Electronic Supplementary Information

Synthesis, Spectral, Electrochemical, and Nonlinear Optical Properties of *β*-Dicyanovinyl Appended 'Push-Pull' Porphyrins

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Experimental Section

Materials required

Benzaldehyde, N-Bromosuccinamide, P_2O_5, K_2CO_3, basic Al_2O_3, $M(OAc)_2•nH_2O$ (M = Ni and Zn), sodium bicarbonate, and calcium hydride were purchased from HiMedia. Pyrrole, DMF, and 1,2-DCE were purchased from SRL. $Cu(OAc)_2•H_2O$, Na_2SO_4, H_2SO_4 and propionic acid were received from Thomas baker. Malononitrile and $POCl_3$ was received from Alpha-Asear. $Pd(PPh_3)_4$ were bought form Sigma-Aldrich (India). Silica gel (mesh size = 100-120) was bought from Rankem and used as received. All the chemicals were employed as received except NBS which was recrystallized in hot water and $TBAPF_6$ which was recrystallized in ethanol. The chemicals utilized in this project were of analytical grade and distilled before use. The 4-(N,N-Diphenylamino)phenyl boronic acid was synthesized according to the literature.[1]

Methods

The electronic absorption spectra of synthesized porphyrins were recorded on Shimadzu UV-2600 spectrophotometer utilising a pair of quartz cells having a volume of 3.5 ml and10 mm path length and emission spectra were recorded on using a Hitachi F-4600 spectrophotometer using a quartz cell of 10 mm path length. NMR (^1H and ^{13}C) spectra were recorded using a Bruker AVANCE 500 MHz in $CDCl_3$ at 298 K and reported with chemical shifts on the δ scale in ppm. Electrochemical studies were carried out using a CH instrument (CH 620E), where a three-electrode assembly was employed, which comprised of a platinum working electrode, Ag/AgCl as a reference electrode and a Platinum-wire as a counter electrode to measure the redox potential. All measurements were done in triple distilled DCM containing 0.1 M $TBAPF_6$ as supporting electrolyte at a scan rate of 0.1 V/s and temperature was maintained at 298 K. The solvent was degassed by argon gas purging while doing the experiment. MALDI-TOF-MS were measured using a Waters Synapt G2-Si Q TOF Mass spectrometer using HABA (2-4-hydroxyphenylazo)benzoic acid) as a matrix. The ground state geometry optimization was carried out by DFT calculations using B3LYP basis set with the LANL2DZ functional using the G16 program suite.

The third-order nonlinear optical properties of all the porphyrins are investigated using single beam Z-scan technique in a liquid solution in a 1 mm thickness quartz cuvette. In single beam Z-scan a 800 nm (120 fs, 1 kHz) femtosecond Gaussian laser beam is focused with a convex lens of 15 cm focal length and the transmittance through the sample is recorded with a photodetector at each z potion across the Rayleigh range suing a computer controlled LabView program. The detailed experimental arrangements are published elsewhere.[1] In material nonlinear absorption (β) and nonlinear refraction are calculated in two different Z-scan configurations. In one mode of configuration, the all the transmitted beam through the sample is recorded using the photodetector, which is called the Open Aperture (OA) Z-scan which is utilized to estimate the two-photon absorption coefficient (β) and two-photon absorption cross-section (σ_{TPA}). In other mode of configuration, the transmitted intensity is recorded using an aperture before the collection, which is called the Closed Aperture (CA) Z-scan, which is envisaged to estimate the nonlinear refractive index (n_2).

The excited state dynamics of the porphyrins are investigated using ultrafast transient absorption spectroscopy via femtosecond optical pump-probe technique. In pump-probe technique a 400 nm (120 fs, 1 kHz) femtosecond laser pulse (generated by frequency double of 800 nm (120 fs, 1 kHz) laser pulse) is utilized as pump beam to excite the samples. The pump-induced modifications and excited state dynamics is monitored by a broadband weak femtosecond supercontinuum (350-1000 nm) probe beam which is temporally and spatially overlapped with the pump beam at the sample surface. The temporal evolution is recorded at each delay time between the pump and probe beam. The TAS measurement for all the samples were performed at 4 μJ pump energy at ambient condition. The detail experimental setups can be found elsewhere.[2]

Synthetic Procedures

The precursors were synthesized according to the literature method. H_2TPP(MN) and H_2TPP(MN)Br_2 were prepared with some modification in reaction conditions.[2,3]

Synthesis of H_2TPP(MN)

To the 150 mg of H_2TPPCHO in 25 ml $CHCl_3$, 1.5 equiv. of malononitrile was introduced followed by basic Al_2O_3, then the reaction mixture was allowed to reflux for 2 hrs. The completion of the reaction was monitored via UV/Vis. and TLC. After completion of the reaction, the solvent was reduced over rotary evaporator and crude product was obtained which was purified on silica column chromatography utilizing 7:3 ($CHCl_3$: Hexane) solvent system. Yield obtained was 84% (135 mg).

UV/Vis ($CHCl_3$): λ_{max}, nm (log ε) 453 (5.42), 531 (4.55), 577 (4.15), 615 (3.98), 674 (4.16).

Copper and nickel metalation was done as reported.

Zinc metalation of H_2TPP(MN)

To the 45 mg of H_2TPP(MN) in 15 ml distil. $CHCl_3$, 10 equiv. of $Zn(OAc)_2$•$2H_2O$ dissolved in 5 ml methanol was added and refluxed for 15 min. The reaction was monitored by TLC and absorption spectroscopy. After termination of the reaction, solvent was rotaory evaporated. The crude porphyrin was dissolved in $CHCl_3$ and washed with distilled water thrice to remove excess of zinc salt. Further purification was done via silica column chromatography using $CHCl_3$ as eluent. The ZnTPPMN was obtained in 90% (45mg, 0.058 mmol) yield.

UV/Vis ($CHCl_3$): λ_{max}, nm (log ε) 338(sh), 402(3.85), 460(4.33), 568(3.20), 619(3.36).

^{1}HNMR (400 MHz, $CDCl_3$) δ (ppm): 9.50 (s, 1H, *β*-pyrrole-H), 8.955 (d, 1H, J = 5Hz, *β*-pyrrole-H), 8.896-8.822 (m, 5H, *β*-pyrrole-H), 8.189-8.130 (m, 6H, meso-*o*-Ph-H), 7.985 (d, 2H, meso-*o*-Ph-H), 7.88 (t, 1H, J = 10 Hz, meso-*m,* and *p*-Ph-H), 7.813-7.710 (m, 11H, meso-

m, and *p*-Ph-H), 7.14 (s, 1H, DCV-H). **MALDI-TOF-MS** (*m/z*): found $[M]^+$ = 754.781, calcd. 754.174.

Synthesis of H_2TPP(MN)Br_2

200 mg of H_2TPP(CHO)Br_2 dissolved in 30 ml $CHCl_3$ was charged with 2 equiv. of malononitrile and basic alumina then the reaction mixture was allowed to reflux for 2 h instead of 8 h. The completion of reaction was confirmed via TLC and optical absorption spectra. The solvent was removed over rotary evaporator and crude porphyrin was further purified over silica column chromatography utilizing 1:1 ($CHCl_3$:Hexane) solvent system as eluent. The yield obtained was 81% (172 mg, 0.201 mmol).

