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Chapter 3 - Design, synthesis, and characterization of photoinitiators for two-photon polymerization

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Synthesis of new photoactive materials for Laser Micromachining and Microfabrication

by

Reece Whitby

Abstract

This thesis describes the synthesis of a number of novel photoinitiator materials based around triphenylamine to aid in the development and optimisation of the two-photon polymerisation technique. Such materials should allow for improved writing speeds, smaller fabricated feature sizes and low laser powers to initiate polymerisation. Two-photon polymerisation allows for the fabrication of intricate three-dimensional structures, but suffers from slow writing speeds and sufficiently optimised photoinitiators. This work starts with an introduction to the two-photon polymerisation technique, used for fabricating micro/nano-scale three-dimensional polymeric structures, and in particular when using a 780 nm femtosecond Ti:Sapphire laser. This is followed by a description of the synthesis, analysis and characterisation of a number of newly synthesised photoinitiators. The latter part consists of a detailed analysis of the two-photon polymerisation work carried out using these newly synthesised photoinitiators.

An in depth analysis of the factors that allow for more efficient photoinitiators was conducted, and identified the key parameters and molecular properties that should lead to better performing materials. Following this, the design and synthesis of three suites of new photoinitiators containing a variety of electron donors and acceptors was conducted in order to maximise two-photon absorption cross-sections - a key parameter for any successful compound. The general suites of compounds prepared were: (i) branched triphenylamine-π-ester systems; (ii) triphenylamine-π-acceptor and acceptor-π-acceptor systems and (iii) triphenylamine: α,β-unsaturated ketone systems. It was found the two-photon cross sections of up to 590 GM were achievable and this is above the 500 GM that was targeted at the outset of this work.

For each class of compound studied, fluorescence measurements were performed, and these showed the strong influence that solvent viscosity had on the molecular properties of the multi-branched structures reported here, particularly the fluorescence quantum yield, and ultimately, the two-photon polymerisation thresholds. Furthermore, the effect of incorporating ketone functionality as a means to reduce fluorescence quantum yields – and which leads to more efficient photoinitiation (through increasing inter system crossing to the
active triplet state) - was also studied. This indeed proved to be a valid approach and fluorescence quantum yields for some of the ketone containing molecules were below 1%. In-depth studies were also performed to assess the photoinitiators ability to initiate the polymerisation of acrylates when exposed to an 800 nm femtosecond Ti:Sapphire laser on a fabrication stage. It was found that high quality structures with micrometre resolutions could made using writing speeds as fast as 200 μm/s and at laser powers as low as 27 μW.

Furthermore, it was shown that making use of dipolar photoinitiators is advantageous over larger multi-polar species, even though the latter species can display seemingly improved properties. It was concluded that in more complex, multibranched systems, that localisation of the excited state to a single branch effectively negates the molecular properties exhibited by larger species. Moreover, given the difficulty in synthesising larger photoinitiators this work suggests that pursuing such a pathway is unlikely to yield large improvements in polymerisation thresholds. Overall it is concluded that improving dipolar species to maximise their two-photon absorption cross-sections, minimise their fluorescence quantum yields and improve their solubility in a variety of monomer materials is likely to be a more fruitful endeavour.
Acknowledgements

This thesis represents the culmination of three years’ research conducted at the Photonics team, Callaghan Innovation and the Photon Factory, University of Auckland. I would like to thank everyone who contributed to the completion of my thesis whether it through personal or professional support.

First of all I would like to express my gratitude to my supervisors Andrew Kay and Jianyong Jin for their support, guidance and knowledge throughout the course of my PhD.

I would also like to thank all the members of the Photonics team for their support throughout my research. To Stefaan Janssens and Sebastiampillai Raymond for performing z-scan and fluorescence lifetime measurements used in this work. Also, David Clarke for his invaluable knowledge of chemistry and spectroscopy. To Robert Breukers for his chemistry knowledge and proof reading skills.

At the Photon Factory I’d like to thank their director Cather Simpson for her continued support and enthusiasm throughout my time in Auckland. I would also like to thank Yael Ben-Tal and Ryan MacMillan for conducting countless two-photon polymerisation tests and Reece Oosterbeek for managing the work at the Photon Factory.

I would like to thank the Ministry for Business and Innovation for the funding under the Laser Micromachining project with the University of Auckland.

I would personally like to thank Elyse McMinn for her continued and unwavering support during my PhD.

Finally, I would like to thank all my friends and family for their support and to everyone who made my time in New Zealand an unforgettable experience.
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Table 4 - Measured values of fluorescence intensity, $\lambda_{max}$ and $\phi_f$ of PIs 6 - 8 in various viscous solvents. QBS was used as a reference standard; conc = $2 \times 10^{-6}$ mol.L$^{-1}$. An excitation wavelength of 365 nm was used an all remaining settings remained constant. Included are viscosity values (cP) with units in mPa·s. MeOH = Methanol (0.543 cP), EG = Ethylene Glycol (16.1), DEG = Diethylene Glycol (35.7) and Acrylates = a 50:50 by weight mixture of the acrylates SR415 (225 cP) and SR351 (106 cP). $^a$ $k_r$ = radiative decay constant ($k_r$ = $\phi_f$/$\tau$) s$^{-1}$. $^b$ $k_n$ = nonradiative decay constant (see Equation 1).

Table 5 - $\delta_{2PA}$ of PIs as measured at 780 nm in CHCl$_3$ at a concentration of $2 \times 10^{-5}$ mol.L$^{-1}$. $^a$ 1 GM = 1 x $10^{50}$ cm$^3$s photons$^{-1}$ molecule$^{-1}$. The stated values of $\delta_{2PA}$ have a standard accuracy of ± 10%. $^b$ Stokes shift (nm) = ($\lambda_{em}$ - $\lambda_{max}$) $^d$. Fluorescence quantum yield with rhodamine 6G as a reference standard; concentration of $2 \times 10^{-6}$ mol.L$^{-1}$, 500 nm excitation.

Table 6 - $\delta$ values of the solvents used.

Table 7 - $\lambda$ = one-photon maxima (nm), measured at $1.0 \times 10^{-5}$ mol.L$^{-1}$. $^b$ $\varepsilon$ = molar extinction coefficient x $10^5$ (M$^{-1}$ cm$^{-1}$) $^c$. Fluorescence quantum yield with rhodamine 6G as a reference standard; concentration of $2 \times 10^{-6}$ mol.L$^{-1}$, 500 nm excitation.

Table 3 - Photoluminescence maxima and stokes shifts in various solvents, conc = $2 \times 10^{-6}$ mol.L$^{-1}$. $\lambda$ = wavelength maxima (nm), 532 nm excitation. $^b$ $\lambda$ maximum emission, 385 nm excitation. $^c$ Stokes shift (nm) = ($\lambda_{em}$ - $\lambda_{max}$) $^d$. Fluorescence quantum yield with QBS as a reference standard; concentration of $2 \times 10^{-6}$ mol.L$^{-1}$ in MeOH, 365 nm excitation.
Table 1: A comparative table of photophysical properties of structurally similar analogues from Chapter 2 (6) and Chapter 4 (31 and 35).

<table>
<thead>
<tr>
<th>λ&lt;sup&gt;max&lt;/sup&gt; (nm)</th>
<th>Fluorescence quantum yield with rhodamine 6G as a reference standard, concentration of 2 x 10&lt;sup&gt;-6&lt;/sup&gt; mol.L&lt;sup&gt;-1&lt;/sup&gt;</th>
<th>500 nm excitation</th>
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</thead>
<tbody>
<tr>
<td>350</td>
<td>A = one-photonic maxima (mm), 380 nm emission.</td>
<td>Em&lt;sub&gt;max&lt;/sub&gt; = 1.0 x 10&lt;sup&gt;4&lt;/sup&gt; mol.L&lt;sup&gt;-1&lt;/sup&gt;.</td>
</tr>
<tr>
<td>360</td>
<td>A = one-photonic maxima (mm), 380 nm emission.</td>
<td>Em&lt;sub&gt;max&lt;/sub&gt; = 1.0 x 10&lt;sup&gt;4&lt;/sup&gt; mol.L&lt;sup&gt;-1&lt;/sup&gt;.</td>
</tr>
<tr>
<td>370</td>
<td>A = one-photonic maxima (mm), 380 nm emission.</td>
<td>Em&lt;sub&gt;max&lt;/sub&gt; = 1.0 x 10&lt;sup&gt;4&lt;/sup&gt; mol.L&lt;sup&gt;-1&lt;/sup&gt;.</td>
</tr>
<tr>
<td>380</td>
<td>A = one-photonic maxima (mm), 380 nm emission.</td>
<td>Em&lt;sub&gt;max&lt;/sub&gt; = 1.0 x 10&lt;sup&gt;4&lt;/sup&gt; mol.L&lt;sup&gt;-1&lt;/sup&gt;.</td>
</tr>
<tr>
<td>390</td>
<td>A = one-photonic maxima (mm), 380 nm emission.</td>
<td>Em&lt;sub&gt;max&lt;/sub&gt; = 1.0 x 10&lt;sup&gt;4&lt;/sup&gt; mol.L&lt;sup&gt;-1&lt;/sup&gt;.</td>
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<tr>
<td>400</td>
<td>A = one-photonic maxima (mm), 380 nm emission.</td>
<td>Em&lt;sub&gt;max&lt;/sub&gt; = 1.0 x 10&lt;sup&gt;4&lt;/sup&gt; mol.L&lt;sup&gt;-1&lt;/sup&gt;.</td>
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<tr>
<td>410</td>
<td>A = one-photonic maxima (mm), 380 nm emission.</td>
<td>Em&lt;sub&gt;max&lt;/sub&gt; = 1.0 x 10&lt;sup&gt;4&lt;/sup&gt; mol.L&lt;sup&gt;-1&lt;/sup&gt;.</td>
</tr>
<tr>
<td>420</td>
<td>A = one-photonic maxima (mm), 380 nm emission.</td>
<td>Em&lt;sub&gt;max&lt;/sub&gt; = 1.0 x 10&lt;sup&gt;4&lt;/sup&gt; mol.L&lt;sup&gt;-1&lt;/sup&gt;.</td>
</tr>
<tr>
<td>430</td>
<td>A = one-photonic maxima (mm), 380 nm emission.</td>
<td>Em&lt;sub&gt;max&lt;/sub&gt; = 1.0 x 10&lt;sup&gt;4&lt;/sup&gt; mol.L&lt;sup&gt;-1&lt;/sup&gt;.</td>
</tr>
<tr>
<td>440</td>
<td>A = one-photonic maxima (mm), 380 nm emission.</td>
<td>Em&lt;sub&gt;max&lt;/sub&gt; = 1.0 x 10&lt;sup&gt;4&lt;/sup&gt; mol.L&lt;sup&gt;-1&lt;/sup&gt;.</td>
</tr>
<tr>
<td>450</td>
<td>A = one-photonic maxima (mm), 380 nm emission.</td>
<td>Em&lt;sub&gt;max&lt;/sub&gt; = 1.0 x 10&lt;sup&gt;4&lt;/sup&gt; mol.L&lt;sup&gt;-1&lt;/sup&gt;.</td>
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<tr>
<td>460</td>
<td>A = one-photonic maxima (mm), 380 nm emission.</td>
<td>Em&lt;sub&gt;max&lt;/sub&gt; = 1.0 x 10&lt;sup&gt;4&lt;/sup&gt; mol.L&lt;sup&gt;-1&lt;/sup&gt;.</td>
</tr>
<tr>
<td>470</td>
<td>A = one-photonic maxima (mm), 380 nm emission.</td>
<td>Em&lt;sub&gt;max&lt;/sub&gt; = 1.0 x 10&lt;sup&gt;4&lt;/sup&gt; mol.L&lt;sup&gt;-1&lt;/sup&gt;.</td>
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<tr>
<td>480</td>
<td>A = one-photonic maxima (mm), 380 nm emission.</td>
<td>Em&lt;sub&gt;max&lt;/sub&gt; = 1.0 x 10&lt;sup&gt;4&lt;/sup&gt; mol.L&lt;sup&gt;-1&lt;/sup&gt;.</td>
</tr>
<tr>
<td>490</td>
<td>A = one-photonic maxima (mm), 380 nm emission.</td>
<td>Em&lt;sub&gt;max&lt;/sub&gt; = 1.0 x 10&lt;sup&gt;4&lt;/sup&gt; mol.L&lt;sup&gt;-1&lt;/sup&gt;.</td>
</tr>
<tr>
<td>500</td>
<td>A = one-photonic maxima (mm), 380 nm emission.</td>
<td>Em&lt;sub&gt;max&lt;/sub&gt; = 1.0 x 10&lt;sup&gt;4&lt;/sup&gt; mol.L&lt;sup&gt;-1&lt;/sup&gt;.</td>
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Table 2: Dielectric constants (e) and solvent polarity parameter (E(30)) values of the solvents used.

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<tr>
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<th>E(30)</th>
<th>e</th>
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<td>DMF</td>
<td>25</td>
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<tr>
<td>DMSO</td>
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<td>1.0</td>
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<tr>
<td>DMSO</td>
<td>25</td>
<td>1.0</td>
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<tr>
<td>DMSO</td>
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<tr>
<td>DMSO</td>
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<tr>
<td>DMSO</td>
<td>25</td>
<td>1.0</td>
</tr>
<tr>
<td>DMSO</td>
<td>25</td>
<td>1.0</td>
</tr>
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</table>

The stated values of λ<sub>max</sub> have a standard accuracy of ± 10%.

For further details, see Chapters 2 and 4.
Table 1 - The optimal processing windows for PI 6. Variable writing speeds of 50, 100, 150 and 200 μm/s were used; also, variable power ranges to give a full description of the processing window. An average is taken for the high and low power limits given to one significant figure. ...

Table 2 - The optimal processing windows for PI 7. Variable writing speeds of 50, 100, 150 and 200 μm/s were used; also, variable power ranges to give a full description of the processing window. An average is taken for the high and low power limits given to one significant figure. ...

Table 3 - The optimal processing windows for PI 8. Variable writing speeds of 50, 100, 150 and 200 μm/s were used; also, variable power ranges to give a full description of the processing window. An average is taken for the high and low power limits given to one significant figure. ..........................
### List of abbreviations

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
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</thead>
<tbody>
<tr>
<td>µm</td>
<td>Micrometre</td>
</tr>
<tr>
<td>µm/s</td>
<td>Micrometre per second</td>
</tr>
<tr>
<td>µW</td>
<td>Microwatt</td>
</tr>
<tr>
<td>1PA</td>
<td>One-photon absorption</td>
</tr>
<tr>
<td>2D</td>
<td>Two-dimensional</td>
</tr>
<tr>
<td>2PA</td>
<td>Two-photon absorption</td>
</tr>
<tr>
<td>2PF</td>
<td>Two-photon fluorescent</td>
</tr>
<tr>
<td>3D</td>
<td>Three-dimensional</td>
</tr>
<tr>
<td>3PA</td>
<td>Three-photon absorption</td>
</tr>
<tr>
<td>4PA</td>
<td>Four-photon absorption</td>
</tr>
<tr>
<td>h</td>
<td>Reduced Planck constant</td>
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<tr>
<td>β</td>
<td>Nonlinear absorption coefficient</td>
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<tr>
<td>δ&lt;sub&gt;2PA&lt;/sub&gt;</td>
<td>Two-photon absorption cross section</td>
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<tr>
<td>ε</td>
<td>Molar extinction coefficient</td>
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<tr>
<td>ε&lt;sub&gt;r&lt;/sub&gt;</td>
<td>Dielectric constants</td>
</tr>
<tr>
<td>λ</td>
<td>Wavelength</td>
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<tr>
<td>λ&lt;sub&gt;Em&lt;/sub&gt;</td>
<td>Fluorescence emission wavelength</td>
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<tr>
<td>τ</td>
<td>Fluorescence lifetime</td>
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<tr>
<td>φ&lt;sub&gt;F&lt;/sub&gt;</td>
<td>Fluorescence quantum yield</td>
</tr>
<tr>
<td>φ&lt;sub&gt;ISC&lt;/sub&gt;</td>
<td>Intersystem crossing (triplet quantum yield)</td>
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<tr>
<td>ω</td>
<td>Angular frequency</td>
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</table>

#### A

- A: Acceptor (electron)
- A<sub>3</sub>-π-(D-Core), D<sub>3</sub>-π-(A-Core): Octupolar, 3 branched
- A-π-D: Dipolar

#### B

- BDMB: 2-benzyl-2-dimethylamino-4-morpholinobutyrophenone
<table>
<thead>
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<th>Abbreviation</th>
<th>Description</th>
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<td>bs</td>
<td>Broad singlet</td>
</tr>
<tr>
<td>BS</td>
<td>Beam splitter</td>
</tr>
<tr>
<td>C</td>
<td>Concentration</td>
</tr>
<tr>
<td>CAD</td>
<td>Computer-aided-design</td>
</tr>
<tr>
<td>CCVJ</td>
<td>9-(2-carboxy-2-cyano)vinyl julolidine</td>
</tr>
<tr>
<td>Ch</td>
<td>Chopper</td>
</tr>
<tr>
<td>cP</td>
<td>Viscosity</td>
</tr>
<tr>
<td>CT</td>
<td>Charge transfer</td>
</tr>
<tr>
<td>CW</td>
<td>Continuous-wave</td>
</tr>
<tr>
<td>D</td>
<td>Doublet</td>
</tr>
<tr>
<td>d</td>
<td>Donor (electron)</td>
</tr>
<tr>
<td>D</td>
<td>Photodiode</td>
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<tr>
<td>DANS</td>
<td>4-(N,N-dimethylamino)-4-nitrostilbene</td>
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<tr>
<td>DCVJ</td>
<td>9-(dicyanovinyl)-julolidine</td>
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<td>DDA</td>
<td>6-Diisopropyl-N,N-dimethylaniline</td>
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<td>DEDC</td>
<td>7-diethylamino-3-(2' benzimidazolyl)coumarin</td>
</tr>
<tr>
<td>DIHP</td>
<td>Diphenyliodonium hexafluorophosphate</td>
</tr>
<tr>
<td>ESA</td>
<td>Excited state absorption</td>
</tr>
<tr>
<td>Eₜ(30)</td>
<td>Solvent polarity parameter</td>
</tr>
<tr>
<td>F</td>
<td>Femto-second</td>
</tr>
<tr>
<td>fs</td>
<td>Femto-second</td>
</tr>
<tr>
<td>GM</td>
<td>Göppert-Mayer - 1 x 10⁻⁵⁰cm⁴s photons⁻¹ molecule⁻¹</td>
</tr>
<tr>
<td>GW</td>
<td>Gigawatt</td>
</tr>
<tr>
<td>ΔG</td>
<td>Gibbs free energy</td>
</tr>
<tr>
<td>H</td>
<td>1-hydroxy-cyclohexyl-phenyl-ketone</td>
</tr>
<tr>
<td>HCl</td>
<td>Hydrochloric acid</td>
</tr>
<tr>
<td>HgO</td>
<td>Mercury (II) oxide</td>
</tr>
<tr>
<td>HRMS</td>
<td>High-resolution mass spectrometry</td>
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<tr>
<td>----------------------</td>
<td>-----------------------------------</td>
</tr>
<tr>
<td>Hz</td>
<td>Hertz</td>
</tr>
<tr>
<td>I</td>
<td>Peak intensity</td>
</tr>
<tr>
<td>ICT</td>
<td>Intramolecular charge transfer</td>
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<tr>
<td>J</td>
<td>Radiative decay constant</td>
</tr>
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<td>K</td>
<td>Bimolecular quenching rate constant</td>
</tr>
<tr>
<td>k_f</td>
<td>Nonradiative decay constant</td>
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<tr>
<td>L</td>
<td>Lens</td>
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<tr>
<td>LIGA</td>
<td>Lithography, electroplating and molding</td>
</tr>
<tr>
<td>LMM</td>
<td>Laser micromachining</td>
</tr>
<tr>
<td>m</td>
<td>Multiplet</td>
</tr>
<tr>
<td>M</td>
<td>Mirror</td>
</tr>
<tr>
<td>MEMS</td>
<td>Microelectromechanical systems</td>
</tr>
<tr>
<td>MHz</td>
<td>Megahertz</td>
</tr>
<tr>
<td>mol.L^{-1}</td>
<td>Moles per litre</td>
</tr>
<tr>
<td>MPMT</td>
<td>Minimum power and minimum exposure time</td>
</tr>
<tr>
<td>mW</td>
<td>milliwatts</td>
</tr>
<tr>
<td>N</td>
<td>Avogadro’s number</td>
</tr>
<tr>
<td>Na</td>
<td>Numerical aperture</td>
</tr>
<tr>
<td>NA</td>
<td>Neutral density filter</td>
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<td>ND</td>
<td>Neodymium-doped Yttrium Aluminium garnet; Nd: Y_3Al_5O_{12}</td>
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<td>Nd:YAG</td>
<td>Neodymium-doped Yttrium Aluminium garnet; Nd: Y_3Al_5O_{12}</td>
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<td>N-DPD</td>
<td>1,5-bis(4-dimethylamino)phenylpenta-1,4-diyn-3-one</td>
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<tr>
<td>NEP</td>
<td>Noise-equivalent power</td>
</tr>
<tr>
<td>NIR</td>
<td>Near-infrared region</td>
</tr>
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<td>nm</td>
<td>Nanometre</td>
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<td>Abbreviation</td>
<td>Description</td>
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<tr>
<td>NMR</td>
<td>Nuclear magnetic resonance</td>
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<td>OROMCERS</td>
<td>Organically modified ceramics</td>
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<td>Photoacid generator</td>
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<td>Ph-N</td>
<td>Phenyl-nitrogen</td>
</tr>
<tr>
<td>PI</td>
<td>Photoinitiator</td>
</tr>
<tr>
<td>ppm</td>
<td>Particles per million</td>
</tr>
<tr>
<td>ps</td>
<td>Picosecond</td>
</tr>
<tr>
<td>PSF</td>
<td>Point-spread function</td>
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<td>q</td>
<td>Quartet</td>
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<tr>
<td>RAPID</td>
<td>Resolution augmentation through photoinduced deactivation</td>
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<td>Rf</td>
<td>Retardation factor</td>
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<td>s</td>
<td>Singlet NMR</td>
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<td>S&lt;sub&gt;1&lt;/sub&gt;</td>
<td>Singlet excited state S&lt;sub&gt;1&lt;/sub&gt;</td>
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<td>Structure-activity relationships (SAR)</td>
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<td>Scanning electron microscopy</td>
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<td>SR351</td>
<td>Trimethylolpropane triacrylate</td>
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<td>SR415</td>
<td>Ethoxylated (20) trimethylpropane triacrylate monomer</td>
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<td>Stimulated-emission-depletion</td>
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<td>C&lt;sub&gt;10&lt;/sub&gt;-TCF</td>
<td>2-(3-cyano-5,5-didecyl-4-methylfuran-2(5H)-ylidene)malononitrile</td>
</tr>
<tr>
<td>t</td>
<td>Triplet</td>
</tr>
<tr>
<td>T&lt;sub&gt;1&lt;/sub&gt;</td>
<td>Triplet state</td>
</tr>
<tr>
<td>TAT</td>
<td>Triazatruxene</td>
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<td>TCF</td>
<td>2-(3-cyano-4,5,5-trimethylfuran-2(5H)-ylidene)malononitrile</td>
</tr>
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<td>Abbreviation</td>
<td>Description</td>
</tr>
<tr>
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<td>-------------</td>
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<tr>
<td>Ti: Sapphire</td>
<td>Titanium-sapphire laser</td>
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<td>TICT</td>
<td>Twisted intramolecular charge-transfer</td>
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<td>TLC</td>
<td>Thin-layer chromatography</td>
</tr>
<tr>
<td>TPA</td>
<td>Triphenylamine</td>
</tr>
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<td>TPEF</td>
<td>Two-photon excited fluorescence</td>
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<td>TPP</td>
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<td>U</td>
<td>Ultraviolet</td>
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# Chapter 1. Synthesis of New Photoactive Materials for Laser Micromachining and Microfabrication

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1.1. Abstract

Over the last two decades, a considerable amount of research has been conducted in the areas of photonics, materials science and engineering to aid in the development of two-photon polymerisation (TPP) processes for two-dimensional (2D) and three-dimensional (3D) micro/nanofabrication. The development of two-photon absorbing (2PA) chromophores for not only TPP, but a wide range of applications has led to the fabrication of a considerable number of micro-structures. In TPP, a near-infrared, ultrashort-pulsed laser is focused onto a photocurable resin containing a suitable 2PA chromophore. This results in a radical or cationic polymerisation process that is confined within the focal volume of the laser allowing excellent control of feature size and resolution using this technique.

This section contains a review of the fundamental principles of 2PA and TPP. Also reviewed is the excellent progress achieved by various groups in the design of new 2PA molecules, polymer materials used for TPP and its applications.
1.2. Introduction

In the past decade, there has been a rapid advancement in micro/nanofabrication techniques capable of producing 3D structures using a number of methods and materials. 3D fabrication is of great importance to fields such as nanotechnology, biotechnology and information technology in the creation of devices such as microfluidic devices, biochips, photonic crystals and microelectromechanical systems (MEMS). This had led to the development of a number of novel 3D microfabrication techniques.

Photolithography has been the dominant technique in creating micro/nano-scale devices over the last fifty years. The shrinking of electronic components such as transistors in silicon wafers and the use of mass production has revolutionised the computing world. The achievements made by the semiconductor industry have been impressive. Commercially chips with 14 nm transistors are now available, however the limit of this silicon-based technology is expected to be reached within the next five to ten years once sub 10 nm components are required. Although, capable of producing extraordinarily complex structures, such techniques are not truly able to produce 3D structures. This is because control for these techniques in the vertical direction is far behind what is capable in the horizontal plane. Furthermore, the processing of materials used in lithographic techniques often use harsh conditions such as HF or reactive ions to etch in 2D structures.

To extend the range of materials that can be used in lithography alternatives have been developed such as dip-pen nanolithography, nanoimprint lithography, and soft lithography. While these techniques have some advantages over photolithography such as higher resolution, more material options and softer processing conditions they all essentially remain tools for 2D micro-fabrication.

Research efforts to extend fabrication into the third dimension have been extensive and a number of techniques have been developed for 3D micro and nanofabrication. The most important techniques include ink-based writing, self-assembly, layer-by-layer assembly, LIGA (lithography, electroplating and molding), micro-stereolithography and multiphoton fabrication. Ink-based writing can be performed with drop or filament-based techniques, which are referred to as ink-jet printing and robotic deposition, respectively. A nozzle can deliver inks of polymers, colloids or polyelectrolytes and structures can be made with resolutions of
approximately 1 – 100 µm. Although 3D control is possible in principle, it has so far proven difficult in practice, due to the inks not being sufficiently rigid upon deposition to create arbitrary structures.

Another process which can achieve 3D fabrication was developed in the early 1980’s and is known as LIGA.¹⁹ LIGA is a German acronym for X-ray lithography; *Lithographie, Galvanoformung, Abformung* (Lithography, Electroplating, and Molding). In this method, X-rays are used to create patterns. As X-rays have extremely short wavelengths this allows for micrometre resolutions to be achieved at depths of up to 1 cm. This has enabled access to high-aspect-ratio patterns such as channels and gears that can be used as molds for the electrodeposition of metals. Structures made with LIGA have good resolution but are limited by the shallow penetration depth of X-rays.

Micro-stereolithography uses a laser to harden the surface of a prepolymer resin into a 2D pattern.²⁰,²¹ Additional resin is then reflowed over the pattern to create a new surface, which is then hardened and this process is repeated until the object is completed. Complexities that are orders of magnitude greater than for other lithographic processes are possible, but the slow fabrication time and high precision required are stumbling blocks for microstereolithography to be used as a high-throughput technology.

TPP was proposed as a potential solution to these challenges and was first demonstrated in 1997. TPP offers a means of creating high resolution 3D fabricated structures with high throughput.¹⁶ In TPP a resin is polymerised not by absorbing one ultraviolet (UV) photon, but simultaneously two photons at longer wavelengths, usually in the near-infrared region (NIR). This has several advantages over conventional one-photon initiated polymerisation. Firstly, many polymer materials have negligible absorption at NIR wavelengths, so the laser can penetrate deeply into a material and initiate polymerisation within the material, without causing polymerisation outside the focal volume. Secondly, as TPP depends nonlinearly upon the laser intensity used, it is possible to localise the photochemical reaction within the focal point of the laser beam. This allows resolutions beyond the diffraction limit of the laser light to be achieved.¹⁵ Structure sizes below 100 nm are regularly achieved using this technique.²²-²⁵ This has led to the design of 2PA molecules as photoinitiators (PIs) for microfabrication and the development of polymerisable materials, which exhibit novel functionalities. As with any new technology the fundamental aspects have received considerable attention in the early stages of development, however the
technology has only now matured enough that widespread applications are becoming feasible. Furthermore, in the future TPP is expected to be an important tool in commercial and industrial settings rather than just a proof-of-principle example used in research laboratories.

This review summarises the most important research to date on the fundamental principles behind TPP, the material considerations and applications of the TPP technique. This review is organised into three main sections; (i) two-photon absorption (2PA) fundamental principles and the types of 2PA materials, (ii) Laser Micromachining (LMM) and TPP fundamentals and (iii) the applications of TPP. As the scope of research in these areas is vast and very diverse, covering all aspects is beyond the scope of this review. However, this review will cover the major fundamental principles behind the technology and bring together much of the cutting-edge research in the field.

1.2.1 Two-photon absorption fundamentals

2PA was first theoretically predicted in 1931 by Maria Göppert-Mayer in her doctoral dissertation at the University of Göttingen.26 The theory was not experimentally confirmed until 1961, a year after the invention of the laser. The first observation of 2PA by Kaiser and Garret was in a CaF$_2$:Eu$^{2+}$ crystal excited by intense coherent radiation from a pulsed ruby-crystal laser.27 The main difference between one-photon absorption (1PA) and 2PA is that 1PA depends linearly on the light’s intensity (I), whereas 2PA depends on the square of the light intensity (I$^2$). Consequently, it wasn’t until the invention of the laser that sufficiently high photon intensities were available to excite 2PA electronic transitions (Figure 1).

![Figure 1](image_url) - Fluorescence from a solution of Rhodamine B caused by single-photon excitation from a UV lamp (left) and by two-photon excitation from a mode-locked Ti: sapphire laser operating at a wavelength of 800 nm (right). The integrated
The intensity in each transverse section of the beam does not depend upon the position for single-photon excitation but is tightly peaked in the focal region for two-photon excitation.\textsuperscript{12}

Up until the mid-1980’s, continuous-wave lasers were used to achieve a sufficient square intensity of photons at the focal volume to drive 2PA to a significant degree – however this meant that applications for 2PA were initially limited.\textsuperscript{14} This situation has now changed with the development of the relatively simple, cheap solid-state pulsed femtosecond lasers that emerged in the late 1980’s and early 1990’s, these pulsed lasers made use of the higher peak powers that were possible with these new systems.

A Ti: Sapphire (Titanium-Sapphire) laser is able to typically produce pulses in the femtosecond (fs) range and at a repetition rate of 80 MHz.\textsuperscript{28} Even though light sources such as Ti: sapphire lasers are able to produce peak powers of tens of watts this is many magnitudes higher than is necessary for efficient 2PA. They can operate in the range of 700 – 1100 nm but most commonly at 800 nm. As 2PA is a third-order non-linear optical phenomenon, the energy absorbed by the two-photon process is quadratically proportional to the intensity of the incident light (Figure 1).

The non-linear intensity dependence of the absorption allows for the excitation to be confined within the focal point of the laser beam where the intensity is greatest. Furthermore, as the absorbance in a given volume is proportional to the intensity squared multiplied by the number of molecules in that volume, the absorption scales inversely with area, unlike 1PA which is linear.\textsuperscript{12}

Virtual state 2PA involves the simultaneous absorption of two photons (Energies $E_1 + E_2$) by a molecule, as a result of absorption two photons are lost from the excitation beams thus reducing their intensity, this brings the molecule into an excited state (State f in Figure 2) at an energy equivalent to $E_1 + E_2$ above the ground state $g$.\textsuperscript{29} 2PA can occur via either a degenerate ($E_1 = E_2$) or non-degenerate ($E_1 \neq E_2$) absorbance. The photons can have the same energy, $E_1$ (degenerate case, $E_f = 2E_1$) or different energies $E_1$ and $E_2$ (non-degenerate case $E_f = E_1 + E_2$) as shown in Figure 2. After the excitation, the system quickly relaxes back to the lowest vibronic level of the lowest energy excited state $r$ and then the system will return to the ground state by radiative or nonradiative pathways (dashed arrow).

In applications of 2PA, objective lens with high numerical aperture (NA) are used to create the required photon density needed to give sufficient non-linear absorption in a given medium. For an ultrafast laser with a pulse duration $\tau$ and a pulse repetition of $f_p$, the
number of photons absorbed per molecule per pulse is given by Equation 1 in which \( p_0 \) is the time-averaged laser power, where \( \lambda \) is the excitation wavelength and \( \delta \) is the two-photon absorption cross section (\( \delta_{2PA} \)) (Equation 1).  

\[
\text{Equation 1}
\]

\[
N_\alpha \approx \frac{p_0^2 \delta}{\tau f_p^2} \left( \frac{(NA)^2}{2\hbar c \lambda} \right)^2
\]

\( \text{Equation 1} \)

For example, the \( \delta_{2PA} \) for the fluorophore Rhodamine B is 220 GM at a wavelength of 840 nm. The value for Rhodamine B is moderate and values greater than this would be preferable to maximise sensitivity. Due to materials design and the availability of high peak power of fast pulsed laser systems higher order absorptions like three-photon absorption

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\text{Figure 2 - Schematic energy level diagram showing the excitation of a molecule from the ground state, } g, \text{ to an excited state, } f \text{ (2PA), located at energy } E_f \text{ above the } g \text{ state by the absorption of two photons (vertical solid arrows). } R = \text{ first lowest energy excited state. Image reproduced from Two-photon absorption: an overview of measurements and principles.}\]

\( \delta \) or \( \delta_{2PA} \) is measured in units known as Göppert-Mayer (GM) and 1 GM is equal to \( 1 \times 10^{-50} \text{cm}^4\text{s photons}^{-1} \text{ molecule}^{-1} \). It is the optimisation of the 2PA cross-section that will form a key component of this work.
(3PA) and four-photon absorption (4PA) have been reported.\textsuperscript{32,33} Applications such as three and four photon pumped lasing have been reported using high peak power of short-pulsed laser systems in the 1.3 – 2 µm wavelength range with femtoseconds durations, to sufficiently stimulate higher order absorptions.\textsuperscript{34,35}

1.2.2 Evaluation the two-photon absorption cross-section

The main techniques used to quantify δ\textsubscript{2PA} are known as z-scan and two-photon excited fluorescence (TPEF).\textsuperscript{29,36,37} There are also other techniques which provide less direct information on 2PA cross sections like degenerate four-wave mixing\textsuperscript{38} and the white-light continuum method,\textsuperscript{39} these techniques are beyond the scope of this review. Consequently, below are described the two techniques have been considered as part of this work for measuring δ\textsubscript{2PA}; z-scan and TPEF.

1.2.3 z-scan technique

In a z-scan measurement, the pulse energy is kept constant but changes in intensity are achieved by moving the sample along the z-axis of a focused beam. The transmittance is measured at each position of the sample via measuring the light intensity at the detector as a function of sample position along the z-axis, hence the name “z-scan”. The experimental setup is shown in Figure 3. If the apparatus is in the open-aperture setup, then the output reflects the intensity dependent transmission and can be used to obtain δ\textsubscript{2PA}. Under such conditions, the δ\textsubscript{2PA} is characterised by a decrease in transmittance which is used to calculate the extent of the non-linear process.\textsuperscript{40}

![Figure 3 – Experimental setup z-scan measurements. L, lens; BS, beam splitter; M, mirror; S, sample.](image-url)
If the apparatus uses a narrow aperture ("closed-aperture") then the output is sensitive to intensity-dependent changes in the refractive index due to third-order non-linear polarisability or thermal effects, which can cause self-focusing or defocusing of the beam. Such effects can also interfere with true measurements for $\delta_{2PA}$ when measured by open-aperture z-scan techniques.\textsuperscript{41} Firstly, light can be lost due to self-focusing if the aperture is too narrow or far from the sample. Secondly, nonlinear scattering can artificially enhance the $\delta_{2PA}$. Finally, a build-up of excited state populations by 1PA or 2PA can lead to non-linear transmission through excited state absorption (ESA); this can be reduced by using wavelengths which reduce 1PA absorption by way of very short laser pulses and low repetition rates.\textsuperscript{42}

1.2.4 Two-photon excited fluorescence

TPEF was first reported by Xu and Webb in 1996.\textsuperscript{31} The TPEF technique measures the fluorescence signal caused by 2PA and derives the TPEF cross section by comparison to a known reference compound or to one-photon excited fluorescence. The use of this referencing allows a large number of variables to be eliminated, such as the excitation $\lambda$ dependence, the sample concentration. However, uncertainty in the one-photon extinction coefficient, $\varepsilon$; leads to uncertainty in the value of $\delta_{2PA}$. The number of fluorescence photons collected per unit of time in TPEF is proportional to the total number of photons absorbed per unit time and the fluorescence quantum efficiency of the molecule. If 2PA occurs during this process the number of fluorescence photons is then proportional to the $\delta_{2PA}$ of the molecule and to the square of the incident intensity.

The TPEF method has been optimised by Rebane and Drobizhev and they reported accurate reference 2PA spectra for a wide range of commercial dyes.\textsuperscript{43,44} The TPEF signal intensity increases with the square of the laser intensity, therefore it is necessary to avoid overestimation of the $\delta_{2PA}$ value due to fluorescence from 1PA. The two limitations of this technique are; firstly, it cannot be applied to spectral regions which exhibit 1PA, and secondly the sample must be photoluminescent, although, the first issue is true to all techniques for measuring reliable 2PA cross sections.
1.2.5 Conclusion

The z-scan and TPEF technique for measuring $\delta_{2PA}$ have advantages and disadvantages, thus considerations around the measured molecules and equipment to perform accurate measurements must be considered. Generally the higher laser intensities required for 2PA measurements can lead to other non-linear phenomena occurring, which is a particular problem with the z-scan technique, which can make interpretation difficult, but detailed analysis of z-scan data using a range of pulse widths and pump-probe data, can give accurate $\delta_{2PA}$ resulting from 1PA and ESA.\textsuperscript{45}

The TPEF technique is free from these background problems and due to its sensitivity allows for samples of lower concentration to be used, compared with z-scan, which needs sample concentrations several orders of magnitude higher than is required for TPEF measurements. Higher concentrations can become problematic with sparingly soluble compounds and can also lead to aggregation phenomena. The main drawback of TPEF, is the requirement that chromophores must exhibit fluorescence in the particular solvent used. This limits the range of molecules and solvents that can be used. However, the sensitivity of the technique means fairly low quantum fluorescence yield ($\phi_F$) are sufficient to analyse the $\delta_{2PA}$. However, an accurate value of $\phi_F$ is needed to give a correct value for $\delta_{2PA}$ and this can be a challenging if $\phi_F$ is very low.\textsuperscript{46}

There are considered three extrinsic factors that need to be considered during the experimental determination of $\delta_{2PA}$. Firstly, the time scales involved in various absorption mechanisms and the response speed of the measurement technique. Secondly, the perturbation of the state structure by the surroundings, and lastly, the intensity at which other nonlinear absorptions may cause permanent changes in molecular structure. In other words for meaningful comparisons of $\delta_{2PA}$, the experimental conditions should be kept the same. The suite of compounds studied in this research was chosen for their potentially high $\phi_T$, which may follow on from low $\phi_F$. Based on the above factors, and experimental facilities available, it was decided to use z-scan as the method to evaluate $\delta_{2PA}$ in this work. The suite of compounds studied in this research were synthesised for their high triplet quantum yields ($\phi_T$) ($\approx$ low $\phi_F$). Therefore, z-scan is likely to be favoured over TPEF.
1.3. Multiphoton absorbing materials

Multiphoton absorption is a third-order non-linear optical phenomenon requiring a centrosymmetric change in electronic distribution associated with the transition within the chromophore. Since the first reported demonstration of 2PA by an organic dye molecule in 1963⁴⁷, there has been considerable interest in such compounds, but it has only been over the last two decades that considerable research efforts have produced a great variety of organic 2PA dyes.

Generally, organic 2PA materials can be divided into three main classes:

1. Dipolar; A-π-D
3. Octupolar; 3 branched, A₃-π-(D-Core), D₃-π-(A-Core)

This is not an exhaustive list, as molecules such as porphyrins, dendrimers, proteins and polymer materials can also exhibit 2PA.

Furthermore, several key factors are involved in the magnitude of δ₂PA in organic molecules:

I. Donor Strength
II. Acceptor Strength
III. π-conjugation length
IV. Intramolecular Charge Transfer (ICT)
V. Structural Conformation/Geometry

Again, although not an exhaustive list, the above factors are generally the most important in determining the magnitude of δ₂PA. δ₂PA is by definition a molecular property and so its magnitude is determined by the molecular structure.

There is a strong correlation between ICT processes and 2PA activity. The permanent ground state dipole moment, as well as the transition state dipole moment, are both determinants of the magnitude of 2PA.⁴⁸ With respect to the 2PA, it is necessary to have electron rich donor (D) and electron poor acceptor (A) moieties to facilitate the ICT process though both are not alone sufficient for good 2PA activity.⁴⁹ The extent of π-conjugation is also an important factor as it leads to states with extended charge separation.⁵⁰-⁵²
Molecular co-planarity is also critical for efficient ICT, e.g. the detrimental effects of meta-linkages can be seen with phenylethynyl-linked dipolar chromophores.\textsuperscript{53} The ground-state dipole strength in non-symmetric molecules or the multipolar transition-dipole strength in centrosymmetric molecules has been shown to greatly affect 2PA in organic molecules.\textsuperscript{54,55} Increasing the number of conjugation paths in a molecule, e.g. connecting several linear paths together to form 2D or 3D configurations has been shown both theoretically and experimentally to increase 2PA.\textsuperscript{54,56,57} Solvent polarity and polarisability (expressed as dielectric constants - $\varepsilon_r$) also play a role, as solvent polarity can positively or negatively influence $\delta_{2PA}$. Furthermore, hydrogen bonding and the ability of a given solvent to promote aggregation are also important considerations.\textsuperscript{58-61}

A number of review articles have been written on 2PA chromophore molecules examining structural, theoretical and experimental factors affecting the design and synthesis of such molecules.\textsuperscript{12,24,46,62,63} The following section reviews the literature around 2PA and effectively assesses what influences the design and applications of high-quality 2PA materials.

1.3.1 Dipolar molecules

Dipolar chromophores have been explored to improve on the fundamental aspects needed to create efficient 2PA molecules, including increasing donor and acceptors strength, $\pi$-conjugation length and structural confirmation. Since work on non-centrosymmetric optically nonlinear molecules like 4-(N,N-dimethylamino)-4-nitrostilbene (DANS) revealed that the degree of ground-state polarity is correlated with $\beta$, the second-order hyperpolarisability of various types of D-$\pi$-A dipolar chromophores have been explored.\textsuperscript{64} Structure-activity relationships (SAR) for organic dyes were not well established until Reinhardt et al. studied a series of D-$\pi$-A conjugated benzenoid molecules.\textsuperscript{65} For this work, dipolar D-$\pi$-A molecules were synthesised, linear and nonlinear photophysical measurements were taken, and structure activity relationships were then formulated (Figure 4).

For the compounds in Figure 4, $\delta_{2PA}$ (z-scan) measurements were performed in tetrahydrofuran (THF) using a 800 nm nano-second pulsed beam, provided by a dye laser system pumped with a frequency-doubled and Q-switched Nd:YAG (neodymium-doped
yttrium aluminium garnet; Nd:Y₃Al₅O₁₂ laser source. The starting molecule iii contains a weak thiophene donor, fluorene π-bridge and pyridine acceptor and was shown to be of low δ₂PA. However, replacement of the thiophene donor with the strong diphenylamino donor group and increasing π-conjugation length as seen in v give an almost 10-fold increase in δ₂PA activity. For ii a 5-fold increase in δ₂PA is overserved when the π-conjugation is increased relative to i, highlighting the importance on conjugation on δ₂PA.

