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Synthesis, Spectroscopic, Electrochemical Redox, Solvatochromism and Anion Binding Properties of β-Tetra- and -Octaphenylethynyl Substituted *Meso*-Tetraphenylporphyrins†

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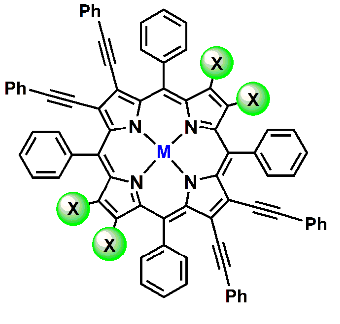
β-Tetra/octa-phenylethynyl substituted porphyrins and their metal (Co(II), Ni(II), Cu(II) and Zn(II)) complexes have been synthesized and characterized. $H_2TPP(PE)_8$ exhibited remarkable red shift in the Soret ($\Delta\lambda_{max}$ = 92 nm) band and longest wavelength band, $Q_x(0,0)$ ($\Delta\lambda_{max}$ = 117 nm), as compared to H_2TPP. Interestingly, $MTPP(PE)_8$ exhibited 450-500 mV anodic shift in first ring reduction potentials as compared to MTPP which is ascribed to electron accepting nature of phenylethynyl groups and extended π-conjugation whereas the first ring oxidation potentials remain unaltered. Hence, we observed significant reduction in HOMO-LUMO gap. The fluorescence quantum yields and lifetime values of free base and Zn(II) porphyrins are found to be 10-20 and 2-6 times, respectively lower than MTPPs. These porphyrins display a strong solvatochromism that is reflected by a large red-shift in their absorption and emission maxima upon increasing the solvent polarity. These porphyrins exhibited lower radiative rate constants (k_r) and enhanced nonradiative rate constants (k_{nr}) as compared to MTPPs. The decrement in fluorescence lifetime values, quantum yields, radiative rate constants (k_r) and profound solvatochromism with enhanced nonradiative rate constants (k_{nr}) have been interpreted in terms of intramolecular charge transfer (ICT) from porphyrin core to phenylethynyl moieties and extended π-conjugation. Further, $ZnTPP(PE)_8$ was utilized for the colorimetric “naked-eye” sensing of CN^-, F^-, Cl^-, Br^-, $H_2PO_4^-$ and CH_3COO^- ions through axial coordination of anions to Zn(II) metal centre. The electron deficient nature of Zn(II) centre of $ZnTPP(PE)_8$ was further proved by axial ligation studies with anions in toluene. $ZnTPP(PE)_8$ exhibited extremely high binding constants (10^{12} – 10^7 M^{-2}) with anions.

Introduction

Substituted porphyrins have unique electronic and optical properties that empower their use as model compounds of biological importance and potential material applications.[1,2] Functionalized porphyrins and their metal complexes were employed in dye-sensitized solar cells[1d,3] (DSSC), catalysis[4], photodynamic therapy (PDT)[5], anion sensing[6] and non-linear optical (NLO) studies[7] owing to their unique physicochemical properties such as high thermal and chemical stability and strong absorption in the visible region. The structural, spectral and electrochemical redox properties of porphyrins can be tuned by peripheral functionalization of porphyrin ring.[8] Particularly, the β-functionalization of *meso*-tetraphenylporphyrins exerts much larger steric and electronic effects on the porphyrin π-system.[8]

Notably, *meso*-phenylethynyl appended ‘push-pull porphyrins’ have attracted attention as potential NLO materials[9] and sensitizers in porphyrin-sensitized solar cells (PSSC).[3,10] The substitution of β-phenylethynyl groups at the porphyrin periphery induces interesting changes in optical absorption and electrochemical redox properties.[11] In general, β-ethynyl linker minimizes the steric interaction between the *meso*-aryl and β-phenyl groups.[11] These planar porphyrins are potential precursors for photochemical or thermal Bergman cyclization reactions.[11a-b] The distinctive physicochemical properties and potential applications of β-phenylethynyl substituted porphyrins[11] prompted us to synthesize and explore the unique properties of β-tetra- and -octaphenylethynyl



X = H, $MTPP(PE)_4$
X = PE, $MTPP(PE)_8$
M = 2H, Co(II), Cu(II), Ni(II), and Zn(II)

Chart 1. Chemical structures of β-phenylethynyl substituted porphyrins.

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†Electronic Supplementary Information (ESI) available: Fluorescence, ^1H NMR and MALDI-TOF mass spectra, cyclic voltammograms, HOMO-LUMO diagrams, solvent dependent UV-Visible and fluorescence spectral profiles, UV-Vis spectral titrations of $ZnTPP(PE)_8$ with different anions.
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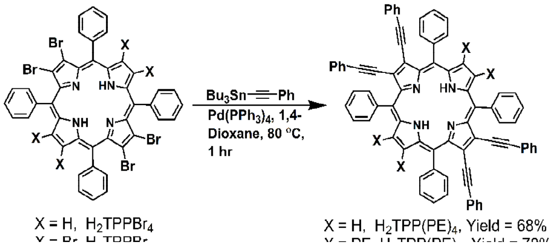
substituted porphyrins and their metal complexes.

Herein, we report the facile synthesis, photophysical, electrochemical redox, solvatochromism and anion binding properties of two series of β-phenylethynyl substituted porphyrins viz. 2,3,12,13-*tetrakis*(phenylethynyl)-5,10,15,20-tetraphenylporphyrin ($H_2TPP(PE)_4$), 2,3,7,8,12,13,17,18-*octakis* (phenylethynyl)-5,10,15,20-tetraphenylporphyrin ($H_2TPP(PE)_8$), and their metal (Co(II), Ni(II), Cu(II), Zn(II)) complexes (Chart 1). These porphyrins were characterized by UV-Visible, fluorescence, ^{1}H NMR and mass spectroscopic techniques. To the best of our knowledge, photophysical, electrochemical redox, solvatochromism, and anion binding properties of β-tetra- and -octaphenylethynyl appended *meso*-tetraphenylporphyrins have not been studied so far.

Results and Discussion



Scheme 1. Synthetic route to β-phenylethynyl substituted porphyrins.

