

Electronic Supplementary Information

Bis(naphthobipyrrolyl)methene derived Hexapyrrolic BODIPY as a Single Molecule Helicate with Near Infrared Emission

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Content

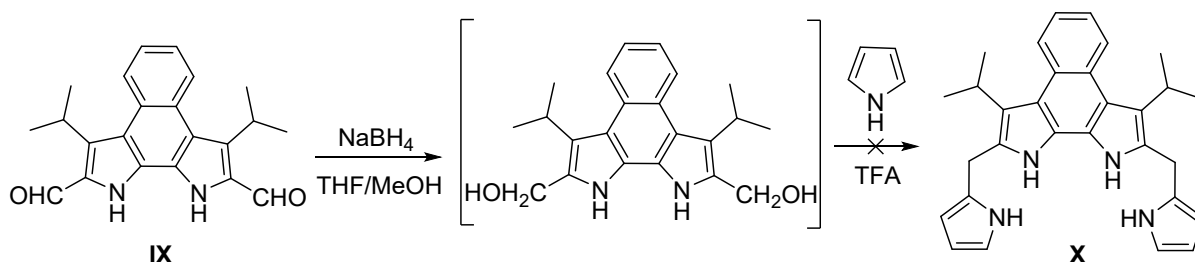
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1. Instrumentation and reagents:

NMR spectra were recorded on a Bruker Ascend-500 and Bruker Avance-500 MHz FT NMR spectrometer using tetramethylsilane (TMS, $\delta = 0$) as an internal standard at room temperature. Mass spectral determinations were carried out by Bruker Maxis HRMS by ESI techniques. UV Visible-NIR spectra were recorded on a Perkin Elmer Lambda 35 UV-Visible spectrometer. Fluorescence spectra were recorded on a JASCO FP-8500 spectrofluorometer. The standard approach of time-correlated single-photon counting (TCSPC) was used to study time resolved photoluminescence (TRPL). Using a picosecond pulsed diode laser with an output of 670 nm, TCSPC experiments were carried out. Dilute Ludox solution, a light scattering solution was used to measure the instrument response function (IRF). To estimate emission lifetimes, TRPL curves were fitted by mono-exponential fitting parameters using the deconvolution method accompanying with the IRF. The residual calculations (χ^2) were used to estimate the fit's reliability. Spectroscopic grade solvents were used for all optical measurements. Commercially available solvents were distilled before use. Reagents were used as received. Cyclic voltammetric (CV) and differential pulse voltammetric (DPV) measurements were done using a Zahner Zennium Electrochemical Workstation, and electrodes were purchased from CH Instruments Inc. All measurements were done in dichloromethane under the flow of nitrogen, and 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF₆) used as a supporting electrolyte, glassy carbon as a working electrode, platinum wire as counter electrode, and Ag/AgCl as a reference electrode were used. Ferrocenium/Ferrocene, Fc⁺/Fc, couple was used as an external reference for calibration. All cyclic voltammetric data were recorded at a 100 mV/s scan rate.

All crystallographic data were collected in Rigaku XtaLAB Synergy, single source X-ray diffractometer. Mo-K α ($\lambda = 0.71073$ Å) radiation was used to collect the X-ray reflections of the crystal. Data reduction was performed using CrysAlisPro 1.171.40.35a.^{S1} Intensities for absorption were corrected using CrysAlisPro 1.171.40.35a.^{S1} and refined using SHELXL2018/3.^{S2a,S2b} with anisotropic displacement parameters for non-H atoms. Crystallographic data (including the structure factor) for all structures in this paper have been deposited in the Cambridge Crystal Crystallographic Data Centre as supplementary publication number 2262189-2262190.

2. Experimental Procedures:



Scheme S1. Attempted synthesis of tetrapyrrole.

Synthesis of 1

IV (200 mg, 0.69 mmol, 1 eq) and **V** (247 mg, 1.03 mmol, 1.5 eq) were taken in two necked RB fitted with a condenser. Then degassed isopropanol was added to it under N₂ atmosphere. After dissolving the compounds, POCl₃ (63 μ L, 0.6 mmol, 1 eq) was added and refluxed for 4-5 h. Then it was cooled to room temperature and quenched with excess triethyl amine. Precipitate formed was filtered and washed with cold methanol. The residue was recrystallised with chloroform and methanol to obtain the desired product as pure green colour solid. Weight obtained: 88mg; Yield: 26%

¹H NMR (500 MHz, CDCl₃) δ in ppm: 12.60 (s, 2H), 11.72 (s, 2H), 11.29 (br, 2H), 8.45 (d, J = 8.03Hz, 2H), 8.35 (d, J = 8.09 Hz, 2H), 7.95 (s, 1H), 7.52 (t, J=7.22Hz, 2H), 7.45 (t, J=7.55Hz, 2H), 4.43 (s, 4H), 4.32 (m, J=6.92Hz, 6H), 3.94 (m, J=6.93Hz, 2H), 2.21 (s, 6H), 1.88 (s, 6H), 1.71 (d, J=7.07Hz, 12H), 1.63 (d, J=7.16Hz, 12H), 1.29 (t, J=7.01Hz, 6H). ¹³C NMR (125.7MHz, CDCl₃) δ in ppm: 163.3, 148.0, 137.1, 136.9, 130.8, 129.3, 126.9, 126.4, 125.9, 125.7, 125.5, 124.4, 121.5, 119.5, 118.1, 117.6, 116.9, 59.7, 27.3, 26.1, 25.2, 23.8, 22.7, 14.5, 11.0, 8.9. HRMS (ESI+): m/z calculated for C₆₁H₆₉N₆O₄ (M-Cl)⁻: 949.5380, found: 949.5383.

Synthesis of 2:

1 (10 mg, 0.01 mmol, 1 eq) was dissolved in dry toluene (7 mL) under N₂ atmosphere. After it gets dissolved, triethyl amine (46 μ L, 0.2 mmol, 20 eq) was added to it and stirred at room temperature for 15 min. To this, BF₃·OEt₂ (80 μ L, 0.6 mmol, 60 eq) was added and refluxed for 30 min. After that the reaction mixture was cooled to room temperature and washed with water to remove any salt formed. Organic layer was passed over anhyd. Na₂SO₄ and concentrated under reduced pressure. It was purified by silica gel column chromatography (EtOAc:hexane :: 1:19). Weight obtained: 6 mg; Yield: 60%

^1H NMR (500 MHz, CDCl_3) δ in ppm: 10.51 (br, 2H), 9.41 (s, 2H), 8.39 (d, $J=8.06\text{Hz}$, 2H), 8.31 (d, $J=7.88\text{Hz}$, 2H), 7.96 (s, 1H), 7.48 (t, $J=7.27\text{Hz}$, 2H), 7.44 (t, $J=7.39\text{Hz}$, 2H), 4.35 (s, 4H), 4.18 (m, $J=7.26\text{Hz}$, 6H), 3.97 (br, 2H), 2.14 (s, 6H), 1.77 (s, 6H), 1.67 (d, $J=7.07\text{Hz}$, 12H), 1.56 (d, $J=7.27\text{Hz}$, 12H), 1.24 (t, $J=7.16\text{Hz}$, 6H). ^{13}C NMR (125.8 MHz, CDCl_3) δ in ppm: 163.3, 145.1, 135.3, 135.0, 130.0, 128.7, 127.9, 127.0, 125.9, 125.6, 125.3, 124.4, 123.8, 120.5, 117.8, 117.4, 60.0, 27.4, 26.0, 25.7, 24.3, 22.5, 14.4, 10.8, 8.6. ^{19}F NMR (376.4 MHz, CDCl_3) δ in ppm: -139.97. HRMS (ESI+): m/z calculated for $\text{C}_{61}\text{H}_{67}\text{N}_6\text{O}_4\text{BF}_2$ (M^+): 996.5284, found: 996.5285.

