Electronic Supplementary Material (ESI) for ChemComm.

Supplementary Information for:

Quinoxaline-fused octaphyrin(2.0.0.0.2.0.0.0). A rudimentary chemosensor

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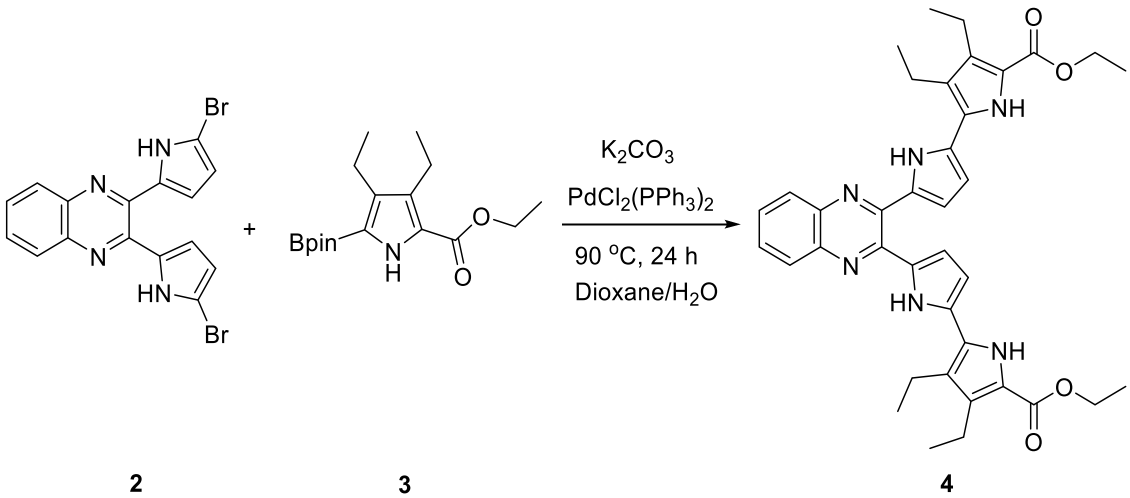
Contents

I. Synthetic Experimental

General

All reagents and solvents were purchased from commercial suppliers and used without further purification. Analytical thin-layer chromatography (TLC) was performed using commercial pre-coated silica gel plates containing a fluorescent indicator. Column chromatography was carried out using silica gel (0.040-0.063 mm). ^{1}H NMR, ^{13}C NMR, and ^{19}F NMR spectra were recorded on Bruker AV400 and AV600 instruments. UV-Vis spectra were measured on a Varian Cary 5000 spectrophotometer. Mass spectra (MS) were taken on LTQ Orbitrap Elite (ESI) or Bruker (Autoflex Speed) matrix-assisted laser desorption ionization time-of-flight mass spectrometry (MALDI-TOF MS). X-ray crystallographic analyses were carried out on Bruker X8 APEX II instruments. Further details of the structures and their refinement are given in a later section.



2 **3** **4**

Scheme S1. Synthesis of compound **5**.

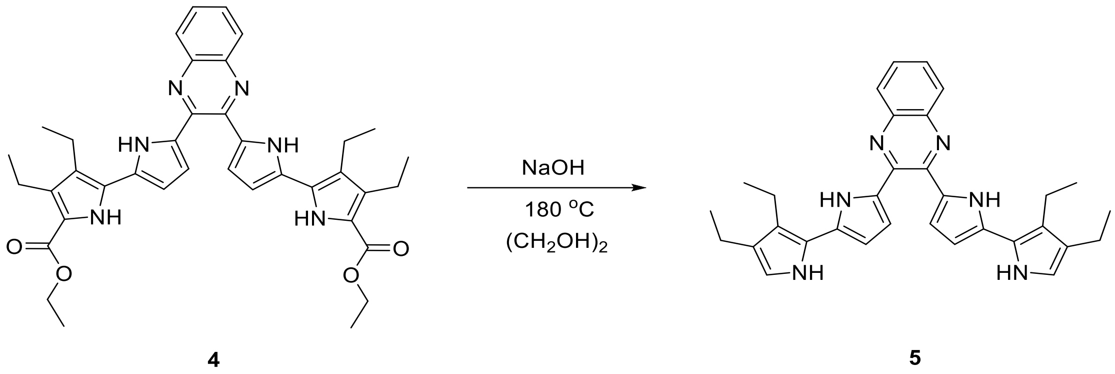
Compound **4**

Compound **2** was prepared using Sessler's method[S1] and compound **3** was made according to a reported procedure.[S2] To a 50 mL round bottom flask equipped with a stirring bar and septum was charged compound **2** (209 mg, 0.5 mmol), **3** (642 mg， 2 mmol), K_2CO_3 (207.3 mg, 1.5 mmol) and $Pd(PPh_3)_2Cl_2$ (17.5 mg, 0.025 mmol). The flask was purged with N_2 for 15 min before 25 mL of a 1,4-dioxane-H_2O mixture (4:1 v/v) was injected. The reaction mixture was then allowed to proceed for 24 h at 90 °C. When the reaction was deemed complete, the mixture was cooled to r. t. and washed with water. The organic layer was extracted with dichloromethane (DCM) and evaporated to dryness. The resulting yellowish oil was then passed through a silica gel column using petroleum ether/ethyl acetate (6:1) as the eluent. This gave compound **4** (120 mg) in 37% yield.

MS (ESI, $[M+1]^+$) Calculated for $C_{38}H_{43}N_6O_4$: 647.330. Found: 647.331.

^{1}H NMR (400 MHz, DMSO-d_6) δ 12.02 (s, 2H), 11.65 (s, 2H), 8.03 (dd, *J* = 6.3, 3.4 Hz, 2H), 7.73 (dd, *J* = 6.3, 3.5 Hz, 2H), 6.59 (s, 2H), 6.49 (s, 2H), 4.29 (q, *J* = 7.1 Hz, 4H), 2.70 (d, *J* = 7.5 Hz, 4H), 2.62 (d, *J* = 7.6 Hz, 4H), 1.31 (t, *J* = 7.1 Hz, 6H), 1.11 (dd, *J* = 7.4, 5.7 Hz, 12H).

^{13}C NMR (100 MHz, DMSO-d_6) δ 161.3, 144.6, 139.4, 133.5, 129.7, 129.5, 128.4, 127.5, 125.5, 123.6, 117.5, 114.7, 108.6, 59.7, 18.0, 17.8, 16.5, 15.5, 14.9.



Scheme S2. Synthesis of compound **6**.

