

SUPPLEMENTARY INFORMATION

For

Effective Tuning of the Electronic and Photophysical Properties of Tetrathiafulvalene Pyrroles via Aromatic Heterocycle Annulation

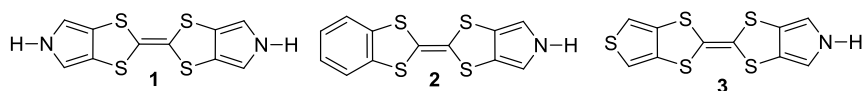
Jung Su Park^{*a}, Jihae Kim^a, Yong-Hoon Kim,^b and Jonathan L. Sessler^{*c}

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1. Synthesis and Characterization:

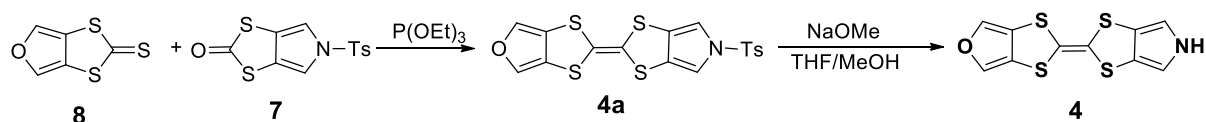
1. Synthesis of Annulated TTF-pyrroles

Compounds **1**,^[1] **2**,^[2] **3**^[3] were prepared according to literature procedures.



Synthesis of **4**:

The synthetic precursors **7**^[1] and **8**^[4] were prepared according to literature procedures.

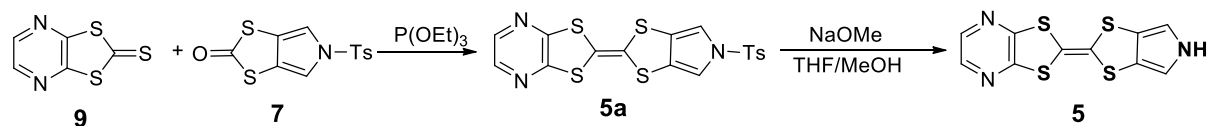


In accord with the scheme given above, a mixture of 5-tosyl-5H-[1,3]dithiolo[4,5-c]pyrrol-2-one (1.20 g, 3.85 mmol) and [1,3]dithiolo[4,5-c]furan-2-thione (1.00 g, 5.78 mmol) in neat triethylphosphite (50 ml) was stirred for 6 hours at 140 °C and then cooled to room temperature. Addition of 100 ml of MeOH into the reaction mixture led to precipitation of a yellow solid (**4a**), which was then collected by filtration. To a solution of **4a** in a mixture of methanol (100 ml) and THF (100 ml) were added 10 equivalents of sodium methoxide (30% in MeOH). The mixture was then heated to 50 °C for 30 min and concentrated under reduced pressure until the volume was 50 ml. The reaction mixture was poured into 200 ml of an aqueous solution of NH₄Cl. The yellow precipitate that resulted was collected by filtration and washed with water. The yellow solid obtained in this way was purified by column chromatography (silica gel, CH₂Cl₂ / hexanes = 2:1, eluent) to give **4** in the form of a yellow solid (0.21 g, 0.19 mmol, 19%).

4: ESI-MS: *m/z* calcd for C₁₀H₅NOS₄: 282.9254; found: 282.9254; ¹H NMR (400MHz, (CD₃)₂SO, 25°C, TMS) δ[ppm]: 11.15 (s, br, 1H), 7.66 (s, 2H), 6.81 (d, 2H, 2.8Hz), ¹³C NMR (400MHz, (CD₃)₂SO, 25°C, TMS) δ[ppm]: 111.11, 116.93, 117.07, 124.50, 124.48, 134.35

Synthesis of **5**:

The synthetic precursor **9**^[5] was prepared according to a literature procedure.

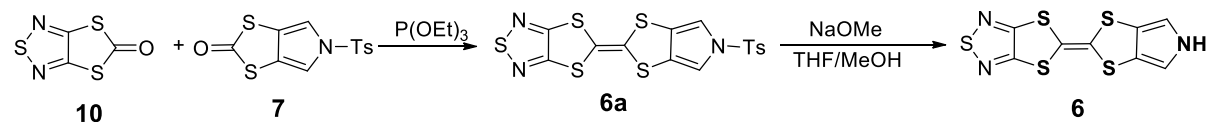


In accord with the scheme given above, a mixture of 5-tosyl-5H-[1,3]dithiolo[4,5-c]pyrrol-2-one (1.20 g, 3.85 mmol) and [1,3]dithiolo[4,5-b]pyrazine-2-thione (1.08 g, 5.78 mmol) in neat triethylphosphite (50 ml) was stirred for 6 hours at 140 °C and then cooled to room temperature. Addition of 100 ml of MeOH into the reaction mixture led to precipitation of an orange solid (**5a**), which was collected by filtration. To a solution of **5a** in a mixture of methanol (100 ml) and THF (100 ml) were added 10 equivalents of sodium methoxide (30% in MeOH). The mixture was then heated to 50 °C for 30 min and concentrated under reduced pressure until the volume was 50 ml. The reaction mixture was poured into 200 ml of an aqueous solution of NH₄Cl. The orange precipitate that resulted was collected by filtration and washed with water. The yellow solid obtained in this way was purified by column chromatography (silica gel, CH₂Cl₂ eluent) to give **5** in the form of an orange solid (0.30 g, 0.26 mmol, 26%).

5: ESI-MS: *m/z* calcd for C₁₀H₅N₃S₄: 294.9366; found: 294.9366; ¹H NMR (400MHz, (CD₃)₂SO, 25°C, TMS) δ[ppm]: 11.22 (s, br, 1H), 8.25 (s, 2H), 6.87 (d, 2H, 2.8Hz), ¹³C NMR (400MHz, (CD₃)₂SO, 25°C, TMS) δ[ppm]: 98.70, 111.13, 116.44, 126.18, 140.32, 156.18.

Synthesis of **6**:

The synthetic precursor **10**^[6] was prepared according to a literature procedure.



In accord with the scheme given above, a mixture of 5-tosyl-5H-[1,3]dithiolo[4,5-c]pyrrol-2-one (2 g, 6.42 mmol) and [1,3]dithiolo[4,5-c][1,2,5]thiadiazol-5-one (1.68 g, 9.63 mmol) in neat triethylphosphite (60 ml) was stirred for 6 hours at 140 °C and then cooled to room temperature. Addition of 100 ml of MeOH into the reaction mixture led to precipitation of a yellow solid (**6a**), which was collected by filtration. To a solution of **6a** in a mixture of methanol (120 ml) and THF (120 ml) were added 10 equivalents of sodium methoxide (30% in MeOH). The mixture was then heated to 50 °C for 30 min and concentrated under reduced pressure until the volume was 50 ml. The reaction mixture was poured into 200 ml of an aqueous solution of NH₄Cl. The orange precipitate that resulted was collected by filtration and washed with water. The yellow solid obtained in this way was purified by column chromatography (silica gel, CH₂Cl₂ eluent) to give **6** in the form of a yellow solid (0.12 g, 0.061 mmol, 6.2%).

6: ESI-MS: m/z calcd for $C_8H_3N_3S_5$: 300.8931; found: 300.8931; 1H NMR (400MHz, $(CD_3)_2SO$, 25°C, TMS) δ [ppm]: 11.26 (s, br, 1H), 6.88 (d, 2H, 4Hz), 6.87 (d, 2H, 2.8Hz), ^{13}C NMR (400MHz, $(CD_3)_2SO$, 25°C, TMS) δ [ppm] : 104.65, 114.54, 116.28, 129.96, 158.69.

2. Spectral Characterization:

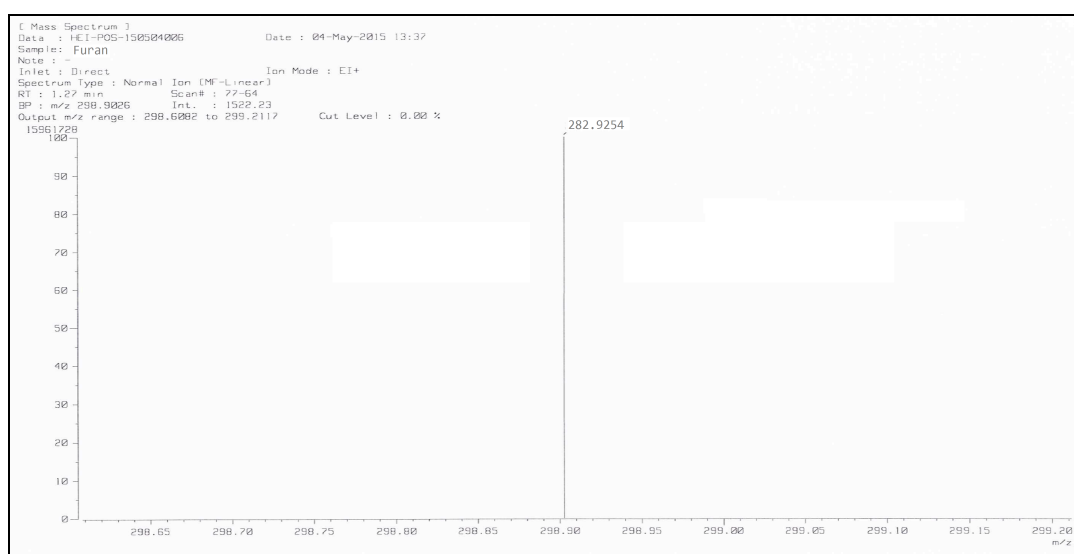


Figure S1. HR-mass spectrum of 4.

