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Switching between Porphyrin, Porphodimethene and Porphyrinogen using Cyanide and Fluoride ions mimicking Volatile Molecular Memory and 'NOR' Logic Gate

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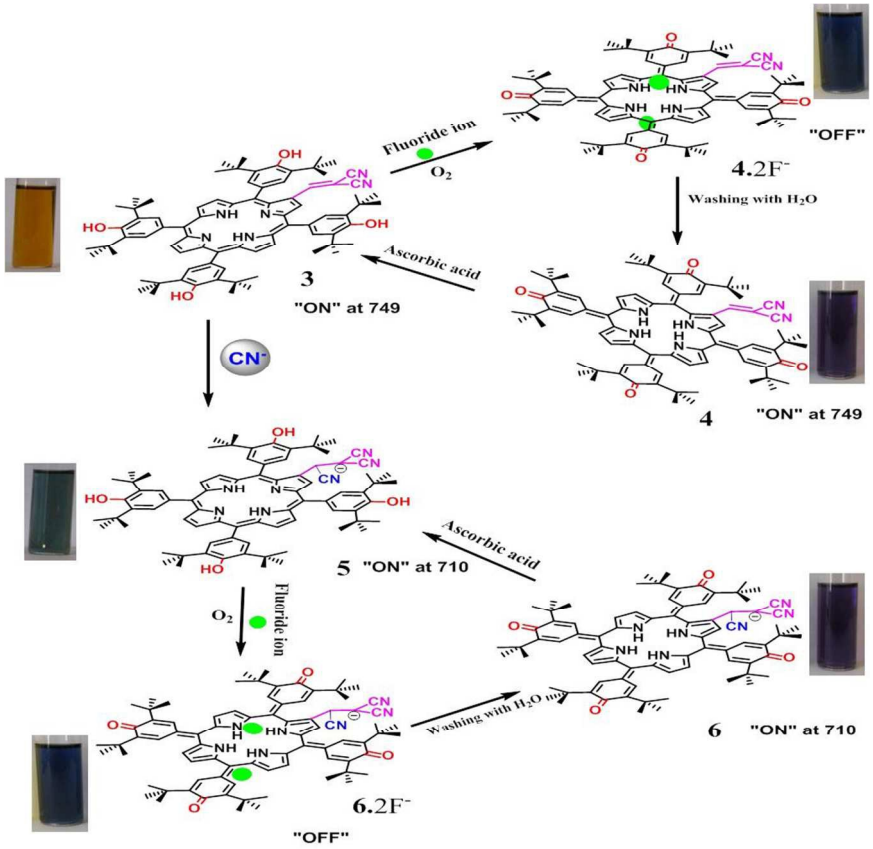

β-substituted porphyrins were developed as a quantitatively operating "lab-on-a-molecule" for the detection of F^- and CN^- ions, by switching between porphyrin, porphodimethene and porphyrinogen along with distinct solution colour changes and reversibility.

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β-functionalization of *meso*-tetrakis(3,5-di-*tert*-butyl-4-hydroxyphenyl)porphyrin with electron acceptors such as formyl and dicyanovinyl has been reported for the first time. 2-formyl-5,10,15,20-tetrakis(3',5'-di-*tert*-butyl-4'-hydroxyphenyl) porphyrinatocopper(II) (Cu-TDtBHPP-CHO) crystallizes in triclinic space group P_1, [a = 10.8479(4) Å, b = 14.6207(5) Å, c = 15.9745(5) Å, V = 2198.97(13) Å^3] exhibits almost planar structure and square planar geometry. β-formyl/dicyanovinyl substituted porphyrins such as Cu-TDtBHPP-CHO, Ni-TDtBHPP-CHO, Cu-TDtBHPP-MN (**1**), Ni-TDtBHPP-MN (**2**) and H_2-TDtBHPP-MN (**3**) exhibited red-shifted optical absorption features ($\Delta\lambda_{max}$ = 13-40 nm) in CH_2Cl_2 as compared to the corresponding MTPPs. β-dicyanovinyl substituted porphyrins were developed as a quantitatively operating 'lab-on-a-molecule' for the visual detection of F^- and CN^- ions. Having CN^- ion responsive dicyanovinyl moiety and F^- ion responsive redox-active 3,5-di-*tert*-butyl-4-hydroxyphenyl groups, they detect simultaneously F^- and CN^- ions by switching unique structural changes between porphyrin, porphodimethene and porphyrinogen along with distinct colour changes which were monitored by UV-Vis-NIR, Fluorescence and NMR spectroscopic techniques.

