Photoinitiators for two-photon polymerisation: Effect of branching and viscosity on

polymerisation thresholds

Electronic supplementary information

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 POCl₃ (22.68 mmol, 2.11 ml) dropwise over 15 minutes. 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-formyltriphenylamine (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).¹ 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, 39.9 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.¹ 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 C₂₀H₁₅NO₂ 301.1103, m/z [M⁺H] 302.1185 (100%), [M⁺Na] 324.1005 (40%); Δ = 1.3 ppm.

Synthesis of 4,4',4"-trisformyltriphenylamine (3). $POCl_3$ (94.98 ml, 1.019 mol, 156.25 g) was added dropwise over 1 h to a stirred solution of triphenylamine (10 g, 40.76 mmol) in

DMF (72.2 ml, 68.44 g, 937.55 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 4M 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 redissolved in DMF (23 eq, 72.2 ml, 68.44 g, 937.55 mmol) and cooled to 0°C under Argon, to the stirred solution was added POCl₃ (94.98 ml, 1.019 mol, 156.25 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 4M NaOH. After extraction with CH₂Cl₂ (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.² Yellow/green solid; R_f 0.25 (DCM); mp 231-233°C (Lit. 230–232 °C).¹ 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, 312.12 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).³ 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, 227.3 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 affording ethyl 4-((diethoxyphosphoryl)methyl)benzoate (5) 68 g, 99% yield. Tan oil, R_f 0.5 (petroleum spirit 60-80°C).^{4, 5} 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 $C_{14}H_{21}O_5P$ 300.1127, m/z [M⁺Na] 323.1019 (100%); Δ = -1.5 ppm.



Figure S1 - Preparation of triphenylamine aldehydes (1 – 3) using Vilsmeir- Haack formylation conditions.



Figure S2 - Preparation of the phosphonate intermediate Ethyl 4-((diethoxyphosphoryl)methyl)benzoate (5).

Photoinitiator	Solvent	λ^{1}_{max} a	٤ ^b	λ^2_{max} c	٤b
6	Toluene	-	-	387	2.78
	Diisopropyl Ether	283	5.93	383	3.43
	Dioxane	298	2.41	385	2.64
	CHCl ₃	288	3.72	388	2.76
	DMF	-	-	387	3.23
	MeOH	296	2.85	384	3.49
7	Toluene	-	-	410	4.41
	Diisopropyl Ether	285	6.33	404	4.94
	Dioxane	297	3.21	407	4.83
	CHCl ₃	286	7.43	411	6.14
	DMF	-	-	411	5.19
	MeOH	295	3.79	406	5.46
8	Toluene	-	-	413	10.69
	Diisopropyl Ether	286	7.66	408	8.85
	Dioxane	305	4.73	412	7.97
	CHCl ₃	301	5.98	415	8.74
	DMF	-	-	416	8.50
	MeOH	304	5.86	410	9.48

Table S1 - UV/Vis absorption properties of compounds 6 – 8; concentration of 1.0×10^{-5} mol L a. λ^1 wavelength maxima (nm) of TPA peak, some values omitted due to solvent cut-off overlap. b. ε = molar extinction coefficient x 10⁴; (, M⁻¹CM⁻¹); A = ε clc: A = absorbance, I = path length, c = concentration. c. λ^2 wavelength maxima (nm) of peak 2.



Figure S3 – Normalised UV/Vis spectrum of PI 6 in various solvents.



Figure S4 – Normalised UV/Vis spectrum of PI 7 in various solvents.



Figure S5 – Normalised UV/Vis spectrum of PI 8 in various solvents.

