Supporting Information

Diphenyl Sulfone-based Symmetrical A– π –D– π –A Dyes as Efficient Initiators for One-photon and Two-photon Initiated Polymerization

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Index

Part I. Instruments and experimental conditions (Page 2-3)

Part II. Synthesis and characterizations of the intermediate and target products (Page 4-12)

Part III. Figures and Tables involved in the manuscript (Page 13-16)

Part I. Instruments and experimental conditions

UV-vis absorption and fluorescence experiments

The UV-vis spectra were recorded using a UV-5200 (UNICO) UV-vis spectrophotometer. The fluorescence properties of the DSOs were studied using a F-4500 (Hitachi High-Technologies Corporation) fluorescence spectrophotometer. Both the two experiments were carried out in a 2×10^{-5} M solution. The fluorescence quantum yields of DSOs were determined using quinine sulfate dehydrate (0.1 M sulfuric acid aqueous solution) as a reference by eqn (1):

$$\Phi = \frac{A_{ref} n^2 F}{A n_{ref}^2 F_{ref}} \Phi_{ref}$$
(1)

where Φ is the quantum yield, *n* is the refractive index of solvent, *A* is the absorbance of solution at the exciting wavelength, and *F* is the integrated area of the emission spectrum.^{1, 2}

The photo-stability of DSOs and steady-state photolysis of DSOs/ION and DSOs/SON systems were carried out under a 405 nm LEDs light source (\sim 400 mW cm⁻²). The interaction between DSOs and onium salts (1:10 in M/M) was monitored by UV-vis spectrophotometer and fluorescence spectrophotometer.

Two-photon excited fluorescence experiment

Two-photon excited fluorescence (TPEF) spectra were recorded on an SD2000 spectrometer with a femtosecond laser (Tsunami, Spectra-Physics). This laser provided pulses of 100 fs of duration at a repetition rate of 80 MHz and was tunable in the wavelength range of 720–880 nm. The laser beam was focused into a quartz cell of 1 cm path length by using a 5 cm focal-length lens. The excitation intensity was 8.2 GW/cm², and the laser spot diameter is 2 mm. To calculate the two-photon absorption (TPA) cross-sections (σ), Rhodamine B in methanol solution (1.0×10^{-6} M) was utilized as reference. For the DSOs, a THF solution (1.0×10^{-6} M) was prepared for detection. All the samples and standard were tested under the same experimental conditions. The TPA cross-sections were calculated by the eqn (2) and the TPEF cross section of Rhodamine B were obtained from reference.³

$$\sigma = \frac{\Phi_{ref} c_{ref} n_{ref} F}{\Phi cn F_{ref}} \sigma_{ref}$$
⁽²⁾

where Φ is the fluorescence quantum yield of the sample as stated in eqn (1), *c* and *n* are the concentration and refractive index of the samples and reference, and *F* is the integral of the TPEF spectrum.

One-photon initiated polymerization experiments

One-photon initiated polymerization experiments were carried out with a 405 nm LED light source (~200 mW cm⁻²). All samples were placed in a plastic mold circle (4.6 mm × 1 mm) and clamped between two microscope slides (75 mm × 25 mm × 1 mm). The sandwich structure was kept together using paper clips placed on the sides. So-prepared samples were irradiated at different time intervals by manually controlling the curing light. N-methylpyrrolidone and epichlorohydrin (100 μ L/1g) was added to the FRP and CP experiments samples to increase the compatibility of initiators and resins. The evolution of double bond content of TPGDA and the epoxy group content of E51 were obtained immediately after each exposure interval on a Nicolet 5700 instrument (Thermo Electron Corporation, Waltham, MA). The double bond conversion was calculated from the decay of the absorption band located at 6167 cm⁻¹ as described by Stansbury and Dickens.⁴ The double bond conversion was calculated by following eqn (3):

Double Bond Conversion% =
$$\left[1 - \frac{S_t}{S_0}\right] \times 100\%$$
 (3)

where S_0 and S_t stand for the peak area of the double bond at initial time and time t.