3. Result and Discussion

3.1. NMR spectra of synthesized Compounds

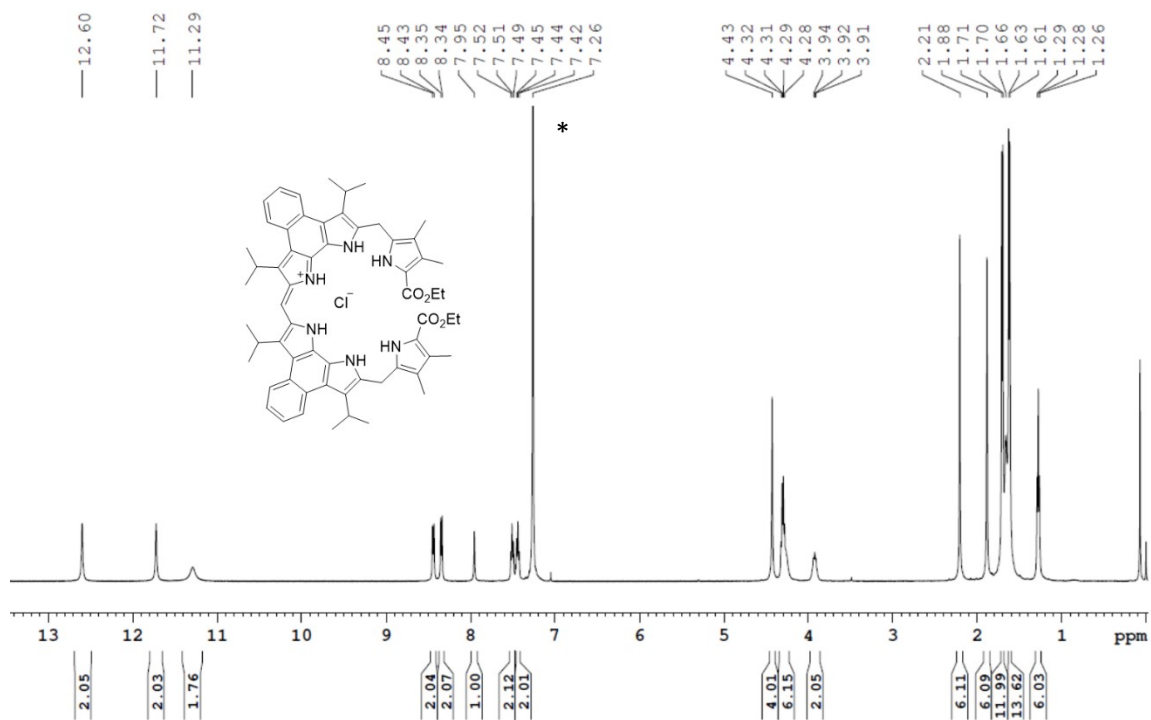


Figure S1. ^1H NMR spectrum of **1** in CDCl_3 recorded at 25 °C (*Asterisk indicates water and residual solvent impurity).

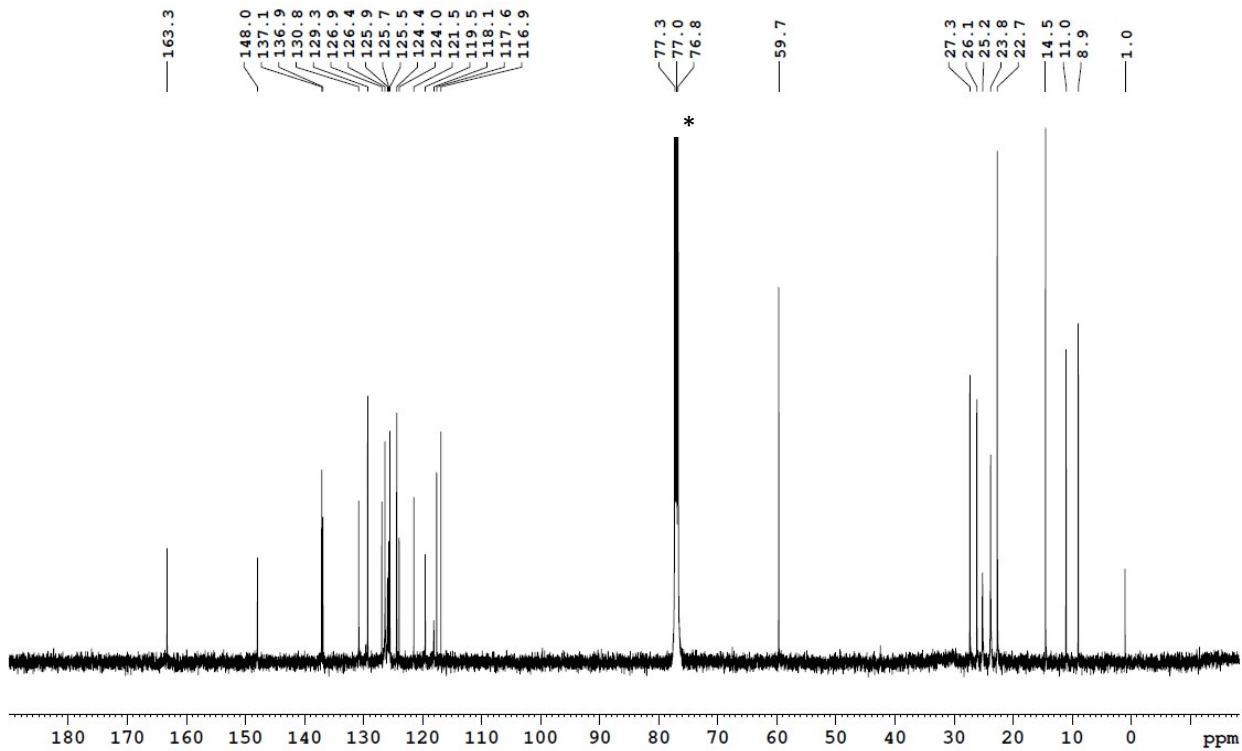


Figure S2. ^{13}C NMR spectrum of **1** in CDCl_3 in recorded at 25 °C (*Asterisk residual solvent impurity).