Tetrapyrrole macrocycles compose a class of compounds that are vital in biochemical systems and perhaps even a cursory look at the role and functions of the porphyrins in biological systems will validate this statement.[1] Additionally synthetic porphyrins have become one of the most extensively studied class of compounds because of their vital role in catalysis,[2] dye-sensitized solar cells (DSSCs),[3] photodynamic therapy (PDT),[4] nonlinear optics (NLO)[5] and electronic materials.[6] In 1983, L. R. Milgrom reported synthesis of *meso*-tetrakis(3,5-di-*tert*-butyl-4-hydroxyphenyl)porphyrin (H_2-TDtBHPP) and its facile aerial oxidation to quinonoidal compounds.[7] Except the formation of oxoporphyrinogen[7] from phenol-substituted porphyrin and N-alkylation/arylation of this porphyrinogen with identical and non-identical groups,[8] the structural modifications have not been explored because of complex tautomeric mixtures and the formation of radical species when modification of the porphyrins was attempted.[9] Of late, conventional porphyrinogens and its N-alkyl/arylated derivatives have also become an increasingly studied class of tetrapyrroles due to their rich synthetic and coordination chemistry and are variously available as sensing probes for anions,[10] molecular chirality recogination,[11] discrimination of alcohols[12] and colorimetric indicator for traces of water in THF.[13] Despite widespread applications, phenol-substituted porphyrin and oxoporphyrinogens were stubborn towards synthetic modifications at β-positions. In 2014, Hill *et al* attempted nitration reaction on the copper(II) or nickel(II) complexes of *meso*-tetrakis(3,5-di-*tert*-butyl-4-hydroxyphenyl)porphyrin but ended with *o*-quinone-substituted porphyrins in reasonable yields.[14] Also, Webre *et al* ended up with β-brominated oxoporphyrinogens during the bromination of *meso*-tetrakis(3,5-di-*tert*-butyl-4-hydroxyphenyl)porphyrin.[15] Herein, first time, we have successfully achieved the β-functionalization of *meso*-tetrakis(3,5-di-*tert*-butyl-4-hydroxyl) porphyrin with electron acceptors with each compound being stable in neutral solution and stable towards aerial oxygen. They exhibit optical properties typical of porphyrin derivatives possessing both charge transfer and electronic coupling with strong electron acceptors.[16] We report herein the synthesis, structural, spectroscopic and electrochemical characterization of electron acceptors appended β-substituted *meso*-tetrakis-(3,5-di-*tert*-butyl-4-hydroxyl)porphyrin (H_2-TDtBHPP).

Complexation of anionic species by molecules containing an appropriate binding site is an area of recent substantial interest in supramolecular chemistry.[17] Detection of fluoride and cyanide ions is an active area of research because of their positive and negative impact on human health and environment.[18] A large number of porphyrin-based receptors for anions have been constructed through the

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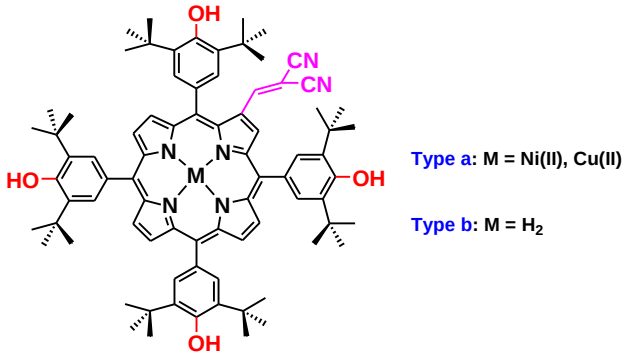
functionalization of β-positions and derivatization of *meso*-positions having appropriate binding pockets.[19] Among the class of the porphyrinoids calixpyrroles,[20] phlorins,[21a] corroles,[21b] sapphyrins,[21c] N-confused porphyrins,[21d,e] and oxoporphyrinogens[10] are excellent multifunctional candidates for anion sensor applications. The concept of "lab-on-a-molecule" can be used for designing sensors capable of distinguishing interfering species. Innovative molecular designs like "lab-on-a-molecule" and multichannel molecular probes for sensing multiple cations or anions are successfully demonstrated[22] in the literature. Thilagar *et al* reported first metalloporphyrin-based "lab-on-a-molecule" system for the independent discrimination of toxic F^- and CN^- ions having triarylboryl units at *meso*-position.[23] However, no such design has been developed yet with β-substituted porphyrins for simultaneous detection of F^- and CN^- ions.

The level of miniaturization of information storage and processing technology is ubiquitous and ever changing.[24] Data might be stored in binary form, based on the changes in the optical or electronic properties, and can be tunned using external stimulus, such as light, temperature, chemical concentration, voltage etc. which is of great interest for the development of molecular memory and logic functions. In this work, we have developed tunable two-input/multi-output system using the changes in the fluorescence and/or optical absorbance with appropriate molecular inputs mimicking first porphyrin based 'NOR' molecular logic-gate. We have also developed memory elements due to fluorescence switching which are based on the subtle structural modifications at the β-position. These memory elements operate primarily by using fluoride and cyanide anions as specific writing components.



M = Cu(II), **1**; M = Ni(II), **2**; M = 2H, **3**

Chart 1. Molecular structures of porphyrin derivatives (**1-3**).

We have synthesized the β-substituted porphyrin derivatives **1**, **2** and **3** as shown in Chart 1. Derivatives **1**, **2** and **3** posses four redox active 3,5-di-tert-butyl-4-hydroxyphenyl groups as well as a dicyanovinyl group. Each compound is stable in neutral solution as well as towards aerial oxygen.

