

Electronic Supplementary Information for

Meso- β , β - β' Trifused Porphyrins: Synthesis, Spectral, Electrochemical and DFT Studies and Their Femtosecond Third-Order Nonlinear Optical Properties

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Table of Contents		Page No.
Experimental Section		S4-S8
Fig. S1	(a) Basic skeleton of ZnTFPMB(MN) ₂ showing labelled carbon atoms, (b) displacement of porphyrin 24-core atoms from the mean plane of ZnTFPMB(MN) ₂ in angstroms.	S9
Table S1	Crystallographic data of ZnTFPMB(MN) ₂ .	S9
Table S2	Selected average bond lengths and angles of ZnTFPMB(MN) ₂ .	S10
Fig. S2	Comparative absorption spectra of compounds indicated in CH ₂ Cl ₂ at 298 K.	S11
Fig. S3	Comparative absorption spectra of compounds indicated in CH ₂ Cl ₂ at 298 K.	S11
Fig. S4	Comparative absorption spectra of compounds indicated in CH ₂ Cl ₂ at 298 K.	S12
Fig. S5	Comparative emission spectra of compounds indicated in CH ₂ Cl ₂ at 298 K.	S12
Fig. S6	Comparative emission spectra of compounds indicated in CH ₂ Cl ₂ at 298 K.	S13
Fig. S7	Comparative emission spectra of compounds indicated in CH ₂ Cl ₂ at 298 K.	S13
Fig. S8	Comparative fluorescence lifetime decay profile of H ₂ TPCMB(IND) ₂ and H ₂ TPCMB(MN) ₂ .	S14

Fig. S9	Fluorescence lifetime decay profile of H ₂ TFPMB(IND) ₂ .	S14
Fig. S10	Fluorescence lifetime decay profile of ZnTFPMB(IND) ₂ .	S15
Fig. S11	¹ H NMR spectrum of H ₂ TPCMB(IND) ₂ in CDCl ₃ at 298 K.	S15
Fig. S12	¹ H NMR spectrum of H ₂ TFPMB(IND) ₂ in CDCl ₃ at 298 K.	S16
Fig. S13	¹ H NMR spectrum of ZnTFPMB(IND) ₂ in CDCl ₃ at 298 K.	S16
Fig. S14	¹ H NMR spectrum of ZnTFPMB(MN) ₂ in CDCl ₃ at 298 K.	S17
Fig. S15	¹ H NMR spectrum of ZnTFPMB(VCN) ₂ in CD ₃ OD+CDCl ₃ at 298 K.	S17
Fig. S16	¹³ C NMR spectrum of ZnTFPMB(VCN) ₂ in CD ₃ OD+CDCl ₃ at 298 K.	S18
Fig. S17	MALDI-TOF mass spectrum of H ₂ TPCMB(IND) ₂ in positive ion mode at 298 K.	S18
Fig. S18	MALDI-TOF mass spectrum of H ₂ TFPMB(IND) ₂ in positive ion mode at 298 K.	S19
Fig. S19	MALDI-TOF mass spectrum of CuTFPMB(IND) ₂ in positive ion mode at 298 K.	S19
Fig. S20	MALDI-TOF mass spectrum of ZnTFPMB(IND) ₂ in positive ion mode at 298 K.	S20
Fig. S21	MALDI-TOF mass spectrum of CuTFPMB(MN) ₂ in positive ion mode at 298 K.	S20
Fig. S22	MALDI-TOF mass spectrum of ZnTFPMB(MN) ₂ in positive ion mode at 298 K.	S21
Fig. S23	MALDI-TOF mass spectrum of CuTFPMB(VCN) ₂ in positive ion mode at 298 K.	S21
Fig. S24	MALDI-TOF mass spectrum of ZnTFPMB(VCN) ₂ in positive ion mode at 298 K.	S22
Fig. S25	Cyclic voltammograms of IND-appended porphyrinoids in CH ₂ Cl ₂ at 298 K using TBAPF ₆ as a supporting electrolyte. Scan rate = 100 mV/s.	S22
Fig. S26	Cyclic voltammograms of MN-appended porphyrinoids in CH ₂ Cl ₂ at 298 K using TBAPF ₆ as a supporting electrolyte. Scan rate = 100 mV/s.	S23
Fig. S27	Complete FMO profile of compounds indicated.	S23
Fig. S28	Complete FMO profile of compounds indicated.	S24
Fig. S29	Complete FMO profile of compounds indicated.	S24
Fig. S30	Optimized geometry (top view a, b, c) and (side view d, e, f) of H ₂ TFPMB(IND) ₂ , CuTFPMB(IND) ₂ and ZnTFPMB(IND) ₂ respectively.	S25

	The unfused <i>meso</i> -phenyl groups are omitted for clarity in the side views.	
Fig. S31	Optimized geometry (top view a, b, c) and (side view d, e, f) of H ₂ TFPMB(MN) ₂ , CuTFPMB(MN) ₂ and ZnTFPMB(MN) ₂ respectively. The unfused <i>meso</i> -phenyl groups are omitted for clarity in the side views.	S25
Fig. S32	Optimized geometry (top view a, b, c) and (side view d, e, f) of H ₂ TFPMB(VCN) ₂ , CuTFPMB(VCN) ₂ and ZnTFPMB(VCN) ₂ respectively. The unfused <i>meso</i> -phenyl groups are omitted for clarity in the side views.	S26
Table S3	Selected average bond lengths and angles of synthesized IND-appended porphyrinoids.	S27
Table S4	Selected average bond lengths and angles of synthesized MN-appended porphyrinoids.	S28
Table S5	Selected average bond lengths and angles of synthesized π -extended trifused porphyrins.	S29
Table S6	Theoretically calculated ground state dipole moment and HOMO-LUMO energy gap of synthesized porphyrinoids.	S30
Fig. S33	Comparative (theoretical and experimental) absorption spectra of H ₂ TPCMB(IND) ₂ .	S30
Fig. S34	Comparative (theoretical and experimental) absorption spectra of H ₂ TFPMB(IND) ₂ .	S31
Fig. S35	Comparative (theoretical and experimental) absorption spectra of CuTFPMB(IND) ₂ .	S31
Fig. S36	Comparative (theoretical and experimental) absorption spectra of ZnTFPMB(IND) ₂ .	S32
Fig. S37	Comparative (theoretical and experimental) absorption spectra of H ₂ TPCMB(MN) ₂ .	S32
Fig. S38	Comparative (theoretical and experimental) absorption spectra of H ₂ TFPMB(MN) ₂ .	S33
Fig. S39	Comparative (theoretical and experimental) absorption spectra of CuTFPMB(MN) ₂ .	S33
Fig. S40	Comparative (theoretical and experimental) absorption spectra of ZnTFPMB(MN) ₂ .	S34
Fig. S41	Comparative (theoretical and experimental) absorption spectra of H ₂ TFPMB(VCN) ₂ .	S34

Fig. S42	Comparative (theoretical and experimental) absorption spectra of CuTFPMB(VCN) ₂ .	S35
Fig. S43	Comparative (theoretical and experimental) absorption spectra of ZnTFPMB(VCN) ₂ .	S35
Table S6	Calculated electronic excitation energies, major orbital contribution, theoretical and experimental absorption maxima, and oscillatory strength of investigated porphyrins.	S36
	References	S37

EXPERIMENTAL SECTION

Chemicals and Instruments

Benzaldehyde and Pyrrole were purchased from SRL India and TCI Chemicals, respectively. Metal salts, K₂CO₃, N-bromosuccinimide (NBS) and DDQ were purchased from SRL, India. Malononitrile, Indane-1,3-dione, Methylacrylate and TBACN were taken from Sigma Aldrich and used as received. TBAPF₆ is purchased from Sigma Aldrich. The chloroform, dichloromethane, hexane and toluene solvents were distilled or dried before use. HPLC-grade solvent methanol, DMF and DMSO were purchased from Merck and used without further purification. Silica gel (100-200 mesh) was purchased from Finar Chemicals, India. TBAPF₆ was recrystallized three times from hot ethanol and dried under a vacuum. NBS was recrystallized from hot water and dried for 12 h at 70 °C under vacuum. Pd(OAc)₂ was purchased from Loba Chemie and used as received. Precoated thin layered silica gel chromatographic plates were purchased from E. Merck.

The electronic absorption spectra were recorded using a UV-1800 Shimadzu UV-Vis Spectrophotometer with a pair of 1 cm path-length quartz cells. The emission spectra were recorded on a HORIBA Fluoromax spectrofluorometer using a quartz cell of 10 mm path length. Fluorescence lifetime data was collected on the Edinburg FLS-1000-xs-t instrument with picosecond pulsed diode laser sources of wavelength 450 nm. ¹H NMR spectra were recorded using a JEOL ECX 500 MHz spectrometer using CDCl₃ and CD₂Cl₂ as a solvent. Bruker Ultraflexextreme-TN MALDI-TOF mass spectrometer was used to record mass spectra. The single crystal X-ray diffraction data were collected on a Bruker Apex-II CCD diffractometer. The cyclic voltammetry (CV) studies were carried out using CH instruments

(CHI 7044E). A three-electrode assembly that consisted of a platinum working electrode, Ag/AgCl as a reference electrode, and Pt wire as a counter electrode was used. The porphyrin concentration was maintained at ~1 mM during electrochemical measurements. The whole experiment was performed under an inert atmosphere.

A femtosecond pulsed laser carried out the NLO experiments [M/s Coherent, Libra] with a pulse width of ~50 fs, a repetition rate of 1 kHz, and a wavelength of 800 nm. A lock-in amplifier and a photodiode were used to gather the signals using the LabVIEW program. We employed the 1D translational stage to scan the sample within the Rayleigh range to collect NLO absorption and refraction data, and more information is available in our earlier reports.^{1,2}

Synthesis of *trans*-Mono Benzochlorin; H₂TPCMB(IND)₂

1,3-Indanedione (106 mg, 0.725 mmol) and K₂CO₃ (100 mg, 0.724 mmol) were dissolved in 3 ml of DMSO and purged with argon for 10 min. To this, 60 mg H₂TPP(NO₂)MB (0.072 mmol) was added and the resulting solution was stirred at 80 °C for 3 hours. The reaction was monitored by TLC and UV-Vis spectroscopy. After the completion of the reaction, the solution was allowed to cool to room temperature, and 15 ml CHCl₃ was added. The resulting mixture was washed three times with brine solution and the organic layer was separated and passed over anhydrous sodium sulphate. The solvent was removed under reduced pressure, and the crude product was purified using silica gel column chromatography using CHCl₃ as an eluent. The desired compound was recrystallized using CHCl₃/MeOH (3:1) mixture.

H₂TPCMB(IND)₂: Yield: 74% (57 mg, 0.053 mmol), UV/vis (CH₂Cl₂): λ_{max} (nm) (ε × 10⁻³ M⁻¹ cm⁻¹): 414(sh) (83), 436 (344), 519 (22), 564 (4), 616 (8), 674 (40). ¹H NMR (500 MHz, CDCl₃) δ(ppm): 8.60 – 8.59 (m, 2H, β-H), 8.25 (d, *J* = 7.2 Hz, 2H, β-H), 8.22 (d, *J* = 4.7 Hz, 2H, *meso*-Ph-H), 8.03 (d, *J* = 7.7 Hz, 2H, *meso*-Ph-H), 7.97 (d, *J* = 7.4 Hz, 2H, *meso*-Ph-H), 7.94 – 7.82 (m, 8H, *meso*-Ph-H), 7.77 (t, *J* = 7.4 Hz, 2H, *meso*-Ph-H), 7.72 – 7.68 (m, 4H, *meso*-Ph-H), 7.56 (d, *J* = 7.5 Hz, 2H, IND-Ph-H), 7.50 (t, *J* = 7.5 Hz, 2H, IND-Ph-H), 7.45 (t, *J* = 7.4 Hz, 2H, IND-Ph-H), 7.30 – 7.28 (d, *J* = 7.5 Hz, 4H, IND-Ph-H & Benzo-CH), 4.88 (d, *J* = 2.8 Hz, 2H, β-CH of Chlorin), 3.89 (s, 6H, -COOCH₃), 3.26 (d, *J* = 2.9 Hz, 2H, -CH of Chlorin), -1.78 (s, 2H, inner NH). MALDI-TOF-MS. Found: *m/z* 1071.807 ([M+H]⁺) Calcd: *m/z* 1071.332. Elemental analysis calcd. for C₇₀H₄₆N₄O₈: C, 78.49; H, 4.33; N, 5.23%. Found: C, 77.54; H, 3.83; N, 4.47%.

Synthesis of Trifused Mono Benzoporphyrin; H₂TFPMB(IND)₂ and Its Metal Complexes; MTFPMB(IND)₂ where M = Cu(II) and Zn(II)

40 mg H₂TPCMB(IND)₂ was dissolved in 10 mL of CHCl₃. To this, 10 equiv. DDQ was added and the resulting reaction mixture was refluxed for 10 hours. The progress of the reaction was monitored by UV-Vis and TLC. After completion of the reaction, the mixture was washed three times with water to remove excess DDQ. The organic layer was passed over anhydrous sodium sulfate and the solvent was evaporated under reduced pressure. The crude product was purified by silica gel column chromatography using CHCl₃ as an eluent.

H₂TFPMB(IND)₂: Yield: 85% (34 mg, 0.032 mmol), UV/vis (CH₂Cl₂): λ_{max} (nm) (ε × 10⁻³ M⁻¹ cm⁻¹): 478 (406), 572 (22), 619 (21), 650 (10), 714 (9). ¹H NMR (500 MHz, CDCl₃) δ(ppm): 9.52 (d, *J* = 4.6 Hz, 2H, β-H), 8.72 (d, *J* = 4.8 Hz, 2H, β-H), 8.17 (d, *J* = 7.7 Hz, 2H, Fused-*meso*-Ph-H), 8.10 (d, *J* = 6.8 Hz, 4H, Fused-*meso*-Ph-H), 8.05 – 7.97 (m, 4H, *meso*-Ph-H), 7.97 – 7.86 (m, 6H, *meso*-Ph-H), 7.83 (t, *J* = 7.5 Hz, 4H, *meso*-Ph-H & IND-Ph-H), 7.49 (t, *J* = 7.8 Hz, 2H, IND-Ph-H), 7.30 (s, 2H, Benzo-CH), 7.04 (d, *J* = 7.7 Hz, 2H, IND-Ph-H), 6.91 (d, *J* = 7.8 Hz, 2H, IND-Ph-H), 3.90 (s, 6H, -COOCH₃), -0.27 (s, 2H, inner NH). MALDI-TOF-MS. Found: *m/z* 1065.647 ([M+H]⁺) Calcd: *m/z* 1065.285. Elemental analysis calcd. for C₇₀H₄₀N₄O₈: C, 78.94; H, 3.79; N, 5.26%. Found: C, 77.82; H, 3.12; N, 4.52%.

10 mg of H₂TFPMB(IND)₂ was dissolved in 5 mL of CHCl₃ in two different round bottom flasks. To this, 10 equiv. of M(OAc)₂.xH₂O (M = Cu(II) and Zn(II)) in 1 mL of MeOH was added and the resulting solution was refluxed for 1 hour. After completion of the reaction, the solvent was removed under reduced pressure and the crude products were redissolved in CHCl₃ and washed twice with water to remove excess metal salts. The organic layer was separated and dried over anhydrous sodium sulfate. The desired metal complexes were purified by silica gel column chromatography using acetone/CHCl₃ (1:99) as an eluent and recrystallized using CHCl₃/MeOH (3:1) mixture.

CuTFPMB(IND)₂: Yield: 85% (9 mg, 0.008 mmol), UV/vis (CH₂Cl₂): λ_{max} (nm) (ε × 10⁻³ M⁻¹ cm⁻¹): 480 (363), 606 (32), 651 (15). MALDI-TOF-MS. Found: *m/z* 1126.677 ([M+H]⁺) Calcd: *m/z* 1126.199. Elemental analysis calcd. for C₇₀H₃₈N₄O₈Cu: C, 74.63; H, 3.40; N, 4.97%. Found: C, 73.73; H, 2.90; N, 4.12%.

ZnTFPMB(IND)₂: Yield: 76% (8 mg, 0.007 mmol), UV/vis (CH₂Cl₂): λ_{max} (nm) (ε × 10⁻³ M⁻¹ cm⁻¹): 459(sh) (39), 485 (189), 537 (9), 614 (10), 661 (4). ¹H NMR (400 MHz, CDCl₃) δ(ppm): 9.55 (d, *J* = 4.7 Hz, 2H, β-H), 8.75 (d, *J* = 4.6 Hz, 2H, β-H), 8.23 (d, *J* = 7.9 Hz, 2H, Fused-*meso*-Ph-H), 8.13 (s, 4H, Fused-*meso*-Ph-H), 8.03 (dt, *J* = 7.3, 3.7 Hz, 4H, Fused-*meso*-Ph-H & IND-Ph-H), 7.95 – 7.81 (m, 10H, Unfused-*meso*-Ph-H), 7.54 – 7.49 (m, 4H, Benzo-CH &

IND-Ph-H), 7.07 – 7.02 (m, 2H, IND-Ph-H), 6.96 – 6.91 (m, 2H, IND-Ph-H), 3.92 (s, 6H, -COOCH₃). MALDI-TOF-MS. Found: m/z 1127.527 ([M+H]⁺) Calcd: m/z 1127.198. Elemental analysis calcd. for C₇₀H₃₈N₄O₈Zn: C, 74.51; H, 3.39; N, 4.96%. Found: C, 73.32; H, 2.95; N, 4.02%.

Synthesis and characterization data of H₂TPCMB(MN)₂, H₂TFPMB(MN)₂ and H₂TFPMB(VCN)₂ will be found in recently reported literature by our group.³

Synthesis of MTFPMB(MN)₂ where M = Cu(II) and Zn(II)

10 mg of H₂TFPMB(MN)₂ was dissolved in 5 mL of CHCl₃ in two different round bottom flasks. To this, 10 equiv. of M(OAc)₂.xH₂O (M = Cu(II) and Zn(II)) in 1 mL of MeOH was added and the resulting solution was refluxed for 1 hour. After completion of the reaction, the solvent was removed under reduced pressure and the crude products were redissolved in CHCl₃ and washed twice with water to remove excess metal salts. The organic layer was separated and dried over anhydrous sodium sulfate. The desired metal complexes were purified by silica gel column chromatography using acetone/CHCl₃ (1:99) as an eluent and recrystallized using CHCl₃/MeOH (3:1) mixture.

