Electronic Supplementary Information (ESI)

A new synthesis of porphyrin via a putative *trans*-manganese(IV)-dihydroxide intermediate

Sruti Mondal, Kasturi Sahu, Bratati Patra, Subhrakant Jena, Himansu S. Biswal,*and Sanjib Kar*

School of Chemical Sciences, National Institute of Science Education and Research (NISER), Bhubaneswar, Khordha, 752050, India and Homi Bhabha National Institute, Training School Complex, Anushakti Nagar, Mumbai, 400 094, India

E-mail: himansu@niser.ac.in, *sanjib@niser.ac.in*

Experimental section

Synthesis of 5,15-bis(4-cyanophenyl)-10-(pentafluorophenyl)tetrapyrrane

The following synthesis was performed by following a protocol reported earlier.[1] 0.100 g (0.4 mmol) of 5-(4-cyanophenyl)dipyrromethane and 49.3 μL (0.4 mmol) of 2,3,4,5,6-Pentafluorobenzaldehyde were dissolved in 50mL MeOH and 25 mL water (2:1) mixture. Subsequently, 5 mL of aqueous HCl (36%) was added to it. The reaction mixture was kept on stirring for 2 hours at room temperature. The crude product was washed and extracted several times with chloroform and water and dried over anhydrous Na_2SO_4. The solvent was evaporated to dryness. The reaction mixture was purged through a silica gel (100-200 mesh) column. The final product was eluted using EtOAc/hexane mixture as eluent.

For 5,15-bis(4-cyanophenyl)-10-(pentafluorophenyl)tetrapyrrane

Yield: 30% (41 mg). Anal. Calcd (found) for $C_{39}H_{25}F_5N_6$: C, 69.64 (69.77); H, 3.75 (3.84); N, 12.49 (12.37). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.14 – 7.86 (br s, 4H), 7.53 (m, 5H), 6.79 – 6.60 (m, 2H), 6.15 (dt, *J* = 11.2, 3.0 Hz, 2H), 5.97 – 5.53 (m, 9H), 5.42 (d, *J* = 6.3 Hz, 2H), 5.31 (s, 1H) (Fig. S13); The electrospray mass spectrum in acetonitrile showed peaks centred at *m/z* = 695.1893 correspond to [M+Na^+] (695.196 calcd for $C_{39}H_{25}F_5N_6Na$) (Fig. S14).

1. B. Koszarna and D. T. Gryko, *J. Org. Chem.* 2006, **71**, 3707-3717.

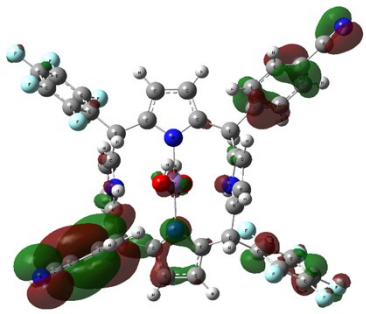
Fig. S13 ^{1}H NMR spectrum of 5,15-bis(4-cyanophenyl)-10-(pentafluorophenyl)tetrapyrrane in $CDCl_3$.

Fig. S14 ESI- MS spectrum in CH_3CN shows the (a) measured spectrum, (b) isotopic distribution pattern of 5,15-bis(4-cyanophenyl)-10-(pentafluorophenyl)tetrapyrrane.

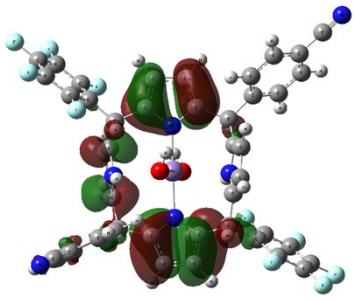
Table S1 UV−Vis. Data [a]

Compound	UV−vis. Data [a] λ_{max} / nm (ε / $M^{-1}cm^{-1}$)
7-Mn [a]	416 (10,860), 470 (7970), 576 (4020), 621 (7140).

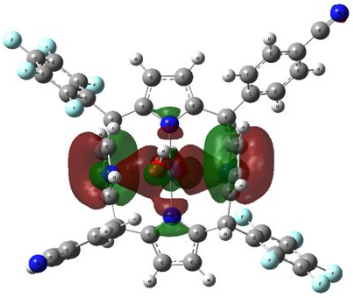
[a] In dichloromethane.



SOMO-11(227A)



LUMO(239A)



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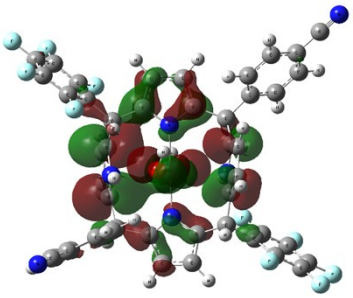

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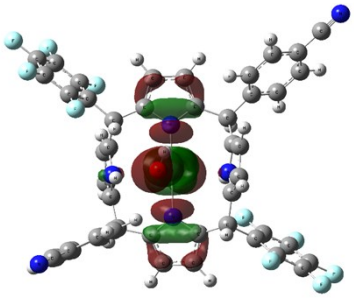
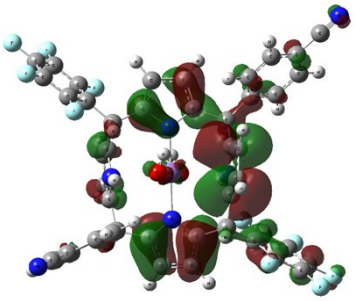
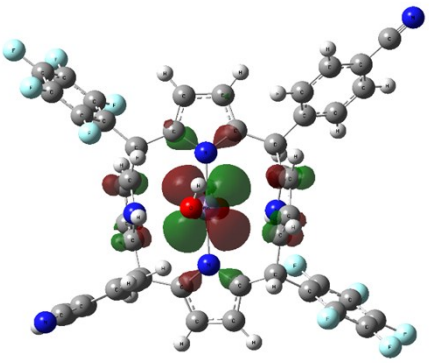


LUMO+1(240A)

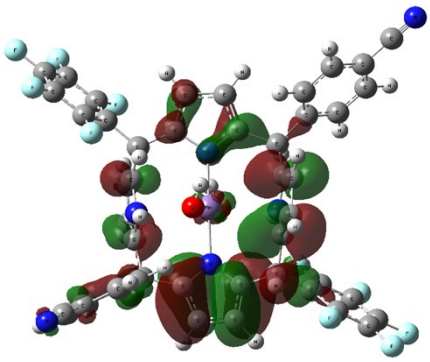


SOMO-2(233B)

Table S2 Composition of selected molecular orbitals of **7-Mn**.



