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Synthesis, Structural, Photophysical, Electrochemical Redox and Axial Ligation Properties of Highly Electron Deficient Perchlorometalloporphyrins and Selective CN⁻ Sensing by Co(II) Complexes

Nivedita Chaudhri^a, Ray J. Butcher^b and Muniappan Sankar^{a*}

A straightforward synthetic route has been adopted to synthesize highly nonplanar electron deficient perchlorometalloporphyrins. Herein, we report the synthesis and characterization of MTPP(NO₂)Cl₇ where (M = Co["], Ni["], Cu["] and Zn["]). Further, we examined their electronic spectral and electrochemical redox properties and the results are compared with MTPPCl₈. MTPP(NO₂)Cl₇ exhibited red-shifted (~10-15 nm) absorption spectra relative to MTPPCl₈ due to strong electron withdrawing nature of nitro group. Mixed β -substitution alters the electrochemical redox properties to such an extent that an appreciable increment in anodic shift in reduction potential (200-300 mV) is observed for MTPP(NO₂)Cl₇ relative to MTPPCl₈ whereas only a minimal shift (15-50 mV) in the oxidation potential is observed. Nonplanarity of macrocyclic core was investigated by Single crystal X-ray analysis and DFT calculations. Higher ΔC_{β} (0.706 Å) for **1d** as compared to **2d** (0.642 Å) is undoubtedly signifying nonplanarity induced by nitro group. To substantiate the effect of mixed substitution, we performed axial ligation studies of Zn(II) complexes with nitrogenous bases and basic anions and found higher log β_2 values as well as a linear relation between log β_2 and pK₈ as compared to perbromoporphyrins. Highly electron deficient β substituted Co(II) porphyrins (**1a** and **2a**) were utilized as novel sensors for selective rapid visual detection of CN⁻ ions.

Introduction

Porphyrins with exhaustive substitution are of considerable interest due to their critical role in modulating physicochemical properties¹, nonplanar conformation² and acid base properties of central coordination entity H_2N_4 of the macrocycle.³ The distortion in tetrapyrrole macrocycles caused by steric interactions involving the peripheral substituents have been investigated in order to recognize the functional consequences of similar distortions observed in various proteins.^{2,4} Introduction of bulky groups at the β -pyrrolic positions distorts the macrocyclic ring and this effect is more when more than four halogens or electron withdrawing groups are present at the β -pyrrolic positions.⁵ In particular, substitution with halogens at β -positions of porphyrins seems to confer some unusual optical properties,⁶ enhanced electrochemical redox stability⁷ and increased catalytic

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efficiency to the metal complexes.^{8,9} The β -substitution by halogens results into π -electron density redistribution over the macrocyclic conjugation pathway as well as on nitrogen atoms involving in conjugation and hence alters the acid-base and axial ligation properties of the metalloporphyrins.¹⁰ Axial ligation dynamics are strongly metal centre dependent based on the metal electronic configuration. As the porphyrin macrocycle can accommodate wide variety of metal ions, the ligand binding and dissociation dynamics can vary according to the electronic structure and ionic radius of the metal ion as well as substitution on porphyrin macrocycle. Although βsubstituted, mainly halogenated porphyrins had appeared by the mid-1970s¹¹, later high-valent metalloporphyrins have been employed as robust catalyst for the oxidation of organic substances in presence of good oxygen donors, and the effectiveness of these catalysts has been traced to the stereochemical features of the porphyrins.¹²

The degree of nonplanarity is totally built upon the nature of substituents. The fully β -substituted (dodecasubstituted) porphyrins exhibited saddle confirmation of the porphyrin core with displacement of C_{β} in the range of 1-1.2 Å from the porphyrin mean plane.¹³ Dodecasubstituted porphyrins fall into two classes namely symmetrically β -substituted and asymmetrically β -substituted porphyrins. Symmetrically β -octasubstituted porphyrins have been widely explored due to their ease of synthesis and exhibited interesting electronic spectral, electrochemical redox and structural features in

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solution as well as solid state.¹⁴ Contrary to the well-studied symmetrically β -substituted octaalkyl¹⁵ and octahaloporphyrins¹⁶ due to their rich spin state and catalytic studies. However, the chemistry of the unsymmetrically dodeca-substituted porphyrins having two or more β -substituents largely unexplored.^{10,130,130,17}

The mixed β -substitution triggered by nitro group is also of particular interest as a consequence of its versatility and its feasible conversion into several other functional groups and wide range applications.¹⁸ Metalloporphyrin based sensors with different metal center have been reported to exhibit excellent selectivity for specific ions.¹⁹ Cyanide is an important target anion due to its toxic nature. Cyanide anion is known to inhibit the process of cellular respiration by interacting with cytochrome c and inhibits the mitochondrial electron transport chain and causes hypoxia.²⁰ Thus to design an anion receptor with high selectivity has been the area of intensive research. Metalloporphyrins were utilized for the detection of CN⁻ ions due to intrinsic affinity of cyanide for many metal ions such as zinc, rhodium, copper coordinated to porphyrins.²¹ Although the fluorescence or visual detection of cyanide ion by Co(II) or Zn(II) complexes of organic ligands is known in literature²² whereas this is the first report on selective naked-eye detection of cyanide ions by Co(II)-porphyrin with low detection limit (< 1.5μ M).