Figure 4 - Structure-Activity relationship table devised by Reinhardt et al. in 1998 based on systematic changes made to the structure and the effects these had on 2PA cross-section and two-photon upconverted fluorescence.⁶⁵

Belfield et al. varied the acceptor strength on some diphenylaminofluorene based molecules to assess the relative strength of differing acceptor groups on dipolar (D-π-A) systems (Figure 5).⁶⁶ The group obtained a large amount of data from linear and nonlinear photophysical studies, crystallographic studies, and quantum mechanical calculations to explain the effective increases in δ₂PA.
An analogue with the electron acceptor 2-pyran-4-ylidene malononitrile group exhibited a nearly 3-fold enhancement of $\delta_{2PA}$ (1650 GM at 840 nm), relative to other members of the series. As seen in Figure 5, increasing the $\pi$-electron accepting strength gives improvements in $\delta_{2PA}$ by way of improving ICT character between donor and acceptors. Kannan et al. synthesised diphenylaminofluorene $\pi$-donor based chromophores with various $\pi$-electron acceptors. They also modified the pendant alkyl groups on the fluorene core, and $\delta_{2PA}$ values of between 390 GM and 1156 GM were observed as measured by an 800 nm, 8 ns pulsed-beam, Nd:YAG laser source. While the strength of the electron acceptors has an effect on measured $\delta_{2PA}$, changes in linear absorption due to these structural changes means comparisons can be difficult. Thus, without performing $\delta_{2PA}$ measurements at varying wavelengths as a function of structure, comparisons can be difficult to fully define. Marder et al. synthesised dipolar chromophores with a pyrrole donor and thiazole acceptors and found these to have a $\delta_{2PA}$ of up to 1500 GM as measured by a 100 fs white-light continuum source as a probe and pump wavelength of 1800 nm. The $\delta_{2PA}$ of these molecules are orders of magnitude higher than would generally be expected for such dipolar systems, which often ranged from tens to the few hundreds of GM values. These molecules were specifically designed for applications in telecommunications, which make use of the NIR region of the spectrum.

Figure 5 – Increasing acceptor strength and its effects on 2PA cross-sections.\textsuperscript{66}
1.3.2 Quadrupolar molecules

Quadrupolar molecules consist of an electric charge distributed across two connected dipoles, for example centrosymmetric quadrupolar structures with A-π-A and A-π-D-π-A confirmations. As with dipolar molecules, significant research has been conducted on SARs of quadrupolar dyes.\textsuperscript{50,58,69-79} Furthermore, many of the structural considerations found for dipolar molecules are applicable to quadrupolar systems, but some differences are also clear.

Marder \textit{et al.} showed that for linear, centrosymmetric quadrupolar 2PA materials ICT plays an important role in the enhancement of $\delta_{2PA}$.\textsuperscript{50,80} Their investigations revealed that the following structural factors enhanced 2PA efficiency: (i) extension of π-conjugation, (ii) the introduction of acceptors onto a molecule’s central motif, (iii) increased donor strength on the pendant ends, and, (iv) the reversal of the direction of CT from D-π-D to A-π-A. For their study a series of dipolar and quadrupolar chromophores were synthesised, and the use of dialkylamino groups as electron donors as well as electron deficient phenylene cores were explored. The modification of the phenylene molecular core with π-acceptors (CN) and σ-acceptors (R-SO$_2$R$_1$) were investigated as shown in Figure 6. Chromophores VI, VII and VIII exhibit very high $\delta_{2PA}$ values, namely 1400, 4100 and 3000 GM respectively.

![Figure 6](Image)

\textbf{Figure 6} – A series of dipolar and quadrupolar chromophores measuring the influence of π and σ-acceptors on $\delta_{2PA}$ and solvatochromism. From: \textit{The Influence of σ and π Acceptors on Two-Photon Absorption and Solvatochromism of Dipolar and Quadrupolar Unsaturated Organic Compounds}.\textsuperscript{81}
This correlates with the increasing strength of the electron withdrawing groups on the central benzene ring; \( \text{SO}_2\text{R} > \text{CN} > \text{F} \). However, the unsymmetrical IX has the lowest observed \( \delta_{2PA} \) (260 GM) in the distyrylbenzene series, even though the cyano group reduces electron density equivalent to the four fluorine atoms in 1,2,4,5-tetrafluorobenzene. Therefore, retaining the symmetry of quadrupolar molecules is an important factor in increasing \( \delta_{2PA} \) values, because ICT can simultaneously occur from both donor moieties to the central ring.\(^\text{81}\)

*Lee et al.* in a number of publications examined the role of \( \pi \)-centres and donor strength on \( \delta_{2PA} \).\(^{82-87}\) A number of \( \pi \)-centres were considered and studied including fluorene, dithienothiophene (DTT), oligothiophenes, and phenylenevinylene, examples of which can be seen in Figure 7.

![Figure 7](image)

**Figure 7** – Quadrupolar D-\( \pi \)-D chromophores TP-Flu-TP\(^1\) - Fluorene\(^\text{82}\) (950 GM), TP-DTT-TP\(^\text{85}\) (1140 GM) and generic \( \pi \)-centres oligothiophene and phenylenevinylene.

The group synthesised a number of DTT and fluorene molecules (Figure 7) exhibiting high \( \delta_{2PA} \); TP-Flu-TP\(^1\) (950 GM; \( \lambda_{\text{max}} = 705 \text{ nm} \)) and TP-DTT-TP (1140 GM; \( \lambda_{\text{max}} = 780 \text{ nm} \)). The increase in \( \delta_{2PA} \) is thought to relate to the higher planarity (DTT > fluorene). They also found that much larger \( \delta_{2PA} \) were observed in symmetric chromophores (D-\( \pi \)-D or A-\( \pi \)-A) over equivalent asymmetric chromophores, and increasing the donor strength (triphenylamine (TPA) > carbazole) had a significant, beneficial effect.
Extension of the structures to D-π-A-π-D, A-π-D-π-A and similar configurations have been proposed as a way of increasing effective ICT across chromophore molecules. Cho et al. synthesised a series of D-π-D (XII) and D-π-A-π-D (2a) derivatives which exhibited large $\delta_{2PA}$ values as shown in Figure 8. For XII the $\delta_{2PA} = 1370$ GM and XIII $\delta_{2PA} = 3130$ GM - both measured at 840 nm. The large increase is due to the increased conjugation pathway and increased ICT between the acceptor and donors.

Another important consideration in chromophore design for enhancing 2PA is the use of ethynylene and vinylene bonds which can have a considerable effect on $\delta_{2PA}$ as can be seen in Figure 9. In general, ethynylene sp (-C≡C-) systems are less conjugated than corresponding vinylene sp$^2$ (-C=C-) systems. This is due to a $\pi$-$\pi$ and $\pi^*$-$\pi^*$ energy mismatch at the C(sp$^1$)-C(sp$^2$) connections. Blanchard-Desce et al. showed that for systems similar to that of XIV and XV (Figure 9) double bonds have greater beneficial effects on $\delta_{2PA}$ than that of equivalent triple bond connected materials. They concluded that replacing a
triple bond with a double bond leads to significant increases in $\delta_{2PA}$, in particular in the NIR region and regardless of the nature of the end groups (i.e. donor or acceptor).

![Figure 9](image)

**Figure 9** – Molecules structures synthesised by Blanchard-Desce et al. The ethylene bridged XIV and vinylene XV.

### 1.3.3 Octupolar molecules

Historically, unlike dipolar and quadrupolar compounds, octupolar molecules have received less attention, however in recent years this has changed. The ability of octupolar molecules to have a large $\delta_{2PA}$ and novel molecular structures has prompted a number of research groups to investigate octupolar molecules. Common core structures that have been investigated include TPA, 1,3,5-tricyano-2,4,6-tris(styryl)benzene, triazatruxene (TAT) and triazine moieties.

![Figure 10](image)

**Figure 10** - A series of 1,3,5-tricyanobenzene core octupolar molecules assessing the effect on branch size and electron donor strengths on $\delta_{2PA}$. Image reproduced from 91.
Cho et al. over the last decade have produced a number of octupolar molecules based around the acceptor core 1,3,5-tricyano-2,4,6-tris(styryl)benzene (Figure 10).\textsuperscript{91-93} The cooperative branching effect, large π-conjugation and use of strong electron donors and acceptors in these types of molecules has resulted in large \( \delta_{2PA} \) values between 50 GM and 2620 GM being measured using nanosecond pulsed TPEF measurements.\textsuperscript{91}

For XVI \( f \) the \( \delta_{2PA} = 197 \) GM at 800 nm which is in stark contrast to XVII \( i \) \( \delta_{2PA} = 2620 \) GM at 800 nm (Figure 10). This shows the effect of increasing donor strength and increasing π-conjugation. However, for XVIII \( i \) the \( \delta_{2PA} = 2480 \) GM at 990 nm and this value was only slightly lower than that of the larger molecule 3i (2620 GM).

Chi et al. created a series of star-shaped octupolar triazatruxene (TAT) chromophores with intramolecular “push-pull” character for potential application as two-photon fluorescent (2PF) probes (Figure 11).\textsuperscript{94} The use of a \( C_3 \)-symmetry planar TAT moiety was seen as a good option for developing efficient octupolar 2PA active materials. The TATs contain a conjugated core and can be thought of as an extended delocalised π-system in which three carbazole units share one aromatic ring. Furthermore, the three nitrogen atoms can act as electron donors and the addition of acceptor groups provides for star-shaped octupolar molecules (Figure 11).

![Figure 11](image-url)

The results showed that molecules with moderate to high 2PA activity could be created, with \( \delta_{2PA} \) values of between 280 and 1620 GM in the 740–860 nm range when measured by TPEF.
A well-used substrate is that of triphenylamine (TPA), either as an electron donor core or donor end-cap for a variety of chromophores. Wu et al. synthesised a series of multi-branched benzyldiene cyclopentanone dyes which exhibited large $\delta_{2PA}$ values. They assessed the effect of increasing branches around a TPA core in D-$\pi$-A, A-$\pi$-D-$\pi$-A and D-$\pi$-A$_3$ configurations as shown in Figure 12. The dipolar XXI exhibited a $\delta_{2PA} = 781$ GM, quadrupolar XXII $\delta_{2PA} = 2475$ GM and octupolar XXIII $\delta_{2PA} = 3299$ GM as measured using the TPEF method. The large increase in $\delta_{2PA}$ with increasing branches is attributed to interbranch vibronic coupling and electronic coupling. This is particularly clear between XXI and XXII, a smaller but significant increase is observed between XXII and XXIII.

![Synthesised multi-branched cyclopentanone chromophores. From Multibranched benzylidene cyclopentanone dyes with large two-photon absorption cross-sections.](image)

**Figure 12** - Synthesised multi-branched cyclopentanone chromophores. From Multibranched benzylidene cyclopentanone dyes with large two-photon absorption cross-sections.

### 1.3.4 Other two-photon absorbing molecules

Besides the more standard chromophores based around dipolar, quadrupolar and octupolar structures, examples of 2PA activity in materials such as polymers, dendrimers, metal complexes, nanoparticles and porphyrins have been found. Due to their size and

...
complexity such molecules can exhibit extremely high $\delta_{2PA}$, with values upwards of 100,000 GM possible, e.g. large cyclic oligothiophene macrocycles produced by Goodson, Iyoda and co-workers. However, many of these molecules are simply too large and difficult to synthesise to be commonly used in applications such as TPP.

Wang et al. synthesised a family of dendrimers with a naphthalene core and TPA branching for use as TPP PIs. These molecules showed exceptionally large $\delta_{2PA}$ values ranging from 959 – 9575 GM (780 nm), and it was found that as branching, and therefore, $\pi$-conjugation increased so did $\delta_{2PA}$. The dendrimers were found to effectively polymerise acrylates at low lasing powers, with one synthesised dendrimer ($\delta_{2PA} = 5582$ GM) shown to be most effective and lasing powers as low as 2.4 mW were observed to be sufficient to induce TPP. Although, dendrimer PIs with higher $\delta_{2PA}$ values were also prepared, their poor solubility in the appropriate acrylate resins was an issue and thus they were ineffective as TPP PIs.

As mentioned in 1.3.2, Quadrupolar molecules, the use of C=C bonds is a more effective strategy for improving $\delta_{2PA}$ in comparison with equivalent C≡C molecules, however, for certain systems this is not always the case. When steric congestion is an important issue, as in meso-linked porphyrins, acetylenic systems tend to be more conjugated. This is because the acetylene linker, unlike a vinylene linker, cannot twist out of plane.

This thesis will predominantly focus on dipolar and quadrupolar molecules for the synthetic and two-photon polymerisation tests. Examples of octupolar molecules will also be synthesised, but factors including synthetic difficulty and solubility become dominant factors in their applicability for the work carried out.

1.4. Laser micromachining

There is a growing demand for 3D micro/nano-fabrication techniques for a variety of industries and applications including MEMS, microfluidics, biomedical applications and many applications in photonics. Several approaches have been used in creating 3D microstructures, including (1) modified lithographic techniques (such as gray-scale lithography and moving mask lithography); (2) direct laser writing processes using multiphoton polymerisation, laser induced chemical vapour deposition and laser ablation; and (3) focused ion beam processing. Modified lithographic processes
have been employed very successfully over many years in the mass production and large-scale patterning applications but their ability to create 3D microstructures is insufficient for many emergent technologies. Presently focused ion-beam processes provide excellent resolution on the order of tens of nanometres but the slow throughput of such techniques limits their potential for mass production of micro/nano-devices. Multiphoton fabrication is an attractive tool for 3D micro/nano-fabrication for several reasons: (1) it can generate any kind of 3D structure based on computer generated models, (2) resolutions below 100 nm are possible, (3) the procedure is relatively fast and easy to process, (4) fabricated structures can be integrated into larger more complex structures and (5) resolutions below the diffraction limit of the laser wavelength can be achieved.

1.4.1 Two-photon polymerisation

Since its inception in 1997, TPP has been under intense investigation for the fabrication of 3D micro/nano-devices.\textsuperscript{16} TPP allows for such fabrication due to the nature of the 2PA process, which allows for polymerisation to be confined within the focal point of a femtosecond (fs) pulsed laser, where photon density is sufficient to drive the two-photon excitation of a PI which leads to monomer polymerisation.\textsuperscript{115} Currently, fs-pulsed Ti:Sapphire lasers are most widely employed for TPP. There are several reasons for this. Firstly, they produce ultra-high peak powers for a given average power with a very short pulse width of approximately 100 fs or less. Secondly, Ti:Sapphire lasers operate in the NIR region, which is close to the half-wavelength (laser $\lambda/2 = \lambda_{\text{max}}$ of PI/resin) of many UV-curable resins used in TPP. Finally, many photopolymers are transparent at 800 nm thus reducing scattering effects.\textsuperscript{23,24}

For TPP, there are two crucial components in the prepolymer resin: the PI and the monomers. Other components can also be introduced to the mixture, for example, solvents which assist casting, polymerisation inhibitors to stabilise the resin and influence feature size, and other additives like dye molecules (e.g. Azo dyes for photoswitching properties).\textsuperscript{12} A schematic of the experimental setup which is commonly employed for TPP processes is shown in Figure 13. The excitation source is mode-locked fs-pulsed Ti:Sapphire laser 800 nm. The repetition rates for such a laser is on the order of 80 MHz and the average power can range from a hundred milliwatts (mW) to more than a watt (W). A Faraday
rotator is often used in the beam path to prevent interference from reflected light and dispersion of laser light can be compensated for by a pair of prisms to obtain the shortest possible pulses at the sample medium. Light intensity can be controlled by a device such as an acoustooptics modulator, an electrooptic modulator or a shutter. A microscope is used as a convenient method to position or switch samples rapidly. The sample is placed upon a computer-controlled stage with can be moved in 3D relative to the focal point of the laser or alternatively scanning mirrors can be employed. The transmitted light is used to view the sample with a charge-coupled device (CCD) camera and a computer screen, which allows for real-time monitoring of the sample and process. With such a set-up, it is possible to fabricate voxel structures of less than 100 nm with 800 nm laser light using the TPP process in a variety of materials.22,116,117

![Figure 13](image-url)

**Figure 13** – The TPP setup we employed for our polymerisation work outlined in Chapter 5. The system is based at the Photon Factory, University of Auckland.

### 1.4.2 Photoinitiators

Photopolymerisation is a light-induced reaction which converts liquid or gel monomers or oligomers into a solid polymer structure. This reaction often requires the use of a PI which is a light-sensitive molecule that can produce a radical or cationic species upon irradiation of
a suitable wavelength of light. PIs are commonly divided into two groups depending on the active species they produce; radicals or cations. Radical PIs have commonly been employed for free-radical polymerisation of acrylates and vinyl ethers. Cationic PIs were introduced later and are usually used in ring-opening polymerisations of epoxides and vinyl ethers. Typically, commercially available UV PIs such as those shown in Figure 14 were often used for early demonstrations of TPP. These types of molecules are simple to synthesise, highly soluble in a variety of monomers, exhibit high linear absorption in the UV-region, and possess high quantum radical yields and high initiation velocities.

For applications like TPP, a laser is focused into the monomer resin mixture, the PI will absorb two photons and produce a radical or cationic species and initiate polymerisation. As a 2PA PIs absorption is proportional to the square of the light intensity \( (I^2) \), polymerisation is confined within the focal point of the laser allowing for micro/nano-scale features. Several research groups have designed, synthesised and tested PIs for TPP, and these often exhibit high \( \delta_{2PA} \) which allows for low lasing powers to be used. Extensive work on the design of TPA chromophores based on the structure-activity relationships has been done in the past.\(^\text{46,118,119}\) However, many of these studies have focused on maximising \( \delta_{2PA} \) but not necessarily for the use in TPP so many TPA chromophores are likely to be ineffective for such an application.

Efficient PIs must balance a number of key parameters to be effective; a high value of \( \delta_{2PA} \), low \( \phi_F \), a high initiation velocity and solubility in the prepolymer resin.\(^\text{119}\) Early research focused on increasing \( \delta_{2PA} \), as many commercial PIs had relatively small \( \delta_{2PA} \) (<20 GM) and
required high lasing powers and exposure times, both of which adversely affect resolution and structure quality. Therefore, a well-designed molecule should have a much greater $\delta_{2PA}$ enabling the use of lower-power and less costly pulsed laser systems. However, a large $\delta_{2PA}$ doesn’t necessarily equate to an effective PI as a multitude of factors affect the polymerisation process.

1.4.3 Radical polymerisation mechanisms

Radical PIs can produce radical species by a number of routes: photoscission reactions, inter-molecular hydrogen abstraction, intra-molecular Y hydrogen abstraction, electron transfer and H-atom abstraction by the excited triplet state. Of these, photoscission is the most common pathway in the production of initiating species; an example of which is shown in Figure 15. Radical PIs are classified as Type I or Type II; a Type I PI will undergo a unimolecular cleavage upon irradiation to produce radical species. A Type II PI will undergo a bimolecular reaction upon irradiation and the resultant excited triplet state of the PI interacts with a second molecule (a co-initiator) to generate radicals to begin the polymerisation process. Type I PIs can also be utilised as Type II PIs by selecting a suitable co-initiator.

![Figure 15 - The formation of free radicals by α-scission from Darocur 1173.](image)

Free-radical polymerisation is a chain reaction in which the radical species reacts with a monomer molecule and regenerates the active species at the chain end. Free radical polymerisation is thought to consist of at least three kinds of reactions:
• The first step is the initiation step where two photons are absorbed by the PI (I) to form (I*) and in the presence of a monomer form the active species R• (step 1a).

• In the propagation step, the initiator fragment (R•) reacts with a monomer molecule (M) to form the first species that is capable of being polymerised. Monomers continue to build up in this manner forming macroradicals (RMM ....) (Step 1b).

• The final step is the termination during which the radical is deactivated and the final polymer chains are formed (RM\textsubscript{n+m}R). This step usually involves the reaction between two polymer species (RM\textsubscript{n} + RM\textsubscript{m}) and proceeds by two mechanisms; combination or disproportionation leading to the formation of one or two polymer chains respectively (Step 1c).

In addition, to the mechanisms mentioned above, other reactions such as chain transfer and chain inhibition can take place which complicates the reaction pathway. Factors such as oxygen inhibition by oxygen scavenging or promoting by forming peroxy radicals which can also be an important issue.$^{127}$

1.4.4 Alpha-scission

Scission at the α-carbon of an alkyl ketone, often called the Norrish Type I reaction, is the most common radical production mechanism.$^{12,128}$ Light is absorbed by the PI to form an excited triplet state that produces two active radical species via cleavage of the C=O-alkyl bond.$^{129}$ For maximum efficiency, the alkyl group needs to be fully substituted thereby giving more stable intermediates. This process is outlined more specifically for the commercial Type I radical PI, Darocur 1173 in Figure 15.
1.4.5 Beta-scission

The process of β-scission occurs where there is a weak bond from the α-carbon to a hetero atom, commonly Cl, S, N, etc. A weak bond in the β-position makes it susceptible to cleavage due to low triplet state bond energies of the carbon-hetero atom bond. The formed radicals as with α-scission are both active species. Furthermore, if a C-Cl bond is β-cleaved the chlorine radical can abstract a hydrogen atom from a donor to produce HCl, the formation of acid can be detrimental to the final structure and a thus knowledge of radical production is necessary when selecting PIs.

1.4.6 Two-photon induced polymerisation mechanism

The mechanism for TPP is shown in Figure 17: a PI is excited by two-photons to the singlet excited state leading to intersystem crossing to the triplet state, this triplet state is believed to be responsible for the activity of two-photon PIs. Hydrogen atom abstraction from the triplet excited state to a monomer initiates polymerisation, due to the intrinsic nature of 2PA this process only occurs within the focal point of the laser, where photon density is sufficient to drive the initial two-photon transition.
Perry et al. showed that a class of D-π-D chromophores (Figure 18) undergo photoinduced electron transfer to initiate polymerisation, and the chromophores exhibited negative ΔG values, indicating that photoinduced electron transfer is energetically favourable. Although, several chromophores exhibited Gibbs free energy (ΔG) ΔG > 0 they were found to still initiate polymerisation of acrylates.\textsuperscript{133} This intramolecular photoinduced electron transfer is also thought to be the dominant process for initiation in related chromophores including D-π-A and A-π-A type systems.\textsuperscript{12,24,130,134,135}

![Molecular structures of PIs and monomers synthesised by Perry and Marder et al.\textsuperscript{131}](image)

The mechanism for TPP follows that of any UV initiated polymerisation reaction (viz. Figure 17), and the production of active species is dependent on the type of PI present. The use of 2PA rather than heat or UV has distinct advantages such as solvent elimination, high reaction rates at room temperature, smaller feature sizes, polymerisation inside the resin and much greater degree of control over the polymerisation all of which allow for 3D structures to be created in a bottom-up process. This is due to the use of an 800 nm fs-pulsed laser, the material is
1.4.7 Type I photo initiators

As described in Figure 17, Type I PIs undergo bond cleavage from the excited triplet state to produce radical species which are capable of initiating polymerisation in an appropriate medium. There are many examples of commercial Type I PIs that are available and most are based on aromatic carbonyl compounds like Irgacure 184 (Figure 14) however, many more commercially available PIs are currently available for a variety of materials.\textsuperscript{122} Sun et al. used commercially available 2-benzyl-2-dimethylamino-4-morpholinobutyrophenone (BDMB) and 1-hydroxy-cyclohexyl-phenyl-ketone (HCAP) Type I PIs in the fabrication of a number of novel structures using a commercial urethane acrylate monomer/oligomer.

The acylphosphine oxide PI known as Lucirin TPO-L (Figure 19) has been extensively used in TPP by a number of research groups.\textsuperscript{136-139} The UV/Vis absorption of Lucirin TPO-L arises from the $n \rightarrow \pi^*$ transition. Upon excitation, the molecule photocleaves to form carbonyl and phosphinoyl radicals resulting in the initiation of the polymerisation chain reaction. Although the $\delta_{2PA}$ this compound is very small <1.2 GM, photopolymerisation with this PI is possible with relatively low power using a Ti:sapphire laser system.\textsuperscript{140} Furthermore, its high radical yield, highly reactive radical species and excellent solubility compensate for its low $\delta_{2PA}$. A distinct advantage is that at room temperature it is a liquid and can be easily mixed - and at high weight percentages - with monomer or oligomer resins.

\textbf{Figure 19} – The acylphosphine oxide PI Lucirin® TPO-L, this commercially available PI is commonly employed for TPP applications.

\textit{Watanabe et al.} designed custom D-\pi-A-\pi-D PIs with a cyano-substituted imino core and which exhibited high $\delta_{2PA}$ and which could initiate TPP using a fs-pulsed Ti:Sapphire laser. They also showed that a high $\delta_{2PA}$ alone is not always sufficient to initiate rapid polymerisation.\textsuperscript{141} \textit{Liska et al.} synthesised a series of benzylidene ketone-based two-photon PIs containing dialkylamino groups as donors and double bonds as conjugation bridges. The molecule (2E,5E)-2,5-bis(4-(dimethylamino)benzylidene)cyclopentanone had a $\delta_{2PA}$ of 466
GM as measured by z-scan at 800 nm. Though this molecule had the highest $\delta_{2PA}$ value, the compound $(2E,6E)$-2,6-bis(4-(dimethylamino)benzylidene)-4-methylcyclohexanone, with a relatively modest $\delta_{2PA}$ of 191 GM, was shown to be the most efficient for initiating polymerisation in TPP experiments. Writing speeds as high as 80 mm/s were obtained for the microfabrication of 3D structures using an acrylate based formulation and $(2E,6E)$-2,6-bis(4-(dimethylamino)benzylidene)-4-methylcyclohexanone as the PI. This further reinforces that other factors are important for design considerations and maximising $\delta_{2PA}$ alone will not necessarily translate into an efficient PI. Perry et al. synthesised D-π-D molecules with $\delta_{2PA}$ ranging from 210 GM to 1250 GM (Figure 18). The work showed that symmetric, donor substituted chromophores designed with large $\delta_{2PA}$ and strong D groups can be effective CT molecules to be used in acrylate polymerisation reactions using TPP.

1.4.8 Type II photoinitiators

Type II PIs have been extensively studied for use in UV-initiated free radical polymerisations but also for TPP. Type II PIs are used with a co-initiator, usually an amine species; however ethers and thiols have also been investigated. The mechanism involves a triplet excited state forming an exciplex and removing a $\alpha$-hydrogen from a hydrogen donor (viz co-initiator), which is then followed by electron transfer to produce initiating radicals (Figure 20). The bimolecular photoreaction often leads to the formation of an initiating radical and a second less efficient initiating radical.

![Figure 20](image)

Figure 20 – Reaction mechanism for Type II PIs for free radical polymerisation. Reproduced from reference 148.

Typically Type II PIs are typically based on benzophenone, camphorquinone, xanthene and thioxanthone derivatives which absorb strongly in the UV region, but these molecules often exhibit low $\delta_{2PA}$ activities and there are opportunities for optimisation in this area.
Belfield et al. used an commercially available dye (5,7-diiodo-3-butoxy-6-fluorone, H-Nu 470) in the presence of an aryl amine and a (meth)acrylate monomer, and with a 775 nm fs pulsed Ti:Sapphire laser were able to produce fine structural features. This demonstrates the viability of commercial dyes to be used for this technique. In another example, Campagnola et al. used a variety of xanthene-based chromophores in combination with the co-initiator triethanolamine for the radical polymerisation of acrylates, acrylamides and proteins.\textsuperscript{149,150} The chromophores exhibit $\delta_{2PA}$ values of around 10 GM at 800 nm, and 100 mW fs pulsed Ti:Sapphire laser system was used. Furthermore, using 9-fluorenone-2-carboxylic acid with triethanolamine and with a 780 nm excitation wavelength they were able to produce structures via a three-photon polymerisation process. The maximum single-photon absorption was at 260 nm, and this is one of the first demonstrated uses of three-photon polymerisation.\textsuperscript{150} Li et al. used the coumarin-based PI 7-diethylamino-3-(2′ benzimidazolyl)coumarin (DEDC) and the coinitiator diphenyliodonium hexafluorophosphate (DIHP) for the Type II radical polymerisation of methyl methacrylate.\textsuperscript{151} Watanabe et al. also used this iodonium coinitiator with their own cyano-substituted imino-backbone chromophore and the tertiary amine 6-diisopropyl-$N,N$-dimethylaniline (DDA) as a coinitiator to fabricate structures with acrylates in dioxane.\textsuperscript{152} In a further innovation, Kumbaraci et al. syntheses a naphthodioxinone-1,3-benzodioxole as a photochemically masked one-component type II PI for free radical polymerisation which required no further hydrogen donors.\textsuperscript{153} Upon irradiation, the PI releases 5-benzoyl-1,3-benzodioxole possessing both benzophenone and 1,3-dioxole groups which act as a light absorbing and hydrogen donating sites, respectively. Furthermore, photoexcitation of benzophenone is followed by hydrogen abstraction, thereby generating radicals capable of initiating radical polymerisation.

Although a relatively large number of commercial radical PIs are available, which brings the benefits of accessibility and well-known processing parameters, such compounds are not always adequate for niche applications and emerging technologies. This has driven a large research effort into the optimisation of such radical PIs for a wide variety of applications. A large body of research has been conducted into optimising the crucial structural properties necessary to create effective radical PIs for use in the field of TPP.
1.4.9 Cationic photoinitiators

The development of cationic PIs for TPP has also been investigated in some detail. A cationic PI works by a generation of a strong Brønsted acid upon excitation that is capable of initiating photopolymerisation, by for example, ring-opening of epoxides. As this process is catalytic each photoacid generator (PAG) molecule can initiate multiple polymerisation reactions and is regenerated. Research into cationic photoinitiated polymerisations of epoxides, vinyl ethers and methylenedioxyxolanes has been growing due to the oxygen insensitivity of the cationic polymerisation process.\(^{154}\) Irradiation of the PI generates a low concentration of strong acid that protonates the epoxides on the oligomer. The protonated oxonium ions will then react with neutral epoxides, and subsequent heating of the polymer activates the cross-linking and regenerates the catalyst.\(^{155}\) Diaryliodonium and triaryl sulfonium salts are two typical classes of commercial cationic PIs that are used in TPP. Commercially available triarylsulphonium A (CD-1010, Sartomer) and diaryliodonium B (CD1012, Sartomer) salts were found to initiate the polymerization of multifunctional epoxide and vinyl ether monomers (Figure 21).\(^{156}\) Other examples of triarylsulphonium salts (\(\text{Ar}_3\text{S}^\text{+}\text{MX}\)) with complex metal halide anions such as \(\text{BF}_4^-, \text{AsF}_4^-, \text{PF}_6^-,\) and \(\text{SbF}_6^-\) are known and represent a new class of highly efficient PIs for cationic polymerization.\(^{157}\) Kubisa and Penczek et al. reviewed the mechanisms associated with cationic polymerisation and provide an in-depth analysis.\(^{158}\)

![Figure 21](image)

**Figure 21** - A. The cationic triarylsulphonium PI (CD-1010, Sartomer); B. Diaryliodonium PI (CD-1012, Sartomer)

Commercial PAG systems are highly sensitive to UV irradiation but, are far from optimised for two-photon excitation because of their small \(\delta_{2PA}\).\(^{13}\) To address this, Zhou et al. created a hybrid 2PA chromophore molecule using a bis-styrylbenzene conjugated bridge linked
directly to a dialkylsulfonium group (Figure 22). The $\delta_{2PA}$ for this molecule was estimated to be 690 GM at 710 nm as measured by the TPEF method, and this value is orders of magnitude higher than currently available PAGs. The PAG BSB-S$_2$ in Figure 22 was employed in a positive-tone photoresist. The resin used was an acrylate polymer system containing acid-cleavable tetrahydropropanyl (THP) ester groups which give carboxylic groups upon cleavage. Exposure of the resin activates the photoacid, which after a post exposure bake rendered the polymer soluble in aqueous base.

![2PA-absorber](image)

**Figure 22** - A two-photon photo-acid generator based on the linking of a two-photon absorbing chromophore and a photocleavable group.

### 1.5. Materials for two-photon polymerisation

Much of the initial work done in the field used commercially available monomer materials such as urethanes, acrylates and epoxides in the fabrication of 3D structures. Recently TPP of more exotic materials (OROMCERS ® (Organically Modified Ceramics; a Trademark of the Fraunhofer-Gesellschaft Zur Förderung der Angewandten Forschung e.V., Munich, Germany) have been demonstrated.

The resins most commonly used for TPP act as negative-tone photoresists (Figure 23). For negative-tone photoresists, polymerisation occurs in the regions which are exposed leaving unexposed material to be removed.
An example of a commonly used commercial negative-tone photoresist is SU-8. The main components of SU-8 are a Bisphenol A Novolak epoxy oligomer (EPONR SU-8 resin, Shell Chemical) and up to 10 wt% triarylsulphonium hexafluoroantimonate salt (CYRACURER UVI, Union Carbide) PAG. Positive-tone photoresists whereby unexposed regions are hardened have also been demonstrated, however their use is less common than negative-tone photoresists (Figure 23). AZ9262 is a commercially available positive-tone novolac-type photoresist from Hoechst. This material is made up of two diazonaphthoquinone (DNQ) photoactive compounds and a mixture of two cresol novolacs.

1.5.1 Radical polymerisation – acrylates

Acrylates exhibit several properties which make them attractive for use in TPP applications. A wide variety of acrylate monomers and their co-polymers are commercially available, they are transparent at visible and near-IR wavelengths - which allows for laser systems in these wavelength regions to be used, and they are easily processed via spin coating or drop casting. Furthermore, the non-polymerised components are easily removed by common solvents such as ethanol and due to their highly cross-linked structures they resist swelling and shrinkage during the development steps.
One of the most well-known structures made by TPP are the microbull structures fabricated by Kawata et al. in 2001, as shown in Figure 24.\textsuperscript{164} The 10 µm long and 7 µm bulls showed the potential for high resolutions at the microscale, and each is roughly the size of a red blood cell. The work made use of the commercially available resin (SCR500; JSR, Japan) which consisted of urethane acrylate monomers and oligomers as well as PIs. This material was used due to its optical transparency to infrared lasers, allowing for deep penetration through the material.

A downside to acrylic based resins are that in the pure form they are liquid, making spin casting or dip coating difficult, however samples can be prepared by placing a drop onto a glass cover. Though for TPP, this can be insufficient in controlling the film thickness and it allows for mobility in the un-polymerised material. A solution to this is to blend polymer binders into the sample along with an easily removed solvent.

\textbf{Figure 24} – A Ti:Sapphire laser operating in mode-lock at 76MHz and 780nm wavelength with a 150-femtosecond pulse width was used as an exposure source. a-c, The bull sculpture was produced by raster scanning; the process took 180 min. d-f, the surface of the bull was defined by TPP and was then fully solidified by illumination under a mercury lamp, this reduced the TPP-scanning time to 13 mins.\textsuperscript{164}
Literature examples have made use of 70% multifunctional acrylate monomer (SR9008:SR368, 1:1, Sartomer Co. Ltd.) and 29.9% poly-(styrene-co-acrylonitrile) along with 0.1% of a custom PI. Several other examples of this kind of blending of monomers, binders and PIs have been used to demonstrate TPP in the lab. In some cases the samples are dissolved in a suitable solvent (chloroform, dioxane etc.) and the constituent parts are blended and cast into films. The solvent is then allowed to evaporate leaving a rigid film which can be used to fabricate micro structures without fear of reflow in the sample; however the use of solvents can increase the preparation time considerably.

1.5.2 Cationic polymerisation - epoxides

An example of a commonly used commercial negative-tone photoresist is SU-8. SU-8 is an epoxy resin material containing 8 epoxy groups in each monomer unit, it makes use of a PAG triaryl sulfonium salt as the cationic PI. Irradiation from a laser source generates a strong acid which acts as a catalyst in the cross-linking process. Heating of the polymer activates the cross-linking and regenerates the acid catalyst. The first SU-8 products were introduced in 1996 by MicroChem. Now the resist is available in a wide range of formulations to give varying film thicknesses ranging from 2 - 300 µm or using a multicoating process to give films of up to 3 mm. Due to the number of epoxy groups in SU-8 the final products are highly cross-linked making them inert to solvents, acids and bases. This also results in high thermal and mechanical stability in the processed materials. Because of its commercial availability and sought-after thermal and chemical properties, SU-8 is an attractive choice for cationic polymerisation.

Even so SU-8 requires a number of processing steps involving spin-coating the photoresists, soft baking, masked irradiation and a final developmental baking step. However, Misawa et al. showed that the post-exposure baking can be eliminated because of the heating during exposure. The resulting features are roughly twice the resolution as those that underwent a post-exposure treatment. Another commercial epoxy based resin that has been used but less extensively than SU-8 in TPP is SCR-701 (JRC). Originally developed for microstereolithography it has since been used in the creation of microgears and nanotweezers by Maruo et al.
1.5.3 Sol-Gel hybrid and ORMOCER materials

Although TPP began with the use of more conventional polymer materials like acrylates and epoxy resins, over recent years research has begun to focus on photosensitive sol-gel hybrid materials.\(^{169}\) In order to combine the advantageous properties of organic and inorganic materials a wide range of strategies have been reported to produce these organic-inorganic materials. These can range from physically blending materials, multi-step chemical synthesis and one step synthesis.\(^{170,171}\) Such materials are often referred to as ORMOCER\(^{\circledR}\)s. ORMOCER\(^{\circledR}\) materials have been researched due to their wide range of physical and chemical properties which arise from the synergistic properties resulting from the organic-inorganic hybrid structure. The materials can comprise a combination of properties of organic polymers such as toughness, functionalisation, and processing at low temperatures with those of glass-like inorganic materials such as hardness, chemical and thermal stability and optical transparency (Figure 25).\(^{172}\)

Figure 25 - Multifunctional precursors for ORMOCER\(^{\circledR}\) synthesis and their resulting influence on the materials properties. (Reprinted from Two-photon polymerization of inorganic-organic hybrid polymers as scalable technology using ultra-short laser pulses.)\(^{173}\)

ORMOCER\(^{\circledR}\)s consists of an inorganic (-O-Si-O-) backbone, which can be functionalised with organic groups such as acrylates and or epoxides, the organic side chains can cross-link the resin into a durable hybrid material. Commercially available ORMOCER\(^{\circledR}\)s have been used extensively for TPP for the creation of a number of different structures such as photonic
crystals and other optical devices. The versatility of the sol-gel process has allowed research groups to chemically modify the material and estimate the mechanical and optical properties from such modifications (Figure 25). Farsari (Foundation for research and technology, FORTH) and Chichkov (Nanotechnology department, Laser Zentrum Hannover (LZH)) created a novel zirconium/silicon hybrid sol-gel at their labs and used it for the TPP of a woodpile photonic crystal. An important feature of this particular material is it does not shrink during photopolymerisation unlike many commercial ORMOCER®s meaning pre-compensation techniques are not required at the design stage.

Uhlig et al. used ORMOCER® materials to construct optical waveguide structures for use in large-area panels. Houbertz et al. used ORMOCER® materials for electro-optical applications related to large-area panels using TPP as a technique for the creation of waveguide structures. In 2008 they also used an acrylate-modified inorganic-organic hybrid material and a TPP process to create optical interconnects in printed circuit boards. Tian et al. used the newly developed material SZ2080 to generate woodpile photonic crystals. The material was used due to its negligible shrinking after TPP. SZ2080 is a 20:80 Zirconium-silicon sol-gel and in this case was used in conjunction with the PI 4, 4’-bis(diethylaminobenzophenone). Woods et al. used silanol terminated dimethyl diphenyl polysiloxane (wt. % OH 0.7-1.3, mole % diphenysiloxane 2.5-3.5), acryloxymethyl trimethoxy silane and dioctyl tin dilaurate with the co-initiator Irgacure 379. The specific two-photon PI 1,5-bis(4-dimethylamino)phenylpenta-1,4-diyn-3-one (N-DPD) was also utilised. This silanol terminated polysiloxane was functionalised with acrylate functional groups and TPP was employed to fabricate 3D optical waveguides.

Although ORMOCER® and other silicate based materials have allowed for the fabrication of a number of high-resolution 3D structures with good optical properties. The versatility of the sol-gel chemistry process allows for multiple metal alkoxides to be used in the co-polymerisation giving a more controlled fine tuning of properties. Duan et al. used Ti⁴⁺ metal ions as a dopant in the commercial photopolymerisable urethane acrylate resin, SCR500 and used 2,2-diethoxy-acetophenone as the PI. They investigated the optical and photopolymerisation properties of the material for applications in photonic structures. Several groups have used this approach with metal ions and metal nanoparticles to optimise properties for use in 3D structure fabrication. Tribuzi et al. fabricated microstructures with gold nanoparticles through an indirect doping process so as
not to interfere with the TPP process. The indirect doping of gold nanoparticles into the polymeric microstructures consisted of using a mixture of acrylate monomers with an aqueous solution of HAuCl$_4$ and the effect of the nanoparticles was shown to be negligible to the rate of polymerisation. Such microstructures exhibit a strong emission, arising from fluorescence by the gold nanoparticles.

1.6. Spatial resolution in two-photon polymerisation

A hugely important aspect of TPP is the size and shape of the volume elements (voxels) created during TPP and accurate measurement of such features is a considerable challenge. The resolution of fabricated microstructures is determined by the size of these voxels. Theoretically the highest resolution possible by a focused laser beam is given by Abbe’s diffraction limit (Equation 2), where $\lambda$ is the laser wavelength and NA is the numerical aperture of the focusing objective.

$$\text{Diffraction limit} = \frac{0.5\lambda}{NA}$$

Equation 2 – Abbe’s diffraction limit.

However, due to the intrinsic properties of 2PA PIs, resolutions below the diffraction limit can be achieved by control of the laser pulse energy, and the number of applied pulses, as explained below. Theoretical studies determining voxel size in TPP have been conducted. The voxel shape is in part determined by the point-spread function (PSF) of the light intensity near the focus. The probability for 2PA is proportional to the intensity squared ($I^2$), which narrows the PSF of the beam near the focal point so that it becomes smaller than the diffraction limit. However, this alone does not explain the decreasing voxel size. Furthermore, a number of key factors affect voxel growth. These include diffusion of PIs/cointiators, dissolved oxygen in the sample, trace solvent, the radical quantum yield of the PIs and viscosity of the resin. The optical system used is also important. Factors that need to be considered include the stability of the laser source, the accuracy of the positioning system, the pulse width and the pulse duration.
A number of theoretical and experimental studies on the size, shape and analysis of voxels during TPP have been conducted in the last decade.193,194 These studies have shown there to be two different types of growth that determine the shapes of voxels: focal spot duplication and voxel growth.116,192 In focal spot duplication, voxels initially take on focal spot shapes that are defined by $I^2$ relative to the threshold level. In this mode voxel growth occurs in all dimensions but becomes especially large with increasing laser power. In voxel growth, the voxel shape is determined by the exposure time. Immediately after exposure the produced voxels will grow due to the interactions of active monomers interacting with other monomers, i.e. at the point where radical chain reactions occurs.116

For both mechanisms, the combination of low laser power and an appropriate exposure time is important for the determination of a voxels aspect ratio.24 A regime of minimum power and minimum exposure time (MPMT) is important for reducing voxel size. The MPMT regime consists of two steps. Firstly, the laser power is reduced and then exposure time is decreased to reduce voxel growth.195 As radicals are produced upon exposure, quenching is a competing effect and is usually considered detrimental to the voxel growth process. In TPP, the presence of quenching species such as oxygen can be used to reduce the diffraction limit and produce very high-resolution structures. This can be done by modifying the light at the focal point to produce radicals, which overcome the quenching species and initiate polymerisation in the region where the exposure energy is sufficiently high.

As the post-fabrication steps often require solvent washing or post-baking to remove or solidify the materials, shrinkage can occur. If computer-aided-design (CAD) has been used it can lead to feature sizes smaller than were intended, and to prevent this, the CAD design can precompensate for this shrinkage.196 Consequently, by considering the shrinkage rate, any changes to the anticipated shape and any size disparities can be corrected at the design stage.