The precursors, β-bromoporphyrins viz. H_2TPPBr_4 and H_2TPPBr_8 were synthesized using reported procedures.[12] $H_2TPP(PE)_4$ and $H_2TPP(PE)_8$ were synthesized in 68-70% yield by Stille coupling of H_2TPPBr_4 or H_2TPPBr_8 with tributyl(phenylethynyl)stannane in refluxing 1,4-dioxane for 1 hour under argon atmosphere as shown in scheme 1.[11a,11l] Notably, we could obtain desired products in lesser time scale (1 hour) as compared to reported literature.[11a,11l] Further, Co(II), Cu(II) and Zn(II) complexes were prepared by refluxing 10 equiv. of $M(OAc)_2{\bullet}nH_2O$ in $CHCl_3$/MeOH mixture whereas Ni metallation was carried out by refluxing in DMF with 10 equivalents of $Ni(OAc)_2{\bullet}4H_2O$. ^{1}H NMR and mass spectra of synthesized porphyrins were shown in Figures S1-S15 in the electronic supplementary information (ESI). It is known from the literature that $MTPP(PE)_8$ (M = 2H and Zn(II))[11a] and MT(*p*-^{t}Bu-Ph)P(PE)$_4$ (M = Co(II), Cu(II) and Zn(II))[11l] exhibited planar conformation (Figures S16-17 and Table S1 in the ESI) whereas $NiTPP(PE)_8$ showed moderately nonplanar conformation due to smaller size of Ni(II) ions and effective bonding of Ni(II) ion with porphyrin nitrogens.[11a]

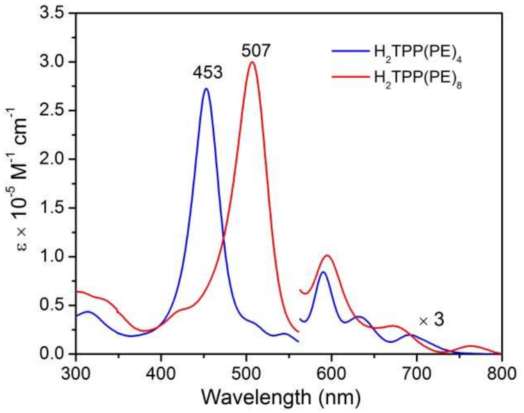


Figure 1. UV-Visible absorption spectra of $H_2TPP(PE)_4$ and $H_2TPP(PE)_8$ in CH_2Cl_2.

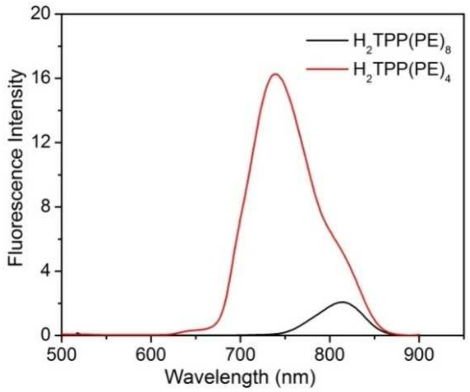


Figure 2. Fluorescence spectra of $H_2TPP(PE)_4$ and $H_2TPP(PE)_8$ in CH_2Cl_2 at 298 K.

The optical absorption spectra of $H_2TPP(PE)_4$, $H_2TPP(PE)_8$ and their metal complexes were recorded in CH_2Cl_2 at 298 K. Representative absorption spectra of $H_2TPP(PE)_4$ and $H_2TPP(PE)_8$ are shown in Figure 1. Table 1 lists the absorption spectral data of these porphyrins in CH_2Cl_2 at 298 K. Free base porphyrins exhibited a characteristic Soret band (B band) and three Q bands whereas metal derivatives exhibited a Soret and two Q bands.[8e] $H_2TPP(PE)_4$ exhibited red shift in B ($\Delta\lambda_{max}$ = 36 nm) and $Q_x(0,0)$ ($\Delta\lambda_{max}$ = 45 nm) bands whereas $H_2TPP(PE)_8$ exhibited larger red shift in Soret band ($\Delta\lambda_{max}$ = 92 nm) and $Q_x(0,0)$ band ($\Delta\lambda_{max}$ = 117 nm) as compared to H_2TPP suggesting that each of the PE group shifts ~9-11 nm.

Table 1. Optical absorption spectral data of synthesised porphyrins in CH_2Cl_2 at 298 K. Values in the parenthesis represent logε values.

Porphyrin	B band, nm	Q band(s), nm
$H_2TPP(PE)_4$	453(5.43)	590(4.45), 633(4.11), 692(3.76)
$H_2TPP(PE)_8$	507(5.48)	594(4.53), 672(3.99), 764(3.44)
$CoTPP(PE)_4$	452(5.39)	589(4.35), 622(4.44)
$CoTPP(PE)_8$	496(5.58)	604(4.65), 647(4.47)
$NiTPP(PE)_4$	457(5.20)	625(4.42)
$NiTPP(PE)_8$	497(5.54)	604(4.63), 651(4.47)
$CuTPP(PE)_4$	453(5.36)	574(4.21), 625(4.57)
$CuTPP(PE)_8$	505(5.50)	618(4.70), 661(4.20)
$ZnTPP(PE)_4$	457(5.50)	579(4.35), 627(4.68)
$ZnTPP(PE)_8$	505(5.47)	619(4.51)

The observed remarkable red shift both in Soret and Q bands was interpreted in terms of extended conjugation by PE groups with porphyrin π-system as well as electron withdrawing nature of PE substituents.[11a,11c]

Table 2. Electrochemical redox data of synthesized porphyrins (in V *vs* Ag/AgCl) in CH_2Cl_2 containing 0.1 M $TBAPF_6$ with a scan rate of 0.1 V/s at 298 K.

Porphyrin	Oxidation (V)		Reduction (V)		ΔE (V)
	I	II	I	II	
H_2TPP	1.00	1.34	-1.23	-1.54	2.23
$H_2TPP(PE)_4$	1.03	1.21^a	-0.88	-0.98^a	1.91
$H_2TPP(PE)_8$	0.99	1.12	-0.79	-1.06	1.78
NiTPP	1.02	1.32	-1.28	-1.72	2.30
$NiTPP(PE)_4$	1.07	1.25	-0.96	-1.21	2.03
$NiTPP(PE)_8$	1.14	1.25	-0.80	-1.07	1.94
CuTPP	0.97	1.35	-1.30	-1.71^a	2.30
$CuTPP(PE)_4$	0.97	1.34	-0.95	-1.22	1.92
$CuTPP(PE)_8$	0.94	1.46	-0.84	-1.06	1.78
ZnTPP	0.84	1.14	-1.36	-1.77	2.20
$ZnTPP(PE)_4$	0.88	1.09	-1.18	-1.36^a	2.06
$ZnTPP(PE)_8$	0.87	1.10	-0.92	-1.35^a	1.79

^{a}data obtained from DPV

The B and Q bands of these porphyrins exhibited an interesting trend in red-shift: $H_2TPP < H_2TPP(PE)_4 < H_2TPP(PE)_8$. The metal complexes exhibited blue-shift in both B and Q bands due to stabilisation of HOMOs.[13]

The synthesized free base and Zn(II) porphyrins were characterized by fluorescence spectroscopy to elucidate the effect of polyphenylethynyl substituents on porphyrin π-system. Figure 2 represents the steady state emission spectra of $H_2TPP(PE)_4$ and $H_2TPP(PE)_8$. The representative emission spectra of $ZnTPP(PE)_n$ (n = 4, 8) are shown in Figure S18 in the ESI. Significant red shifted emission ($\Delta\lambda_{max}$ = 76-90 nm) was observed for $MTPP(PE)_8$ as compared to $MTPP(PE)_4$. However, weak fluorescence with feeble fluorescence intensities and decreased quantum yields were observed for $MTPP(PE)_8$ (M = 2H and Zn(II)) as compared to $MTPP(PE)_4$ or MTPP (*vide infra*).