CuTFPMB(MN)₂: Yield: 85% (9 mg, 0.009 mmol), UV/vis (CH₂Cl₂): λ_{max} (nm) (ε × 10⁻³ M⁻¹ cm⁻¹): 481 (256), 612 (20), 659 (22). MALDI-TOF-MS. Found: m/z 965.752 ([M]⁺) Calcd: m/z 965.169. Elemental analysis calcd. for C₅₈H₃₀N₈O₄Cu: C, 72.08; H, 3.13; N, 11.59%. Found: C, 71.16; H, 2.70; N, 10.82%.

ZnTFPMB(MN)₂: Yield: 84% (9 mg, 0.009 mmol), UV/vis (CH₂Cl₂): λ_{max} (nm) (ε × 10⁻³ M⁻¹ cm⁻¹): 462(sh) (88), 488 (359), 623 (18), 674 (21). ¹H NMR (500 MHz, CDCl₃) δ (ppm): 9.47 (d, *J* = 4.7 Hz, 2H, β-H), 8.70 (d, *J* = 4.7 Hz, 2H, β-H), 8.47 (d, *J* = 7.7 Hz, 2H, Fused-*o*-Ph-H), 8.33 (d, *J* = 8.1 Hz, 2H, Fused-*p*-Ph-H), 8.02 (d, *J* = 6.6 Hz, 4H, Fused-*m*-Ph-H), 7.91 (t, *J* = 7.6 Hz, 2H, Unfused-*meso*-Ph-H), 7.84 (dt, *J* = 14.9, 7.6 Hz, 6H, Unfused-*meso*-Ph-H), 7.69 (t, *J* = 7.4 Hz, 2H, Unfused-*meso*-Ph-H), 7.36 (s, 2H, Benzo-CH), 3.84 (s, 6H, -COOCH₃). MALDI-TOF-MS. Found: m/z 967.732 ([M+H]⁺) Calcd: m/z 967.168. Elemental analysis calcd. for C₅₈H₃₀N₈O₄Zn: C, 71.94; H, 3.12; N, 11.57%. Found: C, 70.83; H, 2.76; N, 10.73%.

Synthesis of π-Extended Trifused Porphyrins; MTFPMB(VCN)₂ where M = Cu(II) and Zn(II)

10 mg of H₂TFPMB(VCN)₂ was dissolved in 5 mL of CHCl₃ in two different round bottom flasks. To this, 10 equiv. of M(OAc)₂.xH₂O (M = Cu(II) and Zn(II)) in 1 mL of MeOH was

added and the resulting solution was refluxed for 1 hour. After completion of the reaction, the solvent was removed under reduced pressure and the crude products were redissolved in CHCl_3 and washed twice with water to remove excess metal salts. The organic layer was separated and dried over anhydrous Na_2SO_4 . The desired metal complexes were purified by silica gel column chromatography using CHCl_3 as eluent and recrystallized using $\text{CHCl}_3/\text{MeOH}$ (3:1) mixture.

CuTFPMB(VCN)₂: Yield: 84% (9 mg, 0.010 mmol), UV/vis (CH_2Cl_2): λ_{max} (nm) ($\epsilon \times 10^{-3} \text{ M}^{-1} \text{ cm}^{-1}$): 334 (39), 441 (77), 517 (50), 730 (180), 786 (15), 854 (22). MALDI-TOF-MS. Found: m/z 913.454 ($[\text{M}]^+$) Calcd: m/z 913.162. Elemental analysis calcd. for $\text{C}_{56}\text{H}_{30}\text{N}_6\text{O}_4\text{Cu}$: C, 73.55; H, 3.31; N, 9.19%. Found: C, 72.82; H, 2.92; N, 8.75%.

ZnTFPMB(VCN)₂: Yield: 75% (8 mg, 0.009 mmol), UV/vis (CH_2Cl_2): λ_{max} (nm) ($\epsilon \times 10^{-3} \text{ M}^{-1} \text{ cm}^{-1}$): 340 (30), 444 (66), 525 (44), 748 (14), 805 (16), 844 (19). ^1H NMR (500 MHz, $\text{CD}_3\text{OD}+\text{CDCl}_3$) δ (ppm): 9.02 (d, $J = 8.3$ Hz, 2H, Fused-*meso*-Ph-H), 8.96 (d, $J = 8.2$ Hz, 2H, Fused-*meso*-Ph-H), 8.69 (d, $J = 4.5$ Hz, 2H, β -H), 8.05 (d, $J = 4.5$ Hz, 2H, β -H), 7.98 (t, $J = 7.4$ Hz, 2H, Fused-*meso*-Ph-H), 7.90 (d, $J = 7.2$ Hz, 6H, Unfused-*meso*-Ph-H), 7.84 (t, $J = 7.4$ Hz, 2H, Fused-*meso*-Ph-H), 7.76 (t, $J = 7.4$ Hz, 4H, Unfused-*meso*-Ph-H), 6.98 (s, 2H, Benzo-CH), 3.85 (s, 6H, $-\text{COOCH}_3$). ^{13}C NMR (126 MHz, $\text{CD}_3\text{OD}+\text{CDCl}_3$) δ (ppm): 169.06, 155.85, 139, 133.48, 133.39, 132.30, 131.41, 129.69, 129.04, 128.39, 127.88, 125.59, 125.51, 118.01, 110.58, 52.59. MALDI-TOF-MS. Found: m/z 914.505 ($[\text{M}]^+$) Calcd: m/z 914.162. Elemental analysis calcd. for $\text{C}_{56}\text{H}_{30}\text{N}_6\text{O}_4\text{Zn}$: C, 73.41; H, 3.30; N, 9.17%. Found: C, 72.10; H, 2.72; N, 8.59%.

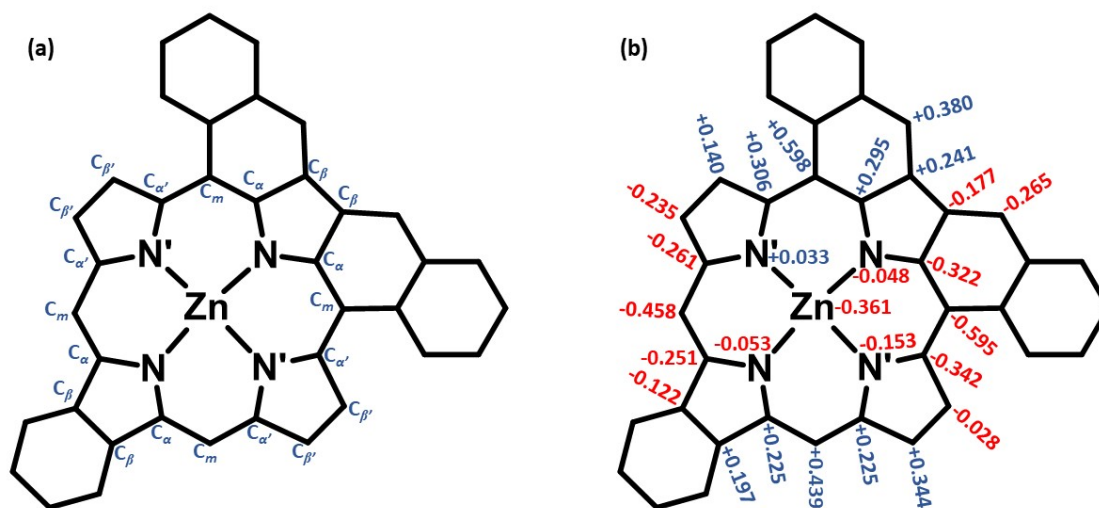


Fig. S1 (a) Basic skeleton of ZnTFPMB(MN)₂ showing labeled carbon atoms, (b) displacement of porphyrin 24-core atoms from the mean plane of ZnTFPMB(MN)₂ in angstroms.

Table S1 Crystallographic Data of ZnTFPMB(MN)₂.

	ZnTFPMB(MN)₂
Empirical Formula	C ₆₁ H ₃₈ Cl ₃ N ₈ O ₆ Zn
Formula Wt.	1150.71 g/mol
Crystal System	<i>Triclinic</i>
Space Group	<i>P</i> $\bar{1}$
a (Å)	9.431(3)
b (Å)	16.704(6)
c (Å)	19.162(7)
α (°)	64.511(15)
β (°)	81.957(16)
γ (°)	85.757(16)
Volume (Å ³)	2697.8(16)
Z	2
D _{calcd} (g/cm ³)	1.417
Wavelength (Å)	0.71073
T (K)	296(2)
No. of total reflns.	34685
No. of Indepnt. reflns.	9264
R	0.0818
GOOF	0.997
CCDC	2392230

Table S2 Selected average bond lengths and angles of ZnTFPMB(MN)₂.

Bond Length (Å)	
M-N	1.380(5)
M-N'	2.038(3)
N-C _α	1.375(5)
N'-C _{α'}	1.380(5)
C_α-C_β	1.451(6)
C_{α'}-C_{β'}	1.441(6)
C _β -C _β	1.386(6)
C _{β'} -C _{β'}	1.346(6)
C _α -C _m	1.415(6)
C _{α'} -C _m	1.416(5)
ΔC_β (Å)	0.728
Δ24 (Å)	0.560
Δ38 (Å)	0.562
ΔM	0.367
Bond Angles (°)	
M-N-C _α	126.37(2)
M-N'-C _{α'}	125.82(3)
N-M-N	162.66(14)
N'-M-N'	162.82(14)
N-C _α -C _m	124.37(3)
N'-C _{α'} -C _m	125.27(4)
N-C _α -C _β	110.17(3)
N'-C _{α'} -C _{β'}	108.45(4)
C _β -C _α -C _m	125.35(4)
C _{β'} -C _{α'} -C _m	126.02(4)
C _α -C _m -C _{α'}	124.37(4)
C _α -C _β -C _β	106.42(4)
C _{α'} -C _{β'} -C _{β'}	107.75(4)
C _α -N-C _α	106.80(3)
C _{α'} -N-C _{α'}	107.45(2)

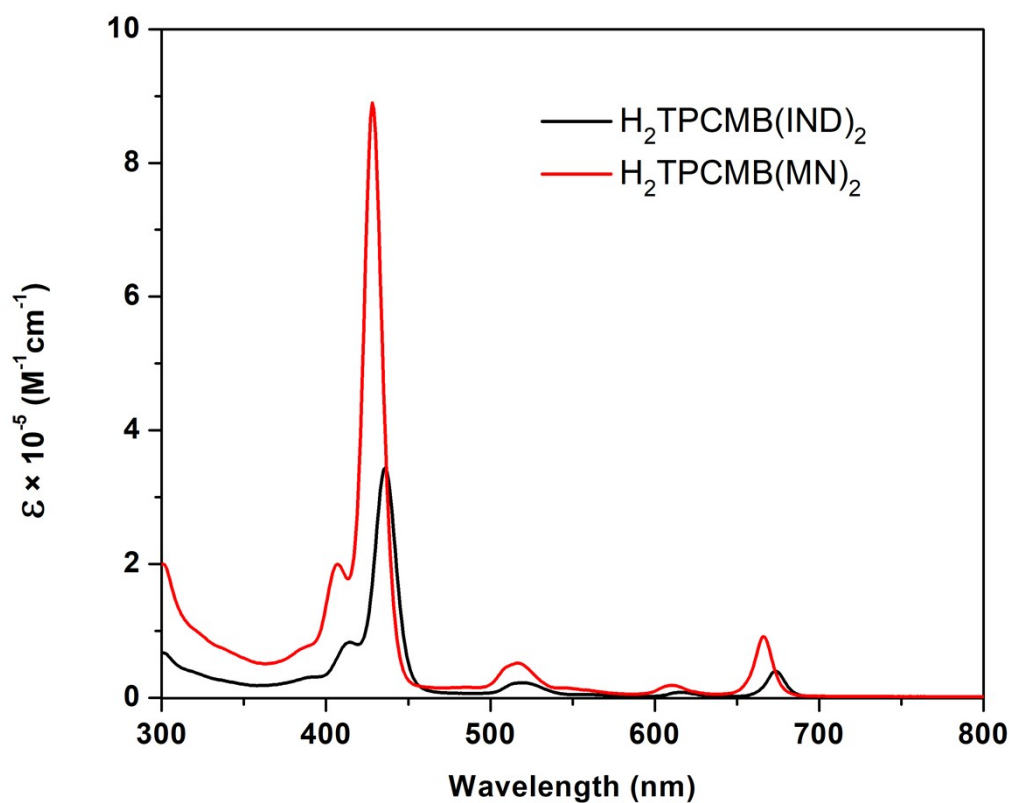


Fig. S2 Comparative absorption spectra of compounds indicated in CH_2Cl_2 at 298 K.

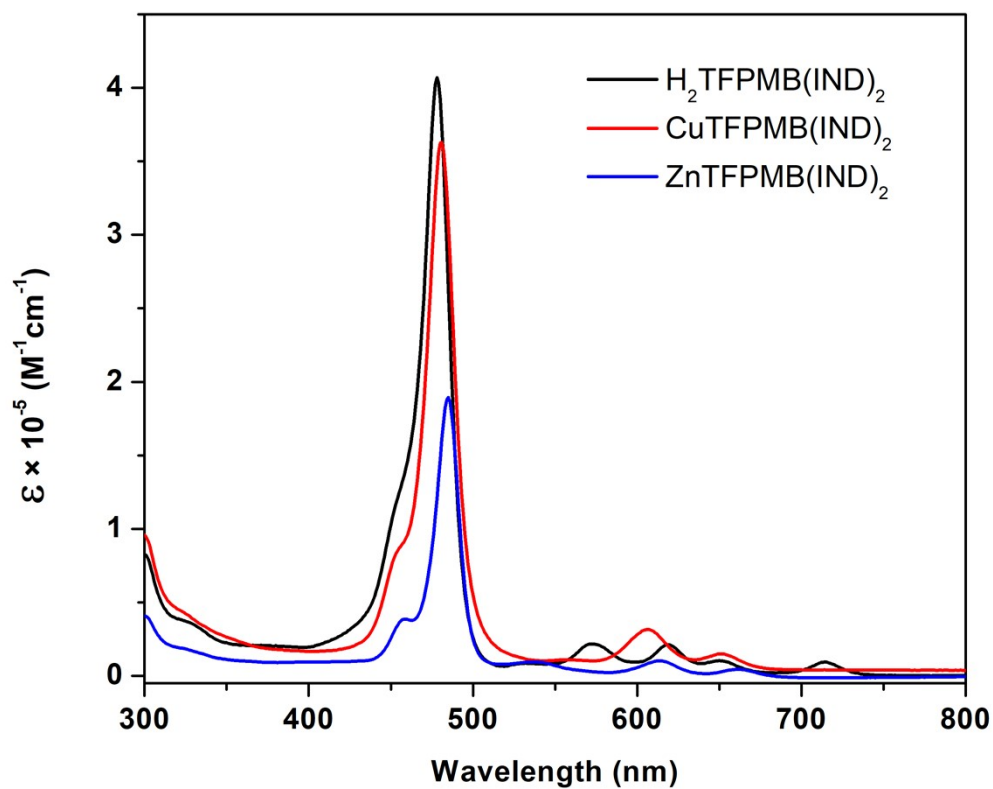


Fig. S3 Comparative absorption spectra of compounds indicated in CH_2Cl_2 at 298 K.

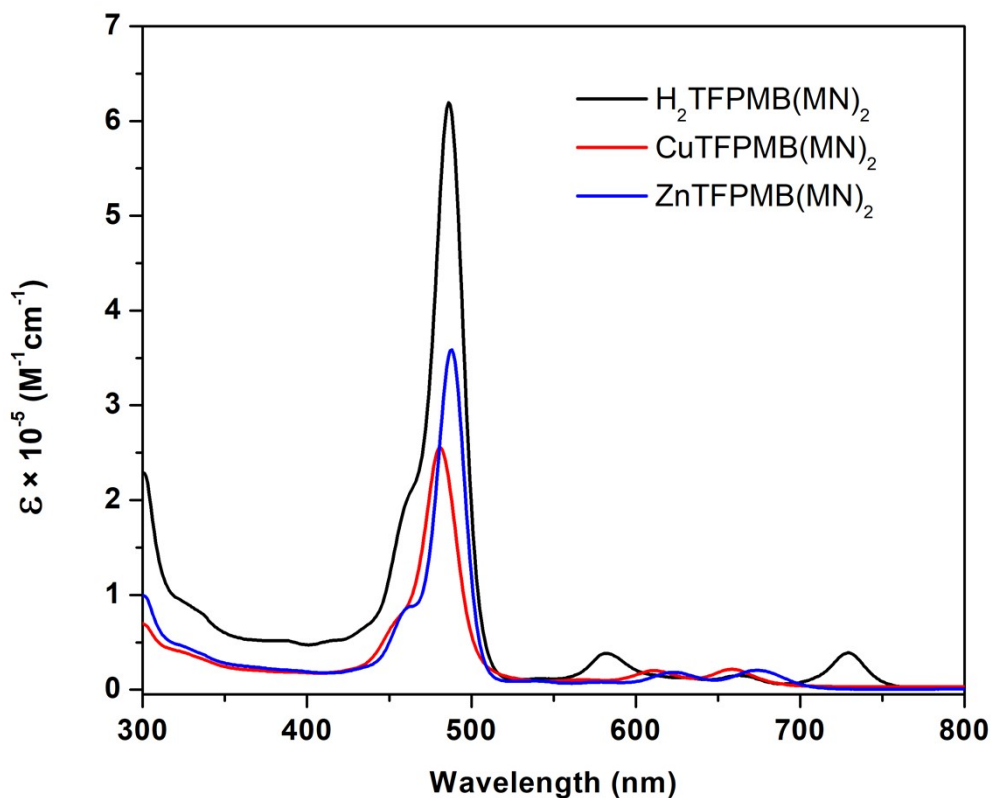


Fig. S4 Comparative absorption spectra of compounds indicated in CH_2Cl_2 at 298 K.