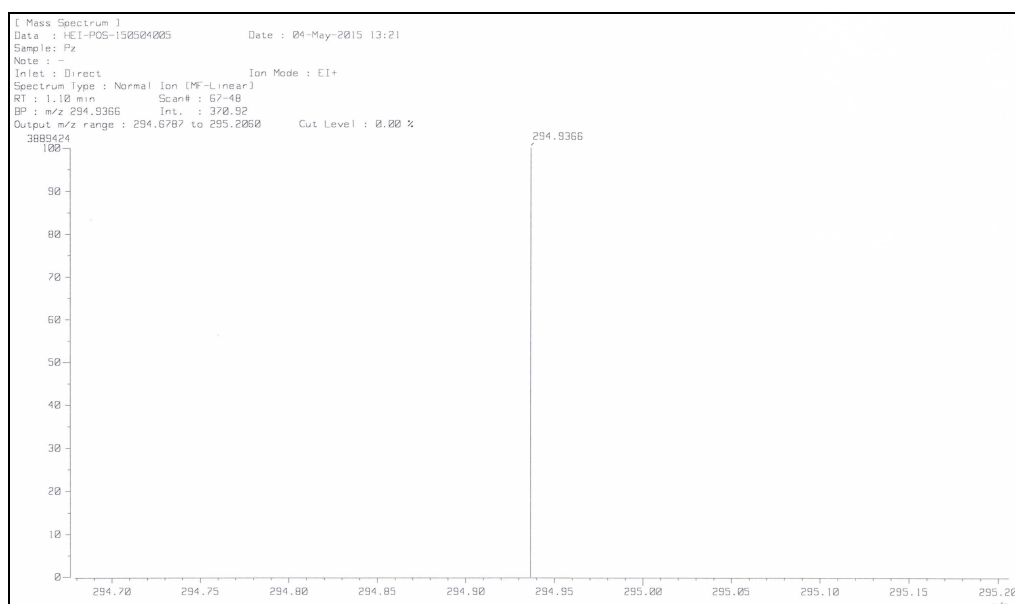


Figure S2. HR-mass spectrum of **5**.

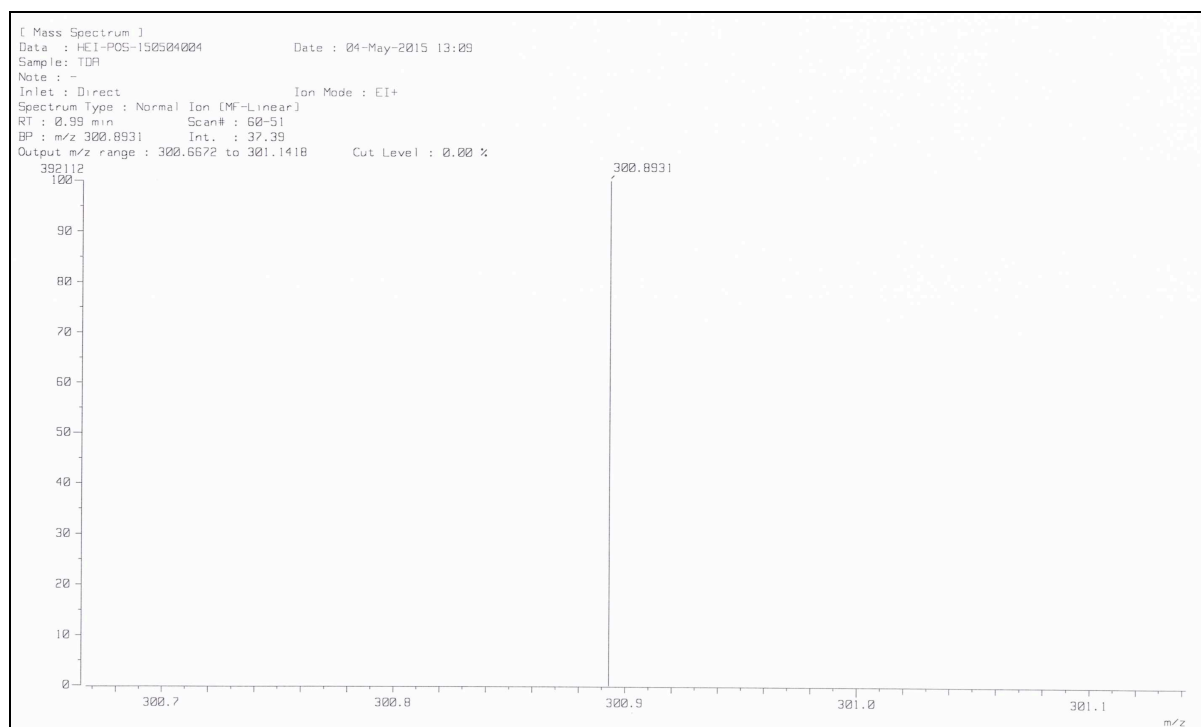


Figure S3. HR-mass spectrum of **6**.

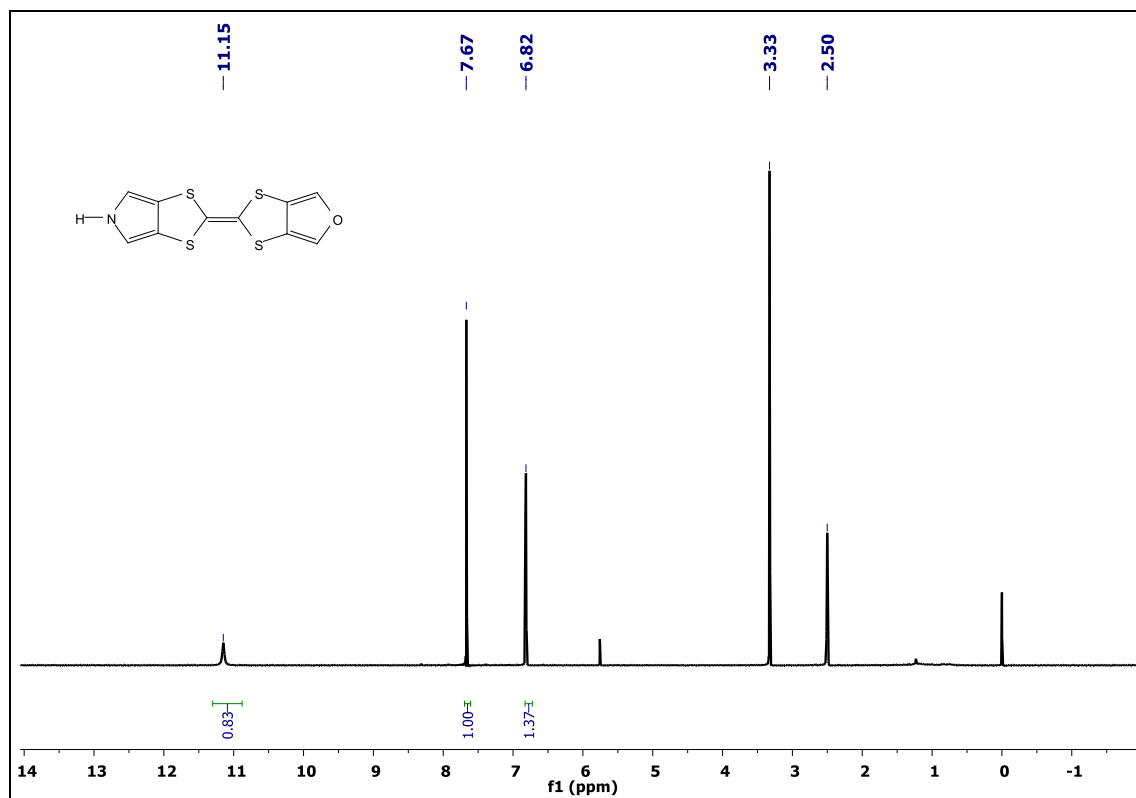


Figure S4. ¹H NMR spectrum of **4** recorded in (CD₃)₂SO at ambient temperature.

