Electronic Supporting Information for

One/two-Photon-Sensitive Photoacid Generators Based on Benzene Oligomer-containing D-π-A-type Aryl

Dialkylsulfonium Salts

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Table of Contents:

General experimental procedures and characterization	S2
Preparation of 3-Methylthiotriphenylamine (Pre-Mono)	S2
4-N, N'-diphenylamino-4'-bromobiphenyl (1)	S2
4-(4'-N, N'-diphenylamino)phenylphenylboronic acid (2)	S3
4-N, N'-diphenylamino-4'-bromotriphenyl (3)	S3
3-methylthio-4'-N,N-diphenylamino-biphenyl (Pre-Bi)	S3
Preparation of PAGs	S 4
¹ H NMR, ¹³ C NMR and MS spectra of PAGs	S8
Scheme S1: Proposed photolysis mechanism for Tri-Ben in acetonitrile	S14
Fig. S13: Optimized geometry of four PAGs (DFT B3LYP/6-31G(d) level)	S15
Fig. S14. The UV-vis absorption spectra and emission spectra of Precursors	S15
Fig. S15: The UV-vis spectra of the photodecomposition process of four PAGs	S16
Fig. S16. Number of photogenerated acid as function of the number of the absorbed photon	S17
Fig. S17: The UV-vis spectra of four PAGs with RDMb as acid indicator	S18
Fig. S18: Partial ¹ H NMR spectra of four PAGs in CD ₃ CN	S19
Fig. S19: Conversion curves for cationic photopolymerization of DVE	S19
Fig. S20. The TGA curves of four PAGs	S20
Fig. S21: The photolithography patterns of SU-8 resins containing PAG (1 wt %)	S20
Fig. S22: Transmittance Vs Intensity of Laser in the nonlinear absorption experiments	S21
Table S1. The solubility of four PAGs in normal organic solvents	S21
Table S2 The dihedral angles data in the conjugated systems of four PAGs	S21
Table S3. TD-DFT electronic transitions of PAGs (TD-DFT/6-31G(d) level)	S22
Reference	S22

General experimental prodecures and characterizaion

The theoretical absorption spectra have been computed based on density functional theory (DFT) and time-dependent DFT (TD-DFT). The overall computation strategy was defined as follows: After initial AM1 optimization calculations (vacuum), subsequent optimization of geometrical structures of the compounds were carried out using the B3LYP/6-31G(d) level of calculation. Finally, the TDDFT vertical transitions have been computed using the same level of calculations. All calculations have been performed using GAUSSIAN 09 package.^{S1}

The steady-state fluorescence experiments of precursors were performed on a Varian Cary Eclipses fluorescence spectrometer. Emission spectra were spectrally corrected, and fluorescence quantum yields include the correction due to the solvent refractive index and were determined relative to quinine bisulfate in 0.05 molar sulfuric acid ($\Phi_f = 0.52$).^{S2}

Preparation of 3-Methylthiotriphenylamine (Pre-Mono). 3-Iodothioanisole (2.22 g, 8.86 mmol) was added to a mixture of diphenylamine (1.5 g, 8.86 mmol), Cu powder (28.3 mg, 0.44 mmol) and K₂CO₃ (1.29 g, 9.30 mmol) in 1, 2-dichluorbenzene (30 mL) under nitrogen atmosphere at room temperature. The resultant mixture was stirred for 10 min and refluxed at 200 °C for 24 h. The reaction mixture was cooled to r.t. and the inorganic compounds were filtered and then the 1,2-dichlorobenzene was distilled at low presure and extracted three times with CH₂Cl₂ (3 × 60 mL), and dried over anhydrous magnesium sulfate. The product was purified by flash column chromatography with 2% ethyl acetate in n-hexane as eluent to give 1.96 g of a colorless oil (75.9 %). ¹H NMR (400 MHz, CDCl₃) δ 7.22 (t, *J* = 7.9 Hz, 4H, PhH), 7.12 (t, 1H, PhH), 7.07 (t, *J* = 7.6 Hz, 4H, PhH), 6.99 (t, *J* = 11.9 Hz, 4.4 Hz, 3H, PhH), 6.85 (d, *J* = 7.8 Hz, 1H, PhH), 6.81 (d, *J* = 8.1 Hz, 1H, PhH), 2.34 (s, 3H, CH₃).