Since TPP was first demonstrated to create spiral structures with diameters of 6.0 µm, spiral widths of 1.3 µm and an axial pitches of 10.3 µm the resolution of the TPP process has been rapidly increasing and voxel sizes in the nanometre range are now possible.16

In 2007, Haske et al. demonstrated woodpile photonic crystal structures with line widths of 80 nm for long, free-spanning lines and 65 nm line widths in a blend of acrylate monomers.22 Emons et al. used a zinc-hybrid sol-gel material to produce structures with a
resolution of as low as 45 nm.\textsuperscript{197} By varying material type, laser pulse length and energy they achieved the maximum resolution possible with the materials and laser system used but higher resolution structures are believed to be possible with the use of other techniques. These more innovative techniques include multiphoton polymerisations that are based on stimulated-emission-depletion (STED) fluorescence microscopy, a technique developed by Hell and Wichmann \textit{et al.}\textsuperscript{198,199} They include single-photon excitation,\textsuperscript{200} a one-colour scheme,\textsuperscript{201} a multiphoton two-colour scheme,\textsuperscript{202,203} and diffusion-assisted STED.\textsuperscript{204} In STED, fluorescent molecules are excited firstly by a short laser pulse then a second laser pulse, which is of a substantially longer wavelength is used to de-excite the molecules through stimulated emission. This depletion must occur after the vibrational relaxation is complete in the excited state but before fluorescence has occurred. Spatial phase shaping of the depletion beam causes de-excitation to occur everywhere except in the region at the centre of the original focal volume. The size of the region depends on the intensity of the depletion beam and the corresponding degree of saturation of stimulated emission. The fluorescence can be localised within an area much smaller than the excitation wavelength.\textsuperscript{161,181} Resolutions of 5.6 nm using visible light and nitrogen vacancy centres in diamond have been reported by Hell \textit{et al.}\textsuperscript{205}

In theory such a technique should be applicable to TPP. For example, Li \textit{et al.} fabricated 3D structures to a resolution down to 40 nm using a technique inspired by STED called resolution augmentation through photoinduced deactivation (RAPID) lithography.\textsuperscript{201} In RAPID, lithography using one laser beam is used to initiate photopolymerisation in a negative-tone photoresist and a second laser beam is used to deactivate the PI, preventing photopolymerisation occurring. Multiphoton absorption of pulsed 800 nm light is used to initiate the cross-linking in the polymer photoresist and 1PA of continuous-wave (CW) 800 nm light is used simultaneously to deactivate the photopolymerisation. Resolutions of 100 nm and below have been readily achieved with a number of material types and fabrication techniques, and such developments are likely to continue until a physical minimum feature size is reached.
1.7. Applications of two-photon polymerisation

Although TPP is at a relatively early stage in its development it has potential applications in a number of fields including photonics, MEMS and medical applications. The majority of the work has been limited to research lab demonstrations of its potential and thus far has not been widely adopted by the industry as a means of micro/nano-scale device creation.

1.7.1 Photonics

A major area of research for TPP and the 3D structures it can create has been in the area of photonics and optics. TPP allows for the miniaturisation of standard optical components like lenses, waveguides and arrays of them, and also in the fabrication of hybrid refractive-diffractive components containing both elements. The creation of Bragg Grating structures, optical waveguides and optical circuits has also been demonstrated in a variety of polymeric materials.

Since the concept of 3D photonic crystal structures was introduced in 1987 they have also been the subject of intense research. Photonic crystals with a fully 3D bandgap in the visible range remain a challenge and microfabrication with high refractive index materials is required. The first photonic crystal fabricated by TPP was in 1999 by Misawa et al. and Cumpston et al., with both groups creating log stack structures. Cumpston et al. measured a photonic band gap near 4.0 µm and the gap was found to be red-shifted as the lattice spacing increased. Wegener et al. demonstrated the use of SU-8 for the fabrication of a functional photonic crystal at telecommunication wavelengths. Due to shrinkage in SU-8, the photonic crystal required large supporting walls.

The group also fabricated 3D woodpile photonic crystals, where they altered elementary cells of the periodic structure to create defects. They also produced a 3D-2D-3D photonic crystal, the first of its kind in 2006 (Figure 26).
Figure 26 - 3D photonic crystal heterostructures comprising waveguide structure. Reproduced from Wegener (2006).  

More complex photonic crystal geometries have been demonstrated such as a colloidal photonic crystal,\textsuperscript{220} a diamond unit cell structure,\textsuperscript{221} a spiral unit cell,\textsuperscript{222,223} a slanted pore structure,\textsuperscript{224} and quasicrystalline lattice.\textsuperscript{225} The above demonstrations all have defined photonic band gaps between the polymer material and the surrounding medium, the change in transmission in the band gap, however, is typically less than 50%.\textsuperscript{12} To create a full-stop band gap structure the incorporation of much higher refractive index materials will be needed. An approach to solve this problem is the incorporation of high refractive index materials into the structures like metal oxides. Farsari et al. reported the creation of a metallic 3D photonic crystal with bandgaps in the NIR to optical region. They prepared woodpile structures and metallised them with silver, and the structures had 900 and 600 nm periodicity and a resolution below 100 nm. They used sol-gel chemistry, direct laser writing and electroless plating metallisation techniques allowing them to create the desired structure.\textsuperscript{106} The group also reported 3D structuring and metallisation of a zirconium-based organic-inorganic photosensitive material doped with metal-binding tertiary amine moieties.\textsuperscript{226} The group fabricated a functional photonic crystal, where they made a crystal structure made of a photosensitive sol-gel material that contained the nonlinear optical chromophore Disperse Red 1, an azo dye chromophore.\textsuperscript{227} They used this material to create 3D photonic crystals with band stops in the NIR region. The optical properties of such a crystal can be controlled by the materials optical nonlinearity and the photochemical switching capabilities of the azo dye chromophore.\textsuperscript{228}
Kawata et al. used SCR500 resin doped with titanium (IV) ethoxide to create structures with an improved band gap.\textsuperscript{185} Prasad et al. fabricated highly conductive gold nanostructures by simultaneous TPP and photoreduction within a polymer matrix. The nanostructures were directly written in a gold-precursor-doped photoresist using a femtosecond laser source. A 2PA dye induced simultaneous reduction of the gold in the resin and the polymerisation of the negative photoresist. This gave gold-nanoparticle-doped polymeric lines which exhibit both plasmonic effects and conductivity due to the concentration of gold nanoparticles present.\textsuperscript{229}

Jung et al. fabricated a 15 nm polymer tip probe on an optical fibre via TPP and O\textsubscript{2} plasma ashing.\textsuperscript{230} They used the resin SCR500 to fabricate the conical polymer tip with a 125 nm curvature radius, then the tip was sharpened with an O\textsubscript{2} plasma ashing process and, as a result, the apex radius of curvature was reduced down to 15 nm. In order to evaluate the performance of the 15 nm curvature radius polymer tip, a 30 nm thick gold layer with holes of 250 nm radius and a single layer of polystyrene beads with a 350 nm radius were imaged using a tuning-fork-based atomic force microscope. The images obtained with the 15 nm tip were improved in depth and width compared with the 125 nm tip due to reductions of imaging artefacts.

1.7.2 Microelectromechanical systems (MEMS)

TPP has the potential for the 3D fabrication of MEMS due to its resolution, accuracy and range of materials that can be fabricated. Structures such as microgears, nanotweezers, springs and cantilevers are some of the possible items that can be created. Maruo et al. have demonstrated the fabrication of optically driven micromachines (Figure 27).\textsuperscript{168}
Figure 27 - Sequential images taken while driving the optically driven micropump. The micropump was made from an epoxy-type photopolymer (D-MEC Co., Ltd., SCR-701) with a Ti:Saph 752 nm laser operating at 150 μW with a writing speed of 30 μM/s. Image reprinted from Optically driven micropump produced by three-dimensional two-photon microfabrication.²³¹

They created microturbines, microgears and micromanipulator arms and used a laser system to optically move the fabricated devices. The group also produced an optically driven micro pump in which two-lobed rotors are incorporated into a microchannel as shown in Figure 27. The confinement of each rotor to its own microchannel prevents the rotors from moving unless continuously irradiated with light.²³¹

The two built-in rotors, 9 μM in diameter, are cooperatively driven by means of time-dividing scanning of a single laser beam. They also demonstrated that a tracer particle could be moved by simultaneously rotating the two rotors. The velocity of tracer particle was proportional to the rotors, in the range of 0.2 – 0.7 μM/s. Such a device has potential applications in a biochip system.

Chichkov and Farsari et al. reported the design and fabrication of a complex, readily assembled micro check valve using TPP.²³² They used a zirconium containing organic–inorganic hybrid photosensitive sol-gel which is known for its negligible shrinking properties during TPP. Such a device has applications in microfluidics and they evaluated its flow performance using parameters exhibited in human veins (Figure 28a). Maruo et al. used an epoxy based photopolymer to fabricate 3D microstructures to high resolutions with
potential applications as carbon electrodes in fuel cells. They used epoxy resorcinol diglycidyl ether within the photopolymer due to its high carbon content and high bond energies to ensure good structural fidelity.\textsuperscript{233} \n
Wang et al. prepared a nickel-phosphorus (Ni-P)/polymer composite and demonstrated a method for fabricating 3D micromachines by using TPP of the polymer and electroless plating of the Ni-P alloy to give a high mechanical performance and remotely controllable composites.\textsuperscript{234} The material exhibited magnetic properties and had a good responsiveness to magnetic fields which could be used to manipulate the 3D micromachine they created. Sun et al. used TPP in the fabrication of remote-controllable micromachines with a novel ferrofluid resin composed of methacrylate groups, modified Fe\textsubscript{3}O\textsubscript{4} nanoparticles and photoresists.\textsuperscript{235} They created a micro spring and a microturbine and demonstrated the remote manipulation of these devices using an external magnet.

\section*{1.7.3 Medical devices and applications}

MEMS devices have also attracted attention for biomedical applications. For example, in the creation of microfluidic devices, microvalves, microneedles for drug delivery and scaffolds for tissue engineering (Figure 28).\textsuperscript{176,232,236} Ovsianikov et al. used poly(ethylene glycol) diacrylate (PEGda) materials and TPP to create biocompatible tissue scaffolds.\textsuperscript{237} They obtained feature sizes of 200 nm and were able to use a biocompatible tissue scaffold which exhibited high reproducibility, which would allow for studying cellular processes in 3D and for better understanding of in vitro tissue formation. Basu et al. cross-linked cytoplasmic proteins in a live cell to fabricate channels or compartments to isolate cellular processes.\textsuperscript{238} They also reported the cross-linking of different types of collagen using a benzophenone dimer as the PI to create 3D tissue scaffolds. They also evaluated the bioactivity and enzyme degradation during the process.\textsuperscript{239}
Kumi et al. demonstrated high-speed TPP to create microfluidic devices.\textsuperscript{240} They used a fluorine-based PAG in conjunction with the epoxy resin SU-8 to create master structures for microfluidic devices with high aspect ratios and uniform, rectangular cross-sections. They made polydimethylsiloxane (PDMS, silicone) molds with 20 µm wide channels and aspect ratios between five and ten were created from the master structures. Ovsianikov, Chichkov and co-workers created Lego\textsuperscript{®}-like interlocking tissue engineering scaffolds and microneedle arrays with unique geometries using TPP.\textsuperscript{241} They used an Ormocer\textsuperscript{®} material with Irgacure 369 PI to fabricate the devices and the surfaces demonstrated acceptable cell viability and cell growth profiles against B35 neuroblast-like cells and HT1080 epithelial-like cells. The group also used Ormocer\textsuperscript{®} materials to TPP arrays of in-plane and out-of-plane hollow microneedles with 800 µm lengths and base diameters of 150 – 300 µm with various aspect ratios.\textsuperscript{242} The fracture and penetration properties were examined using compression load testing and were shown to penetrate cadaveric porcine adipose tissue without fracture. Such arrays have applications in transdermal drug delivery. An example is shown in Figure 28c.

1.8. Conclusion

The applications and devices that have been discussed are an overview of a much broader spectrum of information that is currently in the literature, this review has covered the most important aspects in the field. Clearly, TPP has made it possible to fabricate complex 3D structures with nanometre resolution in a variety of materials. The work from a broad range of fields including photonics, materials science, synthetic organic chemistry and

\textsuperscript{176}Figure 28 – a. A microvalve designed to prohibit reversal of blood flow in human veins. b. A high-porosity tissue engineering scaffold. c. A micro-needle array for transdermal drug delivery.
engineering has allowed for such applications to be possible. A wide range of 2PA PIs which work at a broad range of wavelengths are now reported in the literature, but few are available commercially. These can be used to polymerise a variety of material types; depending on the intended application, desired material properties and functionality, and resolution required in the fabricated product. Although such materials and techniques are available, there is still a great deal of improvement that can be made in these areas. The technology is sufficiently mature that a shift from fundamental work to applications in the commercial sector is now feasible. TPP has the potential to be especially important in the fields of medicine, biology, microelectronics, photonics and nanotechnology. To date, the use of TPP in mass production is not yet a reality due to obstacles such as slow writing speeds, the commercial availability of 2PA PIs, and the cost of laser and fabrication setups. However, TPP has the potential to be an important industrial tool in the near future for the fabrication of micro/nanoscale devices.

1.9. Thesis aims and objectives

The field of TPP is a relatively young one but has garnered a large research interest, whether in PI development, polymer chemistry, laser system development or novel device creation for a variety of applications. Many efficient 2PA PIs have been designed in recent years for TPP, and many of these molecules have been Type I radical PIs, which undergo electron transfer from the excited triplet state to appropriate monomers to initiate polymerisation. Currently, the lack of commercially available highly 2PA PIs for acrylate polymerisation is an area of concern. In particular there is a need in industry to access this technique for the manufacture of high-value micro/nano-scale devices and products.

The work herein is aimed at further building on this existing knowledge to create highly active PIs for TPP, which fully address the issues currently holding back the commercial and industrial development of TPP. This will involve:

2. Incorporation of synthetic features to maximise photoinitiator solubility.
3. Assess improvements in photoinitiator properties and how these translate to efficient two-photon polymerisation.
4. Create feature sizes of < 200 nm.

1.10. References

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Chapter 2. Design, synthesis and characterisation of branched triphenylamine photoinitiators for two-photon polymerisation

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2.1. Introduction

The development of PIs for TPP has been an area of intense research for nearly two decades.1–5 While many active 2PA materials have been developed in recent years, and which seek to maximise their two photon cross section \( \delta_{2PA} \), they often neglect other key factors which make them useful for TPP.6–10 These include not only a large \( \delta_{2PA} \), but also a low fluorescence quantum yield \( \phi_F \), ease of preparation and good solubility in pre-polymer resins. Thus, a large \( \delta_{2PA} \) does not necessarily translate into an efficient PI, as many early 2PA materials possessed high \( \delta_{2PA} \) but exhibited a large \( \phi_F \) and/or poor monomer solubility.3 This being due to the fact that a low \( \phi_F \) doesn’t necessarily equate to a high \( \phi_T \), which is the active component in PIs. Fluorescence can lead to poor efficiency during TPP, as relaxation of the excited state via fluorescence and initiation from the triplet state are competitive pathways. Therefore minimising fluorescence is considered a key factor for maximising a PIs ability to initiate polymerisation.11

The presence of carbonyl groups leads to low-lying \( n\pi^* \) excited states associated with high \( \phi_T \).12 For aromatic ketones, conjugation reduces the energy gap between the singlet and triplet levels, which in turn leads to increased rate coefficients for intersystem crossing and higher triplet quantum yields.13,14 The reactive nature of the \( n^2 \rightarrow n\pi^* \) triplet state transition is responsible for the high reactivity of aromatic ketone based PIs. Conversely, while increasing the \( \pi \)-conjugation length and branching can increase the \( \delta_{2PA} \), it can also be detrimental to TPP due to the increasing strength of the \( \pi \rightarrow \pi^* \) character in the triplet excited state.13,15 Thus, the presence of carbonyl groups can potentially provide a dual-role as both a strong electron acceptor and as an efficient spin-orbit coupling agent that promotes intersystem crossing to the triplet states (Introduction – Figure 18).16–18 A number of research groups have utilised carbonyl moieties in the creation of high \( \delta_{2PA} \) PIs, which possess high sensitivity and low polymerisation thresholds.2,3,11,18–22 These have often focussed around several well-known functional components, including \( \alpha,\beta \)-unsaturated ketones3,17,22, thioxanthones1–16, keto-coumarins20,23 and acylo-phosphine oxides.24

Liska et al. produced a number of aromatic ketone PIs based on a D-\( \pi \)-A-\( \pi \)-D configuration. By modifying the aromatic ketone acceptor groups with dialkylamino donor groups they produced efficient PIs, which displayed excellent processing windows (power range of high quality polymerisation) and polymerisation thresholds of 2.5 mW. The synthesised PIs...
displayed reasonable $\delta_{2PA}$ between 250 – 440 GM, whilst the $\phi_F$ yields measured were all below 0.01. In later work, Liska et al. synthesised a series of benzylidene ketone-based two-photon PIs containing dialkylamino groups as electron donors and alkene connectors for the π-conjugated component (Figure 1). The PI (2E,5E)-2,5-Bis(4-(dimethylamino)benzylidene)-cyclopentanone (3b) exhibited a $\delta_{2PA}$ of 466 GM at 800 nm. Though this PI had the greatest measured value of $\delta_{2PA}$, the initiator (2E,6E)-2,6-Bis(4-(dimethylamino)benzylidene)-4-methylcyclohexanone (3e) with a relatively modest $\delta_{2PA}$ of 191 GM was shown to be most efficient compound for TPP, with a processing window of 10 – 20 mW shown to be most effective.

Although the $\delta_{2PA}$ for 3e was roughly half that of 3b, the $\phi_F$ values were 5 – 10 times lower than those of its analogues, something which is necessary for efficient PIs. This in turn leads to lower radiative deactivation and a higher population of active states required for polymerisation. Duan et al. also observed how a lowering of $\phi_F$ had a positive effect on initiator efficiency. Alongside this, they showed that electron donors can increase the reduction potential necessary to form radicals and thus facilitate the polymerisation process.

Gryko et al. synthesised a series of π-expanded α,β-unsaturated 1,3-diketones for use as TPP PIs, examples of which are shown in Figure 2, viz. a D-π-A configuration, with the 1,3-diketone as a strong electron withdrawing group (A), an anthracene core (π) and long chain dialkyl amino group (D). These PIs were found to possess excellent solubility, low $\phi_F$, good $\delta_{2PA}$ and broad processing windows. The PIs displayed $\delta_{2PA}$ between 600-2500 GM at 725 nm, $\phi_F$ yields below 0.01 and processing windows of 10-65 mW at 800 nm.
As mentioned earlier, it has been shown that an effective strategy to improve PI efficiency requires compounds with a high $\delta_{ZPA}$, low $\phi_F$ and monomer solubility. As such, it was decided to explore the use of the strong electron donor TPA as the base for new PI materials. The TPA donor core possesses a propeller shape with $C_3$ symmetry, thus allowing for dipolar, quadrupolar and octupolar branching. Furthermore, it is proposed to make use of the ester functional group to act as an electron acceptor and to assess the carbonyl groups ability to reduce $\phi_F$. The use of such functionality should maximise triplet quantum yields and directly translate into improved polymerisation thresholds. Consequently, this chapter is concerned with the design and synthesis of a series of branched D-(π-(C=O)-OEt)$_n$ PIs with $n = 1, 2, 3$ viz 6 - 8. Investigation of the photophysical properties of the PIs were conducted via UV-Vis absorption, fluorescence, fluorescence lifetimes ($\tau$) and z-scan measurements. Finally, TPP structuring tests conducted at different laser intensities and writing speeds were performed to evaluate the efficiency of these PIs for TPP (Chapter 5).

2.2. Results and Discussion

The series of PIs 6 - 8 under investigation are shown in Figure 3. All three contain the TPA donor core with a conjugated ethyl ester terminal group giving rise to dipolar (6), quadrupolar (7) and octupolar (8) features. The syntheses of the TPA derivatives are presented in Figures 4 - 6. The key reactions in the synthesis are the Vilsmeier-Haack formylation used in forming TPA aldehydes 1 - 3 from previously described methods.
Secondly, the Horner-Wadsworth-Emmons reaction,\textsuperscript{31} used to couple aldehydes 1 - 3 and phosphonate derivative 5 yielding the target PIs 6 – 8 as shown in Figure 3.

![Figure 3 - Molecular structures of synthesised PIs 6 - 8.](image)

### 2.2.1 Synthesis of starting materials: 1-5

Figure 4 shows the synthesis of the TPA aldehydes 1 – 3, using the Vilsmeier-Haack formylation reaction.\textsuperscript{29,30} 4-Formyltriphenylamine (1) was prepared as per a general synthetic methodology by reacting triphenylamine with DMF and POCl\textsubscript{3} at 95 °C for 24 h. The use of 1.05 eq POCl\textsubscript{3} ensured no further formylation occurs in the vacant \textit{para} positions. Hydrolysis of the imine intermediate yielded crude 1 as a brown oil, which was purified by column chromatography to give a yellow solid in 60% yield. 4,4′-diformyltriphenylamine (2) was prepared in the same manner, however 10.5 eq. of POCl\textsubscript{3} was required to optimally form the desired product in an appreciable yield. Furthermore, a shorter reflux time of 6 h
was employed in order to avoid product degradation. Purification of the crude brown oil gave 2 as a yellow solid in 40% yield.

Several literature reports have shown that 4,4',4''-trisformyltriphenylamine (3) can be synthesised in one step from triphenylamine by using a large excess of POCl₃. However, when it was attempted to repeat this, little to none of the desired product was isolated.³²,³³ Mallegol et al. proposed an alternative two-stage synthetic route to 3 as previous attempts resulted in low yields and mixtures of 4-formyltriphenylamines due to deactivation of the 4-position by the imine intermediates.³⁰ Thus, TPA was first reacted with 25 eq POCl₃ and 23 eq DMF in the first stage, followed by hydrolysis of the di-imine and purification to give 2. In the second stage, 25 eq POCl₃ and 23 eq DMF was used to form 3. This allowed for 3 to be isolated along with 2 as a by-product in 12% and 8% yields, respectively. The

![Figure 4 – Preparation of triphenylamine aldehydes (1 – 3) using Vilsmeir-Haack formylation conditions.](image-url)
triphenylamine-based aldehydes 1-3 were isolated as pale yellow, dark yellow and a green/yellow solid, respectively.

The preparation of the desired phosphonate species ethyl 4-((diethoxyphosphoryl)methyl)benzoate 5 for coupling to 1-3 are outlined in Figure 5.

![Figure 5 – Preparation of the phosphonate intermediate ethyl 4-((diethoxyphosphoryl)methyl)benzoate (5).](image)

The starting material ethyl 4-methylbenzoate was converted into ethyl 4-(bromomethyl)benzoate (4) by way of an azobisisobutyronitrile (AIBN) radical initiated bromination using N-bromosuccinimide (NBS) and overnight reflux in CHCl₃. The solution was cooled to r.t. to give a solid precipitate of succinimide salts. These were removed via vacuum filtration, washed with cold chloroform, the organics combined and the solvent removed in vacuo to yield 4, as a white solid (73%).³⁴ The material was used without further purification and converted into 5 by refluxing in triethyl phosphate at 145 – 150 °C for 6 h. The solution was cooled and excess triethyl phosphate was removed in vacuo to yield 5 as a pale yellow oil (99% yield).³⁴

2.2.2 Synthesis of photo initiators 6 - 8

The starting aldehydes 1 – 3 were subjected to Horner-Wadsworth-Emmons coupling conditions with the ethyl ester phosphonate 5 to form the desired alkene bond(s), which yielded the target PIs 6 – 8. A previous literature report for the synthesis of 6 is known, and made use of a palladium (Pd)-catalysed coupling between an alkene moiety and para-bromo TPA.³⁵ Herein describes a differing synthetic route to 6 and using this synthetic procedure it was possible to readily synthesise PIs 7 and 8. The final coupling steps are shown in Figure 6.
Figure 6 – Horner-Wadsworth-Emmons coupling of TPA aldehydes (1 – 3) with the corresponding phosphonate (5) to yield PIs 6 – 8.

In the case of 6, the starting aldehyde 1 was treated with 5 and t-BuOK in THF at 0 °C. The mixture was stirred at room temperature overnight producing a bright yellow solution. The solution was quenched with aqueous NH₄Cl and the organics were removed in vacuo. The solids were re-dissolved in DCM and washed successively with NH₄Cl and brine, the organics were combined, dried over MgSO₄ and the solvents were removed in vacuo. Purification was achieved by column chromatography (10% CHCl₃: petroleum spirit 60-80 °C) to yield semi-pure 6 (approximately 80-90% pure). However, significant impurity was still present as shown by TLC analysis. Subsequent column purification was needed, initially with 100% petroleum spirit 60-80 °C followed by slowly increasing solvent polarity by incremental
increases of ethyl acetate by 1%. Alongside this, 2-3 drops of methanol were added to sharpen the bands running through the column and this gave a product of 95% purity. Final purification was achieved by re-crystallisation from 10% DCM: petroleum spirit 60-80 °C to yield pure 6 as a yellow crystalline solid (300 mg, 15% yield). This multi-step purification led to a somewhat lower product yield, this was due to the relatively large number of by-products in the reaction that were of similar Rf values to the desired 6. The final structure was confirmed by 1H NMR, with the loss of the 1H aldehyde singlet at 9.95 ppm seen in starting material 1 being replaced with two 1H coupled doublets at 7.15 and 7.00 ppm (J = 16.51 Hz) showing the formation of the new HC=CH bond. Further to this, a 2H quartet at 4.38 ppm and a 3H triplet at 1.40 ppm were detected and show the presence of the ethyl ester moiety from starting material 5. Further confirmation of the structure were obtained by 13C NMR and HRMS.

For compound 7, the starting aldehyde 2 was treated with phosphonate 5 and t-BuOK in THF at 0 °C. The mixture was stirred at r.t. overnight producing a bright yellow solution. The solution was quenched with aqueous NH4Cl and the solvents were removed in vacuo. The solid was re-dissolved in DCM and washed successively with NH4Cl and brine, the organics combined, dried over MgSO4 and solvent removed in vacuo. The solid was loaded onto silica gel and purified via column chromatography (10% CHCl3: petroleum spirit 60-80 °C) to approximately 80-90% purity. However, as with 6, significant impurities were present as seen by TLC analysis. With subsequent column purification using 100% petroleum spirit 60-80°C and slowly increasing solvent polarity by incrementally increases of ethyl acetate by 1%. Alongside this, 2-3 drops of methanol were added to sharpen the bands running through the column. This gave a product of 95% purity (by NMR analysis). Recrystallisation from 10% DCM: petroleum spirit 60-80 °C yielded pure diethyl 4,4'-(1E,1'E)-(((phenylazanediyl)bis(4,1-phenylene))bis(ethene-2,1-diyl))dibenzoate (7) as a yellow solid (100 mg, 5%). The final structure of 7 was confirmed by 1H NMR, the loss of the 2H singlet aldehyde at 9.85 ppm was replaced with 2H doublet at 7.03 ppm, whilst the second 2H doublet was obscured by two phenyl protons at 7.18 – 7.14 ppm. For the ethyl ester moiety, a 4H quartet was observed at 4.38 ppm along with a 6H triplet at 1.40 ppm. Further analysis was conducted with 13C NMR and HRMS, and both support the proposed structure.
To prepare 8, the starting aldehyde 3 was treated with phosphonate 5 and t-BuOK in THF at 0 °C. The mixture was stirred at r.t. overnight producing a bright yellow solution. The solution was quenched with aqueous NH₄Cl and the solvents were removed in vacuo. The solid material was dissolved in DCM and washed successively with NH₄Cl and brine, the organics combined, dried over MgSO₄ and the solvent removed in vacuo. The solid was loaded onto silica gel and purified via column chromatography (10% CHCl₃: petroleum spirit 60-80 °C) to yield pure triethyl 4,4',4''-((1E,1'E,1''E)-(nitrilotris(benzene-4,1-diyl))tris(ethene-2,1-diyl))tribenzoate (8) as a yellow solid; 400 mg, 46% yield. In contrast to 6 and 7, which required multiple column purification steps and recrystallisations, purification of 8 was easily achieved and in comparatively high yield. Compound 8 was confirmed by ¹H NMR, the loss of the 3H singlet at 9.85 ppm followed by the formation of two 3H doublets at 7.18 and 7.05 ppm indicating the formation of three new HC=CH bonds was successful. Alongside this, a 6H quartet at 4.38 ppm and a 9H triplet at 1.41 ppm show the coupling of the starting material 5 with that of 3. In the ¹³C spectrum, the aldehyde C=O at 190.42 ppm was replaced with the up field carbonyl C=O at 166.42 ppm. Final confirmation was given by HRMS for the calculated C₅₁H₄₅NO₆+H 767.3347, m/z [M] 767.3248; Δ = 0.7 ppm.

All the final PIs exhibit a deep fluorescent yellow colour in solution under visible light and fluoresce under 265 nm light and particularly strongly when exposed to 354 nm light. Compounds 6, 7 and 8 are all yellow solids which display excellent solubility in the order 6 > 7 > 8 in solvents such as DCM, ethyl acetate, and DMF. Solubility in the acrylate monomers SR415 and SR351 (Chapter 5 > 5.4.3 Monomer system) were also good, however as the branched chains increased 6 > 7 > 8 the solubilities were observed to decrease. In the case for 8, stirring and heating to 40 °C were necessary to re-dissolve the PI in SR415 and SR351 as it began precipitate out of the monomer mixtures over the course of several weeks.

2.3. Photophysical properties

The one-photon photophysical properties for 6, 7 and 8 are summarised in Table 2 and Table 3. Details of the solvents which were utilised for our measurements including, Eₜ(30), solvent type and dielectric constants (εᵣ) are described in Table 1. As can be seen in Graphs
1 - 3 data with toluene, DMF and diisopropyl ether as solvent have been obtained, with data below 300, 280 and 260 nm respectively omitted due to the UV/Vis cut-off limit of these solvents.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>(\varepsilon_r)</th>
<th>(E_r(30))</th>
<th>Solvent Type</th>
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<td>non polar</td>
</tr>
<tr>
<td>Diisopropyl ether</td>
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<td>34.1</td>
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<td>Acetonitrile (MeCN)</td>
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<td>polar aprotic</td>
</tr>
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<td>Methanol (MeOH)</td>
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<td>55.4</td>
<td>polar protic</td>
</tr>
</tbody>
</table>

*Table 1 - Dielectric constants (\(\varepsilon_r\)) and solvent polarity parameter \(E_r(30)\) values of the solvents used.*

2.3.1 UV/Vis Absorption Spectra

The measurements were performed at a concentration of \(1.0 \times 10^{-5}\) mol.L\(^{-1}\) and spectra were normalised with respect to the \(\lambda_{\text{max}}\) of peak 2 (P2), the ICT band. For 6, a previous synthetic procedure was described, however it was an intermediate in their synthetic route and no photophysical data were presented.\(^{35}\) Yang et al. synthesised the methyl ester derivative of 6, which exhibited a \(\lambda_{\text{abs}}\) maxima of 383 nm in acetonitrile, a \(\lambda_{\text{Em}}\) at 516 nm and a \(\phi_F\) of 18% which is consistent with the data presented for 6.\(^{37}\) For 6 in acetonitrile our \(\lambda_{\text{max}}\) was also at 383 nm, which suggested that the ethyl group had no overall effects on the electronic structure of 6. Although as seen in the \(\lambda_{\text{Em}}\) at 516 nm in acetonitrile for the literature methyl derivative, a 9 nm red-shift was seen in the \(\lambda_{\text{Em}}\) for 6 to 525 nm. For 6 – 8 two main bands exist, a \(\pi-\pi^*\) absorption band around 300 nm and a charge transfer (CT) band around 400 nm can be seen.

In methanol, the absorption maxima occurred at 384 nm for 6, 404 nm for 7 and 410 nm for 8. Thus, the absorptions were red-shifted around 26 nm as branching was increased, indicating additive behaviour.\(^{38}\) Notably, a 20 nm red-shift between 6 and 7 indicated that an enlargement of the degree ICT occurs when a second conjugated chain is introduced.\(^{39}\)
Table 2 – UV/Vis absorption spectrum properties of compounds 6 – 8; concentration of $1.0 \times 10^{-5}$ mol.L$^{-1}$. $\lambda_{\text{max}}$ wavelength maxima (nm), some values omitted due to solvent cut-offs. $^b$ $\epsilon = \text{molar extinction coefficient} \times 10^3$ (M$^{-1}$cm$^{-1}$); $A = \epsilon lc$: $A = \text{absorbance}$, $l = \text{path length}$, $c = \text{concentration}$.

However, only a 6 nm shift between 7 and 8 was observed, and this suggests that the cross-conjugation effect becomes less important as more branches are added.$^{21}$ The molar extinction coefficient ($\epsilon$) increased with the number of branches and values of 3.49, 5.46 and $9.48 \times 10^3$ in methanol were seen for 6, 7 and 8, respectively. The value of $\epsilon$ was approximately proportional to the number of branches and suggested independent behaviour of the branches in these molecules.$^{40-42}$
The PIs 6 – 8 do not appear to exhibit strong solvatochromic behaviour, with absorption shifts of < 10 nm seen in all three molecules for both $\lambda_{\text{max}}$ peaks across a range of solvents.

Furthermore, the absorption spectra of 6 - 8 in toluene were slightly red-shifted relative to the other non-polar solvents. This was rationalised by the stabilisation of the chromophores $\pi$-electrons by the toluene $\pi$-system.\textsuperscript{43,44}
For \( 7 \), for the \( \lambda^2 \) absorption band (P2), a very small shoulder at \( \sim 380 \) nm can be seen. In order to ascertain whether this was caused by aggregation, UV/Vis data for \( 7 \) were obtained at varying concentrations in dioxane, where a change in the size of the shoulder would indicate the presence of aggregation. However, this proved not to be the case as the shoulder remained a constant size irrespective of concentration used. This therefore suggested a splitting of the absorption bands. This splitting results from the coupling between branches in quadrupolar compound \( 7 \), as described by the Frenkel exciton model (Figure 7); which can also be applied to H- and J-aggregates and assumes electrostatic interaction of the chromophores.\(^{45-48}\)

![Schematic electronic level diagram based on the Frenkel exciton model.](image)

**Figure 7** - Schematic electronic level diagram based on the Frenkel exciton model. An electronic level diagram is described for dipolar \( 6 \) (1 branch, left), quadrupolar \( 7 \) (2 branch, middle) and octupolar \( 8 \) (3 branch, right). \( g \) denotes the ground state, \( e, e' \) and \( e'' \) the excited states and \( V \) the coupling energy between adjacent branches.\(^{38}\)

The model predicts that in quadrupolar molecules like \( 7 \), the singlet excited state splits into two bands (2e and 2e’) which are positioned symmetrically with respect to the excited state of the linear molecule, in this case \( 6 \). Both states are one-photon allowed while the lower energy state has a stronger oscillator strength. For the octupolar \( 8 \), the excited state was split into three states (3e, 3e’ and 3e’’). The two states (3e and 3e’) are degenerate and lie at the low-energy side of the dipolar \( 6 \) excited state, which are both one and two-photon allowed, while the third high energy state (3e’’) was predicted to be two-photon allowed only and as such, isn’t observed in the absorption spectrum. As predicted by the model, no shoulder was observed for \( 8 \) due to the third state (3e’’) being two-photon allowed and thus, not contributing to the linear absorption. Also, half-bandwidth broadening of the absorption peak of \( 7 \) relative to \( 6 \) and \( 8 \) was observed and related to the presence of these
two split excited states, both being one-photon allowed because of the angle formed between the two branches (Figure 7).\textsuperscript{41,49}

![Graph 3 - UV/Vis absorption spectrum of PI 8 in various solvents, details in Table 2.](image)

2.3.2 Photoluminescence

A detailed description of the measurement methods is described in the Experimental > Instrumentation > Photophysics section. Measurements were performed in a number of polar and non-polar solvents and the results are described in Table 3. While the $\lambda_{\text{max}}$ values for 6 – 8 display very little solvent dependence, the $\lambda_{\text{Em}}$ are increasingly red-shifted with increasing solvent polarity. For 6 in non-polar toluene and in polar methanol, $\lambda_{\text{Em}}$ were observed at 455 and 535 nm, respectively, while for 7 they occur at $\lambda_{\text{Em}}$ at 461 nm and 534 nm and for 8 at $\lambda_{\text{Em}}$ of 468 nm and 547 nm. Thus, the observed $\lambda_{\text{Em}}$ were red-shifted in methanol meaning that the excited states were more polar and therefore more stable with increasing solvent polarity.\textsuperscript{44} Thus the investigated chromophores 6 - 8 show a marked positive solvatochromism: increasing solvent polarity leads to a marked bathochromic shift of the emission band and band broadening. Also, importantly 6 - 8 have very similar emission spectra (Graph 4, Graph 5 and Graph 6). This suggested that $\lambda_{\text{Em}}$ originates from an excited state that is dipolar in nature i.e. the main emitting species are localised on a single branch.\textsuperscript{40,46}
Blanchard-Desce et al. synthesised a series of multi-branched TPA molecules and assessed the effects of branching on linear and non-linear photophysical properties, which also included quantum mechanical calculations. From their calculations, the TPA moiety adopted a propeller-shaped structure, and the phenyl rings were twisted with respect to the trigonal planar central nitrogen, this also being consistent with crystallographic data. The bond-length alternation parameter - defined as the variations in bond order across the single and double bonds - reflects the degree of conjugation along the molecular backbone. This can also be used to measure the level of polarisation in a molecule and is a generic phenomenon observed in many extended molecular systems such as conjugated polymers. They showed that in the ground state, the molecular geometries for their two and three-branched molecules were similar to that of the dipolar single-branched species. However, the excited state geometries were found to be different. In the dipolar species, the structure of the branch becomes planar with a vanishing bond-length alternation parameter. For multi-branched structures, upon excitation the structures lose their symmetry: generally, one branch adopts a geometry similar to that of the corresponding

<table>
<thead>
<tr>
<th>Photoinitiator</th>
<th>Solvent</th>
<th>( \lambda_{\text{max}}^a )</th>
<th>( \lambda_{\text{Em}}^b )</th>
<th>ST(^c )</th>
<th>( \phi^d )</th>
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<td>Toluene</td>
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<td>455</td>
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<tr>
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<td>Dioxane</td>
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<td>465</td>
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<td></td>
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<td>DMF</td>
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<td>MeOH</td>
<td>420</td>
<td>547</td>
<td>127</td>
<td>0.019</td>
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Table 3 - Photoluminescence maxima and stokes shifts in various solvents, conc = 2 x 10\(^{-6}\) mol.L\(^{-1}\). \( ^a \lambda = \text{wavelength maxima (nm), 532 nm excitation.} \)
\( ^b \lambda_{\text{max}} \text{emission, 385 nm excitation.} \)
\( ^c \text{Stokes shift (nm) = } (\lambda_{\text{Em}} - \lambda_{\text{max}}) \)
\( ^d \text{Fluorescence quantum yield with QBS as a reference standard; concentration of } 2 \times 10^{-6} \text{ mol.L}^{-1} \text{ in MeOH, 365 nm excitation.} \)
A common feature of the PIs investigated is that they exhibit large Stokes shifts \( ST = \lambda_{Em} - \lambda_{max} \), which increases with solvent polarity as shown in Figure 4. These are consistent with the stabilisation of highly polar emitting excited states by polar solvents. The large ST indicated that significant reorganisation takes place after excitation and prior to emission, and is related to the electronic redistribution occurring upon excitation.\(^{52}\) Individually, the ST of 6 - 8 followed the same trend with increasing polarity, however comparisons between each in the same solvent system suggest that for multi-branched species like 7 and 8 the excited state polarities are lower than that of 6. In non-polar toluene, STs of 62, 41 and 42 nm were observed for 6, 7 and 8 respectively, whereas in polar methanol the values were 151, 131 and 127 nm.

The ground and lowest-energy excited states of donor-acceptor molecules are described as a combination of neutral and zwitterionic states represented by the corresponding molecular resonance forms.\(^{53,54}\) Katan et al. performed calculations showing that ICT occurs upon excitation of chromophores, and in particular electron density is shifted from the
donor TPA core to the conjugated branch(es). Thus, in the ground state, the molecules exist in the neutral state, whereas the excited state possesses greater zwitterionic character.\textsuperscript{38,41,50,52}

![Graph 5](image)

Graph 5 - The measured fluorescence emission spectra of 7 ($\lambda_{\text{exc}} = 385$ nm). The measurements were performed in a variety of solvents with increasing polarity defined by $E_r(30)$ values.

The PIs 6 – 8 exhibited reduced $\phi_F$ with increased branching based on measurements done in methanol. Namely, the dipolar compound 6 has a $\phi_F$ of 0.18 in contrast to 7 (0.027) and 8 (0.017) as measured with quinine bisulphate (QBS) as a reference standard. This was expected as the increased $\pi$-conjugation and presence of the carbonyl containing acceptor groups greatly influence the observed reduction in overall $\phi_F$ as described in the introduction to this chapter. From a molecular structure point of view, multibranched molecules tend to adopt twisted configurations and this non-radiative dissipation of excitation energy, which will in turn decrease the molecular $\phi_F$.\textsuperscript{55,56}
Graph 6 - The measured fluorescence emission spectra of 8 ($\lambda_{\text{exc}} = 385$ nm). The measurements were performed in a variety of solvents with increasing polarity defined by $E_T(30)$ values.

2.3.3 Effects of solvent viscosity on photophysical properties

To test the effect of solvent viscosity, the fluorescence intensity was measured in methanol, ethylene glycol (EG) and diethylene glycol (DEG) and a 50:50 by weight mixture of the acrylates SR415 and SR351. The results are detailed in Graph 7 and Table 4. A concentration of $2 \times 10^{-6}$ mol.L$^{-1}$ was utilised throughout and $\phi_F$ values were determined using QBS as an internal standard. The fluorescence emission of 6 – 8 in methanol and acrylates are shown in Graph 7. For 6 in methanol, a broad emission band with $\lambda_{\text{max}}$ of 536 nm, fluorescence intensity of 297.08 and $\phi_F$ of 0.0198 was seen. The values for 7 and 8 were much lower in intensity and in turn, display lower $\phi_F$ values of 0.021 and 0.019, respectively. This can be rationalised by the effect of phenyl rotation on the CT state: i.e. in low viscosity solvents, the rotation of the C-N bond on the branches compete to become part of the dipolar CT state and this in turn reduces fluorescence emission and $\phi_F$. As seen in Table 4, for 6 the viscosity of the solvent was found to have a small effect on $\phi_F$, likely due to the smaller effect on emission from rotation of the phenyl rings around the Ph-N bond. When changing the solvent from methanol to the acrylate mixture, a 2.7 times increase in fluorescence emission
was found. Importantly, a much larger increase in intensity for 7 and 8 was observed in acrylates, with the $\phi_f$ of 7 rising to 0.182 and for 8 to 0.183.

![Graph 7](image-url)  
**Graph 7** – Fluorescence emission intensity of 6 - 8 in MeOH and fluorescence intensity of 6 - 8 in 50:50 by weight mixture of the acrylates SR415 and SR351.

