Supporting Information

Redox-controlled near-infrared-to-near-infrared optical switching in TPA dimers

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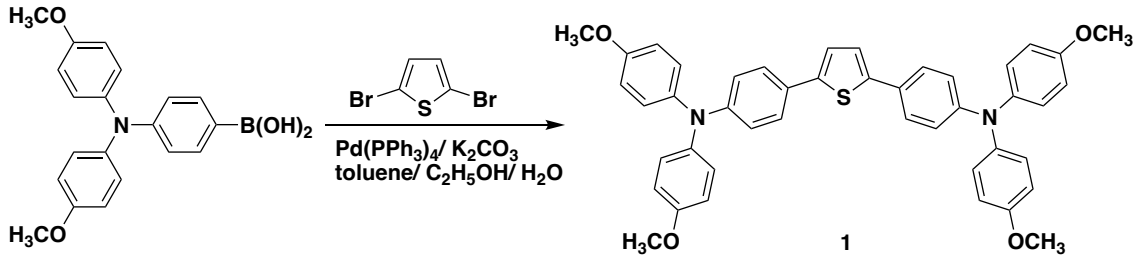
1. General

^{1}H and ^{13}C NMR spectra were recorded on a JEOL JNM-ECZL400 spectrometer. Chemical shifts are reported in parts per million (ppm, δ scale) from residual protons in the deuterated solvent for ^{1}H NMR (δ 7.26 ppm for chloroform) and from the solvent carbon for ^{13}C NMR (δ 77.16 ppm for deuterated chloroform). Cyclic voltammograms (CVs) and differential pulse voltammograms (DPVs) were recorded on a Potentiometer/galvanostat analyzer ECstat-302. UV-vis-NIR absorption spectra were recorded on V-670 UV-Vis-NIR Spectrophotometer. Emission spectra were recorded on JASCO FP-8600 Spectrophotometer. ESR spectra were recorded on Bruker Magnettech ESR5000 Spectrophotometer. Analytic thin layer chromatography (TLC) was performed on Merck, pre-coated plate silica gel 60 F_{254} (0.25 mm thickness). Unless otherwise noted, all materials were obtained from commercial suppliers and used without further purification. All reactions were performed under nitrogen atmosphere. HRMS (DART) spectra were recorded with a Thermo Fisher Scientific LTQ Orbitrap XL instrument. Melting points were recorded on a Yanagimoto micro-melting apparatus and are uncorrected.

2. Syntheses of compounds 1–4

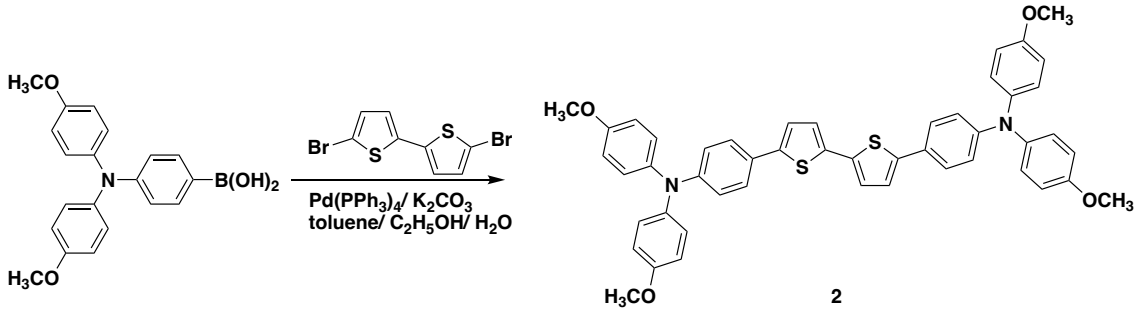
4,4'-(thiophene-2,5-diyl)bis(*N*,*N*-bis(4-methoxyphenyl)aniline) **(1)**



A mixture of 4-[bis(4-methoxyphenyl)amino]phenylboronic acid (0.265 g, 0.758 mmol), 2,5-dibromothiophene (0.0665 g, 0.275 mmol), tetrakis(triphenylphosphine)palladium(0) (17.6 mg, 0.015 mmol), potassium carbonate (0.269 g, 1.27 mmol) in toluene (3 mL), ethanol (2 mL) and water (1 mL) was purged with nitrogen and stirred for 10 minutes, then heated at 90 °C under nitrogen for 24 h. After cooling to room temperature, the mixture was extracted with chloroform (3 × 50 mL). The combined organic phase was dried over Na_2SO_4 and the solvent was evaporated in vacuo. The residue was purified by recrystallization from ethanol/ ethyl acetate to afford yellow-brown powder (0.131 g, 77.0%).

m.p.: 86.0–86.5 °C.
IR (ATR): 1491, 1234, 823 cm^{-1}.
^1H NMR (400 MHz, $CDCl_3$): δ 3.79 (s, 12H), 6.83 (d, 8H, *J*=8.9 Hz), 6.91 (d, 4H, *J*=8.7 Hz), 7.06 (d, 8H, *J*=8.9 Hz), 7.10 (s, 2H), 7.40 (d, 4H, *J*=8.7 Hz).
^{13}C NMR (100 MHz, $CDCl_3$): δ 55.6, 114.8, 120.8, 122.6, 126.2, 126.7, 126.8, 140.8, 142.6, 148.1, 156.0.
HRMS(DART): *m/z*: Calcd. for $C_{44}H_{38}N_2O_4S$ $[M]^+$: 690.2547; Found: 690.2526.

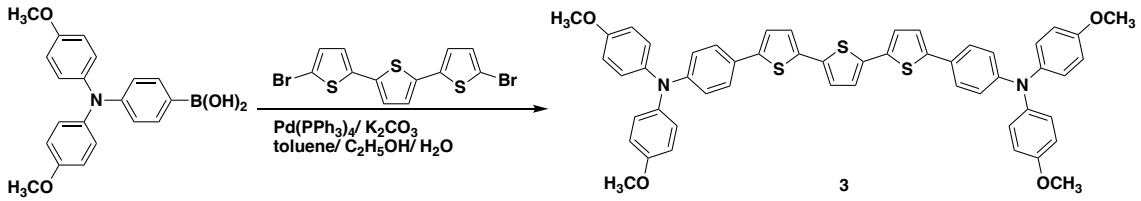
4,4'-([2,2'-bithiophene]-5,5'-diyl)bis(*N*,*N*-bis(4-methoxyphenyl)aniline) **(2)**



A mixture of 4-[bis(4-methoxyphenyl)amino]phenylboronic acid (0.330 g, 0.944 mmol), 5,5'-dibromo-2,2'-bithiophene (0.110 g, 0.341 mmol), tetrakis(triphenylphosphine)palladium(0) (26.0 mg, 0.023 mmol), potassium carbonate (0.341 g, 1.61 mmol) in toluene (3 mL), ethanol (2 mL) and water (1 mL) was purged with nitrogen and stirred for 10 minutes, then heated at 90 °C under nitrogen for 24 h. After cooling to room temperature, the mixture was extracted with chloroform (3 × 50 mL). The combined organic phase was dried over Na_2SO_4 and the solvent was evaporated in vacuo. The residue was purified by recrystallization from ethyl acetate to afford orange powder (0.237 g, 90.2%).

m.p.: 173.5–174.0 °C.
IR (ATR): 1490, 1237, 797 cm^{-1}.
^1H NMR (400 MHz, $CDCl_3$): δ 3.80 (s, 12H), 6.83 (d, 8H, *J*=8.9 Hz), 6.91 (d, 4H, *J*=8.9 Hz), 7.04–7.09 (m, 12H), 7.38 (d, 4H, *J*=8.9 Hz).
^{13}C NMR (100 MHz, $CDCl_3$): δ 55.6, 114.8, 120.6, 122.4, 124.2, 126.3 (overlapped two peaks), 126.8, 135.7, 140.7, 143.2, 148.3, 156.1.
HRMS(DART): *m/z*: Calcd. for $C_{48}H_{40}N_2O_4S_2$ $[M]^+$: 772.2424; Found: 772.2421.

4,4'-([2,2':5',2''-terthiophene]-5,5''-diyl)bis(*N*,*N*-bis(4-methoxyphenyl)aniline) **(3)**

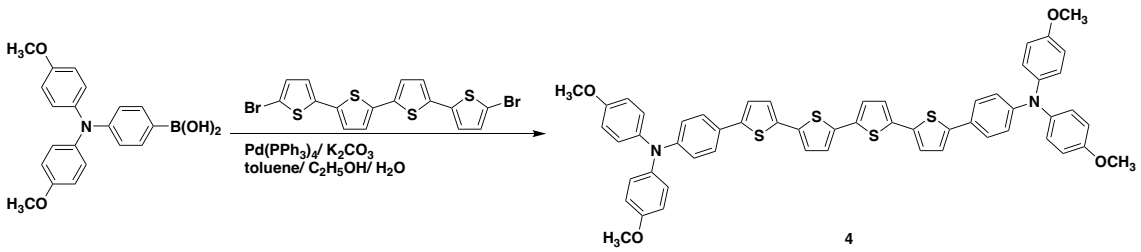


3

A mixture of 4-[bis(4-methoxyphenyl)amino]phenylboronic acid (0.517 g, 1.48 mmol), 5,5''-dibromo-2,2':5',2''-terthiophene (0.202 g, 0.497 mmol), tetrakis(triphenylphosphine)palladium(0) (40.5 mg, 0.036 mmol), potassium carbonate (0.539 g, 2.54 mmol) in toluene (5 mL), ethanol (3 mL) and water (2 mL) was purged with nitrogen and stirred for 10 minutes, then heated at 90 °C under nitrogen for 24 h. After cooling to room temperature, the mixture was extracted with chloroform (3 × 50 mL). The combined organic phase was dried over Na_2SO_4 and the solvent was evaporated in vacuo. The residue was purified by recrystallization from ethyl acetate to afford orange powder (0.346 g, 81.2%).

m.p.: 110.5–111.0 °C.
IR (ATR): 1491, 1236, 823 cm^{-1}.
^1H NMR (400 MHz, $CDCl_3$): δ 3.80 (s, 12H), 6.84 (d, 8H, *J*=8.9 Hz), 6.91 (d, 4H, *J*=8.9 Hz), 7.04–7.09 (m, 14H), 7.38 (d, 4H, *J*=8.7 Hz).
^{13}C NMR (100 MHz, $CDCl_3$): δ 55.6, 114.8, 120.5, 122.4, 124.0, 124.6, 126.1, 126.3, 126.8, 135.1, 136.2, 140.6, 143.6, 148.4, 156.1.
HRMS(DART): *m/z*: Calcd. for $C_{52}H_{43}N_2O_4S_3$ $[M+H]^+$: 855.2379; Found: 855.2389.

4,4'-([2,2':5',2":5",2"'-quaterthiophene]-5,5"'-diyl)bis(*N*,*N*-bis(4-methoxyphenyl)aniline) **(4)**



A mixture of 4-[bis(4-methoxyphenyl)amino]phenylboronic acid (0.121 g, 0.347 mmol), 5,5"'-dibromo-2,2':5',2":5",2"'-quaterthiophene [1] (0.0535 g, 0.109 mmol), tetrakis(triphenylphosphine)palladium(0) (36.0 mg, 0.030 mmol), potassium carbonate (0.162 g, 0.766 mmol) in toluene (40 mL), ethanol (20 mL) and water (10 mL) was purged with nitrogen and stirred for 10 minutes, then heated at 90 °C under nitrogen for 24 h. After cooling to room temperature, the mixture was extracted with chloroform (3 × 50 mL). The combined organic phase was dried over Na_2SO_4 and the solvent was evaporated in vacuo. The residue was purified by column chromatography on silica gel using *n*-hexane/chloroform (1:1) as the eluent to afford orange powder. (0.0535 g, 55.2%).

m.p.: 116.0–116.5 °C.
IR (ATR): 1237, 825, 789 cm^{-1}.
^1H NMR (400 MHz, $CDCl_3$): δ 3.80 (s, 12H), 6.84 (d, 8H, *J*=8.9 Hz), 6.91 (d, 4H, *J*=8.9 Hz), 7.06–7.09 (m, 16H), 7.38 (d, 4H, *J*=8.9 Hz).
^{13}C NMR (100 MHz, $CDCl_3$): δ 55.6, 114.9, 120.5, 122.4, 124.0, 124.3, 124.7, 126.1, 126.4, 126.8, 135.0, 135.6, 136.6, 140.7, 143.8, 148.5, 156.2.
HRMS(DART): *m/z*: Calcd. for $C_{56}H_{45}N_2O_4S_4$ $[M+H]^+$: 937.2257; Found: 937.2273.

3. DFT Calculations

Density functional theory (DFT) calculations were performed using Gaussian 16 program [2]. Geometries were optimized at the (U)B3LYP/6-31+G(d,p) level of theory [3] with the conductive polarizable continuum model (CPCM) [4] using dichloromethane as a solvent. TD-DFT calculations were carried out using (U)B3LYP. The data are summarized in Table S1 as well as Figures S1–S9.

Table S1. Comparison of different functionals employed in TD-DFT calculations performed with the 6-31+G(d,p) basis set.

Compound	Exp [nm]	Calcd. [nm]	Oscillator strength f	Composition
1	400	462	1.5900	182→183
$\mathbf{1}^{\bullet+}$	1775	1745	0.9894	181B→182B
$\mathbf{1}^{2+}$	1077	1179 (CS)[1)]	2.3417	181→182
		1194 (OS)[2)]	1.3476	181A→182A
2	427	514	1.8936	203→204
$\mathbf{2}^{\bullet+}$	1948	1954	1.1701	202B→203B
$\mathbf{2}^{2+}$	1303	1286 (CS)[1)]	2.9174	202→203
		1435 (OS)[2)]	1.7744	202B→203B
3	445	555	2.1442	224→225
$\mathbf{3}^{\bullet+}$	2028	2217	1.3041	223B→224B
$\mathbf{3}^{2+}$	1557	1424 (CS)[1)]	3.2419	223→224
		1670 (OS)[2)]	2.0206	223A→224A
4	457	594	2.7785	245→246
$\mathbf{4}^{\bullet+}$	1756	2507	1.7737	244B→245B
$\mathbf{4}^{2+}$	1744	1574 (CS)[1)]	3.6462	244→245
		1875 (OS)[2)]	2.2932	244B→245B

1) CS: calculated as a closed-shell singlet 2) OS: calculated as an open-shell singlet

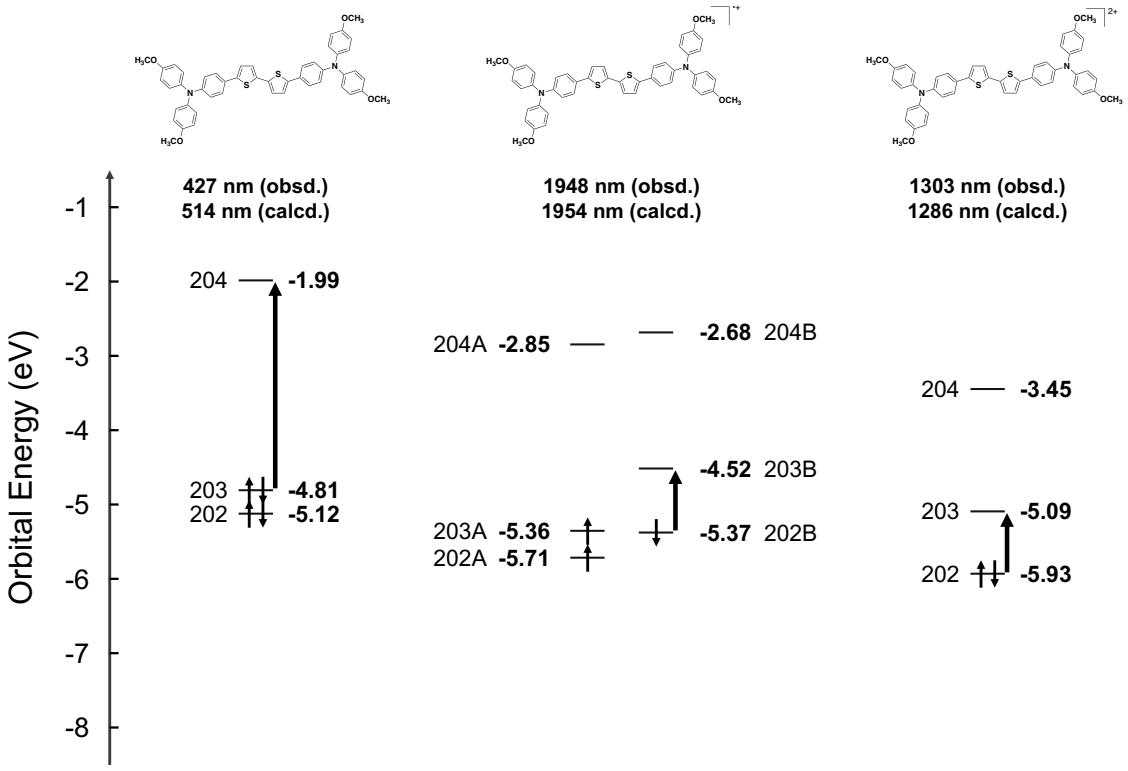


Figure S1. Calculated energy levels of compound **2** and its radical cation and dication at the (U)B3LYP/6-31+G(d,p) level of theory with the conductive polarizable continuum model using dichloromethane as a solvent.

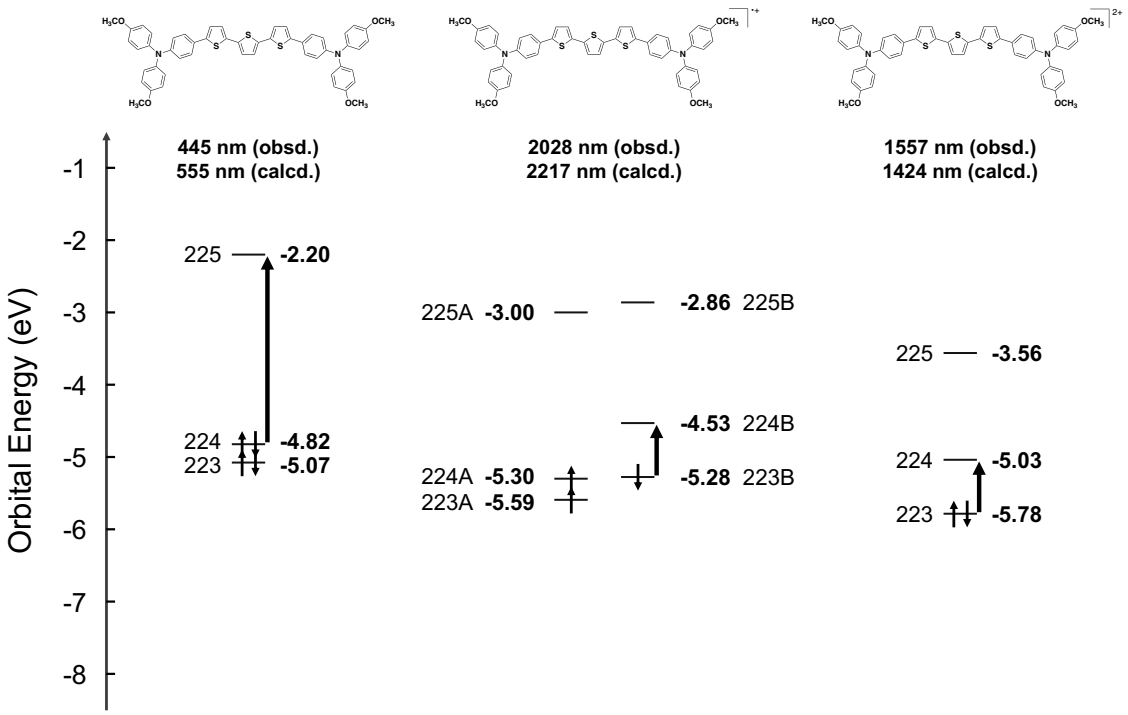


Figure S2. Calculated energy levels of compound **3** and its radical cation and dication at the (U)B3LYP/6-31+G(d,p) level of theory with the conductive polarizable continuum model using dichloromethane as a solvent.

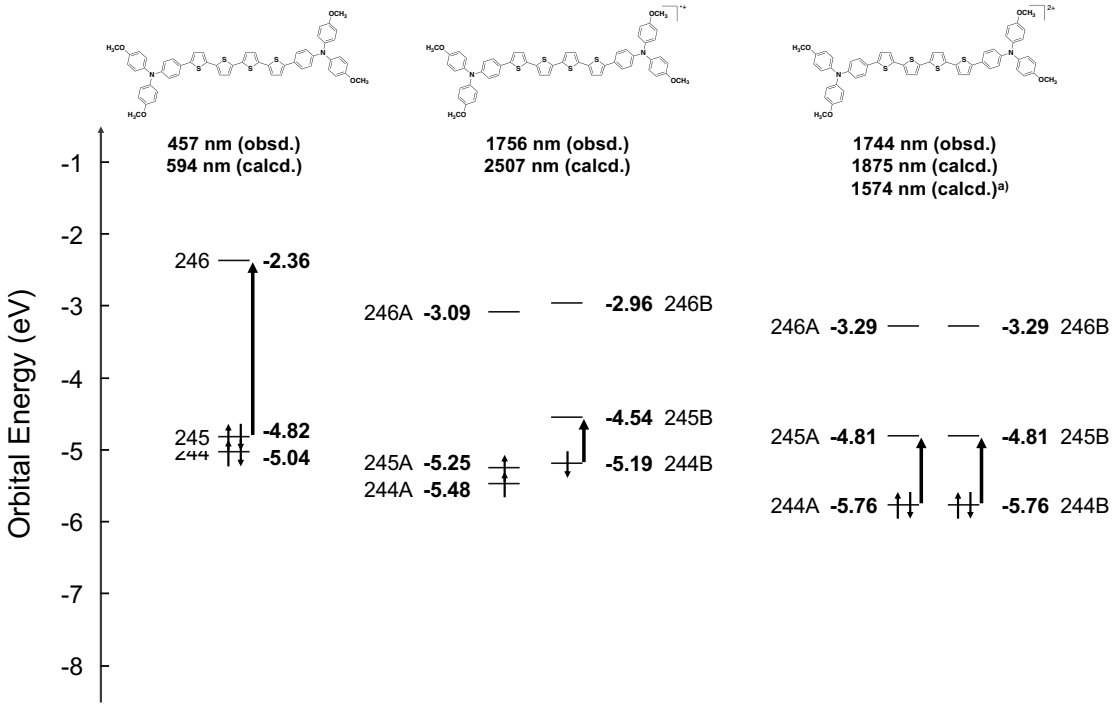


Figure S3. Calculated energy levels of compound **4** and its radical cation and dication at the (U)B3LYP/6-31+G(d,p) level of theory with the conductive polarizable continuum model using dichloromethane as a solvent. The dication of compound **4** was calculated as an open-shell singlet. a) The value calculated for the closed-shell singlet dication.

