RSC Advances

ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/advances

Journal Name

RSCPublishing

ARTICLE

Colorimetric “Naked eye” detection of CN^-, F^-, CH_3COO^- and $H_2PO_4^-$ ions by highly nonplanar electron deficient perhaloporphyrins

Nivedita Chaudhri and Muniappan Sankar*

Cite this: DOI: 10.1039/x0xx00000x

Received 00th January 2012,
Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

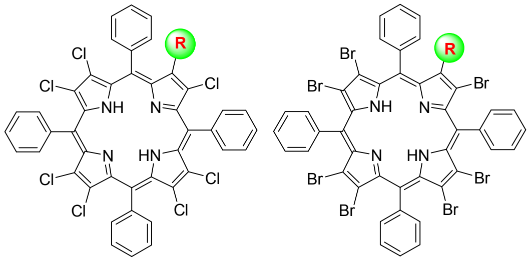
www.rsc.org/

Highly nonplanar perhaloporphyrin-based receptors have been synthesized and characterized by various spectroscopic techniques. Nonplanar and electron deficient nature was authenticated by electronic spectral, electrochemical redox and protonation-deprotonation studies. The colorimetric “naked eye” anion sensing ability of these sensors was probed by spectroscopic and electrochemical studies. These receptors were found to be highly selective and sensitive for the basic anions such as CN^-, F^-, OAc^- and $H_2PO_4^-$ over tested anions and were able to detect these anions even at nanomolar concentration *via* anion induced deprotonation. These perhaloporphyrin receptors have been recovered from receptor-anion host-guest complexes formed during sensing event by acid treatment and were reused for the detection of basic anions without loss of their sensing ability.

Introduction

Porphyrinoids are the class of tetrapyrrole pigments widely occurs in nature.[1a] These pigments are highly coloured and exhibit varying degrees of π-conjugation leading to different nonplanar conformation of the porphyrin macrocycle which are responsible for variety of biological functions.[1] Inspired by nature’s fundamental biological processes involving enzyme-substrate or host-guest interactions which are regulated by light, ions and small molecule concentrations, the design of effective anion receptors containing responsive functional groups as an integral part of a host macrocyclic framework has been an active area of research.[2] Now-a-days the need for a suitable method of anion recognition, extraction and transportation is severely felt and as a consequence, the field of anion supramolecular chemistry has grown rapidly over recent decades.[3] In order to achieve an enhanced selectivity and sensitivity towards a particular anion, a fine tuning of binding sites is required which is often difficult because of their wide range of geometries, larger size, high solvation energies and accessibility in a very narrow pH range as compared to their cationic counterparts.[4] Cyanide is extremely toxic to living organisms, it binds strongly to iron in heme and the active site of cytochrome c which completely stops the O_2 transport in the blood and the mitochondrial electron-transport chain, thus inhibiting cellular respiration.[5a] The selective recognition of fluoride ions is of great importance for monitoring F^- ion metabolism in nature, the analysis of drinking water and in the treatment of osteoporosis.[5b,5c] Phosphate ions are playing a vital role in biological processes like signalling, energy transduction, information storage and expression.[6a] The acetate ions are the most common building blocks in biosynthesis and a critical component of numerous metabolic processes. The rate of OAc^- production and oxidation has been frequently used an indicator of organic decomposition in marine sediments.[6b]

Calixpyrroles,[7] phlorins,[8a] corroles,[8b,8c] sapphyrins,[8d,8e] N-confused porphyrins,[8f,8g] oxoporphyrinogens[8h,8i] and porphyrins[8j] are excellent multifunctional candidates for a great variety of anion sensor applications *via* NH groups of the pyrrole units. Several porphyrins bearing NH groups at the *ortho*-positions of the *meso*-aryl substituents have been utilized as effective anion sensors.[9a,9b] Recently, porphyrin bearing NH groups at the *para*-positions of the *meso*-phenyl ring have been demonstrated for $H_2PO_4^-$ ion sensing.[9c] Many transformation and modifications have been carried out on porphyrin macrocycles for selective ion recognition.[8j,9,10] The β-functionalisation of *meso*-tetraarylporphyrins is of great importance since the electronic properties of the porphyrin macrocycle can be altered by small changes in the substituents leading to larger steric and electronic effects on the porphyrin π-system[1b,1c,10a,10b,11] than substituents at the *meso*-aryl positions. A few β- and *meso*-substituted porphyrins are known which utilize their protonated inner core as effective hydrogen bond makers for anion recognition.[10] In most of the cases, planar porphyrins can recognize anions *via* peripheral functional groups[9a,9b] in which inner core NH groups are less effectively available for H-bond formation due to tautomerism.[9c] Recently, cyanide sensing through chemodosimetric method by a new calix[4] pyrrole derivative,[12a] Pd-calixphyrin,[12b] and subphthalocyanine dye[12c] have been reported in the literature. Also, metalloporphyrin-based cyanide ion sensors through coordinative interactions are known.[12d,12e] However, highly sensitive free base porphyrin-based chemosensors for CN^- ions with very low detection limits (in ppb range) are not known in the literature. In general, acidic receptors can recognize basic anions through deprotonation is quite common in organic hosts[13a-13c] whereas it is very difficult to deprotonate imino protons of planar porphyrins under ambient conditions.[13d,13e] So herein, we tried to make highly nonplanar electron deficient perhaloporphyrins (chart 1) which can be utilized as anion sensors through pyrrolinic NH deprotonation as a detection mechanism for the first time in porphyrin chemistry.



