Supporting Information

Sulfur-doped anthanthrenes as effective organic photocatalysts for metal-free ATRP and PET-RAFT polymerization under blue and green light

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Contents

1. Photoreaction Setup

As shown above (**Figure S1**), all polymerization reactions were conducted in a 6 W blue photo-reactor placed 1 cm from light, which was purchased from http://www.geaochem.com/ (Model: H106062, GEAO CHEMICAL). The reactor has a fan for cooling and its light intensity to be ~30 mW/cm^2.

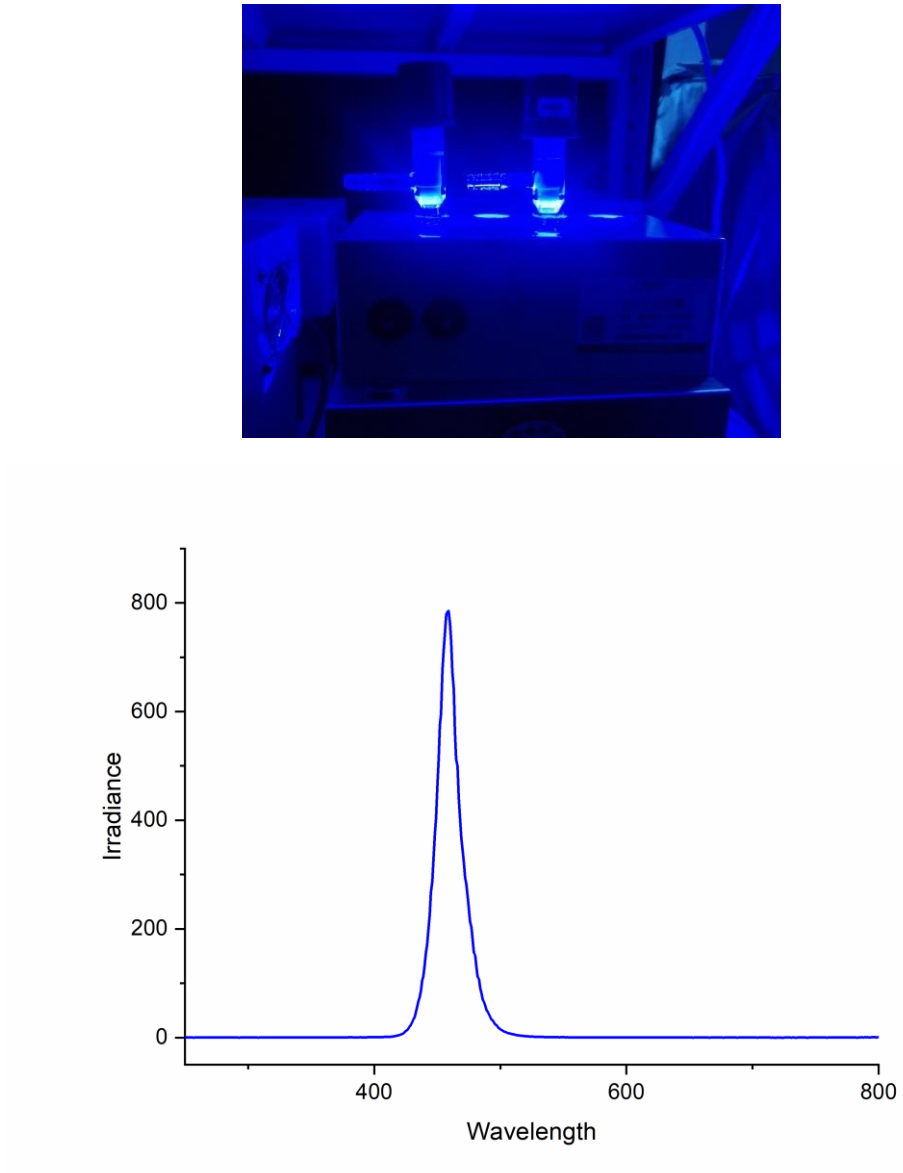
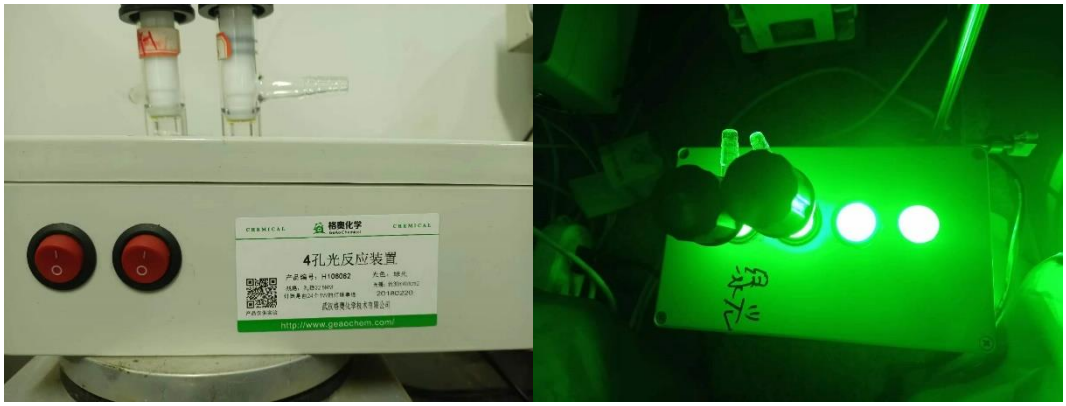


Figure S1. The reaction setup of ATRP polymerizations with 6 W blue LEDs (λ_{max} = 460 nm).



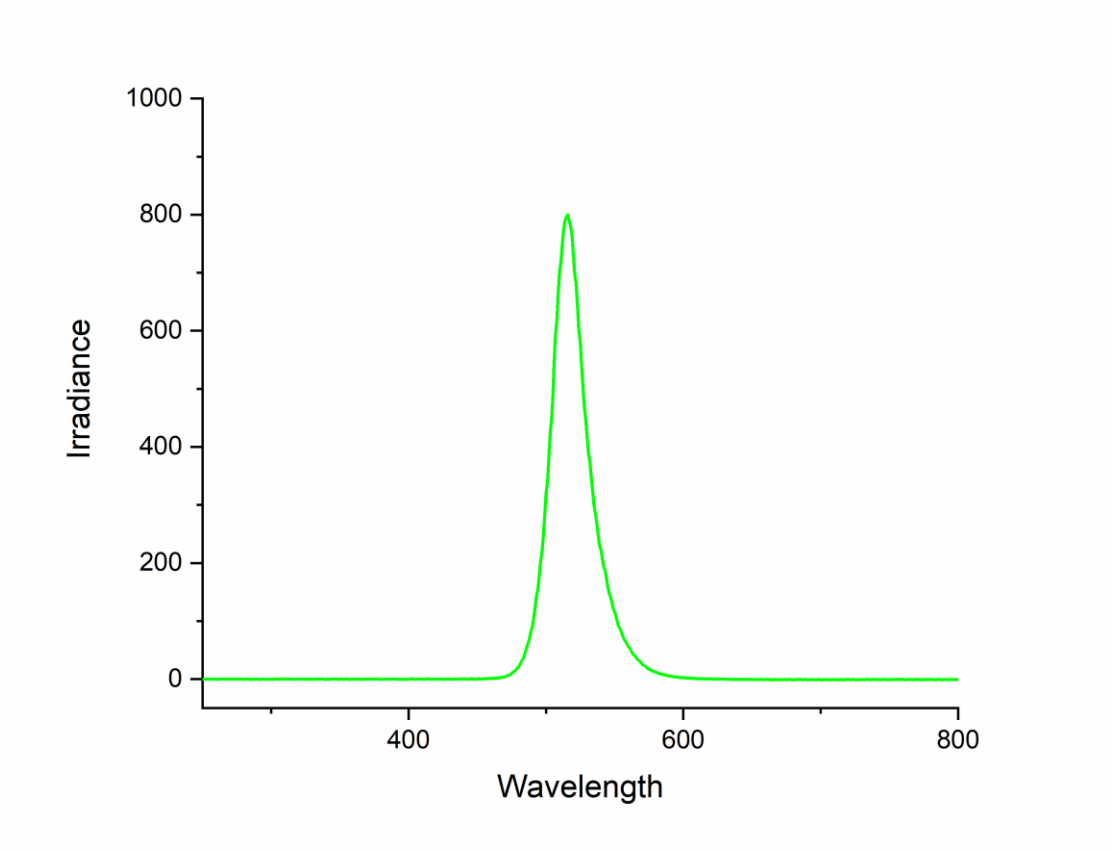
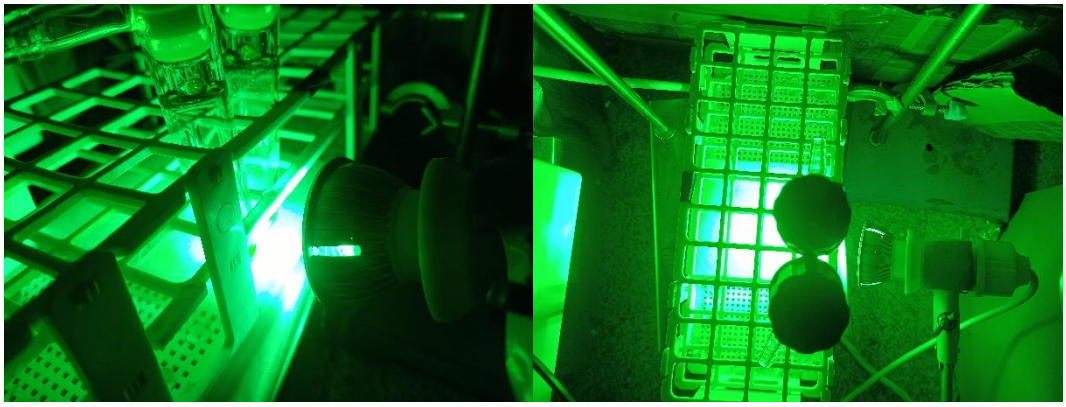


Figure S2. The reaction setup of ATRP polymerizations with 6 W green LEDs (λ_{max} = 516 nm).



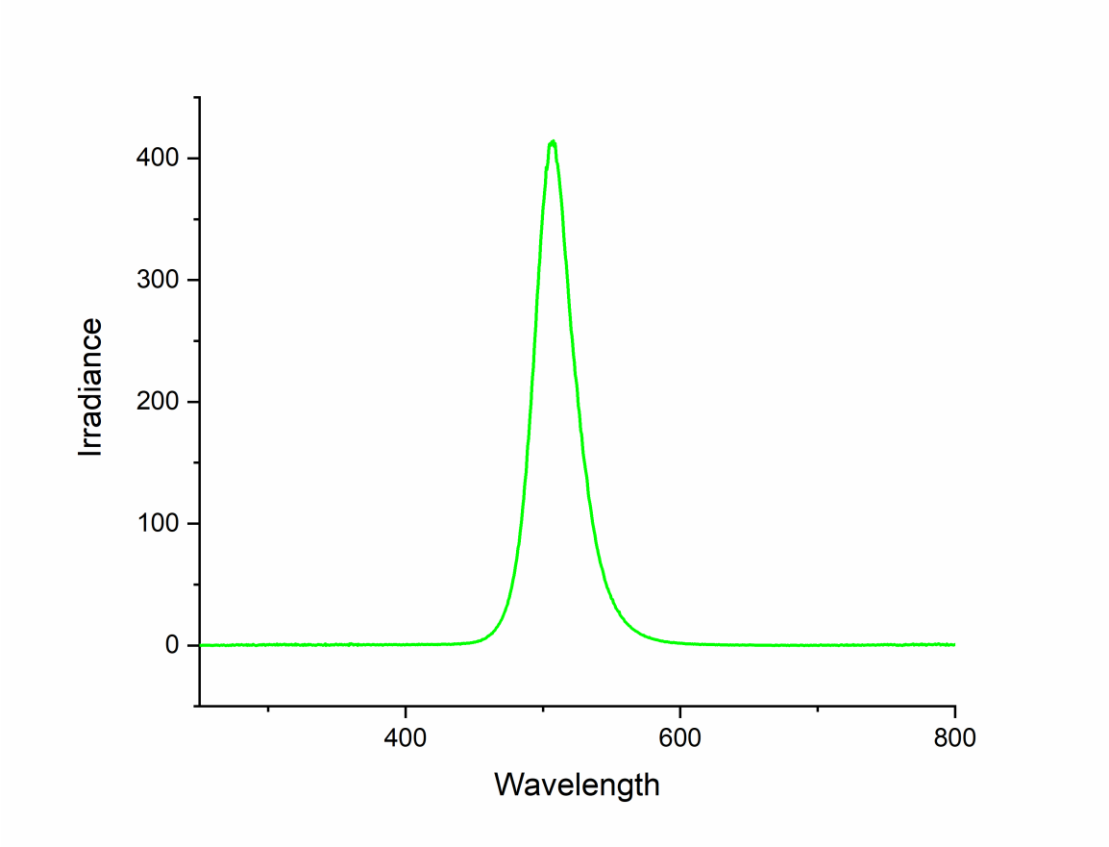
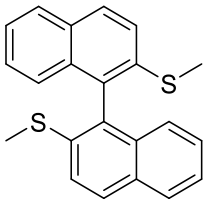


Figure S3. The reaction setup of PET-RAFT polymerizations with 3 W green bulbs (λ_{max} = 516 nm).

2. Synthesis and Characterization of (SDA)s and SeDA

Synthesis of 2,2’-bis(methylthio)-1,1’-binaphthalene (SDA-1a)



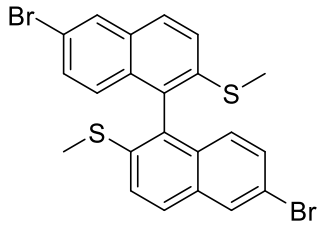
SDA-1a

The synthesis of SDA and SeDA photocatalysts was performed according to literature procedure.[3,4] A solution of 2,2'-dibromo-1,1'-binaphtyl 1.24 g, 3 mmol) in THF (12 mL) in a dried 50 mL round-bottom flask was cooled to -78 ºC and n-BuLi solution (1.6 M in cyclohexane, 1.89 mL, 3.03 mmol) was added. After stirring for 1 h, 1,2-dimethyldisulfane (0.53 mL, 6 mmol) was added and 10 min later the reaction was allowed to warm to room temperature. The solution was concentrated on a rotary evaporator and then purified by flash chromatography (cyclohexane) to yield (2'-bromo-[1,1'-binaphthalen]-2-yl)(methyl)sulfane (0.93 g, 82 % yield) as a colorless solid. Notice: Product decomposition in solution after prolonged exposure in air.

^{1}H NMR (500 MHz, Chloroform-*d*): δ 7.97 (d, J = 8.8 Hz, 2H), 7.88 (d, J = 8.1 Hz, 2H), 7.58 (d, J = 8.8 Hz, 2H), 7.38 (t, J = 7.8, 6.7 Hz, 2H), 7.26 – 7.21 (m, 2H), 7.00 (d, J = 8.6 Hz, 2H), 2.42 (s, 6H).

^{13}C NMR (126 MHz, Chloroform-*d*): δ 136.68, 132.67, 132.48, 131.46, 129.06, 128.30, 127.11, 125.32, 124.96, 123.26, 15.88.

Synthesis of (6,6'-dibromo-[1,1'-binaphthalene]-2,2'-diyl)bis(methylsulfane) (SDA-2a)



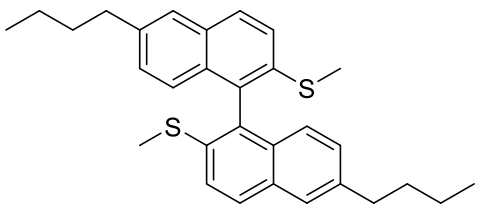
SDA-2a

2,2'-bis(methylthio)-1,1'-binaphthalene 1.04 g (3.0 mmol) was dissolved in 15 mL CH_2Cl_2 and stirred at 0 °C. 0.7 mL (12.0 mmol) Bromine was added in one portion with stirring and a stream of nitrogen was bubbled through the solution to remove the evolving HBr. The reaction mixture was stirred for 5 h while the flask was allowed to warm to room temperature. The reaction mixture was quenched by the addition of saturated $Na_2S_2O_3$ solution (20 mL) and extracted with CH_2Cl_2 (3 × 50 mL). During this procedure, the product precipitates as a white solid and was filtered off and dried in vacuo to give desired product (1.4 g, 92%) as a white powder.

^{1}H NMR (500 MHz, Chloroform-*d*): δ 8.05 (s, 2H), 7.90 (d, J = 8.8 Hz, 2H), 7.60 (d, J = 8.7 Hz, 2H), 7.32 (d, J = 9.0 Hz, 2H), 6.83 (d, J = 9.1 Hz, 2H), 2.44 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 137.65, 132.56, 131.80, 131.04, 130.61, 130.38, 128.31, 126.55, 124.26, 119.44, 14.19.

Synthesis of (6,6'-dibromo-[1,1'-binaphthalene]-2,2'-diyl)bis(methylsulfane) (SDA-2b)



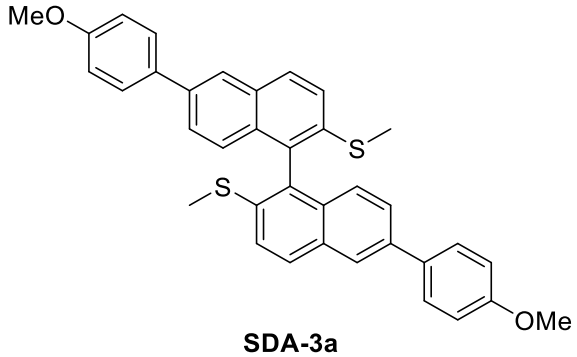
SDA-2b

To a suspension of **SDA-2a** (390 mg, 0.773 mmol) and [Pd(dppf)Cl_2] (29 mg, 0.039 mmol) in dry THF (25 mL) under N_2, *n*-BuMgBr was added dropwise (3.8 mL, 3.8 mmol, 1 M solution in THF) at 0 °C. The mixture was stirred under reflux at 90 °C for 2.5 h and then at r.t. overnight. sat. NH_4Cl (aq.) solution (20 mL) was added, and the mixture extracted with EtOAc (3 × 20 mL). The combined organic phases were washed with brine, dried over $MgSO_4$, filtered and concentrated in vacuo. The crude product was purified by column chromatography (SiO_2, petroleum ether/CH_2Cl_2 10:1), to afford **SDA-2b** (230 mg, 65%) as a white glue.