Results and Discussion

Synthesis and Characterization

Herein, a straightforward synthetic route has been adopted to prepare synthetically nonviable mixed dodecasubstituted porphyrins through direct functionalization instead of taking β -substituted pyrrole, which is economically challengeable (Scheme1). **1b** was synthesized by direct chlorination of NiTPPNO₂^{23a} using N-chlorosuccinimide (NCS).^{23b} Along with desired product, we also obtained **2b** as the side product, this is possibly due to replacement of nitro group by chloro group at high temperature.

 $MTPP(NO_2)Cl_7$ and $MTPPCl_8$ (where $M = Co^{II}$, Cu^{II} , Zn^{II}) were prepared by acid demetallation of respective Ni(II) complexes followed by conventional metallation with different metal acetates in $CHCl_3/MeOH$ mixture in good yields. These metalloporphyrins were characterized by various spectroscopic techniques including UV-Visible, Fluorescence, ¹H NMR, ESI-MS and cyclic voltammetric studies and elemental analyses. The structural aspects were justified by single crystal X-ray analysis and DFT calculations.



Scheme 1. Facile synthetic route to mixed β -substituted perchlorometalloporphyrins which are inaccessible by conventional synthesis.

Crystal Structure Discussion

To determine the correct conformational features and the extend of sterics offered by NO₂ substituent as compared to chloro at β -positions; we have examined the crystal structures of MTPP(NO₂)Cl₇ (M = Co(II) & Zn(II)), and MTPPCl₈ (M = Ni(II) and Zn(II)). The crystallographic data of CoTPP(NO₂)Cl₇(CH₃OH) (**1a**•CH₃OH), NiTPPCl₈ (**2b**), ZnTPP(NO₂)Cl₇(CH₃OH)(**1d**•CH₃OH), ZnTPP(NO₂)Cl₇(Py) (**1d**.Py) and ZnTPPCl₈(CH₃OH) (**2d**•CH₃OH) are listed in Table S1, electronic supplementary Information (ESI).

The ORTEP top views and displacement of macrocyclic core from mean plane for ZnTPP(NO₂)Cl₇(CH₃OH) (1d•CH₃OH) and ZnTPPCl₈(CH₃OH) (2d•CH₃OH) are shown in Fig. 1. The top ORTEP views for $MTPP(NO_2)CI_7$ (M = Co(II) and Zn(II)) and NiTPPCl₈ (1b) are shown in Fig. S1, ESI. Selected average bond lengths and bond angles of these five porphyrins are listed in Table S2 in the ESI. All the crystallized porphyrins have shown the saddle shape conformation of macrocyclic core with very high ΔC_{β} (±0.642-±1.028 Å) and $\Delta 24$ values (Fig. S3 in the ESI), which clearly describing severe nonplanar nature of macrocyclic core. This is further supported by the increment in $C_{\beta}-C_{\alpha}-C_{m}$ angle (~127°) with simultaneous decrement in the N- C_{α} - C_{m} angle (~124°) accompanied with larger C_{β} - C_{β} bond length (~1.345 Å) as compared to reported planar porphyrins. The nonplanarity of the macrocyclic core is enhanced by the steric repulsion among the peripheral substituents, which

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implements the relief of the strain through bond lengths and angles. The decreased N-M-N values (171°-162°) also indicates the saddle shape conformation of the macrocyclic core. The higher ΔC_{β} for **1d** as compared to **2d** reflecting the impact of NO₂ group over Cl group (effect of mixed β -substitution).



Fig. 1 ORTEP diagrams showing top views of (a) ZnTPP(NO₂)Cl₇ (1d) and (b) ZnTPPCl₈ (2d). Displacement of porphyrin core atoms (in Angstroms) from the porphyrin mean plane for ZnTPP(NO₂)Cl₇ (1d) and ZnTPPCl₈ (2d), respectively



The packing diagram of **1a** is showing that the NO₂ group of one porphyrin unit is interacting with the hydrogen of another unit. Fig. S2 shows the packing diagram of $ZnTPP(NO_2)Cl_7$ (**1d**) and $ZnTPPCl_8$ (**2d**), respectively. Both the porphyrins have shown two molecules in a unit cell.

NMR and Electronic Spectral Studies

¹H NMR spectra of Ni(II) and Zn(II) complexes were recorded in CDCl₃ at 298K. The ¹H NMR spectra of Ni(II) complexes are shown in Figs. S4 and S5 in the ESI. The spectral data for MTPPCl₈ where M = 2H, Co(II), Ni(II), Cu(II) and Zn(II) are exactly matching with the reported literature.^{1a,16d,19d} The integrated intensities of the protons are in accordance with the proposed structure. MTPP(NO₂)Cl₇ shown an asymmetric multiplet for *ortho*-phenyl proton relative to their corresponding homosubstituted MTPPCl₈ (Fig. S4 in the ESI) which has indicated the reduced symmetry offered by mixed substitution. The ESI mass spectra of MTPP(NO₂)Cl₇ were recorded in CH₃CN and the observed mass values are matching with the proposed structures (Figs. S6-S9 in the ESI).