R = NO$_2$, H$_2$TPP(NO$_2$)Cl$_7$ (**1**)
R = Cl, H2TPPCl$_8$ (**2**)

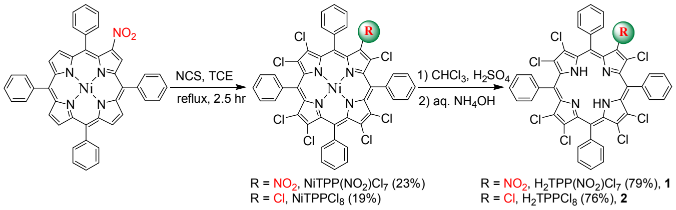
R = NO$_2$, H$_2$TPP(NO$_2$)Br$_7$ (**3**)
R = Br, H$_2$TPPBr$_8$ (**4**)

Chart 1. Molecular structures of synthesized porphyrins (**1** - **4**).

Results and Discussion

Synthesis and Characterization

Herein, we report a straightforward synthetic route for the preparation of **1** and **2** which gives the direct substitution at β-pyrrole position of the macrocycle (scheme 1). **3** and **4** having idiosyncratic nature have also been synthesized using modified literature methods.[14]



Scheme 1. Straightforward synthetic route for the preparation of **1** and **2** *via* direct β-substitution.

The representative UV-Visible spectra of **1** and **3** were shown in toluene (figure S1, ESI). The table S1 in ESI lists the electronic absorption spectral data of **1-4** in toluene at 298 K. **1** exhibited similar spectral features to **2** and showed red-shifted absorption in Soret (6 nm) and in $Q_x(0,0)$ band (12 nm) relative to **2** possibly due to the electron withdrawing nature of the nitro group and increased nonplanarity by mixed susbtitution.[15] Interestingly, **3** has shown red-shifted absorption in B (12 nm) and $Q_x(0,0)$ band (17 nm) relative to **1** possibly due to increased nonplanarity produced by larger size of bromo substituents. The B and $Q_x(0,0)$ bands of **1-4** showed an interesting trend in red-shift and aligns in the following order: **2** < **1** < **4** < **3**. In ^{1}H NMR of **1**, the *meso-o*-phenyl protons showed an asymmetric multiplet (figure S2, ESI) in contrast to **2** indicating the lower symmetry of the molecular structure. Figure S3 in ESI shows the ^{1}H NMR spectra of imino proton region of **1-4** in CDCl$_3$ at 298 K. Interestingly, the downfield shift of NH or the acidity of imino-protons of **1-4** has shown the following order: **3** > **4** > **1** > **2** which readily reflects the extend of nonplanarity of the porphyrin core and electron withdrawing effect of nitro substituent.[16] The negative ion mode ESI mass spectrum of **1** is shown in figure S4 in ESI.

The single crystals of **2** were obtained by vapour diffusion of CH$_3$CN into the toluene solution of **2**. The crystallographic data of **2**•2CH$_3$CN•2H$_2$O is listed in table S2 in ESI. The top and side ORTEP views of **2** are shown in figure S5 in ESI. The nonplanarity of the porphyrin macrocycle is induced by the steric repulsion among the peripheral substituents, which enforces the relief of the strain through bond lengths and angles. The selected average bond lengths and bond angles of **2** are listed in table S3 in ESI which are in accordance with the reported literature.[1b,1c,15a,16] Notably, **2** has exhibited severe nonplanar saddle-shape conformation (figure S5b in ESI) with the displacement of the β-pyrrole carbons, ($\Delta C_\beta = \pm$ 1.21 Å) and 24 atoms core ($\Delta 24$ = 0.57 Å) from the porphyrin mean plane. This is further supported by the increment in C_β-C_α-C_m angle (~129º) with concomitant decrement in the N-C_α-C_m angle (~124º) along with larger C_β-C_β bond length (1.345(11) Å) as compared to reported planar porphyrins.[1c] We have observed higher ΔC_β for **2** than expected due to the strong hydrogen bonding interaction between solvate water molecules and the porphyrin core NH with a distance of 2.831 Å. It is known that **4** has greater extend of nonplanarity (saddle-shape conformation) in comparison to **2** as evidenced from the single crystal X-ray structures.[1b,1c,15a,16]

The ground state geometry optimisation of H$_2$TPP(NO$_2$)Cl$_7$ (**1**) in gas phase was carried out by DFT calculations using B3LYP functional with 6-311G(d,p) basis set. Figure S6 in ESI represents the fully optimised geometry of **1** which exhibits severe nonplanar saddle-shape conformation as shown in figure S6b in ESI. The selected average bond lengths and bond angles of **1** are listed in table S4 in ESI. The displacement of the β-pyrrole carbons, ($\Delta C_\beta = \pm$ 1.21 Å) and 24 atoms core ($\Delta 24$ = 0.52 Å) from the porphyrin mean plane of **1** authenticate the highly nonplanar conformation of the porphyrin core. This is further evidenced by the increment in C_β-C_α-C_m angle with concomitant decrement in the N-C_α-C_m angle along with larger C_β-C_β bond length. The observed higher ΔC_β and $\Delta 24$ values of **1** in gas phase is possibly due to enhanced nonplanarity provided by mixed β-substitution. The pictorial representation of frontier ortibtals of **1** is shown in figure S7 in ESI. The HOMO and HOMO-1 orbitals are found to be a_{2u} and a_{1u}, respectively as expected for electron withdrawing β-substituted porphyrins. The results obtained from single crystal structure and DFT calculations are in good agreement with electronic spectral and NMR studies.