^{1}H NMR (400 MHz, Chloroform-*d*): δ 7.90 (s, 2H), 7.66 (s, 2H), 7.55 (d, J = 8.7 Hz, 2H), 7.10 (d, J = 8.8 Hz, 2H), 6.93 (d, J = 8.7 Hz, 2H), 2.71 (t, J = 7.8 Hz, 4H), 2.42 (s, 6H), 1.69 – 1.61 (m, 4H), 1.42 – 1.34 (m, 4H), 0.93 (t, J = 7.3 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 139.85, 135.31, 132.73, 131.67, 131.21, 128.71, 128.52, 126.67, 124.91, 123.39, 35.77, 33.44, 22.64, 16.04, 14.14.

Synthesis of (6,6'-bis(4-methoxyphenyl)-[1,1'-binaphthalene]-2,2'-diyl)bis(methylsulfane) (SDA-3a)



SDA-3a

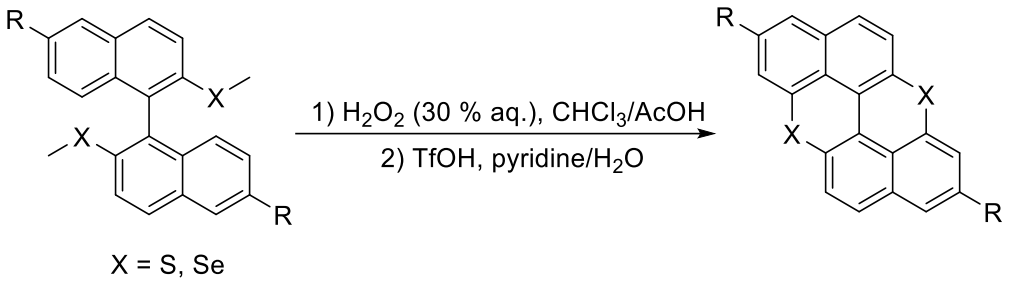
To a suspension of **SDA-2a** (200 mg, 0.773 mmol) and [Pd(dppf)Cl_2] (29 mg, 0.039 mmol) in dry THF (25 mL) under N_2, 4MeOPhMgBr was added dropwise (3.8 mL, 3.8 mmol, 1 M solution in THF) at 0 °C. The mixture was stirred under reflux at 90 °C for 2.5 h and then at r.t. overnight. sat. NH_4Cl (aq.) solution (20 mL) was added, and the mixture extracted with EtOAc (3 × 20 mL). The combined organic phases were washed with brine, dried over $MgSO_4$, filtered and concentrated in vacuo. The crude product was purified by column chromatography (SiO_2, petroleum ether/CH_2Cl_2 10:1), to afford **SDA-3a** (200 mg, 47%) as a white glue.

^{1}H NMR (500 MHz, Chloroform-*d*): δ 8.05 (s, 2H), 8.03 (d, J = 9.2 Hz, 2H), 7.64 – 7.60 (m, 6H), 7.50 (dd, J = 8.8, 2.0 Hz, 2H), 7.09 (d, J = 8.8 Hz, 2H), 6.99 (d, J = 8.8 Hz, 4H), 3.86 (s, 6H), 2.47 (s, 6H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 159.29, 137.59, 136.42, 133.54, 132.37, 131.85, 131.57, 129.25, 128.41, 126.70, 125.46, 123.71, 114.41, 55.47, 15.94.

Acid-mediated Cyclization of Arylmethyl Sulfide[1,2]

Oxidation and Cyclization of SDA-1, SDA-2, SDA-3, and SeDA.

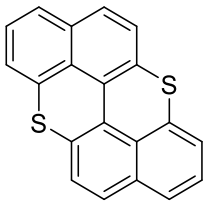


The arylated compound (0.2 mmol, 1.0 eq) and H_2O_2(30 % (w/w) in H_2O) (0.34 mL, 15 eq) were dissolved in 1:1(v/v) $CHCl_3$:CH_3COOH mixture (12 mL). The mixture was stirred at room temperature until the complete conversion of arylmethyl sulfide on TLC (within 1 hour). The reaction mixture was quenched with saturated NaOH aq. solution at 0 °C, until pH~12. The aqueous layer was extracted with DCM three times. Combined organic extract was dried over Na_2SO_4. After evaporation of the solvents, the mixture was purified by column chromatography (eluent: hexane/EtOAc = 1/1).

The corresponding sulfoxide was placed in a Schlenk tube and DCE (3.0 mL) was added. With continuous N_2 streaming into the tube, TfOH (1.5 mL) was added dropwise. After stirring 24 hours at room temperature, 1 mL of H_2O and 4 of pyridine were added and heated at 100 °C for 1 h. After cooling to rt, the solvent was removed in vacuo, and diluted with H_2O and DCM. The organic layer was separated and the aqueous layer was extracted with DCM three times. The combined organic extracts was washed with H_2O and brine, dried over Na_2SO_4, and concentrated in vacuo. The obtained crude material

was purified through column chromatography (eluent: hexane/DCM= 20/1) and GPC ($CHCl_3$) to give the cyclized product.

Thioxantheno[2,1,9,8-klmna]thioxanthene (SDA-1):

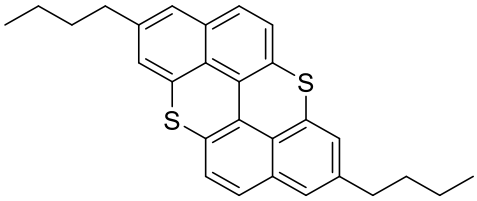


SDA-1

^{1}H NMR ((500 MHz, Methylene Chloride-d_2): δ 7.28 (d, J = 8.7 Hz, 1H), 7.14 (dd, J = 8.1, 1.3 Hz, 1H), 7.02 (dd, J = 8.1, 7.3 Hz, 1H), 6.86 (dd, J = 7.3, 1.3 Hz, 1H), 6.79 (d, J = 8.6 Hz, 1H);

^{13}C NMR (151 MHz, Methylene Chloride-d_2): δ 136.21, 131.64, 131.43, 130.68, 128.18, 127.78, 127.45, 127.39, 127.21, 122.89. HRMS (ESI^+): m/z [M] calcd for ($C_{20}H_{10}S_2$): 314.0224; found: 314.0230.

2,8-dibutylthioxantheno[2,1,9,8-klmna]thioxanthene (SDA-2):



SDA-2

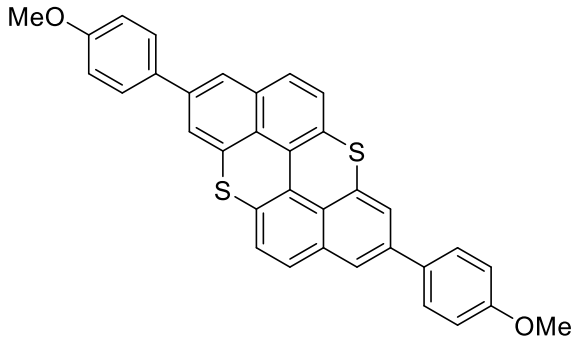
^{1}H NMR (500 MHz, Methylene Chloride-d_2): δ 7.18 (d, J = 8.6 Hz, 2H), 6.89 (s, 2H), 6.74 (d, J = 8.3 Hz, 2H), 6.72 (s, 2H), 2.48 (t, 4H), 1.58 – 1.51 (m, 4H), 1.37 – 1.29 (m, 4H), 0.90 (t, J = 7.4 Hz, 6H).

^{13}C NMR (126 MHz, Methylene Chloride-d_2): δ 141.14, 134.47, 129.30, 128.35, 128.04, 125.37, 124.09, 122.05, 34.78, 32.87, 22.34, 13.72.

HRMS (ESI$^+$): m/z [M] calcd for ($C_{28}H_{26}S_2$): 426.1476; found: 426.1467.

Crystals suitable for X-Ray diffraction were obtained by slow diffusion of EtOH into the solution of **SDA-2** in chloroform (CCDC: 2328161).

2,8-bis(4-methoxyphenyl)thioxantheno[2,1,9,8-klmna]thioxanthene (SDA-3):

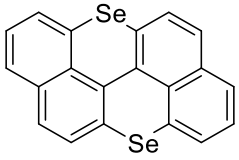


SDA-3

^{1}H NMR (500 MHz, Chloroform-*d*): δ 7.52 (d, J = 7.7 Hz, 4H), 7.29 (d, J = 8.1 Hz, 2H), 7.26 (s, 2H), 7.09 (s, 2H), 6.97 (d, J = 7.7 Hz, 4H), 6.81 (d, J = 7.7 Hz, 2H), 3.86 (s, 6H).

HRMS (APCI$^+$): m/z [M+H]$^+$ calcd for ($C_{34}H_{23}O_2S_2$): 527.1137; found: 527.1139.

Selenoxantheno[2,1,9,8-klmna]selenoxanthene (SeDA):



SeDA

^{1}H NMR (500 MHz, Chloroform-*d*): δ 7.45 (d, J = 8.4 Hz, 2H), 7.36 (dd, J = 7.9, 1.4 Hz, 2H), 7.28 (td, J = 7.3, 1.1 Hz, 2H), 7.19 (d, J = 8.4 Hz, 2H), 7.14 (dd, J = 8.0, 7.2 Hz, 2H);

^{13}C NMR (126 MHz, $CDCl_3$): δ 135.02, 131.69, 130.02, 128.98, 126.77, 126.39, 125.71, 124.86.

3. Characterization of Catalyst Properties

UV-Vis Absorption Spectra

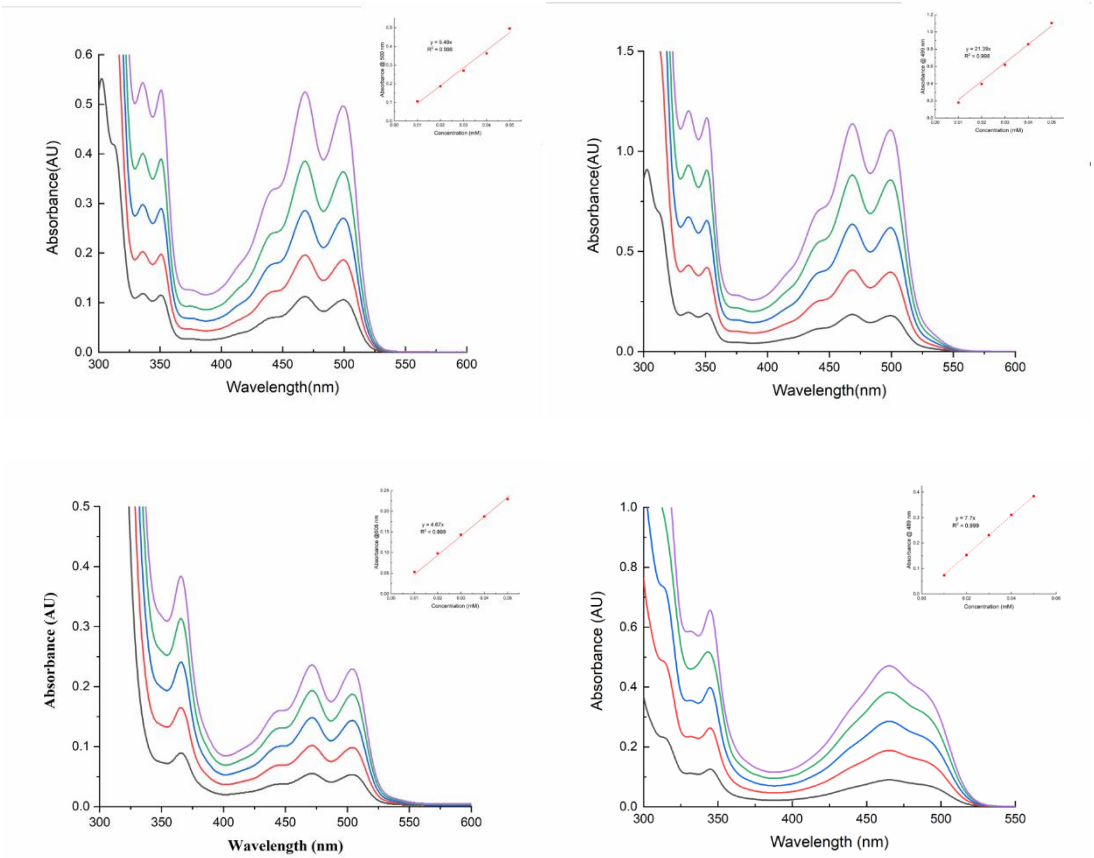
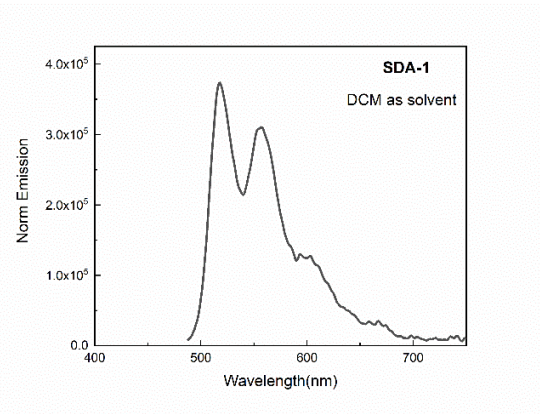
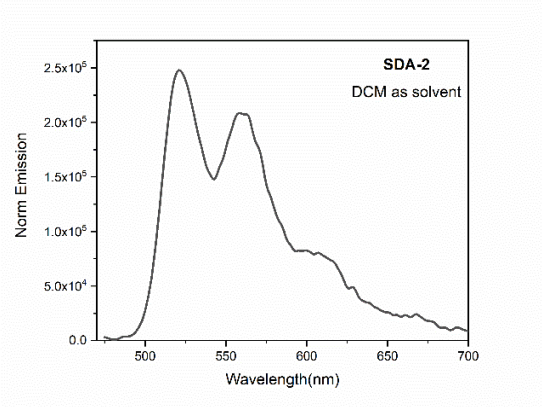


Figure S4. UV-Vis spectra of catalysts **SDA-1**, **SDA-2**, **SDA-3** and **SeDA** at different concentration in DCM.

Fluorescence Spectroscopy





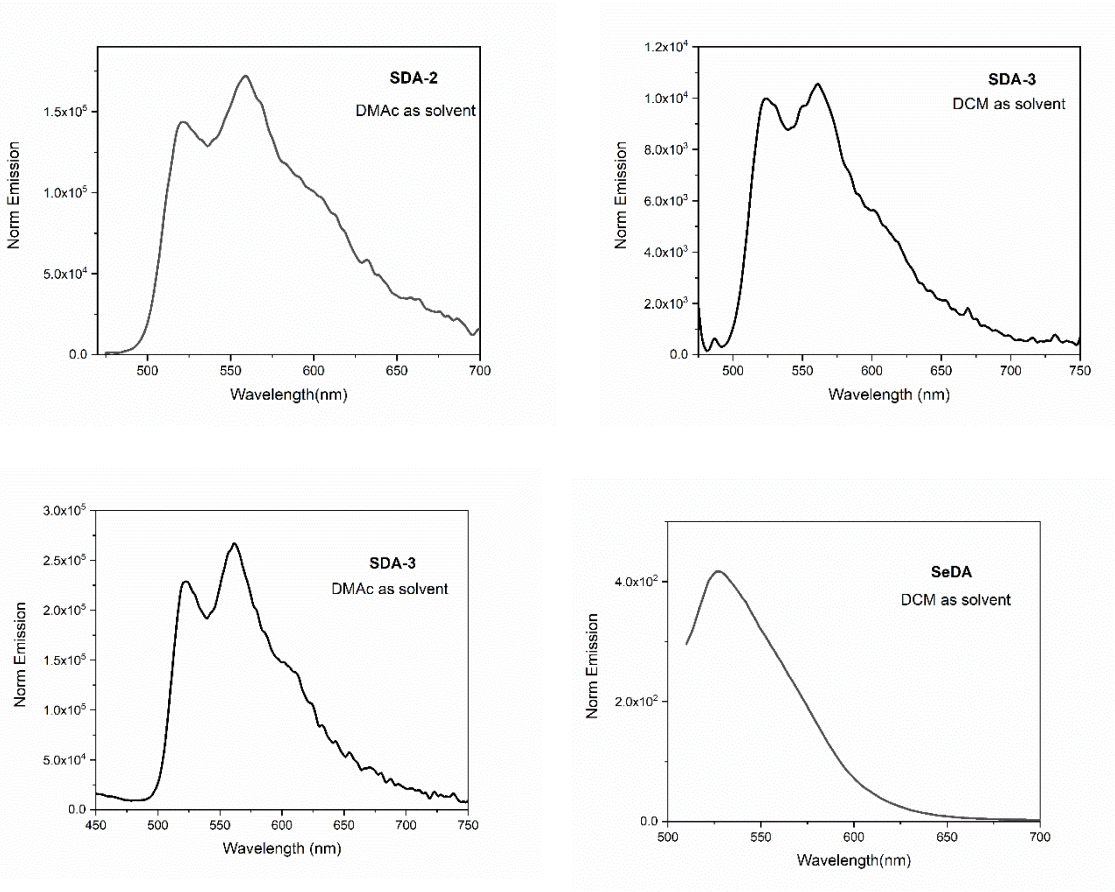
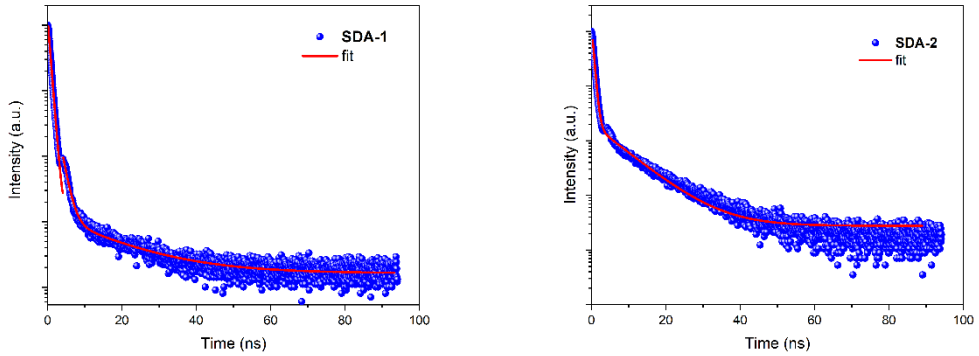


Figure S5. Fluorescence emission spectra of **SDAs** and **SeDA**.