The UV-Visible spectra of all metal derivatives were recorded in CH₂Cl₂ at 298 K. Table 1 lists the electronic spectral data of synthesized porphyrins in CH₂Cl₂ at 298 K. MTPP(NO₂)Cl₇ exhibited similar spectral features to MTPPCl₈ and showed red shift in Soret band ($\Delta \lambda_{max} = 4-12$ nm) as well as in Q_{x(0,0)} band ($\Delta \lambda_{max} = 8-14$ nm) relative to MTPPCl₈ (Fig. S10), this attributes to the strong electron withdrawing nature of nitro group which pulls the electron density from the porphyrin ring which stabilize the LUMO results in reduced HOMO-LUMO gap, and also from induced nonplanarity due to more electrostatic repulsion between mixed β -substituents. The comparative optical absorption spectra of **1d** and **2d** complexes is shown in Fig. 3a.

HOMOs of normal porphyrins usually situated at β -pyrrole positions and substitution at this position with more electron withdrawing substituents will further lift the degeneracy of a_{1u} and a_{2u} orbitals by stabilization of a_{1u} relative to a_{2u} which resulted into the depletion of intensity gap ratio between $Q_{X(0,0)}$ and $Q_{X(1,0)}$ for **1d** as compared to **2d** as shown in inset of Fig. 3a. Fig. 3b represents the comparative emission spectra of **1d** and **2d** complexes in CH₂Cl₂ at 298K. Due to heavy atom effect, these perchlorinated-2-nitrotetraphenylporphyrins also exhibited very feeble emission intensity with very low quantum yields like bromo derivatives.^{10a} **1d** exhibited relatively more intense and red-shifted emission spectra relative to **2d**.

Table 1 or	ntical absorptio	on and emission	spectral data ^a	of MTPP(NO2)Cl- and MTPPClo
able T Ob	Jucai absorpti		i spectiai uata	

porphyrin	B band	Q (band)s	λ_{em}	ϕ_{f}		
1a	447(186.2)	562(16.59), 605(9.77)				
2a	437(147.9)	556(12.30)				
1b	448(128.8)	562(10.96), 604(6.31)				
2b	439(190.5)	554(15.13)				
1c	449(117.5)	576(12.88), 624(6.46)				
2c	437(158.4)	571(17.78), 610(6.16)				
1d	459(158.5)	593(9.12), 647(8.31)	729	0.0009		
2d	455(204.3)	592(10.2), 646(9.55)	708	0.0019		
$^{a}\lambda$ /nm. The values in parentheses refer to $\epsilon \times 10^{-3}$ Lmol ⁻¹ cm ⁻¹ .						

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Fig. 3 (a) Electronic absorption spectra of 1d (8.45×10^{-6} M) and 2d (7.09×10^{-6} M) in CH₂Cl₂, inset shows expended region for Q bands. (b) Electronic emission spectra of 1d and 2d in CH₂Cl₂ at 298 K.

Electrochemical Studies

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A wide variety of highly substituted halogenated porphyrins have been examined in non-aqueous media. The electrochemical behaviour of perhalogenated porphyrins have been well documented in the literature.^{7b,17b,24} To analyse the influence of nitro groups at β -position on the redox potentials of porphyrin core, the electrochemical redox properties of MTPP(NO₂)Cl₇ were examined by cyclic voltammetric studies in distilled CH₂Cl₂ at 298 K under argon using 0.1 M TBAPF₆ as the supporting electrolyte. For comparison, the MTPPCl₈ were also investigated under similar conditions and the electrochemical redox data was found in good agreement with reported value in literature.^{14c,16d} Comparative cyclic voltammograms of 1a and 2a are shown in Fig. 4. Fig. S11 in the ESI represents the comparative cyclic voltammograms of $MTPP(NO_2)Cl_7$ (M = Cu(II) and Ni(II) and $MTPPCI_8$ (M = Cu(II) and Ni(II)). The observed behaviour of 1a is quite similar to 2a containing two reversible reduction and three reversible oxidations but there is a remarkable shift in redox potentials. Table 2 lists the electrochemical redox data of metal complexes of MTPP(NO₂)Cl₇ and MTPPCl₈ in CH₂Cl₂. The β -nitro substituted porphyrins are easier to reduce and harder to oxidize as compared to homosubstituted porphyrins. Interestingly, nitro bearing porphyrins exhibited a significant anodic shift (190-325 mV) in the first ring reduction potentials as compared to



Fig. 4 Comparative Cyclic voltammograms of **1a** and **1b** in CH_2Cl_2 under argon at room temperature with 0.1 M TBAF₆ as the supporting electrolyte at a scan rate of 100 mV/s.

