

Supporting Information

***N*-phenylphenothiazine radical cation with extended π -systems: enhanced heat resistance of triarylamine radical cations as near-infrared absorbing dyes**

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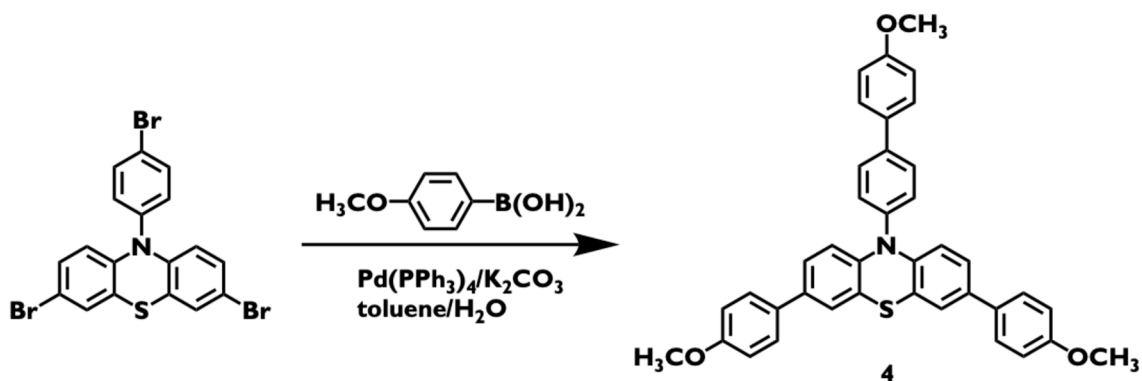
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1. General

¹H and ¹³C NMR spectra were recorded on a JEOL JNM-GSX400 spectrometer. Chemical shifts are reported in parts per million (ppm, δ scale) from residual protons in the deuterated solvent for ¹H NMR (δ 7.26 ppm for chloroform, δ 5.33 ppm for dichloromethane) and from the solvent carbon for ¹³C NMR (δ 77.16 ppm for deuterated chloroform and δ 54.24 ppm for deuterated dichloromethane). Fluorescence spectra were recorded on a JASCO FP-8600 Fluorescence Spectrometer. UV-vis-NIR absorption spectra were recorded on a JASCO V-670 UV-vis-NIR Spectrophotometer. TG-DTA were recorded on a RIGAKU EVO2G TG-DTA8122. Analytic thin layer chromatography (TLC) was performed on Merck, pre-coated plate silica gel 60 F₂₅₄ (0.25 mm thickness). Unless otherwise noted, all materials were obtained from commercial suppliers and used without further purification. Dry tetrahydrofuran (THF) was purchased from Wako pure chemical industries. 3,7-Dibromo-10-(4-bromophenyl)-10*H*-phenothiazine was synthesized by the method described in the literature.¹ All reactions were performed under nitrogen atmosphere. HRMS (APCI+) 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 4–6

10-(4'-Methoxy-[1,1'-biphenyl]-4-yl)-3,7-bis(4-methoxyphenyl)-10*H*-phenothiazine (**4**)



A mixture of 3,7-dibromo-10-(4-bromophenyl)-10*H*-phenothiazine (0.498 g, 0.973 mmol), 4-methoxyphenylboronic acid (1.20 g, 7.90 mmol), tetrakis(triphenylphosphine)palladium(0) (60.8 mg, 0.053 mmol), potassium carbonate (1.1 g, 8.0 mmol) in toluene (12 mL) and water (4 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 × 20 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 methanol/chloroform (1/1) to afford green crystals (0.440 g, 76.2%).

m.p. : 218.0-218.5 °C.

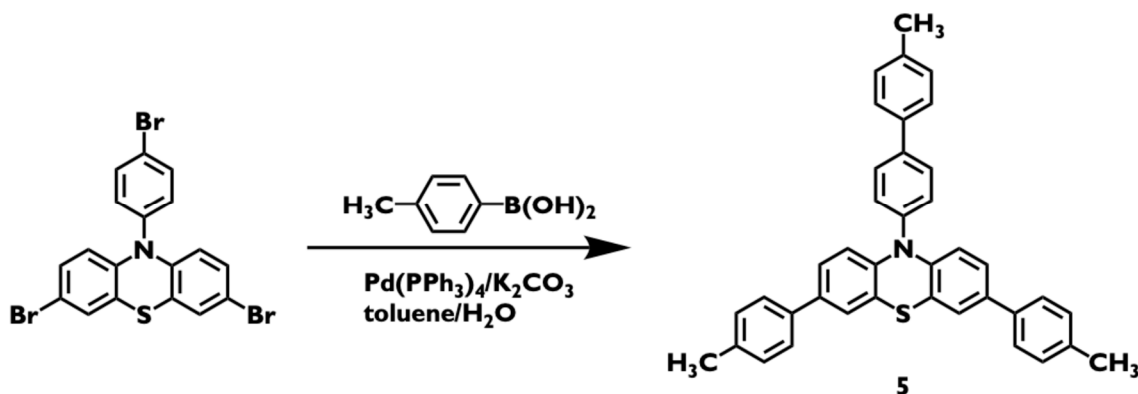
IR : 2951, 1462, 1236, 799 cm^{-1} .

^1H NMR (400 MHz, CD_2Cl_2): δ 3.78 (s, 6H), 3.84 (s, 3H), 6.31 (d, 2H, $J=8.4$ Hz), 6.90 (d, 4H, $J=8.4$ Hz), 7.00-7.06 (m, 4H), 7.22 (d, 2H, $J=2.0$ Hz), 7.40-7.44 (m, 6H), 7.62 (d, 2H, $J=8.8$ Hz), 7.80 (d, 2H, $J=8.8$ Hz).

^{13}C NMR (100 MHz, CD_2Cl_2): δ 55.4, 55.3, 114.2, 114.4, 116.4, 120.2, 124.5, 125.0, 127.3, 128.2, 129.0, 131.0, 132.1, 132.4, 135.0, 139.5, 140.8, 142.8, 159.1, 159.7.

HRMS(DART): m/z : Calcd. for $\text{C}_{39}\text{H}_{32}\text{NO}_3\text{S}$ $[\text{M}+\text{H}]^+$: 594.2098; Found: 594.2098.

10-(4'-Methyl-[1,1'-biphenyl]-4-yl)-3,7-bis(4-methylphenyl)-10*H*-phenothiazine (**5**)



A mixture of 3,7-dibromo-10-(4-bromophenyl)-10*H*-phenothiazine (0.511 g, 0.997 mmol), 4-methylphenylboronic acid (1.08 g, 7.88 mmol), tetrakis(triphenylphosphine)palladium(0) (57.9 mg, 0.05 mmol), potassium carbonate (1.2 g, 8.7 mmol) in toluene (12 mL) and water (4 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 × 20 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 methanol/chloroform (1/1) to afford green crystals (0.412 g, 75.7%).

m.p. : 200.5-201.0 °C.

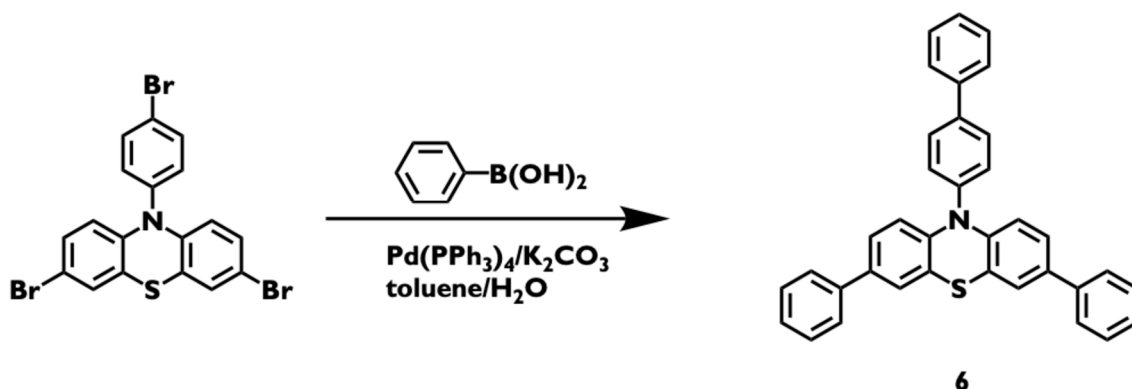
IR : 2918, 1457, 798 cm^{-1} .

^1H NMR (400 MHz, CD_2Cl_2): δ 2.32 (s, 6H), 2.40 (s, 3H), 6.32 (d, 2H, $J=8.8$ Hz), 7.08 (dd, 2H, $J=8.6, 2.0$ Hz), 7.18 (d, 4H, $J=7.6$ Hz), 7.26 (d, 2H, $J=2.0$ Hz), 7.38 (d, 4H, $J=8.4$ Hz), 7.45 (d, 2H, $J=8.4$ Hz), 7.58 (d, 2H, $J=8.0$ Hz), 7.83 (d, 2H, $J=8.4$ Hz).

^{13}C NMR (100 MHz, CD_2Cl_2): δ 21.8, 20.9, 116.4, 120.2, 124.7, 125.2, 126.0, 127.0, 129.3, 129.5, 129.7, 131.0, 135.3, 136.7, 137.0, 137.1, 137.8, 139.8, 141.1, 143.1.

HRMS(DART): m/z : Calcd. for $\text{C}_{39}\text{H}_{32}\text{NS}$ $[\text{M}+\text{H}]^+$: 546.2250; Found: 546.2250.

10-([1,1'-Biphenyl]-4-yl)-3,7-diphenyl-10*H*-phenothiazine (**6**)



A mixture of 3,7-dibromo-10-(4-bromophenyl)-10*H*-phenothiazine (0.572 g, 1.12 mmol), phenylboronic acid (1.05 g, 8.61 mmol), tetrakis(triphenylphosphine) palladium(0) (60.2 mg, 0.05 mmol), potassium carbonate (1.1 g, 8.0 mmol) in toluene (15 mL) and water (5 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 × 20 mL). The combined organic phase was dried over Na₂SO₄ and the solvent was evaporated in vacuo. The residue was purified by recrystallization from methanol/chloroform (1/1) to afford orange crystals (0.425 g, 75.4%).

m.p. : 174.0-174.5 °C.

IR: 3022, 1459, 754 cm⁻¹.

¹H NMR (400 MHz, CD₂Cl₂): δ 6.34 (d, 2H, *J*=8.4 Hz), 7.11 (dd, 2H, *J*=8.6, 2.0 Hz), 7.25-7.29 (m, 4H), 7.35-7.42 (m, 5H), 7.47-7.51 (m, 8H), 7.69 (d, 2H, *J*=7.2 Hz), 7.86 (d, 2H, *J*=8.4 Hz).