$1^{\bullet+}$

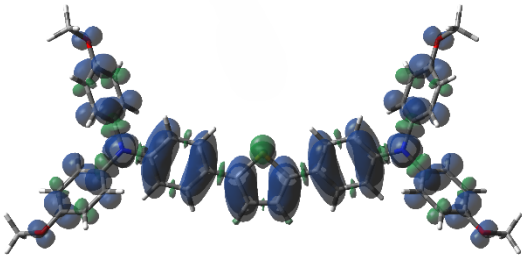


Figure S4. Spin density plots of radical cation $\mathbf{1}^{\bullet+}$.

$2^{\bullet+}$

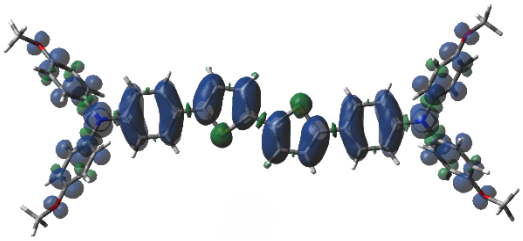


Figure S5. Spin density plots of radical cation $\mathbf{2}^{\bullet+}$.

$3^{\bullet+}$

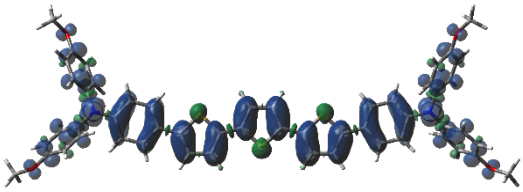


Figure S6. Spin density plots of radical cation $\mathbf{3}^{\bullet+}$.

$\mathbf{4}^{\bullet+}$	$\mathbf{4}^{2+}$

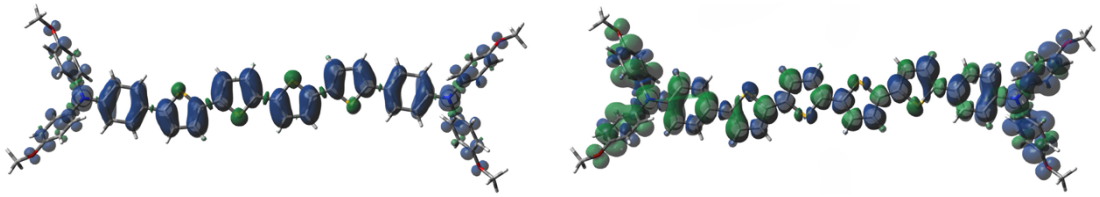


Figure S7. Spin density plots of radical cation $\mathbf{4}^{\bullet+}$ and open-shell singlet dication $\mathbf{4}^{2+}$.

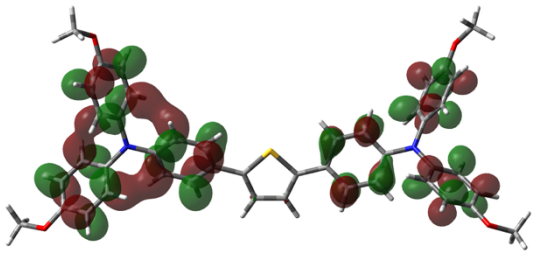
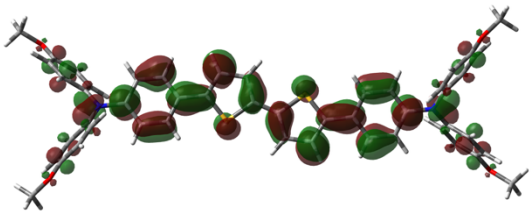
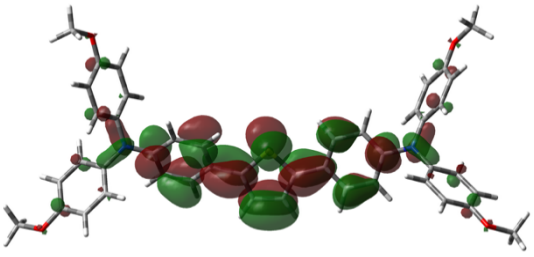
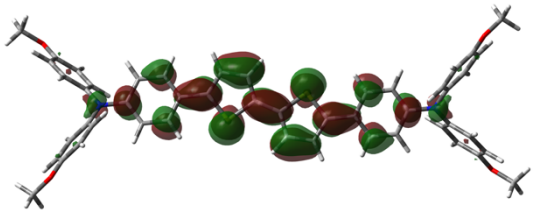
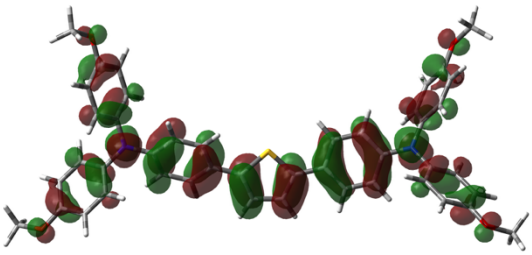
1	2
	
LUMO+1 -0.96 eV	**LUMO+1** -1.09 eV
	
LUMO -1.67 eV	**LUMO** -1.99 eV
	
HOMO -4.80 eV	**HOMO** -4.81 eV

Figure S8. HOMO, LUMO, and LUMO+1 orbitals of **1** and **2** with calculated energy levels.

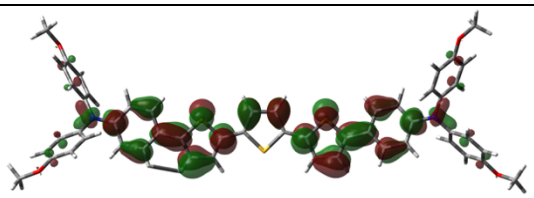
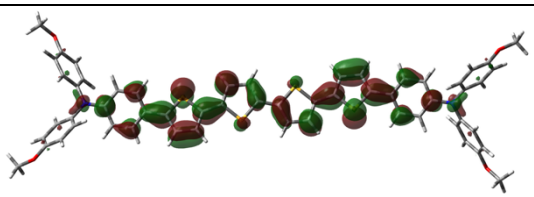
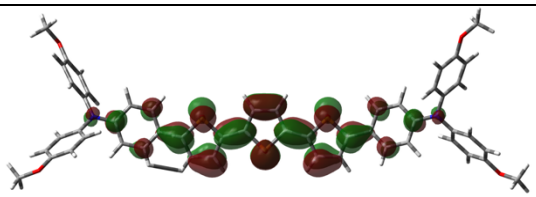
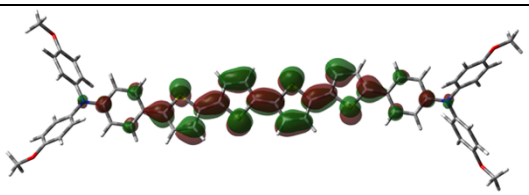
3	4
	
LUMO+1 -1.42 eV	**LUMO+1** -1.69 eV
	
LUMO -2.20 eV	**LUMO** -2.36 eV
	
HOMO -4.82 eV	**HOMO** -4.82 eV

Figure S9. HOMO, LUMO, and LUMO+1 orbitals of **3** and **4** with calculated energy levels.

Computed Geometries

4,4'-(thiophene-2,5-diyl)bis(*N*,*N*-bis(4-methoxyphenyl)-aniline) (1) in dichloromethane

C	**1.26114**	**-1.29836**	**-0.56374**
C	**0.68724**	**-2.44973**	**-1.06534**
C	**-0.73376**	**-2.44511**	**-1.04668**
C	**-1.28535**	**-1.28869**	**-0.53289**
S	**-0.00256**	**-0.18237**	**-0.06165**
H	**1.26753**	**-3.28152**	**-1.44806**
H	**-1.33138**	**-3.28197**	**-1.39006**
C	**-2.69841**	**-0.93595**	**-0.37446**
C	**-3.13149**	**0.04696**	**0.53773**
C	**-3.69275**	**-1.58127**	**-1.13902**
C	**-4.47763**	**0.36453**	**0.68759**
H	**-2.40756**	**0.55770**	**1.16666**
C	**-5.03986**	**-1.26902**	**-0.99782**
H	**-3.40655**	**-2.32152**	**-1.87981**
C	**-5.46415**	**-0.28775**	**-0.07819**
H	**-4.76944**	**1.11687**	**1.41215**
H	**-5.77150**	**-1.77755**	**-1.61622**
C	**2.68102**	**-0.96351**	**-0.42245**
C	**3.12534**	**0.35763**	**-0.21507**
C	**3.67208**	**-1.96476**	**-0.49573**
C	**4.47565**	**0.66578**	**-0.08482**
H	**2.40481**	**1.16830**	**-0.15239**

C	5.02483	-1.66395	-0.38625	C	8.93965	-1.28147	-0.17215
H	3.38395	-3.00090	-0.64241	C	7.47861	-1.61512	1.71705
C	5.45895	-0.33912	-0.17448	C	9.85903	-2.18803	0.36729
H	4.77190	1.69543	0.08281	H	9.16233	-0.80025	-1.11934
H	5.75391	-2.46356	-0.45866	C	8.37618	-2.53235	2.25166
C	-7.23285	1.35369	0.42411	H	6.56153	-1.38756	2.25131
C	-8.15162	1.56353	1.45825	C	9.57637	-2.82407	1.58285
C	-6.73498	2.47159	-0.26911	H	10.77496	-2.39252	-0.17380
C	-8.57801	2.85222	1.79839	H	8.16896	-3.02205	3.19810
H	-8.54686	0.71258	2.00415	N	-6.82824	0.03188	0.06613
C	-7.13716	3.75726	0.07413	N	6.82842	-0.03122	-0.05577
H	-6.02801	2.32901	-1.08031	O	-10.76099	-3.90525	-0.66569
C	-8.06551	3.95850	1.10883	O	-8.40617	5.25970	1.36346
H	-9.29349	2.97393	2.60265	O	10.39837	-3.73156	2.19506
H	-6.75188	4.61907	-0.46192	O	8.79538	4.91411	-1.83844
C	-7.83429	-0.95901	-0.14592	C	-11.90509	-3.68148	-1.49175
C	-8.93368	-0.69536	-0.97025	H	-11.61255	-3.49000	-2.53051
C	-7.75386	-2.21302	0.48579	H	-12.49071	-4.59957	-1.44247
C	-9.93958	-1.64875	-1.16345	H	-12.50584	-2.84424	-1.11833
H	-9.01287	0.26729	-1.46555	C	-9.34927	5.52517	2.40338
C	-8.73773	-3.17437	0.28445	H	-8.97646	5.17963	3.37438
H	-6.91347	-2.43315	1.13654	H	-9.46985	6.60835	2.42502
C	-9.84146	-2.89898	-0.53940	H	-10.31595	5.05396	2.19150
H	-10.77718	-1.40603	-1.80611	C	11.63445	-4.06578	1.56120
H	-8.67393	-4.14198	0.77246	H	12.11717	-4.79104	2.21638
C	7.32905	1.23649	-0.48212	H	11.46590	-4.51782	0.57708
C	7.02523	1.73732	-1.76074	H	12.27684	-3.18397	1.45580
C	8.15174	1.99745	0.35547	C	9.64291	5.72485	-1.02251
C	7.52013	2.96758	-2.17799	H	9.87045	6.60907	-1.61803
H	6.39603	1.15738	-2.42856	H	9.13407	6.02663	-0.09988
C	8.67135	3.22776	-0.06242	H	10.57354	5.20134	-0.77510
H	8.39761	1.62633	1.34554				
C	8.35075	3.72211	-1.33319	**Radical cation of 4,4'-(thiophene-2,5-diyl)bis(*N*,*N*-bis(4-**			
H	7.28428	3.35290	-3.16512	**methoxyphenyl)aniline) ($1^{+\cdot}$) in dichloromethane**			
H	9.30783	3.78646	0.61306	C	1.27037	-1.33269	-0.33019
C	7.74493	-0.98004	0.49075	C	0.69873	-2.56545	-0.66830

C	-0.69877	-2.56544	-0.66832	C	-8.89477	-1.02703	-0.71944
C	-1.27041	-1.33270	-0.33023	C	-7.67260	-2.01591	1.12007
S	-0.00003	-0.15926	-0.01520	C	-9.88555	-2.00298	-0.59614
H	1.28557	-3.44740	-0.89258	H	-8.98887	-0.26500	-1.48619
H	-1.28559	-3.44740	-0.89262	C	-8.64996	-2.99362	1.24480
C	-2.66572	-0.98859	-0.23769	H	-6.82475	-2.01133	1.79733
C	-3.10203	0.26960	0.25312	C	-9.76479	-2.99646	0.38741
C	-3.67342	-1.90483	-0.64211	H	-10.73215	-1.98156	-1.27097
C	-4.44041	0.59603	0.33363	H	-8.57470	-3.75746	2.01181
H	-2.37496	0.99695	0.60113	C	7.22080	1.35658	-0.03721
C	-5.01449	-1.59148	-0.56025	C	6.78280	2.21286	-1.06291
H	-3.39587	-2.86956	-1.05144	C	8.11456	1.84252	0.92337
C	-5.43809	-0.32804	-0.07158	C	7.22084	3.52898	-1.11217
H	-4.73180	1.55941	0.73438	H	6.10678	1.84053	-1.82575
H	-5.75122	-2.30998	-0.89894	C	8.56534	3.16313	0.87688
C	2.66567	-0.98858	-0.23766	H	8.45954	1.18835	1.71742
C	3.10196	0.26974	0.25283	C	8.11550	4.01611	-0.14256
C	3.67339	-1.90493	-0.64177	H	6.89198	4.19312	-1.90477
C	4.44034	0.59618	0.33336	H	9.25286	3.51172	1.63749
H	2.37488	0.99720	0.60058	C	7.78207	-1.02473	0.12884
C	5.01446	-1.59156	-0.55992	C	8.89456	-1.02715	-0.71968
H	3.39587	-2.86978	-1.05084	C	7.67269	-2.01579	1.12016
C	5.43805	-0.32800	-0.07155	C	9.88532	-2.00312	-0.59646
H	4.73170	1.55967	0.73387	H	8.98853	-0.26519	-1.48651
H	5.75120	-2.31018	-0.89834	C	8.65004	-2.99353	1.24481
C	-7.22080	1.35655	-0.03737	H	6.82495	-2.01112	1.79755
C	-8.11471	1.84256	0.92306	C	9.76471	-2.99650	0.38721
C	-6.78257	2.21281	-1.06300	H	10.73181	-1.98178	-1.27143
C	-8.56539	3.16319	0.87649	H	8.57490	-3.75729	2.01190
H	-8.45988	1.18840	1.71704	N	-6.78512	-0.00563	0.00707
C	-7.22051	3.52896	-1.11233	N	6.78505	-0.00560	0.00712
H	-6.10648	1.84042	-1.82574	O	-10.66879	-3.99341	0.59191
C	-8.11529	4.01615	-0.14285	O	-8.48817	5.31804	-0.28035
H	-9.25307	3.51182	1.63693	O	10.66871	-3.99349	0.59163
H	-6.89149	4.19306	-1.90488	O	8.48857	5.31795	-0.28004
C	-7.78212	-1.02473	0.12887	C	-11.83006	-4.05354	-0.24369

H	-11.55216	-4.19463	-1.29377	C	3.09212	0.33222	0.19282
H	-12.39703	-4.91701	0.10303	C	3.65239	-1.85064	-0.74111
H	-12.43812	-3.14862	-0.13805	C	4.42401	0.63807	0.29598
C	-9.40531	5.87657	0.66680	H	2.36819	1.05880	0.54709
H	-8.98775	5.85408	1.67913	C	4.98761	-1.56316	-0.62275
H	-9.55495	6.91028	0.35649	H	3.36860	-2.80067	-1.17702
H	-10.36279	5.34501	0.64742	C	5.41849	-0.30469	-0.10570
C	11.82971	-4.05387	-0.24432	H	4.72689	1.58465	0.72597
H	12.39662	-4.91743	0.10226	H	5.72295	-2.28077	-0.96470
H	11.55146	-4.19496	-1.29431	C	-7.21117	1.34516	-0.02659
H	12.43797	-3.14906	-0.13892	C	-8.14147	1.79353	0.92175
C	9.40566	5.87641	0.66718	C	-6.75704	2.22517	-1.02788
H	9.55565	6.91002	0.35671	C	-8.60527	3.10553	0.89114
H	8.98793	5.85419	1.67944	H	-8.49073	1.11959	1.69654
H	10.36302	5.34460	0.64807	C	-7.21791	3.53027	-1.06525
				H	-6.06492	1.87421	-1.78591
Dication of 4,4'-(thiophene-2,5-diyl)bis(*N*,*N*-bis(4-				C	-8.14357	3.98498	-0.10495
methoxyphenyl)aniline) (1^{2+}) in dichloromethane				H	-9.31229	3.43242	1.64298
C	1.26765	-1.23409	-0.45336	H	-6.88871	4.21315	-1.84100
C	0.68917	-2.44694	-0.90966	C	-7.73002	-1.03841	0.14874
C	-0.68919	-2.44695	-0.90964	C	-8.89635	-1.01383	-0.62892
C	-1.26767	-1.23411	-0.45332	C	-7.54287	-2.06723	1.09197
S	-0.00001	-0.09248	-0.02941	C	-9.86031	-2.00811	-0.48886
H	1.27694	-3.29977	-1.22257	H	-9.04290	-0.22486	-1.35858
H	-1.27696	-3.29979	-1.22252	C	-8.50021	-3.05678	1.23801
C	-2.64534	-0.91936	-0.33426	H	-6.65976	-2.07232	1.72195
C	-3.09215	0.33219	0.19292	C	-9.66623	-3.04034	0.44663
C	-3.65241	-1.85067	-0.74104	H	-10.74538	-1.97548	-1.11128
C	-4.42404	0.63804	0.29606	H	-8.37528	-3.84584	1.97166
H	-2.36822	1.05877	0.54719	C	7.21122	1.34515	-0.02667
C	-4.98763	-1.56320	-0.62268	C	6.75723	2.22512	-1.02807
H	-3.36861	-2.80070	-1.17692	C	8.14143	1.79354	0.92174
C	-5.41851	-0.30473	-0.10563	C	7.21818	3.53019	-1.06549
H	-4.72692	1.58460	0.72606	H	6.06517	1.87415	-1.78614
H	-5.72297	-2.28082	-0.96462	C	8.60530	3.10551	0.89109
C	2.64532	-0.91933	-0.33433	H	8.49057	1.11963	1.69661

C	8.14378	3.98491	-0.10513
H	6.88909	4.21304	-1.84130
H	9.31222	3.43242	1.64301
C	7.72996	-1.03843	0.14876
C	8.89634	-1.01389	-0.62884
C	7.54273	-2.06724	1.09198
C	9.86026	-2.00821	-0.48871
H	9.04295	-0.22493	-1.35850
C	8.50002	-3.05683	1.23809
H	6.65958	-2.07229	1.72191
C	9.66608	-3.04044	0.44677
H	10.74535	-1.97562	-1.11109
H	8.37502	-3.84587	1.97173
N	-6.75385	-0.00675	0.00478
N	6.75384	-0.00675	0.00474
O	-10.53810	-4.05091	0.66331
O	-8.53215	5.27429	-0.22782
O	10.53789	-4.05106	0.66346
O	8.53248	5.27417	-0.22807
C	-11.75747	-4.09946	-0.09274
H	-11.54881	-4.19632	-1.16288
H	-12.28323	-4.98541	0.26048
H	-12.36684	-3.20955	0.09353
C	-9.49093	5.80918	0.69699
H	-9.10259	5.78258	1.71996
H	-9.64572	6.84253	0.38983
H	-10.43628	5.26067	0.63838
C	11.75739	-4.09953	-0.09239
H	12.28313	-4.98546	0.26090
H	11.54889	-4.19640	-1.16256
H	12.36667	-3.20959	0.09398
C	9.49100	5.80917	0.69694
H	9.64576	6.84253	0.38981
H	9.10247	5.78252	1.71984
H	10.43642	5.26077	0.63850

4,4'-([2,2'-bithiophene]-5,5'-diyl)bis(*N*,*N*-bis(4-methoxyphenyl)aniline) (2) in dichloromethane

C	-0.66229	0.29070	0.29981
C	-1.03702	1.61422	0.43434
C	-2.44118	1.81825	0.40006
C	-3.17563	0.65946	0.23805
S	-2.08930	-0.71855	0.10569
H	-0.32289	2.41735	0.58020
H	-2.89723	2.79397	0.52110
C	0.66230	-0.29056	0.29991
C	1.03701	-1.61407	0.43460
S	2.08934	0.71869	0.10600
C	2.44117	-1.81811	0.40040
H	0.32287	-2.41718	0.58044
C	3.17564	-0.65935	0.23830
H	2.89720	-2.79383	0.52150
C	-4.62888	0.49514	0.16554
C	-5.25825	-0.74555	0.39059
C	-5.46604	1.59062	-0.13367
C	-6.63964	-0.89038	0.31902
H	-4.66087	-1.62086	0.62984
C	-6.84848	1.45978	-0.18874
H	-5.03063	2.56563	-0.32850
C	-7.46932	0.21246	0.03276
H	-7.08083	-1.86576	0.49130
H	-7.45517	2.33022	-0.41271
C	4.62889	-0.49505	0.16574
C	5.25828	0.74565	0.39067
C	5.46603	-1.59057	-0.13339
C	6.63967	0.89046	0.31906
H	4.66092	1.62098	0.62986
C	6.84847	-1.45974	-0.18851
H	5.03061	-2.56559	-0.32815
C	7.46933	-0.21241	0.03288
H	7.08088	1.86585	0.49125
H	7.45515	-2.33021	-0.41242