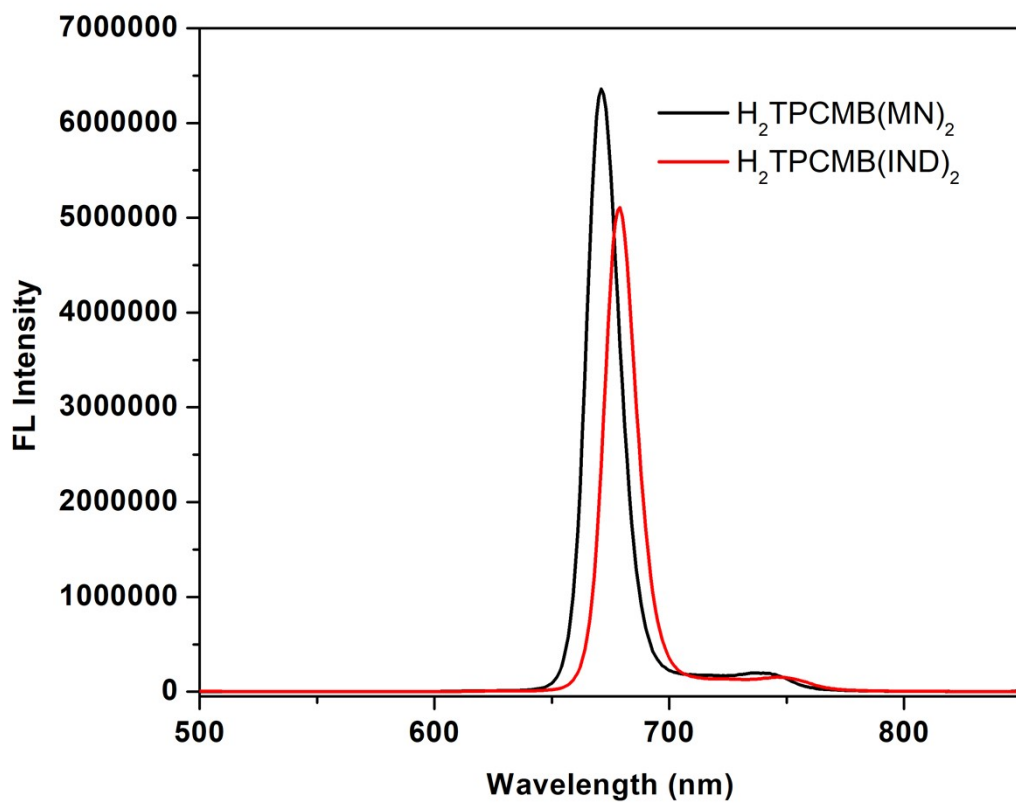


Fig. S5 Comparative emission spectra of compounds indicated in CH_2Cl_2 at 298 K.

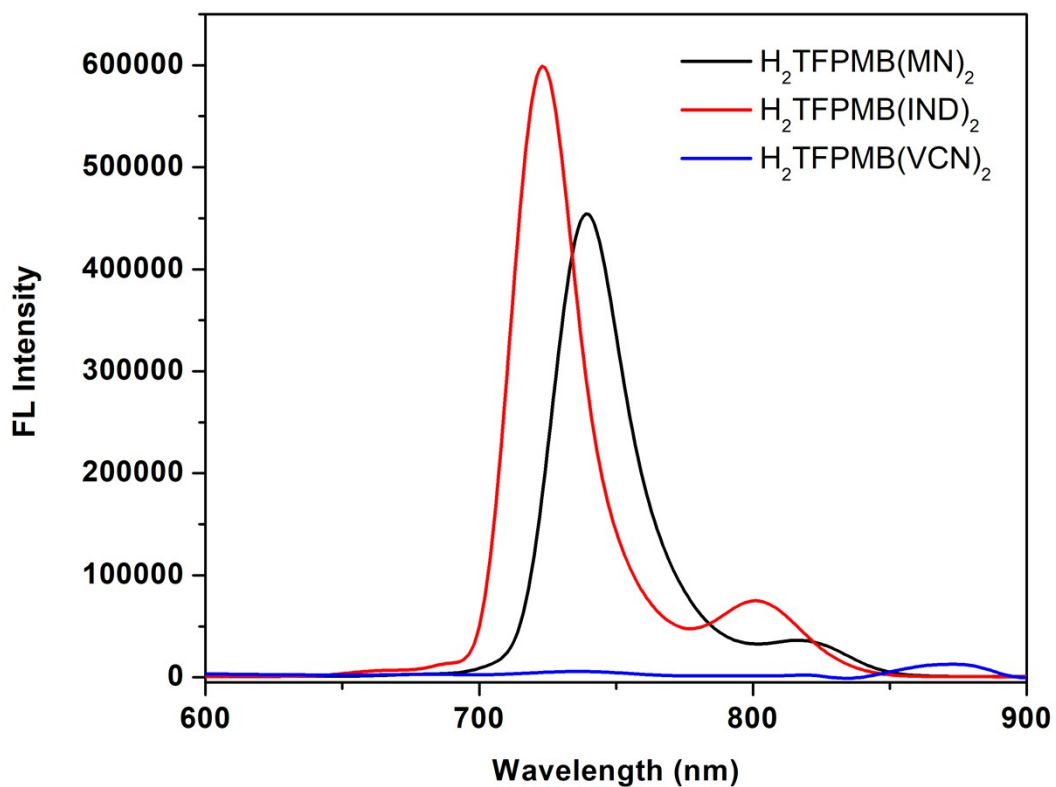


Fig. S6 Comparative emission spectra of compounds indicated in CH₂Cl₂ at 298 K.

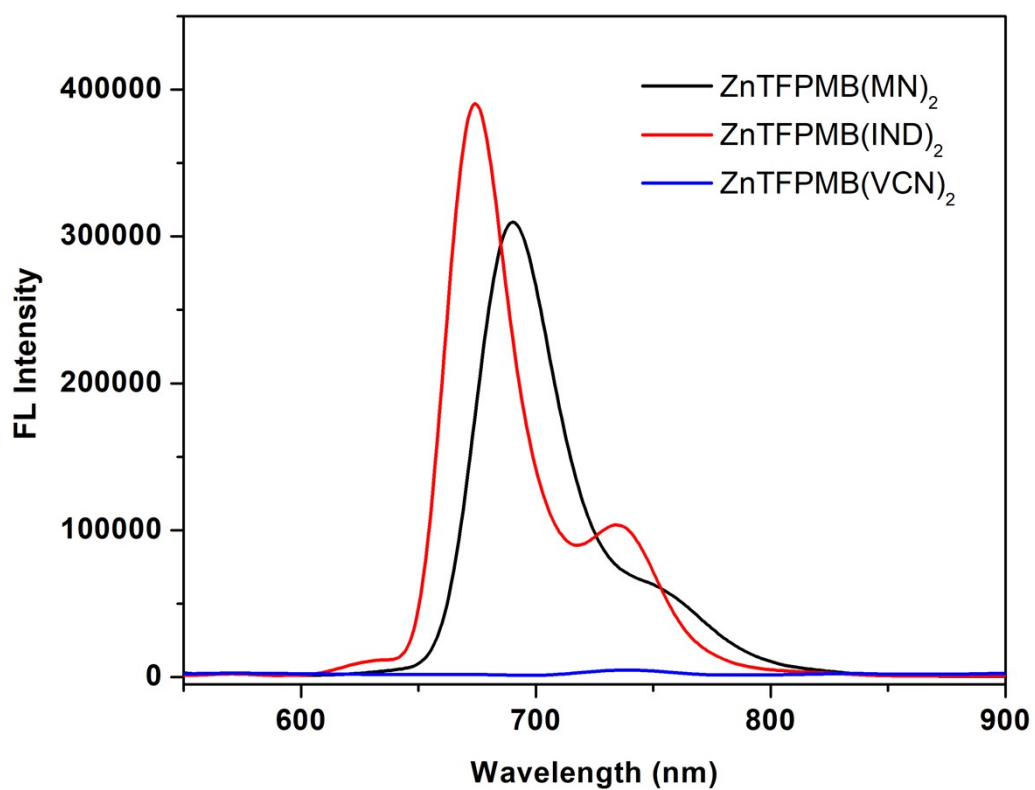


Fig. S7 Comparative emission spectra of compounds indicated in CH₂Cl₂ at 298 K.

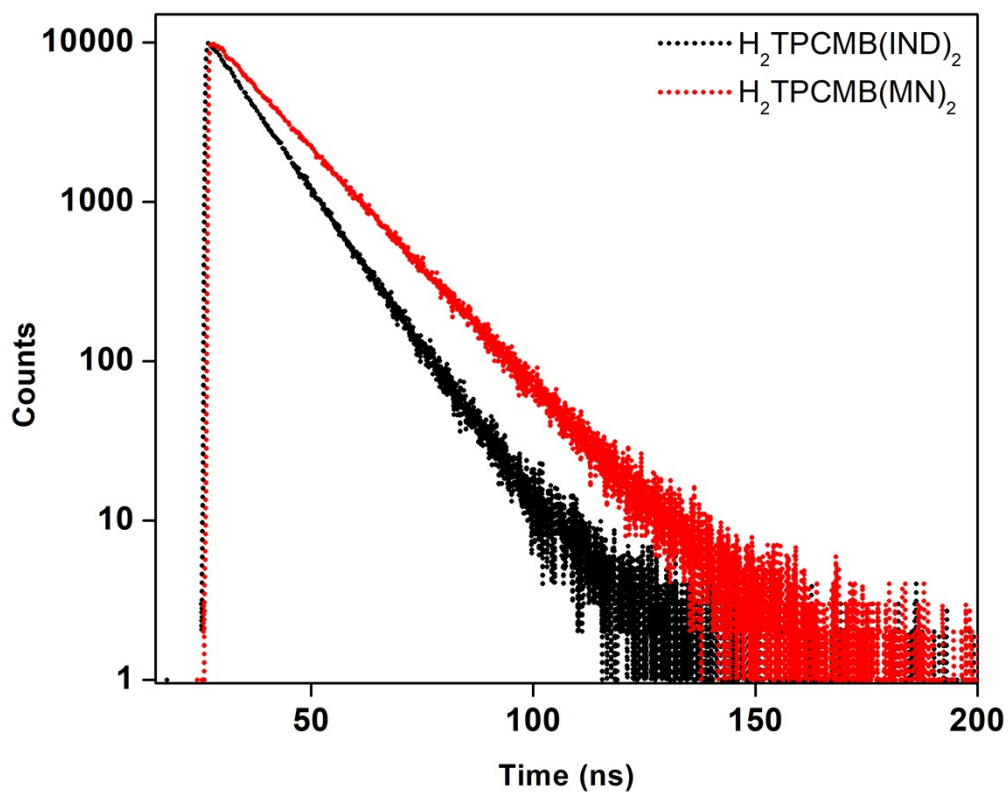


Fig. S8 Comparative fluorescence lifetime decay profile of $H_2TPCMB(IND)_2$ and $H_2TPCMB(MN)_2$.

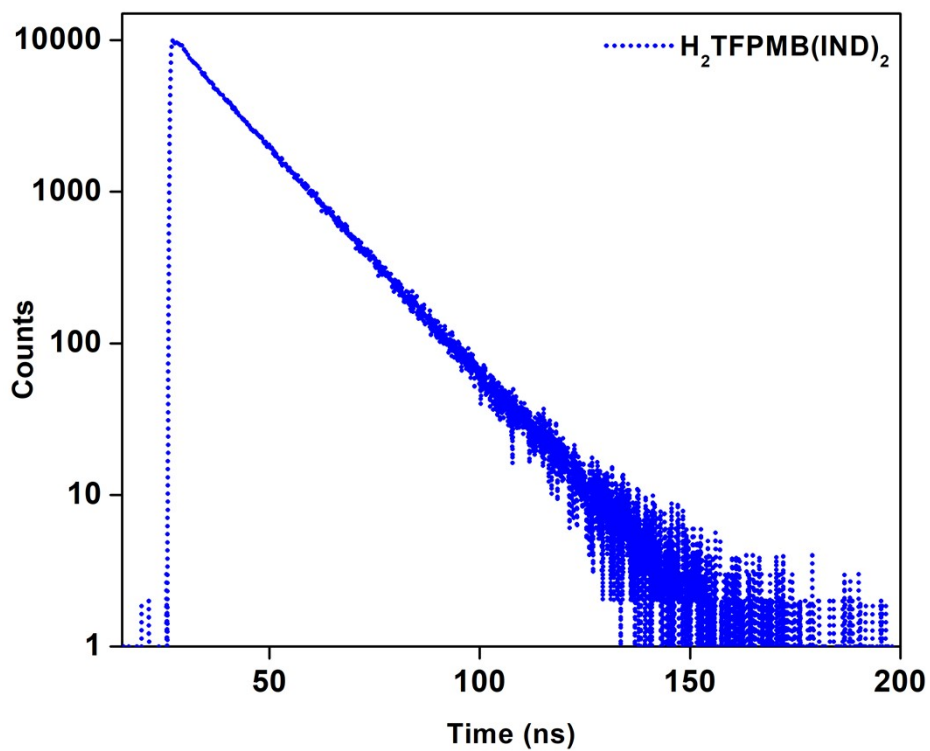


Fig. S9 Fluorescence lifetime decay profile of $H_2TFPMB(IND)_2$.

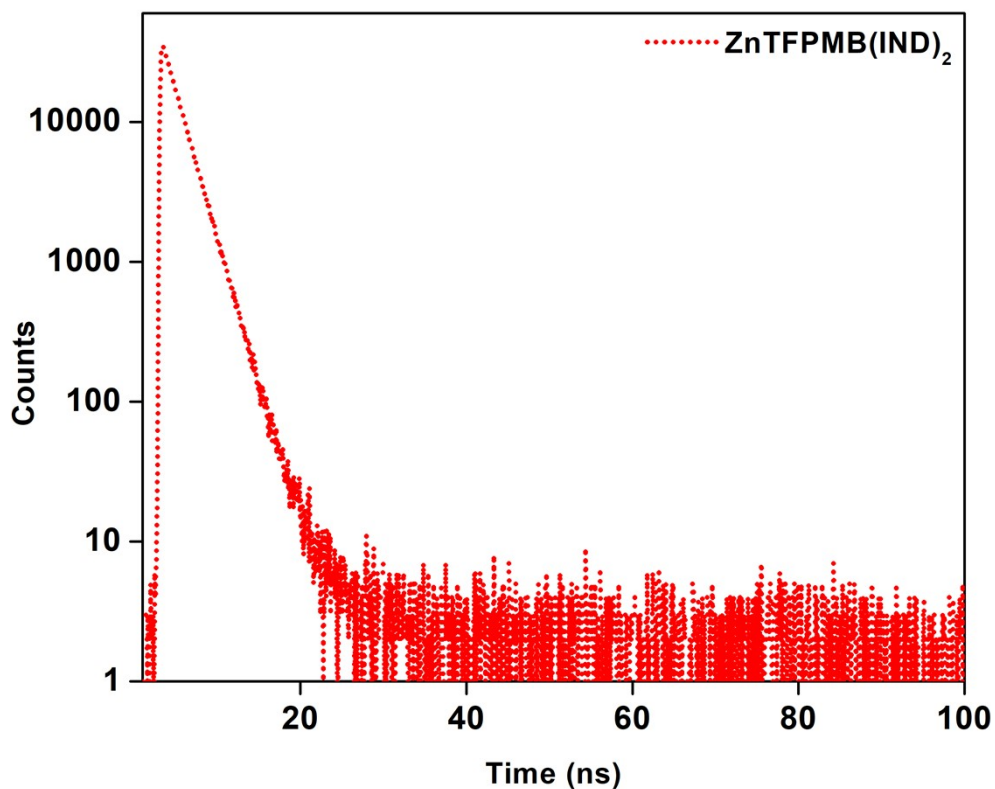


Fig. S10 Fluorescence lifetime decay profile of ZnTFPMB(IND)₂.

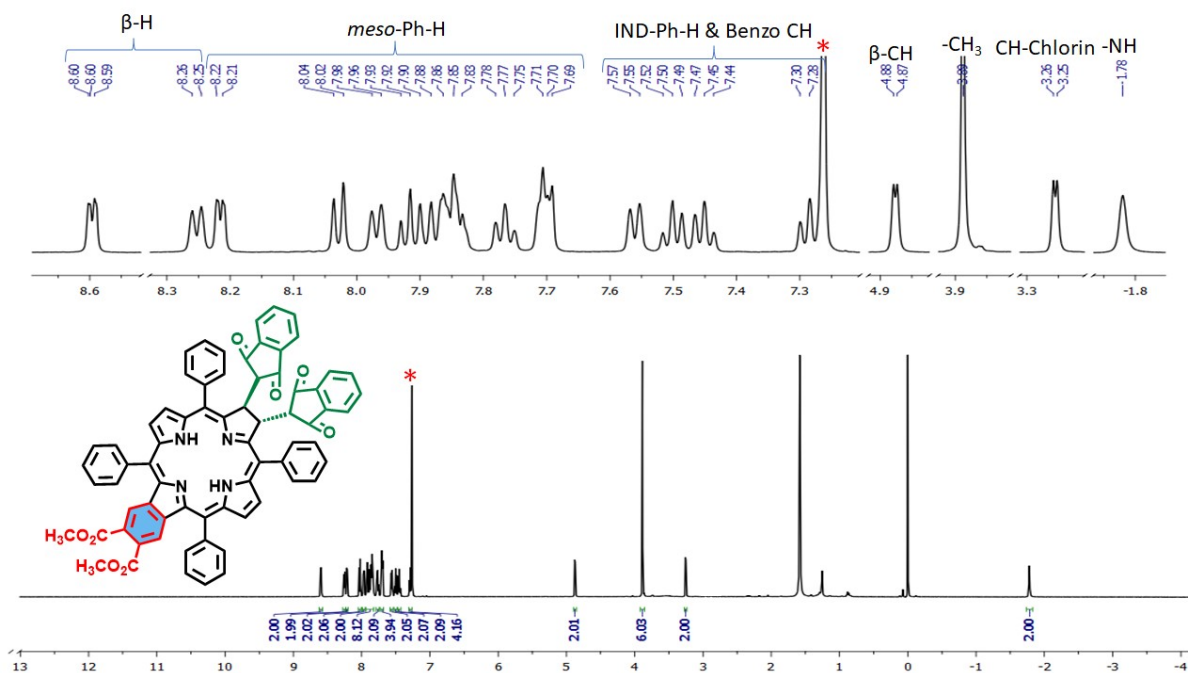


Fig. S11 ¹H NMR spectrum of H₂TPCMB(IND)₂ in CDCl₃ at 298 K.