RESULTS AND DISCUSSION

Bonfantini et al[25] reported the efficient synthesis of 2-formyl-5,10,15,20-tetraarylporphyrins on multi-gram scale by overcoming the shortcomings of literature reported methods.[26] The process involved the demetallation of the intermediate iminium salt that results from Vilsmeier-Haack formylation of the Cu(II)/Ni(II) porphyrins prior to base-catalyzed hydrolysis of the salt to the corresponding free base 2-formylporphyrin. But in case of *meso*-tetrakis-(3,5-di-*t*-butyl-4-hydroxyphenyl)porphyrinatocopper(II) (Cu-TDtBHPP)/ *meso*-tetrakis-(3,5-di-*t*-butyl-4-hydroxyphenyl)porphyrinatonickel(II) (Ni-TDtBHPP), the *in situ* demetallation of iminium salt followed by hydrolysis led to a mixture of free base formyl, metalled formyl and major fraction quinone. The separation involves very tedious column chromatography leading to very low yield of β-formyl substituted free base and metalloporphyrins. To avoid loss of yield and difficult column chromatographic purification, the 2-formyl-*meso*-tetrakis(3,5-di-*tert*-butyl-4-hydroxyphenyl)porphyrinatocopper(II) (Cu-TDtBHPP-CHO)/ 2-formyl-*meso*-tetrakis-(3,5-di-*tert*-butyl-4-hydroxyphenyl)porphyrinatonickel(II) (Ni-TDtBHPP-CHO) were obtained in a good yield (>70%) *via* hydrolysis of the iminium salt using saturated sodium acetate solution. Knoevenagel condensation of β-formyl metalloporphyrins with malononitrile in the presence of catalytic amount of piperidine using modified literature method[16] gave targeted compounds *viz.* Cu-TDtBHPP-MN (**1**) and Ni-TDtBHPP-MN (**2**). 2-dicyanovinyl-*meso*-tetrakis-(3,5-di-*tert*-butyl-4-hydroxyphenyl) porphyrin H_2-TDtBHPP-MN (**3**) has been synthesized by demetallation of the Cu-TDtBHPP-MN(**1**)/Ni-TDtBHPP-MN(**2**) using conc. H_2SO_4. These porphyrins were characterized by various spectroscopic techniques and single crystal XRD analyses (Fig. S1–S11 in the ESI).

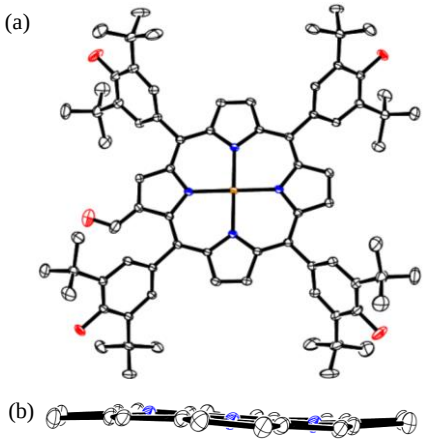


Fig. 1 The ORTEP diagrams showing (a) top and (b) side views of Cu-TDtBHPP-CHO. In side view, *meso*-phenyl and aldehyde groups are not shown for clarity. The aldehyde group is disordered between two inversion-related positions.

The X-ray quality single crystals of Cu-TDtBHPP-CHO were obtained by direct diffusion of hexane into a saturated $CHCl_3$ solution of Cu-TDtBHPP-CHO and the crystallographic parameters are listed in Table S1 in the ESI. It exhibited almost planar structure and square planar geometry. Cu-TDtBHPP-CHO, Ni-TDtBHPP-CHO, Cu-TDtBHPP-MN (**1**), Ni-TDtBHPP-MN (**2**) and H_2-TDtBHPP-MN (**3**) in dichloromethane, gave UV-Visible spectra similar to the analogous TPP complexes. Porphyrins (**1**, **2** and **3**) exhibited characteristic split Soret bands and red-shifted $Q_x(0,0)$ bands (Figure 2a and Table S2, ESI). Importantly, the magnitude of the redox potentials of **1**-**3**

suggests that these compounds are electron deficient, which means that they are nearly 450-400 mV easier to reduce than their parent analogues (Figure 2b and Table S3, ESI).

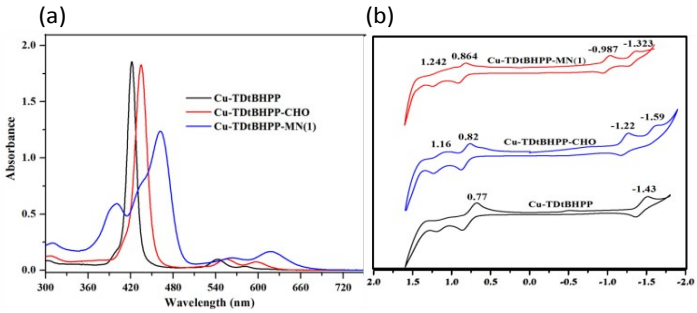


Fig. 2 (a) UV-Vis. spectra of Cu-TDtBHPP, Cu-TDtBHPP-CHO and Cu-TDtBHPP-MN (**1**) in CH_2Cl_2 at 298 K. (b) Cyclic voltammograms of Cu-TDtBHPP, Cu-TDtBHPP-CHO and Cu-TDtBHPP-MN (**1**) in CH_2Cl_2 using Ag/AgCl as the reference electrode.

When cyanide ion was added to Cu-TDtBHPP-MN (**1**) / Ni-TDtBHPP-MN (**2**), both Soret and Q-bands were blue shifted and perturbation in optical spectra was lost as shown in Fig. S12–S13 in the ESI. When **1** (8 μM) was titrated with CN^- ions (0-9.32×10^{-5} M), intensity of the bands at 400, 462, 563 and 618 nm gradually decreased and new bands arose at 423, 546 and 582 nm, with four isosbestic points at 405, 437, 501 and 562 nm, respectively. The colour of the solution changed rapidly from green to reddish pink. Therefore, we expected the addition of one cyanide ion to chemodosimeter *via* nucleophilic addition mechanism. In case of Ni-TDtBHPP-MN (**2**) (Fig. S14 in the ESI), the vinylic proton (H_a) shown at 7.28 ppm completely disappears upon addition of 1 equiv. of cyanide ions. A new signal appears at 4.32 ppm which supports the formation of **[2•CN]**$^-$ adduct. Interestingly, **1** and **2** exhibited 290-350 mV cathodic shift in first ring reduction potentials in the presence of CN^- ions clearly indicating the formation anionic species and interruption of π-conjugation (Fig. S15, ESI). It is important to note that the redox-active 3,5-di-*tert*-butyl-4-hydroxyphenyl groups remain silent to CN^- ions. At this stage, we have two types of β-substituted porphyrins *viz.* dicyanovinyl **(1A)** and tricyanoethylate **(1B)** substituted porphyrins, both of which are responsive to F^- ions (Scheme 1).