¹³C NMR (100 MHz, CD₂Cl₂): δ 116.5, 120.4, 125.0, 125.5, 126.3, 127.1, 127.2, 127.9, 128.9, 129.1, 129.6, 131.1, 135.5, 139.7, 140.0, 140.1, 141.3, 143.3.

HRMS(DART): *m/z*: Calcd. for C₃₆H₂₆N [M+H]⁺: 504.1781; Found: 504.1778.

3. X-Ray diffraction measurements of 4 and 6

CCDC 2393033 and CCDC 2393032 contain the supplementary crystallographic data for **4** and **6**, respectively. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/structures.

Table S1. Crystallographic data for **4** (CCDC 2393033) and **6** (CCDC 2393032).

	4	6
Chemical formula	C ₃₉ H ₃₁ NO ₃ S	C ₃₆ H ₂₅ NS
Formula weight	593.71	503.63
Wavelength / Å	0.71073	0.71073
Cell system	monoclinic	monoclinic
Space group	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> / Å	15.5737(5)	5.6088(2)
<i>b</i> / Å	7.3237(2)	24.8533(9)
<i>c</i> / Å	26.2550(9)	21.5220(6)
β / °	97.319(3)	92.770(3)
<i>V</i> / Å ³	2970.17(16)	2996.60(17)
<i>Z</i>	4	4
<i>D</i> _{calc} / g cm ⁻³	1.328	1.116
<i>F</i> ₀₀₀	1248	1056
μ / cm ⁻¹	0.150	0.131
Crystal size / mm ³	0.23x0.13x0.09	0.44x0.05x0.03
Crystal colour, habit	yellow, block	colorless, needle
transfer factor	0.682-1.000	0.810-1.000
No. of measured reflections	24238	22788
No. of unique reflections.	7179	7131
No. of variables	400	343
Reflections / parameter ratio	17.95	20.79
<i>R</i> _{int}	0.0634	0.0474
2 θ _{max} / °	59.6	59.4
<i>R</i> 1 value ^{a)}	0.0517	0.0612
<i>R</i> value ^{b)}	0.0753	0.0837
<i>wR</i> 2 value ^{c)}	0.1351	0.1377
<i>p</i> and <i>q</i> factors ^{c)}	0.0516, 0.9515	0.0553, 2.0708.
Goodness of fit	1.071	1.044
Min./max. peak in final difference	-0.292/0.555	-0.486/0.607
Fourier map / e Å ⁻³		

a) $R1 = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$ (for $I > 2\sigma(I)$)

b) $R = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$ (for all reflections)

c) $wR^2 = [\sum (w(F_o^2 - F_c^2)^2) / \sum w(F_o^2)^2]^{1/2}$; $w^{-1} = \sigma^2(F_o^2) + (p \cdot P)^2 + q \cdot P$; $P = (F_o^2 + 2F_c^2)/3$ (for all reflections)

4. Solubility tests

To a sample of 5.0 mg, 100 μ L of solvent was added repeatedly. The resulting suspension was shaken and sonicated at room temperature (20–25 °C). The solution was sealed during the dissolution process to prevent volatilization of the solvent. The total amount of solvent was converted to solubility (wt%). The results are summarized in Table S2.

Table S2. Solubility (wt%) of compounds **1-6** in dichloromethane, anisole, toluene and ethyl acetate at room temperature.

Compound	dichloromethane	anisole	toluene	ethyl acetate
1	2.60	1.15	0.54	0.28
2	7.87	5.14	6.18	0.44
3	0.42	0.44	0.33	0.01
4	3.52	2.34	1.08	0.24
5	7.64	9.17	8.15	0.78
6	13.83	5.68	5.68	1.96

5. Cyclic voltammetry

Cyclic voltammograms (CVs) were recorded on a BAS Electrochemical Analyzer CHI-612B. A Pt electrode (surface area: $A = 0.071 \text{ cm}^2$, BAS), an Ag/Ag^+ (Ag wire in 0.01 M AgNO_3 /0.1 M $\text{Bu}_4\text{NPF}_6/\text{CH}_3\text{CN}$), and a Pt wire electrode were used as working, reference, and counter electrodes, respectively. 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 the solutions, beaker-typed three electrode electrochemical cells were constructed with the potentiostat to perform cyclic voltammetry. All CV measurements were performed under a nitrogen atmosphere. The redox potentials were calibrated with ferrocene.

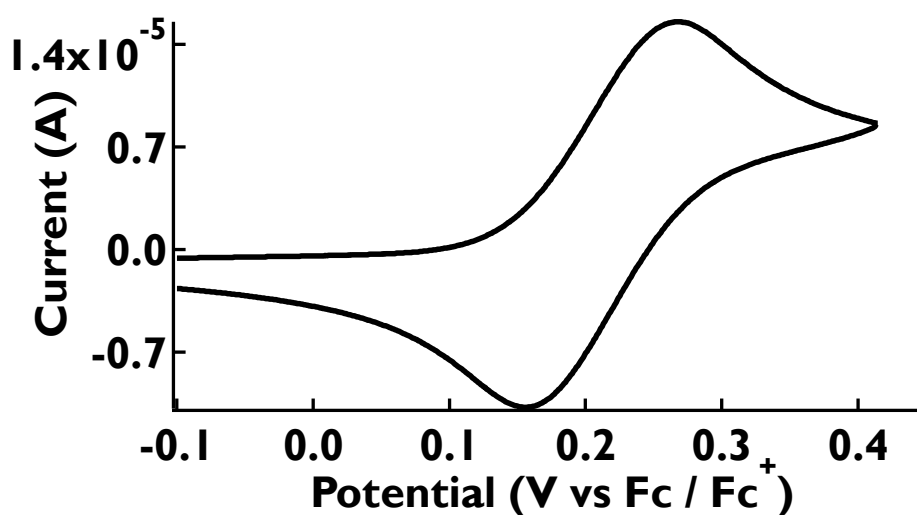


Figure S1. Cyclic voltammogram of **5** in dichloromethane ($1 \times 10^{-3} \text{ M}$) with Bu_4NPF_6 as a supporting electrolyte. The scan rate is 100 mV/s.

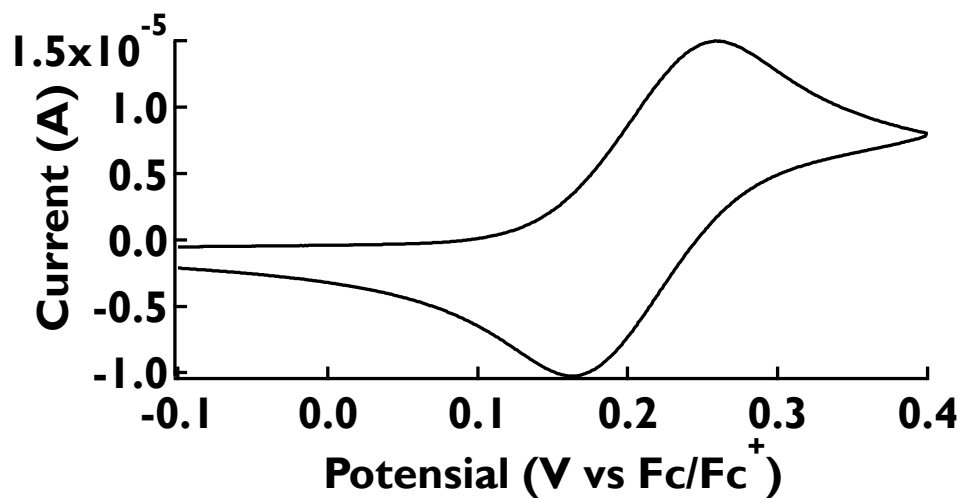


Figure S2. Cyclic voltammogram of **6** in dichloromethane (1×10^{-3} M) with Bu_4NPF_6 as a supporting electrolyte. The scan rate is 100 mV/s.

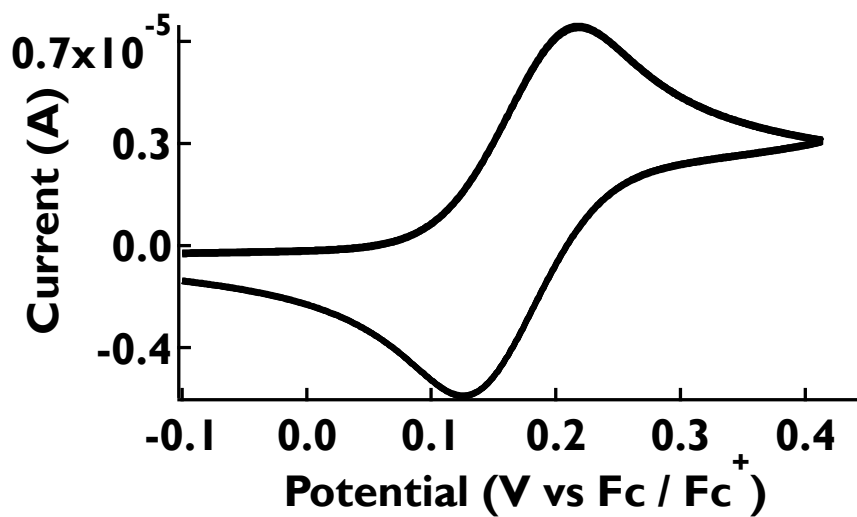


Figure S3. Cyclic voltammogram of **4** in dichloromethane (1×10^{-3} M) repeating sweep ten cycles. The scan rate is 25 mV/s. Bu_4NPF_6 (1×10^{-1} M) was employed as a supporting electrolyte.

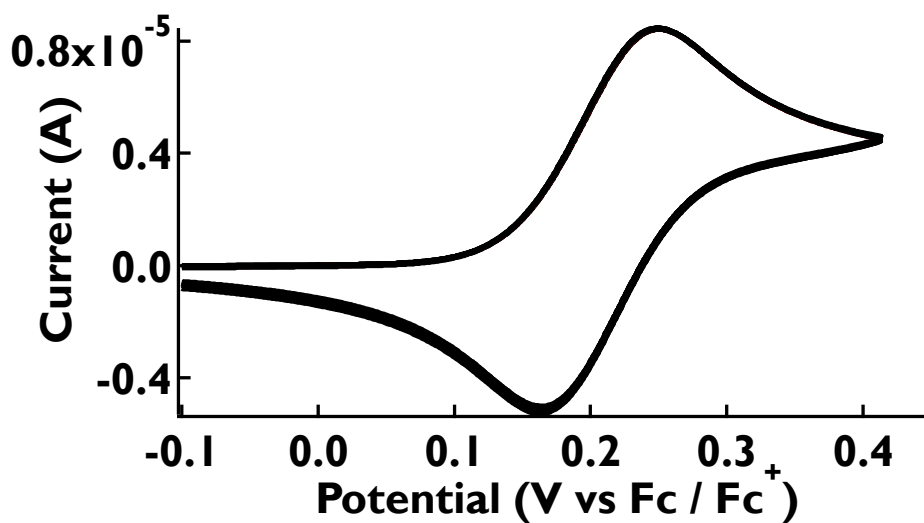


Figure S4. Cyclic voltammogram of **5** in dichloromethane (1×10^{-3} M) repeating sweep ten cycles. The scan rate is 25 mV/s. Bu₄NPF₆ (1×10^{-1} M) was employed as a supporting electrolyte.