Compound **5**

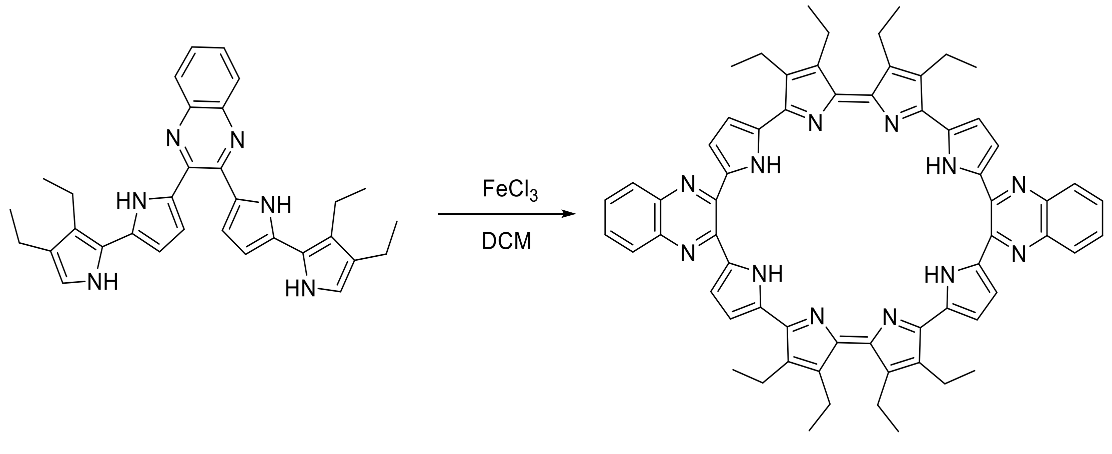
To a 100 mL round bottom flask containing **4** (2.9 g, 4.5 mmol) and NaOH (1.8 g, 45 mmol) was injected 30 mL ethylene glycol before being purged with N_2 for 15 min. The well-sealed flask was quickly heated to 180 °C and the reaction mixture was held at this temperature for 0.5 h. It was cooled to r.t. and 50 mL water were added to the flask and the mixture was cooled in a fridge for 3 h. The product (2.1 g) was collected as an orange solid by filtration in 95%.

MS (ESI, $[M+1]^+$) Calculated for $C_{32}H_{35}N_6$: 503.287. Found: 503.289.

^{1}H NMR (400 MHz, CDCl$_3$) δ 10.22 (s, 2H), 8.02 (s, 2H), 7.74 (dt, *J* = 6.5, 3.3 Hz, 2H), 7.45 (dd, *J* = 6.3, 3.4 Hz, 2H), 7.18 (d, *J* = 3.7 Hz, 2H), 6.53 (t, *J* = 8.4 Hz, 2H), 6.31 (d, *J* = 3.6 Hz, 2H), 2.70

(q, *J* = 7.5 Hz, 4H), 2.53 (q, *J* = 7.5 Hz, 4H), 1.26 (td, *J* = 7.5, 4.3 Hz, 12H).

^{13}C NMR (100 MHz, CDCl$_3$) δ 143.6, 139.5, 129.7, 128.7, 128.2, 127.3, 126.3, 122.0, 120.8, 115.0, 114.9, 107.0, 18.3, 18.0, 15.7, 14.6.



5 **1**

Scheme S3. Synthesis of compound **1**.

Compound **1**

To a 100 mL round bottom flask containing **5** (100 mg, 0.2 mmol) in 50 mL DCM was charged FeCl$_3$ (324.2 mg, 2 mmol). The reaction mixture was stirred for another 0.5 h before 10 mL water were added. The organic layer was extracted with DCM and evaporated. Column chromatography eluted with petroleum ether/DCM (2:1) provided the product as dark blue solid. Yield: 23%.

MS (ESI, [M+1]$^+$) Calculated for $C_{64}H_{61}N_{12}$: 997.514. Found: 997.522. HRMS (ESI, [M+1]$^+$) Calculated for $C_{64}H_{61}N_{12}$: 997.5142. Found: 997.5276.

^{1}H NMR (400 MHz, CDCl$_3$) δ 8.02 (dd, *J* = 6.4, 3.4 Hz, 2H), 7.74 (d, *J* = 4.1 Hz, 2H), 7.68 (dd, *J* = 6.4, 3.4 Hz, 2H), δ 7.28 (s, 2H). 3.01-2.74 (m, 6H), 2.51 (dd, *J* = 13.9, 7.5 Hz, 2H), 1.36 (t, *J* = 7.5 Hz, 6H), 0.94 (t, *J* = 7.5 Hz, 6H).

^{13}C NMR (100 MHz, CDCl$_3$) δ 155.15, 148.4, 145.0, 141.8, 140.3, 140.2, 133.6, 129.7, 128.9, 121.8, 120.3, 20.0, 18.5, 15.5.

II. NMR Spectral Studies

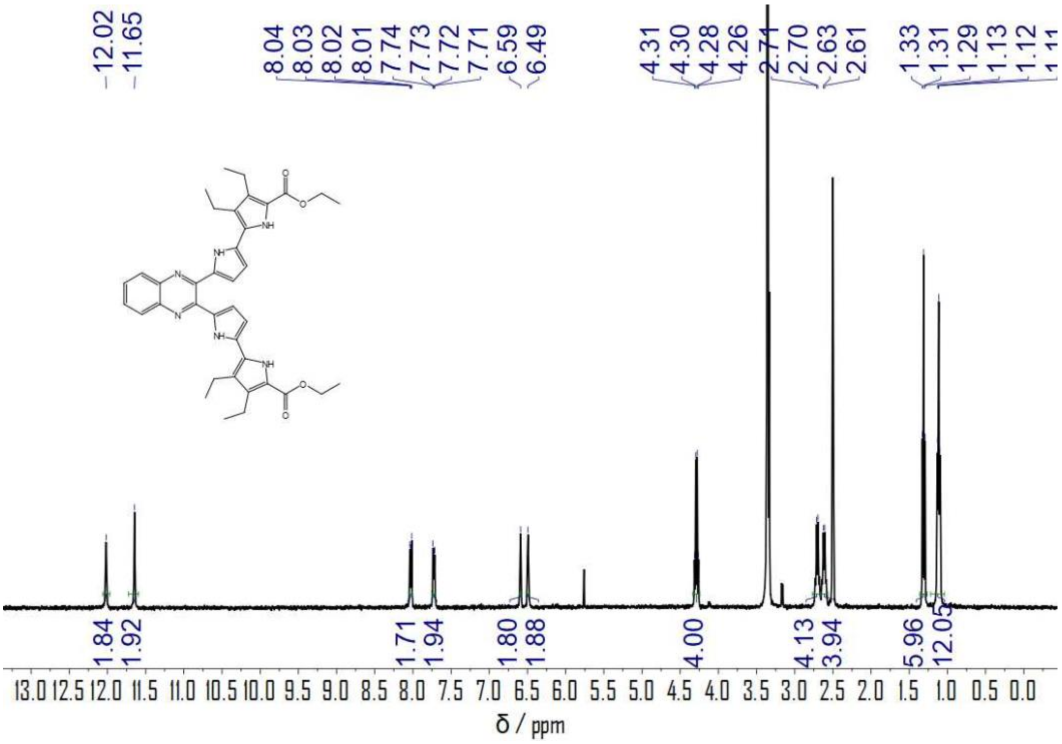


Figure S1. ^{1}H NMR spectrum of **4** recorded in DMSO-d_6 at rt.