Fluorescence

	Solvent	Absorbance	Emission	Stoke shift	Φ_{F}^{c}
		Max ^a	Max ^b	(nm)	
6	Toluene	393	455	62	
	Dioxane	386	465	79	
	CHCl₃	393	487	94	
	DMF	387	526	139	
	MeCN	385	525	140	
	MeOH	384	535	140	19.8
7	Toluene	420	461	41	
	Dioxane	409	469	60	
	CHCl ₃	422	494	72	
	DMF	386	525	139	
	MeCN	404	543	139	
	MeOH	404	534	130	2.1
8	Toluene	426	468	42	
	Dioxane	423	475	52	
	CHCl₃	425	499	74	
	DMF	424	549	125	
	MeCN	410	550	140	
	MeOH	420	547	127	1.9

Table S2 - Photoluminescence maxima and stokes shifts in various solvents, conc = 2×10^{-6} mol/L. a. λ = wavelength maxima (nm), 532 nm excitation. B. λ maximum emission, 385 nm excitation. c. Fluorescence quantum yield with QBS as an internal standard; concentration of 2×10^{-6} MolL in MeOH, 365 nm excitation.



Figure S6 - The measured fluorescence emission spectra of **6** as measured by 385 nm excitation between 420 - 750 nm. The measurements were performed in a variety of solvents with increasing polarity defined by E_{T} (30) values.



Figure S7 - The measured fluorescence emission spectra of **7** as measured by 385 nm excitation between 420 - 750 nm. The measurements were performed in a variety of solvents with increasing polarity defined by $E_{T}(30)$ values.



Figure S8 - The measured fluorescence emission spectra of **8** as measured by 385 nm excitation between 420 - 750 nm. The measurements were performed in a variety of solvents with increasing polarity defined by E_{T} (30) values.

Photoinitiator	Intensity maxima (a.u)	λ Max (nm)	φ _F %
6 - MeOH	297.08	536	19.8
6 - EG	160.82	548	14.5
6 - DEG	306.23	532	20.1
6 - Acrylates	805.76	487	21.6
7 - MeOH	38.97	542	2.1
7 - EG	37.61	550	2.0
7 – DEG	114.18	533	8.8
7 – Acrylates	760.18	495	18.2
8 – MeOH	34.59	546	1.9
8 – EG	36.99	536	2.7
8 - DEG	94.58	540	9.2
8 - Acrylates	701.56	506	18.3

Table S3 - Measured values of fluorescence intensity, λ_{max} and ϕ_F % of PIs 6 – 8 in various viscous solvents. QBS was used as an internal standard; conc = 2 x 10⁻⁶ molL. 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).

An open-aperture z-scan setup was used to study the δ_{2PA} of the synthesised chromophores. A schematic of the setup used is shown in Figure 9.



Figure 9 – Schematic of the z-scan set-up used, (Ch = chopper, L = lens, D = photodiode, M = mirror, ND = neutral density filter and BS = beam splitter). Image reproduced with permission from 6 .

The change in transmittance is measured while the sample is 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 effect can have a profound effect on influence the measurements. As such, a modified zscan setup was used and an optical chopper was incorporated to minimise thermal effects.⁷⁻ ⁹ The chopper frequency was set at 20 Hz and has 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 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. 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 are consistent with the values reported in the literature.¹⁰ All measurements were performed in CHCl₃ with concentrations of 2.0 x 10⁻² mol L.

The open aperture scan can be used to directly obtain the nonlinear absorption coefficient (β). When the third order nonlinear losses are small ($\beta IL_{eff} \ll 1$), the normalised change in transmittance due to two-photon absorption can be approximated by ¹¹;

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

Equation 1

With $q_0 = \beta I_0 L_{eff}$ and $x = z/Z_0$, where Z_0 is the Rayleigh length, I_0 is the peak intensity. $L_{eff} = (1 - e^{-\alpha}L)/\alpha$ 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 twophoton cross section δ_{2PA} can be obtained from β using the following relation;

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

Equation 2

Where N_a is Avogadro's number, C the concentration, \hbar the reduced Planck constant and ω the angular frequency. δ_{2PA} are denoted by GM values, 1 GM is equal to 1 * 10⁻⁵⁰cm⁴s photons⁻¹ molecule⁻¹. Due to the nature of the z-scan measurement, the stated values of δ_{2PA} have a standard accuracy of ± 10%.



Figure S10 - 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 δ_{2PA} of the sample.