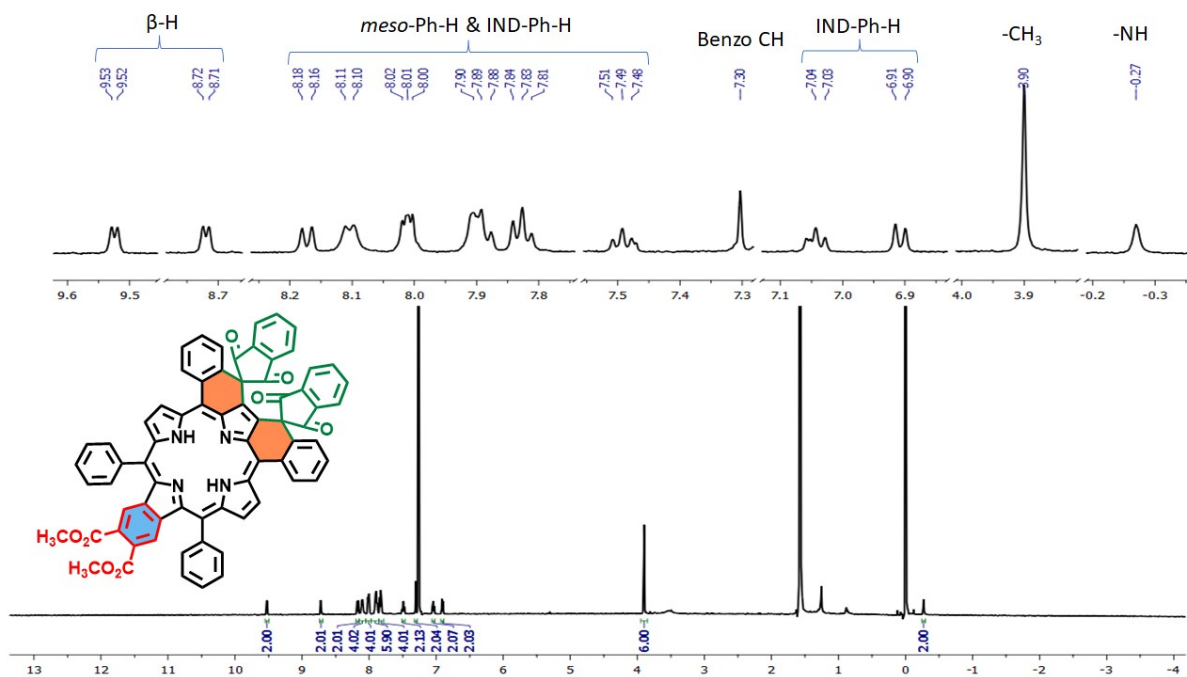


Fig. S12 ¹H NMR spectrum of H₂TFPMB(IND)₂ in CDCl₃ at 298 K.

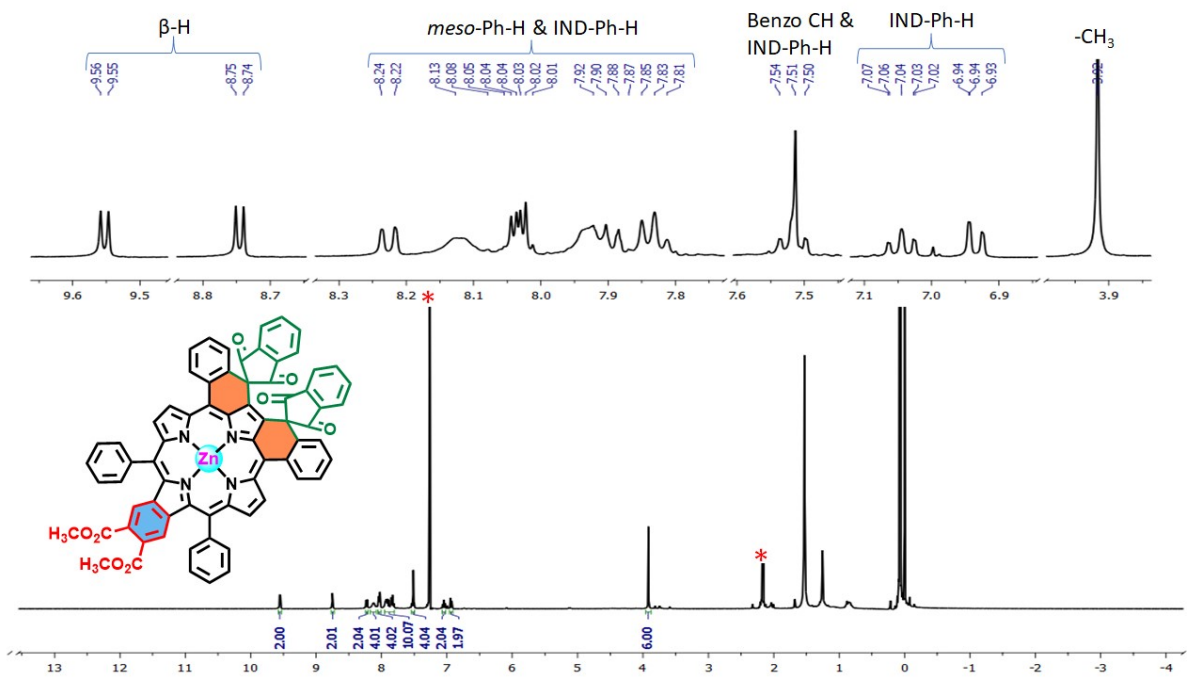
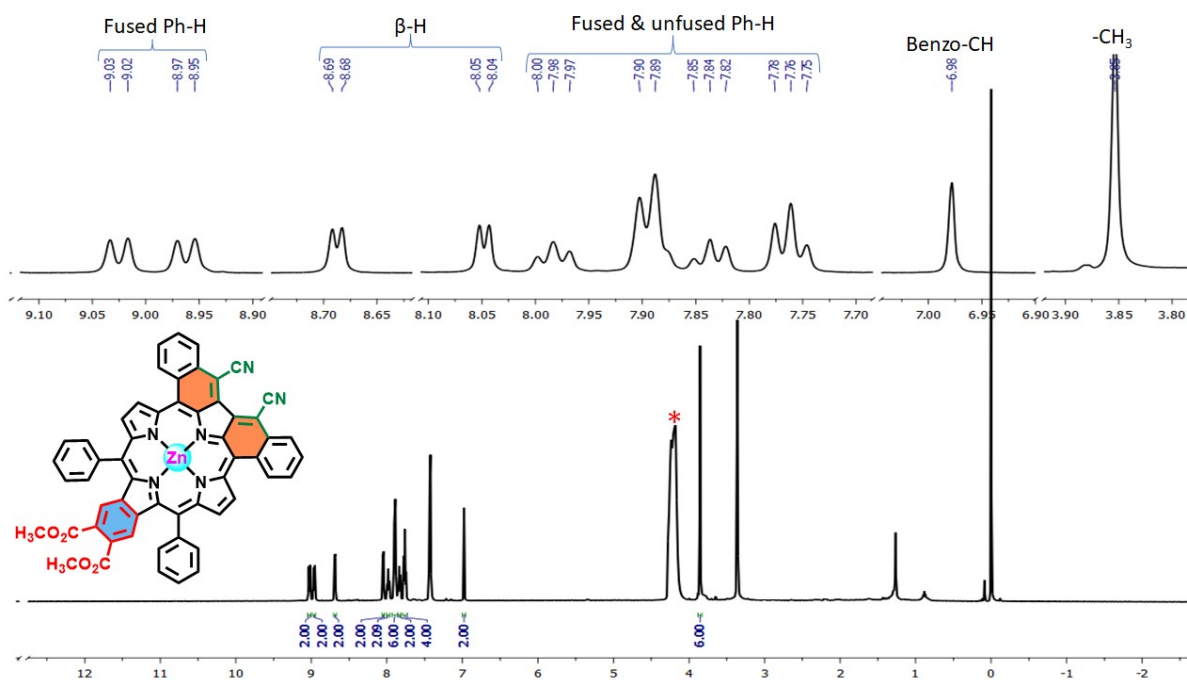
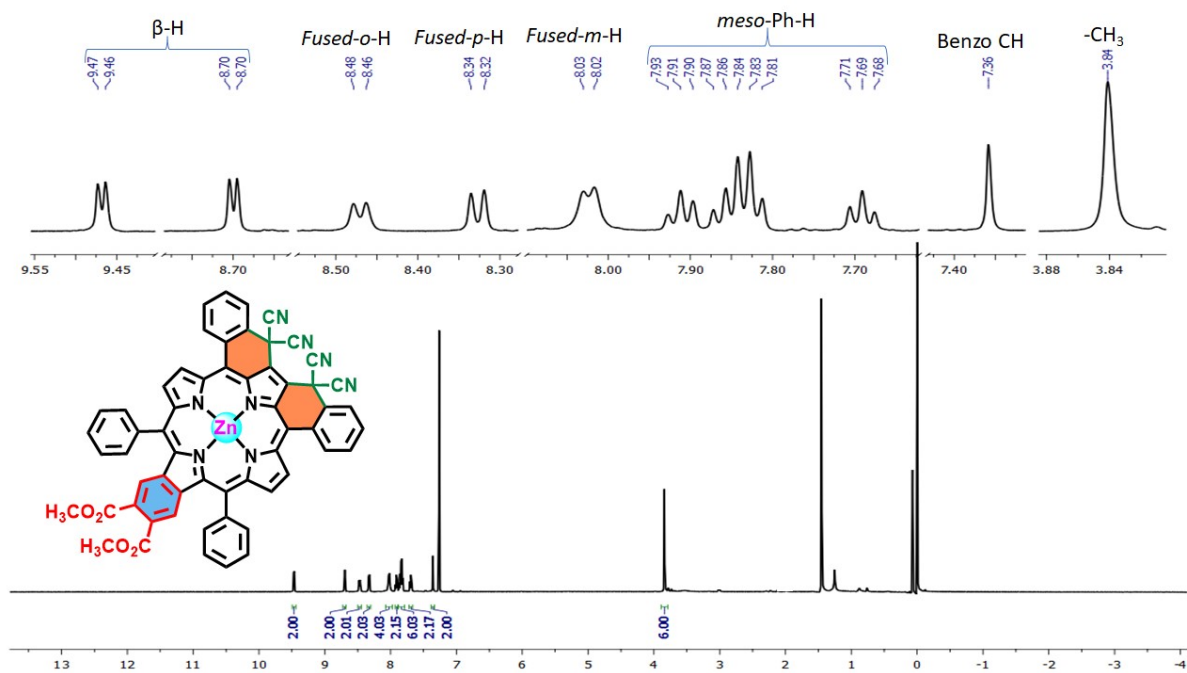


Fig. S13 ¹H NMR spectrum of ZnTFPMB(IND)₂ in CDCl₃ at 298 K.



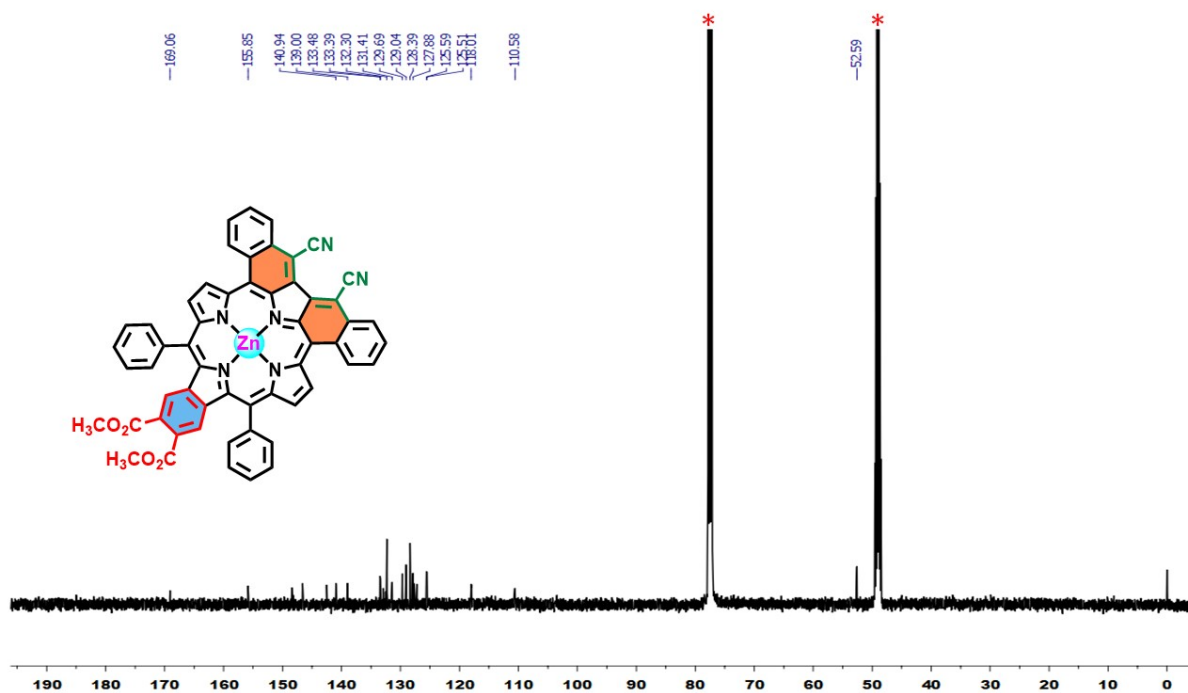


Fig. S16 ¹³C NMR spectrum of ZnTFPMB(VCN)₂ in CD₃OD+CDCl₃ at 298 K.

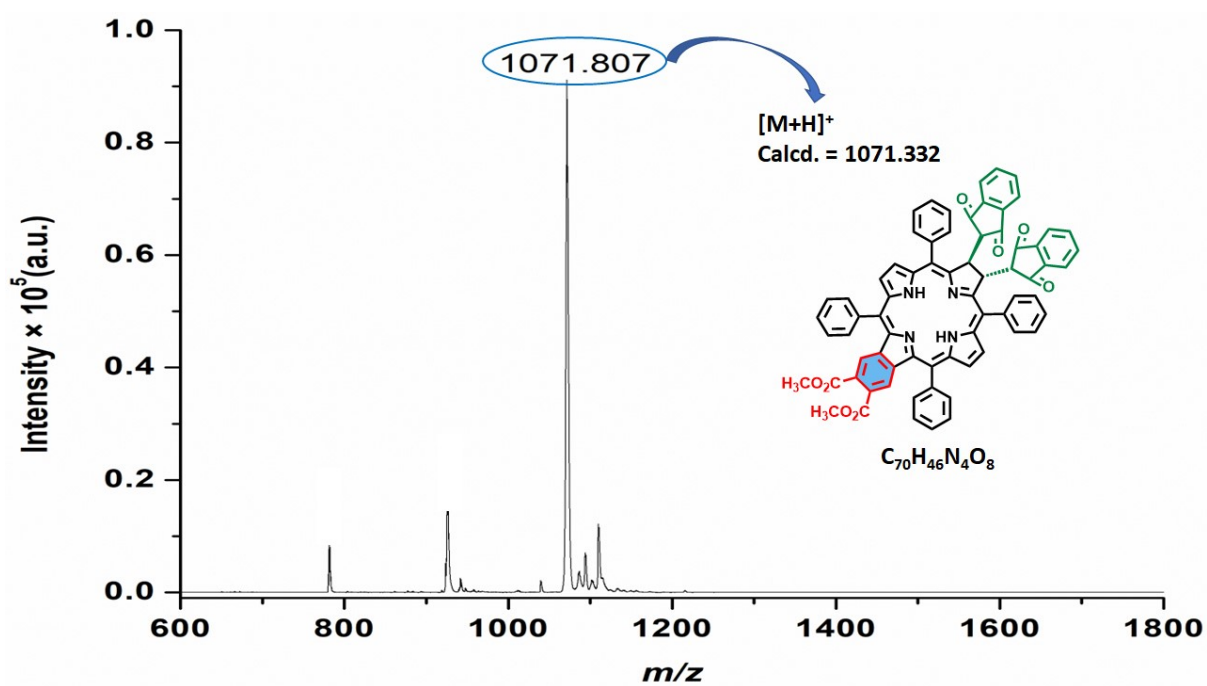


Fig. S17 MALDI-TOF mass spectrum of H₂TPCMB(IND)₂ in positive ion mode at 298 K.

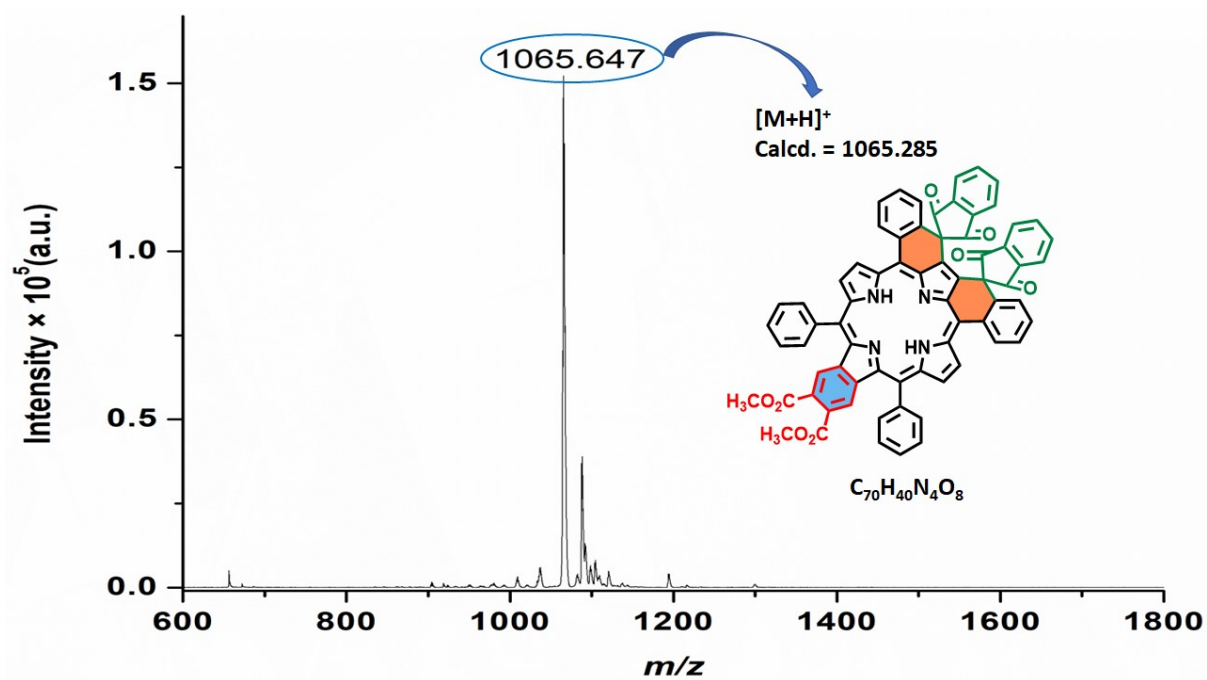


Fig. S18 MALDI-TOF mass spectrum of H₂TFPMB(IND)₂ in positive ion mode at 298 K.