N	8.86819	-0.07444	-0.03113	H	10.64607	1.72120	-0.91671
N	-8.86817	0.07445	-0.03118	C	9.97492	1.98441	2.88656
C	-9.64831	0.92005	-0.87810	H	8.61204	0.35002	2.61195
C	-10.77318	1.58550	-0.37926	C	10.89867	2.85238	2.28113
C	-9.31776	1.08263	-2.23528	H	11.84912	3.40228	0.40949
C	-11.56231	2.39361	-1.20529	H	9.79848	2.06580	3.95459
H	-11.04393	1.47008	0.66561	O	-11.90848	3.33083	-3.44464
C	-10.08372	1.89883	-3.05972	O	-11.50488	-3.75540	3.11187
H	-8.45434	0.56641	-2.64309	O	11.90805	-3.33103	-3.44477
C	-11.21493	2.55901	-2.55219	O	11.50521	3.75538	3.11170
H	-12.42793	2.88985	-0.78343	C	13.06779	-4.02758	-2.98493
H	-9.82740	2.02413	-4.10712	H	13.83063	-3.32988	-2.62079
C	-9.54023	-0.91810	0.74625	H	12.81341	-4.74102	-2.19279
C	-10.45722	-1.79022	0.15013	H	13.45218	-4.56725	-3.85052
C	-9.31300	-1.02408	2.12998	C	12.45316	4.66591	2.55124
C	-11.14329	-2.74734	0.90608	H	12.80242	5.27894	3.38217
H	-10.64576	-1.72151	-0.91669	H	13.30197	4.13193	2.10887
C	-9.97481	-1.98425	2.88664	H	11.98705	5.30728	1.79454
H	-8.61212	-0.34972	2.61194	C	-13.06818	4.02738	-2.98471
C	-10.89841	-2.85240	2.28125	H	-13.45262	4.56709	-3.85026
H	-11.84868	-3.40262	0.40960	H	-13.83101	3.32969	-2.62055
H	-9.79843	-2.06551	3.95470	H	-12.81375	4.74080	-2.19256
C	9.64823	-0.92008	-0.87810	C	-12.45275	-4.66604	2.55147
C	10.77304	-1.58569	-0.37930	H	-13.30156	-4.13216	2.10899
C	9.31763	-1.08256	-2.23527	H	-11.98658	-5.30749	1.79488
C	11.56205	-2.39385	-1.20538	H	-12.80203	-5.27899	3.38246
H	11.04382	-1.47032	0.66556				
C	10.08349	-1.89881	-3.05976	**Radical cation of 4,4'-([2,2'-bithiophene]-5,5'-diyl)bis(*N*,*N*-**			
H	8.45427	-0.56622	-2.64304	**bis(4-methoxyphenyl)aniline) ($2^{+\bullet}$) in dichloromethane**			
C	11.21462	-2.55915	-2.55229	C	-0.65621	0.27279	-0.05859
H	12.42763	-2.89020	-0.78356	C	-1.04215	1.61852	-0.07598
H	9.82712	-2.02403	-4.10716	C	-2.42599	1.80920	-0.07107
C	9.54032	0.91810	0.74625	C	-3.16763	0.62129	-0.04990
C	10.45747	1.79004	0.15010	S	-2.08047	-0.76032	-0.03020
C	9.31303	1.02425	2.12995	H	-0.32823	2.43391	-0.09887
C	11.14361	2.74714	0.90599	H	-2.88340	2.79013	-0.09243

C	0.65621	-0.27277	-0.05856	C	-11.39557	3.13528	-1.31188
C	1.04214	-1.61851	-0.07593	H	-12.40733	2.84728	0.58766
S	2.08046	0.76033	-0.03005	H	-10.19416	3.16566	-3.09755
C	2.42598	-1.80919	-0.07099	C	-9.43463	-1.17946	0.45997
H	0.32822	-2.43390	-0.09886	C	-10.40466	-1.81961	-0.31825
C	3.16762	-0.62128	-0.04983	C	-9.09381	-1.72111	1.71164
H	2.88339	-2.79011	-0.09237	C	-11.02776	-2.98617	0.13134
C	-4.60051	0.46170	-0.04141	H	-10.67681	-1.40771	-1.28468
C	-5.21834	-0.81267	-0.11376	C	-9.70182	-2.88521	2.16231
C	-5.46115	1.58768	0.04186	H	-8.35696	-1.22237	2.33300
C	-6.59121	-0.95989	-0.09922	C	-10.67423	-3.52792	1.37603
H	-4.60886	-1.70682	-0.20407	H	-11.77252	-3.46051	-0.49561
C	-6.83511	1.45281	0.05162	H	-9.44660	-3.30492	3.12995
H	-5.04355	2.58503	0.12175	C	9.67942	-1.09004	-0.43818
C	-7.44170	0.17211	-0.01554	C	10.73869	-1.52012	0.36764
H	-7.02214	-1.95099	-0.17429	C	9.48886	-1.68853	-1.69581
H	-7.45601	2.33675	0.13481	C	11.59828	-2.53447	-0.06067
C	4.60050	-0.46169	-0.04136	H	10.89577	-1.06289	1.33919
C	5.21833	0.81268	-0.11368	C	10.33309	-2.70375	-2.12549
C	5.46113	-1.58767	0.04187	H	8.68237	-1.34999	-2.33829
C	6.59121	0.95989	-0.09916	C	11.39556	-3.13529	-1.31190
H	4.60886	1.70684	-0.20396	H	12.40732	-2.84730	0.58764
C	6.83510	-1.45281	0.05161	H	10.19414	-3.16565	-3.09757
H	5.04353	-2.58502	0.12174	C	9.43464	1.17945	0.45997
C	7.44169	-0.17212	-0.01552	C	10.40463	1.81961	-0.31828
H	7.02213	1.95099	-0.17422	C	9.09386	1.72107	1.71167
H	7.45599	-2.33675	0.13478	C	11.02775	2.98616	0.13132
N	8.82245	-0.03033	0.00033	H	10.67674	1.40774	-1.28472
N	-8.82246	0.03033	0.00034	C	9.70189	2.88516	2.16234
C	-9.67943	1.09004	-0.43817	H	8.35703	1.22232	2.33304
C	-10.73870	1.52012	0.36765	C	10.67428	3.52788	1.37604
C	-9.48888	1.68853	-1.69580	H	11.77249	3.46052	-0.49564
C	-11.59829	2.53446	-0.06066	H	9.44671	3.30485	3.12999
H	-10.89578	1.06288	1.33919	O	-12.17046	4.13164	-1.82486
C	-10.33311	2.70375	-2.12548	O	-11.21571	-4.65953	1.90750
H	-8.68238	1.35000	-2.33828	O	12.17044	-4.13164	-1.82488

O	11.21579	4.65947	1.90751	C	-5.43255	1.58471	0.00345
C	13.27714	-4.60933	-1.05289	C	-6.56121	-0.97832	-0.07730
H	13.99969	-3.80810	-0.86318	H	-4.58891	-1.73255	-0.17952
H	12.93936	-5.03741	-0.10282	C	-6.79899	1.45588	0.00911
H	13.74406	-5.38637	-1.65754	H	-5.01085	2.58046	0.06814
C	12.21725	5.35895	1.16136	C	-7.40985	0.16767	-0.02274
H	12.49903	6.21341	1.77610	H	-6.99988	-1.96639	-0.13870
H	13.09429	4.72553	0.98930	H	-7.41972	2.34050	0.07755
H	11.82013	5.71150	0.20323	C	4.57187	-0.44569	-0.05290
C	-13.27710	4.60939	-1.05283	C	5.19698	0.83693	-0.10019
H	-13.74398	5.38647	-1.65746	C	5.43259	-1.58479	0.00360
H	-13.99971	3.80821	-0.86312	C	6.56122	0.97825	-0.07741
H	-12.93927	5.03744	-0.10276	H	4.58891	1.73244	-0.17971
C	-12.21726	-5.35895	1.16141	C	6.79903	-1.45593	0.00925
H	-13.09427	-4.72547	0.98940	H	5.01089	-2.58053	0.06839
H	-11.82023	-5.71153	0.20327	C	7.40987	-0.16772	-0.02274
H	-12.49906	-6.21338	1.77618	H	6.99987	1.96632	-0.13889
				H	7.41977	-2.34055	0.07778
Dication of 4,4'-([2,2'-bithiophene]-5,5'-diyl)bis(*N*,*N*-bis(4-				N	8.77645	-0.03111	-0.00214
methoxyphenyl)aniline) (2^{2+}) in dichloromethane				N	-8.77642	0.03108	-0.00213
C	-0.65041	0.25831	-0.06742	C	-9.63288	1.07995	-0.46303
C	-1.04718	1.61982	-0.07533	C	-10.71958	1.49208	0.31840
C	-2.41331	1.80174	-0.07031	C	-9.41195	1.67904	-1.71679
C	-3.15876	0.59385	-0.05909	C	-11.57271	2.49909	-0.12867
S	-2.07003	-0.78493	-0.04981	H	-10.89396	1.03360	1.28594
H	-0.33419	2.43584	-0.08913	C	-10.25743	2.68057	-2.16748
H	-2.87790	2.77876	-0.08167	H	-8.59065	1.34359	-2.34146
C	0.65043	-0.25843	-0.06741	C	-11.34415	3.10205	-1.37730
C	1.04721	-1.61994	-0.07527	H	-12.39879	2.80703	0.49966
S	2.07005	0.78482	-0.04986	H	-10.10458	3.14043	-3.13801
C	2.41335	-1.80185	-0.07023	C	-9.39228	-1.16361	0.48680
H	0.33423	-2.43596	-0.08903	C	-10.40342	-1.78634	-0.25574
C	3.15878	-0.59395	-0.05906	C	-9.01252	-1.70100	1.73053
H	2.87794	-2.77886	-0.08155	C	-11.02280	-2.94055	0.21946
C	-4.57185	0.44560	-0.05293	H	-10.70020	-1.37547	-1.21488
C	-5.19697	-0.83701	-0.10010	C	-9.62537	-2.84831	2.20908

H	-8.25284	-1.20572	2.32613	C	-13.24976	4.55440	-1.16941
C	-10.63401	-3.48086	1.45725	H	-13.70408	5.32357	-1.79266
H	-11.79356	-3.40945	-0.37892	H	-13.96727	3.74477	-1.00113
H	-9.34967	-3.26386	3.17246	H	-12.94338	4.98921	-0.21247
C	9.63293	-1.07992	-0.46303	C	-12.21680	-5.28552	1.31178
C	10.71987	-1.49177	0.31823	H	-13.08778	-4.63727	1.17112
C	9.41186	-1.67923	-1.71667	H	-11.86235	-5.65311	0.34332
C	11.57306	-2.49872	-0.12885	H	-12.48546	-6.12814	1.94759
H	10.89441	-1.03309	1.28565				
C	10.25739	-2.68072	-2.16736	4,4'-([2,2':5',2''-terthiophene]-5,5''-diyl)bis(*N*,*N*-bis(4-			
H	8.59042	-1.34399	-2.34125	methoxyphenyl)aniline) (3) in dichloromethane			
C	11.34431	-3.10194	-1.37733	C	2.66806	-1.06902	-0.55519
H	12.39937	-2.80636	0.49932	C	3.23672	-2.28736	-0.87800
H	10.10442	-3.14073	-3.13779	C	4.65383	-2.29337	-0.81122
C	9.39222	1.16363	0.48680	C	5.20448	-1.08283	-0.43595
C	10.40324	1.78649	-0.25580	S	3.92596	0.08800	-0.14042
C	9.01247	1.70096	1.73055	H	2.65256	-3.14963	-1.18058
C	11.02253	2.94076	0.21938	C	-3.21187	-2.30021	-0.94422
H	10.69998	1.37569	-1.21498	S	-3.92382	0.06087	-0.18353
C	9.62523	2.84832	2.20910	C	-4.62950	-2.31555	-0.89311
H	8.25286	1.20558	2.32618	H	-2.61918	-3.15505	-1.25123
C	10.63377	3.48097	1.45723	C	-5.19247	-1.11384	-0.50780
H	11.79315	3.40980	-0.37906	C	-2.65436	-1.08311	-0.59876
H	9.34953	3.26382	3.17250	C	-1.26237	-0.69769	-0.54588
O	-12.11231	4.08516	-1.90661	C	-0.70745	0.56431	-0.43610
O	-11.17208	-4.59464	2.01088	S	0.00927	-1.91246	-0.61477
O	12.11259	-4.08491	-1.90669	C	0.71004	0.56797	-0.42458
O	11.17170	4.59485	2.01080	H	-1.30397	1.46844	-0.38623
C	13.24976	-4.55449	-1.16925	C	1.27330	-0.69114	-0.52516
H	13.96778	-3.74521	-1.00146	H	1.30088	1.47523	-0.36481
H	12.94313	-4.98855	-0.21206	H	-5.21928	-3.18410	-1.16209
H	13.70356	-5.32429	-1.79208	H	5.25342	-3.15995	-1.06469
C	12.21682	5.28540	1.31199	N	-10.74298	0.17315	0.07646
H	12.48590	6.12767	1.94809	C	-11.61709	-0.68749	0.80900
H	13.08747	4.63675	1.17115	C	-11.28982	-1.10659	2.11081
H	11.86260	5.65351	0.34364	C	-12.82926	-1.11164	0.25434

C	-12.14556	-1.93693	2.82551	H	10.59286	3.53474	3.41515
H	-10.35821	-0.77939	2.56171	H	13.25821	4.08847	0.07615
C	-13.70680	-1.93134	0.97269	C	11.75346	-0.68748	-0.21332
H	-13.09855	-0.79617	-0.74883	C	12.80162	-1.01284	0.65419
C	-13.36339	-2.35403	2.26332	C	11.73162	-1.27350	-1.49143
H	-11.89173	-2.26045	3.83018	C	13.81421	-1.89739	0.26655
H	-14.63814	-2.23635	0.51118	H	12.83514	-0.56852	1.64406
C	-11.28670	1.35668	-0.51091	C	12.72208	-2.16856	-1.87914
C	-12.06814	2.23461	0.24764	H	10.93191	-1.02531	-2.18213
C	-11.06937	1.65142	-1.86863	C	13.77402	-2.48589	-1.00404
C	-12.63119	3.38114	-0.32385	H	14.61146	-2.12229	0.96464
H	-12.24706	2.02183	1.29696	H	12.70389	-2.62078	-2.86586
C	-11.60796	2.79793	-2.44122	O	14.70430	-3.36901	-1.48127
H	-10.47363	0.97696	-2.47564	O	12.30014	5.14169	2.42565
C	-12.39678	3.67115	-1.67411	C	15.79616	-3.73162	-0.63385
H	-13.23381	4.03522	0.29462	H	16.39973	-4.43200	-1.21127
H	-11.43935	3.02473	-3.48935	H	16.40199	-2.85663	-0.37187
O	-12.89006	4.76578	-2.33093	H	15.44222	-4.22149	0.28043
O	-14.14038	-3.16150	3.04897	C	13.27514	5.97921	1.80147
C	-13.70014	5.68963	-1.60152	H	14.23987	5.46647	1.71398
H	-13.97774	6.46693	-2.31354	H	12.94070	6.30601	0.81024
H	-14.60530	5.20538	-1.21751	H	13.38199	6.84641	2.45323
H	-13.14156	6.13695	-0.77143	C	-9.37821	-0.13774	-0.06382
C	-15.38961	-3.61984	2.52823	C	-8.40980	0.87660	-0.20672
H	-16.05791	-2.78026	2.30521	C	-8.93132	-1.47596	-0.06476
H	-15.24456	-4.22466	1.62585	C	-7.06318	0.56256	-0.35466
H	-15.82941	-4.23629	3.31231	H	-8.71552	1.91691	-0.20673
N	10.74075	0.23894	0.18330	C	-7.58147	-1.77919	-0.19514
C	11.14189	1.49756	0.72721	H	-9.64802	-2.28229	0.04470
C	10.60755	1.95887	1.94347	C	-6.60723	-0.77096	-0.35218
C	12.09376	2.28648	0.07257	H	-6.35504	1.37720	-0.47769
C	11.00612	3.17933	2.47635	H	-7.28052	-2.82185	-0.17208
H	9.87526	1.35600	2.47122	C	9.37879	-0.07926	0.03476
C	12.51639	3.50724	0.61041	C	8.93102	-1.41519	0.10920
H	12.51771	1.94510	-0.86661	C	8.41494	0.92451	-0.19044
C	11.96696	3.96267	1.81579	C	7.58527	-1.72727	-0.03959

H	9.64309	-2.21033	0.30079
C	7.06991	0.60274	-0.33568
H	8.72463	1.96104	-0.26484
C	6.61486	-0.72950	-0.27010
H	7.27926	-2.76465	0.05451
H	6.36570	1.40571	-0.53511

Radical cation of 4,4'-([2,2':5',2''-terthiophene]-5,5''-diyl)bis(*N*,*N*-bis(4-methoxyphenyl)aniline) ($3^{+\bullet}$) in dichloromethane

C	2.64159	-1.15872	-0.00930
C	3.21061	-2.43545	-0.04836
C	4.60925	-2.43189	-0.04460
C	5.17732	-1.15414	-0.00236
S	3.90922	0.06160	0.03921
H	2.61842	-3.34280	-0.08619
C	-3.21063	-2.43554	0.04788
S	-3.90925	0.06158	-0.03776
C	-4.60926	-2.43200	0.04384
H	-2.61842	-3.34291	0.08510
C	-5.17734	-1.15421	0.00251
C	-2.64161	-1.15877	0.01000
C	-1.26524	-0.79956	0.00546
C	-0.69812	0.48135	0.00398
S	-0.00001	-2.02306	-0.00043
C	0.69808	0.48136	-0.00056
H	-1.29374	1.38682	0.00776
C	1.26521	-0.79954	-0.00417
H	1.29368	1.38685	-0.00274
H	-5.19826	-3.33957	0.08171
H	5.19826	-3.33943	-0.08339
N	-10.69905	0.22289	-0.04494
C	-11.69214	-0.70920	0.39677
C	-11.58502	-1.32347	1.65654
C	-12.79953	-0.99628	-0.40768
C	-12.55779	-2.21520	2.08924
H	-10.73978	-1.09505	2.29786
C	-13.78858	-1.88400	0.02395
H	-12.89386	-0.52526	-1.38085
C	-13.66832	-2.50298	1.27667
H	-12.48162	-2.68879	3.06270
H	-14.63273	-2.08659	-0.62354
C	-11.13950	1.50787	-0.49703
C	-12.00228	2.27647	0.29091
C	-10.73860	2.00035	-1.75112
C	-12.46131	3.51978	-0.15166
H	-12.32054	1.90472	1.25959
C	-11.18149	3.23976	-2.19448
H	-10.08391	1.40551	-2.37997
C	-12.04746	4.00999	-1.39876
H	-13.12675	4.09138	0.48336
H	-10.87816	3.62217	-3.16375
O	-12.43093	5.20817	-1.92418
O	-14.57000	-3.38597	1.79248
C	-13.31797	6.03783	-1.16742
H	-13.48335	6.92553	-1.77746
H	-14.27354	5.53275	-0.98840
H	-12.86724	6.32834	-0.21212
C	-15.72529	-3.72013	1.01694
H	-16.33769	-2.83342	0.81983
H	-15.44128	-4.19278	0.07031
H	-16.29179	-4.42748	1.62214
N	10.69905	0.22290	0.04478
C	11.13958	1.50788	0.49677
C	10.73870	2.00050	1.75081
C	12.00244	2.27635	-0.29122
C	11.18167	3.23992	2.19407
H	10.08396	1.40577	2.37970
C	12.46155	3.51967	0.15125
H	12.32070	1.90450	-1.25985
C	12.04771	4.01002	1.39830
H	10.87836	3.62243	3.16330

H	13.12705	4.09116	-0.48380
C	11.69207	-0.70923	-0.39702
C	12.79944	-0.99645	0.40742
C	11.58490	-1.32341	-1.65682
C	13.78841	-1.88423	-0.02426
H	12.89379	-0.52550	1.38063
C	12.55760	-2.21519	-2.08958
H	10.73967	-1.09488	-2.29812
C	13.66811	-2.50311	-1.27702
H	14.63256	-2.08691	0.62321
H	12.48139	-2.68872	-3.06307
O	14.56972	-3.38612	-1.79289
O	12.43125	5.20823	1.92361
C	15.72495	-3.72048	-1.01735
H	16.29138	-4.42786	-1.62258
H	16.33746	-2.83385	-0.82017
H	15.44086	-4.19315	-0.07075
C	13.31838	6.03773	1.16679
H	14.27391	5.53255	0.98785
H	12.86770	6.32820	0.21145
H	13.48383	6.92547	1.77676
C	-9.34964	-0.10973	-0.03421
C	-8.34937	0.89101	0.04909
C	-8.92774	-1.46138	-0.10550
C	-7.00942	0.55263	0.06208
H	-8.63639	1.93301	0.12445
C	-7.58515	-1.78765	-0.09575
H	-9.66584	-2.25013	-0.18928
C	-6.57632	-0.79439	-0.01003
H	-6.28088	1.35290	0.15216
H	-7.31166	-2.83367	-0.17788
C	9.34962	-0.10969	0.03414
C	8.92771	-1.46134	0.10548
C	8.34936	0.89105	-0.04912
C	7.58512	-1.78759	0.09579
H	9.66581	-2.25009	0.18926
C	7.00941	0.55270	-0.06202
H	8.63639	1.93305	-0.12455
C	6.57630	-0.79432	0.01012
H	7.31161	-2.83360	0.17800
H	6.28087	1.35297	-0.15214

Dication of 4,4'-([2,2':5',2''-terthiophene]-5,5''-diyl)bis(*N*,*N*-bis(4-methoxyphenyl)aniline) (3^{2+}) in dichloromethane

C	2.62465	-1.13333	0.01048
C	3.20394	-2.42361	-0.01196
C	4.58521	-2.41648	-0.00336
C	5.15629	-1.12092	0.02640
S	3.88944	0.09396	0.04931
H	2.61161	-3.33087	-0.04013
C	-3.20394	-2.42362	0.01146
S	-3.88945	0.09398	-0.04839
C	-4.58521	-2.41649	0.00272
H	-2.61161	-3.33090	0.03909
C	-5.15630	-1.12093	-0.02638
C	-2.62466	-1.13332	-0.01016
C	-1.26355	-0.79615	-0.00562
C	-0.68905	0.50091	-0.00342
S	-0.00001	-2.02295	0.00007
C	0.68905	0.50090	0.00453
H	-1.28781	1.40399	-0.00608
C	1.26354	-0.79615	0.00620
H	1.28781	1.40399	0.00746
H	-5.17872	-3.32085	0.02555
H	5.17873	-3.32082	-0.02687
N	-10.65071	0.21679	-0.05121
C	-11.63593	-0.70618	0.42431
C	-11.48796	-1.31841	1.68187
C	-12.77245	-0.97967	-0.34571
C	-12.45347	-2.19853	2.14674
H	-10.62413	-1.09002	2.29752

