Electronic Supplementary Information for

Studies of a bola-type bis(dithiafulvene) system: synthesis crystal structure, and electrochemical properties

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1. NMR, IR and Mass Spectra for Compounds **5** and **6**

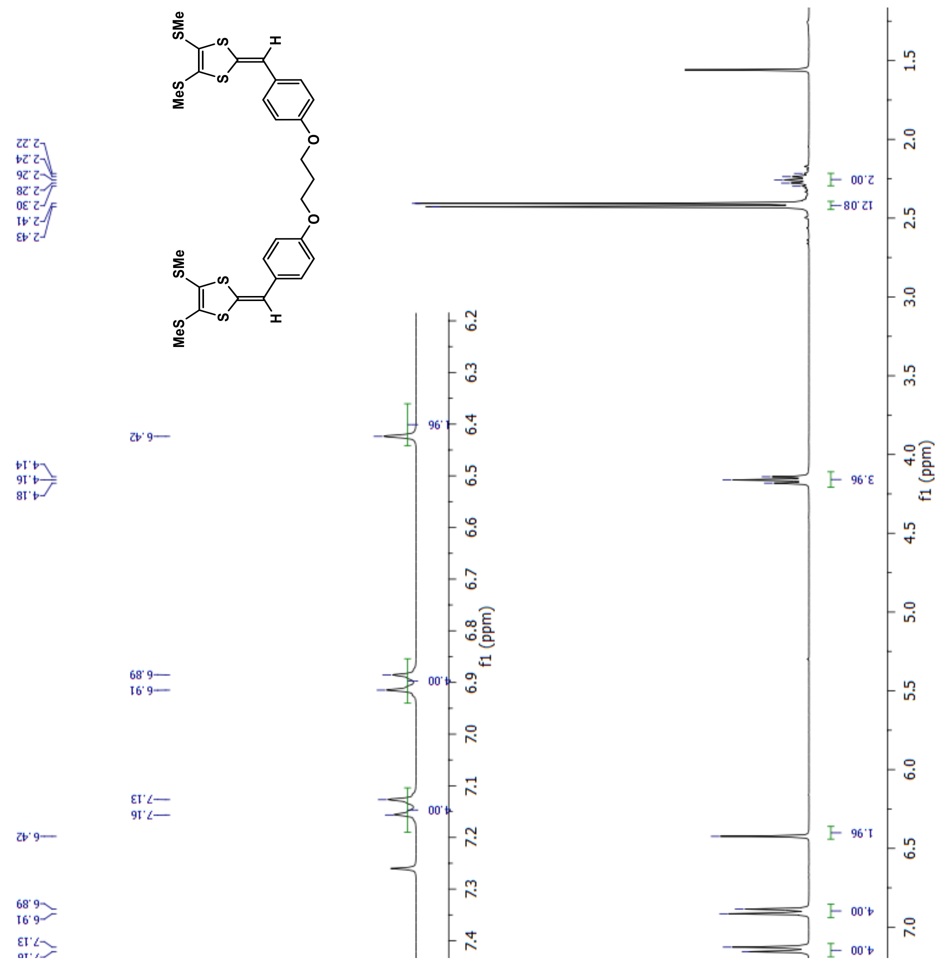


Fig. S-1 ^{1}H NMR (300 MHz, $CDCl_3$) of compound **5**.

