Supporting Information

Carborane based Chalcogen-fused Phenazines for Visible Light induced ATRP

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Experimental Procedures

1. Materials and instrumentation

General. All reactions were performed using standard Schlenk under argon atmosphere. Toluene was distilled from sodium/benzophenone prior to use. selenium (98%), sulfolane (99%), diphenylamine (99%), selenium dioxide (99%), *N*,*N*-dimethylaniline (99%), Pd(PPh_3)$_4$ (99%), *N*,*N*-dimethylaniline (99%), bis(4-bromophenyl)acetylene (99%) were purchased from Energy Chemical Inc. Decaborane (99%) was purchased from Zhengzhou Alfa Chemical Co. Ltd. If no other special indicated, other reagents and solvents were used as commercially available without further purification. Column chromatographic purification of products was accomplished using 200-300 mesh silica gel.

NMR spectra were measured on a Bruker Avance-400 spectrometer in the solvents indicated; chemical shifts are reported in units (ppm) by assigning TMS resonance in the ^{1}H spectrum as 7.26 ppm, $CDCl_3$ or 2.50 ppm, DMSO-d^6 resonance in the ^{13}C spectrum as 77.0 ppm or 35.0 ppm. Coupling constants are reported in Hz with multiplicities denoted as s (singlet), d (doublet), t (triplet), q (quartet) and m (multiplet). UV-vis measurements were performed using UV-2600 Scan spectrophotometer. Cyclic Voltammetry was performed under Ar atmosphere with a CHI 660E potentiostation in a solution of anhydrous THF with 0.1 M tetrabutylammonium hexafluorophosphate as supporting electrolyte, at a scan rate of 50 mV s^{-1}. A glassy carbon was used as working electrode; a platinum wire was used as the auxiliary electrode, and an Ag/AgCl was used as reference electrode. Under these conditions, $E_{1/2}$ = 0.56 V for the $FeCp_2^+$/ $FeCp_2$ couple.

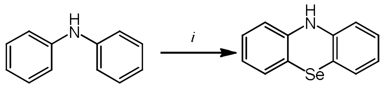
The cyclic voltammetry (CV) were measured using CHI 660E, with a polished gold electrode as the working electrode, a Pt-net as counter electrode, and an Ag wire as reference electrode, using ferrocene/ferrocenium (Fc/Fc$^+$) as internal standard. High-resolution mass spectra (HRMS) were collected on a Bruker maXisUHR-TOF mass spectrometer in an ESI positive mode.

General Polymerization Procedure: A 20 mL vial was charged with a small stirbar and catalysts (***o*-CB-DPE**). Then transferred into a nitrogen-atmosphere glovebox. Next solvent (DMA), monomer (MMA) and initiator (EBP) were added sequentially via pipette. The vial was then sealed with foil paper, placed inside a beaker illuminated by white LED light (390 nm, 5 W) and stirred. To analyze the progress of a polymerization at a given time point, a 0.1 mL aliquot of the reaction media was removed via syringe and injected into a vial containing 0.7 mL CDCl3 with 250 ppm butylated hydroxytoluene (BHT). This aliquot was then analyzed by ^{1}H NMR for conversion, dried under reduced pressure, and then re-dissolved in THF for analysis of Mw and Mn by gel permeation chromatography coupled with multi-angle light scattering.

Isolation Procedure: isolation was performed by pouring the reaction mixture into a 50-fold excess of CH_3OH, causing the polymer to precipitate. After 1 hour of stirring, the precipitate was collected via vacuum filtration and dried under reduced pressure.

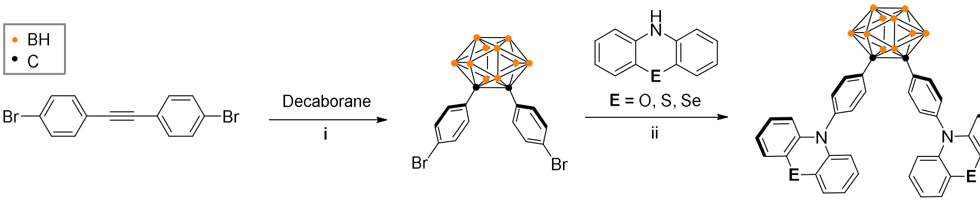
2. Synthetic procedures

Synthesis of 10*H*-phenoselenazine [1]



To a mixture of selenium (1.00 g, 12.79 mmol) in 5 mL of sulfolane, the appropriate diphenylamine (10 mmol), selenium dioxide (1.20 eq.) and iodine (0.1 eq.) were added. The reaction mixture was sealed in a pressure vial with a Teflon bushing and placed in an oil bath at 150 °C for 5 hours. Upon completion, the reaction mixture was cooled to room temperature and was filtered through a Celite plug using dichloromethane (DCM). The solvent was evaporated in vacuo and recrystallized using EtOH and then subsequently purified twice or thrice by flash chromatography using hexane: EtOAc (5: 1) as the eluent. The desired compound 10*H*-Phenoselenazine was obtained in 20% yield. Yellow solid. Mp = 195–197 °C. ^{1}H NMR (400 MHz, DMSO-d^6): δ 8.59 (s, 1 H), 7.11–7.08 (m, 2 H), 7.05–7.00 (m, 2 H), 6.78–6.74 (m, 4 H); ^{13}C NMR (100 MHz, DMSO-d^6): δ 142.58, 129.35, 128.28, 122.61, 115.62, 111.98; HRMS (ESI) m/z calcd. for $C_{12}H_{10}NSe$ [M + H]$^+$ 247.9973, found 247.9979.

Synthesis of *o*-CB-DPE.



1

2

o-CB-DPE E = O, S, Se

(1) Decaborane (1.22 g, 10 mmol) was dissolved in 80 mL of toluene and *N*,*N*-dimethylaniline (1.75 mL, 13.8 mmol) under Ar atmosphere. After the mixture was stirred at room temperature for 1 h. Bis(4-bromophenyl)acetylene **1** (3 g, 9 mmol) was added, and the mixture was additionally refluxed for 2 d. Then cooling to room temperature, insoluble products were removed by filtration, and the solvent was evaporated. The residue was purified by column chromatography on a silica gel (hexane/DCM v/v = 10:1). After evaporation of solvents, recrystallization from DCM/hexane afforded the desired compound **2** as a white powder (3.1 g, 76%)[2].

The date of **2**. melting point: 199-201 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.26-7.32 (m, 8H), 3.05-2.07 (cage 10H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 132.04, 131.75, 129.58, 125.40, 84.12. ^{11}B {^{1}H} NMR (128 MHz, $CDCl_3$): δ –3.03 (2B), -11.14-11.56 (8B). HRMS calcd for $C_{14}H_{18}B_{10}Br_2$ [M+H]$^+$ 455.0779; found: 455.0783.

(2) Phenoxazine (0.916 g, 5 mmol) or Phenothiazine (1.0 g, 5 mmol) or phenoselenazine (1.24 g, 5 mmol) and 1-bromobenzene (0.5 mL, 5.5 mmol) were dissolved in toluene (10 mL) and degassed with nitrogen. $Pd_2(dba)_3$ (138 mg, 0.15 mmol) and $P^tBu_3BF_4$ (73 mg, 0.25 mmol) were added and the mixture stirred for 10 min. Sodium tert-butoxide (0.56 g, 5.75 mmol) was added and the mixture was stirred at 110 °C for 48 h. After cooling to room temperature, the resulting mixture was extracted with dichloromethane followed by purification by column chromatography on silica gel with petroleum ether/dichloromethane (5:1) as the eluent to offer a white solid. The desired compound ***o*-CB-DPO, *o*-CB-DPS** and ***o*-CB-DPSe** were obtained in 58%, 73% and 65% yields respectivly.