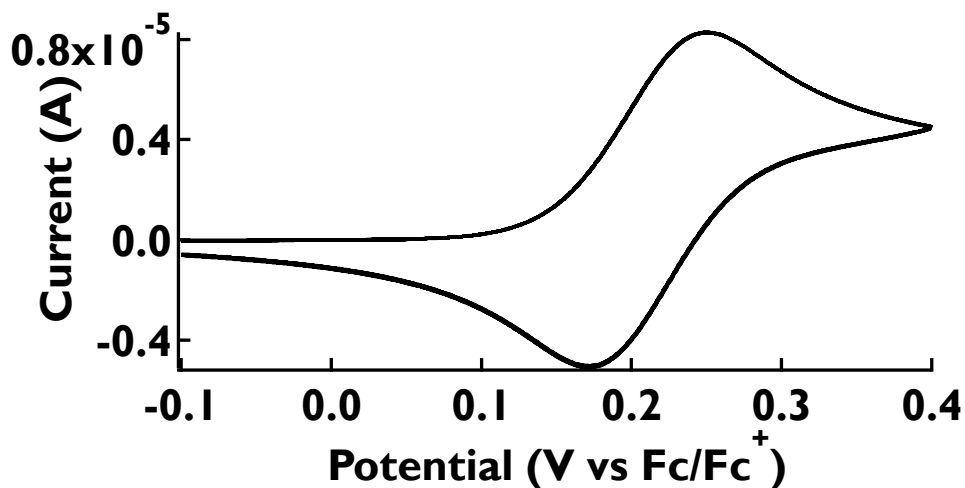


Figure S5. Cyclic voltammogram of **6** in dichloromethane (1×10^{-3} M) repeating sweep ten cycles. The scan rate is 25 mV/s. Bu₄NPF₆ (1×10^{-1} M) was employed as a supporting electrolyte.

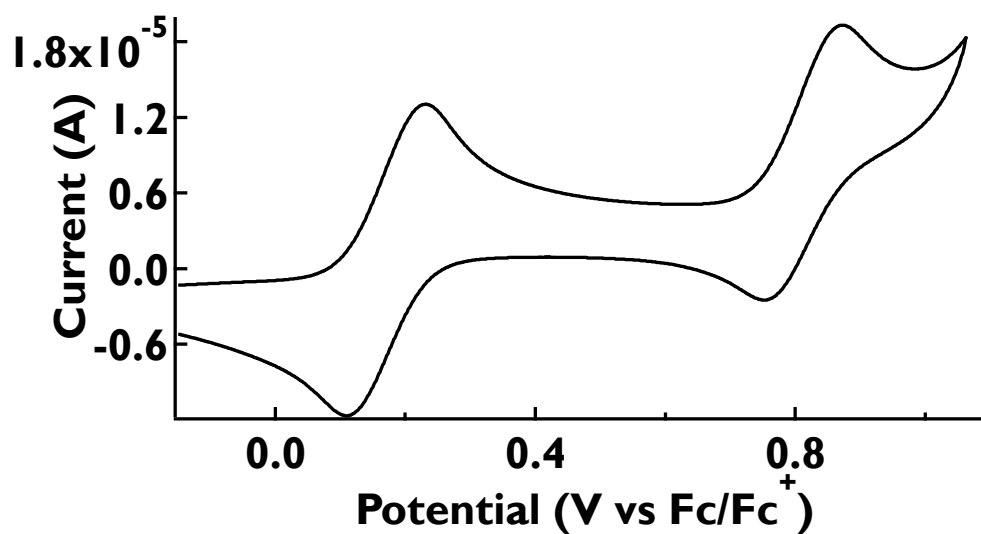


Figure S6. Cyclic voltammogram of **4** in dichloromethane (1×10^{-3} M) with Bu_4NPF_6 as a supporting electrolyte in the range of -0.15 and 1.06 V (vs Fc/Fc^+) The scan rate is 100 mV/s.

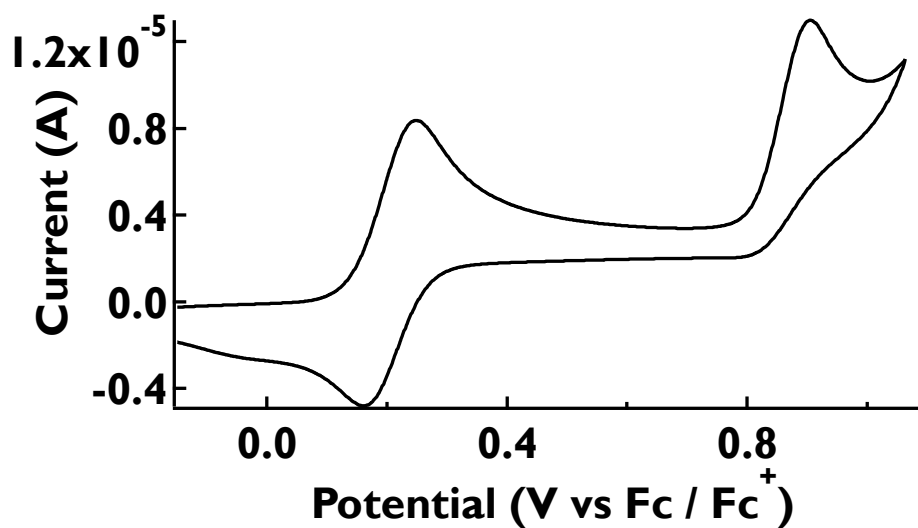


Figure S7. Cyclic voltammogram of **5** in dichloromethane (1×10^{-3} M) with Bu_4NPF_6 as a supporting electrolyte in the range of -0.15 and 1.06 V (vs Fc/Fc^+) The scan rate is 100 mV/s.

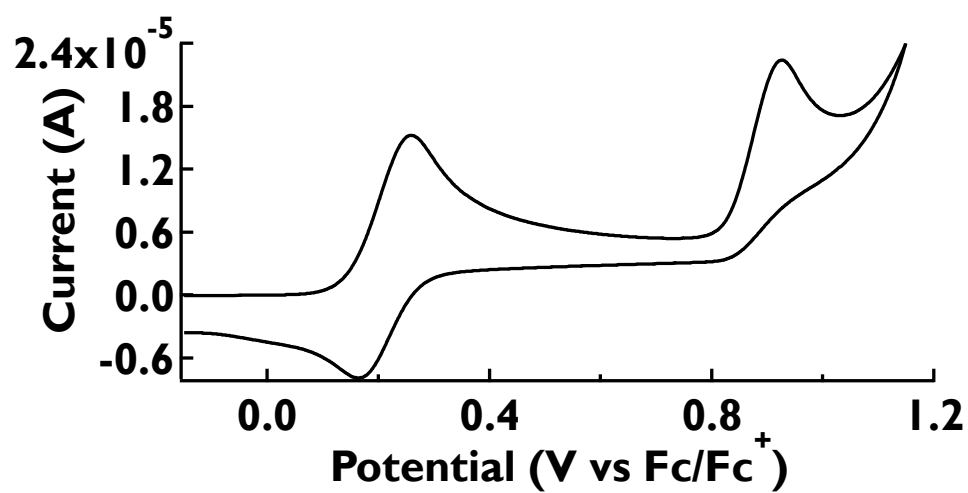


Figure S8. Cyclic voltammogram of **6** in dichloromethane (1×10^{-3} M) with Bu_4NPF_6 as a supporting electrolyte in the range of -0.15 and 1.15 V (vs Fc/Fc^+) The scan rate is 100 mV/s.

6. Absorption and emission spectra

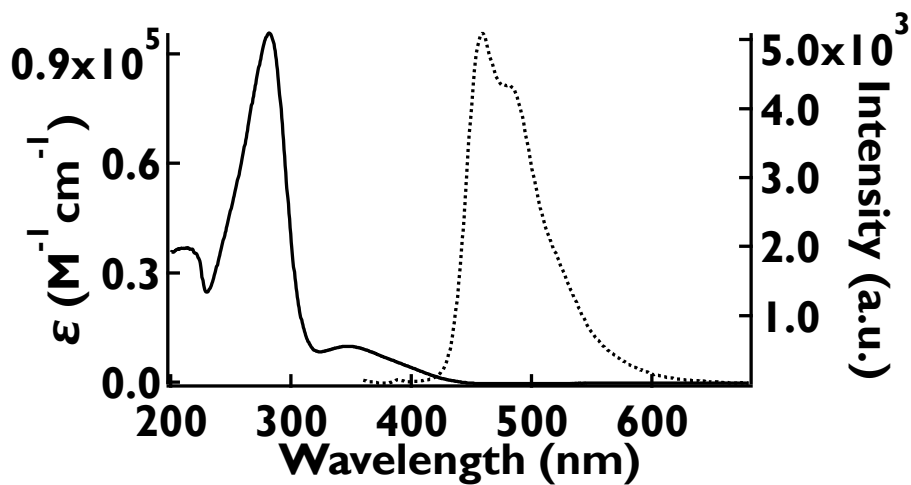


Figure S9. UV-vis (solid line) and fluorescence emission (dotted line) spectra of **5**. The concentration is 1×10^{-5} M for UV-vis and 1×10^{-6} M for fluorescence emission spectra.

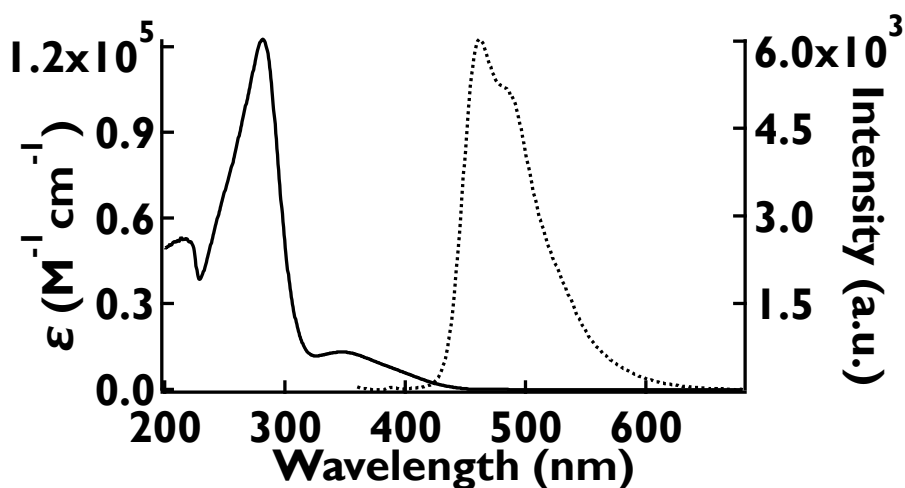


Figure S10. UV-vis (solid line) and fluorescence emission (dotted line) spectra of **6**. The concentration is 1×10^{-5} M for UV-vis and 1×10^{-6} M for fluorescence emission spectra.