Time-resolved emission decay



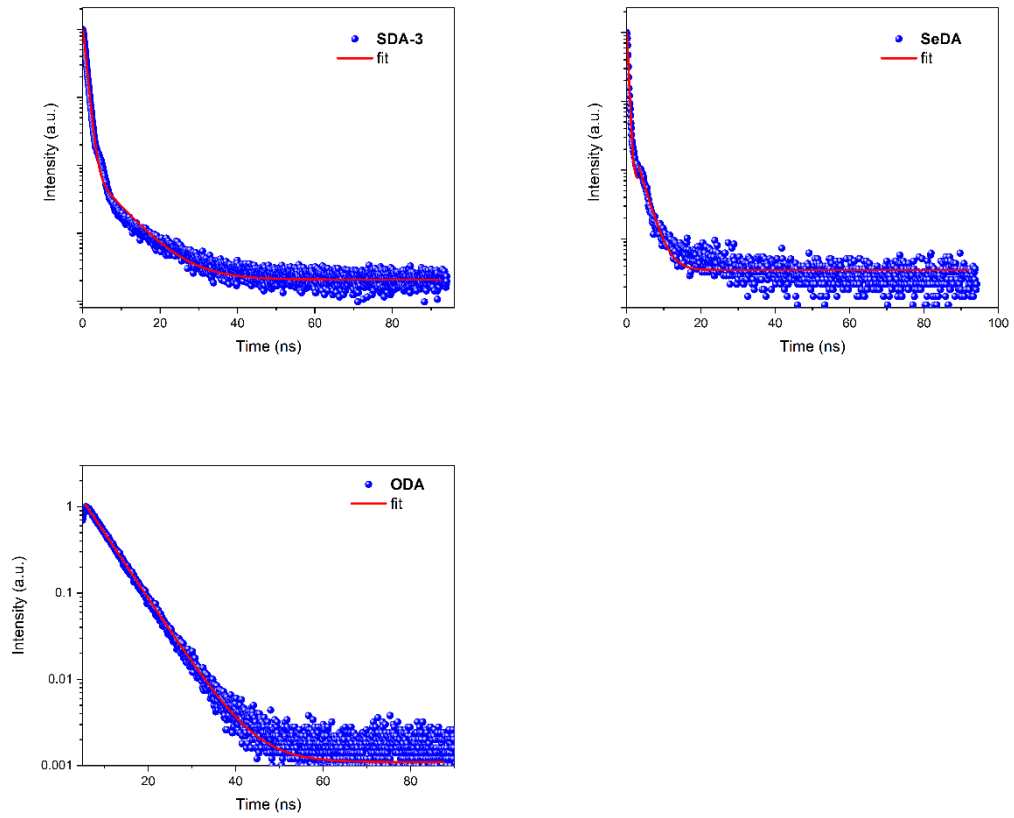


Figure S6. Time-resolved emission decay curves of catalyst **SDA-1** (A), **SDA-2** (B), **SDA-3** (C), **SeDA** (D) and **ODA** (E) in DCM.

Table S1. Lifetime data of PCs in DCM under a N_2 atmosphere at RT.

Entry	PCs	Lifetime	Weight	χ^2
1	SDA-**1**	$\tau_1 = 0.59$	99.3%	1.18
		$\tau_2 = 5.20$	0.7%	
2	SDA-**2**	$\tau_1 = 0.52$	98.5%	1.15
		$\tau_2 = 8.00$	1.5%	
3	SDA-**3**	$\tau_1 = 0.75$	99.1%	1.28
		$\tau_2 = 6.80$	0.9%	
4	SeDA	$\tau_1 = 0.34$	96.8%	1.55
		$\tau_2 = 2.32$	3.2%	
5	ODA	$\tau = 5.62$	100%	1.27

Cyclic Voltammetry

General Procedure: Cyclic voltammograms of the photoredox catalysts were performed in a 3-compartment electrochemical cell with Ag/AgCl as the reference electrode, n-Bu_4NPF_6 in DCM (0.1 M) as the electrolyte solution, glassy carbon electrode for the working and a platinum wire for counter electrodes.

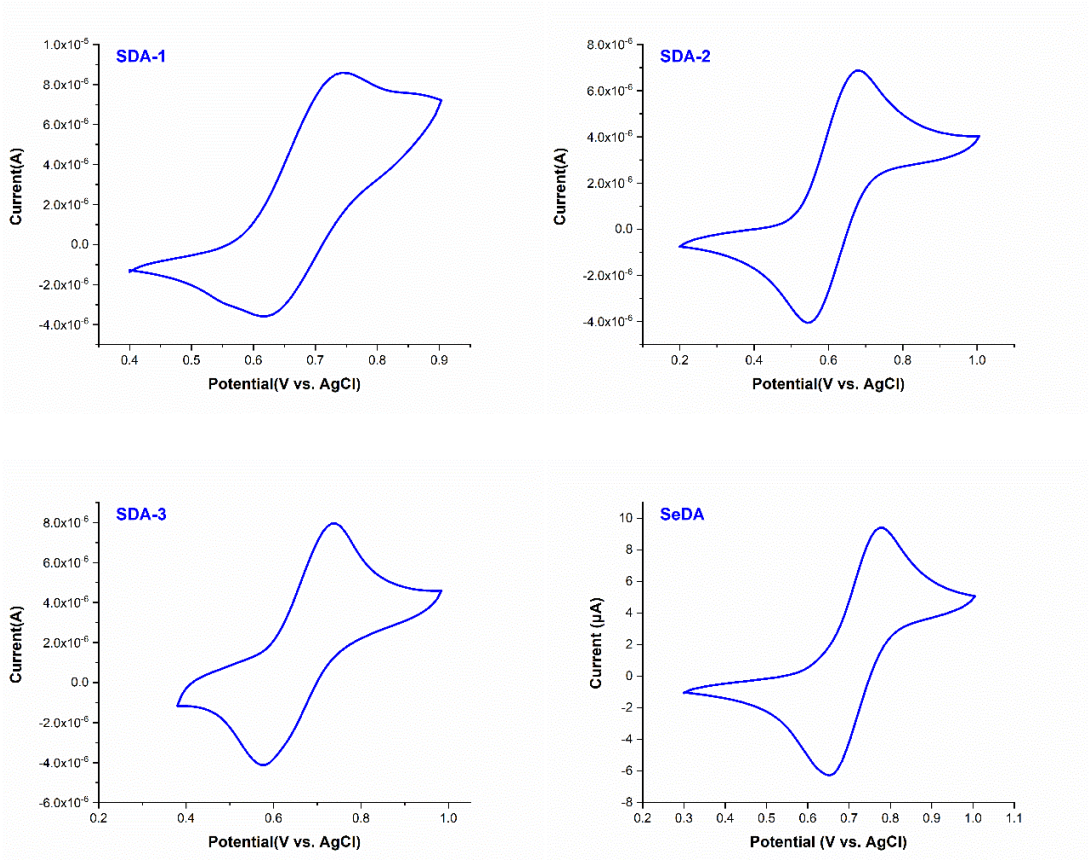


Figure S7. Cyclic voltammograms of the **SDA-1** (A), **SDA-2** (B), **SDA-3** (C) and **SeDA** (D) at 50 mV/s in DCM performed in a 3-compartment electrochemical cell.

Experimental Determination of Excited State Reduction Potentials

The singlet excited reduction potential of PC in DCM vs the saturated calomel electrode (SCE) as determined from the following equation:

$$E^0(PC^{\cdot+}/{}^1PC^*, \text{vs SCE}) = E^0(PC^{\cdot+}/PC, \text{vs SCE}) - E_{s1}$$

Table S2. Experimentally measured excited state reduction potentials of doped catalysts

Molecule	λ_{onset}	E_{s1}[a] (E'_{s1}[b])	$E^0(PC^{\cdot+}/PC)$	$E^{0*}(PC^{\cdot+}/{}^1PC^*)$ (E'[c])	$E^{0*}(PC^{\bullet+}/{}^3PC)$[d]
ODA	468	2.65(2.58)	0.82	-1.83(-1.76)	-1.63[d]
SDA-1	509	2.45(2.23)	0.64	-1.81(-1.59)	-1.55
SDA-2	511	2.42(2.21)	0.56	-1.86(-1.65)	-1.60
SDA-3	514	2.42(2.20)	0.62	-1.80(-1.58)	-1.56
SeDA	509	2.39(2.35)	0.67	-1.72(-1.68)	-1.61

[a] Calculated from the onset of absorption spectra. [b] Calculated from the maximum of emission λ_{max}. [c] Calculated by $E_0(PC^{\cdot+}/PC) - E'_{s1}$. [d] calculated reduction potentials.

Fluorescence Quenching Study

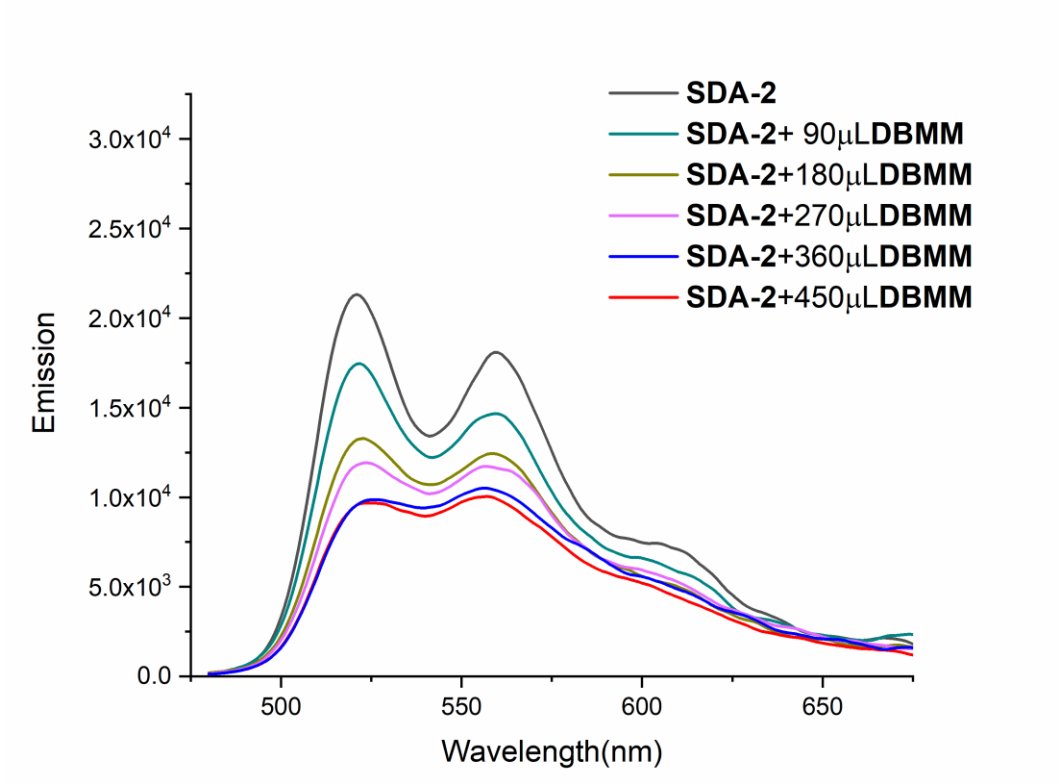


Figure S8. Fluorescence spectra of **SDA-2** using DBMM as quencher.

The solutions of **SDA-2** were excited at 470 nm and the fluorescence spectra were

recorded between 521 and 560 nm. The emission of a 0.20 mM solution of **SDA-2** in DCM was measured at varying volumes of diethyl 2-bromo-2-methylmalonate (DBMM, 157 mM). As shown in **Figure S8** a significant fluorescence quenching by addition of DBMM was observed.

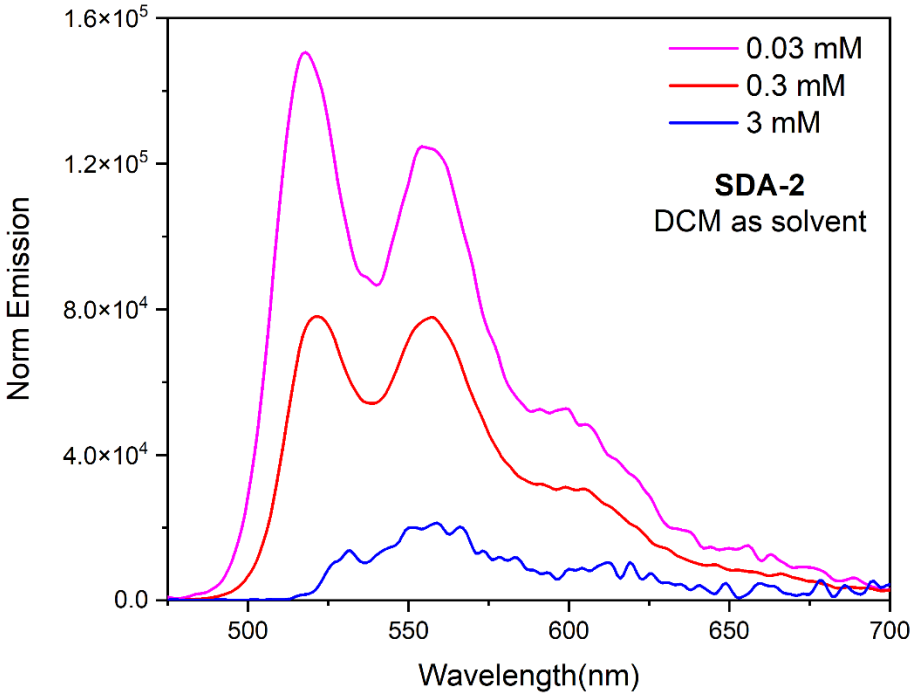


Figure S9. Fluorescence spectra of **SDA-2** at different concentrations in argon saturated DCM.

As the **SDA-2** concentration increases, π-π stacking effect leads to a significant red shift in fluorescence, with the main emission peak shifting from 521 nm to 560 nm.

Crystal Data of SDA-2 (CCDC: 2328161)

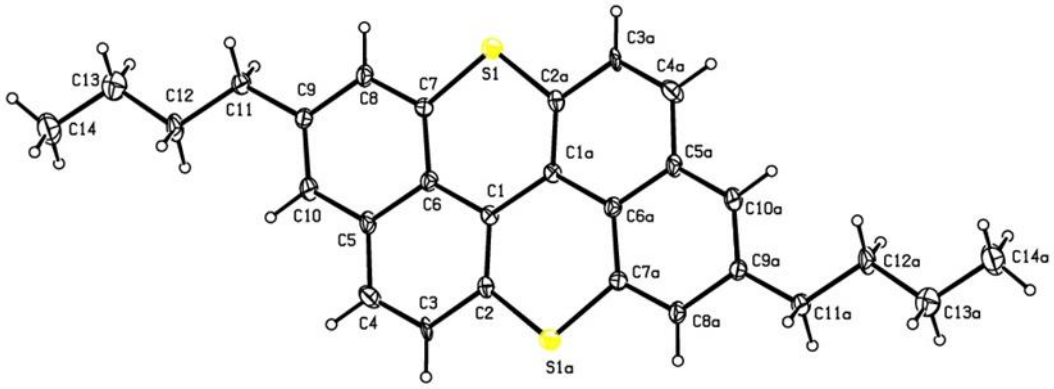


Table S3. Crystallographic information for the structural refinement of **SDA-2**

Empirical formula	$C_{28}H_{26}S_2$
Formula weight	426.61
Temperature/K	293(2)
Crystal system	triclinic
Space group	P-1
a/Å	6.565(6)
b/Å	10.442(4)
c/Å	15.773(4)
α/°	96.93(3)
β/°	94.54(5)
γ/°	90.35(5)
Volume/Å^3	1070.0(10)
Z	2
ρ_{calc}g/cm^3	1.324
μ/mm^{-1}	0.262
F(000)	452.0
Crystal color	Clear orangish
Crystal size/mm^3	0.065 × 0.078 × 0.21
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	3.93 to 59.464
Index ranges	$-9 \le h \le 8$, $-11 \le k \le 13$, $-21 \le l \le 20$

Reflections collected	13806
Independent reflections	4929 [R_{int} = 0.1372, R_{sigma} = 0.2287]
Data/restraints/parameters	4929/0/273
Goodness-of-fit on F^2	1.024
Final R indexes [I>=2σ (I)]	R_1 = 0.1266, wR_2 = 0.3023
Final R indexes [all data]	R_1 = 0.2614, wR_2 = 0.3740
Largest diff. peak/hole / e $Å^{-3}$	1.07/-0.82

4. Polymerization Procedure

General Methods for Kinetic Study and Analysis of Molecular Weight Growth[3]

A typical procedure of kinetics experiments were performed in glovebox using a [MMA]:[DBMM] ratio of 100:1 with 100 ppm **SDA-2** and 1 mL:1.5 mL MMA: DCM. To evaluate the kinetics and growth of molecular weight versus conversion for polymerization, an aliquot of 0.05 mL of reaction mixture was taken and injected into a solution of $CDCl_3$ containing 250 ppm of the radical inhibitor (BHT), at predetermined times after the start of the polymerization as indicated (when the reaction mixture was exposed to light). Another aliquot sample re-dissolved in HPLC grade, unstabilized tetrahydrofuran and the M_n and M_w/M_n were directly analyzed by GPC. Analysis of kinetics and molecular weight growth of other catalysts loading can be found in the supplementary details below.