***o*-CB-DPO** ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.69-7.67 (d, *J* = 8.0 Hz, 4H), 7.21-7.19 (d, *J* = 8.0 Hz, 4H), 6.67-6.64 (m, 4H), 6.59-6.55 (m, 4H), 6.40-6.34 (m, 4H), 5.63-5.61 (m, 4H), 3.14-2.20 (cage, 10H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.82, 141.50, 133.43, 133.40, 130.82, 130.64, 123.43, 121.85, 115.67, 112.95, 83.97; ^{11}B {^{1}H} NMR (128 MHz, $CDCl_3$): δ 11.97- -0.71 (6B), -7.05- -20.11 (4B). HRMS (ESI) m/z calcd. for $C_{38}B_{10}H_{35}N_2O_2$ [M + H]$^+$ 661.3629, found 661.3636.

***o*-CB-DPS** ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.47-7.44 (d, *J* = 12.0 Hz, 4H), 7.19-7.16 (m, 4H), 7.03-7.00 (d, *J* = 12.0 Hz, 4H), 6.96-6.91 (m, 8H), 6.50-6.48 (m, 4H), , 3.02-2.24 (cage, 10H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.84, 142.38, 132.52, 127.78, 127.06, 126.64, 124.31,123.25, 120.73, 85.08; ^{11}B {^{1}H} NMR (128 MHz, $CDCl_3$): δ 23.35- -0.99 (6B), -5.01- -20.14 (4B). HRMS (ESI) m/z calcd. for $C_{38}B_{10}H_{35}N_2S_2$ [M + H]$^+$ 693,3172, found 693,3176.

***o*-CB-DPSe** ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.56-7.54 (d, *J* = 8.0 Hz, 4H), 7.26-7.13 (m, 16H), 6.70-6.68 (d, *J* = 8.0 Hz, 4H), 2.31-2.05 (cage, 10H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 146.73, 141.61, 131.74, 131.26, 129.84, 127.67, 126.83,126.11, 123.32, 115.53, 86.17;

$^{11}B\{^{1}H\}$ NMR (128 MHz, $CDCl_3$): δ 21.08-11.20 (4B), -2.02- -8.19 (6B). HRMS (ESI) m/z calcd. for $C_{38}B_{10}H_{35}N_2Se_2$ [M + H]$^+$ 789.6021, found 789.6029.

3. Single-crystal X-ray structure determination

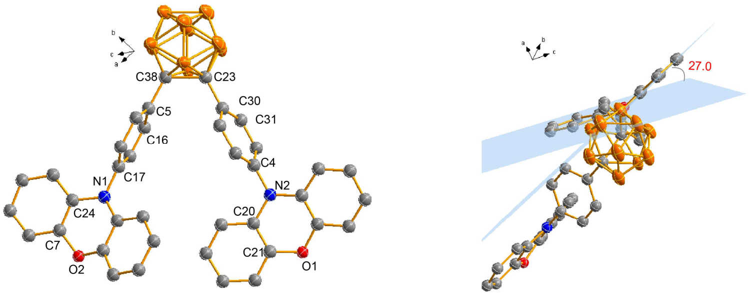


Figure S1. Molecular Structure of ***o*-CB-DPO** with thermal ellipsoids presented at room temperature Selected Bond lengths [Å] and angles [deg]: O2-C7, 1.769(3); N1-C7, 1.438(3); N1-C17, 1.415(3); C2-C13, 1.503(3); B23-B38, 1.760(4); C11-C13, 1.737(3); C11-B19, 1.738(4); C12-C30, 1.402(4); C30-O1-C21, 100.71(13); C15-O2-C24, 98.10(13); C14-N1-C7, 114.4(2); C43-C28-C21, 121.3(3); C17-N1-C7, 118.5(2); C16-C5-C11, 121.4(2); C5-C11-C13, 117.66(19); B23-C11-C13, 59.63(15); C42-C36-C15,119.9(3).

Table 1 Crystal data and structure refinement for ***o*-CB-DPO.**

pirical formula	$C_{38}H_{34}B_{10}N_2O_2$
Formula weight	660.47
Temperature/K	296.15
Crystal system	triclinic
Space group	P-1
a/Å	15.168(10)
b/Å	15.529(10)
c/Å	17.352(11)
α/°	65.517(9)
β/°	76.901(10)
γ/°	82.058(10)
Volume/Å^3	3618(4)
Z	2
ρ_{calc}g/cm^3	1.287
μ/mm^{-1}	0.145
F(000)	1452.0
Crystal size/mm^3	0.23 × 0.18 × 0.15
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	2.886 to 51.048
Index ranges	$-18 \le h \le 18, -18 \le k \le 18, -20 \le l \le 20$
Reflections collected	35568
Independent reflections	13218 [R_{int} = 0.0968, R_{sigma} = 0.1391]
Data/restraints/parameters	13218/0/954
Goodness-of-fit on F^2	0.847
Final R indexes [I>=2σ (I)]	R_1 = 0.0756, wR_2 = 0.2110
Final R indexes [all data]	R_1 = 0.1795, wR_2 = 0.2967
Largest diff. peak/hole / e Å^{-3}	0.73/-1.26

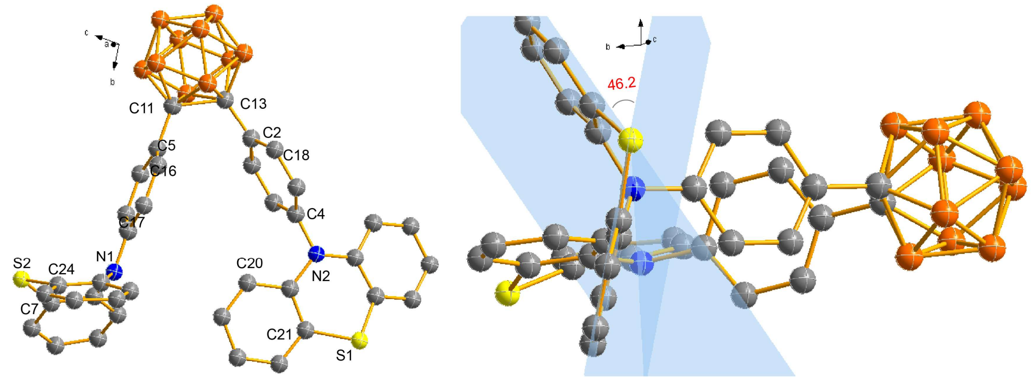


Figure S2. Molecular Structure of ***o*-CB-DPS** with thermal ellipsoids presented at room temperature Selected Bond lengths [Å] and angles [deg]: S2-C24, 1.769(3); N1-C7, 1.438(3); N1-C17, 1.415(3); C2-C13, 1.503(3); B23-B38, 1.760(4); C11-C13, 1.737(3);C11-B19, 1.738(4); C12-C30, 1.402(4); C30-S1-C21, 100.71(13); C15-S2-C24, 98.10(13); C14-N1-C7, 114.4(2); C43-C28-C21, 121.3(3); C17-N1-C7, 118.5(2); C16-C5-C11, 121.4(2); C5-C11-C13, 117.66(19); B23-C11-C13, 59.63(15); C42-C36-C15,119.9(3).

