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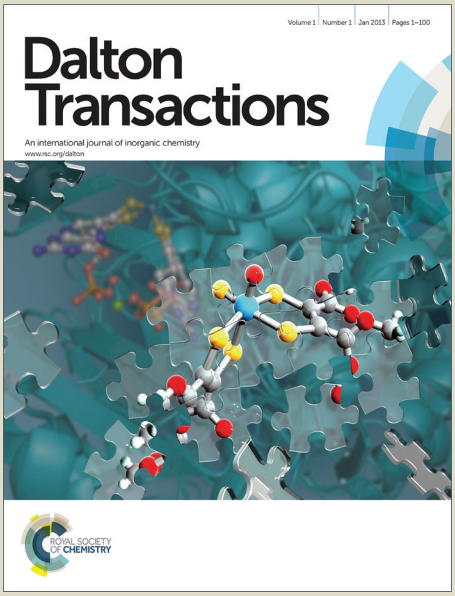

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ARTICLE

Ratiometric Colorimetric "Naked eye" Selective Detection of CN⁻ ions by Electron Deficient Ni(II) Porphyrins and their Reversibility Studies

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Highly electron deficient β-substituted Ni(II) porphyrins (**1**-**5**) were synthesized and utilized as novel sensors for selective rapid visual detection of CN⁻ ions. This article describes the single crystal X-ray structures, electronic spectral and electrochemical redox properties of these sensors. The ratiometric and colorimetric responses of these porphyrins were monitored by change in optical absorption spectra. These sensors were found to be highly selective for cyanide ions with extremely high binding constants (10^{16}- 10^{8} M^{-2}) through axial ligation of CN⁻ ions and are able to detect < 0.11 ppm of CN⁻ ions. **1**-**5** were recovered from **1**-**5**•2CN⁻ adduct by acid treatment and reused without loss of their sensing ability. CN⁻ binding strongly perturbs the redox properties of parent porphyrin π-system. The applicability of **1**-**5** as a practical visible colorimetric test kits for CN⁻ ions in an aqueous and non-aqueous media have also been explored. The mode of binding was confirmed by single crystal X-ray, spectroscopic studies and DFT calculations.

Introduction

The design of anion receptors with high selectivity has been the subject of intensive research due to their potential applications in environmental, clinical, chemical and biological sectors.[1-3] Cyanide is one among the toxic anions; even as little as 0.5 - 3.5 mg cyanide per kg of body weight is lethal to humans where it binds with cytochrome c inside the cells and interferes the mitochondrial electron transport chain, thus inhibiting cellular respiration causing hypoxia.[4] Cyanide ions could be absorbed through the lungs, skin, and gastrointestinal tract leading to vomiting, convulsion, loss of consciousness, and eventual death.[5] Despite their toxicity, their outstanding applications in various industrial processes[6] including electroplating, metallurgy, heap leaching of gold ore, polymer synthesis, steel manufacturing and as raw materials for synthetic fibers, resins and herbicides are inevitable, which raises the risk for accidental or intentional release of cyanide ions into environment as a toxic contaminant.[6]

All the above aspects demand an efficient sensing system to monitor cyanide concentration from contaminant sources. A variety of techniques have been developed for the determination of cyanide, including ion chromatography, voltammetry, amperometry, fluorometry, ion selective electrode and potentiometry.[7] But the primary disadvantage of these techniques is the use of time-consuming procedures and sophisticated instrumentation. Nowadays, the most attractive approach focuses on highly selective colorimetric cyanide ion sensors, which allows "naked eye" detection of CN⁻ ions by means of colour change.[8-10] Various approaches to the novel colorimetric chemosensors for anions are chemodosimetric method, displacement assay, nucleophilic addition to carbonyl group or activated carbon-carbon double bond, host-guest interactions through hydrogen bonding, anion induced deprotonation etc.[8-10] However, they do suffer with one or more limitations such as poor selectivity especially in the presence of fluoride or acetate ions. Most of the chemodosimeters are irreversible, others require specific conditions, such as high temperature or basic media, only works in an organic media, complicated multi-step synthesis.[10] All these drawbacks challenge us to fabricate a unique reversible, specific, colorimetric optical probe capable of 'naked eye detection' of CN⁻ ions with extremely low detection limits.

Porphyrin-based receptors for anions have been constructed through the derivatization of *meso*-positions[11] having appropriate binding pockets whereas only a few reports on β-functionalized porphyrins[12] due to their synthetic difficulties. Metalloporphyrins have been utilized for the detection of CN⁻ ions due to intrinsic affinity of cyanide for many metals such as zinc,[7f,13a-d] rhodium,[13e] and copper[13f] coordinated to porphyrins. Recently, cyanide sensing through chemodosimetric method by a new calix[4]pyrrole derivative,[14a] Pd-calixphyrin,[14b] cobalt corrins,[14c-g] and subphthalocyanine dye[14h] have been reported in the literature. In general, square planar Ni(II) porphyrins exhibited very weak axial ligation and extremely low binding constants (β_2 = 0.3 - 38 M^{-2}) with nitrogenous bases.[15] Herein,

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we are reporting an easy, rapid, reusable, selective and sensitive 'naked eye' colorimetric cyanide ion sensing by highly electron deficient planar and nonplanar β-substituted Ni(II) porphyrins (**1-5**, Chart 1) with extremely high binding constants ($\beta_2 = 10^{16} - 10^{8}\ M^{-2}$) through coordinative interactions for the first time in porphyrin chemistry.