<table>
<thead>
<tr>
<th>PI</th>
<th>Solvent</th>
<th>$\lambda_{em}$ Intensity</th>
<th>$\lambda_{em}$ (nm)</th>
<th>$\phi_f$</th>
<th>$\tau$ (ns)</th>
<th>$K_f$ $^a$</th>
<th>$K_{nr}$ $^b$</th>
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<td>536</td>
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<td>$1.26 \times 10^8$</td>
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<td>EG</td>
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<td></td>
<td>DEG</td>
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</tbody>
</table>

*Table 4* – Measured values of fluorescence intensity, $\lambda_{max}$ and $\phi_f$ of Pls 6 – 8 in various viscous solvents. QBS was used as a reference standard; conc = $2 \times 10^{-6}$ mol.L$^{-1}$. An excitation wavelength of 365 nm was used and all remaining settings remained constant. Included are viscosity values (cP) with units in mPa·s. MeOH = Methanol (0.543 cP), EG = Ethylene Glycol (16.1), DEG = Diethylene Glycol (35.7) and Acrylates = a 50:50 by weight mixture of the acrylates SR415 (225 cP) and SR351 (106 cP). $^a$ $k_f$ = radiative decay constant ($k_f = \phi_f / \tau$) s$^{-1}$, $^b$ $k_{nr}$ = nonradiative decay constant (see Equation 1).
Furthermore, the emission of 6 – 8 in acrylates show a similar intensity and shape. This being further evidence that the emission of the excited state was largely confined to a single dipolar branch. For 7 and 8 the excited states were localised to a single dipolar branch and, with molecular rotation of the remaining branches limited by solvent viscosity, this in turn, implies that the fluorescence emission became closer to that of the dipolar 6 (Table 4).\textsuperscript{57,58}

This feature can be explained by the stabilisation of the dipolar CT excited state in 7 and 8 by way of hindering the inter-conversion of CT states by the reduced molecular rotation. These results show the significant role of molecular rotation on fluorescence, and in particular how the hindrance of molecular rotation prevents the destabilisation of the dipolar excited state by inter-conversion of the charge resonance structures.\textsuperscript{57}

For 6 – 8 in methanol, a red-shift was observed compared with measurements obtained in lower polarity solvents as shown in Table 3 and this can be rationalised by increased stabilisation of the CT state in polar solvents. For the PIs 6 – 8 in acrylates, a large blue-shift of 40-50 nm can be seen. As seen in Graph 7, strong emission from the dipolar excited state can be seen for 6, 7 and 8 and the blue-shifts were due to the lower polarity of the acrylate system and thus reduced stabilisation of the CT state. These processes are well described in the literature, in particular for a group of compounds called molecular rotors, two examples of which can be seen in Figure 8. These molecules are a group of twisted intramolecular charge-transfer (TICT) complexes which are used for viscosity sensitive measurements, commonly for biological applications.\textsuperscript{59}

![DCVJ - 1 and CCVJ - 2](image)

**Figure 8** – Structure of two commercially available molecular rotors. 9-(dicyanovinyl)-julolidine (DCVJ, 1) and 9-(2-carboxy-2-cyano)vinyl julolidine (CCVJ, 2). Upon excitation CT takes place between the nitrogen as the electron donor and the nitrile acceptor group with subsequent intramolecular rotation around the julolidine-vinyl bond.

TICT complexes which undergo a twisting motion to form the excited state were first observed by Z. R. Grabowsky in 1973.\textsuperscript{60} Förster and Hoffmann examined this phenomenon in TPA dyes, which were found to display TICT character and they determined the
relationship between $\phi_F$ and viscosity - this was derived analytically and verified experimentally. The relationship shows that as solvent viscosity increased, so did the fluorescence emission intensity and the $\phi_F$. These results have particular importance for these types of multi-branched PIs for use in TPP as the polymerisation process often takes place using viscous monomers. Thus, measurements of ideal properties like $\phi_F$ in solvents without comparison of the same properties under TPP experimental conditions can be misleading. For example, when considering the effect of fluorescence on the TPP mechanism, in a species like 6 with a larger $\phi_F$, relaxation occurs via irradiative processes such as fluorescence or non-radiative relaxation. Lower $\phi_F$ values are desirable as they allow for greater intersystem crossing to the triplet state from the excited state, the former state being responsible for PI activity. As noted earlier, conjugated aromatic ketones reduce the energy gap between singlet and triplet levels leading to higher rates of intersystem crossing (viz triplet quantum yield).

2.3.4 Fluorescence lifetimes

To further investigate these conclusions, fluorescence lifetime ($\tau$) measurements were performed in methanol and acrylates at a concentration of $2 \times 10^{-6}$ mol.L$^{-1}$. These results are shown in Table 4 and the normalised fluorescence lifetime spectra are shown in Graph 8 and Graph 9. The fluorescence decay profiles were acquired using the time correlated single photon counting method and exciting the fluorescence with 375 nm pulsed photodiode with a pulse duration of $\sim$100 ps. Fluorescence decay times were determined by analysis of the decay profiles by an iterative reconvolution method. For 6 in methanol, a lifetime of 1.57 ns was measured and decay occurs from a single excited state. For 7 and 8 in methanol, lifetimes of 0.55 ns and 0.33 ns respectively - via a double exponential decay - were measured, it consists of a very short decay followed by a longer second component. The low $\phi_F$ and shorter lifetimes for 7 and 8 can be attributed to the dominant nonradiative decay mechanisms. The radiative decay constants ($k_r$, $k_r = \phi_F/\tau$) for 6, 7 and 8 in methanol are $1.26 \times 10^8$ s$^{-1}$, $3.82 \times 10^7$ s$^{-1}$ and $5.76 \times 10^7$ s$^{-1}$, respectively. The nonradiative decay constants ($k_{nr}$) can be calculated from $k_r$ and $\phi_F$ according to the following equation:
The calculated $k_{nr}$ values were $5.11 \times 10^8$ s$^{-1}$, $1.78 \times 10^9$ s$^{-1}$ and $2.97 \times 10^9$ s$^{-1}$ in methanol for 6, 7 and 8, respectively. The larger $k_{nr}$ value seen for 7 and 8 explains the shorter lifetime in methanol. In acrylates, the fluorescence lifetimes measured were 2.08 ns, 2.17 ns and 2.26 ns for 6, 7 and 8, respectively. The corresponding $k_f$ values in acrylates were $1.04 \times 10^8$ s$^{-1}$, $8.39 \times 10^7$ s$^{-1}$ and $8.10 \times 10^7$ s$^{-1}$ for 6, 7 and 8. It is worth noting that when compared to methanol relatively large increases were seen for 7 and 8. The $k_{nr}$ values were $3.77 \times 10^8$ s$^{-1}$, $3.77 \times 10^8$ s$^{-1}$ and $3.62 \times 10^8$ s$^{-1}$ for 6, 7 and 8, respectively, suggesting that the radiative pathway became the dominant process. This provides further evidence for emission being limited to a single dipolar branch, such as that observed for 6 and which can be seen in the lifetime decay curves of 6 – 8 in acrylates. As can be seen in Graph 9 the decay curves for 6 – 8 were very closely matched and can be explained by the effect of acrylate viscosity on the emission. As with the $\phi_F$ measurements, as the viscosity of the solvent medium increased so does the emission intensity, which closely matches that of the dipolar 6.

Graph 8 – Normalised fluorescence lifetime of 6 – 8 in MeOH. Excitation at 375 nm with pulse duration of 100 ps, $\tau$ are shown in Table 4.

\[
k_{nr} = \left( \frac{1}{\phi_F} - 1 \right) k_f
\]

**Equation 1** – Equation for calculating nonradiative decay constants using $k_r$ and $\phi_F$. 

Graph 8 – Normalised fluorescence lifetime of 6 – 8 in MeOH. Excitation at 375 nm with pulse duration of 100 ps, $\tau$ are shown in Table 4.
Graph 9 - Normalised fluorescence lifetime of 6 – 8 in acrylate. Excitation at 375 nm with pulse duration of 100 ps, lifetimes are shown in Table 4.

This was due to the diminishing effect of phenyl rotation on the dipolar CT state and thus, the fluorescence spectra intensity and lifetimes of 7 and 8 were close to that of 6. CT state formation involves the rotation of the phenyl ring to form the planar excited state structure with a single branch followed by relaxation to the ground state through radiative decay or non-radiative decay. As such, the lifetime of the CT state is controlled by the rate at which the phenyl group rotates - the faster the rotations the lower the CT stability. The effect of molecular rotation was seen as observed in Graph 7, with an increasing fluorescence contribution for 7 and 8 and as such, the nature of the fluorescence became similar to that of 6 in the presence of highly viscous acrylate monomers (Table 4).

2.3.5 Two-photon absorption cross-section – z-scan

The $\delta_{2PA}$ values for chromophores 6 – 8 were measured at a concentration of $2.0 \times 10^{-2}$ mol.L$^{-1}$ in chloroform and the results are detailed in Table 5. To assess the $\delta_{2PA}$ using the z-scan technique an operating wavelength of 780 nm was used (Ti:Saph fs-laser) with rhodamine 6G in ethanol as a reference. A measured value of the $\delta_{2PA}$ 33 GM was obtained
for rhodamine 6G, this being consistent with previous literature.\(^6^6\) The stated values of \(\delta_{2PA}\) have a standard accuracy of ± 10%. A schematic of the setup is shown in Figure 9 and a full description of the experimental setup is presented in Experimental, z-scan measurements. The measured spectra for PIs 6 – 8 are shown in Graph 10, Graph 11 and Graph 12.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Solvent</th>
<th>(\lambda_{\text{max}}) (nm)</th>
<th>(\delta_{2PA}) (GM)(^a,b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rhodamine 6G</td>
<td>MeOH</td>
<td>-</td>
<td>33</td>
</tr>
<tr>
<td>6</td>
<td>CHCl(_3)</td>
<td>388</td>
<td>126</td>
</tr>
<tr>
<td>7</td>
<td>CHCl(_3)</td>
<td>407</td>
<td>358</td>
</tr>
<tr>
<td>8</td>
<td>CHCl(_3)</td>
<td>415</td>
<td>590</td>
</tr>
</tbody>
</table>

*Table 5 - \(\delta_{2PA}\) of PIs as measured at 780 nm in CHCl\(_3\) at a concentration of 2 x 10\(^{-2}\) mol.L\(^{-1}\).\(^6\). 1 GM = 1 x 10\(^{-50}\) cm\(^4\)s photons\(^{-1}\) molecule\(^{-1}\).\(^b\). The stated values of \(\delta_{2PA}\) have a standard accuracy of ± 10%.

The use of strong electron donors and acceptors leads to states with high charge separation. In addition, the use of long \(\pi\)-conjugation pathways and good planarity further improves charge separation. These are considered critical in maximising ICT, which is fundamental for \(\delta_{2PA}\).\(^7\) As shown in Table 5, as branching increases the \(\delta_{2PA}\) similarly increases linearly with each additional branch. For dipolar 6 the \(\delta_{2PA}\) observed was 126 GM, quadrupolar 7 was 358 GM and for octupolar 8 a measured value of 590 GM. With each successive branch an increase of 232 GM was observed, suggesting excellent cooperative enhancement during two-photon excitation. For all chromophores measured, the one-photon absorption maximum is closely matched to half the wavelength used for two-photon measurements, i.e. 390 nm. For 6 - 8 in chloroform the observed \(\lambda_{\text{max}}\) values were 388, 407 and 415 nm. This suggests that the values obtained were likely to be close to their maximum in this particular solvent. However, assessment over a wider wavelength and power range would be necessary to confirm this. Graph 10, Graph 11 and Graph 12, show the relative position of the sample as it moved through the z-axis and the measured change in transmittance as the sample moved through the focal point. The open aperture scan can be used to directly obtain the nonlinear hyperpolarisability coefficient (\(\beta\)), which can be used to obtain the \(\delta_{2PA}\) using Equation 2. When third order nonlinear losses are small, the normalised change in transmittance caused by a molecule’s \(\delta_{2PA}\) can be approximated as:\(^6^7\)
\[ \delta_{2PA} = \frac{\hbar \omega \beta}{N_a C} \]

Equation 2

Where \( N_a \) is Avogadro’s number, \( C \) the concentration, \( \hbar \) the reduced Planck constant and \( \omega \) the angular frequency. \( \delta_{2PA} \) are denoted by GM values, where 1 GM is equal to \( 1 \times 10^{-50} \text{cm}^4 \text{s photons}^{-1} \text{molecule}^{-1} \).

Graph 10 - Z-scan measurement of PI 6. The measured and averaged transmission as the sample moves through the z-axis. The change in measured transmittance gives details on the \( \delta_{2PA} \) of the sample. Measured values are shown in Table 5.
The measured and averaged transmission as the sample moves through the z-axis. The change in measured transmittance gives details on the $\delta_{2\text{PA}}$ of the sample. Measured values are shown in Table 5.

To obtain a full analysis of the $\delta_{2\text{PA}}$ of these PIs, it would be useful to use a broad wavelength range to find optimum wavelengths to maximise $\delta_{2\text{PA}}$. Alongside this, performing measurements in a range of polar and non-polar solvents would also be advantageous, as these are known to affect $\delta_{2\text{PA}}$. However, given these particular molecules are designed for use in TPP, the most common wavelength for polymerisations are 780 – 800 nm, the results obtained represent an excellent indicator of expected efficacy.
2.4. Experimental

2.4.1 Materials

Commercially available reagents were purchased from Sigma-Aldrich New Zealand, Pure Science Ltd, and SiliCycle Canada and were used without further purification. For our TPP tests the commercially available acrylates SR415 and SR315 and were purchased directly from Sartomer and used without further purification. The solvents used were of reagent and analytical grade and were used without further purification unless otherwise stated. Flash column chromatography was carried out using Silicycle SiliaFlash F60 silica (230 – 400 mesh) with stated solvent systems. Analytical thin-layer chromatography (TLC) analyses were performed on pre-coated plates (Merck aluminium sheets, silica gel 60F 254, 0.2 mm). Visualisation of chromophores was achieved by illumination under ultraviolet light (254 nm).

2.4.2 Instrumentation

$^1$H NMR and $^{13}$C NMR were performed on a BRUKER-500 MHz - FT-NMR spectrometer operating at 500 MHz. The chemical shift (s = singlet, bs = broad singlet, d = doublet, t = triplet, q = quartet, m = multiplet) are stated in ppm using tetramethylsilane (TMS) as the internal standard. NMR solvents used were of ≥ 99.5% purity. High-Resolution Mass Spectrometry was performed using a Waters Q-TOF Premier™ Tandem Mass Spectrometer. Melting points were recorded with an EZ-Melt automated melting point apparatus and are uncorrected.

2.4.3 Photophysics

Linear absorption spectra were obtained using a PerkinElmer Lambda 1050 WB UV/VIS/NIR spectrometer. The light sources were a pre-aligned tungsten-halogen (Vis/NIR) and deuterium source (UV). The detectors were a grid-less photomultiplier tube (175 – 800 nm). Photoluminescence measurements were carried out on a Cary Eclipse fluorescence spectrometer. A Xe-lamp with a pulse width of 2-3 µs and a repetition rate of up to 80 Hz were used. Different slit widths were selected for emission and excitation to vary spectral resolution between 1.5 nm and 20 nm. Measurements were performed with quinine
bisulphate (QBS) in (0.05 mol.L⁻¹) sulphuric acid (φ_F = 0.52) or Rhodamine 6G in ethanol (φ_F = 0.96) as reference standards.\textsuperscript{72}

2.4.4 z-scan measurements

An open-aperture z-scan setup was used to determine the δ_{2PA} of the synthesised chromophores. A schematic of the setup used is shown in Figure 9. The description below relates to the method used for all compounds in this thesis. The change in transmittance was measured while the sample was moved through the focal point of the lens using a translation stage. A Toptica fs fibre laser with pulse duration of 100 fs, a repetition rate of 80 MHz and operating wavelength of 780 nm was used. The resulting optical intensity in the focal point was 4.8 GW/cm². Due to the high repetition rate thermal effects can have an effect on the measurements. As such, a modified z-scan setup was used and an optical chopper was incorporated to minimise thermal effects.\textsuperscript{74-76} The chopper frequency was set at 20 Hz with a duty cycle of 0.82%. This resulted in the sample being illuminated 1.64 ms every 498.36 ms. The rise time was 4.6 μs and is due to the finite size of the beam at the chopper and the transmittance through the sample was measured exactly after the rise time using a digital oscilloscope. The reference detector (D1) was used to account for fluctuations in laser intensity and was also used as the trigger for the oscilloscope.

![Figure 9 – Schematic of the z-scan setup used, (Ch = chopper, L = lens, D = photodiode, M = mirror, ND = neutral density filter and BS = beam splitter). Image reproduced with permission from Synthesis and characterization of strongly two photon absorbing and photoswitchable azo molecules.\textsuperscript{73}](image)

A solution of rhodamine 6G in methanol was used as the reference standard to verify the setup and resulted in a measured δ_{2PA} of 33 GM, which is consistent with the value reported
in the literature. All measurements were performed in DMF or chloroform depending on chromophore solubility with concentrations of $2.0 \times 10^{-2}$ mol.L$^{-1}$, except for 23 which had a concentration of $1.23 \times 10^{-2}$ mol.L$^{-1}$. The open aperture scan can be used to directly obtain the nonlinear absorption coefficient ($\beta$). When the third order nonlinear losses are small ($\beta I L_{\text{eff}} \ll 1$), the normalized change in transmittance due to two photon absorption can be approximated by Equation 3.$^{67}$

$$\Delta T(x) = -\frac{q_0}{2\sqrt{2}} \frac{1}{1 + x^2}$$

Equation 3

With $q_0 = \beta I_0 L_{\text{eff}}$ and $x = z/Z_0$, where $Z_0$ is the Rayleigh length, $I_0$ is the peak intensity. $L_{\text{eff}} = (1 - e^{-\alpha L})/\alpha$ is the effective sample length which in this case is approximately equal to the sample length due to the low absorbance at the wavelength used. The molecular two photon cross section $\delta_{2PA}$ can be obtained from $\beta$ using Equation 4.

$$\delta_{2PA} = \frac{\hbar \omega \beta}{N_a C}$$

Equation 4

Where $N_a$ is Avogadro’s number, $C$ the concentration, $\hbar$ the reduced Planck constant and $\omega$ the angular frequency. $\delta_{2PA}$ are denoted by GM values, where 1 GM is equal to $1 \times 10^{-50}$cm$^4$s photons$^{-1}$ molecule$^{-1}$. GM values were measured at 780 nm and are listed in Table 5. Due to the nature of the z-scan measurement, the stated values of $\delta_{2PA}$ have a standard accuracy of ± 10%.

2.5. Synthesis

**Synthesis of 4-formyltriphenylamine (1).** To a stirred solution of triphenylamine (5.3 g, 21.6 mmol) in DMF (40 ml) at 0 °C under argon was added POCl$_3$ (22.68 mmol, 2.11 ml) dropwise over 15 mins. The resulting mixture was stirred vigorously at 95 °C for 24 h until TLC analysis showed no starting material present. The mixture was allowed to cool to room
temperature, poured into ice-water and neutralised with 4 M NaOH. The solid filtrates were collected, washed and dried under vacuo. Purification by column chromatography (silica gel, DCM: petroleum spirit 60-80 °C, 1:4) affording 4-formytriphenylamine (1) 4.72 g, 80% yield. Pale yellow solid; Rf 0.3 (DCM: petroleum spirit 60-80 °C, 1:4); mp 128 – 130 °C (Lit. mp 129 – 131 °C).²⁹ ¹H NMR (500 MHz, CDCl₃): δ = 9.95 (s, 1H, CHO), 7.70 (d, J = 9.1 Hz, 2H), 7.36 (t, 4H), 7.25-7.15 (m, 6H), 7.05 (d, J = 9.1 Hz, 2H). ¹³C NMR (500 MHz, CDCl₃): 190.47, 152.02, 145.53, 131.30, 130.16, 127.07, 126.27, 125.11, 122.78, 119.37. HRMS: calcd for C₁₉H₁₅NO 273.1154, m/z [M⁺] 273.1148 (30%), [M⁺H] 274.1223 (100%); Δ = 0.7 ppm.

**Synthesis of 4,4′-diformyltriphenylamine (2).** To a stirred solution of triphenylamine (10 g, 40.8 mmol) in DMF (75 ml) at 0 °C under argon was added POCl₃ (428.4 mmol, 40 ml) dropwise over 15 minutes. The resulting mixture was stirred vigorously at 95 °C for 6 h until TLC analysis showed no starting material present. The mixture was allowed to cool to room temperature, poured into ice-water and neutralised with 4M NaOH. The solid filtrates were collected, washed and dried under vacuo. Purification by column chromatography (silica gel, DCM: petroleum spirit 60-80 °C (1:3)) affording 4,4′-diformyltriphenylamine (2) 4.91 g, 40% yield.²⁹ Yellow solid; Rf 0.5 (DCM); mp 142 – 144 °C (Lit. mp 141 – 143 °C ). ¹H NMR (500 MHz, CDCl₃): δ = 9.85 (s, 2 H, CHO), 7.77 (d, J = 9.17 Hz, 4H), 7.40 (d, 2H), 7.26 (t, 1H), 7.18 (m, 6H). ¹³C NMR (500 MHz, CDCl₃): 190.45, 152.01, 145.52, 131.30, 130.16, 127.07, 126.27, 125.12, 122.51. HRMS: calcd for C₂₀H₁₅NO 301.1103, m/z [M⁺H] 302.1185 (100%), [M⁺Na] 324.1005 (40%); Δ = 1.3 ppm.

**Synthesis of 4,4′,4″-triformyltriphenylamine (3).** POCl₃ (95 ml, 1 mol, 156.25 g) was added dropwise over 1 h to a stirred solution of triphenylamine (10 g, 40 mmol) in DMF (72.2 ml, 68.5 g, 938 mmol) under argon at 0°C. The resulting mixture was stirred at 95°C for 4 h. After cooling to r.t., the mixture was poured into ice-water (500 ml) and neutralised with 4 M NaOH. After extraction with DCM (500 ml), the organic layer was washed with brine (3 x 200 ml), dried over MgSO₄ and filtered. The solvents were then removed in vacuo to yield the crude intermediate product. The crude product was re-dissolved in DMF (23 eq, 72.2 ml, 68.5 g, 937 mmol) and cooled to 0 °C under Argon, to the stirred solution was added POCl₃ (95 ml, 1 mol, 156 g). The resulting mixture was stirred at 95 °C for 1.5 h. After cooling to r.t., the mixture was poured into ice-water (500 ml) and neutralised with 4 M NaOH. After extraction with DCM (500 ml), the organic layer was washed with brine (3 x
200 ml), dried over MgSO₄ and filtered. The solvents were then removed in vacuo, the product was loaded onto silica and purified via column chromatography (75% DCM: petroleum spirit 60-80 °C) to yield pure 4,4',4''-trisformyltriphenylamine (3) (1.5 g, 12% yield), 4,4'-diformyltriphenylamine (2) was also isolated (1 g, 8% yield) from the column. Yellow/green solid; Rf 0.25 (DCM); mp 231 – 233 °C (Lit. 230 – 232 °C). 1H NMR (500 MHz, CDCl₃): δ = 9.85 (s, 3 H, CHO), 7.70 (d, J = 8.87 Hz, 6H), 7.15 (d, J = 8.87 Hz, 6H). 13C NMR (500 MHz, CDCl₃): 190.42, 151.20, 132.64, 131.49, 124.54. HRMS: calcd for C₂₁H₁₅NO₃ 329.1052, m/z [M⁺] 329.1061 (10%), [M⁺H] 330.1137 (100%); Δ = 2.1 ppm.

Synthesis of ethyl 4-(bromomethyl)benzoate (4). To a solution of ethyl 4-methylbenzoate (51.25 g, 50 ml, 312 mmol) in CHCl₃ (200 ml) was added AIBN (0.5 g, 15 mmol). The solution was heated to 80 °C and in portions over 30 mins NBS (61.1 g, 343.3 mmol) was added and stirred overnight. The solution was cooled to r.t and filtered to remove succinimide; the filtrate was washed with cold DCM. The solvents were removed in vacuo to yield ethyl 4-(bromomethyl)benzoate (4) 55 g, 73% yield. Off-white solid, Rf 0.5 (petroleum spirit 60-80 °C); mp 34 – 36 °C (Lit. 35 - 36 °C ). 1H NMR (500 MHz, CDCl₃): δ = 8.01 (d, J = 8.09 Hz, 2H), 7.45 (d, J = 8.09 Hz, 2H), 4.38 (s, 2H), 4.36 (q, 2H), 1.40 (t, 3H). Synthesis of ethyl 4-((diethoxyphosphoryl)methyl)benzoate (5). To 4-(bromomethyl)benzoate (4) (55 g, 227 mmol) was added triethyl phosphite (125 ml) and the solution was heated at 150 °C for 6 h. After cooling to r.t, the solvents were removed in vacuo to afford ethyl 4-((diethoxyphosphoryl)methyl)benzoate (5) 68 g, 99 % yield. Tan oil, Rf 0.5 (petroleum spirit 60-80 °C). 1H NMR (500 MHz, CDCl₃): δ = 7.89 (d, 2H), 7.29 (d, 2H), 4.29-4.25 (m, 2H), 3.80-3.75 (m, 4H), 3.11 (d, 2H), 1.22 (t, 3H), 1.18-1.13 (m, 6H). 13C NMR (500 MHz, CDCl₃): 166.32, 136.92, 129.66, 129.49, 126.42, 62.32, 61.18, 34.30, 16.22, 14.10. HRMS: calcd for C₁₄H₂₁O₃P 300.1127, m/z [M⁺Na] 323.1019 (100 %); Δ = -1.5 ppm.

Synthesis of (E)-ethyl 4-(4-(diphenylamino)styryl)benzoate (6). To a solution of t-BuOK (1.35 g, 12 mmol) in THF (20 ml) was added ethyl 4-((diethoxyphosphoryl)methyl)benzoate (5) (3.35 g, 11.15 mmol) dropwise over 30 mins at 0 °C. The solution was stirred for 30 mins and kept below 5 °C, 4-formyltriphenylamine (1) (2.53 g, 9.26 mmol) in THF (10 ml) was slowly added and the solution was allowed to reach r.t and stirred overnight. The solution was quenched with aq. NH₄Cl (25 ml) and THF was removed in vacuo. The solution was extracted into DCM (50 ml) and washed with aq. NH₄Cl (3 x 25 ml) and brine (50 ml). The

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organics were combined, dried over MgSO₄, filtered and dried in vacuo. The solids were loaded onto silica gel and purified via column chromatography (CHCl₃: petroleum spirit 60-80 °C, 1:1) to give pure (E)-ethyl 4-(4-(diphenylamino)styryl)benzoate (6) 300 mg, 15 % yield. Yellow solid, Rf 0.75 (DCM: petroleum spirit 60-80 °C, 1:1). ¹H NMR (500 MHz, CDCl₃): δ 8.00 (d, J = 8.25 Hz, C₆H₄-CO₂Et, 2H), 7.52 (d, J = 8.25 Hz, C₆H₄-CO₂Et, 2H), 7.44-7.41 (m, Ph₂N-C₆H₄, 2H), 7.28-7.24 (m, Ph-NPh₂, 4H), 7.15 (d, J = 16.51 Hz, -N-Ar₁-CH=CH-Ar, 1H), 7.13-7.10 (m, Ph-NPh₂, 4H), 7.06-7.03 (m, Ph-N-C₆H₄-CH=CH, 4H), 7.00 (d, J = 16.51 Hz, -N-Ar₁-CH=CH-, 1H), 4.38 (q, J = 7.1 Hz, 2H), 1.40 (t, J = 7.1 Hz, 3H). ¹³C NMR (500 MHz, CDCl₃): 166.44, 147.97, 147.43, 142.11, 130.71, 129.98, 129.34, 128.90, 127.68, 126.01, 125.79, 124.73, 123.29, 123.18, 60.86, 14.37. HRMS: calcd for C₂₉H₂₅NO₂ 419.1885, m/z [M⁺] 419.1886 (100%), [M⁺H⁺] 420.1950 (100%), [M⁺Na] 442.1788 (100%); Δ = 0.2 ppm.

**Synthesis of diethyl 4,4′-((1E,1′E)-((phenylazanediyl)bis(4,1-phenylene))bis(ethene-2,1-diyl))dibenzolate (7).** To a solution of t-BuOK (0.85 g, 7.9 mmol) in THF (20 ml) was added ethyl 4-((diethoxyphosphoryl)methyl)benzoate (5) (2.27 g, 7.57 mmol) dropwise over 30 mins at 0 °C. The solution was stirred for 30 mins and kept below 5 °C, 4,4′-diformyltriphenylamine (2) (0.95 g, 3.16 mmol) in THF (10 ml) was slowly added and the solution was allowed to reach r.t and stirred overnight. The solution was quenched with aq. NH₄Cl (25 ml) and THF was removed in vacuo. The solution was extracted into DCM (50 ml) and the organics were combined, filtered and dried in vacuo. The solids were loaded onto silica gel and purified via column chromatography (CHCl₃: petroleum spirit 60-80 °C, 1:1) to give pure diethyl 4,4′-((1E,1′E)-((phenylazanediyl)bis(4,1-phenylene))bis(ethene-2,1-diyl))dibenzolate (7) 100 mg, 5% yield. Yellow solid, Rf 0.50 (DCM: petroleum spirit 60-80 °C, 1:1). ¹H NMR (500 MHz, CDCl₃): δ 8.01 (d, J = 8.55 Hz, C₆H₄-CO₂Et, 4H), 7.54 (d, J = 8.55 Hz, C₆H₄-CO₂Et, 4H), 7.42 (d, J = 8.64 Hz, Ar-N-C₆H₄, 4H), 7.30-7.29 (m, 2H), 7.18-7.14 (m, 4H), 7.11-7.07 (m, 5H), 7.03 (d, J = 16.90 Hz, Ar₁-CH=CH-Ar, 2H), 4.38 (q, J = 7.1 Hz, 4H), 1.40 (t, J = 7.1 Hz, 6H). ¹³C NMR (500 MHz, CDCl₃): 166.44, 147.46, 142.00, 131.35, 130.53, 130.00, 129.47, 129.00, 127.76, 126.16, 125.13, 123.84, 60.87, 14.36. HRMS: calcd for C₄₀H₃₅NO₄ 593.2566, m/z [M⁺] 593.2561 (90%), [M⁺H⁺] 594.2628 (100%), [M⁺Na] 616.2456 (50%); Δ = -0.8 ppm.

**Synthesis of triethyl 4,4′,4′′-((1E,1′E,1′′E)-(nitrilotris(benzene-4,1-diyl))tris(ethene-2,1-diyl))tribenzoate (8).** To a solution of t-BuOK (454 mg, 4.05 mmol) in THF (20 ml) was added
ethyl 4-((diethoxyphosphoryl)methyl)benzoate (5) (1.05 g, 3.71 mmol) dropwise over 30 mins at 0 °C. The solution was stirred for 30 mins and kept below 5°C, 4,4',4''-trisformyltriphenylamine (3) (0.37 g, 1.124 mmol) in THF (10 ml) was slowly added and the solution was allowed to reach r.t and stirred overnight. The solution was quenched with aq. NH₄Cl (25ml) and THF was removed in vacuo. The solution was extracted into DCM (50 ml) and washed with aq. NH₄Cl (3 x 25ml) and brine (50ml). The organics were combined, dried over MgSO₄, filtered and dried in vacuo. The solids were loaded onto silica gel and purified via column chromatography (CHCl₃: petroleum spirit 60-80 °C, 1:9) to yield pure triethyl 4,4',4''-((1E,1'E,1''E)-(nitrilotris(benzene-4,1-diyl))tribenzoate (8) 400 mg, 46% yield. Yellow solid, Rf 0.50 (DCM: petroleum spirit 60-80 °C, 1:1); ¹H NMR (500 MHz, CDCl₃): δ 8.02 (d, J = 8.44 Hz, C₆H₄-CO₂Et, 6H), 7.54 (d, J = 8.44 Hz, C₆H₄-CO₂Et, 6H), 7.45 (d, J = 8.66 Hz, N(C₆H₄)₃, 6H), 7.18 (d, J = 16.50 Hz, Ar₁=CH=CH₂, 3H), 7.13 (d, J = 8.66 Hz, N(C₆H₄)₃, 6H), 7.05 (d, J = 16.50 Hz, Ar₁=CH=CH₂, 3H), 4.38 (q, J = 7.1 Hz, 6H), 1.41 (t, J = 7.1 Hz, 9H). ¹³C NMR (500 MHz, CDCl₃): 166.42, 147.02, 141.90, 131.89, 130.41, 129.10, 127.85, 126.47, 126.10, 124.34, 60.89, 14.37. HRMS: calcd for C₅₁H₄₅NO₆ 767.32, m/z [M⁺] 767.3248 (100%), [M⁺H] 768.3289 (60%), [M⁺Na] 790.3124 (20%); Δ = 0.7 ppm.

2.6. Conclusions

A series of two-photon PIs containing a TPA donor core with phenylene-vinylene π-system linking ethyl ester acceptors was synthesised via Horner–Wadsworth–Emmons reactions. A systematic evaluation of key molecular properties that should determine overall polymerisation thresholds was undertaken, and photophysical measurements confirmed the significant effect of molecular branching on the values obtained for these types of PIs. It was shown that for 8, a large δ₂PA of 590 GM was measured at 780 nm in chloroform using the z-scan technique, while 7 and 6 displayed a linear relationship with branching. Similarly, a φᵣ of 0.198 was exhibited for 6 in methanol which decreased to approximately 0.02 for 7 and 8. However, upon excitation the excited states were confined to a single dipolar branch in all species, which has important consequences for the overall properties. For our measurements in common solvents key molecular properties were similar to those previously reported for similar species in literature. However, measurements done in the
acrylate system used for TPP assessments showed pronounced effects due to the dipolar nature of the PIs. It has been shown that viscosity plays an important role in $\phi_F$, fluorescence lifetimes and PI polymerisation thresholds. In viscous acrylates the $\phi_F$ of 6, 7 and 8 were 0.216, 0.182 and 0.183 and fluorescence lifetimes closely resembled those of the dipolar 6.

These results have significant implications for PI design, where desired properties such as large $\delta_{2PA}$, low $\phi_F$, high $\phi_T$ and monomer solubility are considered key. Common methods for maximising these are by way of increasing $\pi$-conjugation pathways through branching and modifying donors and acceptors. Due to the nature of the excited state, synthesising large multibranch molecules looks a valid strategy for improving the desired properties, although this may not necessarily translate into high efficiency PIs. This will be tested later in this thesis (Chapter 5) where polymerisation thresholds will be assessed for 6 - 8.

2.7. References


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3.1. Introduction

Chromophores with large $\delta_{2PA}$ are important for TPP technology, due to their high sensitivity to polymerisation and use over a wider power range, which allows for dynamic control of microstructure dimensions. The use of D-\( \pi \)-A, D-\( \pi \)-D and A-\( \pi \)-D-\( \pi \)-A type systems - among others have been widely utilised in the creation of novel, high $\delta_{2PA}$ PIs for TPP.\(^1\)\(^-\)\(^5\) As outlined in Chapters 1 - 2, the synthesis of effective 2PA PIs for TPP involves a number of key challenges that are considered crucial to the polymerisation process.

The mechanism of polymerisation for these types of molecules is outlined fully in Chapter 1, Section 1.4.6. To briefly recap, two-photon excitation of a PI excites electrons from the ground state to the excited triplet state through intersystem crossing, followed by electron transfer to an acrylate monomer producing a radical species and initiating polymerisation within the laser focal point.\(^6\)\(^-\)\(^9\) The outlined mechanisms are different to early demonstrations of TPP, which often employed commercially available PIs designed for one-photon initiated polymerisation. As such, these PIs often have very low $\delta_{2PA}$ (<20 GM),\(^10\) thus require longer exposure times and higher powers leading to potential damage of the polymer during fabrication.\(^11\) These are considered Type I PIs due to the intramolecular nature of the mechanism, but differ based on the final radical species producing step, which involves electron transfer or homolytic cleavage. For two-photon optimised molecules, the main process for radical production is via a photoexcited electron transfer from the active triplet state.\(^4\) For early commercial UV-based PIs, \( \alpha \)-homolytic cleavage producing two active radical species is the dominant process and this often occurs in the presence of a carbonyl derived functional group.\(^12\),\(^13\)

The molecules synthesised and described here were based around the well-known triphenylamine (TPA) electron donor core. TPA is desirable due to the electron donor ability of the central nitrogen atom coupled with the propeller shape of the molecule with $C_3$ symmetry, which allow for dipolar, quadrupolar and octupolar features.\(^14\) The combination of TPA with the inclusion of aromatic thiophene and phenyl linkers to extend the $\pi$-conjugation has previously been found to improve ICT and thus, $\delta_{2PA}$.\(^15\)\(^-\)\(^21\) The introduction of electron acceptor groups plays a dual role – through both increased $\pi$-conjugation length and improved ICT between donors and acceptors. Such modifications have yielded efficient 2PA chromophores with exceptionally high $\delta_{2PA}$ values.\(^21\)\(^-\)\(^23\) The use of
acceptor groups has also been shown to assist in reducing $\phi_F$ which can improve the PIs sensitivity during the TPP process.\textsuperscript{9,24} Finally, the solubility of the PI in the acrylate monomers selected for TPP testing was considered to be crucial in allowing for effective polymerisation. Compounds containing the powerful TCF acceptor 2-(3-cyano-4,5,5-trimethylfuran-2(5H)-ylidene)malononitrile, have been well-studied for use in second order nonlinear optics.\textsuperscript{25-28} Cyano groups possess low energy $\pi^*$ orbitals and when linked with conjugated C=C bridges, create powerful electron acceptors.\textsuperscript{29-31} Making use of the previously outlined synthesis of the parent dimethyl TCF system (10) (Figure 1),\textsuperscript{32,33} it was postulated that by preparing molecules containing 2-(3-cyano-5,5-didecyl-4-methylfuran-2(5H)-ylidene)malononitrile (C$_{10}$-TCF, 21) and which would contain solubilising hydrocarbon moieties, the solubility of the PIs would be significantly enhanced (Figure 1).

![Figure 1 - Structure of electron acceptor TCF (10) and C$_{10}$-TCF (21) used in this chapter.](image)

Consequently, a series of dipolar (D-\pi-A) and quadrupolar (A-\pi-D-\pi-A and A-\pi-A) PIs were designed (Figure 2 and Figure 3) and synthesised as described in Figure 5, Figure 6, Figure 8 and Figure 11. Their linear photophysical properties were assessed using UV-Vis measurements and quantum fluorescence measurements in suitable solvents, while non-linear measurements were performed using the z-scan technique to yield information on the two-photon absorption properties of these molecules at 780 nm. Finally, investigations of their potential to initiate the polymerisation of acrylate monomers was explored using an 800 nm fs Ti:Sapphire laser system.

### 3.2. Results and discussion

A number of dipolar (D-\pi-A) and quadrupolar (A-\pi-D-\pi-A, A-\pi-A) were synthesised in order to maximise the overall $\delta_{2PA}$, viz 11, 12b, 16, 17, 22 – 25 (Figure 2 and Figure 3). The synthesis of these molecules was conducted through known intermediates and using well-
known and efficient literature methods such as the Vilsmeier-Haack formylation\textsuperscript{34,35}, Heck-Coupling\textsuperscript{36} and Knoevenagel condensations as outlined below.\textsuperscript{26}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{structures.png}
\caption{Structures of final synthesised PIs 11, 12b, 16 and 17.}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{structures2.png}
\caption{Structures of final synthesised PIs 22 – 25.}
\end{figure}

3.2.1 Synthesis of triphenylamine TCF donor-\(\pi\)-acceptor molecules

The strong electron acceptor 2-(3-cyano-4,5,5-trimethylfuran-2(5H)-ylidene)malononitrile (TCF) (10) was prepared according to the literature method shown in Figure 4.\textsuperscript{33} Initially,
the starting alkyne 2-methylbut-3-yne-2-ol was converted into 3-hydroxy-3-methylbutan-2-one (9) with mercury (II) oxide and dilute sulfuric acid.\textsuperscript{37} Then, 9 was reacted with 4 equivalents of malononitrile to produce 2-(3-cyano-4,5,5-trimethylfuran-2(5H)-ylidene)malononitrile (TCF) (10) as a brown powder without further purification in 55% yield, 350 g.\textsuperscript{33} The product could be used after filtration and ethanol washing which made its large scale synthesis simple and efficient. The structure was confirmed by \textsuperscript{1}H NMR, \textsuperscript{13}C NMR, and HRMS and was consistent with previous reports.\textsuperscript{33}

Figure 4 – Synthesis of the electron acceptor TCF, 10.

The synthesis of TPA aldehydes 1, 2 and 3 are described in Chapter 2 > Experimental. The base-catalysed Knovenagel reaction was employed, using TCF (10) and the corresponding aldehydes 1 and 2, and it was found possible to generate the mono-TCF derivatives 11 and 12b in moderate yields of 37% and 12.5%, respectively (Figure 5). The initial procedure was aimed at synthesising the desired species 12a, however 12b was isolated during the purification stage and any 12a present was lost. The reactions were conducted in methanol at 65 °C over six hours with catalytic triethylamine (NEt\textsubscript{3}), and a noticeable colour change from an orange-brown to a deep blue/purple colour indicated product formation for both 11 and 12b, respectively. The purification of 11 and 12b presented a much greater challenge and required two to three column chromatography procedures to purify to a suitable level. This was due to several factors: strongly coloured products and by-products made identifying the target product difficult and in the case of 12b, as coupling to more than one aldehyde group is possible, thus a complex mixture of products was present. All attempts to isolate 12a were subsequently unsuccessful.
Figure 5 – Synthesis of final compounds 11, 12b and the failed synthesis of 12a from TPA aldehydes 1 and 2.

For 11 the final structure was confirmed by \( ^1 \text{H} \) NMR, with the loss of the 1H singlet at 9.95 ppm seen in 1, and the appearance of two 1H doublets (\( J = 17.07 \) Hz) at 7.89 ppm and 6.99 ppm for the new protons bound to the \( \text{HC}=\text{CH} \) bond. Secondly, the two CH\(_3\) groups on the TCF acceptor moiety were seen as a 6H singlet at 1.77 ppm. Upon attempted purification of the desired 12a, 12b was isolated as the pure final product, as confirmed by \( ^1 \text{H} \) NMR and HRMS. The \( ^1 \text{H} \) NMR showed a clean product, however the presence of a 1H singlet at 9.8 ppm and a 6H singlet at 1.8 ppm indicated the existence of only one TCF acceptor. Furthermore, the loss of one relative 1H singlet at 9.85 ppm seen in 2 was replaced with two 1H coupled doublets (\( J = 16.86 \) Hz) at 7.62 ppm and 6.91 ppm, respectively for the new \( \text{HC}=\text{CH} \) bond. The combination of these integrals indicated that only one \( \text{HC}=\text{CH} \) bond was present.
Compounds 11 and 12b were dark purple solids which displayed moderate solubility in chlorinated solvents like DCM and chloroform as well as high polarity solvents such as DMF, DMSO, and methanol. As 11 and 12b were only moderately soluble, it would be expected that the addition of further TCF branching would further decrease expected solubility (viz. reaction using 3). Furthermore as 11 displayed poor acrylate monomer solubility, no further attempts to synthesise and isolate 12a were conducted. Nonetheless, to mitigate the issue of incomplete coupling between the acceptor and 2, future reactions (preparation of 23 - 25) were performed with a greater excess of TCF and longer reaction times were employed.

3.2.2 Synthesis of triphenylamine π-extended TCF donor-π-acceptor molecules

The synthesis of the dipolar thiophene π-extended compound 16 and dipolar phenyl π-extended molecule 17 and are shown in Figure 6. The synthesis of 4-formyltriphenylamine 1 is described in Chapter 2. The starting aldehyde 1 was converted into 4-vinyltriphenylamine (13) using t-BuOK and methyl(triphenyl)phosphonium bromide by a known literature method. The purification was simple due to the stark difference in polarity and colour between 1 and 13. Purification was achieved by way of a short silica column using petroleum spirit 60-80 °C as eluent, yielding pure 13 as a white solid in 52% yield. The remaining un-reacted aldehyde was recovered by eluting with 25% DCM: petroleum spirit 60-80 °C. Conversion of the starting aldehyde 1 to alkene 13 was observed by NMR spectroscopy due loss of the aldehyde 1H proton at 9.95 ppm. This was replaced by a 1H doublet of doublets at 6.57 ppm, a 1H doublet at 5.56 ppm and a 1H doublet at 5.08 ppm, with these peaks being consistent with previous literature reports for 13. From 13 the synthesis of intermediates (E)-5-(4-(diphenylamino)styryl)thiophene-2-carbaldehyde (14) and (E)-4-(4-(diphenylamino)styryl)benzaldehyde (15) were conducted using a known literature method which utilised a Heck-coupling reaction. In the synthesis of 14, 5-bromothiophene-2-carbaldehyde was coupled with 13 via overnight heating in DMF at 110 °C to yield a crude brown oil which was extracted into DCM, washed, filtered and dried in vacuo. The solids were loaded onto silica gel and purified via column chromatography using 30% DCM: petroleum spirit 60-80 °C to afford 14 as a yellow/orange solid in 38% yield. The product was confirmed by 1H NMR, as indicated by the 1H aldehyde singlet at 9.76 ppm. Alongside this, two coupled (J = 4.04 Hz) 1H doublets were seen at 7.55
and 7.00 ppm showing the presence of the thiophene protons. Furthermore, none of the alkene peaks seen for 13 were observed. The expected two 1H doublets for the newly formed HC=CH bond were obscured by the aromatic region protons. All the peaks were consistent with previous literature reports.39 The synthesis for 15 was conducted in the same manner as for 14 using bromobenzaldehyde, and 15 was isolated as an orange solid in 36% yield and was confirmed by 1H NMR spectroscopy. The aldehyde 1H singlet was observed at 9.95 ppm and the newly formed HC=CH bond were seen as two coupled (J = 16.3 Hz) 1H doublets at 7.40 ppm and 7.19 ppm. Lastly, no alkene peaks seen in 13 were observed with all the peaks observed being consistent with previous literature reports.