C	-13.74824	-1.86235	0.11630	C	11.63590	-0.70621	-0.42441
H	-12.89324	-0.50898	-1.31572	C	12.77238	-0.97981	0.34563
C	-13.59112	-2.48092	1.36756	C	11.48796	-1.31831	-1.68203
H	-12.35353	-2.66777	3.11978	C	13.74815	-1.86250	-0.11641
H	-14.61295	-2.06278	-0.50371	H	12.89314	-0.50921	1.31569
C	-11.10403	1.48702	-0.52973	C	12.45344	-2.19842	-2.14694
C	-11.99416	2.24918	0.23604	H	10.62415	-1.08983	-2.29769
C	-10.68836	1.96351	-1.78611	C	13.59104	-2.48094	-1.36773
C	-12.45913	3.47871	-0.22923	H	14.61281	-2.06303	0.50362
H	-12.31983	1.88627	1.20521	H	12.35352	-2.66758	-3.12002
C	-11.14541	3.18629	-2.25420	O	14.47746	-3.35354	-1.91090
H	-10.02142	1.36590	-2.39882	O	12.42442	5.13562	2.02577
C	-12.03323	3.95626	-1.47971	C	15.66466	-3.68397	-1.17862
H	-13.13967	4.05175	0.38779	H	16.21106	-4.38503	-1.80846
H	-10.83895	3.55735	-3.22651	H	16.27670	-2.79334	-1.00227
O	-12.42428	5.13558	-2.02605	H	15.41647	-4.16219	-0.22534
O	-14.47755	-3.35352	1.91068	C	13.33916	5.96787	1.30082
C	-13.33912	5.96783	-1.30123	H	14.28923	5.45052	1.13124
H	-13.50465	6.83967	-1.93307	H	12.90863	6.28301	0.34459
H	-14.28918	5.45045	-1.13172	H	13.50473	6.83974	1.93262
H	-12.90869	6.28302	-0.34496	C	-9.31294	-0.10700	-0.04869
C	-15.66478	-3.68385	1.17841	C	-8.31378	0.90841	-0.00834
H	-16.27679	-2.79318	1.00213	C	-8.88606	-1.46538	-0.08368
H	-15.41663	-4.16202	0.22509	C	-6.98023	0.57836	0.00494
H	-16.21120	-4.38492	1.80822	H	-8.60905	1.94880	0.04786
N	10.65071	0.21677	0.05117	C	-7.54891	-1.78322	-0.08500
C	11.10408	1.48700	0.52964	H	-9.62330	-2.25646	-0.14260
C	10.68849	1.96353	1.78603	C	-6.53966	-0.77640	-0.03595
C	11.99417	2.24914	-0.23620	H	-6.25355	1.38193	0.07214
C	11.14556	3.18632	2.25406	H	-7.27107	-2.82863	-0.14779
H	10.02158	1.36595	2.39880	C	9.31294	-0.10700	0.04870
C	12.45917	3.47868	0.22901	C	8.88605	-1.46539	0.08357
H	12.31980	1.88620	-1.20538	C	8.31378	0.90842	0.00852
C	12.03334	3.95628	1.47950	C	7.54890	-1.78322	0.08488
H	10.83916	3.55741	3.22638	H	9.62329	-2.25646	0.14242
H	13.13969	4.05169	-0.38806	C	6.98022	0.57837	-0.00473

H	8.60904	1.94882	-0.04761	H	13.90067	2.67828	3.57339
C	6.53965	-0.77640	0.03598	H	16.47666	2.73658	0.12089
H	7.27106	-2.82864	0.14761	C	13.37889	-1.14557	-0.59634
H	6.25354	1.38195	-0.07183	C	14.26618	-1.92597	0.15228
				C	13.11838	-1.51363	-1.92831
4,4'-([2,2':5',2'':5'',2'''-quaterthiophene]-5,5'''-diyl)bis-				C	14.89116	-3.04745	-0.40445
(*N*,*N*-bis(4-methoxyphenyl)aniline) (4) in dichloromethane				H	14.47980	-1.65564	1.18168
C	-0.71114	0.12862	0.01776	C	13.71899	-2.63696	-2.48483
C	-1.38633	1.32546	-0.14300	H	12.44008	-0.91463	-2.52778
C	-2.79549	1.20383	-0.06473	C	14.61356	-3.41193	-1.72823
S	-1.85926	-1.18364	0.26145	H	15.57517	-3.62496	0.20556
H	-0.88179	2.27133	-0.30599	H	13.51703	-2.92042	-3.51309
C	5.01723	1.82401	-0.72115	N	-12.76944	-0.01358	0.01803
S	5.96259	-0.43704	0.08834	C	-13.67515	-1.01021	0.49529
C	6.42900	1.95567	-0.75251	C	-13.53513	-1.55225	1.78528
H	4.34054	2.61572	-1.02387	C	-14.73643	-1.44921	-0.30343
C	7.10968	0.82126	-0.35262	C	-14.42334	-2.51492	2.25102
C	4.58182	0.58235	-0.29575	H	-12.72413	-1.21636	2.42379
C	3.23206	0.08936	-0.14629	C	-15.64763	-2.40308	0.16326
C	2.79475	-1.19830	0.10799	H	-14.86067	-1.04014	-1.30121
S	1.85701	1.18012	-0.27521	C	-15.48954	-2.94640	1.44468
C	1.38592	-1.31804	0.19396	H	-14.31410	-2.93318	3.24679
H	3.46962	-2.03936	0.22087	H	-16.45902	-2.71538	-0.48293
C	0.71003	-0.12543	0.00671	C	-13.30925	1.18728	-0.53779
H	0.88213	-2.25908	0.38483	C	-14.27580	1.92214	0.15667
H	6.92934	2.85669	-1.08763	C	-12.89885	1.64188	-1.80352
H	-3.46992	2.04772	-0.15715	C	-14.83278	3.08383	-0.38953
N	12.77031	0.01489	-0.02670	H	-14.60490	1.58443	1.13444
C	13.60616	0.97089	0.62809	C	-13.43190	2.80507	-2.34689
C	13.30966	1.41477	1.92905	H	-12.15692	1.07922	-2.36140
C	14.75232	1.46594	-0.00292	C	-14.40630	3.53444	-1.64551
C	14.13045	2.33630	2.56905	H	-15.58150	3.62436	0.17679
H	12.43002	1.03425	2.43863	H	-13.11440	3.15571	-3.32396
C	15.59587	2.37866	0.64005	C	11.37909	0.20785	-0.10334
H	14.99699	1.13295	-1.00674	C	10.49243	-0.88696	-0.15263
C	15.28323	2.82338	1.93111	C	10.82310	1.50424	-0.13229

C	9.11854	-0.68991	-0.23767
H	10.88363	-1.89793	-0.12861
C	9.44784	1.69112	-0.20006
H	11.47513	2.36984	-0.09431
C	8.55412	0.60125	-0.26282
H	8.47522	-1.56387	-0.28847
H	9.06278	2.70595	-0.20199
C	-11.37912	-0.20738	0.09546
C	-10.49651	0.88494	0.22113
C	-10.81922	-1.50176	0.04605
C	-9.12211	0.68754	0.29399
H	-10.89231	1.89300	0.27422
C	-9.44464	-1.68914	0.12231
H	-11.46738	-2.36342	-0.06935
C	-8.55485	-0.60194	0.25172
H	-8.48177	1.55663	0.41707
H	-9.05367	-2.69936	0.05022
C	-3.23362	-0.08948	0.15731
C	-4.58390	-0.58532	0.29267
C	-5.02060	-1.83360	0.69721
S	-5.96344	0.44001	-0.08015
C	-6.43258	-1.96525	0.72357
H	-4.34460	-2.62936	0.99075
C	-7.11129	-0.82396	0.34028
H	-6.93564	-2.86928	1.04648
O	-14.87605	4.65860	-2.26850
O	-16.31423	-3.88913	1.99611
O	16.03169	3.71748	2.64753
O	15.16029	-4.49087	-2.36837
C	17.21867	4.24386	2.05097
H	16.98857	4.80196	1.13624
H	17.64767	4.91973	2.79082
H	17.93563	3.44620	1.82512
C	16.07662	-5.31750	-1.64807
H	15.59693	-5.77214	-0.77382
H	16.38032	-6.09968	-2.34391
H	16.95786	-4.74857	-1.33028
C	-17.41660	-4.36562	1.22178
H	-17.07353	-4.85182	0.30140
H	-17.92682	-5.09567	1.85021
H	-18.10690	-3.55155	0.97275
C	-15.86670	5.44333	-1.60162
H	-15.48835	5.83331	-0.64983
H	-16.08817	6.27355	-2.27236
H	-16.77933	4.86265	-1.42501

Radical cation of 4,4'-([2,2':5',2'':5'',2'''-quaterthiophene]-5,5'''-diyl)bis(*N*,*N*-bis(4-methoxyphenyl)aniline) ($4^{+\cdot}$) in dichloromethane

C	-0.70255	0.11150	0.05890
C	-1.39154	1.32957	0.05353
C	-2.78212	1.19323	0.05521
S	-1.84323	-1.23004	0.06497
H	-0.88805	2.28947	0.04968
C	5.00322	1.95000	0.12104
S	5.93509	-0.46662	0.00585
C	6.39819	2.07854	0.11621
H	4.32872	2.79745	0.17090
C	7.08287	0.86208	0.05996
C	4.55788	0.62763	0.06912
C	3.22067	0.13604	0.06323
C	2.78213	-1.19328	0.05639
S	1.84325	1.23000	0.06391
C	1.39155	-1.32962	0.05480
H	3.46305	-2.03647	0.05663
C	0.70257	-0.11154	0.05903
H	0.88807	-2.28952	0.05183
H	6.89933	3.03695	0.16611
H	-3.46304	2.03642	0.05464
N	12.71312	0.00401	-0.01784
C	13.61901	1.02397	0.41591
C	13.46454	1.62917	1.67523

C	14.69074	1.41007	-0.39537	C	-14.39063	3.64310	-1.39053
C	14.35451	2.60711	2.10058	H	-15.48239	3.63269	0.48572
H	12.64719	1.32666	2.32207	H	-13.18188	3.35710	-3.14825
C	15.59833	2.38443	0.02929	C	11.33688	0.21059	0.00236
H	14.82200	0.94786	-1.36851	C	10.43543	-0.87754	0.09945
C	15.42994	2.99245	1.28152	C	10.79036	1.51553	-0.07403
H	14.24081	3.07420	3.07358	C	9.06874	-0.66582	0.11912
H	16.41694	2.66121	-0.62355	H	10.81913	-1.88776	0.17834
C	13.26558	-1.23466	-0.47581	C	9.42215	1.71513	-0.05666
C	14.19717	-1.92583	0.30533	H	11.45094	2.36938	-0.16743
C	12.90498	-1.75792	-1.72966	C	8.51182	0.63342	0.04157
C	14.76473	-3.12138	-0.14409	H	8.41896	-1.53029	0.21931
H	14.48532	-1.53009	1.27399	H	9.05098	2.73036	-0.14381
C	13.45500	-2.95143	-2.17951	C	-11.33688	-0.21057	0.00250
H	12.19578	-1.22283	-2.35312	C	-10.43544	0.87755	0.09979
C	14.39073	-3.64294	-1.39080	C	-10.79034	-1.51550	-0.07396
H	15.48237	-3.63272	0.48552	C	-9.06875	0.66584	0.11960
H	13.18210	-3.35676	-3.14857	H	-10.81916	1.88776	0.17874
N	-12.71312	-0.00400	-0.01784	C	-9.42213	-1.71509	-0.05645
C	-13.61904	-1.02400	0.41575	H	-11.45090	-2.36934	-0.16756
C	-13.46472	-1.62927	1.67504	C	-8.51182	-0.63339	0.04201
C	-14.69069	-1.41005	-0.39567	H	-8.41897	1.53030	0.21999
C	-14.35473	-2.60726	2.10024	H	-9.05092	-2.73030	-0.14373
H	-12.64744	-1.32681	2.32200	C	-3.22065	-0.13608	0.06325
C	-15.59832	-2.38444	0.02882	C	-4.55787	-0.62766	0.06955
H	-14.82185	-0.94777	-1.36880	C	-5.00324	-1.94997	0.12262
C	-15.43005	-2.99254	1.28103	S	-5.93507	0.46656	0.00531
H	-14.24112	-3.07441	3.07321	C	-6.39822	-2.07848	0.11789
H	-16.41687	-2.66117	-0.62411	H	-4.32876	-2.79739	0.17325
C	-13.26553	1.23473	-0.47571	C	-7.08286	-0.86207	0.06058
C	-14.19718	1.92582	0.30543	H	-6.89940	-3.03683	0.16870
C	-12.90485	1.75811	-1.72949	O	-14.87800	4.80087	-1.92222
C	-14.76471	3.12141	-0.14391	O	-16.25176	-3.95487	1.79045
H	-14.48541	1.52998	1.27403	O	16.25160	3.95472	1.79109
C	-13.45484	2.95166	-2.17925	O	14.87818	-4.80063	-1.92259
H	-12.19561	1.22308	-2.35294	C	17.36973	4.38638	1.00977

H	17.04192	4.82909	0.06274	H	0.88597	-2.29240	0.03822
H	17.87459	5.14279	1.61026	H	6.87582	3.02848	0.08223
H	18.05688	3.55617	0.81249	H	-3.44923	2.03988	0.03755
C	15.83951	-5.54892	-1.17226	N	12.65895	0.00713	-0.00776
H	15.42089	-5.88250	-0.21635	C	13.56269	1.01971	0.44785
H	16.08251	-6.41597	-1.78611	C	13.38435	1.61866	1.70751
H	16.74613	-4.96004	-0.99440	C	14.65333	1.39685	-0.34369
C	-17.36971	-4.38659	1.00889	C	14.27335	2.58591	2.15342
H	-17.04169	-4.82921	0.06190	H	12.55639	1.31421	2.33946
H	-17.87460	-5.14308	1.60925	C	15.55392	2.36586	0.09977
H	-18.05690	-3.55643	0.81154	H	14.79881	0.93735	-1.31575
C	-15.83960	5.54893	-1.17202	C	15.36527	2.96958	1.35323
H	-15.42123	5.88254	-0.21601	H	14.14830	3.04674	3.12767
H	-16.08266	6.41597	-1.78584	H	16.38486	2.64292	-0.53673
H	-16.74613	4.95984	-0.99435	C	13.21944	-1.22076	-0.48491
				C	14.17275	-1.90296	0.27936
Dication of 4,4'-([2,2':5',2'':5'',2'''-quaterthiophene]-5,5'''-diyl)bis(*N*,*N*-bis(4-methoxyphenyl)aniline) (4^{2+}) in dichloromethane				C	12.84466	-1.73421	-1.73923
				C	14.74228	-3.08866	-0.18584
				H	14.46883	-1.51138	1.24700
C	-0.69428	0.10210	0.04298	C	13.40381	-2.91468	-2.20674
C	-1.39197	1.33378	0.03973	H	12.12575	-1.19840	-2.35045
C	-2.76577	1.19904	0.03918	C	14.35651	-3.60359	-1.43384
S	-1.83408	-1.24271	0.04570	H	15.47210	-3.59926	0.42979
H	-0.88588	2.29207	0.03788	H	13.12698	-3.31290	-3.17730
C	4.99012	1.94999	0.06474	N	-12.65888	-0.00703	-0.00767
S	5.90984	-0.48818	0.01782	C	-13.56275	-1.01953	0.44788
C	6.36967	2.07230	0.06148	C	-13.38470	-1.61836	1.70764
H	4.31637	2.79892	0.08603	C	-14.65325	-1.39667	-0.34384
C	7.05747	0.83874	0.03952	C	-14.27384	-2.58551	2.15347
C	4.53528	0.61470	0.04498	H	-12.55684	-1.31389	2.33971
C	3.20977	0.14554	0.04326	C	-15.55400	-2.36559	0.09954
C	2.76586	-1.19934	0.03936	H	-14.79851	-0.93726	-1.31597
S	1.83412	1.24240	0.04552	C	-15.36564	-2.96920	1.35311
C	1.39206	-1.33411	0.03993	H	-14.14901	-3.04624	3.12780
H	3.44934	-2.04016	0.03789	H	-16.38484	-2.64264	-0.53708
C	0.69434	-0.10244	0.04299	C	-13.21930	1.22090	-0.48485

C	-14.17243	1.90326	0.27949	C	-3.20971	-0.14583	0.04332
C	-12.84466	1.73418	-1.73928	C	-4.53523	-0.61494	0.04519
C	-14.74197	3.08894	-0.18578	C	-4.99014	-1.95021	0.06517
H	-14.46839	1.51182	1.24721	S	-5.90975	0.48800	0.01771
C	-13.40381	2.91461	-2.20686	C	-6.36969	-2.07246	0.06193
H	-12.12583	1.19826	-2.35053	H	-4.31642	-2.79916	0.08670
C	-14.35640	3.60365	-1.43393	C	-7.05744	-0.83886	0.03982
H	-15.47159	3.59970	0.42994	H	-6.87590	-3.02861	0.08287
H	-13.12707	3.31271	-3.17750	O	-14.84721	4.74710	-1.97987
C	11.29458	0.20864	0.00773	O	-16.18028	-3.92097	1.87941
C	10.39337	-0.89180	0.06140	O	16.17974	3.92147	1.87958
C	10.74471	1.52033	-0.02868	O	14.84721	-4.74715	-1.97965
C	9.03336	-0.68556	0.07892	C	17.31869	4.35284	1.12472
H	10.78274	-1.90074	0.11884	H	17.01209	4.80313	0.17469
C	9.38218	1.71402	-0.02270	H	17.81260	5.10235	1.74212
H	11.40519	2.37627	-0.09241	H	18.00444	3.51952	0.93871
C	8.47094	0.62083	0.03266	C	15.83018	-5.49513	-1.25335
H	8.38450	-1.55293	0.15191	H	15.42932	-5.84368	-0.29569
H	9.00847	2.72933	-0.08460	H	16.07040	-6.35152	-1.88250
C	-11.29453	-0.20861	0.00794	H	16.73246	-4.89774	-1.08516
C	-10.39327	0.89181	0.06157	C	-17.31885	-4.35274	1.12419
C	-10.74470	-1.52032	-0.02831	H	-17.01183	-4.80277	0.17416
C	-9.03327	0.68552	0.07914	H	-17.81257	-5.10256	1.74137
H	-10.78259	1.90076	0.11895	H	-18.00492	-3.51971	0.93817
C	-9.38218	-1.71405	-0.02227	C	-15.83005	5.49522	-1.25355
H	-11.40520	-2.37625	-0.09195	H	-15.42894	5.84415	-0.29613
C	-8.47089	-0.62090	0.03300	H	-16.07061	6.35131	-1.88296
H	-8.38438	1.55286	0.15211	H	-16.73222	4.89779	-1.0848
H	-9.00850	-2.72939	-0.08401				

4. Cyclic voltammetry and Differential pulse voltammetry

Cyclic Voltammograms (CVs) were recorded on ECstat-302. A Pt electrode, a Ag/Ag^+ (Ag wire in 0.01 M $AgNO_3$/0.1 M Bu_4NPF_6/CH_2Cl_2), and a Pt wire electrode were used as working, reference, and counter electrodes, respectively. The working electrode was polished with 5 μm diamond slurry and then with 0.5 μm alumina slurry. After polishing, it was washed with deionized water and acetone, and dried in an oven. A CH_2Cl_2 solution of sample including 1 mM of each sample and 0.1 M of Bu_4NPF_6 was prepared as an electrochemical solution. Using the electrodes and solutions, beaker-type three-electrode electrochemical cells were constructed and connected to a potentiostat to perform cyclic voltammetry. The redox potentials were calibrated with ferrocene as an international standard. The voltammograms are presented following the IUPAC plotting convention, with the potential increasing from left to right and the current plotted with anodic currents upward.

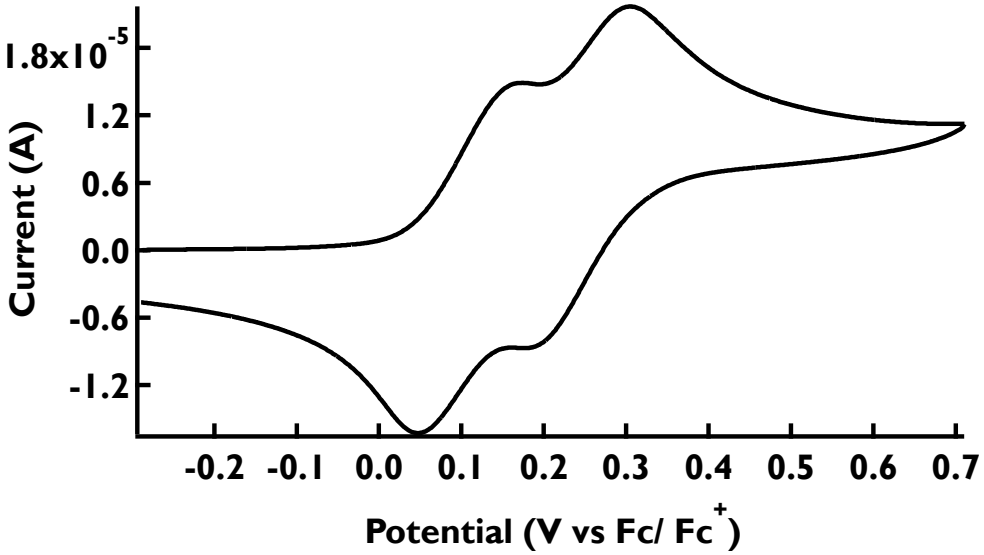


Figure S10. Cyclic voltammogram of **1** in dichloromethane (1×10^{-3} M) with Bu_4NPF_6 as a supporting electrolyte. The scan rate is 100 mV/s.

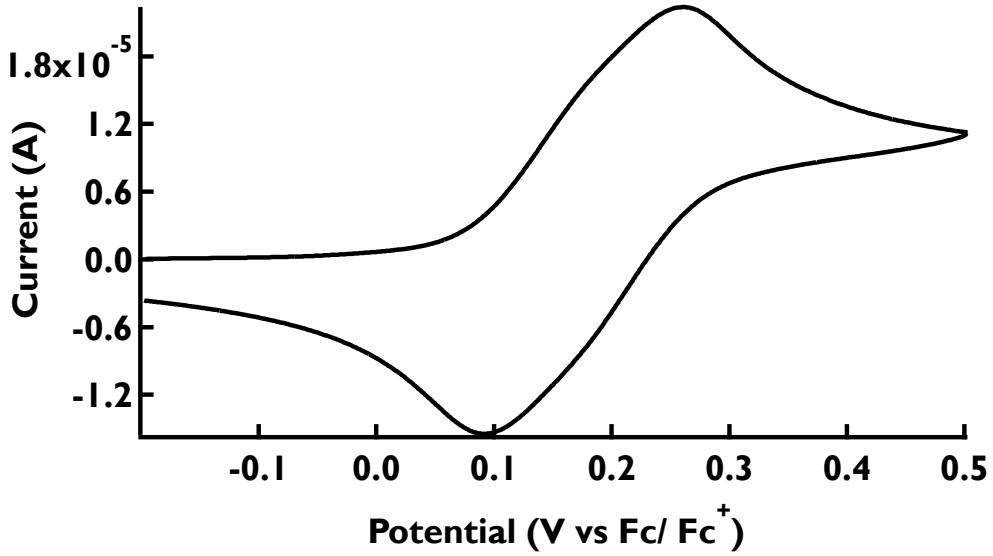


Figure S11. Cyclic voltammogram of **2** in dichloromethane (1×10^{-3} M) with Bu_4NPF_6 as a supporting electrolyte. The scan rate is 100 mV/s.