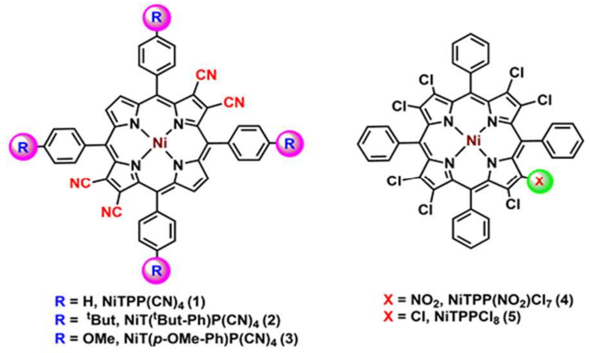


Chart 1 Molecular structures of β-substituted Ni(II) porphyrins (**1-5**).

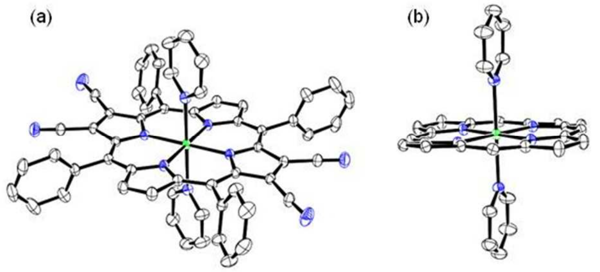
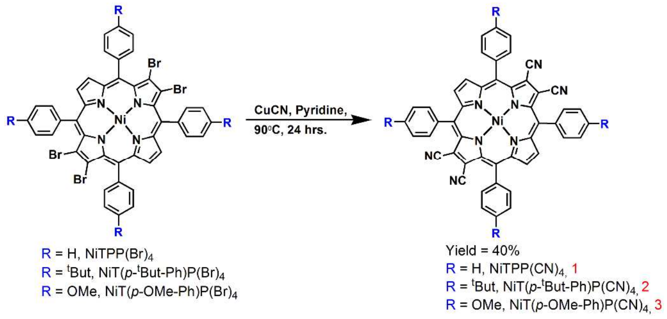


Fig. 1 The ORTEP diagrams showing (a) top and (b) side views of **1** with axial coordination of pyridine molecules. In side view, the β-substituents and *meso*-phenyl groups are not shown for clarity.

Results and Discussion

Synthesis and characterization

Ni(II) β-tetracyano-*meso*-tetraphenylporphyrins (**1-3**) were prepared by nucleophilic substitution at β-pyrrole positions of the tetrabromoporphyrins using modified literature methods[16] as shown in Scheme 1 and Ni(II) perhaloporphyrins (**4-5**) were synthesized by direct substitution at β-pyrrole position of macrocyclic ring according to reported procedure[12b] as shown in Scheme 1 in the electronic supplementary information (ESI). These porphyrins were characterized by various spectroscopic techniques, elemental and single crystal XRD analyses.



Scheme 1 Synthetic route for the preparation of **1**-**3** *via* nucleophilic substitution at β-pyrrole position.

The representative absorption spectra of **1** and **3-5** were shown in CH_2Cl_2 at 298 K (Fig. S1 in ESI). Table S1 in ESI lists the electronic absorption spectral data of **1-5** in CH_2Cl_2. **3** exhibited 10 nm red shift in the Soret band as compared to **1** which is attributed to the electron donating effect of methoxy substituents. **1-3** exhibited considerable gain in the intensity of the longest wavelength $Q_x(0,0)$ band relative to the $Q_x(1,0)$ band due to extensive stabilization of a_{1u} relative to a_{2u} by means of β-cyano substitution which leads to increased transition probability of a_{2u} to $e_g(\pi^*)$ relative to a_{1u} to $e_g(\pi^*)$.[16] **4** has shown red-shifted optical absorption spectra ($\Delta\lambda$ = 9 -13 nm) as compared to **5** due to electron withdrawing nature of nitro group and increased nonplanarity induced by mixed substitution. In ^{1}H NMR spectra of **1-3**, the β-pyrrole protons exhibited a singlet at 8.74 - 8.81 ppm indicating the antipodal positions of β-cyano groups (Figs. S2-S4 in ESI).

The X-ray quality single crystals of **1**(Pyridine)$_2$ and **3** were obtained by direct diffusion of hexane into $CHCl_3$/pyridine and pure $CHCl_3$ solutions of **1** and **3**, respectively. The single crystals of **4-5** were obtained by direct diffusion of hexane into saturated toluene solution of **4** and **5**. The crystallographic data of these porphyrins are listed in Table S2 in ESI. ORTEP top and side views of these porphyrins are shown in Figs. 1 and S5 in ESI. The selected bond lengths and bond angles are given in Table S3 in ESI. Notably, **1** and **3** have shown planar conformation of porphyrin macrocycle (ΔC_β = 0.06 - 0.07 Å and $\Delta 24$ = 0.05 - 0.06 Å) whereas **4-5** exhibited nonplanar conformations with the displacements of β-pyrrole carbons, $\Delta C_\beta = \pm 0.9$ Å and the 24 atoms core, $\Delta 24 = \pm 0.53$ Å, which is attributed to the steric hindrance between β-substituents and *meso*-phenyl groups.[17] **1** and **3** exhibited longer C_β'-C_β' bond distance (1.37 Å) for β-pyrrole carbons having CN substituents as compared to antipodal β-pyrrole carbons bearing no substitution (C_β-C_β = 1.32 Å) which is further supported by increment in C_β'-C_α'-C_m angle (125º) with concomitant decrement in N′-C_α'-C_m (125.7º). Similarly, **4** and **5** exhibited longer C_β-C_β distance (1.35 Å) with increment in C_β-C_α-C_m