Por	Oxidation			Reduction			٨E
FUI.	Ι	Ш	Coll/III	Coll/I	Ι	II	ΔL
1a	1.34	1.51	1.00	-0.27	-1.12	-1.60 ^d	2.46
2a	1.13	1.25	0.91	-0.37	-1.44	-	2.57
1b	1.27	-	-	-	-0.64	-0.89	1.91
2b	1.22	-	-	-	-0.85	-1.16	2.07
1c	1.13	1.63	-	-	-0.66	-0.89	1.79
2c	1.04	-	-	-	-0.85	-1.11	1.89
1d	0.99	1.23	-	-	-0.92	-1.18	1.91
2d ^c	0.98	1.22	-	-	-1.12	-1.47 ^d	2.10

 $^{\rm a}$ In V, vs Ag/Agcl electrode, $^{\rm d}$ data obtained from differential pulse voltammetry $^{\rm c}$ in 5% THF in CH_2Cl_2

Axial Ligation Studies

To demonstrate the effect of basicity of axial ligands and electron withdrawing substituents (chloro, nitro) on the acidity of Zn(II) center of the porphyrin ring, we have examined the axial ligation studies of ZnTPP(NO₂)Cl₇ (**1d**) and ZnTPPCl₈ (**2d**) with various nitrogenous bases (pyridine, N-methylimidazole, 4-dimethylaminopyridine and piperidine) and basic anions such as CN⁻, OAc⁻, F⁻ and H₂PO₄⁻ in the form of their respective tetrabutylammonium salts in toluene at 298 K.

Fig. 5a represents the concomitant decrement in the absorbance of ZnTPP(NO₂)Cl₇ (1d) (8.29 × 10⁻⁶ M) at 460 nm with emergence of a new B-Band at 465 nm accompanied by 5 nm red shift upon sequential addition of pyridine (4-150 μ M). As axial ligation proceeds, the decrement in the Q_(1,0) band with 16 nm red-shift with simultaneous increment in Q_(0,0) band accompanied with 29 nm red-shift was observed. A plot of [base] *vs.* [base]/(Δ A) show a straight line which in turn

indicates the 1:1 complexation of porphyrin:base as shown in inset of Fig. 5a.

The equilibrium constants (K_{eq}) were calculated using literature method. 10a,25 The equation for the analysis is as follow:

$1/K_{eq} = [base]/\{[por.]L(\epsilon_p-\epsilon_{pa})/(Ao-An)-1\}$ Eq.1

Where ϵ_p is molar extinction coefficient for the Zn(II) complexes and ϵ_{pa} is molar extinction coefficient for porphyrin:anion/base complex, respectively. A_0 is the initial absorbance and A_n is the absorbance in presence of added base or anion at a particular wavelength. L is the path length of the cell.



Fig. 5 (a) Axial ligation of pyridine to **1d** $(8.29 \times 10^{-6} \text{ M})$ in toluene at 298K. (b) Axial ligation of CN⁻ ion to **1d** $(8.29 \times 10^{-6} \text{ M})$ in toluene at 298K. Main plots show the spectral changes in Soret region and insets show plot [Pyridine] *vs.* [Pyridine]/ Δ A.



Fig. 6 (a) comparative plot of log K_{eq} Vs p_{Ka} is given for **1d** and **2d**. (b) Comparative plot of log K_{eq} Vs p_{Ka} is given for ZnTPP(NO₂)Br₇ and ZnTPPBr₈ (values are taken from ref^{10a}).

Similar UV-Vis spectral changes have been perceived for ZnTPPCl₈ (2d) with pyridine (Fig. S12 in the ESI), which also shown 1:1 stoichiometry (porphyrin to pyridine) indicated by slope of regression line. The axial ligation of other bases also performed with 1d and 2d and found to be axially ligated with porphyrins in 1:1 stoichiometric ratio. Table 3 lists the equilibrium constant data, which clearly reveals that 1d having higher equilibrium constant values as compared to 2d, this again attributing to the enhanced nonplanarity by mixed substitution and increased acidic nature of Zn(II) core of porphyrin due to substitution with electron withdrawing nitro group.

Table. 3 Equilibrium constants $^{a}\left(K_{eq}\right)$ for the ligation of nitrogenous bases with
Zn(II) complexes of perchloroporphyrins in toluene at 298 K.

Base	1d		2d		рКа
	К	P:B	К	P:B	
Piperidine	2076.97	1:1	1710.31	1:1	11.22
4-DMAP	212.12	1:1	163.00	1:1	9.70
N-Methylimidazole	219.68	1:1	159.37	1:1	7.33
Pyridine	57.01	1:1	46.85	1:1	5.23
Pyridine ^a The K _{en} values refers to (57.01 ×10 ³ K _{eo} /M ⁻¹)	1:1 within th	46.85 ne error range	1:1 of ± 6%,	5. Pre

to porphyrin and B refers to base. To gain insight into the electronic effect of chloro vs. bromo on the ligation properties, we compared the data of perchlorinated porphyrins with perbrominated porphyrins reported in litrature.^{10a} Data listed in table 3 revealing high binding constant for chloro complexes as compared to bromo derivatives is straightforward indication of higher electron deficient nature of porphyrin. The plot constructed for **1d** and **2d** between logK_{eq} and the pKa values of used bases is shown in Fig. 6 which displayed a linear relation with K_{eq}. **1d** showing comparative impartial straight line as compared to ZnTPP(NO₂)Br₇ with higher correlation coefficient. Among all used bases, the trend in K_{eq} values was found to be in

Table. 4 The overall binding constants $(\beta_2)^a$ for the ligation of basic anions with $Zn^{(0)}$ complexes of perchloroporphyrins in toluene at 298K.

accordance with their pK_a values, higher the pKa value greater

is the equilibrium constant.