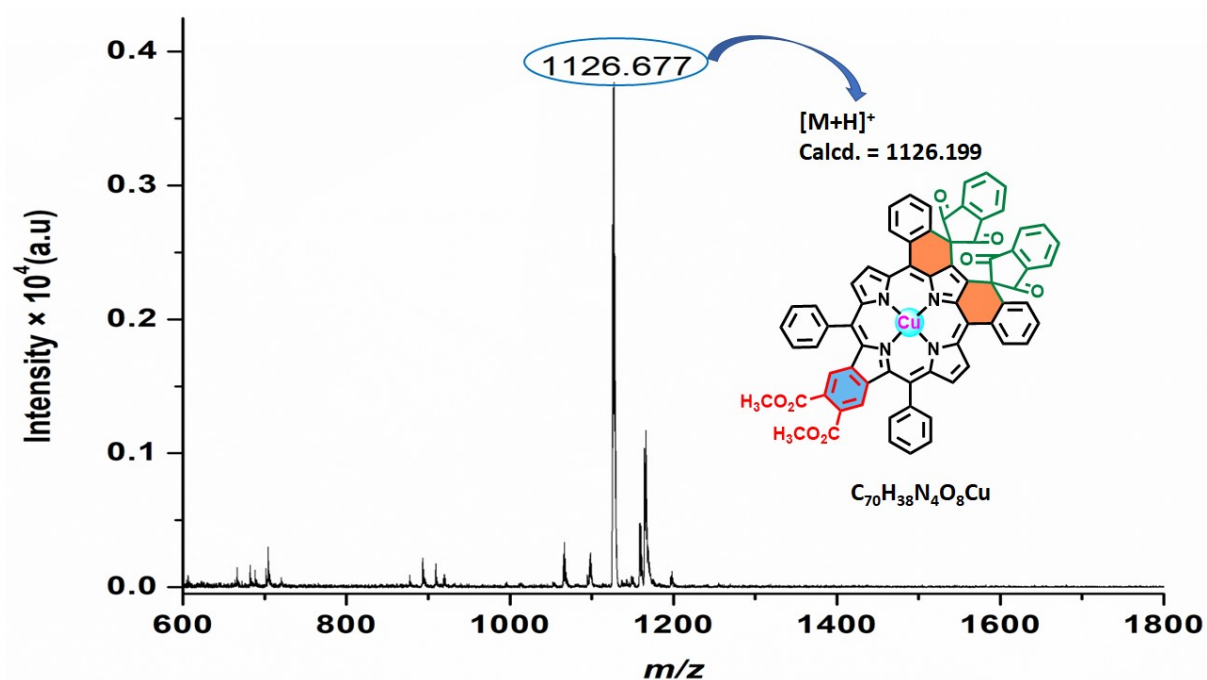


Fig. S19 MALDI-TOF mass spectrum of CuTFPMB(IND)₂ in positive ion mode at 298 K.

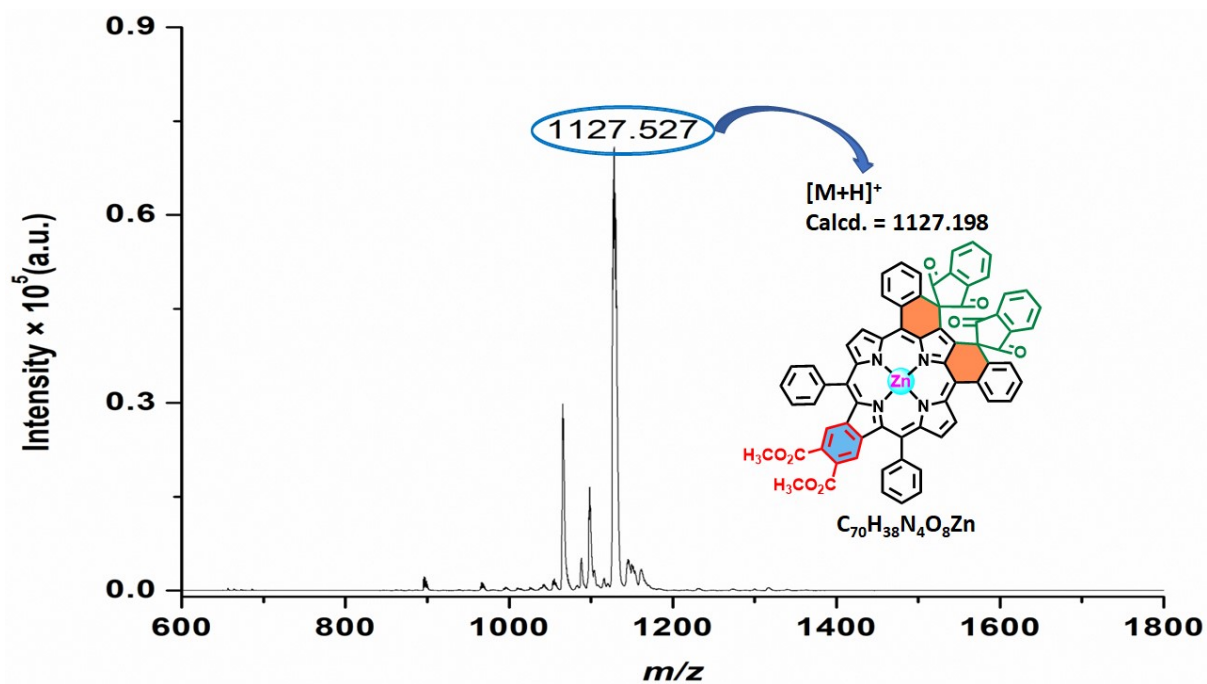


Fig. S20 MALDI-TOF mass spectrum of ZnTFPMB(IND)₂ in positive ion mode at 298 K.

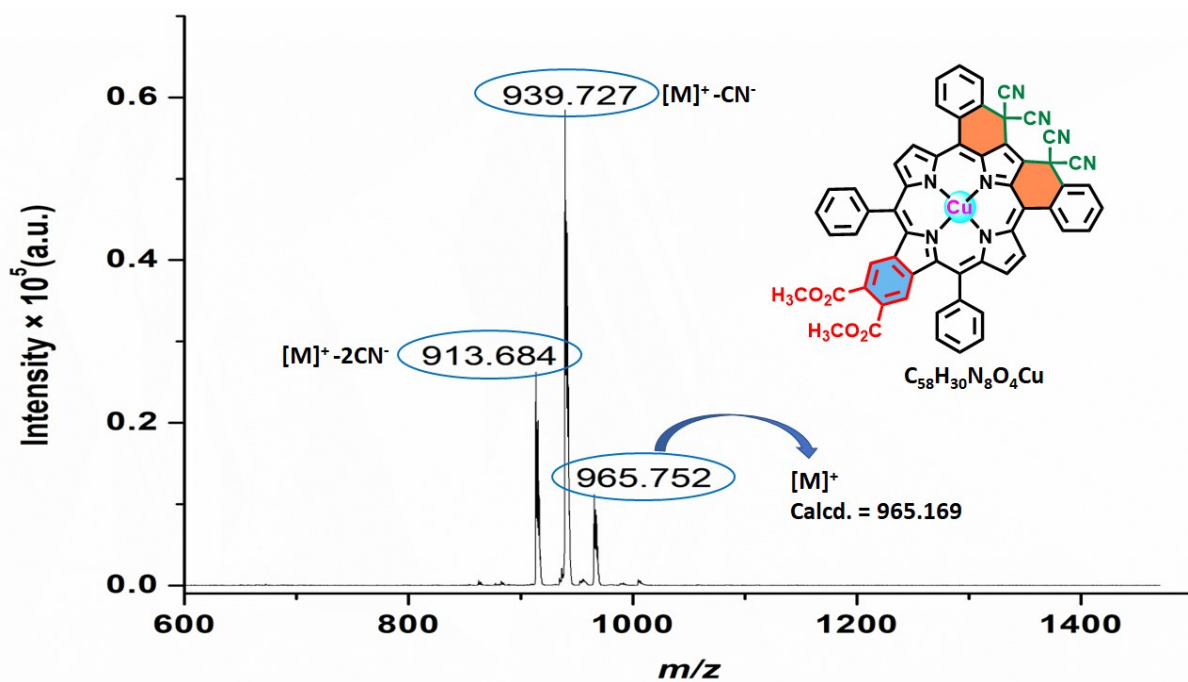


Fig. S21 MALDI-TOF mass spectrum of CuTFPMB(MN)₂ in positive ion mode at 298 K.

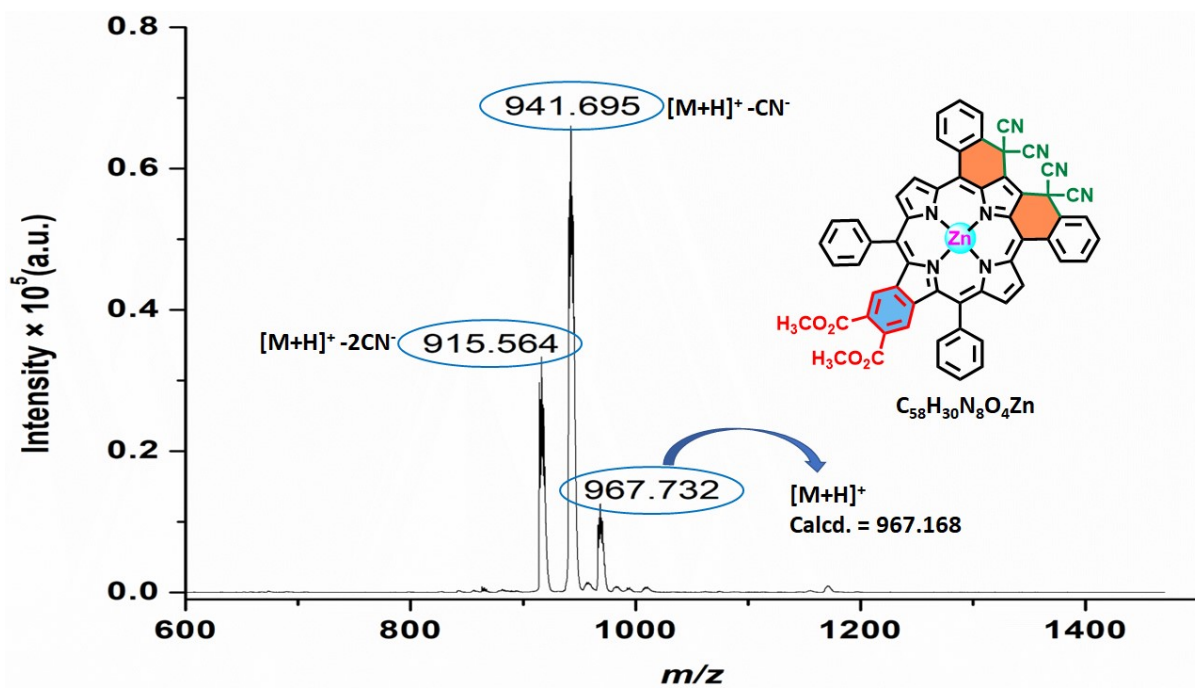


Fig. S22 MALDI-TOF mass spectrum of ZnTFPMB(MN)₂ in positive ion mode at 298 K.

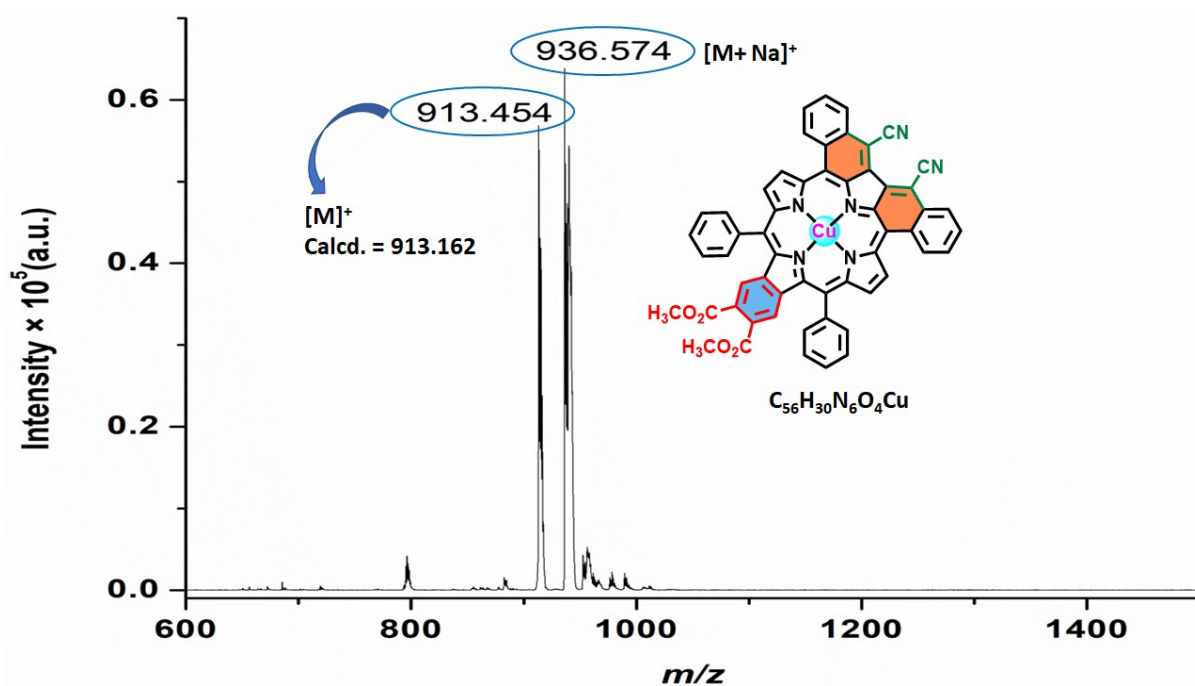


Fig. S23 MALDI-TOF mass spectrum of CuTFPMB(VCN)₂ in positive ion mode at 298 K.

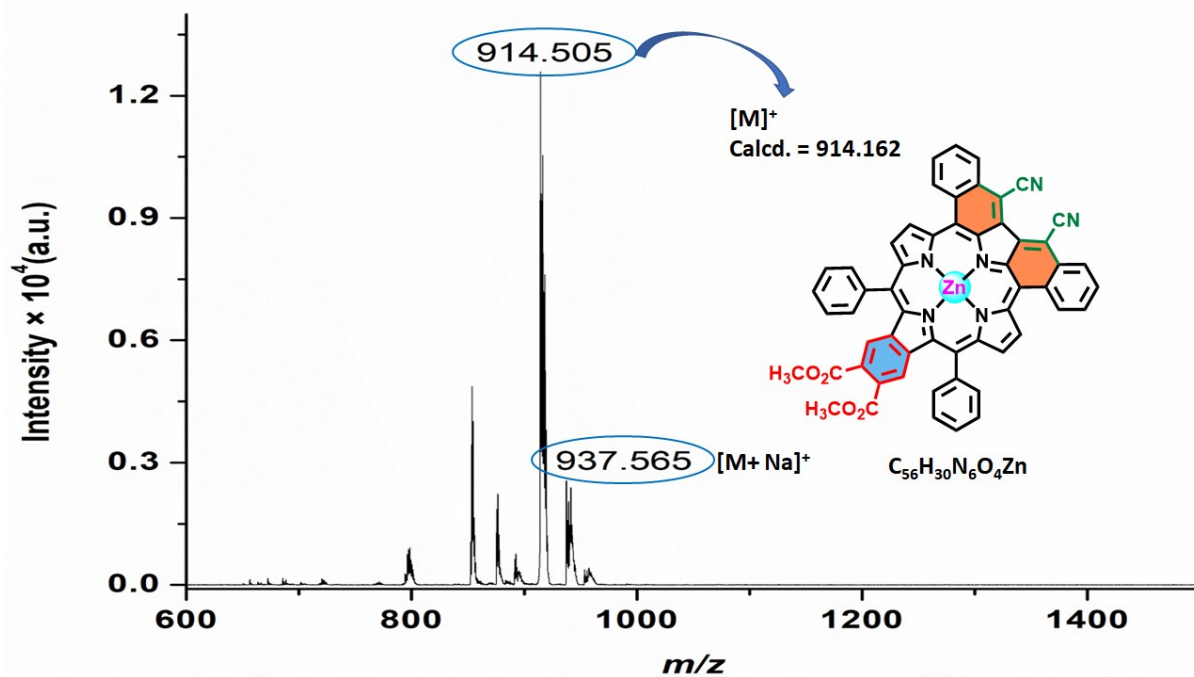


Fig. S24 MALDI-TOF mass spectrum of ZnTFPMB(VCN)₂ in positive ion mode at 298 K.

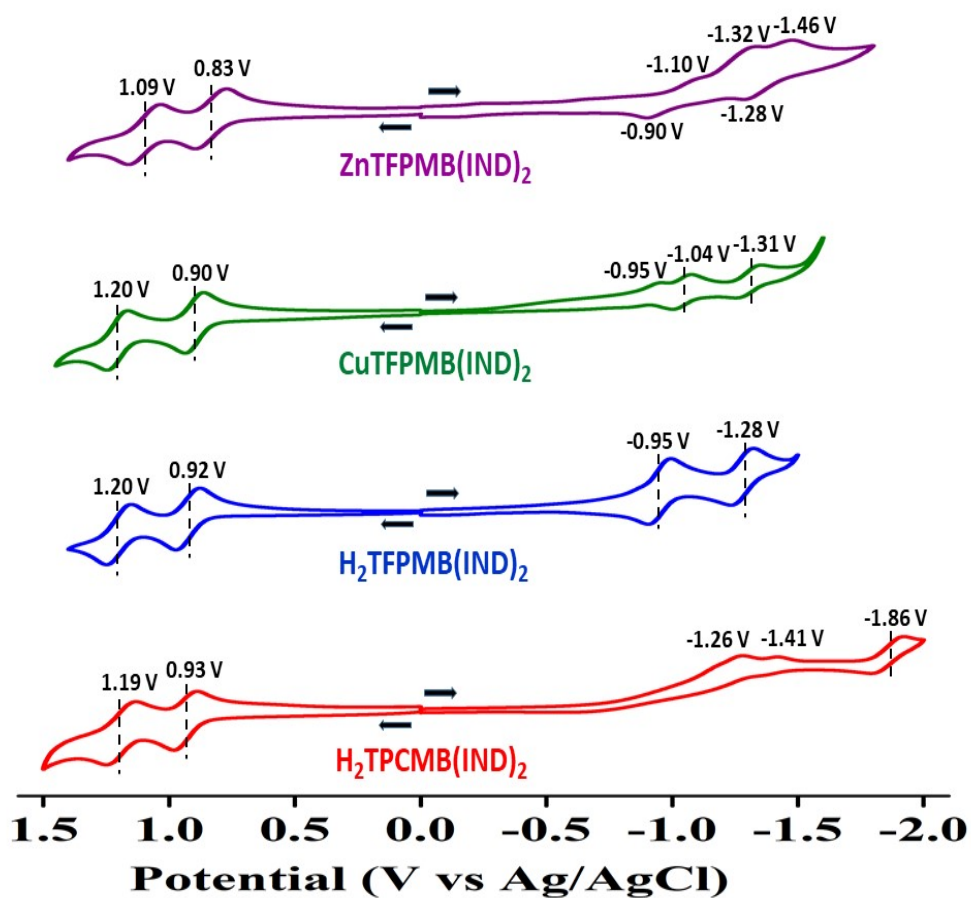


Fig. S25 Cyclic voltammograms of IND-appended porphyrinoids in CH₂Cl₂ at 298 K using TBAPF₆ as a supporting electrolyte. Scan rate = 100 mV/s.