UV/Vis ($CHCl_3$): λ_{max}, nm (log ε) 376 (sh), 451 (4.97) 538 (3.99), 582 (3.65), 623 (3.51), 688 (3.69).

Copper and nickel metalation was done as reported.

Synthesis of ZnTPP(MN)Br_2

To the 45 mg of H_2TPP(MN)Br_2 dissolved in 15 ml dry $CHCl_3$, 10 equiv. of $Zn(OAc)_2{\bullet}2H_2O$ in 5 ml methanol was added and allowed to reflux for 15 min. The reaction was monitored by TLC and optical absorption spectroscopy. After confirmation, the excess solvent was removed on rota-evap. To remove the excess zinc salt, work up was done thrice with distilled water and crude porphyrin was collected in $CHCl_3$. Further purification was done via silica column chromatography using $CHCl_3$ as eluent. The ZnTPP(MN)Br_2 was obtained in 82% (40mg, 0.043 mmol) yield.

UV/Vis ($CHCl_3$): λ_{max}, nm (log ε) 344(sh), 400(4.72), 459(5.31), 572(4.21), 622(4.33).

^{1}HNMR (500 MHz, $CDCl_3$) δ (ppm): 9.51 (s, 1H, *β*-pyrrole-H), 8.84 (s, 1H, *β*-pyrrole-H), 8.75 (s, 1H, *β*-pyrrole-H), 8.150-7.660 (m, 20H, meso-*o,p*-Ph-H), 7.19 (s, 1H, DCV-H). **MALDI-TOF-MS** (*m/z*): found $[M + H]^+$ = 912.725, calcd. 912.973.

Synthesis of H_2TPP(MN)(TPA)$_2$

To the double neck round bottom flask, 50 mg of H_2TPP(MN)Br_2 (0.0589 mmol) was added and to this 4-(N,N-Diphenylamino)phenylboronic acid (12 equiv., 204 mg) dissolved in toluene was introduced followed by addition of K_2CO_3 (24 equiv., 195.36). Argon purging was done for 15-20 mins to make the inert atmosphere. Next to this, $Pd(PPh_3)_4$ (0.19 equiv., 13.46 mg) was added and then RB containing reaction mixture was heated at 95 ºC for 20 h. The monitoring of the reaction was done via UV-Vis and TLC. The reaction mixture was brought down to room temperature after which solvent (toluene) was reduced over rota-evap. Work-up was done thrice with distilled water and organic layer was obtained in chloroform. To obtain the pure compound silica column chromatography was done where polarity of solvent was varied from hexane to $CHCl_3$:MeOH (99.5:0.5) mixture. The dark green porphyrin (52 mg, 0.044 mmol) was obtained in 75 % yield.

UV/Vis ($CHCl_3$): λ_{max}, nm (log *ε*) 306 (sh), 457(4.85), 535(4.08), 584(3.81), 684(3.55). **^{1}HNMR (500 MHz, $CDCl_3$)** δ (ppm): 9.467(s, 1H, *β*-pyrrole-H), 8.834(d, 1H, J = 5 Hz, *β*-pyrrole-H), 8.74(d, 1H, J = 4.5 Hz, *β*-pyrrole-H), 8.616(t, 2H, J = 4 Hz, *β*-pyrrole-H), 8.297-8.227 (m, 2H, meso-*o*-Ph-H), 8.136(d, 2H, J = 7 Hz, meso-*o*-Ph-H), 7.915(t, 5H, J = 7 Hz, meso-*o, m, and p*-Ph-H), 7.864-7.795(m, 5H, meso-*m, p*-Ph-H), 7.518(t, 2H, J = 7 Hz, meso-*m, p*-Ph-H), 7.390(t, 4H, J = 7.5 Hz, meso-*m, and p*-Ph-H), 7.276-7.238(m, 8H, TPA-Ph-H), 7.048-6.967(m, 8H, TPA-Ph-H), 6.789(t, 4H, J = 7.5 Hz, TPA-Ph-H), 6.665-6.615(dd, 4H, J = 3 Hz, TPA-Ph-H), **^{13}C NMR (500 MHz, $CDCl_3$)** δ (ppm): -2.265(s, 2H, -NH). 155.63, 148.17, 147.64, 145.10, 141.38, 141.20, 141.04, 140.89, 135.79, 135.63, 135.51, 134.93, 132.30, 129.09, 128.50, 127.85, 127.47, 127.39, 127.21, 126.34, 124.38, 123.92, 123.73, 123.05, 122.90, 122.35, 121.87, 121.78, 121.32, 119.20, 116.22, 114.24, 113.46. **MALDI-TOF-MS** (*m/z*): found $[M + H]^+$ = 1178.418, calcd. 1178.435.

Metalation of H_2TPP(MN)(TPA)$_2$

20 mg H_2TPP(MN)(TPA)$_2$ was taken in 10 ml chloroform, thereafter 10 equiv. of $M(OAc)_2$•nH_2O (M = Cu, and Zn) in 3 ml MeOH was added. Then the reaction mixture was refluxed for 15 mins to 30 mins, and reaction was ceased only after checking *via* UV/Vis and TLC (single fraction). The solvent was removed over rota-evaporator. Excess metal acetate was removed by three times water wash and the crude porphyrin was purified using silica column by eluting with chloroform.

For nickel metalation, 20 mg of H_2TPP(MN)(TPA)$_2$ and 10 equiv. of $Ni(OAc)_2$•$4H_2O$ was dissolved in 8 ml DMF and refluxed for 3 h. Insertion of nickel was confirmed *via* UV/Vis (2 Q-bands) and TLC (single spot). The reaction mixture was brought down to room temperature and thereafter 20 ml distilled water was added to the reaction mixture, which facilitated the precipitate formation of porphyrin and solubilized the DMF. Later, reaction mixture was filtered and washed several times with water, the residue (porphyrin) was dried in hot air oven at 100 ºC. To obtain clean NMR, silica column chromatography was done in $CHCl_3$.

CuTPP(MN)(TPA)$_2$, Yield = 93%, **UV/Vis ($CHCl_3$):** λ_{max}, nm (log *ε*) 308 (sh), 397 (4.72), 458 (5.12), 566 (4.10), 619 (4.33). **MALDI-TOF-MS** (*m/z*): found $[M + H]^+$ = 1239.401, calcd. 1239.965. Anal. Calcd for $C_{84}H_{54}CuN_8$: C, 81.43; H, 4.39; N, 9.04. Found C, 81.67; H, 4.56; N, 9.23.

ZnTPP(MN)(TPA)$_2$, Yield = 87%, **UV/Vis ($CHCl_3$):** λ_{max}, nm (log *ε*) 308(sh), 403 (4.22), 466(4.68), 572 (3.52), 626 (3.77). **^{1}HNMR (500 MHz, $CDCl_3$)** δ (ppm): 9.634(s, 1H, *β*-

pyrrole-H), 8.88(d, 1H, J = 5 Hz, *β*-pyrrole-H), 8.788(d, 1H, J = 5 Hz, *β*-pyrrole-H), 8.607(t, 2H, J = 4.5 Hz, *β*-pyrrole-H), 8.221(dd, 2H, J = 5 Hz, meso-*o*-Ph-H), 8.114(d, 2H, J = 7 Hz, meso-*o*-Ph-H), 7.907(t, 1H, J = 7.5 Hz, meso-*o*-Ph-H), 7.874-7.785(m, 10H, meso-*o, m, and p*-Ph-H), 7.504(t, 2H, J = 8 Hz, meso-*m, p*-Ph-H), 7.370-7.316(m, 6H, meso-*m, p*-Ph-H and TPA-Ph-H), 7.284(s, 2H, TPA-Ph-H), 7.058(d, 9H, J = 8.5 Hz, TPA-Ph-H), 6.998(t, 6H, J = 7.5 Hz, TPA-Ph-H), 6.860 (d, 4H, J = 6.5 Hz, TPA-Ph-H), 6.686(d, 4H, J = 7 Hz, TPA-Ph-H). **^{13}C NMR (500 MHz, CDCl$_3$) δ (ppm):** 132.54, 129.09, 123.74, 122.32, 122.07, 29.70. **MALDI-TOF-MS** (*m/z*): found $[M + H]^+$ = 1241.351, calcd. 1241.799.