A wide variety of perhaloporphyrins have been examined in non-aqueous media.[13e,17] Cyclic voltammograms and DPVs of **1-4** in CH_2Cl_2 containing $TBAPF_6$ as supporting electrolyte were shown in Figure S8 in ESI and the redox data is listed in table S5 in ESI. Interestingly, the mixed substituted porphyrins (**1** and **3**) exhibited ~200 mV anodic shift in the reduction as compared to homo substituted porphyrins (**2** and **4**) whereas in oxidation only 60 mV anodic shift was observed. This can be attributed to the strong electron withdrawing nature of the nitro substituent. Notably, the bromoporphyrins (**3** and **4)** exhibited 90 mV cathodic shift in the oxidation potentials relative to their corresponding chloroporphyrins (**1** and **2**) is ascribed to enhanced nonplanarity provided by bulkier bromo groups.[15,16]

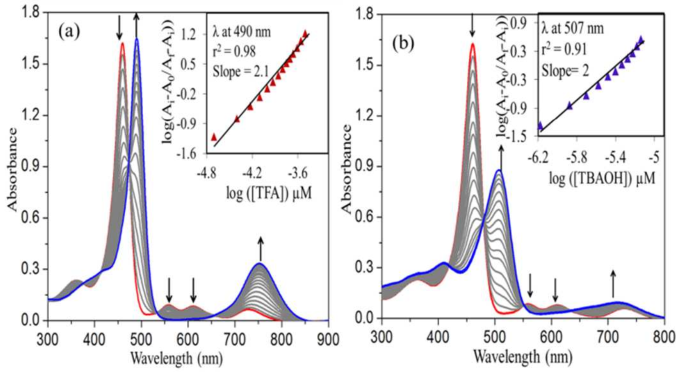


Figure 1. UV-Visible spectral titrations of **1** with TFA (a) and TBAOH (b) in toluene at 298 K. Insets shows the corresponding Hill plots.

Protonation and Deprotonation Studies

To examine the effect of mixed substitution on nonplanarity, we have carried out protonation and deprotonation studies of **1-4** in toluene using trifluroacetic acid (TFA) and tetrabutylammonium hydroxide (TBAOH), respectively. Figure 1 shows the UV-Visible spectral changes of **1** while increasing the conc. of TFA (20 - 60 μM) and TBAOH (0.07 - 11 μM), respectively. The protonation and deprotonation constants of **1-4** are calculated using Hill equation[18] (table 1). Figure 1a represents the concomitant decrement in absorbance of **1** at 461 nm and rising of a new band at 490 nm upon increasing [TFA]. As protonation proceeds, the multiple Q bands are disappearing and a new single broad band rises at 752 nm accompanied with the red-shift of 22 nm in $Q_x(0,0)$ band. In all cases, we have obtained diprotonated porphyrin species which is further confirmed by Hill plot having the slope value of ~ 2 as shown in figures 1a inset and S9 in ESI. **4** has shown highest protonation constant (logβ$_2$) as compared to all other porphyrins.[16b] **3** and **4** have shown 15-18 times higher logβ$_2$ values as compared to **1** and **2**. The protonation constants of **1-4** have shown the following order: **4** > **3** > **2** > **1** which reveals the extent of basicity of inner core nitrogens. The deprotonation of free base porphyrin is influenced by the electronic nature of the substituents, the extent of nonplanarity of the porphyrin core and the basicity of the base employed. Figure 1b shows the concomitant decrement in the absorbance of **1** at 461 nm while increasing [TBAOH] and the new band rises at 507 nm. During deprotonation, the new band grows at 721 nm with the disappearance of multiple Q bands of **1**. The figures 1b inset and S10 in ESI show the Hill plot with the slope value of 2 indicating the formation of dianionic species in all cases. **3** have shown highest deprotonation constant (logβ$_2$ = 11.6) which is 7 folds greater than **1** is ascribed to the increased nonplanarity of the porphyrin macrocycle. The logβ$_2$ values of **1-4** have shown the following order: **3** > **4** > **1** > **2** which suggests that porphyrins bearing mixed substitution with bulky bromo groups favour the high degree of deprotonation.

Table 1. Protonation and deprotonation constants (β_2 and logβ_2)[a] of **1-4** in Toluene at 298 K.

Porphyrin	Protonation			Deprotonation		
	logβ_2	β_2	n[b]	logβ_2	β_2	n[b]
1	8.51	3.30×10^{8}	2.1	10.77	5.91×10^{10}	2.0
2	9.21	1.90×10^{9}	2.0	10.21	1.65×10^{10}	1.9
3	9.70	5.07×10^{9}	2.1	11.60	4.06×10^{11}	2.1
4	10.53	3.43×10^{10}	2.1	10.40	2.53×10^{10}	2.0

[a]Within the error ±0.07 for logβ_2 and ±10% for β_2; [b]n refers stoichiometry

Anion Sensing

The anion recognition properties of **1-4** were studied in toluene with different anions such as CN^-, F^-, Cl^-, Br^-, I^-, NO_3^-

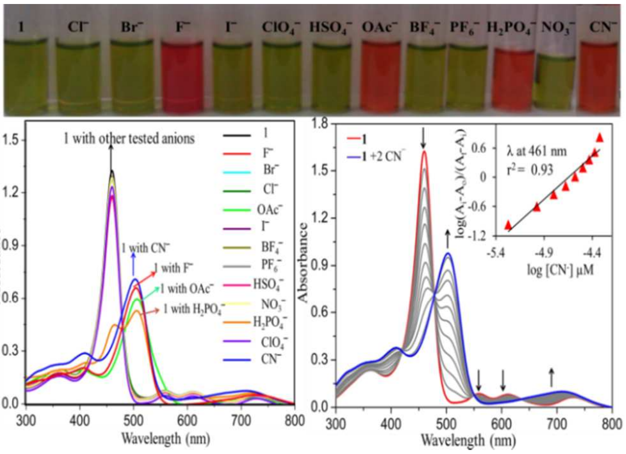


Figure 2. Colorimetric response of **1** with various anions (top). Optical absorption spectra of **1** with tested anions (bottom left) and UV-Visible spectral titration of **1** with CN^- ions (bottom right) in toluene at 298 K.

HSO_4^-, PF_6^-, ClO_4^-, BF_4^-, CH_3COO^- and $H_2PO_4^-$ ions using UV-Visible spectroscopy with the addition of the aliquot anion in the form of TBA salt. Among all, CN^-, F^-, CH_3COO^- and $H_2PO_4^-$ were selectively interacts with **1-4** and showing considerable red-shift (43-48 nm) in the UV- Visible spectra as shown in figures 2a and S11 in ESI whereas there were no shifts observed for other anions. Interestingly, the green colour solution of **1** was turned to dark pink upon addition of aliquots of CN^-, F^-, OAc^- and $H_2PO_4^-$ solution which enables the naked eye detection of these anions in solution (Figure 2). The UV-Visible spectra obtained for **1** with CN^-, F^-, OAc^- and $H_2PO_4^-$ resemble the optical absorption spectrum of $\mathbf{1}^{2-}$ obtained by the addition of TBAOH indicating the possibility of dianion formation during the addition of anions (table S6 in ESI).