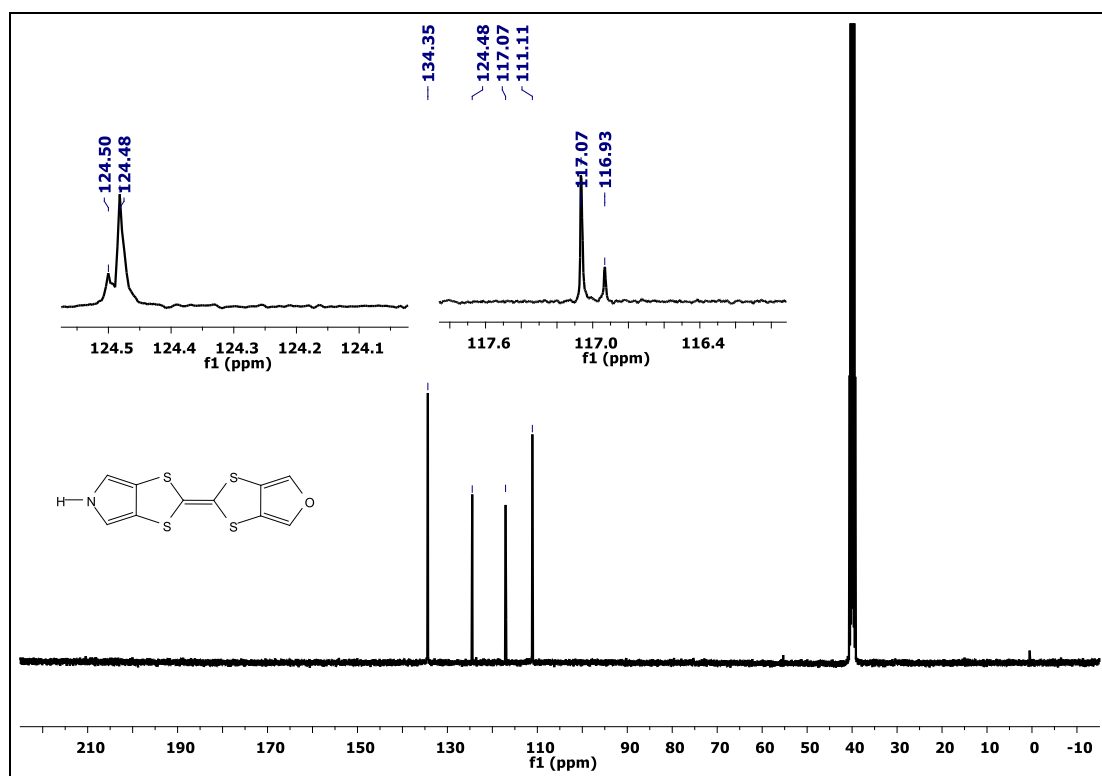


Figure S5. ^{13}C NMR spectrum of **4** recorded in $(\text{CD}_3)_2\text{SO}$ at ambient temperature.

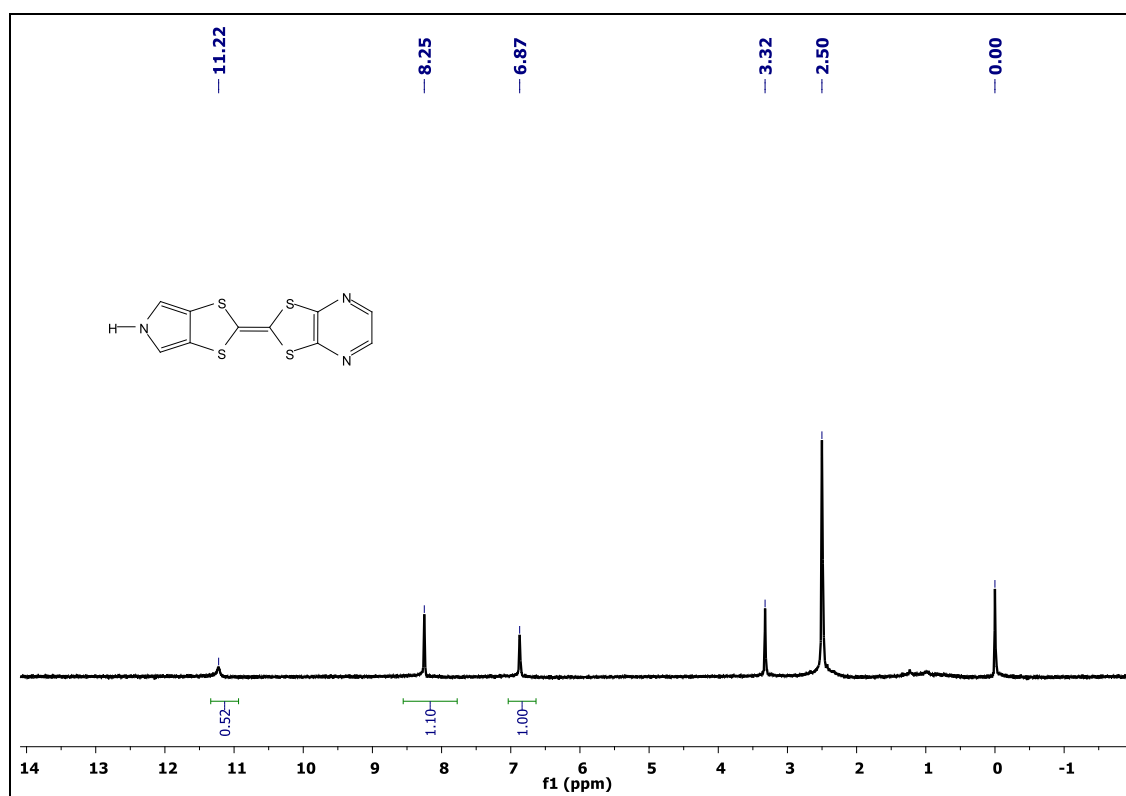


Figure S6. ^1H NMR spectrum of **5** recorded in $(\text{CD}_3)_2\text{SO}$ at ambient temperature.

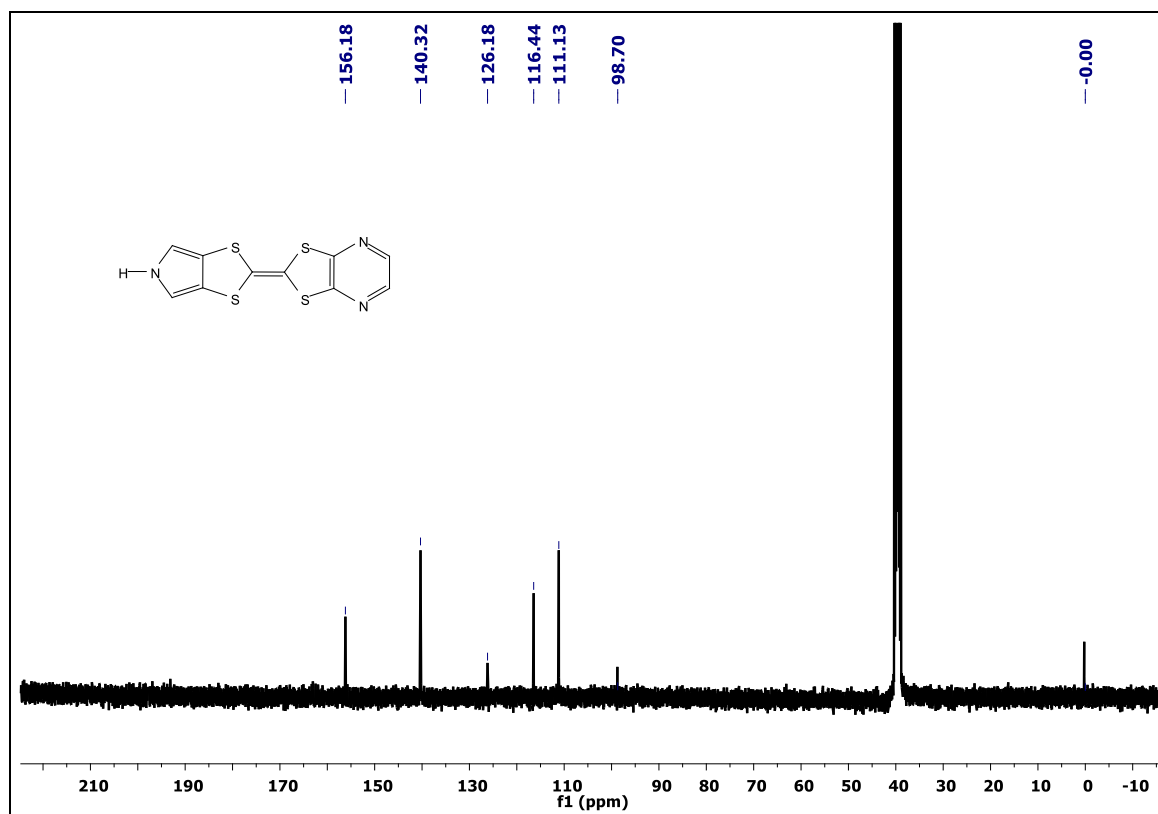


Figure S7. ^{13}C NMR spectrum of **5** recorded in $(\text{CD}_3)_2\text{SO}$ at ambient temperature.