^{1}H NMR spectrum of $H_2TPP(PE)_4$ exhibits characteristic resonances arising from β-pyrrole protons, *meso*-phenyl, β-phenylethynyl (PE) and imino hydrogens (NH) while $H_2TPP(PE)_8$ is devoid of β-protons. The *ortho* protons of *meso*-phenyl of $H_2TPP(PE)_8$ are marginally ($\Delta\delta$ = 0.17 ppm) downfield shifted while *meta*- and *para*-protons of *meso*-phenyl and β-phenyl-ethynyl protons are marginally ($\Delta\delta$ = 0.03-0.06 ppm) upfield shifted as compared to $H_2TPP(PE)_4$. Notably, the core imino protons of $H_2TPP(PE)_8$ (-1.34 ppm) are downfield shifted as compared to $H_2TPP(PE)_4$ (-2.55 ppm) which are interpreted in terms of the electron withdrawing and conjugative effect of PE groups.[11c,11l] ^{1}H NMR spectra of $MTPP(PE)_4$ (M = Ni(II) and Zn(II)) complexes are devoid of imino protons, indicating that metal got inserted into the porphyrin ring. The *meso*-phenyl proton resonances of $MTPP(PE)_4$ (M = Ni(II) and Zn(II)) are 0.05-0.06 ppm upfield shifted as compared to corresponding free base porphyrins. The integrated intensities of proton resonances of these β-phenylethynyl substituted porphyrins are in consistent with the proposed structures (Figures S1-S6, ESI).

Electrochemical Redox Properties

To examine the influence of phenylethynyl (PE) substituents on porphyrin π-system, the electrochemical redox behaviour of these porphyrins was studied by cyclic voltammetry in CH_2Cl_2 at 298 K. Under similar conditions, the corresponding MTPP derivatives were also examined and the electrochemical redox data (*vs* Ag/AgCl) is listed in Table 2.

The cyclic voltammograms of $CuTPP(PE)_n$ (n = 0, 4 and 8) complexes are shown in Figure 3. These porphyrins exhibited two successive reversible one-electron oxidations and one-electron reductions (Figure S19, ESI).[14] However, the first oxidation and first reduction of Co(II) complexes is a metal centered process which is well documented in literature.[14,15]

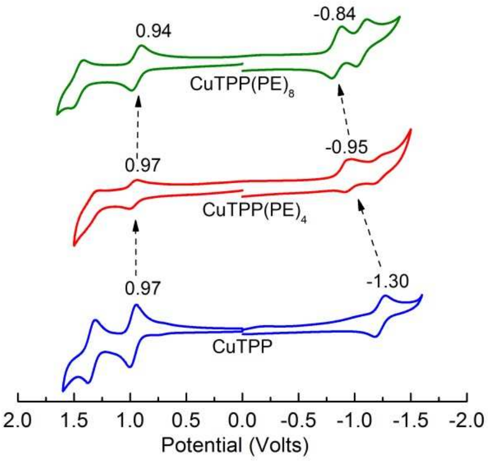


Figure 3. Cyclic Voltammograms of $CuTPP(PE)_n$ (n = 0, 4 and 8) in CH_2Cl_2 containing 0.1 M $TBAPF_6$ using Ag/AgCl as reference electrode with a scan rate of 0.1 V/s at 298 K.

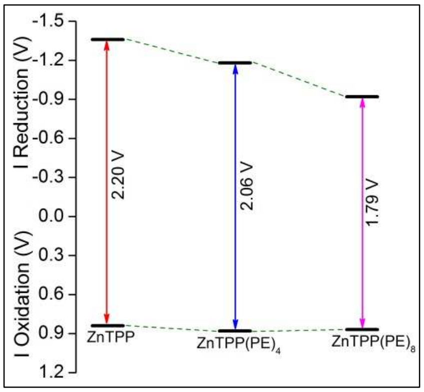


Figure 4. Variation of LUMO levels of $ZnTPP(PE)_4$ and $ZnTPP(PE)_8$ in reference to ZnTPP.

Analysis of electrochemical redox data of $MTPP(PE)_n$ (n = 0, 4, and 8; M = 2H, Ni(II), Cu(II), Zn(II)) revealed marginal changes in first ring oxidation (10 - 100 mV) and a drastic anodic shift (450-500 mV) in first ring reduction potential with increase in number of phenylethynyl groups (Figures 3 and S19, ESI). The anodic shift in first ring reduction potentials were interpreted in terms of electron withdrawing and conjugative effects of PE substituents. Similarly, for $CoTPP(PE)_n$ (n = 4, 8) complexes, the $Co^{II/III}$ oxidation potentials marginally shifted (anodic shift) by ~0.06 V while the $Co^{II/I}$ reduction is shifted anodically by 0.23-0.49 V as compared to CoTPP[14] (Table S2, ESI). The first reduction potential of these porphyrins followed the trend 2H > Ni(II) > Cu(II) > Zn(II) according to the difference in their electronegativity. As we increase the number of phenylethynyl groups, the HOMO-LUMO gap of $MTPP(PE)_n$ decreases (0.38 - 0.55 V) as compared to MTPP as shown in Figures 4 and S20, ESI due to extensive stabilization of LUMO. The electrochemical redox data of these porphyrins clearly indicate the electron deficient nature of porphyrin π-system.[11c]

Photophysical Studies

In order to understand the effect of polyphenylethynyl substitution, we have carried out quantum yield and life time measurements. Table 3 lists emission spectral data and the comparative values of quantum yields, Stokes shifts, radiative (k_r) and non-radiative (k_{nr}) rate constants of synthesized porphyrins.

Table 3. Photophysical data of $MTPP(PE)_n$ (M = 2H and Zn; n = 0, 4, 8) in CH_2Cl_2 at 298 K.