NiTPP(MN)(TPA)$_2$, Yield = 87%, **UV/Vis (CHCl$_3$):** λ_{max}, nm (log *ε*) 306 (sh), 437 (5.05), 551 (4.03), 596 (4). **^{1}HNMR (500 MHz, CDCl$_3$)** δ (ppm): 9.237(s, 1H, *β*-pyrrole-H), 9.171(s, 1H, *β*-pyrrole-H), 8.585(d, 1H, J = 5 Hz, *β*-pyrrole-H), 8.561(d, 1H, J = 5 Hz, *β*-pyrrole-H), 8.341(d, 1H, J = 5 Hz, *β*-pyrrole-H), 8.313(d, 1H, J = 5 Hz, meso-*o*-Ph-H), 7.993(d, 2H, J = 6.5 Hz, meso-*o*-Ph-H), 7.946(d, 2H, J = 6 Hz, meso-*o*-Ph-H), 7.734-7.628(m, 7H, meso-*o, m, and p*-Ph-H), 7.568(d, 4H, J = 6 Hz, meso-*m, p*-Ph-H), 7.414(t, 2H, J = 5 Hz, meso-*m, p*-Ph-H), 7.266(s, 3H, TPA-Ph-H), 7.235(s, 4H, TPA-Ph-H), 7.051-6.976(m, 14H, TPA-Ph-H), 6.717(dd, 4H, J = 3 Hz and 2.5 Hz, TPA-Ph-H), 6.626(dd, 4H, J = 2 Hz and 2 Hz, TPA-Ph-H), **^{13}C NMR (500 MHz, CDCl$_3$)** δ (ppm): 148.49, 148.22, 147.80, 145.82, 145.63, 145.33, 143.22, 142.15, 141.48, 140.67, 140.55, 140.17, 139.73, 139.61, 139.54, 139.19, 135.41, 134.17, 134.12, 133.85, 133.74, 133.46, 133.25, 132.91, 132.76, 132.45, 132.43, 131.72, 129.50, 129.10, 128.99, 128.19, 127.61, 127.21, 126.17, 123.93, 122.78, 122.49, 121.97, 119.31, 118.88, 118.41, 31.45, 30.60, 30.22, 29.70. **MALDI-TOF-MS** (*m/z*): found $[M + 4\% CHCl_3 – 2CN]^+$ = 1186.342, calcd. 1186.875.

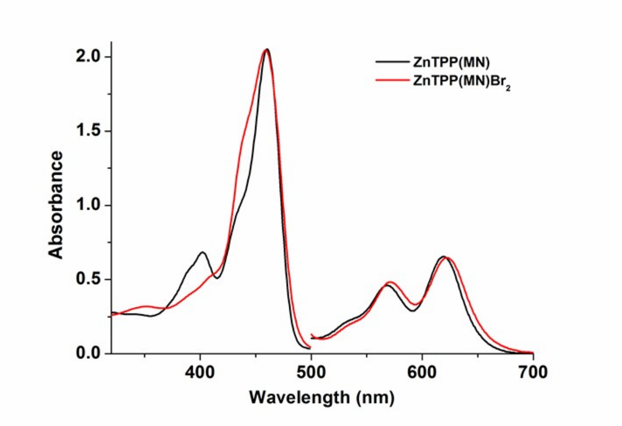


Figure S1. The optical absorption spectra of ZnTPP(MN) and ZnTPP(MN)Br_2 in $CHCl_3$ at 298 K.

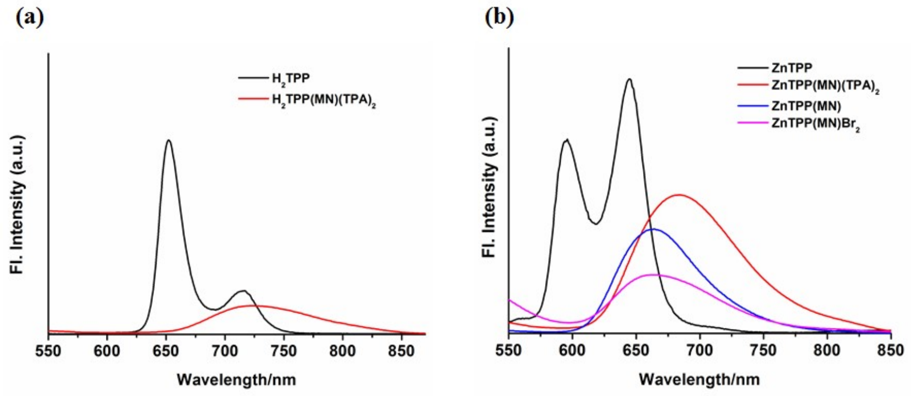


Figure S2. Comparable emission spectra of (a) H_2TPP and $H_2TPP(MN)(TPA)_2$ (b) ZnTPP, $ZnTPP(MN)(TPA)_2$, ZnTPP(MN), and $ZnTPP(MN)Br_2$ in $CHCl_3$ at 298 K.

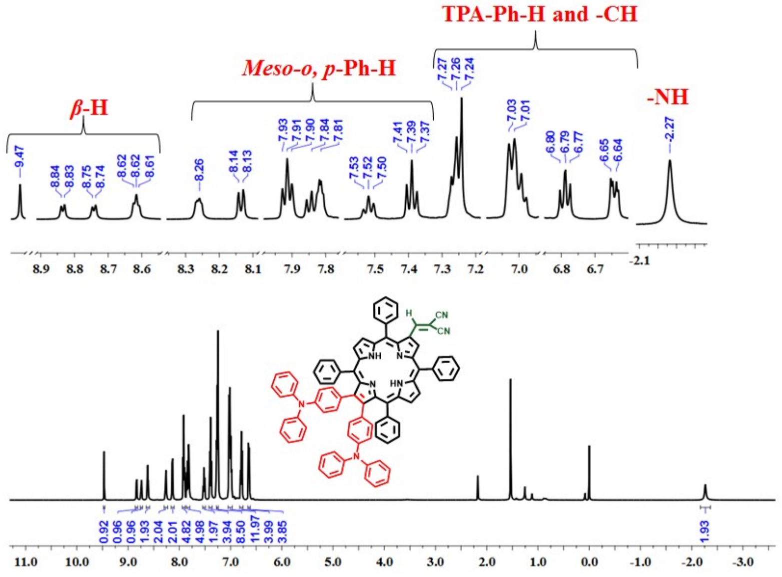


Figure S3. ^{1}H NMR spectrum of $H_2TPP(MN)(TPA)_2$ in $CDCl_3$ at 298 K.