The synthesis for 16 and 17 involved the base catalysed Knovenagel coupling of aldehydes 14 and 15 with 10. This procedure was conducted in the same manner as for compound 11, with the full scheme shown in Figure 6. Heating at 65 °C for 6 h in methanol with a catalytic amount of triethylamine yielded the desired products, indicated by the distinct colour change from yellow/orange to a deep blue/purple for both 16 and 17. As with the previous syntheses detailed here, the purification of 16 and 17 proved difficult and required several purification steps to yield a suitably pure product. As such, overall yields were greatly diminished, with final yields of 9% (16) and 10% (17).

Thus, both products proved problematic to purify via column chromatography alone – due to an impurity which was close in Rf to the product on TLC. Consequently, the partly purified products were dissolved in the minimum volume of DCM and precipitated with a large volume of petroleum spirit 60-80 °C (> 500 ml) and filtered. This process was repeated several times to yield 16 and 17 as pure products.

The successful isolation of 16 was confirmed by NMR and HRMS. The 1H NMR spectrum showed the presence of two HC=CH bonds as four 1H doublets, the first pair at 8.11 and 6.72 ppm (J = 15.2 Hz) and a second pair at 7.40 and 7.23 ppm (J = 16.1 Hz). A 6H singlet was observed at 1.77 ppm for the two CH₃ groups from the TCF acceptor moiety. Furthermore, the 1H aldehyde singlet seen for 14 was no longer evident. The 1H NMR spectrum for 17 was similar to that described for 16, with one of the HC=CH groups appearing as 1H doublets at 7.22 and 7.00 ppm (J = 16.2 Hz). However, for the HC=CH group...
located between the TCF and phenyl ring one doublet was seen at 7.63 ppm ($J = 16.7 \, \text{Hz}$) whilst the other was masked by the aromatic protons in a 5H multiplet at 7.09 – 7.04 ppm. The two methyl CH$_3$ groups on the TCF group were seen as a 6H singlet at 1.78 ppm. The HRMS data for the final products 16 and 17 are presented and further analysis by $^{13}$C NMR spectroscopy is in the *Experimental* section.

Figure 6 – Synthetic route of the dipolar thiophene π-extended 16 and phenyl π-extended 17 as synthesised from 4-formyltriphenylamine 1.
Compounds 16 and 17 are both dark purple solids which display poor solubility in low polarity solvents like toluene and petroleum spirit 60 - 80 °C, but, reasonable solubility in DMF, DMSO and methanol. Importantly, the solubility in our reference acrylate system was also relatively poor. Initially, it was planned to synthesise a full series of D-π-extended-A molecules, which included the dipolar molecules 11, 16 and 17 (Figure 5 and Figure 6) alongside quadrupolar A-π-D-π-A system 12b (Figure 5) and octupolar A_3-π-D molecules based on the same donors and acceptors. The two most important considerations were the issue of product solubility, ease of synthesis and purification. Due to the derivatives containing the parent TCF (10) yielding only moderately soluble compounds (11, 16 and 17), additional branching using the parent TCF (10) moiety would be expected to further decrease solubility. This is despite the fact that the proposed quadrupolar and octupolar molecules would likely possess a greatly enhanced δ_{2PA}. Therefore, due to the difficulty in the synthesis and purification of the dipolar (11, 16 and 17) and quadrupolar (12b) species, along with their poor solubility, further attempts to synthesise multi-polar analogues containing the parent TCF (10) were discontinued.

3.2.3 Synthesis of triphenylamine C_{10}-TCF donor-π-acceptor molecules

As outlined previously (Chapter 1), PIs which possess a high δ_{2PA} and high solubility are desirable. Whereas, TCF 10 is a strong electron acceptor due to presence of multiple cyano moieties, these adversely affect solubility in solvents and monomers. The dimethyl groups do little to improve this, however more soluble derivatives of 10 are known and have been investigated in previous work. Thus, the acceptor 2-(3-cyano-5,5-didecyl-4-methylfuran-2(SH)-ylidene)malononitrile (C_{10}-TCF ) 21 was synthesised by the previously described synthetic route conducted within our research group. In order to prepare 21, the synthesis of a bis-C_{10}H_{21} containing α-hydroxy ketone (20) was required (Figure 7). Thus, firstly, an acetal ester was generated by the reaction of ethyl pyruvate and triethyl orthoformate with catalytic H_2SO_4 as per a previous literature method. This yielded 2,2-diethoxypropanoate 18, which was used without further purification.
Figure 7 – Synthetic procedure of the C$_{10}$-TCF electron acceptor 21. Initial starting materials ethyl pyruvate and triethyl orthoformate are used to produce 2,2-diethoxypropanoate 18. This was followed by a Grignard reaction yielding 19 (not isolated) with subsequent acid hydrolysis forming $\alpha$-hydroxy ketone 20. Finally, a Knoevenagel condensation produces the final C$_{10}$-TCF acceptor 21.

Secondly, a standard Grignard reagent was formed by reacting magnesium with 1-bromodecane and this was coupled with 18 to give the desired 11-(1,1-diethoxyethyl)henicosan-11-ol 19. This was not isolated and was acid hydrolysised to yield the 3-decyl-3-hydroxytridecan-2-one 20 as a yellow oil in 63% yield, and which was used without further purification. Finally, treatment of 20 with four equivalents of malononitrile in pyridine at room temperature for 3 days yielded 2-(3-cyano-5,5-didecyl-4-methylfuran-2(5H)-ylidene)malononitrile 21 as brown semi-solid in 56% yield. The product was confirmed by $^1$H NMR spectroscopy, as a 3H singlet at 2.29 ppm and the two terminal CH$_3$ groups at 0.89 ppm were observed. This was consistent with literature data from our group for a close analogue of 21, which had C$_{10}$ as the pendant alkyl chain rather than the C$_{10}$ presented here. Further confirmation was provided by HRMS and $^{13}$C NMR analysis. The synthesis of dipolar (E)-2-(3-cyano-5,5-didecyl-4-(4-(diphenylamino)styryl)furan-2(5H)-ylidene)malononitrile 22 and quadrupolar 2,2',4,4'-(((1E,1'E)-(phenylazanediyl)bis(4,1-phenylene))bis(ethene-2,1-diyl))bis(3-cyano-5,5-didecylfuran-4(5H)-yl)-2(5H)-ylidene))dimalononitrile 23 are shown in Figure 8. The synthesis was performed under similar conditions as those outlined for 11 and 12b. However, a 72 h reaction time - and in the case of 23 - extra equivalents of 21 were used to mitigate the likelihood of any aldehyde groups being left un-reacted.
Figure 8 - The synthetic procedure of TPA-C_{10}-TCF 22 and 23.

The synthesis of 22 was conducted in a similar manner as for 11, i.e. via the base catalysed Knovenagel condensation of 4-formyltriphenylamine 1 with two equivalents of C_{10}-TCF 21. The crude blue-purple oil was loaded onto silica gel and eluted with 15 % DCM: petroleum spirit 60-80 °C. As with 11, several deeply coloured by-products were present and identification of the desired product proved difficult. Thus, several purification steps were necessary, which reduced the final yield to 4%, but this gave 250 mg of pure product. The structure was confirmed by NMR spectroscopy which showed the loss of the 1H singlet aldehyde at 9.95 ppm, which was replaced with two coupled 1H doublets at 7.59 and 6.84 ppm (J = 16.02 Hz), respectively. Further to this, the presence of the 42 alkyl chain hydrogens as a 2H multiplet at 2.16 - 2.10, a 2H multiplet at 1.94 - 1.88, a 28H broad singlet at 1.23 ppm, a 2H broad singlet at 1.2 - 1.12 and 1.08 - 1.00, and a 6H triplet at 0.87 ppm, also confirmed the structure. An example of the alkyl region for 22 can be seen in Figure 9 and was consistent with other C_{10}-TCF containing species 23 and 25 (described below). HRMS analysis confirmed the final product had the molecular formula C_{48}H_{58}N_{4}OH (found 707.4689, Δ 0.0 ppm).
Figure 9 – $^1$H NMR of 22 showing the C$_{10}$ alkyl hydrogens. A total of 42 hydrogens were seen per each additional C$_{10}$-TCF moiety.

The synthesis of 23 followed the same procedure as for 22, with the starting material 4,4'-diformyltriphenylamine (2) being treated with 4 equivalents of C$_{10}$-TCF 21 to give a crude blue-purple oil which was loaded onto silica. The product was eluted with 25% DCM: petroleum spirit 60-80 °C and as with 22 required several column runs to yield pure product, albeit in a very low yield of 0.2%. This low yield was due to the presence of multiple deeply coloured by-products, which were of similar polarity as to the target product, making isolating the desired 23 difficult. As such, a large amount of the product was lost as impure fractions from the column runs and it was decided that further efforts to purify this crude material were overly time consuming. The HC=CH bonds formed between the aldehyde and methyl group of 21 were confirmed from the $^1$H NMR spectrum via two coupled 2H doublets being observed at 7.61 and 6.92 ppm ($J = 16.25$ Hz). Alongside this, the 2H aldehyde singlet seen for starting material 2 at 9.85 ppm was no longer present. Lastly, the four terminal CH$_3$ groups were shown as a 12H triplet at 0.87 ppm and were consistent with 22 (Figure 9). The HRMS showed the final product to have the molecular formula C$_{78}$H$_{101}$N$_7$O$_2$Na 1190.7906; Δ = 0.3 ppm.
3.2.4 Synthesis of quadrupolar acceptor-π-acceptor molecules

Given the utility of the TCF acceptor system, it was decided to also explore its use in the development of quadrupolar A-π-A systems. Consequently the synthesis of the quadrupolar A-π-A PIs 24 and 25 (Figure 11) was undertaken. Initially, 24 was a by-product formed during an alternative synthesis of 17 (Figure 10). In the alternative synthesis of 17, it was planned to react TCF 10 and terephthalaldehyde to give compound A (Figure 10) which could then undergo Horner-Wadsworth-Wittig coupling with a triphenylamine-phosphonate derivative (Figure 10, B) to give 17. However, it was found that the t-BuOK base used to catalyse the formation of A from terephthalaldehyde and 10, led to formation of the bis-adduct 24 and which led to difficulties in purifying compound A. As a consequence, the proposed methodology outlined in Figure 10 was abandoned, but compound 24 was still considered of potential interest. 24 has been previously reported alongside several other TCF containing materials, although, few details are given on its physical and photophysical properties.\(^{43}\)

![Chemical structure](image)

**Figure 10** – An attempted synthesis of 17 via an alternative procedure making use of a TPA-phosphonate B and TCF-phenylaldehyde A.

To optimise the preparation of 24, to a solution of 10 in methanol was added terephthalaldehyde (0.5 equivs), catalytic NEt\(_3\) and NH\(_4\)OAc, which produced a dark brown solution. The solution was heated to 65 °C overnight forming a dark red suspension. Upon cooling the solids were filtered and washed with methanol to yield a red solid (24) in 68%
yield, 0.68 g. The material was of sufficient purity to be used without further purification. From $^1$H NMR analysis the $\text{HC} = \text{CH}$ groups formed were apparent as two coupled 2H doublets at 8.06 and 6.81 ppm ($J = 16.47$ Hz). The phenyl hydrogens were observed as two coupled 2H doublets at 7.69 and 7.40 ppm ($J = 4.89$ Hz). Finally, a 12H singlet was observed at 1.79 ppm for the four CH$_3$ groups present on the TCF acceptor moieties. No CH$_3$ 3H singlet at 2.40 ppm was observed indicating the consumption of the TCF 10 starting material. Lastly, the HRMS showed the correct molecular ion. [calculated for C$_{30}$H$_{20}$N$_6$O$_2$Na 519.1545, found m/z [M$^+$Na] 519.1545 (100%); $\Delta = 0.0$ ppm].

**Figure 11** – Synthesis of A-π-A molecules 24 and 25 via a base catalysed Knoevenagal condensation.

In the case of the synthesis of 25, terephthalaldehyde, catalytic NEt$_3$ and NH$_4$OAc were added to a solution of 21 in methanol giving a dark brown suspension. The solution was heated to 65 °C overnight, whereupon a dark red suspension formed indicating product formation. Upon cooling the solids were filtered and washed with methanol to yield a red solid in 22.5% yield. The material was of sufficient purity to be used without further purification. From $^1$H NMR analysis, the two protons of the $\text{HC} = \text{CH}$ bonds formed were seen as two coupled 2H doublets at 7.63 and 7.11 ppm ($J = 16.48$ Hz). The phenyl hydrogens are observed as apparent 4H singlet at 7.74 ppm. Finally, the four C$_{10}$ alkyl chains were observed and were consistent with what was seen with the previous C$_{10}$-TCF containing
species (Figure 9). Lastly, the HRMS showed the molecular ion calculated for \( \text{C}_{66}\text{H}_{92}\text{N}_{6}\text{O}_{2}\text{Na} \) 1023.7168, found m/z [M+Na] 1023.7167 (100%); \( \Delta = -0.1 \) ppm.

### 3.2.5 Photophysical properties

The linear photophysical properties are described in Tables 2 - 8 and include the absorption maxima (\( \lambda_{\text{max}} \)), molar extinction coefficients (\( \varepsilon \)), and fluorescence emission (\( \lambda_{\text{Em}} \)), Stokes shifts (ST) and \( \phi_{\text{F}} \). A detailed description of the measurements are described in *Experimental > Instrumentation > Photophysics*. The data for toluene and DMF below 300 and 270 nm respectively, were omitted due to the UV/Vis cut-off limit of these solvents.

### 3.2.6 UV/Vis spectra

The UV/Vis spectra were measured in a variety of non-polar and polar solvents as detailed in Table 1. All spectra were performed at a concentration 1.0 \( \times \) 10\(^{-5} \) mol.L\(^{-1} \) and have been normalised in relation to the longest wavelength maxima. Across the series (Graphs 1-7), there were absorption maxima at 500 – 600 nm and these are attributed to strong ICT absorption bands.\(^{45} \) The absorption bands at approximately 250 - 350 nm are related to localised \( \pi-\pi^* \) transitions of the phenylene moieties.\(^{46} \) However, across the series these are greatly affected by solvent polarity and type. The very large absorptions for 12b at around 350 are due to the presence of the phenylene \( \pi-\pi^* \) transition, which is increased by the presence of the electron withdrawing aldehyde group. These chromophores possess CT ground states, and it is well-known in the literature that solvent polarity can shift these CT bands.\(^{47,48} \) Surprisingly, the \( \lambda_{\text{max}} \) show little to no solvatochromic behaviour across the series and generally the greatest red-shifts in the maxima were observed in chloroform, with small increases in the value of \( \lambda_{\text{max}} \) seen with higher polarity solvents.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>( \varepsilon )</th>
<th>( E_{\text{r}}(30) )</th>
<th>Solvent Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>Toluene</td>
<td>2.38</td>
<td>33.9</td>
<td>non polar</td>
</tr>
<tr>
<td>Dioxane</td>
<td>2.3</td>
<td>36</td>
<td>non polar</td>
</tr>
<tr>
<td>Chloroform (CHCl(_3))</td>
<td>4.81</td>
<td>39.1</td>
<td>non polar</td>
</tr>
<tr>
<td>Dimethylformamide (DMF)</td>
<td>36.7</td>
<td>43.2</td>
<td>polar aprotic</td>
</tr>
<tr>
<td>Acetonitrile (MeCN)</td>
<td>36.6</td>
<td>45.6</td>
<td>polar aprotic</td>
</tr>
<tr>
<td>Methanol (MeOH)</td>
<td>32.7</td>
<td>55.4</td>
<td>polar protic</td>
</tr>
</tbody>
</table>

*Table 1 - Dielectric constants (\( \varepsilon \)) and solvent polarity parameter \( E_{\text{r}}(30) \) values of the solvents used.*\(^{44} \)
Graph 1 - Normalised UV/Vis absorption spectrum of PI 11 in various solvents, details in Table 2.

In comparing 11 (Graph 1) and 12b (Graph 2), the $\lambda_{\text{max}}$ values were all blue-shifted in 12b and this suggested a decrease in the overall ICT character.\textsuperscript{49} The differences were c. 20 – 30 nm and were consistent across the range of solvents used. Due to the strong electron accepting nature of the formyl group, the ICT was effectively split between the two competing branches upon excitation.

<table>
<thead>
<tr>
<th>11</th>
<th>$\lambda_{\text{max}}$\textsuperscript{a}</th>
<th>$\varepsilon$\textsuperscript{b} (10\textsuperscript{3})</th>
<th>$\lambda_{\text{Em}}$\textsuperscript{c}</th>
<th>ST\textsuperscript{d}</th>
<th>$\Phi_{\text{F}}$\textsuperscript{e}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Toluene</td>
<td>547</td>
<td>5.93</td>
<td>628</td>
<td>81</td>
<td>-</td>
</tr>
<tr>
<td>Dioxane</td>
<td>531</td>
<td>2.75</td>
<td>640</td>
<td>109</td>
<td>-</td>
</tr>
<tr>
<td>CHCl\textsubscript{3}</td>
<td>560</td>
<td>1.50</td>
<td>681</td>
<td>121</td>
<td>0.022</td>
</tr>
<tr>
<td>DMF</td>
<td>550</td>
<td>3.96</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>MeCN</td>
<td>542</td>
<td>2.36</td>
<td>706</td>
<td>164</td>
<td>-</td>
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<tr>
<td>MeOH</td>
<td>551</td>
<td>5.81</td>
<td>675</td>
<td>124</td>
<td>-</td>
</tr>
<tr>
<td>Acrylate</td>
<td>550</td>
<td>4.71</td>
<td>656</td>
<td>106</td>
<td>0.048</td>
</tr>
</tbody>
</table>

\textsuperscript{a} $\lambda = \text{one-photon maxima (nm), measured at 1.0 \times 10^{-5} \text{ mol.L}^{-1}$.
\textsuperscript{b} $\varepsilon = \text{molar extinction coefficient \times 10}^{3} (\text{M}^{-1}\text{cm}^{-1})$.
\textsuperscript{c} $\lambda = \text{emission maxima (nm), 525 nm emission}$.
\textsuperscript{d} Stokes shift (nm) = ($\lambda_{\text{Em}} - \lambda_{\text{max}}$).
\textsuperscript{e} Fluorescence quantum yield with rhodamine 6G as a reference standard; concentration of $2 \times 10^{-6} \text{ mol.L}^{-1}$, 500 nm excitation.

As seen with quadrupolar 7 (Chapter 2) and 23 (Graph 6), a shoulder was evident on the high-energy side of the localised $\pi-\pi^{*}$ phenylene absorption band (c. 350 nm) which could indicate a splitting of the one-photon allowed states near the highest energy Franck-Condon states.\textsuperscript{50} This was evidenced by the inhibition of ICT, which in turn leads to an increased
probability of localised absorption and can be seen for 12b (Graph 2). This reduction in ICT was also evidenced by the lower $\varepsilon$ values of 12b when compared with 11.

![Graph 2 - Normalised UV/Vis absorption spectrum of PI 12b in various solvents, details in Table 3.](image)

<table>
<thead>
<tr>
<th>12b</th>
<th>$\lambda_{\text{max}}$</th>
<th>$\varepsilon$ ($10^3$)</th>
<th>$\lambda_{\text{em}}$</th>
<th>ST</th>
<th>$\phi_F$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Toluene</td>
<td>521</td>
<td>1.82</td>
<td>609</td>
<td>88</td>
<td>-</td>
</tr>
<tr>
<td>Dioxane</td>
<td>507</td>
<td>1.79</td>
<td>621</td>
<td>114</td>
<td>-</td>
</tr>
<tr>
<td>CHCl$_3$</td>
<td>539</td>
<td>1.84</td>
<td>648</td>
<td>109</td>
<td>0.0474</td>
</tr>
<tr>
<td>DMF</td>
<td>522</td>
<td>2.02</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>MeCN</td>
<td>517</td>
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<tr>
<td>MeOH</td>
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<td>3.39</td>
<td>667</td>
<td>150</td>
<td>-</td>
</tr>
<tr>
<td>Acrylates</td>
<td>524</td>
<td>1.08</td>
<td>644</td>
<td>120</td>
<td>0.145</td>
</tr>
</tbody>
</table>

Table 3 - a. $\lambda$ = one-photon maxima (nm), measured at 1.0 x $10^{-5}$ mol.L$^{-1}$. b. $\varepsilon$ = molar extinction coefficient x $10^3$ (M$^{-1}$ cm$^{-1}$). c. $\lambda$ emission maxima (nm), 500 nm emission. d. Stokes shift (nm) = ($\lambda_{\text{em}}$ - $\lambda_{\text{max}}$). e. Fluorescence quantum yield with rhodamine 6G as a reference standard; concentration of 2 x $10^{-6}$ mol.L$^{-1}$, 500 nm excitation.

For molecules 16 (Graph 3) and 17 (Graph 4), the $\pi$-conjugation has been increased due to the presence of the thiophene and phenylene linkers respectively. In comparing 16 vs 11, a bathochromic shift of the absorption maxima was observed across the varying solvents which was consistent with previous literature reports.$^{51}$
Graph 3 - Normalised UV/Vis absorption spectrum of PI 16 in various solvents, details in Table 4.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>$\lambda_{\text{max}}$</th>
<th>$\varepsilon$</th>
<th>$\lambda_{\text{Em}}$</th>
<th>ST</th>
<th>$\phi$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Toluene</td>
<td>595</td>
<td>2.33</td>
<td>738</td>
<td>143</td>
<td>-</td>
</tr>
<tr>
<td>Dioxane</td>
<td>581</td>
<td>2.33</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>CHCl$_3$</td>
<td>628</td>
<td>3.15</td>
<td>805</td>
<td>177</td>
<td>0.002</td>
</tr>
<tr>
<td>DMF</td>
<td>591</td>
<td>2.00</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>MeCN</td>
<td>576</td>
<td>3.25</td>
<td>-</td>
<td>-</td>
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</tr>
<tr>
<td>MeOH</td>
<td>585</td>
<td>3.54</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Acrylates</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Table 4 - a, $\lambda$ = one-photon maxima (nm), measured at $1.0 \times 10^{-5}$ mol.L$^{-1}$. b, $\varepsilon$ = molar extinction coefficient x $10^3$ (M$^{-1}$cm$^{-1}$). c, $\lambda$ emission maxima (nm), 600 nm emission. d, Stokes shift (nm) = ($\lambda_{\text{Em}}$ - $\lambda_{\text{max}}$). e, Fluorescence quantum yield with rhodamine 6G as a reference standard; concentration of $2 \times 10^{-6}$ mol.L$^{-1}$, 500 nm excitation.

Furthermore, the molar absorptivity of 16 was generally similar to that of 11, with the exception of toluene (5.93 vs. 2.33) and methanol (5.81 vs. 3.54) which displayed significantly lower values. For 17 the absorption maxima in various solvents display a hypsochromic shift relative to 11 and a reduction is also seen in the values of $\varepsilon$. Therefore, the replacement of the phenyl (17) unit by a thienyl (16) unit results in a red shift in the absorption band, indicating that the reduced aromaticity in the connecting unit does not lead to a large reduction of the electronic gap between ground and excited states. 52
Graph 4 - Normalised UV/Vis absorption spectrum of PI 17 in various solvents, details in Table 5.

<table>
<thead>
<tr>
<th>17</th>
<th>λ_{max}^a</th>
<th>ε b \times 10^3</th>
<th>λ_{Em}^e</th>
<th>ST d</th>
<th>φF^e</th>
</tr>
</thead>
<tbody>
<tr>
<td>Toluene</td>
<td>540</td>
<td>1.74</td>
<td>630</td>
<td>80</td>
<td>-</td>
</tr>
<tr>
<td>Dioxane</td>
<td>520</td>
<td>1.22</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>CHCl3</td>
<td>574</td>
<td>4.85</td>
<td>717</td>
<td>143</td>
<td>0.0016</td>
</tr>
<tr>
<td>DMF</td>
<td>520</td>
<td>2.24</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>MeCN</td>
<td>509</td>
<td>1.88</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>MeOH</td>
<td>518</td>
<td>1.71</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Acrylates</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Table 5 - a. λ = one-photon maxima (nm), measured at 1.0 \times 10^{-5} \text{ mol.L}^{-1}. b. ε = molar extinction coefficient x 10^3 (M^{-1}cm^{-1}). c. λ emission maxima (nm), 600 nm emission. d. Stokes shift (nm) = (λ_{Em} - λ_{max}). e. Fluorescence quantum yield with rhodamine 6G as a reference standard; concentration of 2 \times 10^{-6} \text{ mol.L}^{-1}, 500 nm excitation.

For the dipolar 22 (Graph 5) and quadrupolar 23 (Graph 6), the λ_{max} values were generally red-shifted with the addition of a second branch in 23, indicating electronic coupling between the branches.53 The red-shifts in the optical absorption of 23 compared with 22 were also ascribed to a higher degree of exciton delocalisation between the chromophores.47 This also suggests that ICT character was slightly larger for the quadrupolar species 23 and this is consistent across the solvent polarities used. As the level of branching, and therefore the number of acceptors, was increased from 22 to 23, changes were evident in the measured ε values. The values of ε are 27,100 (toluene) and 28,100 (dioxane) for 22, but 44,900 (toluene) and 48,100 (dioxane) for 23. The fact that the ε value is effectively doubled in these solvents was indicative of the branches acting independently.53
Graph 5 - Normalised UV/Vis absorption spectrum of PI 22 in various solvents, details in Table 6.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>( \lambda_{\text{max}} ) (nm)</th>
<th>( \varepsilon \times 10^3 )</th>
<th>( \lambda_{\text{Em}} ) (nm)</th>
<th>ST (nm)</th>
<th>( \Phi_F )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Toluene</td>
<td>557</td>
<td>2.71</td>
<td>635</td>
<td>78</td>
<td>0.045</td>
</tr>
<tr>
<td>Dioxane</td>
<td>535</td>
<td>2.81</td>
<td>639</td>
<td>104</td>
<td>0.078</td>
</tr>
<tr>
<td>CHCl₃</td>
<td>572</td>
<td>4.43</td>
<td>676</td>
<td>104</td>
<td>0.031</td>
</tr>
<tr>
<td>DMF</td>
<td>560</td>
<td>2.96</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>MeCN</td>
<td>550</td>
<td>5.22</td>
<td>711</td>
<td>161</td>
<td>0.0006</td>
</tr>
<tr>
<td>MeOH</td>
<td>562</td>
<td>5.90</td>
<td>678</td>
<td>116</td>
<td>0.0007</td>
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<tr>
<td>Acrylates</td>
<td>560</td>
<td>4.46</td>
<td>656</td>
<td>94</td>
<td>0.055</td>
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</table>

Table 6: \( \lambda_{\text{max}} \) = one-photon maxima (nm), measured at 1.0 x 10⁻⁵ mol.L⁻¹. \( \varepsilon \) = molar extinction coefficient x 10³ (M⁻¹cm⁻¹). \( \lambda_{\text{Em}} \) emission maxima (nm), 525 nm emission. ST = (\( \lambda_{\text{Em}} \) - \( \lambda_{\text{max}} \)). Fluorescence quantum yield with rhodamine 6G as a reference standard; concentration of 2 x 10⁻⁶ mol.L⁻¹, 500 nm excitation.

Conversely, in higher polarity solvents a much smaller difference in \( \varepsilon \) values were observed suggesting the branches were less independent. The red shift in \( \lambda_{\text{max}} \) was further evidence for the enlargement of the ICT upon the introduction of the second conjugated branch, similar behaviour has been observed in other multi-branched structures.⁴⁹

A shoulder was evident on the high-energy side of the main absorption band for 23 (Graph 6) and, as observed for PI 7 (Chapter 2), is related to a splitting of the excited states through interbranch coupling. This coupling splits the excited state into two bands positioned symmetrically with respect to the dipolar species.⁵⁴-⁵⁶ This phenomenon was predicted by the Frenkel exciton model (Chapter 2, Figure 8), which was applied to H- and J-aggregates and assumes electrostatic interactions between the molecules.⁵⁴,⁵⁷,⁵⁸
Graph 6 - Normalised UV/Vis absorption spectrum of PI 23 in various solvents, details in Table 7.

<table>
<thead>
<tr>
<th>23</th>
<th>$\lambda_{\text{max}}$ a</th>
<th>$\varepsilon$ b ($10^3$)</th>
<th>$\lambda_{\text{Em}}$ c</th>
<th>ST d</th>
<th>$\Phi_F$ e</th>
</tr>
</thead>
<tbody>
<tr>
<td>Toluene</td>
<td>572</td>
<td>4.49</td>
<td>628</td>
<td>56</td>
<td>0.055</td>
</tr>
<tr>
<td>Dioxane</td>
<td>554</td>
<td>4.81</td>
<td>634</td>
<td>80</td>
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<td>590</td>
<td>5.18</td>
<td>662</td>
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<td>DMF</td>
<td>577</td>
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<td>-</td>
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</tr>
<tr>
<td>MeCN</td>
<td>574</td>
<td>6.43</td>
<td>711</td>
<td>137</td>
<td>0.0001</td>
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<td>5.45</td>
<td>709</td>
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<td>0.0016</td>
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<td>2.88</td>
<td>662</td>
<td>90</td>
<td>0.066</td>
</tr>
</tbody>
</table>

Table 7 - a. $\lambda$ = one-photon maxima (nm), measured at $1.0 \times 10^{-5}$ mol.L⁻¹. b. $\varepsilon$ = molar extinction coefficient x $10^3$ (M⁻¹cm⁻¹). c. $\lambda$ emission maxima (nm), 550 nm emission. d. Stokes shift (nm) = ($\lambda_{\text{Em}} - \lambda_{\text{max}}$). e. Fluorescence quantum yield with rhodamine 6G as a reference standard; concentration of $2 \times 10^{-6}$ mol.L⁻¹, 500 nm excitation.

Comparing the $\lambda_{\text{max}}$ of TCF compound 11 (Graph 1) and its C₁₀-TCF analogue 22 (Graph 5), some noticeable differences are seen. In general, a 10 nm red shift was observed across the solvent polarities with the addition of the C₁₀-TCF group. This can be explained by the differences in structural confirmation between the two structures.

For the A-π-A species 25 (Graph 7), the absorption maxima display little solvatochromism with the exception of methanol which displays a near 20 nm blue shift in the predominant $\pi-\pi^*$ transition in the 400-450 nm range. In acetonitrile and methanol, a slight broadening of the absorption band can be seen indicating an increasing level of ground-state ICT. However these transitions are still predominantly from a locally excited state, with a 20 nm shift seen for methanol.⁵⁹
Graph 7 – Normalised UV/Vis absorption spectrum of PI 25 in various solvents, details in Table 8.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>(\lambda_{\text{max}})</th>
<th>(\varepsilon) (\times) (10^3)</th>
<th>(\lambda_{\text{em}})</th>
<th>ST</th>
<th>(\phi_F)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Toluene</td>
<td>460</td>
<td>5.64</td>
<td>583</td>
<td>123</td>
<td>-</td>
</tr>
<tr>
<td>Dioxane</td>
<td>456</td>
<td>5.94</td>
<td>513</td>
<td>57</td>
<td>-</td>
</tr>
<tr>
<td>CHCl3</td>
<td>459</td>
<td>6.30</td>
<td>581</td>
<td>122</td>
<td>0.018</td>
</tr>
<tr>
<td>MeCN</td>
<td>452</td>
<td>5.05</td>
<td>579</td>
<td>127</td>
<td>-</td>
</tr>
<tr>
<td>MeOH</td>
<td>434</td>
<td>6.19</td>
<td>554</td>
<td>120</td>
<td>-</td>
</tr>
<tr>
<td>Acrylates</td>
<td>425</td>
<td>8.89</td>
<td>545</td>
<td>120</td>
<td>0.053</td>
</tr>
</tbody>
</table>

Table 8 - \(\lambda\) = one-photon maxima (nm), measured at 1.0 x \(10^{-5}\) mol.L\(^{-1}\). \(\varepsilon\) = molar extinction coefficient \(\times\) \(10^3\) (M\(^{-1}\)cm\(^{-1}\)). \(\lambda_{\text{em}}\) = emission maxima (nm), 440 nm emission. ST = Stokes shift (nm) = \((\lambda_{\text{em}} - \lambda_{\text{max}})\). \(\phi_F\) = Fluorescence quantum yield with rhodamine 6G as a reference standard; concentration of 2 x \(10^{-6}\) mol.L\(^{-1}\), 500 nm excitation.

3.2.7 Photoluminescence

Fluorescence and \(\phi_F\) measurements were performed for 11, 12b, 22, 23 and 25 in various solvents. In general, all species exhibited low fluorescence emissions and \(\phi_F\) values. This was particularly so in polar solvents like methanol, DMF and acetonitrile where the fluorescence emissions were exceptionally low (< 50 a.u.). As such, large slit widths and voltages were used alongside data smoothing to give a more accurate depiction of their fluorescence spectra. For the \(\phi_F\) measurements, Rhodamine 6G in ethanol was used as the reference standard and an emission wavelength of 500 nm was used.\(^{60}\)

Many multi-branch chromophores have no permanent dipole moment. However, for many chromophores, experimental data suggest the existence of polar excited states. In particular, strong fluorescence solvatochromism has been observed for many dipolar,
quadrupolar and octupolar species.\textsuperscript{61-65} Time-resolved fluorescence anisotropy measurements suggest that the initial delocalised excitation is localised to a single dipolar branch, giving a polar excited state.\textsuperscript{61} For our chromophores containing electron-donor and electron-acceptor groups, CT occurs upon excitation from the electron-donor to the electron-acceptor through the $\pi$-conjugation pathway. The CT process is expected to increase the dipole moment in the excited state and would therefore be stabilised by highly polar solvents.\textsuperscript{66}

The fluorescence emission spectra of all the measured PIs display a bathochromic shift of the emission band, thus suggesting the excited state is more polar and therefore, stabilised by increasing solvent polarity.\textsuperscript{67} Such solvatochromic behaviour is typical of compounds with ICT character with an increase in dipole moment upon excitation for TPA-based structures being well known in the literature.\textsuperscript{14,68} The emission intensity in non-polar solvents (toluene, dioxane and chloroform) were significantly larger than the corresponding intensities observed in polar solvents (acetonitrile and methanol). Large Stoke shifts (ST) were observed across the series and indicate that significant electronic reorganisation occurs after excitation and prior to emission.\textsuperscript{69}

The overall $\phi_F$ values, as measured in chloroform, were low across the entire series with values as low as 0.018 for 25. The use of strong donors (TPA) and strong acceptors (TCF & C\textsubscript{10}-TCF) maximise overall CT and this is known to reduce $\phi_F$.\textsuperscript{70} As previously demonstrated in Chapter 2, the local viscosity effects the TICT formed upon excitation leading to higher $\phi_F$. Overall, noticeable increases in the $\phi_F$ were measured in the acrylate system across the measured species, except in the case for 23 which displayed a near two-fold reduction in $\phi_F$.

The fluorescence spectra for 11 (Graph 8), 12\textsubscript{b} (Graph 2) and 22 (Graph 11) and, 23 (Graph 6) show maxima observed at higher-energies in nonpolar solvents, but they all exhibited significant broadening and red-shifting for measurements obtained in higher polarity solvents. The fluorescence intensity was also considerably reduced in higher polarity solvents. It is postulated that conversion from a locally excited state to a ICT state is dependent on the solvent-controlled reaction coordinate.\textsuperscript{71}

Stewart et al. demonstrated that increasing solvent polarity can lead to a decrease in the radiative rate constants whilst the nonradiative rate constant can remain constant.\textsuperscript{72} This means the locally excited state has a fast radiative rate constant, which leads to higher $\phi_F$ in nonpolar solvents. Whereas the ICT state has a much slower radiative rate constant and this
contributes to smaller $\phi_F$. Due to the greater charge separation and excited state twisting, in the ICT state, internal conversion is able to compete and therefore lead to a decrease in the $\phi_F$. Further to this, their results suggest that molecules in the locally excited state remain in a geometry similar to that of the ground state. However, those in the ICT state are stabilised by formation of a TICT state.

To test this hypothesis, $\phi_F$ measurements for 22 were performed across our solvent range. This showed that as solvent polarity increased, the values of the $\phi_F$ dropped sharply. In toluene, dioxane and chloroform $\phi_F$ values of 0.045, 0.078 and 0.038 were measured, respectively. However, in the highly polar solvents acetonitrile and methanol very low values of 0.0006 and 0.0007 were measured, indicating that as polarity was increased the fluorescence emission converts from a locally excited state to one of an ICT state. The locally excited state possesses a fast-radiative decay constant ($k_f$) and this leads to higher $\phi_F$ in nonpolar solvents. The ICT state exhibits a slower radiative rate constant ($k_l$), caused via enhanced charge separation and excited state twisting – which results in internal conversion competing with fluorescence emission and thus this decreases the overall $\phi_F$. It should be noted that attempts were made to perform fluorescence lifetime measurements on 22 in a variety of solvents. However, because of the low signal to noise ratio no values were able to be obtained. This was due to lack of a suitably powerful excitation light-source, with initial attempts made using LED source operating at 500 nm which was found to be unsatisfactory.
Graph 8 - Normalised fluorescence emission of 11 as measured by 525 nm emission between 540 - 800 nm. The measurements were performed at a concentration of $2 \times 10^{-6}$ mol.L$^{-1}$.

For 11 (Graph 8), the $\lambda_{Em}$ displays a 47 nm bathochromic shift in going from non-polar (toluene, 628 nm) to polar (methanol, 675 nm) solvents. Likewise, 12b (Graph 9) exhibits a similar bathochromic shift of 58 nm when measurement in toluene are compared to methanol.

Graph 9 - Normalised fluorescence emission of 12b as measured by 500 nm emission between 540 - 850 nm. The measurements were performed at a concentration of $2 \times 10^{-6}$ mol.L$^{-1}$.
Comparing \(11\) and \(12b\), a blue-shift of the emission band was observed for \(12b\) over the range of solvents used suggesting that the ICT upon excitation was lower for \(12b\) than for \(11\). This was also consistent with the observed blue-shift in \(\lambda_{\text{max}}\) values seen for \(12b\).

![Graph 10](image)

**Graph 10** - Normalised fluorescence emission of \(16\) and \(17\) as measured by 600 nm emission between 620 - 850 nm. The measurements were performed at a concentration of \(2 \times 10^{-6}\) mol.L\(^{-1}\).

For \(16\) and \(17\) (Graph 10) and, as with other molecules in this chapter, the fluorescence emissions are typically very weak, with usable data only able to be obtained in toluene and chloroform. Extremely low \(\phi_F\) values were obtained in chloroform of 0.002 and 0.0016 for \(16\) and \(17\), respectively. The emission spectra of the thiophene \(\pi\)-extended species \(16\) also exhibits a large STs of 143 and 177 nm in toluene and chloroform, respectively. However, for the phenyl \(\pi\)-extended species \(17\) the ST was reduced, and was found to be 80 and 143 nm in toluene and chloroform, respectively. This reduction was attributed to the reduced aromaticity of thiophene (\(16\)) in comparison with the phenylene (\(17\)) with the former consuming more excitation energy and this leads to a red shift in the \(\lambda_{\text{Em}}\).\(^{73}\)

For \(22\) (Graph 11) and \(23\) (Graph 12) the \(\phi_F\) values were larger in non-polar solvents such as toluene, dioxane and chloroform, whereas in acetonitrile and methanol the \(\phi_F\) were relatively weak (c. 100 times smaller). As mentioned previously, in non-polar solvents the fluorescence emission emanates from a locally excited \(n\pi^*\) emission, whereas in polar solvents emission was from a ICT state leading to lower \(\phi_F\). For \(22\), a \(\phi_F\) of 0.03 was measured in chloroform, with the corresponding measurement for \(23\) being 0.011.
Further to this, with the additional branching the excited state was of lower polarity than the equivalent dipolar species and can be rationalised by the lower CT seen for 23 (blue shift in $\lambda_{\text{Em}}, 23$ vs. 22). $^{44, 52}$ This observation was also consistent with previous multi-branched structures outlined for 6 – 8 (Chapter 2).
As with previously synthesised PIs 6 – 8 (Chapter 2), emission spectra for 22 and 23 were similar with band broadening occurring with increased solvent polarity. This indicated that excited state emission occurred from a single dipolar branch in these chromophores.\textsuperscript{53,57} This was consistent with previous reports of TPA containing chromophores, where photoexcitation produced an emissive CT state that was localised to a single branch.\textsuperscript{56,63,64,74,75} There is an observed decrease in the ST of 23 when compared to 22 and this implies that the overall excited state polarity decreases upon the addition of a second branch. This therefore suggested that dipolar 22 possess higher CT character than the quadrupolar compound 23.

Graph 13 - Normalised fluorescence emission of 25 as measured by 450 nm emission between 470 - 800 nm. The measurements were performed at a concentration of 2 x 10\textsuperscript{-6} mol.L\textsuperscript{-1}.

For 25 (Graph 13) large STs were seen in acetonitrile (127 nm) and methanol (120 nm) although they are somewhat smaller in toluene (16 nm) and dioxane (57 nm). This is consistent with the absorption data showing a largely locally excited state with the species remaining in a similar geometry to the ground state upon excitation. Due to the A-\pi-A nature of 25 no strong electron donors are present to facilitate efficient ICT.

All the species here displayed low emissions and thus low \( \phi_r \), and this suggests that they have the potential to be highly active as PIs. As described in previous chapters, a low \( \phi_r \) can lead to higher rate of intersystem crossing to the active triplet state and thus initiate polymerisation. As exemplified by 22 this fluorescence property can be greatly influenced by solvent type and polarity. Rogers \textit{et al.} showed that in low polarity solvents deactivation
of the excited state by fluorescence is the dominant pathway, whereas with increasing solvent polarity the $\phi_F$ decreases. However, they observed no large increase in the formation of the triplet excited state ($\phi_{ISC}$). This was due to the prevalence of the species to undergo internal conversion and would likely be detrimental for initiating polymerisation.

3.2.8 Two-photon absorption cross-section ($\delta_{2PA}$) – z-scan

To assess the synthesised PIs $\delta_{2PA}$ the z-scan technique was utilised. A full description of the experimental set up is located in Chapter 2, Experimental, z-scan measurements. The effective $\delta_{2PA}$ values of our PIs were measured at a concentration of $2.0 \times 10^{-2}$ mol.L$^{-1}$ in DMF with the results being presented in Table 9. The PIs were measured at 780 nm using a Ti:Saph fs-laser with Rhodamine 6G as a reference (33 GM in ethanol), which was consistent with previous literature. The stated values of $\delta_{2PA}$ have a standard accuracy of ± 10%.

<table>
<thead>
<tr>
<th>Photoinitiator</th>
<th>Solvent</th>
<th>$\delta_{2PA}$ (GM)$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rhodamine 6G</td>
<td>EtOH</td>
<td>33</td>
</tr>
<tr>
<td>11</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>12b</td>
<td>DMF</td>
<td>333</td>
</tr>
<tr>
<td>16</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>17</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>22</td>
<td>DMF</td>
<td>390</td>
</tr>
<tr>
<td>23</td>
<td>DMF</td>
<td>507</td>
</tr>
<tr>
<td>24</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>25</td>
<td>DMF</td>
<td>438</td>
</tr>
</tbody>
</table>

Table 9 - $\delta_{2PA}$ of PIs as measured at 780 nm in DMF at a concentration of $2.0 \times 10^{-2}$ mol.L$^{-1}$, 23 was performed at a concentration of $1.26 \times 10^{-2}$ mol.L$^{-1}$. 1 GM = $1 \times 10^{-50}$cm$^4$s photons$^{-1}$ molecule$^{-1}$. a. The stated values of $\delta_{2PA}$ have a standard accuracy of ± 10%.