Porphyrin	$\lambda_{em, nm}$	Stokes shift (cm^{-1})	Φ_f	τ (ns)	k_r (s^{-1})	k_{nr} (s^{-1})	k (s^{-1})
H_2TPP	654,718	165	0.11	9.15	1.2×10^{7}	9.7×10^{7}	1.09×10^{8}
$H_2TPP(PE)_4$	739	919	9.6×10^{-3}	1.57	6.1×10^{6}	6.3×10^{8}	6.37×10^{8}
$H_2TPP(PE)_8$	814 (w)	804	5.2×10^{-3}	1.44	3.6×10^{6}	6.9×10^{8}	6.95×10^{8}
ZnTPP	598,644	372	3.0×10^{-2}	1.59	1.9×10^{7}	6.4×10^{8}	6.62×10^{8}
$ZnTPP(PE)_4$	644	421	1.9×10^{-2}	0.55	3.4×10^{7}	1.8×10^{9}	1.81×10^{9}
$ZnTPP(PE)_8$	736 (w)	2568	2.3×10^{-3}	0.97	2.4×10^{6}	1.0×10^{9}	1.02×10^{9}

W = Weak emission intensity

$MTPP(PE)_n$ (M = 2H, Zn(II); n = 4, 8) exhibit planar conformation as evidenced from their deviation of β-pyrrole carbons from the porphyrin mean plane, ΔC_β (0.040-0.094 Å) and deviation of 24 core atoms from porphyrin mean plane, $\Delta 24$ values (0.032-0.068 Å) (Table S1, ESI).[11a,11l] $MTPP(PE)_4$ and $MTPP(PE)_8$ exhibited decreased fluorescence quantum yields and shorter lifetimes than MTPP which is attributed to intramolecular charge transfer (ICT) from porphyrin core to acceptor PE moieties.[11c,11k,16] The observed radiative rate constants (k_r) of $MTPP(PE)_n$ are nearly 2-8 times lower than H_2TPP whereas nonradiative rate constants (k_{nr}) are 2-7 fold higher than H_2TPP. In X-ray structures, the phenylethynyl groups are almost perpendicular to porphyrin mean plane which indicates some extent of intramolecular charge transfer must be involved in ground and singlet excited state resulting into reduced k_r and enhanced k_{nr}, poor quantum yields, large Stokes shifts and shortened lifetime values as compared to that of MTPP (Table 3). The photophysical data clearly support the possibility of intramolecular charge transfer (ICT) from porphyrin core to phenylethynyl moieties.[11c,11k,16] $ZnTPP(PE)_8$ has exhibited large Stokes shift as compared to other porphyrins in this study due to the absence of well-defined $Q_x(0,0)$ band in the UV-Vis absorption spectrum.

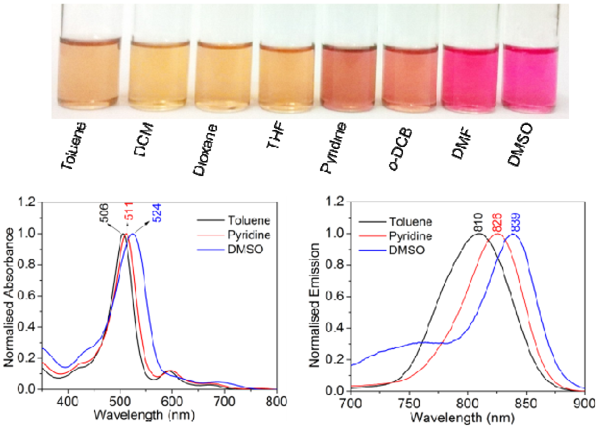


Figure 5. (top) Colorimetric response of $H_2TPP(PE)_8$ in different solvents; (bottom) UV Visible and fluorescence spectra of $H_2TPP(PE)_8$ in different solvents at 298 K.

Table 4. Electronic spectral data of $H_2TPP(PE)_8$ in different solvents at 298 K.

Solvent	B band, nm	Q band(s), nm	λ_{em}, nm
Toluene	506(5.52)	593(4.59), 673(3.97), 759(2.61)	810
DCM	507(5.41)	595(4.48), 672(3.96), 762(3.44)	814
Dioxane	506(5.64)	594(4.68), 672(4.17), 763(3.43)	820
THF	504(5.43)	593(4.48), 669(3.96), 760(3.10)	823
Pyridine	511(5.45)	597(4.53), 674(4.03), 765(3.22)	826
o-DCB	510(5.47)	595(4.57), 673(4.01), 760(3.32)	809
DMF	521(5.30)	605(4.15), 678(3.96)	765
DMSO	524(5.20)	691(3.87)	839

Solvatochromism Studies

In order to gain further insight into the photophysical processes in these compounds, we recorded the absorption and emission spectra of $MTPP(PE)_n$ (M = 2H, Zn(II); n = 0, 4 and 8) in different solvents and the results are summarized in Table 4 and S3 in the ESI. The Soret band of $H_2TPP(PE)_8$ in various solvents lies between 506 and 524 nm and is seen to have red-shift with increasing solvent polarity. This positive solvatochromism[17-19] is ascribed to the possibility of charge transfer between the electron rich porphyrin core and the electron deficient peripheral PE groups. Notably, the β-phenylethynyl substituted porphyrins have been shown to exhibit charge transfer characteristics.[9a-b,11c] The photophysical properties of these porphyrins are unusual in that they evince considerable charge-transfer character mixed into the porphyrin B- and Q-type transitions[9a-b,11c,16] due to π-delocalisation of β-substituent with porphyrin π-system. This is further supported by the increased bandwidth of the Soret band (B band) of $H_2TPP(PE)_8$ (FWHM = 49 nm) and $ZnTPP(PE)_8$ (FWHM = 36 nm) with respect to H_2TPP (FWHM = 14 nm) and ZnTPP (FWHM = 11 nm).[16] Furthermore, the possibility of deprotonation by various solvents listed in Table 4 is ignored as the UV-Vis spectral profiles of deprotonated $H_2TPP(PE)_8$ is completely different as that of solvent dependent profiles