The UV-Visible spectrophotometric titration of **1** with CN^- ions was shown figure 2b. As we increase the concentration of CN^- ions, the decrement in the absorbance of **1** was observed at 461 nm, 559 nm and 612 nm and the concomitant increment at 503 and 711 nm respectively multiple isosbestic points. The Hill plot (figure 2b inset) 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-anion) stoichiometry. Also the similar behaviour was observed for **2-4** with CN^- ions as shown in figure S12 in ESI. Further, we have performed the UV-Visible spectral titrations for **1-4** with F^-, OAc^- and $H_2PO_4^-$ anions and found to have almost similar spectral features with variation in the association constants (figures S13 to S15 in ESI). Table 2 lists the association constants obtained for CN^-, F^-, OAc^- and $H_2PO_4^-$ ions with **1-4** in toluene at 298 K. Each of the system studied displays higher β_2 values which are $>10^8$ M^{-2}, establishing that these porphyrins (**1-4**) are capable of strongly interacting with 2 equiv. of CN^-, F^-, OAc^- and $H_2PO_4^-$ ions.[7-12,13e] Interestingly, **1-4** exhibited much higher association constants (logβ_2 values ranges from 8.7 to 11.4) with anions such as CN^-, F^-, OAc^- and $H_2PO_4^-$ ions as compared to other porphyrins known in the literature.[7-12,13e] Notably, the β_2 values for **1** and **3** are ~ 220 times higher than **2** and **4** for F^- ions which is ascribed to strong electron withdrawing nature of nitro substituent and the effect of mixed substitution. With CN^- ions, **3** and **4** showed two-to-six fold higher β_2 values as compared **1** and **2**. This is ascribed to enhanced nonplanarity of the macrocycle due to bulkier bromo groups relative to their chloro substituents.[16] The general trend in β_2 values for free base porphyrins with anions is found to be **3** > **1** > **4** > **2** (table 2). Among the anions, the general trend in β_2 values was found to be CN^- > F^- > OAc^- > $H_2PO_4^-$ which is slightly different from the expected trend (CN^- > OAc^- > F^- > $H_2PO_4^-$) according to their pK_a values. The higher logβ_2 values of F^- ions are possibly due to smaller ionic size (1.3 Å) and high electronegativity (4.1) of F^- ions.

Table 2. Association constants[a] of **1-4** with various anions in toluene.

Por.	CN^-		F^-		OAc^-		$H_2PO_4^-$	
	logβ_2	n[b]	logβ_2	n[b]	logβ_2	n[b]	logβ_2	n[b]
1	10.57	2.2	10.53	2.7	9.59	2	9.39	2
2	9.56	2.0	9.33	2.3	8.77	2	8.68	2
3	11.36	2.4	11.12	2.8	10.21	2	9.86	2
4	10.23	2.1	8.76	2.3	8.95	2	8.72	2

[a]Within the error ±0.06; [b]n refers to stoichiometry.

The detection limit (LOD) and quantification limit (LOQ) for CN^-, F^-, OAc^- and $H_2PO_4^-$ ions were calculated in presence of **1-4** in toluene at 298 K (table S7, ESI). In all cases, the observed LOD (6 - 10 nM) and LOQ (18 - 31 nM) were found to be extremely low which are in nanomolar scale. Hence these porphyrins **1-4** were highly sensitive for basic anions such as CN^-, F^-, OAc^- and $H_2PO_4^-$ ions. **1-4** have shown positive cooperative binding as evidenced from the plot (figures 3 and S16 in ESI) which indicates the interaction of first anion with N_4 core distorts the macrocycle ring intern that favours second anion binding. The detection of anions further supported by the fluorescence quenching of **1-4** with increasing [F^-] in toluene (figure S17, ESI). We have carried out the ^1H NMR studies for **1-4** in presence of F^- ions and observed that the disappearance of N-H peak while increasing [F^-] indicates the formation of dianionic species (figure S18, ESI).

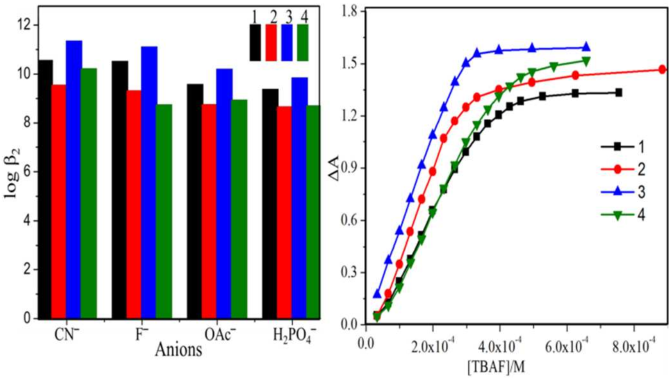


Figure 3. Bar graph constructed logβ_2 *vs.* [Anions] for **1-4** in toluene at 298K (Left). Sigmoidal curve for **1-4**, ΔA *vs.* [TBAF] indicating positive cooperative behaviour (right).