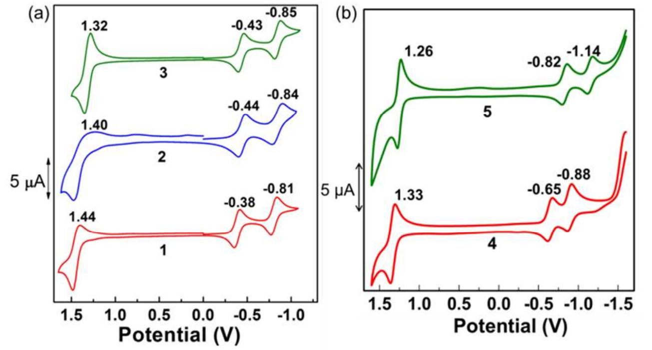


Fig. 2 Cyclic Voltammograms of **1-3** (a) and **4-5** (b) in CH_2Cl_2 containing 0.1 M $TBAPF_6$ as the supporting electrolyte using Ag/AgCl as reference electrode.

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angle (~127º) with concomitant decrement in N-C_α-C_m (~124º), indicating severe steric repulsion between β-substituents which leads to nonplanar conformation of porphyrin macrocycle as compared planar porphyrins.[17] The N-Ni-N bond angles are exactly 180º for planar porphyrins (**1** and **3**) whereas these angles are deviated (171-172º) for porphyrins, **4** and **5** due to nonplanar conformation. The observed UV-Vis and ^{1}H NMR spectroscopic data of these Ni(II) porphyrins is in accordance with obtained single crystal X-ray structures.

To examine the effect of β-susbtituents and nonplanarity of the macrocyle on electrochemical redox potentials, we have carried out cyclic voltammetric studies. Cyclic voltammograms of **1-5** in CH_2Cl_2 containing 0.1 M $TBAPF_6$ as supporting electrolyte are shown in Figure 2. The redox data (*vs* Ag/AgCl) is listed in Table S4 in ESI. **1-5** exhibited one two-electron reversible electrochemical oxidation and two successive one-electron reductions. The first oxidation potentials of **1-3** exhibit 300−480 mV anodic shift in comparison to NiTPP suggesting that each of the β-cyano group shifts ~130 mV anodically which is due to the strong electron-withdrawing nature of the β-cyano substituents.[15b,18] Further, the anodic shift in first oxidation of **4** and **5** as compared to NiTPP is ascribed to the combined effect of electron-withdrawing nature of nitro and chloro substituents as well as the highly nonplanar conformation of macrocycle. The cathodic shift (80-150 mV) in first ring oxidation potentials of **2-3** in comparison to **1** is ascribed to electron donating ^{t}butyl and methoxy substituents present at the *meso*-phenyl rings of **2** and **3**, respectively. The observed redox potentials indicate the highly electron deficient nature of porphyrin π-system.[16,18]

Cyanide Sensing

The anion recognition properties of all synthesized porphyrins (**1-5**) were studied in toluene with various anions, using UV-Visible spectroscopy with the addition of the aliquot anion in the form of TBA salts. Importantly, an additional remarkable feature of these sensors **1-5** was pinpointed, as their ability to specifically recognize cyanide in an admixture of anions. **1-5** have shown red-shifted UV-Visible spectra with colorimetric 'naked eye' detection of cyanide ions (green to yellow for **1-3** and reddish brown to green for **4-5**) whereas no observable shift was found with other tested anions as shown in Figs. 3 and S6 in ESI. **1-5** were titrated with CN^- ions in toluene at 298 K and monitored by UV-Vis absorption spectroscopy. The broad Soret of **1-5** upon addition of CN^- ions is due to charge-transfer transitions.[19] The metal *d*-orbital energies in metalloporphyrins can be perturbed by the presence of axial ligands. Herein, the electron deficient porphyrin π-system makes Ni(II) metal centre to bind with highly basic cyanide (pK_a = 9.3) ions.

UV-Vis titration of **1** with cyanide ions is shown in Fig.4. Both the Soret (35 nm) and Q bands (77 nm) are shifted to longer wavelengths upon increasing the concentration of TABCN indicating the axial coordination of CN^- ions to **1**. For **1**, well-anchored isosbestic points were observed at 457, 526 and 647 nm during the course of the cyanide binding experiment. Stoichiometry for **1** was established using Job's plot (Fig. 4 inset) which has a maxima at a cyanide molar ratio of ~ 0.65 indicating that **1** is capable of binding with 2 equivalents of CN^- ions to form **1**•$2CN^-$ adduct.