Table S2. **Crystal data and structure refinement for *o*-CB-DPS.**

Empirical formula	$C_{38}H_{34}B_{10}N_2S_2$
Formula weight	690.89
Temperature/K	296.15
Crystal system	triclinic
Space group	P-1
a/Å	10.207(5)
b/Å	13.006(6)
c/Å	13.541(6)
α/°	94.160(6)
β/°	90.439(7)
γ/°	97.056(6)
Volume/Å^3	1779.2(14)
Z	2
ρ_{calc}g/cm^3	1.290
μ/mm^{-1}	0.183
F(000)	716.0
Crystal size/mm^3	0.268 × 0.24 × 0.22
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.016 to 53.162
Index ranges	-12 ≤ h ≤ 12, -16 ≤ k ≤ 16, -16 ≤ l ≤ 16
Reflections collected	18906
Independent reflections	7306 [R_{int} = 0.0408, R_{sigma} = 0.0568]
Data/restraints/parameters	7306/0/469
Goodness-of-fit on F^2	1.022
Final R indexes [I>=2σ (I)]	R_1 = 0.0555, wR_2 = 0.1423
Final R indexes [all data]	R_1 = 0.0938, wR_2 = 0.1667
Largest diff. peak/hole / e Å^{-3}	0.99/-0.54

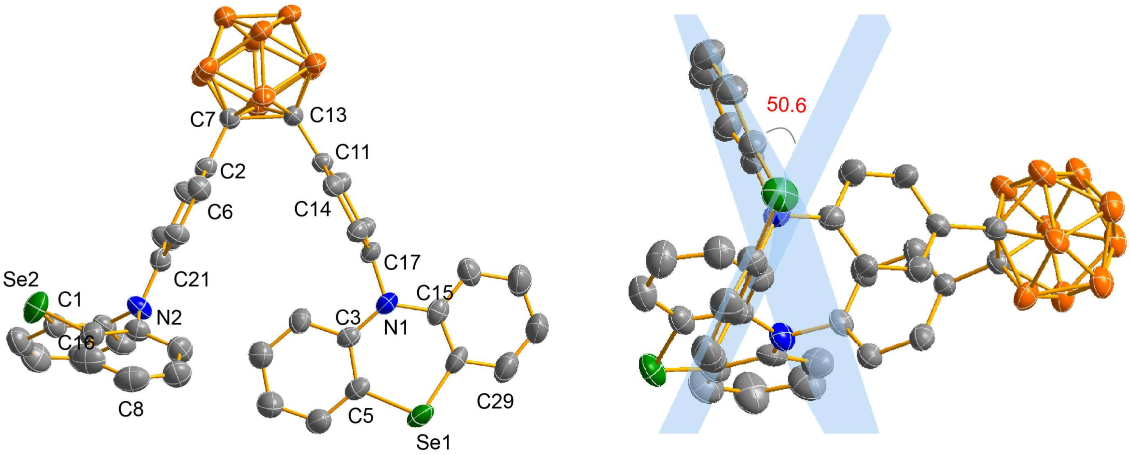


Figure S3. Molecular Structure of ***o*-CB-DPSe** with thermal ellipsoids presented at room temperature Selected Bond lengths [Å] and angles [deg]: Se1-C5,1.884(6); Se2-C1, 1.893(7); N1-C15, 1.449(8); C7-C13, 1.739(8); N2-C21, 1.426(8); C1-Se2-C16, 93.8(3); C35-C1-Se2, 119.7(5); C6-C2-C7, 121.3(5); C18-C2-C6, 118.5(6); C18-C2-C7, 120.1(5); N1-C3-C5, 121.9(5); C33-C3-N1, 119.6(5); C33-C3-C5, 118.4(6); C3-N4-C15, 125.3(5); C3-N4-C17, 113.9(5).

Table S3. Crystal data and structure refinement for ***o*-CB-DPSe.**

Identification code	1
Empirical formula	$B_{10}C_{38}N_2Se_2$
Formula weight	750.42
Temperature/K	296.15
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	14.546(8)
b/Å	10.201(6)
c/Å	24.680(14)
α/°	90
β/°	95.087(8)
γ/°	90
Volume/Å^3	3648(4)
Z	4
ρ_{calc}g/cm^3	1.366
μ/mm^{-1}	2.057
F(000)	1440.0
Crystal size/mm^3	0.23 × 0.18 × 0.15
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.134 to 51.34
Index ranges	$-17 \le h \le 17$, $-12 \le k \le 12$, $-29 \le l \le 29$
Reflections collected	34561
Independent reflections	6866 [R_{int} = 0.1028, R_{sigma} = 0.0866]
Data/restraints/parameters	6866/0/469
Goodness-of-fit on F^2	1.168
Final R indexes [I>=2σ (I)]	R_1 = 0.0690, wR_2 = 0.1840
Final R indexes [all data]	R_1 = 0.1359, wR_2 = 0.2148
Largest diff. peak/hole / e Å^{-3}	0.78/-0.64

4. CV and UV-Vis data

Table S4. Optical and Electronic Properties of ***o*****-CB-DPE**.

Compound	λ_{max} [nm]	Electrochemical		LUMO (eV)[a]	HOMO (eV)	Egap (eV)[b]
		E_{red} (V)	E_{ox} (V)			
***o*-CB-DPO**	379, 301	-3.03-2.05,-1.21	0.21	-3.59	-6.50	2.91
***o*-CB-DPS**	405, 313	-2.85, -1.99, -1.04	0.23	-3.76	-6.70	2.94
***o*-CB-DPSe**	420, 321	-2.83, -2.05, -1.01	0.21	-3.79	-6.75	2,96

[a] Energy levels vs vacuum level were calculated from CV data and from the optically determined energy gap. [b] Energy gap values were calculated from the absorption spectra.

5. ECD and chemical oxidation

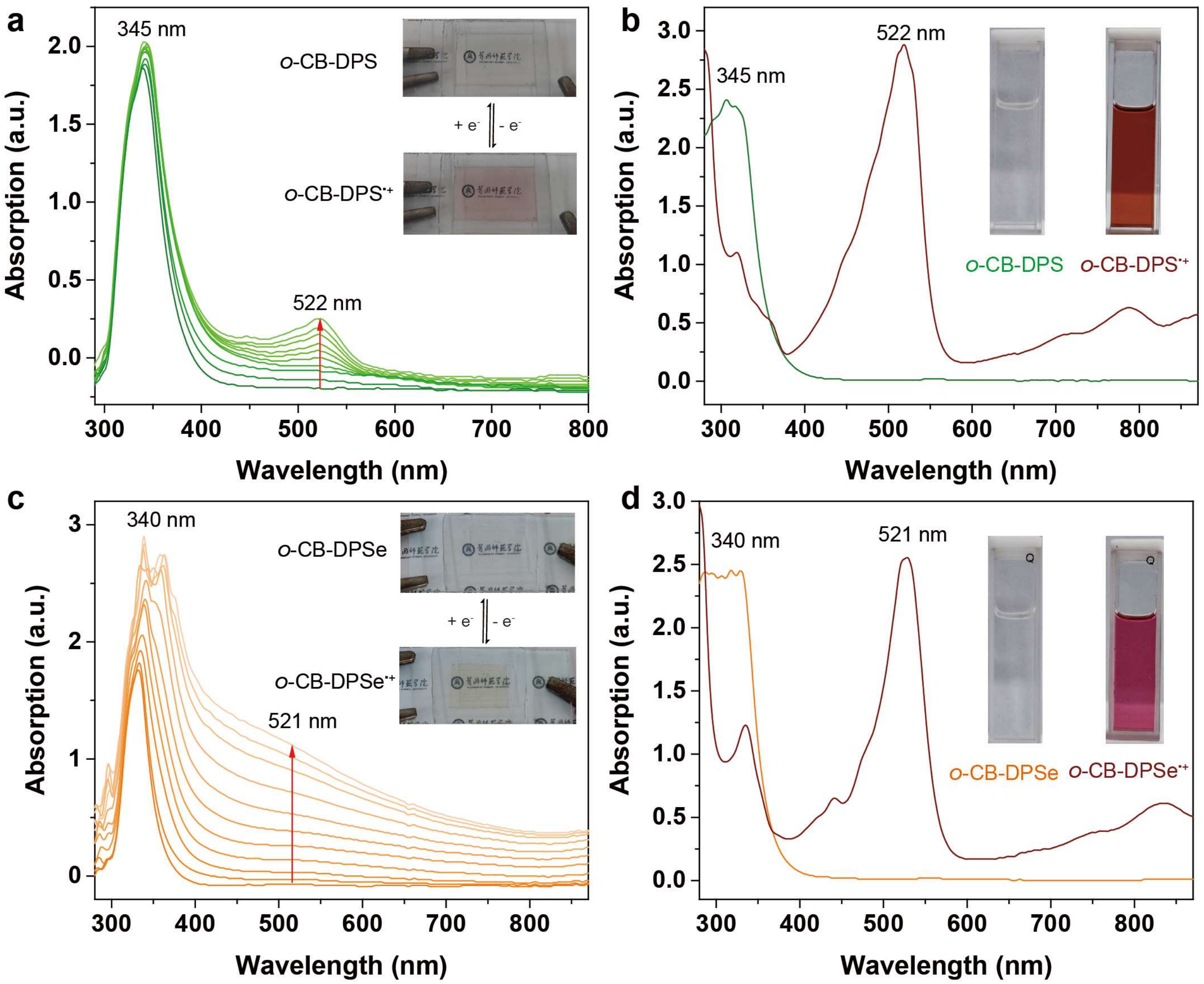


Figure S4. (a, c) Spectroelectrochemistry of ***o*****-CB-DPS/** ***o*****-CB-DPSe** for radical cation formation process and the images of electrochromic device colour changes were shown inside. (b, d) UV-vis absorption spectra of the radical cation species of ***o*****-CB-DPS**$^{\bullet+}$/ ***o*****-CB-DPSe**$^{\bullet+}$and inserted are the photos of the DCM solutions.