To probe further, we have carried out the differential pulse voltammetric (DPV) studies of **1-4** with excess addition of fluoride ions (figure S19, ESI). The observed cathodic shift in oxidation (450 - 530 mV) and in reduction (230 - 360 mV) potentials after addition of aliquots of F^- also supports the formation of dianionic species[13e] (DPV titrations of **1-4** with F^- ions**,** figures 4 and S20 in ESI) whereas the opposite trend (anodic shift) was observed for the protonation of free base dodecaphenylporphyrins.[10a,10b] The cation radicals of **1-4** formed after electrochemical oxidation are unstable and undergo disproportionation hence the peak currents for the anodic and cathodic processes are different.[10a,10b] Also, we have carried out UV-Visible spectral titrations for some planar porphyrins (H_2TPP and $H_2TPP(Ph)_4$) and nonplanar porphyrins (H_2TPPBr_4 and $H_2TPP(Ph)_8$) with F^- ions (figure S21 in ESI) and found no spectral changes were observed even at high conc. of anions which clearly suggests that the highly nonplanar conformation with electron withdrawing substituents is necessary for anion recognition.

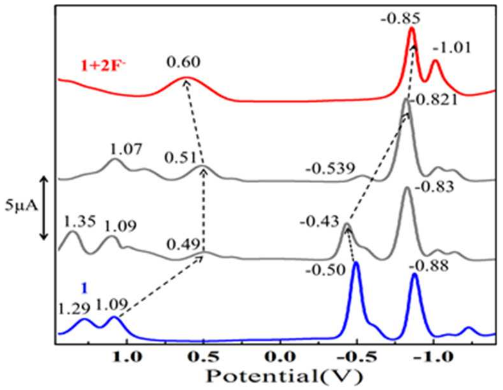


Figure 4. DPV traces of **1** while increasing concentration of F^- ion in CH_2Cl_2containing 0.1 M $TBAPF_6$ at 298 K.

It is known that the perhaloporphyrins, **2** and **4** hydrogen bonds with various polar solvents[19a] including Lewis bases and forms 1:1 host-guest complex[19b] with very low binding constants (0.2 - 16 M^{-1}). In general, **1-4** with anions didn't correspond to the 1:1 host-guest complex neither in the UV-Visible spectral features (figure S22, ESI) nor in binding constant values (very high $\log\beta_2$ values ranges from 8.7 to 11.4) except **3**, which interacts with Cl^- ions through hydrogen bonding (figure S23, ESI) with 1:1 stoichiometry having lower binding constant ($\log\beta_2$ = 3.82). Based on our experimental evidences, we are representing the plausible mechanism of anion recognition by **1-4** (figure 5).

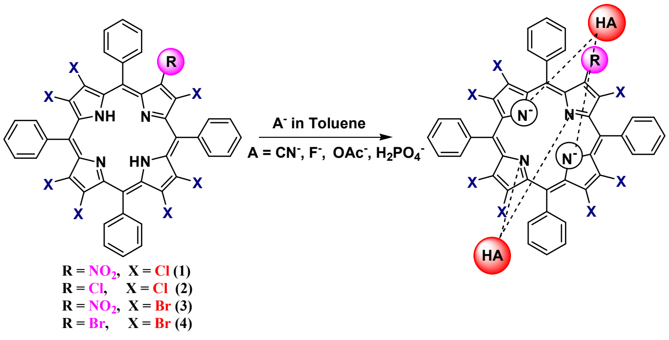


Figure 5. Plausible mechanism for the detection of anions by **1-4**.

Reversibility Studies

Reversibility studies were carried out on these porphyrin-anion host-guest systems to acknowledge the range of their applicability.[20] The reversibility test of these sensors with cyanide ions was studied. For example, **1**•$2CN^-$ was prepared by adding 2 equivalents of cyanide ions to the solution of **1** in toluene which led to the colour change from green to pink (figure 6). It was then treated with aliquots of 1 mM solution of TFA in toluene (figure S24a, ESI). This led to a complete regeneration of **1** which can be visualized by colorimetric change from pink to green accompanied by UV-Visible spectral changes as shown in figure 6. On this basis, we conclude that the formation and dissociation of 1•$2CN^-$ is a reversible process. To confirm the regeneration, the resulting mixture was washed with water and dried over anhydrous Na_2SO_4. Then the recovered **1** was treated with 2 equivalents of CN^- ions (figure S24b, ESI) which exhibited similar binding constant as fresh solution of **1** with cyanide ions. The similar results were obtained for the receptors **2-4** with CN^- ions and TFA solution as shown in figures S25-S27 in ESI. Notably, the receptors **1-4** have exhibited similar results with other anions such as F^-, CH_3COO^- and $H_2PO_4^-$ ions. These results clearly demonstrate that the receptors **1-4** can be recoverable and reusable for basic anions detection.

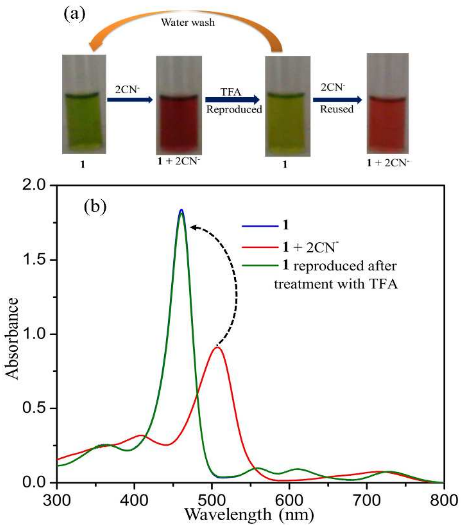


Figure 6. (a) Colorimetric response of **1** for reversibility and reusability test with CN^-; (b) Reversibility test: Treatment of the complex 1•$2CN^-$ with a solution of TFA.

Conclusions

In conclusion, the perhaloporphyrins (**1-4**) were synthesised and exhibited colorimetric responses toward basic anions such as CN^-, F^-, CH_3COO^- and $H_2PO_4^-$ ions and being able to detect these anions in nanomolar concentration. The red-shifted electronic spectral features, the higher β_2 values for deprotonation and anion recognition of **1-4** were interpreted in terms of enhanced nonplanarity and electron withdrawing effect of NO_2 and/or halo substituents. The large anodic shift in voltammetric studies and disappearance of ^1H NMR signals for imino protons strongly supports the anion induced deprotonation. The spectroscopic studies and voltammetric titrations reveal that the formation of dianionic porphyrin species which intern hydrogen bonded with protonated anions (HA). Our results clearly suggest that the highly nonplanar conformation with electron withdrawing substituents is necessary for anion recognition. The reversibility studies unambiguously demonstrated that these receptors **1-4** can be recoverable and reusable for basic anions detection without losing their sensing ability.