Similar UV-Vis spectral profiles were observed for **2-5** with CN^- ions as shown in Fig. S7 in ESI. Stoichiometry for **2-3** was calculated using Job's plot (Fig. S7 in ESI). The binding constants for **1-5** with cyanide ions were calculated using Hill equation[20] and the corresponding binding parameters are presented in Table 1. The stoichiometry for **4** and **5** was confirmed by Hill plot as shown in insets of Fig. S7 in ESI. 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. The magnitude of Hill coefficient (n) for **1-3** clearly reflects the extent of cooperativity between supramolecular binding events.[3d,11b]

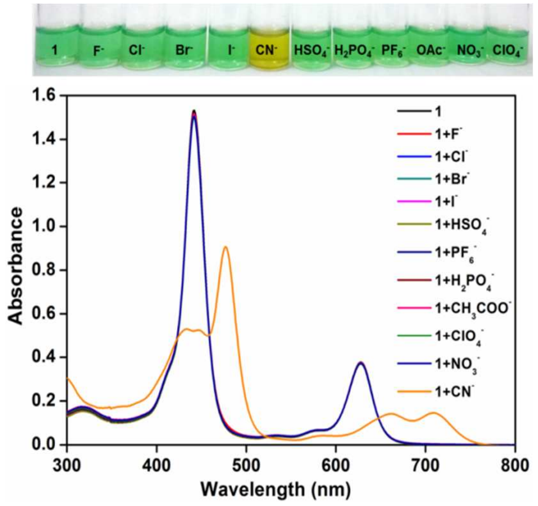

Fig. 3 (Top) Colorimetric response of **1** with tested anions in toluene; (b) UV-Vis spectra of **1** (3.33 × 10^{-6} M) upon addition of excess TBA salts of tested anions in toluene at 298 K.

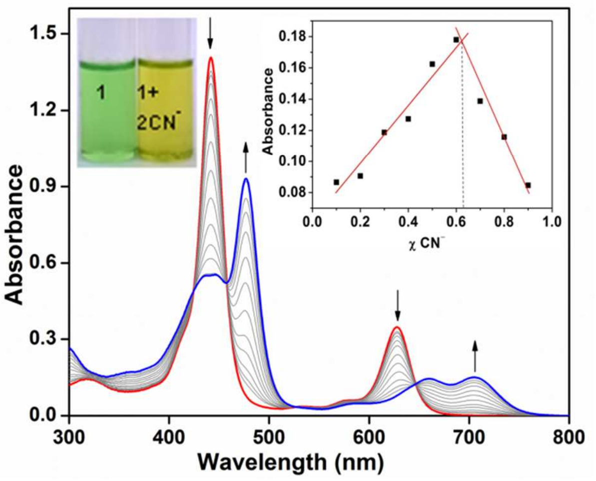

Fig. 4 UV-visible spectral titrations of **1** (9.35 µM) upon addition of aliquots of TBACN (0 - 0.03 M) in toluene, inset shows corresponding Job's plot.

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Table 1. Binding constant data[a] of Ni(II) porphyrins and their CN⁻ ion detection limits in toluene at 298 K.

Porphyrin	β_2	r^2	n	LOD (ppm)	m
1	3.86×10^{16}	0.87	3.33	0.108	2
2	1.95×10^{16}	0.92	3.33	0.108	2
3	6.70×10^{12}	0.90	2.68	0.104	2
4	1.21×10^{9}	0.99	2	0.062	2
5	7.79×10^{8}	0.97	2	0.103	2

[a] Within the error of ±0.04; n = Hill coefficient; LOD = Limit of detection; m = Stiochiometry.

Ni(II) cyanoporphyrins (**1-3**) exhibited very high binding constants, β_2 (10^{16} - 10^{12} M^{-2}) owing to their high electron deficient nature as compared to nonplanar perhaloporphyrins, **4** and **5** (10^{9} – 10^{8} M^{-2}) as indicated by their reduction potentials (Table S5 in ESI). The trend along the series of porphyrins tracks the β_2 values (**1** > **2** > **3** > **4** > **5**), with the more electron deficient porphyrins displaying larger Hill Coefficients (Table 1). The detection limits (LOD) for CN^- ions were calculated in presence of **1-5** in toluene (Table 1).[21] These porphyrins are able to detect as low as ~ 0.11 ppm solution of cyanide ions. Hence these sensors **1-5** were very selective and sensitive for cyanide ions.

Interestingly, the most commonly interfering anions especially basic anions such as fluoride, acetate and dihydrogenphosphate didn't show any response with these sensors. The competition experiments were performed to ascertain the selectivity of synthesized porphyrins using two equivalents of cyanide ions and 10 equivalents of interfering anions in toluene. The representative bar graph observed for **1** is shown in Fig. 5, which clearly demonstrate the tolerance of **1** towards these potentially interfering anions and thus can be used quantitatively and selectively to detect cyanide ions. The similar results were observed for **2-5** as shown in Figure S8 in ESI.