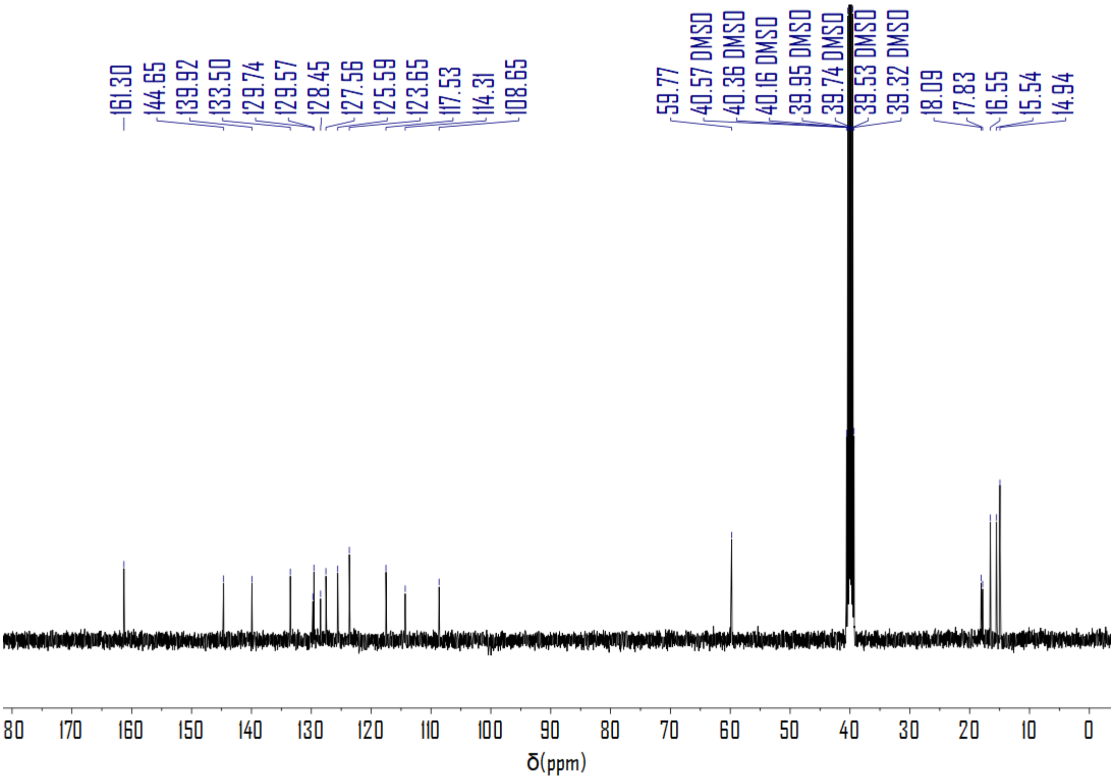


Figure S2. ^{13}C NMR spectrum of **4** recorded in DMSO-d_6 at rt.

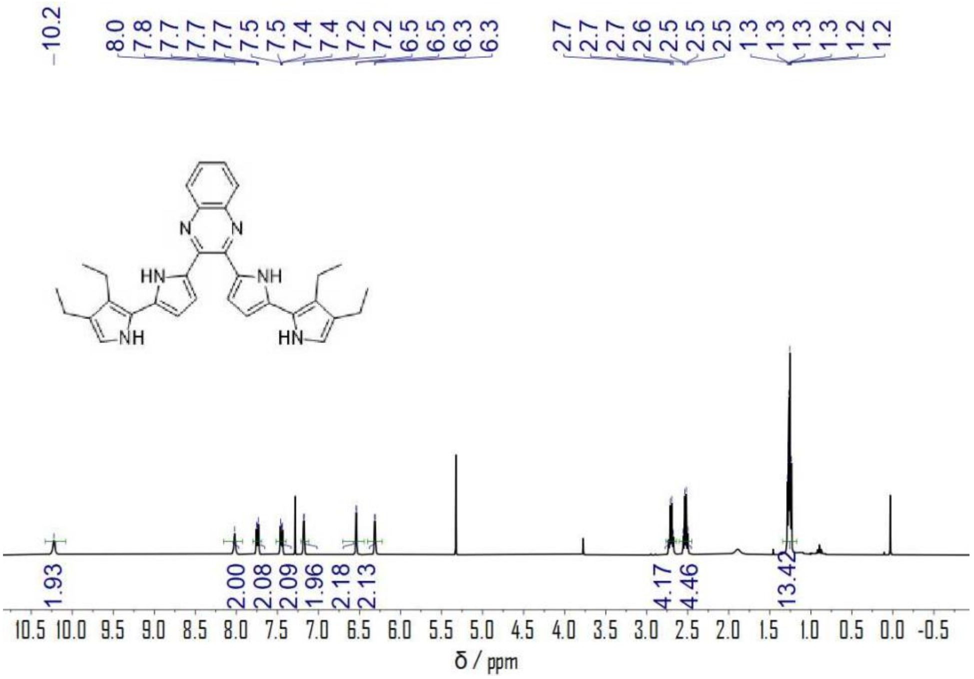


Figure S3. ^1H NMR spectrum of **5** recorded in $CDCl_3$ at rt.

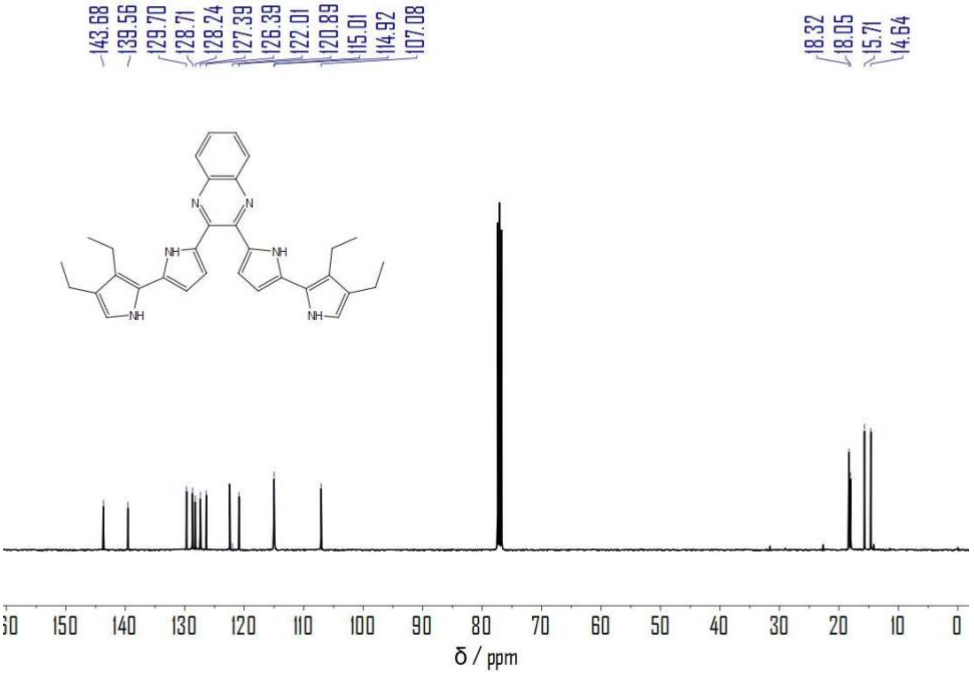
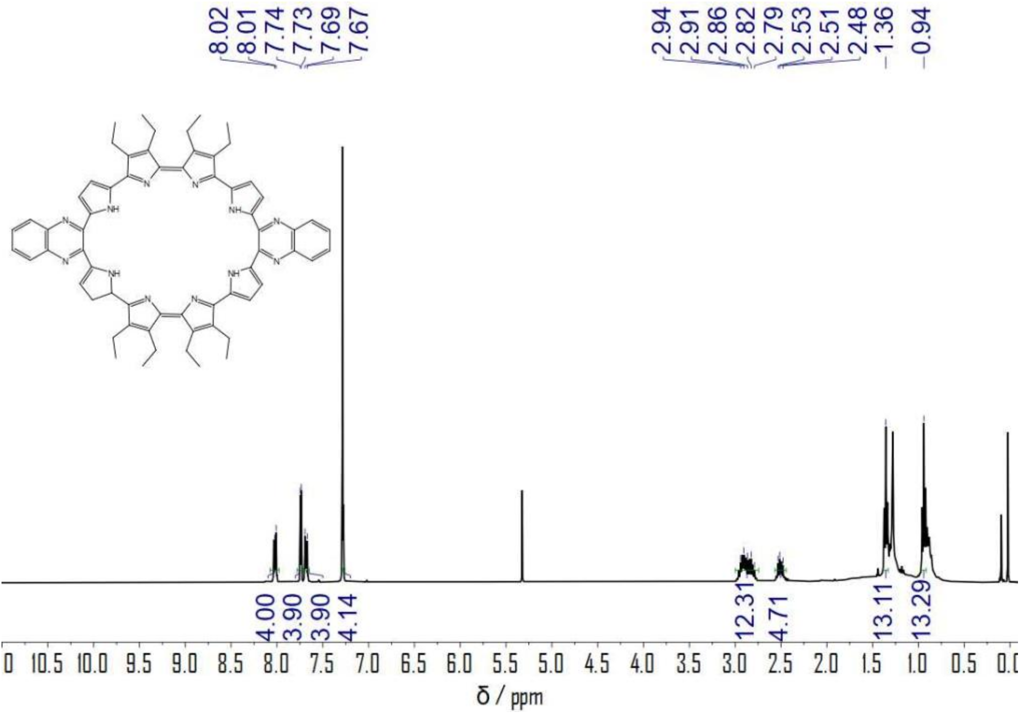