(Figure S21, ESI). The absorption spectra of $H_2TPP(PE)_4$ are nearly independent of solvent polarity and shows no appreciable colour change in different solvents (Figure S22, ESI) with marginal shift (2-7 nm) which indicates weak intramolecular interaction between donor and acceptor groups in the ground state. Notably, $ZnTPP(PE)_4$ and $ZnTPP(PE)_8$ exhibit 13-18 nm shift in their Soret band while increasing solvent polarity from toluene to DMSO. However, there is no regular trend observed with solvent polarities in Zn(II) complexes which is due to combined solvatochromism arising from axial ligation of coordinating solvents and intramolecular interaction between donor (porphyrin core) and acceptor (PE) groups in the ground state (Figure S23, ESI).[19] In pyridine, a highly red-shifted absorption spectrum was observed for Zn(II) complexes which is probably due to the strong axial coordination of pyridine to the zinc metal centre.[20] A distinctive bathochromic shift (20-30 nm) in emission band was also observed (Figures 5 and S23, ESI) for free bases and Zn(II) complexes as we move from less polar solvent (toluene) to more polar solvent (DMSO) along with successive decrease in fluorescence intensity. $H_2TPP(PE)_4$ exhibits broad structureless weak emission in high polar solvents like DMF and DMSO. These results suggests an internal charge transfer which results from stabilization of polar excited state by polar solvents and is well documented with donor-acceptor fluorophores.[17-19,21] $H_2TPP(PE)_8$ exhibited blue shifted emission (negative solvatochromism) in DMF. This is possibly due to less stable and less polar excited state than the ground state which is further supported by the lower life time (0.66 ns) as compared to other solvents such as CH_2Cl_2, toluene, THF and dioxane (life time 1.3 to 1.6 ns) (Table S4, ESI).[17] To investigate further solvetochromism behaviour of PE groups, we recorded the fluorescence life time decay and analysed using a multi exponential decay. In more polar solvents, $H_2TPP(PE)_8$ and $ZnTPP(PE)_8$ exihibited di- or triexponential fluorescence decay, this is may be due to the emission of porphyrin core is partially quenched by the acceptor PE moieties. We observed almost linear fit between Stokes shift of $H_2TPP(PE)_8$ in different solvents and dielectric constant which indicates enhanced charge transfer in polar solvents (Figure S24a,b in ESI). The solvent induced changes were examined according to the Lippert–Mataga method.[22] According to this method, the plot between the observed Stokes shift (ν_{st}) and solvent orientation polarizability (Δf) must be linear for simple solvent-solute interactions whereas nonlinear fit will be observed in case of solvent-solute interactions associated with charge transfer (CT) and hydrogen bonding interactions.[22] In case of $H_2TPP(PE)_8$, we observed nonlinear fit indicating charge transfer interactions mixed into the π-π* transitions. While $ZnTPP(PE)_8$ exhibited more scattered points due to the combined effect of charge transfer and axial ligation (Figure S24c,d in ESI).[20]

Anion Binding Studies

A wide variety of porphyrinoids[6] and organic sensors[23] were utilised for sensing of toxic anions. A qualitative assessment of colorimetric responses of $MTPP(PE)_n$ (M = 2H, Zn and n = 4, 8) to various anions have also been carried out in CH_2Cl_2 at 298 K with various anions in the form of TBA salts.

$H_2TPP(PE)_8$ selectively interacts with F^- and CN^- ions which are reflected by red-shifted UV-Visible spectra with colorimetric 'naked eye' sensing of F^- and CN^- ions (reddish brown to dark pink) whereas no observable shift was found with other tested anions as shown in Figure 6. These anions show sensing *via* anion induced deprotonation mechanism as the UV-Visible spectral profiles obtained for $H_2TPP(PE)_8$ with F^- and CN^- resemble the optical absorption spectrum obtained by the addition of TBAOH (Figure S21, ESI). Further, we have recorded the ^1H NMR of $H_2TPP(PE)_8$ in presence of CN^- and F^- ions in $CDCl_3$ at 298 K. The disappearance of NH signal confirms the anion induced deprotonation mechanism as shown in Figure S25a in the ESI.

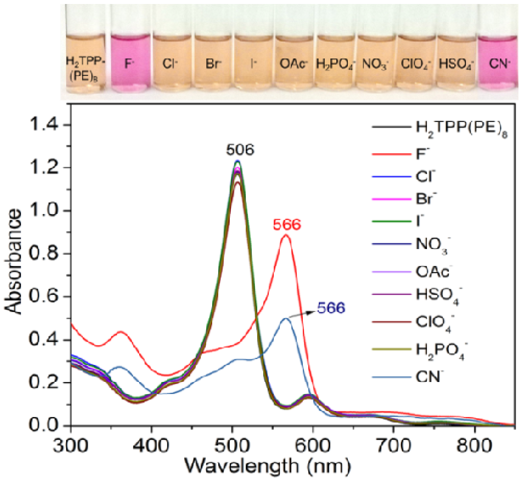


Figure 6. (Top) Colorimetric response of $H_2TPP(PE)_8$ with tested anions in CH_2Cl_2; (bottom) UV-Vis spectra of $H_2TPP(PE)_8$ upon addition of excess of TBA salts of tested anions in CH_2Cl_2 at 298 K.

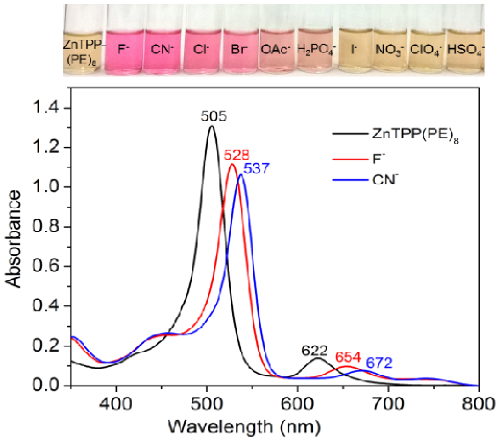


Figure 7. (Top) Colorimetric response of $ZnTPP(PE)_8$ with tested anions in CH_2Cl_2; (bottom) UV-Vis spectra of $ZnTPP(PE)_8$ upon addition of F^- and CN^- ions in the form of TBA salts in CH_2Cl_2 at 298 K.

Table 5. Optical absorption data of $ZnTPP(PE)_8$ (**1**) in presence of different anions in CH_2Cl_2 at 298 K.

Porphyrin	B band, nm	Q band(s), nm	ΔB, nm	ΔQ, nm
1	505(5.52)	622(4.54)	-	-
1+CN^{-}	537(5.43)	672(4.38)	32	50
1+F^{-}	528(5.44)	654(4.32)	23	32
1+Cl^{-}	535(5.41)	665(4.29)	30	43
1+Br^{-}	505(5.39), 533(sh)	622(4.0), 648(sh)	0	0
1+OAc^{-}	528(5.42)	652(4.37)	23	30
1+$H_2PO_4^{-}$	524(5.37)	646(4.34)	19	24

ΔB = Shift in B band w.r.t $ZnTPP(PE)_8$ (**1**) ; ΔQ = Shift in Q band w.r.t $ZnTPP(PE)_8$ (**1**)