These results reported herein will provide a new standpoint to develop recyclable electron deficient nonplanar porphyrin-based anion sensors.

Experimental Section

Materials: Pyrrole, C_6H_5CHO, N-Chlorosuccinimide, $Cu(NO_3)_2•3H_2O$, $Ni(OAc)_2•4H_2O$, $Na_2S_2O_4$, TFA, TBAOH and $NaHCO_3$ were purchased from HiMedia, India and used as received. All solvents employed in the present work were of analytical grade and distilled or dried before use. 1,1,2,2-tetrachloroethane was purchased from Rankem and dried over molecular sieves (4Å) 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 2 days. The tetrabutylammonium salts (TBAX, X = CN^-, F^-, Cl^-, Br^-, I^-, HSO_4^-, BF_4^-, OAc^-, $H_2PO_4^-$, ClO_4^-, PF_6^- and NO_3^-) were purchased from Alfa Aesar and used as received. Dry CH_2Cl_2 for CV analysis 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 3.5 ml volume and 10 mm path length and fluorescence spectra were recorded on Hitachi F-4600 spectrofluorometer using a quartz cell of 10 mm path length. ^1H NMR spectra were recorded on Bruker AVANCE 500 MHz and JEOL ECX 400 MHz spectrometers in $CDCl_3$ and elemental analyses were performed on Elementar vario EL III instrument. ESI mass spectra were recorded on Bruker Daltanics microTOF mass spectrometer in negative ion mode using CH_3CN as solvent. The X-ray quality single crystals of **2** were obtained by vapour diffusion of CH_3CN into the toluene solution of **2**. Single-crystal XRD data of **2** was collected on a Bruker Apex-II CCD diffractometer equipped with a liquid cryostat. The ground state geometry optimisation of **1** in gas phase was carried out by DFT calculations using B3LYP functional with 6-311G(d,p) basis set. Electrochemical measurements were carried out using CH instrument (CH 620E). A three electrode assembly was used consisted of a GC working electrode, Ag/AgCl as a reference electrode and a Pt-wire as a counter electrode. The concentration of **1-4** was maintained ~ 1 mM. All measurements were performed in triple distilled CH_2Cl_2 containing 0.1 M $TBAPF_6$ as supporting electrolyte which was degassed by Argon gas purging. Protonation, deprotonation and anion detection studies were carried out in distilled toluene at 298 K and the concentration of **1-4** were kept ~ 10-13 μM throughout the experiments whereas the stock solution of anions were maintained in between 0.003 to 0.05 M 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.[18] We have calculated the limit of detection (LOD) and limit of quantification (LOQ) for anions in toluene by **1-4** using the formulae LOD = 3.3(SD/S), LOQ = 10(SD/S) where SD stands for standard deviation of blank and S stands for slope of regression line.[19]

Synthetic Procedures

$NiTPP(NO_2)$ was prepared by nitration of NiTPP using copper nitrate in acetic anhydride as reported in literature.[21]

Synthesis of $NiTPP(NO_2)Cl_7$: $NiTPP(NO_2)$ (0.2 gm, 0.28 mmol) was dissolved in 70 ml of 1,1,2,2-tetrachloroethane (TCE) in a 100 mL RB flask. To this, 15 equiv. of N-chlorosuccinimide (0.56 gm, 4.19 mmol) was added and then refluxed for 2.5 hours under argon atmosphere. The solvent was removed under vacuum and the crude porphyrin was purified by silica gel column chromatography using $CHCl_3$/hexane mixture (1:1, v/v) as eluent. The desired product was eluted as second fraction and the yield was found to be 23% (0.062 gm, 0.064 mmol). $NiTPPCl_8$ was collected as first fraction and the yield was found to be 19% (0.050 gm, 0.053 mmol). The spectroscopic data of $NiTPPCl_8$ was in accordance in with reported literature.[22]

$NiTPP(NO_2)Cl_7$: UV/Vis (CH_2Cl_2): λ_{max} in nm (logε) 448 (5.12), 562(4.04), 604(3.80). ^1H NMR in $CDCl_3$ (500 MH_Z): δ_H (ppm) 7.93-7.87(m, 8H, *meso-o*-phenyl-H), 7.73-7.60 (m, 12H, *meso-m,p*-phenyl-H). ESI-MS (m/z): 987.82 $[M•OCH_3]^-$ (calcd., 987.56). $C_{44}H_{20}N_5O_2Cl_7Ni$: C, 55.19%; H, 2.11%; N, 7.31%. Found: C, 55.45%; H, 2.44%; N, 7.57%.

Synthesis of $H_2TPP(NO_2)Cl_7$ (1): $NiTPP(NO_2)Cl_7$ (0.1 gm, 0.10 mmol) was dissolved in 70 ml of distilled $CHCl_3$ in a 250 mL RB flask. To this, 8 mL of conc. H_2SO_4 was added drop wise and allowed to stir for 3 hrs at 0 ºC. Then 100 mL of water was added and extracted into $CHCl_3$. The organic layer was washed with water (2×100 mL) and then neutralized with 100 mL of aq. NH_3 solution (10%). The excess ammonia was removed by washing with water and then dried over Na_2SO_4. The crude porphyrin was purified by silica gel column chromatography using $CHCl_3$ as eluent. The yield of **1** was found to be 79% (0.074 gm, 0.082 mmol) respectively.