General Procedure for PMMA Macroinitiator Synthesis

A typical metal-free organocatalyzed ATRP procedures with the molar ratio of $[MMA]_0$: $[initiator]_0$: $[catalyst]_0$ = 100: 1: 0.01 were showed as follows. In Argon-filled glovebox, the polymerization was conducted with MMA (1.0 mL, 9.35 mmol, 100 eq.) as the model monomer, DBMM (18 μL, 93.5 μmol, 1.0 eq.) as the ATRP initiator, organic photocatalyst (4.70 μmol, 0.5 eq.) and DCM (1.0 mL) as the solvent in a Schlenk tube with a PTFE stirring bar. And then the polymerization was occurred under blue LED

irradiation at room temperature. After the desired time, the tube was opened under argon and 20.0 μL of mixture were syringed out and quenched into $CDCl_3$ containing 250 ppm BHT to determine the monomer conversion by ^1H NMR. After 1H NMR analysis, the sample is dried using compressed air, re-dissolved in HPLC grade, unstabilized tetrahydrofuran and the M_n and M_w/M_n were directly analyzed by GPC.

Polymerization Procedure for Chain Extension from PMMA Macroinitiator

MMA (2.00 mL, 18.8 mmol, 100 eq.), DBMM (72 μL, 283 μmol, 1.5 eq.), and catalyst (0.188 μmol, 0.01 eq.) were dissolved in 2.50 mL DCM and reacted according to the above general polymerization procedure for 16 hours. After that, the tube was opened under argon and 20.0 μL of mixture were syringed out and quenched into $CDCl_3$ containing 250 ppm BHT to determine the monomer conversion by ^1H NMR (Conv. = 70.4%). At this time, the reaction was removed, poured into 250 mL methanol and stirred for 4 h. The resulting precipitate was slowly dripped into room temperature methanol, after stirring for half an hour, then isolated by vacuum filtration and washed with excess methanol. The polymer was then re-dissolved in a minimal amount of DCM again and dripped into 150 mL of methanol and stirred for 2 h to fully remove unreacted monomer, initiator or catalyst. The resulting chain extended PMMA was collected via vacuum filtration and dried in a vacuum over at 40 ^oC overnight obtained 1g of polymer, M_n = 6.1 kDa, $Đ$ = 1.26, and I^* = 92%.

Chain Extension and Block Copolymer Synthesis from PMMA Macroinitiator

Synthesis of PMMA-*b*-PMMA

A Schlenk tube with a PTFE stirring bar was charged with 0.29 mg of PC (9.42×10^{-5} mol, 0.02 eq.) and 26 mg of the PMMA macroinitiator described above (M_n = 6.1 kDa, 1.0 eq.) which were dissolved in 1 mL of DCM. Then 91 µL of MMA were added (0.86 mmol, 200 eq.), reacted according to the above general polymerization procedure for 6 hours. The tube was opened under argon and 20.0 µL of mixture were syringed out and the sample is dried using compressed air, re-dissolved in HPLC grade, unstabilized tetrahydrofuran and the M_n and M_w/M_n were analyzed by GPC.

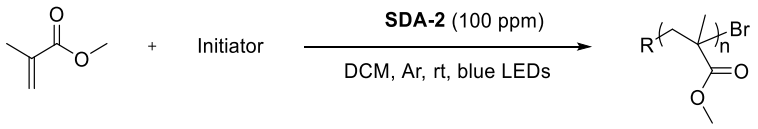
Synthesis of PMMA-*b*-PTFEMA

A Schlenk tube with a PTFE stirring bar was charged with 50 µL of PC (9.42×10^{-5} mol, 0.05 eq.) and 34.2 mg of the PMMA macroinitiator described above (M_n = 6.1 kDa, 1.0 eq.) which were dissolved in 1 mL of DCM. Then 132 µL of TFEMA were added (1.12 mmol, 200 eq.), reacted according to the above general polymerization procedure for 9 hours. The tube was opened under argon and 20.0 µL of mixture were syringed out and the sample is dried using compressed air, re-dissolved in HPLC grade, unstabilized tetrahydrofuran and the M_n and M_w/M_n were analyzed by GPC.

General Procedure for PET-RAFT Polymerizations

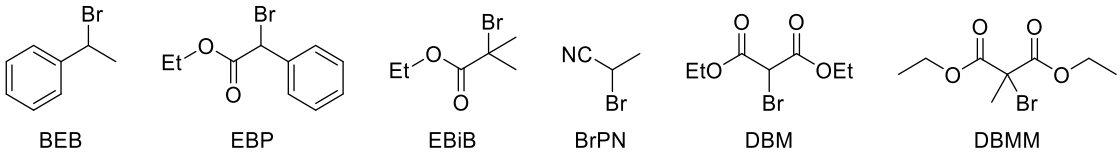
A 10mL Schlenk tube is charged with PC (0.027 μmol, 0.001 eq [5 ppm relative to monomer]), RAFT agent (0.027 mmol, 1 eq.), monomer (2.7 mmol, 100 eq.), and 0.5 mL solvent. This stoichiometry was used in all experiments unless otherwise indicated. And then the polymerization was placed under a 460 nm blue bulb or 516 nm green bulb. After the indicated amount of reaction time, the reaction mixture is removed from the photoreactor and samples of the reaction mixture are removed via syringe for analysis.[4]

Table S4. Initiator screening for O-ATPR of MMA



Entry	Initiator	Time (h)	Conv. (%)[b]	$M_{n,theo}$[c]	$M_{n,GPC}$[d]	$Đ$[d]	I^*(%)[e]
1	BEB	17	86	8.8	183.0	1.80	52
2	EBP	15	80	8.3	7.8	1.40	106
3	EBiB	16	83	8.5	18.4	1.66	46
4	BrPN	16	92	9.4	14.0	1.22	67
5	DBM	16	85	8.8	10.0	1.35	88
6	DBM	16	84	8.7	10.8	1.30	81
7	DBMM	20	88	9.1	10.0	1.30	91

[a]Reaction conditions: [M]=9.4 mol/L, $[MMA]_0/[DBMM]_0/[\textbf{SDA-2}]_0$ = 1000 : 10 : 0.1, MMA/DCM (1:1, v/v) at room temperature under blue LED irradiation for specified time. [b]Determined by ^{1}H NMR. $M_{n,theo}$ = ([monomer]/[initiator] × M_w of monomer × Conv. % + M_w of initiator)/1000. [d]Measured using GPC-MALS. [e]I^* = $(M_{n,theo})/(M_{n,GPC})$ × 100%.



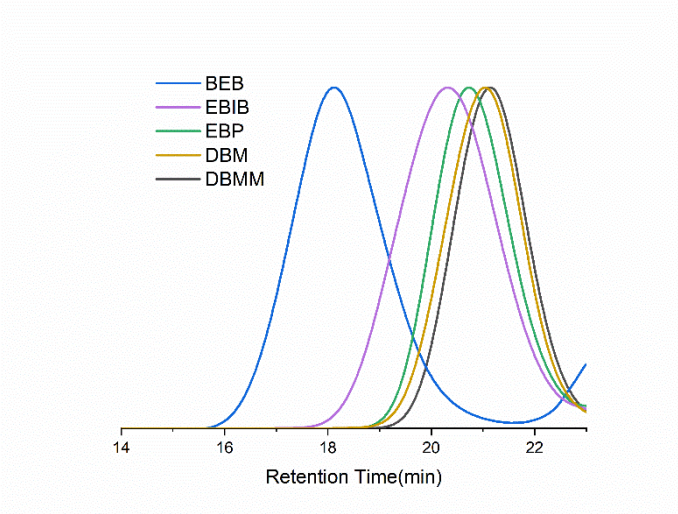


Figure S10. GPC traces of entry 1 (blue), 2 (red), 3 (purple),6 (yellow) and 7 (black).

Table S5. Results of O-ATRP catalyzed by various **SDA-2** loading under various light source.

SDA-2 loading (ppm)	Light Source	Conv.[b]	$M_{n,theo}$[c]	$M_{n,GPC}$[d]	Đ[d]	I^*[e] (%)
100	Blue LEDs	76%	7.9	9.3	1.25	85
50	Blue LEDs	88%	9.1	9.7	1.29	91
30	Blue LEDs	87%	8.9	9.6	1.45	94
25	Blue LEDs	96%	9.9	10.8	1.43	77
10	Blue LEDs	88%	9.1	10.7	1.40	93
5	Blue LEDs	89%	9.2	10.5	1.54	92
100	Green LEDs	75%	7.8	9.9	1.25	79
50	Green LEDs	71%	7.5	10.1	1.44	74
100	White LEDs	64%	6.7	9.8	1.38	68
100	Sunlight	68%	7.1	13.6	1.27	52

[a]Polymerization conditions: [M] = 9.4 mol/L, $[M]_0/[DBMM]_0$ = 100/1. [b]Determined by ^{1}H NMR. [c] [c]Calculated by ($[monomer]_0/[initiator]_0$ × MW of monomer × conv. % + MW of initiator)/1000. [d]Molecular weight ($M_{n,GPC}$) and dispersity ($Đ$) were measured by GPC with poly(methyl methacrylate) (PMMA) standards. [e]Initiator efficiency (I^*) calculated by ($M_{n,theo}/M_{n,GPC}$) × 100%.

Monomer scope in O-ATRP

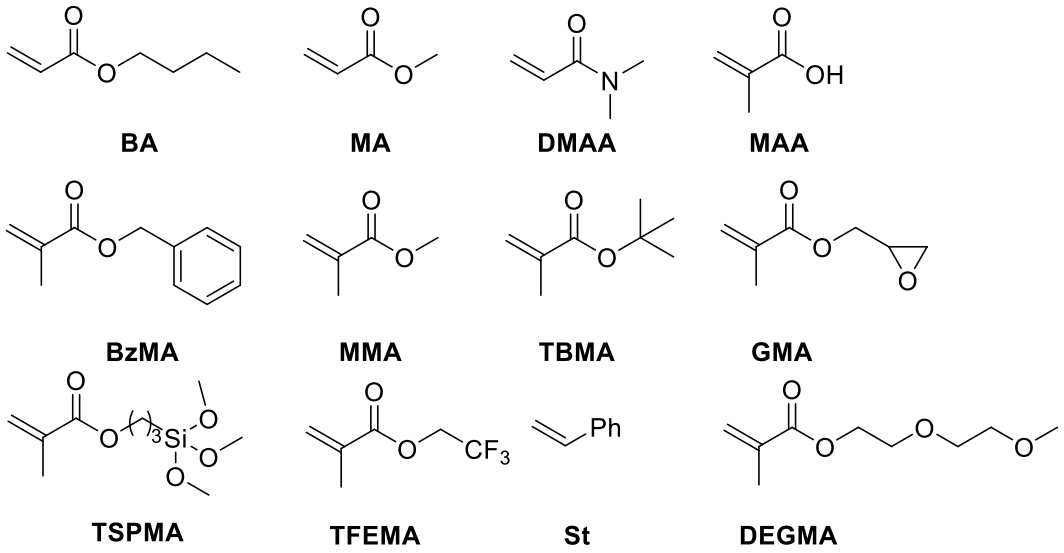


Table S6. Data of M_n and $Đ$ vs Conversion, corresponding to **Figure** 2A left blue line.

Entry	catalyst	initiator	$M_0/I_0/C_0$[a]	time (h)	conv. (%)[b]	$M_{n,GPC}$[c]	$Đ$[c]
1	SDA-2	DBMM	200:1:0.01	1	27	5.6	1.34
2	SDA-2	DBMM	200:1:0.01	3	43	10.3	1.33
3	SDA-2	DBMM	200:1:0.01	5	50	11.1	1.33
4	SDA-2	DBMM	200:1:0.01	7	75	13.8	1.31

[a]$M_0/I_0/C_0$ = $[monomer]_0/[initiator]_0/[catalyst]_0$. [b]Determined by ^1H NMR. [c]Determined by GPC with poly(methyl methacrylate) (PMMA) standards, kDa.

Table S7. Investigations on O-ATRP of more monomers under blue light

Entry	M	Solvent	Time (h)	conv. (%)[b]	$M_{n,th}$[c]	$M_{n,GPC}$[d]	$Đ$[d]
1	MA	THF	8	92.7	8.1	9.0	1.48
2	BA	THF	8	87.1	11.3	11.5	1.52
3	GMA	THF	11	77.6	11.2	11.2	1.50
4	DEGMA	THF	11	81.1	15.3	16.1	1.51

[a]$[M]_0/[EBP]_0/[SDA\text{-}2]_0$ = 100/1/0.01. [b]Determined by ^{1}H NMR. [c] Calculated by (Conv. × $[MMA]_0/[DBMM]_0$) × MW_{MMA}+ MW_{DBMM}. [d] Determined by GPC with poly(methyl methacrylate) (PMMA) standards, kg/mol.

Gel-Permeation Chromatography Traces

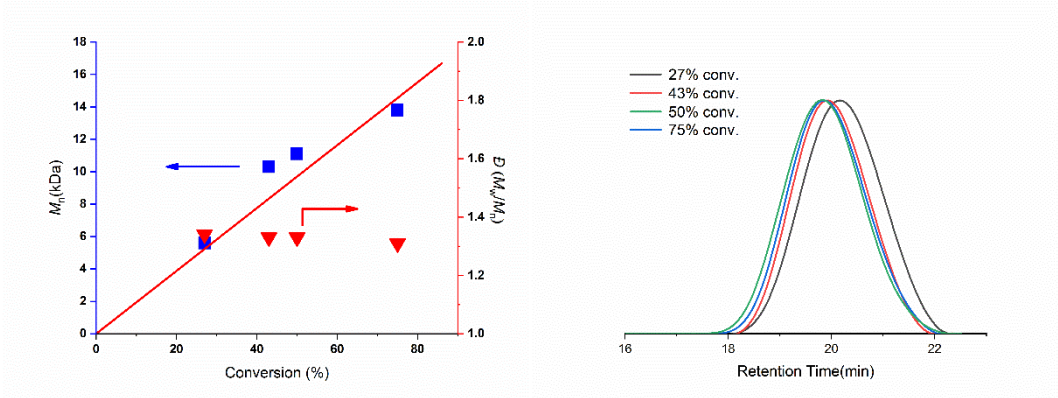


Figure S11. (a) Plot of M_n and $Đ$ versus monomer conversion for the polymerization of MMA under continuous irradiation; **(b)** Overlaid GPC trace for the O-ATRP of MMA using **SDA-2** under 6W blue LED irradiation.

NMR Spectra of Precipitated Polymer Products

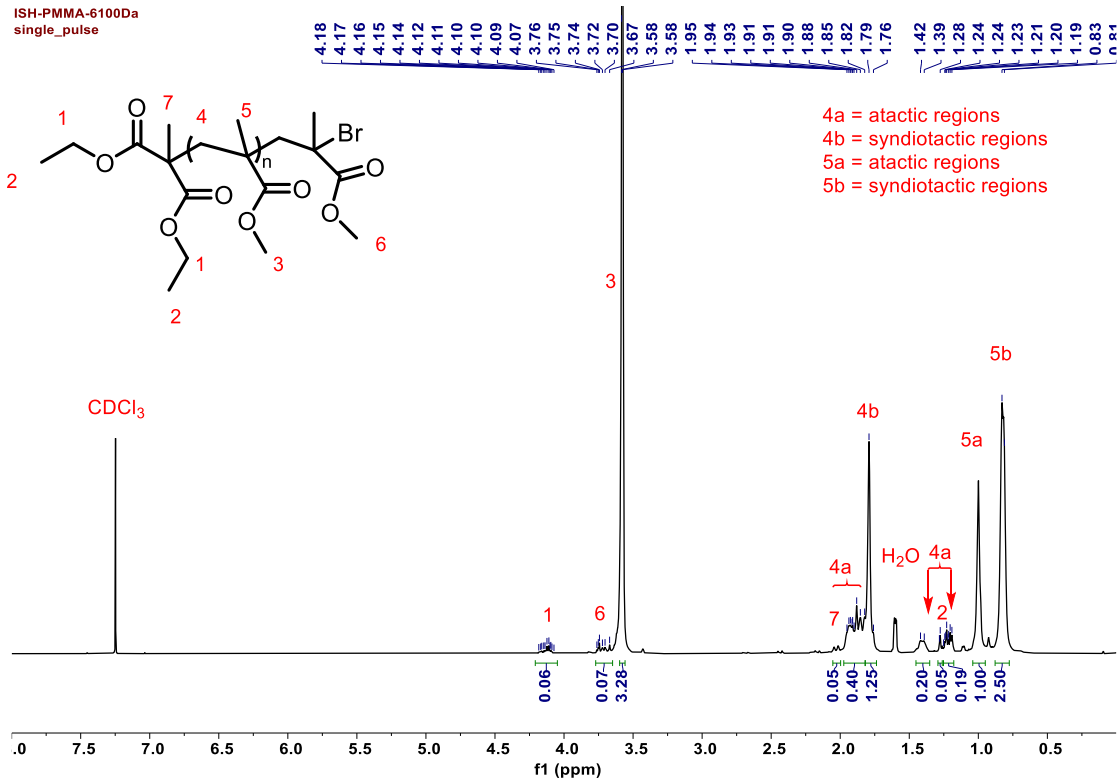


Figure S12. ^{1}H NMR of isolated PMMA ($CDCl_3$, 400 MHz, DP = 65, $M_{n(NMR)}$ = 6.76 kDa).