LUMO(236B)



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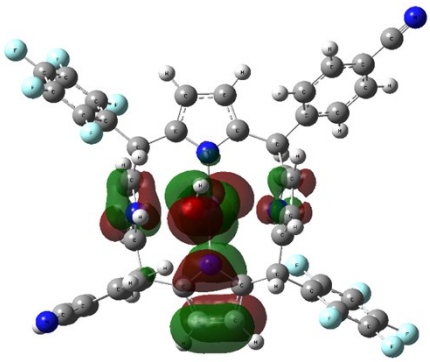

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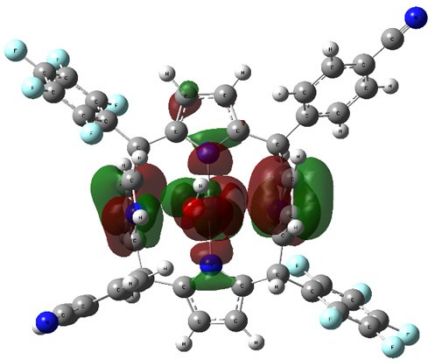

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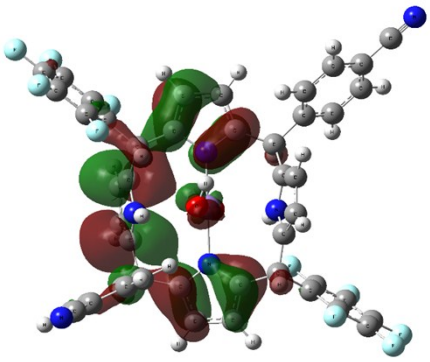
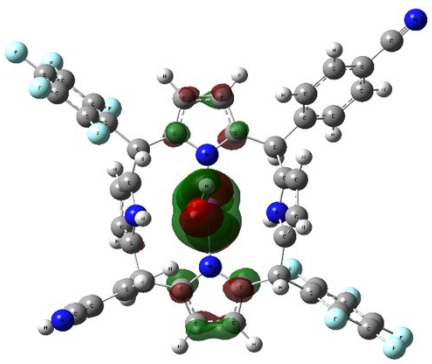


SOMO-3(232B)



LUMO+1(237B)

Table S3 Composition of selected molecular orbitals of **7-Mn**.

State	E(eV)	Transition Orbitals	Contribution	Character
S_{13}	1.76	SOMO-11(227A) to LUMO(239A)	0.99(100%)	ILCT
S_{26}	2.31	SOMO-18(220A) to LUMO239A)	0.11(1.19%)	LMCT
		SOMO-3(235A) to LUMO+1(240A)	0.11(1.30%)	LMCT
		SOMO-2(233B) to LUMO(236B)	0.98(96.30%)	LMCT
		SOMO-1(234B) to LUMO(236B)	0.11(1.20%)	LMCT
S_{29}	2.52	SOMO-6(232A) to LUMO+1(240A)	0.22(4.87%)	LMCT
		SOMO-4(234A) to LUMO+1(240A)	0.66(44.37%)	LMCT
		SOMO-3(232B) to LUMO(236B)	0.69(48.37%)	LMCT
		SOMO-1(234B) to LUMO+1(237B)	0.14(1.92%)	LMCT

Table S4 TD-DFT transitions for **7-Mn**.

Table S5 TD-DFT calculated IR frequencies for **7-Mn**.

Functional Group	IR Frequency(cm^{-1})
Water Stretch	3667.10
	3664.82
Pyrrole NH	3466.32
	3437.08
Pyrrole CH	3235.57 -3176.80
Benzonitrile CH	3153.95-3119.51
PFB	2993-2924
CN Stretch	2257.96
	2257.83
Aromatics C=C bending	1627.74-900
OH bending	700-900

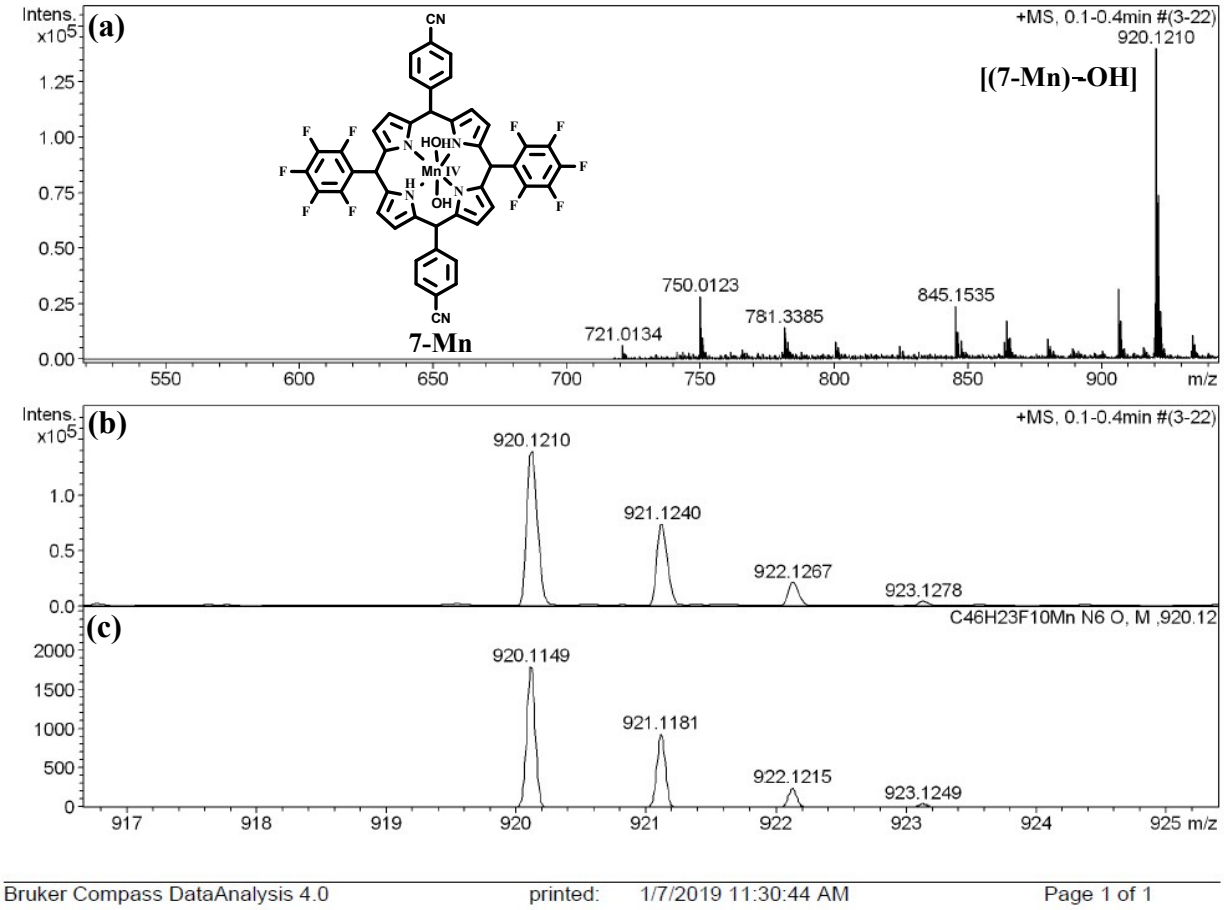


Fig. S1 ESI- MS spectrum in CH_3CN shows the (a) measured spectrum, (b) isotopic distribution pattern (experimental) and (c) isotopic distribution pattern (simulated) of **7-Mn**.