Figure S4. ^{13}C NMR spectrum of **5** recorded in $CDCl_3$ at



rt.

Figure S5. ^{1}H NMR spectrum of **1** recorded in $CDCl_3$ at rt.

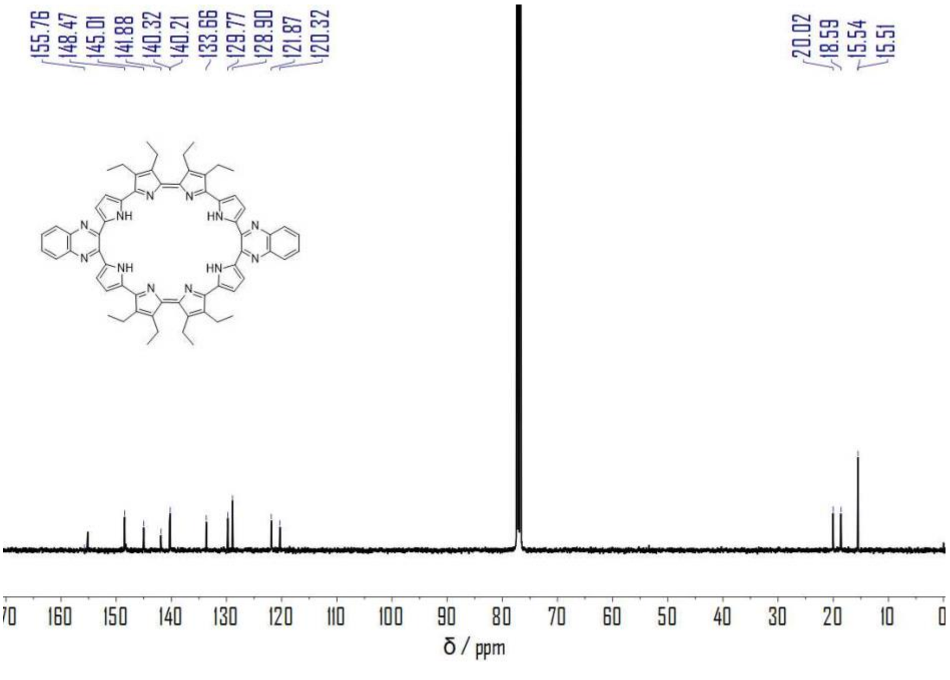
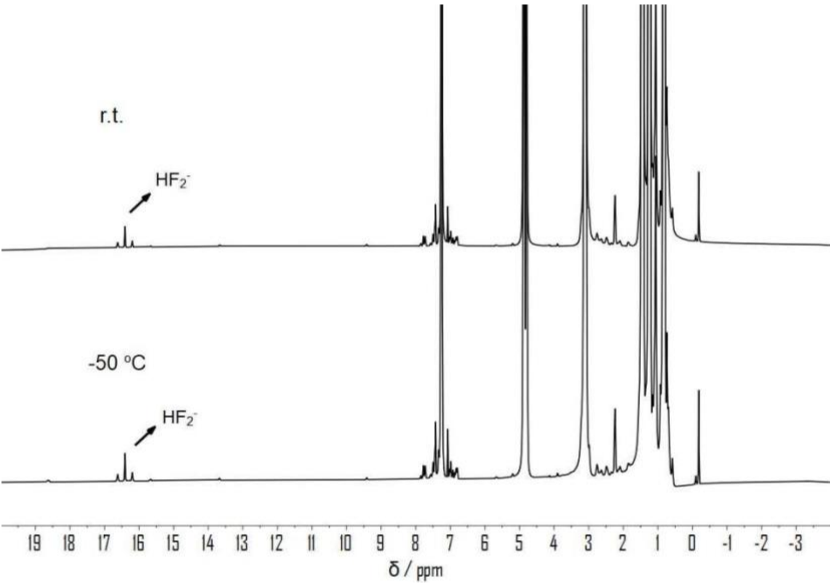


Figure S6. ^{13}C NMR spectrum of **1** recorded in $CDCl_3$ at



rt.

Figure S7. VT ^{1}H NMR spectra of **1** recorded in the presence of 10 equivalents of TBAF in CDCl$_3$.

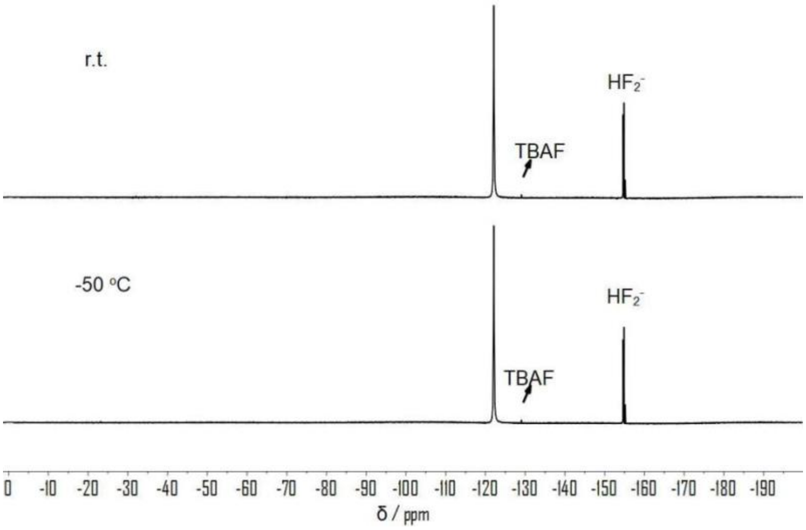


Figure S8. VT ^{19}F NMR spectra of **1** recorded in the presence of 10 equivalents of TBAF in CDCl$_3$.