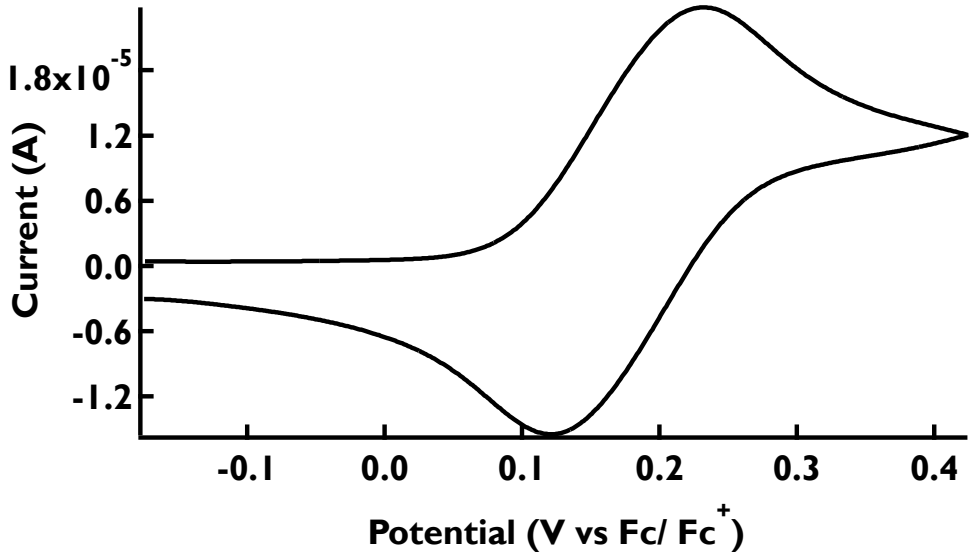


Figure S12. Cyclic voltammogram of **3** in dichloromethane (1×10^{-3} M) with Bu_4NPF_6 as a supporting electrolyte. The scan rate is 100 mV/s.

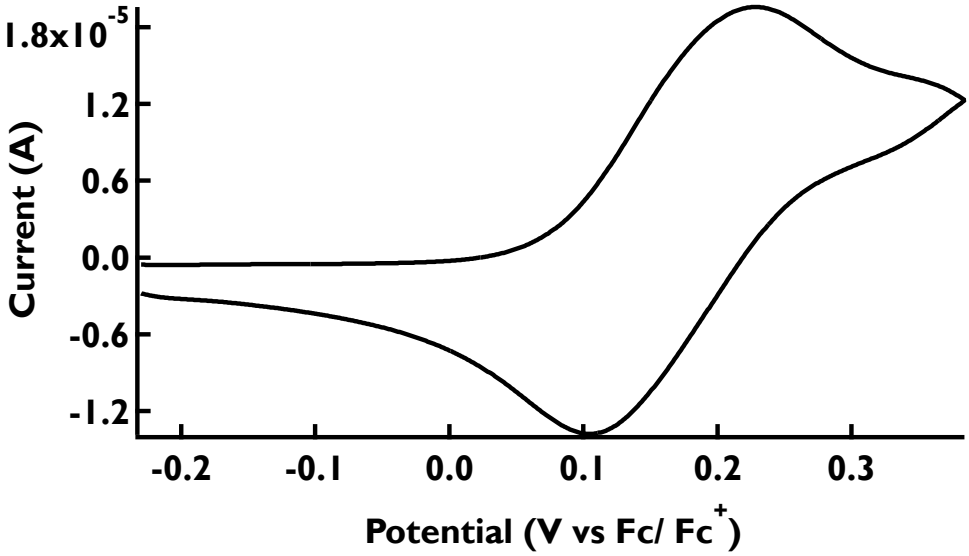


Figure S13. Cyclic voltammogram of **4** in dichloromethane (1×10^{-3} M) with Bu_4NPF_6 as a supporting electrolyte. The scan rate is 100 mV/s.

Differential pulse Voltammograms (DPVs) were recorded under the same solvent/supporting-electrolyte conditions as the CV measurements. The DPV measurement conditions are as follows.: pulse amplitude = 25 mV, potential step (ΔE) = 10 mV, pulse width = 50 ms, and pulse period = 1000 ms. The current was sampled at 33–50 ms (sample 1) and 983–1000 ms (sample 2) within each pulse period. The current range was set to 300 μA.

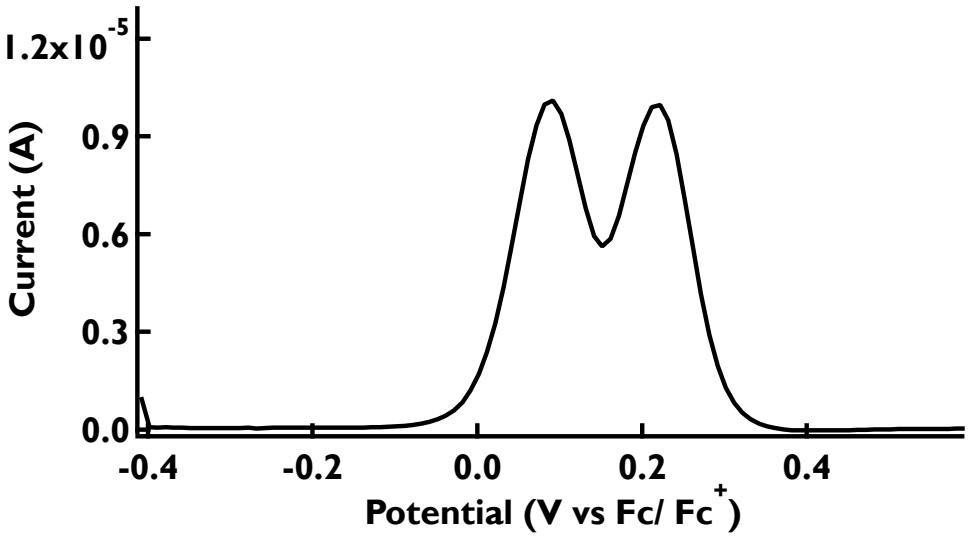


Figure S14. Differential pulse voltammogram of **1** in dichloromethane (1×10^{-3} M) with Bu_4NPF_6 as a supporting electrolyte.

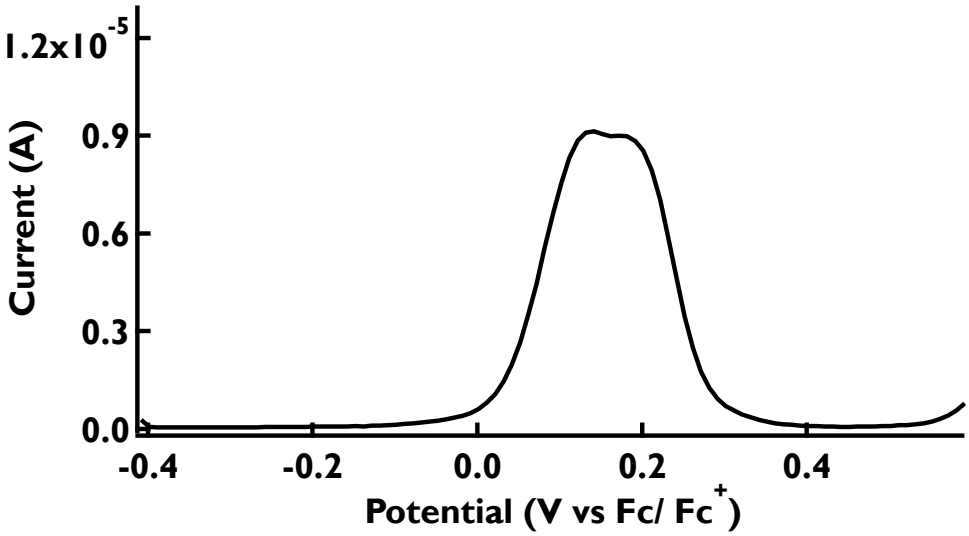


Figure S15. Differential pulse voltammogram of **2** in dichloromethane (1×10^{-3} M) with Bu_4NPF_6 as a supporting electrolyte.

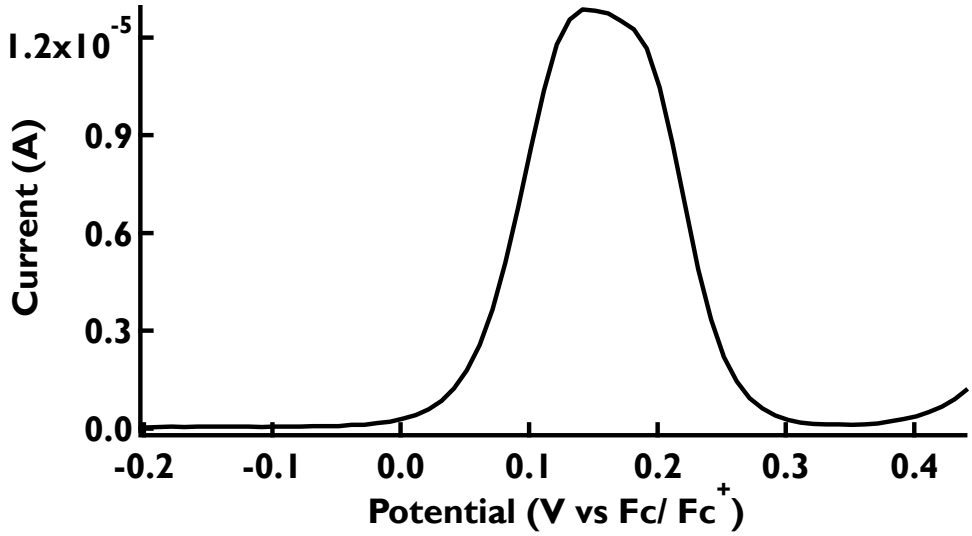


Figure S16. Differential pulse voltammogram of **3** in dichloromethane (1×10^{-3} M) with Bu_4NPF_6 as a supporting electrolyte.

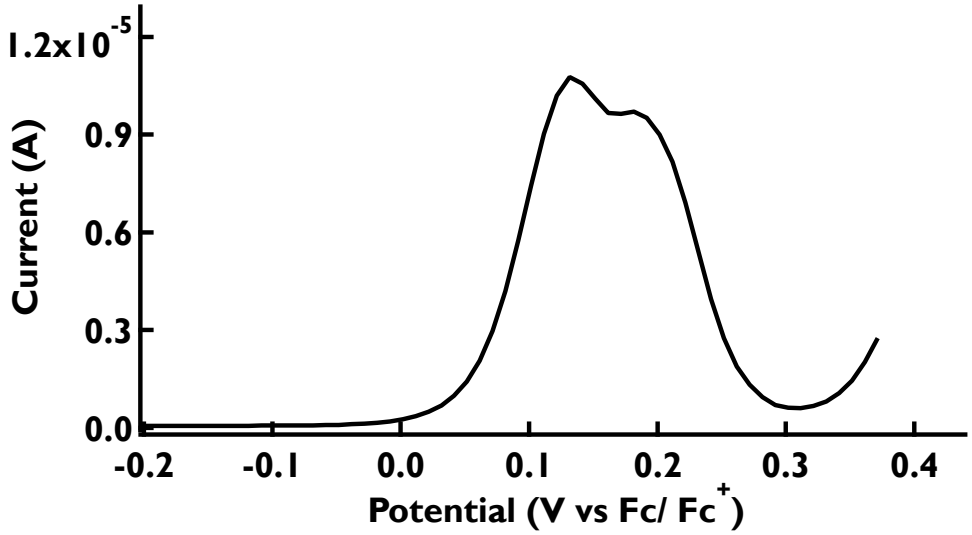


Figure S17. Differential pulse voltammogram of **4** in dichloromethane (1×10^{-3} M) with Bu_4NPF_6 as a supporting electrolyte.

5. Absorption and emission spectra of the neutral species

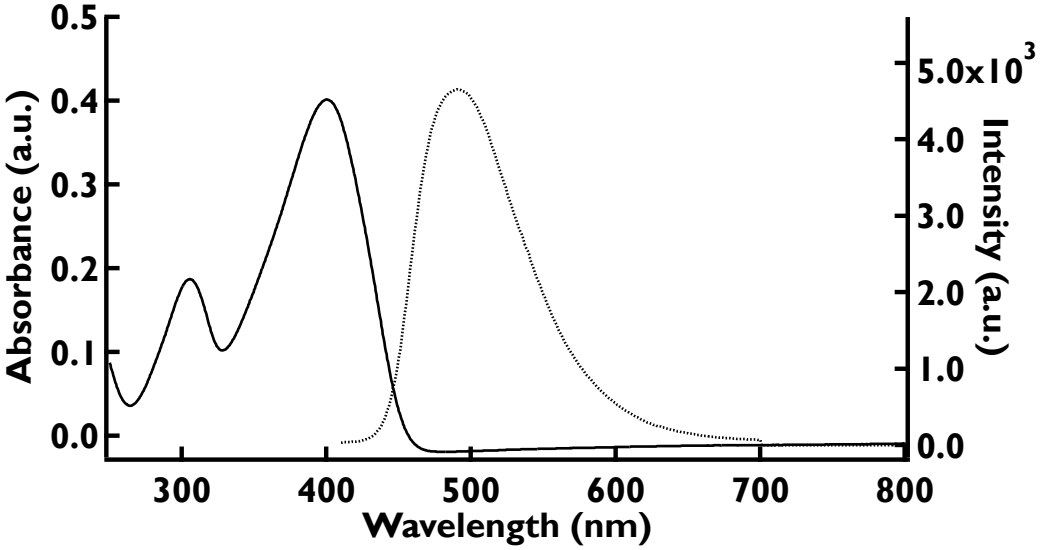


Figure S18. UV-vis (solid line) and fluorescence emission (dotted line) spectra of **1** in dichloromethane. The concentration is 1×10^{-5} M for UV-vis and 1×10^{-6} M for fluorescence emission spectra (Excitation at 400 nm).

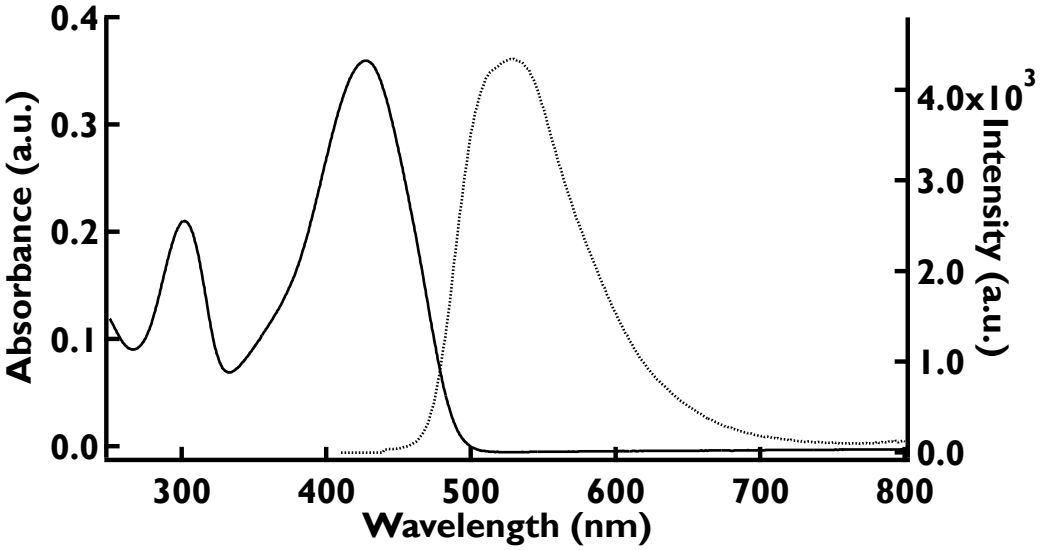


Figure S19. UV-vis (solid line) and fluorescence emission (dotted line) spectra of **2** in dichloromethane. The concentration is 1×10^{-5} M for UV-vis and 1×10^{-6} M for fluorescence emission spectra (Excitation at 427 nm).

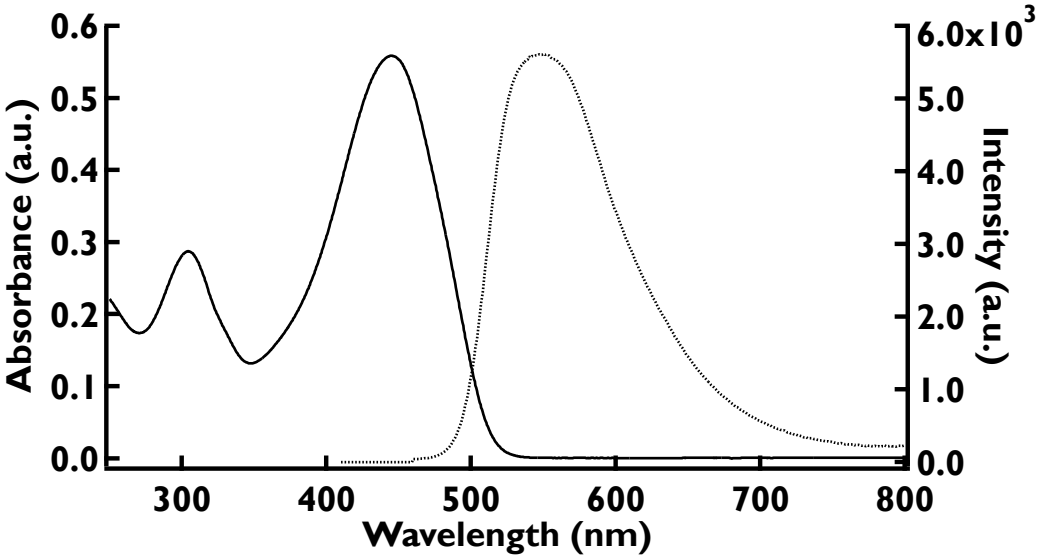


Figure S20. UV-vis (solid line) and fluorescence emission (dotted line) spectra of **3** in dichloromethane. The concentration is 1×10^{-5} M for UV-vis and 1×10^{-6} M for fluorescence emission spectra (Excitation at 445 nm).

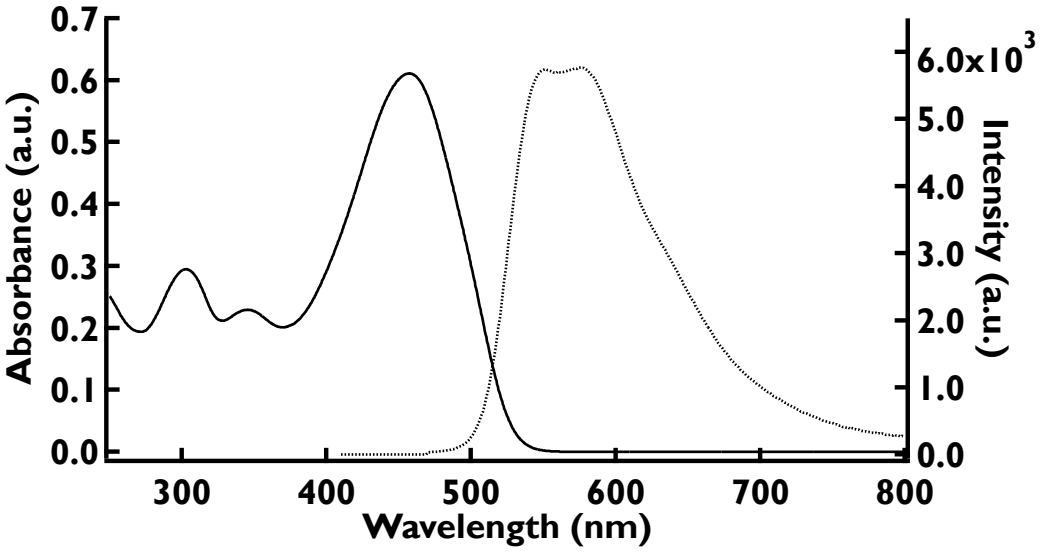


Figure S21. UV-vis (solid line) and fluorescence emission (dotted line) spectra of **4** in dichloromethane. The concentration is 1×10^{-5} M for UV-vis and 1×10^{-6} M for fluorescence emission spectra (Excitation at 457 nm).

6. Absorption spectra of the oxidized species

The absorption spectral changes during the oxidation processes of the compounds were measured as follows. A sample solution (1.0×10^{-5} M in dichloromethane, 3 mL) was prepared and placed in a quartz cell with an optical path length of 10 mm. UV–vis–NIR absorption spectroscopy was carried out at room temperature under ambient atmosphere. To generate the radical cation and dication species, magic blue (2.5×10^{-3} M in dichloromethane) was used as the oxidant. The oxidant was added dropwise (6 μL each) to the sample solution, and absorption spectra were recorded after each addition to monitor spectral changes. Photographs of the solutions were taken using $SbCl_5$ as the oxidant, since neither $SbCl_5$ nor its reduced form absorbs in the visible region.

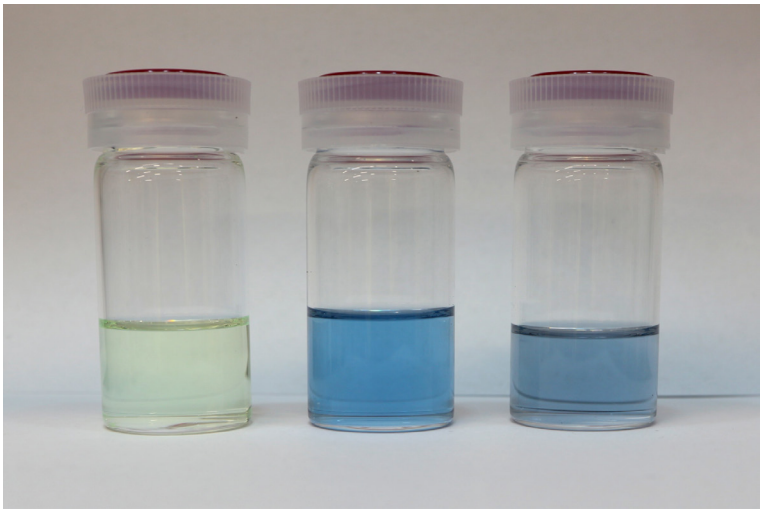


Figure S22. Dichloromethane solution of **1** (left), $\mathbf{1}^{\bullet+}$ (center) and $\mathbf{1}^{2+}$ (right). [**1**] = 1×10^{-5} M. $SbCl_5$ as an oxidant.