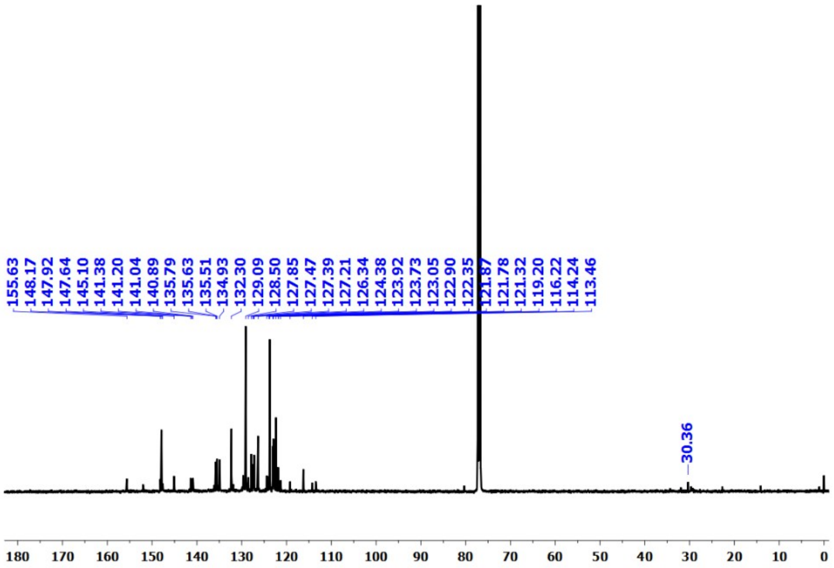


Figure S4. ^{13}C NMR spectrum of $H_2TPP(MN)(TPA)_2$ in $CDCl_3$ at 298 K.

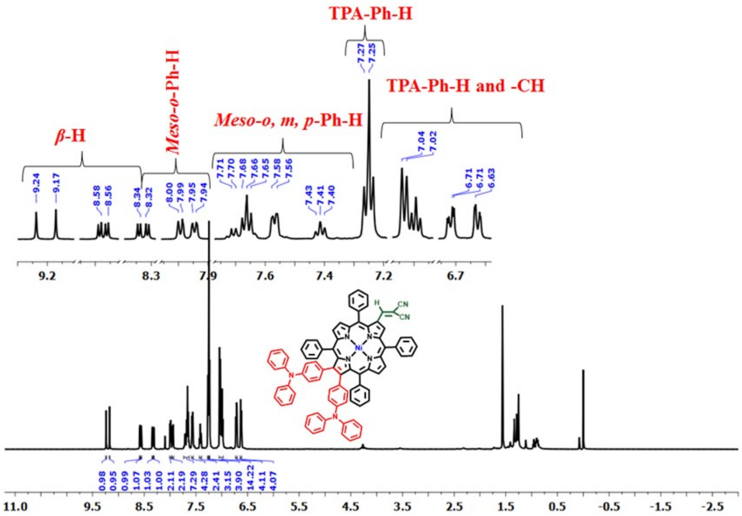


Figure S5. ^{1}H NMR spectrum of $NiTPP(MN)(TPA)_2$ in $CDCl_3$ at 298 K.

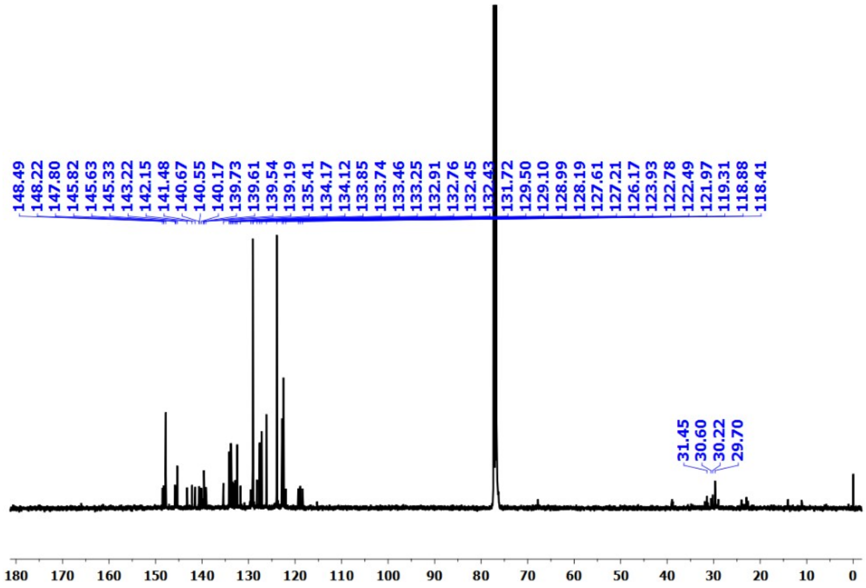


Figure S6. ^{13}C NMR spectrum of NiTPP(MN)(TPA)$_2$ in CDCl$_3$ at 298 K.

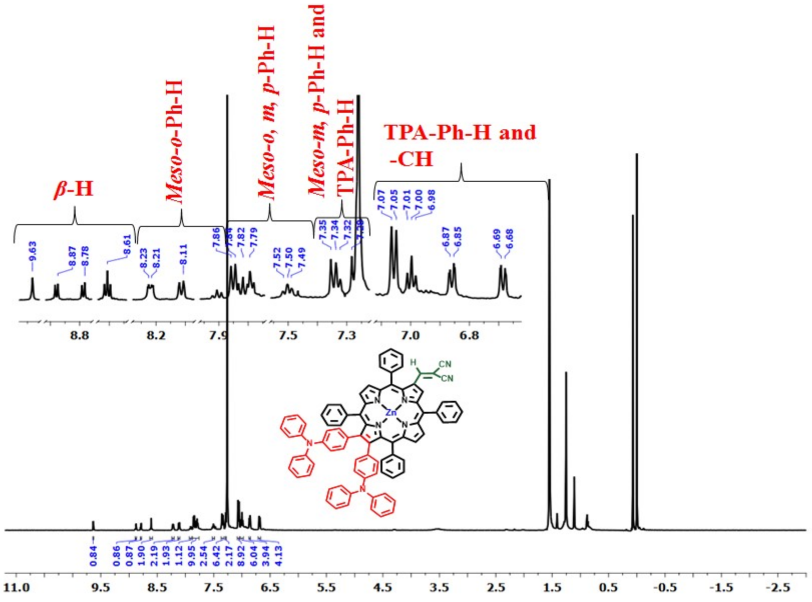


Figure S7. ^{1}H NMR spectrum of ZnTPP(MN)(TPA)$_2$ in CDCl$_3$ at 298 K.