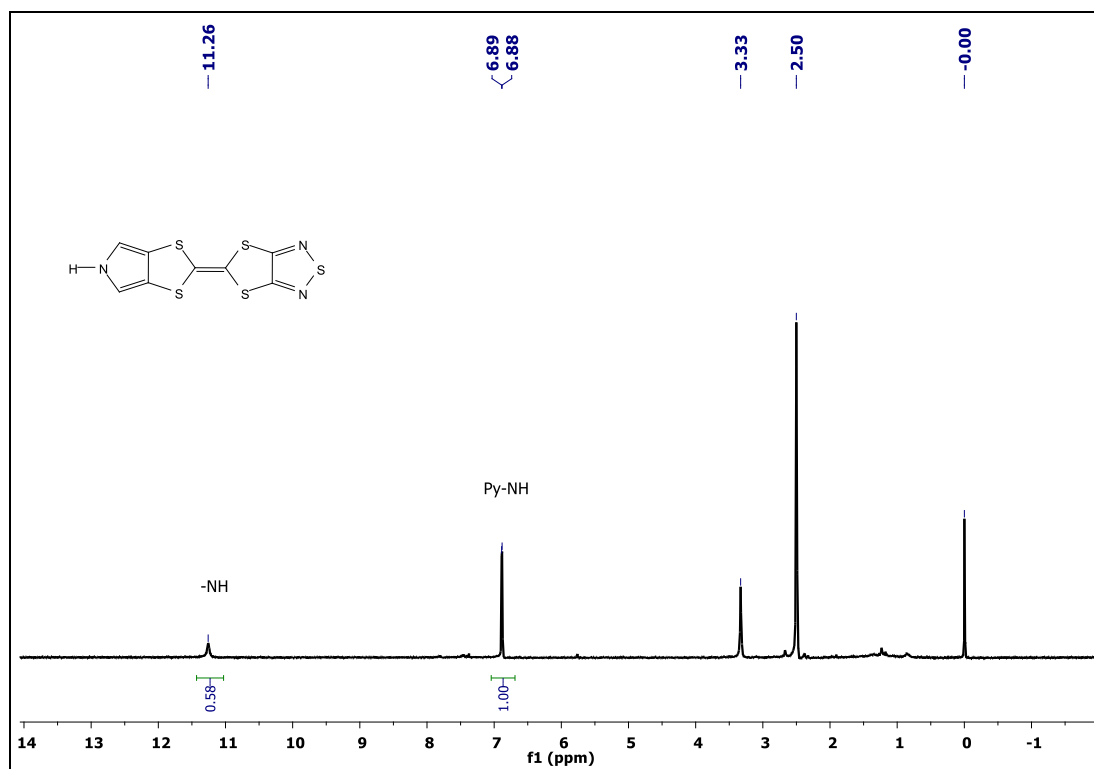


Figure S8. ^1H NMR Spectrum of **6** recorded in $(\text{CD}_3)_2\text{SO}$ at ambient temperature.

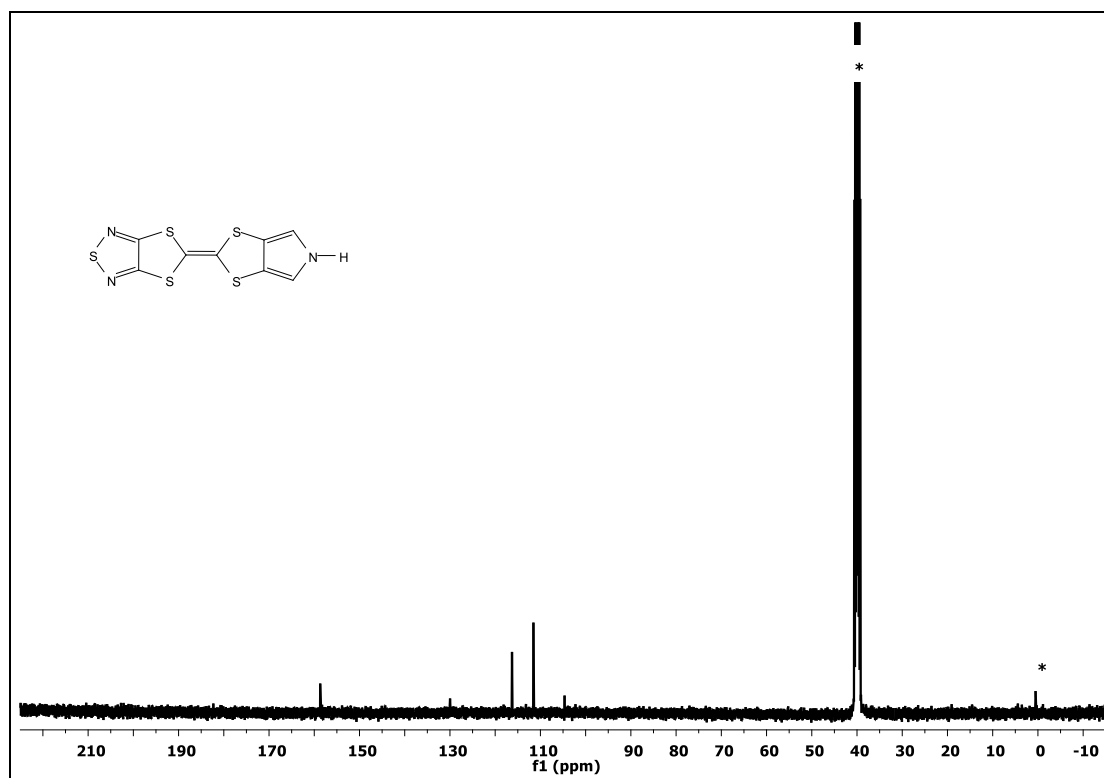


Figure S9. ^{13}C NMR Spectrum of **6** recorded in $(\text{CD}_3)_2\text{SO}$ at ambient temperature.

Table S1. Pyrrole-NH peak chemical shift for compounds **1-6** as seen in the corresponding ^1H NMR spectra recorded in $(\text{CD}_3)_2\text{SO}$ at ambient temperature

Compound	NH peak in ^1H NMR (ppm)
1	11.09
2	11.14
3	11.14
4	11.15
5	11.22
6	11.26