6. Radical cationic stability

The stability of radical cationic intermediates formed by ***O*-CB-DPE** were studied using electrochemical spectroscopy. Monitored the relationship between the maximum absorption peaks of compounds ***O*-CB-DPO** (549 nm), ***O*-CB-DPS** (522 nm) , ***O*-CB-DPSe** (521 nm) and time respectively. The radical cationic generation and quenching time were calculated with 80% total response time.

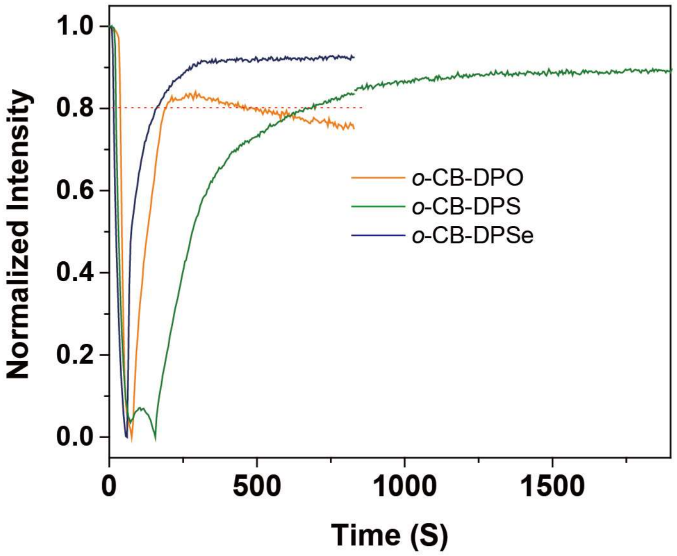


Figure S5. The relationship between the maximum absorption peaks of ***O*-CB-DPE** and time

7. Polymerization

Figure S6a illustrates the kinetic plots (ln[M]$_0$/[M] vs time), and Figure S6b displays the evolution of M$_n$ and M$_w$/M$_n$ with conversion. The linear semilogarithmic plots suggested that the concentration of the propagating radicals was almost constant throughout the polymerization.

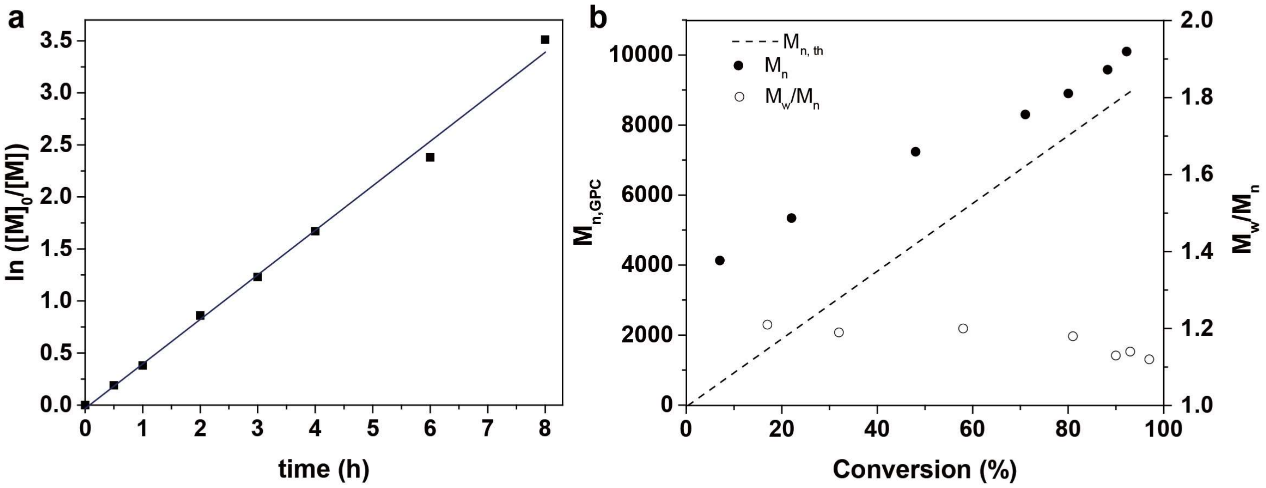
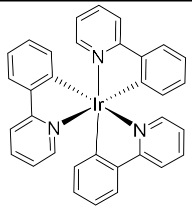
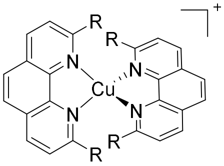
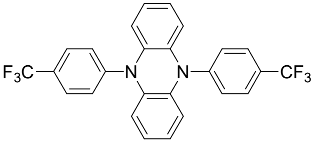
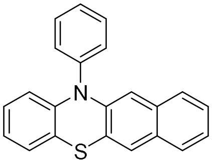
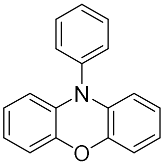
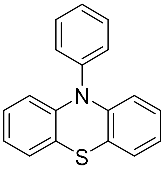
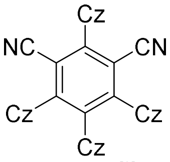
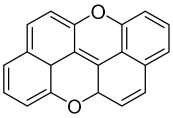
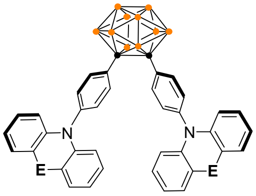


Figure S6 (a) Semilogarithmic kinetic plots of polymerization of MMA with photoinduced metal-free ATRP methods under conditions [MMA]:[EBP]:[1] = 100:1:0.1 in DMA, irradiation by a wight LED light (390 nm, 5 W); (b) number-average molecular weight (Mn, filled symbols) and dispersity (Mw/Mn, open symbols) vs conversion for metal-free ATRP of MMA.

Table S5 Some photocatalysts participate in ATRP reactions.

Classify	Catalysts	MMA convertion (%)	M_w/M_n	Conditions	Reference
Metal photocatalysts	 fac-[Ir(ppy)$_3$][3]	86	1.19	Visible light (50 W fluorescent lamp), 8 h.	*Angew. Chem., Int. Ed.* 2012, **51**, 8850.
	 Cu(phen)$_2^+$: R = H Cu(dap)$_2^+$: R = *p*-OMe-Ph [4]	75	1.09	T = 60 °C, 24 h.	*Macromolecules*, 2016, **49**, 7653.
Metal free photocatalysts	 Diaryl dihydrophenazine [5]	98.4	1.17	white LEDs, 8 h.	*Science*, 2016, 352, 1078.
	 Ph-benzo-PTZ [6]	82	1.30	392 nm LED, 48 h	*Chem. Eur. J.*, 2017, **23**, 597.
	 *N*-Aryl phenoxazines [7]	85.1	1.09	365 nm (54 W), 8 h.	*J. Am. Chem. Soc.*, 2016, **138**, 11399.
	 PTH [8]	90	1.18	380 nm LEDs, 4 h	*J. Am. Chem. Soc.*, 2014, **136**, 16096.
	 4CzIPN [9]	90	1.50	458 nm blue LED, 3.0 h	*Macromol. Rapid Commun.*, 2017, **38**, 1600461.
	 O-doped anthanthrene [10]	88.5	1.25	400 nm, LED, 10 h.	*Nat. Commun.*, 2021,**12**,429.
	 O-CB-DPE (E = O, S, Se)	Up to 97	Low to 1.09	390 nm LED, 8 h	This work