7. Absorption spectra of the oxidized species

Typical procedure for the preparation of radical cationic species for UV measurements is as follows. To a solution of triarylamine in dry dichloromethane (5.0×10^{-4} M, 100 μ L) was added a solution of SbCl_5 in dry dichloromethane (5.0×10^{-4} M, 200 μ L). The obtained solution was diluted to 5 mL with dry dichloromethane.



Figure S11. Dichloromethane solution of **4** in the absence (left) and presence of 2.0 equivalents of SbCl_5 (right). $[\mathbf{4}] = 1 \times 10^{-5}$ M.

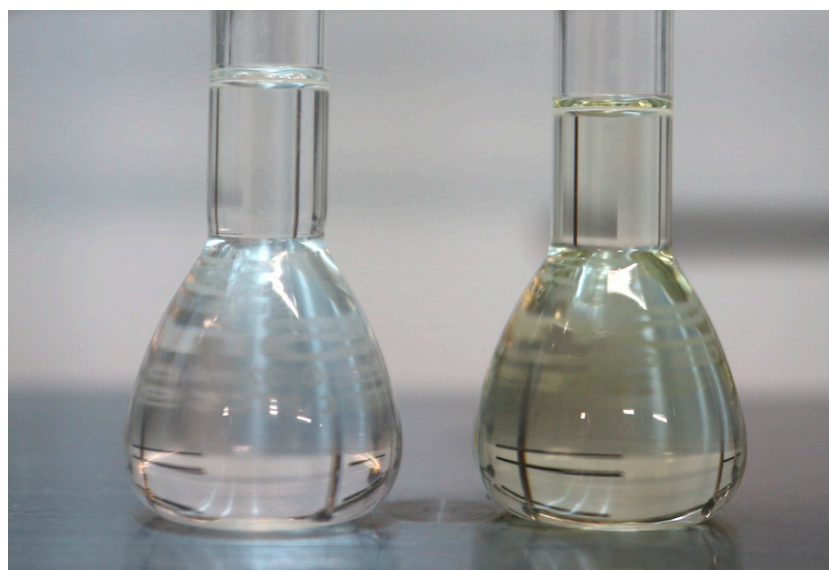


Figure S12. Dichloromethane solution of **5** in the absence (left) and presence of 2.0 equivalents of SbCl_5 (right). $[\mathbf{5}] = 1 \times 10^{-5}$ M.



Figure S13. Dichloromethane solution of **6** in the absence (left) and presence of 2.0 equivalents of SbCl_5 (right). $[\mathbf{6}] = 1 \times 10^{-5} \text{ M}$.

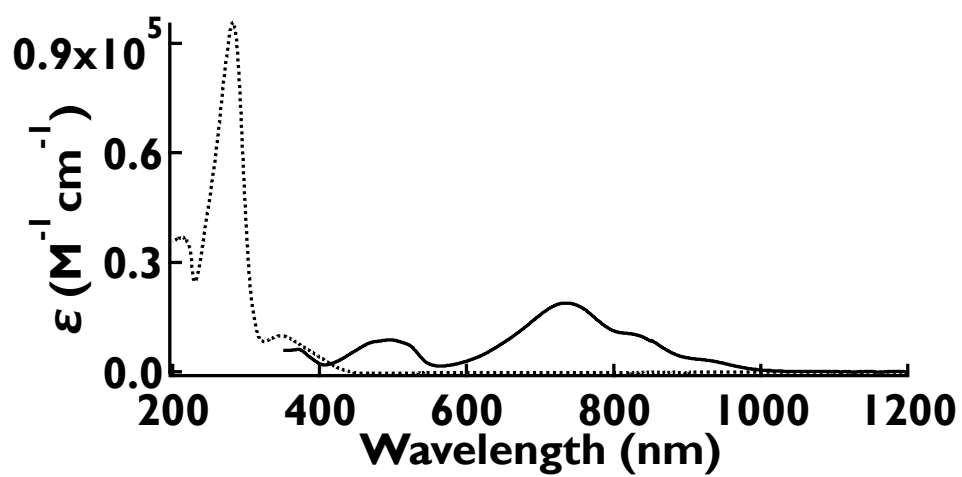


Figure S14. Absorption spectra of **5** before (dotted line) and after oxidation with 2.0 equivalents of SbCl_5 (solid line) in dichloromethane at room temperature. $[\mathbf{5}] = 1 \times 10^{-5} \text{ M}$.

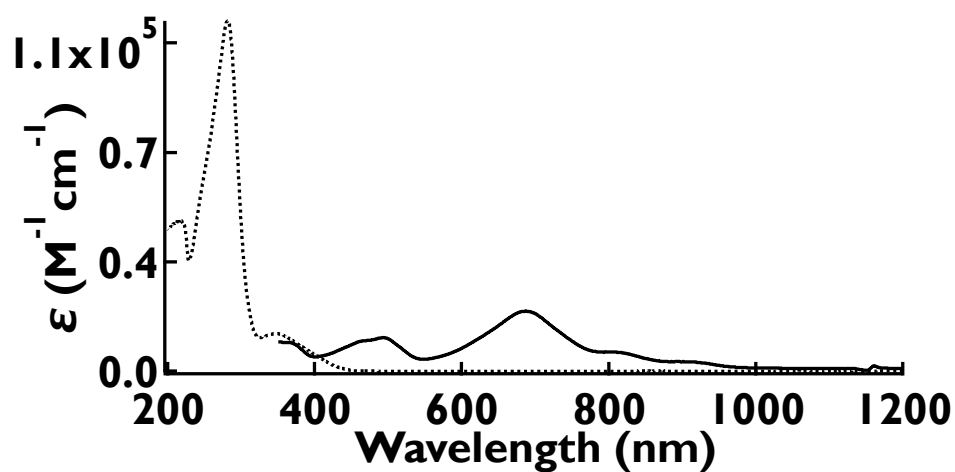


Figure S15. Absorption spectra of **6** before (dotted line) and after oxidation with 2.0 equivalents of SbCl_5 (solid line) in dichloromethane at room temperature. $[\mathbf{6}] = 1 \times 10^{-5}$ M.

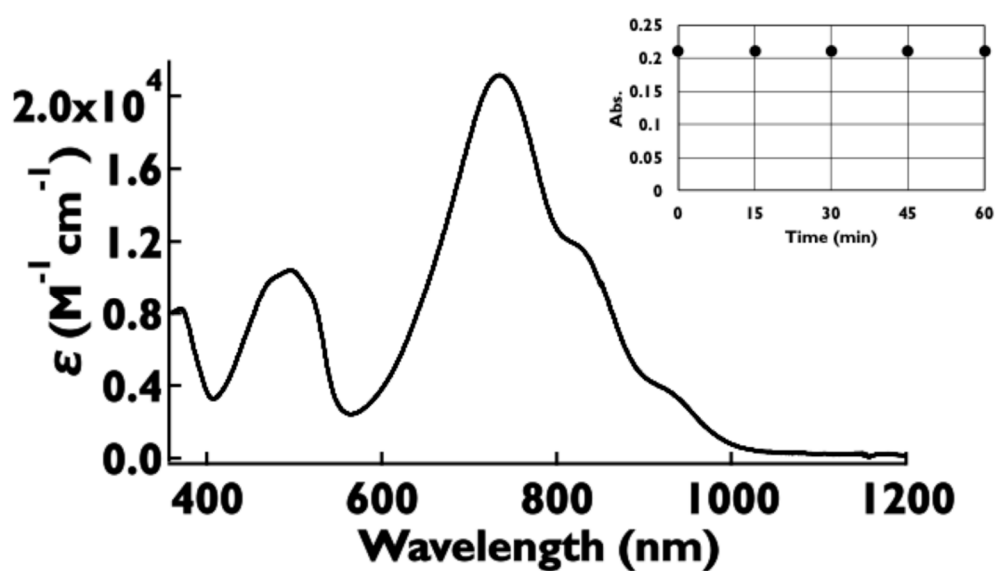


Figure S16. Time-course of absorption spectra of **5** with 2.0 equivalents of SbCl_5 in dichloromethane at room temperature recorded every 15 minutes. The initial concentration of **5** is 1×10^{-5} M. Inset: time-course of the peak intensity at 736 nm.

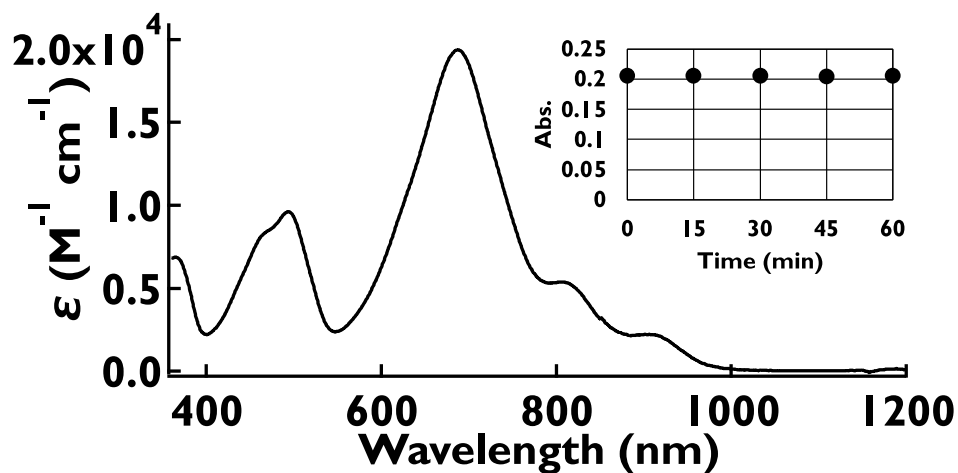


Figure S17. Time-course of absorption spectra of **6** with 2.0 equivalents of SbCl_5 in dichloromethane at room temperature recorded every 15 minutes. The initial concentration of **6** is 1×10^{-5} M. Inset: time-course of the peak intensity at 688 nm.