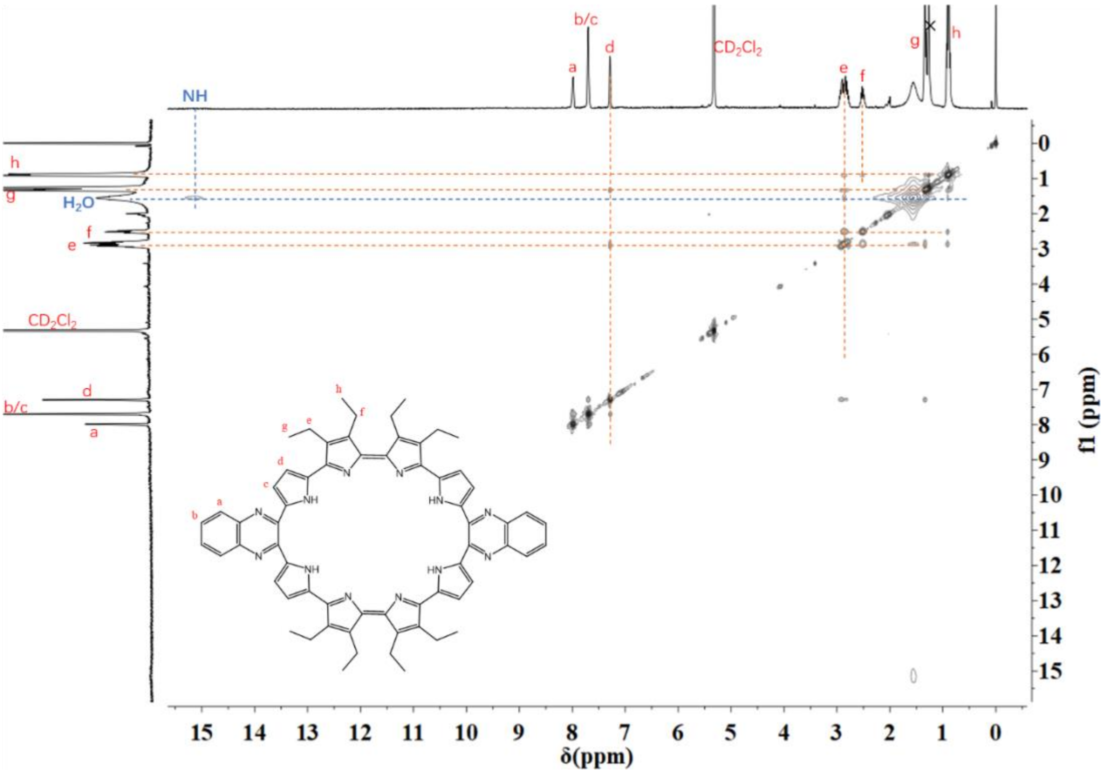


Figure S9. NOESY spectrum of **1** recorded in CD$_2$Cl$_2$.

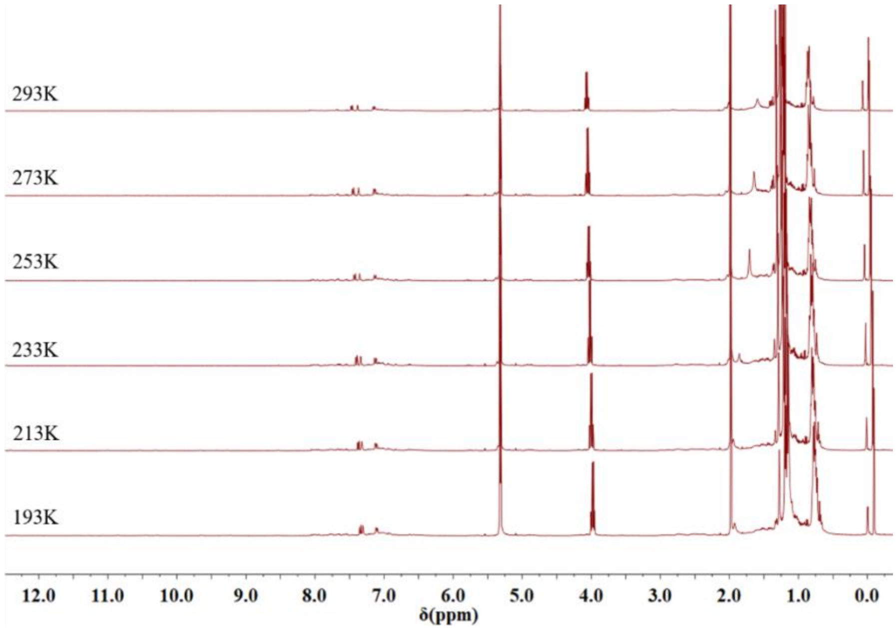


Figure S10. VT ^{1}H NMR spectra of **1** recorded in CD$_2$Cl$_2$.

IX. UV-Vis Spectral Studies

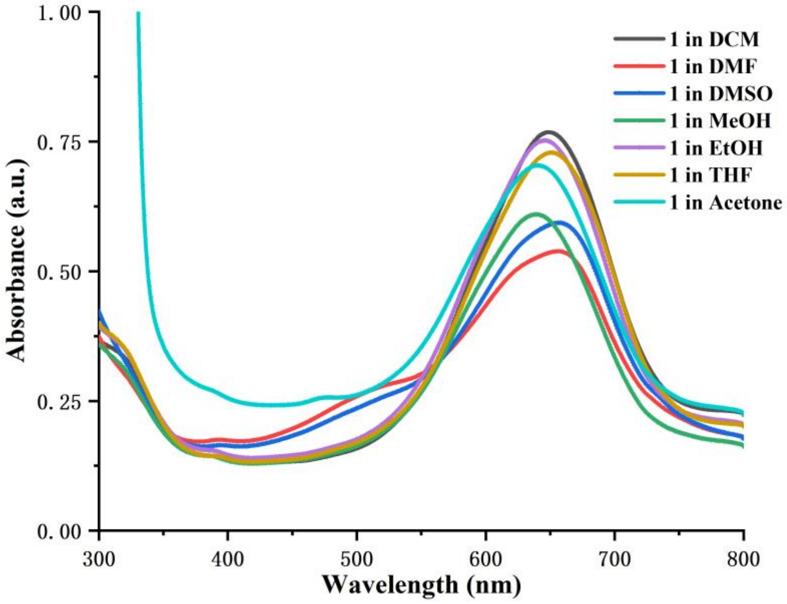


Figure S11. UV-Vis absorption spectra of **1** at the same concentration in DCM, DMF, DMSO, methanol, and ethanol.