Anions	1d			2d		
74110115	β ₂	$\log \beta_2$	P:A	β_2	$\log \beta_2$	A:P
CN ⁻	5.75×10 ¹⁰	10.75	1:2	3.53×10 ¹⁰	10.54	2:1
OAc	2.45×10 ¹⁰	10.38	1:2	2.01×10 ¹⁰	10.30	2:1
H ₂ PO ₄ ⁻	2.33×10 ¹⁰	10.36	1:2	1.12×10^{10}	10.04	2:1
F	9.22×10 ⁸	8.96	1:2	7.78×10 ⁸	8.89	2:1

 $^{\rm a}$ within the error range of ±5% for $\beta_{\rm 2},$ P refers to porphyrin and A refers to anion.

11.8 The effect of electron withdrawing groups on the acidity of Zn^{II} core of the porphyrin π-system further proved by performing again axial ligation studies with highly basic anions such as CN⁷,
 OAc⁷, F⁻ and H₂PO₄ in the form of their tetrabutylammonium salts in toluene at 298 K. Fig. 5b represents the changes in

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Soret Band region upon successive addition of CN⁻ (1-18 µM) to 1d in toluene at 298 K. The UV-vis. spectral features of anion binding are almost similar to that of base binding. While increasing the concentration of cyanide ion to **1d** (8.29×10^{-6} M), the decrement in absorbance at 459, 589, 644 nm and the concomitant increments in the absorbance at 475 and 690 nm was observed with multiple isosbestic points. The overall binding constant and stoichiometry were analyzed by Benesi-Hildebrand method. 1d and 2d both were found to be axially ligated with basic anions in 1:2 (Porphyrin:Anions) stoichiometric ratio (Figs. S13 and S14 in the ESI). Similar spectral changes were observed during titration of 2d (8.38×10⁻⁶ M) with CN⁻ (Fig. S14b). A standard Benesi-Hildebrand plots were also constructed in 1:1 stoichiometric ratio from the titration data of 1d and 2d with cyanide ion as shown in Figure S15 in the ESI. The cyanide binding was not accurately modeled by these plots clearly indicating that the binding of anions with 1d and 2d cannot be fit in 1:1 stoichiometric fashion. Other anions were also tested with both Zn(II) complexes and the data for equilibrium constant is listed in Table 4. Data revealed that as the basicity of anion increases the equilibrium constant also increases.

Selective Cyanide Ion Sensing by Cobalt(II) Complexes

The use of 3d transition metal complexes of porphyrins for anion sensing is cost effective and environmental friendly. The use of free base complexes of perhaloporphyrins for detection of highly basic anions through anion induced deprotonation process^{23b} and Ni(II) complexes of perchloroporphyrins for selective detection of cyanide ions through axial coordination of CN⁻ ion are reported by us.^{19d} The anion recognition properties of Co(II) complexes of these porphyrin were studied in toluene with various anions by UV-Visible spectroscopy with the sequential addition of their TBA salts. Interesting, their remarkable feature was identified to specially recognize cyanide ion in presence of all other anions. 1a and 2a showed remarkable red shifted absorption spectra with cyanide ion with distinct colour change whereas no observable shift was found with other tested anion as shown in Figs. 7 and S16 in the ESI.

UV-Visible spectral titration of **1a** $(1.04 \times 10^{-5} \text{ M})$ with cyanide ion is shown in Fig. 8. As we increase the concentration of cyanide ion $(0.13 \times 10^{-5} - 1.58 \times 10^{-5} \text{ M})$, the decrement in the absorbance of 1a was observed at 447 and 561 nm with the concomitant increment at 397, 489 and 682 nm with multiple isosbestic points. The same behavior was observed for 2a $(1.05 \times 10^{-5} \text{ M})$ with sequential addition of CN⁻ ion as shown in Figure S17 in the ESI. Both the Soret (43-45 nm) and Q bands (113-120 nm) were highly red-shifted upon addition of aliquots of CN⁻ ions to 1a and 2a. The stoichiometry and binding constant were calculated by Benesi-Hildebrand method by plotting a graph between $1/[\Delta A]$ and 1/[CN] which shows a straight line with $r^2 = 0.99$. The representative plot of K_{eq} for cyanide ion sensing is shown as insets of Figs. 8 and S17 (ESI). logK values were found to be 4.89 and 4.59 with 1:1 (porphyrin:cyanide) stoichiometry for 1a and 2a, respectively.

The higher binding constant for **1a** is clearly reflecting the highly electron deficient nature of nitro group.



Fig. 7 (Top) colorimetric changes of **1a** with tested anions in toluene at 298 K. (Bottom) UV-Visible spectral changes of **1a** upon addition of excess of anions in the form of TBA salts in toluene at 298K.



Fig. 8 UV-Visible spectral titration of 1a (1.04×10^{-5} M) upon sequential addition of cyanide ion in toluene at 298K. insight shows Benesi-Hildebrand plot.