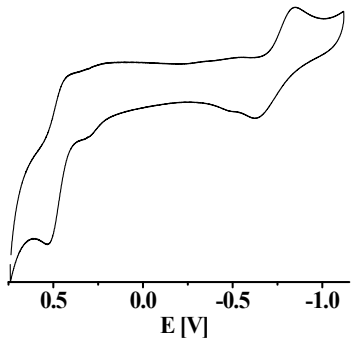


Fig. S2 Cyclic voltammogram (———) of **7-Mn** in CH_3CN. The potentials are vs. ferrocene/ferricinium.

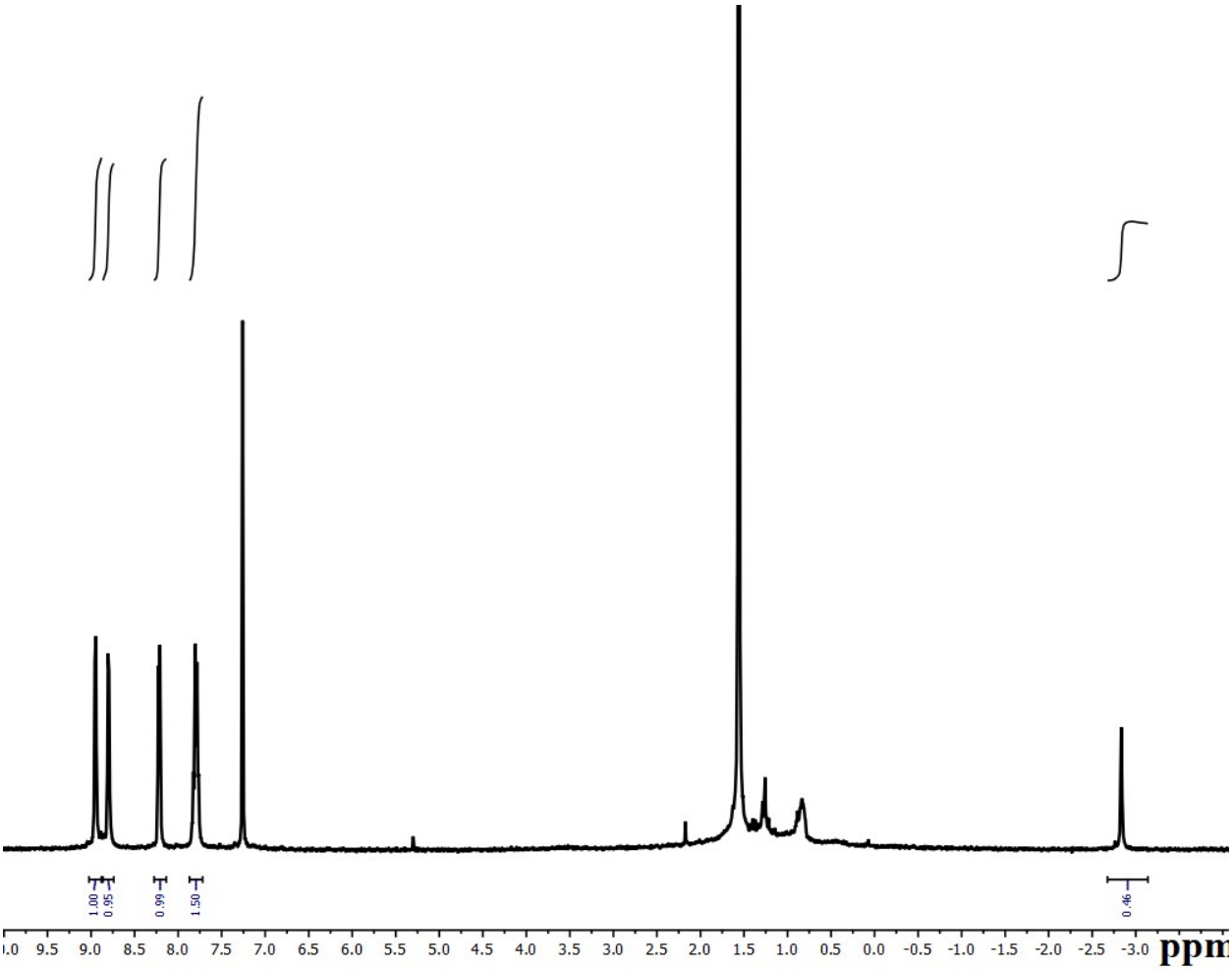


Fig. S3 ^{1}H NMR spectrum of 5,15-Bis(pentafluorophenyl)-10,20-diphenylporphyrin, **1** in $CDCl_3$.

