Supporting Information

Thieno[3,2-*b*]thiophene-based bridged BODIPY dimers: synthesis, electrochemistry, and one- and two-photon photophysical properties

Zhiyong Chai,[a] Tingting Gu,[a] Annaelle Beau,[b,c] Frédéric Bolze,[b] Claude P. Gros,[c] Xu Liang,[d] Donghai Shi[a] and Haijun Xu[a, e]

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1. Experimental section

1.1. General

All chemicals and solvents were of analytical reagent grade and used as received unless otherwise noted. Solvents for reactions were purified and dried according to standard procedures, and then distilled before use. All mixtures of solvents are given in v/v ratio. ^{1}H NMR spectra were collected on Bruker DRX-400 AVANCE III and Bruker DRX-600 AVANCE III spectrometers. Chemical shifts for ^{1}H NMR spectra were recorded in ppm relative to $CDCl_3$ (δ = 7.26 ppm) or DMSO-d_6 (δ= 2.5 ppm) as the internal standard. Mass spectra data were obtained using a Bruker Microflex LRF MALDI-TOF spectrometer.

1.2. Spectroscopic measurements

UV–vis spectra were carried out on a Shimadzu UV-3100 spectrophotometer. All the Spectra and PLQY were measured in FluoroLog-UltraFast (HORIBA Instrument Inc, Edison) equipped with a 450 W CW xenon lamp and an Open-Electrode TECooled CCD Detector (Syn-cerity). Absorption and emission measurements were carried out in 1x1 cm quartz cuvettes with spectroscopic grade solvent, and was kept constant at (298 ± 2) K. An integrating sphere mounted in sample compartment directly for PLQY measure. Nanosecond lifetime and TRES studies were conducted using a TCSPC MCA model equipped with a picosecond photo detector (<200 ps) (PPD850) and picosecond laser (duration is 180 ps, Deltadiode, 100 MHz laser). TRES data were measured by incrementing the monochromator on the emission channel of the time-resolved fluorometer in fixed wavelength intervals at each wavelength. Slices of data were taken in the intensity-wavelength plane to obtain spectra at different times during the decay. Microsecond life-time decays were collected by a MCS mode on TCSPC HUB (DeltaHUB) with a LED source (SpectraLED) as a sample excitation source.

1.3. Two-photon spectroscopy

The two-photon absorption spectra were recorded using the fluorescence induced method as described previously using an Insight SpectraPhysic fs pulsed laser. Rhodamine B (800-900 and 950-1000 nm; Φ = 69%), Fluorescein (900-950 nm; Φ =

95%) and Styryl 9M (950-1000 nm; Φ = 24%) were used as reference at 10^{-4} M as for the sample of interest. Values were collected from 800 nm to 1000 nm with a power varying from 80 to 180 mW with verification of the quadratic power dependency.

1.4. Electrochemistry

Cyclic voltammetry was measured on a CHI–730C Electrochemical Workstation at room temperature. A homemade three-electrode cell with a glassy carbon working electrode, a platinum wire counter elec-trode and a saturated calomel reference electrode (SCE) was used to do the measurement.

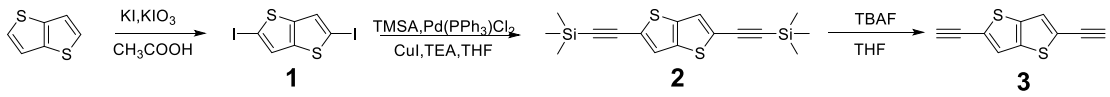


Chart S1. Synthetic procedures to access to compounds **1-3**

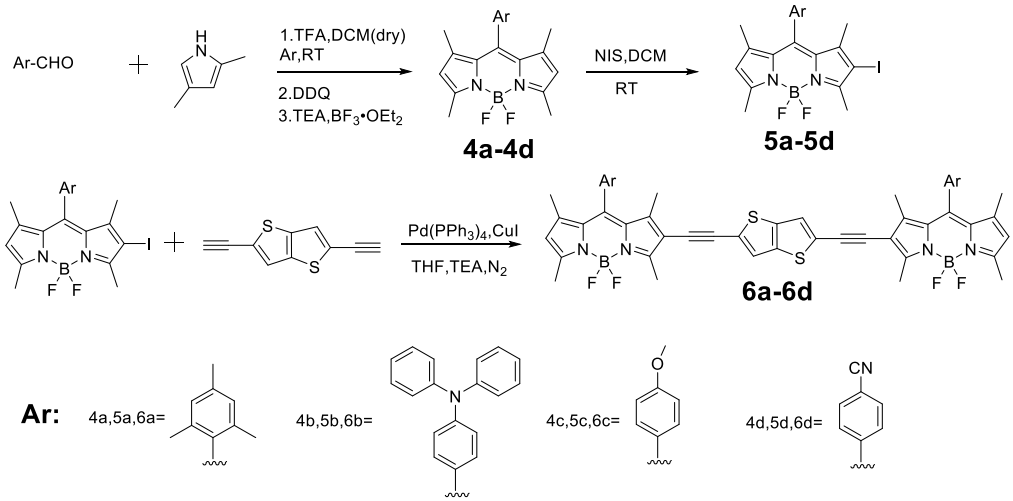
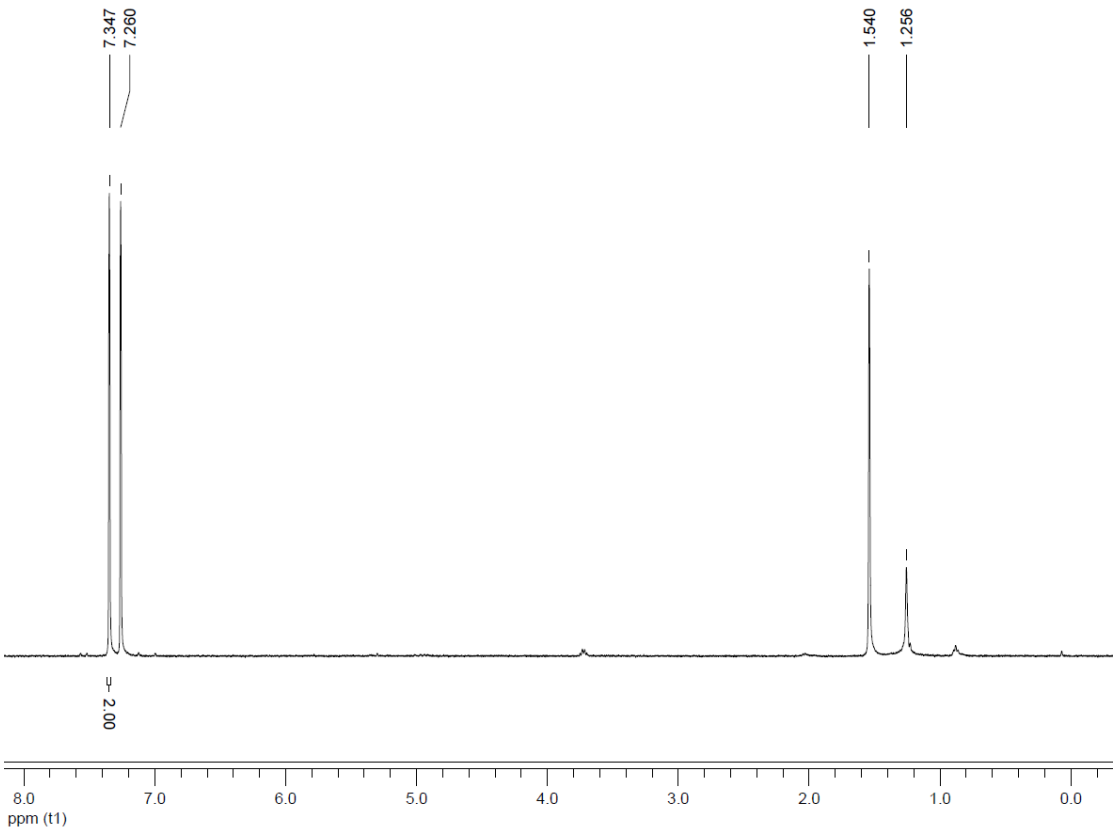
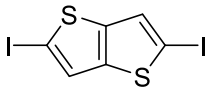


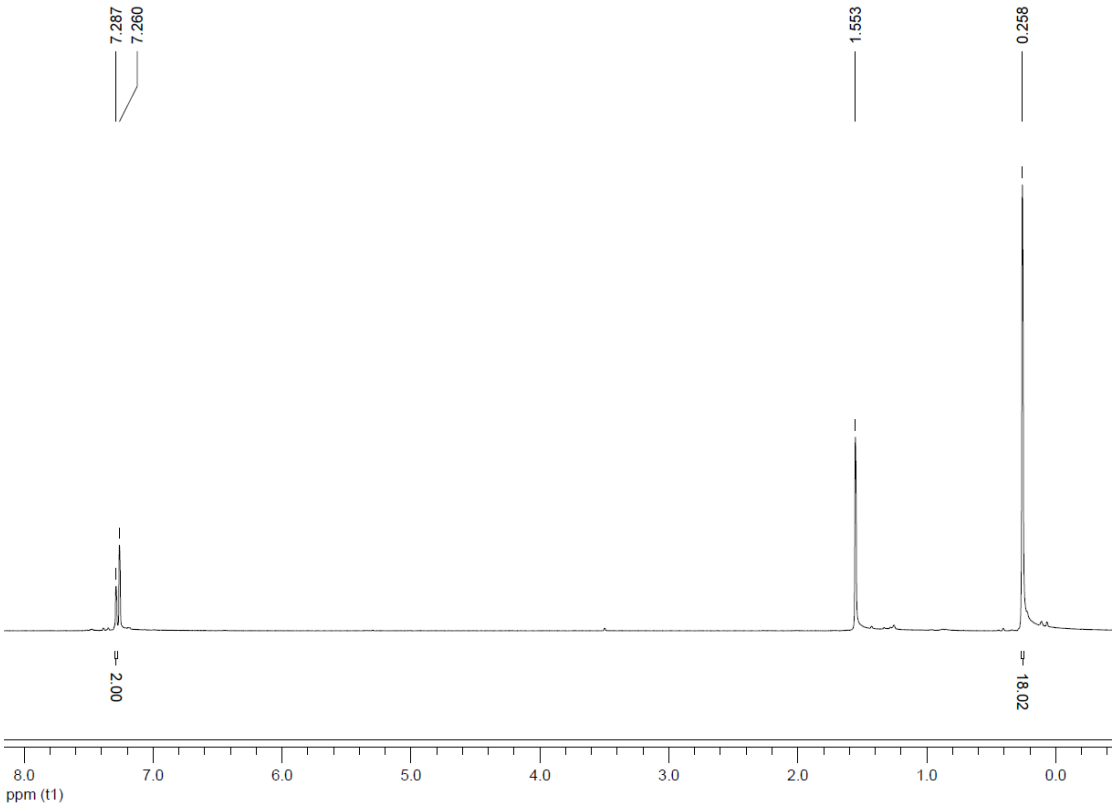
Chart S2. Synthetic procedures to access to compounds **6a-6d**





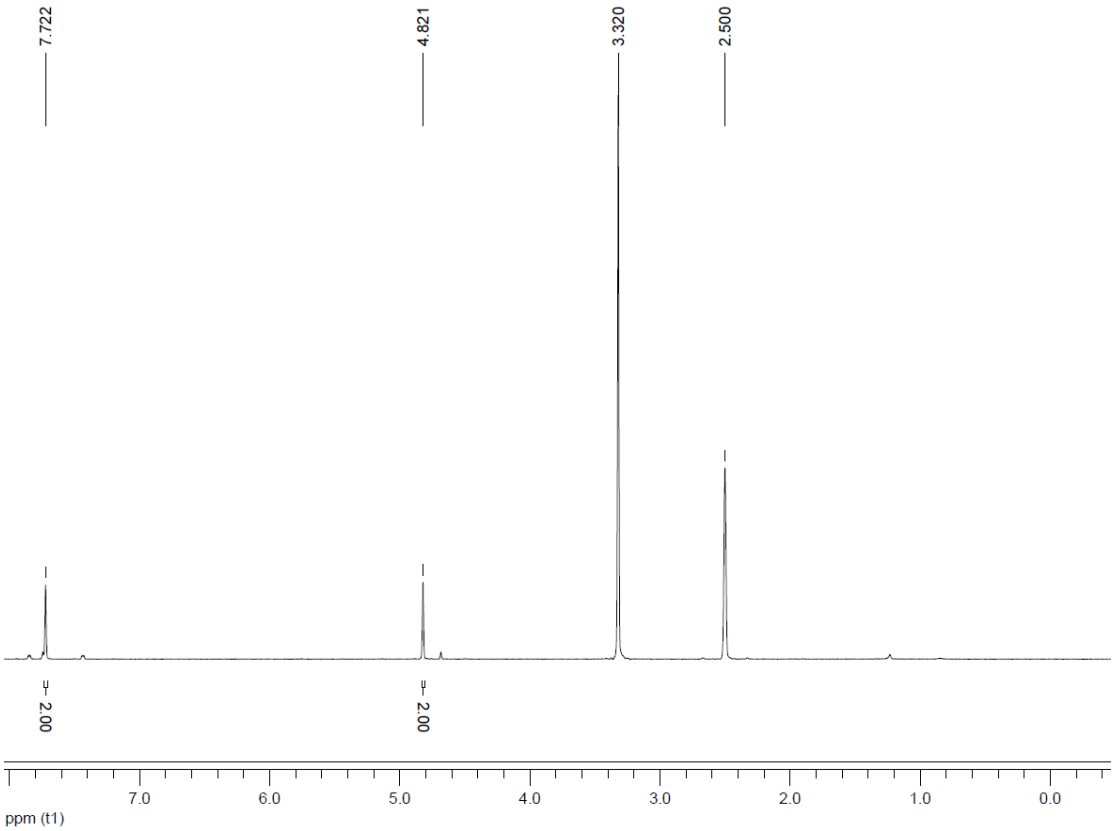
Chemical Formula: $C_6H_2I_2S_2$
Exact Mass: 391.7687
Molecular Weight: 392.0109

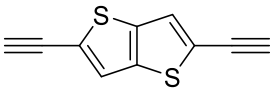
Fig. S1. ^{1}H NMR spectrum of compound **1** ($CDCl_3$, 400 MHz)



Chemical Formula: $C_{16}H_{20}S_2Si_2$
Exact Mass: 332.0545
Molecular Weight: 332.6260