For cationic polymerization of E51, the peak at 6070 cm⁻¹ (epoxy group stretching vibrations, first overtone) was used to monitor the disappearance of epoxy group in this study. The peak at 5980 cm⁻¹ (aromatic C-H stretching vibrations) was choose as reference peak.⁵ The epoxy conversion was also calculated by using eqn (4):

Epoxy Conversion% =
$$\left[1 - \frac{\left(S_t/R_t\right)}{\left(S_0/R_0\right)}\right] \times 100\%$$
 (4)

where S_0 and S_t stand for the peak area of the epoxy group at initial time and time t, R_0 and R_t stand for the peak area of aromatic C-H bond in E51 at initial time and time t.

Two-photon polymerization experiment

The two-photon stereolithography process utilized a 780 nm femtosecond Ti:Sapphire laser system (Tsunami, Spectra-Physics) with a pulse width of 80 fs and a repetition rate of 80 MHz. The laser beam was fixed and tightly focused across a glass cover slip into the liquid photoresist with an oil-immersion objective lens (100 *, NA=1.45). The photo-curable resin was moved through the focus spot by a 3D piezostage (P-563.3CL, Physik Instrumente). For patterning the polymeric microstructures, P-DSO and T-DSO were both used as TPIP initiators (0.1wt%) and TPIP sensitizers for ION (0.1%/1%, w/w). 4-Acryloylmorpholine (50wt%) was added to the oligomer to adjust viscosity and a little of 1,2-dichloroethane was used to increase the compatibility. The fabricated microstructures were developed by ethanol and their scanning electron microscope (SEM) images were carried out on a S-4300 (Hitachi) field-emission scanning electron microscope.

Redox potentials

The oxidation potentials (E_{ox} vs Ag/Ag⁺) of DSOs were measured in acetonitrile/dichloromethane (50%/50%, V/V) by cyclic voltammetry (CHI660E electrochemical workstation) using tetrabutylammonium hexafluorophosphate (0.1 M) as supporting electrolyte. A glass-carbon electrode was used as the working electrode, a platinum wire as the counter electrode and Ag/Ag⁺ as the reference electrode.⁶ The free energy change ΔG for the photoinduced electron transfer between DSOs and ION and SON was calculated from the classical eqn $(\Sigma)^{\frac{1}{2}}$ E_{abc} E_{abc} E_{abc} E_{abc} E_{abc}

$$\Delta G = E_{ox} - E_{red} - E_S + C \tag{5}$$

where E_{ox} , E_{red} , E_S , and C are the oxidation potential of dyes, the reduction potential of ION and SON, the excited singlet state energy of dyes, and the electrostatic interaction energy for the initially formed ion pair (this latter parameter is considered as negligible in polar solvents), respectively.

Electron spin resonance spin trapping (ESR-ST) experiment

ESR-ST experiments were carried out using a Bruker ELEXSYS E500 electronic paramagnetic resonance (EPR) spectrometer. The radicals were generated upon a 405 nm LED exposure at room temperature. In ESR-ST experiments, the radicals were trapped by N-tert-butyl- α -phenylnitrone (PBN) in tert-butylbenzene according to the procedure described in refer.⁸ The ESR spectra simulations were carried out using the Bruker epr. software.

Computational procedure

The molecular structures in the ground state were optimized based on density function theory (DFT) at the Becke 3-Lee-Yang-Parr (B3LYP)/Genecp (6-31G** basis set) level of theory. The frontier molecular orbital properties were analysed and visualized using the Gauss View 5.0 software.

Notes and references

1. A. T. R. Williams, S. A. Winfield and J. N. Miller, The Analyst, 1983, 108, 1067-1071.

- 2. Y. Povrozin and E. Terpetschnig, 2011, 8.
- 3. N. S. Makarov, M. Drobizhev and A. Rebane, Optics Express, 2008, 16, 4029-4047.
- 4. J. W. Stansbury and S. H. Dickens, Dental Materials, 2001, 17, 71-79.
- 5. G. Kortaberria, P. Arruti and I. Mondragon, Macromolecular Symposia, 2003, 198, 389-398.
- 6. G. R. R, K. C. A and L. G. C, Inorganic Chemistry, 1980, 19, 2.
- 7. D. Rehm and A. Weller, Israel Journal of Chemistry, 1970, 8, 259-271.
- A. Criqui, J. Lalevée, X. Allonas and J.-P. Fouassier, *Macromolecular Chemistry and Physics*, 2008, 209, 2223-2231.