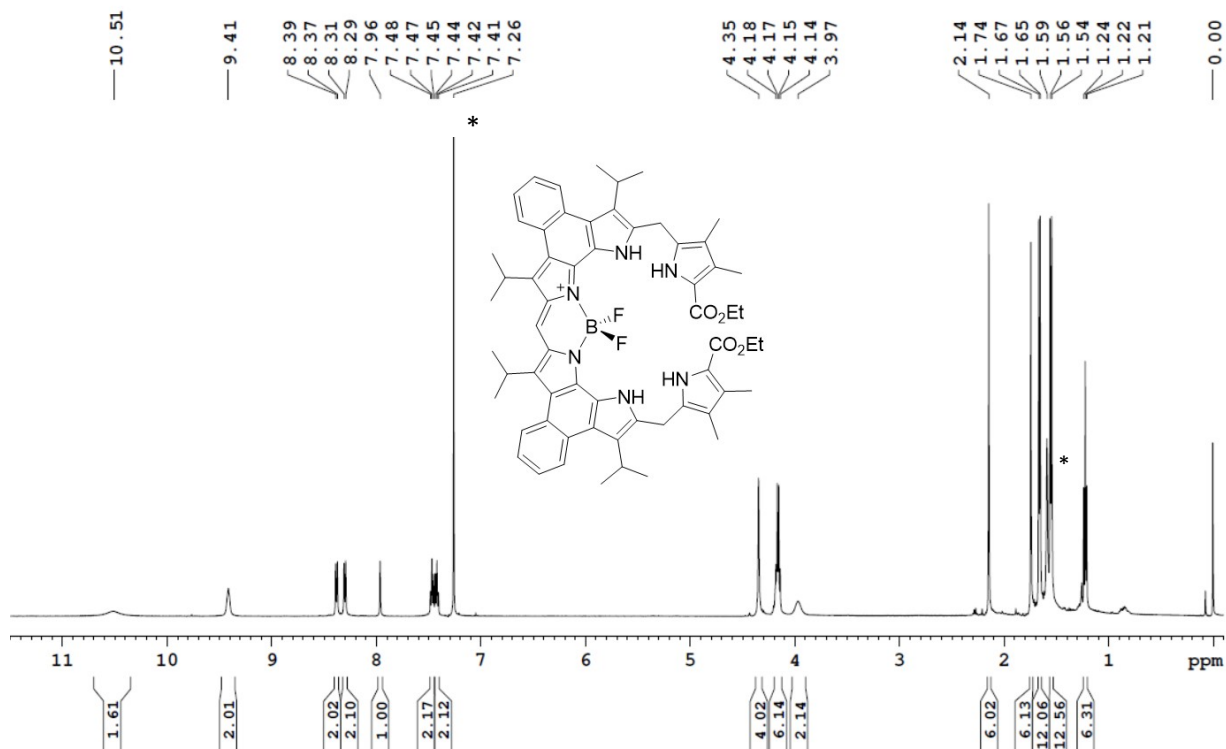


Figure S3. ^1H NMR spectrum of **2** in CDCl_3 recorded at 25 °C (*Asterisk indicates water and residual solvent impurity).

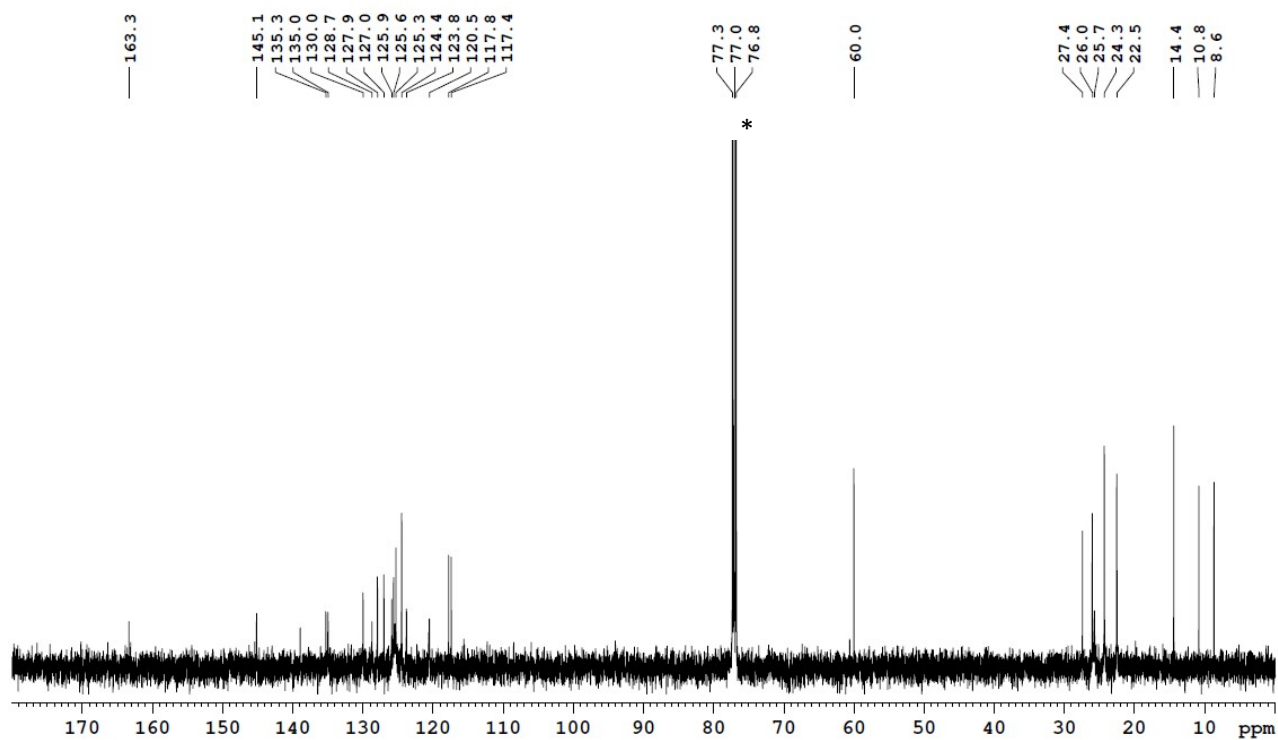


Figure S4. ^{13}C NMR spectrum of **2** in CDCl_3 recorded at 25 °C (*Asterisk indicates residual solvent impurity).

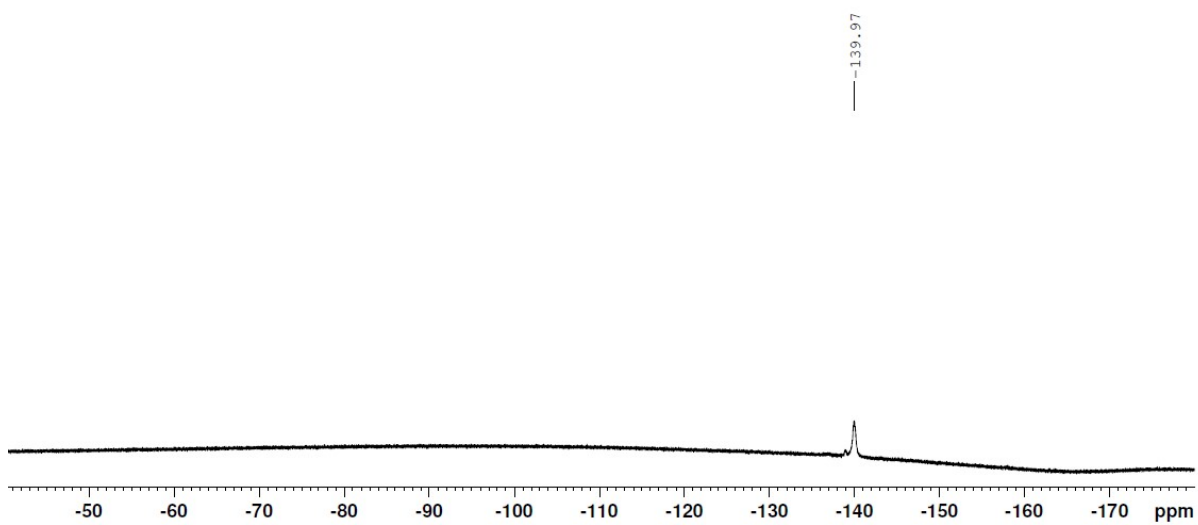


Figure S5. ^{19}F NMR spectrum of **2** in CDCl_3 recorded at 25 °C.