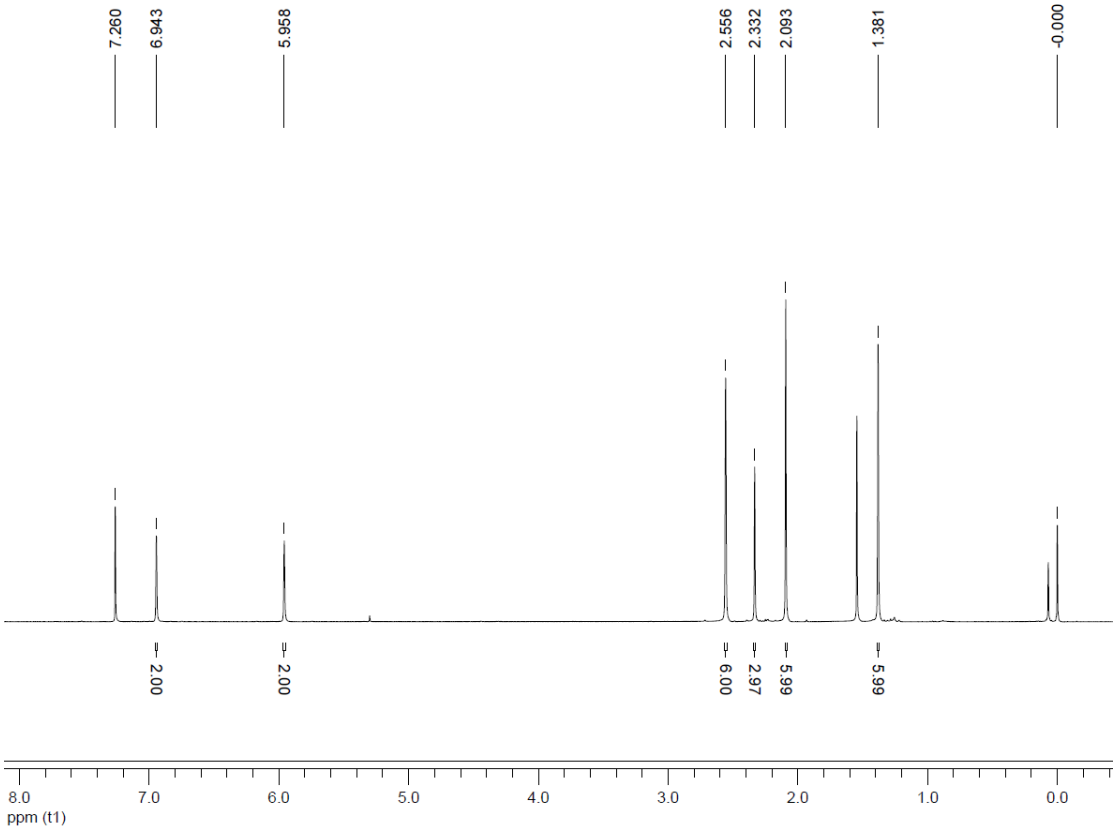
Fig. S2. ^{1}H NMR spectrum of compound **2** ($CDCl_3$, 400 MHz)

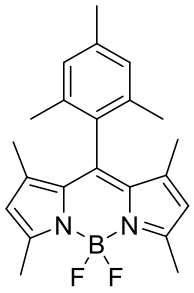




Chemical Formula: $C_{10}H_4S_2$
Exact Mass: 187.9754
Molecular Weight: 188.2620

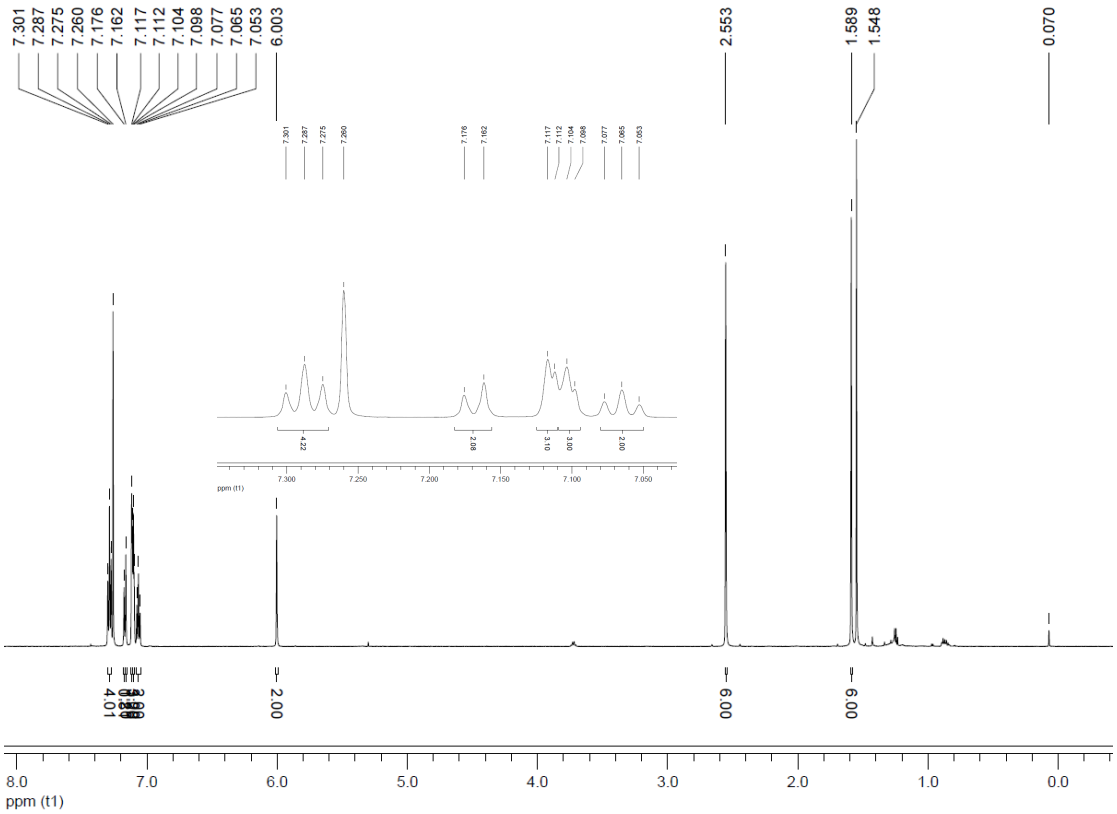
Fig. S3. ^{1}H NMR spectrum of compound **3** (DMSO, 400 MHz)

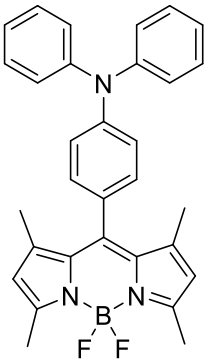




Chemical Formula: $C_{22}H_{25}BF_2N_2$
Exact Mass: 366.2079
Molecular Weight: 366.2628

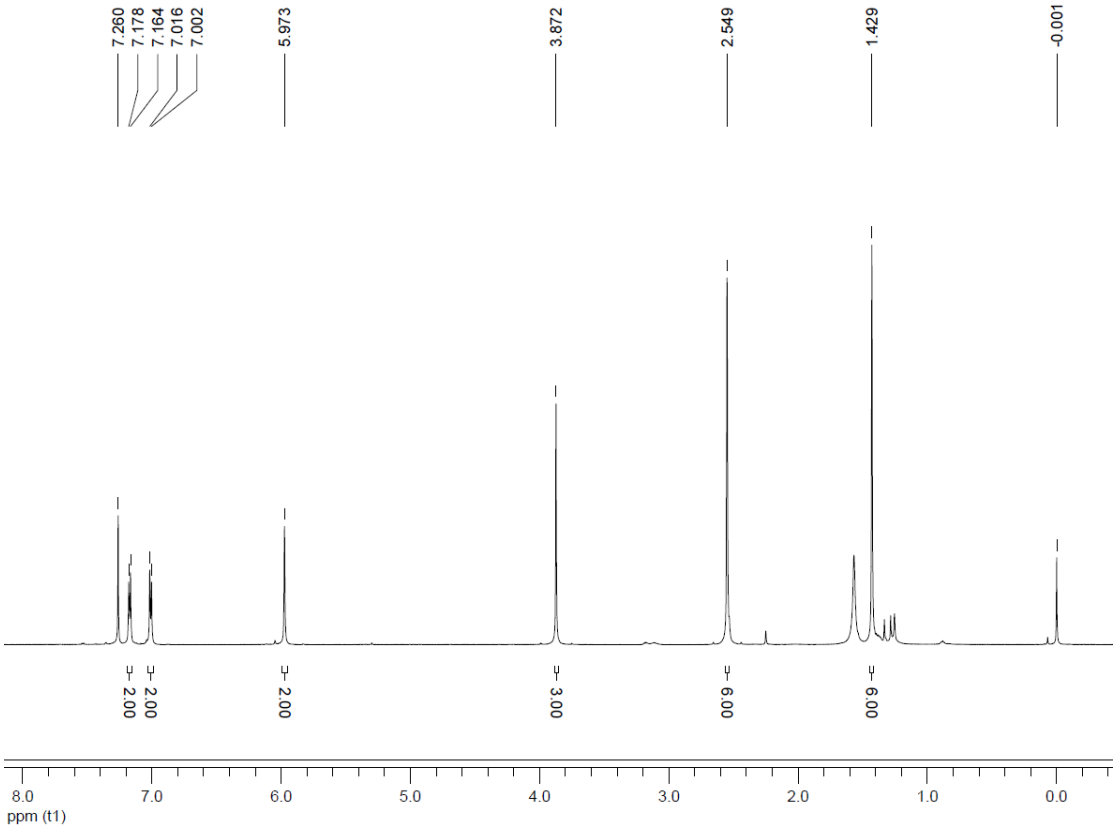
Fig. S4. ^{1}H NMR spectrum of compound **4a** ($CDCl_3$, 400 MHz)

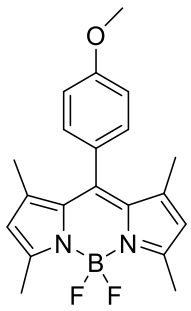




Chemical Formula: $C_{31}H_{28}BF_2N_3$
Exact Mass: 491.2344
Molecular Weight: 491.3928

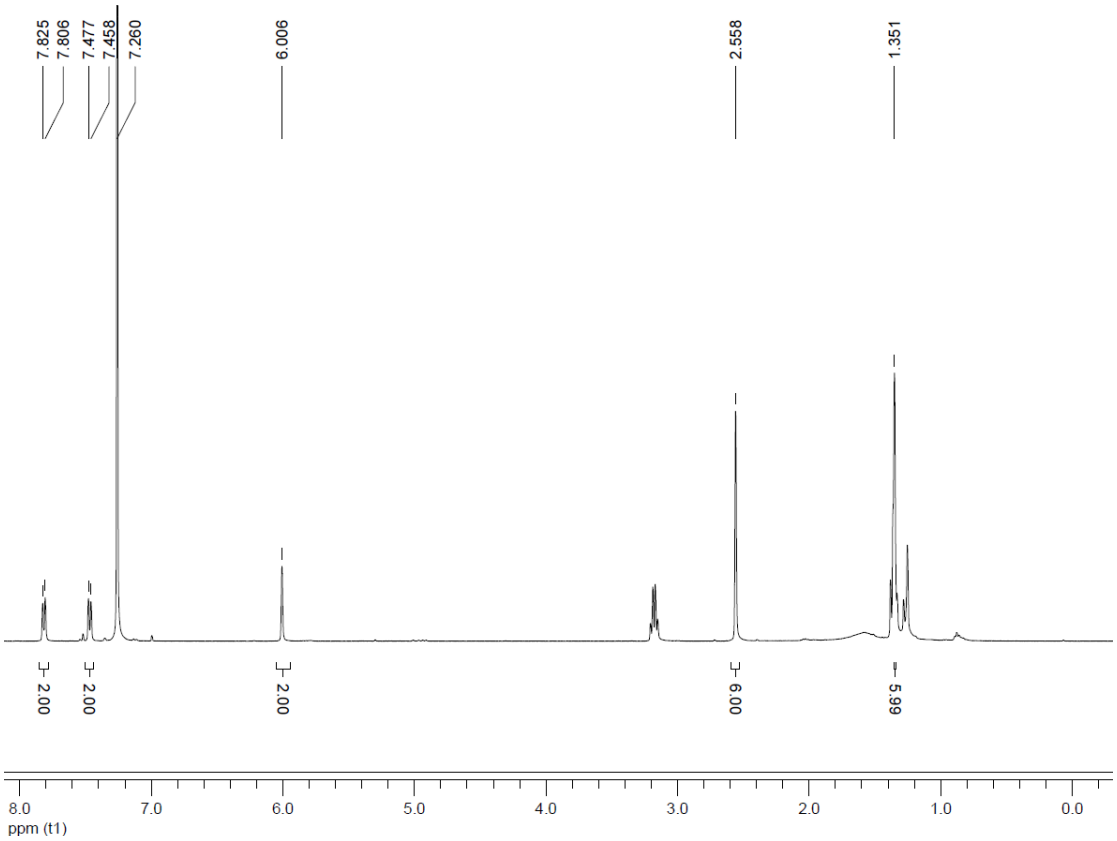
Fig. S5. ^{1}H NMR spectrum of compound **4b** ($CDCl_3$, 600MHz)

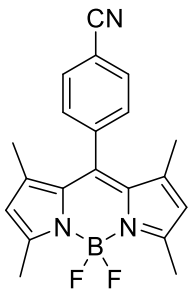




Chemical Formula:
$C_{20}H_{21}BF_2N_2O$
Exact Mass: 354.1715
Molecular Weight: 354.2078

Fig. S6. ^{1}H NMR spectrum of compound **4c** ($CDCl_3$, 600 MHz)