The cyanide detection behaviour of these porphyrins (**1a** and **2a**) was also revealed by differential pulse voltammetric (DPV) studies. The DPV changes of **1a** and **2a** upon addition of cyanide ion were carried out in CH_2Cl_2 at 298 K using 0.1 M TBAPF₆ as supporting electrolytes. Interestingly, the successive addition of cyanide ions into **1a** results in a cathodic shift of 310 mV in the first oxidation potential (Fig. 9) and a dramatic cathodic shift of 700 mV in the first reduction potential

possibly due to cyanide ion induced metal centered oxidation (Co^{III} to Co^{III}) and leads to cyanide coordination to the metal center, **1a**·CN⁻. This cathodic shift in the first redox potentials for **2a** is also pronounced (Fig. S18 in the ESI). Fig. S19 in the ESI represents the DPV titration of **1a** and **2a** after successive addition of cyanide ion.



Fig. 9 DPV (in V vs Ag/ AgCl) traces recorded for 1a (blue) and 1a.2CN^{\cdot} (red) in CH₂Cl₂ containing 0.1M TBAPF₆ with a scan rate of 0.1 Vs⁻¹ at 298 K.

Interestingly, the most common interfering anions especially basic anions such as fluoride, acetate and dihydrogen phosphate were inactive towards these sensors. The ratiometric experiments were performed to ascertain the selectivity of synthesized Co(II) porphyrins using 10 equivalents of interfering anions followed by two equivalents of cyanide ions in toluene. The representative bar graph observed for **1a** is shown in Fig. 10 which clearly demonstrates the tolerance of **1a** towards these potentially interfering anions and thus can be used quantitatively and selectively to detect cyanide ions. Similar results were observed for **2a** as shown in Fig. S20 (ESI).



Fig. 10 Ratiometric absorbance changes (A_{490}/A_{447}) of **1**a (1.04×10^{-5} M) on addition of 1-2 equiv. of CN⁻ and 10 equiv. of other anions. Green bars indicate the blank and in presence of other interfering anions, and purple bars indicate the addition of CN⁻ to the interfering anions

To recognize the range of applicability of **1a** and **2a** the reversibility test has been performed in toluene. **1a** was treated with 2 equivalent of cyanide ion resulted in a red-shift of 43 nm in Soret band (447-490 nm) which corresponds to Co(II) to Co(III) due to cyanide ion binding (scheme 2). The reversibility test was attempted using TFA as shown in Fig. 11.

The addition of TFA to 1a-CN⁻ adduct does not restore the absorption spectra of 1a which clearly indicate that the behaviour of cyanide ion binding is not reversible as indicated by the different spectral behavior of 1a-CN⁻ with TFA and without TFA. Similar behaviour has been found for 2a as shown in Fig. S24, ESI.







Scheme 2. The plausible mechanism for cyanide ion sensing

DFT Studies

The geometry optimization of Zn(II) and Co(II) complexes has been performed on Gaussian 09 using B3LYP functional with LANL2DZ basis set in gas phase. Fig. S22 in ESI shows the top and side views of the fully optimized geometries of 1d and 2d respectively. To get insight into the electronic modulation of porphyrin core after cyanide binding and their impact onto the molecular orbitals, further we performed the geometry optimization of Co(II) complexes (low spin; $S = \frac{1}{2}$) with cyanide ion i.e Co(III) complex, as well as TD-DFT has also been evaluated to obtain the theoretical electronic spectra. Fig. 12 shows the fully optimized geometries of CoTPP(NO₂)Cl₇ (1a) and CoTPP(NO₂)Cl₇.CN⁻ (1a-CN⁻), whereas the optimized geometries of CoTPPCI₈ (2a) complex with and without cyanide ion is given in Fig. S23 in the ESI. The repulsive interaction between β -substituents leads to the saddle shape conformation of the porphyrins core. As expected from Gouterman's four-orbital model the Soret transitions of these metalloperhaloporphyrins were found to involve substantial a_{1u} to e_g character. Fig. S24 in the ESI represents the frontier

molecular orbitals of Zn(II) complexes, **1d** and **2d**, respectively which were exactly matching with FMOs for ZnBr₈ and Znl₈ complexes given by Ghosh *et a*l.²⁶ The HOMO were found as b_2 (a_{2u} type) and HOMO-1 as $b_1(a_{1u}$ type).



Fig. 12 Fully optimized geometries of (a and c) top and side views of CoTPP(NO₂)Cl₇ (1a), (b and d) top and side views of CoTPP(NO₂)Cl₇.CN^{\cdot} (1a.CN^{\cdot}). H atoms in top views and phenyl rings in side views are omitted for clarity