3.2. HRMS data

Display Report

Analysis Info

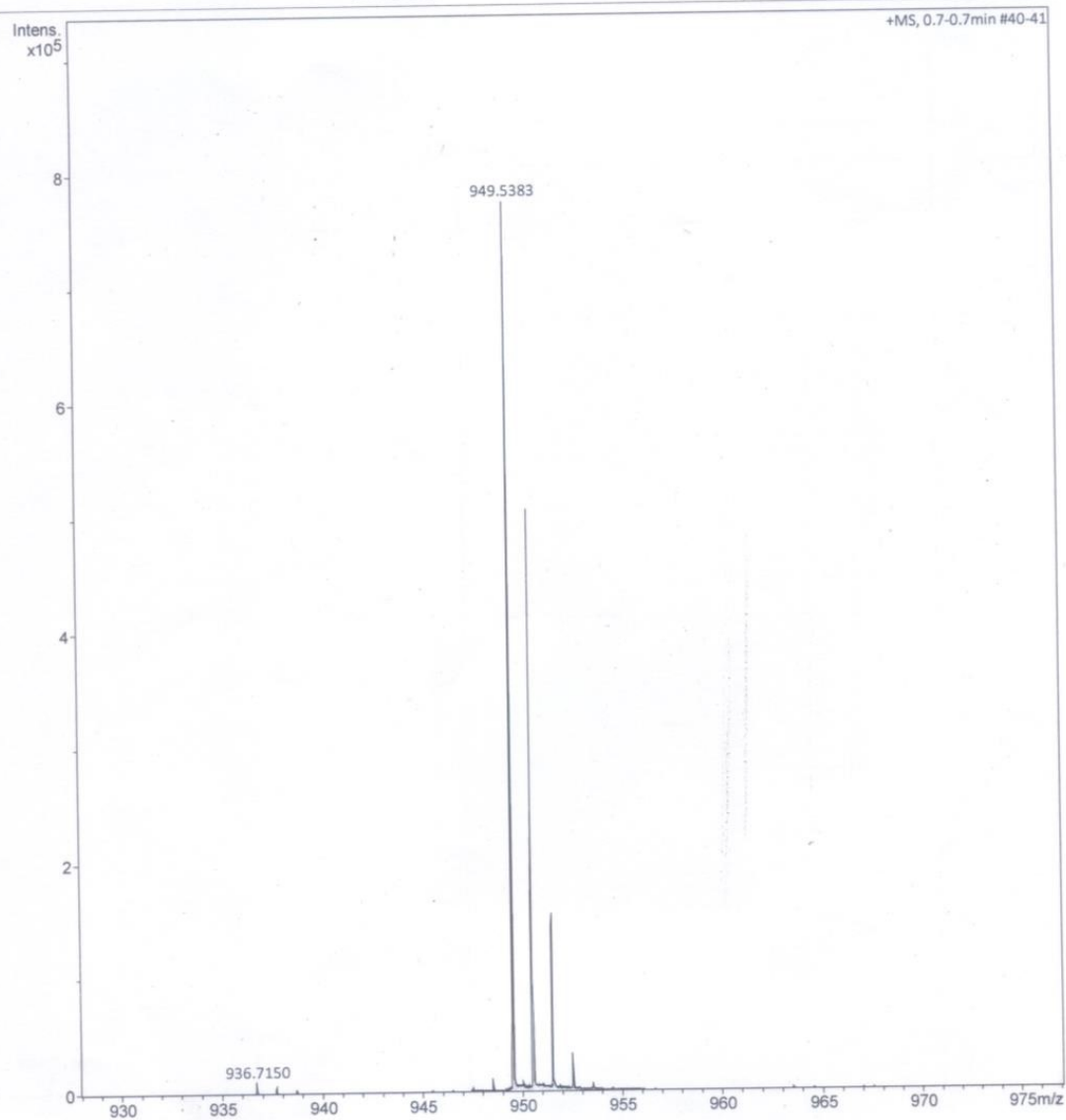
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SSS-HP-ET.d

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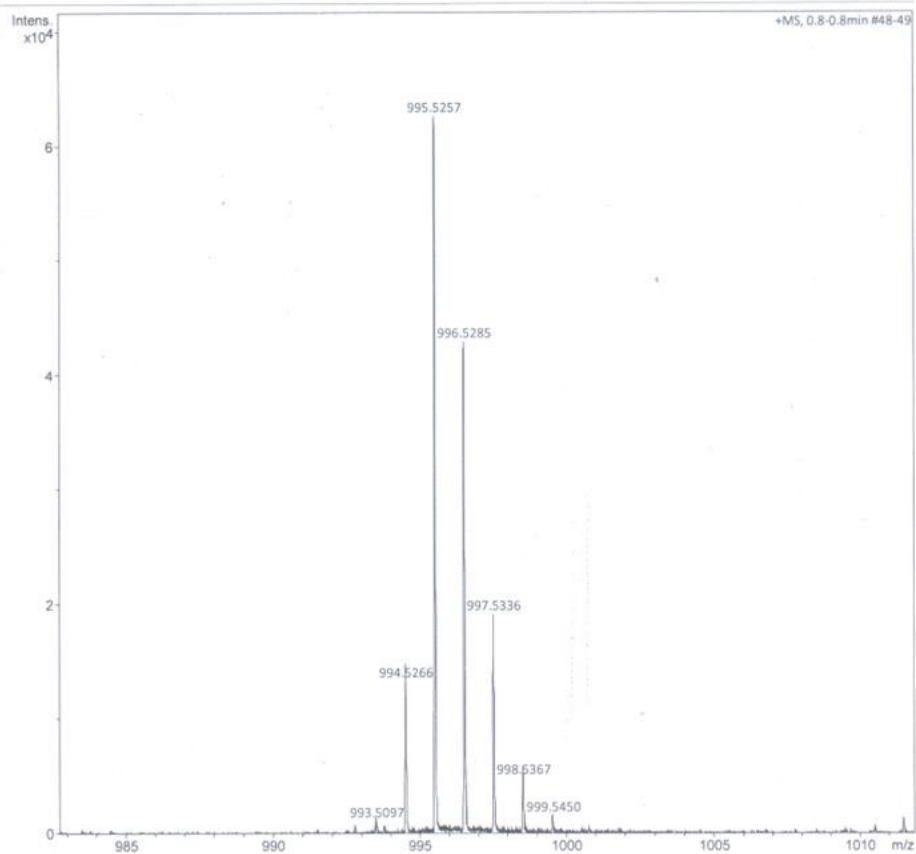
Page 1 of 1

Figure S6. HR-ESI mass spectrum of **1** (m/z calculated for C₆₁H₆₉N₆O₄ (M-Cl⁻): 949.5380, found: 949.5383).

Display Report

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SSS-57-S-1.d
Bruker Compass DataAnalysis 4.2 printed: 1/20/2022 2:51:31 PM by: BDAL Page 1 of 1

Figure S7. HR-ESI mass spectrum of **2** (m/z calculated for C₆₁H₆₇N₆O₄BF₂ (M⁺): 996.5284, found: 996.5285).