Reagents and conditions: (a) AICl₃, 1,2-dichloroethane, reflux; (b) Pd(PPh₃)₂Cl₂, Cul, PPh₃, 2-methyl-3-butyn-2-ol, DMF, Et₃N, 85°C, N₂ atmosphere; then KOH, isopropanol; (d) Pd(PPh₃)₂Cl₂, Cul, PPh₃, DPS-Br, DMF, Et₃N, 85°C, N₂ atmosphere.

Part I. Synthesis and characterizations of the intermediate and target products

Scheme S1 Synthetic routes to the DSOs.

Synthesis of 4-bromo-diphenylsulfone (DPS-Br)

In a three-necked round-bottomed flask (250 mL) equipped with a condenser and a mechanical stirrer, benzenesulfonyl chloride (10.0 mmol) was slowly added to a mixtrue of bromobenzene (12.0 mmol) and aluminum chloride (15.0 mmol) in 1,2-dichloroethane (50 mL) in room temperature. The reaction mixture was heated under reflux and the progress of the reaction was followed by TLC. After completion of the reaction, the reaction mixture was cooled to room temperature and carefully poured into large amount of ice water. The mixture was filtered off and the filtrate was extracted with CH_2Cl_2 (3×20 mL) and the organic phase was washed with 10% NaHCO₃ solution (2×20 mL) and saturated NaCl solution (20 mL). The organic layers were dried over anhydrous Na₂SO₄, concentrated in vacuum, and the residue was recrystallized from ethanol/n-hexane to give 4-bromo-diphenylsulfone as a white crystalline solid, yield 82%. ¹H NMR (400 MHz, CDCl₃): δ (ppm) 7.94-7.92 (d, J=7.2 Hz, 2H), 7.81-7.79 (d, J=7.2 Hz, 2H), 7.65-7.63 (d, J=7.6 Hz, 2H), 7.60-7.57(t, J=7.6 Hz, 6.8 Hz, 1H), 7.53-7.50(t, 7.2 Hz, 2H). ¹³C NMR (CDCl₃) δ (ppm): 127.66, 128.46, 129.20, 129.43, 132.61, 133.46, 140.70, 141.17. IR (KBr) (cm⁻¹): 3084, 3062, 1572, 1469, 1443, 1387, 1321, 1308, 1157, 1105, 1069, 1008, 745, 714, 688.



Fig. S1 ¹H NMR and ¹³C NMR of the DPS-Br.

General procedure for synthesis of bis(ethynyl) aromatic amine derivatives

Typically, Pd(PPh₃)₂Cl₂ (0.4 mmol), CuI (4.0 mmol), PPh₃ (4.0 mmol) and dibromine substituted aromatic amine derivatives (40.0 mmol) were dissolved in a solution of DMF (100 mL) and triethylamine (50 mL). The mixture was nitrogen bubbled for 30 min and then slow heated to 60 °C and remained for 1 h then heated to 85 °C. 2-Methyl-3-butyn-2-ol (144 mmol) was added to the reaction mixture and heated at 85 °C for 6 h under nitrogen atmosphere. TLC was used for monitoring the reaction. The result mixture was cooled to room temperature and allowed to stand overnight. Then the mixture was filtered to remove salts. The filtrate was concentrated by vacuum evaporation for removal of triethylamine and then added into saturated NH₄Cl solution. The resulting mixture was dried with CH_2Cl_2 and the combined organic phase was washed with water and brine. The collected organic layer was dried with anhydrous Na_2SO_4 and using rotary evaporator to remove the solvent to obtain tertiary acetylenic alcohol substituted aromatic amines and purified by silica gel column chromatography using petroleum ether and ethyl acetate as eluent.