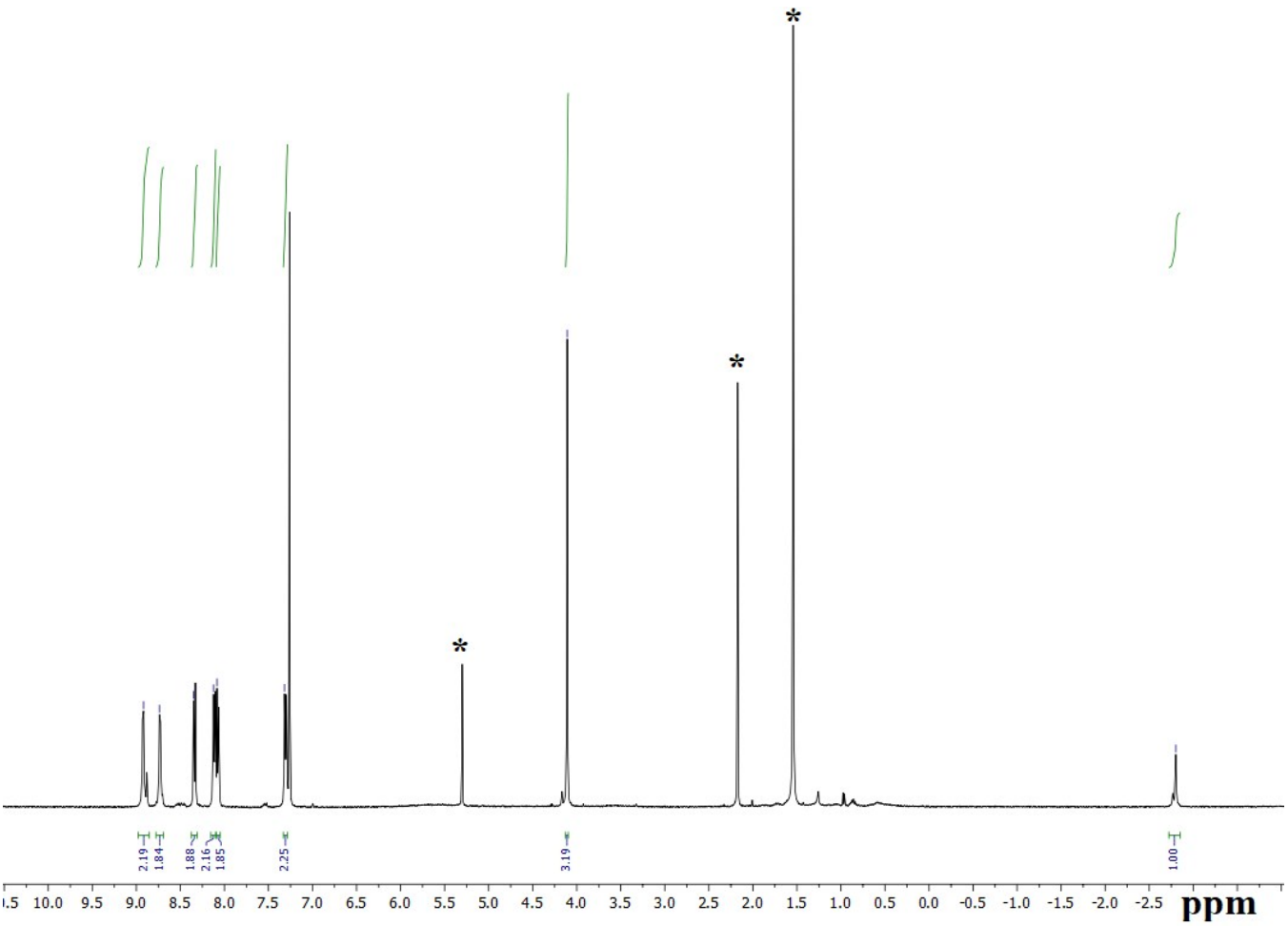


Fig. S4 ^{1}H NMR spectrum of 5,15-Bis(4-cyanophenyl)-10,20-bis(4-methoxyphenyl)porphyrin, **2** in $CDCl_3$.

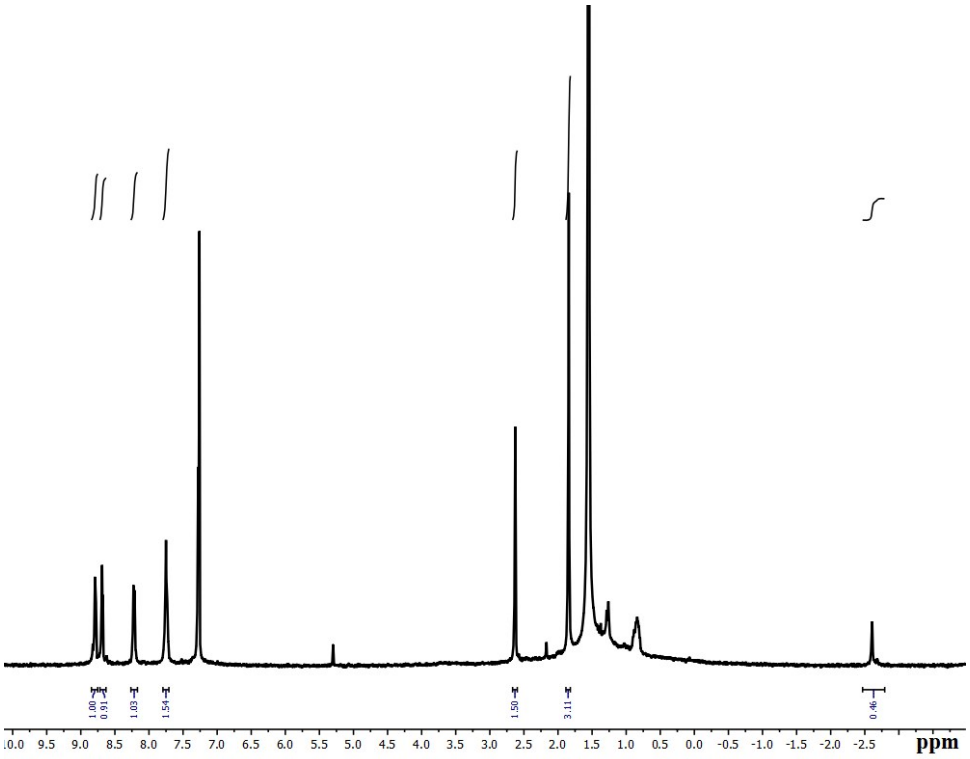


Fig. S5 ^{1}H NMR spectrum of 5,15-Dimesityl-10,20-diphenylporphyrin, **3** in $CDCl_3$.