As can be seen from Table 9 values for 11, 16, 17 and 24, a $\delta_{2PA}$ value could not be determined using our experimental set up at 780 nm. In the case of 11 and 17 an insufficient change in normalised transmittance was seen and thus, a $\delta_{2PA}$ couldn’t be determined at 780 nm. For the $\pi$-extended thiophene species 16 no change in transmittance was observed, which was attributed to linear absorption at this wavelength. This was also an issue for 11 and 17 and therefore to obtain values for these molecules would likely require a longer wavelength, i.e. 1064 nm or greater. In the case of 24, poor solubility of the chromophore in a number of solvents, including DMF and DMSO was the issue.
The $\delta_{2PA}$ values of 12b, 22 and 23 were found to be 333, 390 and 507 GM, respectively. Given the measured $\lambda_{\text{max}}$ values for these PIs were 507, 560 and 577 nm respectively in DMF, this suggests that the likely of $\delta_{2PA}$ values could well be higher if a longer integrating light beam was used. However, measurements at longer wavelengths were not possible with the current experimental setup. For 12b, it was difficult to make statements about the effects of the aldehyde group on measured $\delta_{2PA}$ as measurements on the structurally similar species 11 could not be obtained at 780 nm. However, the measured value for 22, the C$_{10}$-TCF analogue of 11 was 390 GM, which was 57 GM larger than that measured for 12b. This implies that the addition of the aldehyde group in 12b was detrimental to the overall ICT, which is considered key in maximising 2PA. As seen in Graph 2, the relative intensity of the linear absorption at longer wavelengths, which are related to ICT, are smaller than that observed for the $\pi-\pi^*$ transitions (c. 350 nm). This is due to the detrimental effect of the aldehyde on the former process and thus on the overall $\delta_{2PA}$ measured. The experimental values for the dipolar species 22 and quadrupolar 23 were 390 and 507 GM respectively, thus suggesting cooperative enhancement upon two-photon excitation. This was rationalised by the increased $\pi$-conjugation and increased number of C$_{10}$-TCF acceptor groups and was consistent the literature values for these types of species.$^{56,64,77}$ For the quadrupolar 25 a relatively large $\delta_{2PA}$ of 438 GM was measured at 780 nm. Large $\delta_{2PA}$ values have been shown in such A-$\pi$-A molecules, and this is related to the large CT and its ability to maximise $\delta_{2PA}$. However, when comparing structurally similar species it is apparent that D-$\pi$-D and A-$\pi$-D-$\pi$-A chromophores are generally more effective than the corresponding A-$\pi$-A analogues for maximising $\delta_{2PA}$. As was the case with PI 6 – 8, measurements were performed at 780 nm. However, the majority of these chromophores exhibit one-photon absorption maxima at approximately 450 – 600 nm. As such, an assessment of these molecules over a broader wavelength range would help yield a deeper insight into the maximum $\delta_{2PA}$ values that these molecules could achieve. This is likely to be particularly true for 12b, 22, 23 and 25 as their linear $\lambda_{\text{max}}$ values were red-shifted relative to 6 – 8 and lie closer to 500 – 600 nm. Furthermore, this would also aid in the selection of a more appropriate laser wavelength for our TPP experiments, which are outlined in detail in Chapter 5.
3.3. Experimental

3.3.1 Synthesis

**Synthesis of 3-hydroxy-3-methylbutan-2-one (9).** To a solution of H₂O (1 L) and conc. H₂SO₄ (77 ml) was added HgO (45 g). The solution was warmed to 55 ºC to dissolve fully producing a deep red/orange colour. To this solution was added 2-methylbut-3-yn-2-ol (430 g, 500 ml) slowly over 3 h and the solution was stirred overnight. To the stirred solution was added NaCl (250 g) and the mixture extracted with diethyl ether (900 ml). The organic layer was washed with brine, dried over MgSO₄, filtered and the solvents were removed in vacuo to yield pure 3-hydroxy-3-methylbutan-2-one (9) 329 g, 63% yield. The crude material was used in the next stage without further purification.

**Synthesis of 2-(3-cyano-4,5,5-trimethylfuran-2(5H)-ylidene)malononitrile (TCF) (10).** To a solution of 3-hydroxy-3-methylbutan-2-one (9) (329 g, 3.25 mol) in pyridine (1000 ml) was added malononitrile (851.2 g, 12.8 mol) and catalytic amounts of AcOH (10 ml) and NH₄OAc (1 g). The reaction was stirred for 72 h after which the pyridine was reduced to 200 ml and H₂O (300 ml) was added. The solution was evaporated in vacuo successively in this manner three times until a solid formed. The solids were filtered and washed with cold H₂O and then EtOH. The crude solids were dried in a drying pistol setup for 3 h. The TCF product could be used without further purification in 350 g, 55% yield. 2-(3-cyano-4,5,5-trimethylfuran-2(5H)-ylidene)malononitrile (10, TCF): Brown powder; Rf 0.6 (DCM). ¹H NMR (CDCl₃): δ = 2.40 (s, 3H), 1.65 (s, 6H). ¹³C NMR (CDCl₃): 185.71, 177.22, 112.17, 111.45, 109.92, 103.62, 101.30, 23.20, 14.16. HRMS: calcd for C₁₁H₉N₃ONa 222.0643, found m/z [M⁺Na] 222.0647 (20%); Δ = 1.8 ppm.

**Synthesis of (E)-2-(3-cyano-4-(4-(diphenylamino)styryl)-5,5-dimethylfuran-2(5H)-ylidene)malononitrile (11).** To a solution of 4-formyltriphenylamine (1) (1 g, 3.66 mmol) in MeOH (50 ml) was added 10 (0.85 g, 4.4 mmol, 1.1 eq) and a catalytic amount of NEt₃ (3 drops). The solution was stirred rapidly at 65 ºC for 6 h. The colour changed from yellow/brown to a deep blue indicating product formation. The MeOH was removed in vacuo the residue was extracted with DCM (2 x 100 ml) and with H₂O (2 x 100 ml). The organics were combined, dried over MgSO₄ and filtered. The solvent was removed in vacuo to yield deep purple/blue oil. The crude product was loaded on silica gel and purified via column chromatography (DCM: petroleum spirit 60-80 ºC, 1:2.3) affording (E)-2-(3-cyano-4-
(4-(diphenylamino)styryl)-5,5-dimethylfuran-2(5H)-ylidene)malononitrile (11) 0.6 g, 37% yield. Dark purple solid; Rf 0.45 (DCM: petroleum spirit 60-80 °C, 2:3). 1H NMR (CDCl3): δ = 7.89 (d, J = 17.07 Hz, 1H), 7.77 (d, J = 9.39 Hz, 2H), 7.42 (t, J = 7.9 Hz, 4H), 7.23 (t, J = 7.4 Hz, 2H), 7.19 (d, J = 7.63 Hz, 4H), 6.99 (d, J = 17.07 Hz, 1H), 6.88 (d, J = 9.39 Hz, 2H), 1.77 (s, 6H). 13C NMR (CDCl3): 175.81, 173.97, 152.53, 147.23 145.66, 131.09, 129.84, 126.36, 125.91, 125.63, 119.88, 112.15, 111.36, 111.16, 110.86, 97.11, 26.62. HRMS: calcd for C30H22N4O 455.1872, found m/z [M+H]+ 455.1868 (100%); Δ = -0.9 ppm.

Synthesis of 2,2'-(4,4'-((1E,1'E)-(phenylazanediyl))bis(4,1-phenylene))bis(ethene-2,1-diyl))bis(3-cyano-5,5-dimethylfuran-4(5H)-ylidene)malononitrile (12b). To a solution of 4,4'-diformyltriphenylamine (2) (1 g, 3.32 mmol) in MeOH (50 ml) was added TCF (10) (1.5 g, 7.31 mmol, 2.2 eq) and a catalytic amount of NEt3 (3 drops). The solution was stirred rapidly at 65 °C for 6 h. The colour changed from yellow/brown to a deep blue/purple indicating product formation. The MeOH was removed in vacuo, the residue was extracted with DCM (2 x 100 ml) and with H2O (2 x 100 ml). The organics were combined, dried over MgSO4 and filtered. The solvents were removed in vacuo to yield deep purple/blue solid. The crude product was loaded on silica gel and purified via column chromatography (DCM: petroleum spirit 60-80 °C, 1:2.3) affording (E)-2-(3-cyano-4-(4-(4-formylphenyl)(phenyl)amino)styryl)-5,5-dimethylfuran-2(5H)-ylidene)malononitrile (12b) 0.2 g, 12.5% yield. Dark purple solid, Rf 0.20 (DCM: petroleum spirit 60-80 °C, 3:2). 1H NMR (CDCl3): δ = 9.91 (s, 1H), 7.79 (d, J = 8.83 Hz, 2H), 7.60 (d, J = 16.86 Hz, 1H), 7.55 (d, J = 8.83 Hz, 2H), 7.41 (t, J = 7.4 Hz, 2H), 7.20 (d, J = 7.73 Hz, 2H), 7.17 (m, 3H), 7.14 (d, J = 8.81 Hz, 2H), 6.89 (d, J = 16.86 Hz, 1H), 1.78 (s, 6H). 13C NMR (CDCl3): 190.44, 175.50, 173.78, 151.61, 150.90, 146.50, 145.21, 131.67, 131.32, 130.83, 129.85, 128.33, 127.03, 123.10, 112.91, 111.86, 111.09, 110.54, 97.42, 26.54. HRMS: calcd for C31H22N4O2Na 505.1640, found m/z [M+Na]+ 505.1641 (100%); Δ = 0.2 ppm.

Synthesis of 4-vinyltriphenylamine (13). t-BuOK (0.51 g, 4.6 mmol) was added to a solution of methyl(triphenyl)phosphonium bromide (1.97 g, 5.5 mmol) in anhydrous THF (30 ml) at 0 °C. The mixture was allowed to reach room temperature and stirred for 15 minutes after which 4-formyltriphenylamine (1) (1.25 g, 4.57 mmol) was added at 0 °C. The mixture was stirred at room temperature for 3 h, the solution was then poured into water (200 ml). The solids were collected by filtration. The crude product was recrystalised in ethanol to give 4-vinyltriphenylamine (13) 0.65 g, 52% yield. White solid; Rf 0.85 (DCM: petroleum spirit 60-
\[ 80^\circ C, 1:5 \].\(^{38} \] \(^1\)H NMR (CDCl\(_3\)): \( \delta = 7.21 \) (d, 2H), 7.18-7.15 (m, 4H), 7.01 (m, 4H), 6.95 (m, 4H), 6.57 (dd, 1H), 5.56 (d, 1H), 5.08 (d, 1H). \(^{13}\)C NMR (CDCl\(_3\)): 147.66, 136.27, 131.95, 129.75, 127.08, 124.6, 123.62, 122.95, 112.15. HRMS: calcd for C\(_{20}\)H\(_{17}\)N: 272.1439, found m/z [M+H]+ 272.1440 (100%); \( \Delta = 0.4 \) ppm.

**Synthesis of (E)-5-(4-(diphenylamino)styryl)thiophene-2-carbaldehyde (14).** To a solution of 4-vinyltriphenylamine (13) (1.42 g, 5.25 mmol) in anhydrous DMF (20 ml) was added 5-bromo-2-thiophenecarbaldehyde (1 g, 5.24 mmol) and tetra-n-butylammonium bromide (6.17 g, 18.9 mmol). To this mixture was added anhydrous K\(_2\)CO\(_3\) (2.6 g, 18.9 mmol) and Pd(OAc)\(_2\) (10 mol %, 180 mg) and the mixture was stirred under an inert argon atmosphere at 110 °C for 24 h. After cooling to r.t, the solution was poured into H\(_2\)O (100 ml) and extracted with DCM (100 ml). The organics were washed with brine (2 x 100 ml), dried over MgSO\(_4\), filtered and the solvents were removed in **vacuo**. The crude product was loaded on silica gel and purified via column chromatography (DCM: petroleum spirit 60-80 °C, 1:2.3) to afford (E)-5-(4-(diphenylamino)styryl)thiophene-2-carbaldehyde (14) 0.75 g, 38% yield. A semi-pure yellow solid; R\(_f\) 0.6 (DCM). \(^1\)H NMR (CDCl\(_3\)): \( \delta = 9.76 \) (s, 1H), 7.55 (d, \( J = 4.04 \) Hz, 1H), 7.26 (d, 2H), 7.21-7.16 (m, 5H), 7.04-7.02 (d, 4H), 7.00 (d, \( J = 4.04 \) Hz, 1H), 6.99-6.95 (m, 3H), 6.94 (d, 2H). \(^{13}\)C NMR (CDCl\(_3\)): 182.44, 153.20, 148.56, 147.40, 147.21, 141.02, 137.34, 132.66, 131.32, 129.75, 127.92, 125.89, 124.89, 123.61, 122.68, 118.77. HRMS: calcd for C\(_{25}\)H\(_{19}\)NOS 381.1187, found m/z [M+H]+ 382.1268 (100%).

**Synthesis of (E)-4-(4-(diphenylamino)styryl)benzaldehyde (15).** To a solution of 4-vinyltriphenylamine (13) (2.2 g, 8.1 mmol) in anhydrous DMF (20 ml) was added 4-bromobenzylaldehyde (1.8 g, 9.7 mmol) and tetra-n-butylammonium bromide (9.37 g, 29 mmol). To this mixture was added anhydrous K\(_2\)CO\(_3\) (4 g, 29 mmol) and Pd(OAc)\(_2\) (10 mol %, 180 mg) and the mixture was stirred under an inert argon atmosphere at 110 °C for 24 h. After cooling to r.t, the solution was poured into H\(_2\)O (100 ml) and extracted with DCM (2 x 100 ml). The organics were washed with brine (2 x 100 ml), dried over MgSO\(_4\), filtered and the solvents were removed in **vacuo**. The crude product was loaded on silica gel and purified via column chromatography (DCM: petroleum spirit 60-80 °C, 1:2.3) to afford (E)-4-(4-(diphenylamino)styryl)benzaldehyde (15) 1.2 g, 36% yield. Semi-pure yellow/orange solid, \( R_f \) 0.60 (DCM). \(^1\)H NMR (DMSO-D\(_6\)): \( \delta = 9.95 \) (s, 1H), 7.89 (d, \( J = 8.5 \) Hz, 2H), 7.78 (d, \( J = 8.5 \) Hz, 2H), 7.55 (d, 2H), 7.40 (d, \( J = 16.3 \) Hz, 1H), 7.36-7.34 (m, 4H), 7.19 (d, \( J = 16.3 \) Hz, 1H),
7.08 (t, 2H), 7.05 (d, 4H), 6.95 (d, 4H). HRMS: calcd for C_{27}H_{21}NO 375.16, found m/z [M^+] 375.16 (100%), [M^+H] 376.16 (80%).

**Synthesis of 2-(3-cyano-4-((E)-2-(5-((E)-4-(diphenylamino)styryl)thiophen-2-yl)vinyl)-5,5-dimethylfuran-2(5H)-ylidene)malononitrile (16).** To a solution of (E)-5-(4-(diphenylamino)styryl)thiophene-2-carbaldehyde (14) (3 g, 7.87 mmol) in MeOH (100 ml) was added TCF (10) (1.88 g, 9.44 mmol) and a catalytic amount of NEt₃ (3 drops). The solution was stirred rapidly at 65 °C for 6 h. The colour changed from yellow/brown to a deep blue indicating product formation. The MeOH was removed in vacuo, the residue was extracted with DCM (2 x 100 ml) and with H₂O (2 x 100 ml). The organics were combined, dried over MgSO₄ and filtered. The solvent was removed in vacuo to yield a deep purple/blue oil. The crude product was loaded on silica gel and purified via column chromatography (DCM: petroleum spirit 60-80 °C, 1:2.3) affording 2-(3-cyano-4-((E)-2-(5-((E)-4-(diphenylamino)styryl)thiophen-2-yl)vinyl)-5,5-dimethylfuran-2(5H)-ylidene)malononitrile (16) 0.4 g, 9% yield. A dark purple solid; Rₚ 0.50 (DCM). 

**Synthesis of 2-(3-cyano-4-((E)-4-((E)-4-(diphenylamino)styryl)styryl)styryl)-5,5-dimethylfuran-2(5H)-ylidene)malononitrile (17).** To a solution of (E)-4-(4-(diphenylamino)styryl)benzaldehyde (15) (3.45 g, 9.2 mmol) in MeOH (60 ml) was added TCF (10) (2.2 g, 11 mmol) and a catalytic amount of NEt₃ (3 drops). The solution was stirred rapidly at 65 °C for 6 h. The colour changed from yellow/brown to a deep blue indicating product formation. The MeOH was removed in vacuo, the residue was extracted with DCM (2 x 100 ml) and with H₂O (2 x 100 ml). The organics were dried over MgSO₄ and filtered. The solvent was removed in vacuo to yield a deep purple/blue oil. The crude product was loaded on silica gel and purified via column chromatography (DCM: petroleum spirit 60-80 °C, 1:2.3) affording 2-(3-cyano-4-((E)-4-((E)-4-(diphenylamino)styryl)styryl)-5,5-dimethylfuran-2(5H)-ylidene)malononitrile (17) 0.52 g, 10% yield. Dark Purple solid (0.52 g, 10%); Rₚ 0.50 (DCM). 

\[ \text{HRMS (CDCl}_3\text{): } \delta = 7.58 \text{ (d, } J = 16.28 \text{ Hz, 1H}), 7.55 \text{ (d, } J = 8.9 \text{ Hz, 2H),} \]
7.50 (d, J = 8.9 Hz, 2H), 7.33 (d, J = 8.92 Hz, 2H), 7.23-7.19 (m, 4H), 7.14 (d, J = 16.68 Hz, 1H), 7.06 (d, J = 9.83 Hz, 4H), 7.09 – 7.04 (m, 4H), 6.96 (d, J = 16.68 Hz, 1H), 6.92 (d, J = 16.28 Hz, 1H), 7.14 (d, J = 16.68 Hz, 1H), 6.92 (d, J = 16.28 Hz, 1H), 7.06 (d, J = 16.68 Hz, 1H), 6.92 (d, J = 16.28 Hz, 1H), 1.78 (s, 6H).

$^{13}$C NMR (CDCl$_3$): 173.60, 148.47, 147.26, 146.84, 142.78, 131.88, 128.73, 129.42, 127.93, 127.17, 125.11, 124.98, 123.59, 122.77, 113.98, 111.69, 110.34, 97.47, 27.10.

HRMS: calcd for C$_{38}$H$_{28}$N$_4$O$_5$ 556.2263, found m/z [M$^+$] 556.2264 (50%); Δ = 0.2 ppm.

**Synthesis of ethyl 2,2-diethoxypropanoate (18).** A mixture of ethyl pyruvate (99.05 g, 853 mmol), triethyl orthoformate (303.4 g, 2.05 mol) and conc. H$_2$SO$_4$ (9 ml) was stirred at r.t. for 3 hours. The mixture was diluted and extracted with DCM (500 ml) and washed with H$_2$O (500 ml) and sat. brine (2 x 500 ml). The organics were dried over MgSO$_4$, filtered and the solvents removed in vacuo. The pale yellow oil was used without further purification affording ethyl 2,2-diethoxypropanoate (18) 170.6 g, 100% yield.

**Synthesis of ethyl 3-decyl-3-hydroxytridecan-2-one (20).** To magnesium turnings (12.2 g, 506 mmol) in THF (500 ml) under argon was added an iodine chip. The solution was gently heated to 65 °C and several drops of 1-bromodecane was added to initiate the reaction, once the reaction began to reflux 1-bromodecane (112 g, 506.5 mmol) was added dropwise at such a rate as to allowed for a continued gentle reflux. The solution was then stirred for 0.5 h before being cooled to 0 °C. To this solution was slowly added ethyl 2,2-diethoxypropanoate (18) and the reaction mixture was refluxed for 2 h. The reaction mixture was then quenched by the slow addition to H$_2$O:HCl (20:1) (250 ml) and stirred for a further 2 h. The mixture was then concentrated in vacuo to yield a yellow oil, 3-decyl-3-hydroxytridecan-2-one (19). A mixture of EtOH/H$_2$O/HCl (4:4:1) (300 ml) was then added and the mixture refluxed for a further 2 h. The solution was cooled to r.t., concentrated in vacuo, and diluted with DCM (500 ml). The organics were washed with H$_2$O (500 ml) and sat. brine (2 x 500 ml). The organics were combined, dried over MgSO$_4$, filtered and solvent was removed in vacuo. Ethyl 3-decyl-3-hydroxytridecan-2-one (20) 56 g, 63% yield, was obtained as a yellow oil and was used without further purification affording.

**Synthesis of 2-(3-cyano-5,5-didecyl-4-methylfuran-2(5H)-ylidene)malononitrile (21).** To a solution of ethyl 3-decyl-3-hydroxytridecan-2-one (21) (56 g, 158 mmol) in pyridine (500 ml) was added malononitrile (41.74 g, 632.2 mmol) and catalytic amounts of acetic acid and ammonium acetate. The reaction was then stirred for 72 h at r.t producing a red/brown coloured solution. The pyridine volume was reduced in vacuo (100 ml) and H$_2$O (300 ml) was added, this dilution and evaporation was repeated three subsequent times. The crude
oil was diluted with DCM (500 ml) and the organics were washed with H₂O (500 ml) and sat. brine (2 x 500 ml). The organics were combined, dried over MgSO₄, filtered and the solvents were removed in vacuo affording 2-(3-cyano-5,5-didecyl-4-methylfuran-2(5H)-ylidene)malononitrile (21) 40 g, 56% yield. A brown semi-solid; Rf 0.5 (DCM: petroleum spirit 60-80 °C, 1:1). ¹H NMR (CDCl₃): δ 2.29 (s, 3H), 2.04 (m, 2H), 1.75 (m, 2H), 1.26 (bs, 28H), 0.97 (bs, 2H), 0.89 (t, 6H). ¹³C NMR (CDCl₃): 181.61, 176.02, 110.98, 110.52, 108.90, 106.31, 105.12, 36.86, 31.52, 29.67, 29.45, 29.41, 29.22, 29.18, 22.63, 15.22, 14.49, 8.65. HRMS: calcd for C₂₉H₄₅N₃ONa 474.3460, found m/z [M⁺Na] 474.3462 (100%); Δ = 0.4 ppm.

Synthesis of (E)-2-(3-cyano-5,5-didecyl-4-(4-(diphenylamino)styryl)furan-2(5H)-ylidene)malononitrile (22). To a solution of 4-formyltriphenylamine (1) (2.31 g, 8.46 mmol) in MeOH (50 ml) was added 2-(3-cyano-5,5-didecyl-4-methylfuran-2(5H)-ylidene)malononitrile (21) (4.87 g, 10.152 mmol). To this rapidly stirred solution was added NEt₃ (3 drops, catalytic) and NH₄OAc (50 mg, catalytic) and the solution was stirred overnight at 65 °C with the solution being observed to go from a brown colour to deep blue/purple indicating product formation. The solvents were removed in vacuo yielding purple/blue oil. The crude material was loaded onto silica (5 g) and purified by column chromatography (silica gel, DCM: petroleum spirit 60-80 °C (1:5.6)) affording (E)-2-(3-cyano-5,5-didecyl-4-(4-(diphenylamino)styryl)furan-2(5H)-ylidene)malononitrile (22) 250 mg, 4% yield. Purple solid; Rf 0.75 (DCM). ¹H NMR (CDCl₃): δ 7.59 (d, J = 16.02 Hz, 1H), 7.48 (d, J = 9.15 Hz, 2H), 7.36 (t, J = 7.9 Hz, 4H), 7.20 (t, J = 7.4 Hz, 2H), 7.18 (d, J = 7.15 Hz, 4H), 6.99 (d, J = 9.15 Hz, 2H), 6.84 (d, J = 16.02 Hz, 1H), 2.16-2.10 (m, 2H), 1.94-1.88 (m, 2H), 1.23 (bs, 28H), 1.20-1.12 (bs, 2H), 1.08-1.00 (bs, 2H), 0.87 (t, J = 7.00 Hz, 6H). ¹³C NMR (CDCl₃): 176.77, 172.38, 152.48, 146.29, 145.69, 131.08, 129.84, 126.32, 125.93, 125.61, 119.95, 112.17, 111.54, 110.83, 102.92, 98.61, 39.11, 31.85, 29.49, 29.42, 29.23, 29.17, 22.64, 14.08. HRMS: calcd for C₄₈H₅₈N₄O 707.4689, found m/z [M⁺H] 707.4689 (20%); Δ = 0.0 ppm.

Synthesis of 2,2′-(4,4′-((1E,1′E)-((phenylazanediyl)bis(4,1-phenylene))bis(ethene-2,1-diyi))bis(3-cyano-5,5-didecylfuran-4(5H)-yl-2(5H)-ylidene))dimalononitrile (23). To a solution of 4,4′-diformyltriphenylamine (2) (1.89 g, 6.3 mmol) in MeOH (50 ml) was added 2-(3-cyano-5,5-didecyl-4-methylfuran-2(5H)-ylidene)malononitrile (21) (6.6 g, 13.81 mmol). To this rapidly stirred solution was added NEt₃ (3 drops, catalytic) and NH₄OAc (50 mg,
catalytic) and the solution was stirred overnight at 65 °C with the solution being observed to go from a brown colour to deep blue/purple indicating product formation. The solvents were removed in vacuo yielding purple/blue oil. The crude material was loaded onto silica (1 g) and purified by column chromatography (silica gel, DCM: petroleum spirit 60-80 °C (1:3)) affording 2,2’-(4,4’-((1E,1’E)-((phenylazanediyl)bis(4,1-phenylene))bis(ethene-2,1-diyl))bis(3-cyano-5,5-didecylfuran-4(5H)-yl-2(5H)-ylidene))dimalononitrile (23) 30 mg, 0.2% yield. Purple solid; Rf 0.5 (DCM). 

1H NMR (CDCl3): δ 7.61 (d, J = 16.25 Hz, 2H), 7.56 (d, J = 8.8 Hz, 4H), 7.43 (t, J = 7.9 Hz, 2H), 7.31 (t, J = 7.9 Hz, 1H), 7.17 (d, J = 7.78 Hz, 2H), 7.15 (d, J = 8.79 Hz, 4H), 6.92 (d, J = 16.25 Hz, 2H), 2.19-2.12 (m, 4H), 1.95-1.88 (m, 4H), 1.37-1.10 (bs, 60H), 1.04 (bs, 4H) 0.87 (t, J = 7.00 Hz, 12H).

13C NMR (CDCl3): 176.29, 172.04, 150.39, 145.19, 144.99, 130.79, 130.32, 128.75, 126.98, 126.98, 123.34, 113.56, 111.75, 111.15, 110.47, 103.15, 100.52, 39.03, 31.87, 29.71, 29.50, 29.37, 29.25, 29.20, 22.97, 14.10. HRMS: calcd for C78H101N7O2Na 1190.7903, found m/z [M+Na] 1190.7906 (100%); Δ = 0.3 ppm.

Synthesis of 2,2’-(4,4’-((1E,1’E)-1,4-phenylenebis(ethene-2,1-diyl))bis(3-cyano-5,5-dimethylfuran-4(5H)-yl-2(5H)-ylidene))dimalononitrile (24).

To a solution of terephthalaldehyde (306 mg, 2.28 mmol) in MeOH (50 ml) was added 10 (1 g, 5 mmol). To this rapidly stirred solution was added NEt3 (3 drops, catalytic) and NH4OAc (50 mg, catalytic) and the solution was stirred overnight at 65 °C with the solution being observed to go from a brown colour to red/orange colour indicating product formation. The solution was cooled and the red product was filtered off and washed with MeOH yielding pure 2,2’-(4,4’-((1E,1’E)-1,4-phenylenebis(ethene-2,1-diyl))bis(3-cyano-5,5-dimethylfuran-4(5H)-yl-2(5H)-ylidene))dimalononitrile (24) 0.68 g, 60% yield. Red solid; Rf 0.2 (DCM:EtOAc (1:1)). 1H NMR (DMSO-D6): δ 8.06 (d, J = 16.47 Hz, 2H), 7.69 (d, J = 4.89 Hz, 2H), 7.40 (d, J = 4.89 Hz, 2H), 6.81 (d, J = 16.47 Hz, 2H), 1.79 (s, 12H). 13C NMR (DMSO-D6): 192.66, 176.89, 174.30, 145.07, 139.60, 137.68, 129.96, 129.76, 118.14, 112.46, 111.63, 110.59, 99.62, 24.94. HRMS: calcd for C30H20N6O2Na 519.1545, found m/z [M+Na] 519.1545 (100%); Δ = 0.0 ppm.

Synthesis of 2,2’-(4,4’-((1E,1’E)-1,4-phenylenebis(ethene-2,1-diyl))bis(3-cyano-5,5-didecylfuran-4(5H)-yl-2(5H)-ylidene))dimalononitrile (25) To a solution of terephthalaldehyde (0.59 g, 4.4 mmol) in MeOH (50 ml) was added 2-(3-cyano-5,5-didecyl-4-methylfuran-2(5H)-ylidene)malononitrile (21) (5 g, 11.1 mmol). To this rapidly stirred solution was added NEt3 (3 drops, catalytic) and NH4OAc (50 mg, catalytic) and the solution
was stirred overnight at 65 °C with the solution being observed to go from a brown colour to red/orange colour indicating product formation. The solvents were removed in vacuo yielding red oil. The crude material was loaded onto silica (10 g) and purified by column chromatography (silica gel, DCM: petroleum spirit 60-80 °C (1:3)) affording 2,2'-(4,4'-(1E,1'E)-((phenylazanediyl)bis(4,1-phenylene))bis(ethene-2,1-diyl))bis(3-cyano-5,5-didecylfuran-4(5H)-yl-2(5H)-ylidene))dimalononitrile (25) 1 g, 22.5 % yield. Red solid; Rf 0.5 (DCM). 1H NMR (CDCl₃): δ 7.74 (s, 4H), 7.64 (d, J = 16.48 Hz, 2H), 7.10 (d, J = 16.48 Hz, 2H), 2.24-2.18 (m, 4H), 1.98-1.92 (m, 4H), 1.35-1.17 (bs, 60H), 1.06 (bs, 4H) 0.86 (t, J = 7.00 Hz, 12H). 13C NMR (CDCl₃): 175.61, 171.32, 143.80, 137.27, 129.73, 117.32, 111.21, 109.49, 103.57, 38.76, 31.83, 29.47, 29.39, 29.21, 29.15, 22.77, 22.63, 14.07. HRMS: calcd for C₆₆H₉₂N₆O₂Na 1023.7168, found m/z [M+Na] 1023.7167 (100%); Δ = -0.1 ppm.

3.4. Conclusion

A series of TCF containing PIs were synthesised via Knovenagel condensations to produce dipolar and quadrupolar molecules. Key physical and photophysical properties were evaluated to assess their suitability to initiate polymerisation using the TPP technique. Where measurements were possible, the compounds were found to possess δ₂PA values of 333 – 507 GM when measured at 780 nm in chloroform using the z-scan technique. Furthermore, low φₚ values of < 0.1 were seen across the series in chloroform, and in acrylates the values were < 0.15. As expected, the solubility of the compounds was shown to improve with the introduction of large alkyl chains to the side groups of the TCF acceptor and these in turn had little overall effect on photophysical properties. Overall, these molecules display the potential to be effective and efficient PIs for TPP based on their key molecular properties. This will be further evaluated by TPP experiments on some of the compounds in Chapter 5.

3.5. References

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Chapter 4. Design, synthesis and characterisation of triphenylamine α,β-unsaturated ketone photoinitiators

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4.1. Introduction

As previously described in the *Chapter 1 > Introduction*, upon excitation a PI undergoes intersystem crossing to the active triplet state followed by electron transfer, which in turn initiates polymerisation.\(^1\)\(^\text{-}\)\(^2\) To briefly recap, the use of carbonyl moieties is an effective strategy for the creation of highly active PIs as they help to lower \(\Phi_F\), although the true aim is to maximise the \(\Phi_T\).\(^3\) A lower energy gap between the singlet and triplet levels can lead to increased intersystem crossing rates.\(^4\) The use of carbonyl groups in TPP PIs has been well-researched and a range of differing functional groups have been investigated to assess their ability to initiate polymerisation and include: \(\alpha,\beta\)-unsaturated ketones,\(^5\)\(^\text{-}\)\(^7\) thioxanthenes,\(^8\)\(^,\)\(^9\) keto-coumarins\(^10\)\(^,\)\(^11\) and acylo-phosphine oxides.\(^12\) A number of the groups have made use of \(\alpha,\beta\)-unsaturated ketone functionality to produce PIs. Examples of these, synthesised by *Liska et al.*\(^13\) and *Gryko et al.*\(^14\), are described in *Chapter 2 > Introduction*. Several reports have also utilised cycloketones such as cyclopentanone or cyclohexanone as synthons to give quadrupolar molecules, due to their ability to form symmetrical \(\alpha,\beta\)-unsaturated ketones.\(^6\)\(^,\)\(^15\)\(^,\)\(^16\)

Compounds in this chapter belong to a series of D-(C=O)-C=C-R PIs with R = donor or acceptor *viz* 29 – 33 and 35 (Figure 1). As with earlier work, compounds in this chapter will utilise the electron donating TPA as a core component, although the starting material 4-acetyltriphenylamine 26 will be used as a key intermediate, rather than the previously utilised 4-formyltriphenylamine 1. The use of 26, alongside commercially available aldehydes, will be shown to permit ready access to dipolar D-\(\pi\)-A and quadrupolar D-\(\pi\)-D systems *viz* 30 – 33.

Furthermore, the target product 35 is structurally similar to compound 6 (*Chapter 2*), and differs by the inclusion of a carbonyl group in the conjugated interconnect. Investigations of the photophysical properties have been assessed across the synthesised series and include UV/Vis, \(\lambda_{Em}\), \(\Phi_F\) and two-photon absorption data.
4.2. Results and discussion

The described molecules employ an $\alpha,\beta$-unsaturated ketone moiety as a $\pi$-bridge between a triphenylamine (donor) and donor and acceptor groups to yield quadrupolar (D-$\pi$-D) and dipolar (D-$\pi$-A) configurations. The synthesis followed literature procedures to create novel PIs for use in TPP. The starting materials were synthesised using the Vilsmeier-Haack formylation$^{17}$ for preparing 4-formyltriphenylamine 1 and Friedel–Crafts acylation to give 4-acetyltriphenylamine 26, as previously described in the literature.$^{18}$ From these two starting materials, the corresponding ketone 26 or aldehyde 1 were reacted by way of aldol condensations to yield the final $\alpha,\beta$-unsaturated ketone containing PIs (Figure 5-6). An analysis of the reaction mechanism is also presented (Figure 2) and is discussed in 4.2.1.

![Chemical structures](image-url)

Figure 1 – The synthesised $\alpha,\beta$-unsaturated ketones 29 – 33 and 35.
4.2.1 Analysis of aldol condensation mechanism of $\alpha,\beta$-unsaturated ketones

Initially, the proposed synthetic route for preparing $\alpha,\beta$-unsaturated ketone containing PIs involved reacting 4-formyltriphenylamine 1 with commercially available or easily prepared methyl ketones (Route A, Figure 2). Thus, as exemplified in Figure 2, and using 4-nitroacetophenone, it was intended to prepare target PI A–v via a straightforward reaction with aldehyde A–i. However, it should be noted that there is a competing reaction path, route B, that could lead to the undesired ketone dimer, B–iii. While both mechanistic pathways were possible, it was expected that route A would be most favourable.

The first step in the mechanism for both routes is deprotonation of the ketone by a base. For route A, the enol species attacks the aldehyde group forming an intermediate which is protonated to become the aldol intermediate A – iii. Secondly, the $\alpha$-proton in A – iii is removed by base through an enolisation step to provide the intermediate A – iv which undergoes elimination via an E1cB mechanism to form the desired $\alpha,\beta$-unsaturated ketone A – v. In the alternative pathway, route B, the enolate of 4-nitroacetophenone attacks 4-nitroacetophenone itself, and the reaction then proceeds via a similar mechanism as route A to form the diketone B – iii. In this case, the ketone has an electron-withdrawing nitro substituent making the enolate intermediate less reactive. However, the unenolised ketone species is more reactive to attack by the formed enolate (Step B – i). This means cross-condensations between the ketone species is likely very favourable. In turn, this increased the likelihood of by-product formation, making subsequent purification more difficult and reducing the overall yields. Indeed, this proved the case, with initial attempts to form compounds such as A – v using the approach shown in Figure 2, largely unsuccessful due to significant impurities, as well as evidence of the starting aldehyde and ketone being present as shown by TLC.
Figure 2 - Mechanism for the synthesis of α,β-unsaturated ketones, using 4-formyltriphenylamine 1 and 4-nitroacetophenone as the starting materials.

From repeated attempts to form compounds such as A - v with a variety of electron rich and electron poor ketones, it was found that producing the desired PIs using aldehyde 1 as a key synthon was difficult and time-consuming with regards to the purification process. This was
likely due to the fact that the donor ability of the central nitrogen atom of 1 deactivates the aldehyde group to the desired nucleophilic attack. Moreover, in the case of ketones containing electron withdrawing groups such as 1-(4-nitrophenyl)ethan-1-one, the ketone is activated for nucleophilic attack, increasing the propensity for dimer formation. As a consequence, the reaction as shown in Figure 2 could only be accomplished using an aldehyde with an electron donating group, 27, and this did lead to the successful preparation of PI 29. As a result it was decided to investigate the use of 4-acetyltriphenylamine 26 as a replacement for 1, although this would result in the formation of α,β-unsaturated ketones in which the carbonyl moiety was directly attached to the triphenylamine ring (e.g. 30), as opposed to the unsaturated carbon-carbon double bond (e.g. A - v). Although the donor ability of the nitrogen would still have a deactivating effect on the formation of the enolate, once formed it would be more favourable to attack the corresponding aldehyde over an unenolised ketone species (i.e. 26). Thus, the synthesis of compounds 30 - 33 and 35 were attempted as shown in Figure 6 and Figure 7, and found to be successful using standard conditions. A more detailed description of the synthesis and photophysical properties of the molecules is described below.

4.2.2 Synthesis of starting materials: 26, 27 and 28.

To prepare the target compounds 30 - 33 and 35, the key synthon was compound 26. Examples of synthesising 4-acetyltriphenylamine 26 are present in literature and employ the Friedel-Crafts acylation reaction by way of acetyl chloride/ZnCl₂ 18 or acetyl chloride/AlCl₃. 20 The starting material 28 (a precursor to 31) was prepared from a known literature procedure. 21 The same procedure was also utilised in the synthesis of 27 22 (precursor to 29).
Figure 3 - Synthesis of 4-formyltriphenylamine 1 by Vilsmeier-Haack formylation and the corresponding ketone 26 by Friedel-Crafts acetylation of triphenylamine.

The synthesis of 26 was conducted with fewer by-products and a simpler workup in comparison to the preparation of the corresponding aldehyde 1 (Figure 3). Purification was readily achieved by flushing the remaining unreacted TPA through a silica column with petroleum spirit 60-80 °C followed by elution with petroleum spirit 60-80 °C: ethyl acetate (10:1) to give the product as a pure yellow solid in 77% yield. Alternatively, purification was also achieved via recrystallisation from ethyl acetate, again yielding the pure yellow crystalline solid. Confirmation of the isolation of 26 was evident from 1H NMR by a 3H singlet at 2.52 ppm, which was consistent with previous literature reports.

The preparation of intermediates 27 and 28 are shown in Figure 4. The starting materials for 27 were 4-hydroxyacetophenone and 2-ethylhexyl bromide, which were stirred in DMF at 60 °C overnight with K₂CO₃ yielding 27 in 96% yield as a pale tan oil. The product was used without further purification and its formation was confirmed by 1H NMR. Thus, the starting material OH proton observed at approximately 5 ppm was replaced with a series of upfield alkyl multiplet peaks. A 1H doublet of doublets was seen at 3.64 ppm, with the remaining alkyl protons seen between 0.89 - 1.80 ppm and containing a total of 16 protons, which is consistent with the newly formed group. The synthesis of 28 followed the same literature procedure used for 27, and made use of 4-hydroxybenzylaldehyde and ethyl iodide. The crude reaction mixture was extracted to yield 28, which was used without further purification. The structure of 28 was determined by 1H NMR and was consistent with previous literature.
4.2.3 Synthesis of α,β-unsaturated ketone 29

The synthesis of 29 utilised 4-formyltriphenylamine 1 and ethyl hexyl ketone 27. This was accomplished, albeit in 6% yield, as a yellow/orange semi-solid. The reaction was conducted at room temperature in ethanol with 2.5 eq sodium hydroxide. Although it was possible to isolate 29 it proved extremely difficult, requiring a number of column chromatography purifications, attempted recrystallisations and preparative TLC to yield a useable quantity of product. As shown in Figure 2, route A was the desired reaction pathway. However, it was thought that by-product/s could have been formed through the route B mechanism outlined in Figure 2 (i.e. similar species to b – iii may have formed).

Figure 4 – Synthesis of the intermediates 27 from 4-hydroxyacetophenone and 28 and 29 from 4-hydroxybenzylaldehyde.

Figure 5 - Initial synthetic route using 4-formyltriphenylamine 1 and ketone 27 to give α,β-unsaturated ketone 29.
The final product was confirmed by NMR and HRMS. From NMR studies, the 1H singlet peak for starting aldehyde 1 at 9.95 ppm and the 3H singlet at 2.25 ppm in ketone 27 were replaced with two coupled (J = 15.3 Hz) 1H doublets at 7.75 and 7.40 ppm indicating coupling was successful. Furthermore, confirmation of the mass ion calculated for C_{35}H_{37}NO_{2}+H 504.2903 was confirmed as the M^+H mass at 504.2897; Δ = -1.2 ppm.

4.2.4 Synthesis of α,β-unsaturated ketones PIs 30 - 33 and 35

As stated in the mechanistic analysis of the aldol reaction (Figure 2), a more successful approach was thought to involve the use of 4-acetyltriphenylamine 26 as the starting material over the corresponding 4-formyltriphenylamine 1. Indeed 26 was successfully coupled with a range of aldehydes to yield our final PIs designated 30 - 33 and 35 (Figure 6). As noted above, using 26, rather than the corresponding aldehyde 1 also switched the position of the carbonyl C=O and the alkene bonds in the unsaturated backbone relative to compound 30. The syntheses of 30, 31, 32 and 33 were performed via a similar method to that of 29, however sodium methoxide was used as base.

In the case of 30, to a solution of 26 in ethanol was added 4-nitrobenzaldehyde, and this was followed by sodium methoxide which was added in portions over 15 minutes. The reaction mixture was stirred overnight producing a yellow/orange suspension which was washed with water and brine, followed by extraction into DCM. The crude orange/red solid was purified via column chromatography to yield 30 as a deep orange/red solid in 31% yield. The final structure was confirmed by NMR and HRMS. In 1H NMR, the starting ketone CH\textsubscript{3} singlet at 2.52 ppm was replaced with two 1H coupled doublets at 7.79 and 7.63 ppm (J = 15.7 Hz) for the protons attached to the newly formed HC=CH bond. The calculated mass for 30 was C_{27}H_{20}N_{2}O_{3}+H 421.1552 and the molecular ion peak was found at 421.1544; Δ = -1.9 ppm.