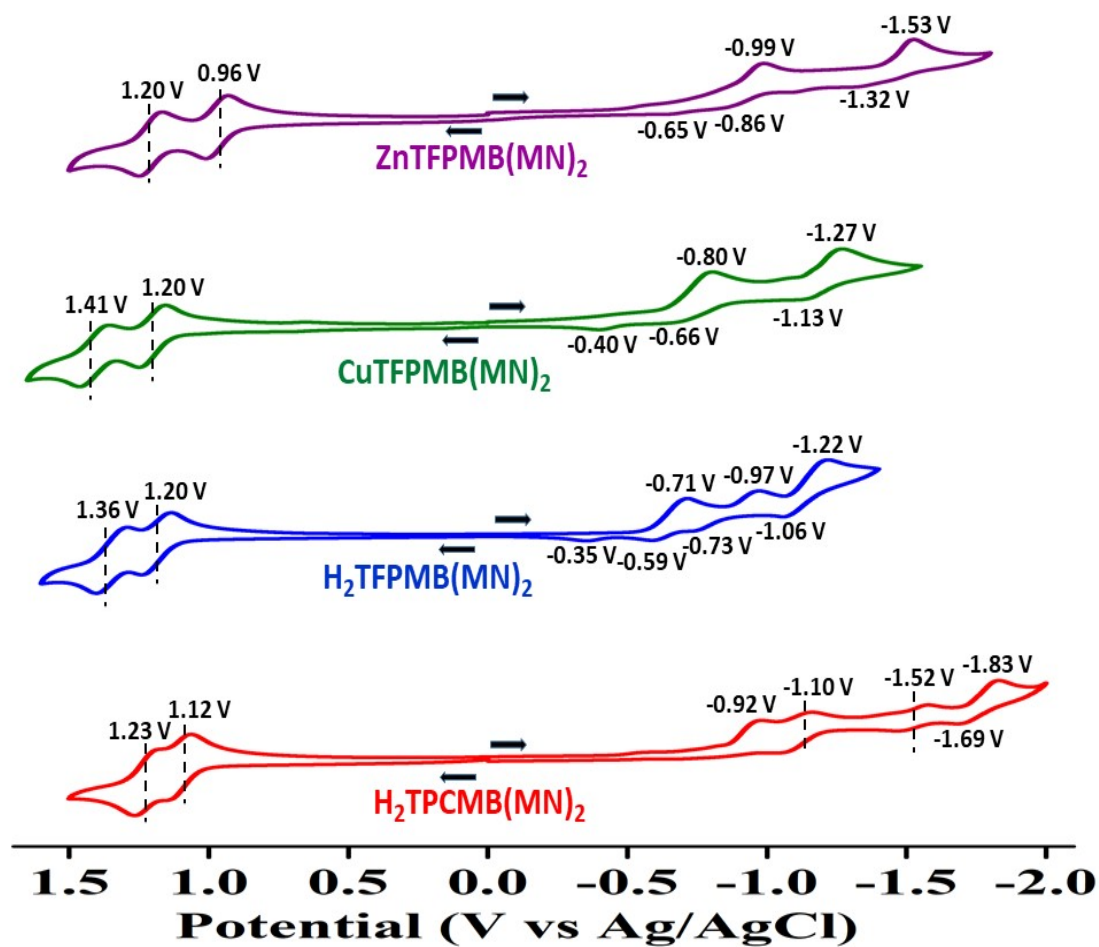


Fig. S26 Cyclic voltammograms of MN-appended porphyrinoids in CH_2Cl_2 at 298 K using TBAPF_6 as a supporting electrolyte. Scan rate = 100 mV/s.

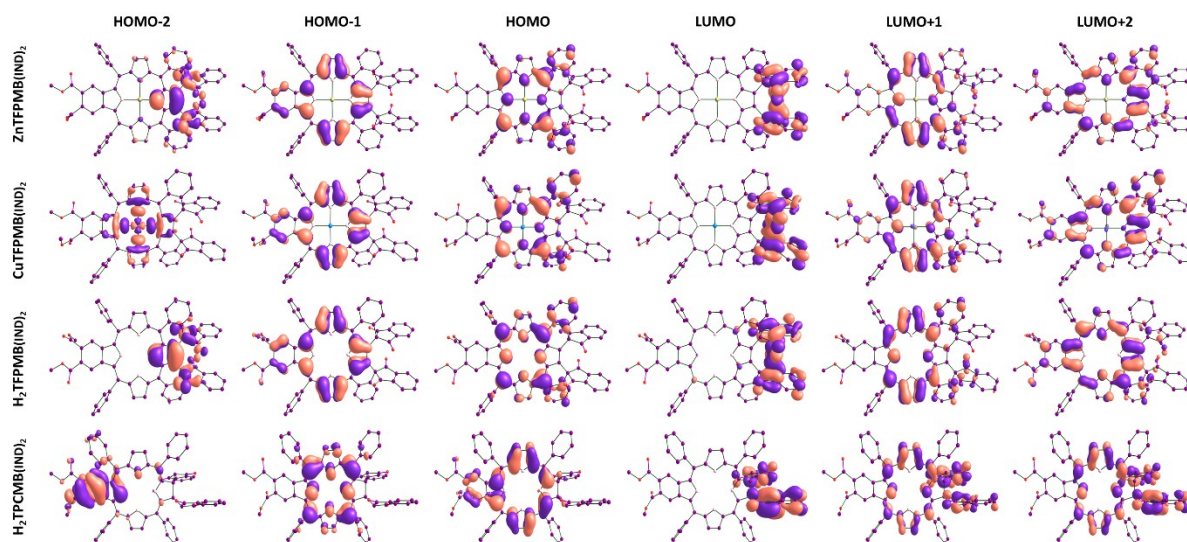


Fig. S27 Complete FMO profile of compounds indicated.

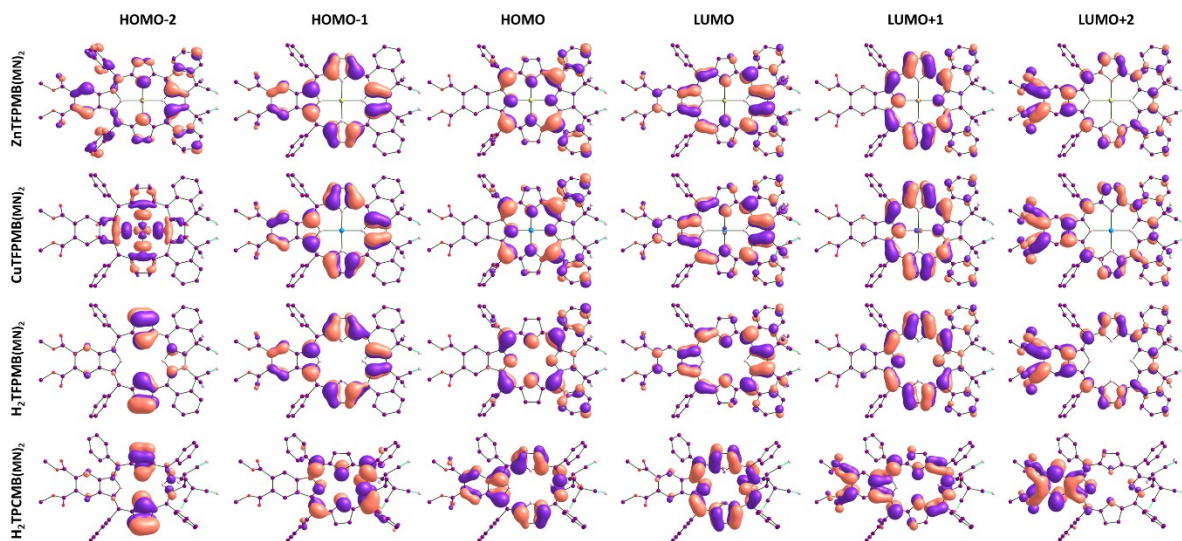


Fig. S28 Complete FMO profile of compounds indicated.

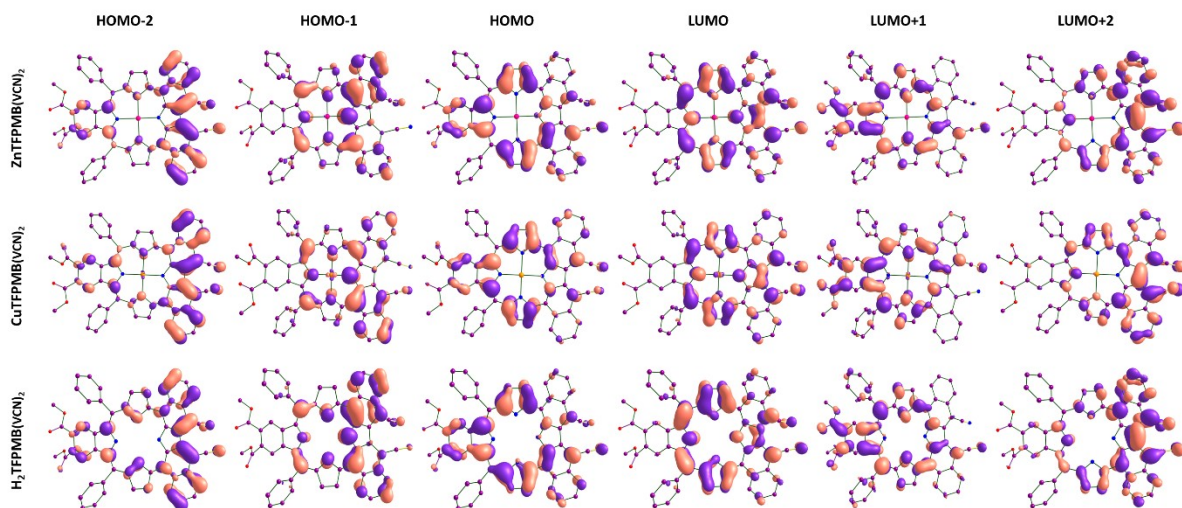


Fig. S29 Complete FMO profile of compounds indicated.

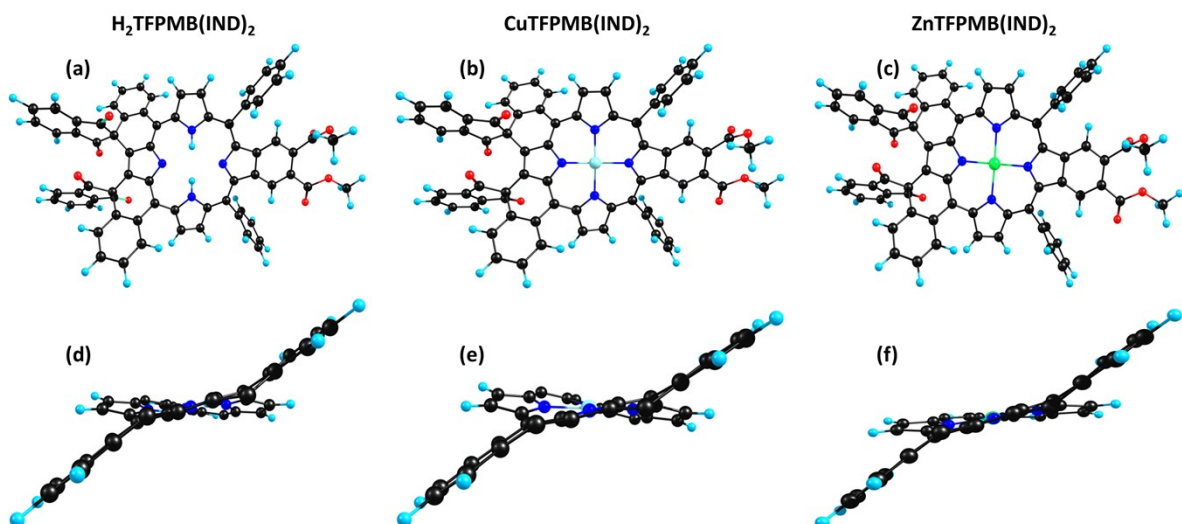


Fig. S30 Optimized geometry (top view a, b, c) and (side view d, e, f) of $\text{H}_2\text{TFPMB}(\text{IND})_2$, $\text{CuTFPMB}(\text{IND})_2$ and $\text{ZnTFPMB}(\text{IND})_2$ respectively. The unfused *meso*-phenyl groups are omitted for clarity in the side views.

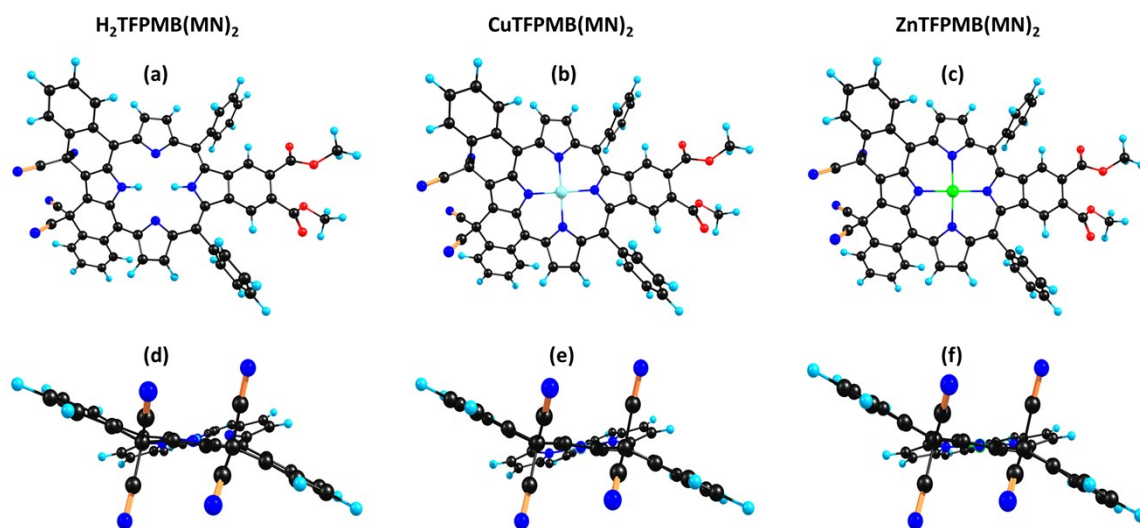


Fig. S31 Optimized geometry (top view a, b, c) and (side view d, e, f) of $\text{H}_2\text{TFPMB}(\text{MN})_2$, $\text{CuTFPMB}(\text{MN})_2$ and $\text{ZnTFPMB}(\text{MN})_2$ respectively. The unfused *meso*-phenyl groups are omitted for clarity in the side views.

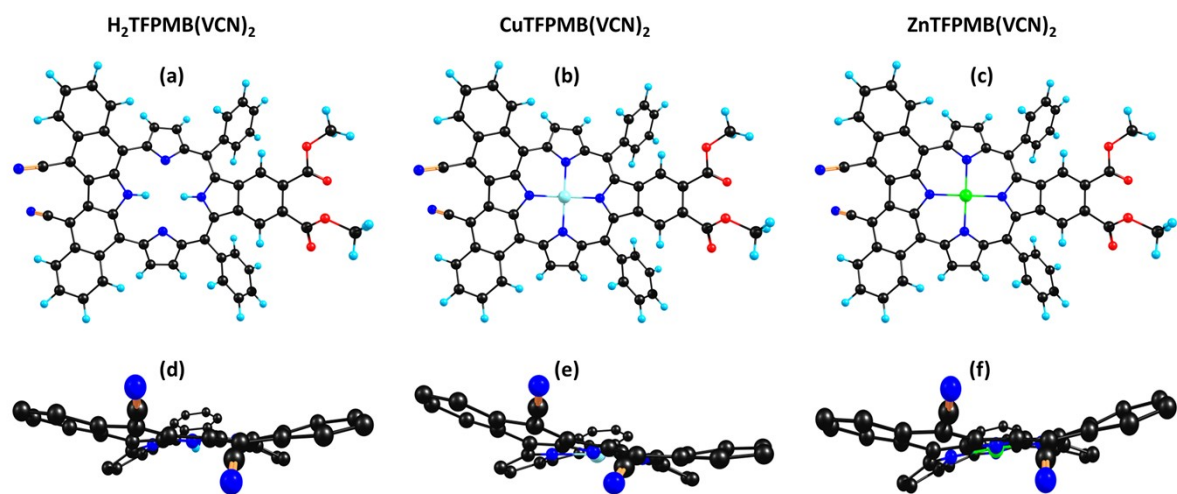


Fig. S32 Optimized geometry (top view a, b, c) and (side view d, e, f) of $\text{H}_2\text{TFPMB}(\text{VCN})_2$, $\text{CuTFPMB}(\text{VCN})_2$ and $\text{ZnTFPMB}(\text{VCN})_2$ respectively. The unfused *meso*-phenyl groups are omitted for clarity in the side views.

Table S3 Selected average bond lengths and angles of synthesized IND-appended porphyrinoids.