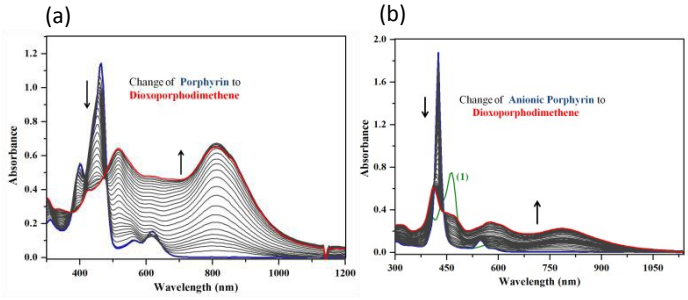
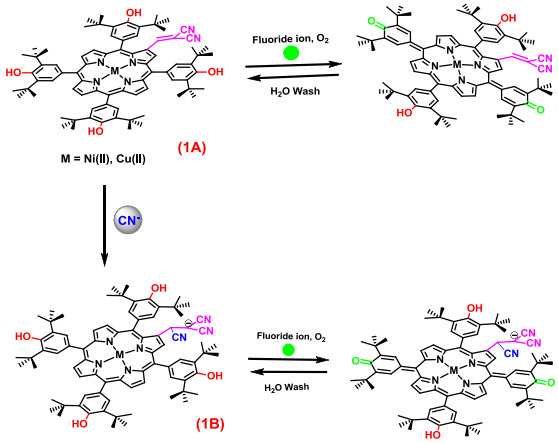


Fig. 3 (a) UV/Vis titration of F^- (0–10^{-3} M) to **1** (8 μM) changing porphyrin to porphodimethene and (b) UV/Vis titration of F^- (0–4 mM) to **1**+CN^- (6 μM) changing anionic porphyrin to anionic porphodimethene.

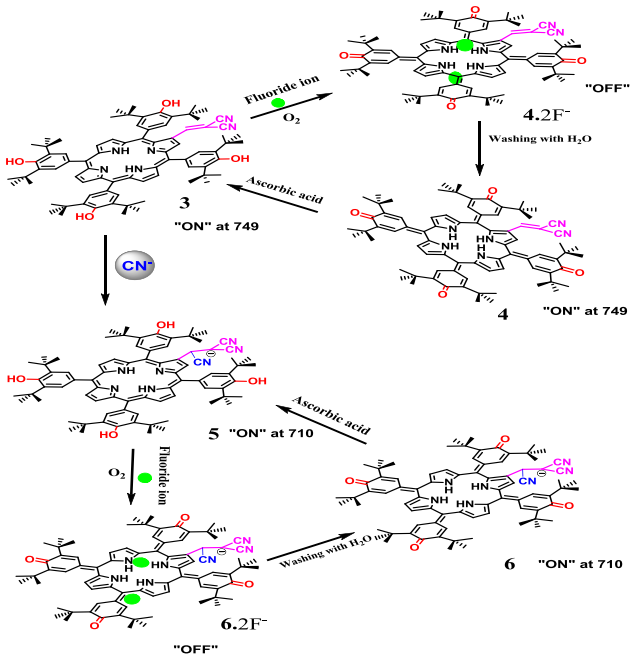
The addition of fluoride ions to these β-modified porphyrin solutions *viz.* **1A** and **1B**, however, produced drastic colour and spectroscopic changes. Addition of F^- ions (0-10^{-3} M) into Cu-TDtBHPP-MN (**1**) solution corresponded to complete removal of the metalloporphyrin B band, and the disappearance of the Q bands (Fig. 3a). The latter was replaced with increased absorbance across the entire visible range and near infrared region (NIR) from 450 to nearly 1200 nm, having more intense bands at 516 and 810 nm respectively, which accounts for their dark colours. The green colour of metalloporphyrin solution changed to deep blue after addition of F^- ions giving porphyrin analogues having absorption in NIR-region (Fig. 4). Switching of metalloporphyrin to porphodimethene (Scheme 1) was also supported by ^{1}H NMR titrations. For Ni-TDtBHPP-MN (**2**), on increasing the conc. of F^- ions from 0 to 5 equiv., both metalloporphyrin and porphodimethene exists in equilibrium. On further addition of F^- ions (10 equiv.), only porphodimethene is present in solution (Fig. S17, ESI). The addition of TBAF solution (0 to 3.5×10^{-3} M) to anionic porphyrin i.e. tricyanoethylate substituted porphyrin (Cu-TDtBHPP-MN+CN^-) solution diminishes the blue shifted bands 423, 546 and 582 nm forming anionic porphodimethene having absorption in the entire UV-Vis-NIR from 350 to 1000 nm as shown in Fig 3b. Hence, the addition of F^- ions to β-substituted porphyrins (**1** and **1**+CN^-) corresponds to oxidation of the macrocycle leading to the formation of a dioxoporphodimethene derivative.