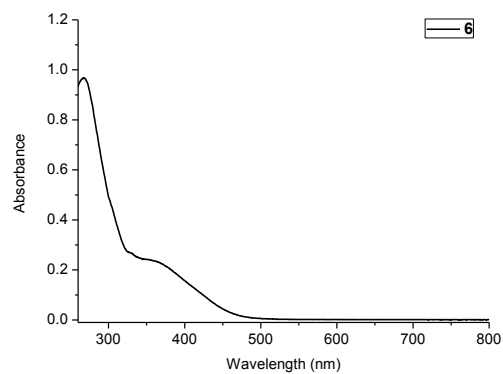
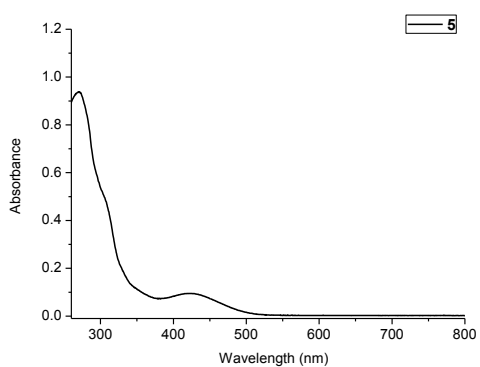
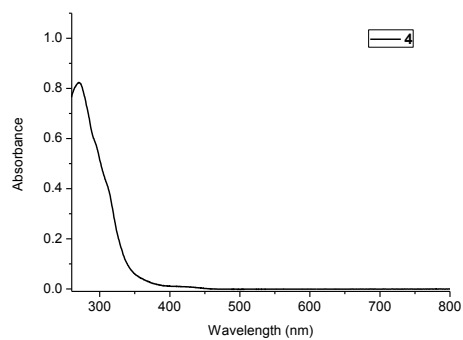
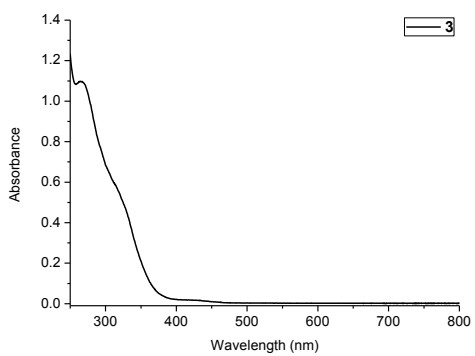
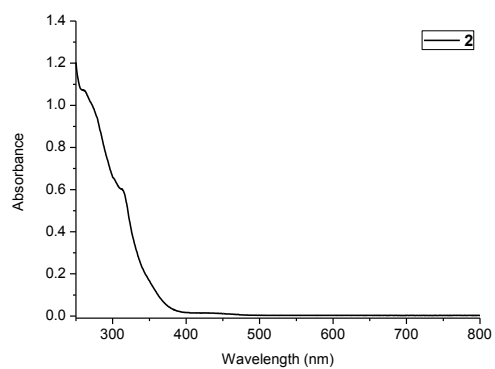
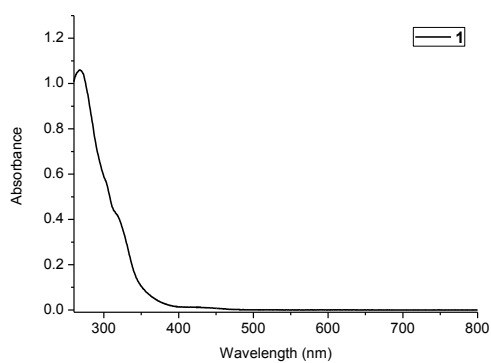


Figure S10. Electronic absorption spectra of 25 μ M solutions of compounds **1-6** in CH_2Cl_2 .

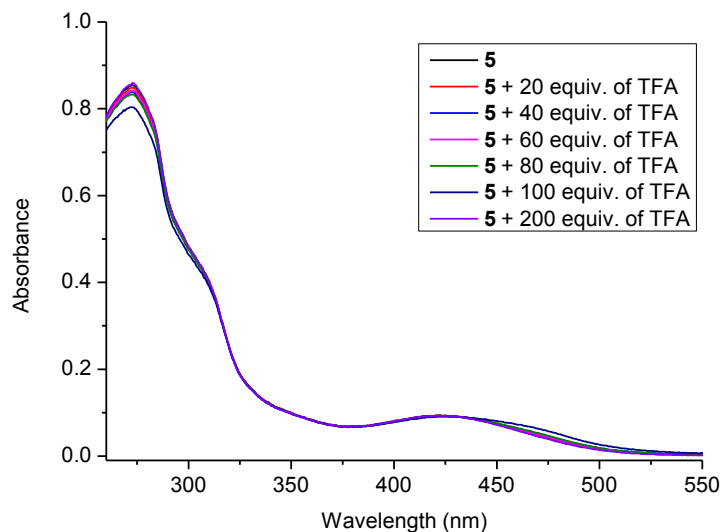


Figure S11. Electronic absorption spectral changes of **5** (25 μM) seen upon the progressive addition of TFA to an initial CH_2Cl_2 solution.

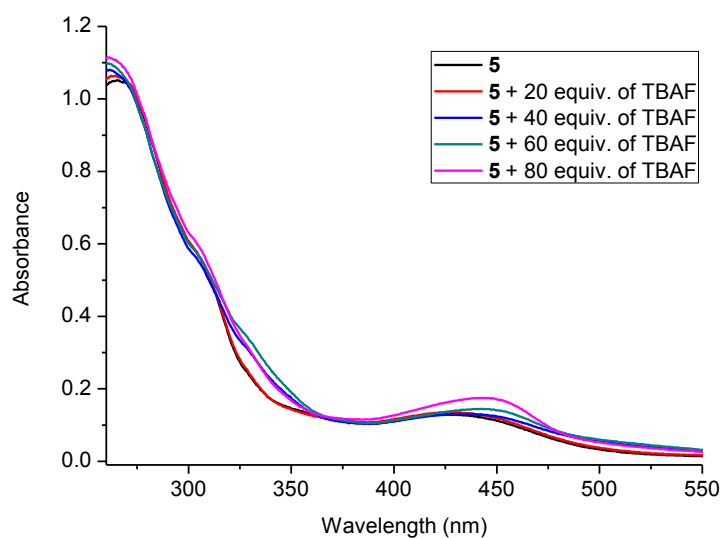


Figure S12. Electronic absorption spectral changes of **5** (25 μM) seen upon the progressive addition of TBAF to an initial CH_2Cl_2 solution.

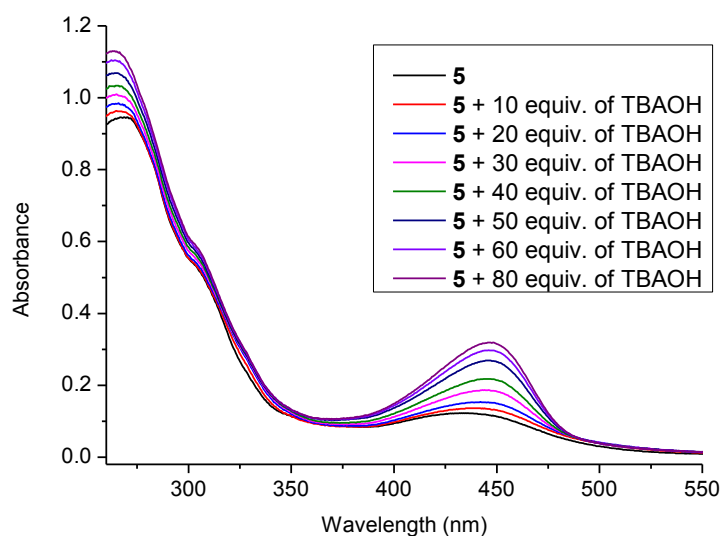


Figure S13. Electronic absorption spectral changes of **5** (25 μM) seen upon the progressive addition of TBAOH to an initial CH_2Cl_2 solution.

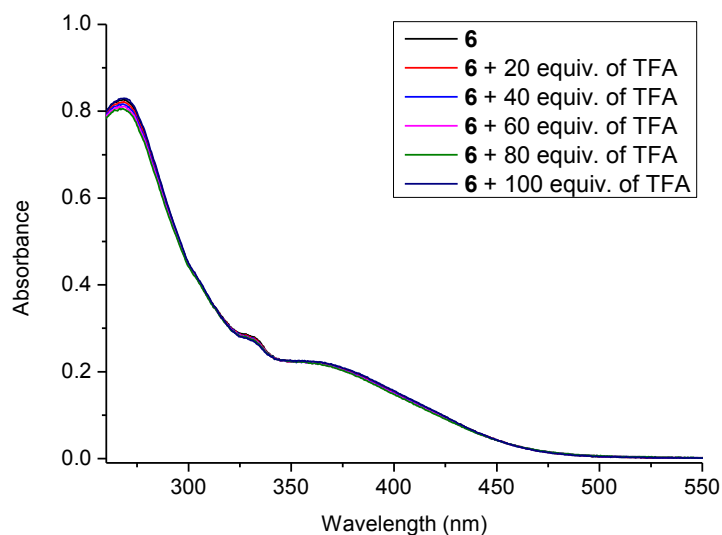


Figure S14. Electronic absorption spectral changes of **6** (25 μM) seen upon the progressive addition of TFA to an initial CH_2Cl_2 solution.

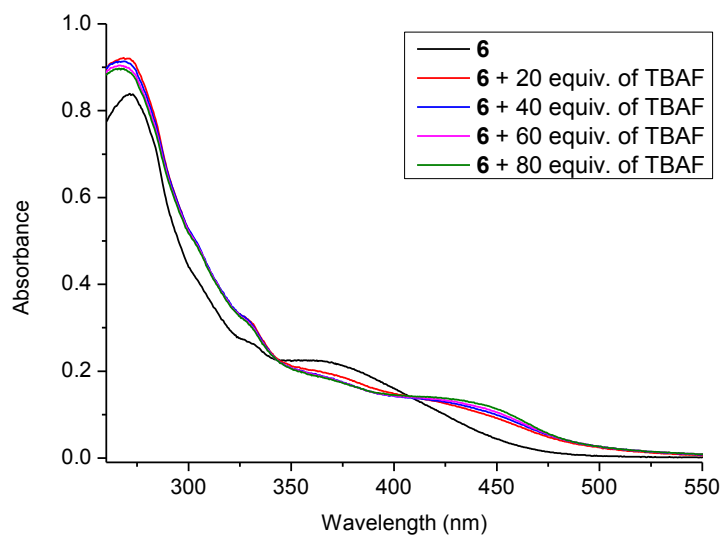


Figure S15. Electronic absorption spectral changes of **6** (25 μM) seen upon the progressive addition of TBAF to an initial CH_2Cl_2 solution.