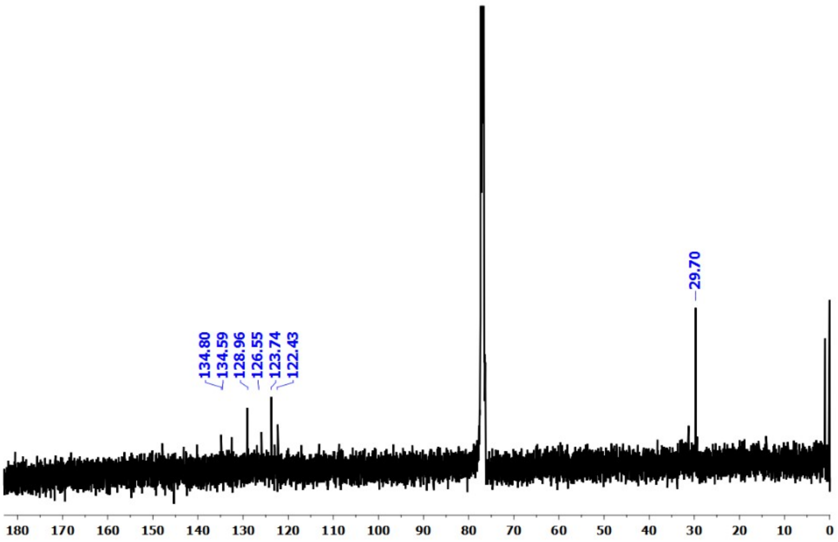


Figure S8. ^{13}C NMR spectrum of ZnTPP(MN)(TPA)$_2$ in CDCl$_3$ at 298 K.

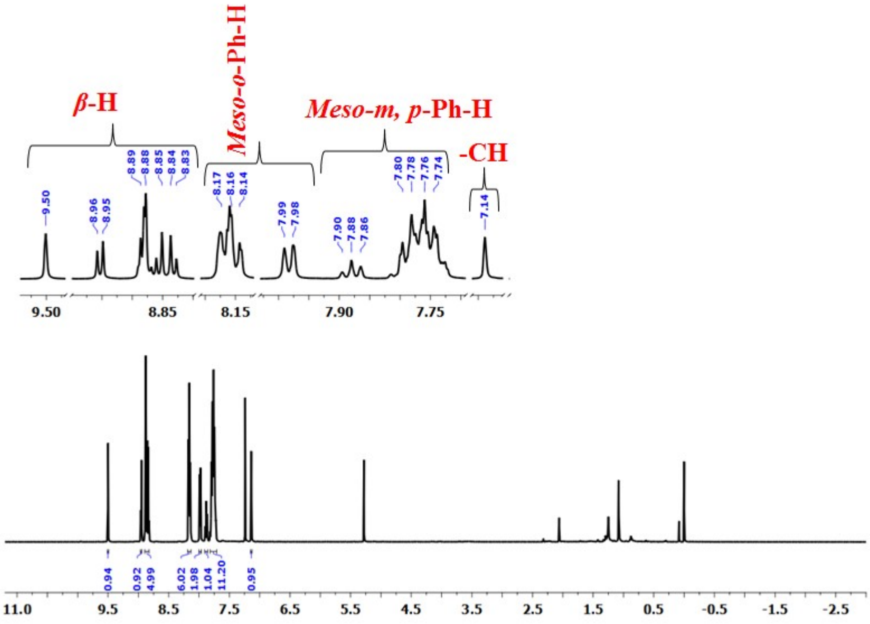


Figure S9. ^{1}H NMR spectrum of ZnTPP(MN) in CDCl$_3$ at 298 K.

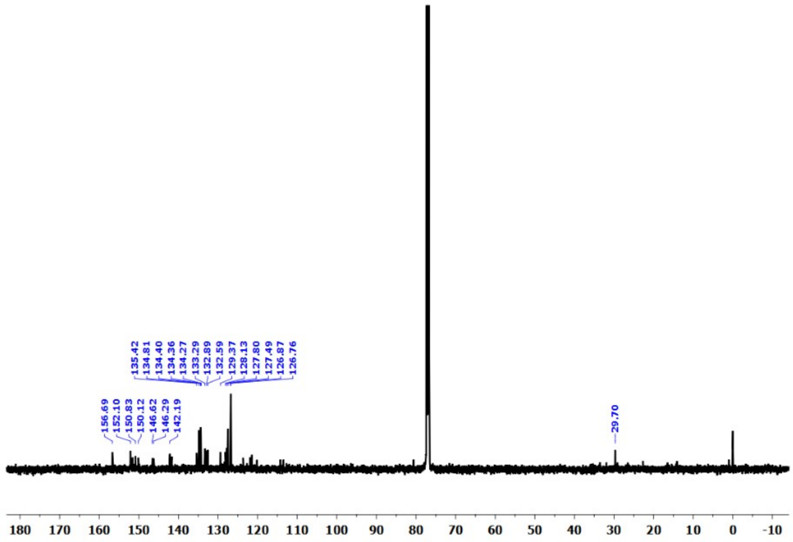


Figure S10. ^{13}C NMR spectrum of ZnTPP(MN) in $CDCl_3$ at 298 K.

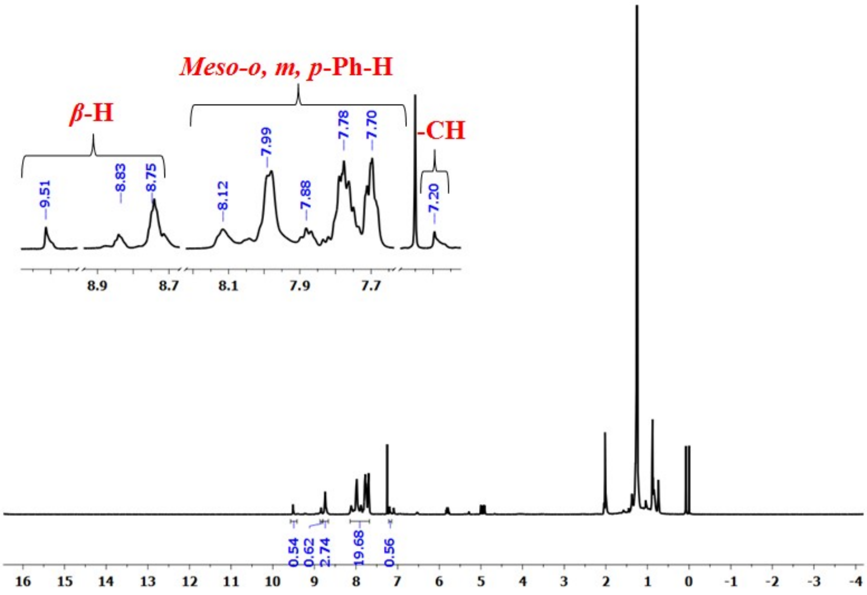


Figure S11. ^{1}H NMR spectrum of $ZnTPP(MN)Br_2$ in $CDCl_3$ at 298 K.

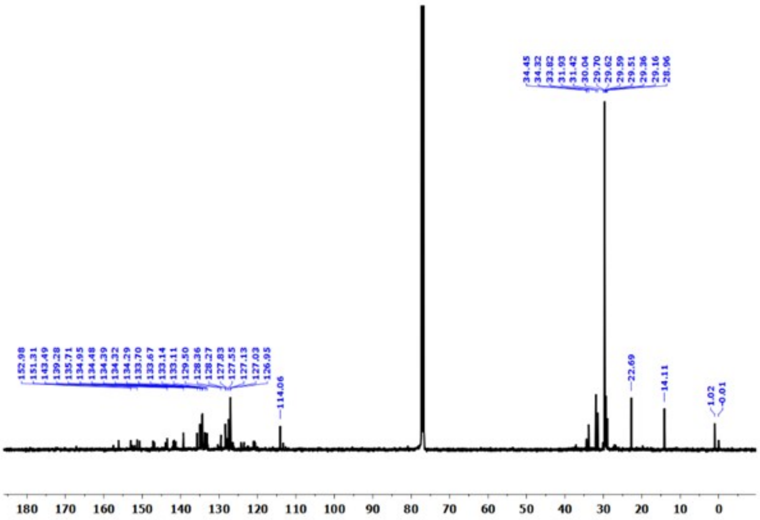


Figure S12. ^{13}C NMR spectrum of ZnTPP(MN)Br_2 in $CDCl_3$ at 298 K.