Scheme 1. The mechanism of switching between porphyrin and porphodimethene as well anionic porphyrin and anionic porphodimethene after addition of CN^- and F^- ions for Cu-TDtBHPP-MN(**1**) / Ni-TDtBHPP-MN(**2**).

Since tricyanoethylate group stands orthogonally to macrocyclic ring, so the absorption spectrum for tricyanoethylate substituted porphyrin (**1B**) is less red shifted to NIR-region as compared to dicyanovinyl substituted porphyrin (**1A**) after the addition of fluoride ions because of disruption of electronic communication between macrocyclic ring and the side arm (Fig. 3 and Fig. S16, S19 in the ESI). Addition of excess of tetra- butylammonium salts of Cl^-, Br^-, I^-, NO_3^-, BF_4^-, PF_6^-, CH_3COO^-, $H_2PO_4^-$ and ClO_4^- to solutions of **1** and **2** in CH_2Cl_2 result in no significant changes in optical absorbance and colour of the porphyrin solution (Fig. 4 and S20-S21 in the ESI). Reduction of porphodimethene or anionic porphodimethene back to porphyrin is readily achieved demonstrating that little or no oxidative disruption of the macrocycle has occurred. Washing these basified solutions

with water regenerated the metalloporphyrin spectrum to a greater extent with marginal shift in $Q_x(0,0)$ bands as in case of Cu-TDtBHPP-MN (**1**) but in case of Ni-TDtBHPP-MN (**2**) the distortion in Q bands is more probably due to autoxidation of the metalloporphyrin by dissolved oxygen (Fig. S22-S23 in the ESI). The regeneration ability of porphodimethene to metalloporphyrin was additionally confirmed by addition of protic solvents such as trifluoroacetic acid (TFA) and CH_3OH (Fig. S24 in the ESI). Hence these metalloporphyrin systems respond reversibly to fluoride ion simply switching between porphyrin/porphodimethene and anionic porphyrin/anionic porphodimethene couples just by washing with water/protic solvents as shown in Scheme 1. On the contrary, no such regeneration was achieved by washing cyanide anionic compounds with water because it is chemodosimetric-response (Fig. S25 in the ESI). It is important to note that phenoxide anion substituents formed after the addition of F^- ion develop double bond character between the phenoxide anion substituent(s) and the macrocycle. Increasing electron density over the porphyrin macrocycle lowers the oxidation potential of **1**-**2** by about 600-700 mV as shown in Fig. S18 in the ESI.



Scheme 2. The mechanism of switching between porphyrin and porphyrinogen as well as anionic porphyrin and anionic porphyrinogen after addition of CN^- and F^- ion for H_2-TDtBHPP-MN (**3**).

3 responds differently as compared to that of **1** and **2** towards F^- ions but similarly towards CN^- ions as shown in Scheme 2. Addition of cyanide ion (0-2.5x10^{-4} M) to **3** (8 µM) displayed similar behaviour as **1** and **2** forming anionic porphyrin **5** with blue shifted absorption spectrum (Fig. S26a in the ESI). The HOMO and LUMO switches after the addition of cyanide ion and is localized on the electron rich tricyanoethylate group (Fig. S41, ESI) of anionic porphyrin species. This observation was also supported by the cyclic voltammetric studies with visual colour change (Fig. 4). Addition of CN^- ions (0-2×10^{-4} M) shifts the emission wavelength from 749 nm to 710 nm with decrement in intensity (Fig. S26b, in the ESI).

Addition of TBAF (0-8.5×10^{-4} M) to the solution of **3** (8 µM) in CH_2Cl_2 results in a non-fluorescent solution (Fig. S27b, ESI) with complete removal of free base porphyrin bands (B and Q) in optical absorption spectra (Fig. S27a, ESI). **3** was oxidised to porphyrinogen [**4•2F**$^-$]. Subsequent removal of F^- ions by washing with water recovers the fluorescence to a small extent (Fig. S28 in the ESI). Noticeably this behaviour is different as reported by Hill *et al*[10a] where non-fluorescent behaviour is retained even after the removal of fluoride ions by washing with water. This result led to the important observation that porphyrinogen having electron acceptor through the olefinic bridge on the β-position is fluorescent whereas conventional porphyrinogen is non-fluorescent.

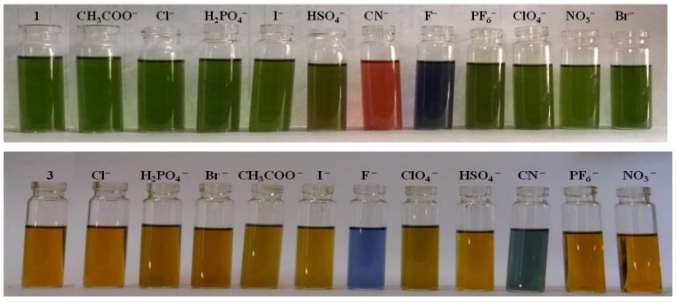


Fig. 4 Visual changes for Cu-TDtBHPP-MN **(1)** and H_2-TDtBHPP-MN **(3)** in the presence of different anions. Changes observed only for F^- and CN^- ions.

The addition of L-ascorbic acid to **4** enhances its fluorescence immediately regenerating original colour of porphyrin **3** (Fig. S28-S29 in the ESI). It is also noted that direct addition of ascorbic acid to **4•2F**$^-$ also regenerates porphyrin **3** spontaneously (Fig. 6c) reverting to the initial fluorescent state. Addition of F^- (0-2×10^{-3} M) to **5** results into a non-fluorescent solution of **6•2F**$^-$ (Fig. S30 in the ESI). Washing the solution with H_2O changes colour of the solution from blue to purple with recovered fluorescence to some extent (Fig. S31).