IV. Mass Spectrometric Studies

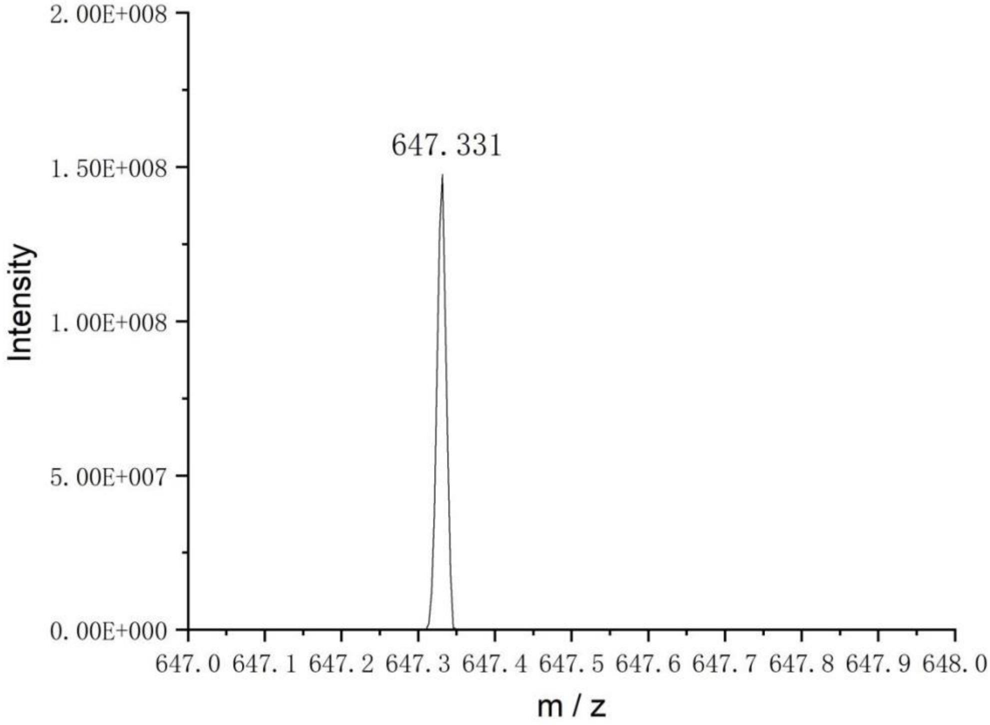


Figure S12. Mass spectrum of **4**.

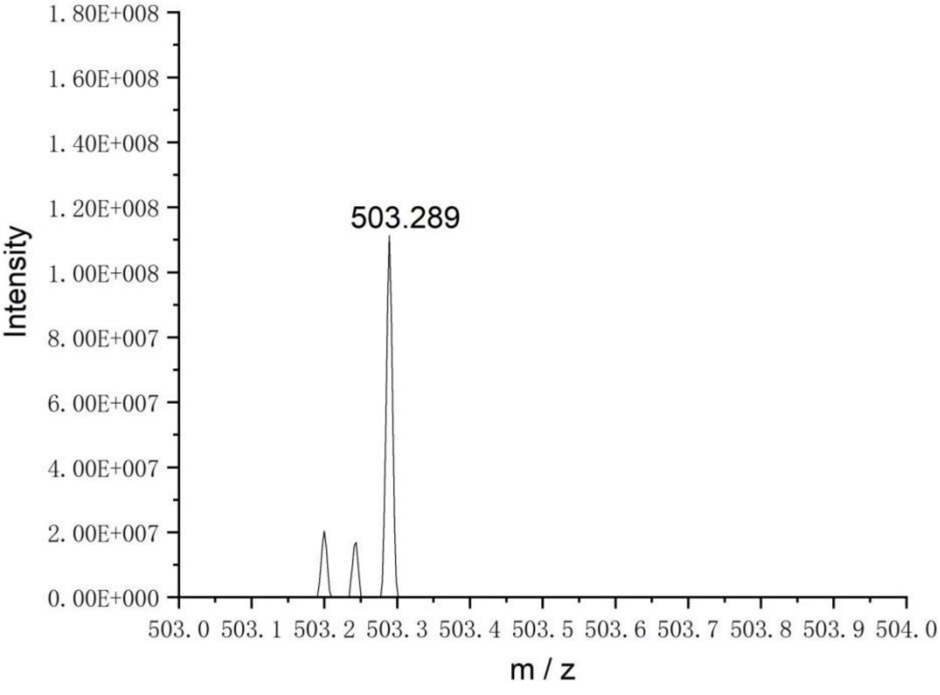


Figure S13. Mass spectrum of **5**.

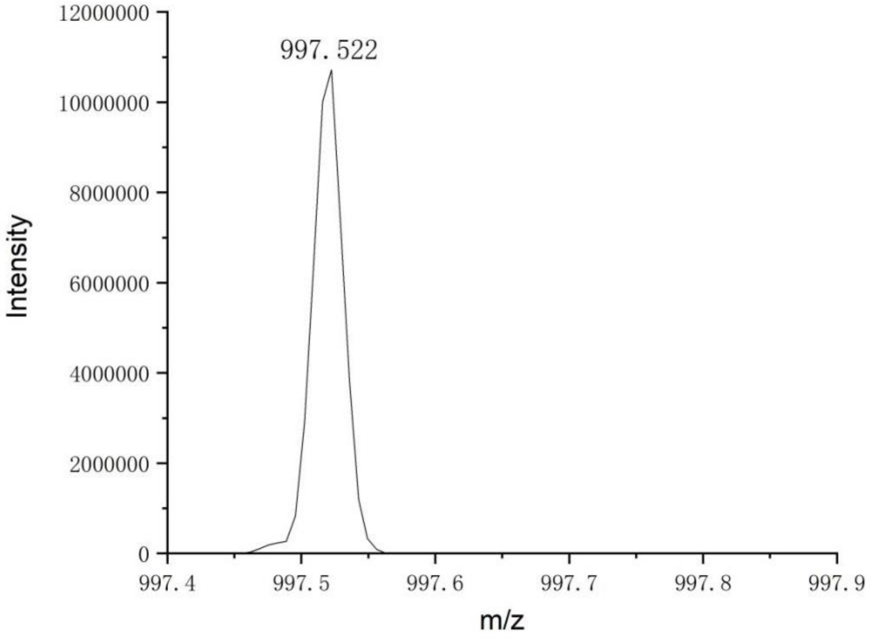


Figure S14. Mass spectrum of **1**.

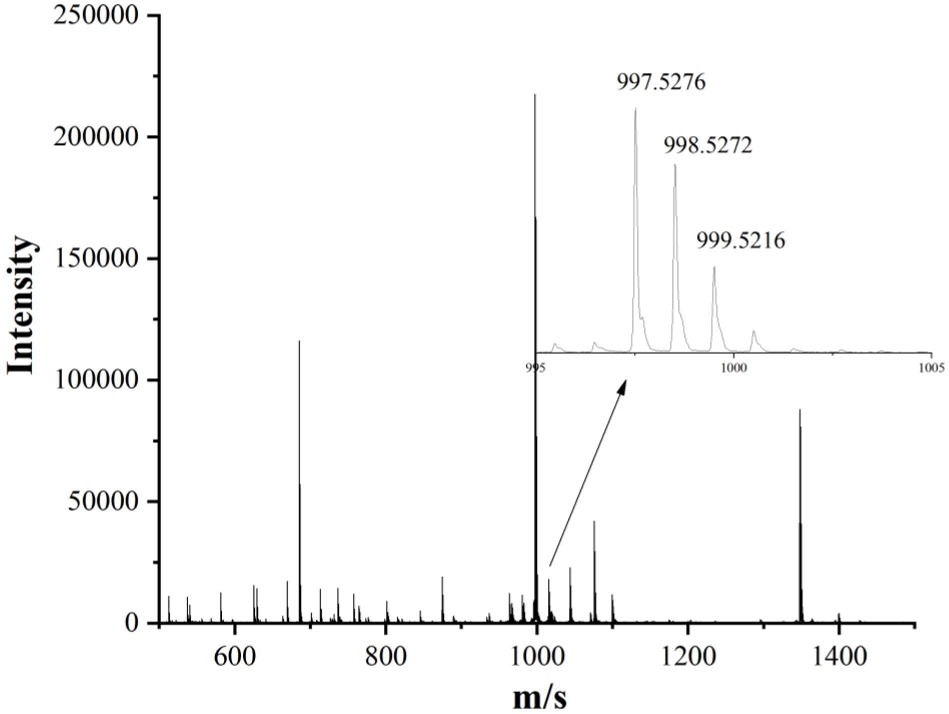


Figure S15. High resolution mass spectrum of **1**.