Chemical Formula:
$C_{20}H_{18}BF_2N_3$
Exact Mass: 349.1562
Molecular Weight:
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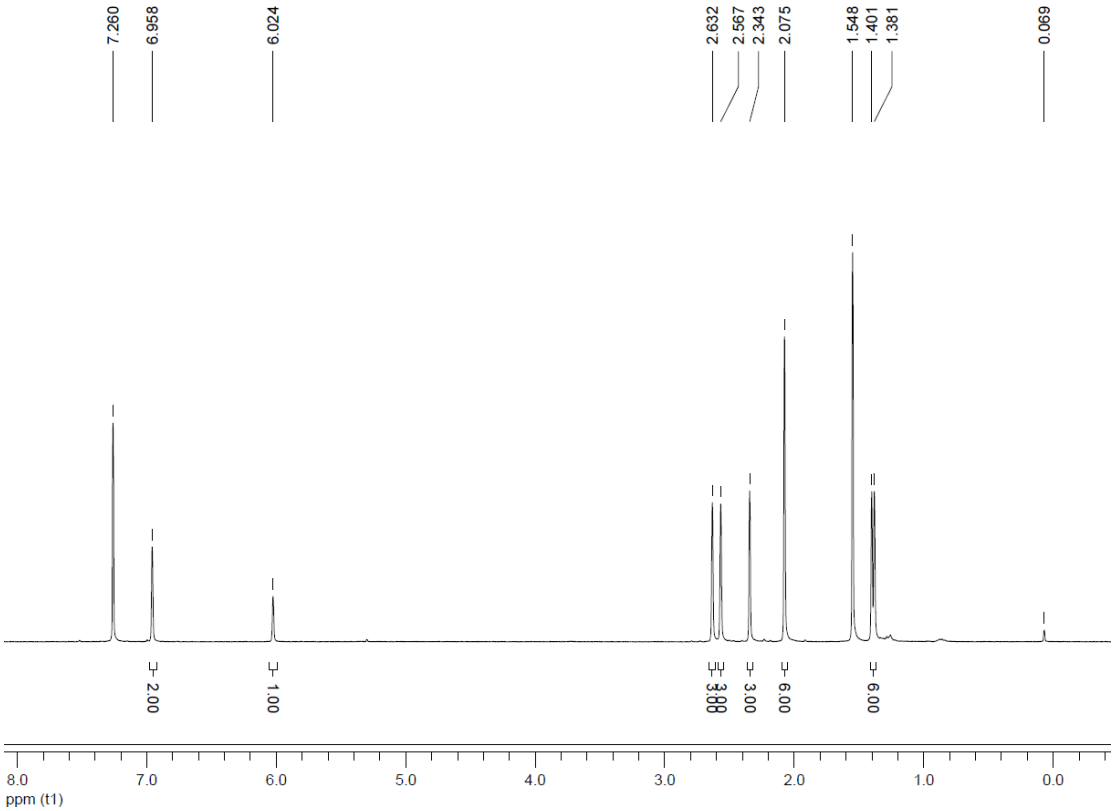
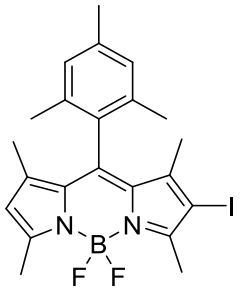
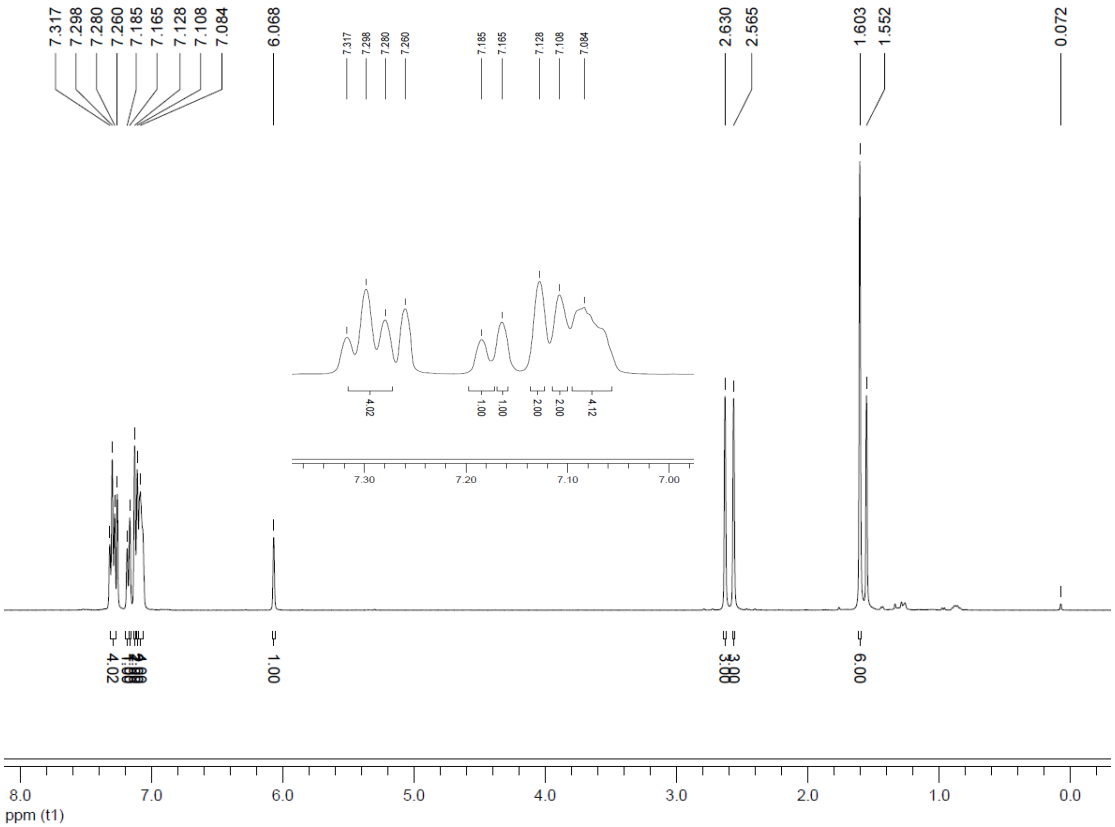
Fig. S7. ^{1}H NMR spectrum of compound **4d** ($CDCl_3$, 400 MHz)

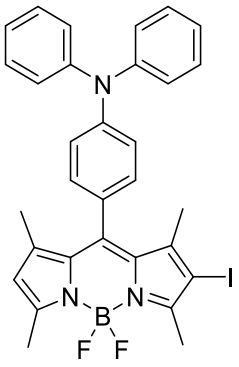




Chemical Formula: $C_{22}H_{24}BF_2IN_2$
Exact Mass: 492.1045
Molecular Weight: 492.1593

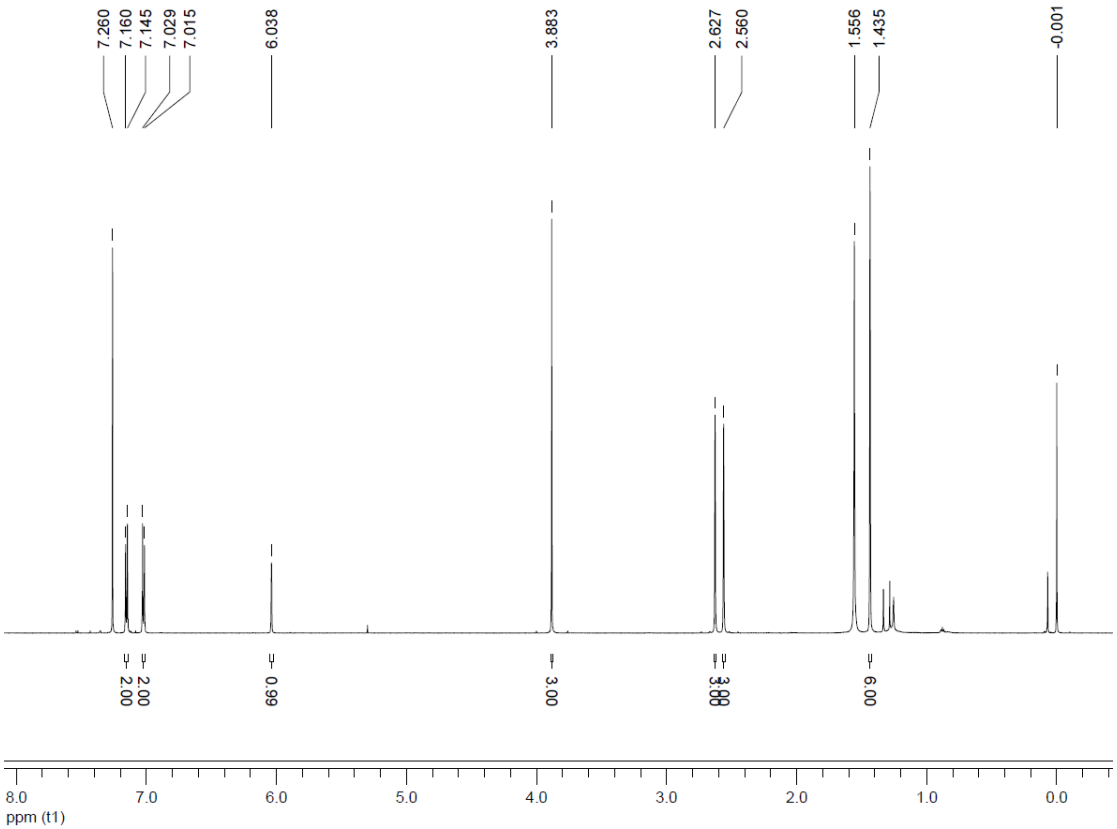
Fig. S8. ^{1}H NMR spectrum of compound **5a** ($CDCl_3$, 400 MHz)

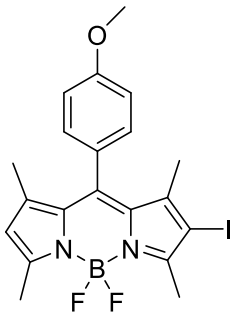




Chemical Formula: $C_{31}H_{27}BF_2IN_3$
Exact Mass: 617.1311
Molecular Weight: 617.2893

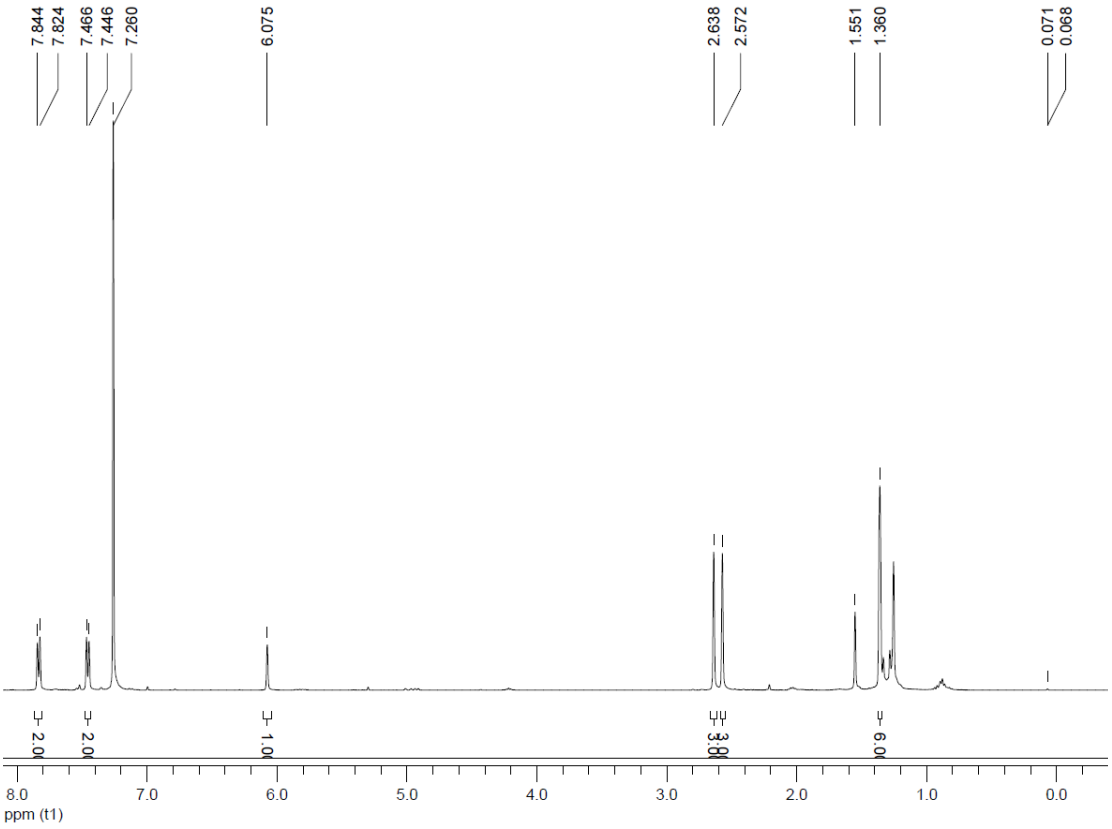
Fig. S9. ^{1}H NMR spectrum of compound **5b** ($CDCl_3$, 600 MHz)

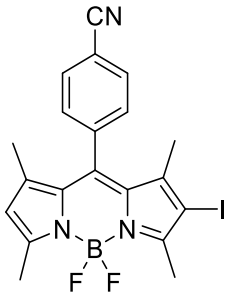




Chemical Formula: $C_{20}H_{20}BF_2IN_2O$
Exact Mass: 480.0681
Molecular Weight: 480.1043

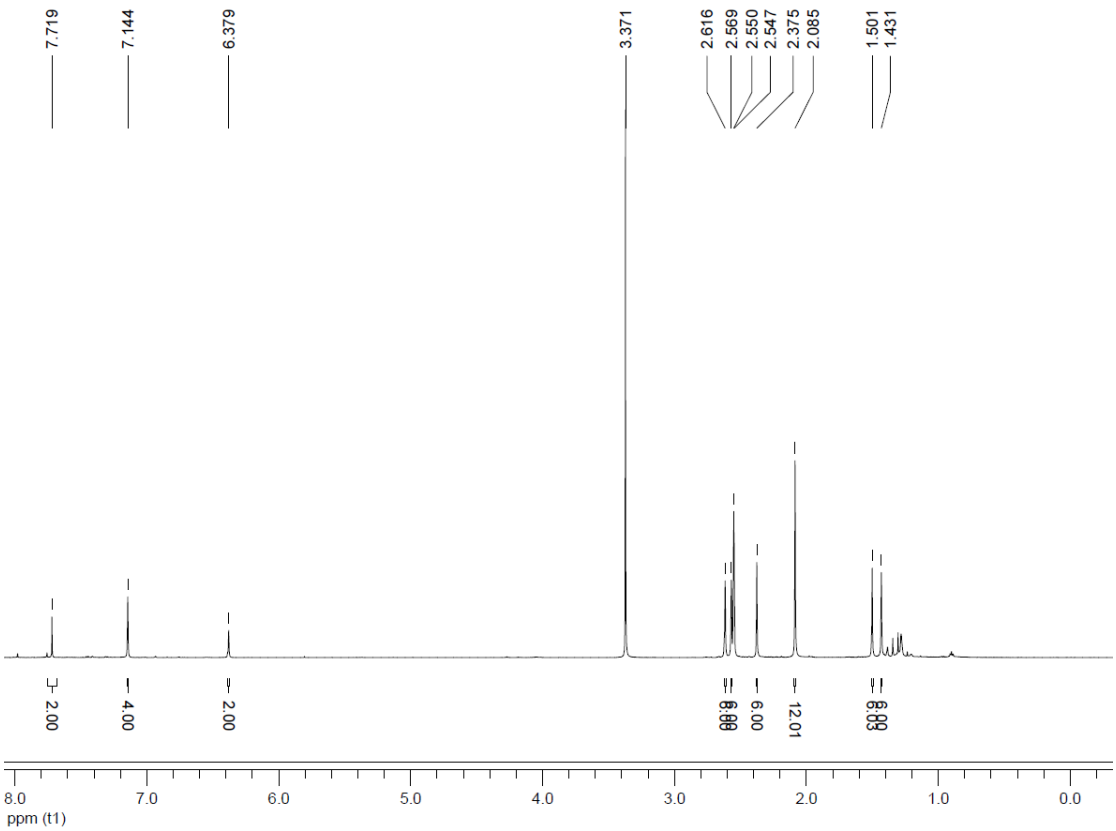
Fig. S10. ^{1}H NMR spectrum of compound **5c** ($CDCl_3$, 600 MHz)