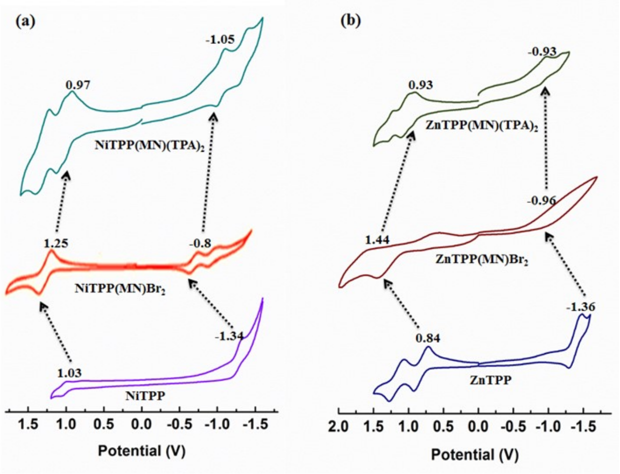


Figure S13. Comparative cyclic voltammograms of (a) NiTPP, NiTPP(MN)Br_2 and NiTPP(MN)$(TPA)_2$ (b) ZnTPP, ZnTPP(MN)Br_2, and ZnTPP(MN)$(TPA)_2$ in DCM containing 0.1 M $TBAPF_6$ at 0.1 V/s scan rate and 298 K.

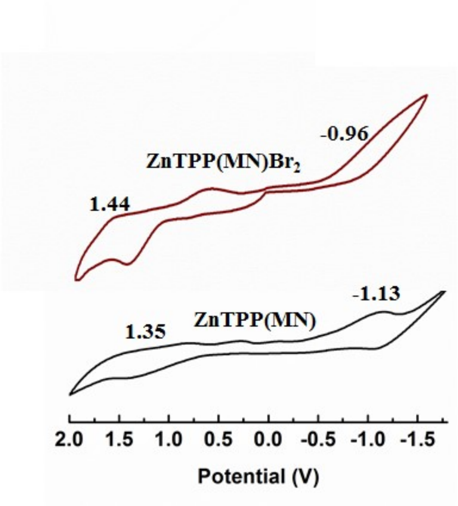


Figure S14. cyclic voltammograms of ZnTPP(MN), and ZnTPP(MN)Br$_2$ in DCM containing 0.1 M TBAPF$_6$ at 0.1 V/s scan rate and 298 K.

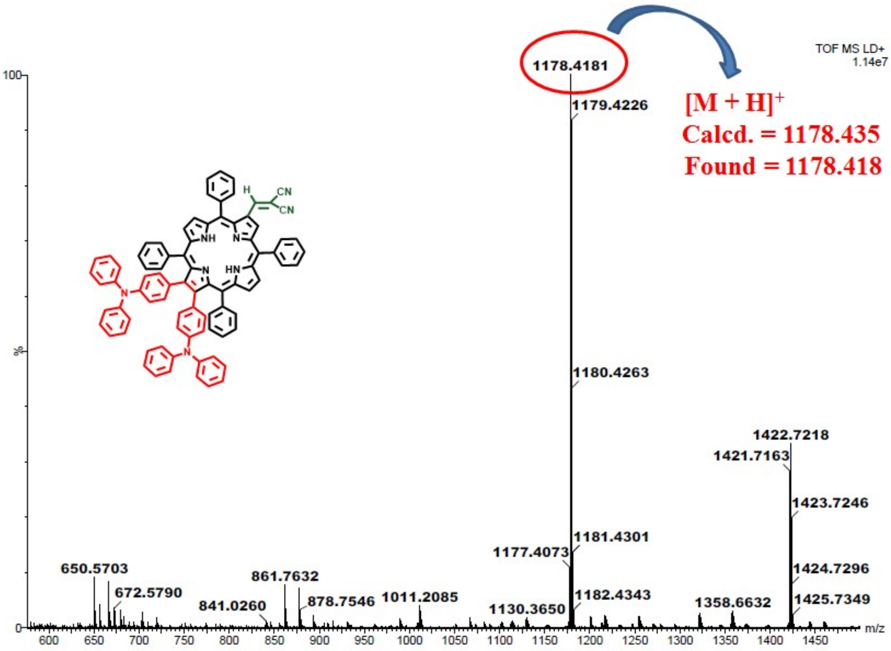


Figure S15. MALDI-TOF-MS spectrum of H$_2$TPP(MN)(TPA)$_2$ using HABA as matrix at 298 K.

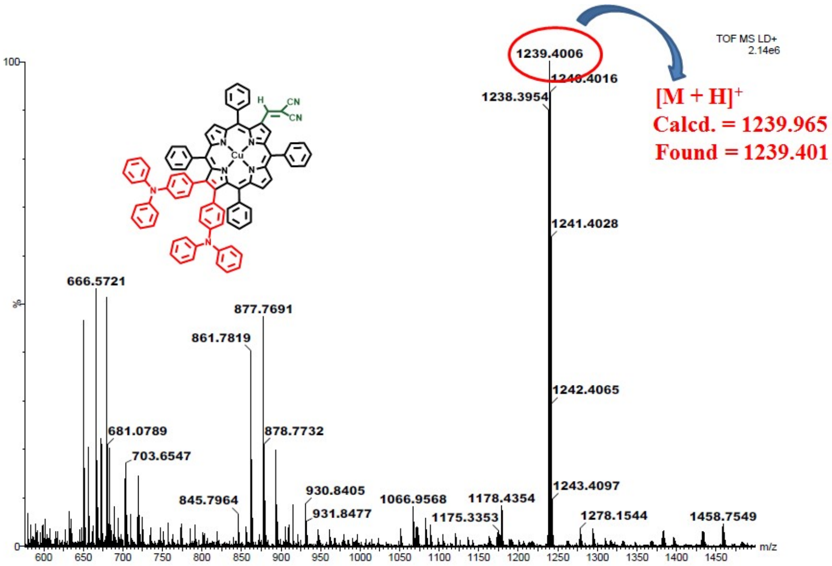


Figure S16. MALDI-TOF-MS spectrum of CuTPP(MN)(TPA)$_2$ using HABA as matrix at 298 K.