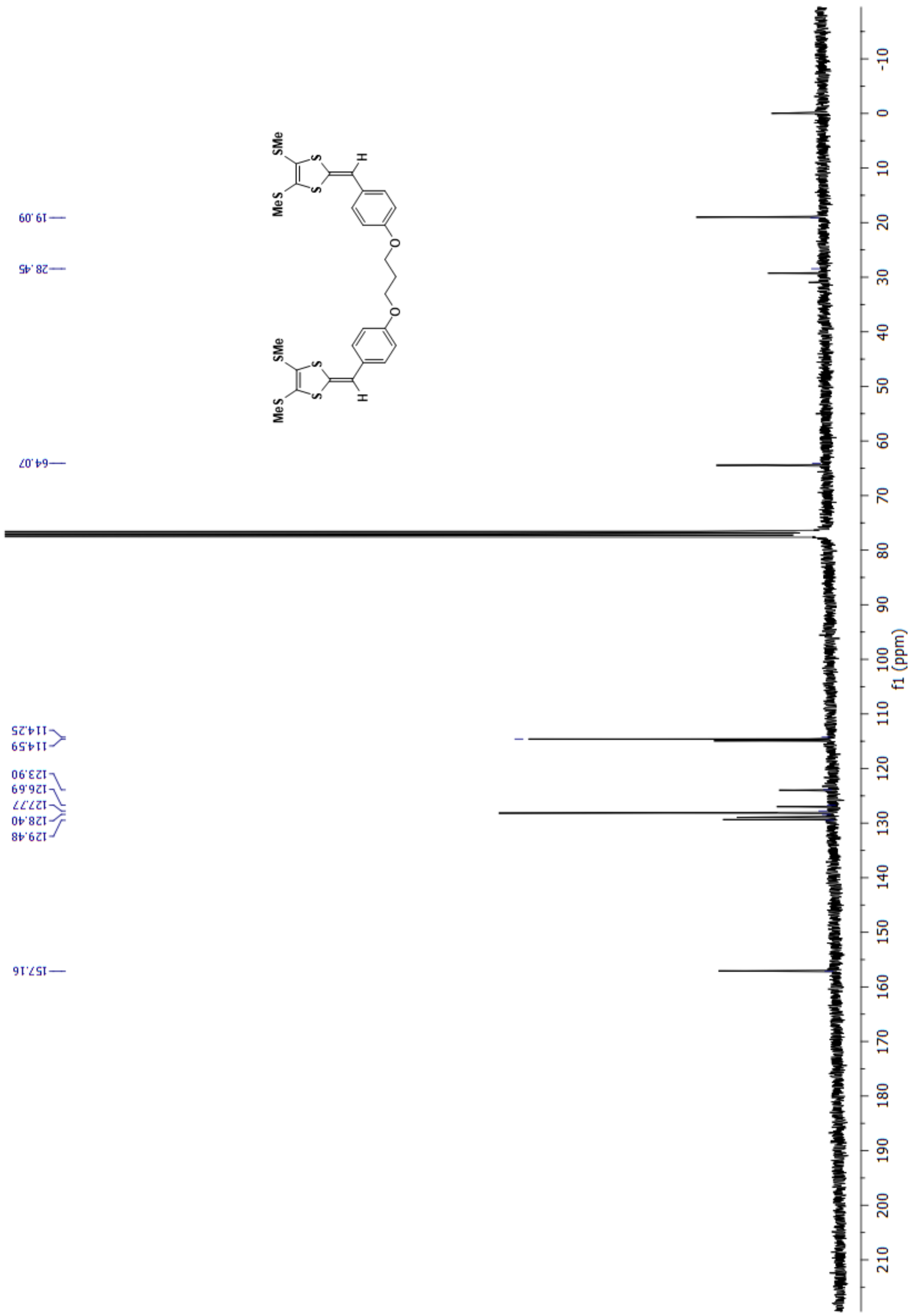


Fig. S-2 ^{13}C NMR (75 MHz, $CDCl_3$) of compound **5**

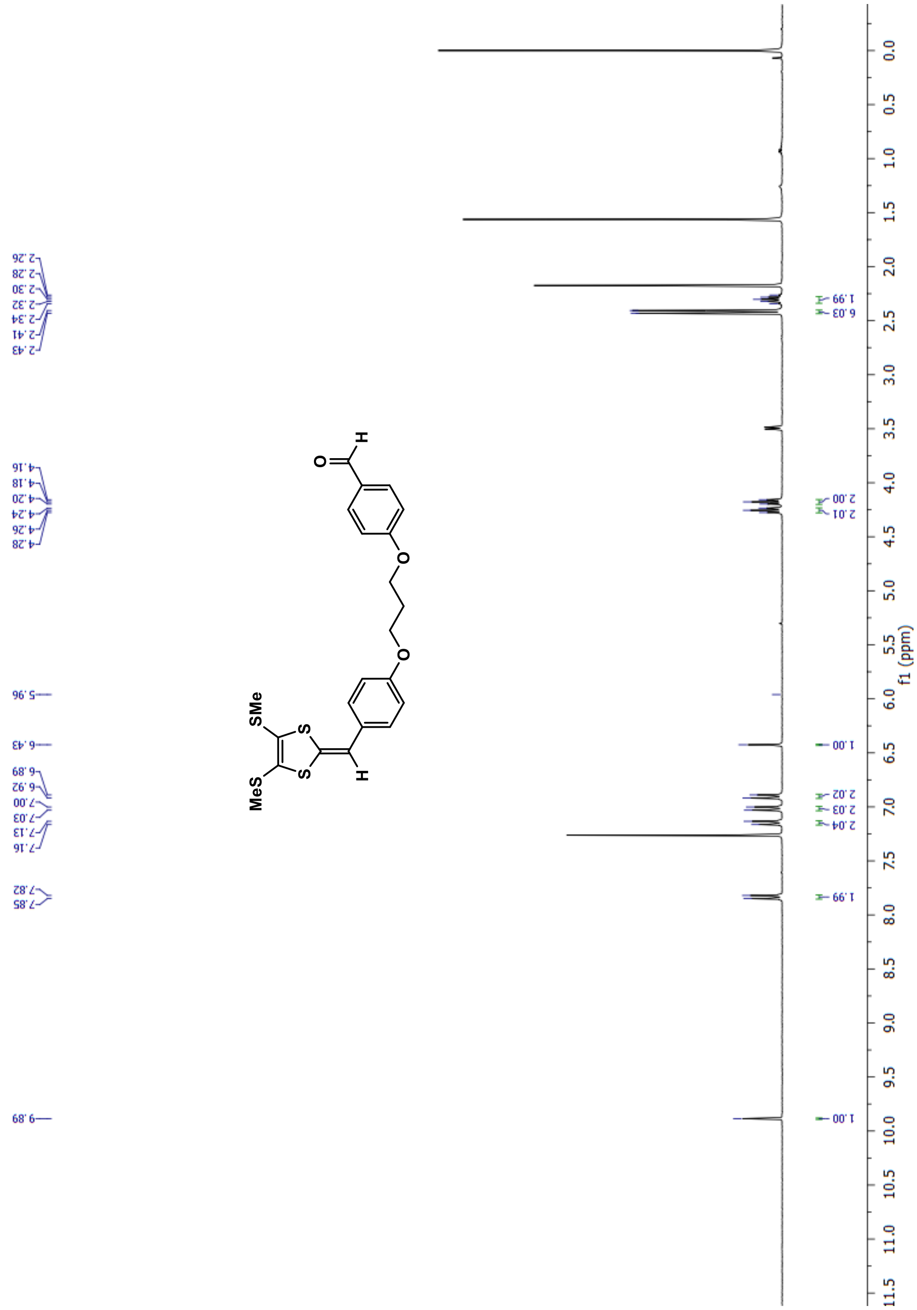


Fig. S-3 ^{1}H NMR (500 MHz, $CDCl_3$) of compound **6**.