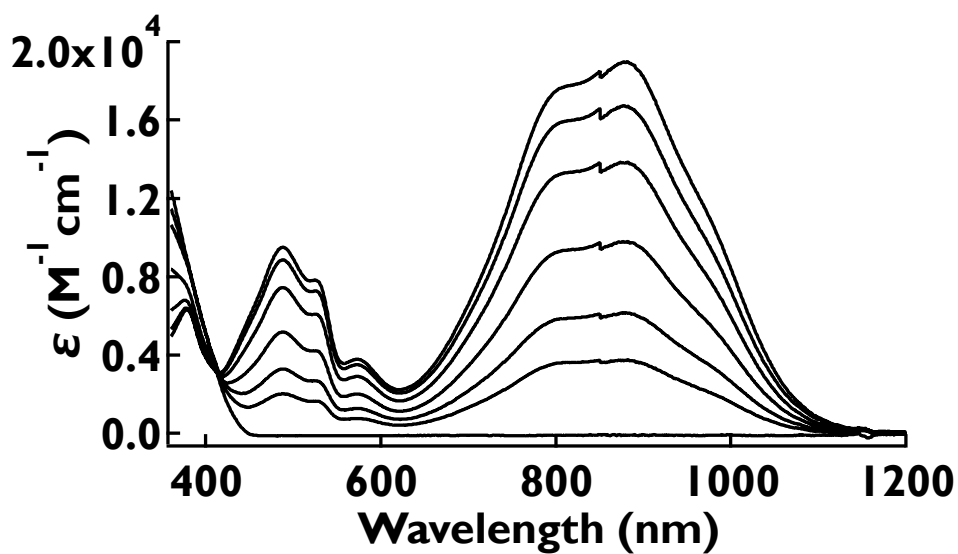


Figure S18. Absorption spectra of **4** after oxidation with 0, 0.3, 0.6, 0.9, 1.2, 1.5 and 2.0 equivalents of SbCl_5 in dichloromethane at room temperature. $[\mathbf{4}] = 1 \times 10^{-5}$ M.

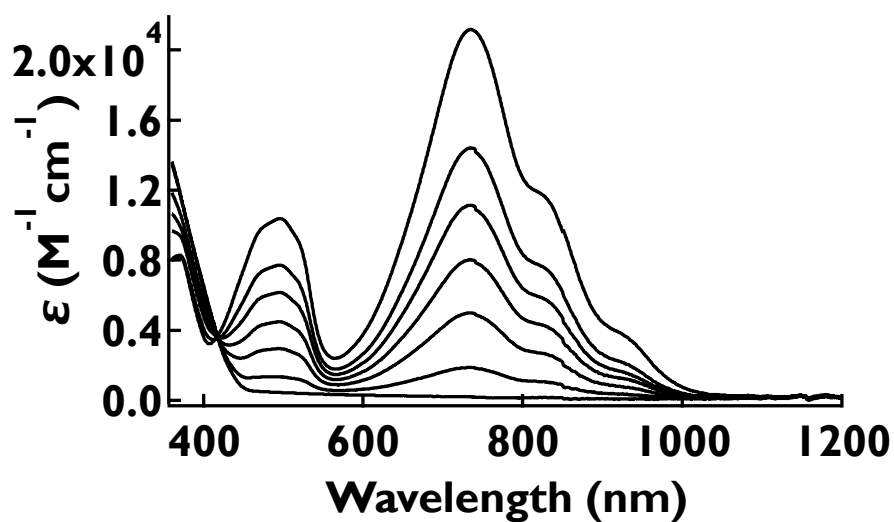


Figure S19. Absorption spectra of **5** after oxidation with 0, 0.3, 0.6, 0.9, 1.2, 1.5 and 2.0 equivalents of SbCl_5 in dichloromethane at room temperature. $[\mathbf{5}] = 1 \times 10^{-5} \text{ M}$.

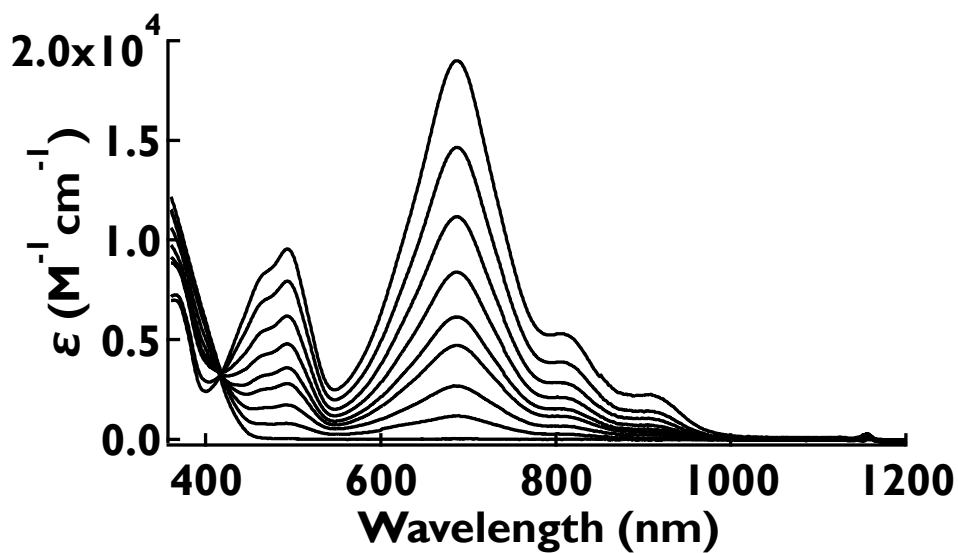


Figure S20. Absorption spectra of **6** after oxidation with 0, 0.1, 0.3, 0.6, 0.9, 1.2, 1.5, 1.8 and 2.0 equivalents of SbCl_5 in dichloromethane at room temperature. $[\mathbf{6}] = 1 \times 10^{-5} \text{ M}$.

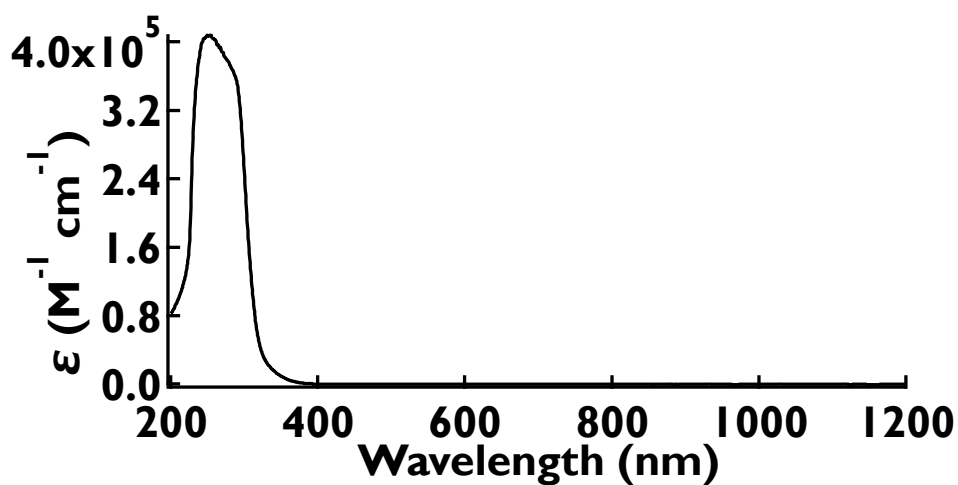


Figure S21. Absorption spectrum of SbCl_5 in dichloromethane at room temperature. $[\text{SbCl}_5] = 1 \times 10^{-5} \text{ M}$.

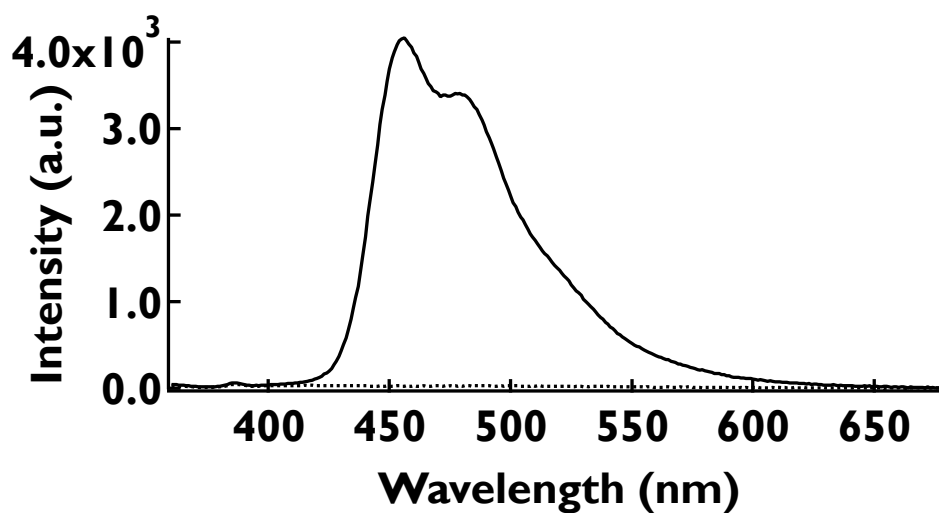


Figure S22. Emission spectra of **4** before (solid line) and after oxidation with 2.0 equivalents of SbCl_5 (dotted line) in dichloromethane at room temperature. Excitation at 346 nm. $[\mathbf{4}] = 1 \times 10^{-6} \text{ M}$.

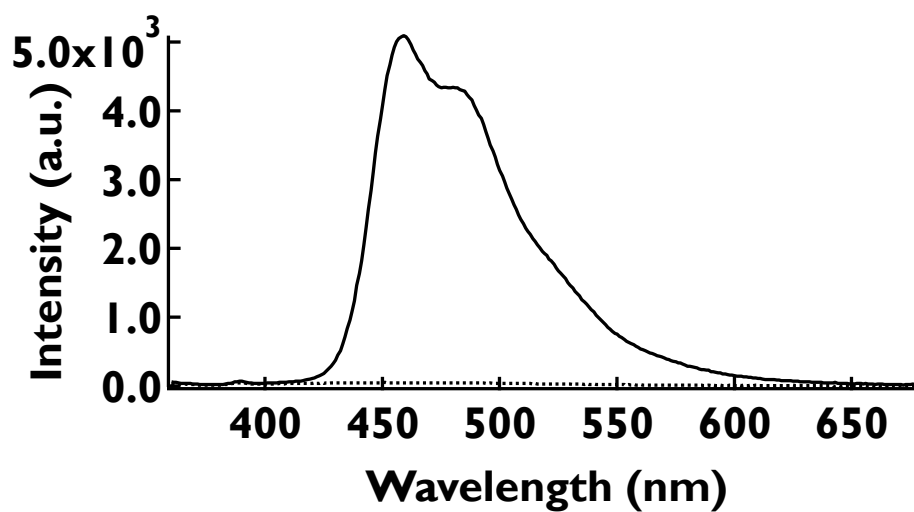


Figure S23. Emission spectra of **5** before (solid line) and after oxidation with 2.0 equivalents of SbCl_5 (dotted line) in dichloromethane at room temperature. Excitation at 348 nm. $[\mathbf{5}] = 1 \times 10^{-6} \text{ M}$.