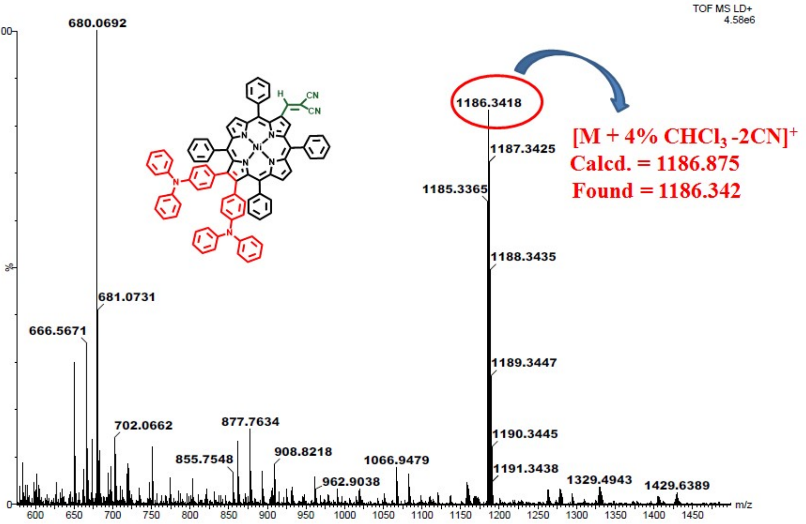


Figure S17. MALDI-TOF-MS spectrum of NiTPP(MN)(TPA)$_2$ using HABA as matrix at 298 K.

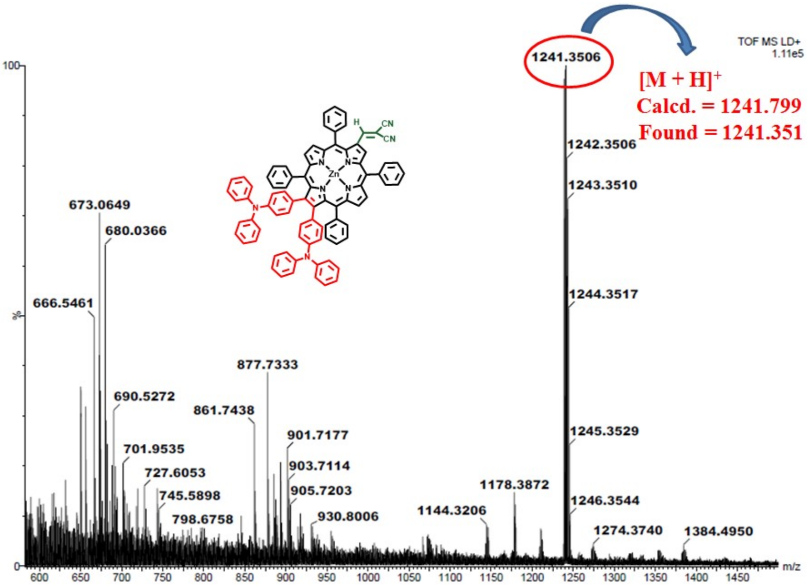


Figure S18. MALDI-TOF-MS spectrum of ZnTPP(MN)(TPA)$_2$ using HABA as matrix at 298 K.

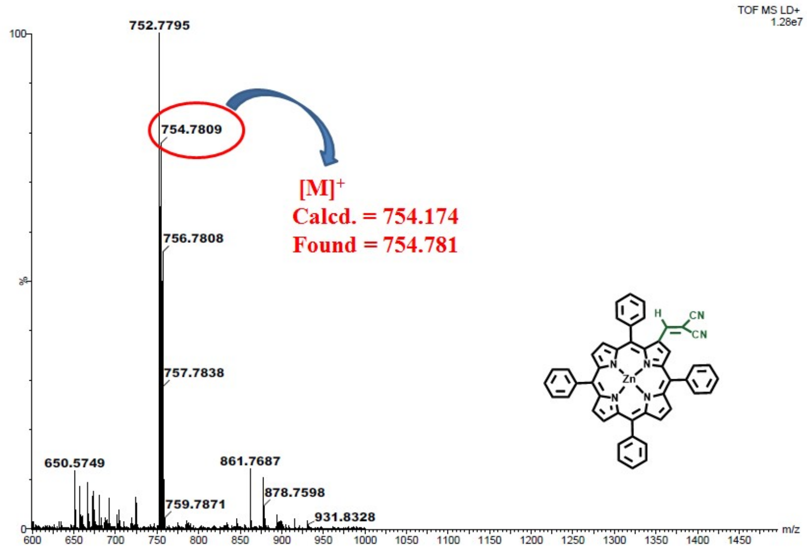


Figure S19. MALDI-TOF-MS spectrum of ZnTPP(MN) using HABA as matrix at 298 K.

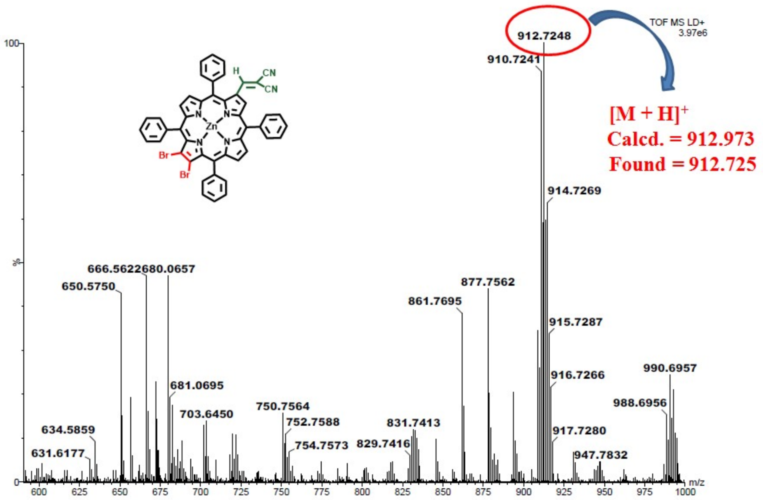


Figure S20. MALDI-TOF-MS spectrum of $ZnTPP(MN)Br_2$ using HABA as matrix at 298 K.

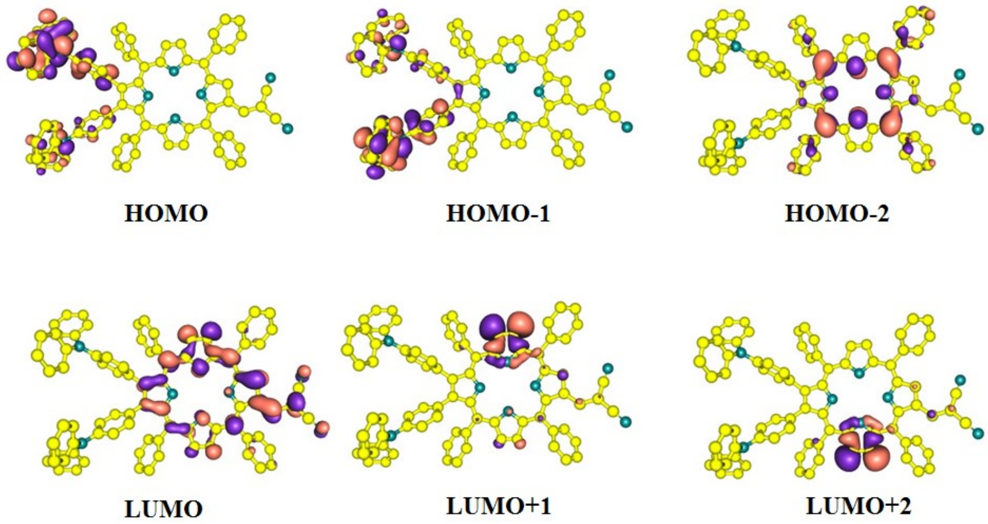


Figure S21. Frontier molecular orbitals of $H_2TPP(MN)(TPA)_2$.