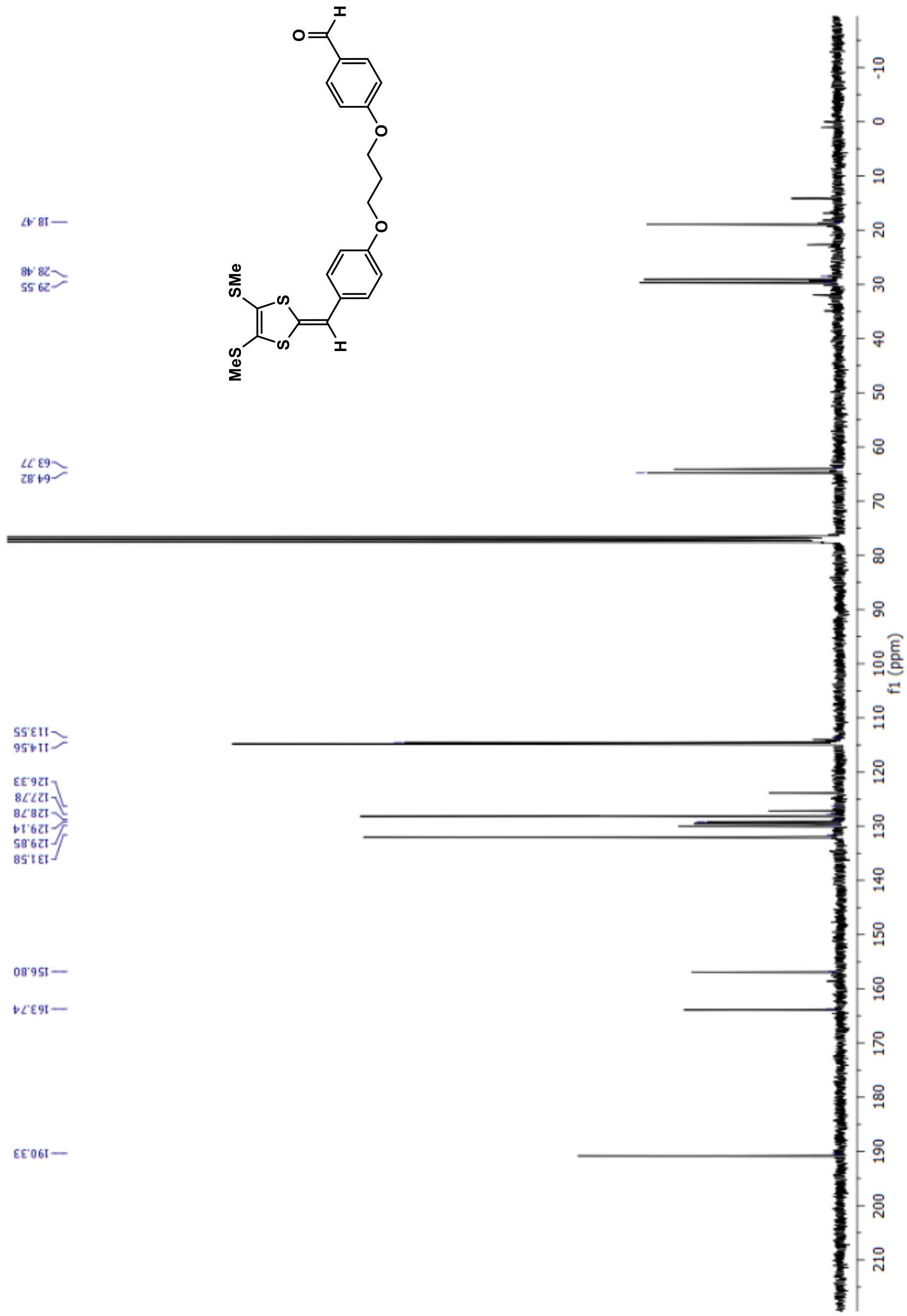


Fig. S-4 ^{13}C NMR (75 MHz, $CDCl_3$) of compound **6**

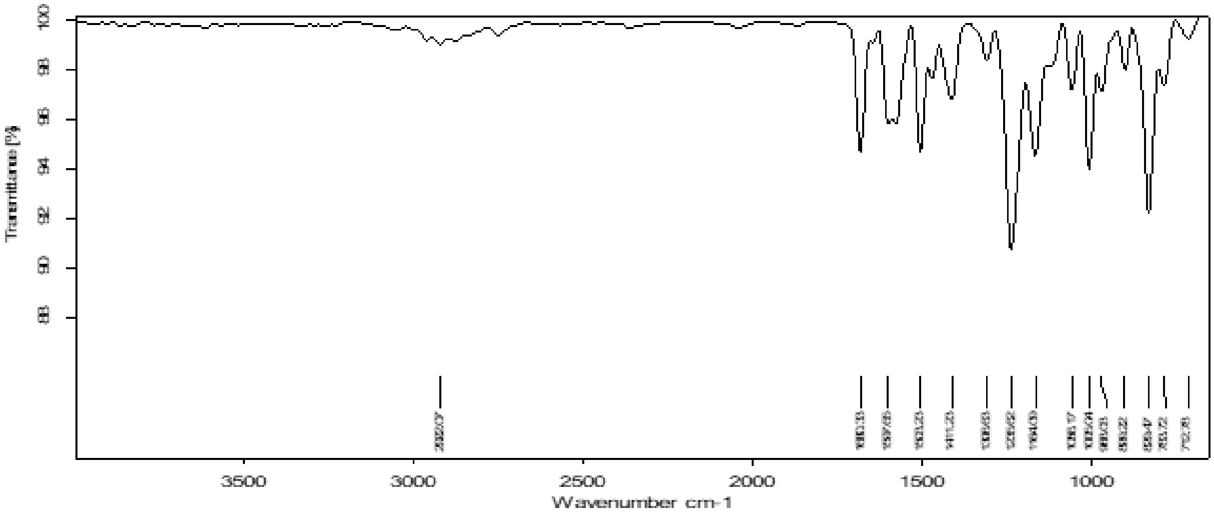


Fig. S-5 IR spectrum of compound **5.**

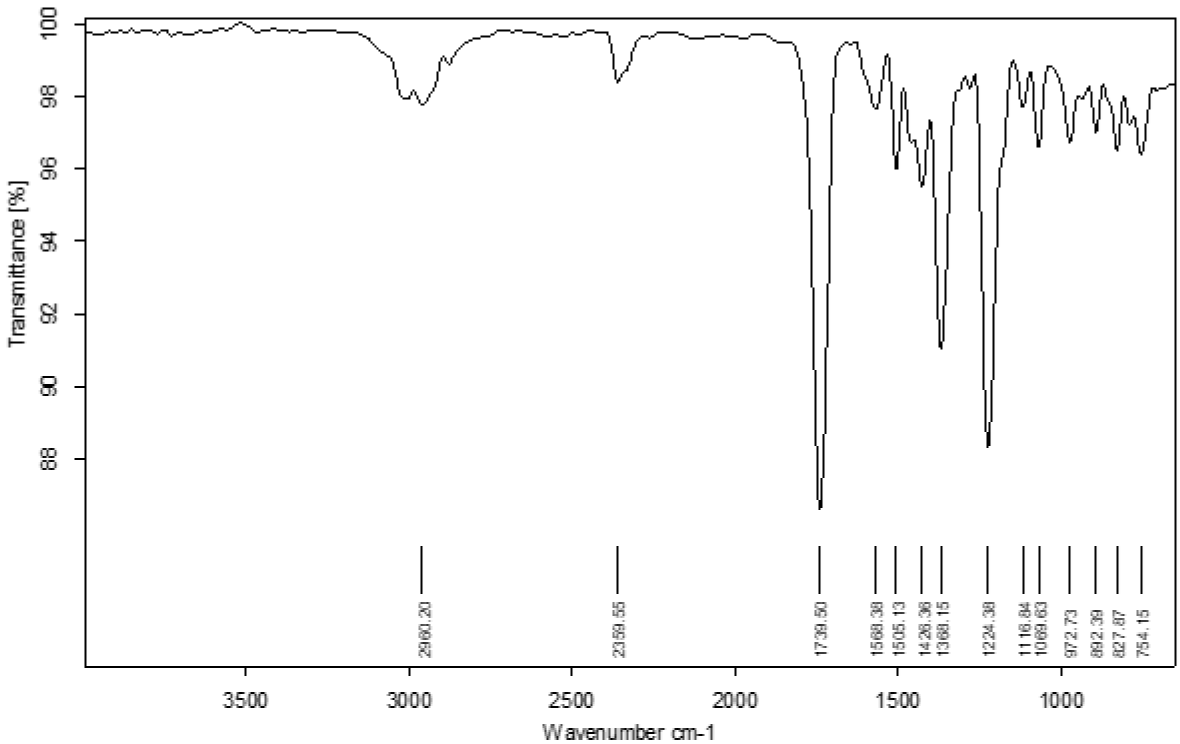


Fig. S-6 IR spectrum of compound **6.**

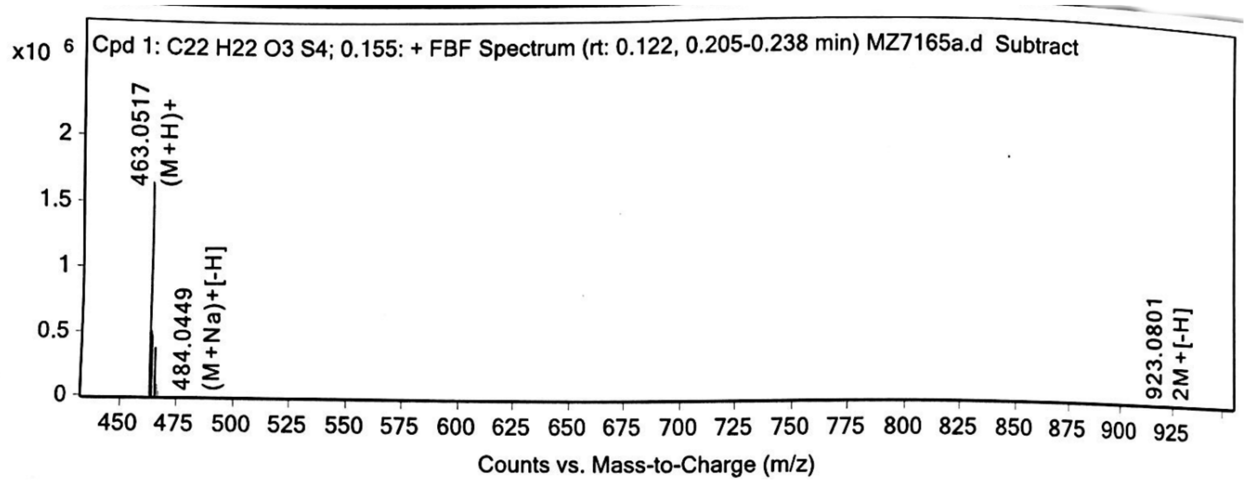


Fig. S-7 Mass spectrum (APPI) of compound **5.**

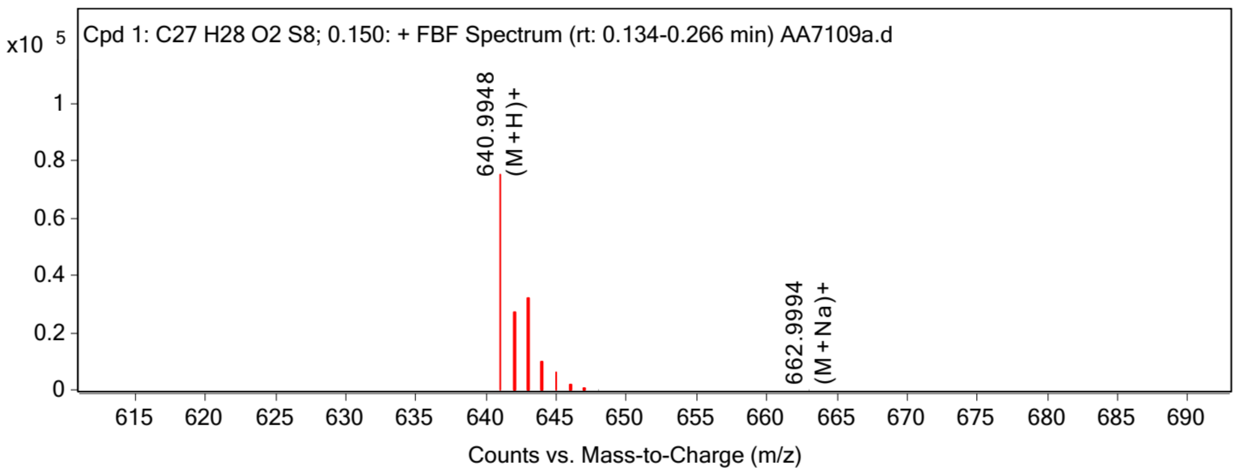


Fig. S-8 Mass spectrum (APPI) of compound **6.**

2. Crystallographic Data for Compounds **5** and **6**

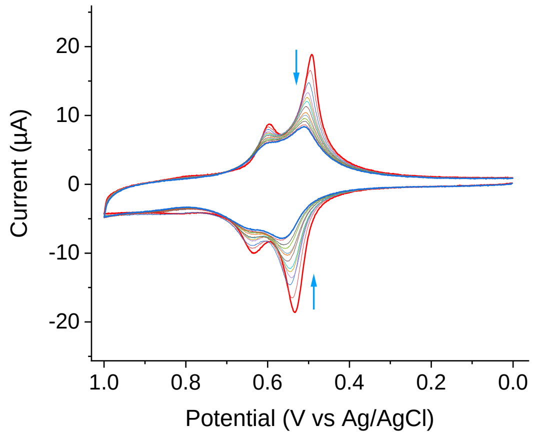
Table S-1 Crystal data and structure refinement for **5**

Empirical formula	$C_{27}H_{28}O_2S_8$
Formula weight	640.97
Temperature/K	100(2)
Crystal system	monoclinic
Space group	$P2/c$
a/Å	21.3010(5)
b/Å	5.21057(12)
c/Å	13.0620(3)
β/°	98.392(2)
Volume/Å^3	1434.23(6)
Z	2
ρ_{calc}mg/mm^3	1.484
μ/mm^{-1}	5.970
F(000)	668.0
Crystal size/mm^3	0.232 × 0.179 × 0.039
2θ range for data collection	4.194 to 154.824°
Index ranges	$-26 \leq h \leq 26$, $-5 \leq k \leq 6$, $-16 \leq l \leq 15$
Reflections collected	18250
Independent reflections	3013[R(int) = 0.0745]
Data/restraints/parameters	3013/0/170