The anionic species formed after deprotonation have stronger hydrogen bonding with protonated anion (HCN or HF) which leads to large spectral shift.[24] While using TBAOH, the formed anionic species and water are in equilibrium with reactant ($H_2TPP(PE)_8$) possibly due to weaker hydrogen bonding interactions (Figure S25b, ESI). Interestingly, $H_2TPP(PE)_4$ doesn't show any UV-Vis spectral change and colorimetric response even towards highly basic anions like F^{-} and CN^{-} (Figure S26, ESI). Notably, $ZnTPP(PE)_8$ is able to sense F^{-}, Cl^{-}, Br^{-}, CN^{-}, CH_3COO^{-} and $H_2PO_4^{-}$ ions which have shown considerable red-shifts in Soret ($\Delta\lambda_{max}$ = 19-32 nm) and Q bands ($\Delta\lambda_{max}$ = 30-50 nm) in CH_2Cl_2. Figure 7 represent the colorimetric 'naked eye' sensing of these anions by $ZnTPP(PE)_8$. Table 5 and S5 list the UV-Vis spectral data of $ZnTPP(PE)_8$, $H_2TPP(PE)_8$ and $ZnTPP(PE)_4$ in presence of different anions in CH_2Cl_2 at 298 K. The shift in B and Q bands are in accordance with the basicities of anions (pK_a) except Cl^{-} ion due to effective CT from chloride ion to porphyrin than F^{-} ion. No observable UV-Vis shifts and observable colour changes are observed with I^{-}, NO_3^{-}, ClO_4^{-} and HSO_4^{-} ions.

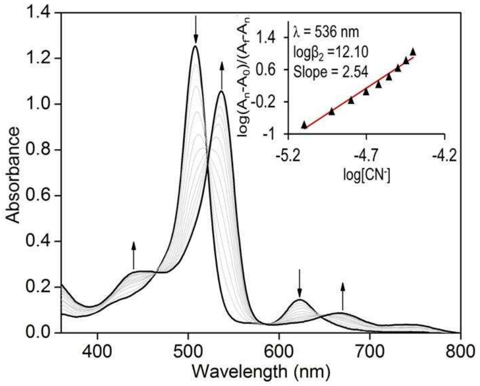


Figure 8. UV-Vis titration of $ZnTPP(PE)_8$ (4 μM) while increasing the concentration of cyanide ions (6 – 47.5 μM) in toluene at 298 K. Inset shows the corresponding Hill plot.

Axial ligation Studies

UV-Vis titrations were carried for $ZnTPP(PE)_n$ with basic anions in order to measure binding constants and stoichiometry of complexation.[20] Figure 8 represents the UV-Vis spectral titration of $ZnTPP(PE)_8$ with CN^{-} ions in toluene at 298 K. Both the Soret ($\Delta\lambda_{max}$ = 32 nm) and Q bands ($\Delta\lambda_{max}$ = 50 nm) are red shifted upon increasing the concentration of TBACN indicating the axial coordination of CN^{-} ions to $ZnTPP(PE)_8$ with well-anchored isosbestic points at 462, 521, 554 and 645 nm during the course of CN^{-} ion binding experiment. Similar, UV-Vis spectral profiles were observed for $ZnTPP(PE)_8$ with F^{-}, Cl^{-}, CH_3COO^{-} and $H_2PO_4^{-}$ ions. Figures S27 and S28 in the ESI represent the UV-Vis titration of $ZnTPP(PE)_8$ with Cl^{-}, CH_3COO^{-}, ions and $ZnTPP(PE)_4$ with CN^{-} ions, respectively in toluene at 298 K. The binding constants were calculated using Hill equation[25] and the corresponding binding data are presented in Table 6. The binding constants are increasing as the basicity of anion increases except for Cl^{-} and F^{-} ions. The higher binding constant was observed for Cl^{-} ions as compared to F^{-} ions with $ZnTPP(PE)_8$ is possibly due to effective charge transfer from Cl^{-} ion to Zn(II) metal center. It is known from the literature that Cl^{-} binds effectively with Zn(II) porphyrins as compared to Br^{-} and I^{-} anions according to their basicity.[20a,e,f] The stoichiometry of complexation was confirmed by Hill plot[25] (Figure 8 inset and Table 6). The Hill plot shows a straight line between log[CN^{-}] and log(A_i-A_0/A_f-A_i) having slope value ~2, which indicates 1:2 (porphyrin-to-cyanide) stoichiometry. These results clearly reveal enhanced the Lewis acidic nature of Zn(II) center due to electron withdrawing nature of polyphenyethynyl groups. To the best of our knowledge, this is first report on Zn(II) porphyrins[20] showing very high binding constants (10^{12} – 10^{7} M^{-2}) with anions as compared to ZnTPP.[20a]

Table 6. Binding constant data of $ZnTPP(PE)_n$ with anions in toluene at 298K and n represents the stoichiometry of complexation.

Porphyrin	Anion	β_2 (M^{-2})	log β_2	n
$ZnTPP(PE)_8$	CN^{-}	1.26×10^{12}	12.10	2.5
	Cl^{-}	8.71×10^{11}	11.94	2.3
	CH_3COO^{-}	2.09×10^{9}	9.32	1.7
	$H_2PO_4^{-}$	3.98×10^{7}	7.60	1.8
	F^{-}	8.13×10^{6}	6.91	1.7
$ZnTPP(PE)_4$	CN^{-}	2.69×10^{9}	9.43	2.1

Conclusions

Phenylethynyl-substituted porphyrins were synthesized by Stille coupling reaction in shorter timescale as compared to literature methods. $H_2TPP(PE)_8$ exhibited red shift of 92 nm in Soret and 117 nm in longest wavelength, $Q_x(0,0)$ bands as compared to H_2TPP. $MTPP(PE)_n$ exhibited only marginal shift in first oxidation potentials (10 - 100 mV) whereas profound anodic shifts were found in the first ring reduction potentials (ΔE_{red} = 450 – 500 mV), which are interpreted in terms of electron withdrawing and conjugative effect of phenylethynyl substituents. Hence, we could observe substantial decrement in the HOMO-LUMO gap. The free base and Zn(II) porphyrins exhibited lower fluorescence quantum yields and lifetime values as compared to MTPPs. $MTPP(PE)_8$ display a strong solvatochromism which is reflected by a large red-shift in their absorption and emission maxima while increasing the solvent polarity. These porphyrins exhibited lower radiative rate constants (k_r) and enhanced nonradiative rate constants (k_{nr}) as compared to MTPP. The decrement in fluorescence lifetime values, quantum yields, radiative rate constants (k_r) and profound solvatochromism with enhanced nonradiative rate constants (k_{nr}) have been interpreted in terms of intramolecular charge transfer (ICT) from porphyrin core to phenyethynyl moieties assosiated with extended π-conjugation. Further, ZnTPP(PE)$_8$ was utilized for the colorimetric "naked-eye" sensing of CN^-, F^-, Cl^-, Br^-, $H_2PO_4^-$ and CH_3COO^- ions through axial coordination of anion to Zn(II) metal centre. The enhanced Lewis acidity of ZnTPP(PE)$_8$ is further proved by axial ligation studies. Furthermore, ZnTPP(PE)$_8$ exhibited extremely high binding constants (10^{12} - 10^7 M^{-2}) with anions as compared to ZnTPP.