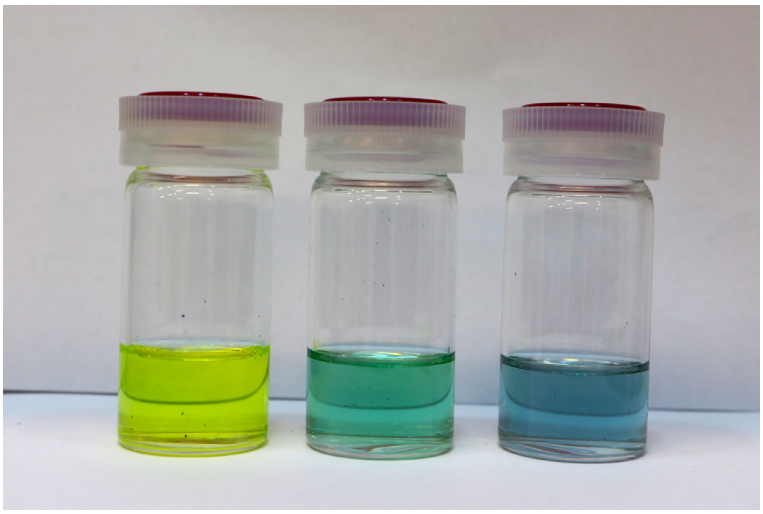


Figure S23. Dichloromethane solution of **2** (left), $\mathbf{2}^{\bullet+}$ (center) and $\mathbf{2}^{2+}$ (right). [**2**] = 1 × 10^{-5} M. $SbCl_5$ as an oxidant.

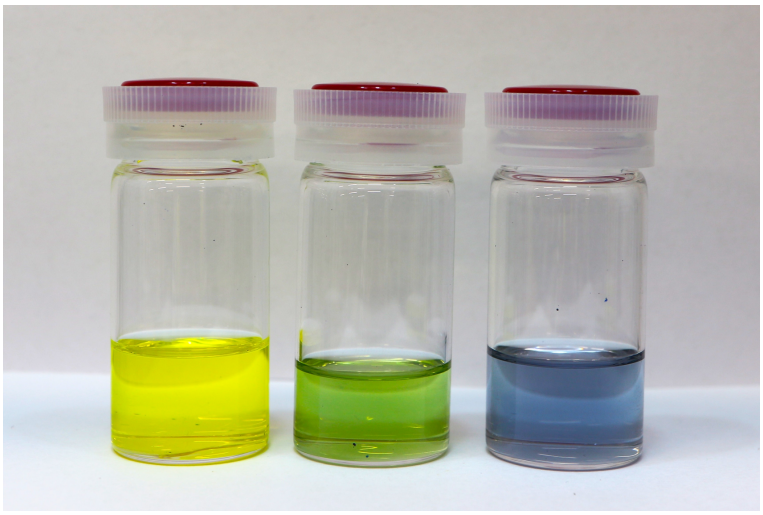


Figure S24. Dichloromethane solution of **3** (left), $\mathbf{3}^{\bullet+}$ (center) and $\mathbf{3}^{2+}$ (right). [**3**] = 1 × 10^{-5} M. $SbCl_5$ as an oxidant.

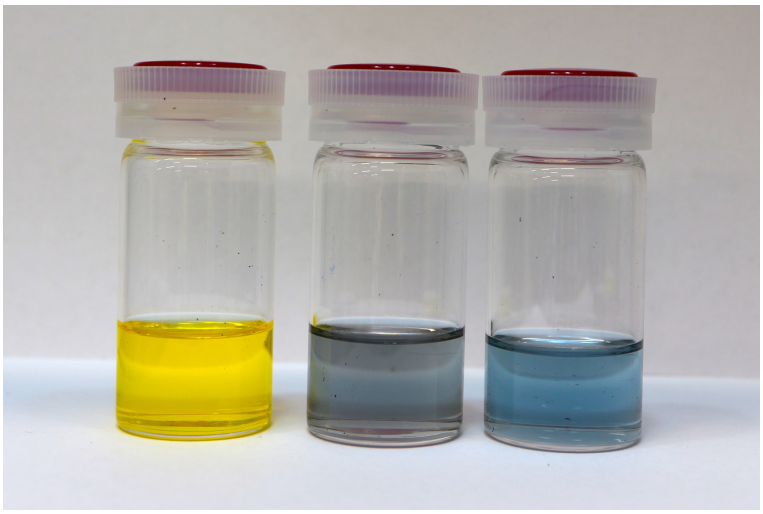


Figure S25. Dichloromethane solution of **4** (left), $\mathbf{4}^{\bullet+}$ (center) and $\mathbf{4}^{2+}$ (right). [**4**] = 1 × 10^{-5} M. $SbCl_5$ as an oxidant.

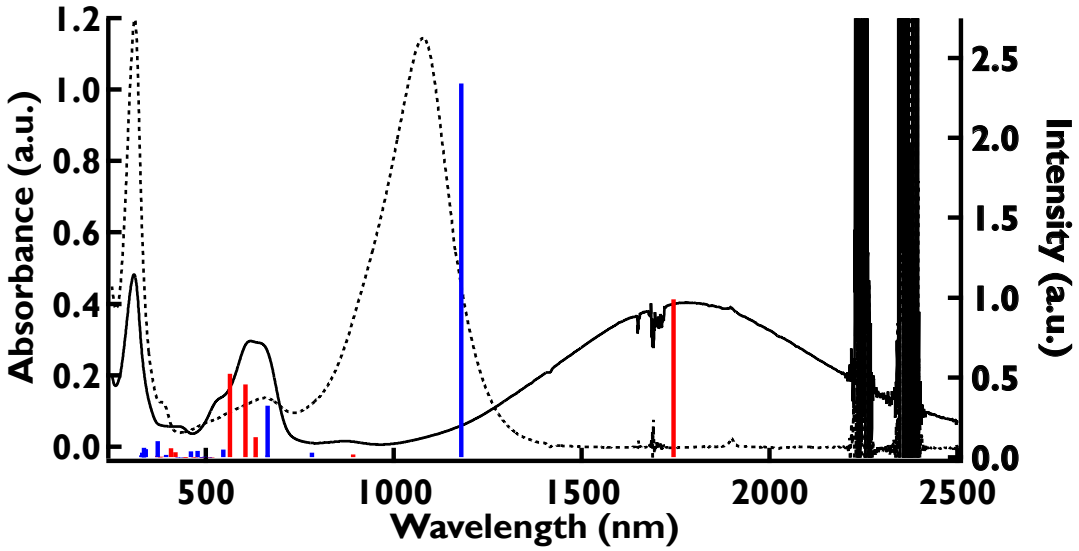


Figure S26. Experimental UV-vis-NIR absorption spectra of $\mathbf{1}^{\bullet+}$ (solid line) and $\mathbf{1}^{2+}$ (dotted line) and TD-DFT calculated energy transition with oscillator strength shown as a vertical red ($\mathbf{1}^{\bullet+}$) and blue ($\mathbf{1}^{2+}$) lines, respectively.

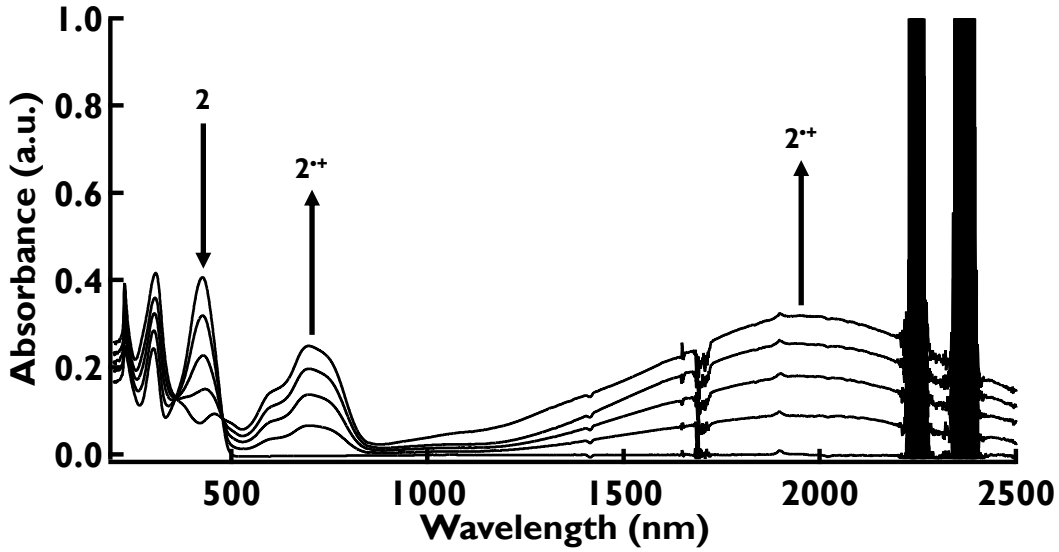


Figure S27. Absorption spectral change from **2** to $\mathbf{2}^{\bullet+}$ upon stepwise addition of magic blue. [**2**] = 1×10^{-5} M.

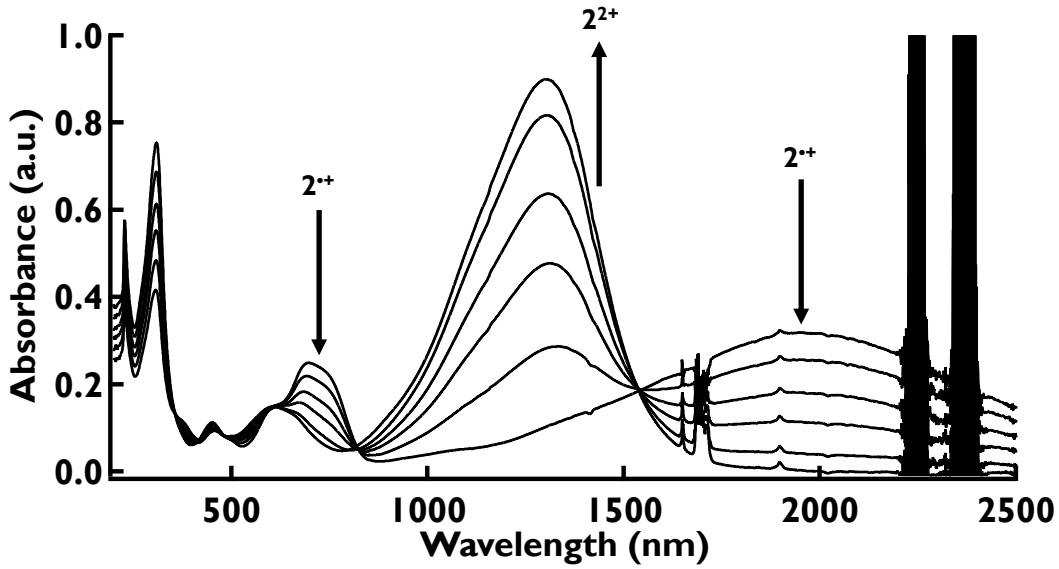


Figure S28. Absorption spectral change from $\mathbf{2}^{\bullet+}$ to $\mathbf{2}^{2+}$ upon stepwise addition of magic blue. [**2**] = 1×10^{-5} M.

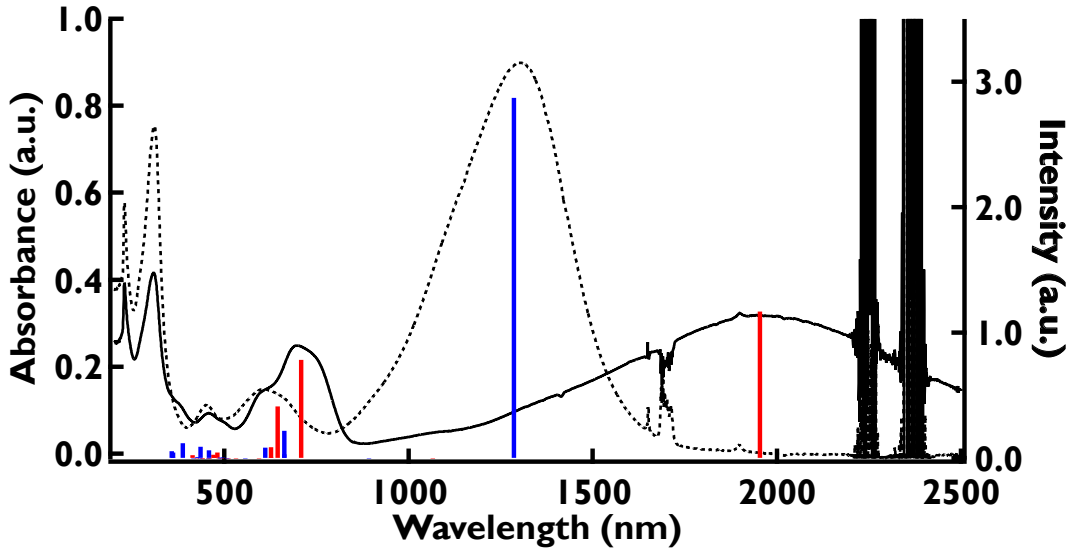


Figure S29. Experimental UV-vis-NIR absorption spectra of $\mathbf{2}^{\bullet+}$ (solid line) and $\mathbf{2}^{2+}$ (dotted line) and TD-DFT calculated energy transition with oscillator strength shown as a vertical red ($\mathbf{2}^{\bullet+}$) and blue ($\mathbf{2}^{2+}$) lines, respectively.

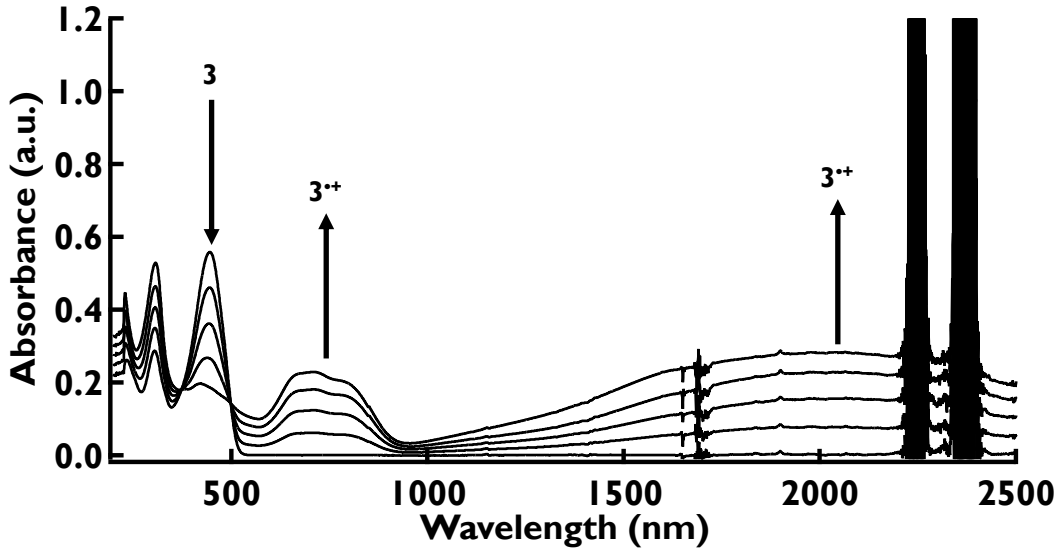


Figure S30. Absorption spectral change from **3** to $\mathbf{3}^{\bullet+}$ upon stepwise addition of magic blue. [**3**] = 1×10^{-5} M.

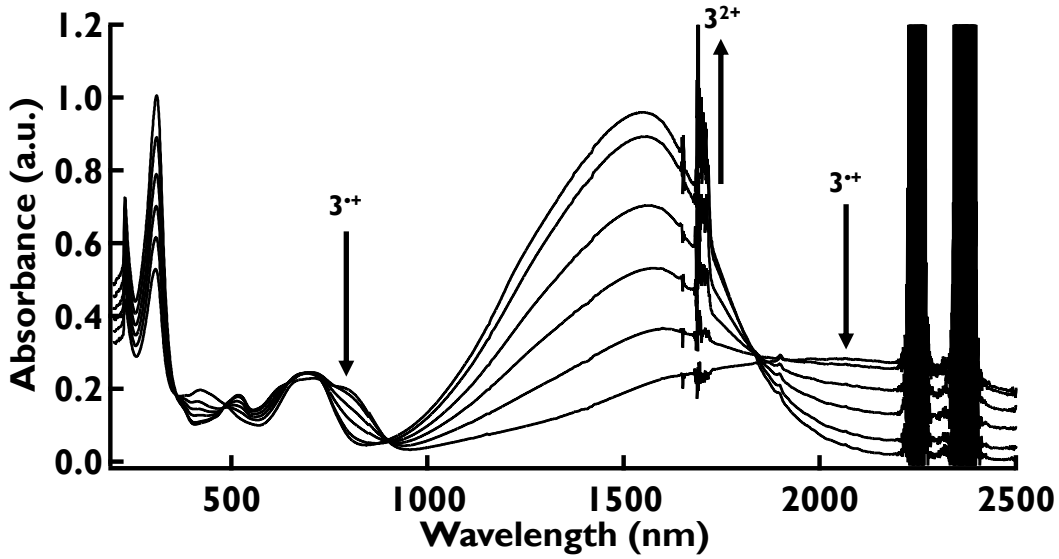


Figure S31. Absorption spectral change from $\mathbf{3}^{\bullet+}$ to $\mathbf{3}^{2+}$ upon stepwise addition of magic blue. [**3**] = 1×10^{-5} M.

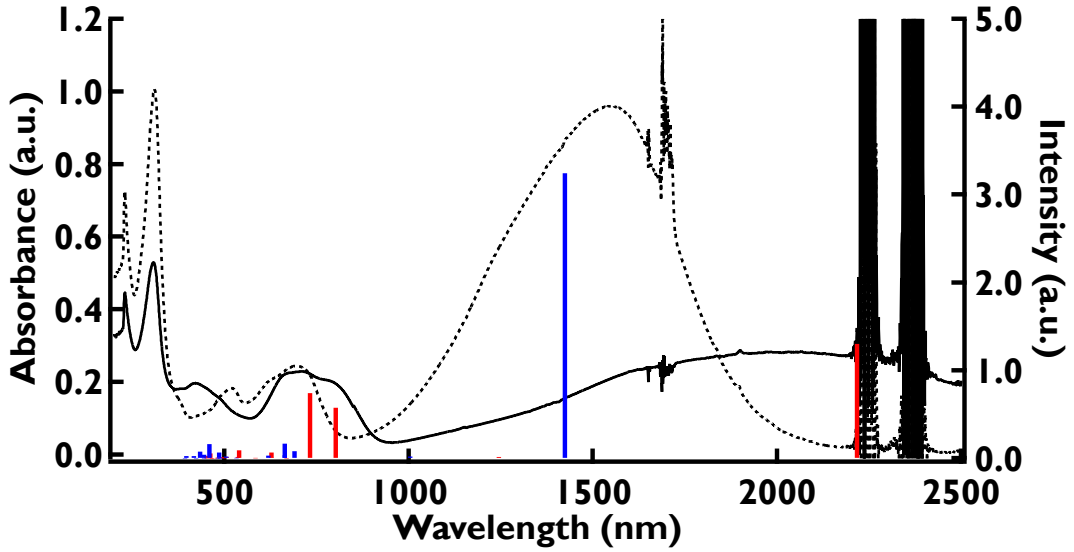


Figure S32. Experimental UV-vis-NIR absorption spectra of $\mathbf{3}^{\bullet+}$ (solid line) and $\mathbf{3}^{2+}$ (dotted line) and TD-DFT calculated energy transition with oscillator strength shown as a vertical red ($\mathbf{3}^{\bullet+}$) and blue ($\mathbf{3}^{2+}$) lines, respectively.

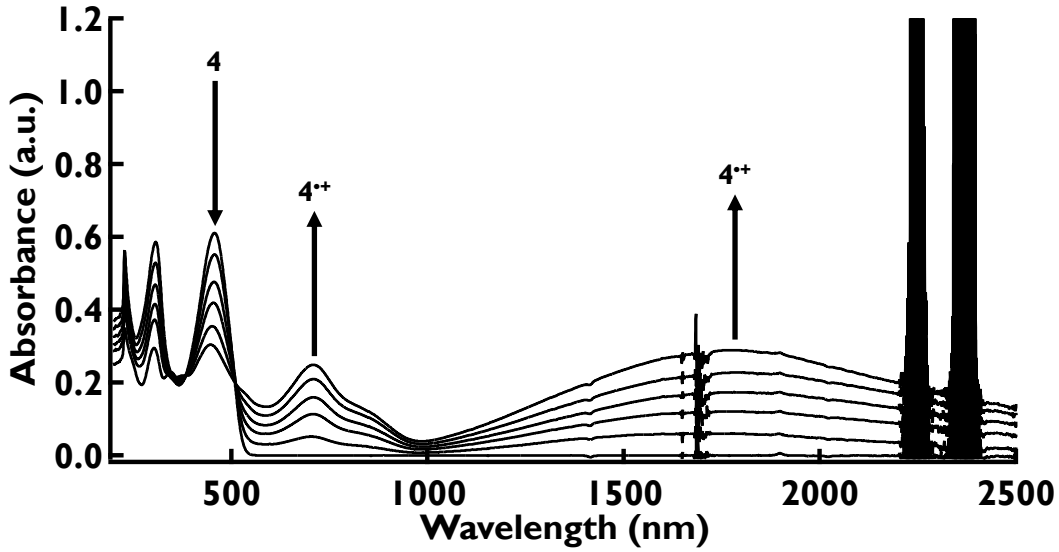


Figure S33 Absorption spectral change from **4** to $\mathbf{4}^{\bullet+}$ upon stepwise addition of magic blue. [**4**] = 1×10^{-5} M.