4-N, N'-diphenylamino-4'-bromobiphenyl (1). 1 was prepared by the same method as **Pre-Mono** by 4-bromo-4'-iodobiphenyl and got a white powder like product, the yield was 74.9 %. ¹H NMR (400 MHz, CDCl₃) δ 7.73 (d, J = 8.3 Hz, 2H, PhH), 7.42 (d, J = 8.6 Hz, 2H, PhH), 7.28 (m, 6H, PhH), 7.12 (d, J = 8.3, 6H, PhH), 7.04 (t, J = 7.3 Hz, 2H, PhH).

4-(4'-N, N'-diphenylamino)phenylphenylboronic acid (2). Compound **1** (4.0 g, 10 mmol) was dissolved in the anhydrous THF (50 mL) and cooled to - 78 °C and dry triisopropyl borate (3.76 g, 20 mmol) was added by syringe. The mixture was stirred for 2 h at this temperature and then the n-BuLi (8 mL, 2.5 mol/L, 20 mmol) was added dropwise. Keep stirring for 2h and then the mixture was moved to room temperature with stirring for another 5 h. The reaction was quenched by water and then diluted hydrochloric acid was added to adjust the pH value to 2. After hydrolysis for 5 h, the mixture was extracted by dichloromethane (3 × 50mL) and dried over anhydrous Na₂SO₄. The crude product was purified by column chromatography on silica gel using dichloromethane/methanol (20/1, v/v) as eluent to afford the desired product as a white solid (2.24 g, 61.2 %). ¹H NMR (400 MHz, DMSO-d₆) δ 8.06 (s, 2H, OH), 7.85 (d, *J* = 7.83 Hz, 2H, PhH), 7.61 (t, *J* = 7.29 Hz, 4H, PhH), 7.32(t, *J* = 7.70 Hz, 4H, PhH), 7.06 (m, 8H, PhH).

4-N, N'-diphenylamino-4'-bromotriphenyl (3). A mixture of compound **2** (1.0 g, 2.74 mmol), 1-bromo-4-iodobenzene (0.77 g, 2.74 mmol), potassium carbonate (1.14 g, 8.22 mmol), Pd(PPh₃)₄ (158.3 mg, 0.14 mmol) and methyl trioctyl ammonium chloride (0.5 mL) in toluene (20 mL), ethanol (12 mL) and water (4 mL) (5: 3: 1, v/v/v) was stirred under N₂ atmosphere at 100 °C for 12 h. The resulting solution was cooled to room tempeture, extracted with dichloromethane (3 × 50 mL), washed with water, and dried over anhydrous MgSO₄. The crude product was purified by column chromatography on silica gel using dichloromethane/petroleum ether (1: 10, v/v) as eluent to afford

the desired product as a white solid (1.07 g, 82.3 %). ¹H NMR (400 MHz, CDCl₃) δ 7.64-7.51 (m, 6H, PhH), 7.47 (t, J = 8.5 Hz, 4H, PhH), 7.24 (d, J = 7.6 Hz, 4H, PhH), 7.13 (d, J = 7.9 Hz, 6H, PhH), 7.02 (t, J = 7.2 Hz, 2H, PhH).

3-methylthio-4'-N,N-diphenylamino-biphenyl (Pre-Bi). A mixture of 4-bromo-triphenylamine (1.0 g, 3.08 mmol), 3-(methylthio)phenylboronic acid (0.52 g, 3.08 mmol), potassium carbonate (1.28 g, 9.24 mmol), Pd(PPh₃)₄ (118.0 mg, 0.15mmol) and methyl trioctyl ammonium chloride (0.5 mL) in toluene (20mL), ethanol (12 mL) and water (4 mL) was stirred under N₂ atmosphere at 100 $^{\circ}$ C for 24 h. The resulting solution was cooled to room tempeture, extracted with dichloromethane (3 × 50 mL), washed with water, and dried over anhydrous MgSO₄. The crude product was purified by column chromatography on silica gel using dichloromethane/petroleum ether (1:5, v/v) as eluent to afford the desired product as a white solid (0.83 g, 82.3 %). ¹H NMR (400 MHz, CDCl₃): δ 7.43 (d, *J* = 8.0 Hz, 3H, PhH), 7.31 (d, *J* = 4.4 Hz, 2H, PhH), 7.24 (d, *J* = 7.6 Hz, 4H, PhH), 7.19 (t, 1H, PhH), 7.12 (d, *J* = 8.0 Hz, 6H, PhH), 7.02 (t, *J* = 7.3 Hz, 2H, PhH), 2.50 (s, 3H, CH₃). ¹³C NMR (101 MHz, CDCl₃): δ 147.68, 147.49, 141.43, 138.95, 134.61, 129.38, 129.22, 127.88, 124.96, 124.91, 124.54, 123.84, 123.63, 123.09, 15.95.