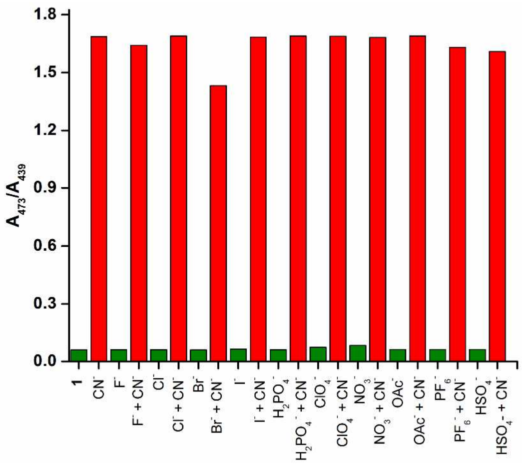

Fig. 5 Ratiometric absorbance changes (A_{473}/A_{439}) of **1** (1.01×10^{-5} M) on addition of 2 equiv of CN^- and 10 equiv of other anions. Green bars indicate the blank and in presence of other interfering anions, and red bars indicate the addition of CN^- to the interfering anions.

Notably, the plots of the absorbance changes (ΔA) *vs* [CN^-] show sigmoidal curves, which indicate that cyanide ions bind to **1-3** in a cooperative manner as shown in Fig. 6a. Nevertheless, in order to get further insight into the binding ability of these sensors **1-5** with CN^- ions, we have carried out differential pulse voltammetric (DPV) studies of **1-5** with addition of cyanide ions (Figs. 6b and S9 in ESI). The addition of cyanide ions to **1** results a cathodic shift of 250 mV in first oxidation and 160 mV in first reduction which is expected upon going from neutral porphyrin to dinegatively charged porphyrin adduct (**1**•$2CN^-$). This shift in potential is further in consistent with rising of HOMO (from DFT studies). Table 2 represents the electrochemical first ring redox data of **1-5** in presence and absence of CN^- ions.

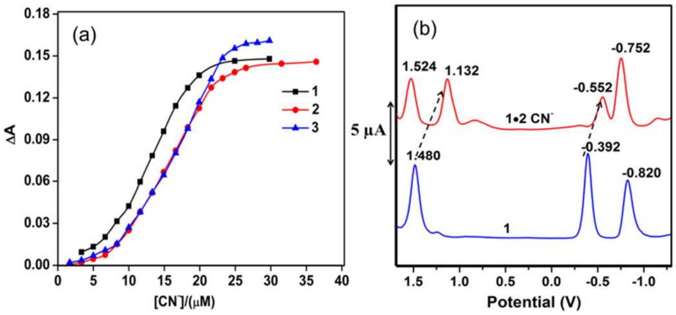

Fig. 6 (a) sigmoidal curve for **1-3**, [CN^-] *vs* ΔA indicating positive cooperative behaviour. (b) DPV (in V vs Ag/ AgCl) traces recorded for **1** (blue) and 1·$2CN^-$(red) in CH_2Cl_2 containing 0.1 M $TBAPF_6$ with a scan rate of 0.1 V/s at 298 K.

Table 2. Electrochemical first ring redox potentials (in mV *vs* Ag/AgCl) upon addition of CN^- ions to **1-5** in CH_2Cl_2 containing 0.1 M $TBAPF_6$ with a scan rate of 0.1 V/s.

Porphyrin	Porphyrin (without CN^-)		Porphyrin•$2CN^-$	
	1st Ox	1st Red	1st Ox	1st Red
1	1480	-392	1132	-552
2	1400	-416	1135	-675
3	1332	-420	1000	-612
4	1340	-630	820	-860
5	1280	-810	783	-1102

Reversibility Studies

To acknowledge the range of applicability, the reversibility and reusability of the sensors **1-5** are the key events that have to be determined.[22] **1** was treated with 2 equivalents of cyanide ions in toluene forming **1**•$2CN^-$ as visualized by colorimetric change from green to yellow accompanied by UV-visible spectral changes as shown in Fig. 7. Switching off the cyanide ion binding was carried out using TFA. As shown in the Fig.7, the addition of aliquots of 1 mM solution of TFA in toluene to the solution containing **1**•$2CN^-$ adduct immediately restored to **1** with colorimetric change from yellow to green.

To confirm the reusability, the resulting mixture was washed with water and dried over anhydrous Na_2SO_4. The recovered **1** was treated with 2 equivalents of CN^- ions, which showed

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similar spectral features as that of fresh solution of **1** with cyanide ions. The similar results were observed for **2-5** indicating their recoverability and reusability (Fig. S10 in ESI).

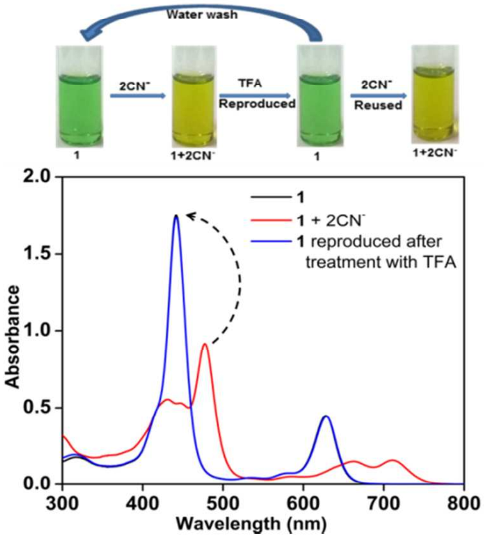

Fig. 7 Colorimetric response of **1** for reversibility and reusability test with CN$^-$ ions (top) and their corresponding UV-Visible spectral changes in toluene at 298 K (bottom).