Goodness-of-fit on F^2	1.102
Final R indexes [I>=2σ (I)]	R_1 = 0.0631, wR_2 = 0.1733
Final R indexes [all data]	R_1 = 0.0658, wR_2 = 0.1752
Largest diff. peak/hole / e Å^{-3}	1.11/-0.58

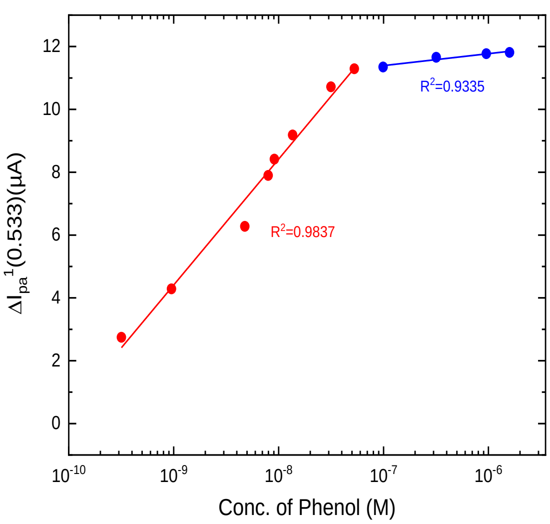
Table S-2 Crystal data and structure refinement for **6**

Identification code	A21C1_twin1_hklf4
Empirical formula	$C_{22}H_{22}O_3S_4$
Formula weight	462.63
Temperature/K	100(2)
Crystal system	triclinic
Space group	*P*-1
a/Å	12.7578(2)
b/Å	13.5031(2)
c/Å	15.2145(2)
α/°	93.6610(10)
β/°	114.2170(10)
γ/°	113.636(2)
Volume/Å^3	2106.47(6)
Z	4
ρ_{calc}g/cm^3	1.459
μ/mm^{-1}	4.327
F(000)	968.0
Crystal size/mm^3	0.124 × 0.101 × 0.048
Radiation	Cu *K*α (λ = 1.54184)
2θ range for data collection/°	6.622 to 155.13
Index ranges	$-16 \le h \le 16$, $-17 \le k \le 17$, $-19 \le l \le 19$
Reflections collected	20864
Independent reflections	20864 [R_{sigma} = 0.0307]
Data/restraints/parameters	20864/0/529
Goodness-of-fit on F^2	1.033
Final *R* indexes [*I*>=2σ (I)]	R_1 = 0.0769, wR_2 = 0.2380
Final *R* indexes [all data]	R_1 = 0.0969, wR_2 = 0.2536
Largest diff. peak/hole / e Å^{-3}	0.92/-0.95