Pre-Tri and **Pre-Tetra** were prepared by compound **1** and **3** with 3-(methylthio)phenylboronic acid using the same method as **Pre-Bi**, respectively.

Pre-Tri. Yield: 80.2 %. ¹H NMR (400 MHz, CDCl₃) δ 7.60 (s, 4H, PhH), 7.48 (d, J = 8.9 Hz, 3H, PhH), 7.33 (d, J = 11.0 Hz, 2H, PhH), 7.23 (d, J = 7.2 Hz, 5H, PhH), 7.12 (d, J = 6.9 Hz, 6H, PhH), 7.01 (t, J = 5.9 Hz, 2H, PhH), 2.49 (s, 3H, CH₃). ¹³C NMR (101 MHz, CDCl₃) δ 147.72, 147.41, 141.50, 139.90, 139.14, 134.43, 129.41, 129.32, 127.75, 127.57, 127.05, 125.42, 125.23, 124.58, 123.92, 123.10, 15.99.

Pre-Tetra. Yield 80.7 %. ¹H NMR (400 MHz, CDCl₃): δ 7.72-7.60 (m, 8H, PhH), 7.50 (d, *J* = 8.6 Hz, 3H, PhH), 7.38 (d, *J* = 7.6 Hz, 1H, PhH), 7.34 (t, *J* = 7.6 Hz, 1H, PhH), 7.25 (d, *J* = 7.6 Hz, 5H, PhH), 7.13 (d, *J* = 7.6 Hz, 6H, PhH), 7.02 (t, *J* = 7.3 Hz, 2H, PhH), 2.52 (s, 3H, CH₃). ¹³C NMR (101 MHz, CDCl₃): δ 147.70, 147.37, 141.43, 139.91, 139.73, 139.65, 139.13, 138.93, 134.44, 129.38, 129.31, 127.70, 127.62, 127.39, 127.37, 127.07, 125.48, 125.25, 124.55, 123.97, 123.89, 123.07, 15.97.

Preparation of [3-(*N***,***N***-Diphenyl)amino]phenyl 4-cyanobenzyl methyl sulfonium hexafluorophosphate (Mono-Ben).** In the dark romm, Pre-Mono (300.0 mg, 1.03 mmol), silver trifluoromethanesulfonate (529.0 mg, 2.06 mmol) and Cs_2CO_3 were added into anhydrous CH_2Cl_2 (30 mL) under N₂ atmosphere at room temperature. Then 4-cyanobenzyl bromide (403.8 mg, 2.06 mmol) dissolved in 5 mL of anhydrous CH_2Cl_2 were synringed in half hour. The mixture was stirred for 96 h in the dark then the crude product was directly purified by column chromotography on silica gel using chloroform/methanol (10: 1, v/v) as eluent to afford the desired product as yellow solid. The product was used in the ion-metathesis described below without further purification.

A fresh 50 mL portion of aqueous KPF₆⁻ (4.60 g, 25 mmol) was added to a solution of prepared Mono-Ben in 20 mL of acetone. The mixture was stirred for 2 h at room temperature in the dark. The solid was collected by filtration and redissolved in 10 mL of acetone. The above anion-exchange was repeated three times and giving a final yield of 411.2 mg (74.4 %). ¹H NMR (400 MHz, CD₃CN) δ 7.74 (d, *J* = 7.7 Hz, 2H, PhH), 7.47 (t, *J* = 8.1 Hz, 1H, PhH), 7.36 (t, *J* = 7.3 Hz, 4H, PhH), 7.31 (d, *J* = 7.7 Hz, 2H, PhH), 7.27 (d, *J* = 7.8 Hz, 1H, PhH), 7.22 (d, *J* = 10.0 Hz, 1H, PhH), 7.19 (t, *J* = 7.4 Hz, 2H, PhH), 7.03 (d, *J* = 7.9 Hz, 4H, PhH), 7.00 (s, 1H, PhH), 4.89-4.54 (m, 2H, CH₂), 3.12 (s, 3H, CH₃). ¹³C NMR (101 MHz, CD₃CN) δ 149.57, 145.81, 132.78, 132.38, 131.53, 131.17, 129.64,

126.20, 125.15, 124.73, 122.08, 121.23, 117.64, 113.30, 49.67, 24.21. EI-MS (m/z): calcd for $C_{27}H_{23}F_6N_2PS$, 522.1224, found: 407.1580, $[M-PF_6^{-1}]^+$.