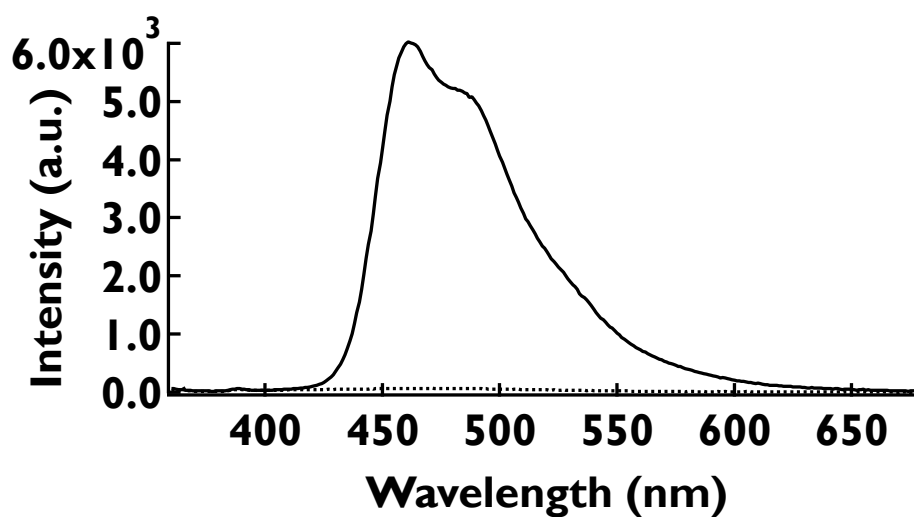
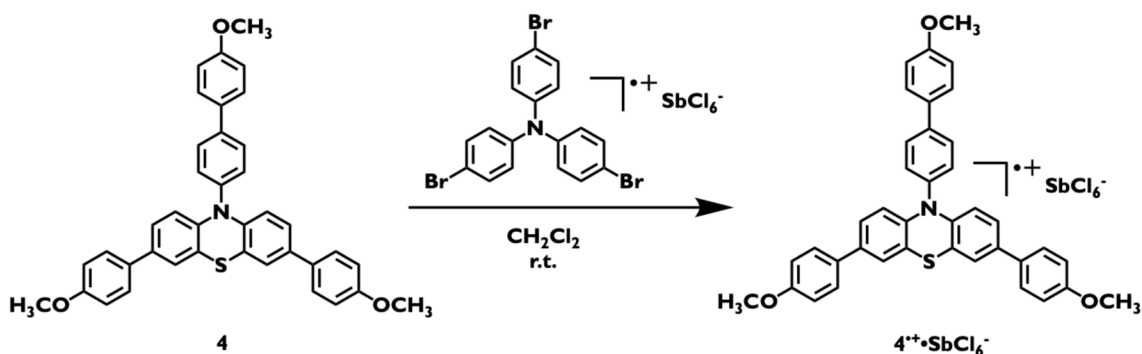


Figure S24. Emission spectra of **6** before (solid line) and after oxidation with 2.0 equivalents of SbCl_5 (dotted line) in dichloromethane at room temperature. Excitation at 348 nm. $[\mathbf{6}] = 1 \times 10^{-6} \text{ M}$.

8. Attempt to isolate radical cation salts ($4^{\bullet+} \cdot \text{SbCl}_6^-$)



To a solution of **4** (115 mg, 2.0×10^{-1} mmol) in CH_2Cl_2 (5 ml) was added tris(4-bromophenyl)ammonium hexachloroantimonate (173 mg, 2.0×10^{-1} mmol), and the mixture was stirred at room temperature for 2 min under nitrogen atmosphere. After the mixture was evaporated, the residue was washed with Et_2O . The insoluble material was collected by filtration to give $4^{\bullet+} \cdot \text{SbCl}_6^-$ (149 mg, 81.8 %) as reddish brown solid. The absorption spectrum of the isolated $4^{\bullet+} \cdot \text{SbCl}_6^-$ was completely consistent with that of the radical cation of **4** generated in solution.

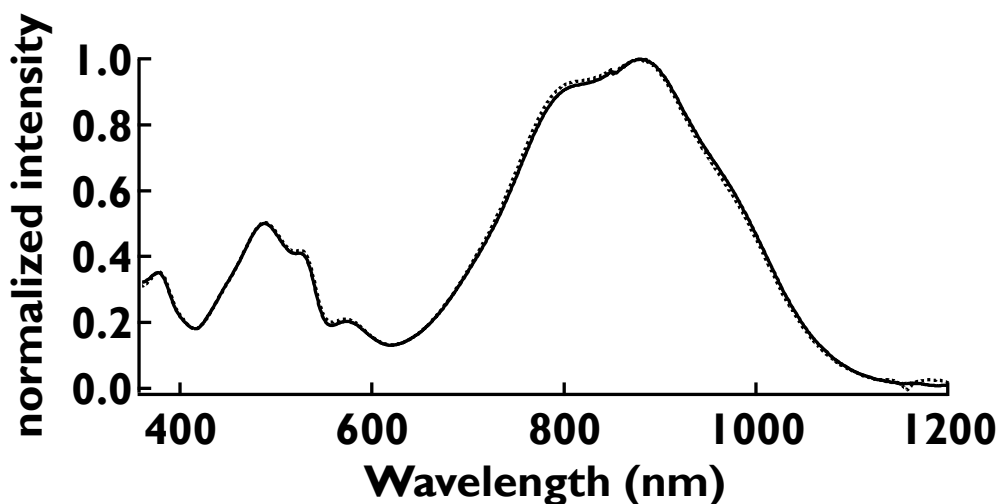


Figure S25. Absorption spectra of isolated $4^{\bullet+} \cdot \text{SbCl}_6^-$ (solid line) and **4** after oxidation with 2.0 equivalents of SbCl_5 (dotted line) in dichloromethane at room temperature.

9. TG-DTA for $1^{+} \cdot \text{SbCl}_6^{-}$

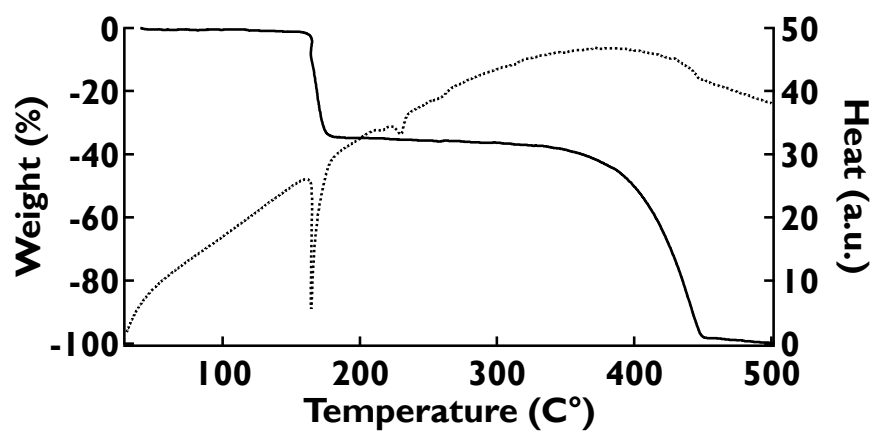


Figure. S26. TG-DTA charts for $1^{+} \cdot \text{SbCl}_6^{-}$ under N_2 purge. Solid and dotted lines represent TG and DTA, respectively.

10. ESR spectra

Typical procedure for the preparation of radical cationic species for ESR measurements is as follows. To a solution of triarylamine in dry dichloromethane (5.0×10^{-4} M, 100 μ L) was added a solution of SbCl_5 in dry dichloromethane (5.0×10^{-4} M, 200 μ L). The obtained solution was diluted to 5 mL with dry dichloromethane.