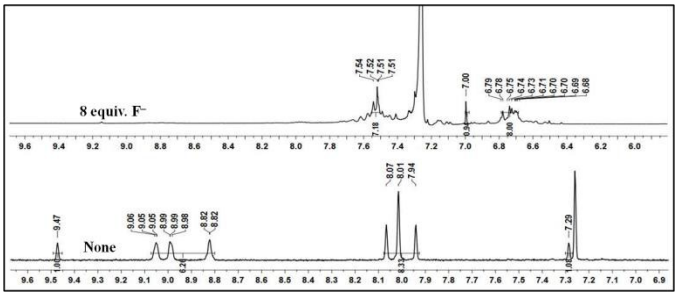


Fig. 5 ^{1}H-NMR spectra of **3** in the absence and presence of F^- ions in $CDCl_3$.

Further addition of L-ascorbic acid converts **6** to **5** with original anionic porphyrin colour (Fig. S31-S32). Again in case of **6•2F**$^-$, the direct addition of ascorbic acid restores the fluorescence and optical absorption spectra to original anionic porphyrin **5** (Fig. 6d). This volatile behaviour is typical of anion-responsive molecular switches as shown in Fig. 6 and S33 in the ESI. Fluoride anions induce oxidative conversion from **3** to **4.2F**$^-$ with subsequent complexation of **3** with F^- (writing) then, **4.2F**$^-$ is reduced to **3** by using ascorbic acid (erasing). A similar

type of "writing-erasing" type memory element was developed with **5**. **1** and **2** also present a memory cycle using optical absorbance as shown in Fig. S34-S35 in the ESI. It may be noted here that **1**-**2** (**Type a**) and **3** (**Type b**) molecular systems result in different memory cycles. In case of **1**-**2** transformation from porphyrin to porphodimethene is achieved by the addition of fluoride ions with consequently switching to porphyrin just by washing with water without addition of any reducing agent. But **3** presented different memory cycle in which switching between porphyrin and porphyrinogen requires the addition of reducing agent (washing with water just restores the fluorescence to a small extent). Further, the detection limits (LOD) of cyanide ions using **1**, **2** and **3** were found to be 4, 3.6 and 6.4 μM, respectively whereas for fluoride ions found to be 30, 27 and 40 μM (Fig. S37-S39 in the ESI). In fact, these porphyrins require slightly higher concentrations of fluoride ions for oxidation than CN^- ions which undergo nucleophilic substitution reaction.

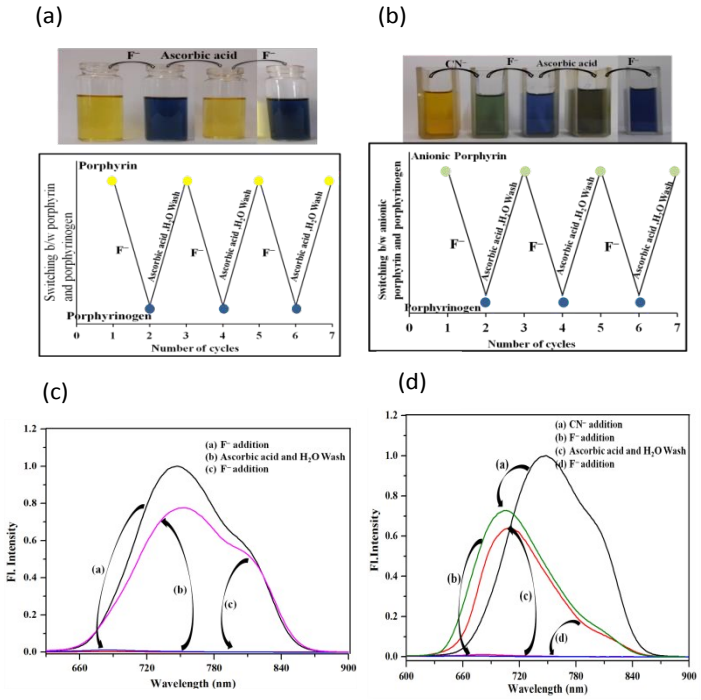


Fig. 6 Repeated memory cycles using **3** (a) and **5** (b), in which each state was detected by its emission intensity (749 nm for **3**; 710 nm for **5**) obtained from 10^{-6} M solutions of **3** and **5** in CH_2Cl_2. Photographs showed each solution of **3** and **5** under 'naked-eye'. Fluorescence emission spectral changes upon addition of F^- into 10^{-6}M solutions of **3** (c) and **5** (d) in CH_2Cl_2.