	H ₂ TPCMB(IND) ₂	H ₂ TFPMB(IND) ₂	ZnTFPMB(IND) ₂	CuTFPMB(IND) ₂
Bond Length (Å)				
M-N			2.078	2.018
M-N'			2.040	1.988
N-C _α	1.372	1.374	1.387	1.387
N'-C _{α'}	1.388	1.384	1.394	1.392
C_α-C_β	1.505	1.469	1.463	1.460
C_{α'}-C_{β'}	1.437	1.437	1.456	1.454
C _β -C _β	1.486	1.403	1.413	1.412
C _{β'} -C _{β'}	1.374	1.377	1.377	1.375
C _α -C _m	1.407	1.410	1.416	1.409
C _{α'} -C _m	1.408	1.411	1.421	1.414
ΔC_β (Å)	0.277	0.776	0.705	0.804
Δ24 (Å)	0.156	0.586	0.535	0.619
Δ38 (Å)		0.597	0.546	0.624
ΔM			0.002	0.000
Bond Angles (°)				
M-N-C _α			125.91	126.16
M-N'-C _{α'}			125.96	126.28
N-M-N			179.86	179.92
N'-M-N'			178.27	178.45
N-C _α -C _m	125.03	125.24	125.40	125.40
N'-C _{α'} -C _m	128.00	126.29	125.80	125.65
N-C _α -C _β	110.64	110.56	109.36	109.71
N'-C _{α'} -C _{β'}	106.22	106.23	108.77	109.08
C _β -C _α -C _m	124.30	124.10	125.20	124.76
C _{β'} -C _{α'} -C _m	125.75	127.23	125.33	125.01
C _α -C _m -C _{α'}	126.09	123.97	124.28	122.44
C _α -C _β -C _β	104.26	105.92	106.55	106.46
C _{α'} -C _{β'} -C _{β'}	108.44	108.30	107.41	107.29
C _α -N-C _α	109.25	107.01	108.18	107.67
C _{α'} -N-C _{α'}	110.68	110.87	107.55	107.12

Table S4 Selected average bond lengths and angles of synthesized MN-appended porphyrinoids.

	H ₂ TPCMB(MN) ₂	H ₂ TFPMB(MN) ₂	ZnTFPMB(MN) ₂	CuTFPMB(MN) ₂
Bond Length (Å)				
M-N			2.073	2.013
M-N'			2.045	1.993
N-C _α	1.383	1.366	1.388	1.388
N'-C _{α'}	1.383	1.383	1.394	1.393
C _α -C _β	1.487	1.443	1.459	1.457
C _{α'} -C _{β'}	1.461	1.463	1.458	1.455
C _β -C _β	1.491	1.413	1.429	1.408
C _{β'} -C _{β'}	1.360	1.360	1.415	1.374
C _α -C _m	1.395	1.406	1.418	1.412
C _{α'} -C _m	1.416	1.414	1.421	1.413
ΔC _β (Å)	0.390	0.745	0.713	0.784
Δ24 (Å)	0.243	0.553	0.530	0.598
Δ38 (Å)		0.559	0.533	0.598
ΔM			0.000	0.000
Bond Angles (°)				
M-N-C _α			125.79	126.05
M-N'-C _{α'}			125.96	126.29
N-M-N			180.00	180.00
N'-M-N'			177.66	178.06
N-C _α -C _m	126.04	126.24	125.80	125.79
N'-C _{α'} -C _m	126.45	125.65	125.77	125.62
N-C _α -C _β	106.11	106.55	109.01	109.35
N'-C _{α'} -C _{β'}	110.52	110.19	108.78	109.09
C _β -C _α -C _m	127.79	127.11	125.13	124.69
C _{β'} -C _{α'} -C _m	122.95	123.93	125.35	125.04
C _α -C _m -C _{α'}	125.00	123.71	124.00	120.66
C _α -C _β -C _β	104.96	107.55	106.78	106.68
C _{α'} -C _{β'} -C _{β'}	106.73	106.80	107.43	107.31
C _α -N-C _α	113.44	111.78	108.41	109.40
C _{α'} -N-C _{α'}	105.44	105.90	107.47	107.06

Table S5 Selected average bond lengths and angles of synthesized π -extended trifused porphyrins.

	H ₂ TFPMB(VCN) ₂	ZnTFPMB(VCN) ₂	CuTFPMB(VCN) ₂
Bond Length (Å)			
M-N		2.086	2.034
M-N'		2.067	2.020
N-C _α	1.381	1.391	1.392
N'-C _{α'}	1.383	1.396	1.396
C_α-C_β	1.441	1.458	1.456
C_{α'}-C_{β'}	1.461	1.452	1.449
C _β -C _β	1.445	1.443	1.439
C _{β'} -C _{β'}	1.362	1.376	1.375
C _α -C _m	1.411	1.420	1.412
C _{α'} -C _m	1.422	1.427	1.419
ΔC_β (Å)	0.709	0.606	0.680
Δ24 (Å)	0.364	0.317	0.380
Δ38 (Å)	0.336	0.318	0.360
ΔM		0.062	0.000
Bond Angles (°)			
M-N-C _α		125.32	125.70
M-N'-C _{α'}		125.12	125.49
N-M-N		177.17	178.95
N'-M-N'		175.74	175.07
N-C _α -C _m	126.18	125.74	125.75
N'-C _{α'} -C _m	124.97	125.56	125.22
N-C _α -C _β	106.99	109.53	109.87
N'-C _{α'} -C _{β'}	110.22	109.00	109.35
C _β -C _α -C _m	126.67	124.65	124.23
C _{β'} -C _{α'} -C _m	124.75	125.39	125.32
C _α -C _m -C _{α'}	123.29	123.43	121.82
C _α -C _β -C _β	106.94	106.11	106.06
C _{α'} -C _{β'} -C _{β'}	106.77	107.39	107.26
C _α -N-C _α	111.83	108.32	107.06
C _{α'} -N-C _{α'}	105.75	107.01	106.41

Table S6 Theoretically calculated ground state dipole moment and HOMO-LUMO energy gap of the synthesized porphyrinoids.

Porphyrinoids	Theoretically calculated Dipole moment (D)	HOMO-LUMO Energy Gap (eV)
H ₂ TPCMB(IND) ₂	10.62	2.485
H ₂ TFPMB(IND) ₂	10.27	2.337
CuTFPMB(IND) ₂	10.58	2.253
ZnTFPMB(IND) ₂	10.49	2.292
H ₂ TPCMB(MN) ₂	6.74	2.343
H ₂ TFPMB(MN) ₂	11.59	2.337
CuTFPMB(MN) ₂	11.74	2.357
ZnTFPMB(MN) ₂	11.85	2.340
H ₂ TFPMB(VCN) ₂	9.38	1.992
CuTFPMB(VCN) ₂	8.60	1.933
ZnTFPMB(VCN) ₂	8.78	1.955

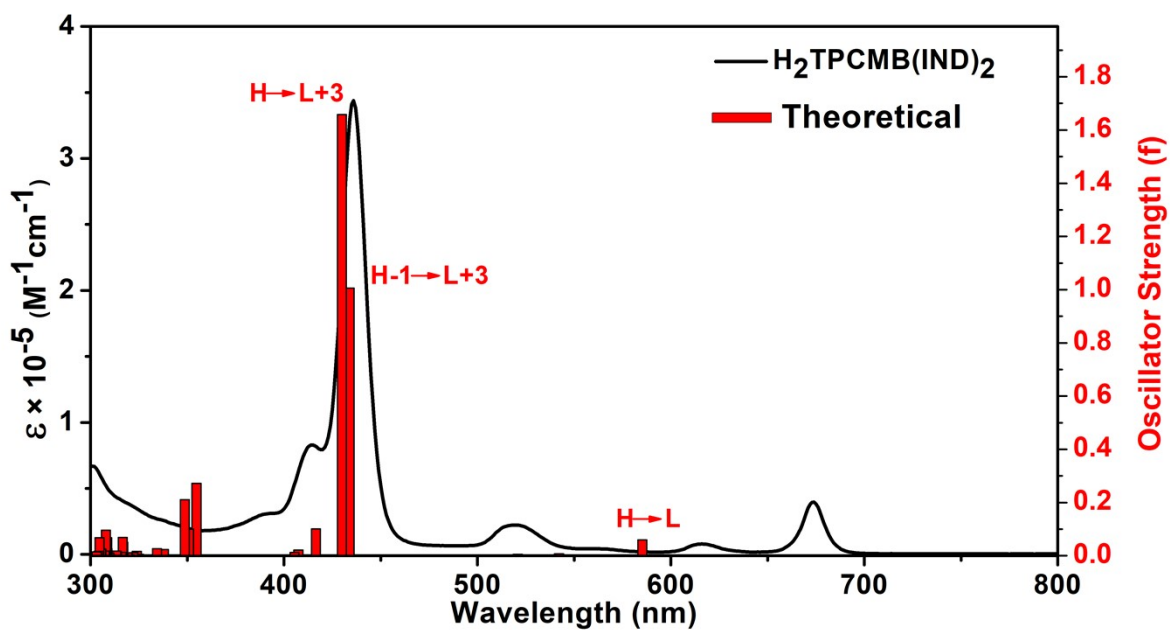


Fig. S33 Comparative (theoretical and experimental) absorption spectra of H₂TPCMB(IND)₂.

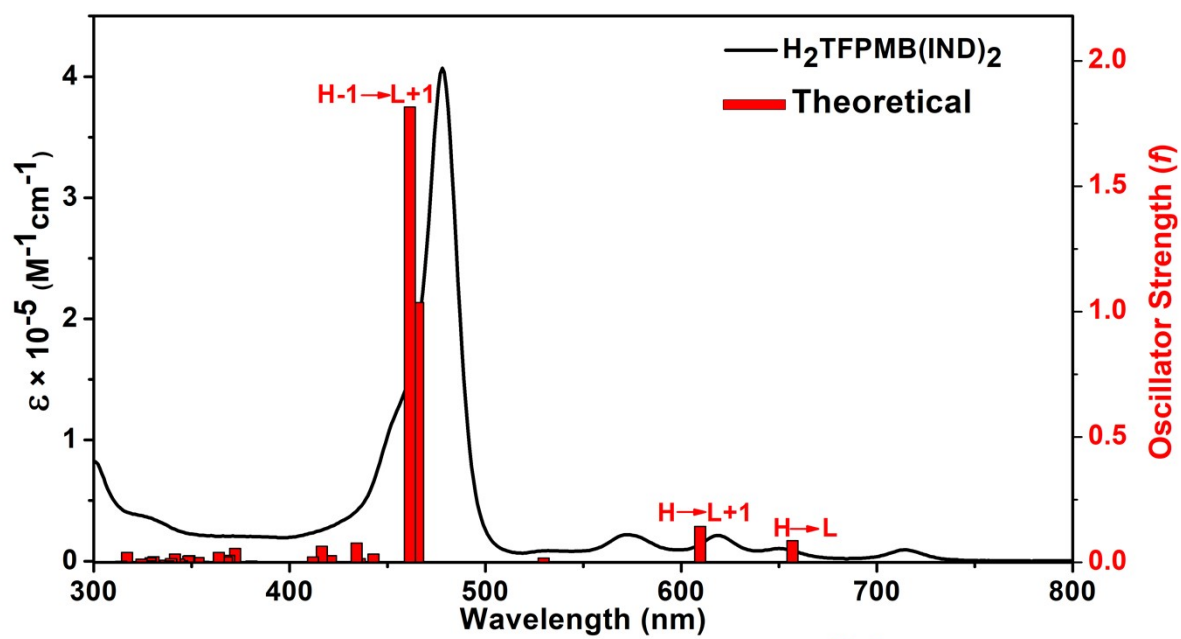


Fig. S34 Comparative (theoretical and experimental) absorption spectra of $H_2TFPMB(IND)_2$.

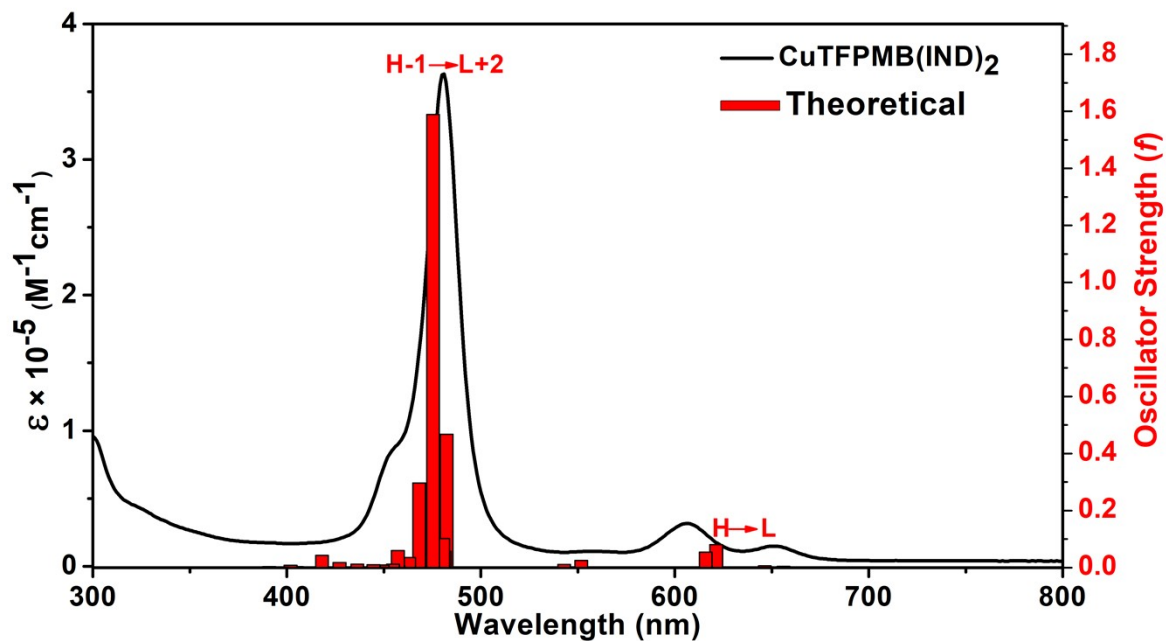


Fig. S35 Comparative (theoretical and experimental) absorption spectra of $CuTFPMB(IND)_2$.

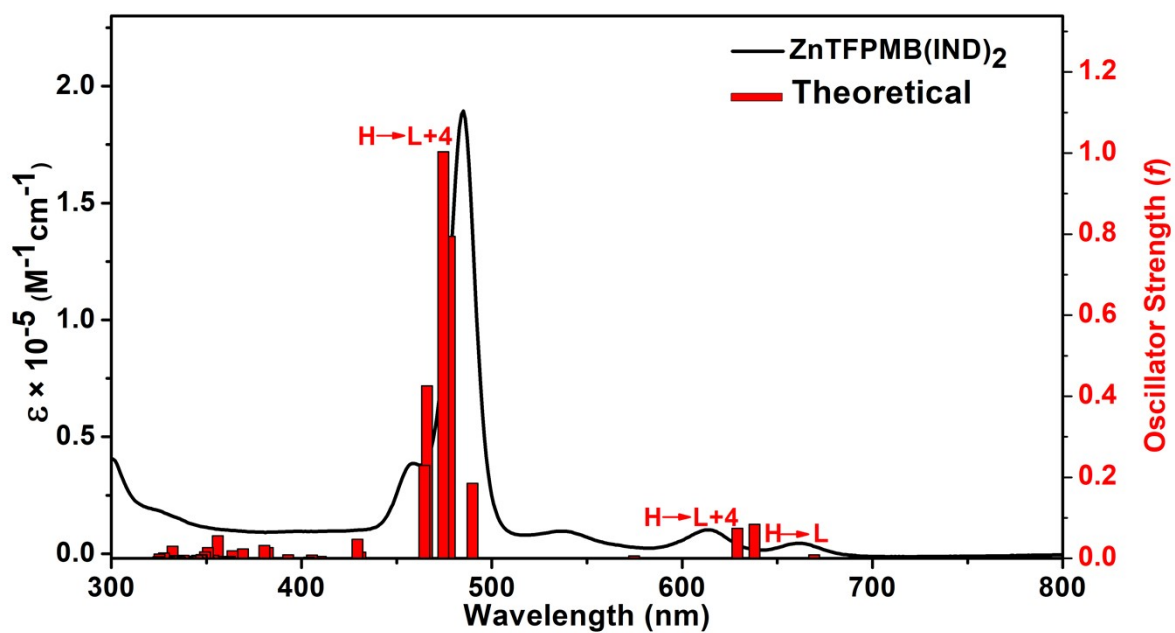


Fig. S36 Comparative (theoretical and experimental) absorption spectra of ZnTFPMB(IND)₂.

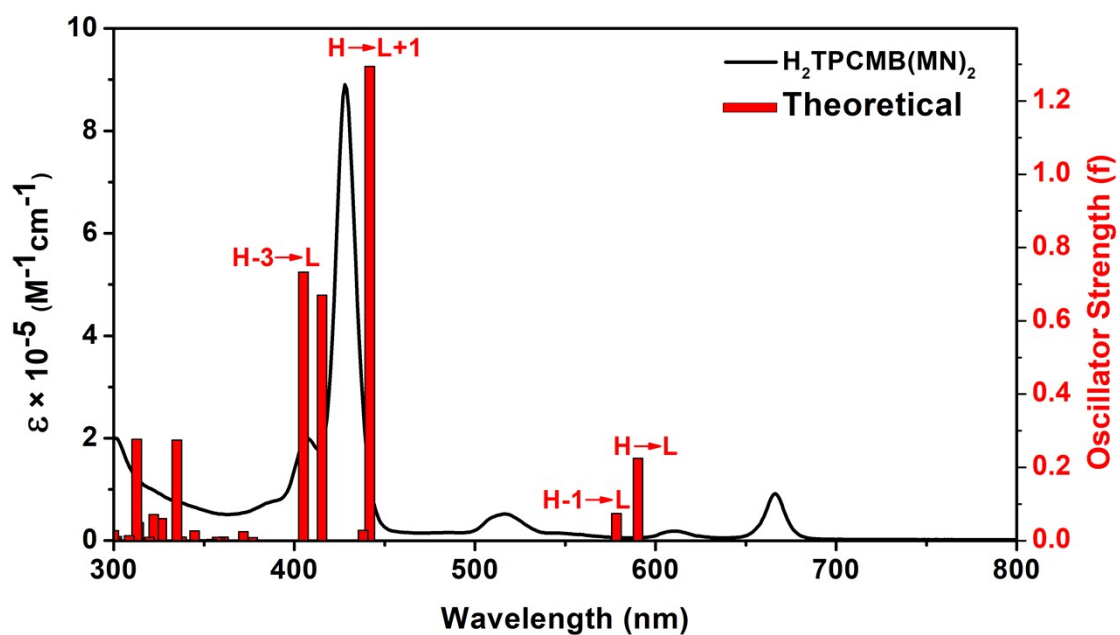


Fig. S37 Comparative (theoretical and experimental) absorption spectra of H₂TPCMB(MN)₂.