Bi-Ben, Tri-Ben and Tetra-Ben were prepared using the same method with respective precursors.

Bi-Ben (257.9 mg, 59.6 %): ¹H NMR (400 MHz, CD₃CN) δ 7.98 (d, *J* = 7.7 Hz, 1H, PhH), 7.84 (s, 1H, PhH), 7.69 (d, *J* = 8.3 Hz, 2H, PhH), 7.66 (d, *J* = 8.3 Hz, 1H, PhH), 7.61 (d, *J* = 8.4 Hz, 1H, PhH), 7.51 (d, *J* = 7.2 Hz, 2H, PhH), 7.34 (dd, *J* = 15.5, 7.9 Hz, 6H, PhH), 7.15-7.05 (m, 8H, PhH), 4.98-4.72 (m, 2H, CH₂), 3.24 (s, 3H, CH₃). ¹³C NMR (101 MHz, CD₃CN) δ 148.36, 146.88, 142.77, 132.73, 132.24, 132.21, 131.20, 131.02, 130.54, 129.21, 128.28, 127.68, 127.61, 124.63, 123.54, 122.19, 122.09, 117.52, 113.26, 49.64, 24.06. EI-MS (m/z): calcd for C₃₃H₂₇F₆N₂PS, 628.1537, found: 483.1894, [M-PF₆⁻]⁺.

Tri-Ben (263.3, 58.4 %): ¹H NMR (400 MHz, CD₃CN) δ 8.05 (d, *J* = 7.6 Hz, 1H, PhH), 7.95 (s, 1H, PhH), 7.77-7.66 (m, 8H, PhH), 7.59 (d, *J* = 8.6 Hz, 2H, PhH), 7.37 (d, *J* = 8.1 Hz, 2H, PhH), 7.30 (t, *J* = 7.9 Hz, 4H, PhH), 7.10-7.01 (m, 8H, PhH), 4.99-4.74 (m, 2H, PhH), 3.26 (s, 3H, CH₃). ¹³C NMR (101 MHz, CD₃CN) δ 147.49, 147.19, 142.88, 140.36, 135.97, 132.83, 132.79, 132.23, 132.09, 131.25, 131.11, 129.64, 129.21, 129.02, 128.24, 127.37, 126.71, 124.27, 123.15, 122.95, 122.25, 117.55, 113.34, 49.74, 24.15. EI-MS (m/z): calcd for C₃₃H₂₇F₆N₂PS, 704.1855, found: 559.2208, [M-PF₆-]⁺.

Tetra-Ben (213.4 mg, 50.8 %): ¹H NMR (400 MHz, CD₃CN) δ 8.05 (d, J = 7.4 Hz, 1H, PhH), 7.96 (s, 1H, PhH), 7.81 (d, J = 7.6 Hz, 2H, PhH), 7.77-7.63 (m, 10H, PhH), 7.57 (d, J = 7.7 Hz, 2H, PhH), 7.37 (d, J = 7.6 Hz, 2H, PhH), 7.29 (t, J = 7.4 Hz, 4H, PhH), 7.06 (t, J = 8.3 Hz, 8H, PhH), 4.99-4.77 (m, 2H, PhH), 3.25 (s, 3H, CH₃). ¹³C NMR (101 MHz, CD₃CN) δ 147.26, 142.82, 140.34, 139.36, 137.84, 136.55, 133.48, 132.90, 132.80, 132.27, 131.27, 131.13, 129.20, 129.12, 128.33, 127.42,

127.27, 127.14, 127.06, 126.57, 124.19, 123.10, 123.07, 122.32, 117.58, 113.32, 49.76, 24.17. EI-MS (m/z): calcd for $C_{33}H_{27}F_6N_2PS$, 780.8025, found: 635.2520, [M-PF₆⁻]⁺.

¹H NMR, ¹³C NMR and MS spectra of PAGs



Fig. S1: The ¹H NMR spectrum of Mono-Ben in CD₃CN.



Fig. S2: The ¹³C NMR spectrum of Mono-Ben in CD₃CN.



Fig. S3: The MS of Mono-Ben.



Fig. S4: The ¹H NMR spectrum of Bi-Ben in CD₃CN.