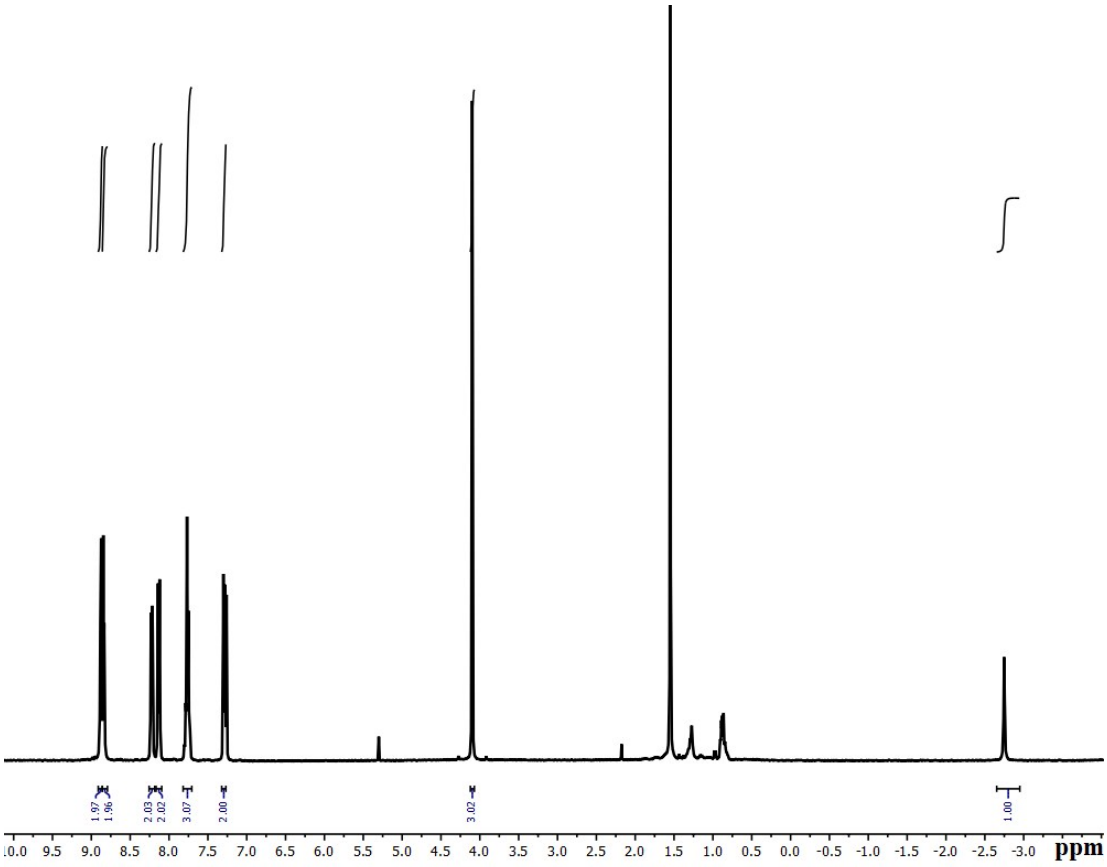


Fig. S6 ^{1}H NMR spectrum of 5,15-Bis(4-methoxyphenyl)-10,20-diphenylporphyrin, **4** in $CDCl_3$.

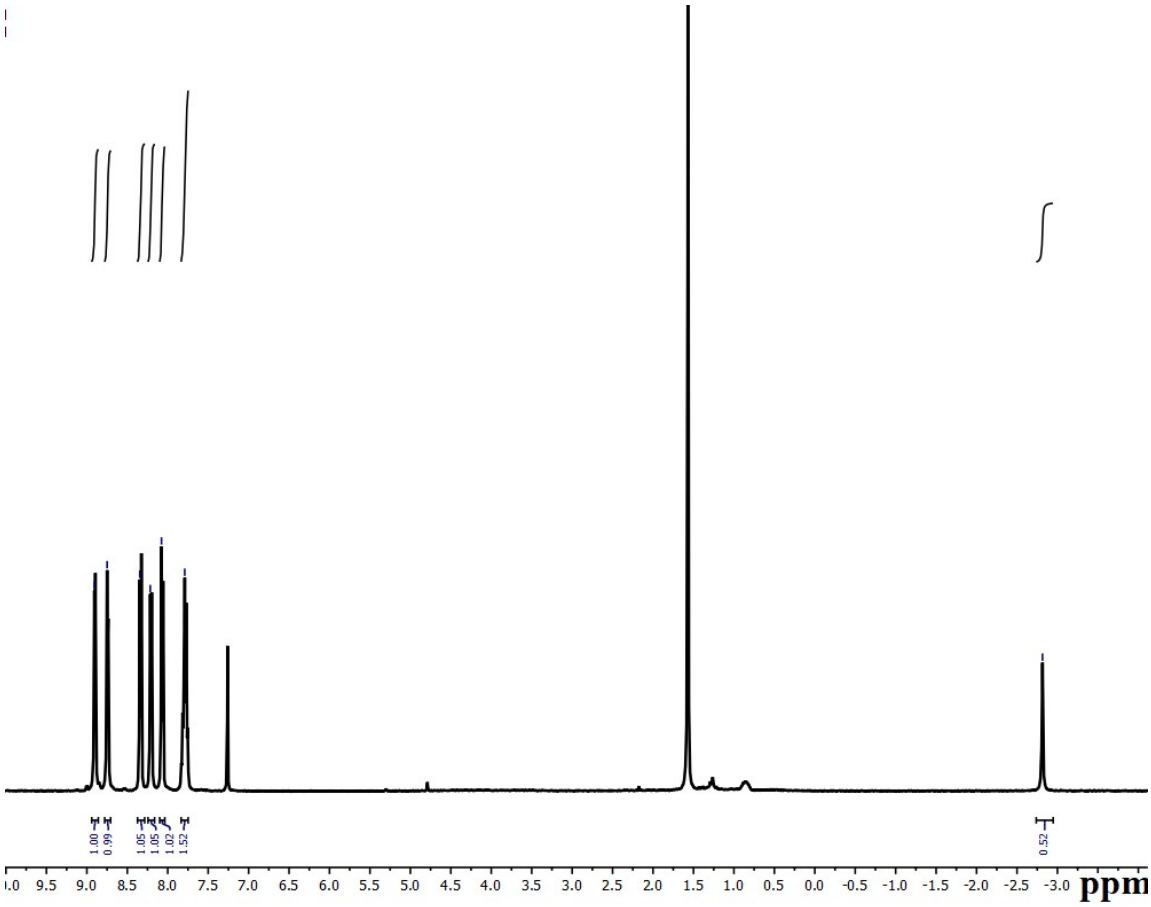


Fig. S7 ^{1}H NMR spectrum of 5,15-Bis(4-cyanophenyl)-10,20-diphenylporphyrin, **5** in $CDCl_3$.