3.3. Optical Properties of 1 and 2

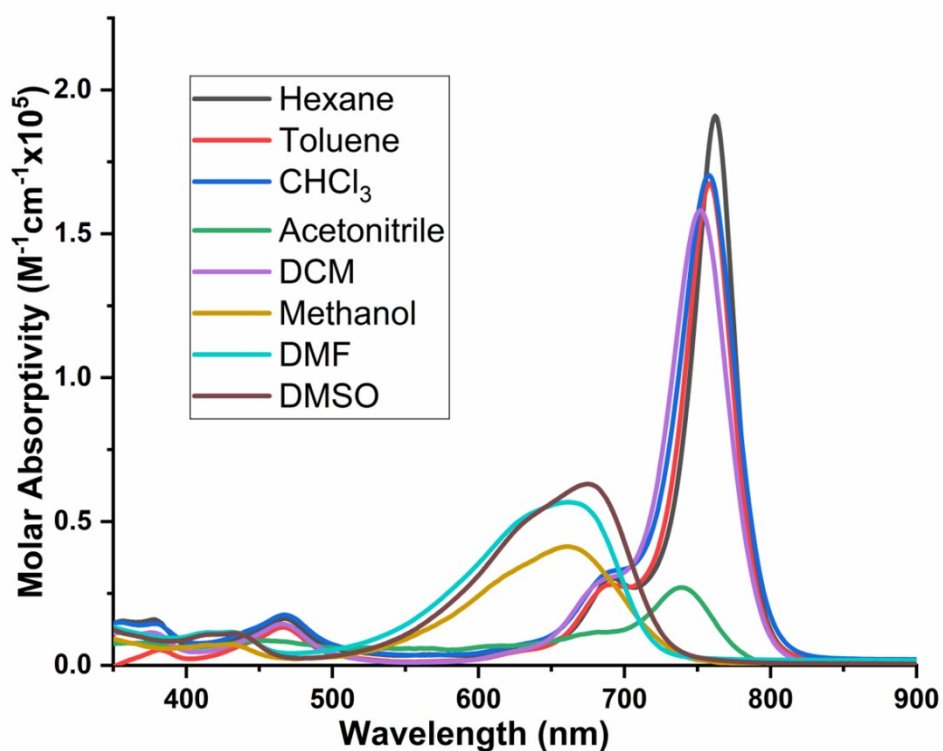


Figure S8. Absorption spectra of 1 in various solvents recorded at 25 °C.

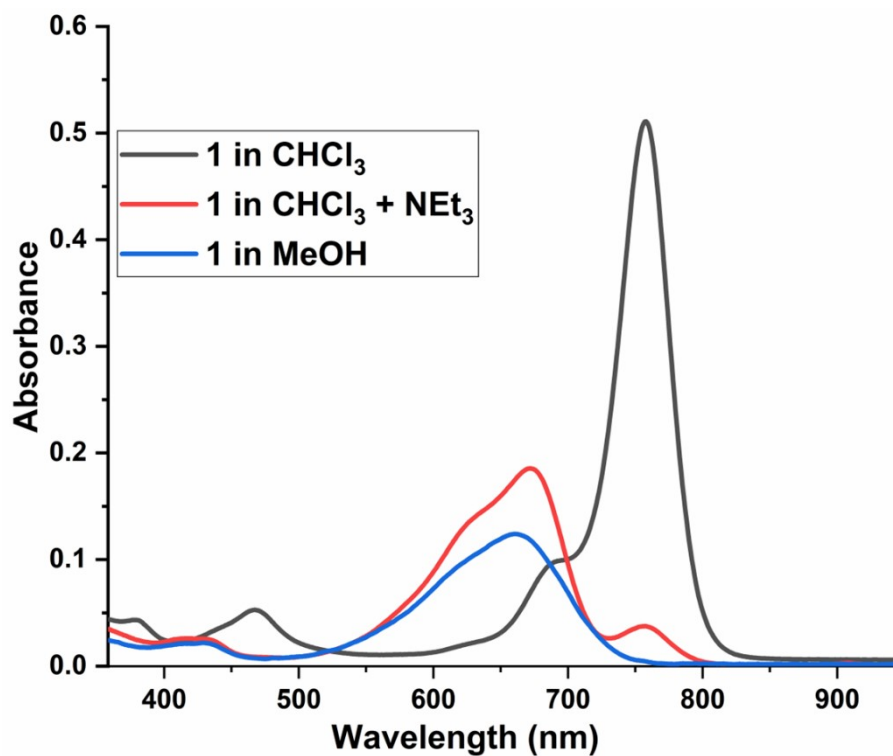
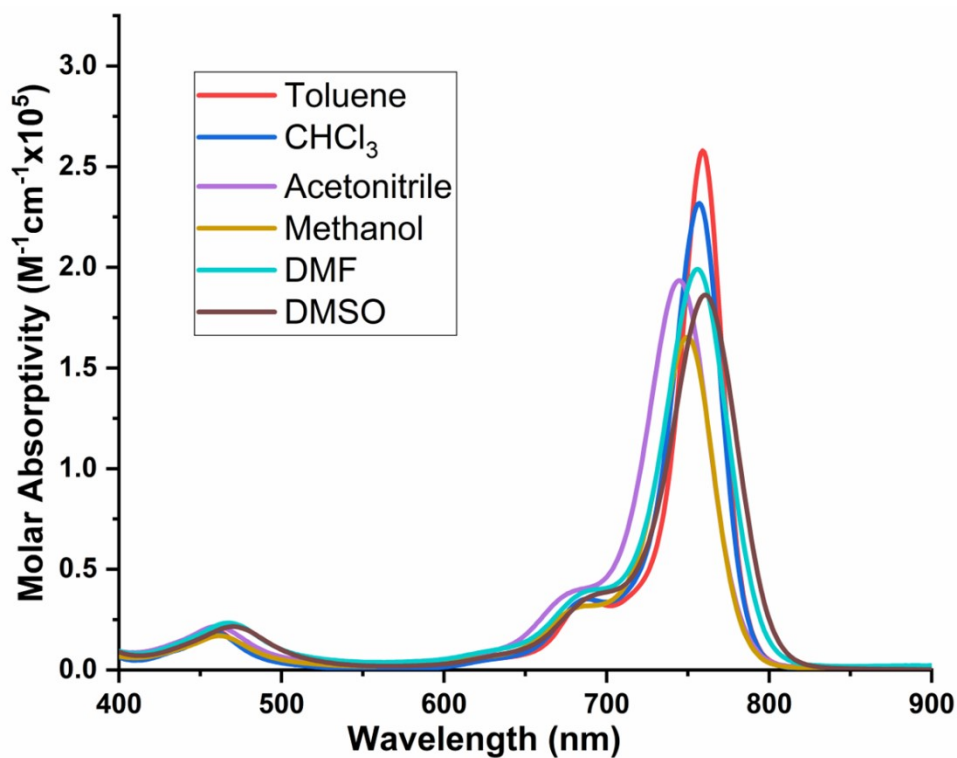


Figure S9. Absorption spectra of 1 upon deprotonation.

Table S1. Summary of absorption properties of **1**.

Sl. No	Solvent	λ_{abs} (nm)	Absorption coefficient ϵ ($\text{M}^{-1}\text{cm}^{-1} \times 10^5$)	FWHM (cm^{-1})
1	Hexane	762	1.91	623
2	Toluene	758	1.67	698
3	CHCl_3	758	1.70	808
4	DCM	752	1.58	855
5	Acetonitrile	739	0.27	1075
6	Methanol	660	0.41	2745
7	DMF	662	0.56	2788

**Figure S10.** Absorption spectra of **2** in various solvents recorded at 25°C.**Table S2.** Summary of photophysical properties of **2**.