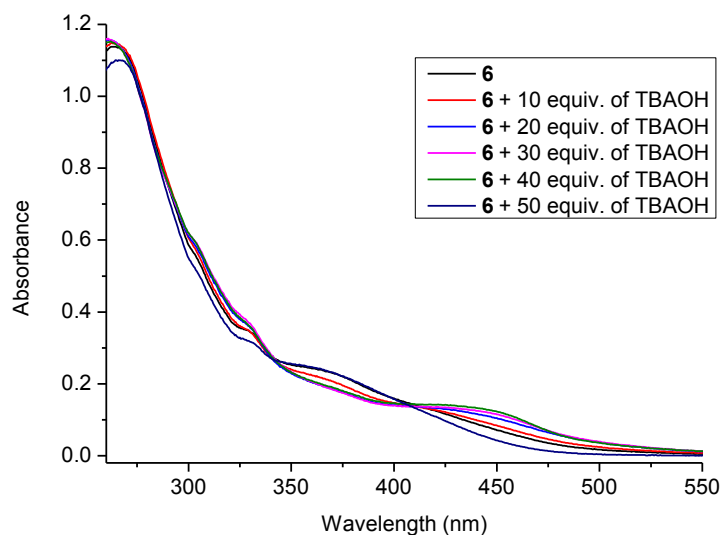


Figure S16. Electronic absorption spectral changes of **6** (25 μM) seen upon the progressive addition of TBAOH to an initial CH_2Cl_2 solution.

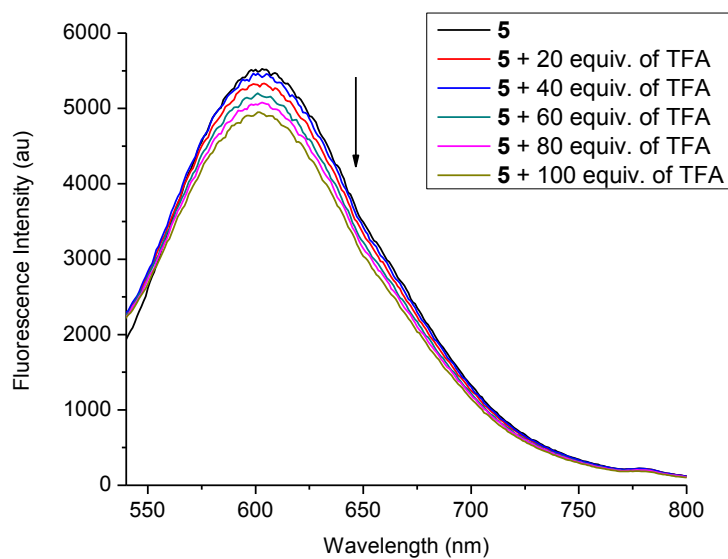


Figure S17. Fluorescence spectral changes of **5** (25 μM) seen upon the progressive addition of trifluoroacetic acid (TFA) to an initial CH₂Cl₂ solution.

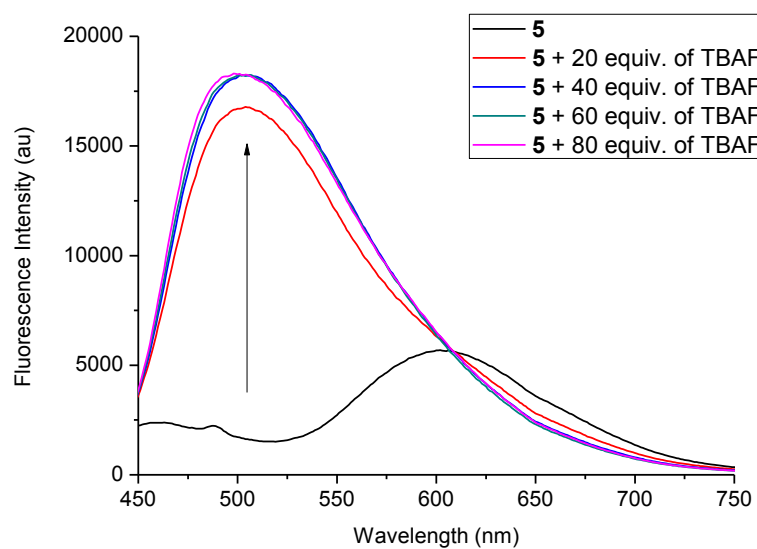


Figure S18. Fluorescence spectral changes of **5** (25 μM) seen upon the progressive addition of tetrabutylammonium fluoride solution (TBAF) to an initial CH₂Cl₂ solution.

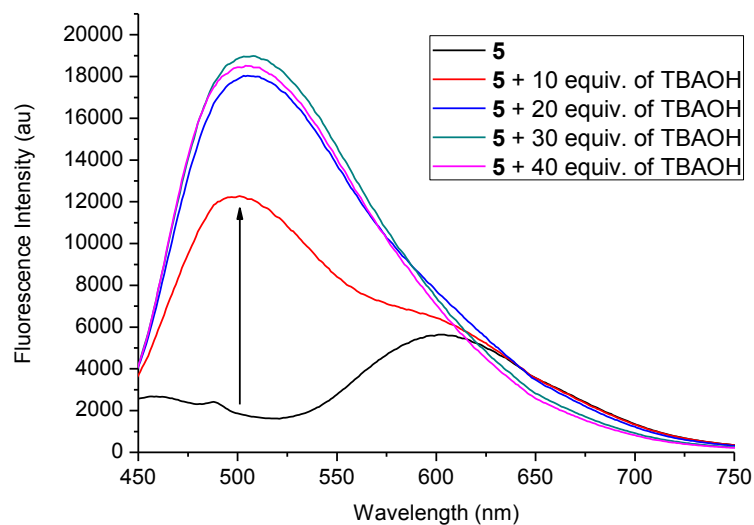


Figure S19. Fluorescence spectral changes observed for **5** (25 μM) upon the progressive addition of tetrabutylammonium hydroxide to an initial CH_2Cl_2 solution.

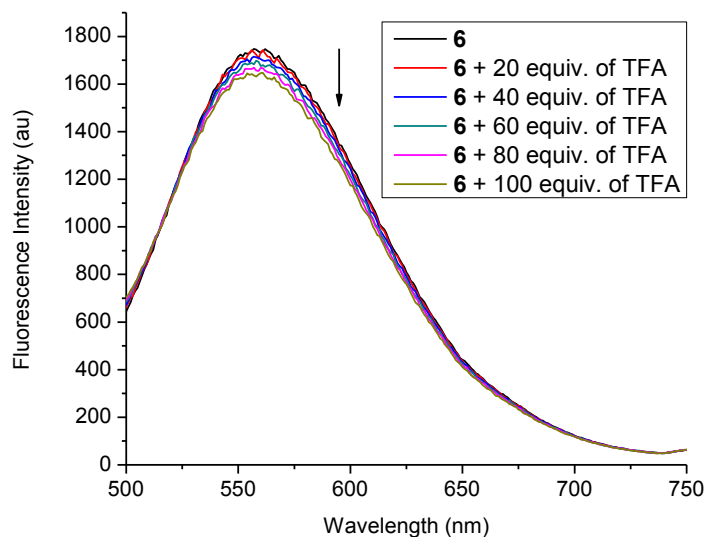


Figure S20. Fluorescence spectral changes observed for **6** (25 μM) upon the progressive addition of TFA to an initial CH_2Cl_2 solution.

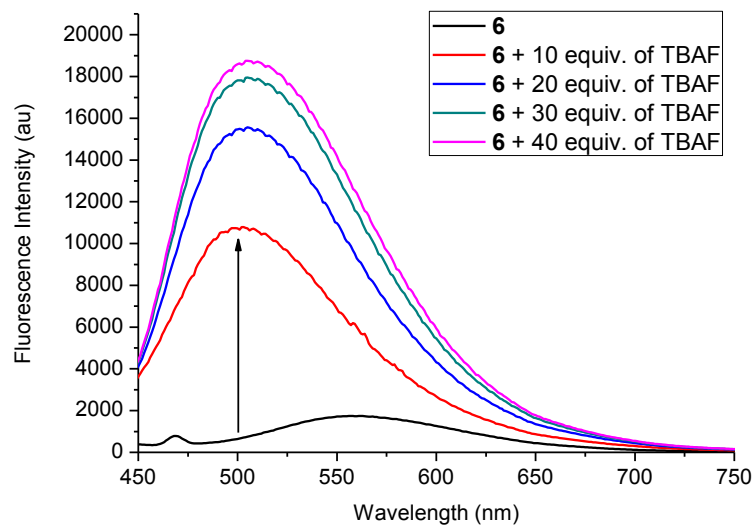


Figure S21. Fluorescence spectral changes of **6** (25 μM) upon the progressive addition of tetrabutylammonium fluoride solution (TBAF) to an initial CH₂Cl₂ solution.