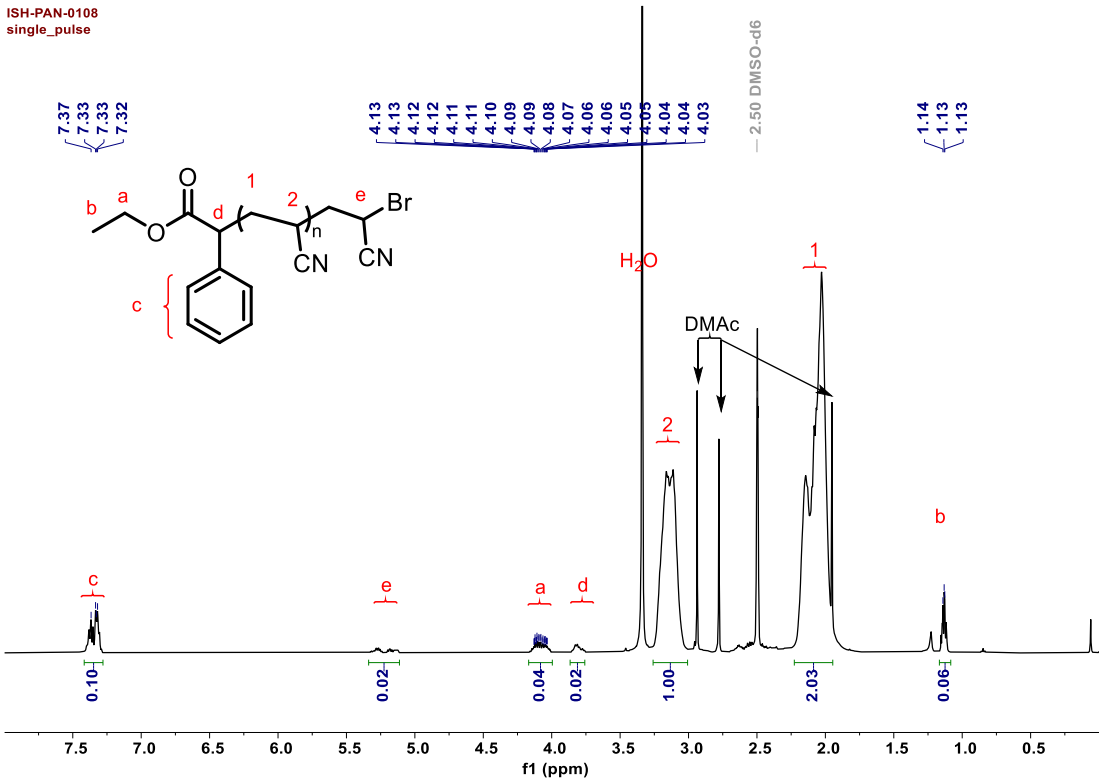
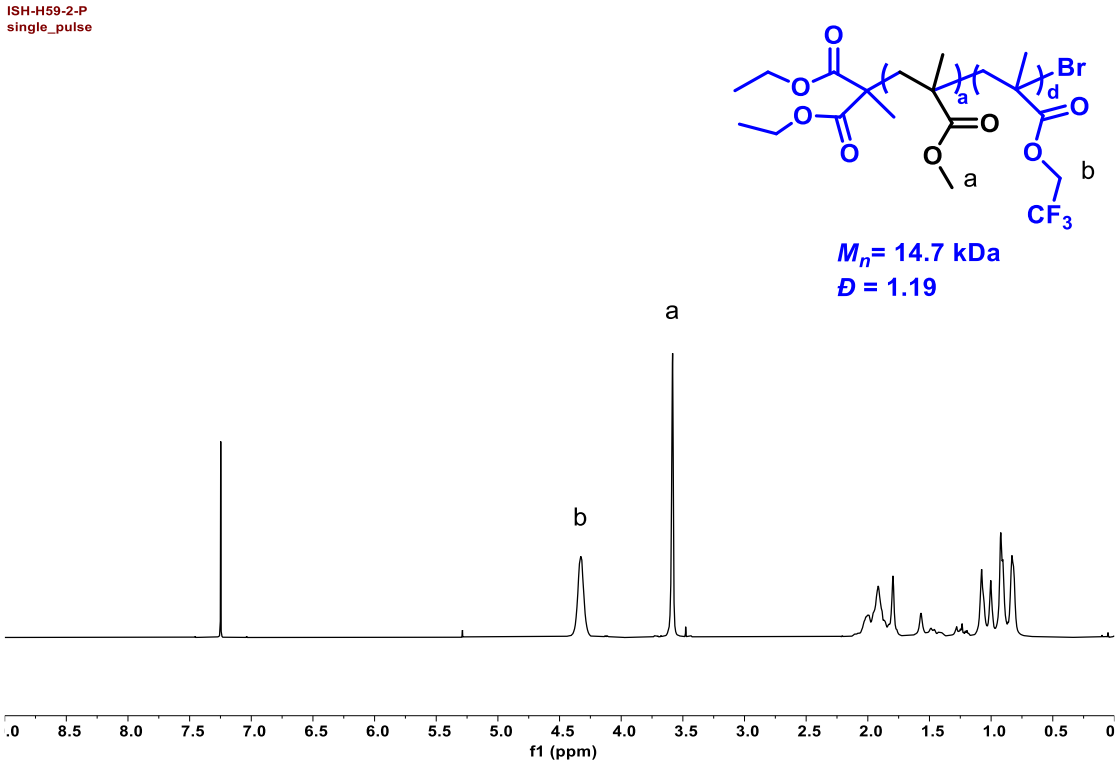


Figure S13. ^{1}H NMR of isolated PAN (DMSO-d_6, 500 MHz, DP = 50, $M_{n(NMR)}$ = 2.89 kDa).



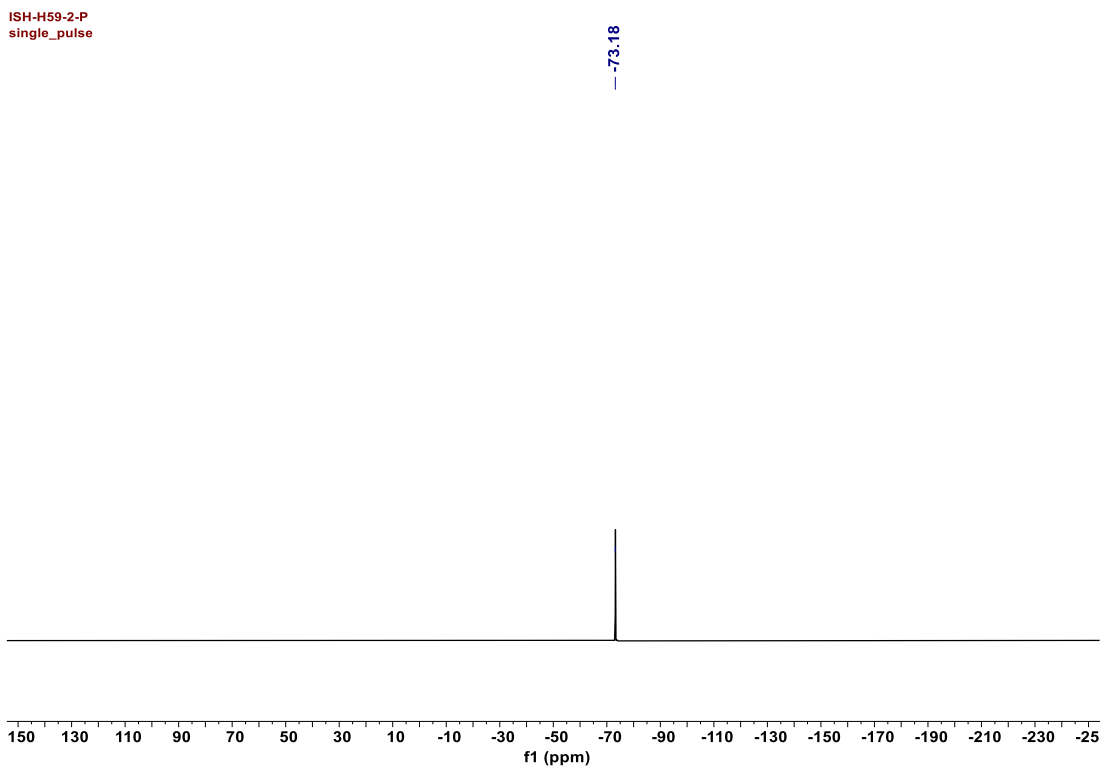


Figure S14. ^{1}H NMR and ^{19}F spectrum of isolated PMMA-*b*-TFEMA prepared by O-ATRP using **SDA-3** (50 ppm) as the catalyst. ($CDCl_3$)

5. NMR Spectra

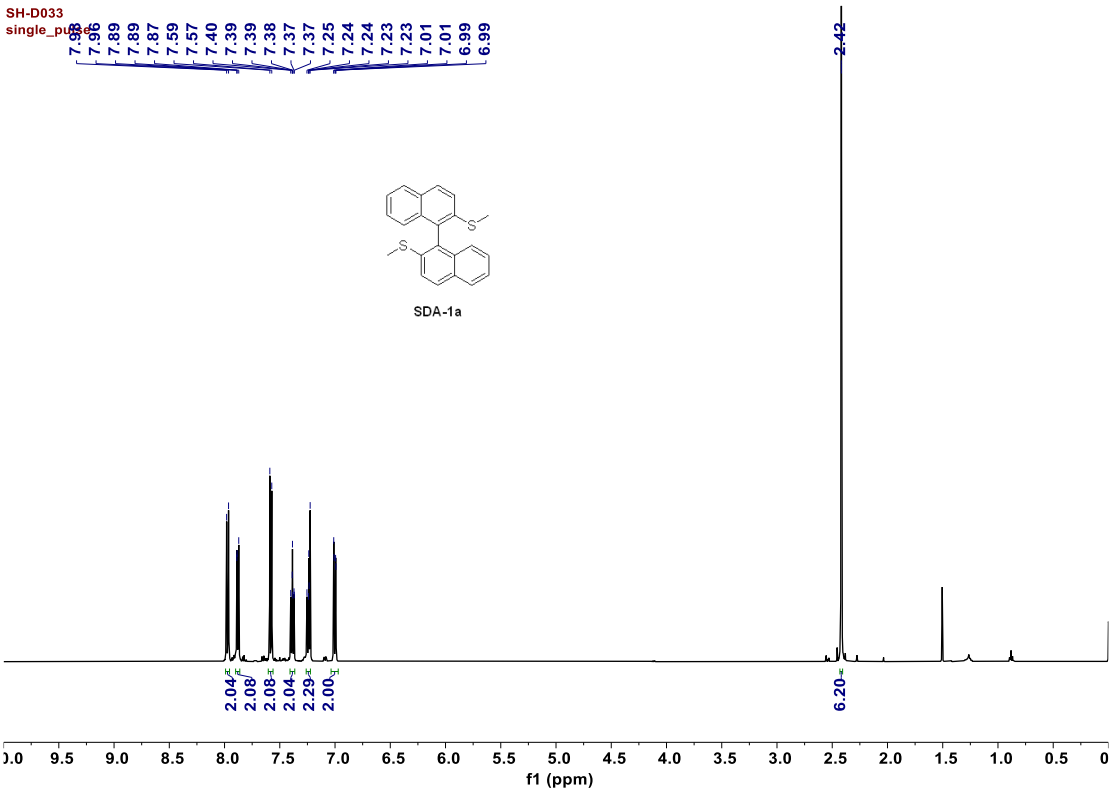


Figure S15. ^{1}H NMR of **SDA-1a** in $CDCl_3$.

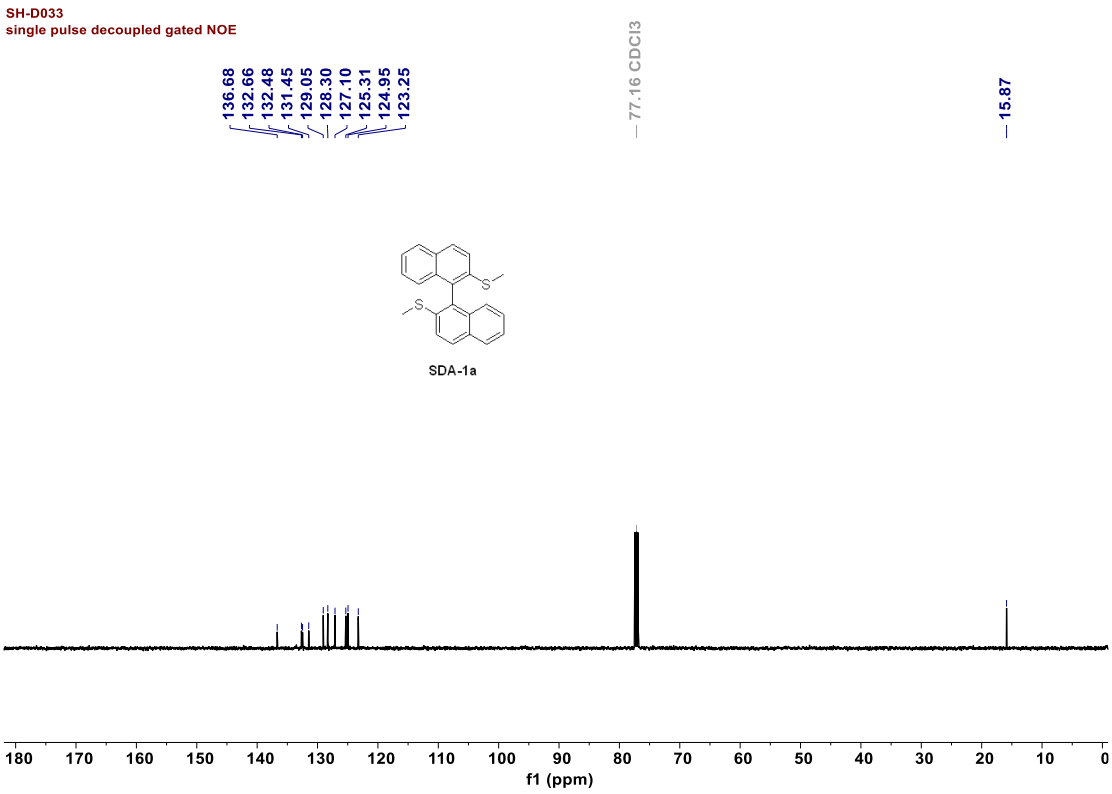


Figure S16. ^{13}C NMR of **SDA-1a** in $CDCl_3$.

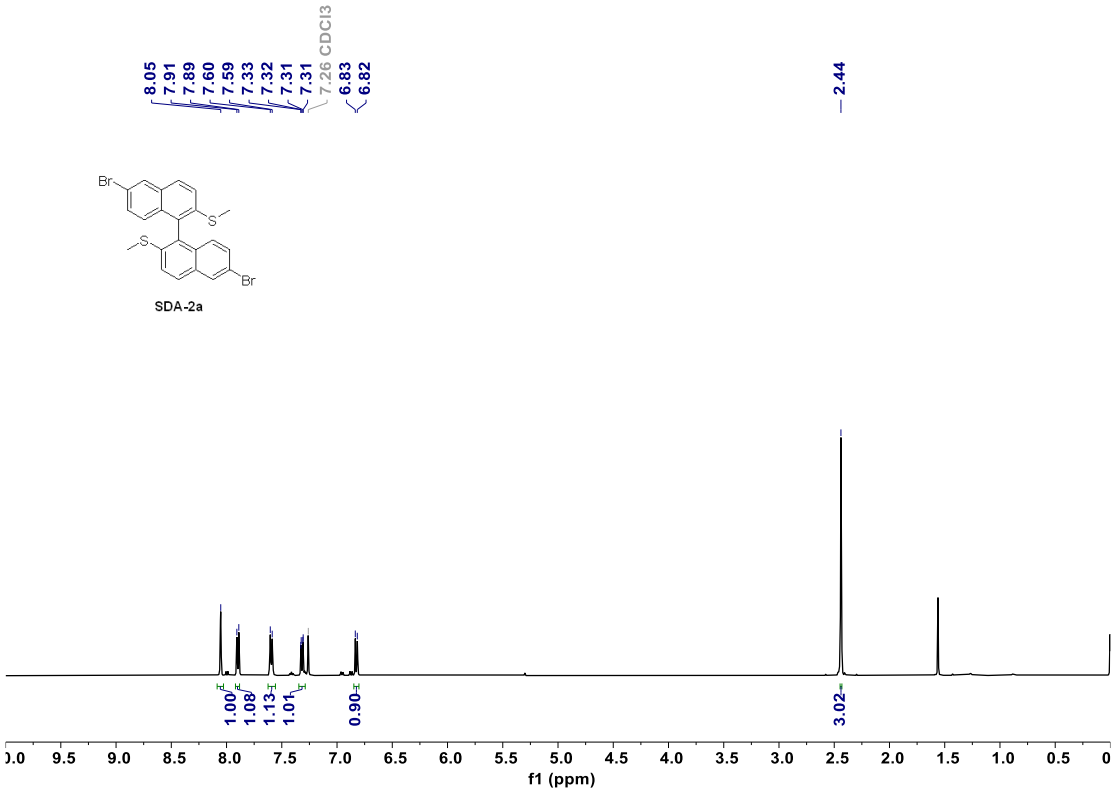


Figure S17. ^{1}H NMR of **SDA-2a** in $CDCl_3$.