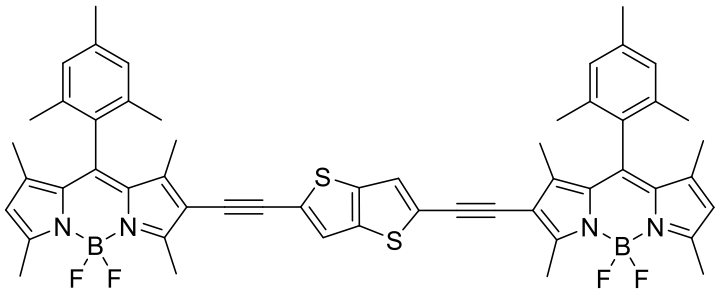




Chemical Formula: $C_{20}H_{17}BF_2IN_3$
Exact Mass: 475.0528
Molecular Weight: 475.0883

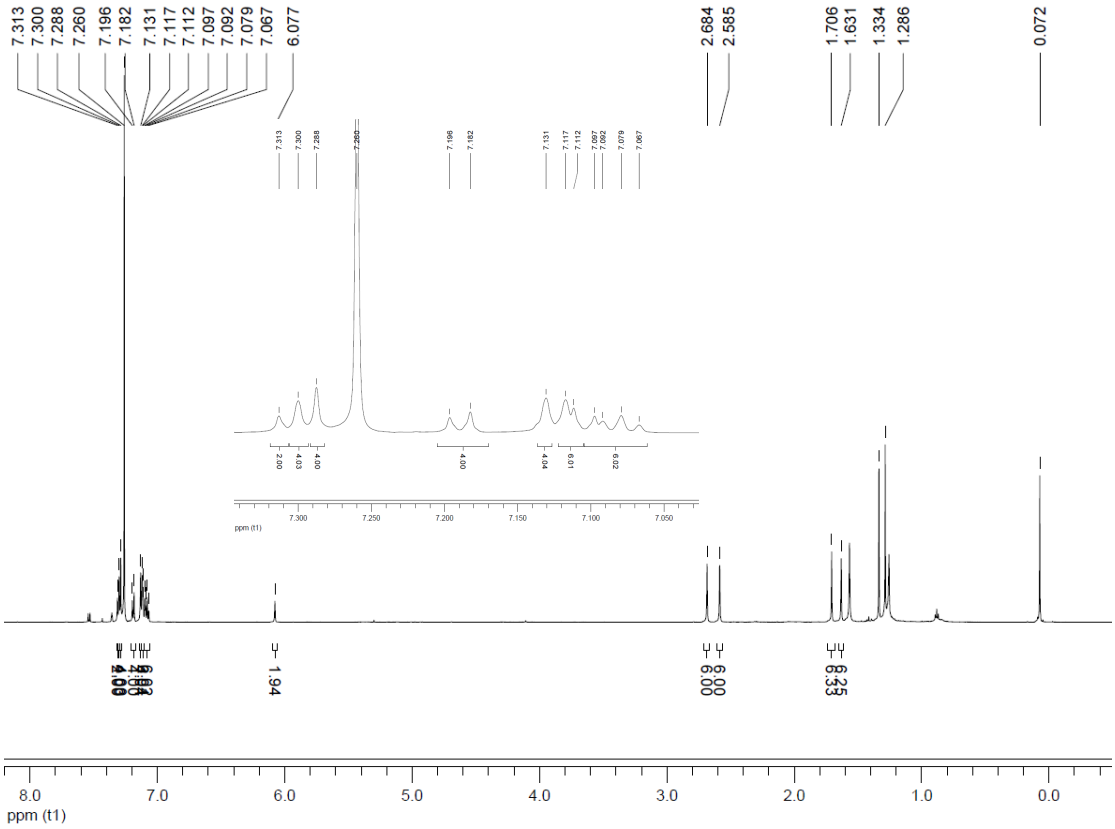
Fig. S11. ^{1}H NMR spectrum of compound **5d** ($CDCl_3$, 600 MHz)

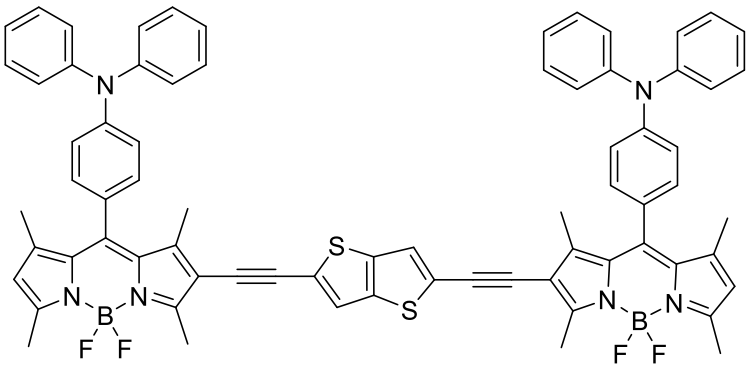




Chemical Formula: $C_{54}H_{50}B_2F_4N_4S_2$
Exact Mass: 916.3599
Molecular Weight: 916.7556

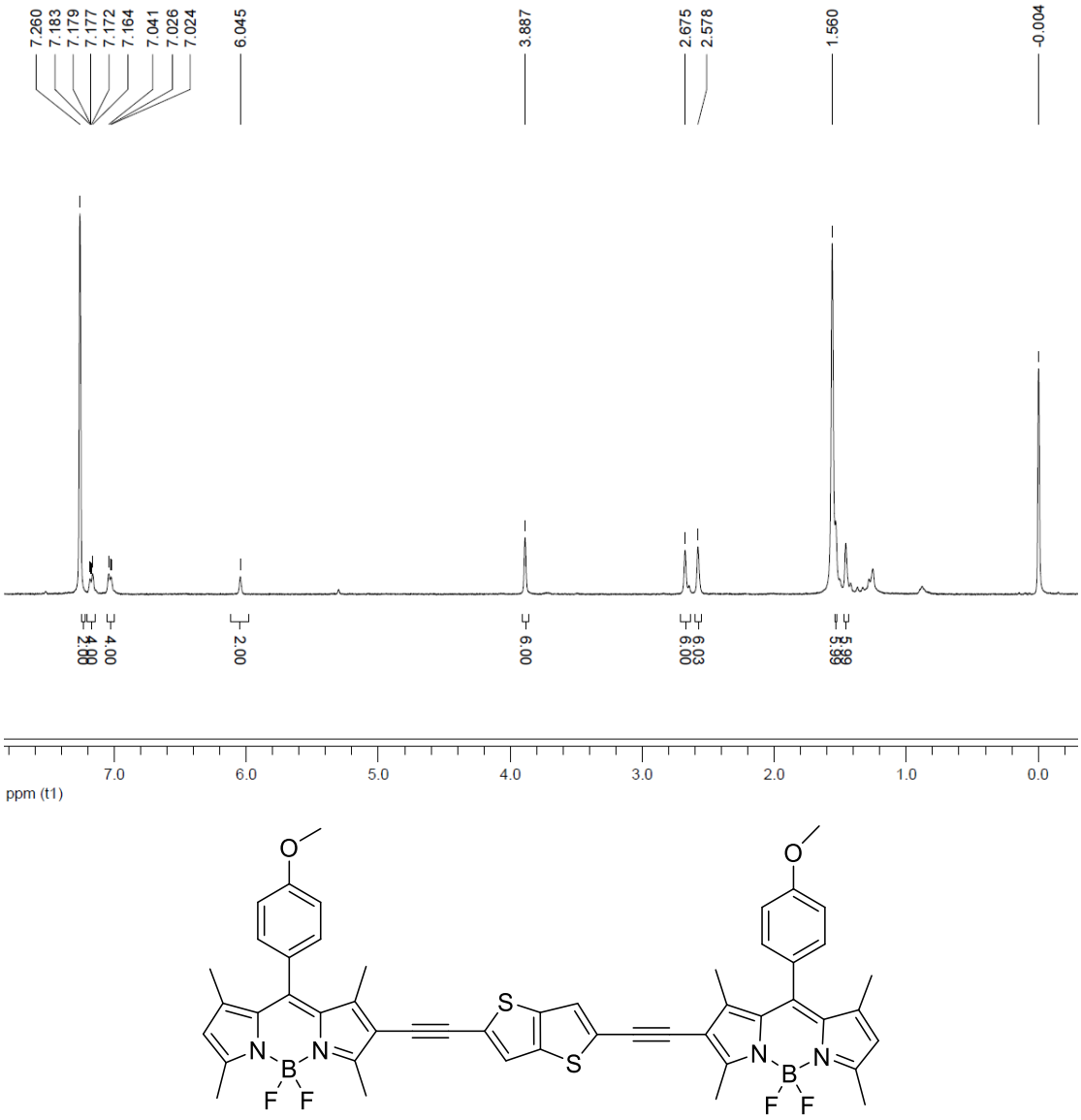
Fig. S12. ^{1}H NMR spectrum of compound **6a** (DMSO,600 MHz)





Chemical Formula: $C_{72}H_{56}B_2F_4N_6S_2$
Exact Mass: 1166.4130
Molecular Weight: 1167.0156

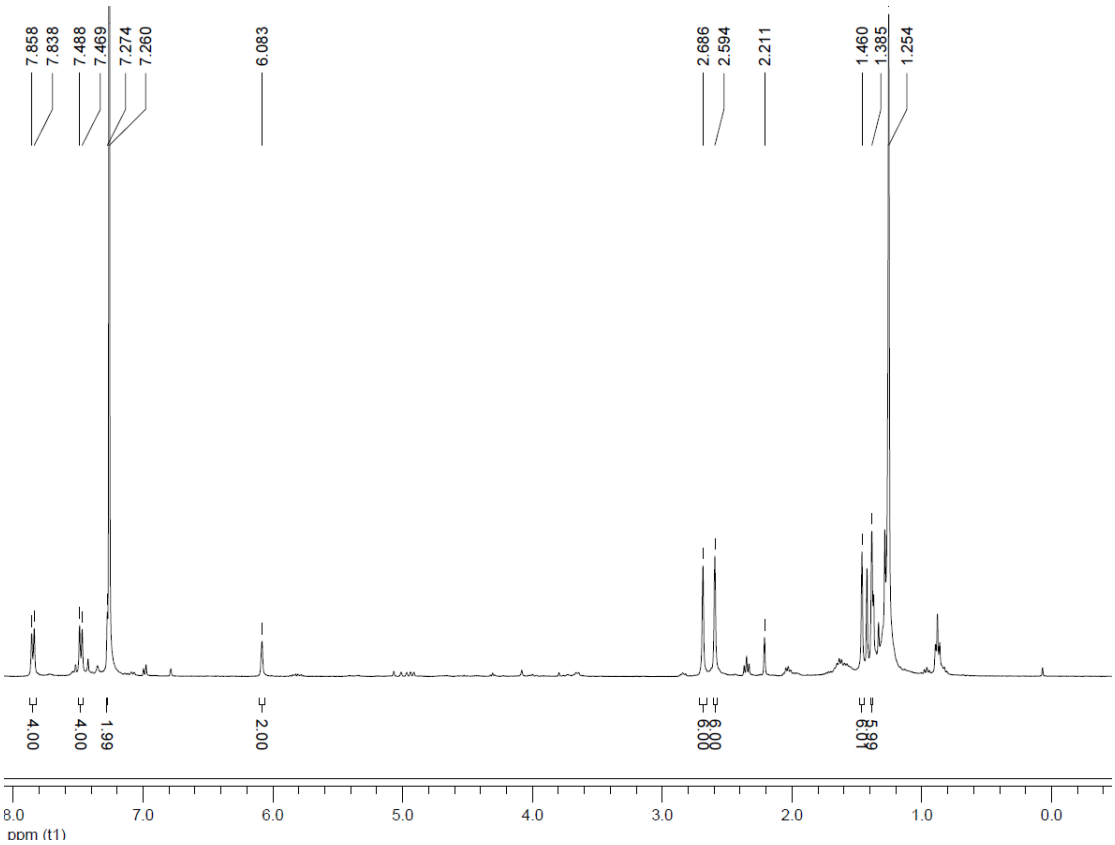
Fig. S13. ^{1}H NMR spectrum of compound **6b** ($CDCl_3$, 600 MHz)

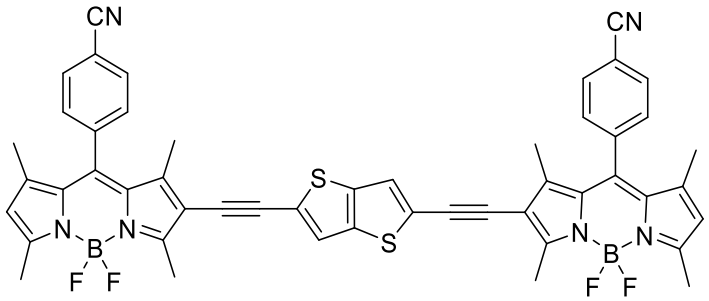


Chemical Formula: $C_{50}H_{42}B_2F_4N_4O_2S_2$
Exact Mass: 892.2871
Molecular Weight: 892.6456

Fig. S14. ^{1}H NMR spectrum of compound **6c** ($CDCl_3$, 600 MHz)

.





Chemical Formula: $C_{50}H_{36}B_2F_4N_6S_2$
Exact Mass: 882.2565
Molecular Weight: 882.6136

Fig. S15. ^{1}H NMR spectrum of compound **6d** ($CDCl_3$, 400 MHz)

.