Solvents	Absorption Properties			Emission Properties			
	λ_{abs} (nm)	Absorption Coefficient, ϵ ($\text{M}^{-1}\text{cm}^{-1} \times 10^5$)	FWHM (cm^{-1})	λ_{emi} (nm) ^a	Stokes Shift (cm^{-1})	FWHM (cm^{-1})	ϕ_f ^b
Toluene	759	2.57	541	768	155	593	0.25
CHCl_3	757	2.31	633	767	173	698	0.27
Acetonitrile	756	1.99	834	765	155	837	0.16
Methanol	745	1.93	752	766	368	750	0.21
DMF	750	1.65	845	775	430	831	0.14
DMSO	761	1.86	852	782	353	885	0.16

a: λ_{exc} = 670 nm, b: all fluorescence quantum yields are measured with respect to **VIII** as standard.

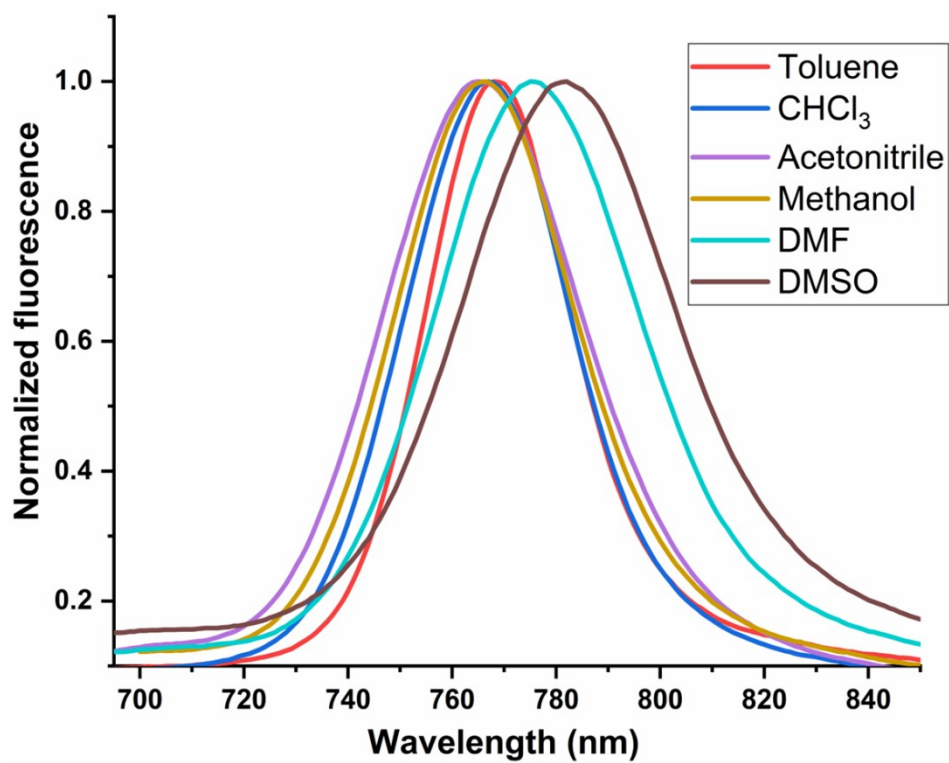


Figure S11. Emission spectra of **2** in various solvents recorded at 25°C ($\lambda_{\text{exc}}=670$ nm).

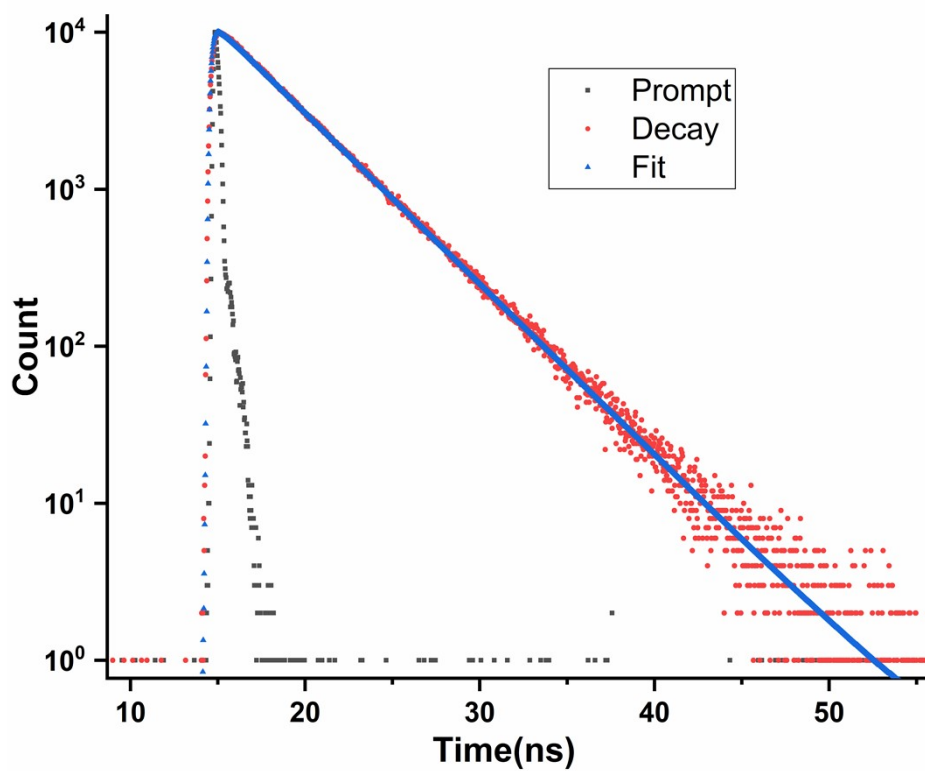


Figure S12. Fluorescence decay profile of **2** in chloroform ($\lambda_{\text{exc}}=670$ nm).

3.4. Electrochemical Analysis

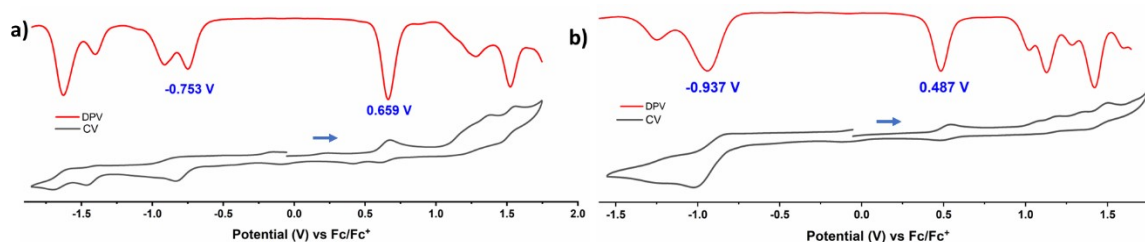


Figure S13. Cyclic voltammogram and differential pulse voltammogram of a) **1** and b) **2** recorded in dichloromethane solution.

Table S3. Oxidation potential (E_{ox}^1) and Reduction potential (E_{red}^1) vs Fc/Fc+ in V and electrochemical HOMO-LUMO gaps (ΔE) of **1** and **2** in dichloromethane.