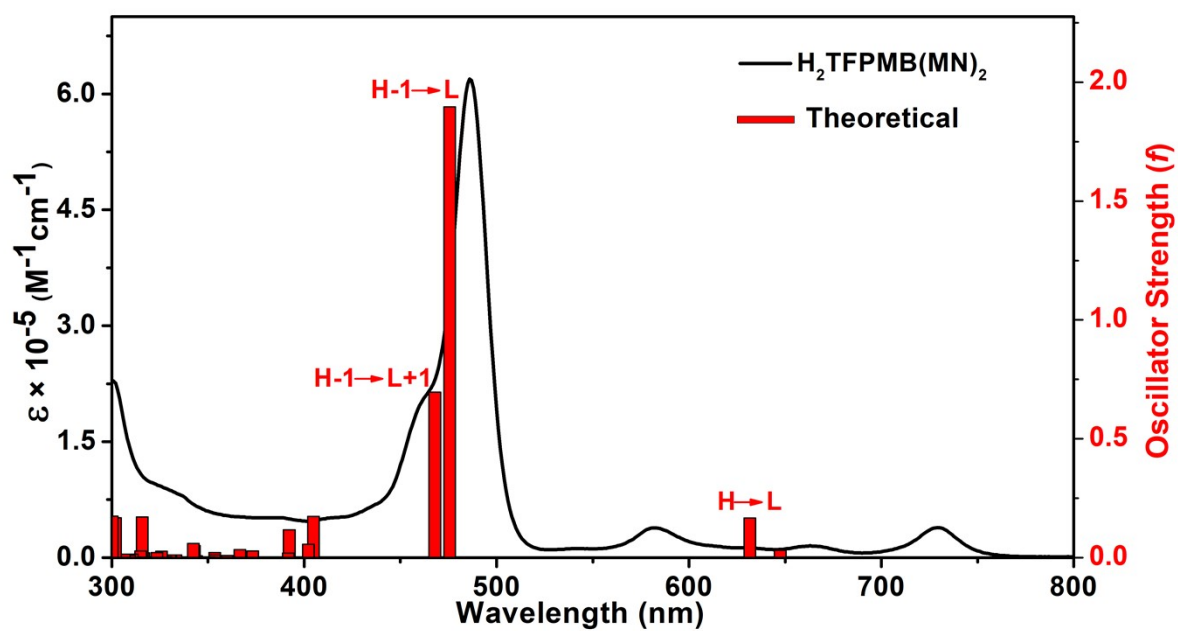


Fig. S38 Comparative (theoretical and experimental) absorption spectra of $H_2TFPMB(MN)_2$.

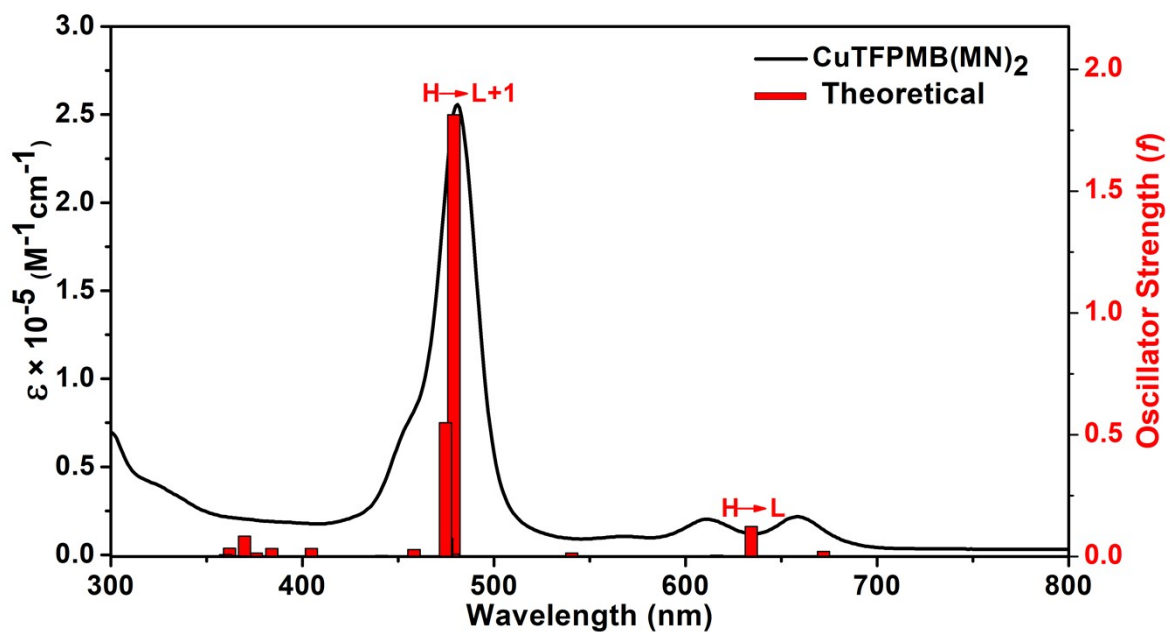


Fig. S39 Comparative (theoretical and experimental) absorption spectra of $CuTFPMB(MN)_2$.

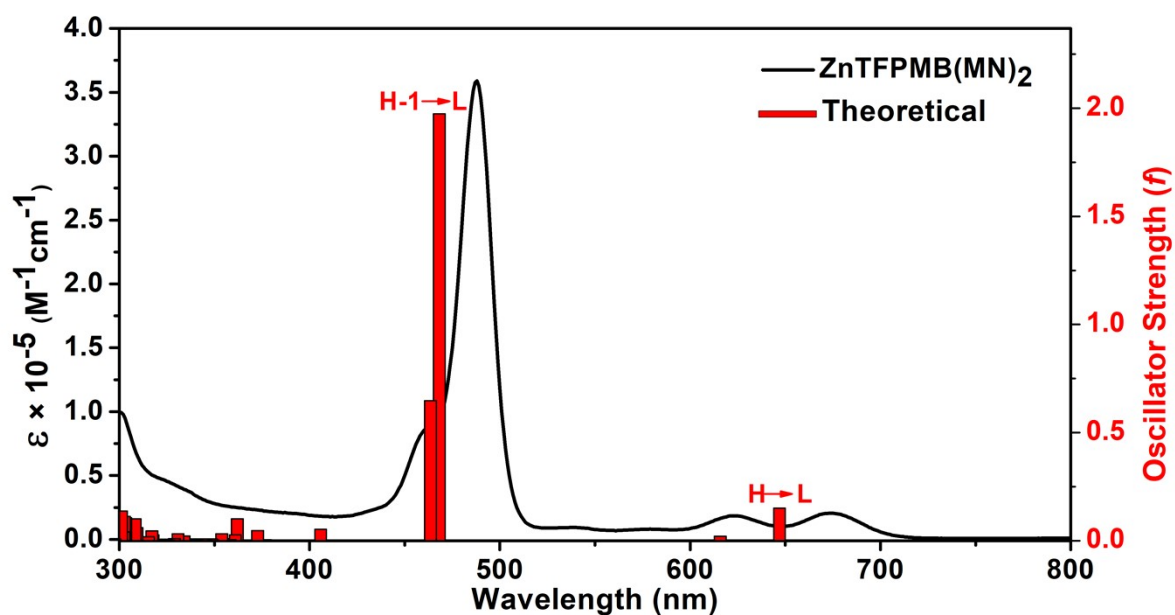


Fig. S40 Comparative (theoretical and experimental) absorption spectra of ZnTFPMB(MN)₂.

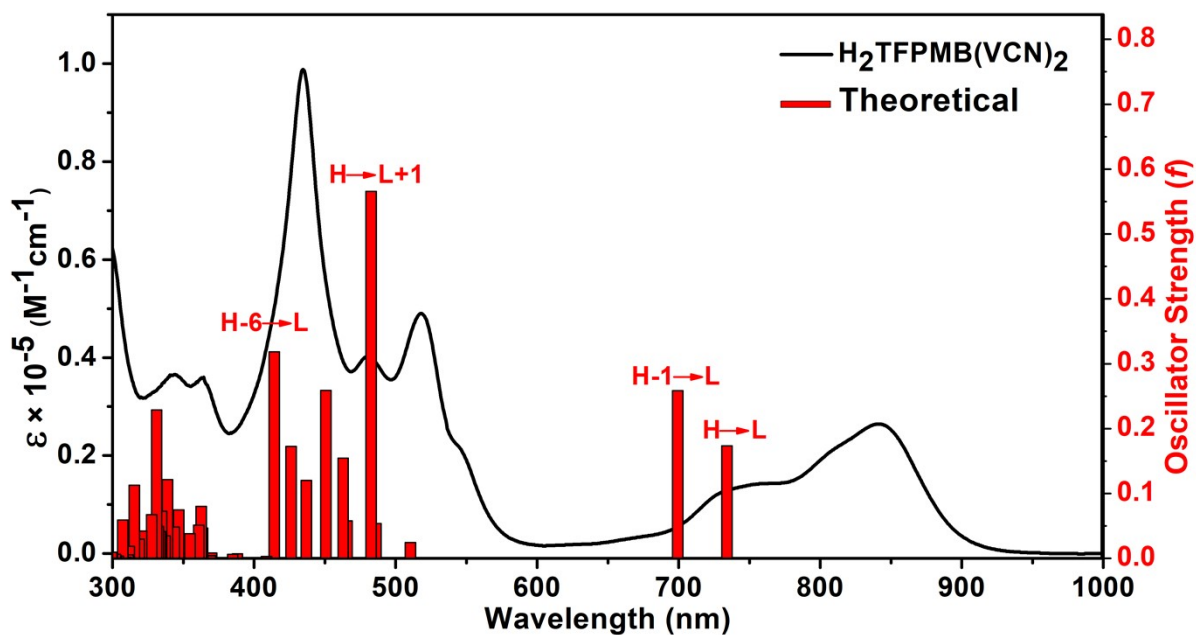


Fig. S41 Comparative (theoretical and experimental) absorption spectra of H₂TFPMB(VCN)₂.

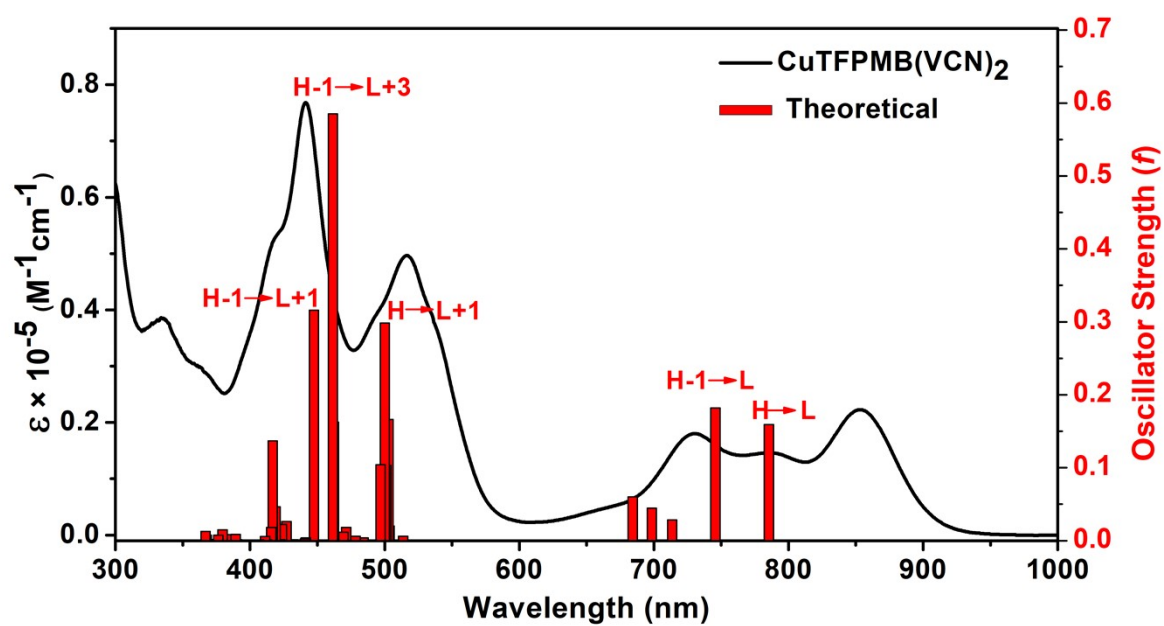


Fig. S42 Comparative (theoretical and experimental) absorption spectra of CuTFPMB(VCN)₂.

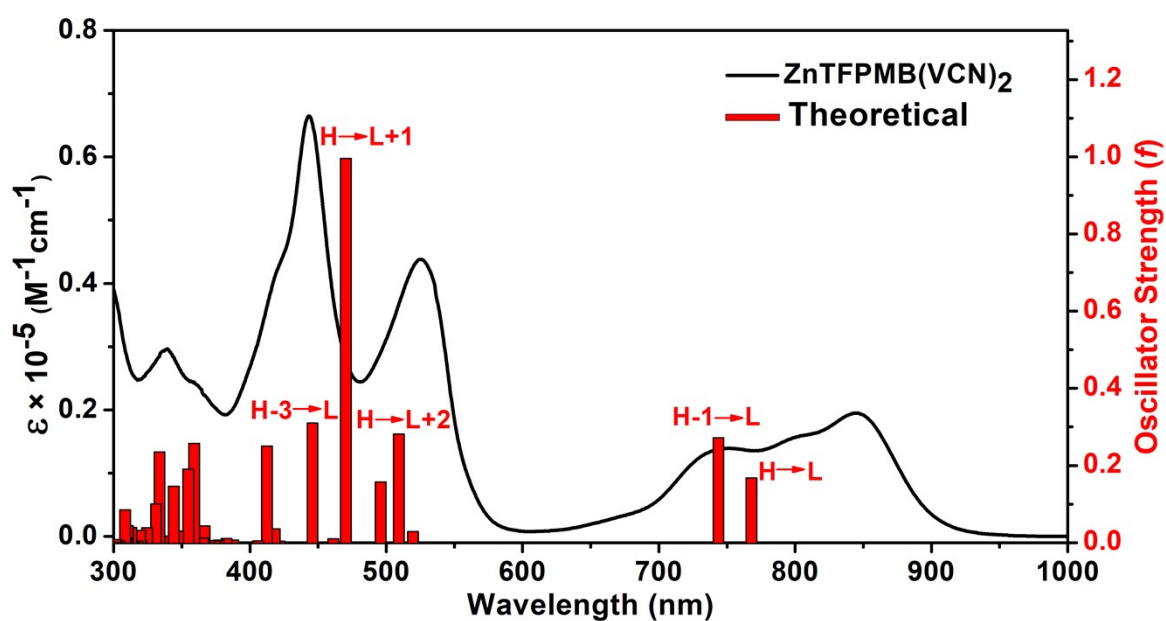


Fig. S43 Comparative (theoretical and experimental) absorption spectra of ZnTFPMB(VCN)₂.

Table S7 Calculated electronic excitation energies, major orbital contribution, theoretical and experimental absorption maxima, and oscillatory strength of investigated porphyrins.

Porphyrinoids	Excited state energy (eV)	Contribution	Coefficient (%)	λ (nm)	Oscillatory strength (<i>f</i>)	Experimental λ_{max} (nm) in CH ₂ Cl ₂
H ₂ TPCMB(IND) ₂	2.8836	HOMO→LUMO+3	44	430	1.8419	
	2.8571	HOMO-1→LUMO+3	46	434	1.1174	436
	2.1186	HOMO→LUMO	58	585	0.0669	674
H ₂ TFPMB(IND) ₂	2.6872	HOMO-1→LUMO+1	48	461	2.017	478
	2.0334	HOMO→LUMO+1	54	610	0.1587	619
	1.8875	HOMO→LUMO	56	657	0.096	714
CuTFPMB(IND) ₂	2.6082	HOMO-1→LUMO+2	44	475	1.765	480
	1.9954	HOMO→LUMO	59	621	0.0901	651
ZnTFPMB(IND) ₂	2.6132	HOMO→LUMO+4	44	474	1.2390	485
	1.9434	HOMO→LUMO	57	638	0.1036	661
H ₂ TPCMB(MN) ₂	3.0609	HOMO-3→LUMO	62	405	0.7326	407
	2.8068	HOMO→LUMO+1	57	442	1.2945	428
	2.1437	HOMO-1→LUMO	60	578	0.0742	610
	2.1005	HOMO→LUMO	66	590	0.2246	666
H ₂ TFPMB(MN) ₂	2.6500	HOMO-1→LUMO+1	63	468	0.7737	
	2.6070	HOMO-1→LUMO	57	476	2.1071	486
	1.9629	HOMO→LUMO	64	632	0.1851	730
CuTFPMB(MN) ₂	2.5879	HOMO→LUMO+1	53	479	2.0147	481
	1.9548	HOMO→LUMO	59	634	0.1376	659
ZnTFPMB(MN) ₂	2.6480	HOMO-1→LUMO	56	468	2.1938	488
	1.9164	HOMO→LUMO	65	647	0.1671	674
H ₂ TFPMB(VCN) ₂	2.9917	HOMO-6→LUMO	66	414	0.4366	434
	2.5666	HOMO→LUMO+1	53	483	0.7759	480
	1.7710	HOMO-1→LUMO	69	700	0.3546	754
	1.6870	HOMO→LUMO	70	735	0.2381	840
CuTFPMB(VCN) ₂	2.7712	HOMO-1→LUMO+1	44	447	0.3511	441
	2.6865	HOMO-1→LUMO+3	46	462	0.6502	
	2.4793	HOMO→LUMO+1	41	500	0.3315	517
	1.6628	HOMO-1→LUMO	58	746	0.2023	730
	1.5785	HOMO→LUMO	68	785	0.1769	854
ZnTFPMB(VCN) ₂	2.7805	HOMO-3→LUMO	37	446	0.3826	444
	2.6359	HOMO→LUMO+1	39	470	1.2293	444
	2.4347	HOMO→LUMO+2	48	509	0.3478	525
	1.6671	HOMO-1→LUMO	67	744	0.3355	748
	1.6145	HOMO→LUMO	68	768	0.2069	844

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