In 2002 Scheiner and his coworker explained that for a simple CoTPP, the porphyrin MOs (a_{2u} and a_{1u}) lie in between ${}^{1}e_{g}$ (d π) and dz^2 of the metal due to the stabilization of MOs of porphyrin by metal (Co) and Porphyin orbital interaction.²⁷ However, the introduction of electron withdrawing substituents at porphyrin periphery switches the HOMO from metal ${}^{1}e_{g}$ to a_{2u} type. The open shell molecular orbitals and spin density profile of CoTPP(NO₂)Cl₇ is clearly indicating the significant orbital interaction of the metal (dx^2-y^2) and a_{2u} of porphyrin. SUMOs (b₂ and b₁) of electron deficient saddle shaped porphyrins are in good agreement with the reported in literature.^{26,28,29} The axial coordination of the cyanide ion changed the spin and multiplicity of system which again perturbed the FMOs. Fig. S27 represents the theoretical UV-Vis. spectra of 1a and 2a obtained by TD-DFT in gas phase which are fairly matching with the experimental UV-vis. spectra. The broader absorption for 1a as compared to 2a due to the presence of nitro group is also confirmed by TD spectra. The obtained UV-Vis spectra of 1a and 2a with cyanide ion are given in Figs. S28 and S29, respectively. The spectral features and absorption spectral data are also matching with the experimental UV-Visible spectra. Red-shifts in the Soret band of cobalt complexes and charge transfer band upon axial coordination of cyanide ion were also observed in TD-DFT spectra.

Experimental Section

Materials:

2, 2-tetrachloroethane was purchased from Rankem and dried before use over molecular sieves (4Å). Silica gel (100-200 mesh) was purchased from Rankem used as received. TBAPF₆ received from HiMedia and recrystallized twice with ethanol and dried at 50 °C under vacuum for 2 days. Pyridine was purchased from Thomas Baker and piperidine purchased from SDFCL was of analytical grade and used without further purification. N-Methylimidazole and dimethylaminopyridine were purchased from HiMedia and used as received. The tetrabutylammonium salts (TBAX, X = CN⁻, F⁻, OAc⁻ and H₂PO₄⁻) were purchased from Alfa Aesar and used as received. Dry CH₂Cl₂ for CV analysis distilled twice with P₂O₅ and third time from CaH₂ whereas dry toluene (for UV-Visible spectral studies) was dried and distilled from sodium benzophenone mixture.

Instrumentation and Methods:

Optical absorption and emission spectra were recorded on Agilent Cary 100 UV-Vis. spectrophotometers and Hitachi F-4600 spectrofluorometer, respectively using a pair of quartz cells of 10 mm path length and 3.5 ml volume. ¹H NMR spectra were recorded on Bruker AVANCE 500 MHz spectrometer in CDCl₃. The ESI mass spectra were recorded on Bruker Daltonics microTOF mass spectrometer in the negative ion mode using CH₃CN as solvent. Elemental analyses were performed on Elementar vario EL III instrument. The X-ray quality single crystals of 1a, 1d, and 2d were obtained by vapour diffusion of methanol onto a CHCl₃ solution of respective porphyrins. 1d was also crystalized with vapour diffusion of hexane onto the CHCl₃ solution of **1d** with few drops of pyridine, and the single crystals of 2b were obtained by vapour diffusion of methanol onto the toluene solution of 2b. The single crystal XRD data were analysed on a Bruker Apex-II CCD diffractometer equipped with graphite-monochromated Mo K_{α} (λ = 0.7107 Å) by the ω -2 θ scan. Crystallographic data are summarized in the table S1 in the ESI. ORTEP views for ZnTPP(NO₂)Cl₇(CH₃OH) (1d•CH₃OH), ZnTPPCl₈(CH₃OH) (2d•CH₃OH), MTPP(NO₂)Cl₇ (M = Co(II) and Zn(II)) and NiTPPCl₈ (1b) are shown in Figures 1 and S1 in the ESI. Selected average bond lengths and bond angles of these five porphyrins are listed in Table S2 in the ESI. The octachlorometalloporphyrins were solved in a straight forward manner whereas mononitroheptachloroporphyrins were tough to solve since nitro group disordered over chloro group(s). The correct occupancies of nitro and chloro groups were in the corresponding crystallographic information files. The ground state geometry optimization for Co(II) and Zn(II) complexes was performed using B3LYP as functional and LANL2DZ as the basis sets. Electrochemical redox studies were carried out with a BAS Epsilon electrochemical workstation using a three electrode assembly consists of GC working electrode, Ag/AgCl as a reference electrode and Pt-wire as a counter electrode. All measurements were carried out in triple distilled CH₂Cl₂ which was degassed by Argon, containing 0.1 M TBAPF₆ as the supporting electrolyte with scan rate of 100 µA. The concentration of all metal complexes was maintained- $1\,\mu\text{M}$ throughout the whole experiment. Axial ligation studied were carried out in distilled toluene at room temperature,

equilibrium constant were calculated using already given equation in axial ligation studies. Using the above equation the K_{eq} can be evaluated by taking the negative of the 1/intercept.

Synthetic procedures

1b and **2b** were synthesized by chlorination of NiTPPNO₂ with 15 equivalents of N-chlorosuccinimide (NCS) in 1,1,2,2-Tetrachloroethane.^{23b} Free base porphyrins, H₂TPP(NO₂)Cl₇ and H₂TPPCl₈ were prepared by acid demetalltion of **1b** and **2b** using con. H₂SO₄.^{23b}

General Procedure for the Synthesis of $MTPP(NO_2)Cl_7$ and $MTPPCl_8$ (where M = Co^{II}, Cu^{II} and Zn^{II}):

Free base porphyrins, $H_2TPP(NO_2)CI_7$ and H_2TPPCI_8 (25-30 mg) were dissolved in 20-25 ml of distilled CHCI₃. To this, 10 equiv. of the corresponding metal acetate hydrate in 2 mL of methanol was added and refluxed for 30 minutes at 75 °C on water bath. The solvent was removed by rotary evaporation and the crude porphyrin was washed with water to remove excess of metal salt and purified by silica-gel column chromatography using chloroform as eluent. Further, these metalloporphyrins were recrystallized by chloroform and methanol mixture (1:5, v/v) and dried in vacuum oven for overnight at 75-80 °C. Yields were found to be in the range of 80-90%.