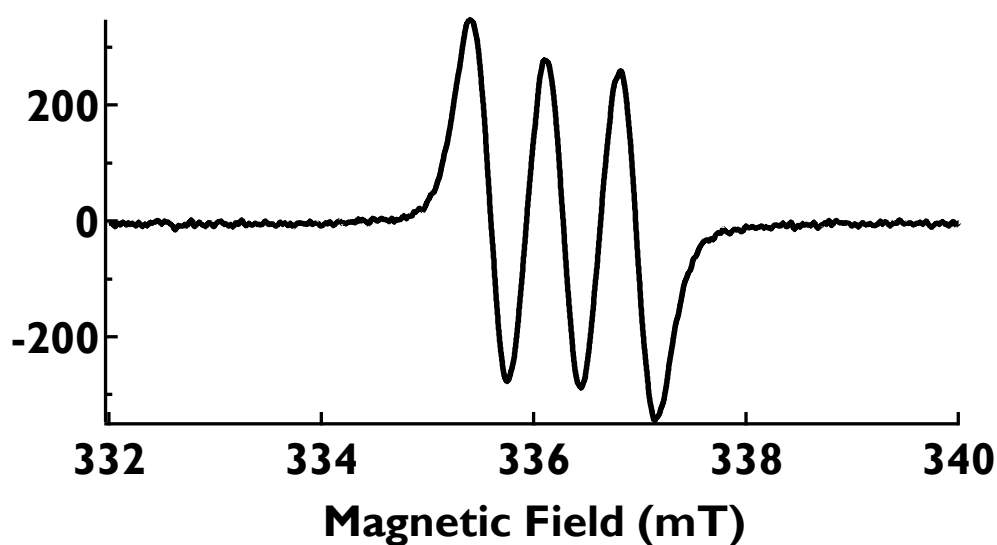


Figure S27. ESR spectrum of $4^{+\bullet}$ in CH_2Cl_2

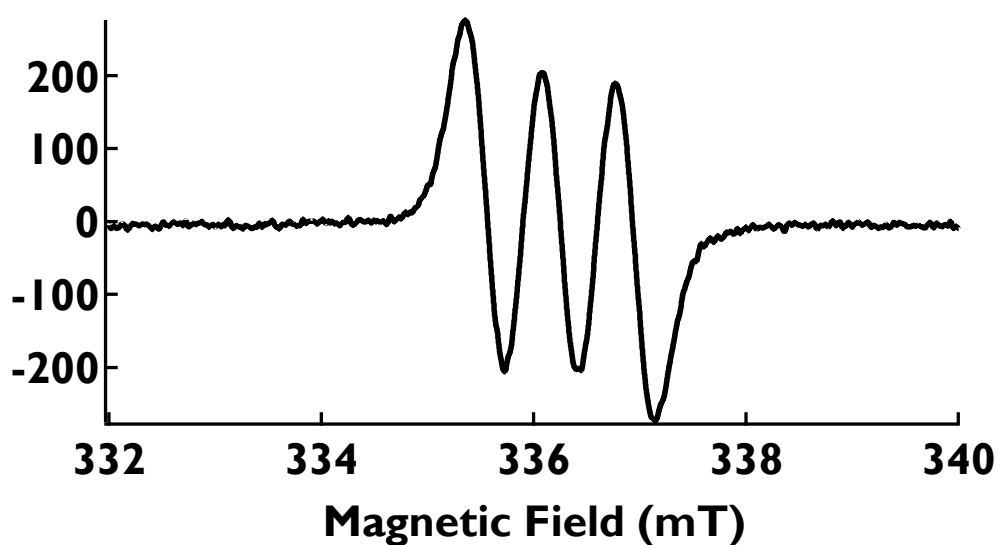


Figure S28. ESR spectrum of $5^{+\bullet}$ in CH_2Cl_2

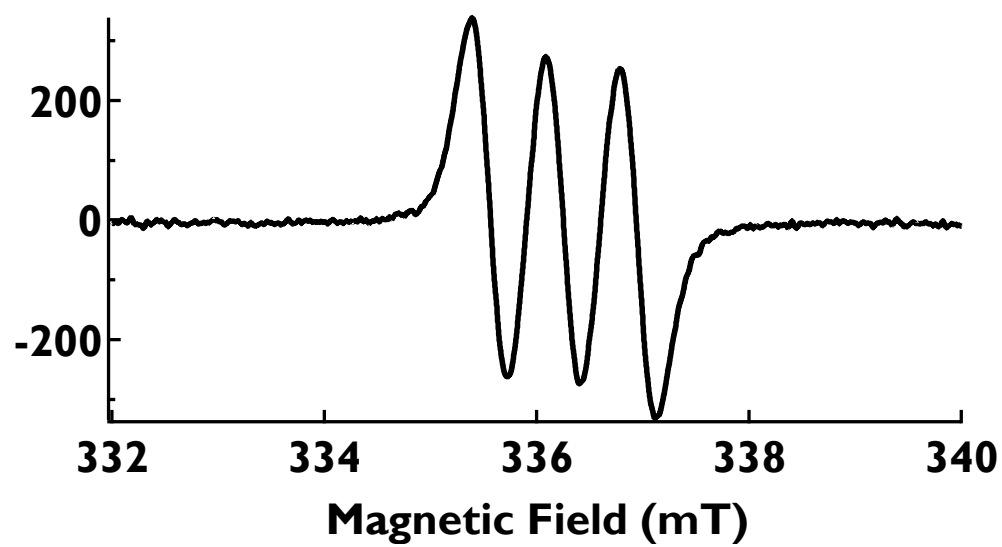


Figure S29. ESR spectrum of $6^{\bullet+}$ in CH_2Cl_2

11. ^1H and ^{13}C NMR spectra

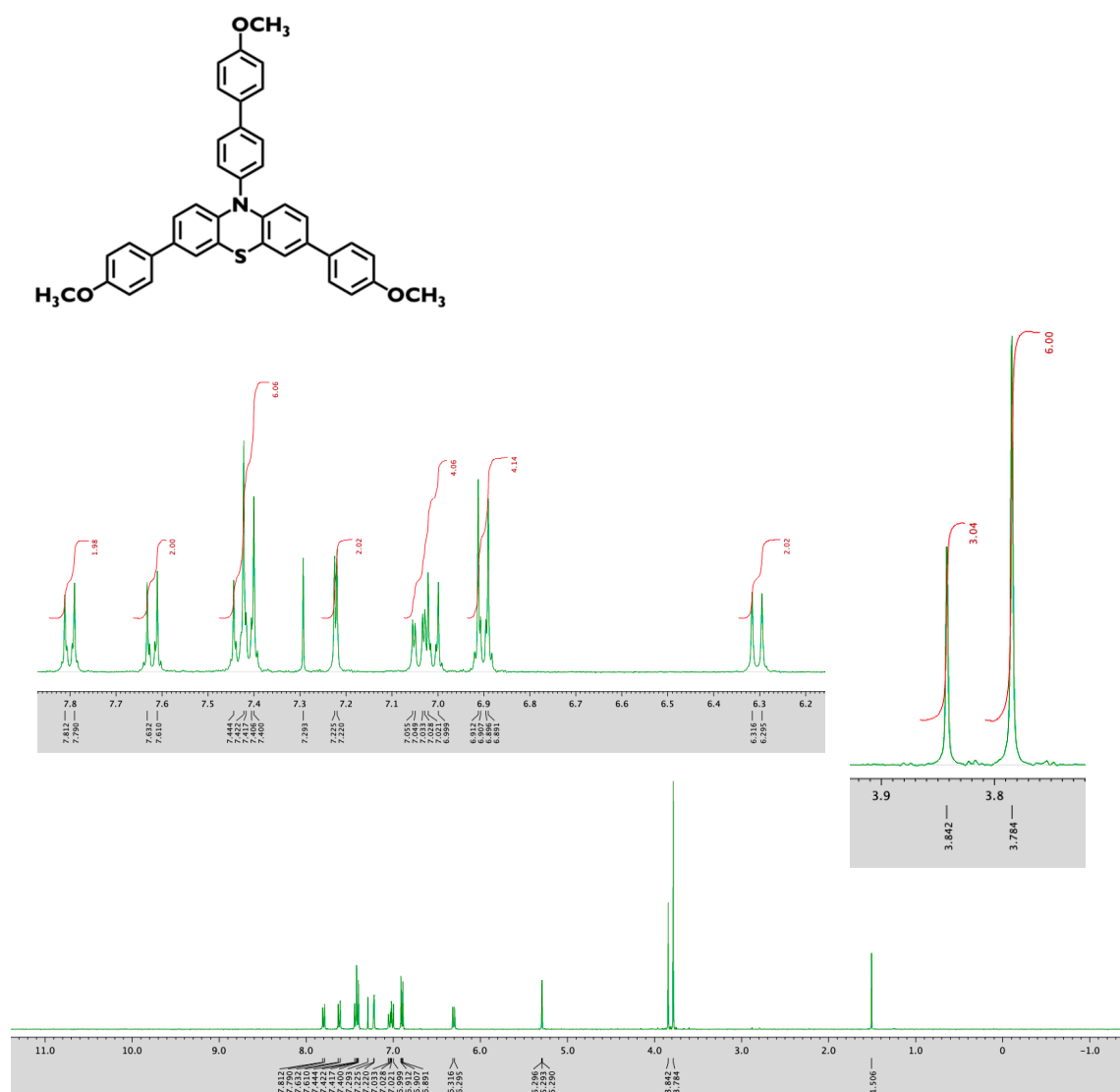
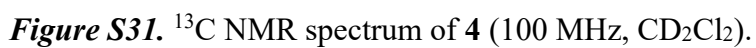


Figure S30. ^1H NMR spectrum of **4** (400 MHz, CD_2Cl_2).



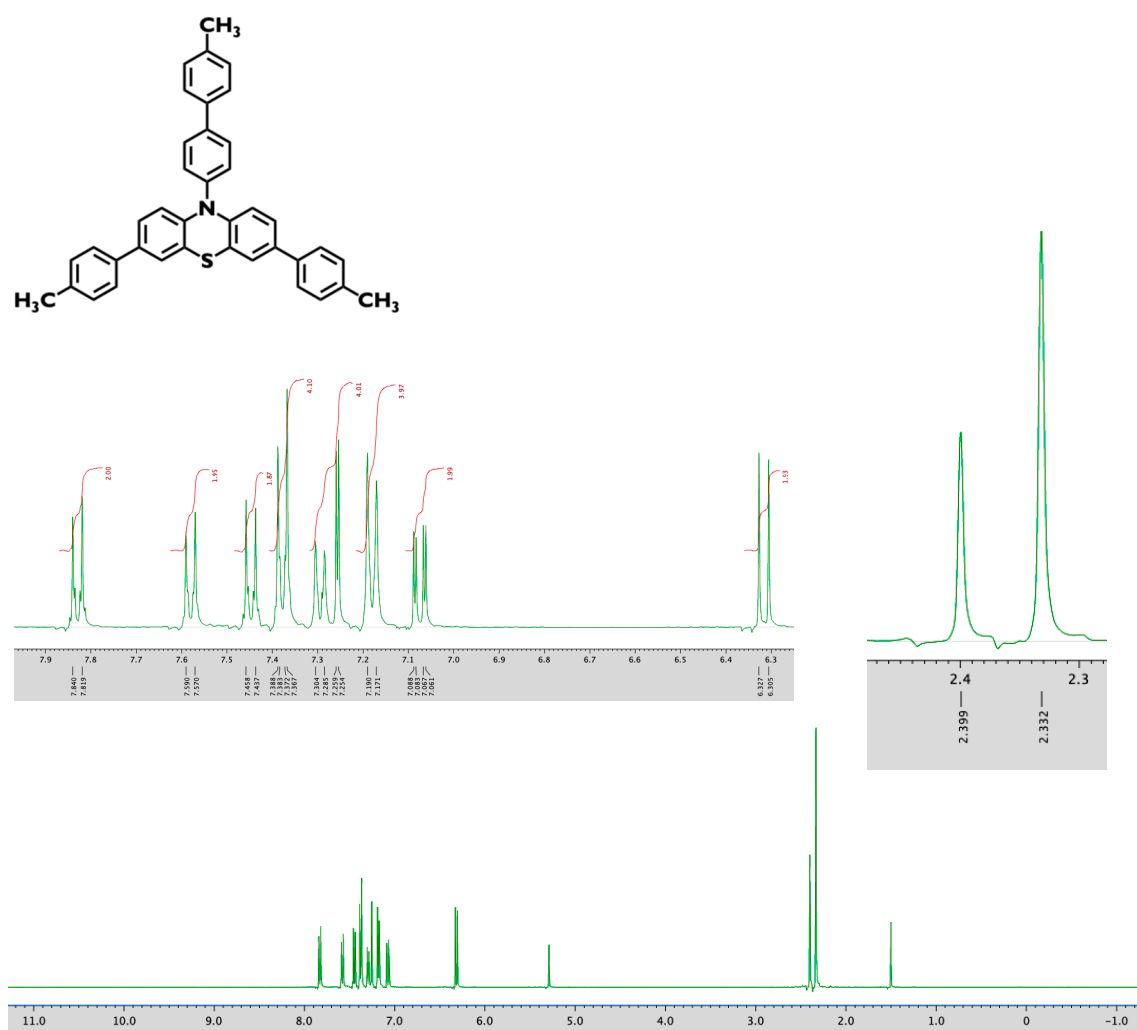


Figure S32. ^1H NMR spectrum of **5** (400 MHz, CD_2Cl_2).