In the synthesis of 31, a solution of 26 in ethanol was added to previously synthesised 28, after which sodium methoxide was added in portions over 15 minutes. The suspension was stirred vigorously overnight to form a yellow suspension. The suspension was poured into water (250 ml) and extracted into DCM. The organics were washed with 2M HCl and brine, the solvents
were subsequently removed in \textit{vacuo}. The crude yellow material was eluted with DCM: petroleum spirit 60-80 °C through a silica column to give a semi-pure yellow solid. TLC analysis showed several by-products with closely matched \( R_f \) values. The solids were recrystallised from the minimum amount of hot petroleum spirit 60-80 °C/ethyl acetate (4:1) to yield pure yellow crystals of \textbf{31} in 14.5\% yield. The final structure was confirmed by NMR and HRMS. The \( \text{CH}_3 \) peak of \textbf{26} at 2.52 ppm was replaced with two coupled \( 1H \) doublets at 7.77 and 7.41 ppm (\( J = 16.05 \text{ Hz} \)) for the protons attached to the newly formed \( \text{HC=CH} \) bond. No aldehyde peak at 9.86 ppm from the starting material \textbf{28} was seen. Two peaks were observed as a \( 2H \) quartet and \( 3H \) triplet at 4.07 and 1.43 ppm in the final product, and are consistent with the ethyl ether moiety. Further confirmation was seen in the HRMS data calculated for \( \text{C}_{29}\text{H}_{25}\text{NO}_2+\text{H} \ 420.1964 \), found 420.1967; \( \Delta = 0.7 \text{ ppm} \).
The synthesis of 32 was conducted using terephthalaldehyde as the limiting reagent in ethanol followed by the addition of 26. Sodium methoxide was added in portions over 15 minutes and the yellow/orange suspension was stirred overnight producing an orange/red suspension. The solution was poured into water, extracted with DCM, and the organics were washed with 2M HCl and brine. The solvents were combined and removed in vacuo yielding an orange/red
crude solid. The product was eluted through silica with DCM: petroleum spirit 60-80 °C which yielded a semi-pure orange solid. TLC analysis showed the product alongside some closely matched impurities with a similar Rf. The crude material was recrystallised from the minimum amount of hot petroleum spirit 60-80 °C and ethyl acetate (4:1) to afford 32 as a red/orange solid in 9% yield. The final product was confirmed by NMR and HRMS. From the 1H NMR spectrum, no aldehyde peak was seen for the starting dialdehyde material and no CH3 peak was observed at 2.52 ppm from starting material 26. Secondly, two coupled 2H doublets were seen at 7.78 and 7.56 ppm (J = 15.42 Hz) indicating the successful formation of the new HC=CH bond. Lastly, a 4H singlet at 7.65 ppm indicated the presence of the central phenyl ring protons. The HRMS calculated for C48H36N2O2+H was 673.2855 with an experimental mass of 673.2861 (Δ = 0.9 ppm).

The synthesis of 33 was conducted in the same manner as 30 – 32, with 4-(diethylamino)benzaldehyde being used to form the final product 34. The crude orange material was eluted from a silica column with DCM: petroleum spirit 60-80 °C which yielded a semi-pure orange/red solid, this purification step was repeated twice more to afford 33 as a pure orange/red solid in 14.5% yield. Confirmation of the final product was evident via the 1H NMR spectrum which showed the CH3 singlet seen in starting material 26 being replaced by a 1H doublet at 7.77 ppm (J = 15.87 Hz), with the second doublet obscured by a 4H triplet at 7.31 ppm, thus giving a 5H multiplet. Furthermore, two coupled 2H doublets at 7.89 and 6.66 ppm (J = 8.75 Hz) indicate the presence of the new phenyl ring. A 4H quartet at 3.41 ppm and a 6H triplet at 1.20 ppm further confirm successful coupling of 4-(diethylamino)benzaldehyde with 26. Final confirmation was given by HRMS as calculated for C31H30N2O+H 447.2436, found m/z [M+H] 447.2439 (100%); Δ = 0.7 ppm.

The preparation of 35, first required the synthesis of ethyl 4-formylbenzoate 34 and the method used followed a previously described literature procedure.24 Thus, to a solution of 4-formylbenzoic acid in DMF was added iodoethane and K2CO3. The mixture was stirred overnight and followed by an aqueous workup to yield a pale tan oil in 92% yield, 9.28 g. 1H NMR analysis confirmed the presence of the new ethyl group, which was presented as a 2H
quartet at 4.42 ppm and a 3H triplet at 1.42 ppm, and these were consistent with the literature values.\textsuperscript{24}

\begin{figure}
\centering
\includegraphics[width=\textwidth]{figure7}
\caption{Synthesis of ethyl 4-formylbenzoate 34 and synthesis of PI 35.}
\end{figure}

Compound 35, was of particular interest due to its structural similarity to the PI (E)-ethyl 4-((diphenylamino)styryl)benzoate (6, Chapter 2). The synthesis of (E)-ethyl 4-(3-((diphenylamino)phenyl)-3-oxoprop-1-en-1-yl)benzoate 35 was carried out in slightly different fashion to that of PIs 30–33. Initially, sodium methoxide and methanol were used as the base reaction conditions. After extensive purification by way of column chromatography and recrystallisations, TLC analysis showed the ‘clean’ product. However, upon \textsuperscript{1}H NMR analysis, it was observed that the use of sodium methoxide and methanol caused the ethyl ester group to undergo transesterification to give a mixture of ethoxy and methoxy substituted products. This was seen by 3H singlet at 3.94 ppm (methyl ester), along with a 2H quartet at 4.39 ppm and a 3H triplet at 1.40 ppm (ethyl ester). Approximately, 40% of the product was the target compound 35, and the remaining 60% was the undesired methyl ester product. Interestingly, in the synthesis of 32 no methyl ester analogue was seen in the final product even though sodium methoxide was used as the base.
For subsequent attempts sodium ethoxide was used in the place of sodium methoxide, and the product 35 was observed by TLC, but a similar light yellow product of closely matched $R_f$ was seen just below the desired product. This yellow product varied slightly in colour to the desired product and in its fluorescence under 248/355 nm light. $^1$H NMR analysis showed the desired product as expected, but also another compound with similar structural characteristics. As shown in the mechanism outlined in Figure 2, an $\alpha,\beta$-hydroxy ketone (A-iii) is formed as an intermediate in the reaction mechanism. It was proposed that the corresponding intermediate, compound 35a, was also isolated from the reaction mixture. This was evident from the $^1$H NMR spectrum, which showed a 1H doublet at 3.55 ppm, an OH singlet at 4.0 ppm and a 2H multiplet at 3.32 – 3.19 ppm. Evidence for the desired product was seen due to the two 1H doublets at 7.80 and 7.60 ppm, indicating the presence of the HC=CH bond protons. Using the above $^1$H NMR spectrum, the integration of the 1H doublet at 3.55 ppm and 2H multiplet at 3.32 – 3.19 ppm as compared with the two 1H doublets at 7.80 and 7.60 ppm showed the ratio of aldol intermediate 35a to product 35 was around 2:1.

![35a](image_url)

**Figure 8** – The aldol intermediate 35a which was isolated alongside 35.

To mitigate the formation of 35a, it was decided to produce sodium ethoxide *in-situ* by way of treating the ethanolic mixture with sodium metal and within 15 mins the colour changed to a vibrant yellow, indicating product formation. The reaction mixture was stirred for 3 hours, and the precipitate was filtered. From TLC analysis, the product appeared to remain in the filtrate and this solution was concentrated in vacuo and worked up in a standard manner. The shorter reaction time and use of freshly prepared sodium ethoxide produced fewer side products in the crude material, but as in the previous attempts the aldol intermediate was still present. The
crude material was combined and repeated recrystallisation from ethanol was performed in order to remove the aldol species 35a before a final recrystallisation from petroleum spirit 60-80 °C removed the high Rf species (0.95, DCM). This yielded 35 as a pure yellow solid in 5.3% yield, 220 mg.

Analysis of the 1H NMR showed the formation of a new HC=CH bond, with two coupled 1H doublets (J = 15.85 Hz) at 7.79 and 7.59 ppm which were consistent with the previously synthesised species. Also, a 2H quartet at 4.40 ppm and 3H triplet at 1.41 ppm showed the presence of an ethyl ester group and that coupling had been successful. Furthermore, no peaks were seen for the aldol intermediate 35a previously described. Final confirmation of the mass ion calculated for C30H25NO3+H 470.1732 was obtained as the M+H mass at 470.1734; Δ = 0.4 ppm.

4.3. Photophysical properties

4.3.1 UV/Vis absorption spectra

The UV/Vis absorption spectra were measured in a variety of non-polar and polar solvents as detailed in Table 1. All spectra were obtained at a concentration 1.0 x 10⁻⁵ mol.L⁻¹ and have been normalised in relation to the longest wavelength maxima. For spectra obtained in toluene and DMF, data below 300 and 280 nm, respectively, have been omitted due to the UV/Vis transmission limit of these solvents.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>ε_r</th>
<th>E_r(30)</th>
<th>Solvent Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>Toluene</td>
<td>2.38</td>
<td>33.9</td>
<td>non polar</td>
</tr>
<tr>
<td>Chloroform (CHCl₃)</td>
<td>4.81</td>
<td>39.1</td>
<td>non polar</td>
</tr>
<tr>
<td>Dimethylformamide (DMF)</td>
<td>36.7</td>
<td>43.2</td>
<td>polar aprotic</td>
</tr>
<tr>
<td>Acetonitrile (MeCN)</td>
<td>36.6</td>
<td>45.6</td>
<td>polar aprotic</td>
</tr>
<tr>
<td>Methanol (MeOH)</td>
<td>32.7</td>
<td>55.4</td>
<td>polar protic</td>
</tr>
</tbody>
</table>

Table 1 - Dielectric constants (ε_r) and solvent polarity parameter E_r(30) values of the solvents used.²⁵

Across the series very little solvatochromic behavior was observed, with only small shifts in λ_max observed. The absorption bands due to local π-π* transitions are considered to be solvent
insensitive, whereas the more polar CT bands are more susceptible to environmental dielectric changes.\textsuperscript{26} Due to the structural features and π-conjugation of these molecules, they display three predominant localised absorptions: π-π* and CT bands.

The UV/Vis absorption spectra for \textsuperscript{29} are shown in Graph 1 and details are shown in Table 2. The peaks around 300 nm were due to locally excited π-π* transitions, and these peaks were also enlarged by n-π* absorption from the ester group. The \( \lambda_{\text{max}} \) peak originated from the CT process upon excitation. The \( \varepsilon \) values for \textsuperscript{29} were calculated with respect to the \( \lambda_{\text{max}} \) and ranged from 20,000 to 27,500 M\(^{-1}\)cm\(^{-1}\) being typical of a ππ \( \rightarrow \) ππ* transition and increased proportionally with increasing solvent polarity.

![Graph 1 - UV/Vis absorption spectra of 29 in various solvents at a concentration of 1.0 x 10\(^{-5}\) mol.L\(^{-1}\), details are shown in Table 2.](image)

<table>
<thead>
<tr>
<th>Solvent</th>
<th>( \lambda_{\text{max}} ) ( ^{a} )</th>
<th>( \varepsilon ) ( ^{b} ) (10(^{3}))</th>
<th>( \lambda_{\text{em}} ) ( ^{c} )</th>
<th>ST ( ^{d} )</th>
<th>( \Phi_{\text{f}} ) ( ^{e} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Toluene</td>
<td>406</td>
<td>2.00</td>
<td>480</td>
<td>74</td>
<td>-</td>
</tr>
<tr>
<td>CHCl(_3)</td>
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<td>2.42</td>
<td>540</td>
<td>123</td>
<td>0.29</td>
</tr>
<tr>
<td>DMF</td>
<td>409</td>
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<td>561</td>
<td>152</td>
<td>-</td>
</tr>
<tr>
<td>MeCN</td>
<td>406</td>
<td>2.64</td>
<td>568</td>
<td>162</td>
<td>-</td>
</tr>
<tr>
<td>MeOH</td>
<td>417</td>
<td>2.75</td>
<td>597</td>
<td>180</td>
<td>-</td>
</tr>
</tbody>
</table>

\textsuperscript{a} \( \lambda = \) one-photon maxima (nm), measured at 1.0 x 10\(^{-5}\) mol.L\(^{-1}\). \textsuperscript{b} \( \varepsilon = \) molar extinction coefficient \( \times 10^{3} \) (M\(^{-1}\)cm\(^{-1}\)); \( A = \varepsilon l c \): \( A = \) absorbance, \( l = \) path length, \( c = \) concentration. \textsuperscript{c} \( \lambda_{\text{em}} = \) emission maxima (nm), 410 nm emission. \textsuperscript{d} ST = Stokes shift.
\((\text{nm}) = (\lambda_{\text{Em}} - \lambda_{\text{max}}) \). Fluorescence quantum yield with Rhodamine 6G as a reference standard; concentration of \(2 \times 10^6\) mol.L\(^{-1}\), 500 nm excitation.

The spectra for 30 are depicted in Graph 2 and details are described in Table 3. Unlike the other molecules in this series the variations in \(\lambda_{\text{max}}\) were much greater, particularly with respect to toluene which exhibited a large blue shift relative to the other solvents. The absorption displayed a band with strong \(\pi-\pi^*\) absorption around 280 – 330 nm and a CT band around 400 nm. The strong \(\pi-\pi^*\) absorption is caused by the local absorption of the phenylene, carbonyl and nitro groups present.

![Graph 2 - UV/Vis absorption spectra of 30 in various solvents at a concentration of 1.0 x 10^5 mol.L^{-1}, details are shown in Table 3.](image)

**Table 3** - a. \(\lambda\) = one-photon maxima (nm), measured at 1.0 x 10^5 mol.L\(^{-1}\). b. \(\varepsilon\) = molar extinction coefficient x 10^3 (M\(^{-1}\)cm\(^{-1}\)); A = elc: A = absorbance, l = path length, c = concentration. c. \(\lambda_{\text{Em}}\) = emission maxima (nm), 400 nm emission. d. ST = Stokes shift (nm) = \((\lambda_{\text{Em}} - \lambda_{\text{max}})\). Fluorescence quantum yield with Rhodamine 6G as a reference standard; concentration of \(2 \times 10^6\) mol.L\(^{-1}\), 500 nm excitation.
Furthermore, a significant portion of this higher energy band was due to the n-π* absorption of the nitro group.\(^{27}\) The values of \(\varepsilon\) were comparatively lower than the other molecules in this series as the CT absorption band was relatively small. However, they also displayed a trend of increasing extinction coefficient with increasing solvent polarity.

The spectra for 31 are depicted in Graph 3 and details are described in Table 4. The value of \(\lambda_{\text{max}}\) displayed no clear trend with increasing solvent polarity, although a general increase in \(\varepsilon\) can be seen. The spectra displayed a broad absorption, with the \(\lambda_{\text{max}}\) band being attributed to CT absorption. Alongside this, a π-π* absorption band was present at approximately 300 nm from local absorption of the carbonyl and phenylene groups. A significant contribution was also seen from the n-π* absorption around 330 nm, although as a broader absorption band rather than the more distinct absorption bands seen in the other compounds.

<table>
<thead>
<tr>
<th>31</th>
<th>(\lambda_{\text{max}})(^a)</th>
<th>(\varepsilon)(^b) ((10^3))</th>
<th>(\lambda_{\text{em}})(^c)</th>
<th>ST(^d)</th>
<th>(\phi_f)(^e)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Toluene</td>
<td>381</td>
<td>1.94</td>
<td>452</td>
<td>71</td>
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<tr>
<td>CHCl(_3)</td>
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</tr>
<tr>
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<tr>
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<td>MeOH</td>
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<td>2.39</td>
<td>521</td>
<td>127</td>
<td>-</td>
</tr>
</tbody>
</table>

Table 4 - \(^a\). \(\lambda\) = one-photon maxima (nm), measured at 1.0 x 10\(^{-5}\) mol.L\(^{-1}\). \(^b\). \(\varepsilon\) = molar extinction coefficient \(\times 10^3\) (M\(^{-1}\)cm\(^{-1}\)); A = \(\varepsilon\)lc: A = absorbance, l = path length, c = concentration. \(^c\). \(\lambda_{\text{em}}\) = emission maxima (nm), 380 nm emission. \(^d\). ST = Stokes shift (nm) = \((\lambda_{\text{em}} - \lambda_{\text{max}})\). \(^e\). Fluorescence quantum yield with Rhodamine 6G as a reference standard; concentration of 2 \(\times 10^{-6}\) mol.L\(^{-1}\), 500 nm excitation.
The spectra for 32 are depicted in Graph 4 and details are shown in Table 5. The $\lambda_{\text{max}}$ displayed a small variance across the solvent polarities and this was consistent with the other compounds in this series. Much larger $\varepsilon$ values were observed for 32 and were due to the contribution of ICT from the two donor TPA groups towards the two carbonyl groups. As solvent polarity increased a small increase in $\varepsilon$ was also observed. The main absorption band (ICT band) was evident at approximately 420 nm, alongside this a strong $\pi$-$\pi^*$ absorption was evident at about 300 nm from the phenylene and carbonyl groups present. Furthermore, an n-$\pi^*$ band at approximately 350 nm was seen and was attributed to the existence of the two carbonyl groups.

<table>
<thead>
<tr>
<th></th>
<th>$\lambda_{\text{max}}$ a</th>
<th>$\varepsilon$ b ($10^3$)</th>
<th>$\lambda_{\text{em}}$ c</th>
<th>ST d</th>
<th>$\phi$ e</th>
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<tr>
<td>Toluene</td>
<td>413</td>
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<td>CHCl₃</td>
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<td>4.72</td>
<td>586</td>
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</table>

Table 5 - a. $\lambda$ = one-photon maxima (nm), measured at $1.0 \times 10^{-5}$ mol L$^{-1}$. b. $\varepsilon$ = molar extinction coefficient x $10^3$ (M$^{-1}$cm$^{-1}$); A = $\varepsilon$lc: A = absorbance, I = path length, c = concentration. c. $\lambda_{\text{em}}$ = emission maxima (nm), 410 nm emission. d. ST = Stokes shift (nm) = $(\lambda_{\text{em}} - \lambda_{\text{max}})$. e. Fluorescence quantum yield with rhodamine 6G as a reference standard; concentration of $2 \times 10^{-6}$ mol L$^{-1}$, 500 nm excitation.
Graph 4 - UV/Vis absorption spectra of 32 in various solvents at a concentration of $1.0 \times 10^{-5}$ mol.L$^{-1}$; details are shown in Table 5.

The spectra for 33 are depicted in Graph 5 and detailed fully in Table 6. A relatively small $\pi-\pi^*$ band around 290 nm was seen along with a much stronger CT band around 430 nm. The strong electron donating properties of the TPA and diethylaniline end groups facilitate CT towards the central carbonyl group, which act as an electron acceptor. As with 32, diethylaniline behaved as an electron donor and contributed to the overall ICT. This was apparent due to the slightly larger $\varepsilon$ values for 32, which were roughly 10,000 M$^{-1}$cm$^{-1}$ higher than those seen in 33 and indicated the higher degree of ICT seen in 32. Furthermore, as solvent polarity increased so did the value for $\varepsilon$.

For 33, the relative absorbance was much lower below 370 nm than for 32, and was related to the presence of fewer localised absorbing groups i.e. the $\alpha,\beta$-unsaturated ketone.
The spectra for 35 are depicted in Graph 6 and full details are described in Table 7. The $\lambda_{\text{max}}$ values display little notable change with solvent polarity and the values for $\varepsilon$ were reasonably low as well.

**Graph 5** - UV/Vis absorption spectra of 33 in various solvents at a concentration of $1.0 \times 10^{-5}$ mol.L$^{-1}$, details are shown in Table 6.

**Graph 6** - UV/Vis absorption spectra of 35 in various solvents at a concentration of $1.0 \times 10^{-5}$ mol.L$^{-1}$, details are shown in Table 7.
The spectra exhibited a strong π-π* absorption around 290 nm and a weaker CT band around 380 nm (which was used to normalise the spectra). The strong π-π* absorption was due to the phenylene and carbonyl groups.

<table>
<thead>
<tr>
<th></th>
<th>$\lambda_{\text{max}}$</th>
<th>$\varepsilon$</th>
<th>$\lambda_{\text{em}}$</th>
<th>ST</th>
<th>$\phi$</th>
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<td>1.64</td>
<td>521</td>
<td>135</td>
<td>-</td>
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</tbody>
</table>

Table 7 - a. $\lambda$ = one-photon maxima (nm), measured at $1.0 \times 10^{-5}$ mol.L$^{-1}$. b. $\varepsilon$ = molar extinction coefficient $\times 10^3$ (M$^{-1}$cm$^{-1}$); A = $\varepsilon$lc: A = absorbance, l = path length, c = concentration. c. $\lambda_{\text{em}}$ = emission maxima (nm), 380 nm emission. d. Stokes shift (nm) = ($\lambda_{\text{em}}$ - $\lambda_{\text{max}}$). e. Fluorescence quantum yield with Rhodamine 6G as a reference standard; concentration of $2 \times 10^{-6}$ mol.L$^{-1}$, 500 nm excitation.

4.3.2 Photoluminescence

A detailed description of the experimental technique is described in *Experimental > Instrumentation > Photophysics*. Measurements were performed in a number of polar and non-polar solvents, with their properties detailed in Table 1. Across this series of PIs it was observed that with increasing solvent polarity a bathochromic shift in the $\lambda_{\text{em}}$ was generally observed and this suggested the excited states were more polar, and therefore more stabilised with increasing solvent polarity.$^{28}$ The large STs observed indicated significant electronic reorganisation takes place after excitation and prior to emission.$^{29}$ Furthermore, the fluorescence spectra across the series exhibit a general trend with increasing solvent polarity resulting in a lower emission intensity and a broadening of the emission band. Across the series, the strong influence of solvent on emission intensity is also observed. Thus, in low and moderately polar solvents a reasonably strong $\lambda_{\text{em}}$ is observed, but in more polar solvents, the fluorescence is reduced due to the increasing degree of ICT.$^{30}$ As described in *Chapter 3*, in low polarity solvents emission emanates from a locally excited state, whereas in higher polarity solvents emission occurs from an ICT state.$^{31}$ This is explained by the decrease in radiative rate constants while nonradiative decay remains unchanged.$^{32}$ A reduced $k_r$ in polar solvents as emission is from an nπ* excited state, which is symmetry forbidden. This enlargement of ICT is
seen in the increasing values of $\varepsilon$ with increasing solvent polarity and was consistent across the series, with 36 being the only exception. Alongside this, in highly polar solvents the hydrogen bonding interactions of the solvent on the highly polar CT state of the excited species may also be contributing to the quenching of the $\lambda_{\text{Em}}$ intensity.\textsuperscript{28} The spectra of 30 (Graph 8, toluene), 31 (Graph 9, methanol), 32 (Graph 10, DMF acetonitrile and methanol) and 35 (Graph 12, methanol) all show a sharp band in the 400 – 450 nm region. This is likely related to the need for intense excitation energies that are required in higher polarity solvent to produce a suitable $\lambda_{\text{Em}}$.

As described in Table 2, large STs for 29 were seen in the $\lambda_{\text{Em}}$ with increased solvent polarity and is consistent with a stabilisation of the polar excited state. The addition of the alkyl ether group leads to a large increase in $\lambda_{\text{Em}}$ displayed across the solvents (Graph 7). This could also be weak emission from an $n\pi^*$ state with a weak absorption that is masked by the tail of the strong CT or $\pi\rightarrow\pi^*$ transition. As such, a relatively large $\phi_F$ was measured in chloroform of 0.292. Such a large $\phi_F$ would be likely to negatively impact the level of intersystem crossing to the active triplet state, and thus make 29 a poor candidate for TPP. As solvent polarity
increases the $\lambda_{Em}$ intensity decreases, and this is consistent with a transition from a locally excited state to one of a ICT state leading to the reduction and was described previously.

**Graph 8** - Fluorescence emission of 30 as measured by 400 nm emission between 420 - 800 nm. The measurements were performed at a concentration of $2 \times 10^{-6}$ mol.L$^{-1}$.

For 30 a small $\phi_F$ value was measured in chloroform of 0.0023. Measured $\lambda_{Em}$ values of 566, 502 and 510 nm were measured in toluene, chloroform and DMF, respectively. Thus, the presence of the nitro electron withdrawing group appears to significantly reduce both the measured $\phi_F$, and fluorescence emission intensity (Graph 8). Furthermore, the obtained $\lambda_{Em}$ intensities are extremely small even in low polarity solvents. The measured $\lambda_{Em}$ in toluene displays a significant red shift relative to chloroform and DMF. For 31, a $\phi_F$ value of 0.058 was measured in chloroform, while with increasing solvent polarity, there is a significant bathochromic shift in $\lambda_{Em}$ (Graph 9). Alongside this, a large drop in emission intensity and broadening of the emission band is observed and is consistent with highly polar excited states, which are stabilised by solvents of high polarity.
Graph 9 - Fluorescence emission of 31 as measured by 380 nm emission between 400 - 750 nm. The toluene and chloroform samples were at a concentration of $2 \times 10^{-6}$ mol.L$^{-1}$; DMF and MeCN were measured at $1 \times 10^{-5}$ mol.L$^{-1}$.

Graph 10 - Fluorescence emission of 32 as measured by 410 nm emission between 430 - 750 nm. Emission data in toluene and chloroform were at a concentration of $2 \times 10^{-6}$ mol.L$^{-1}$; DMF, MeCN and MeOH were measured at $1 \times 10^{-5}$ mol.L$^{-1}$.

For 32, a low $\phi_F$ value of 0.0075 was measured in chloroform. Furthermore, as seen in Table 5, 32 displays a large ST and the value obtained is greater than other species present in this series (Graph 10). Due to the large $\pi$-conjugation pathway and presence of two strong electron donor
groups, 32 possesses a strongly polar excited state which should be stabilised by polar solvents. Interestingly, the ST value for toluene was 104 nm followed by 172 nm in chloroform with the maximum value measured being in acetonitrile at 188 nm. Alongside this, very weak $\lambda_{Em}$ intensities were observed and this was particularly true with increasing solvent polarity. This is attributed to the prevalence of locally excited state emissions in non-polar toluene, whereas the emission in polar solvents originates from ICT.\textsuperscript{31}

**Graph 11** - Fluorescence emission of 33 as measured by 420 nm emission between 440 - 750 nm. The measurements were performed at a concentration of $2 \times 10^{-6}$ mol.L\textsuperscript{-1}.

For 33, a $\phi_F$ value of 0.082 was measured in chloroform. The observed STs do increase with increasing solvent polarity and suggest the existence of a polar excited state, however they are generally lower than the other PIs in this series (Graph 11). In comparison to 32, a significant blue shift can be seen in the emission suggesting a low level of ICT upon excitation. This is caused by the stronger electron donating ability of the TPA group compared with the diethylaniline group and the larger $\pi$-conjugation system. The measured $\lambda_{Em}$ intensities in 33 were much stronger and were due to the dominant locally excited state emission in solvents such as toluene, chloroform and acetonitrile. Whereas in methanol a weaker fluorescence and slight increase in ST was seen, and this is indicative of the transition to a ICT emission. As
previously, with 35 an increase in solvent polarity was accompanied by an increase in the $\lambda_{\text{em}}$ maxima, this is expected with highly polar excited states that are stabilised by polar solvents (Graph 12). The measured $\Phi_F$ in chloroform was found to be 0.094.

Graph 12 - Fluorescence emission of 35 as measured by 380 nm emission between 400 - 750 nm. The measurements were performed at a concentration of $2 \times 10^{-6}$ mol.L$^{-1}$ except MeOH, which was performed at $1 \times 10^{-5}$ mol.L$^{-1}$.

4.3.3 Two-photon absorption cross-section ($\delta_{2\text{PA}}$) – z-scan

To assess the $\delta_{2\text{PA}}$ values of the synthesized PIs, the z-scan technique was used in the same manner as previously described. The full experimental setup is described in Chapter 2, Experimental, z-scan measurements. The obtained effective $\delta_{2\text{PA}}$ of this series of PIs were measured at a concentration of $2.0 \times 10^{-2}$ mol.L$^{-1}$ in chloroform and the results are presented in Table 8. The PIs were measured at 780 nm using a Ti:Saph fs-laser with rhodamine 6G as a reference (33 GM in ethanol), which was consistent with previous literature. The stated values of $\delta_{2\text{PA}}$ have a standard accuracy of ± 10%.
<table>
<thead>
<tr>
<th>Photoinitiator</th>
<th>Solvent</th>
<th>$\delta_{2PA}$ (GM)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rhodamine 6G</td>
<td>MeOH</td>
<td>33</td>
</tr>
<tr>
<td>29</td>
<td>CHCl₃</td>
<td>101</td>
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<tr>
<td>30</td>
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<td>371</td>
</tr>
<tr>
<td>35</td>
<td>CHCl₃</td>
<td>86</td>
</tr>
</tbody>
</table>

Table 8 - $\delta_{2PA}$ of PIs as measured at 780 nm and a concentration of $2.0 \times 10^{-2}$ mol.L$^{-1}$. 1 GM = $1 \times 10^{-50}$ cm$^4$s photons$^{-1}$ molecule$^{-1}$.

As can be seen in Table 8, $\delta_{2PA}$ values were obtained for all the synthesised PIs and were in the range of 78 GM for 30 to 371 GM for 33. Overall the measured values were relatively moderate compared to our previously synthesised PIs. The two-species containing the ether moieties 29 and 31 have moderate $\delta_{2PA}$ values of 101 GM and 147 GM at 780 nm, respectively. The ether groups act as relatively weak electron donor, therefore the $\delta_{2PA}$ values were relatively modest. Alongside this, the position of the $\alpha,\beta$-unsaturated ketone group was reversed in 29 and suggests a lowering of the $\delta_{2PA}$ occurred if the $\text{-C=C-}$ (29), rather than carbonyl component (31) was attached directly to the TPA ring.

The $\delta_{2PA}$ for 30 was found to be 78 GM, and in this case the use of the strong electron withdrawing nitro group should facilitate efficient CT from the donor core to acceptor. However, this doesn’t appear to be the case, as evident in the low molar extinction coefficient ($1.68 \times 10^3$ M$^{-1}$cm$^{-1}$ in chloroform) suggesting poor ICT upon excitation. This is due to the $\alpha,\beta$-unsaturated ketone group acting as a poor $\pi$-conjugation pathway and therefore poor ICT occurs upon excitation. This was evident by the strong $\pi-\pi^*$ absorption seen in Graph 2, whereas ICT absorptions for this compound at longer wavelengths are less intense.

Much higher responses were seen for the D-$\pi$-D PIs 32 and 33 with $\delta_{2PA}$ values of 211 GM and 371 GM at 780 nm, respectively. Thus, the presence of strong electron donors appears to give a significant improvement in the measured $\delta_{2PA}$. Due to the strong donating ability of the TPA and diethyl aniline groups present, it was possible that these could act as ‘independent’ groups with the carbonyl group acting as the electron acceptor. Thus, the overall $\delta_{2PA}$ value seen for 32 and 33 could be a combination of two loosely independent conjugation pathways.
For **35** a value for the $\delta_{2PA}$ of only 86 GM was measured at 780 nm. Thus, in comparison with structurally similar species like **6** (126 GM) and **31** (147 GM) a moderate drop in GM was seen. This is likely due to a combination of factors, including the $\alpha,\beta$-unsaturated ketone acting as an electron acceptor from the donor TPA and secondly, the second ester carbonyl acting as another electron acceptor meaning the overall ICT process was adversely affected.

As evidenced by the PIs synthesised in *Chapter 2* and *3* and detailed in *Chapter 5*, the use of $\delta_{2PA}$ values as an indication of PI efficiency can be misleading and TPP tests would need to be carried out to give meaningful data on the efficacy of a compound for use in TPP. As stated in *Chapters 2* and *3* an assessment of the $\delta_{2PA}$ values over a broad wavelength range would likely give a detailed, and insightful description of the $\delta_{2PA}$. However, unlike the molecules synthesised in *Chapter 3* the one-photon maxima of these species are close to 400 nm which suggests that the measured values could be close to their maxima due to measurements being done at 780 nm.

**4.3.4 Comparison of photoinitiators: 6, 31 and 35**

During this work, the PIs **6**, **31** and **35** have been prepared and they share common structural similarities, as outlined in Figure 9 and Table 9 contains their key photophysical data.

![Figure 9 – Structures of photoinitiators 6, 31 and 35 from Chapter 2 and Chapter 4, respectively.](image-url)
Firstly, to compare the compounds, 6 contained a vinylene connecting group whereas 31 and 35 are connected by the α,β-unsaturated ketone moiety. As such this has important consequences for the π-conjugation pathway, with a reduction in effective conjugation for 31 and 35 compared with 6. Secondly, 6 can be considered a dipolar D-π-A, while 31 has a quadrupolar D-π-A-π-D conformation and 35 a quadrupolar D-π-A-π-A species.

<table>
<thead>
<tr>
<th>PI</th>
<th>Solvent</th>
<th>λ&lt;sub&gt;max&lt;/sub&gt;</th>
<th>ε (10&lt;sup&gt;4&lt;/sup&gt;)</th>
<th>λ&lt;sub&gt;Em&lt;/sub&gt;</th>
<th>ST</th>
<th>φ&lt;sub&gt;F&lt;/sub&gt;</th>
<th>δ&lt;sub&gt;2PA&lt;/sub&gt;(GM)</th>
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<tbody>
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</table>

Table 9 – A comparative table of photophysical properties of structurally similar analogues from Chapter 2 (6) and Chapter 4 (31 and 35).

From Table 9 it was observed that these structural differences and similarities have consequences for the overall molecular properties of these PIs. Across the three PIs an indication of the ICT efficiency is evident in the variation of the ε across the series. As shown in Table 9 a general trend is seen, with the values of ε increasing in the order 35 < 31 < 6 and this suggests an enlargement of ICT. This is due to the overall reduction in ICT from the donor core to the carbonyl acceptor and was particularly evident when comparing 6 and 35. Furthermore, this reduction of ICT partly explains the measured δ<sub>2PA</sub>, as ICT is considered one of the key factors in maximising δ<sub>2PA</sub>. The quadrupolar nature of 31 when compared with the dipolar 6 explains the increase in δ<sub>2PA</sub> observed, even though the effective π-conjugation pathway is
shorter in 31.35 Across all three compounds, in their emission spectra, large STs are observed and this is consistent with the formation of highly polar excited states, which are stabilised by polar solvents.

The presence of an extra carbonyl group appears to have reduced the overall $\phi_F$ values, with a value of 0.198 seen for 6, 0.094 for 35 and 0.058 for 31, with the former in methanol and the latter two measured in chloroform. The additional carbonyl groups in 31 and 35 could also further reduce the energy gap between the singlet and triplet levels, and thus give potential improvements in polymerisation thresholds.4 As seen with compounds 6 – 8 in Chapter 2, the overall $\delta_{2PA}$ can sometimes give little guidance in likely polymerisation thresholds, particularly in viscous media, where excitation can be limited to a single dipolar branch. Nonetheless, the reduction in ICT upon excitation may reduce the ability to initiate polymerisation for 31 and 35, although the reduced $\phi_F$ may prove enough to negate this effect. Nonetheless, it is anticipated that there would be greater TPP activity in 31 when compared 35, due to the lower $\phi_F$, higher $\delta_{2PA}$ and higher molar absorptivity seen in 31. However, further investigations into the properties of these three PIs would give a better indication of their relative activities.

4.4. Experimental

4.4.1 Synthesis

Synthesis of 1-(4-(diphenylamino)phenyl)ethanone (26). Triphenylamine (20 g, 81.6 mmol) and zinc chloride (12.2 g, 89.7 mmol) were added to a stirred solution of DCM (200 ml). A solution of acetyl chloride (7.05 g, 89.7 mmol) was added dropwise over 5 minutes, after which the solution was refluxed for 20 h. After cooling to r.t, the solution was carefully poured into 2 M aq. HCl solution (500 ml) and separated with DCM. The organics were washed with sat. K$_2$CO$_3$ (2 x 200 ml) and brine (200 ml). They were dried over MgSO$_4$, filtered and the solvents removed in vacuo. Purification by column chromatography (silica gel, DCM: petroleum spirit 60-80 °C 1:4) afforded 1-(4-(diphenylamino)phenyl)ethanone (26) in 18 g, 77% yield.18 Yellow solid; Rf 0.4 (DCM: petroleum spirit 60-80 °C, 1:4); mp 142-144 °C. (lit.: 143-145 °C.23). $^1$H NMR (CDCl$_3$): δ = 7.79 (d, J = 8.45 Hz, 2H), 7.31 (t, 4H), 7.15 - 7.09 (m, 6H), 6.98 (d, J = 8.45 Hz, 2H),
2.52 (s, 3H). $^{13}$C NMR (CDCl$_3$): 196.43, 152.19, 146.54, 129.90, 129.40, 129.21, 125.71, 124.65, 122.95, 119.72, 26.23. HRMS: calcd for C$_{20}$H$_{17}$NO+H 288.1388, found m/z [M$^+$H] 288.1385 (100%); $\Delta$ = -1.0 ppm.

**Synthesis of 1-(4-(octan-3-yl)oxy)phenyl)ethanone (27).** 4-Hydroxyacetophenone (21.9 g, 161 mmol), 2-ethylhexyl bromide (32.6 g, 169 mmol) and K$_2$CO$_3$ (24.5 g, 177 mmol) were added to a stirred solution of DMF. The rapidly stirred solution was heated at 60 °C overnight. The solution was allowed to cool and poured into H$_2$O (500 ml) and extracted with DCM (250 ml), the organics were successively washed with H$_2$O (2 x 200 ml) and sat. brine (2 x 200 ml). They were dried over MgSO$_4$, filtered and the solvents removed in vacuo. The pale tan oil was used without further purification affording 1-(4-(octan-3-yl)oxy)phenyl)ethanone (27) 38.47 g, 96% yield. $^1$H NMR (CDCl$_3$): $\delta =$ 7.63 (d, J = 9.3 Hz, 2H), 6.65 (d, J = 9.3 Hz, 2H), 3.64 (dd, J = 7.17 Hz, 1H), 2.25 (s, 3H), 1.28-1.10 (m, 5H), 1.09-1.02 (m, 5H), 0.69-0.61 (m, 6H). $^{13}$C NMR (CDCl$_3$): 197.14, 163.49, 130.62, 115.45, 114.21, 70.78, 39.29, 30.47, 26.25, 23.82, 22.99, 14.02, 11.06. HRMS: calcd for C$_{16}$H$_{24}$O$_2$+H 249.1855, found m/z [M$^+$H] 249.1858 (100%); $\Delta$ = 1.2 ppm.

**Synthesis of 4-ethoxybenzaldehyde (28).** 4-Hydroxybenzaldehyde (5 g, 40.97 mmol), iodoethane (6.7 g, 43 mmol) and K$_2$CO$_3$ (6.8 g, 49 mmol) were added to a stirred solution of DMF. The rapidly stirred solution was heated at 60 °C overnight. The solution was allowed to cool and poured into H$_2$O (500 ml) and extracted with DCM (250 ml), the organics were successively washed with H$_2$O (2 x 200 ml) and sat. brine (2 x 200 ml). They were dried over MgSO$_4$, filtered and the solvents removed in vacuo. The pale tan oil was used without further purification affording 4-ethoxybenzaldehyde (28) 5.85 g, 95 % yield.$^{21}$ $^1$H NMR (CDCl$_3$): $\delta =$ 9.86 (s, 1H), 7.81 (d, J = 8.9 Hz, 2H), 6.97 (d, J = 8.9 Hz, 2H), 4.10 (q, 2H), 1.44 (t, 3H).

**Synthesis of (E)-3-(4-(diphenylamino)phenyl)-1-(4-(octan-3-yl)oxy)phenyl)prop-2-en-1-one (29).** To a solution of 4-formyltriphenylamine (1) (0.9 g, 3.27 mmol) and 1-(4-(octan-3-yl)oxy)phenyl)ethanone (27) (0.81 g, 3.2 mmol) in MeOH (50 ml) was added KOH (0.46 g, 8.15 mmol). The solution was stirred overnight and a deep orange colour was observed. The solution was poured in H$_2$O (250 ml) and extracted with DCM (200 ml). The organics were washed with 2 M aq. HCl (3 x 100 ml) and sat. brine (2 x 200 ml). They were combined, dried over MgSO$_4$, filtered and the solvents were removed in vacuo. Purification by column
chromatography (silica gel, EtOAc: petroleum spirit 60-80 °C 1:25) affording (E)-3-(4-(diphenylamino)phenyl)-1-(4-(octan-3-yloxy)phenyl)prop-2-en-1-one (29) 100 mg, 6% yield. Orange/yellow semi-solid; Rf 0.6 (DCM: petroleum spirit 60-80 °C, 1:5). ¹H NMR (CDCl₃): δ = 8.00 (d, J = 9.07 Hz, 2H), 7.75 (d, J = 15.3 Hz, 1H), 7.49 (d, J = 9.07 Hz, 2H), 7.40 (d, J = 15.3 Hz, 1H), 7.29 (t, J = 15.99 Hz, 4H), 7.13 (d, J = 7.5 Hz, 4H), 7.09 (t, J = 7.4 Hz, 2H), 7.02 (d, J = 9.07 Hz, 2H), 6.96 (d, J = 9.07 Hz, 2H), 3.91 (dd, J = 5.70, 1.5 Hz, 1H), 1.57 - 1.37 (m, 5H), 1.36 - 1.29 (m, 5H), 0.96 - 0.88 (m, 6H). ¹³C NMR (CDCl₃): 188.73, 163.14, 146.95, 143.66, 131.22, 130.64, 129.6, 128.25, 128.19, 125.40, 123.59, 121.78, 119.42, 114.29, 70.78, 39.34, 30.51, 29.08, 23.86, 23.03, 14.31, 11.42. HRMS: calcd for C₃₅H₃₇NO₂⁺H 504.2897, found m/z [M⁺H] 504.2897 (100%); Δ = -1.2 ppm.

Synthesis of (E)-1-(4-(diphenylamino)phenyl)-3-(4-nitrophenyl)prop-2-en-1-one (30). To a stirred solution of (1-(4-(diphenylamino)phenyl)ethanone) 26 (0.5 g, 1.74 mmol) and 4-nitrobenzaldehyde (0.32 g, 2.1 mmol) in EtOH (50 ml) was added NaOMe (0.28 g, 5.2 mmol) in portions over 15 mins. The solution was stirred at r.t overnight after which the solution was poured in H₂O (250 ml) and extracted with DCM (200 ml). The organics were washed with 2 M aq. HCl (3 x 100 ml) and sat. brine (2 x 200 ml). They were combined, dried over MgSO₄, filtered and the solvents were removed in vacuo. Purification by column chromatography (silica gel, DCM: petroleum spirit 60-80 °C 1:1) affording (E)-1-(4-(diphenylamino)phenyl)-3-(4-nitrophenyl)prop-2-en-1-one (30) 225 mg, 31% yield. Orange/red solid; Rf 0.75 (DCM). ¹H NMR (CDCl₃): 188.73, 163.14, 146.95, 143.66, 131.22, 130.64, 129.6, 128.25, 125.40, 123.59, 121.78, 119.42, 114.29, 70.78, 39.34, 30.51, 29.08, 23.86, 23.03, 14.31, 11.42. HRMS: calcd for C₂₇H₂₆N₂O₃H 421.1552, found m/z [M⁺H] 421.1544 (100%); Δ = -1.9 ppm.

Synthesis of (E)-1-(4-(diphenylamino)phenyl)-3-(4-ethoxyphenyl)prop-2-en-1-one (31). To a stirred solution of (1-(4-(diphenylamino)phenyl)ethanone) 26 (2.14 g, 7.5 mmol) and 4-ethoxybenzaldehyde (28) (1.68 g, 11.2 mmol) in EtOH (50 ml) was added NaOMe (1 g, 18.6 mmol) in portions over 15 mins. The solution was stirred at r.t. overnight after which the solution was poured in H₂O (250 ml) and extracted with DCM (200 ml). The organics were
washed with 2 M aq. HCl (3 x 100 ml) and sat. brine (2 x 200 ml). They were combined, dried over MgSO₄, filtered and the solvents were removed in vacuo. Purification by column chromatography (silica gel, DCM: petroleum spirit 60-80 °C 1:1) affording (E)-1-(4-(diphenylamino)phenyl)-3-(4-ethoxyphenyl)prop-2-en-1-one (31) followed by recrystallisation (petroleum spirit 60-80 °C: EtOAc; 10:1) yielded pure 450 mg, 14.5% yield. Yellow crystalline solid; Rf 0.75 (DCM). ¹H NMR (CDCl₃): δ = 7.89 (d, J = 9.23 Hz, 2H), 7.77 (d, J = 16.05 Hz, 1H), 7.57 (d, J = 8.83 Hz, 2H), 7.41 (d, J = 16.05, 1H), 7.36 – 7.29 (m, 4H), 7.17 (d, J = 9.81 Hz, 4H), 7.13 (m, 2H), 7.04 (d, J = 8.83 Hz, 2H), 6.91 (d, J = 9.23 Hz, 2H), 4.07 (q, J = 7.0 Hz, 2H), 1.43 (t, J = 7.0 Hz, 3H).

¹³C NMR (CDCl₃): 188.33, 160.87, 146.61, 143.49, 131.05 130.04, 127.81, 125.92, 124.55, 120.02, 119.54, 114.87, 63.64, 14.73. HRMS: calcd for C₂₉H₂₅NO₂+H 420.1964, found m/z [M+H] 420.1967 (100%); Δ = 0.7 ppm.