Experimental Section

Chemicals and materials

All the reagents employed in the present work were purchased from Sigma Aldrich and used as received without further purification. All solvents employed in the present work were of analytical grade and distilled or dried before use. Silica gel (100 - 200 mesh) used for column chromatography was purchased from Rankem and used as received. The tetrabutylammonium salts (TBAX, X = CN^-, F^-, Cl^-, Br^-, I^-, HSO_4^-,OAc^-, $H_2PO_4^-$, ClO_4^-, PF_6^- and NO_3^-) used for sensing applications were purchased from Alfa Aesar and used as received.

Instrumentation and methods

UV-Vis absorption spectra were measured in distilled dichloromethane or toluene using Agilent Cary 100 spectrophotometer with a pair of quartz cells of 10 mm path length and the fluorescence spectra were recorded on Hitachi F-4600 spectrofluorometer using a quartz cell of 10 mm path length. ^{1}H NMR spectra were recorded on Bruker AVANCE 500 MHz and JEOL ECX 400 MHz spectrometers using $CDCl_3$ as a solvent. MALDI-TOF-MS spectra were measured using a Bruker UltrafleXtreme-TN MALDI-TOF/TOF spectrometer using HABA as a matrix. Electrochemical measurements were carried out using CHI 620E electrochemical workstation. A three electrode assembly was used consisting of a Pt disk working electrode, Ag/AgCl as a reference electrode and a Pt-wire as a counter electrode. These cyclic voltammetric studies were carried out under Ar atmosphere. Fluorescence life time measurements in ns time domain were recorded in CH_2Cl_2 using Horiba Jobin Yvon "fluorocube fluorescence life time system" equipped with NanoLED (635 nm) source. The binding constants were calculated using Hill equation.[25]

General procedure for the synthesis of β- tetra- or octaphenylethynyl substituted *meso*-tetraphenylporphyrins

H_2TPPBr_4 or H_2TPPBr_8[12] (0.108 mmol) and $Pd(PPh_3)_4$ (20 mol%) were dissolved in 50 mL of distilled 1,4-dioxane and purged with Ar gas for 15 minutes. To this, tributyl(phenylethynyl)-stannane (10 equiv. for H_2TPPBr_4 and 20 equiv. for H_2TPPBr_8) in 10 mL of degassed dioxane was added and heated to 80 °C for 1 hour under Ar atmosphere. After completion of the reaction, the solvent was removed by vacuum distillation. The crude porphyrin was redissolved in $CHCl_3$ (20 mL) and purified on silica column using $CHCl_3$/hexane mixture (7:3, v/v) to 100% $CHCl_3$ as eluent. The desired products were recrystallized from $CHCl_3/CH_3OH$ mixture (1:3, v/v). Yields were found to be 68% and 70% for β-tetra- and octa-phenylethynyl substituted porphyrins, respectively.

2,3,12,13-tetra(phenylethynyl)-5,10,15,20-tetraphenyl porphyrin, (H_2TPP(PE)$_4$)

Yield = 68%; UV/Vis. (CH_2Cl_2): λ_{max}(nm) (logε) 453 (5.43), 544 (4.32), 590 (4.45), 632 (4.11); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.71 (s, 4H, β-pyrrole-H) , 8.25 (d, 8H, J = 6.5 Hz, *meso-o*-phenyl-H), 7.80-7.69 (m, 12H, *meso-m*- and *p*-phenyl-H), 7.36-7.33 (m, 8H, β-pyrrole-*o*-PE-H), 7.29-7.26 (m, 12H, β-pyrrole-*m*- *and* *p*-PE-H), -2.55 (s, 2H, imino-H). MALDI-TOF-MS (m/z): found 1016.44 $[M+H]^+$, calcd. 1016.24. Anal. calcd. for $C_{76}H_{46}N_4$: C, 89.91; H, 4.57; N, 5.52. Found: C, 89.73; H, 4.64; N, 5.61.

2,3,7,8,12,13,17,18-octa(phenylethynyl)-5,10,15,20-tetraphenyl-porphyrin (H_2TPP(PE)$_8$)

Yield = 70%; UV/Vis. (CH_2Cl_2): λ_{max}(nm) (logε) 507 (5.48), 590 (4.45), 633 (4.11), 692 (3.76); ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 8.42 (d, 8H, J = 7.5 Hz, *meso-o*-phenyl-H), 7.77 (t, 8H, J = 7.5 Hz, *meso-m*-phenyl-H), 7.65 (t, 4H, J = 7.5 Hz, *meso-p*-phenyl-H), 7.29 (d, 16H, J = 7.3 Hz, β-pyrrole-*o*-PE-H), 7.26-7.20 (m, 24H, β-pyrrole-H, *m*- and *p*-PE-H), -1.34 (s, 2H, imino-H). MALDI-TOF-MS (m/z): found 1417.15 $[M+H]^+$, calcd. 1417.72. Anal. calcd. for $C_{108}H_{62}N_4$: C, 91.63; H, 4.41; N, 3.96. Found: C, 91.55; H, 4.60; N, 3.72.

Synthesis of Co(II), Ni(II), Cu(II) and Zn(II) complexes

Corresponding free base porphyrins viz. (H_2TPP(PE)$_4$ or H_2TPP(PE)$_8$ (0.02 mmol) was dissolved in 15 mL of $CHCl_3$. To this, 10 equiv. of $M(OAc)_2{\bullet}nH_2O$ (M = Co(II), Cu(II) and Zn(II)) in 2 mL of methanol was added and refluxed on water bath for 50 minutes. The solvent was then evaporated to dryness and redissolved in minimum amount of $CHCl_3$ and washed with water (2×15 mL).The crude product was purified by column chromatography on silica column using $CHCl_3$ as eluent. Yields were found to be 85-90%. Further, Ni(II) complexes were prepared by refluxing free bases and $Ni(OAc)_2{\bullet}2H_2O$ (10 equiv.) in DMF for 2 hours under Ar atmosphere followed by the precipitation with water. The crude product was purified on silica column using $CHCl_3$ as eluent. The yield was found to almost quantitative.

NiTPP(PE)$_4$: Yield = 90%; UV/Vis. (CH_2Cl_2): λ_{max}(nm) (logε) 457 (5.20), 625 (4.42); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.57 (s,4H, β-pyrrole-H), 8.00-7.98(m, 8H, *meso-o*- phenyl-H), 7.66-7.61(m, 12H, *meso-m* and *p*-phenyl-H), 7.27-7.26 (m, 20H, β-pyrrole-*o, m* and *p*-PE-H); MALDI-TOF-MS (m/z): found 1070.82 $[M]^+$, calcd. 1070.29. Anal. calcd. for $C_{76}H_{44}N_4Ni{\bullet}0.5H_2O$: C, 84.45; H, 4.20; N, 5.18. Found: C, 84.31; H, 4.11; N, 5.34.