For the practical application of **1-5**, test kits were prepared by immersing Whatman filter papers in toluene solution of **1-5** (1 mM) and then dried in air. These test kits coated with **1** were exposed to different anion solutions (1 mM) in toluene for 1 - 2 seconds, the colour change from green to yellow was observed only with CN$^-$ ion in toluene (Fig. 8a) whereas there was no colour change observed for other anions. Notably, the similar results were observed when these test kits were exposed to neutral aqueous solutions of various anions (Fig. 8b). Test strips prepared for **2-5** exhibited similar colorimetric changes with cyanide ions in toluene and aqueous solutions as shown in the Figs. S11 and S12 in ESI.

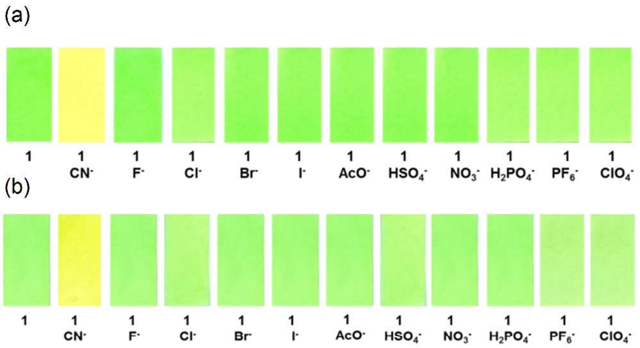

Fig. 8 Photographs of test kits with **1** (1 mM) for detecting the cyanide ion in (a) toluene solution (b) neutral aqueous solution with other anions.

DFT Calculations

The ground state geometry optimization of **1** and **4** in gas phase was carried out by DFT calculations using B3LYP functional with LANL2DZ basis set. Fig. 9 and S13 in ESI represent the fully optimized geometries of **1**•2CN$^-$ and **4**•2CN$^-$ which exhibit planar and severe nonplanar conformations, respectively. The pictorial views of frontier molecular orbitals (FMOs) of **1**, **4**, **1**•2CN$^-$ and **4**•2CN$^-$ were shown in Figs. S14-S17 in ESI.

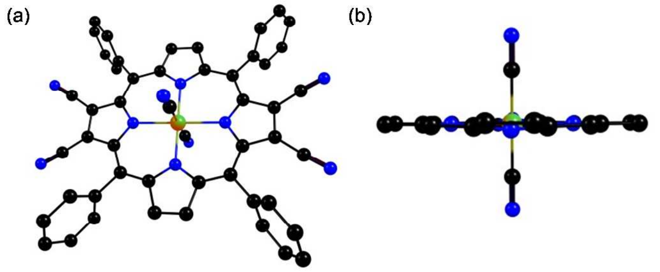

Fig. 9 B3LYP/LANL2DZ-Optimized geometry showing (a) top as well as (b) side views of NiTPP(CN)4•2CN$^-$; hydrogens are omitted for clarity. In side view, the β-cyano and *meso*-phenyl substituents are not shown for clarity.

The HOMO and HOMO-1 are found to be a_{1u} and a_{2u}, respectively as expected for **1** containing β-cyano substituents whereas switching was observed for **1**•2CN$^-$. This indicates perturbation of FMOs upon axial ligation by cyanide ions. The "a_{2u}-type" singly occupied b_2 and SUMO b_1 for saddle shaped **4** are in accordance with the reported literature.[23] The switching of these orbitals occur upon cyanide binding. UV-Vis spectra obtained for **1**, **4**, **1**•2CN$^-$ and **4**•2CN$^-$ using TD-DFT calculations are in accordance with experimental UV-Vis spectra (Figs. S18-19 in ESI). The observed broad features of Soret band of **1-5**•2CN$^-$ is possibly due to ligand to metal charge transfer[19] as reflected in FMO diagrams (Figs. S15 and S17 in ESI).

1-5 remained EPR inactive in presence of excess cyanide ions which indicate the axial ligation of CN$^-$ ions to Ni(II) metal centre. This is further evidenced by single crystal X-ray structure of **3** with axial coordination of CN$^-$ ion and charge balanced by TBA cation which is present in the crystal lattice (Fig. S20 in ESI). CN$^-$ strongly coordinates to Ni(II) metal centre with a distance 1.970(5) Å. Further, Ni(II) ion is 0.309 Å deviated from the porphyrin mean plane in order to bind with cyanide ion effectively. The longer Ni(II)–N$_{core}$ distance in **1**(Py)$_2$ and **3**•CN$^-$ as compared to **3-5** is due to axial coordination of pyridine and cyanide ion, respectively which leads porphyrin core expansion.[15b] To the best of our knowledge, single crystal X-ray structure of five coordinate Ni(II) porphyrin complex is not known in the literature. However, electronic absorption spectral studies revealed stable six coordinate Ni(II) porphyrin complexes in solution which is confirmed by time-dependent absorption spectral profiles **1-5** in presence of cyanide ions (Fig. S21 in ESI). Further, the six coordinate complex of **1** in presence of cyanide ions (**1**•2CN$^-$) was confirmed by MALDI-TOF mass spectrometry analysis (Fig. S22 in ESI). Also, we have recorded the UV-Vis spectra for some Ni(II) porphyrins (NiTPP, NiOPP, NiDPP, NiT(2,6-