8. GPC traces of each polymer

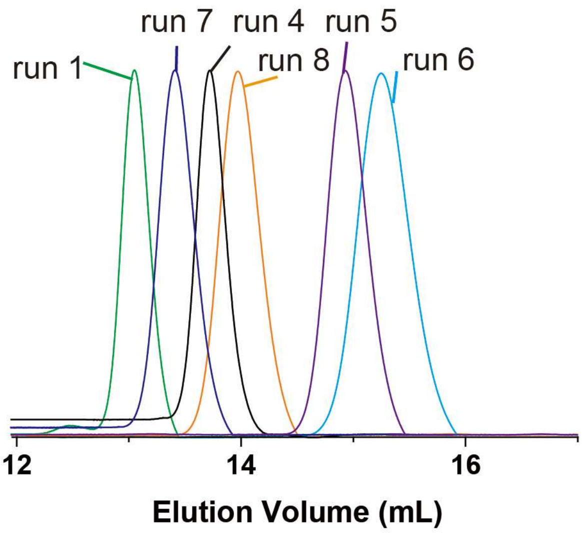
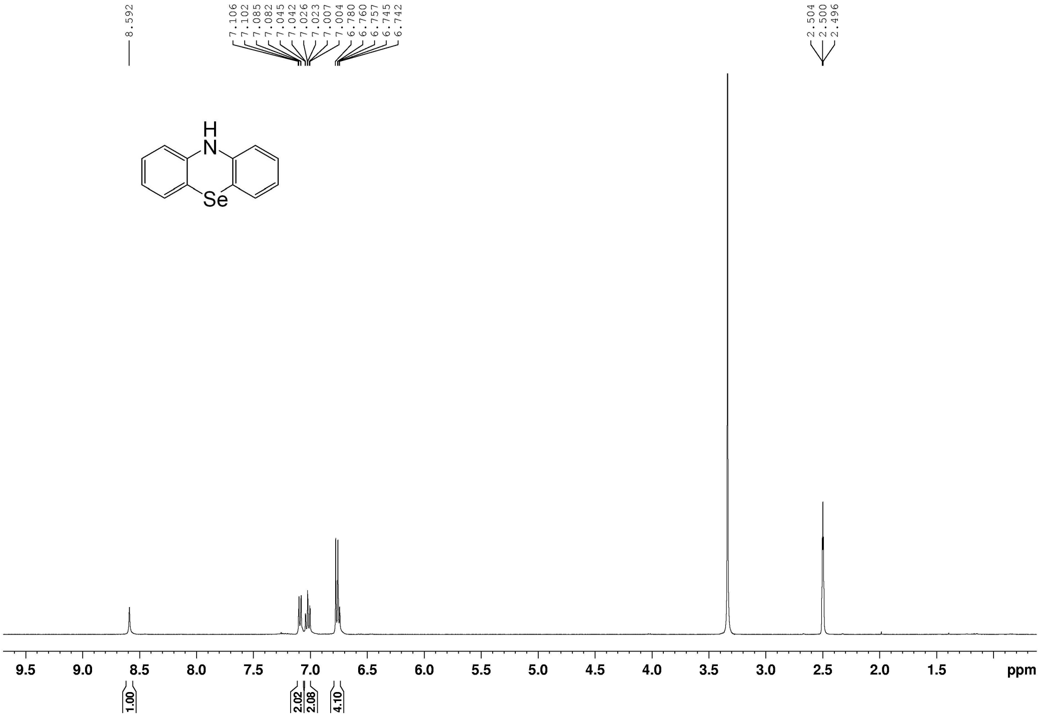
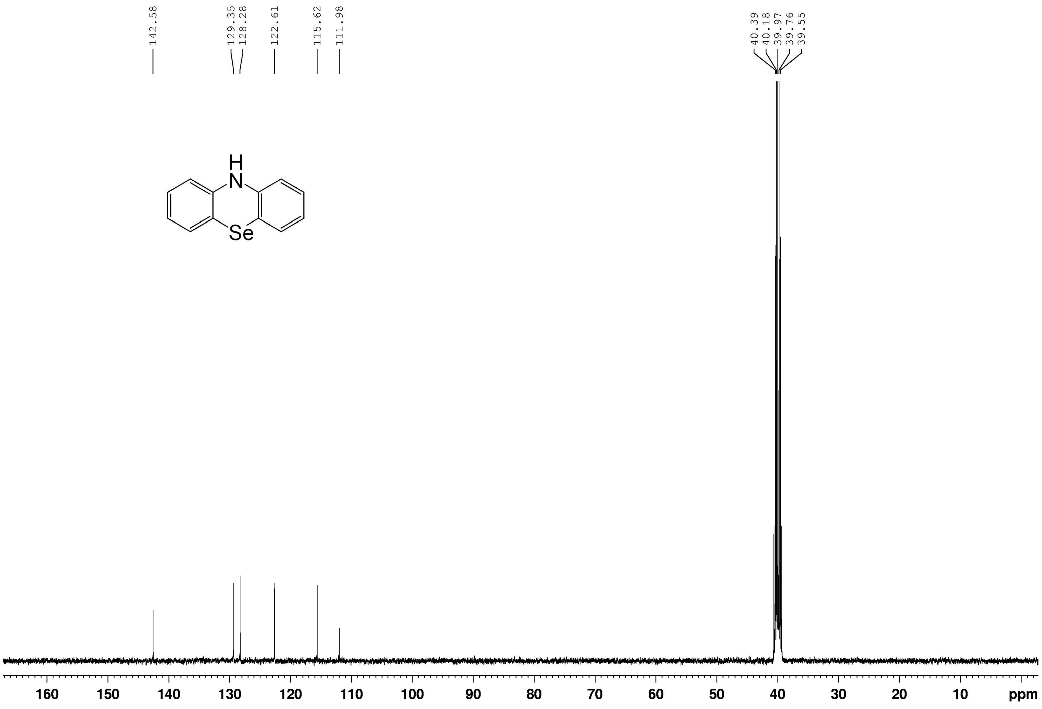