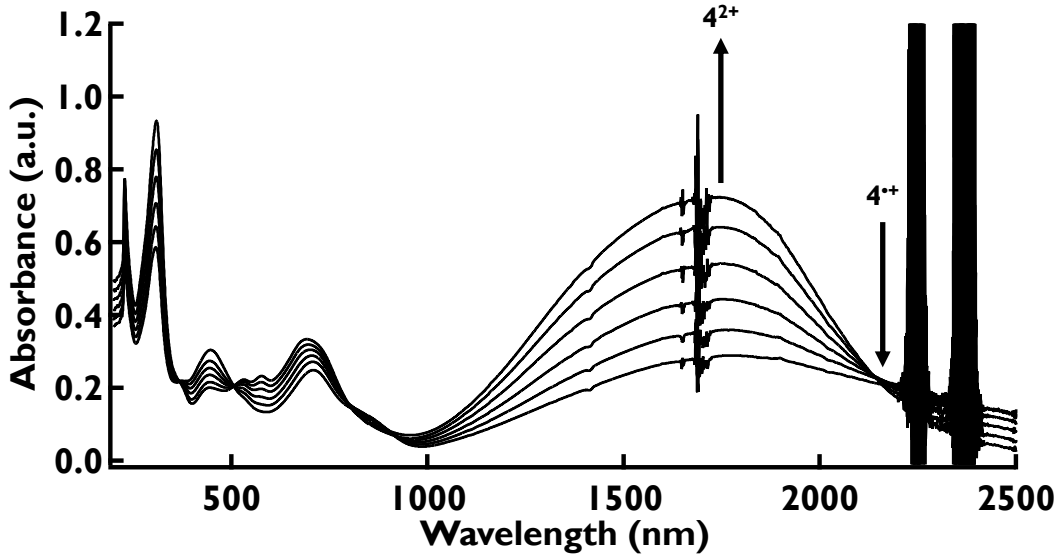


Figure S34. Absorption spectral change from $\mathbf{4}^{\bullet+}$ to $\mathbf{4}^{2+}$ upon stepwise addition of magic blue. [**4**] = 1×10^{-5} M.

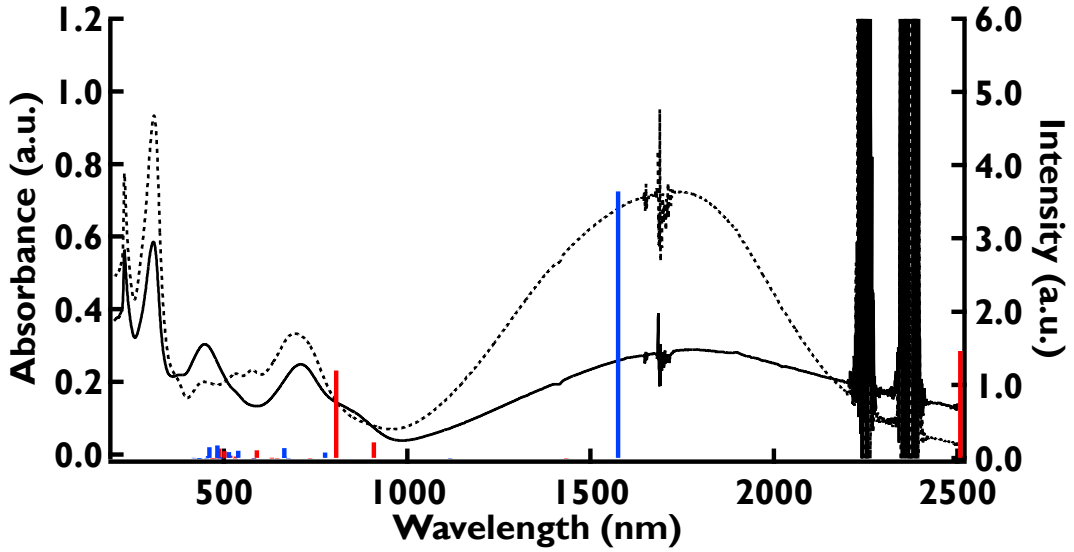


Figure S35. Experimental UV-vis-NIR absorption spectra of $\mathbf{4}^{\bullet+}$ (solid line) and $\mathbf{4}^{2+}$ (dotted line) and TD-DFT calculated energy transition with oscillator strength shown as a vertical red ($\mathbf{4}^{\bullet+}$) and blue ($\mathbf{4}^{2+}$) lines, respectively.

7. ESR spectra

ESR measurements were performed under the following experimental conditions. Samples were prepared as 5 mL dichloromethane solutions with a concentration of 1.0×10^{-4} M and placed in quartz tubes. Measurements were carried out at room temperature under ambient atmosphere. Radical cations and dications were generated by stepwise addition of oxidant solutions ($SbCl_5$ in dichloromethane), and the spectral changes during this process were monitored. The magnetic field was swept from 330 to 340 mT with a field modulation of 100 kHz and 0.3 mT amplitude. The microwave power was set to 10 mW to avoid saturation of the signal.

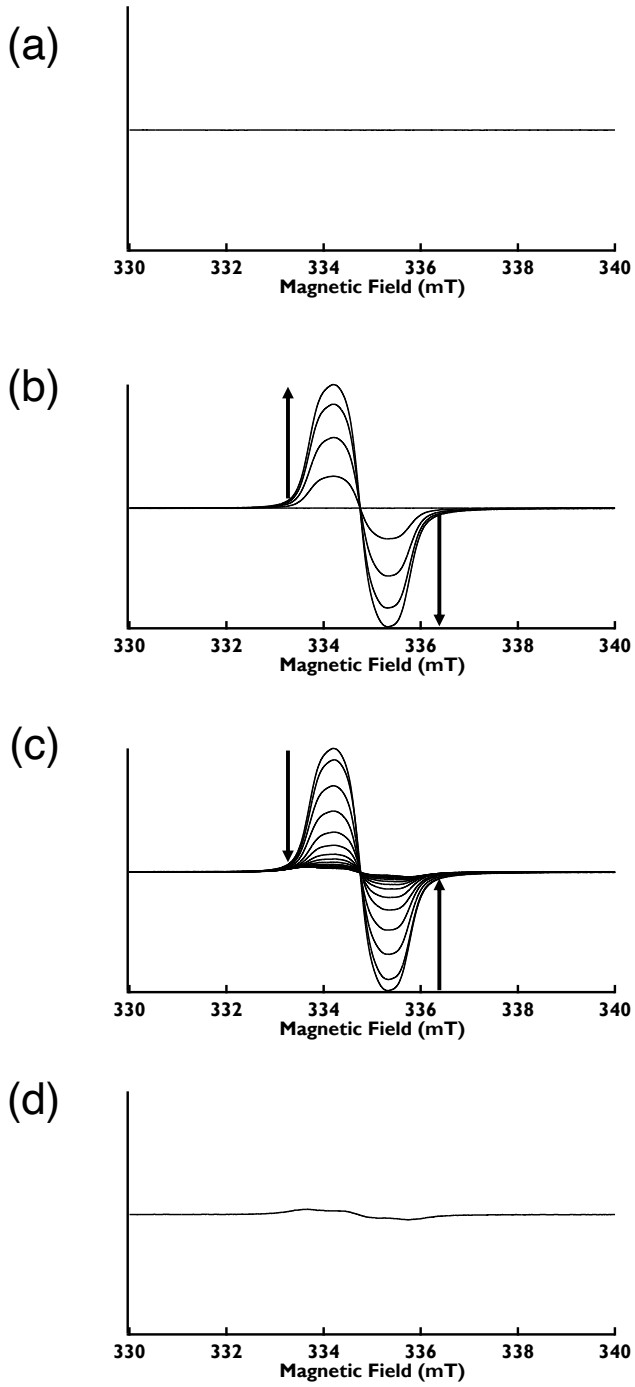


Figure S36. ESR spectra of **1** in dichloromethane at 298 K: (a) neutral **1** (no signal); (b) after stepwise additions of $SbCl_5$, showing the growth of the radical-cation signal; (c) upon further additions of $SbCl_5$, showing progressive bleaching due to formation of the dication; (d) after exhaustive oxidation with excess $SbCl_5$. The *g* value of $\mathbf{1}^{\bullet+}$ is 2.000. Experimental particulars (stock solution concentration and aliquot volumes) are provided in the SI.

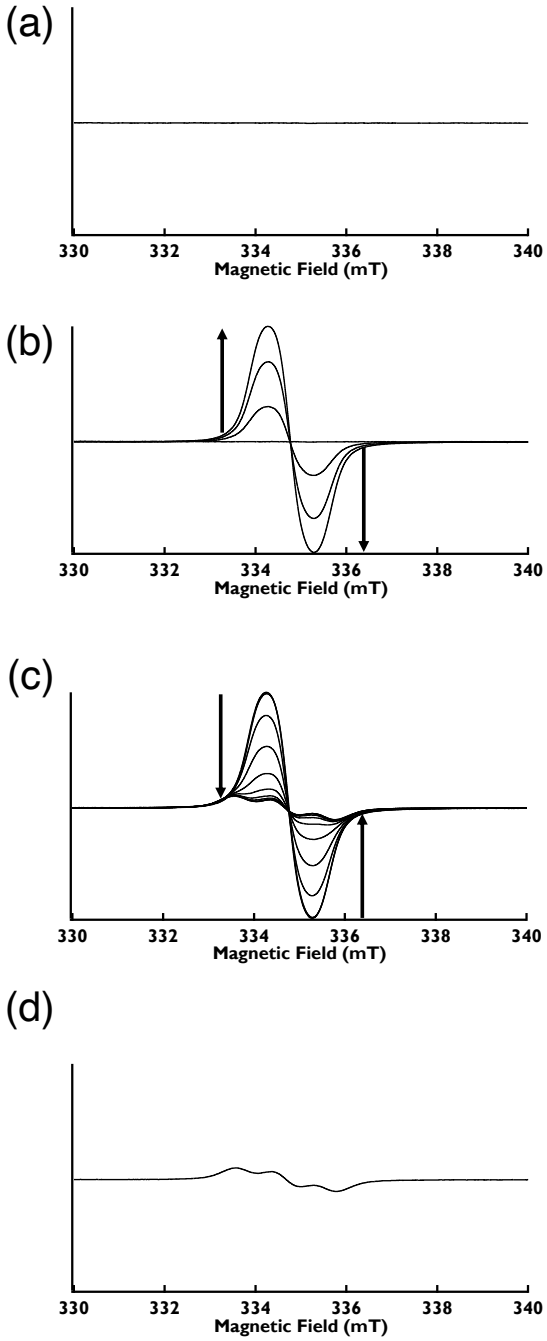


Figure S37. ESR spectra of **2** in dichloromethane at 298 K: (a) neutral **2** (no signal); (b) after stepwise additions of $SbCl_5$, showing the growth of the radical-cation signal; (c) upon further additions of $SbCl_5$, showing progressive bleaching due to formation of the dication; (d) after exhaustive oxidation with excess $SbCl_5$. The *g* value of $\mathbf{2}^{\bullet+}$ is 2.000. Experimental particulars (stock solution concentration and aliquot volumes) are provided in the SI.

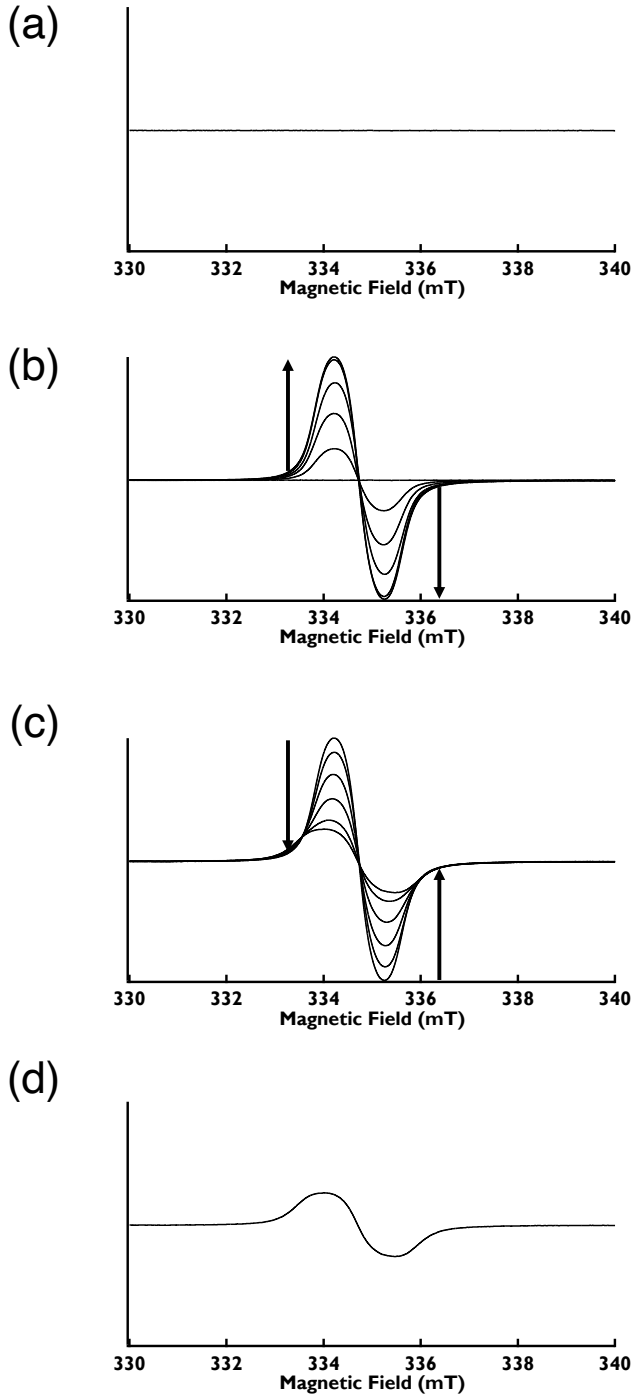


Figure S38. ESR spectra of **3** in dichloromethane at 298 K: (a) neutral **3** (no signal); (b) after stepwise additions of $SbCl_5$, showing the growth of the radical-cation signal; (c) upon further additions of $SbCl_5$, showing progressive bleaching due to formation of the dication; (d) after exhaustive oxidation with excess $SbCl_5$. The *g* value of $\mathbf{3}^{\bullet+}$ is 2.000. Experimental particulars (stock solution concentration and aliquot volumes) are provided in the SI.

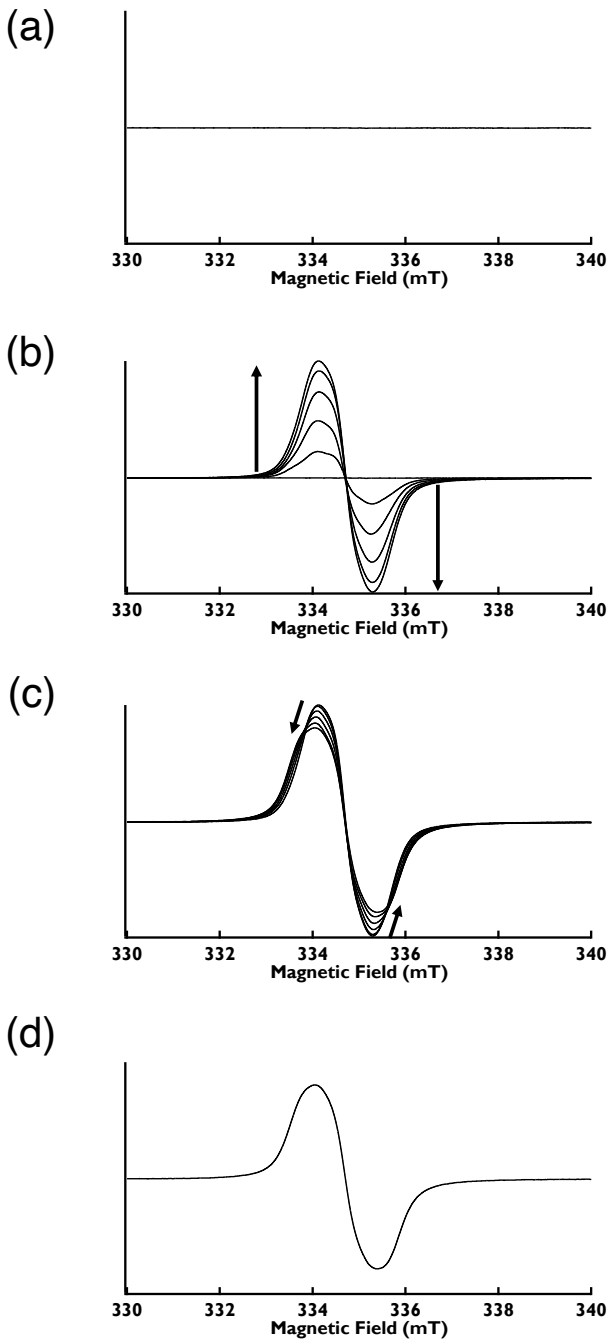


Figure S39. ESR spectra of **4** in dichloromethane at 298 K: (a) neutral **4** (no signal); (b) after stepwise additions of $SbCl_5$, showing the growth of the radical-cation signal; (c) upon further additions of $SbCl_5$, showing progressive bleaching due to formation of the dication; (d) after exhaustive oxidation with excess $SbCl_5$. The *g* value of $\mathbf{4}^{\bullet+}$ is 2.001. Experimental particulars (stock solution concentration and aliquot volumes) are provided in the SI.

8. ^{1}H and ^{13}C NMR spectra

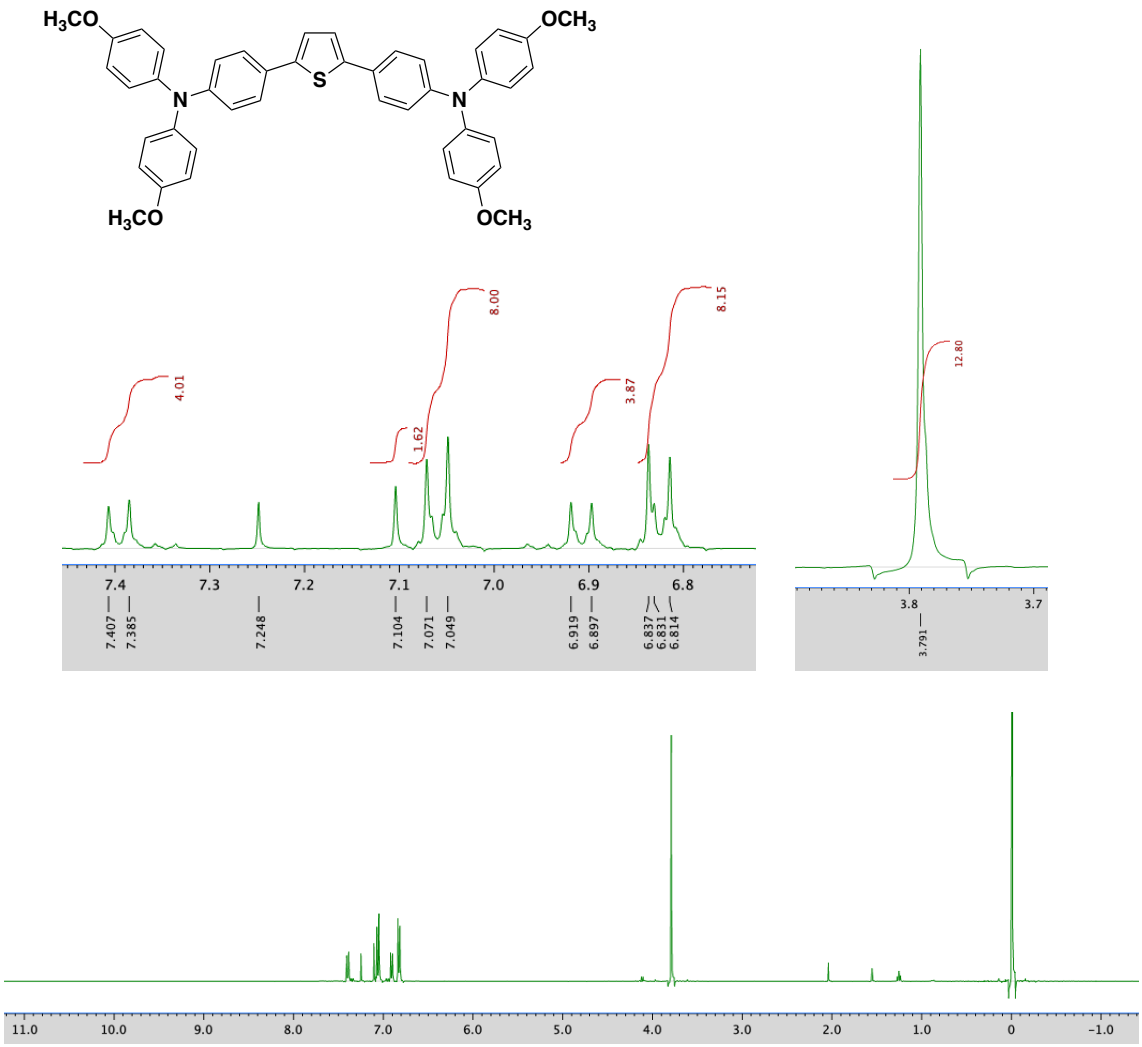


Figure S40. ^{1}H spectrum of **1** (400 MHz, $CDCl_3$).

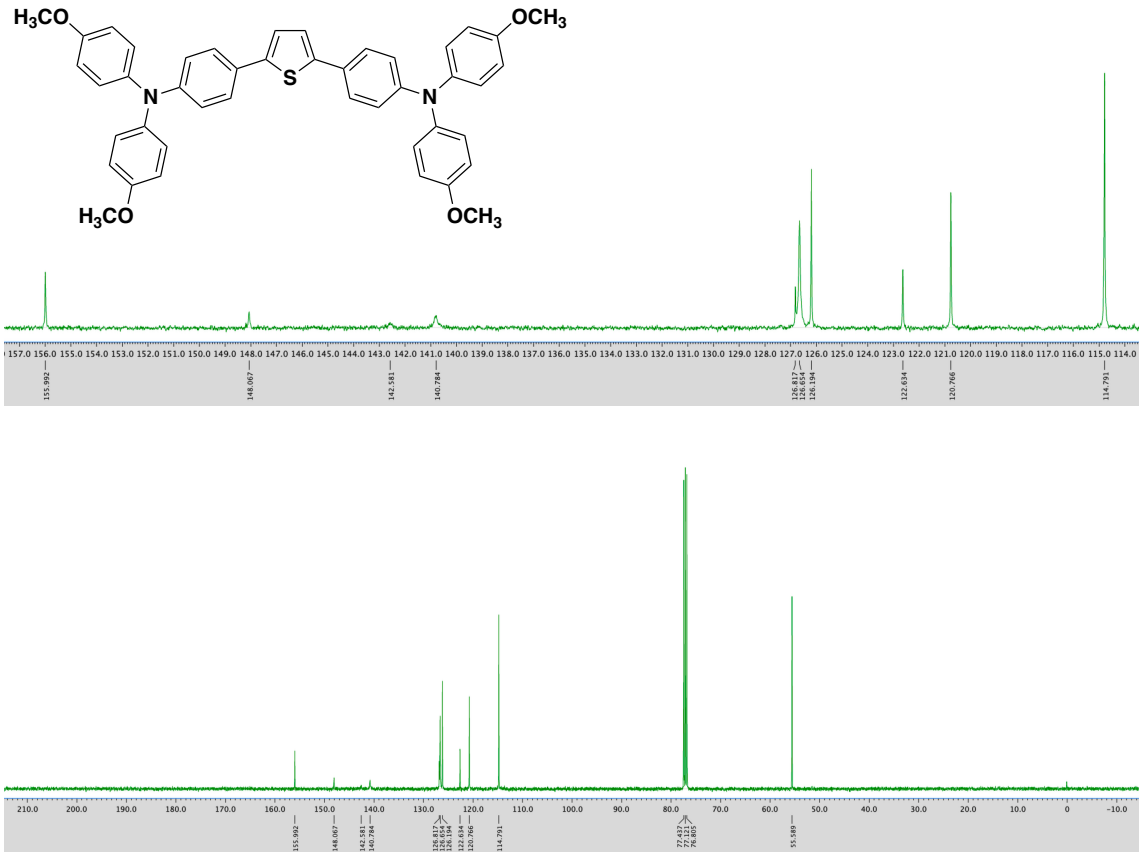


Figure S41. ^{13}C spectrum of **1** (100 MHz, $CDCl_3$).