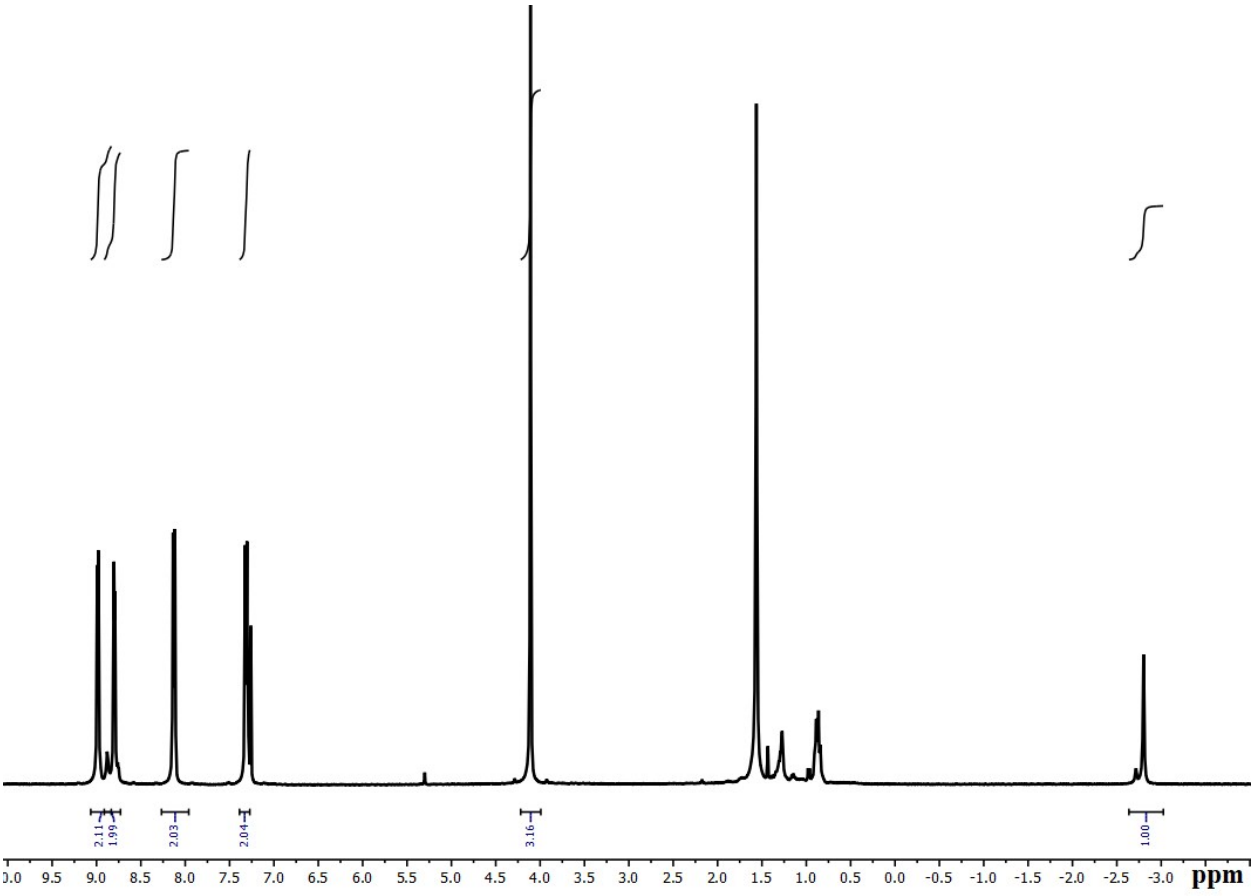


Fig. S8 ^{1}H NMR spectrum of 5,15-Bis(4-methoxyphenyl)-10,20-bis(pentafluorophenyl)porphyrin, **6** in $CDCl_3$.

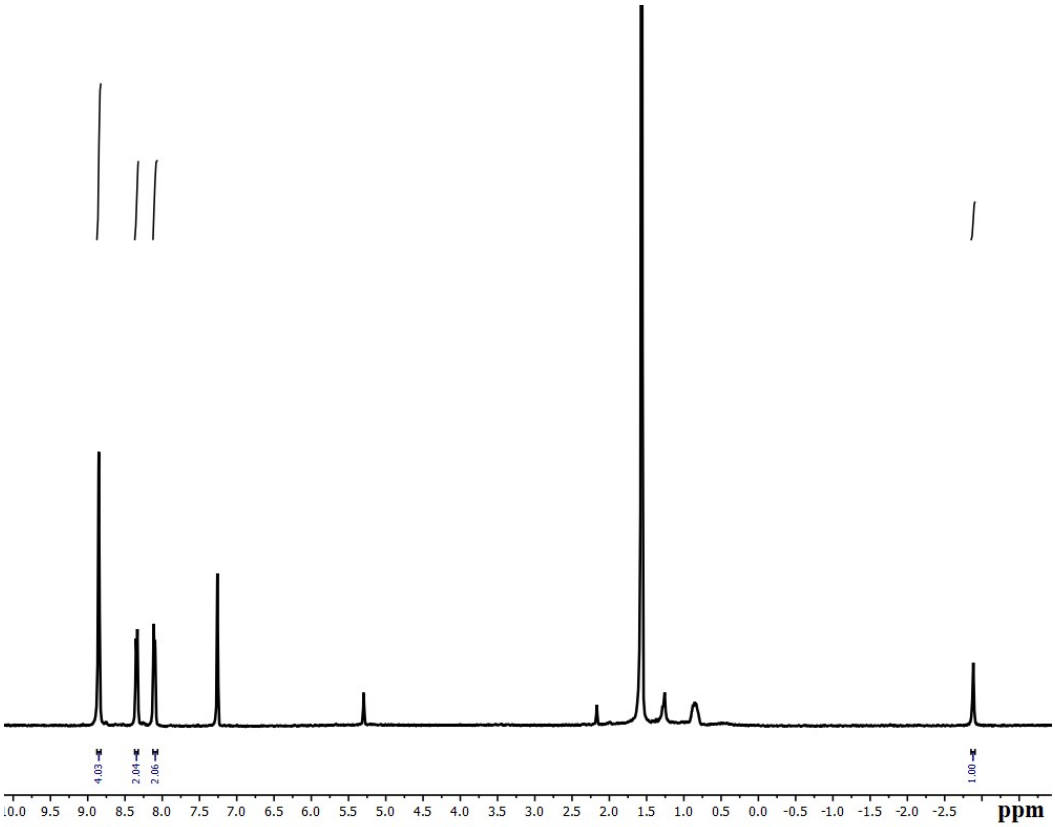


Fig. S9 ^{1}H NMR spectrum of 5,15-bis(4-cyanophenyl)-10,20-bis(pentafluorophenyl)porphyrin, **7** in $CDCl_3$.