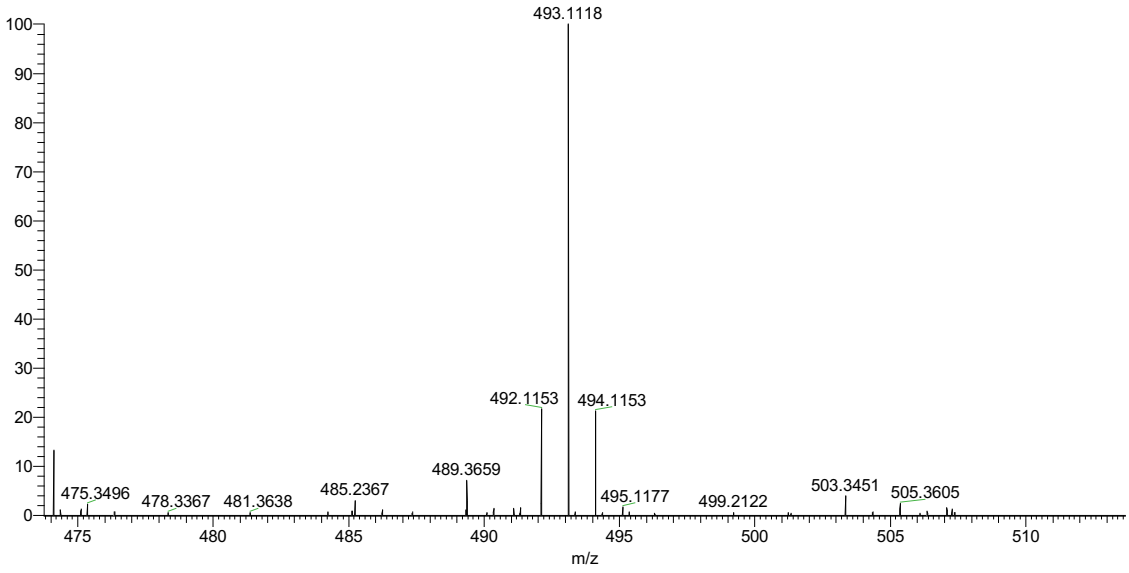


Fig. S16. High Resolution ESI-Mass spectrum of compound **5a**

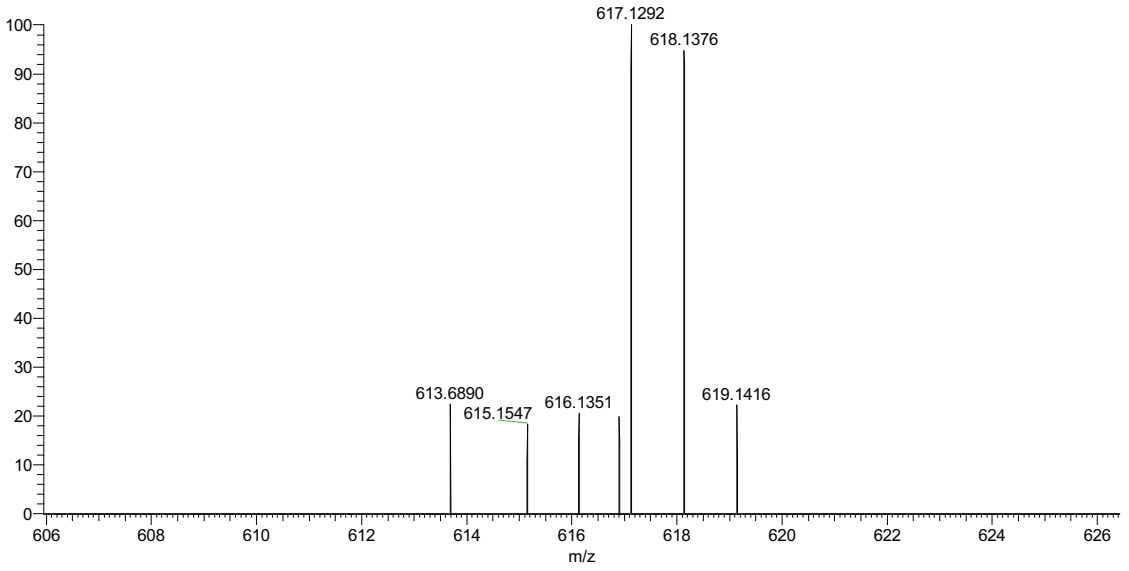


Fig. S17. High Resolution ESI-Mass spectrum of compound **5b**

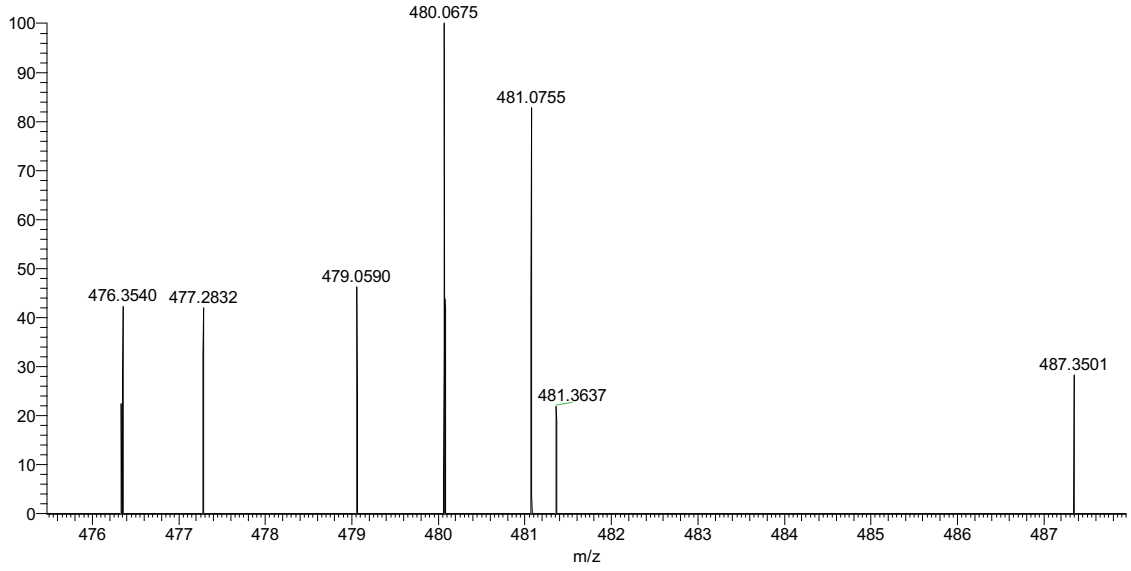


Fig. S18. High Resolution ESI-Mass spectrum of compound **5c**

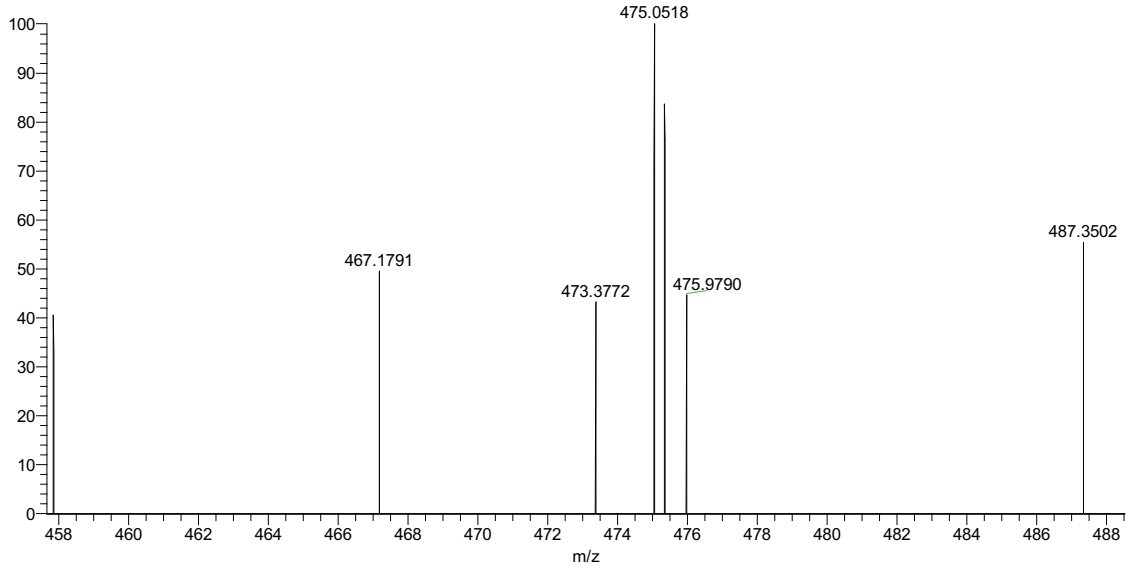
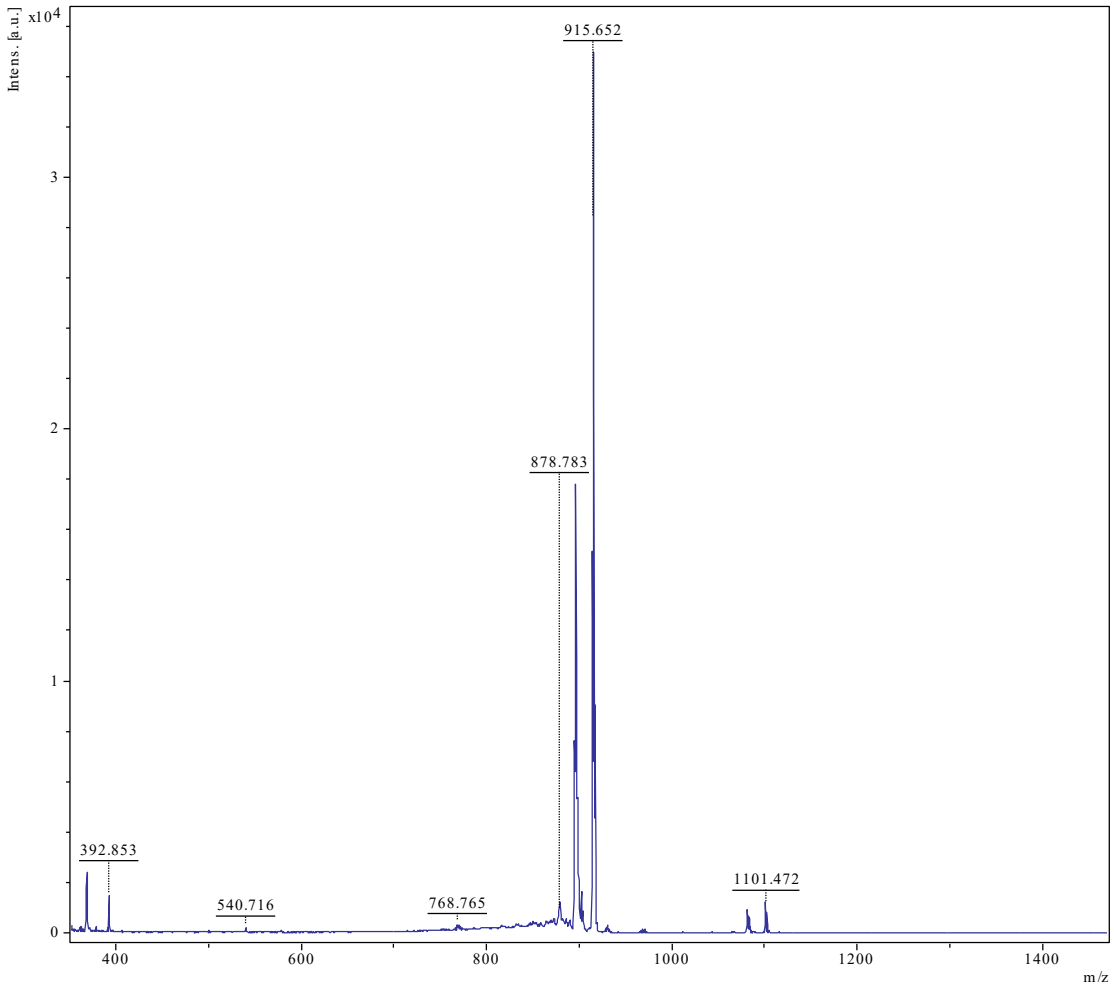


Fig. S19. High Resolution ESI-Mass spectrum of compound **5d**



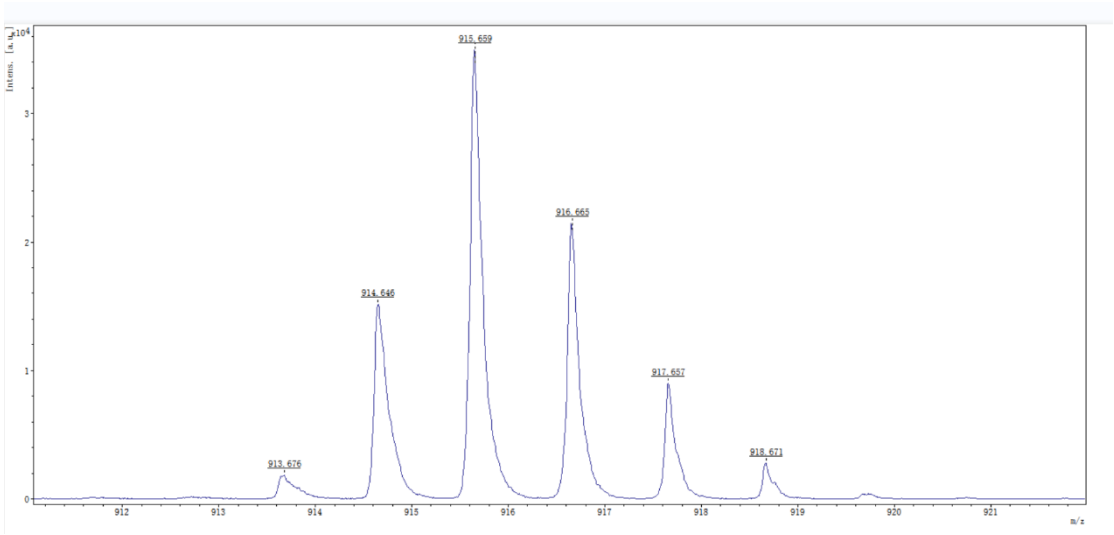
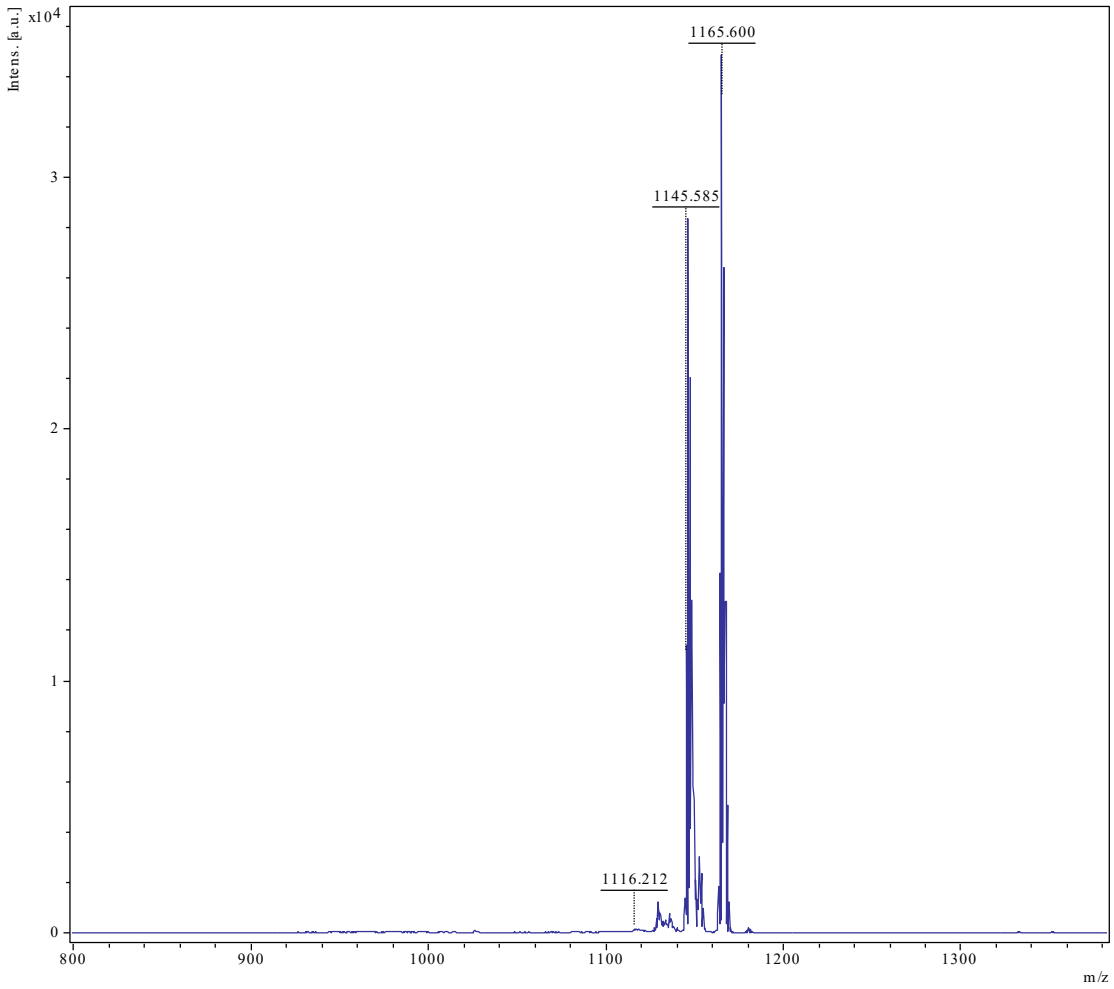