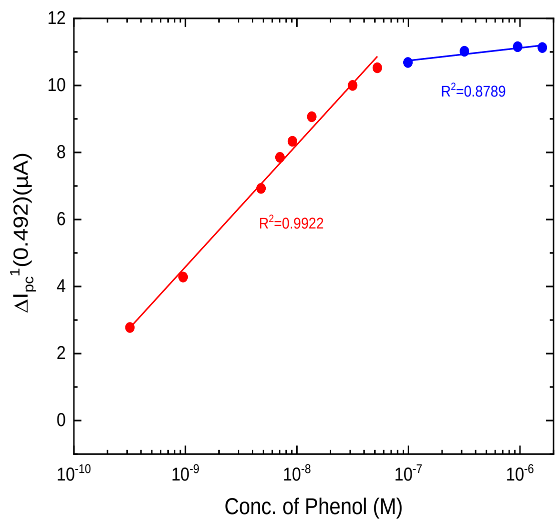
3. CV Titration Results of poly-[**5**]//poly-[**7**] Film with Phenol and Catechol



A

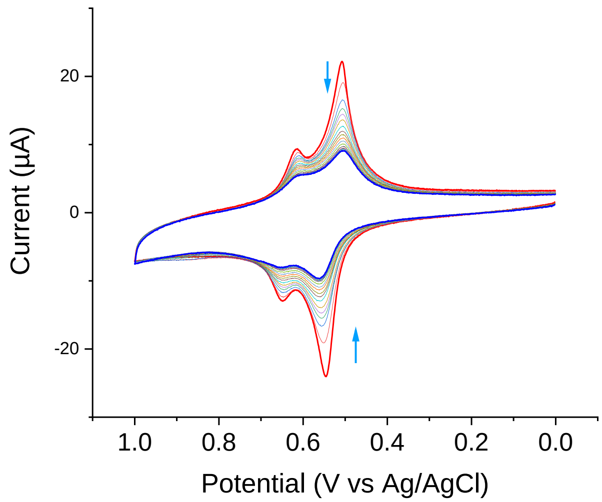


B

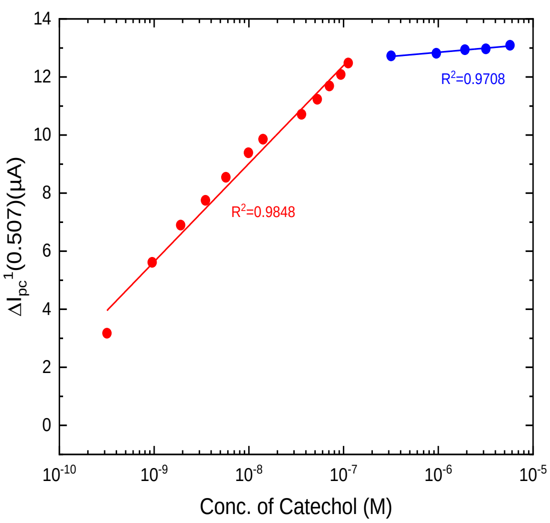


C

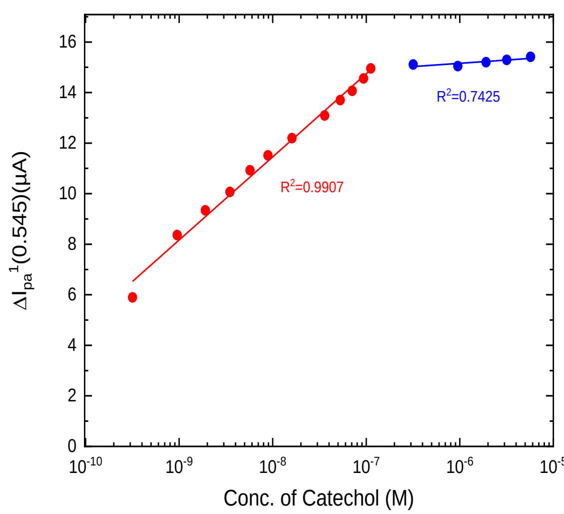
Fig. S-9 (A) CV scans monitoring the responses of the poly-[**5**]//poly-[**7**] thin film to the titration of phenol (0 to 1.59 $\times 10^{-6}$ M) inCH_3CN with Bu_4NBF_4 (0.1 M) as the electrolyte. Scan rate = 100 mV/s. (B) Correlation of the change in the intensity of the first anodic peak with the concentration of phenol. (C) Correlation of the change in the intensity of the first cathodic peak with the concentration of phenol.



A



B



C

Fig. S-10 (A) CV scans monitoring the responses of the poly-[**5**]//poly-[**7**] thin film to the titration of catechol (0 to 5.72 $\times 10^{-6}$ M) inCH_3CN with Bu_4NBF_4 (0.1 M) as the electrolyte. Scan rate = 100 mV/s. (B) Correlation of the change in the intensity of the first anodic peak with the concentration of catechol. (C) Correlation of the change in the intensity of the first cathodic peak with the concentration of catechol.

4. CV Titration Results of poly-[**7**] Film with Cannabidiol, Phenol, and Catechol

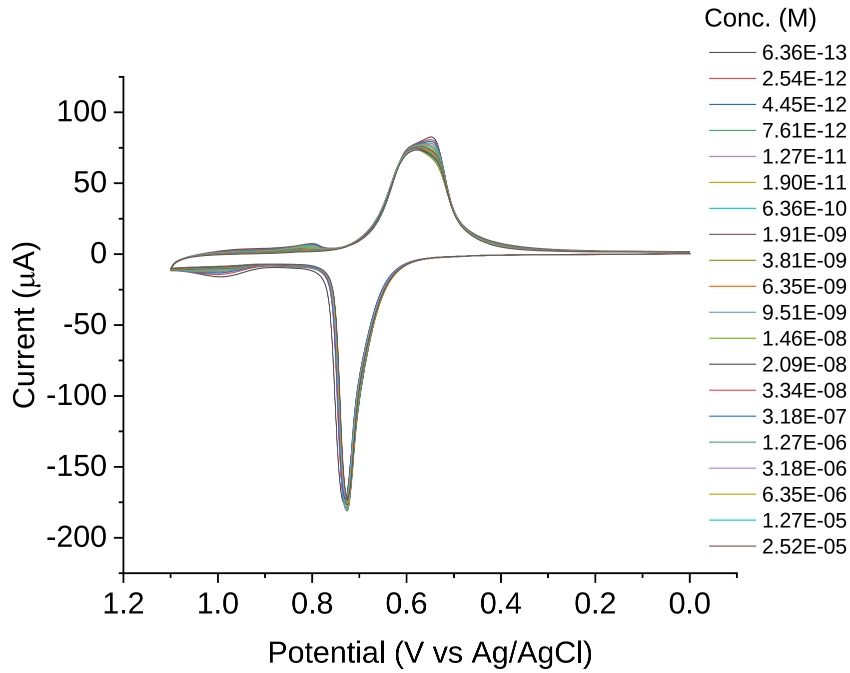


Fig. S-11 CV scans monitoring the responses of the poly-[**7**] thin film to the titration of cannabidol (0 to 2.52 $\times 10^{-5}$ M) inCH_3CN with Bu_4NBF_4 (0.1 M) as the electrolyte. Scan rate = 100 mV/s.