Figure S7.GPC traces of each polymer

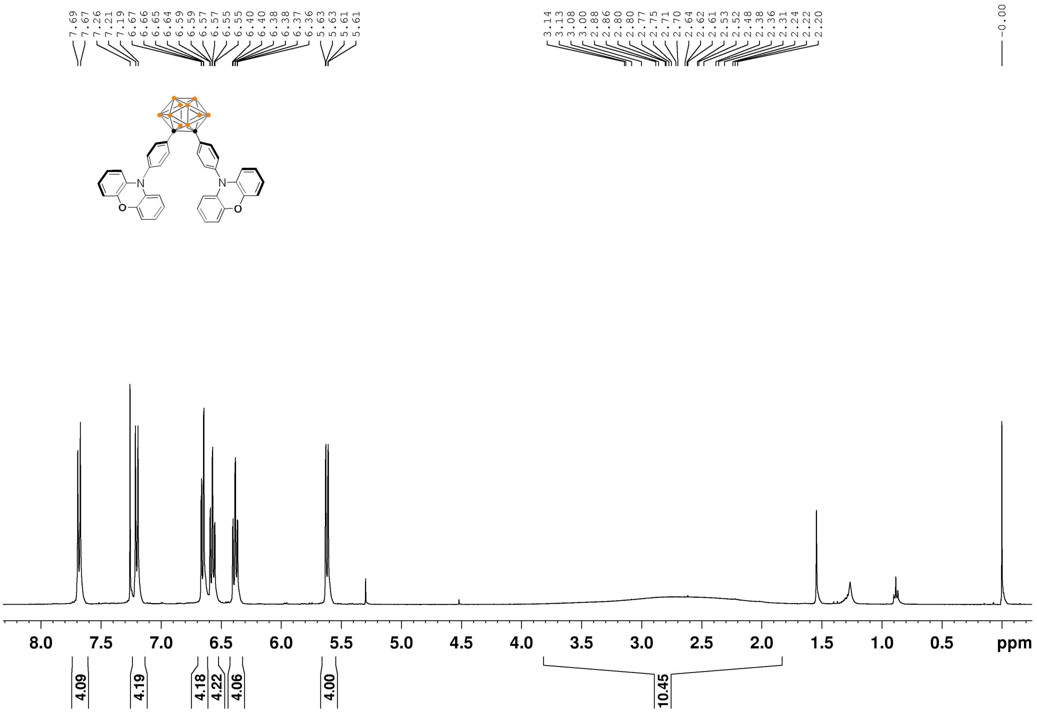
9. ^{1}H, ^{13}C ^{11}B NMR spectra

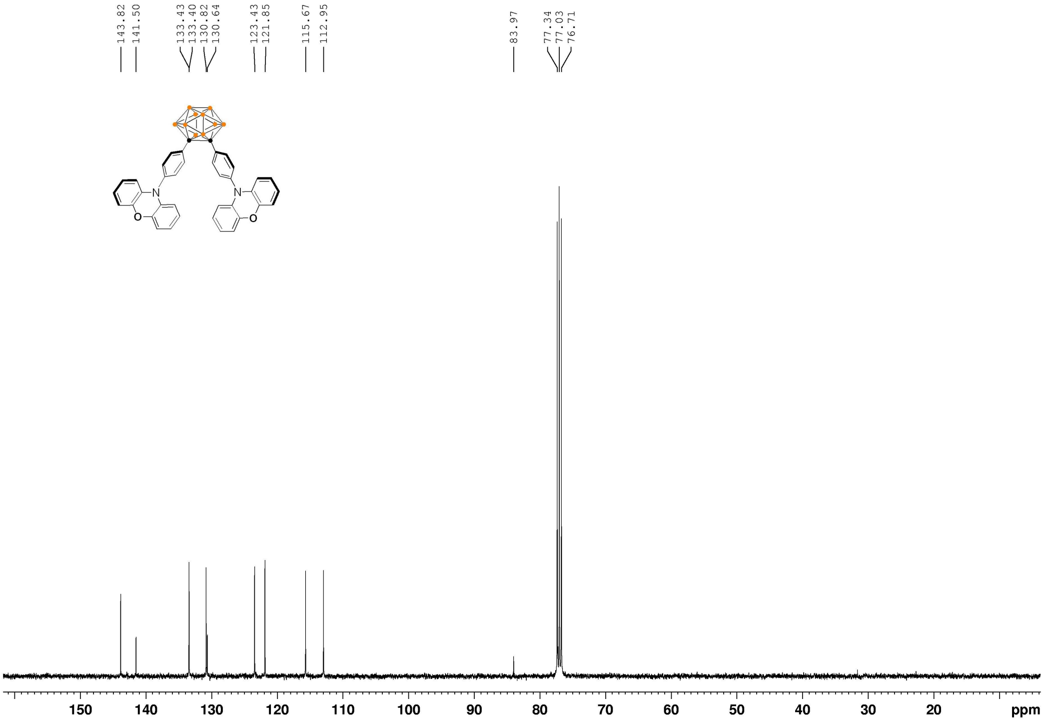
^{1}H NMR (CDCl$_3$, 400 MHz) and ^{13}C NMR (CDCl$_3$, 100 MHz) spectra of **2**

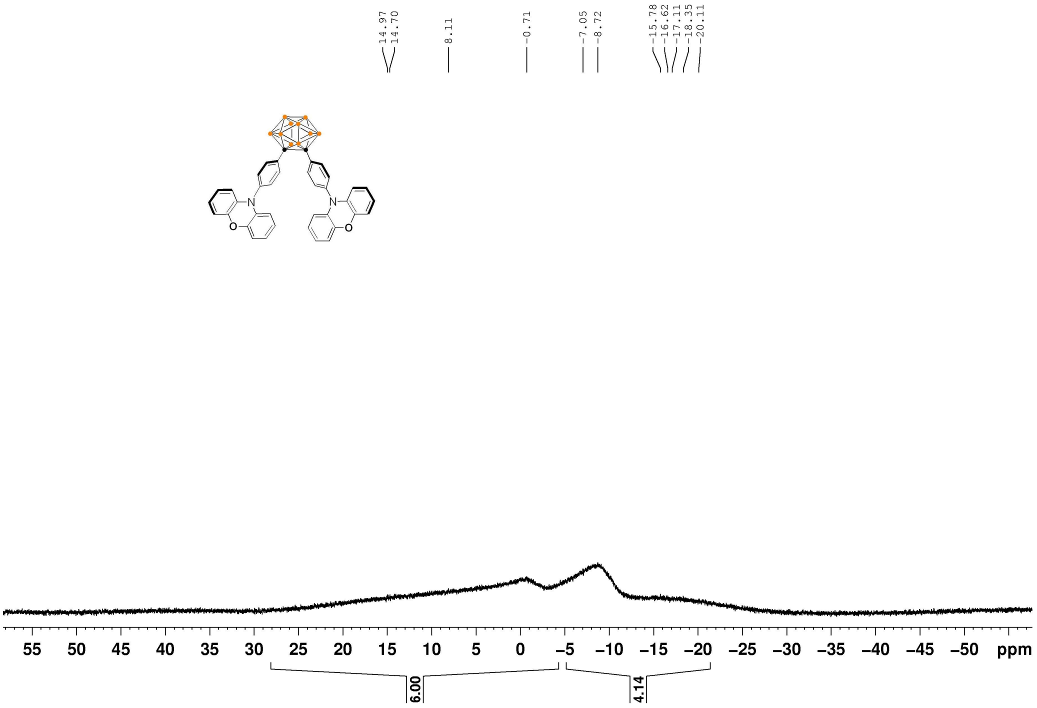




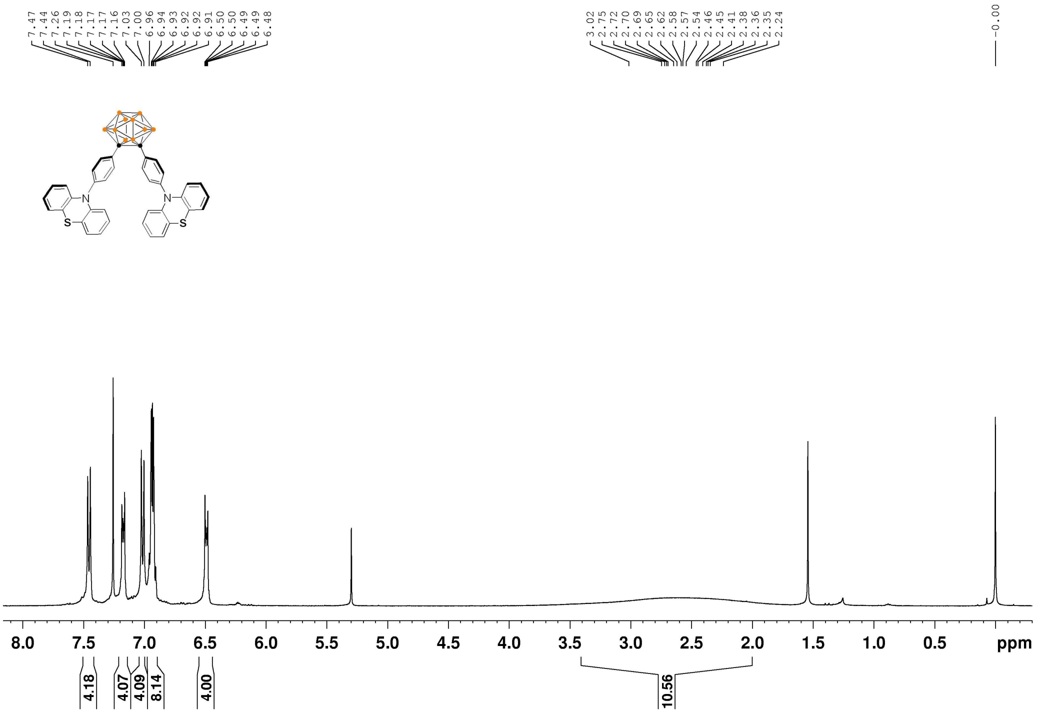
^{1}H NMR (CDCl$_3$, 400 MHz), ^{13}C NMR (CDCl$_3$, 100 MHz) and ^{11}B {^{1}H} NMR spectra of ***o*-CB-DPO**