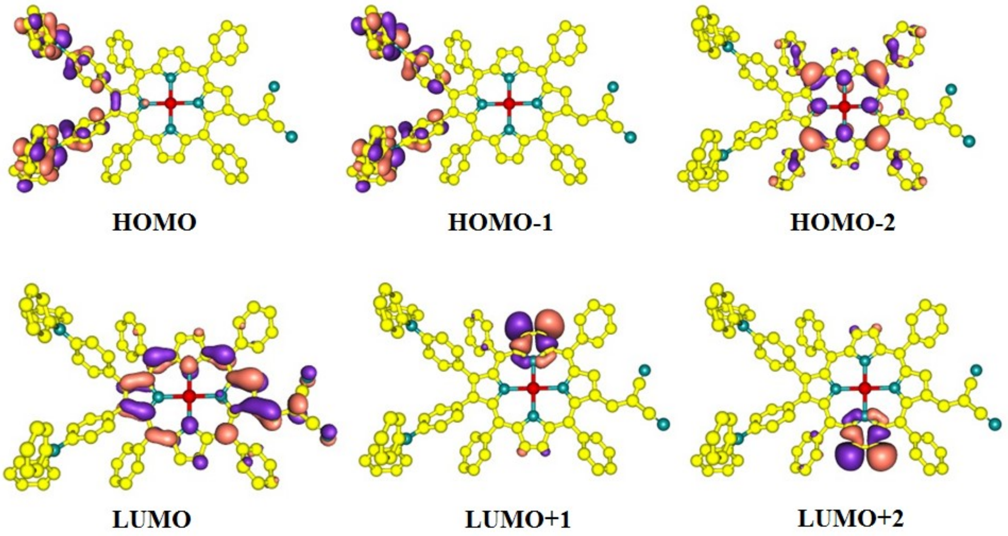


Figure S22. Frontier molecular orbitals of $ZnTPP(MN)(TPA)_2$.

Table S1. The photophysical data of synthesized porphyrins in $CHCl_3$ at 298 K.

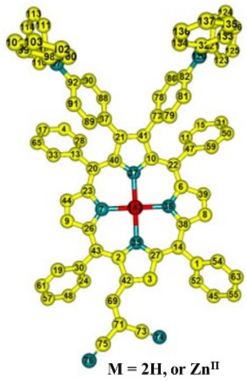
Porphyrins	**λ_{ex} (nm)**		**λ_{em} (nm)**	**ϕ_f**	**FWHM**
	B-band	Q-band			
ZnTPP(MN)	338(sh), 402(3.85), 460(4.33)	568(3.20), 619(3.36)	664	0.0112	35
$ZnTPP(MN)Br_2$	344(sh), 400(3.72), 459(4.57)	572(3.47), 622(3.60)	663	0.006	44
$H_2TPP(MN)(TPA)_2$	306(sh), 457(5.17)	535(4.08), 584(3.81), 684(3.56)	772	0.065	68
$CuTPP(MN)(TPA)_2$	308(sh), 397(4.721), 458(5.12)	566(4.10), 619(4.33)			46
$NiTPP(MN)(TPA)_2$	306(sh), 437(5.05)	551(4.04), 596(4)			32
$ZnTPP(MN)(TPA)_2$	308(sh), 403(4.22), 466(4.68)	572(3.51), 626(3.77)	684	0.022	41

In the parenthesis is log ε.

Table S2. Comparative redox potential data of porphyrins in CH_2Cl_2 containing 0.1 M $TBAPF_6$ and 0.1 V/s scan rate at 298 K.

Porphyrins	**Oxidation (V)**				**Reduction (V)**			**$\Delta E_{1/2}$**
	I	**II**	**III**	**IV**	**I**	**II**	**III**	
H_2TPP	1.08	1.34			-1.15	-1.54		2.23
H_2TPP(MN)	1.15	1.39			-0.77	-1.04		1.92
H_2TPP(MN)Br_2	1.13	1.29			-0.75			1.89
H_2TPP$(TPA)_2$CHO	1.10				-0.94			2.05
H_2TPP(MN)$(TPA)_2$	**0.68**	**1.02**	**1.21**		**-0.452**	**-0.74**		**1.13**
CuTPP	0.97	1.35			-1.33	-1.70		2.30
CuTPP(MN)	1.12	1.48			-0.89	-1.23		2.02
CuTPP(MN)Br_2	1.11	1.48			-0.84	-1.11		1.95
CuTPP$(TPA)_2$CHO	1.06	1.47			-0.97	-1.34		2.03
CuTPP(MN)$(TPA)_2$	**0.98**	**1.08**	**1.23**		**-0.85**	**-1.15**	**-1.35**	**1.83**
NiTPP	1.02	1.32			-1.28	-1.72		2.30
NiTPP(MN)	1.15	1.32	1.89		-0.88	-1.22		2.03
NiTPP(MN)Br_2	1.25				-0.81	-1.06		2.05
NiTPP$(TPA)_2$CHO	1.03	1.26	1.5	2.0	-1.05			2.09
NiTPP(MN)$(TPA)_2$	**0.97**	**1.08**	**1.31**		**-1.05**	**-1.34**		**2.02**
ZnTPP	0.84	1.15			-1.36	-1.77		2.20
ZnTPP(MN)	0.82				-1.13			1.94
ZnTPP(MN)Br_2	1.44				-0.96			
ZnTPP$(TPA)_2$CHO	1.04	1.55			-1.11	-1.36		2.16
ZnTPP(MN)$(TPA)_2$	**0.93**	**1.05**	**1.27**		**-0.93**	**-1.16**		**1.86**

Table S3. Average bond angle (Å) and bond length (°) of optimized geometry of $H_2TPP(MN)(TPA)_2$ and $ZnTPP(MN)(TPA)_2$ using B3LYP as functional and LANL2DZ as basis set.

		
Bond length (Å)		
	$H_2TPP(MN)(TPA)_2$	**$ZnTPP(MN)(TPA)_2$**
N- C_α	1.384	1.394
N - C_α'	1.401	1.414
C_α - C_β	1.443	1.461
C_α' - C_β'	1.468	1.460
C_β - C_β	1.397	1.395
C_β' - C_β'	1.248	1.258
C_α - C_m	1.412	1.426
C_α' - C_m	1.403	1.408
Δ24	0.187	0.199
ΔC_β	0.361	0.414
ΔM		0.051
Bond Angle (°)		
N - M - N		178.89
N′ - M - N′		178.09
M - N - C_α		125.73
M - N′ - C'_α		125.67
N - C_α - C_m	124.57	124.52
N′ - C_α' - C_m	128.32	124.74
N - C_α - C_β	106.51	109.33
N′ - C_α' - C_β'	107.68	105.75
C_β - C_α - C_m	128.87	127.14
C_β'- C_α' - C_m	123.73	124.51
C_α - C_m- C_α'	124.02	123.66
C_α - N- C_α	111.11	107.25
C_α' - N- C_α'	105.28	107.49
C_{87} - C_{21} – C_{41}	124.44	126.19
C_{77} - C_{41} – C_{21}	123.69	125.94

References:

1. J. N. Acharyya, D. N. Rao, M. Adnan, C. Raghavendar, R. B. Gangineni and G. V. Prakash, *Adv. Mater. Interfaces*, 2020, **7**, 2000035.
2. J. N. Acharyya and G. V. Prakash, *Optik.*, 2021, **247**, 167944.