To further investigate the interaction of fluoride ions with **3**, we have carried out ^1H NMR studies. Addition of 9.2 equiv of F^- to a $CDCl_3$ solution of **3** (6 mM) resulted in new resonances at 7.52, 7.00 and 6.74 ppm with disappearance of the resonances due to **3** in the ^1H NMR spectrum (Fig. 5). It should be noted that oxidation from **3** to **4•2F**$^-$ and from **5** to **6•2F**$^-$ does not occur in the presence of Cl^-, Br^-, I^-, NO_3^-, BF_4^-, PF_6^-, CH_3COO^-, CN^-, $H_2PO_4^-$ and ClO_4^- ions (Fig. S36 in the ESI). To gain an insight into their geometry and electronic structure, computational studies were performed on compounds by using density functional methods (DFT) at the B3LYP/LANL2DZ level. In our calculations, all of the compounds were fully optimized to a stationary point on the Born-Oppenheimer potential energy surface. To gain more confidence in the computed structures, especially the nonplanarity factors, the computed structures were compared with the X-ray structure. Figure S41 illustrates the first HOMO and first LUMO of H_2-TDtBHPP, **3**, **4•2F**$^-$, **4**, **5** and **6•2F**$^-$ while Table S4 lists the energies of the first two HOMOs and first two LUMOs along with the calculated HOMO-LUMO gap. The HOMO and LUMO orbitals for compound H_2-TDtBHPP were found to be mainly on the porphyrin π-ring system, while for H_2-TDtBHPP-MN (**3**) and anionic porphyrin (**5**) formed after the addition of CN^- ion, these orbitals were spread to dicyanovinyl/tricyanoethylate unit due to extended conjugation and charge transfer. But in case of porphyrinogens (**4•2F**$^-$, **4**, **5** and **6•2F**$^-$), these orbitals were dispersed to the oxo-cyclohexadienylidene rings of the porphyrinogen macrocycle due to extension of conjugation caused by oxidation. The calculated HOMO-LUMO gap followed the trend **4** < **4•F**$^-$ < **3** < **H_2-TDtBHPP**. These results suggest a decreased HOMO-LUMO gap for the porphyrinogens/porphodimethene as compared to the parent porphyrin, and gap decreases with β-substitution of parent porphyrin as shown in Table S4-S5 in the ESI.

Table 1. Tunable two-input/multi-output system for **3** using CN^- and F^- ions as inputs.

Memory element		$\lambda_{abs.}$ 426 nm	$\lambda_{abs.}$ 464 nm	$\lambda_{abs.}$ 638 nm	λ_{em} 749 nm	λ_{em} 710 nm
INPUT = CN^-	INPUT = F^-					
0	0	"0"	"1"	"0"	"1"	"0"
1	0	"1"	"0"	"0"	"0"	"1"
0	1	"0"	"0"	"1"	"0"	"0"
1	1	"0"	"0"	"1"	"0"	"0"

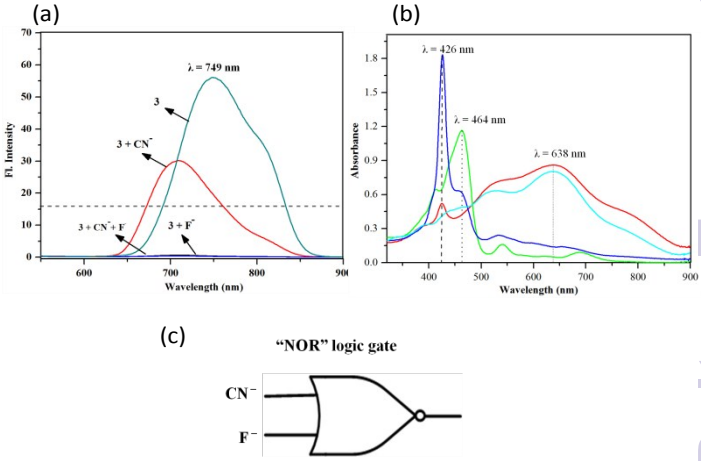


Fig. 7 (a) Emission spectra of **3** under different input conditions. (b) Absorption spectra of **3** under different input conditions. (c) The logic circuit incorporating the truth table constitutes the two input NOR logic gate.

A tunable two-input/multi-output system was also depicted on the basis of a single molecule (**Type a** (**1**-**2**) and **Type b** (**3**)) by using UV-Vis. and fluorescence spectroscopic techniques. By using F^- and CN^- ions as two inputs, multiple "ON = 1" and "OFF = 0" outputs were obtained at different wavelengths as

shown in Table 1 and S6-S7 in the ESI. The logic characteristic of 'NOR' gate for **3** was determined by observing the fluorescence spectrum at 749 nm and absorption spectrum at 464 nm having fluoride and cyanide as possible input conditions. The output corresponds to the response of fluorescence emission at 749 nm and absorption at 464 nm based on the interaction of **3** with F^- and CN^- ions (Table 1). In order to elucidate the design of the logic gate, we assign logic 0 and logic 1 to the inputs and outputs. The four possible input combinations are (0, 0), (1, 0), (0, 1) and (1, 1) as shown in Table 1. In the absence of two chemical inputs (CN^- = 0, F^- = 0), the emission/absorption intensity is significantly high. Otherwise the fluorescence output/ absorption output is low as shown in Table 1.

Conclusions

In conclusion, β-functionalization of *meso*-tetrakis(3,5-di-*tert*-butyl-4-hydroxyphenyl)porphyrin with electron acceptors such as formyl and dicyanovinyl are reported in very good yields. Each of these compounds is stable in neutral solution and stable towards aerial oxygen. Further, this molecular system provides a unique example of "lab-on-a-molecule" for the simultaneous detection of F^- and CN^- ions by switching between different porphyrinoid states *viz.,* porphyrin, porphodimethene and porphyrinogen with proper reversibility. Each state has a unique colour enabling 'naked-eye' colorimetric detection of toxic ions. A "writing-erasing" or volatile type memory element was also developed with these systems by using fluoride and cyanide anions as specific writing components. Tunable outputs ("ON = 1" and "OFF = 0") at particular wavelength using F^- and CN^- ions as two inputs mimics first porphyrin-based 'NOR' molecular logic-gate.