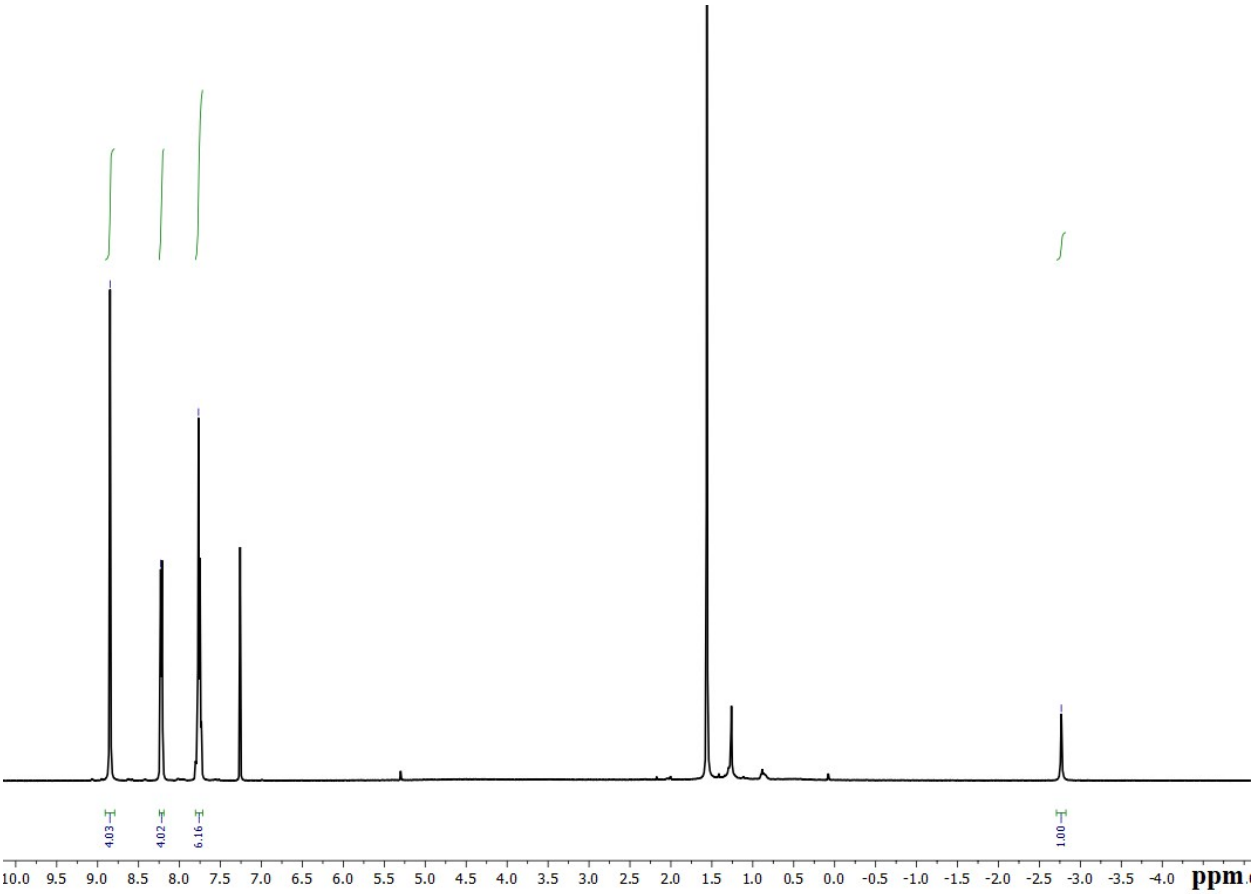


Fig. S10 ^{1}H NMR spectrum of 5,10,15,20-Tetraphenylporphin, **8** in $CDCl_3$.

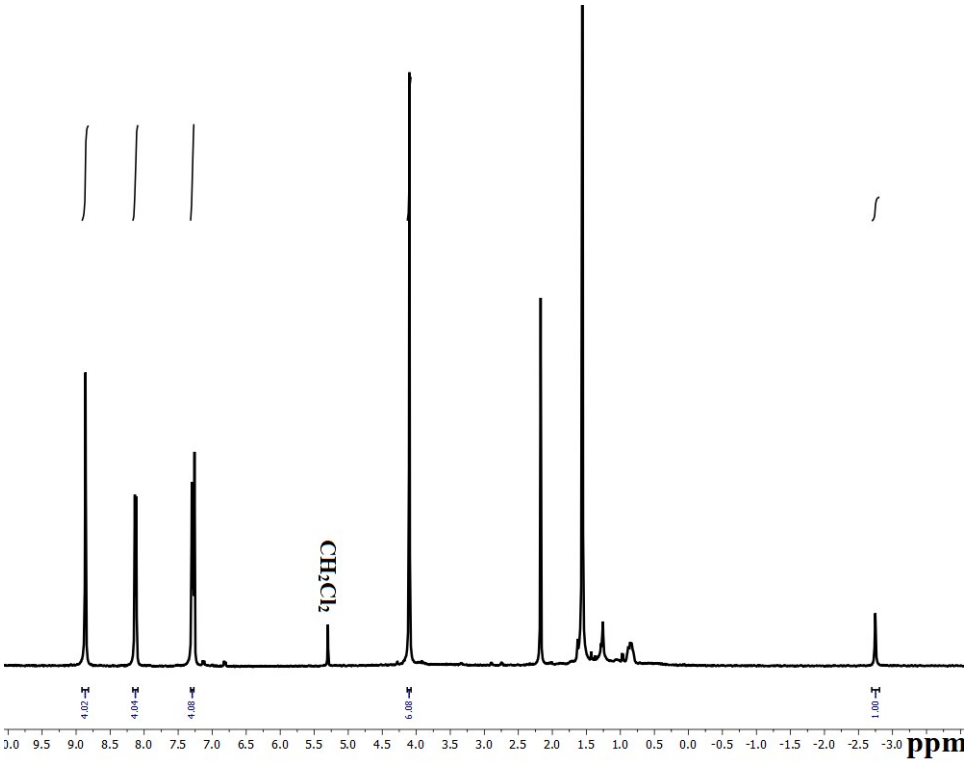


Fig. S11 ^{1}H NMR spectrum of 5,10,15,20-Tetrakis(4-methoxyphenyl)porphyrin, **9** in $CDCl_3$.

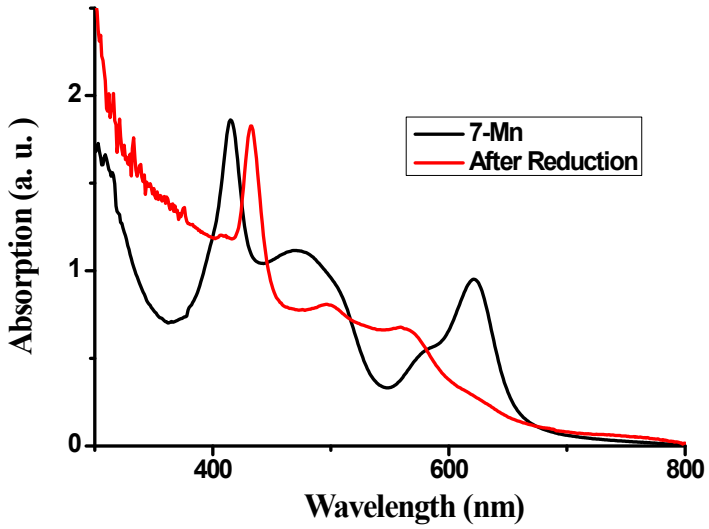


Fig. S12 Chemical reduction of **7-Mn** via $LiAlH_4$ in DCM solution at RT. Black line indicates the absorption spectra before reduction and red line indicates the species obtained after reduction.