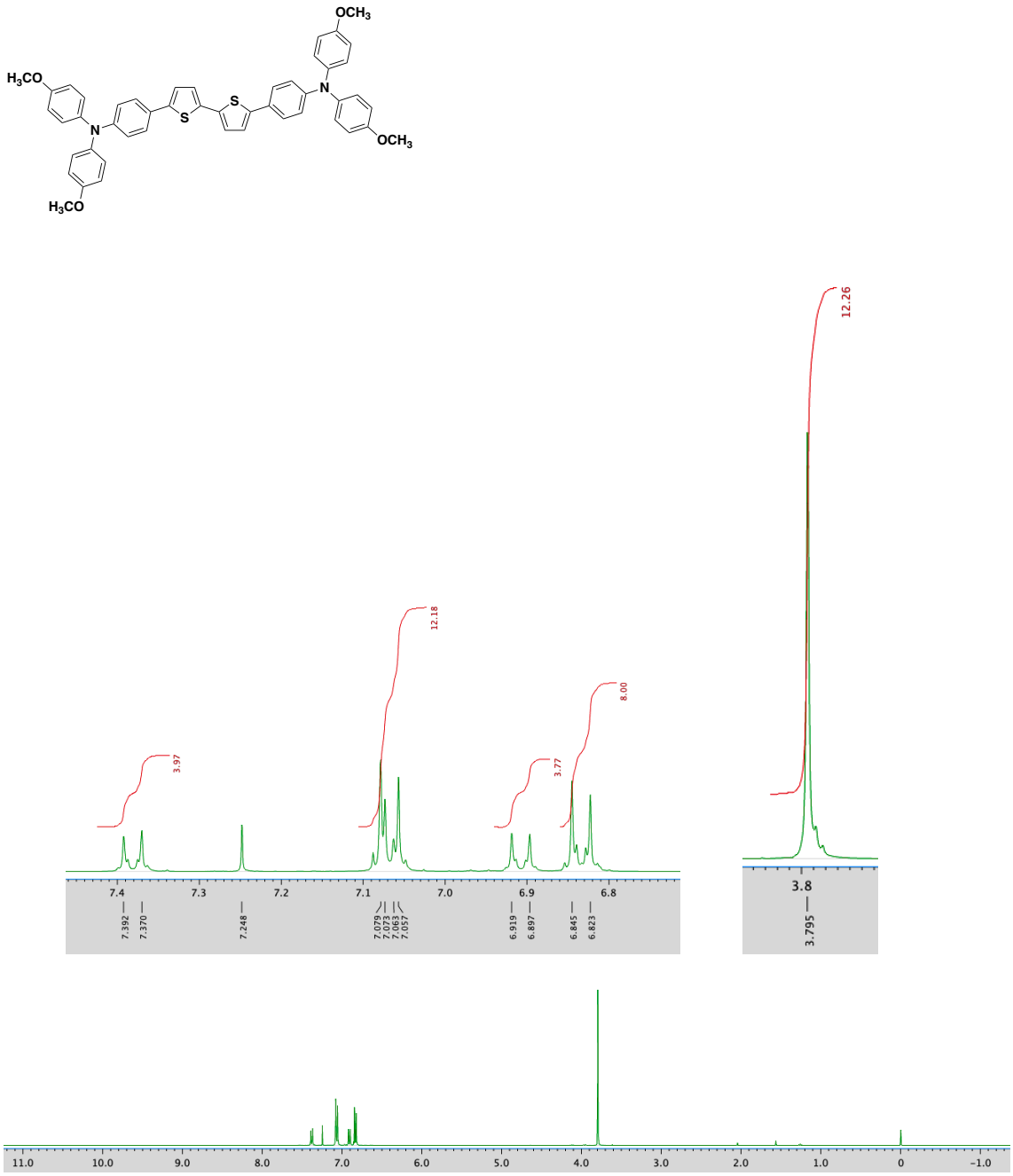


Figure S42. ^{1}H spectrum of **2** (400 MHz, $CDCl_3$).

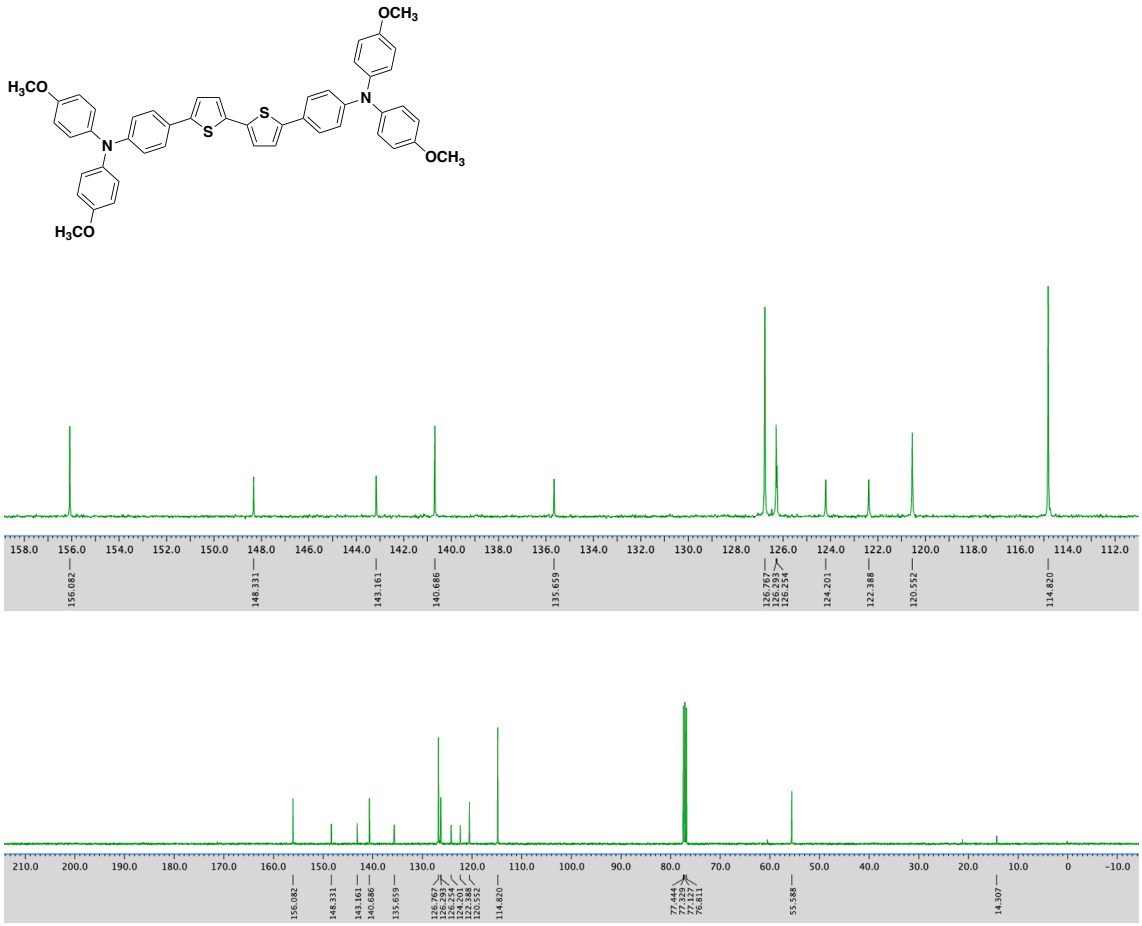


Figure S43. ^{13}C spectrum of **2** (100 MHz, $CDCl_3$).

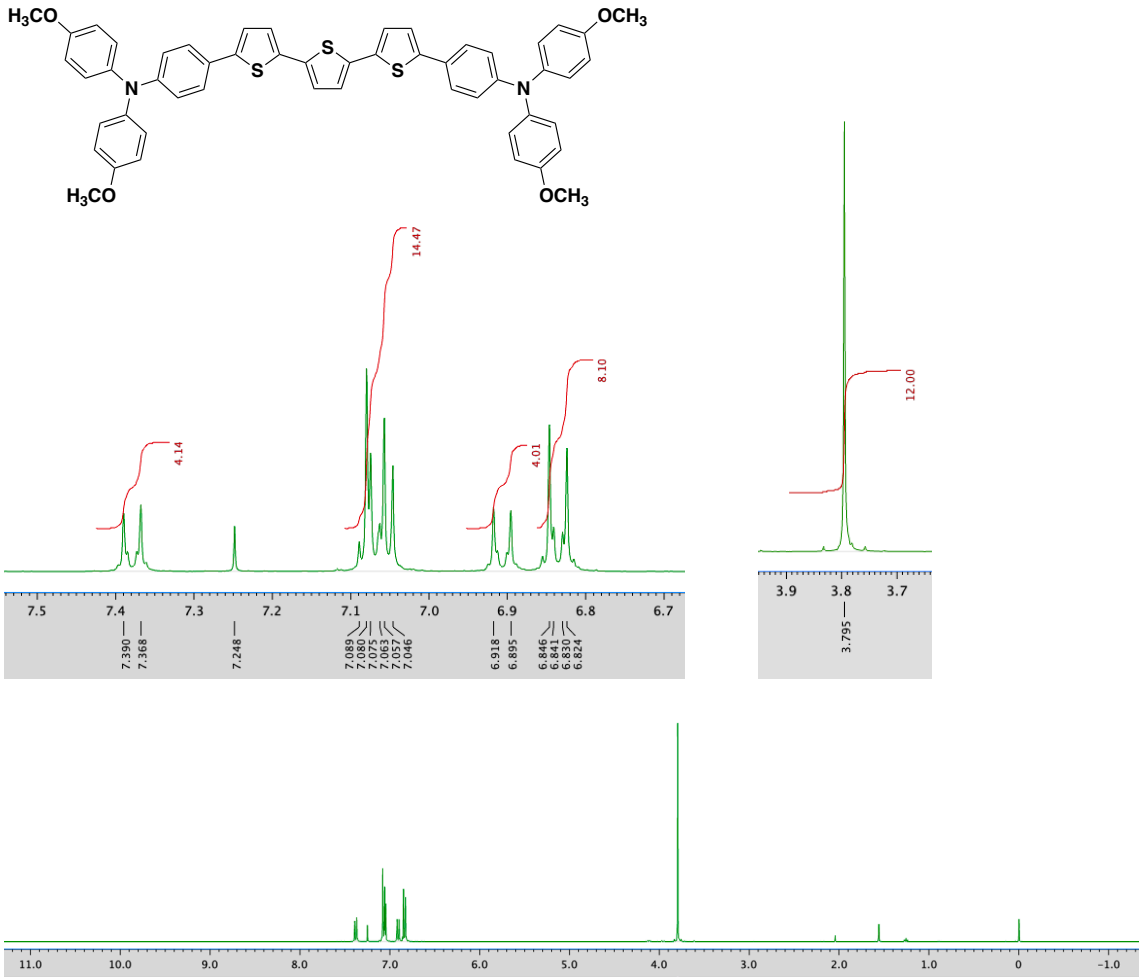


Figure S44. ^{1}H spectrum of **3** (400 MHz, $CDCl_3$).

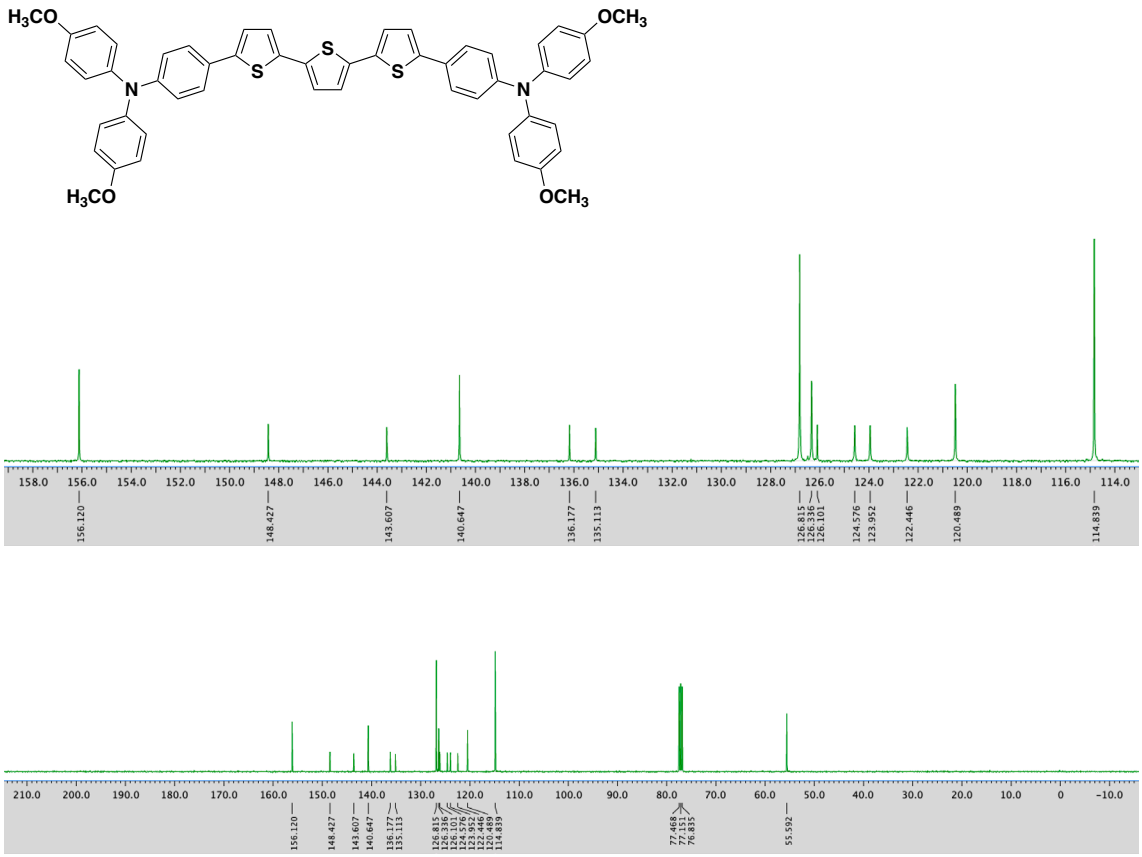


Figure S45. ^{13}C spectrum of **3** (100 MHz, $CDCl_3$).

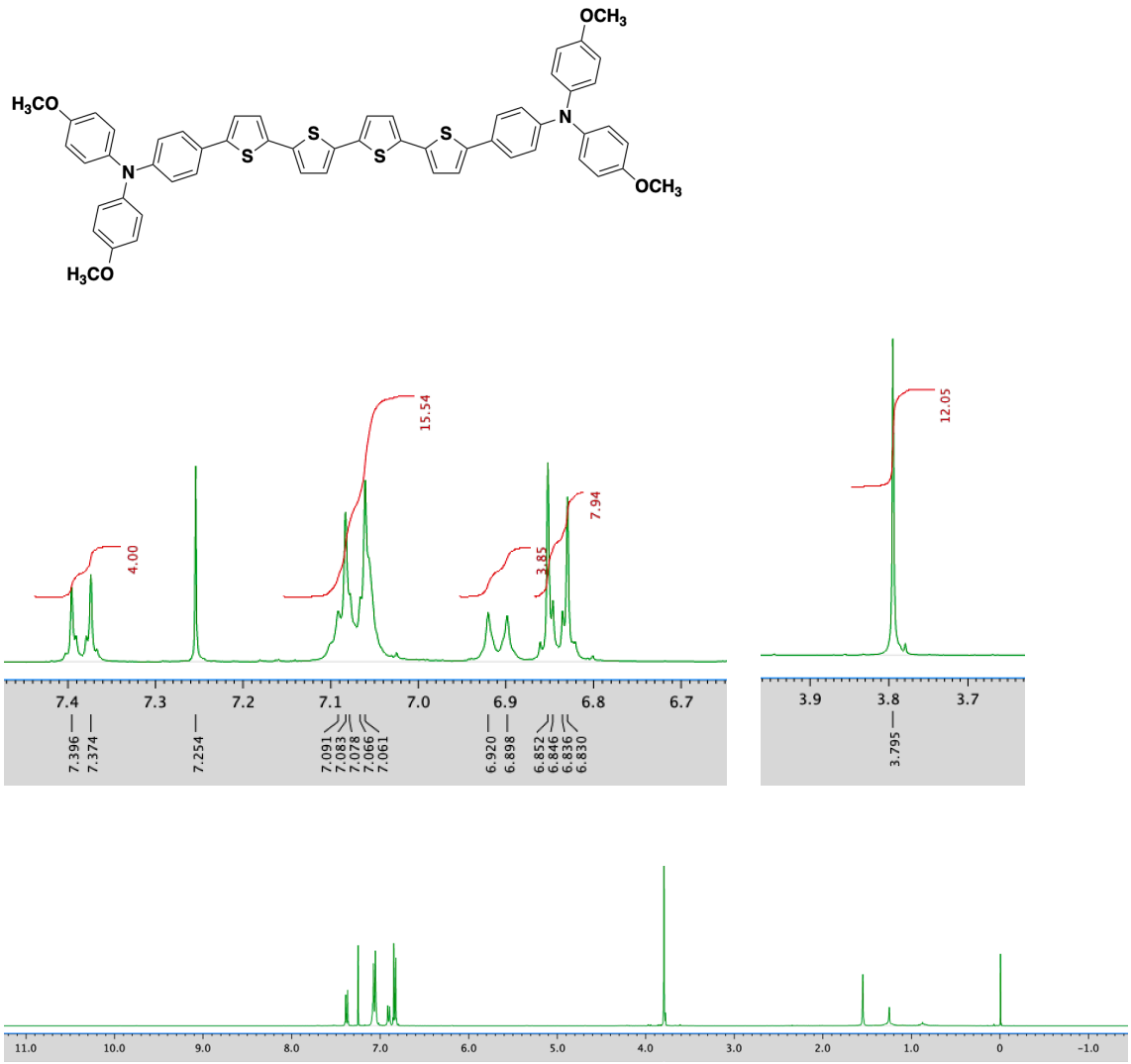


Figure S46. ^{1}H spectrum of **4** (400 MHz, $CDCl_3$).

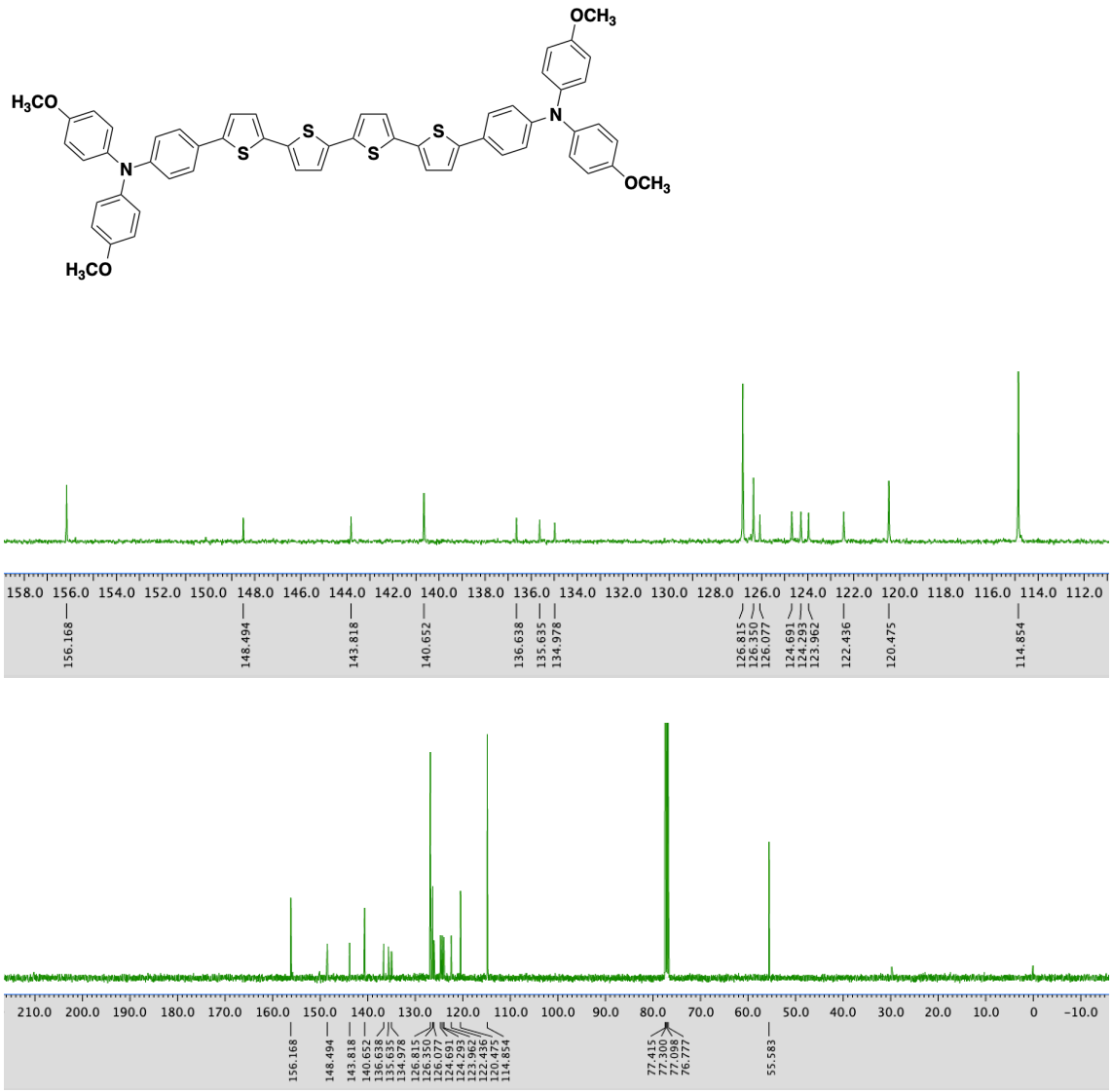


Figure S47. ^{13}C spectrum of **4** (100 MHz, $CDCl_3$).

9. References

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