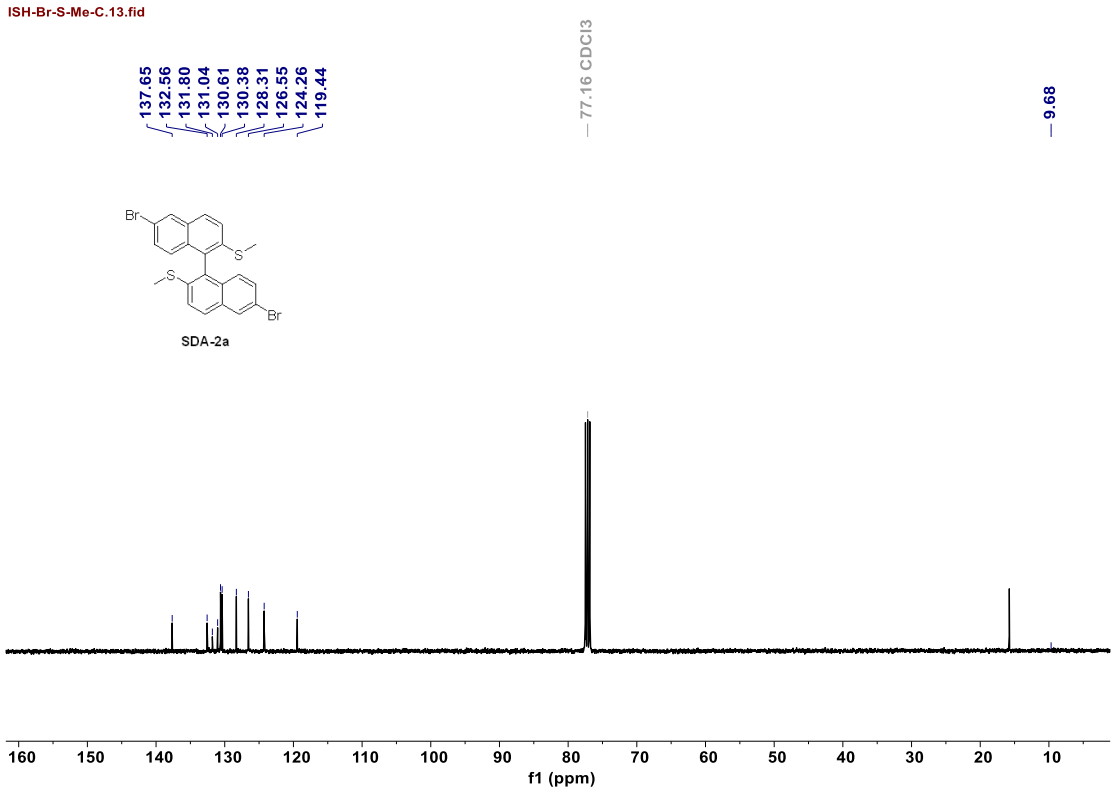


Figure S18. ^{13}C NMR of **SDA-2a** in $CDCl_3$.

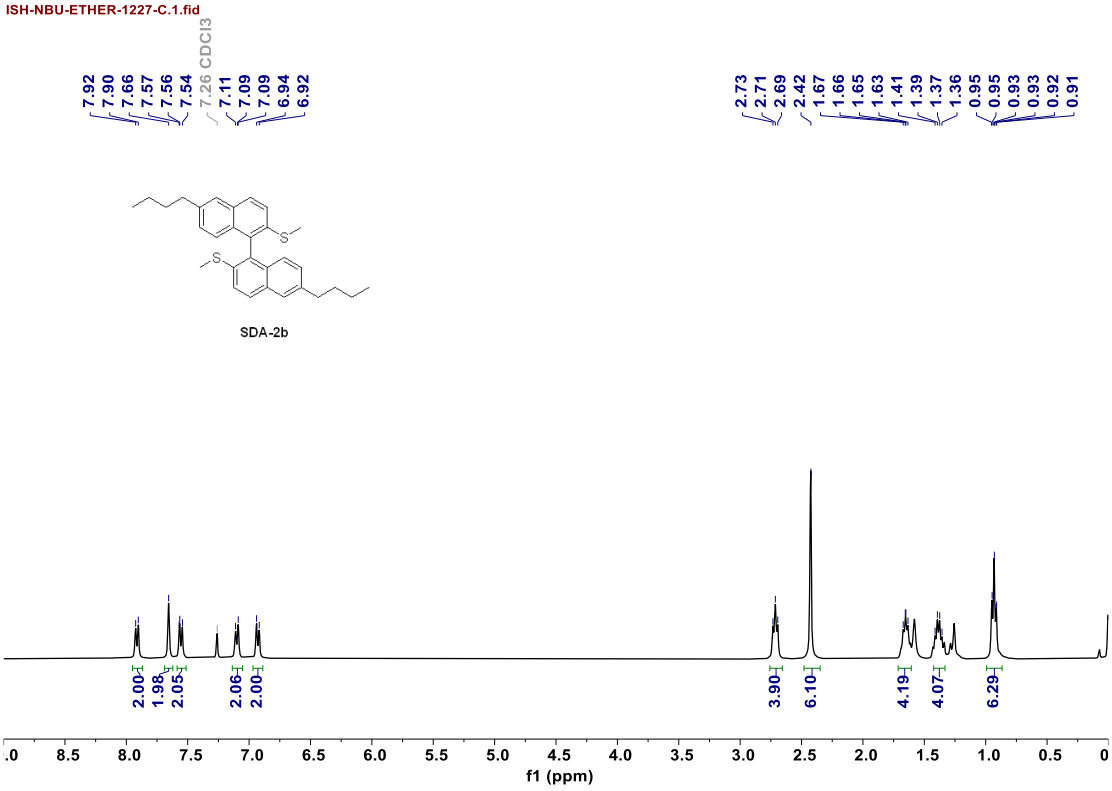


Figure S19. ^{1}H NMR of **SDA-2b** in $CDCl_3$.

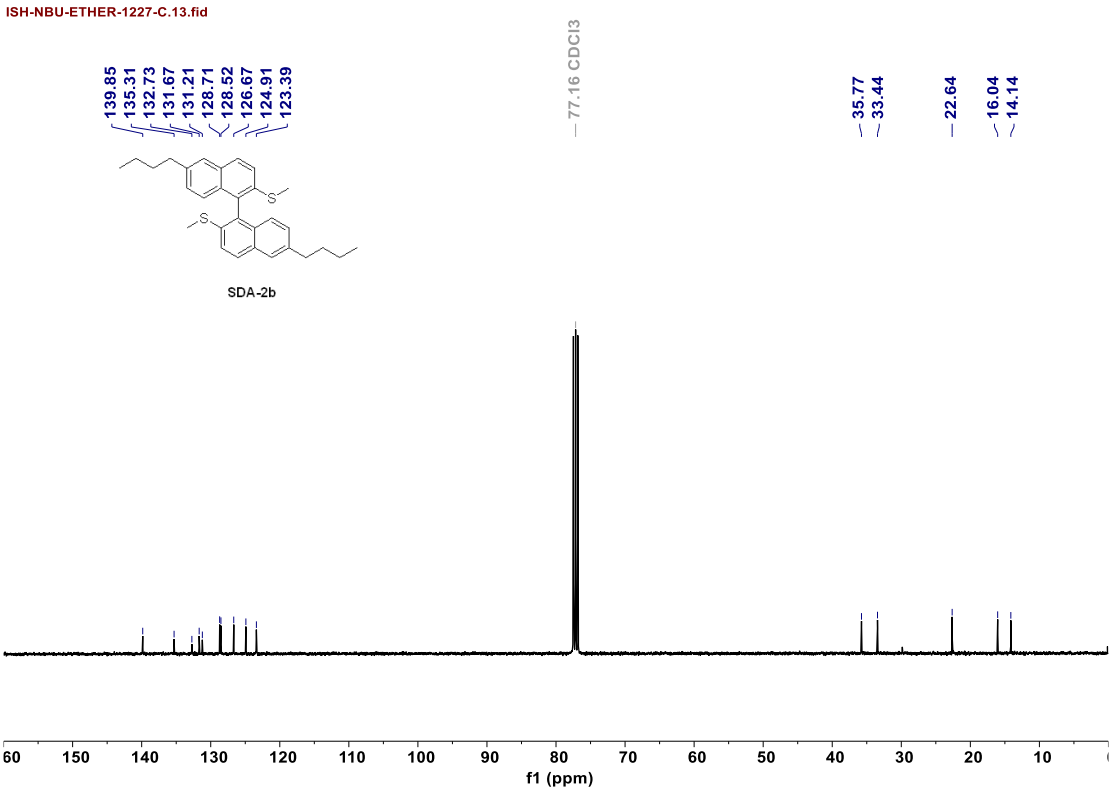


Figure S20. ^{13}C NMR of **SDA-2b** in $CDCl_3$.

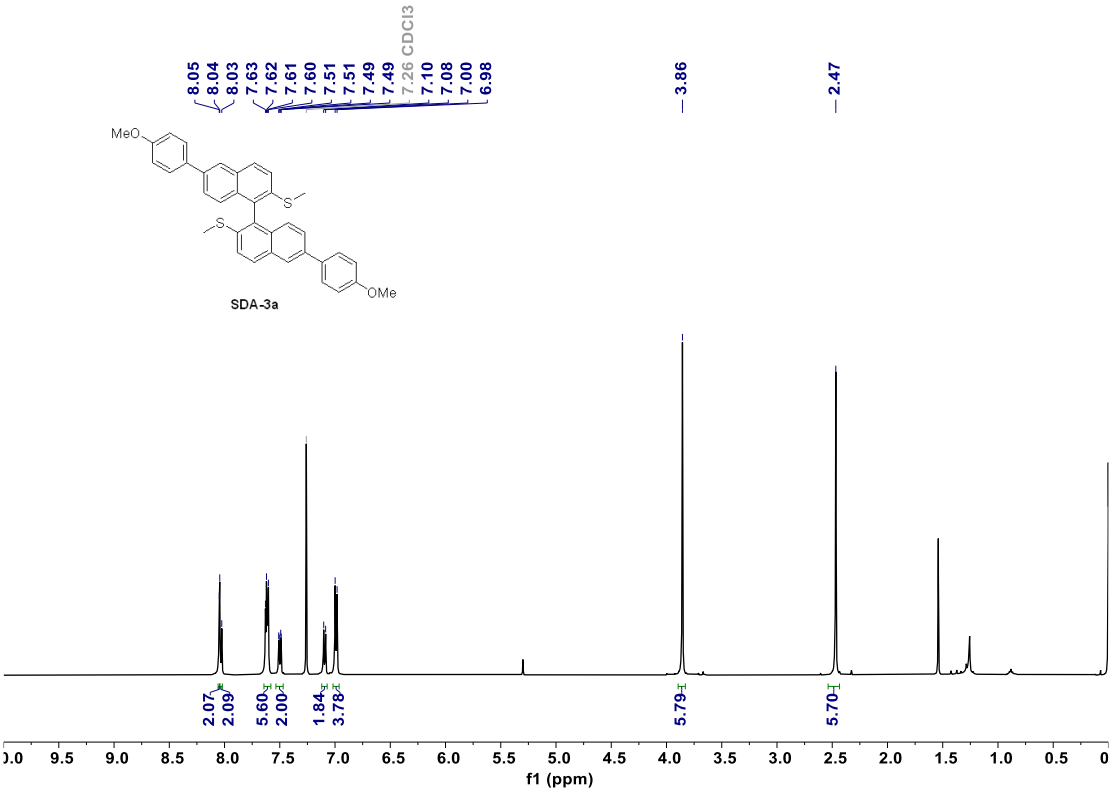


Figure S21. ^{1}H NMR of **SDA-3a** in $CDCl_3$.

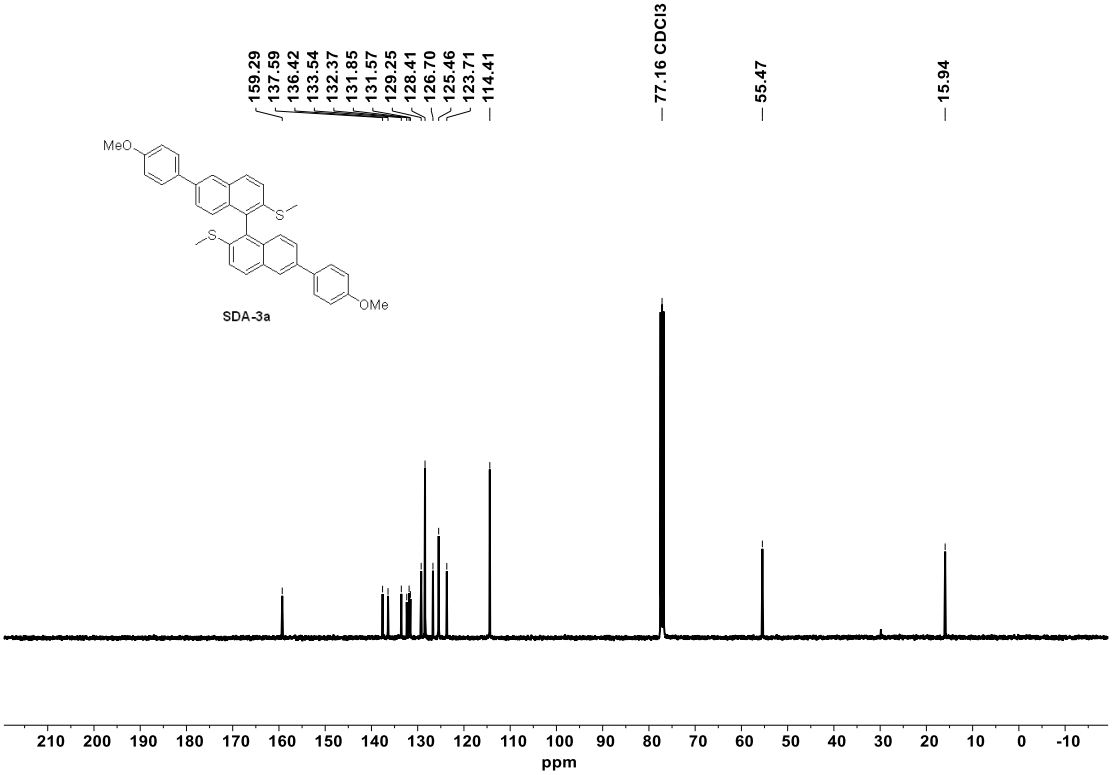


Figure S22. ^{13}C NMR of **SDA-3a** in $CDCl_3$.

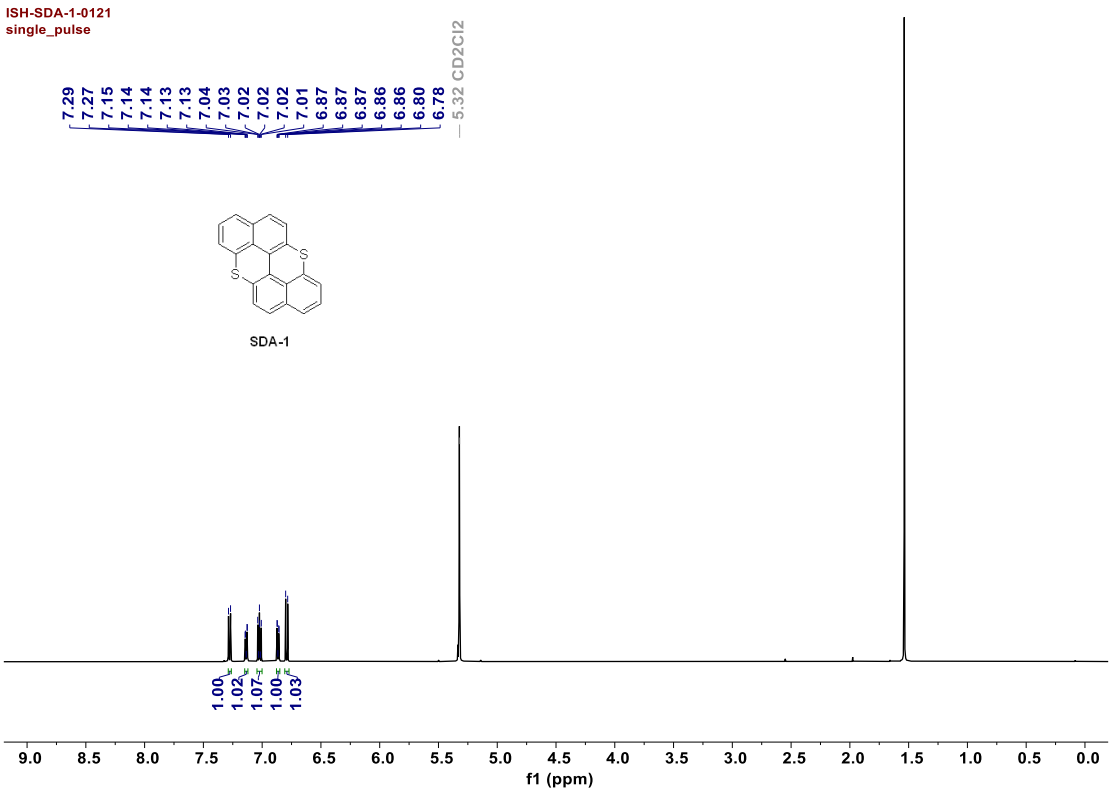


Figure S23. ^{1}H NMR of **SDA-1** in CD_2Cl_2.