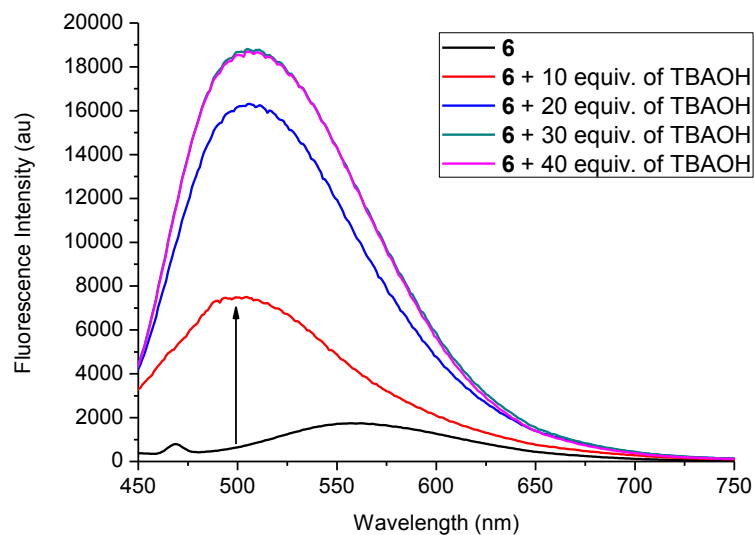


Figure S22. Fluorescence spectral changes of **6** (25 μM) upon the progressive addition of tetrabutylammonium hydroxide solution (TBAOH) to an initial CH₂Cl₂ solution.

4. Electrochemical Studies

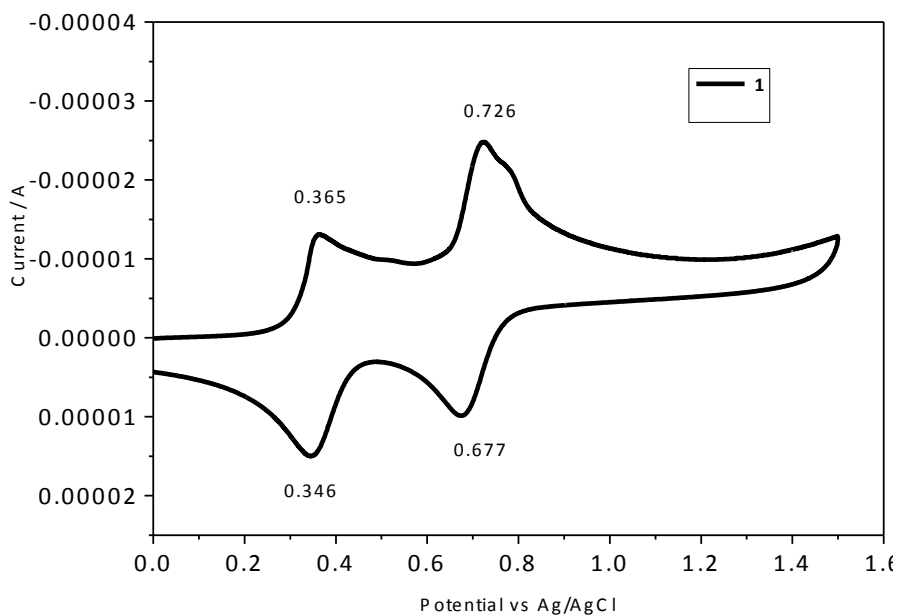


Figure S23. Cyclic voltammogram of **1** in acetonitrile containing 1 M TBAPF₆ at a glassy carbon electrode vs. a Ag/AgCl reference electrode with scan rate of 100 mV/s.

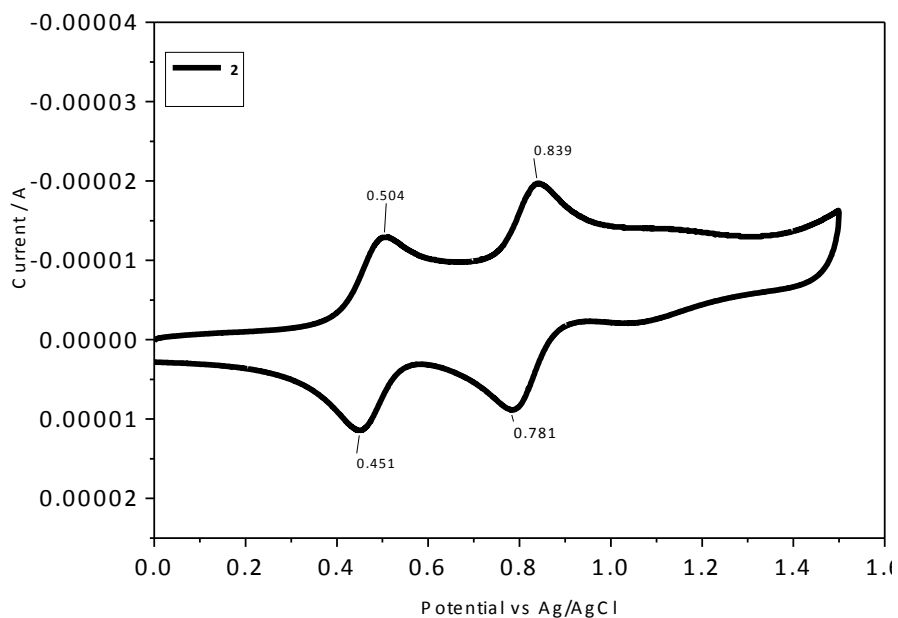


Figure S24. Cyclic voltammogram of **2** in acetonitrile containing 1 M TBAPF₆ at a glassy carbon electrode vs. a Ag/AgCl reference electrode with a scan rate of 100 mV/s.

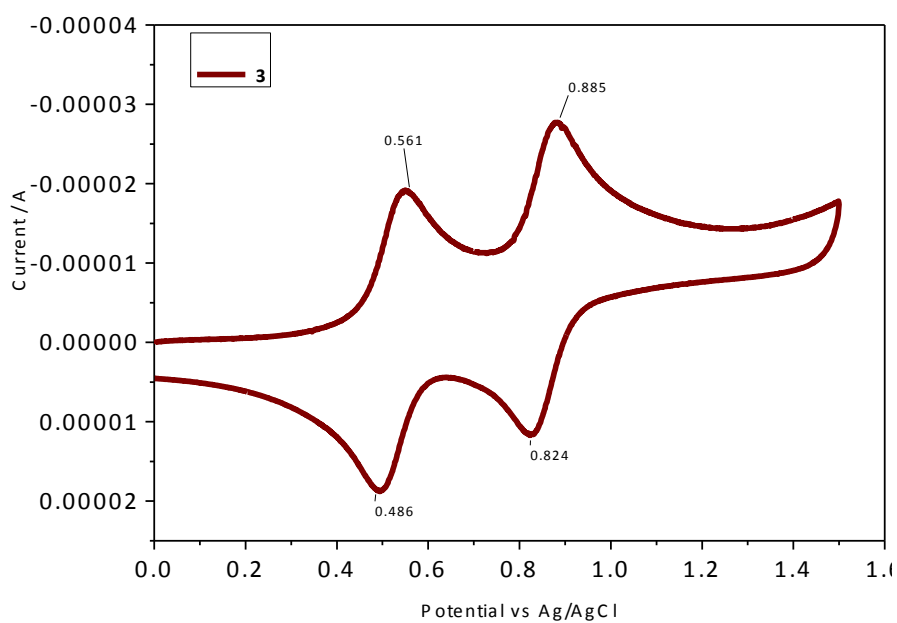


Figure S25. Cyclic voltammogram of **3** in acetonitrile containing 1 M TBAPF₆ at a glassy carbon electrode vs. Ag/AgCl reference electrode with scan rate of 100 mV/s.