The above obtained product (7.1 mmol) was dissolved in 60 mL of isopropanol, to which pulverized KOH (71 mmol) was added. The mixture was refluxed under nitrogen atmosphere with stirring for about 4 h. After that the mixture was cooled and poured into water, the product was extracted with CH₂Cl₂, washed with water and brine and dried over anhydrous Na₂SO₄. Then the solvent was evaporated and crude product was purified by column chromatography (silica gel, pure petroleum ether) to give the bis(ethynyl) aromatic amine product.

3,6-diethynyl-9-dodecyl-9H-carbazole (CzC₁₂C₂)

¹H NMR (400 MHz, DMSO-*d*₆) δ (ppm): 8.40 (d, *J* = 1.4 Hz, 2H), 7.64 (s, 1H), 7.62 (s, 1H), 7.56 (dd, *J* = 8.4, 1.6 Hz, 2H), 4.40 (t, *J* = 7.0 Hz, 2H), 1.73 (q, *J* = 7.1 Hz, 2H), 1.27-1.12 (m, 18H), 0.84 (t, *J* = 6.8 Hz, 3H).¹³C NMR (DMSO-*d*₆) δ (ppm): 140.19, 129.68, 124.53, 121.56, 112.24, 109.93, 84.66, 78.69, 42.44, 31.25, 28.91, 28.81, 28.79, 28.63, 28.37, 26.27, 22.05, 13.91. Yield: 70%.



Fig. S2 ¹H NMR and ¹³C NMR of the $CzC_{12}C_2$.

3,7-diethynyl-10-dodecyl-10H-phenothiazine (PTZC₁₂C₂)

¹H NMR (400 MHz, DMSO-*d*₆) δ 7.29 (dd, *J* = 8.4, 2.0 Hz, 2H), 7.21 (d, *J* = 1.9 Hz, 2H), 6.98 (d, *J* = 8.5 Hz, 2H), 4.12 (s, 2H)3.85 (t, *J* = 6.9 Hz, 2H), 1.63 (p, *J* = 7.2 Hz, 2H), 1.39-1.14 (m, 18H), 0.85 (t, *J* = 6.8 Hz, 3H). ¹³C NMR (400 MHz, DMSO-*d*₆) δ 144.43, 131.38, 129.79, 123.08, 115.92, 115.89, 82.60, 80.60, 46.56, 31.28, 28.98, 28.94, 28.83, 28.76, 28.69, 28.37, 25.86, 25.80, 22.08, 13.92. Yield: 65%.



Fig. S3 ¹H NMR and ¹³C NMR of the $PTZC_{12}C_2$.

4, 4'-diethynyltriphenylamine (TPAC₂)

¹H NMR (400 MHz, DMSO-*d*₆) δ 7.42-7.33 (m, 6H), 7.20-7.14 (m, 1H), 7.11-7.06 (m, 2H), 6.99-6.91 (m, 4H), 4.09 (s, 2H). ¹³C NMR (400 MHz, *d*₆-DMSO) δ 147.00, 145.88, 133.11, 132.99, 132.69, 129.89, 125.55, 124.68, 123.30, 122.83, 115.58, 83.39, 80.03. Yield: 62%.



Fig. S4 ¹H NMR and ¹³C NMR of the TPAC₂.







Fig. S5 ¹H NMR and ¹³C NMR of the DSOs.

Part II. Figures and Tables involved in the manuscript

	Toluene	Ethyl acetate	THF	Acetonitrile	DMSO			
C-DSO	2.42	< 1.0	8.22	< 1.0	1.21			
P-DSO	> 10.0	9.26	> 10.0	< 1.0	> 10.0			
T-DSO	> 10.0	5.98	> 10.0	2.10	5.81			

Table S1 Solubility of the DSOs in different solvents at 25 °C (g/100 mL).



Fig. S6 The UV-vis absorption spectra of DSOs in the different solvents: (a) C-DSO; (b) P-DSO; (c) T-DSO.