Synthesis of (2E,2'E)-3,3'-(1,4-phenylene)bis(1-(4-(diphenylamino)phenyl)prop-2-en-1-one) (32). To a stirred solution of (1-(4-(diphenylamino)phenyl)ethanone) 26 (1 g, 3.5 mmol) and terephthalaldehyde (0.21 g, 1.6 mmol) in EtOH (50 ml) was added NaOMe (0.38 g, 7.1 mmol) in portions over 15 mins. The solution was stirred at r.t overnight, after which the solution was poured in H₂O (250 ml) and extracted with DCM (200 ml). The organics were washed with 2 M aq. HCl (3 x 100 ml) and sat. brine (2 x 200 ml). They were combined, dried over MgSO₄, filtered and the solvents were removed in vacuo. Purification by column chromatography (silica gel, DCM: petroleum spirit 60-80 °C 1:1) affording semi-pure 33. Recrystallisation (petroleum spirit 60-80 °C: EtOAc; 5:1) afforded pure (2E,2'E)-3,3'-(1,4-phenylene)bis(1-(4-(diphenylamino)phenyl)prop-2-en-1-one) (32) 261 mg, 9 % yield. Orange/red solid; Rf 0.75 (DCM). ¹H NMR (CDCl₃): δ = 7.91 (d, J = 9.16 Hz, 4H), 7.78 (d, J = 15.42 Hz, 2H), 7.65 (s, 4H), 7.56 (d, J = 15.42 Hz, 2H), 7.33 (t, J = 7.8 Hz, 8H), 7.18 – 7.12 (m, 12H), 7.03 (d, J = 9.16 Hz, 4H). ¹³C NMR (CDCl₃): 187.88, 152.26, 146.21, 142.38, 136.98, 130.48, 130.21, 129.66, 128.81, 127.81, 125.79, 124.77, 122.84, 119.78. HRMS: calcd for C₄₈H₃₆N₂O₂+H 673.2855, found m/z [M+H] 673.2861 (100%); Δ = 0.9 ppm.

Synthesis of (E)-3-(4-(diethylamino)phenyl)-1-(4-(diphenylamino)phenyl)prop-2-en-1-one (33). To a stirred solution of (1-(4-(diphenylamino)phenyl)ethanone) 26 (2 g, 6.9 mmol) and 4-(diethylamino)benzaldehyde (1.85 g, 10.5 mmol) in MeOH (100 ml) was added NaOMe (1.51 g,
27 mmol) in portions over 15 mins. The solution was stirred at r.t. overnight after which the solution was poured into H$_2$O (250 ml) and extracted with DCM (200 ml). The organics were washed with 2 M aq. HCl (3 x 100 ml) and sat. brine (2 x 200 ml). They were combined, dried over MgSO$_4$, filtered and the solvents were removed in vacuo. Purification by column chromatography (silica gel, DCM: petroleum spirit 60-80 °C 1:1) affording (E)-3-(4-(diethylamino)phenyl)-1-(4-(diphenylamino)phenyl)prop-2-en-1-one (33) 450 mg, 14.5% yield. Orange/red solid; Rf 0.75 (DCM). $^1$H NMR (CDCl$_3$): δ = 7.89 (d, J = 8.75 Hz, 2H), 7.77 (d, J = 15.87 Hz, 1H), 7.51 (d, J = 8.75 Hz, 2H), 7.31 (t, J = 7.3 Hz, 5H), 7.16 (d, J = 8.59 Hz, 4H), 7.12 (t, J = 7.4 Hz, 2H), 7.04 (d, J = 8.75 Hz, 2H), 6.66 (d, J = 8.75 Hz, 2H), 3.41 (q, J = 7.1 Hz, 4H), 1.20 (t, J = 7.1 Hz, 6H). $^{13}$C NMR (CDCl$_3$): 188.54, 151.54, 146.79, 144.67, 130.54, 129.83, 129.53, 125.77, 124.31, 120.33, 116.22, 111.32, 44.49, 12.61. HRMS: calcd for C$_{31}$H$_{30}$N$_2$O+H 447.2436, found m/z [M$^+$H] 447.2439 (100%); Δ = 0.7 ppm.

Synthesis of ethyl 4-formylbenzoate (34). To a stirred solution of 4-formylbenzoic acid (8.5 g, 56.6 mmol) in DMF (200 ml) was added K$_2$CO$_3$ (15.6 g, 113 mmol) and iodoethane (11 g, 68 mmol). The reaction mixture was stirred rapidly at r.t. overnight and completion of the reaction was monitored by TLC analysis. After which, the mixture was poured into H$_2$O (500 ml) and extracted with diethyl ether (3 x 200 ml). The organics were combined, dried over MgSO$_4$, filtered and the solvents were removed in vacuo. The crude oil was used without further purification. Ethyl 4-formylbenzoate (34) 9.28 g, 92% yield. Pale oil; Rf 0.6 (DCM).$^2$4 $^1$H NMR (CDCl$_3$): δ = 10.10 (s, 1H), 8.20 (d, J = 9.12 Hz, 2H), 7.95 (d, J = 9.12 Hz, 2H), 4.42 (q, 2H), 1.42 (t, 3H).

Synthesis of (E)-ethyl 4-(3-(4-(diphenylamino)phenyl)-3-oxoprop-1-en-1-yl)benzoate (35). To a rapidly stirred solution of (1-(4-(diphenylamino)phenyl)ethanone) 26 (2.68 g, 9.3 mmol) and ethyl 4-formylbenzoate (1.99 g, 11.8 mmol) in EtOH (100 ml) was added sodium metal (0.65 g, 27.9 mmol) in portions. The solution was stirred for 3 h and the precipitates were filtered off. The precipitate was recrystallised in EtOH and finally in petroleum spirit 60-80 °C affording (E)-ethyl 4-(3-(4-(diphenylamino)phenyl)-3-oxoprop-1-en-1-yl)benzoate 35 220 mg, 5.3% yield. Yellow crystalline solid; Rf 0.8 (DCM). $^1$H NMR (CDCl$_3$): δ = 8.07 (d, J = 8.77 Hz, 2H), 7.91 (d, J = 9.26 Hz, 2H), 7.79 (d, J = 15.84 Hz, 1H), 7.67 (d, J = 8.77 Hz, 2H), 7.59 (d, J = 15.84 Hz,
1H), 7.33 – 7.30 (m, 4H), 7.17 (m, 6H), 7.03 (d, J = 9.26 Hz, 2H), 4.40 (q, J = 7.1 Hz, 2H), 1.41 (t, J = 7.1 Hz, 3H). $^{13}$C NMR (CDCl$_3$): 187.76, 166.03, 152.35, 146.40, 141.97, 139.43, 131.62, 130.24, 130.07, 129.65, 128.05, 126.09, 124.81, 124.05, 119.69, 61.17, 14.32. HRMS: calcd for C$_{30}$H$_{25}$NO$_3$+Na 470.1732, found m/z [M+Na] 470.1734 (100%); $\Delta$ = 0.4 ppm.

4.5. Conclusions

A series of TPA based $\alpha,\beta$-unsaturated ketones PIs with dipolar and quadrupolar geometries were synthesised via aldol condensation reactions. Their synthesis, physical and photophysical properties has been described in detail. The use of 4-acetyltriphenylamine as a starting material improved access to the compounds, through improved yields and fewer by-products. Nonetheless, further development of the synthetic conditions used would likely result in improvements in overall yields beyond the moderate yields of < 40% obtained here. Moderate $\delta_{2PA}$ values were measured for these species in the range of 78 – 371 GM, at 780 nm using the z-scan technique. The majority of the synthesised species exhibited $\phi_F$ of less than 0.1, with 30 and 32 displaying measured values of less than 0.01. However for 29, a much larger value was measured, namely 0.3, and suggests it would likely be unsuitable for efficient two-photon polymerisation. The one-photon absorption data shows strong linear absorptions occur at around 380 – 420 nm for these species suggesting the use of an 800 nm laser wavelength for fabrication would likely be close to optimal. Two-photon polymerisation tests were unable to be conducted on the PIs presented in this chapter in the latter stages of this project due to a malfunction of the laser system, further tests will be conducted in the future.

4.6. References

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(27) Hui, Y. H. *Handbook of food science, technology, and engineering*; CRC press, 2006; Vol. 149.


Chapter 5. Two-photon polymerisation of synthesised photoinitiators

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5.1. Introduction

Since its inception in 1997, TPP has been under intense investigation for the fabrication of 3D micro/nano-devices. Photopolymerisation initiated by a 2PA PI is a growing field for producing micro/nano-scale 3D structures in a variety of materials. The TPP technique takes advantage of the 2PA processes that occur in suitable PIs. To drive the two-photon transition sufficient photon densities are required and this only occurs at the focal point of a laser. Commonly, fs or ns lasers are sufficient to drive this process, however for the studies described in this chapter the use of a fs-pulsed Ti:Sapphire laser at 800 nm was sufficient. Importantly, the use of near-infrared lasers implies the linear absorption of the chosen liquid-state monomers are negligible. Therefore, polymerisation can occur within the material, rather than at the surface, which occurs in conventional UV-initiated polymerisations. After polymerisation, the remaining un-polymerised material can be easily washed away leaving the desired 3D structures. Alongside the considerable materials development work conducted by a number of research groups, many have also developed fabrication stages and experimental setups in the pursuit of high-throughput and high quality fabrication. A number of papers and reviews have been published on this subject matter. As noted earlier, in the last decade considerable progress has been made in developing highly active 2PA PIs for TPP applications. In-depth descriptions of the key physical properties are described in Chapter 1 > Two-photon polymerisation > Photoinitiators and Chapter 2 > Introduction. Furthermore, as described in Chapters 2 – 4, a series of PIs were designed, synthesised and characterised. To conclude this work, investigations of their suitability for TPP have been conducted and made use of a reference acrylate system. These tests have established optimum processing parameters including necessary polymerisation power thresholds, writing speeds and feature sizes.

Consequently, the TPP setup has been used to investigate the multibranched species 6, 7 and 8 from Chapter 2 and molecules 22 and 23 from Chapter 3. Several reasons exist for the selection of these particular compounds, however the biggest issue was the poor solubility of several of our designed molecules in our reference monomer system. The reference monomer system chosen consisted of the commercially available acrylates SR415 and SR351 (5.4.3), as these materials have been previously used in literature studies. Finally, the ideal processing
parameters for each PI were determined by changing laser intensity and writing speed using the same PI concentration. A full description of the setup is detailed in the Experimental section.

5.2. Results and discussion

5.2.1 Two-photon polymerisation mechanism

In the early years of research into this technique several groups studied and discussed the mechanism for TPP. The mechanism for TPP is described in Figure 1: a PI in the ground state is two-photon excited to the singlet excited state $S_1$. From the $S_1$ state the molecule can relax back to the ground state through fluorescence, which can be measured by its $\phi_F$. Alternatively, the molecule can undergo intersystem crossing ($\phi_{ISC}$, triplet quantum yield) to the triplet state $T_1$, leading to electron transfer and polymerisation of the monomer species.$^{17,20}$ The molecules can also relax by non-radiative processes. In order for the molecule to be an effective PI for TPP it is necessary to maximise the probability of intersystem crossing ($\phi_{ISC}$) to the active $T_1$ state. Alongside this, a high $\delta_{2PA}$ is also desirable to improve a PIs sensitivity.

Cumpston et al. synthesised a series of D-π-D chromophores for use in TPP. They investigated the electron transfer processes in these compounds using three techniques: (1) steady-state fluorescence quenching, (2) fluorescence lifetime shortening and (3) the appearance of electronic absorption bands due to the presence of a radical cation.$^{20}$ Further work by Perry et al. confirmed that a photoinduced electron transfer mechanism was involved.$^{17}$ In this work by Perry et al. they selected a number of D-π-D molecules and commercially available acrylates for their TPP studies. It was found that quenching of the fluorescence emission and shortening of the excited state lifetime in the presence of acrylates occurred. The bimolecular quenching rate constant ($K_q$), was determined by the change in fluorescence intensity as a function of monomer concentration using the Stern-Volmer equation. Secondly, they determined the free energy, $\Delta G$, of the electron transfer in the excited state and found that when $\Delta G$ was negative that photoinduced electron transfer was thermodynamically favourable. However, some PIs exhibited a $\Delta G > 0$ suggesting the electron transfer was thermodynamically unfavourable for these species. Although, for these molecules a substantial $K_q$ was measured and these
molecules were found to initiate polymerisation, albeit to a lesser degree, than the chromophores with negative ΔG values. Since these initial studies several other groups have investigated the TPP mechanism and investigated the types of molecules that can improve TPP thresholds - a number of reviews are available.\textsuperscript{3,6,8,12,19,22-24} As the molecules described here are of a similar nature to these previously designed and tested species, the mechanism by which they undergo TPP is expected to be identical.

Figure 1 – A Jablonski electron state diagram of a PI showing the mechanism for TPP by way of electron transfer from the photoinduced T\textsubscript{1} state to a monomer species.

5.3. Two-photon polymerisation

A general description of the TPP structuring procedure is outlined in Experimental > General procedure, with a description of the PI properties is shown in Experimental > Photoinitiators
including $\phi_T$, $\delta_{2PA}$ and solubility in the acrylate system employed. For initial tests, glass slides were employed as the substrate. A few drops of the monomer and PI mixture were placed onto a slide and flattened using a small custom built device and this gave a smooth placement of the resin across the slide, roughly 1-2 mm in thickness. In turn, this helped to reduce any optical effects that may occur at the surface.

5.3.1 Photoinitiators 6 – 8

The designed PIs 6 - 8 described in Chapter 2 are shown in Figure 12. Descriptions of the PIs optimum processing windows at varying speeds are given in Table 1 - 3. In order to assess the activity of these PIs, defined structures were created by TPP (lateral dimensions: 150 µm x 150 µm and 50 µm in height). The laser power employed was in the microwatt (µW) range, and variable writing speeds were also used, namely: 50, 100, 150 and 200 µm/s. A 1:1 by weight mixture of commercially available acrylate monomers (SR415:SR351) was used and a PI concentration $6.3 \times 10^{-6}$ mol.L$^{-1}$ was employed throughout.

<table>
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<tr>
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Table 1 - The optimal processing windows for PI 6. Variable writing speeds of 50, 100, 150 and 200 µm/s were used; also, variable power ranges to give a full description of the processing window. An average is taken for the high and low power limits given to one significant figure.
This monomer system has been employed in previous studies and exhibited good results for TPP structuring tests.\textsuperscript{16,25} Scanning electron microscopy (SEM) was used to assess the quality of the fabricated structures, and to categorise the quality of the fabricated structures as seen in Figure 16.

Although optimum processing windows were generally within $50 - 100 \, \mu W$ for high quality structures, the PIs displayed polymerisation over a much wider power ranges up to $350 \, \mu W$, where polymerisation was still observed albeit in very poor quality. It should also be noted that power limits are given as ± \mu W values, due to the inherent uncertainty in power measurements. To aid in assessing the PIs, the averaged high and low powers are given. For compound \textit{6} in Table 1, a number of tests were performed to obtain accurate power ranges for polymerisation. Examples of the structuring tests are shown in Figure 2.

![Figure 2 – A SEM image taken structuring tests of 6 over varying writing speeds and powers. A. The horizontal arrow describes the decreasing power from left to right. B. From top to bottom decreasing writing speeds from 200 to 100 \mu m/s however, the 50 \mu M/s structure isn’t shown. C. A fabricated structure which was ‘knocked over’ during post processing. D. shows that at the powers below the optimum polymerisation threshold no structures are observed, a small amount of polymerisation is seen at a writing speed of 100 \mu m/s.](image)

As can be seen in the average values for the lower power levels, as writing speed increased so did the overall power required for high quality polymerization; this trend was also observed in the upper limits. For \textit{6} a minimum of 30 \mu W was required at a writing speed of 50 \mu m/s, however earlier tests all showed a minimum of 45 \mu W at the same writing speed. The earlier
tests also indicated that increasing the writing speed had minimal effect on the lowest polymerisation limit i.e. for 50, 100 and 150 μm/s it remained at around 45 μW, and an increase in the lowest limit was only observed at 200 μm/s, at which point it increased to 61 μW. For run 4 at 50 μm/s, a narrower power range was observed but as the writing speeds were increased the values matched more closely to the values observed in earlier tests. Interestingly, the upper limits of the optimal power range were more varied between tests but showed the expected trend: i.e. as writing speed increased so does the power needed. Thus, the upper power limits appear to be more affected by writing speed than the corresponding lower power limits, although this could be attributed to the relatively arbitrary nature of assigning structure quality. Consequently, it was concluded for 6 that the average minimum power needed ranged from 41 – 60 μW across all writing speeds, while the upper limit range was 89 – 145 μW.

Figure 3 shows an example of tests performed at a power of 53 μW. Immediately noticeable in A232 (left), are the large polymerised ‘filament’ type structure that seem to originate from the base of the structure. This could be down to over polymerisation of the material continuing after the initial writing was performed, however it is very difficult to quantify its origin or cause.
is uncertain. The structures produced at this power are relatively consistent irrespective of writing speeds, are of good quality, and all of them display reasonably stable, smooth and straight walls (Figure 4).

Figure 4 - C232 (left) and D232 (right) created using TPP with PI 6 at a power of 53 µW ± 1 µW. C232 was produced at a writing speed of 100 µm/s and D232 at 50 µm/s.

<table>
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<td>Run 6</td>
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<td>High</td>
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<td>138±9</td>
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<td>61±7</td>
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<tr>
<td>Run 7</td>
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<td>Average Range</td>
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<td>64</td>
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<td>92</td>
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</table>

Table 2 - The optimal processing windows for PI 7. Variable writing speeds of 50, 100, 150 and 200 µm/s were used; also, variable power ranges to give a full description of the processing window. An average is taken for the high and low power limits given to one significant figure.

The experimental results for PI 7 are described in Table 2. For 7, the minimum energy for polymerisation was found to be 61 µW and this was relatively consistent as writing speeds
increased, and in particular for runs 5 and 6. The upper power limits showed an increase in power as writing speeds increased, and this was consistent with tests conducted with 6. The averaged minimum power required was between 62 – 68 μW across all writing speeds while the average maximum power needed ranged between 121 – 160 μW.

Surprisingly, when compared with the dipolar 6, quadrupolar compound 7 had a higher polymerisation threshold. To eliminate factors such as variability in laser power or variation in the laser system, it was useful to compare the data acquired on the same day for both 6 (runs 1 and 2) and 7 (run 5). It showed a 16 μW increase in the required minimum power was needed to obtain high quality structures for 7 at low writing speeds, while at higher writing speeds the power levels required were similar.

A noticeable difference was seen in the quality of the fabricated structures of 7 relative to those of 6. This could be simply down to the post processing or that the power levels used were closer to the low end of the ‘good quality’ polymerisation thresholds. The structures were generally of good quality, but some imperfections and inconsistencies were evident as seen in both Figure 5 and Figure 6. This was most noticeable as a curvature that was seen in the side

Figure 5 - E117 (left) and F117 (right) created using TPP with PI 7 at a power of 68 μW ± 1 μW. E117 was produced at a writing speed of 200 μm/s and F117 at 150 μm/s.
walls (Figure 5 and Figure 6) and were likely due to post processing conditions affecting the side walls.

![Image of Figure 6 - G117 (left) and H117 (right) created using TPP with PI 7 at a power of 68 µW ± 1 µW. G117 was produced at a writing speed of 100 µm/s and H117 at 50 µm/s.]

Excellent polymerisation thresholds were observed for 8 and powers as low as 27 µW were found to be suitable for creating good quality structures (Table 3). Previous tests with 6 and 7 showed greater variability in the upper polymerisation thresholds than 8; for the latter, these were relatively consistent even with increasing writing speeds.

As with 6, for structures prepared using 8, polymeric filaments can be seen emanating from the fabricated structure but these were much more common and consistent across the writing speeds (Figures 7 and 8). It was postulated that the source of these features was related to the sensitivity of the molecules, which caused polymerisation to continue, albeit in poorly defined, outside of the focal point i.e. after the laser has passed the PI it continued to initiate polymerisation for a short period of time.
<table>
<thead>
<tr>
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<td>Run 9</td>
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<td>34±12</td>
</tr>
<tr>
<td>Average</td>
<td>High</td>
<td>85</td>
<td>111</td>
<td>120</td>
</tr>
<tr>
<td></td>
<td>Low</td>
<td>30</td>
<td>29</td>
<td>29</td>
</tr>
<tr>
<td>Average Range</td>
<td>55</td>
<td>82</td>
<td>91</td>
<td>91</td>
</tr>
</tbody>
</table>

Table 3 - The optimal processing windows for PI 8. Variable writing speeds of 50, 100, 150 and 200 µm/s were used; also, variable power ranges to give a full description of the processing window. An average is taken for the high and low power limits given to one significant figure.

Figure 7 - I55 (left) and J55 (right) created using TPP with PI 8 at a power of 36.7 µW ± 0.7 µW. I55 was produced at a writing speed of 200 µm/s and J55 at 150 µm/s.

As remarked previously, PI 7 showed a higher polymerisation threshold relative to 6. Even though several key properties such a higher δ<sub>2PA</sub> and lower φ<sub>F</sub> was seen for 7 when compared to 6 these parameters appear to be negated during TPP. Overall, the results from our TPP tests
showed that for general performance $8 > 6 > 7$ with minimum power thresholds present at 27 μW, 45 μW and 61 μW, respectively, at a writing speed of 50 μm/s. *Chapter 2* provides an in-depth discussion and set of results, which explain these trends. In particular, the findings from our own work and that of others describe how in multi-branched molecules such as these, the excited states were confined to a single dipolar branch in all species.  

Figure 8 - K55 (left) and L55 (right) created using TPP with PI 8 at a power of 36.7 μW ± 0.7 μW. K55 was produced at a writing speed of 100 μm/s and L55 at 50 μm/s.

This has important implications, mainly relating to how the excited state was affected by the remaining branches in their ground states. The most important consequence of this being the limitation on phenyl-N rotation which occurred as ground state branches compete to disrupt the CT state. This reduced overall fluorescence and was particularly the case in low viscosity solvents such as methanol. However, in the acrylate system this took on an added importance and it was shown how low viscosity environments negatively affect (i.e. increase) the $\phi_F$, such that for 7 ($\phi_F = 0.182$) and 8 ($\phi_F = 0.183$) they become close to those seen in dipolar 6 ($\phi_F = 0.216$). Such viscosity dependent phenomena were also seen when comparing the fluorescence emission intensities, fluorescence lifetimes and radiative, and non-radiative decay constants of 6 - 8 (*Chapter 2, Table 5*).
5.3.2 Photoinitiators 22 and 23

The structures of 22 and 23 are shown in Figure 13 and a general description of their key molecular properties are described in Experimental > Photoinitiators. As with the PIs from Chapter 2 it was of interest to see how branching affected the polymerisation thresholds. Unlike the tests conducted for 6 – 8 a smaller set of tests were performed, and are described in further detail below. Several TPP tests were performed employing laser powers from 260 μW to 20 μW over the four writing speeds used previously, as depicted in Figure 9 - 12.

![Image](image_url)

**Figure 9** – A poor quality structure produced using PI 22 at 165 μW and writing speed of 50 μm/s.

The relatively poor qualities of the fabricated structures across the varying powers were obvious. For PI 22 full tests were performed from 260 μW down to 100 μW. The structures produced in this power range were often of poor quality and became abysmal at the lower limit of this range (Figure 9). Several subsequent runs on 22 show similarly consistent results and again, only poor quality structures were observed throughout. Several tests using 23 yielded a reasonable power range, however the fabricated structures were again of poor quality, albeit relatively improved compared with those seen for 22. With
poor quality structures, such as that seen for 22, were seen across power ranges from 260 \( \mu W \) down to 41 \( \mu W \) (Figure 10). The lower power range used represented a reasonable improvement relative to 22. The structure fabricated in Figure 10 was produced at 41 \( \mu W \) and a writing speed of 50 \( \mu m/s \). Several repeat tests were performed and showed similar power thresholds across the tests, however no improvements in structure quality were evident.

![SEM image of a poor quality structure produced using PI 23 at 41 \( \mu W \) and writing speed of 50 \( \mu m/s \).](image)

The SEM images taken of structures fabricated using 23 are depicted in Figure 11. Power levels ranged from 260 \( \mu W \) for structures on the left of Figure 11a to 225 \( \mu W \) on the right of the figure, with an approximate 10 \( \mu W \) reduction in power used to form each fabricated structure. Several of the fabricated structures toppled over during the post processing, however it was possible to view the filament like side-walls produced (Figure 11b). Overall the structures were of poor quality, possessing over-polymerised walls and clearly incomplete polymerisation had taken place, resulting in holes and imperfections throughout. Earlier experimental data for 22 and 23 suggested they had the potential to be efficient Pls. This is because both possess good \( \delta_{2PA} \) and low \( \phi_F \) in both chloroform, and importantly, the acrylate system.
Two main issues were found in the failure of 22 and 23 to act as efficient PIs. Firstly, the samples of 22 and 23 had been dissolved in the monomer (as with previous runs for 6 - 8), however several weeks passed before the samples were used for structuring tests.

It was observed that the initial mixtures were much lighter in colour than when first prepared, owing to the fact that a visible amount of PI had begun to crystalise out of solution and could be seen floating on the resin surface. To combat this, the solutions were stirred and heated to 40 – 50 °C and this went someway to helping redissolve the materials. This appeared to work to an extent, as the acrylate mixture again became a much darker purple colour. However, visibly undissolved PI was still present. This continued to be a problem for both samples and further attempts to redissolve the material failed, meaning tests were almost certainly conducted without the desired PI concentration.

Furthermore, it was postulated that over time the PI precipitates out of solution and begins to form aggregates. This resulted in difficulties to break up and redissolve the PIs into the acrylate mixture. Similar push-pull type molecules have been studied within the Photonics group, Callaghan Innovation and it was found that aggregation phenomena regularly occurred in compounds akin to 22 and 23. This is due to the presence of large π-systems present, coupled with a high degree of charge separation, which allows π-stacking to occur. This was likely to have a negative impact on the laser beam used for TPP, due to scattering the laser light, which
impacted the laser. Polymerisation could be initiated by aggregates in the monomer resin that sit outside of the desired focal point. A potential indicator of this was the existence of large amounts of polymerised ‘specks’ surrounding our fabricated structures (See Figure 9 and Figure 10) and which were not previously seen for fabrication studies done using 6 – 8.

The second reason 22 and 23 failed to act as efficient PIs was because the one-photon maxima for both PIs are approximately 525 – 550 nm, which suggested that a more optimum laser for fabrication would be a 1054 nm fs laser system, rather than the 800 nm used here. As previously stated in Chapter 3, to better evaluate this, the two-photon absorption spectra would need to be assessed over a wide wavelength range to find the optimum wavelength needed. Although the PIs 22 and 23 have proved to be relatively poor PI for our tests, future studies could benefit from the use of differing laser wavelengths or finding more suitable acrylates to mitigate aggregation of the PIs.

5.4. Experimental

5.4.1 Instrumentation

For imaging of our structures, a sputter coater and SEM setup were used. The sputter coater was a Polaron Equipment Limited SEM Coating Unit E5000. This allowed for the deposition of gold onto the surface structures under an inert argon atmosphere. In this case deposition thicknesses of ~ 56 nm were sufficient. The SEM setup employed was a JCM-6000PLUS NeoScope Benchtop SEM, 60,000 x resolution.

5.4.2 Photoinitiators

A number of PIs have been designed and synthesised and their linear, non-linear photophysical and physical properties have been examined and these are described in Chapters 2 – 4. The PIs were designed for use as radical PIs in the polymerisation of acrylate monomers. A large number of PIs were developed, however the majority of the TPP tests were performed with PIs 6 – 8 (Figure 12). There are several reasons for this, firstly they all exhibited reasonable
solubility in the chosen monomer system (although 8, over time, does begin to precipitate out from the resin). Secondly, these PIs exhibited no linear absorption between 780 – 800 nm. Thirdly, they all possess good $\delta_{2PA}$ values of between 126 – 590 GM. Lastly, the $\phi_F$ of these PIs were relatively low. These factors were considered to be of particular importance to the effectiveness of a PI during radical TPP. For all tests, including with the reference PI, a concentration of $6.3 \times 10^{-6}$ mol.L$^{-1}$ was employed.

Likewise, based on the photophysical data and machining results obtained for 6 - 8, the PIs 22 and 23 (Figure 13) were chosen for TPP studies. Both compounds displayed good $\delta_{2PA}$ values of 390 GM (22) and 507 GM (23). Alongside this, the presence of long alkyl chains ($C_{10}$) were found to assist with overall PI solubility. Finally, both displayed very low $\phi_F$ in both chloroform
of 0.031 (22) and 0.097 (23) and a $\phi_F$ in the acrylate mixture of 0.055 and 0.066 for 22 and 23, respectively.

Figure 13 – Structures of PIs 22 and 23 from Chapter 3 - A novel series of triphenylamine based dipolar and quadrupolar photoinitiators for use in two-photon polymerisation.

5.4.3 Monomer system

To fully assess the effectiveness of the synthesised PI a reference acrylate monomer system was used (Figure 14). Sartomer 415 is an ethoxylated (20) trimethylopropane triacrylate monomer (MW = 1176) which has low toxicity and is water soluble, and which forms flexible and low shrinkage films. The second monomer was Sartomer 351 trimethylolpropane triacrylate (MW = 296) which is a low viscosity, low volatility liquid monomer. No further modifications were made to the acrylate reference system beyond dissolving the desired amount of PI. A 1:1 by weight mixture of the two monomers was used throughout our TPP structuring tests.
5.4.4 Laser system, fabrication stage and macros

A femto-second Ti:Saph laser system (Coherent Legend) was employed for the TPP structuring and operated in the wavelength of 790 – 800 nm as shown in Figure 15.

The laser power was measured using a Coherent PowerMax-USB UV/VIS Quantum Power Sensor with 100 nW noise-equivalent power (NEP). An Altechna ultraFAST Watt Pilot was
employed to attenuate the laser power delivered to the sample. The power increments were limited by the capabilities of the attenuator. Due to the discrete nature of the steps in power, the measured threshold power levels where TPP quality became poor were subjective in nature. Similarly, the ranges of laser power used for a sample were given as +/- values. High neutral-density (ND) filters were also used to further reduce laser power. This was achieved by firstly a 0.5 ND filter and secondly the beam was passed through a 3.0 ND filter. These filters, along with the attenuator, allowed for a finer control of the power. As the attenuator changes the power by a percentage it gave more discrete control. The beam was analysed with a spectrometer to pinpoint its operating wavelength during the tests. A Gaussian beam shape was utilised and a beam profiler was used to ensure consistent a beam shape was used throughout. The beam was focused using a THORLABS Aspheric Condenser lens with a 0.79 numerical aperture (NA). A pulse picker was used to achieve a repetition rate of 500 Hz. A JPSA IX-100-C stage was used to position the sample with precise movements in the X-Y-Z axes, this stage has a minimum step size of 0.1 μm.

To evaluate the PI efficiency a structure macro was produced, and this was used to guide the fabrication stage to produce the desired structures. An example of the structure can be seen in Figure 16, image D. This structure was 150 μm x 150 μm in the X-Y direction and 50 μm in the Z direction. Each structure was made up of ten 5 μm layers creating a ‘four-square’ structure, which allowed the laser to move in small step sizes and polymerise the exposed material to produce a consistent structure. The macro was written to operate at four different writing speeds of 50, 100, 150 and 200 μm/s, and this was achieved by increasing the linear spacing between laser pulses.

5.4.5 General procedure

To a clean glass slide was placed a few small drops of pre-prepared resin/PI mixture, followed by smoothing the resin surface with the flattening device. The slide was placed upon the machining stage and fixed into place. The objective camera of the stage was used to focus onto the glass surface, in order to give a rough placement of where polymerisation will occur. Low
power trials were performed and the z-axis position was modified to allow for accurate focus onto the glass slide surface. Once the z-axis position was found, full tests were performed using the outlined macro above. Tests were performed at writing speeds of 50, 100, 150 and 200 µm/s and the supplied power was modified using the attenuator until structures were no longer observed using the objective camera. Once complete, the slide was removed and placed in a glass petri dish where ethanol was carefully added to dissolve any remaining resin. The slide was dried and sputter coated with gold. Finally, images were obtained using SEM imaging at x200 magnification. This process was then repeated for subsequent tests.

5.4.6 Qualitative analysis of structures

Images of polymerised structures were obtained by way of SEM imaging and given a general structural quality label. The initial assessments of these structures were predominantly subjective in nature and were deemed suitable for this work. To categorise the quality of structures produced, we opted to use a colour coded system as shown in Figure 16. Optimal structures have thin, stable walls like those shown in green (D). Over polymerised structures, due to too high lasing powers, resulted in misshaped and poor quality structures as exemplified in orange (B) and yellow (C). Under-polymerised or extremely poor structures were categorised in red (A), whilst powers which produced no structure were denoted in black (not shown).
5.4.7 Polymerisation thresholds

Full descriptions of the TPP tests are displayed in Graph 1, Graph 2 and Graph 3. These were performed over a large power range and tests to give an accurate assessment of PI activity.
Graph 1 – The full qualitative analysis of PI 6 over a wide power range, writing speeds and test runs.

Graph 2 - The full qualitative analysis of PI 7 over a wide power range, writing speeds and test runs.
Graph 3 - The full qualitative analysis of PI 8 over a wide power range, writing speeds and test runs.

5.5. Conclusion

Overall, the described PIs 6 – 8 exhibited excellent polymerisation thresholds with powers as low as 27 μW for 8 over a broad range of writing speeds. All three compounds display similar average powers at each writing speed, being of the order of 48 – 91 μW across the series. While the optimum power ranges for each PI have been described, they all exhibit the ability to initiate polymerisation over a much broader power range (as much as 350 μW). However, structures produced outside the optimum range are generally of poor quality. The overall yields and ease of synthesis/isolation followed the order: 6 < 7 < 8. This is an important consideration for PI design, as molecules may be excellent PIs but difficult and lengthy synthesis and purification procedures may reduce their suitability for larger scale use. Thus, a balance must be found between ease of synthesis and overall TPP thresholds. In this instance, the use of 6
over 8 would be favourable as polymerisation thresholds are within one order of magnitude of one another.

In contrast to PIs 6 – 8, for 22 and 23 problems of processability and PI aggregation were detrimentally affecting the quality and reproducibility of TPP using these PIs. While they were shown to initiate polymerisation in the μW region, with 23 showing the broadest power range (260 – 41 μW), consistently poor quality structures were seen across the power ranges. Although the PIs 22 and 23 performed poorly in tests, future studies could benefit from using differing laser wavelengths or finding more suitable acrylates to mitigate aggregation of the PIs.

5.6. References

(8) Maria, F.; Maria, V.; Boris, N. C. Journal of Optics 2010, 12, 124001.


6.1. Summary and Conclusion

In this thesis, photoinitiators excited by two-photon absorption for polymerisation of acrylates were synthesised and studied. Such photoinitiators can be easily blended into acrylate resins at low concentrations to allow for efficient polymerisation of micro/nanoscale 3D structures using an 800 nm femto-second laser system. Early studies made use of commercially available photoinitiators for fabrication although their desired properties are often mediocre for two-photon polymerisation. As such, efforts have been made to improve on the key molecular properties to maximise their potential for use in two-photon polymerisation. An in-depth study was performed to assess the key properties of photoinitiators to maximise their potential; namely 2PA, fluorescence yields and solubility.

The introduction detailed the previous work conducted in the varying fields related to two-photon polymerisation. These include designing and synthesising two-photon absorbing molecules, the two-photon polymerisation technique, photoinitiator design and key molecular properties and finally the types of materials that are compatible with this technique. So far, the use of two-photon polymerisation has been limited to proof of principle demonstrations of its potential. This is due to a number of factors including, suitable photoinitiators, slow writing speeds and the initial cost of setup all being factors.

The work was aimed at further building on this existing knowledge to create highly active PIs for TPP, which fully address the issues currently holding back the commercial and industrial development of TPP. In the introduction four key aims were outlined:

2. Incorporation of synthetic features to maximise photoinitiator solubility
3. Assess how improvements in photoinitiator properties translate to efficient two-photon polymerisation
4. Create feature sizes of <200 nm.

In Chapter 2 a series of multi-branched triphenylamine ethyl esters were synthesised and their photophysical properties were studied. The synthesis made use of the Vilsmeier-Haack formylation to create synthetically useful intermediates, followed by Horner–Wadsworth–Emmons reactions to couple these yielding one, two and three branch
products. From the experiments conducted it was clear that increasing the level of branching led to a desired decrease in fluorescence quantum yield and proportional increase in two-photon absorption, with 8 exhibiting a measured value of 590 GM. Furthermore, the use of ethyl ester acceptor moieties ensured good acrylate monomer solubility. However, upon excitation the excited states were confined to a single dipolar branch in all species, which has important consequences for the overall properties. For our measurements in common solvents key molecular properties were similar to those previously reported for similar species in the literature. However, measurements performed in the acrylate system used for TPP assessments show pronounced effects due to the dipolar nature of the PIs. It has been shown that viscosity plays an important role in $\Phi_F$, fluorescence lifetimes and PI polymerisation thresholds. In viscous acrylates the $\Phi_F$ of 6, 7 and 8 were 0.216, 0.182 and 0.183 and fluorescence lifetimes closely resembled those of the dipolar 6. These results have significant implications for PI design, where desired properties such as large $\delta_{2PA}$, low $\Phi_F$, high $\Phi_T$ and monomer solubility are considered key.

Due to the nature of the excited state, synthesising large multibranched molecules looked a valid strategy for improving the desired properties, although there was always an awareness that this may not necessarily translate into high efficiency PIs, as demonstrated by the lower polymerisation threshold of 6 relative to 7. This would imply that the synthesis of simple dipolar species which are designed to maximise the desired properties are likely to give similar polymerisation thresholds to their more complex quadrupolar and octupolar analogues and other more difficult to synthesise PIs.

In Chapter 3 dipolar and quadrupolar derivatives were synthesised with the aim of maximising two-photon absorption and to assess its effect on polymerisation thresholds. The use of triphenylamine as a strong electron donor and tricyanofuran derivatives as electron acceptors were utilised, and were coupled using Knoevenagel condensation reactions. The properties of these compounds were assessed by UV/Vis absorption spectroscopy, fluorescence spectroscopy and z-scan to assess their suitability as photoinitiators. They possessed good $\delta_{2PA}$ values of 333 – 507 GM when measured at 780 nm in chloroform using the z-scan technique, although several compounds were unable to be evaluated due to their linear absorption sitting too far from the $\lambda/2$ of the incident laser. Furthermore, low $\Phi_F$ values of < 0.1 were seen across the series in chloroform and in acrylates values were < 0.15. As expected, the solubility of the compounds was shown to
improve with the introduction of large alkyl chains to the side groups of the TCF acceptor and these, in turn, had little overall effect on photophysical properties. The two-photon polymerisation properties of 22 and 23 were assessed and polymerisation was initiated in the µW region. However issues persisted, with aggregation of the photoinitiators in the acrylate resin being a significant issue leading to a reduction in dissolved photoinitiator. This culminated in poor quality polymerisation for both species. Further studies are required at higher wavelengths and differing monomer systems to avoid these adverse effects.

In Chapter 4 a series of single branched α,β-unsaturated ketones were produced, utilising aldol condensation chemistry. Moderate $\delta_{2PA}$ values were measured for these species in the range of 78 – 371 GM as measured at 780 nm using the z-scan technique. The majority of the synthesised species exhibited $\phi_F$ of below 0.1, with 31 and 33 displaying measured values of less than 0.01. However for 30, a much larger value was measured, namely 0.3, meaning it would likely be unsuitable for efficient two-photon polymerisation. The one-photon absorption data showed strong linear absorptions to occur at around 380 – 420 nm for these species meaning the use of an 800 nm laser wavelength for fabrication would likely be close to optimal.

Chapter 5 detailed the two-photon polymerisation tests conducted on selected photoinitiators 6, 7, 8, 22 and 23 in acrylate monomers. The chapter described the fabrication setup, laser system and procedure used to assess the polymerisation threshold of the selected photoinitiators. Overall, the described PIs 6 – 8 exhibit excellent polymerisation thresholds with powers as low as 27 μW for 8 over a broad range of writing speeds. All three display similar average powers at each writing speed, and these are in the range of 48 – 91 μW across the series. From a synthesis point of overall yields and synthetic difficulty follows: 6 < 7 < 8. This was an important consideration for PI designs, as molecules may be excellent PIs but difficult and lengthy synthetic procedures reduce their suitability for larger scale use. A balance must be found between ease of synthesis and overall TPP thresholds. In this instance, the use of 6 over 8 would likely be favourable as polymerisation thresholds are within a magnitude of order of one another.

In contrast with PIs 6, 7, 8, the molecules 22 and 23 exhibited issues of processability and PI aggregation which detrimentally affected the quality and reproducibility of these PIs. They were shown to initiate polymerisation in the µW region with 23 showing the broadest power range (260 – 41 μW), however across the power range consistently poor quality
structures were seen. Although the PIs 22 and 23 have proved to be relatively poor PIs for our tests, future studies could benefit from differing laser wavelengths or finding more suitable acrylates to mitigate aggregation of the PIs.

6.2. Future Work

A number of investigations could be conducted to build on the work presented in this thesis. Firstly, assessing the limits of the feature sizes possible using the photoinitiators from Chapter 2 to assess their ability in creating features sizes below 200 nm. The use of a differing monomer system could assist in achieving this and might provide a solution to photoinitiator aggregation. Secondly, assessing the two-photon absorption values of all species over a broader wavelength with a tuneable laser system would be a great benefit. This would then assist in selecting the most suitable polymerisation wavelength for each photoinitiator to maximise their effectiveness. For example, studying the polymerisation thresholds of the Chapter 3 photoinitiators with a longer wavelength c. 1064 nm laser. Two-photon polymerisation measurements should also to be conducted on the photoinitiators presented in Chapter 4, although these should be conducted with the current fabrication setup using an 800 nm laser for fabrication.
Appendix

7.1. Structures of photoinitiators

Chapter 2:

Figure 1 – Structures of photoinitiators from Chapter 2 and Chapter 3.
Chapter 3 (continued):

![Chemical structures](image)

Chapter 4:

![Chemical structures](image)

Figure 2 - Structures of photoinitiators from Chapter 3 and Chapter 4.
7.1.1 $^1$H NMR Spectra - Chapter 2:

Figure 3 – $^1$H NMR and expansion of aromatic region of photoinitiator 6, performed in chloroform-d.
Figure 4 - $^1$H NMR and expansion of aromatic region of photoinitiator 7, performed in chloroform-d.
Figure 5 - $^1$H NMR and expansion of aromatic region of photoinitiator 8, performed in chloroform-d.
Figure 6 - $^1$H NMR and expansion of aromatic region of photoinitiator 11, performed in chloroform-d.
Figure 7 - $^1$H NMR and expansion of aromatic region of photoinitiator 12b, performed in chloroform-d.
Figure 8 - $^1$H NMR and expansion of aromatic region of photoinitiator 16, performed in chloroform-d.
Figure 9 - $^1$H NMR and expansion of aromatic region of photoinitiator 17, performed in chloroform-d.
Figure 10 - $^1$H NMR and expansion of aromatic region of photoinitiator 22, performed in chloroform-d.
Figure 11 - $^1$H NMR and expansion of aromatic region of photoinitiator 23, performed in chloroform-d.
Figure 12 - $^1$H NMR and expansion of aromatic region of photoinitiator 24, performed in dimethyl sulfoxide-d6.
Figure 13 - $^1$H NMR and expansion of aromatic region of photoinitiator 25, performed in chloroform-d.
7.1.3 $^1$H NMR Spectra - Chapter 4

Figure 14 - $^1$H NMR and expansion of aromatic region of photoinitiator 29, performed in chloroform-d.
Figure 15 - $^1$H NMR and expansion of aromatic region of photoinitiator 30, performed in chloroform-d.
Figure 16 - $^1$H NMR and expansion of aromatic region of photoinitiator 31, performed in chloroform-d.
Figure 17 - $^1$H NMR and expansion of aromatic region of photoinitiator 32, performed in chloroform-d.
Figure 18 - $^1$H NMR and expansion of aromatic region of photoinitiator 33, performed in chloroform-d.
Figure 19 - $^1$H NMR and expansion of aromatic region of photoinitiator 35, performed in chloroform-d.