$H_2TPP(NO_2)Cl_7$: UV/Vis (CH_2Cl_2): λ_{max} in nm (logε) 461 (5.18), 562(3.88), 615(3.85), 732(3.78). ^1H NMR in $CDCl_3$ (500 MH_Z): δ_H (ppm) 8.23-8.15 (m, 8H, *meso-o*-phenyl-H), 7.82-7.72 (m, 12H, *meso-m, p*-phenyl-H). ESI-MS (m/z):

900.58 $[M]^-$ (calcd., 900.86). $C_{44}H_{22}N_5O_2Cl_7$: C, 58.66%; H, 2.46%; N, 7.77%. Found: C, 58.37%; H, 2.62%; N, 7.56%.

The demetallation of $NiTPPCl_8$ was carried out using concentrated H_2SO_4 as per the reported procedure[23] and the spectroscopic data was in accordance to with the proposed structure of **2**.

Acknowledgements

We are grateful for the financial support provided by Council of Scientific and Industrial Research (01(2694)/12/EMR-II), Science and Engineering Research Board (SB/FT/CS-015/2012) and Board of Research in Nuclear Sciences (2012/37C/61BRNS/253). NC thanks Council of Scientific and Industrial Research (CSIR), India for the fellowship.

Notes and references

Department of Chemistry, Indian Institute of Technology Roorkee, Roorkee - 247667, India. Tel: +91-1332-28-4753; Fax: +91-1332-27-3560; E-mail: sankafcy@iitr.ac.in.

†Electronic Supplementary Information (ESI) available: UV-Visible absorption, fluorescence and ^1H NMR spectra of **1**-**4**, CV and DPV figures of **1**-**4**, UV-Visible titrations for protonation, deprotonation and anion sensing studies, evidences for the dianion formation through ^1H NMR and electrochemical studies.

1 (a) L. R. Milgrom, *The Colours of Life*: *An Introduction to the Chemistry of Porphyrins and Related Compounds*, Oxford University Press, New York, 1997; (b) J. A. Shelnutt, X.-Z. Song, J.-G. Ma, S.-L. Jia, W. Jentzen and C. J. Medforth, *Chem. Soc. Rev.,*1998, **27**, 31; (c) M. O. Senge, *The Porphyrin Handbook*, Vol. 1, Eds.: K. M. Kadish, K. M. Smith and R. Guilard, *Academic Press*, *San Diego*, 2000, 239; (d) M. O. Senge, *Chem. Commun*., 2006, 243.

2 (a) D. S. Kim and J. L. Sessler, *Chem. Soc. Rev.*, 2014, DOI: 10.1039/c4cs00157e; (b) V. V. Roznyatovskiy, C.-H. Lee and J. L. Sessler, *Chem. Soc. Rev.*, 2013, **42**, 1921; (c) P. D. Beer and P. A. Gale, *Angew. Chem. Int. Ed*., 2001, **40**, 486; (d) E. Matthews and P. D. Beer, *Supramol. Chem*., 2005, **17**, 411.

3 (a) A. Bianchi, K. Bowman-James and E. Garcia-Espana, *Supramolecular Chemistry of Anions, Ed*., Wiley-VCH, New York, 1997; (b) J. L. Sessler, P. A. Gale and W.-S. Cho, *Anion Receptor Chemistry*, RSC Publishing, Cambridge, UK, 2006; (c) L. C. Gilday, N. G. White and P. D. Beer, *Dalton Trans*., 2012, **41**, 7092.

4 (a) P. D. Beer and P. A. Gale, *Angew. Chem.*, 2001, **113**, 502; (b) E. Matthews and P. D. Beer, *Supramol. Chem*., 2005, **17**, 411.

5 (a) B. Vennesland, E. E. Comm, C. J. Knownles, J. Westly and F. Wissing, Cyanide in Biology, *Academic press, London*, 1981; (b) M. S. Frant and J. Ross, *Science*, 1966, **154**, 1533; (c) D. Briancon, *Rev. Rheum.,*1997, **64**, 78.

6 (a) R. L. P. Adams, J. T. Knowler and D. P. Leader, *The Biochemistry of the Nucleic Acids, Ed*., Chapman and Hall, New York, 11th ed., 1992; (b) X. F. Shang and X. F. Xu, *BioSystems*, 2009, **96**, 165.

7 (a) C.-H. Lee, H. Miyaji, D.-W. Yoon and J. L. Sessler, *Chem. Commun.,* 2008, 24; (b) S. K. Kim and J. L. Sessler, *Acc. Chem. Res.*, 2014, **47**, 2525; (c) P. Anzenbacher, R. Nishiyabu and M. A. Palacois, *Coord. Chem. Rev*., 2006, **250**, 2929; (d) P. A. Gale and C.-H. Lee, *Top. Heterocycl. Chem.,* 2010, **24**, 39.

8 See for selected examples: (a) A. J. Pistner, D. A. Lutterman, M. J. Ghidiu, Y.-Z. Ma and J. Rosenthal, *J. Am. Chem. Soc.,* 2013, **135**, 6601; (b) C. I. M. Santos, E. Oliveira, J. F. B. Barata, M. A. F. Faustino, J. A. S. Cavaleiro, M. G. Neves and C. Lodeiro, *J. Mater. Chem.,* 2012, **22**, 13811; (c) P. Yadav and M. Sankar, *Dalton Trans.*, 2014, **43**, 14680; (d) J. L. Sessler and J. M. Davis, *Acc. Chem. Res.*, 2001, **34**, 989; (e) D. G. Cho, *Syntheses and studies of sapphyrins and anion receptors*, Umi Dissertation Publishing, 2012; (f) D. H. Won, M. Toganoh, H. Uno and H. Furuta, *Dalton Trans*., 2009, 6151; (g) Y. Xie, T. Marimoto and H. Furuta, *Angew. Chem. Int. Ed*., 2006, **45**, 6907; (h) F. D'Souza, N. K. Subbaiyan, Y. Xie, J. P. Hill, K. Ariga, K. Ohkubo and S. Fukuzumi, *J. Am. Chem. Soc*., 2009, **131**, 16138; (i) J. P. Hill, A. L. Schumacher, F. D'Souza, J. Labuta, C. Redshaw, M. R. J. Elsegood, M. Aoyagi, T. Nakanishi and K. Ariga, *Inorg. Chem*., 2006, **45**, 8288; (j) M. Takeuci, T Shioya and T. M. Swager, *Angew. Chem. Int. Ed*., 2001, **40**, 3372.