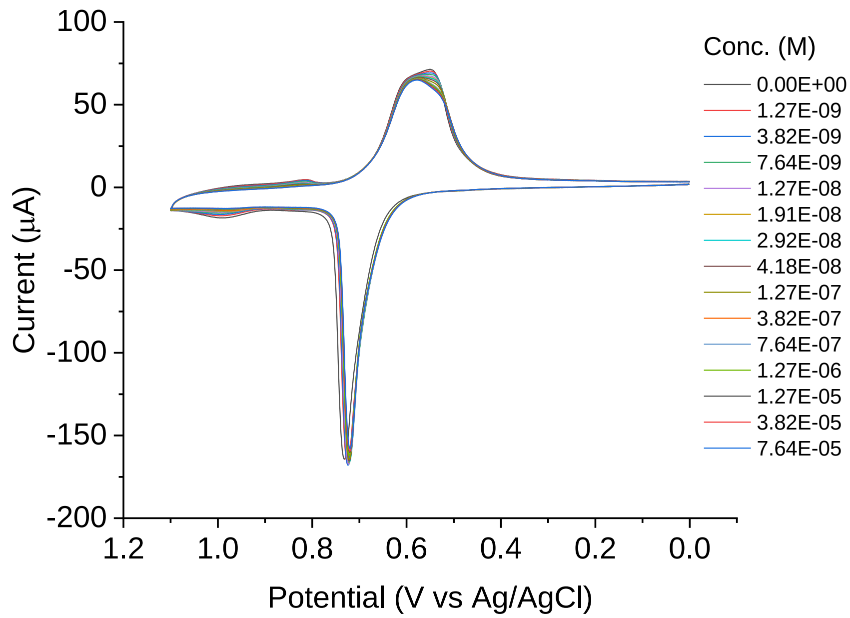


Fig. S-12 CV scans monitoring the responses of the poly-[**7**] thin film to the titration of phenol (0 to 7.64 $\times 10^{-5}$ M) inCH_3CN with Bu_4NBF_4 (0.1 M) as the electrolyte. Scan rate = 100 mV/s.

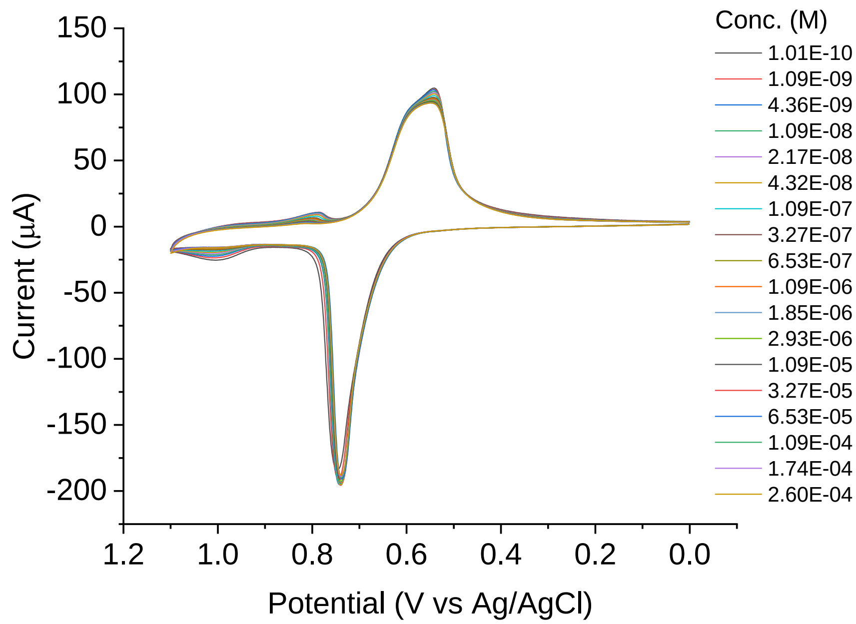


Fig. S-13 CV scans monitoring the responses of the poly-[**7**] thin film to the titration of catechol (0 to 2.60×10^{-4} M) inCH_3CN with Bu_4NBF_4 (0.1 M) as the electrolyte. Scan rate = 100 mV/s.

5. Effects of Trace Amounts of Water on the CV Properties of Poly-[**5**]//Poly-[**7**] Film

To investigate whether trace amounts of water in organic solvents can exert significant effects of the CV behavior of the poly-[**5**]//poly-[**7**] film, a comparative study was conducted in which two thin films of poly-[**5**]//poly-[**7**] were prepared through multi-cycle CV scans. Figure S-14A shows the CV profiles of the thin film prepared and measured in ACS grade CH_3CN (water < 0.03% wt) without any further purification. Figure S-14B shows the CV profiles of the thin film prepared and measured in ACS grade CH_3CN dried through a solvent purification system. Comparison of the data from the two sets of experiments confirms that trace amounts of water in organic solvents have rather insignificant effects on the CV properties of the poly-[**5**]//poly-[**7**] film.

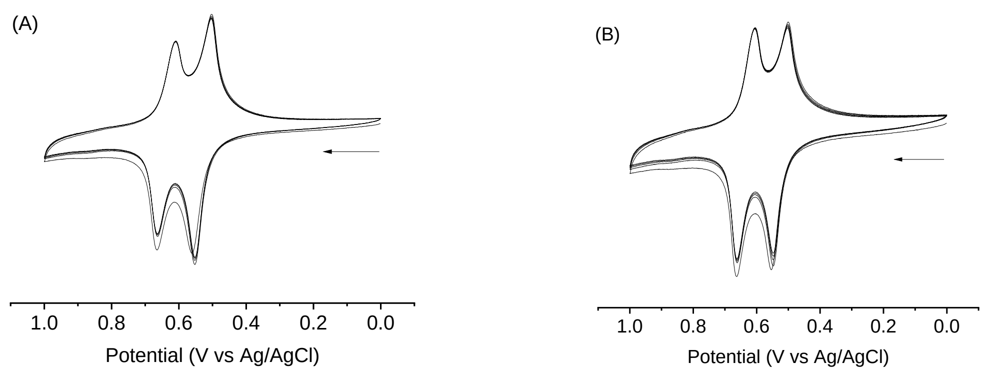


Figure S-14 (A) Multi-cycle CV scans of poly-[**5**]/poly-[**7**] prepared and measured in ACS grade acetonitrile without further drying. (B) Multi CV scans of poly-[**5**]/poly-[**7**] prepared and measured in ACS grade acetonitrile after drying through a solvent purification system. Bu_4NBF_4 (0.1 M) as the electrolyte. Scan rate = 100 mV/s. The arrows indicate the initial scan directions.