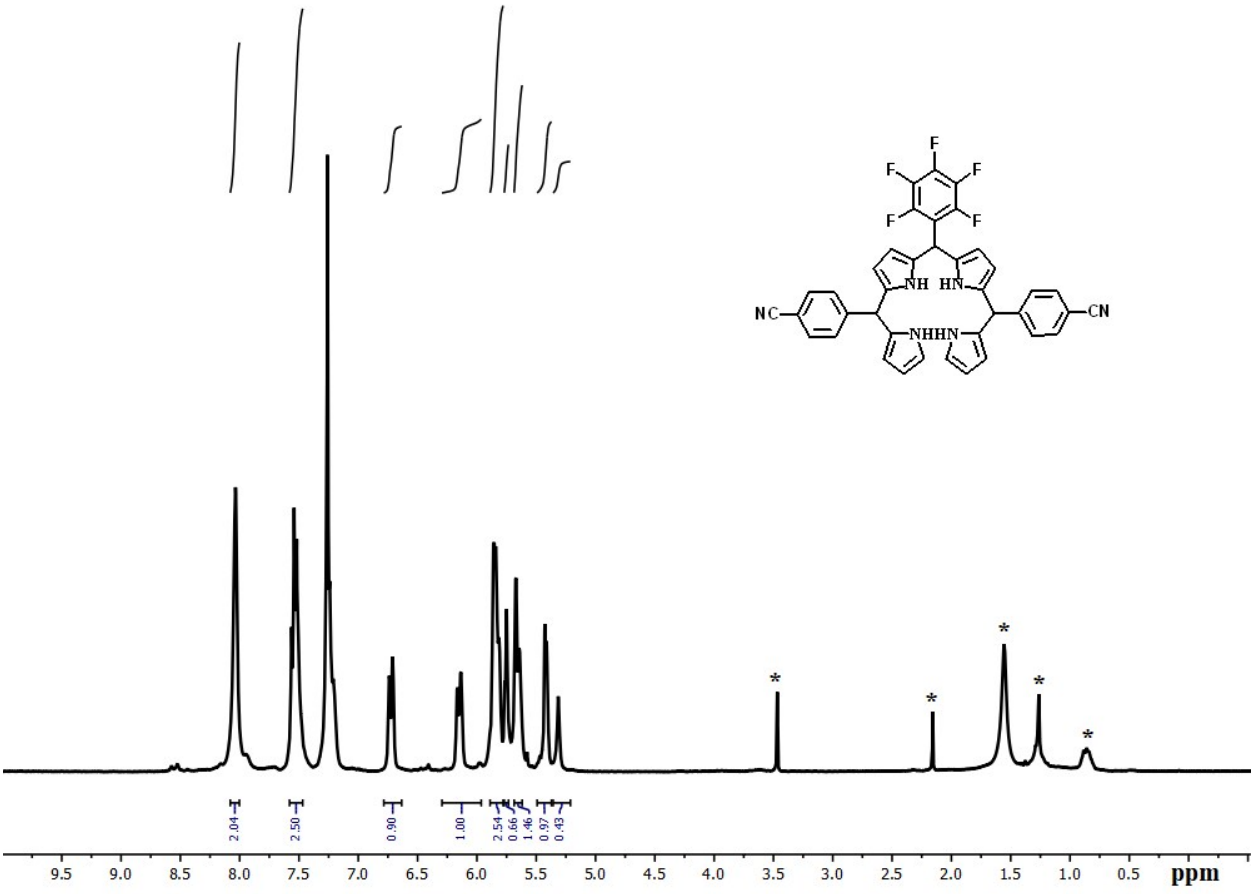


Fig. S13 ^{1}H NMR spectrum of 5,15-bis(4-cyanophenyl)-10-(pentafluorophenyl)tetrapyrrane in $CDCl_3$.

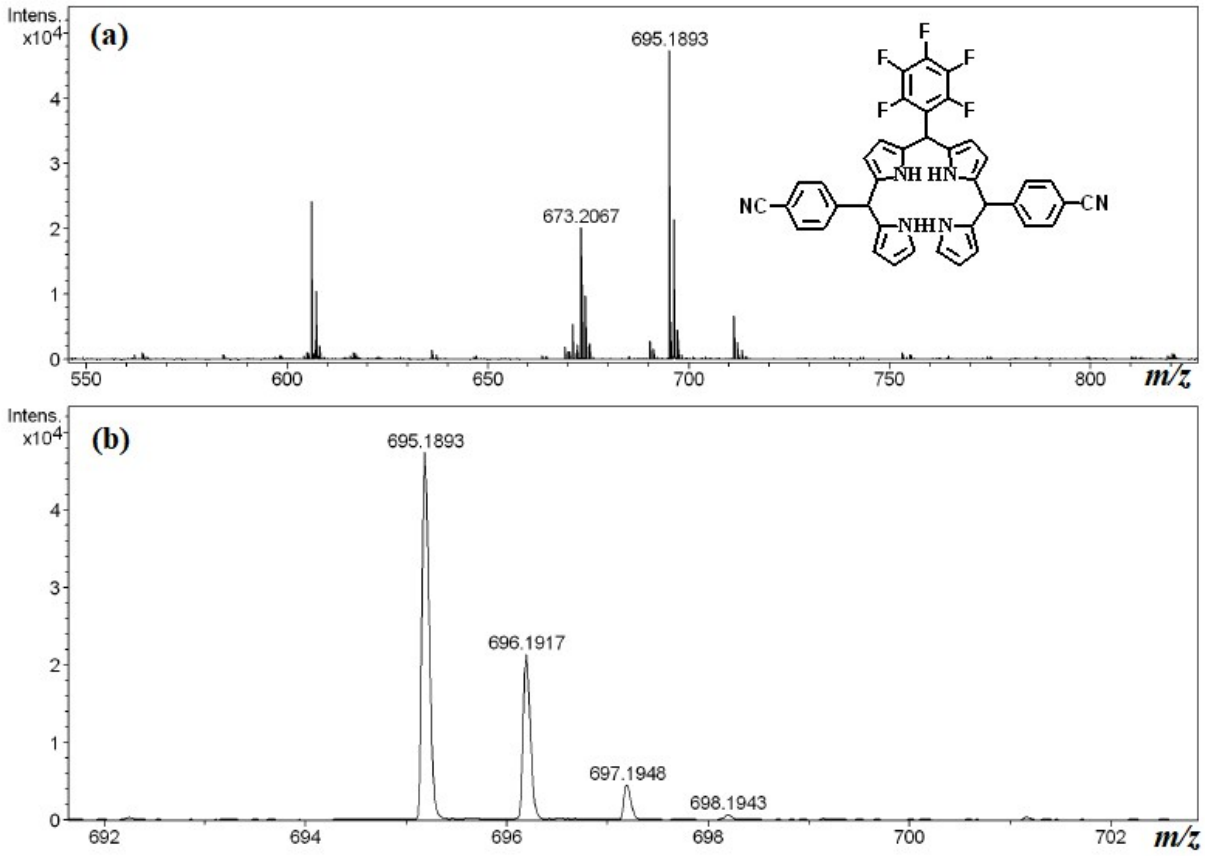


Fig. S14 ESI- MS spectrum in CH_3CN shows the (a) measured spectrum, (b) isotopic distribution pattern of 5,15-bis(4-cyanophenyl)-10-(pentafluorophenyl)tetrapyrrane.