Fig. S20. MALDI-TOF MS spectrum of compound **6a**



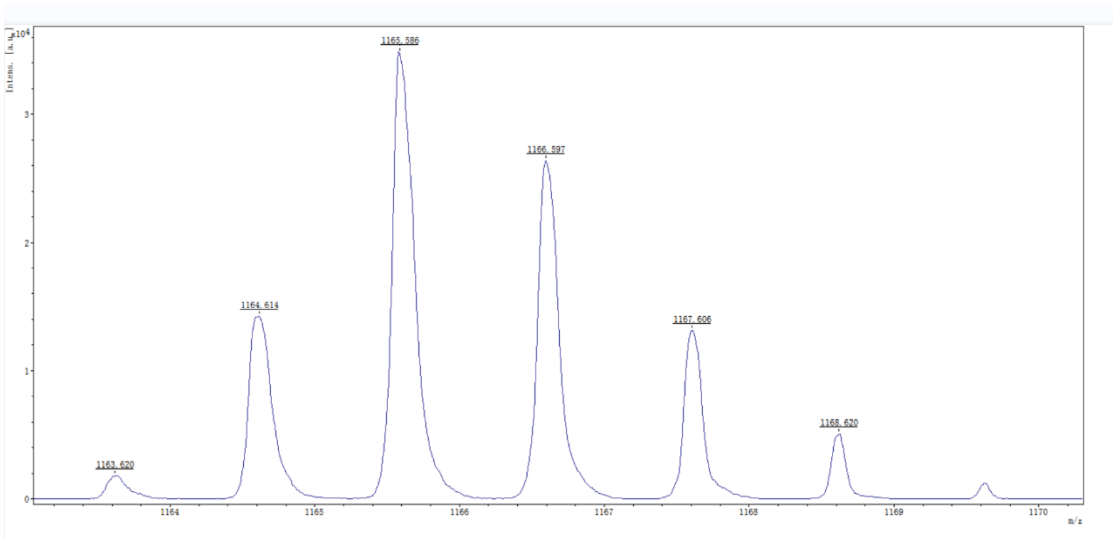


Fig. S21. MALDI-TOF MS spectrum of compound **6b**

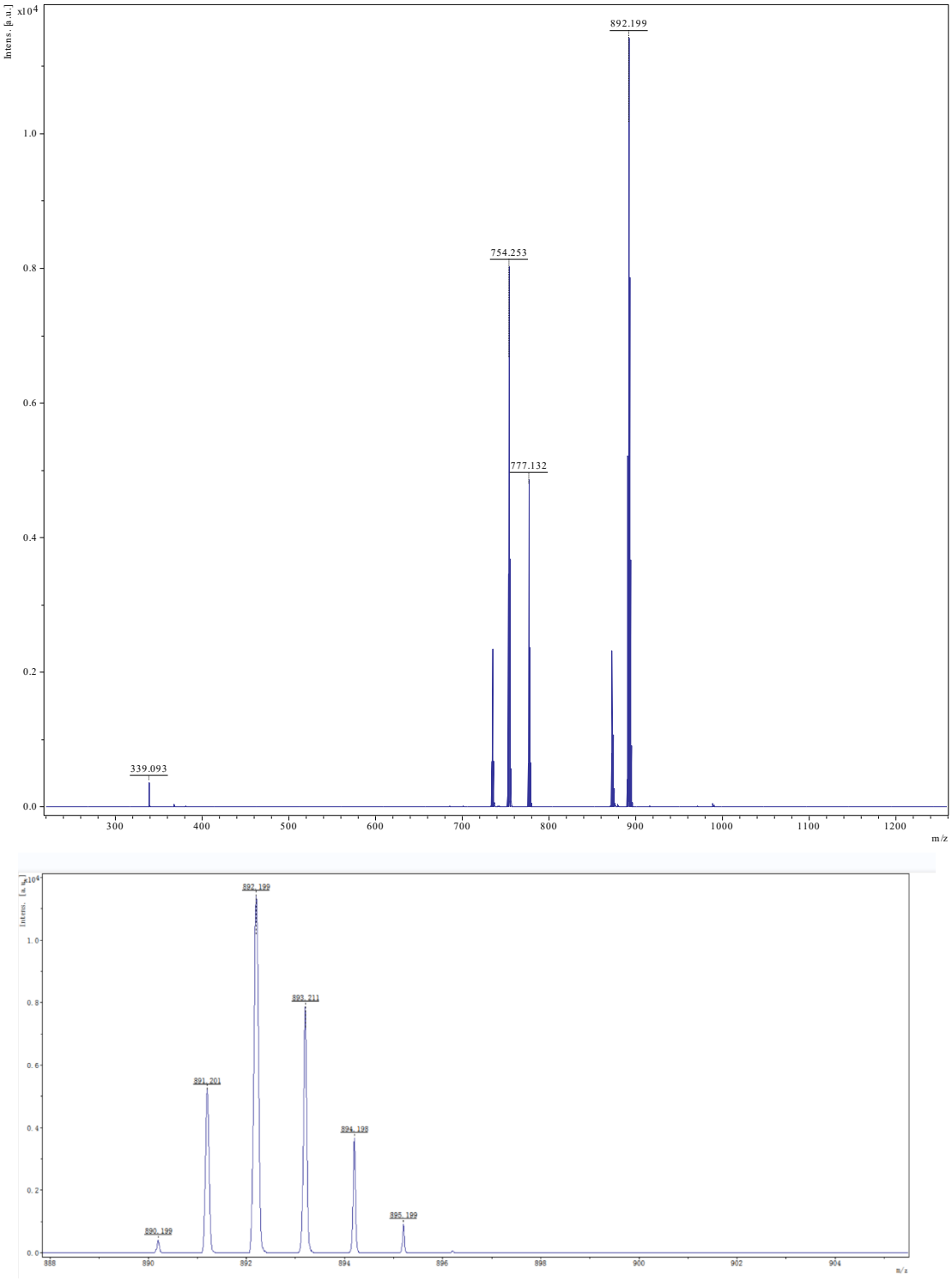


Fig. S22. MALDI-TOF MS spectrum of compound **6c**

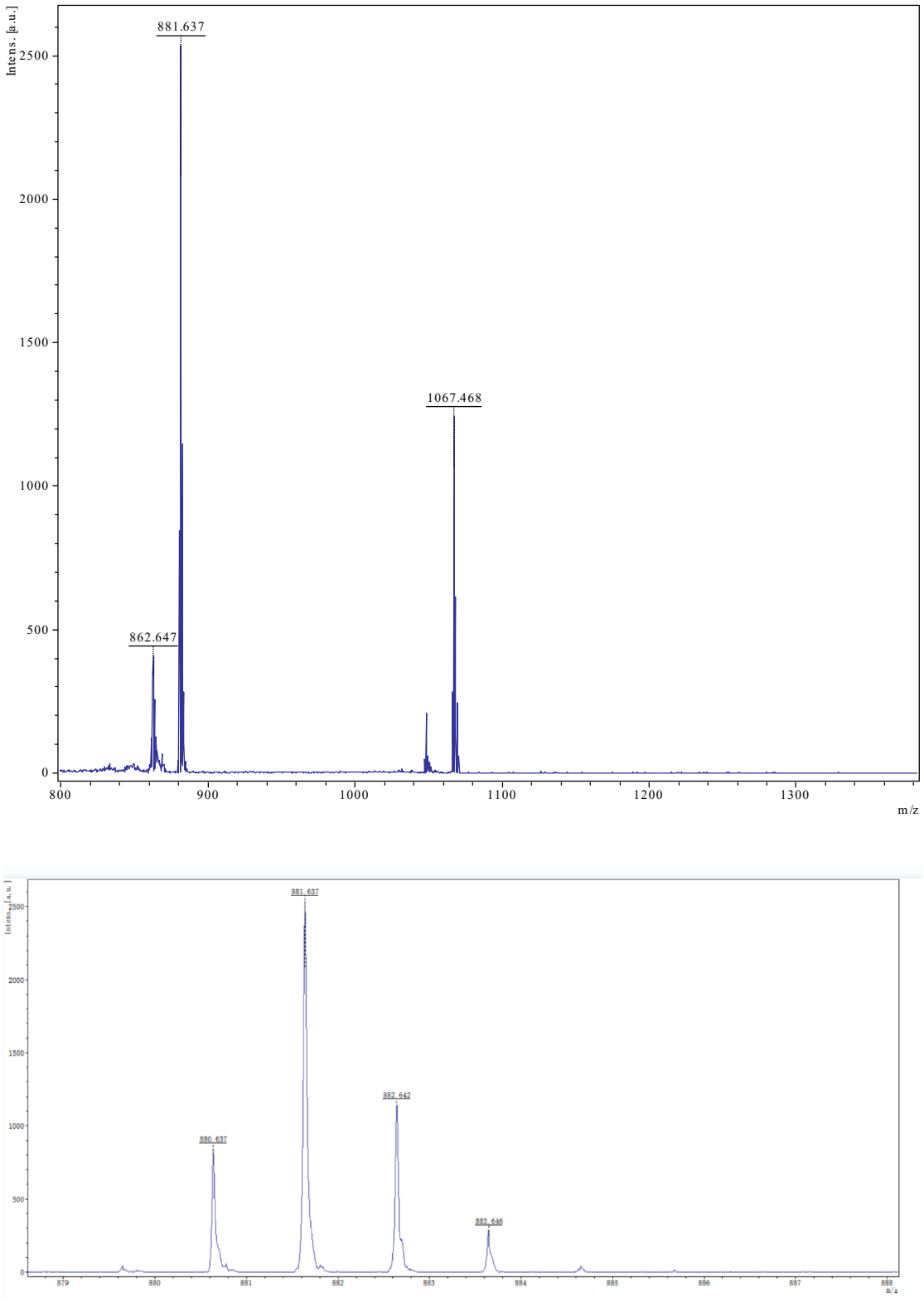


Fig. S23. MALDI-TOF MS spectrum of compound **6d**

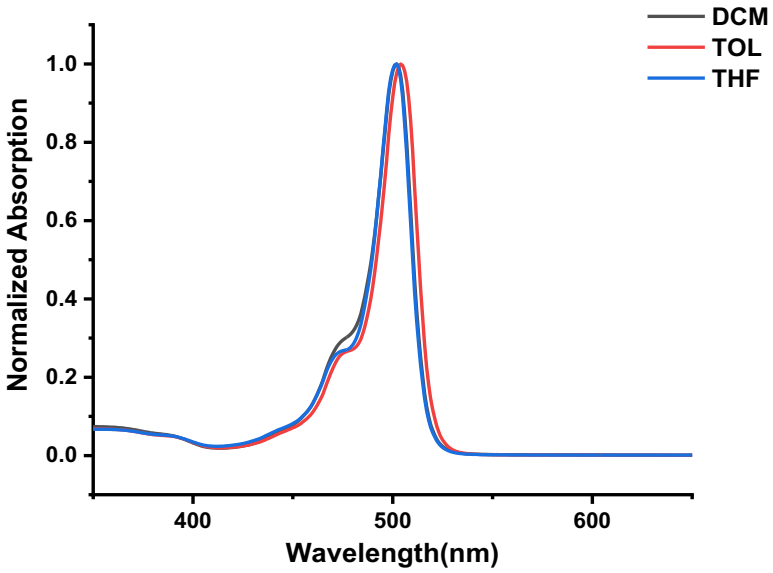


Fig. S24. Normalized Emission spectra of compound **4a** in different solvents

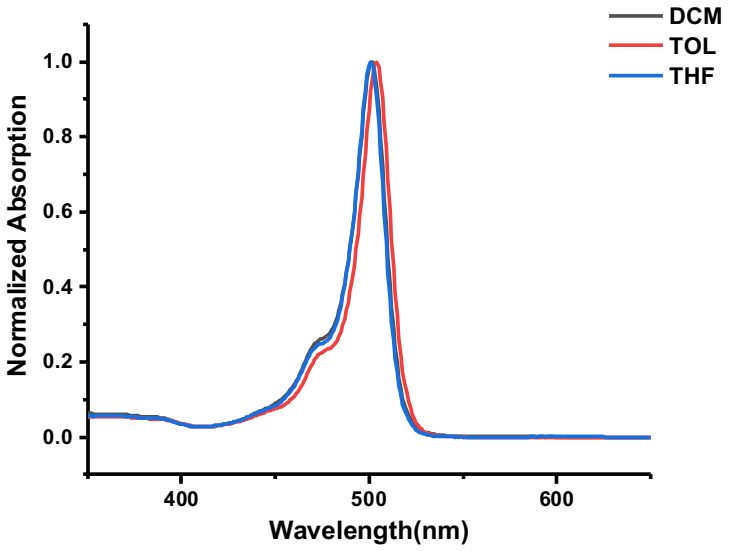


Fig. S25. Normalized Emission spectra of compound **4b** in different solvents

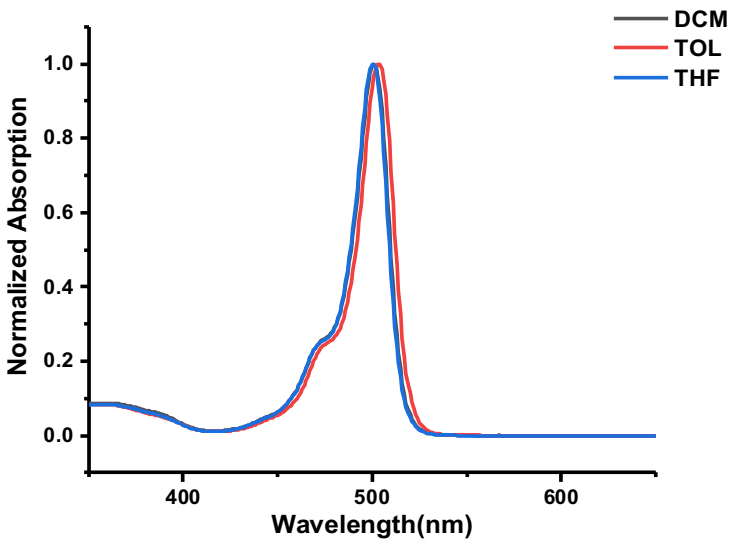


Fig. S26. Normalized Emission spectra of compound **4c** in different solvents

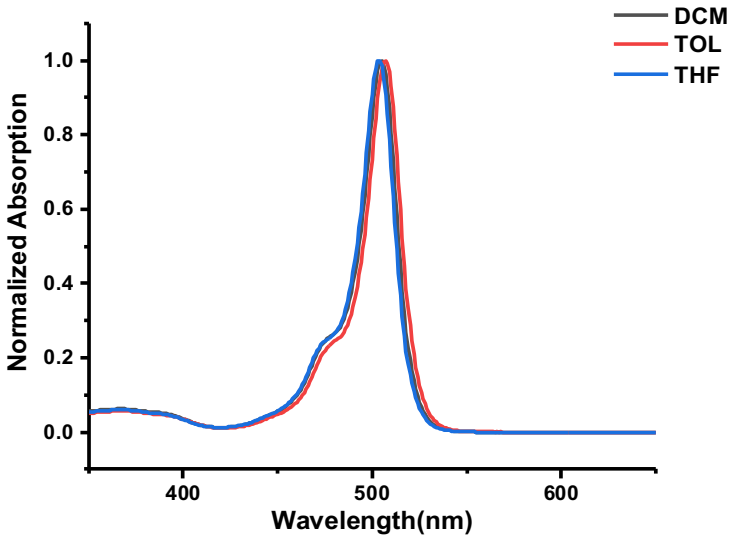


Fig. S27. Normalized Emission spectra of compound **4d** in different solvents

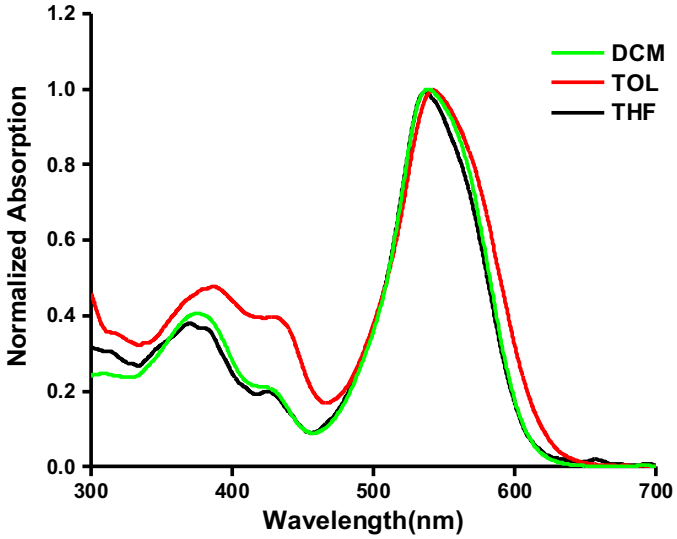


Fig. S28. UV-vis spectra of compound **6a** in different solvents

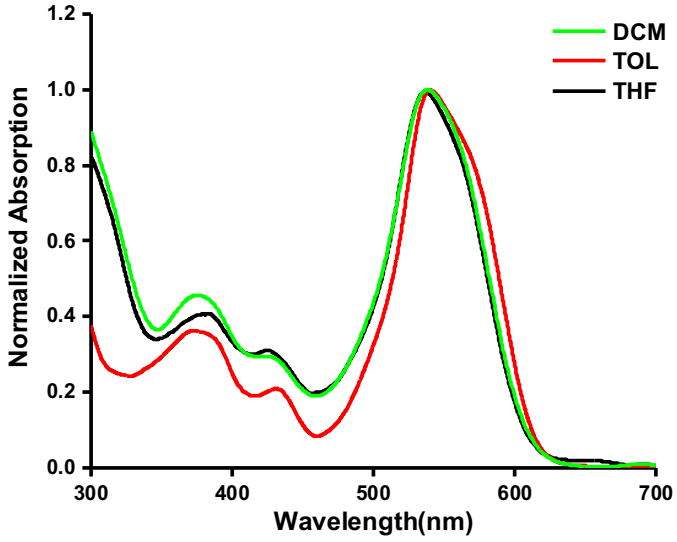


Fig. S29. UV-vis spectra of compound **6b** in different solvents