	Solvent	$\lambda_{max,1}{}^a$	$\lambda_{max,2}{}^{a}$	€ _{max,1} ^b	$\epsilon_{max,2}{}^{b}$	ε ₄₀₅ ^b	λ_{ex}^{c}	$\lambda_{em}{}^c$	Δv^d	Φ ^e
C-DSO	Toluene	318	369	3.29	3.38	0.003	369	394	1720	0.82
	DCM	319	372	3.24	3.41	0.10	369	433	4006	0.63
	THF	318	368	3.37	3.39	0.05	369	422	3404	0.81
	Acetonitrile	317	365	3.46	3.41	0.12	367	463	5650	0.47
	DMSO	319	374	3.00	3.11	0.37	370	470	5750	
P-DSO	Toluene	288	395	3.89	1.64	1.55	314	506	12084	0.28
	DCM	291	401	3.76	1.68	1.66	281	523	16467	0.20
	THF	293	395	3.76	1.78	1.71	298	520	14326	0.22
	Acetonitrile	288	396	3.76	1.69	1.63	286	545	16616	0.04
	DMSO	293	407	3.62	1.60	1.60	300	554	15283	
T-DSO	Toluene		393		3.86	3.22	374	433	3643	0.68
	DCM		395		4.37	4.02	375	479	5790	0.43
	THF		392		4.90	4.00	377	462	4880	0.53
	Acetonitrile		390		4.54	3.48	375	517	7324	0.17
	DMSO		396		3.58	3.33	379	521	7191	

Table S2 The linear optical properties of dyes.

^a Absorption peak position in nm (2.0×10⁻⁵ M).

 $^{\rm b}$ Molar extinction coefficients in 10^4 mol^-1 L cm^-1.

^c Excitation and Emission wavelength of SPEF in nm (2.0×10⁻⁵ M).

^d Stokes shift in cm⁻¹.

e Quantum yields determined by using quinine sulfate dehydrate as the standard.



Fig. S7. The TPEF spectra of DSOs under different excitation laser wavelengths: (a) C-DSO; (b) P-DSO; (c) T-DSO.

Wavelength	(nm)	C-l	DSO	P-DSO		T-DSO			
	-	σ (GM)	ησ (GM)	σ (GM)	ησ (GM)	σ (GM)	ησ (GM)		
720		262	213	1059	233	1030	546		
730		252	204	939	206	847	449		
740		239	194	871	192	743	394		
750		285	231	956	212	775	411		
760		252	204	888	195	727	385		
770		117	95	506	111	493	261		
780		67	54	392	86	385	204		
790		47	38	409	90	460	244		
800		21	17	413	91	500	265		
810		16	13	627	138	776	411		
820				525	115	670	355		
830				316	69	360	191		
840				266	58	208	110		
850				252	55	130	69		

Table S3. The TPA cross-section (σ) and TPA action cross-section ($\eta\sigma$) data of DSOs.



Fig. S8 One-photon initiated polymerization profiles of TPGDA and E51 in the presence of the DSOs/ONI systems under 405 nm LED (TPGDA and E51: 100 wt%; all the ratios are weight percentages): (a) and (d) C-DSO/ION system; (b) and (e) P-DSO/ION system; (c) and (f) T-DSO/ION system.



Fig. S9. Photolysis of DSOs in the absence of ION, (a) C-DSO; (b) P-DSO, (c) T-DSO.



Fig. S10 UV-vis spectra (a) and fluorescence spectra (b) of C-DSO/ION at different irradiation times in THF solution ($c_{C-DSO} = 2.0 \times 10^{-5}$ M, $c_{ION} = 2.0 \times 10^{-4}$ M); (c) Photo-stability and photo bleaching kinetics of DSOs/ION measured under 405 nm LED ($c_{DSOs} = 2.0 \times 10^{-5}$ M, $c_{ION} = 2.0 \times 10^{-4}$ M); (d) Photo bleaching kinetics of P-DSO/ION and P-DSO/SON measured under 405 nm LED ($c_{P-DSO} = 2.0 \times 10^{-5}$ M, $c_{ION} = 2.0 \times 10^{-6}$ M); (e) Photo bleaching kinetics of P-DSO/ION and P-DSO/SON measured under 405 nm LED ($c_{P-DSO} = 2.0 \times 10^{-5}$ M, $c_{ION} = 2.0 \times 10^{-6}$ M).