V. X-ray Experimental

Compound 1. A yellow needle crystal of $C_{64}H_{60}N_{12}$ having approximate dimensions of 0.1 x 0.06 x 0.05 mm^3 was mounted on a glass fibre. All measurements were made on a Bruker APEX-II CCD diffractometer with graphite monochromated Mo-K radiation. The data were collected at a temperature of 100.0 K. Of the 112054 reflections that were collected, 6328 were unique (R_{int} = 0.045); equivalent reflections were merged. Data were collected and integrated using the Bruker SAINT software package. The structure was solved by direct methods. All non-hydrogen atoms were refined anisotropically. All refinements were performed using the SHELXTL crystallographic software package Bruker-AXS. All C-H hydrogen atoms were placed in calculated positions but were not refined. Because the crystal is very thin and slim, the high-theta-angle diffraction reflections could not be found even though the exposure time had been adjusted to be 60 seconds. In the refinement, there are Q peaks at the suitable distance of all the eight pyrrolic nitrogen atoms. Presumably these should be the disordered hydrogen atoms which have eventually been assigned with an occupancy of 0.5.

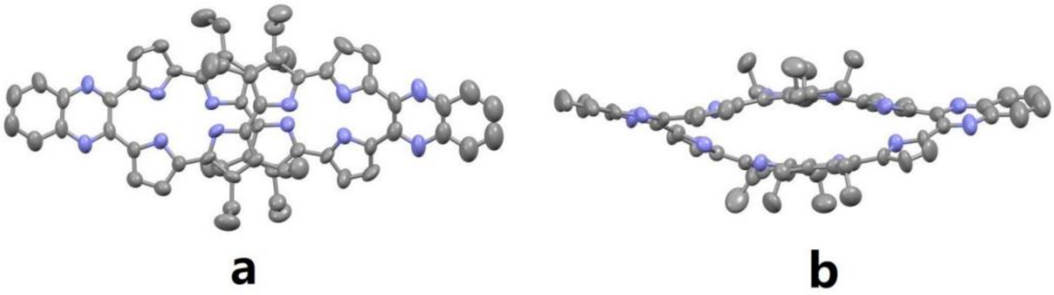


Figure S16. Crystal structure of compound **1**. a) Top view; b) side view. Hydrogen atoms are not shown for clarity.

Table S1. Crystal data of compound **1**.

Empirical Formula		$C_{64}H_{60}N_{12}$
Formula Weight		997.24
Temperature		100(1) K
Wavelength		0.71073 Å
Crystal Dimensions		0.1 x 0.06 x 0.05 mm^3
Crystal System		Monoclinic
Space Group		P 1 21/n 1
Lattice Parameters	*a*/Å	21.533(3)
	b/Å	17.889(3)
	c/Å	27.961(5)
	α/deg	90
	β/deg	93.891(4)
	γ/deg	90
	V/$Å^3$	10746(3)
Z Value		8
F_{000}		4224
No. of Reflections Measure	Total:	80925
	Unique:	10015
R1; *wR2* (refined on F^2, all data)		0.1722; 0.1183
Goodness of Fit Indicator (GOF)		0.909
R1; *wR2* (refined on F, I>2σ(*I*))		0.0559; 0.0884
CCDC number		2178803

VI. Electrochemistry

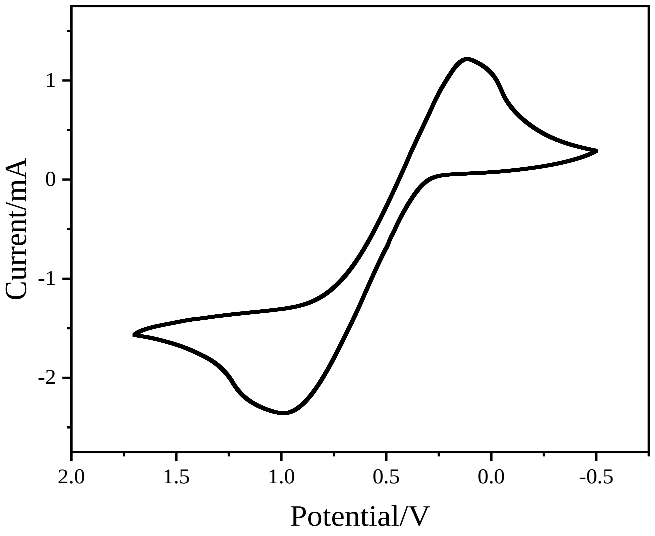


Figure S17. Cyclic voltamagram of **1** (1 mM in 1% CH_2Cl_2). The measurement was carried out at a scan rate of 0.05 $V\cdot s^{-1}$ with 0.1 M TBA•PF_6 as the supporting electrolyte.