6. Understanding the Adsorption of Phenols on Poly-[**5**]//Poly-[**7**] Film

To shed light on the adsorption process of phenols on the film of poly-[**5**]//poly-[**7**] film, a control experiment was undertaken as follows. A poly-[**5**]//poly-[**7**] film was first prepared and them immersed into a solution of phenol (6.30 $\times 10^{-4}$ M) in CH_3CN for a certain period of time. Next, the thin film was subjected to thorough rinsing with CH_2Cl_2. After that, the thin film was examined by CV scans in CH_3CN in the presence of Bu_4NBF_4.

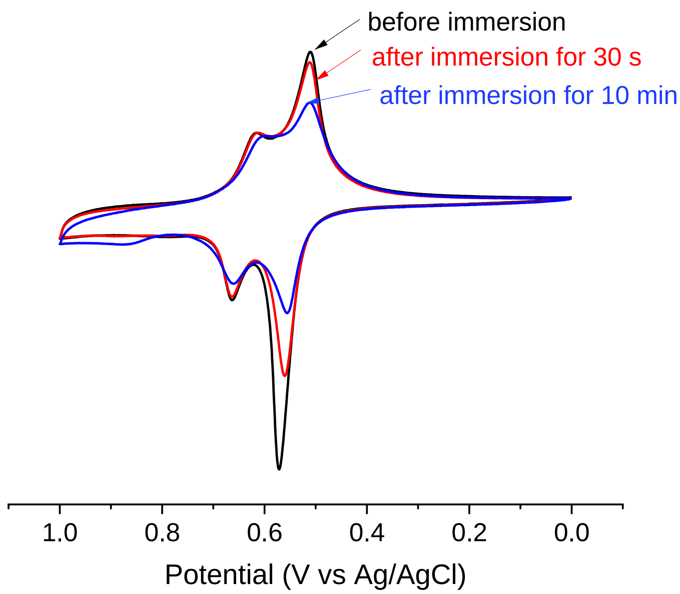


Figure S-15 CV profiles of a poly-[**5**]//poly-[**7**] film measured before and after immersion in a phenol solution (6.30 $\times 10^{-4}$ M in CH_3CN) followed by thorough rinsing with CH_2CH_2. Bu_4NBF_4 (0.1 M) as the electrolyte. Scan rate = 100 mV/s.

As shown in Figure S-15, the thin film after immersion in a phenol solution followed by thorough CH_2Cl_2 rinsing shows attenuated redox currents and slightly shifted redox potentials. The results confirm that phenols can be irreversibly trapped in neutral poly-[**5**]//poly-[**7**] film.

7. Results of DFT and TD-DFT Calculations

Table S-3 Summary of TD-DFT results for **5** calculated at the B3LYP/6-311+G(2d,p) level (in CH_2Cl_2)

λ_{abx} (nm)	*f*	Major contributions
385.2	0.047	H-1→L (50%), H→L (48%)
382.5	0.090	H-1→L+1 (46%), H→L+1 (51%)
370.0	0.233	H-1→L+3 (21%), H-1→L+4 (14%), H→L+3 (21%), H→L+4 (18%)
368.4	0.163	H-1→L+2 (21%), H-1→L+5 (15%), H→L+2 (18%), H→L+5 (19%)
339.4	0.005	H-1→L+1 (50%), H→L+1 (47%)
337.5	0.796	H-1→L+5 (17%), H→L+2 (16%), H→L+3 (10%), H→L+4 (16%), H→L+5 (11%)
333.8	0.533	H-1→L+4 (15%), H→L+2 (14%), H→L+3 (17%), H→L+4 (10%), H→L+5 (14%)
332.4	0.007	H-1→L+2 (56%), H→L+2 (43%)
330.6	0.002	H-1→L+3 (55%), H→L+3 (43%)
310.9	0.027	H-1→L+6 (41%), H→L+6 (36%)
310.3	0.028	H-1→L+7 (38%), H→L+6 (10%), H→L+7 (38%)
289.9	0.013	H-4→L (89%)
289.7	0.016	H-5→L+1 (62%), H-2→L+1 (21%)
281.0	0.011	H-1→L+8 (29%), H-1→L+11 (11%), H→L+8 (28%), H→L+11 (10%)
279.0	0.007	H-1→L+10 (25%), H-1→L+11 (14%), H→L+10 (27%), H→L+11 (16%)
276.6	0.022	H-1→L+9 (37%), H→L+9 (39%)
276.5	0.049	H-6→L (35%), H-3→L (51%)
274.8	0.039	H-7→L+1 (24%), H-5→L+1 (12%), H-2→L+1 (45%)
273.9	0.011	H-1→L+8 (12%), H-1→L+10 (15%), H-1→L+11 (17%), H→L+8 (11%), H→L+10 (14%), H→L+11 (17%)
263.9	0.115	H-2→L+3 (70%)
259.7	0.140	H-3→L+2 (67%)
259.5	0.029	H-1→L+18 (11%), H→L+10 (11%), H→L+12 (16%), H→L+18 (10%)
258.9	0.014	H-1→L+13 (10%), H-1→L+16 (14%), H→L+13 (12%), H→L+16 (12%)
258.2	0.006	H-1→L+12 (22%), H→L+12 (22%)
256.8	0.011	H-1→L+12 (11%), H-1→L+18 (18%), H→L+18 (17%)

Table S-4 Summary of TD-DFT results for **6** calculated at the B3LYP/6-311+G(2d,p) level (in CH_2Cl_2)

λ_{abx} (nm)	*f*	Major contributions
383.7	0.048	H→L+1 (98%)
368.0	0.227	H→L+2 (51%), H→L+4 (40%)
336.1	0.699	H→L+2 (46%), H→L+4 (50%)
311.6	0.031	H→L+5 (88%)
290.1	0.013	H-2→L+1 (94%)
280.3	0.018	H→L+6 (64%), H→L+7 (21%)

279.6	0.087	H-1→L (90%)
276.8	0.507	H-3→L (82%)
276.5	0.047	H-4→L+1 (35%), H-1→L+1 (50%)
273.1	0.009	H→L+6 (29%), H→L+7 (55%)
262.9	0.014	H-7→L (68%), H-3→L+3 (29%)
259.2	0.137	H-1→L+2 (73%)
256.7	0.028	H-2→L+2 (57%), H→L+8 (15%)
256.5	0.009	H-2→L+2 (13%), H→L+8 (18%), H→L+10 (15%), H→L+13 (40%)
251.4	0.005	H-4→L+1 (29%), H-1→L+1 (13%), H→L+11 (30%)
250.3	0.004	H→L+8 (12%), H→L+10 (19%), H→L+11 (14%), H→L+12 (14%)
249.8	0.050	H-4→L+1 (17%), H-1→L+1 (16%), H→L+9 (18%), H→L+11 (14%), H→L+12 (12%)
243.9	0.027	H-2→L+4 (10%), H-1→L+4 (61%)
241.4	0.037	H-4→L+2 (32%), H-2→L+4 (13%), H→L+16 (17%)
241.0	0.015	H-5→L+2 (11%), H-2→L+4 (51%)
239.4	0.001	H-3→L+1 (96%)
238.3	0.014	H→L+9 (23%), H→L+12 (26%), H→L+17 (15%)