9 (a) D. P. Cormode, M. G. B. Drew, R. Jagessar and P. D. Beer, *Dalton Trans.,* 2008, 6732; (b) P. D. Beer, D. P. Cormode and J. J. Davis, *Chem. Commun*., 2004, 414. (c) J. M. M. Rodrigues, A. S. Farinha, P. V. Muteto, S. M. Woranovicz-Barreira, F. A. A. Paz, M. G. Neves, J. A. S. Cavaleiro, A. C. Tome, M. T. Gomes, J. L. Sessler and J. P. C. Tome, *Chem. Commun*., 2014, **50**, 1359.

10 (a) R. Harada and T. Kojima, *Chem. Commun.,* 2005, 716; (b) T. Honda, T. Kojima and S. Fukuzumi, *Chem. Commun.,* 2009, 4994; (c) M. M. Kruk, A. S. Starukhina, N. Zh. Mamardashvilib, G. M. Mamardashvilib, Y. B. Ivanovab and O. V. Maltsevab, *J. Porphyrins Phthalocyanines*, 2009, **13**, 1148.

11 (a) N. Agarwal and M. Ravikanth, *Tetrahedron*, 2004, **60**, 4739; (b) M.O Senge, T. P. Forsyth, L. T. Nguyen and K. M. Smith, *Angew. Chem. Int. Ed. Engl.*, 1994, **30**, 2485; (c) N. Agarwal, C-H. Hung and M. Ravikanth, *Tetrahedron*, 2004, **60**, 10671.

12 (a) S.-J. Hong, J. Yoo, S.-H. Kim, J. S. Kim, J. Yoon and C.-H. Lee, *Chem. Commun*., 2009, 189; (b) M. G. D. Holaday, G. Tarafdar, B. Adinarayana, M. L. P. Reddy and A. Srinivasan *Chem. Commun*., 2014, **50**, 10834. (c) E. Palomares, M. V. Martinez-Diaz, T. Torres and E. Coronado, *Adv. Funct. Mater*., 2006, **16**, 1166; (d) Y.-H. Kim and J.-I. Hong, *Chem. Commun*., 2002, 512; (e) L. D. Chen, X. U. Zou and P. Bühlmann, *Anal. Chem*., 2012, **84**, 9192.

13 (a) V. Amendola, D. Esteban-Gomez, L. Fabbrizzi and M. Licchelli, *Acc. Chem. Res.,* 2006, **39**, 343; (b) A. Basu, S. K. Dey and G. Das, *RSC Adv.,* 2013, **3**, 6596; (c) Q. Wang, Y. Xie, Y. Ding, X. Li and W. Zhu, *Chem. Commun*., 2010, **46**, 3669; (d) G. Lu, X. Zhang, X. Cal, Y. Fang, M. Zhu, W. Zhu, Z. Ou and K. M. Kadish, *J. Porphyrins Phthalocyanines*, 2013, **17**, 941; (e) Y. Fang, P. Bhyrappa, Z. Ou and K. M. Kadish, *Chem. Eur. J*., 2014, **20**, 524.

14 (a) P. Bhyrappa and V. Krishnan, *Inorg. Chem*., 1991, **30**, 239; (b) P. Bhyrappa and P. Bhavana, *J. Chem. Soc. Perkin Trans. 2*, 2001, 238.

15 (a) M. O. Senge, V. Gerstung, K. Ruhlandt-Senge, S. Runge and I. Lehmann, *J. Chem. Soc., Dalton Trans*., 1998, 4187. (b) L. Jaquinod, R. G. Khoury, K. M. Shea and K. M. Smith, *Tetrahedron,* 1999, **5**, 13151; (c) P. Bhyrappa, M. Sankar and B. Varghese, *Inorg. Chem*., 2006, **45**, 4136.

16 (a) T. Wijesekera, A. Matsumoto, D. Dolphin and D. Lexa, *Angew. Chem. Int. Ed. Engl*., 1990, **29**, 1028; (b) P. Bhyrappa and V. Krishnan, *Chem. Lett.*, 1993, 869.

17 K. M. Kadish, G. Royal, E. V. Caemelbecke and L. Gueletti, *The Porphyrin Handbook*, *Vol. 9*, Eds.: K. M. Kadish, K. M. Smith and R. Guilard, *Academic Press*, *San Diego*, 2000, 1.

18 (a) A. V. Hill, *J. Physiol. (London)*, 1910, **40**, IV-VII; (b) A. Pfeil and J.-M. Lehn, *J. Chem. Soc., Chem. Commun*., 1992, 838.

19 (a) P. Bhyrappa and P. Bhavana, *Chem. Phys. Lett.*, 2001, **342**, 39; (b) P. Bhyrappa and P. Bhavana, *Chem. Phys. Lett.*, 2002, **357**, 108.

20 A. S. F. Farinha, M. J. F. Calvete, F. A. A. Paz, A. C. Tome, J. A. S. Cavaleiro, J. L. Sessler and J. P. C. Tome, *Sensors Actuat. B-Chem*, 2014, **201**, 387.

21 V. M. Patel, J. A. Patel, S. S. Havele and S. R. Dhaneshwar, *Int. J. Chem. Tech. Res*., 2010, **2,** 756-761.

22 A. Giraudeau, H. J. Callot and M. Gross, *Inorg. Chem.*, 1979, **18**, 201.

23 G. A. Spyroulias, A.P. Despotopoulos, C. P. Raptopoulou, A. Terzis, D. de Montauzon, R. Poilblanc, and A. G. Coutsolelos, *Inorg. Chem*., 2002, **41**, 2648.