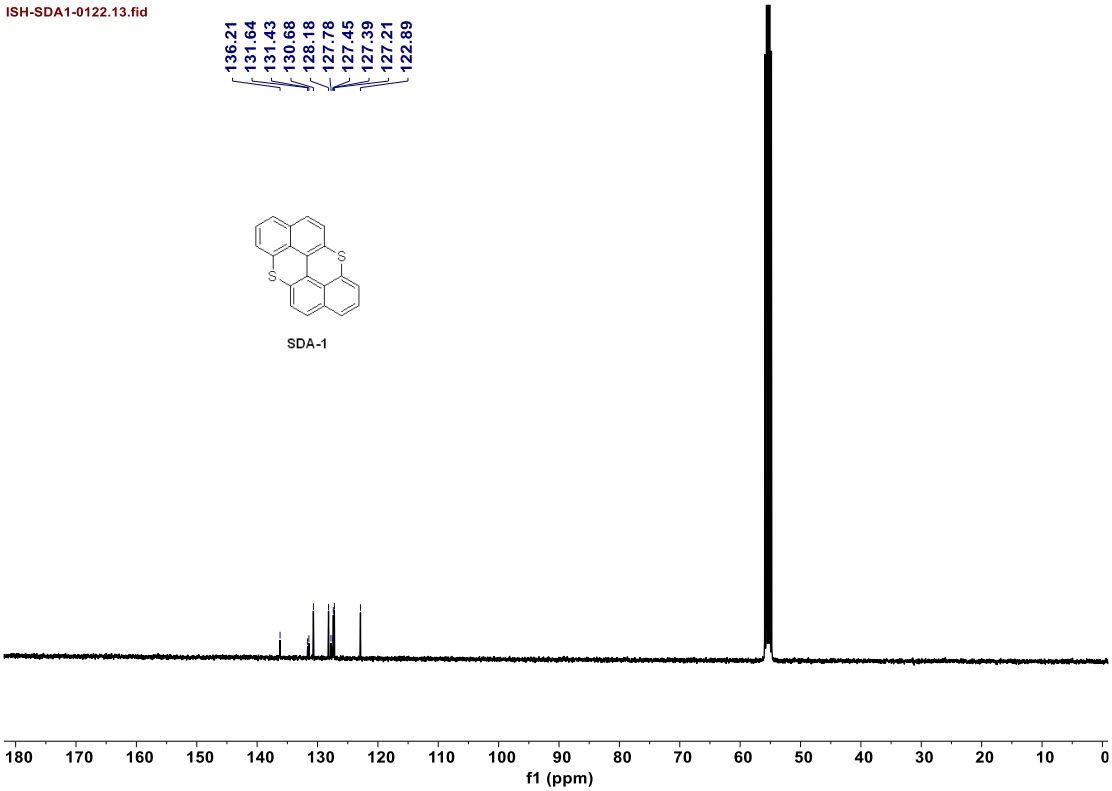


Figure S24. ^{13}C NMR of **SDA-1** in CD_2Cl_2.

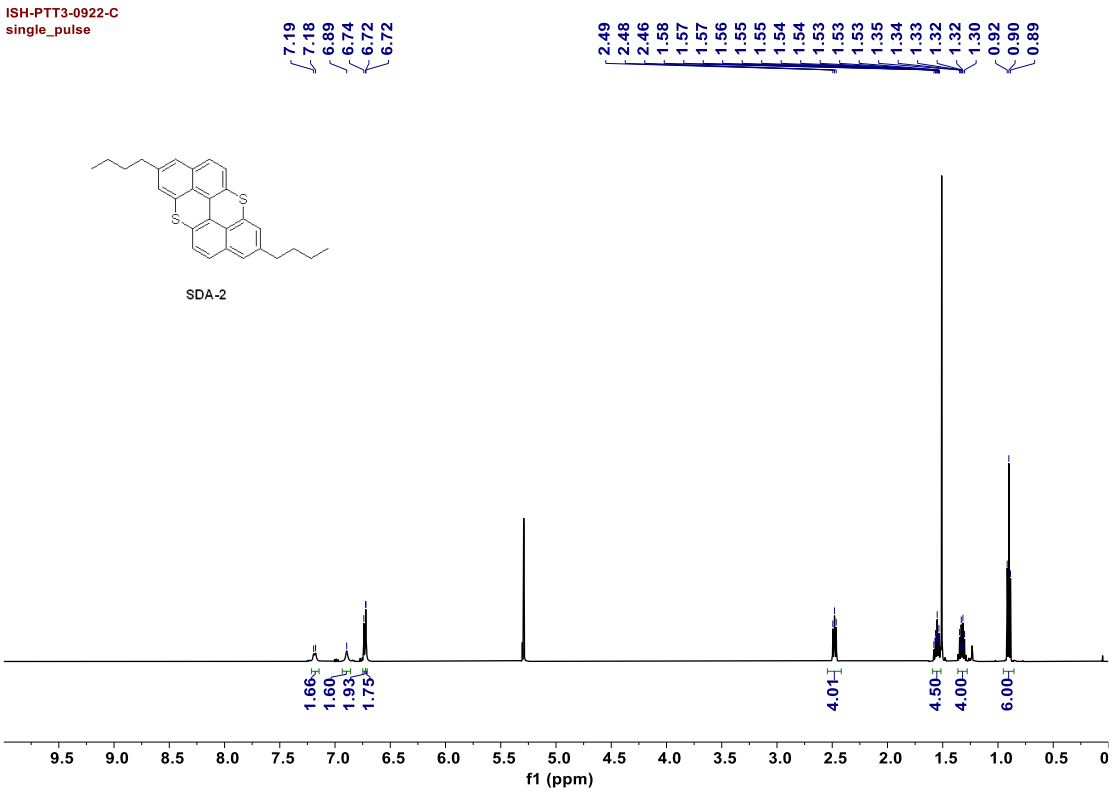


Figure S25. ^{1}H NMR of **SDA-2** in $CDCl_3$.

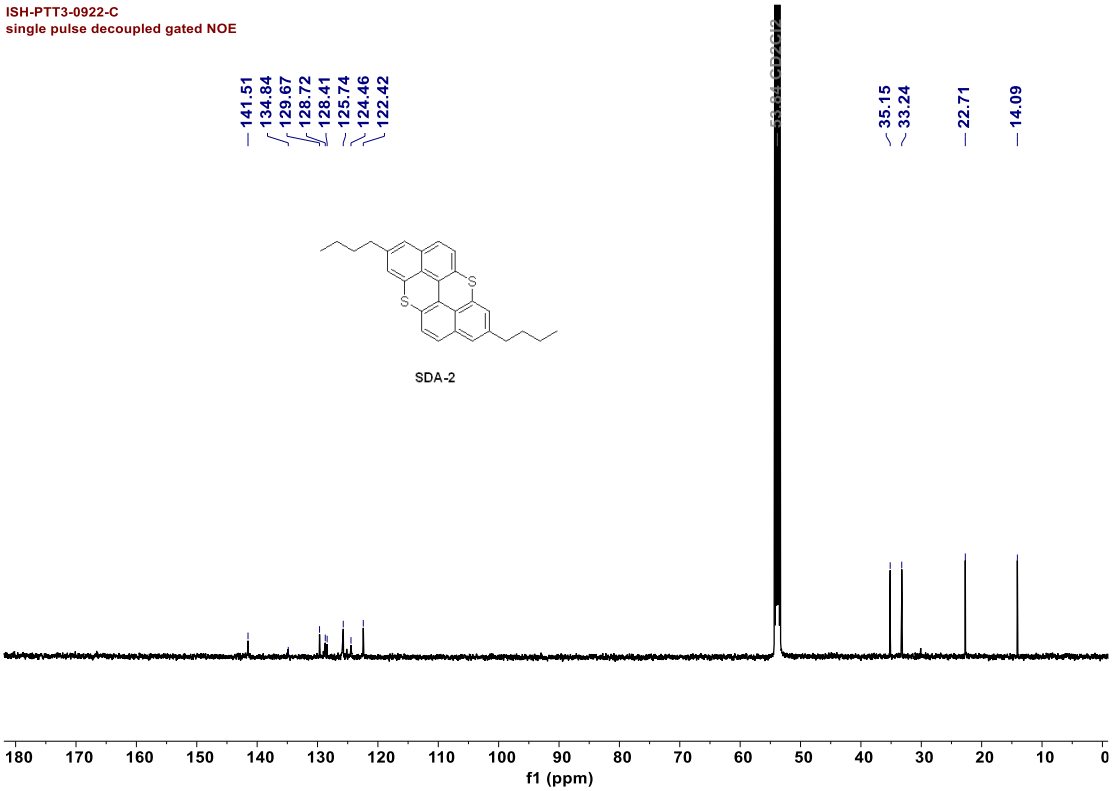


Figure S26. ^{13}C NMR of **SDA-2** in CD_2Cl_2.

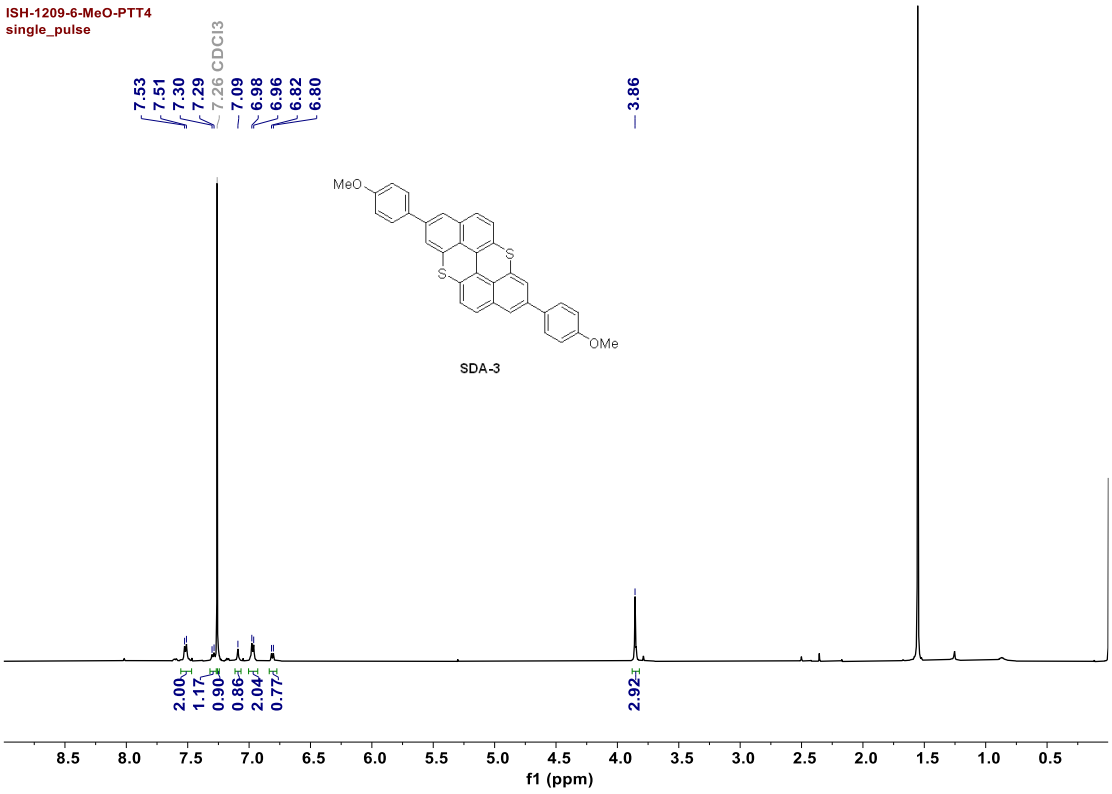


Figure S27. ^{1}H NMR of **SDA-3** in $CDCl_3$.

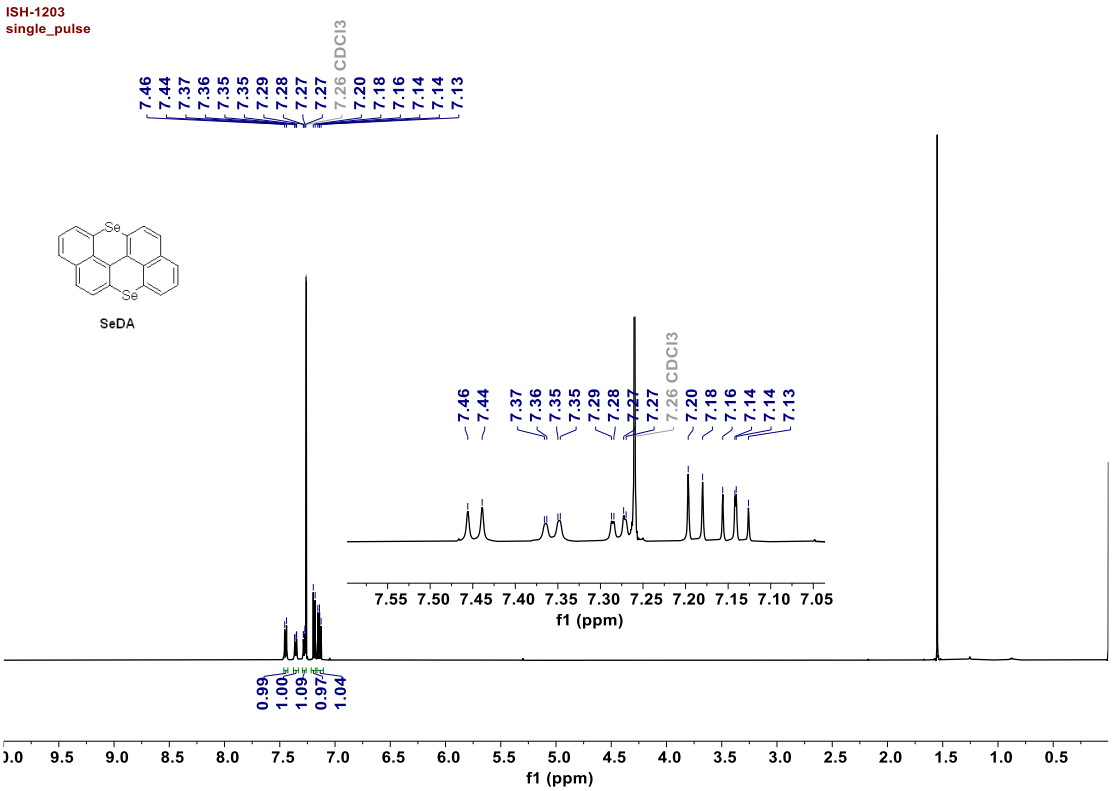


Figure S28. ^{1}H NMR of **SeDA** in $CDCl_3$.

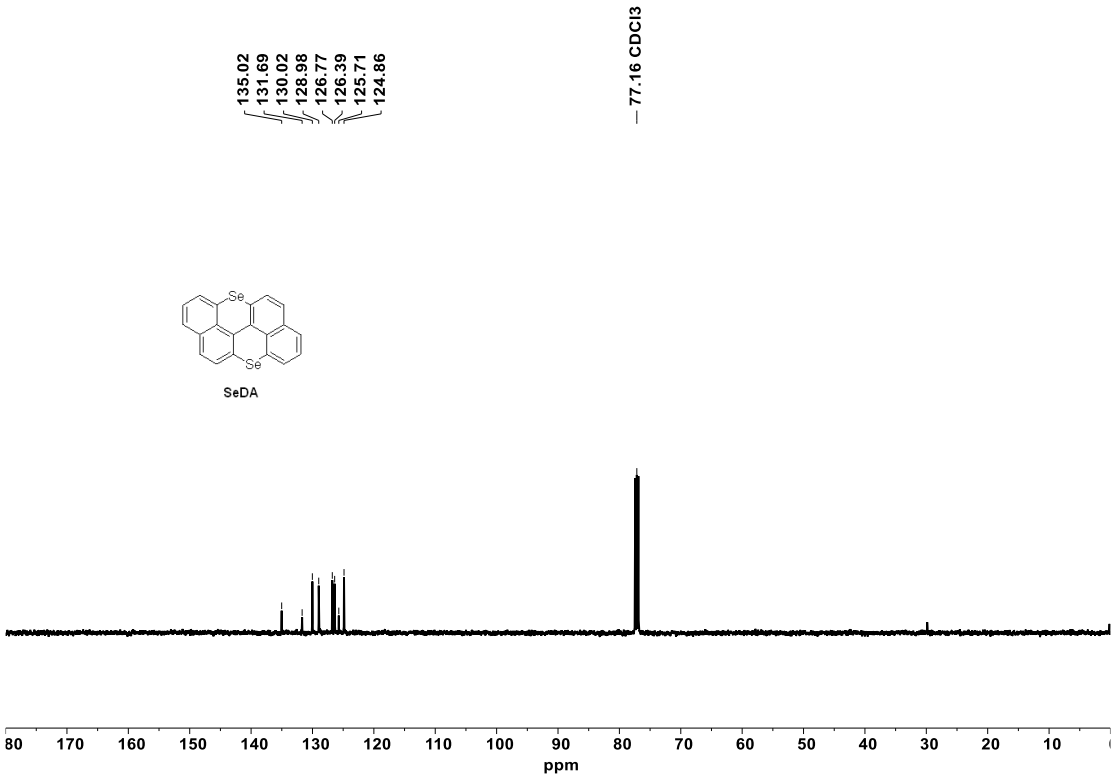


Figure S29. ^{13}C NMR of **SeDA** in $CDCl_3$.