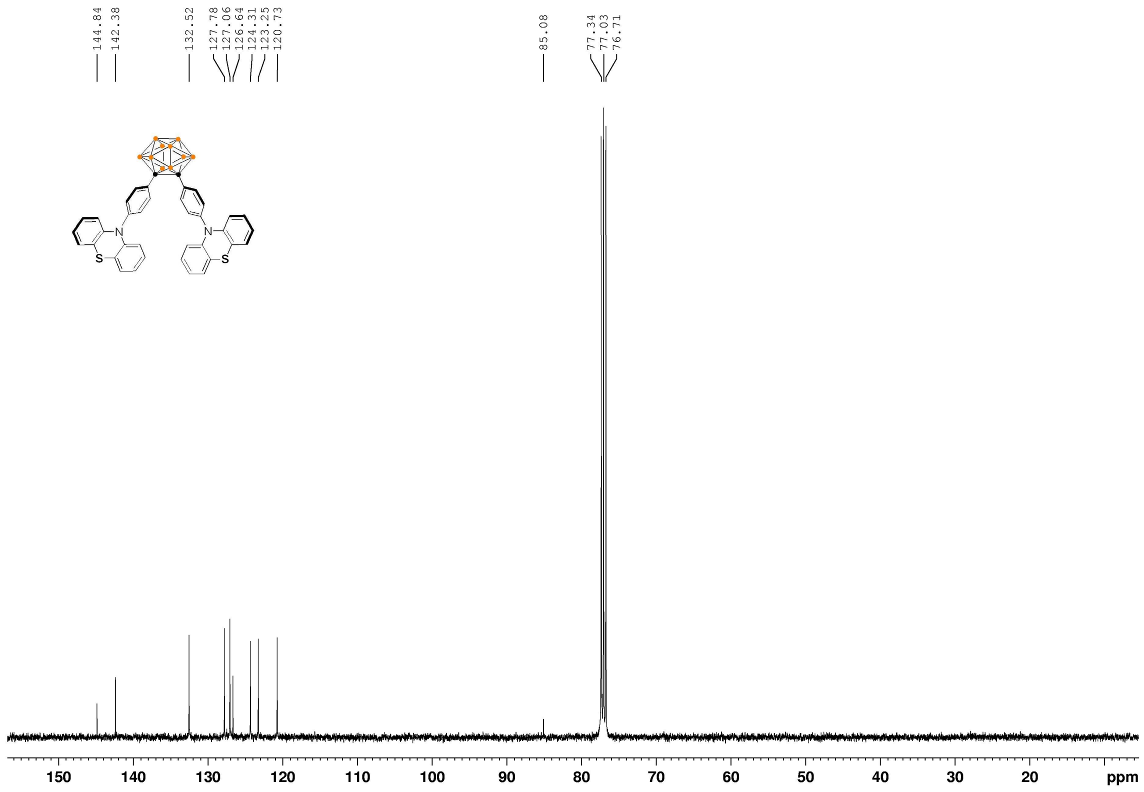


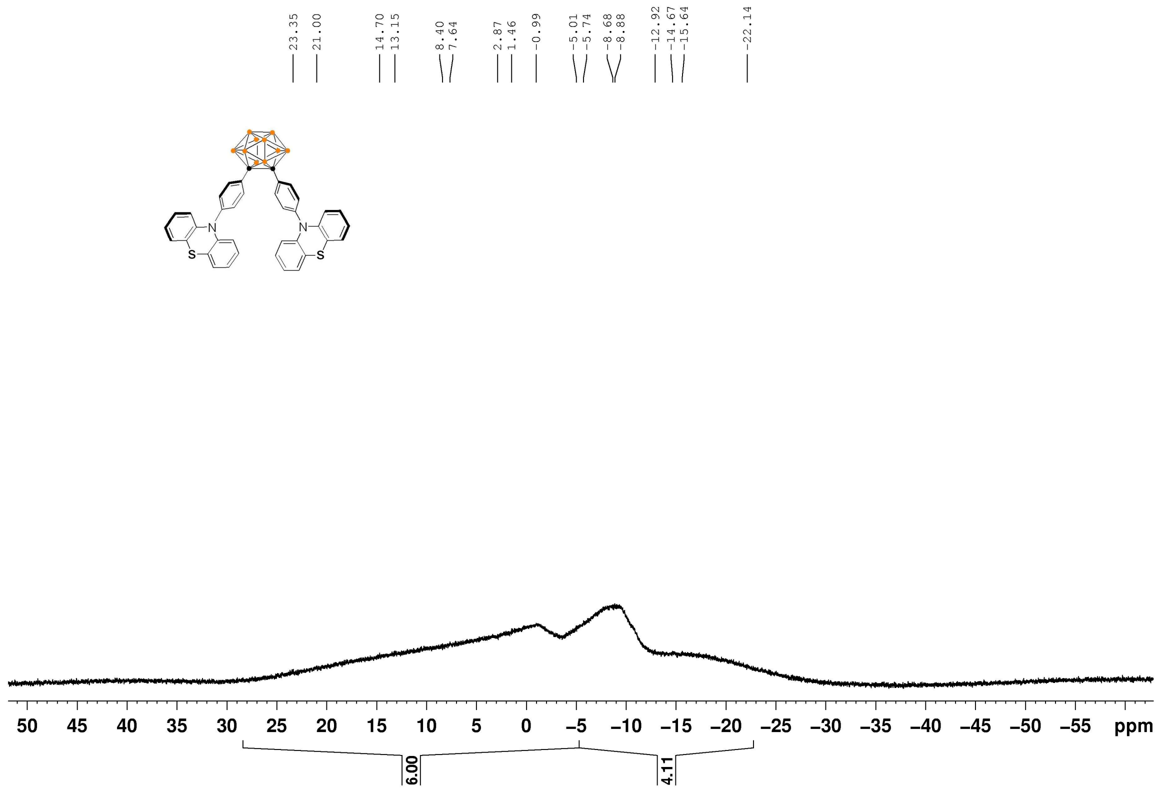




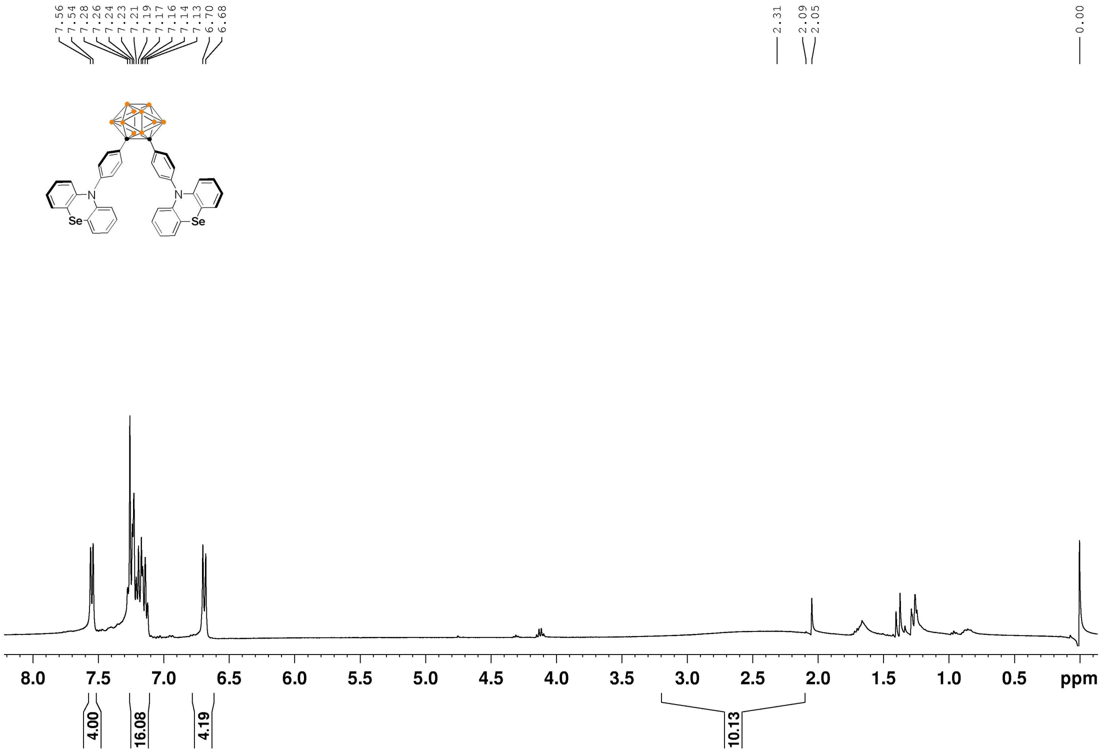
^{1}H NMR (CDCl$_3$, 400 MHz), ^{13}C NMR (CDCl$_3$, 100 MHz) and ^{11}B {^{1}H} NMR spectra of ***o*-CB-DPS**