VII. Calculations

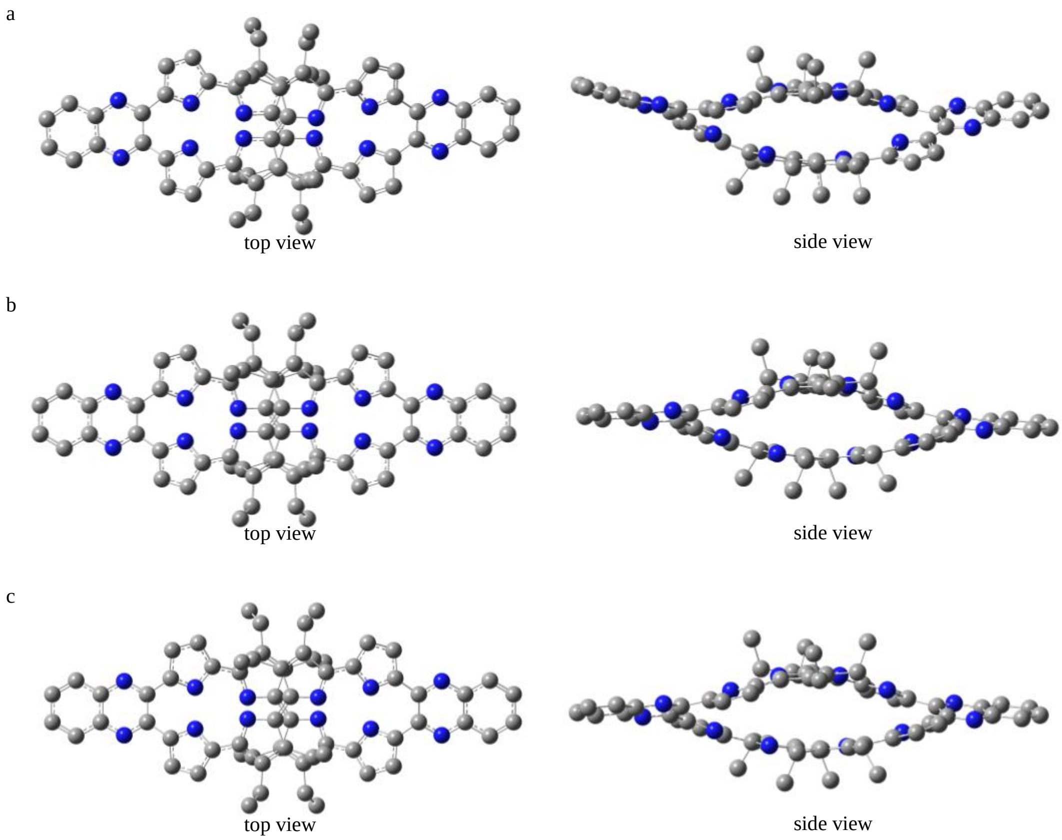


Figure S18. a) Crystal structure of octaphyrin **1**; b) Optimized structure of **1** in the gas state; c) Optimized structure of **1** in DCM solution. Hydrogen atoms are not shown for clarity.

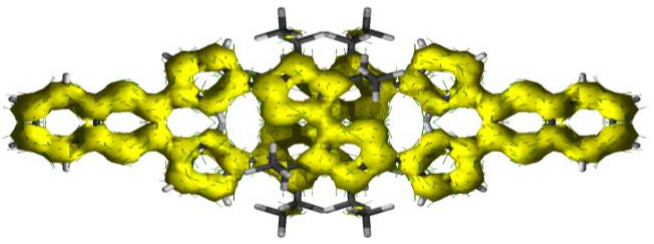


Figure S19. AICD (Anisotropy of the induced current density)[3] isosurface of octaphyrin **1** (isosurface value: 0.05). AICD was calculated using CSGT (Continuous Set of Gauge Transformation) method and plotted using POV-Ray. Note： The GIAO/B3LYP/6-311+G(d,p) method was applied for the NICS (nucleus-independent chemical shift) calculations.[4,5] NICS values were computed at the geometrical center of the heavy atoms of the macrocycle at 1 Å above and below the ring center together with its out-of-plane tensor component [NICS(1)$_{zz}$]. The NICS(1)$_{zz}$ value of 0.505 is taken as evidence that **1** is nonaromatic.

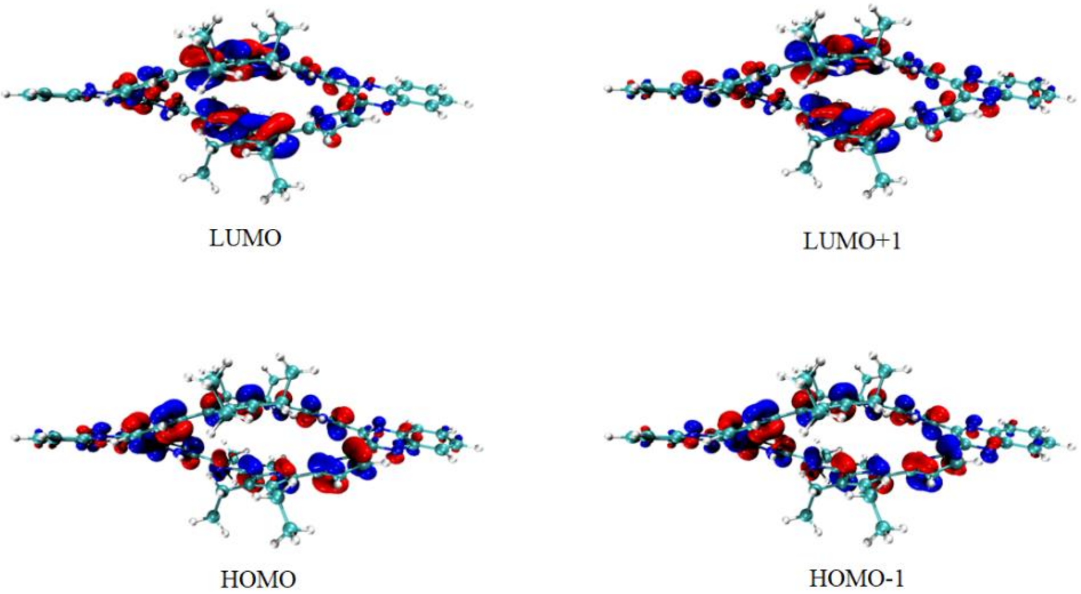


Figure S20. The contour of LUMO, LUMO+1, HOMO and HOMO-1 orbitals.

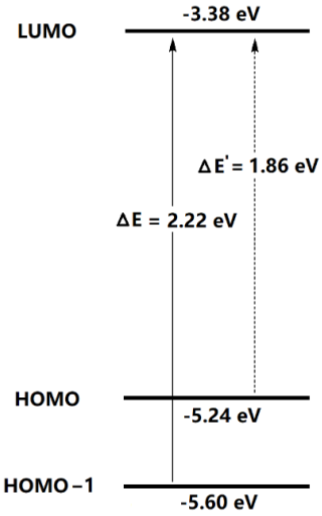


Figure S21. Calculated energy levels and band gaps.

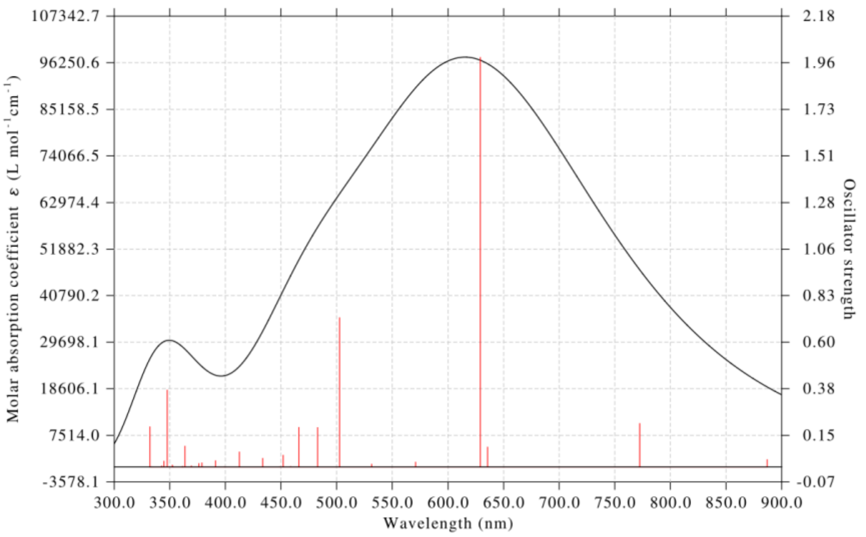


Figure S22. Calculated UV-Vis absorption bands.

VIII. Supporting References

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S5. Z. Chen, C. S. Wannere, C. Corminboeuf, R. Puchta, P. Schleyer, *Chem. Rev.* 2005**, 105**, 3842–3888.