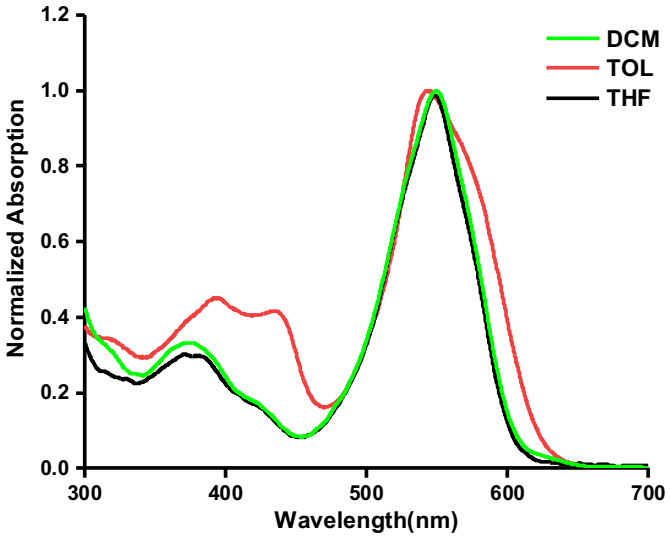


Fig. S30. UV-vis spectra of compound **6c** in different solvents

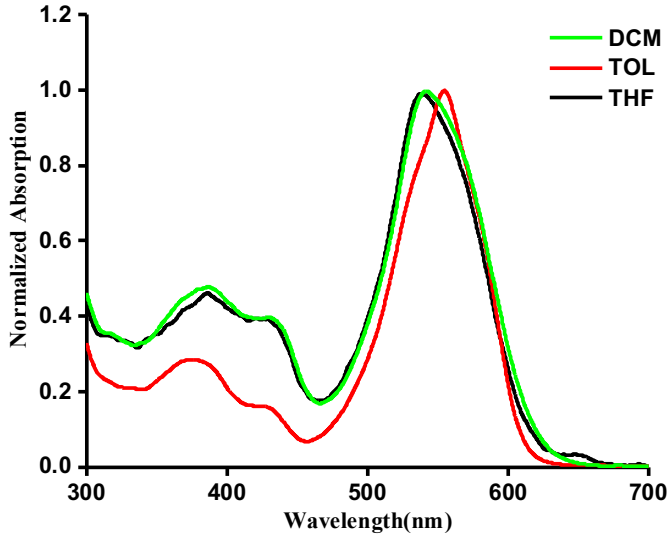


Fig. S31. UV-vis spectra of compound **6d** in different solvents

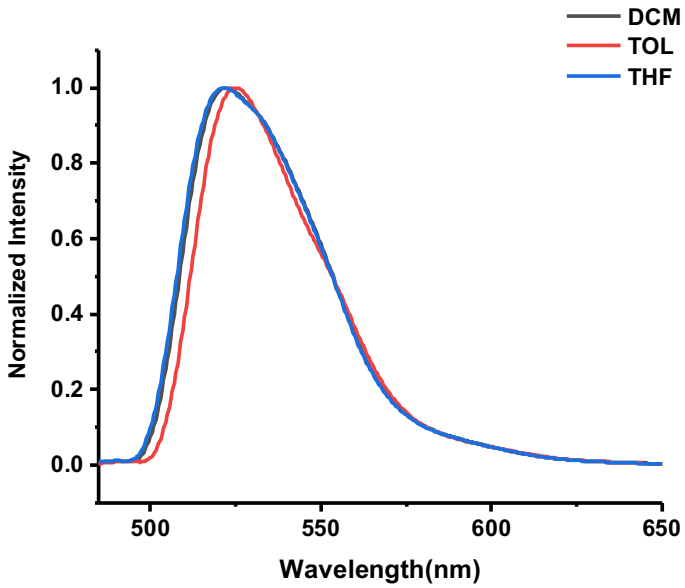


Fig. S32. Normalized Emission spectra of compound **4a** in different solvents

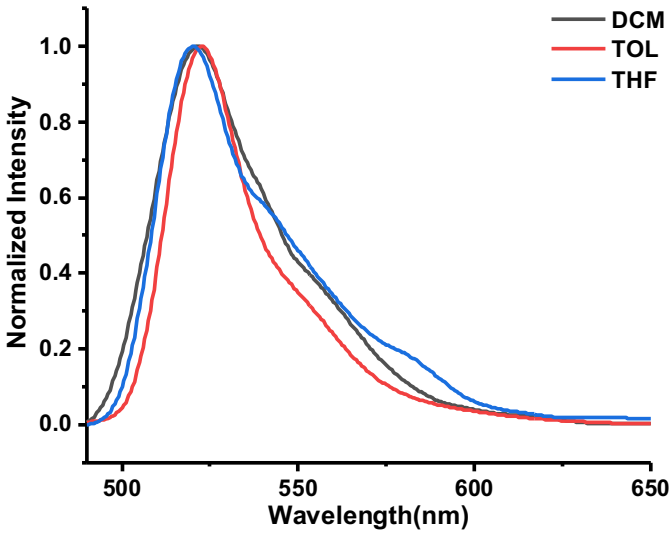


Fig. S33. Normalized Emission spectra of compound **4b** in different solvents

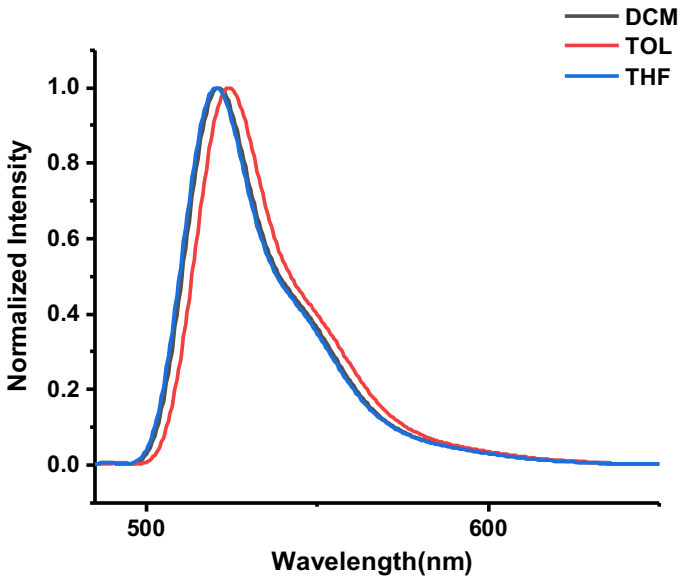


Fig. S34. Normalized Emission spectra of compound **4c** in different solvents

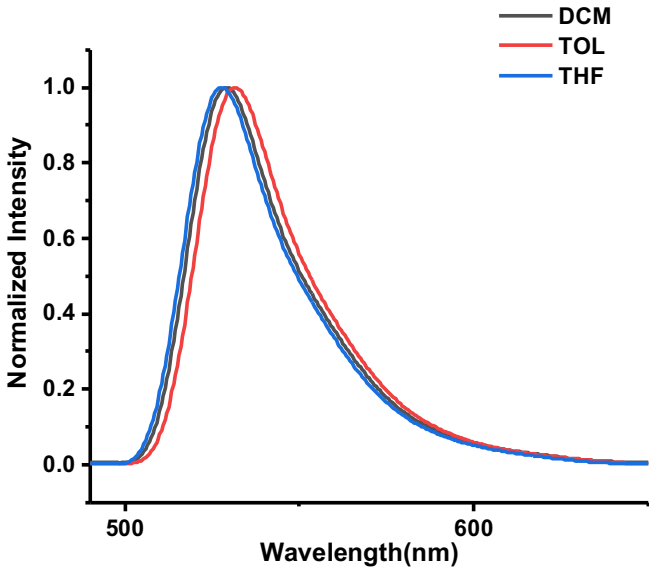


Fig. S35. Normalized Emission spectra of compound **4d** in different solvents

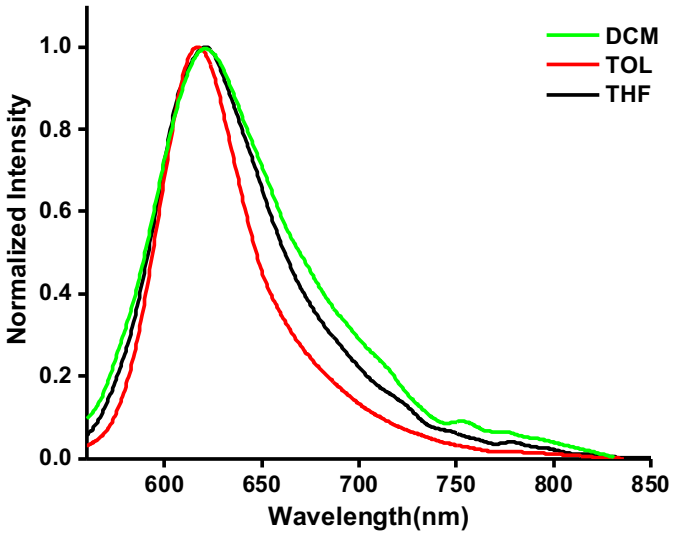


Fig. S36. Normalized Emission spectra of compound **6a** in different solvents

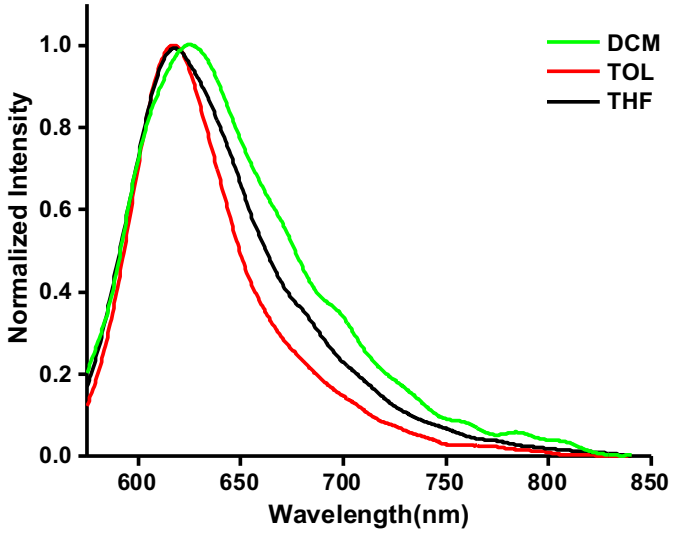


Fig. S37. Normalized Emission spectra of compound **6b** in different solvents

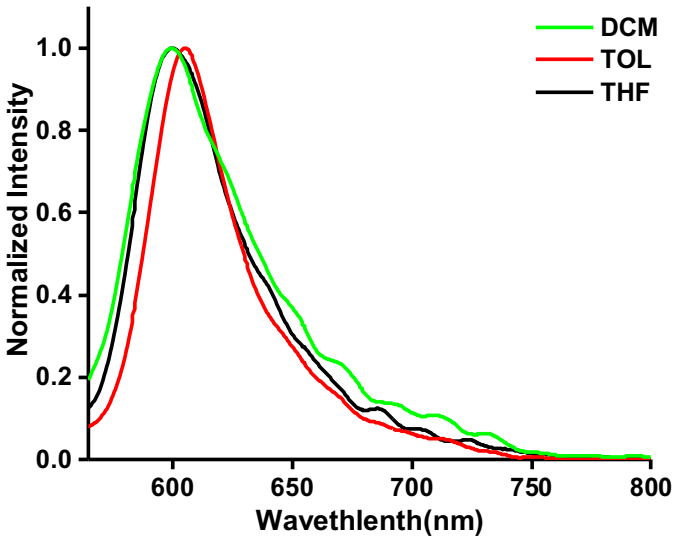