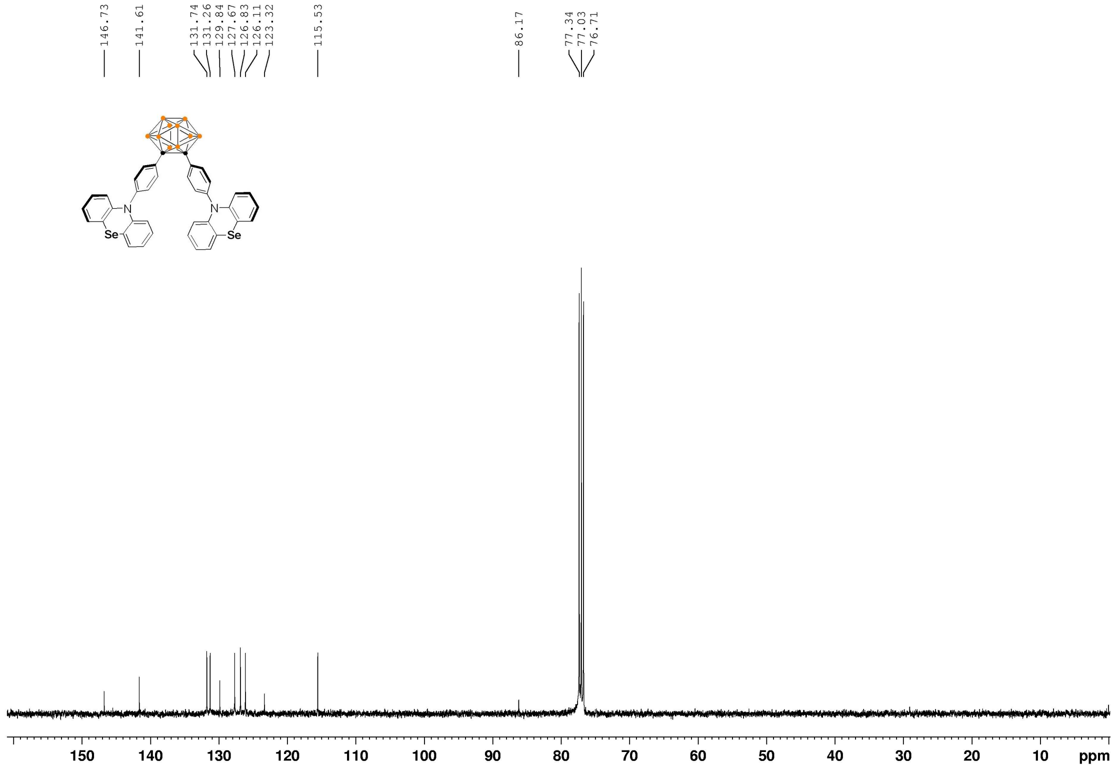


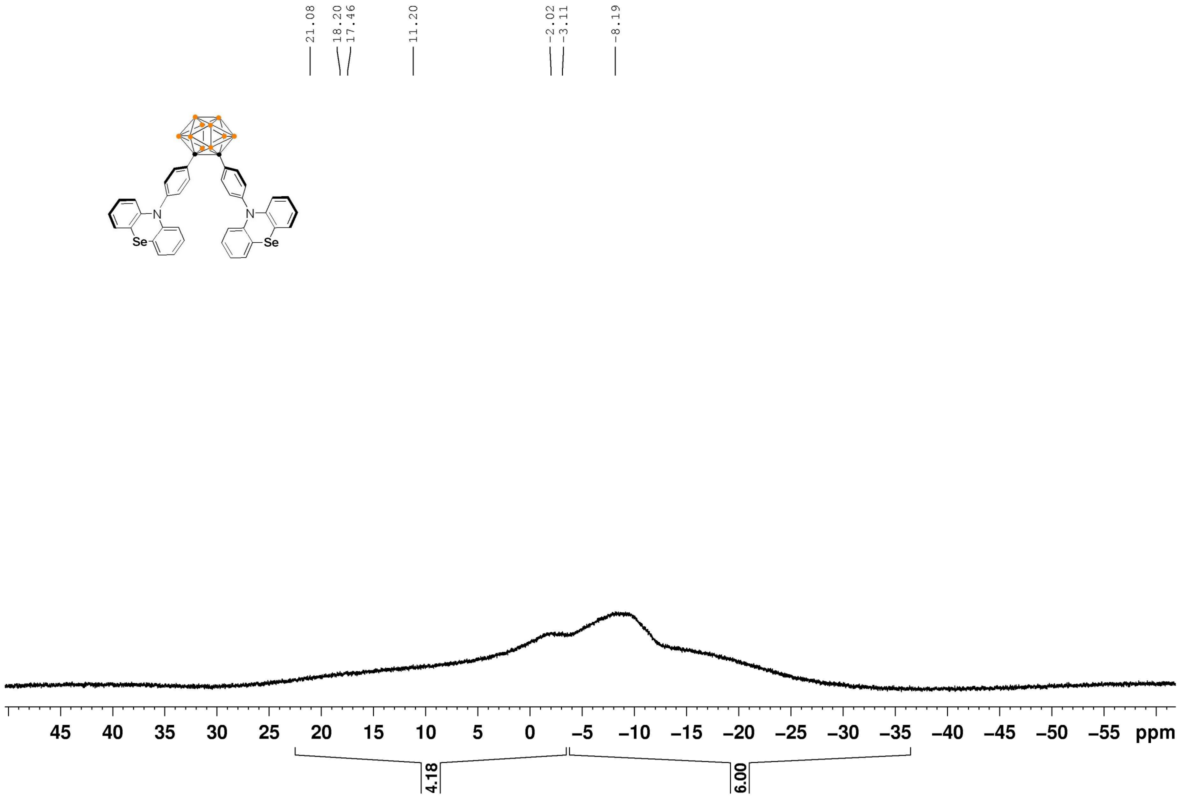




^{1}H NMR (CDCl$_3$, 400 MHz), ^{13}C NMR (CDCl$_3$, 100 MHz) and ^{11}B {^{1}H} NMR spectra of ***o*-CB-DPSe**


7.56
7.54
7.28
7.26
7.24
7.23
7.21
7.19
7.17
7.16
7.14
7.13
6.70
6.68
2.31
2.09
2.05
0.00
N
Se
N
Se
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
4.00
16.08
4.19
10.13


146.73
141.61
131.74
131.26
129.84
127.67
126.83
126.11
123.32
115.53
86.17
77.34
77.03
76.71
N
Se
N
Se
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


21.08
18.20
17.46
11.20
-2.02
-3.11
-8.19
N
Se
N
Se
45 40 35 30 25 20 15 10 5 0 −5 −10 −15 −20 −25 −30 −35 −40 −45 −50 −55 ppm
4.18
6.00

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