ZnTPP(PE)$_4$: Yield = 89%; UV/Vis. (CH_2Cl_2): λ_{max}(nm) (logε) 457 (5.50), 579 (4.35), 627 (4.68); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.69 (s, 4H, β-pyrrole-H), 8.20-8.15 (m, 8H, *meso-o*-phenyl-H), 7.73-7.67 (m, 12H, *meso-m* and *p*-phenyl-H), 7.40-7.36 (m, 8H, β-pyrrole-*o*-PE-H),7.30-7.26 (m, 12H, β-pyrrole-*m*- and *p*-PE-H); MALDI-TOF-MS (m/z): found 1078.74 $[M]^+$, calcd.

1078.60. Anal. calcd. for $C_{76}H_{44}N_4Zn$: C, 84.63; H, 4.11; N, 5.19. Found: C, 84.70; H, 4.18; N, 5.04.

$CoTPP(PE)_4$: Yield = 92%; UV/Vis. (CH_2Cl_2): λ_{max}(nm) (logε) 452 (5.39), 589 (4.35), 622 (4.44); MALDI-TOF-MS (m/z): found 1073.03 $[M+H]^+$, calcd. 1073.15. Anal. calcd. for $C_{76}H_{44}N_4Co$: C, 84.14; H, 4.14; N, 5.23. Found: C, 84.15; H, 4.18; N, 5.19.

$CuTPP(PE)_4$: Yield = 90%; UV/Vis. (CH_2Cl_2): λ_{max}(nm) (logε) 453 (5.36), 574 (4.21), 625 (4.57); MALDI-TOF-MS (m/z): found 1076.86 $[M]^+$, calcd. 1076.76. Anal. calcd for $C_{76}H_{44}N_4Cu$: C, 84.78; H, 4.12; N, 5.20. Found: C, 84.61; H, 4.19; N, 5.25.

$NiTPP(PE)_8$: Yield = 88%; UV/Vis. (CH_2Cl_2): λ_{max}(nm) (logε) 497 (5.54), 604 (4.63), 651 (4.47); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.23 (d, 8H, J = 8Hz, *meso-o*-phenyl-H), 7.71 (t, 8H, J = 8Hz,*meso-m*-phenyl-H), 7.61 (t, 4H, *meso-p*-phenyl-H), 7.30-7.22 (m, 40H, β-pyrrole-*o, m-* and *p*-PE-H); MALDI-TOF-MS (m/z): found 1472.11 $[M+H]^+$, calcd. 1472.47.

$ZnTPP(PE)_8$: Yield = 87%; UV/Vis. (CH_2Cl_2): λ_{max}(nm) (logε) 505 (5.47), 619 (4.51); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.34 (d, 8H, J = 8Hz, *meso-o*-phenyl-H), 7.72 (t, 8H, J = 8Hz, *meso-m*-phenyl-H), 7.60 (t, 4H, J = 4Hz, *meso-p*-phenyl-H), 7.36-7.31 (m, 16H, β-pyrrole-*o*-PE-H), 7.27-7.20 (m, 24H, β-pyrrole-*m*-and *p*-PE-H); MALDI-TOF-MS (m/z): found 1478.09 $[M+H]^+$, calcd. 1478.42.

$CoTPP(PE)_8$: Yield = 91%; UV/Vis. (CH_2Cl_2): λ_{max}(nm) (logε) 496 (5.58), 604 (4.65), 647 (4.47); MALDI-TOF-MS (m/z): found 1473.18 $[M+H]^+$, calcd. 1473.63. Anal. calcd. for $C_{108}H_{60}N_4Co$: C, 88.09; H, 4.11; N, 3.80. Found: C, 87.96; H, 4.04; N, 3.97.

$CuTPP(PE)_8$: Yield = 94%; UV/Vis. (CH_2Cl_2): λ_{max}(nm) (logε) 505 (5.50), 618 (4.70), 661 (4.20); MALDI-TOF-MS (m/z): found 1478.06 $[M+H]^+$, calcd. 1478.24

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Synthesis, Spectroscopic, Electrochemical Redox, Solvatochromism and Anion Sensing Properties of β-Tetra- and -Octaphenylethynyl Substituted Meso-Tetraphenylporphyrins

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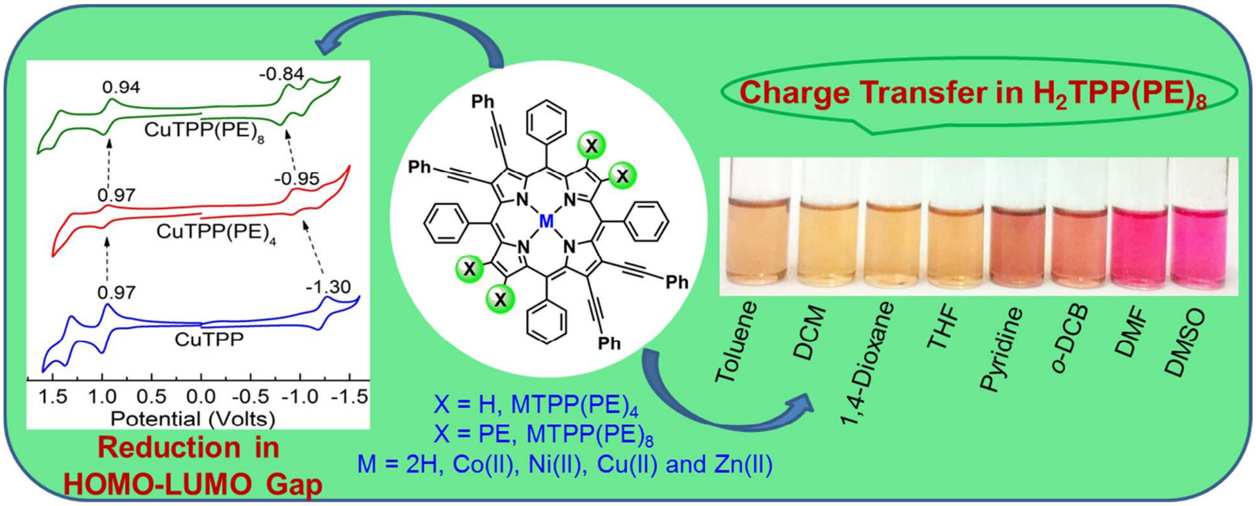

β-phenylethynyl substituted porphyrins exhibited unique photophysical properties and solvatochromic behavior due to intramolecular charge transfer (ICT) from porphyrin core to phenylethynyl moieties. Further, Zn(II) porphyrins were utilized for anion sensing.