The spectroscopic data of MTPPCI_8 was exactly matches with the reported literature.

$MTPP(NO_2)CI_7$ (where M = Co'', Ni'', Cu'' and Zn''):

CoTPP(NO₂)Cl₇: UV/Vis (CH₂Cl₂): λ_{max} (nm) ($\epsilon \times 10^{-3}$ L mol⁻¹ cm⁻¹) 447(186.2), 562(16.59), 605(9.77). ESI-MS (m/z): found 992.821 [M+K]⁺, calcd 992.840. Anal. Calcd for C44H20N5O2Cl7Co: C, 55.18; H, 2.10; N, 7.31, Found: C, 54.98; H, 2.12; N, 7.40. NiTPP(NO₂)Cl₇: UV/Vis (CH₂Cl₂): λ_{max} (nm) ($\epsilon \times 10^{-1}$ ³ L mol⁻¹ cm⁻¹) 448(128.8), 562(10.96), 604(6.31). ¹H NMR in CDCl₃ (500 MH₇): δ_H (ppm), 7.94-7.87 (m, 8H, meso-o-Ph-H), 7.73-7.60(m, 12H, meso-m,p-Ph-H). ESI-MS (m/z): found calcd 991.84. Anal. Calcd 991.80 [M+K]⁺, for C₄₄H₂₀N₅O₂Cl₇Ni•(0.5CH₂Cl₂): C, 53.45; H, 2.12; N, 7.00, Found: C, 53.19; H, 2.09; N, 7.34. CuTPP(NO₂)Cl₇: UV/Vis (CH₂Cl₂): λ_{max} (nm) ($\epsilon \times 10^{-3}$ L mol⁻¹ cm⁻¹) 449(117.5), 575(12.88), 605(6.46). ESI-MS (m/z): found 996.90 [M+K]⁺, calcd 996.84. Anal. Calcd for $C_{44}H_{20}N_5O_2Cl_7Cu$: C, 54.91; H, 2.09; N, 7.28. Found: C, 54.48; H, 2.10; N, 7.50. ZnTPP(NO₂)Cl₇: UV/Vis (CH₂Cl₂): λ_{max} (nm) ($\epsilon \times 10^{-3}$ L mol⁻¹ cm⁻¹) 457(158.5), 590(9.12), 647(8.31). ¹H NMR in CDCl₃ (500 MH_z): δ_H (ppm) 7.51-7.47 (m, 8H, meso-o-Ph-H), 7.20-7.13 (m 10H, *meso-m,p*-Ph-H), 7.04-7.01 (t, ³J_{H,H} = 8Hz, 2H, meso-m,p-Ph-H). ESI-MS (m/z): found 997.190 [M+K]⁺, calcd 997.836. Anal. Calcd for C44H21N5O2.5Cl7Zn•(0.5CH3OH): C, 54.53; H, 2.26; N, 7.14, Found: C, 54.30; H, 2.48; N, 7.00.

Conclusions

Facile synthesis of perchloro-2-nitro-tetraphenylporphyrin metal (Co^{II} , Ni^{II} , Cu^{II} and Zn^{II}) complexes has been reported. The new porphyrin derivatives were characterized by various

spectroscopic techniques and single crystal X-ray analysis. The results were compared with homosubstituted MTPPCl₈ to highlight the effect of nitro group over their macrocyclic conformation as well as their spectral properties. Nitro bearing porphyrins exhibited 10-15 nm red-shift in the electronic spectra and dramatic anodic shift in the reduction potentials. The lower $C_{\beta}'-C_{\alpha}'-C_m$ and higher $\Delta 24$ values for **1d** as compared to **2d** indicate the effect of mixed β -substitution induced nonplanarity by the nitro group. The axial ligation studies of Zn(II) perchloroporphyrins with nitrogenous bases and basic anions revealed the higher Lewis acidity of the metal centre compared to perbromoporphyrins which is further evidenced by higher $log\beta_2$ values. The electron deficient Co(II) porphyrins (1a and 2a) were utilized as sensors for the selective rapid visual detection of cyanide ions for the first time in porphyrin chemistry.

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Graphical Abstract



We report the facile synthesis of perchlorinated-2-nitro-*meso*-tetraphenylporphyrin metal complexes and their characterization by single crystal X-ray, spectroscopic and electrochemical analysis. The axial ligation studies of Zn(II) perchloroporphyrins with nitrogenous bases and basic anions revealed the higher Lewis acidity of the metal centre as compared to known porphyrins. Co(II) porphyrins were utilized as selective rapid visual cyanide ion sensors for the first time in porphyrin chemistry.