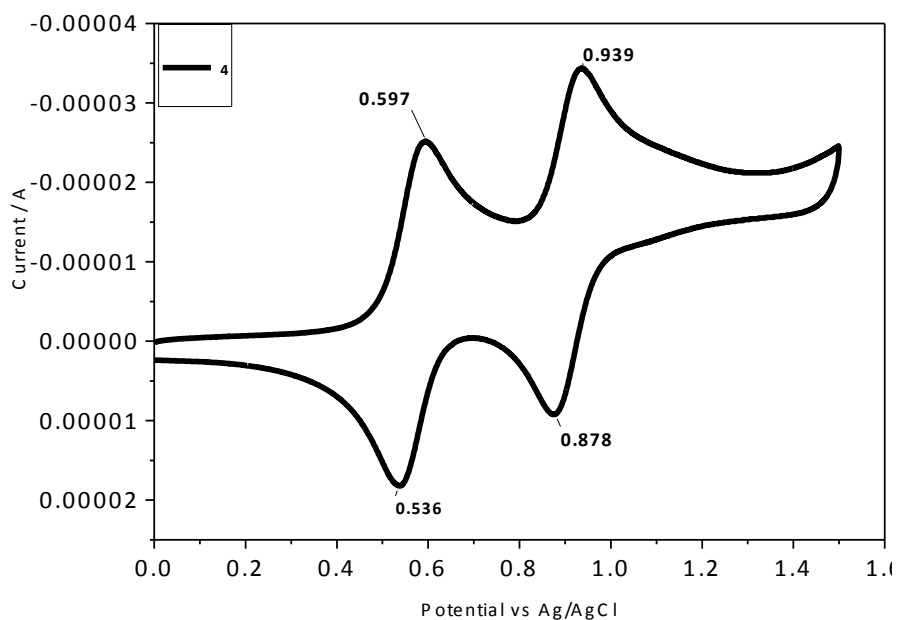


Figure S26. Cyclic voltammogram of **4** in acetonitrile containing 1 M TBAPF₆ at a glassy carbon electrode vs. a Ag/AgCl reference electrode with a scan rate of 100 mV/s.

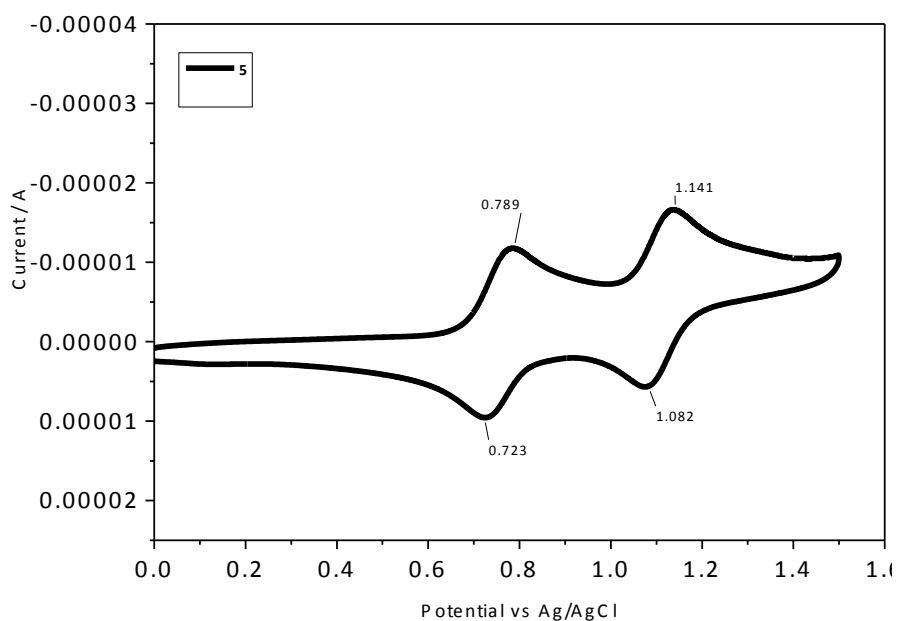


Figure S27. Cyclic voltammogram of **5** in acetonitrile containing 1 M TBAPF₆ at a glassy carbon electrode vs. a Ag/AgCl reference electrode with a scan rate of 100 mV/s.

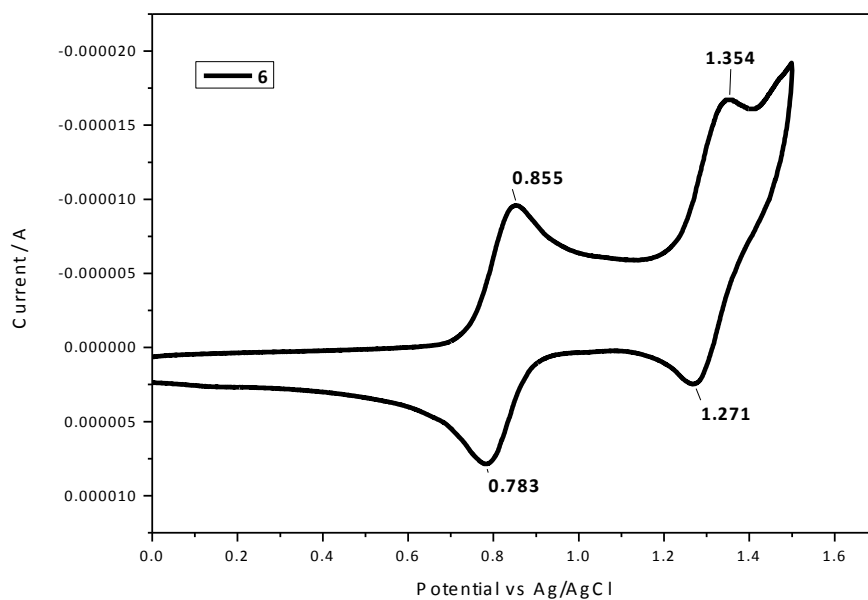


Figure S28. Cyclic voltammogram of **6** in acetonitrile containing 1 M TBAPF₆ with scan rate of 100 mV/s vs. a Ag/AgCl reference electrode with a scan rate of 100 mV/s.

4. Single crystal X-ray data of 5

The X-ray crystallographic data for the structure of **5** were collected on a Nonius Kappa CCD diffractometer using a graphite monochromator with MoK α radiation ($\lambda = 0.71073 \text{ \AA}$). The data were collected at 153 K using an Oxford Cryostream low temperature device. Details of crystal data, data collection and structure refinement are listed in Table S2. Data reduction were performed using DENZO-SMN.^[7] The structure was solved by direct methods and refined by full-matrix least-squares on F^2 with anisotropic displacement parameters for the non-H atoms using SHELXL-97.^[8] The hydrogen atoms were calculated in ideal positions with isotropic displacement parameters set to 1.2xUeq of the attached atom (1.5xUeq for methyl hydrogen atoms). All the calculations were carried out with the SHELXTL program. Further details of the individual structures can be obtained from the Cambridge Crystallographic Data Centre by quoting reference numbers CCDC-1404846.

Table S2. Crystal data and structure refinement for **5**.

Parameter	
Chemical formula	C ₁₀ H ₅ N ₃ S ₄
Formula mass	295.41
Crystal system	Monoclinic
Space group	P 2 ₁ /n
Crystal color	Orange
a (Å)	8.1660(4)
b (Å)	9.3650(5)
c (Å)	15.1600(9)
α (deg)	90
β (deg)	102.045(2)
γ (deg)	90
Volume (Å ³)	1133.83(11)
Z	4
Temperature (K)	153(2)
θ range	2.63 to 27.50 deg
Completeness to θ	99.3 %
Reflections collected / unique	4691 / 2598
R _{int}	0.0693
Absorption correction	Gaussian
Data/restraints/parameters	2598 / 0 / 154
Goodness-of-fit on F^2	1.041
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0638,$ $wR_2 = 0.1086$
R indices (all data)	$R_1 = 0.1265,$ $wR_2 = 0.1257$
CCDC number	CCDC-1404846

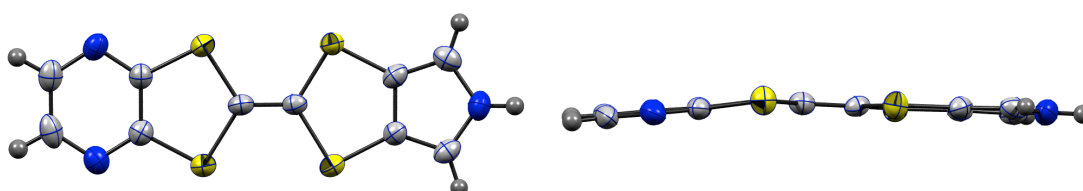


Figure S29. Two views of the X-ray single crystal structure of 5. Displacement ellipsoids are scaled to the 50% probability level.

5. DFT Calculations for 1-6

The geometry-optimized structures and associated energetic calculations were carried out at the B3LYP 6–31G*(d) level of theory using the commercially available Spartan'10 Window program.

6. References for ESI

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- [8] Sheldrick, G. M. SHELXL97. *Program for the Refinement of Crystal Structures*. University of Gottingen, Germany. **1994**.