Fig. S38. Normalized Emission spectra of compound **6c** in different solvents

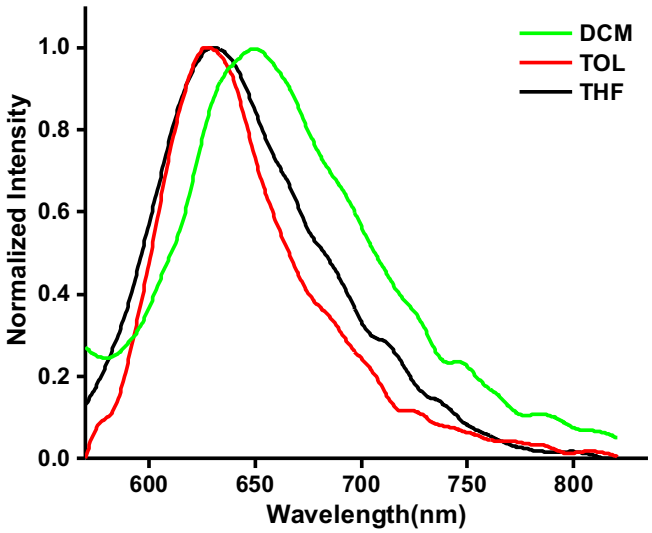


Fig. S39. Normalized Emission spectra of compound **6d** in different solvents

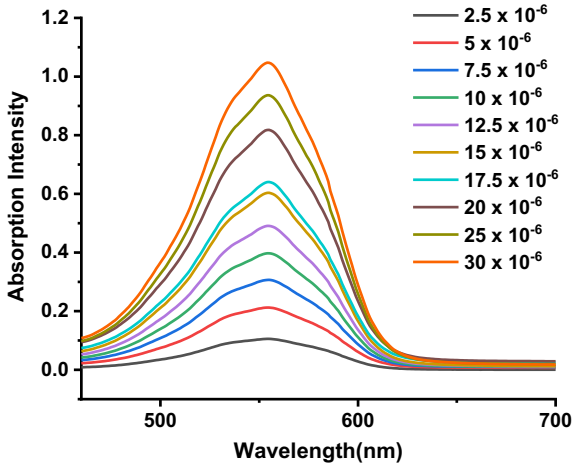


Fig. S40. UV-vis spectra of compound **6c** in different concentrations in toluene

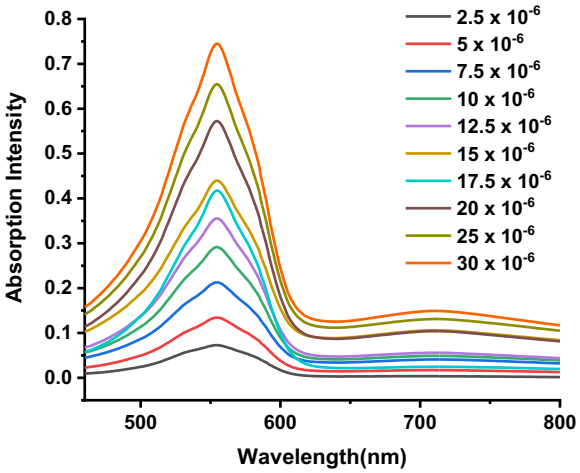


Fig. S41. UV-vis spectra of compound **6d** in different concentrations in toluene

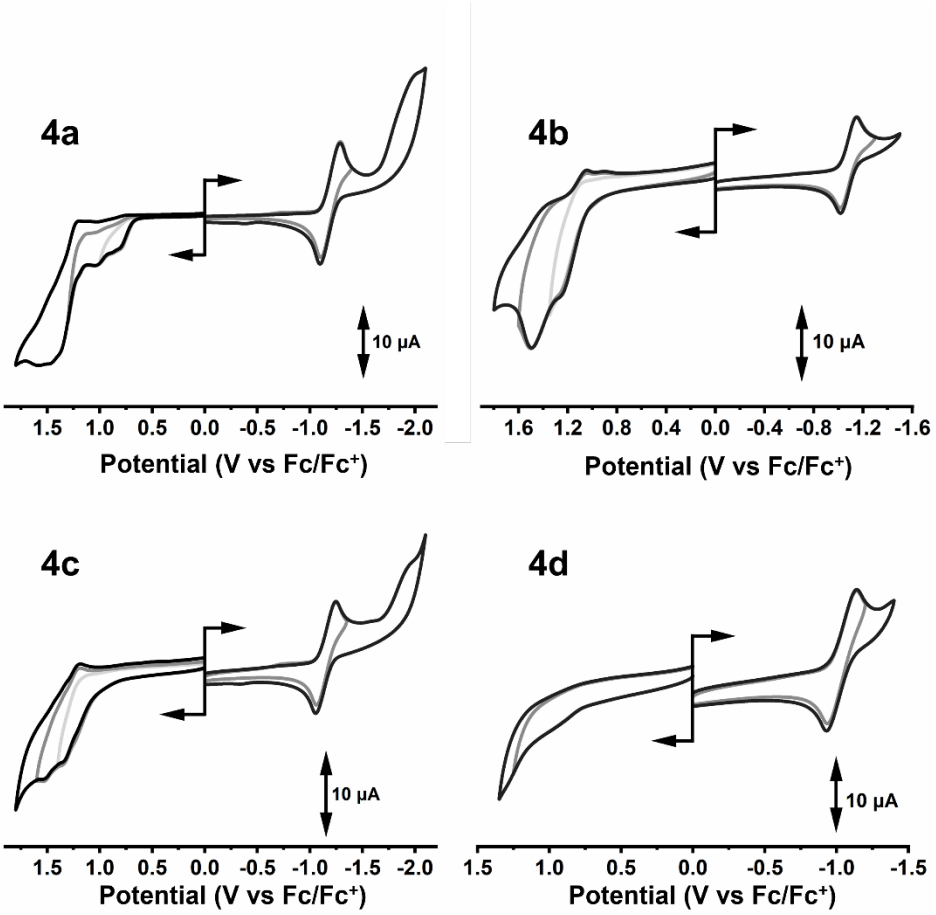


Fig. S42. Cyclic voltammograms of compounds **4a-4d** in CH_2Cl_2 containing 0.1 M TBAP at scan speed of 0.1 V/s

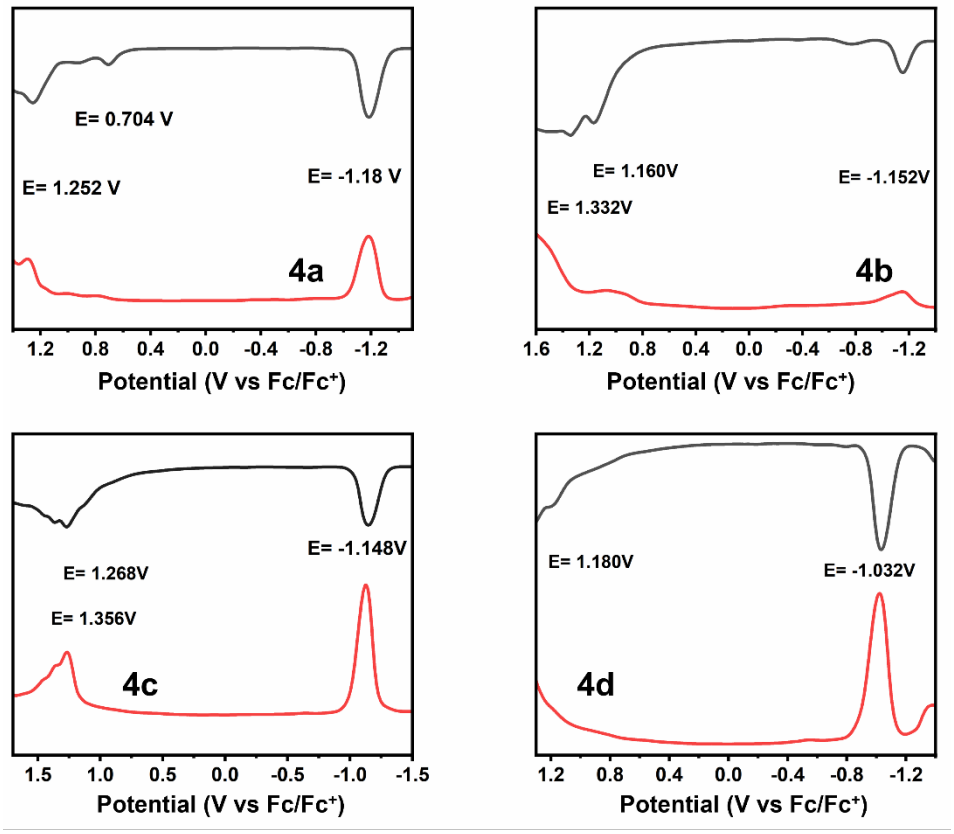


Fig. S43. DPV of compounds **4a-4d**

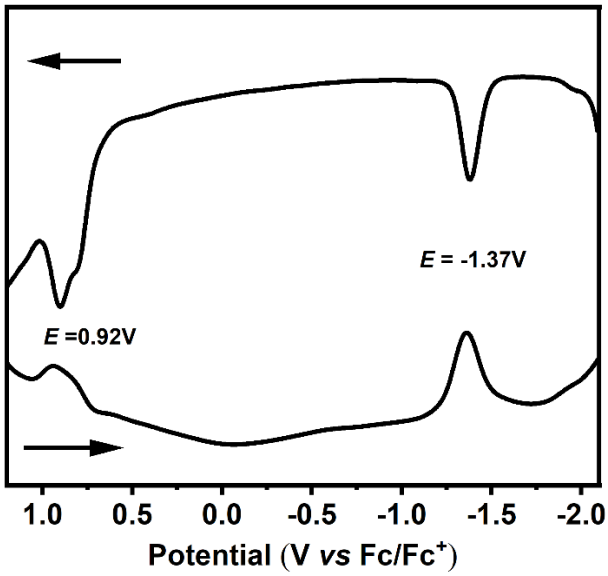


Fig. S44. DPV of compound **6a**

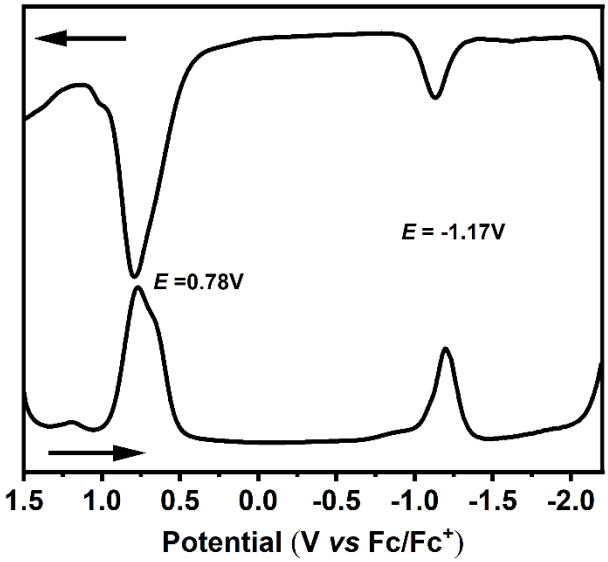


Fig. S45. DPV of compound **6b**

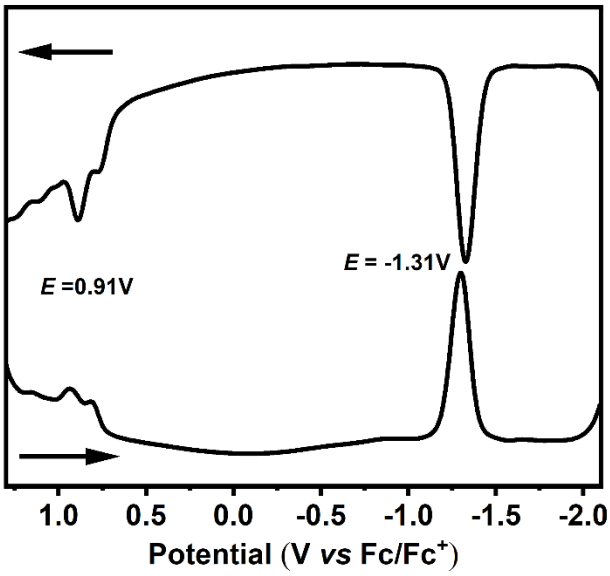


Fig. S46. DPV of compound **6c**

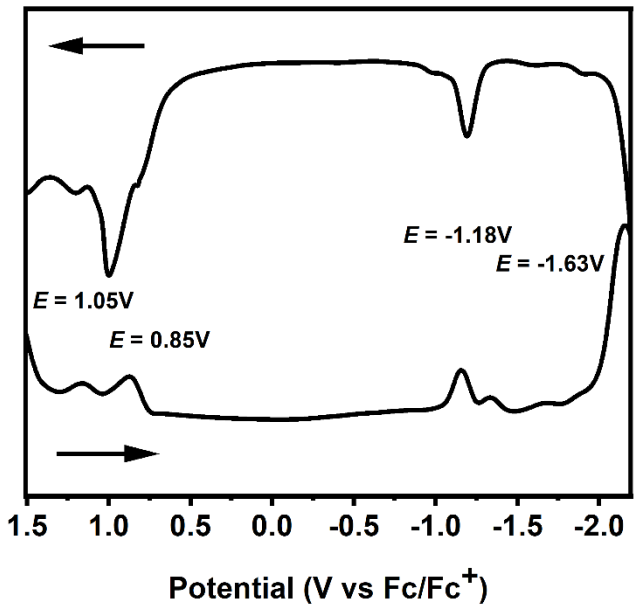


Fig. S47. DPV of compound **6d**