Figure S11 - z-scan measurement of PI **7**. The measured and averaged transmission as the sample moves through the z-axis. The change in measured transmittance gives details on the δ_{2PA} of the sample.



Figure S12 - z-scan measurement of PI **8**. The measured and averaged transmission as the sample moves through the z-axis. The change in measured transmittance gives details on the δ_{2PA} of the sample.

Two-photon polymerisation

Monomer system

To fully assess the effectiveness of the synthesised photoinitiators a reference acrylate monomer system was used.^{12, 13} Sartomer 415 (SR415) is an ethoxylated trimethylopropane triacrylate monomer (MW = 1176) which has low toxicity and is water soluble, and which

forms flexible and low shrinkage films.¹⁴ The second monomer was Sartomer 351 (SR351) trimethylolpropane triacrylate (TMPTA) (MW = 296) which is a low viscosity, low volatility liquid monomer.¹⁵ No further modifications were made to the acrylate reference system beyond dissolving the desired amount of PI. An employed 50:50 by weight mixture of the two monomers was used throughout our TPP structuring tests.



Figure S13 – The qualitative standards we adopted for our assignments of polymerisation thresholds. (a) No desired structure is red, (b) Very poor quality is orange, (c) Poor quality is yellow and (d) Good quality is green.



Figure S14 – Qualitative analysis of PI 6. Multiple tests were performed to determine accurate polymerisation thresholds.

Definition of "6" optimal processing windows					
		50um/s	100um/s	150um/s	200um/s
21 Oct	High	77±8	139±9	155±7	170±6
	Low	45±8	45±8	61±7	61±7
21 Oct	High	122±6	139±9	139±9	139±9
	Low	45±8	45±8	45±8	61±7
22 Oct	High	93±7	123±6	139±9	139±9
	Low	45±8	45±8	45±8	61±7
2 Dec	High	65±8	117±8	117±8	133±7
	Low	30±9	58±9	58±9	58±9
Average	High	89	130	138	145
	Low	41	48	52	60
Average Range		48	82	86	85

Table S4 - The optimal processing windows for PI **6**. Variable writing speeds of 50, 100, 150 and 200 μ m/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 S15 - Qualitative analysis of PI 7. Multiple tests were performed to determine accurate ideal polymerisation thresholds.

Definition of "7" optimal processing windows					
		50um/s	100um/s	150um/s	200um/s
21 Oct	High	122±6	122±6	155±7	170±6
	Low	61±7	61±7	61±7	61±7
23 Oct	High	122±6	138±9	155+7	170±6
	Low	61±7	61±7	61±7	61±7
12 Jan	High	120±3	139±1	139±9	139±9
	Low	64±2	70±3	76±2	81±2
Average	High	121	133	150	160
	Low	62	64	66	68
Average Range		59	69	84	92

Table S5 - The optimal processing windows for PI 7. Variable writing speeds of 50, 100, 150 and 200 μ m/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 S16 - Qualitative analysis of PI 8. Multiple tests were performed to determine accurate ideal polymerisation thresholds.

Definition of "8" optimal processing windows					
		50um/s	100um/s	150um/s	200um/s
22 Oct	High	76±8	108±8	108±8	108±8
	Low	27±8	27±8	27±8	27±8
23 Oct	High	76±8	92±7	92±7	92±7
	Low	27±8	27±8	27±8	27±8
18 Jan	High	104±16	132±12	159±14	159±14
	Low	36±4	34±12	34±12	34±12
Average	High	85	111	120	120
	Low	30	29	29	29
Average Range		55	82	91	91

Table S6 - The optimal processing windows for PI **8**. Variable writing speeds of 50, 100, 150 and 200 μ m/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.

Two-photon polymerisation setup



Figure S17 - A schematic diagram for our TPP setup located at the Photon Factory, University of Auckland.

NMR spectra



Figure 18 – 1H NMR spectrum of 6 with expansion of the aromatic region



Figure 19 - 1H NMR spectrum of 7 with expansion of the aromatic region



Figure 20 - 1H NMR spectrum of 8 with expansion of the aromatic region

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