6. Computational detail

All of the theoretical calculations were performed in Gaussian16 package. Geometries optimization calculations were carried out by a hybrid functional PBE0 with 6-31G* basis set for all atoms. Vibrational frequencies were calculated analytically at the same level to obtain the thermodynamic corrections. No imaginary frequency was obtained at optimized geometries for all species. The DCM solvation model using the self-consistent reaction field (SCRF) method with the solvents of acetonitrile was employed to account the solvent effect. The changes in Gibbs free energy are reported in the content. The redox potentials of triplet state were calculated by the energy differences of triplet states and cation radical,

$$\Delta G_{red}\ (PC^{+}/^{3}PC) = G(^{3}PC) - G(PC^{\bullet+}),$$

with the corrections to SHE (–4.48V) and to SCE (–0.244V) in acetonitrile,

$$E^{0}\ (PC^{+}/^{3}PC) = \Delta G_{red}\ (PC^{+}/^{3}PC)/\ 23.06 - 4.48 - 0.244,\ \text{in V}.$$

Computational geometries and energies

SDA-1, R=H

Triplet state

C	-2.457745	-2.561898	-0.404639
C	-1.128673	-2.889426	-0.211004
C	-0.178851	-1.907198	0.048622
C	-0.500265	-0.489486	0.054585
C	-1.929246	-0.174809	-0.023883
C	-2.885465	-1.209953	-0.272271
C	0.500263	0.489480	0.054579
C	1.929245	0.174810	-0.023889
C	2.433844	-1.126236	0.143733
C	3.800827	-1.416357	0.071915
H	4.142531	-2.438910	0.208416
C	4.710031	-0.398391	-0.187950
C	4.254058	0.899167	-0.358921
C	2.885457	1.209955	-0.272279
H	-3.193691	-3.330190	-0.621007
H	-0.815097	-3.929780	-0.252741
C	2.457728	2.561896	-0.404692
C	1.128654	2.889421	-0.211062
C	-2.433840	1.126238	0.143732
C	-3.800819	1.416375	0.071883
C	-4.710025	0.398416	-0.187999
C	0.178843	1.907195	0.048606
C	-4.254060	-0.899149	-0.358943
H	-4.142509	2.438933	0.208375
H	-4.955779	-1.705925	-0.554517
H	0.815064	3.929770	-0.252825
H	3.193670	3.330182	-0.621094
H	4.955769	1.705950	-0.554495
S	-1.394364	2.482074	0.519657
S	1.394381	-2.482097	0.519573

H -5.770879 0.622463 -0.254311

H 5.770888 -0.622434 -0.254230

Energies (0K) = -1563.347555

Energies (0K) + ZPE = -1563.113384

Enthalpies (298K) = -1563.097338

Free Energies (298K) = -1563.156312

Cation radical

C 2.527302 -2.556608 -0.000576

C 1.209480 -2.891745 -0.000450

C 0.216652 -1.884086 -0.000169

C 0.525682 -0.502763 -0.000115

C 1.928289 -0.166226 -0.000069

C 2.923433 -1.194932 -0.000307

C -0.525697 0.502764 -0.000157

C -1.928309 0.166223 -0.000156

C -2.417473 -1.164492 0.000279

C -3.780665 -1.458963 0.000685

H -4.106637 -2.495678 0.001105

C -4.720811 -0.434587 0.000501

C -4.292838 0.879549 -0.000112

C -2.923460 1.194950 -0.000405

H 3.293329 -3.326557 -0.000826

H 0.906672 -3.935233 -0.000548

C -2.527291 2.556620 -0.000857

C -1.209477 2.891749 -0.000711

C 2.417499 1.164502 0.000273

C 3.780662 1.458944 0.000430

C 4.720838 0.434545 0.000207

C -0.216640 1.884078 -0.000234

C 4.292850 -0.879546 -0.000176

H 4.106660 2.495659 0.000696

H 5.010110 -1.695369 -0.000355

H -0.906665 3.935236 -0.000955

H -3.293324 3.326566 -0.001287

H -5.010169 1.695307 -0.000339

S 1.374211 2.542910 0.000656

S -1.374220 -2.542900 0.000222

H 5.779759 0.672587 0.000330

H -5.779757 -0.672537 0.000838

Energies (0K) = -1563.235387

Energies (0K) + ZPE = -1562.997428

Enthalpies (298K) = -1562.981726

Free Energies (298K) = -1563.039776

SDA-2,R=*n*-Bu

Triplet state

C 2.031008 -2.790300 0.507545

C 0.724601 -2.940312 0.080612

C -0.051459 -1.836267 -0.257970

C 0.426865 -0.471292 -0.111196

C 1.846774 -0.341785 0.218014

C 2.625959 -1.496109 0.541874

C -0.440311 0.623836 -0.202991

C -1.886451 0.485466 -0.379024

C -2.504417 -0.730693 -0.715675

C -3.886549 -0.849106 -0.887851

H -4.313466 -1.814732 -1.150900

C -4.723697 0.252378 -0.714620

C -4.137234 1.469768 -0.381570

C -2.749559 1.614678 -0.221086

H 2.627178 -3.654678 0.783958

H 0.293769 -3.935466 -0.002011

C -2.199887 2.896109 0.071816

C -0.828641 3.065879 0.124054

C 2.520669 0.891381 0.232696

C	3.878062	1.001677	0.546411
C	4.627983	-0.126774	0.877321
C	0.035469	1.988437	-0.043344
C	3.984889	-1.360442	0.870405
H	4.351180	1.981356	0.545075
H	4.546468	-2.258676	1.119950
C	-6.216180	0.111311	-0.829199
C	-6.870049	-0.229438	0.514646
H	-6.457682	-0.674094	-1.556706
H	-6.645343	1.046444	-1.211294
C	-8.384450	-0.375711	0.414300
H	-6.433496	-1.161063	0.901749
H	-6.621850	0.553961	1.244730
C	-9.031876	-0.712374	1.751232
H	-8.812372	0.557016	0.020391
H	-8.624092	-1.157620	-0.320148
H	-10.119361	-0.813388	1.656643
H	-8.642872	-1.656672	2.152204
H	-8.832998	0.069534	2.494783
C	6.098164	-0.014120	1.172126
C	6.950718	-0.097034	-0.099076
H	6.397414	-0.815112	1.859887
H	6.301350	0.937617	1.679704
C	8.444866	0.014875	0.183647
H	6.741412	-1.046509	-0.611848
H	6.644708	0.700683	-0.790729
C	9.289556	-0.065781	-1.081251
H	8.644596	0.963316	0.702105
H	8.742028	-0.783332	0.878472
H	10.359237	0.016123	-0.855744
H	9.130632	-1.017951	-1.602707
H	9.033308	0.740592	-1.779748
H	-0.412878	4.056966	0.290275
H	-2.869437	3.738407	0.217261

H -4.765237 2.348759 -0.249740

S 1.722538 2.386565 -0.204342

S -1.579483 -2.186003 -1.014825

Energies (0K) = -1877.521141

Energies (0K) + ZPE = -1877.058738

Enthalpies (298K) = -1877.030999

Free Energies (298K) = -1877.119582

Cation radical

C -1.956990 -2.841961 -0.398873

C -0.604119 -2.904449 -0.273734

C 0.162500 -1.717672 -0.196366

C -0.418799 -0.428572 -0.244567

C -1.852458 -0.382467 -0.376776

C -2.618592 -1.587981 -0.452755

C 0.401911 0.769744 -0.160901

C 1.834889 0.722871 -0.023712

C 2.584964 -0.476016 0.038587

C 3.973788 -0.488618 0.167377

H 4.486659 -1.445629 0.203805

C 4.707577 0.695088 0.246978

C 3.997531 1.890442 0.187454

C 2.602902 1.927822 0.055892

H -2.548662 -3.750705 -0.457785

H -0.099973 -3.866101 -0.232757

C 1.942365 3.182933 -0.002050

C 0.590239 3.245816 -0.132257

C -2.601884 0.819053 -0.441889

C -3.988035 0.828252 -0.568502

C -4.721349 -0.359120 -0.641154

C -0.177857 2.059565 -0.211953

C -4.016234 -1.553401 -0.581962

H -4.512500 1.780407 -0.616024

H -4.548857 -2.499801 -0.639220

C	6.207130	0.718420	0.399112
C	6.924989	-0.620115	0.278218
H	6.439356	1.168117	1.375574
H	6.610312	1.419023	-0.345172
C	8.438929	-0.475165	0.403929
H	6.565877	-1.309699	1.055206
H	6.683987	-1.085034	-0.688411
C	9.170575	-1.805970	0.291961
H	8.802215	0.211792	-0.373063
H	8.678171	-0.003067	1.367047
H	10.254645	-1.674141	0.384771
H	8.851773	-2.501719	1.078002
H	8.975697	-2.286226	-0.674992
C	-6.220198	-0.331858	-0.734445
C	-6.889816	-0.265274	0.644364
H	-6.567072	-1.228728	-1.261885
H	-6.532489	0.535703	-1.329034
C	-8.411935	-0.229937	0.554038
H	-6.575074	-1.132693	1.241165
H	-6.531181	0.625581	1.178854
C	-9.081305	-0.167692	1.920639
H	-8.718228	0.637541	-0.047078
H	-8.762628	-1.118894	0.011470
H	-10.173276	-0.143518	1.829194
H	-8.818013	-1.039905	2.531735
H	-8.773892	0.728923	2.473003
H	0.086816	4.207768	-0.175183
H	2.534343	4.091349	0.058647
H	4.530814	2.836862	0.242036
S	-1.862150	2.382352	-0.377308
S	1.848205	-2.038578	-0.039555

Energies (0K) = -1877.373931

Energies (0K) + ZPE = -1876.908672

Enthalpies (298K) = -1876.881007

Free Energies (298K) = -1876.969318

SDA-3,R=*p*-MeOC$_6$H$_4$

Triplet state

C	2.105788	-2.807844	0.175362
C	0.742161	-2.958550	0.004481
C	-0.077816	-1.860053	-0.232658
C	0.427110	-0.497168	-0.241990
C	1.881916	-0.372336	-0.184473
C	2.702847	-1.520176	0.046257
C	-0.436287	0.605737	-0.223248
C	-1.888577	0.480272	-0.121021
C	-2.567544	-0.739628	-0.281194
C	-3.955355	-0.849061	-0.182244
H	-4.417435	-1.827074	-0.286497
C	-4.745430	0.271922	0.093791
C	-4.094327	1.496364	0.254668
C	-2.701496	1.625761	0.146582
H	2.738847	-3.667085	0.374474
H	0.297991	-3.950147	0.047832
C	-2.100442	2.912230	0.268660
C	-0.742959	3.064672	0.055849
C	2.555701	0.848937	-0.354939
C	3.946109	0.957562	-0.299274
C	4.744433	-0.165533	-0.058084
C	0.068839	1.968395	-0.217457
C	4.098308	-1.391718	0.110717
H	4.404795	1.936365	-0.410268
H	4.684067	-2.294253	0.265328
H	-0.297272	4.055842	0.094014
H	-2.726746	3.769414	0.496044
H	-4.674839	2.396959	0.437840
S	1.698676	2.333955	-0.707386

S	-1.722391	-2.221308	-0.673969
C	-6.213561	0.161447	0.206412
C	-6.936410	-0.747729	-0.573869
C	-6.935758	0.969647	1.101022
C	-8.320897	-0.857256	-0.479247
H	-6.415801	-1.371557	-1.296105
C	-8.312103	0.871041	1.208808
H	-6.407144	1.671156	1.741283
C	-9.019648	-0.044421	0.418160
H	-8.841930	-1.567644	-1.112177
H	-8.863174	1.490724	1.910720
O	-10.359069	-0.067094	0.592935
C	-11.114103	-0.981760	-0.180892
H	-10.820182	-2.018801	0.022923
H	-12.154493	-0.838005	0.116909
H	-11.014624	-0.778085	-1.254250
C	6.215361	-0.055458	0.010848
C	6.963086	-0.871700	0.866835
C	6.915654	0.870649	-0.781162
C	8.350304	-0.782674	0.940038
H	6.454310	-1.581557	1.514039
C	8.294913	0.969838	-0.721795
H	6.373819	1.506540	-1.476606
C	9.027330	0.142694	0.140360
H	8.888387	-1.428520	1.625621
H	8.830951	1.679073	-1.346298
O	10.367533	0.312109	0.127409
C	11.149119	-0.513212	0.971981
H	12.186619	-0.220604	0.799500
H	10.901232	-0.356211	2.028936
H	11.026753	-1.574327	0.721954

Energies (0K) = -2253.735743

Energies (0K) + ZPE = -2253.272675

Enthalpies (298K) = -2253.241804

Free Energies (298K) = -2253.335816

Cation radical

C	2.091601	2.922674	0.020379
C	0.737187	3.046228	0.014422
C	-0.086318	1.895200	0.014160
C	0.439077	0.580963	0.014487
C	1.872845	0.470688	0.018412
C	2.697562	1.639192	0.027689
C	-0.439070	-0.580958	0.014490
C	-1.872838	-0.470688	0.018441
C	-2.574840	0.761775	0.015791
C	-3.962186	0.835194	0.029543
H	-4.434510	1.813210	0.059667
C	-4.758599	-0.318793	0.037342
C	-4.096070	-1.544905	0.034056
C	-2.697558	-1.639189	0.027718
H	2.726562	3.803827	0.021692
H	0.277424	4.030901	0.011351
C	-2.091594	-2.922673	0.020412
C	-0.737180	-3.046223	0.014463
C	2.574858	-0.761772	0.015663
C	3.962209	-0.835177	0.029280
C	4.758603	0.318825	0.037175
C	0.086331	-1.895192	0.014162
C	4.096077	1.544926	0.034005
H	4.434538	-1.813192	0.059232
H	4.662955	2.470945	0.013053
H	-0.277416	-4.030897	0.011435
H	-2.726559	-3.803824	0.021744
H	-4.662967	-2.470911	0.013030
S	1.763804	-2.291422	0.010740
S	-1.763793	2.291425	0.010748
C	6.228982	0.235344	0.046001

C	6.901927	-0.830076	-0.564696
C	7.005789	1.229239	0.668403
C	8.289889	-0.913240	-0.565931
H	6.340174	-1.604749	-1.080012
C	8.386258	1.157457	0.679688
H	6.520235	2.057557	1.177420
C	9.044127	0.084938	0.060163
H	8.771983	-1.748822	-1.061478
H	8.981160	1.920471	1.173317
C	-6.228981	-0.235309	0.046134
C	-7.005829	-1.229252	0.668449
C	-6.901909	0.830163	-0.564489
C	-8.386287	-1.157481	0.679634
H	-6.520272	-2.057548	1.177497
C	-8.289873	0.913327	-0.565812
H	-6.340106	1.604934	-1.079602
C	-9.044126	-0.084946	0.060088
H	-8.981271	-1.920474	1.173199
H	-8.771931	1.749021	-1.061212
O	-10.389594	-0.104194	0.119943
O	10.389590	0.104143	0.120061
C	-11.100746	0.966874	-0.478270
H	-12.157848	0.751572	-0.313062
H	-10.848443	1.925264	-0.008689
H	-10.906855	1.023448	-1.556118
C	11.100693	-0.967042	-0.478016
H	12.157784	-0.752075	-0.312318
H	10.847936	-1.925418	-0.008657
H	10.907215	-1.023414	-1.555951

Energies (0K) = -2253.625463

Energies (0K) + ZPE = -2253.157927

Enthalpies (298K) = -2253.127512

Free Energies (298K) = -2253.219684

SeDA

Triplet state

C	1.734656	-3.066366	0.701392
C	0.384985	-3.070055	0.411983
C	-0.271251	-1.900007	0.049118
C	0.373078	-0.596805	0.056028
C	1.841711	-0.645925	0.164373
C	2.490825	-1.874252	0.519850
C	-0.373069	0.596798	0.056047
C	-1.841702	0.645930	0.164367
C	-2.687984	-0.450113	-0.077517
C	-4.079309	-0.372812	0.033679
H	-4.679894	-1.256034	-0.167204
C	-4.682602	0.819518	0.412158
C	-3.889821	1.928828	0.653958
C	-2.490805	1.874253	0.519889
H	2.244425	-3.974938	1.007599
H	-0.181643	-3.997174	0.454969
C	-1.734616	3.066342	0.701530
C	-0.384936	3.070033	0.412122
C	2.687987	0.450134	-0.077490
C	4.079299	0.372863	0.033782
C	4.682602	-0.819465	0.412276
C	0.271275	1.900009	0.049174
C	3.889840	-1.928801	0.653986
H	4.679877	1.256098	-0.167063
H	4.341954	-2.875811	0.937712
H	0.181699	3.997146	0.455145
H	-2.244373	3.974899	1.007800
H	-4.341930	2.875835	0.937703
H	5.762722	-0.878152	0.512494
H	-5.762726	0.878234	0.512312
Se	2.003333	2.112873	-0.597049

Se -2.003365 -2.112895 -0.596942

Energies (0K) = -5565.377241

Energies (0K) + ZPE = -5565.144086

Enthalpies (298K) = -5565.127449

Free Energies (298K) = -5565.188849

Cation radical

C 1.826632 -3.132586 -0.002679

C 0.471741 -3.116432 -0.001593

C -0.234985 -1.890163 -0.000368

C 0.394516 -0.621798 -0.000443

C 1.849303 -0.657582 -0.000757

C 2.546460 -1.913426 -0.001955

C -0.394521 0.621795 -0.000662

C -1.849310 0.657584 -0.000751

C -2.697320 -0.480346 0.000630

C -4.088399 -0.392315 0.001136

H -4.674202 -1.308097 0.002328

C -4.725057 0.841920 -0.000112

C -3.950416 1.983614 -0.001840

C -2.546467 1.913433 -0.002065

H 2.376375 -4.069141 -0.003764

H -0.090129 -4.046622 -0.001777

C -1.826622 3.132586 -0.003335

C -0.471736 3.116426 -0.002414

C 2.697333 0.480351 0.000562

C 4.088397 0.392317 0.000712

C 4.725056 -0.841931 -0.000749

C 0.234992 1.890150 -0.000682

C 3.950423 -1.983616 -0.002140

H 4.674232 1.308082 0.001825

H 4.411163 -2.967150 -0.003214

H 0.090136 4.046615 -0.003054

H -2.376366 4.069141 -0.004717

H	-4.411187	2.967134	-0.002862
H	5.808881	-0.899851	-0.000722
H	-5.808881	0.899868	0.000269
Se	2.047646	2.204624	0.002188
Se	-2.047650	-2.204620	0.001715

Energies (0K) = -5565.268040

Energies (0K) + ZPE = -5565.030069

Enthalpies (298K) = -5565.013897

Free Energies (298K) = -5565.074265

7. Reference

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