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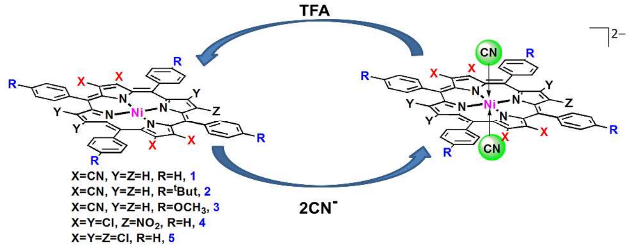
DCP)P and NiT(p-^{t}But-Ph)PBr$_4$) with CN$^-$ ions and found no spectral changes (Fig. S23 in ESI) observed even with excess of CN$^-$ ions which clearly suggests that highly electron deficient Ni(II)-porphyrin metal centre is necessary for CN$^-$ ion recognition. Further, it is revealed that the reduction potential positive than -0.8 V makes them a suitable candidate for CN$^-$ ion detection (Fig. S24 and Table S5 in ESI). Based on our experimental and theoretical studies, we are representing the plausible mechanism of cyanide ion recognition and their reversibility with TFA of **1**-**5** in Scheme 2.



Scheme 2 Schematic representation of CN$^-$ ions binding to **1-5** and their reversibility in presence of trifluroacetic acid (TFA) followed by reusability after water wash.

Conclusions

In summary, we have demonstrated that **1-5** displays a specific, colorimetric and ratiometric response to cyanide ions over the other coexisting anions in toluene. Highly electron deficient planar porphyrins, **1-3** exhibit very high binding constants β_2 (~ 10^{16} - 10^{12} M^{-2}) and bind with 2 equivalent of cyanide ions in a highly cooperative fashion as compared to nonplanar porphyrins **4** and **5**. Cyanide binding also perturbs the redox chemistry and each of the Ni(II) porphyrin•2CN$^-$ adduct is much more easily oxidized than the parent porphyrin. These porphyrins are being able to detect (LOD) < 0.11 ppm of cyanide ions. The reversibility studies revealed that the sensors **1-5** can be recoverable and reusable for cyanide detection without losing their sensing ability.

Experimental section

Materials

Pyrrole, benzaldehyde, Ni(OAc)$_2$•4H$_2$O, TFA, pyridine and Na$_2$SO$_4$ were purchased from HiMedia, India and used as received. 4-Anisaldehyde was purchased from SDFCL and p-^{t}Bu-benzaldehyde and copper(I) cyanide were purchased from Alfa Aesar and used as received. All solvents employed in the present work were of analytical grade and distilled or dried before use. Silica gel (100 - 200 mesh) was purchased from Rankem and used as received. TBAPF$_6$ was recrystallised twice with ethanol and dried at 50 ºC under vacuum for 3 days. The tetrabutylammonium salts (TBAX, X = CN$^-$, F$^-$, Cl$^-$, Br$^-$, I$^-$, HSO$_4^-$,OAc$^-$, H$_2$PO$_4^-$, ClO$_4^-$, PF$_6^-$ and NO$_3^-$) were purchased from Alfa Aesar and used as received. Dry CH$_2$Cl$_2$ for CV studies was distilled thrice from CaH$_2$ and the toluene (for UV-Visible spectral studies) was dried and distilled from sodium-benzophenone mixture.

Instrumentation and methods

Optical absorption spectra were recorded on Agilent Cary 100 spectrophotometer using a pair of quartz cells of 10 mm path length. ^{1}H NMR spectra were recorded on Bruker AVANCE 500 MHz and JEOL ECX 400 MHz spectrometers in CDCl$_3$. MALDI-TOF-MS spectra were measured using a Bruker UltrafleXtreme-TN MALDI-TOF/TOF spectrometer using HABA as a matrix and ESI mass spectra were recorded on Bruker Daltanics microTOF mass spectrometer in positive ion mode using CH$_3$CN as solvent. The X-ray quality single crystals of **1**(Pyridine)$_2$ and **3** were obtained by direct diffusion of hexane into CHCl$_3$/pyridine and pure CHCl$_3$ solutions of **1** and **3**, respectively. The single crystals of **4-5** were obtained by direct diffusion of hexane into saturated toluene solution of **4** and **5**. X-ray quality single crystals of **3**•CN$^-$ was obtained by direct diffusion of n-hexane into the CHCl$_3$ solution of **3** containing small amount of TBACN. Single-crystal XRD data of **1**, **3-5** and **3**•CN$^-$ were collected on a Bruker Apex-II CCD diffractometer equipped with a liquid cryostat. The single crystals obtained were mounted on mounting loops. All diffraction data were collected using Bruker APEXII diffractometer at 293 K equipped with graphite-monochromated Mo $K\alpha$ (λ = 0.71073 Å) by the ω-2θ scan. The structures were solved by direct methods by using SIR97 and SHELX-97.[25] In case of **1**(Py)$_2$ and **3**, SQUEEZE procedure[26] was implemented in order to correct electron density contribution from disordered solvent molecules. The crystallographic data of these Ni(II) porphyrins are summarized in Table S2 in ESI. CCDC-1043611 (**1**(pyridine)$_2$), 1043609 (**3**), 1043615 (**4**), 1044025 (**5**) and 1043610 (**1**•CN$^-$) contain the crystallographic supplementary data. The elemental analyses were carried out using Elementarvario EL III instrument. The ground state geometry optimization of **1** and **4** (with and without cyanide ions) in gas phase was carried out by DFT calculations using B3LYP functional with LANL2DZ basis set. Electrochemical measurements were carried out using CH instrument (CH 620E). A three electrode assembly was used consisted of a platinum button working electrode (2 mm diameter), Ag/AgCl as a reference electrode and a platinum wire as a counter electrode. The concentration of **1-5** was maintained~1 mM. All measurements were performed in triple distilled CH$_2$Cl$_2$ containing 0.1 M TBAPF$_6$ as supporting electrolyte which was degassed by Argon gas purging. For UV-Vis titrations, the concentrations of **1-5** were kept in the range of 9 - 13 μM throughout the experiments whereas the stock solution of anions was maintained in between 4 to 8 mM as per their need. The temperature inside the cell was 298±0.2 K. The association constants (β_2) and stoichiometry for anion binding were calculated using Hill equation.[20] The limit of detection (LOD) values has been calculated by using the intercept of plotted graph between $(A_{min}-A)/(A_{min}-A_{max})$ and log[A$^-$].[24] For the practical utility of these sensors, the test strips were prepared by cutting the Whatman filter paper (grade 1) and dipped in 1 mM toluene solution of **1-5** for few seconds and dried. These test strips were dipped in different anion solutions for 1-2 seconds. The colour change from green to yellow (**1-3**) and brown to green (**4-5**) were observed only with cyanide ions. The similar results were observed when these test strips were exposed to neutral aqueous solution of tested anions.