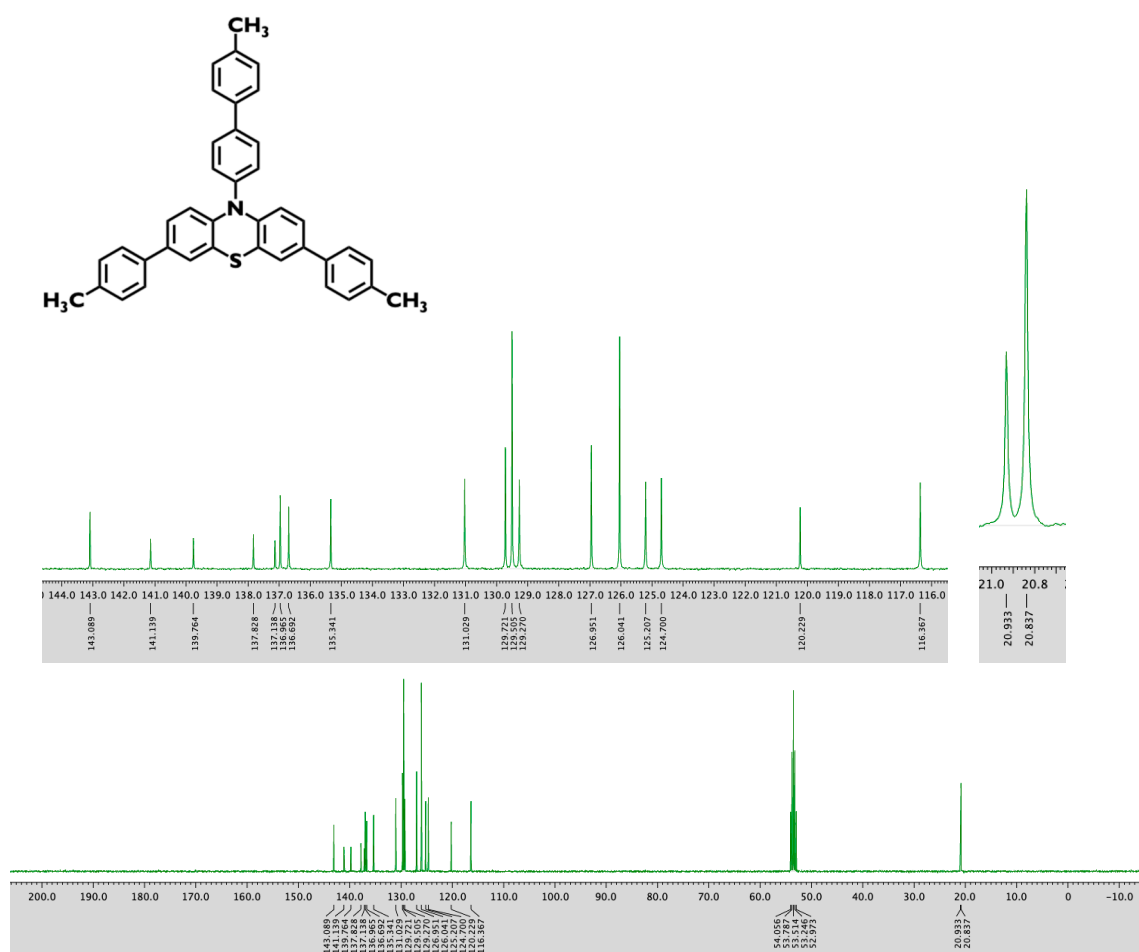


Figure S33. ^{13}C NMR spectrum of **5** (400 MHz, CD_2Cl_2).

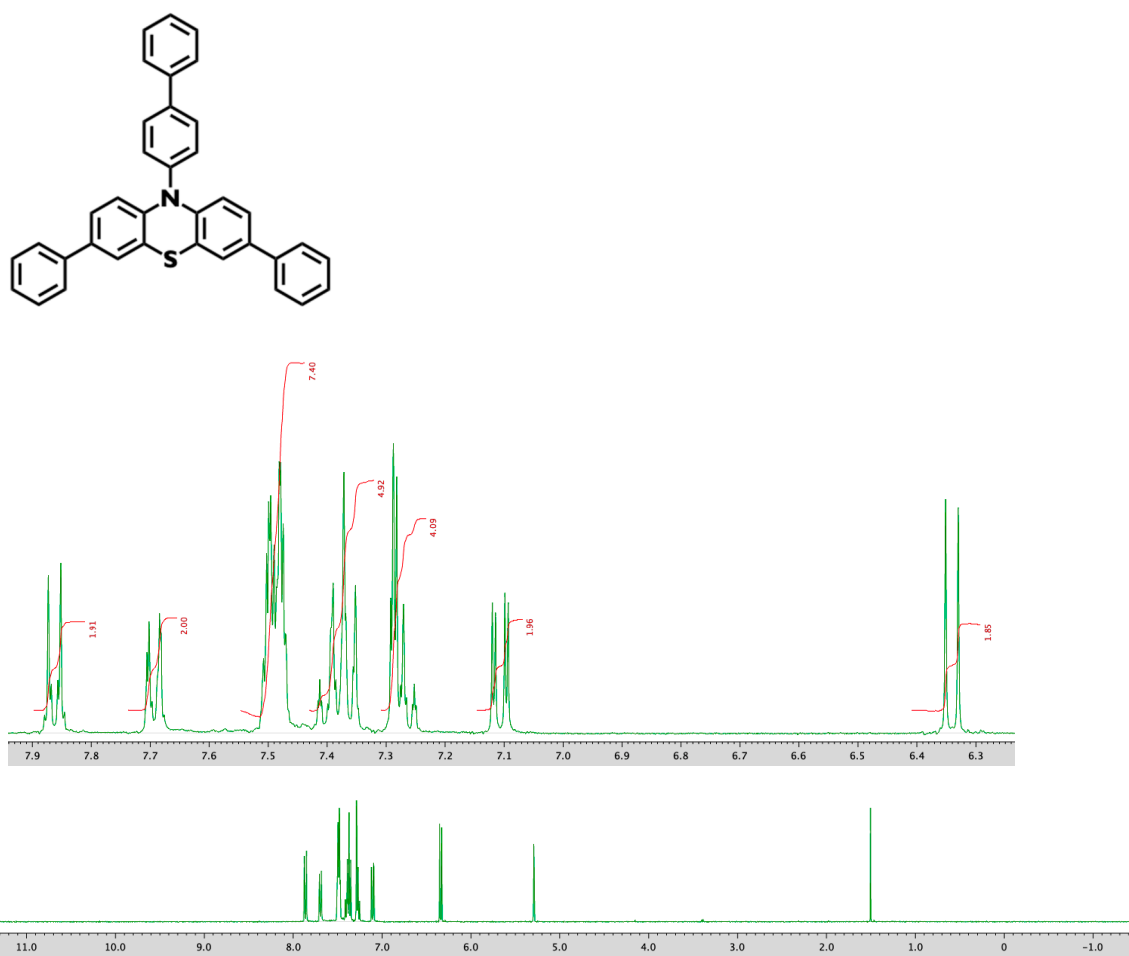


Figure S34. ^1H NMR spectrum of **6** (400 MHz, CD_2Cl_2).

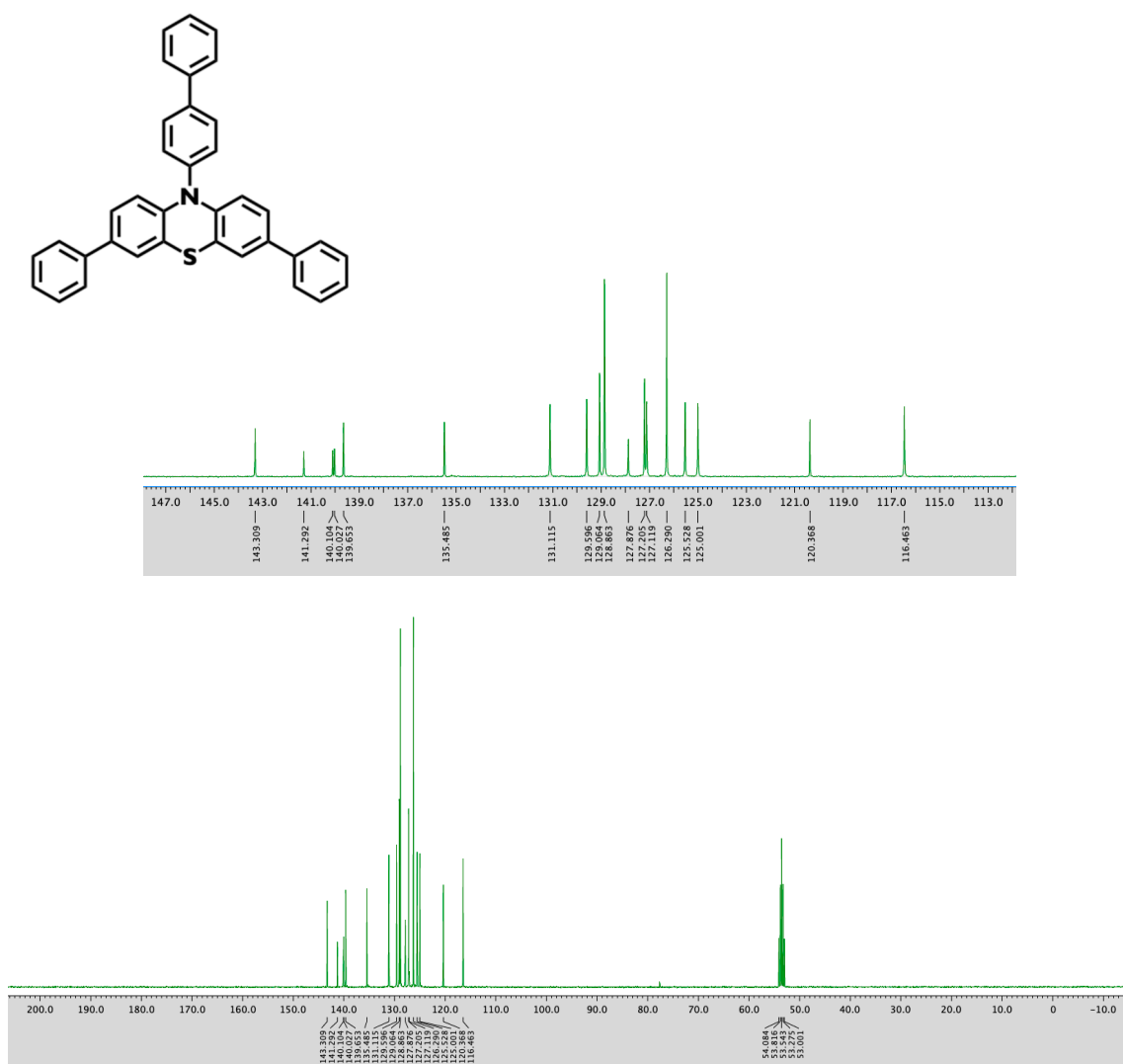


Figure S35. ¹³C NMR spectrum of **6** (400 MHz, CD₂Cl₂).

12. References

1. Li M, Li T, Gong C, Ding D, Du J, Zhou X, Song Y, Yang YF, She Y, Jia J. *J Mater Chem C*. 2023; 11: 13897–13904.