Compound	E_{ox}^1	E_{red}^1	ΔE (eV)
1	0.659	-0.753	1.41
2	0.487	-0.937	1.42

Note: scan rate: 100 mV s^{-1} ; 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF₆) used as a supporting electrolyte, glassy carbon as a working electrode, platinum wire as counter electrode, and Ag/AgCl as a reference electrode were used.

4. Crystal structure diagrams

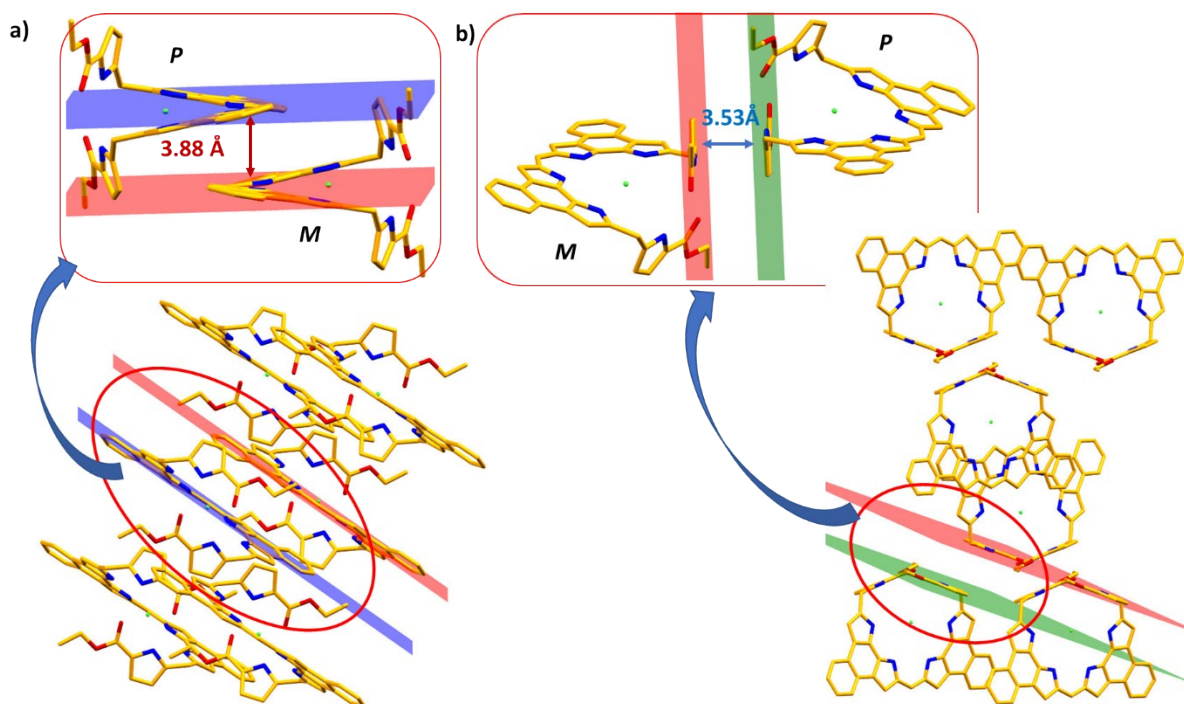


Figure S14. Crystal packing of **1** along a) c-axis and b) b- axis showing π - π stacking.

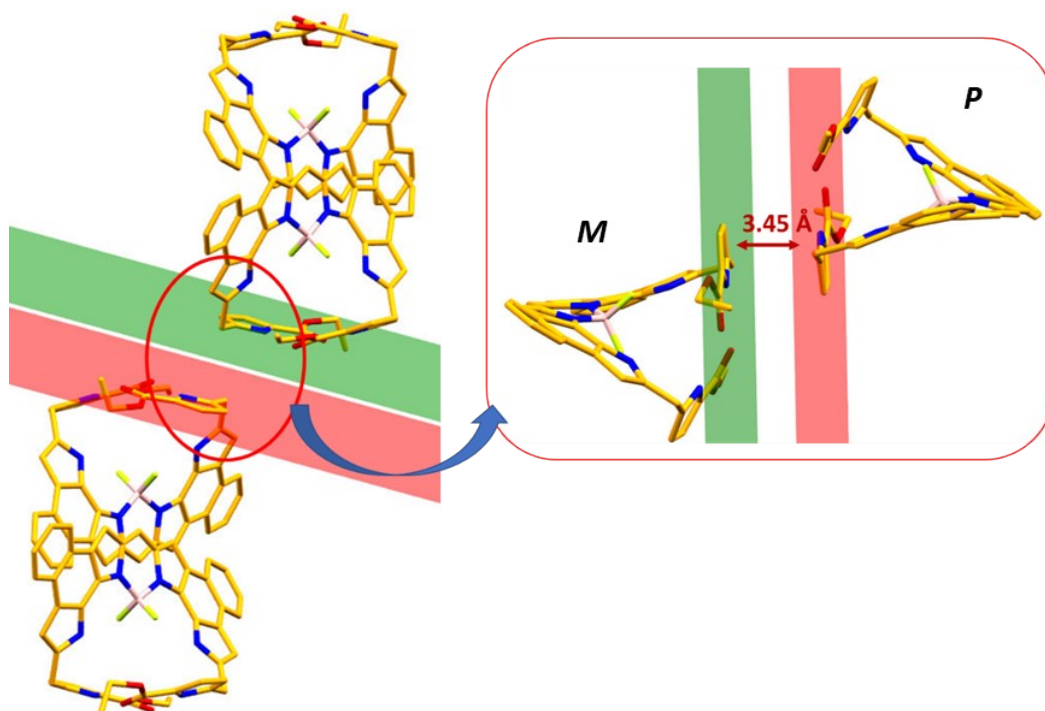


Figure S15. Crystal packing of **2** along c-axis showing π - π stacking.

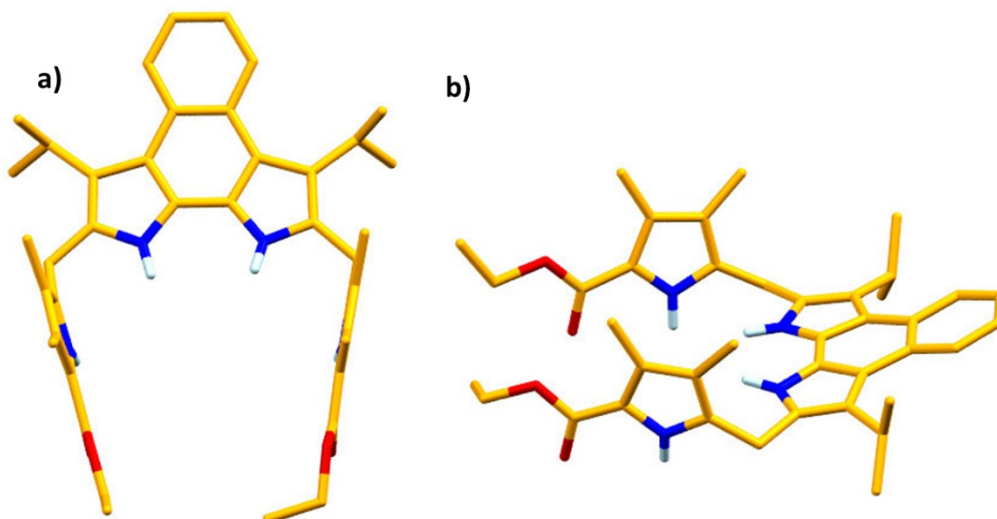


Figure S16. Crystal structure of **VI**: a) front view; b) side view.