Fig. S6: The MS of Bi-Ben.



Fig. S7: The ¹H NMR spectrum of Tri-Ben in CD₃CN.



Fig. S8: The ¹³C NMR spectrum of tri-Ben in CD₃CN.



Fig. S9: The MS of Tri-Ben.



Fig. S10: The ¹H NMR spectrum of Tetra-Ben in CD₃CN.



Fig. S11: The ¹³C NMR spectrum of Tetra-Ben in CD₃CN.



Fig. S12: The MS of Tetra-Ben.



Scheme S1: Proposed photolysis mechanism for Tri-Ben in acetonitrile.



Fig. S13: Optimized geometry of four PAGs (DFT B3LYP/6-31G(d) level).



Fig. S14: The UV-vis absorption spectra and emission spectra of four Precursors in acetonitrile.



Fig. S15: The UV-vis spectra of the photodecomposition process of four PAGs in acetonitrile under irradiation of 365 nm UV light (0.5 mW cm^{-2}).



Fig. S16: Number of photogenerated acid as function of the number of the absorbed photon in acetonitrile (Black Squares: Mono-Ben; Red Circles: Bi-Ben; Blue Triangles: Tri-Ben; Cyan

Triangles: Tetra-Ben.).



Fig. S17: The UV-vis spectra of four PAGs with Rhodamine B as acid indicator under irradiation of

365 nm UV light (0.5 mW cm⁻²).



Fig. S18: Partial ¹H NMR spectra of four PAGs in CD₃CN.



Fig. S19: Conversion vs. time curves for cationic photopolymerization of divinyl monomer DVE containing PAG (1 wt %). λ_{exc} : 365 nm , Irradiance: 5 mW cm⁻².



Fig. S20: The TGA curves of four PAGs.





Fig. S21: The photolithography patterns of SU-8 resins containing PAG (1 wt %), λ_{exc} : 365 nm , Irradiance: 160 mJ cm⁻². Upper is the photo of 21 step sensitivity guide (Stouffer).



Fig. S22: Transmittance Vs Intensity of Laser in the nonlinear absorption experiments of PAGs in DMF. (Concentration: 0.001-0.01 mol/L; λ_{exc} : 700 nm; 1K Hz).

PAGs	CH ₃ Cl	CH_2Cl_2	Acetonitrile	Acetone	DMF
Mono-Ben	\checkmark \checkmark	\checkmark	\checkmark \checkmark	$\sqrt{}$	$\sqrt{}$
Bi-Ben	\checkmark \checkmark	\checkmark	\checkmark \checkmark	\checkmark \checkmark	\checkmark \checkmark
Tri-Ben	\checkmark \checkmark	\checkmark	\checkmark \checkmark	\checkmark \checkmark	\checkmark \checkmark
Tetra-Ben	\checkmark	\checkmark	\checkmark	\checkmark \checkmark	\checkmark \checkmark

Table S1. The solubility of four PAGs in normal organic solvents.

 \checkmark : Soluble; $\checkmark \checkmark$: Easy to dissolve.

Table S2 The dihedral angles data in the conjugated systems of four PAGs (DFT/6-31G(d) level)

PAGs	DA-1 ^a	DA-2	DA-3
Mono-Ben	-	-	-
Bi-Ben	31.79°	-	-
Tri-Ben	30.12°	32.01°	-
Tetra-Ben	33.27°	34.38°	36.12°

^a Dihedral angle, as shown in Fig. S14.

Transition	Mono	-Ben	Bi-B	Bi-Ben		Tri-Ben		Tetra-Ben	
	E _{th} /eV	f	E _{th} /eV	f	E _{th} /eV	f	E _{th} /eV	f	
$S_0 \rightarrow S_1$	3.98	0.08	3.98	1.10	3.80	1.55	3.87	1.99	
$S_0 \rightarrow S_2$	4.55	0.40	4.12	0.05	4.40	0.02	4.41	0.04	
$S_0 \rightarrow S_3$	4.85	0.32	4.52	0.03	4.42	0.05	4.53	0.10	
$S_0 \rightarrow S_4$	4.94	0.11	4.68	0.25	4.58	0.26	4.56	0.27	
$S_0 \rightarrow S_5$	5.09	0.03	-	_a	4.80	0.11	4.56	0.20	

Table S3. TD-DFT electronic transitions of PAGs (TD-DFT/6-31G(d) level).

Reference

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