Table S-5 Cartesian coordinates for optimized **5** and **6** at the B3LYP/6-311+G(2d,p) level (in CH_2Cl_2)

5 (*E* = -4382.208480 Hartree)				**6** (*E* = -2670.414334 Hartree)			
H	-3.48526500	2.83003500	1.94723600	H	0.15509700	1.75874400	-1.30890300
C	-3.72557300	2.73262500	0.89553400	C	0.35314600	0.78032200	-0.88851100
C	-4.33892600	2.52979500	-1.79081400	C	0.82748000	-1.73571100	0.15078600
C	-2.93003900	3.39770300	-0.04190500	C	-0.72466100	-0.00207000	-0.46548000
C	-4.80805800	1.97202000	0.48994200	C	1.65007600	0.30897800	-0.78502800
C	-5.14168000	1.83614600	-0.87144500	C	1.92918000	-0.96287400	-0.24869000
C	-3.24947400	3.29639300	-1.39774300	C	-0.47923900	-1.27478900	0.05354400
H	-5.41019600	1.50403600	1.25654400	H	2.44591300	0.93871000	-1.15830900
H	-2.66430100	3.80582900	-2.15002600	H	-1.28827700	-1.91224400	0.38087400
H	-4.57149200	2.46273800	-2.84778800	H	0.99902400	-2.72689000	0.55552500
O	-1.88906500	4.12054900	0.45914800	O	-1.96196100	0.55470400	-0.60932000
C	-1.03171700	4.81939300	-0.45342600	C	-3.10540200	-0.20268200	-0.20398600
H	-0.59827600	4.11236100	-1.16580100	H	-3.14681400	-1.13882100	-0.77073100
H	-1.61372200	5.56179100	-1.00765400	H	-3.02618100	-0.44733500	0.86048900
C	0.05492800	5.50595800	0.35594900	C	-4.33164000	0.65275800	-0.47570600
H	-0.40784300	6.16059500	1.09935500	H	-4.37485700	0.89831100	-1.53933700
H	0.63351000	6.14293900	-0.31847500	H	-4.24981600	1.59060500	0.07860200
C	0.99446800	4.55602000	1.07836500	C	-5.60785300	-0.06329200	-0.07035800
H	1.69057000	5.12035600	1.70599200	H	-5.73288700	-0.99524900	-0.62980900
H	0.43478000	3.86343800	1.71264300	H	-5.60803700	-0.29487900	0.99900600
O	1.72781000	3.82021900	0.08987400	O	-6.70189800	0.81856200	-0.36661900
C	2.62391200	2.88040000	0.50342200	C	-7.96456600	0.41544300	-0.09955600
C	4.53899900	0.89589300	1.14566200	C	-10.64711900	-0.21385000	0.36925300
C	3.29281600	2.18130300	-0.50541700	C	-8.97587000	1.33663300	-0.42693800
C	2.90116700	2.57735400	1.83836600	C	-8.29885200	-0.82062300	0.46285700
C	3.83940500	1.59856000	2.13947400	C	-9.63515200	-1.12051900	0.69043500
C	4.22645000	1.20943300	-0.19110300	C	-10.29608800	1.02453700	-0.19522100

H	3.05975100	2.40598400	-1.53910600	H	-8.69004600	2.28637000	-0.86130700
H	2.39663400	3.08989900	2.64498400	H	-7.53736900	-1.54149000	0.72175600
H	4.04029900	1.37582100	3.18151700	H	-9.89678500	-2.07840600	1.12689400
H	4.69014300	0.67349700	-1.00786600	H	-11.07815200	1.73026900	-0.44596000
C	5.51631200	-0.09982700	1.56758800	C	-12.04180500	-0.57383800	0.62735600
H	5.45422400	-0.36975600	2.61841100	H	-12.18432300	-1.57769300	1.07290200
C	-6.25059300	1.04424400	-1.38878900	O	-13.00915900	0.13074500	0.39262700
H	-6.48706400	1.23436900	-2.43226700	C	3.26153700	-1.53238500	-0.09008600
C	-7.01171500	0.10781900	-0.78912500	H	3.27040500	-2.59948300	0.11501400
S	-8.37104100	-0.65158300	-1.65684000	C	4.47485600	-0.94812500	-0.13712400
S	-6.87129700	-0.52188200	0.86600800	S	5.96467400	-1.91212800	0.02359000
C	-8.63180000	-1.97882100	-0.51463800	S	4.84417400	0.77442800	-0.37377400
C	-7.95626300	-1.91234700	0.64809000	C	7.07051200	-0.55388900	0.25648700
S	-9.86498900	-3.17718800	-0.90299400	C	6.56023100	0.67973300	0.08691500
S	-8.00227200	-3.06579600	1.98725000	S	8.73001200	-0.98395900	0.70326700
C	-9.26256100	-3.86490600	-2.49330000	S	7.47098600	2.18728200	0.13737700
H	-9.25129700	-3.10699600	-3.27268900	C	9.63734200	-0.71803000	-0.86894100
H	-9.97981600	-4.64248100	-2.75366900	H	9.20278400	-1.32019900	-1.66356900
H	-8.27607400	-4.30424000	-2.36354300	H	10.65624100	-1.05148900	-0.67315600
C	-9.55042400	-2.59823400	2.85568200	H	9.64207300	0.33629300	-1.13524000
H	-9.58842200	-3.23337200	3.74055800	C	6.68071800	3.07101700	1.53851200
H	-9.51601600	-1.55394500	3.15775600	H	7.21554000	4.01690900	1.61727800
H	-10.41674000	-2.79401400	2.22788000	H	5.62983500	3.26378500	1.33676000
C	6.49014500	-0.72098900	0.87387500	H	6.80223000	2.50165700	2.45724100
S	6.93456100	-0.48127400	-0.83080900				
S	7.50938200	-1.96716500	1.63770000				
C	8.73454800	-2.04464200	0.36697800				
C	8.48198400	-1.35715800	-0.76200100				
S	10.16777500	-3.01605900	0.74197900				
S	9.47342600	-1.36988400	-2.21857900				
C	9.87285400	-4.53994900	-0.23614500				
H	10.68797100	-5.21352300	0.02765700				
H	9.90641200	-4.32456000	-1.30153600				
H	8.92289500	-4.99058600	0.04203100				
C	9.95859000	0.39346600	-2.37300900				
H	10.58438800	0.44046000	-3.26354600				
H	10.53312700	0.70181900	-1.50247200				
H	9.08662800	1.02877500	-2.50814100				