General procedure for the Synthesis of Nickel(II) complexes of β-tetracyano-*meso*-tetraphenylporphyrins (1-3):

NiTPPBr$_4$ (0.5 g, 0.507mmol) and copper(I)cyanide (1.816 g, 20.27mmol) were taken in 250 mL two neck RB. To this, 50 mL of pyridine was added and heated at 90 ºC for 24 hours under argon atmosphere. At the end of this period, the reaction mixture was cooled and filtered through G-4 sintered crucible to remove excess copper cyanide. Solvent was removed under vacuum and then the crude product was loaded on silica column and purified using CHCl$_3$ as eluent. The similar procedure was employed for the preparation of **2-3**. The yield was found to be ~ 40% in all cases (**1-3**).

NiTPP(CN)$_4$ (1): UV/Vis (CH$_2$Cl$_2$): λ_{max} (nm) (logε) 440 (5.10), 630(4.50). ^{1}H NMR in CDCl$_3$: δ (ppm) 8.77 (s, 4H, *β*-pyrrole-H), 7.89-7.83 (m, 12H, *meso-o- and m*-phenyl-H), 7.75-7.71 (m, 8H, *meso-m-* and *p*-phenyl-H). ESI-MS (m/z): found 771.9 [M+H]$^+$, calcd. 771.2. Anal. Calcd for $C_{48}H_{24}N_8Ni$: C, 74.73; H, 3.14; N, 14.53%. Found: C, 74.52; H, 3.39; N, 14.65%.

NiT(*p*-^{t}But-Ph)P(CN)$_4$ (2): UV/Vis (CH$_2$Cl$_2$): λ_{max} (nm) (logε) 445 (5.13), 632(4.47).^{1}H NMR in CDCl$_3$: δ (ppm) 8.81 (s, 4H, *β*-pyrrole-H), 7.77-7.70 (m, 16H, *meso-o- and m*-phenyl-H), 1.54 (s, 36H, CH$_3$ of ^{t}But). ESI-MS (m/z): found 1020.7 [M+H•Na]$^+$, calcd. 1020.0. Anal. Calcd for $C_{64}H_{56}N_8Ni$: C, 77.19; H, 5.67; N, 11.25%. Found: C, 77.31; H, 5.50; N, 11.43%.

NiT(*p*-OMe-Ph)P(CN)$_4$ (3): UV/Vis (CH$_2$Cl$_2$): λ_{max} (nm) (logε) 450 (5.07), 636(4.54). ^{1}H NMR in CDCl$_3$: δ (ppm) 8.74 (s, 4H, *β*-pyrrole-H), 7.75 (d, 8H, *J* = 8.5 Hz, *meso-o*-phenyl-H), 7.24 (d, 8H, *J* = 8.5 Hz, *meso-m*-phenyl-H), 4.04 (s, 12H, OCH$_3$ *meso-m*-phenyl-H). MALDI-TOF-MS (m/z): found 892.6 [M+H]$^+$, calcd. 892.6. Anal. Calcd for $C_{52}H_{32}N_8O_4Ni{\bullet}0.5H_2O$: C, 69.35; H, 3.69; N, 12.44%. Found: C, 69.40; H, 3.78; N, 12.55%.

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Notes and references

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†Electronic Supplementary Information (ESI) available: UV-Vis and ^{1}H NMR spectra, crystallographic and electrochemical redox data, UV-Vis titrations of **1-5** for cyanide ion sensing and their reversibility studies, DPV traces in presence and absence of cyanide ions, DFT optimized structures and their frontier molecular orbitals (FMOs) of **1**, **4**, **1•**2CN$^-$ and **4•**2CN$^-$**.** CCDC-1043609, 1043610, 1043611, 1043615 and 1044025. See DOI: 10.1039/b000000x/

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