5. Computational studies

All quantum mechanical calculations are performed by Gaussian 09 programme^{S3} provided by CMSD facility at University of Hyderabad. Ground state optimisation has been performed by density functional theory (DFT) using Becke's three-parameter hybrid exchange functional and the Lee-Yang-Parr correlation functional (B3LYP) employing 6-31G+(D,P) basis set. The molecular orbitals were visualized using Gauss view 5.

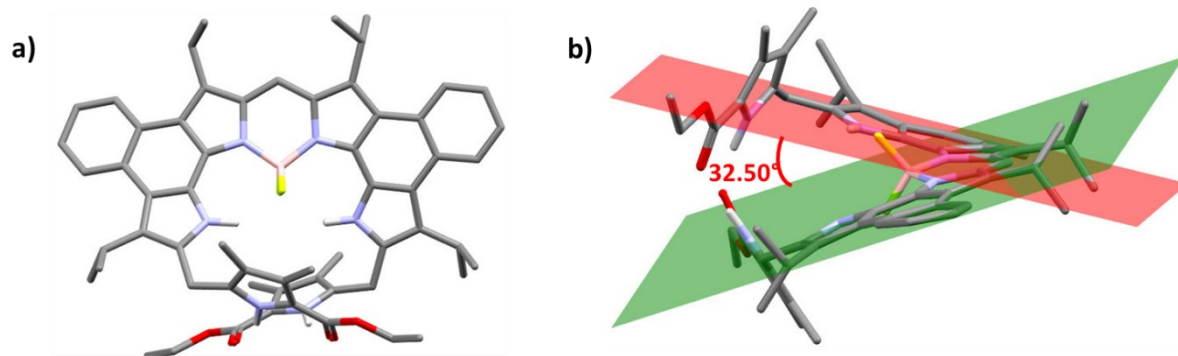


Figure S17. Optimized geometry of **2** in gas phase calculated by DFT/B3LYP method and 6-31G(D,P) basis set: a) front view; b) side view showing dihedral angle between naphthobipyrrolic units.

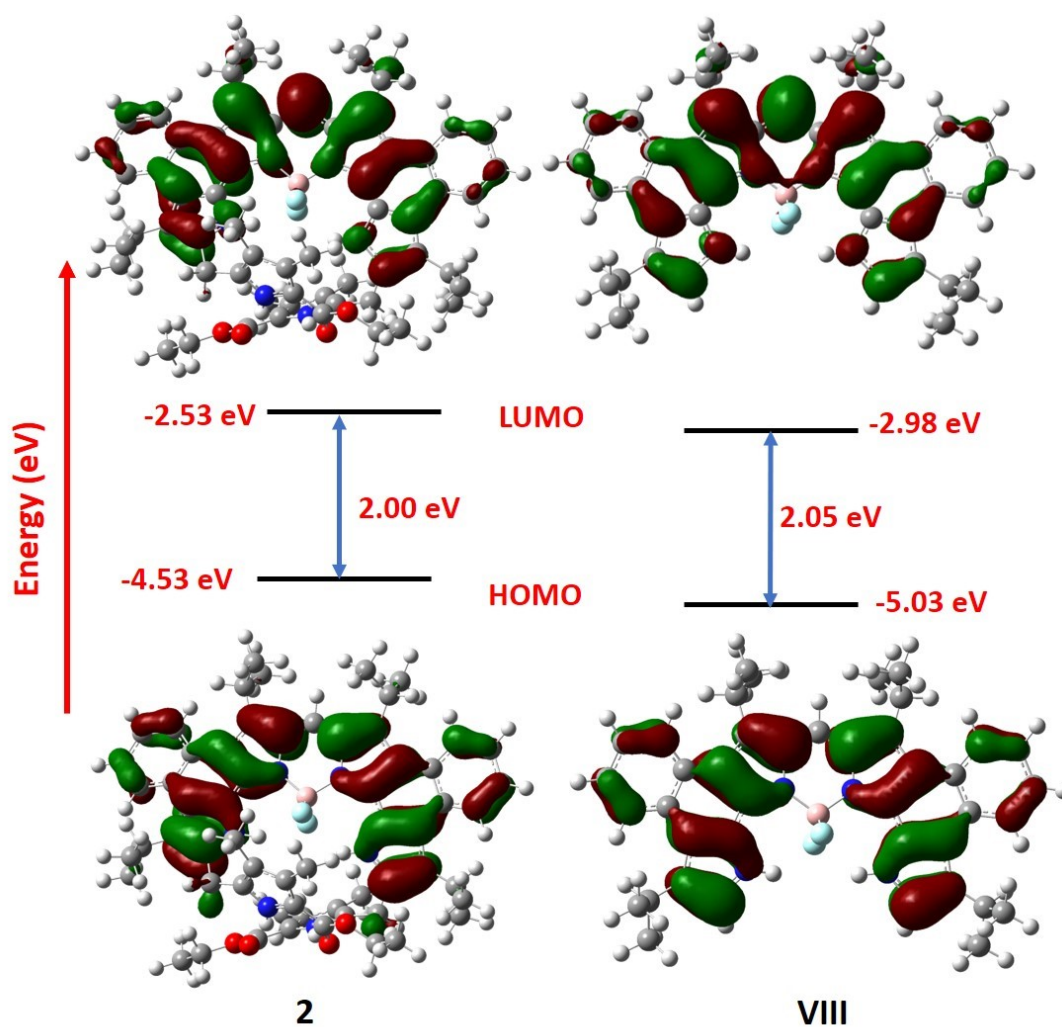


Figure S18. Frontier orbital diagram of **2** and **VIII** showing HOMO-LUMO.

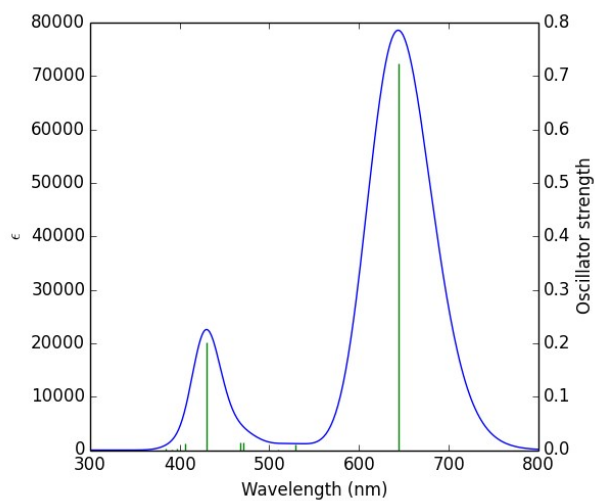


Figure S19. Theoretical absorption spectrum of **2**.

Table S4. Orbital contribution of computed possible transitions of **2** in gas phase.

Sl. No.	Wavelength (nm)	Oscillation strength	Major contribution
1	644	0.72	HOMO→LUMO (100%)
2	430	0.20	HOMO-5 →LUMO (87%)

6. Reference

1. CrysAlisPRO, Oxford Diffraction /Agilent Technologies UK Ltd, Yarnton, England.
2. a) SHELXL -Version 2014/7; Program for the Solution and Refine-ment of Crystal Structures, University of Göttingen, Germany, 1993-2014; b) Sheldrick, G. M. A short history of SHELX. *Acta Cryst.* **2008**, A64, 112.
3. Gaussian 09, (Revision C.01), M. J. Frisch et al. Gaussian, Inc., Wallingford CT, **2010**.