EXPERIMENTAL SECTION

Materials and Measurements

All chemicals used for synthesis were obtained from chemical companies and used without further purification. Tetra-n-butylammonium salts and L-ascorbic acid were purchased from Alfa Aesar and HiMedia respectively. The X-ray quality single crystals of Cu-TDtBHPP-CHO were obtained by direct diffusion of hexane into a saturated $CHCl_3$ solution of Cu-TDtBHPP-CHO. The single crystals obtained were mounted on mounting loops. All diffraction data were collected by using a Bruker APEXII diffractometer at 25°C equipped with graphite-monochromated Mo Kα (λ = 0.71073 Å) by the ω-2θ scan. Crystallographic parameters are summarized in Table S1 in the ESI. The structure was solved using P-1 space group where aldehyde group is disordered between two inversion-related positions. The hexane solvent was squeezed out. CCDC-1451709 (Cu-TDtBHPP-CHO) contains the supplementary crystallographic data. Spectroscopic grade solvents were used for all spectroscopic measurements. UV/Vis, fluorescence, UV/Vis/NIR and ^{1}H-NMR spectra were obtained using Agilent Cary 100 spectrophotometer, F-4600 (Hitachi), LAMBDA 950 (Perkin Elmer), Bruker AVANCE 500 MHz and JEOL ECX 400 MHz instruments, respectively. Elemental analyses were performed using an Elementar vario EL III instrument. MALDI-TOF-MS spectra were measured using a Bruker UltrafleXtreme-TN MALDI-TOF/TOF spectrometer using HABA as a matrix. The ground state geometry optimisation was carried out by DFT calculations using B3LYP functional with LANL2DZ basis set using G09 program suite.[27] A three electrode assembly was used consisted of a platinum working electrode, Ag/AgCl as a reference electrode and a Pt-wire as a counter electrode. All measurements were performed in triple distilled CH_2Cl_2 containing 0.1M $TBAPF_6$ as supporting electrolyte, which was degassed by argon gas purging.

General procedure for formylation: To a mixture of phosphoryl chloride (236 mmol) in dimethylformamide (362 mmol) was added a solution of metal complex (3.71 mmol) in 1,2-dichloroethane. The mixture was heated under reflux for 18 h. Saturated sodium acetate solution was added and the mixture was warmed under stirring for a further 2 h. The product was extracted with chloroform, dried over sodium sulfate, and evaporated to dryness. The crude porphyrin was purified on silica column using $CHCl_3$/hexane mixture (7:3, v/v) to 100% $CHCl_3$ as eluent.

2-formyl-*meso*-tetrakis-(3',5'-di-*tert*-butyl-4'-hydroxyphenyl)-porphyrinatocopper(II) (Cu-TDtBHPP-CHO): Yield 72%. UV/Vis (CH_2Cl_2): λ_{max} (nm) 435, 555, 598. MALDI-TOF-MS (m/z): found, 1218.303 (calcd., 1217.124). Anal. Calcd for $C_{77}H_{92}CuN_4O_5$: C, 75.98; H, 7.62; N, 4.60%. Found: C, 76.01; H, 7.39; N, 4.42%.

2-formyl-*meso*-tetrakis-(3',5'-di-*tert*-butyl-4'-hydroxyphenyl)-porphyrinatonickel(II) (Ni-TDtBHPP-CHO): Yield 70%. UV/Vis (CH_2Cl_2): λ_{max} (nm) 436, 545, 586. ^{1}H NMR in $CDCl_3$ (500 MHz): δ_H (ppm) 9.34 (s, 1H, -CHO), 9.09 (s, 1H, β-H), 8.875 (d, 1H, J = 5Hz, β-H), 8.779-8.81 (m, 4H, β-H), 8.755 (d, 1H, J = 5Hz, β-H), 7.825 (s, 2H, *meso*-*o*-phenyl-H), 7.794 (s, 2H, *meso*-*o*-phenyl-H), 7.78 (s, 2H, *meso*-*o*-phenyl-H), 7.748 (s, 2H, *meso*-*o*-phenyl-H), 5.583 (s, 1H, -OH), 5.492-5.483 (m, 3H, -OH), 1.55-1.57 (m, 72H); MALDI-TOF-MS (m/z): found 1213.32, [M+], calcd. 1212.27. Anal. Calcd for $C_{77}H_{92}NiN_4O_5$: C, 76.29; H, 7.65; N, 4.62%. Found: C, 76.56; H, 7.89; N, 4.41%.

Synthesis of Cu-TDtBHPP-MN (1): Cu-TDtBHPP-CHO (200 mg, 0.164 mmol) was taken in 30 mL of distilled $CHCl_3$. To this, malononitrile (0.229 mmol) and catalytic amount of piperidine was added and refluxed for 6 hrs. Solvent was rotary evaporated to dryness under vacuum. The crude porphyrin was purified on silica column using $CHCl_3$ as eluent. Yield was found to be 77% (160 mg).
Cu-TDtBHPP-MN(1): UV/Vis (CH_2Cl_2): λ_{max} (nm) 400, 462, 563, 618. MALDI-TOF-MS (m/z): found 1265.85 [M+], calcd. 1265.17. Anal. Calcd for $C_{80}H_{92}CuN_6O_4$: C, 75.95; H, 7.33; N, 6.64%. Found: C, 75.96; H, 7.12; N, 6.92%.

Synthesis of Ni-TDtBHPP-MN (2): **2** was prepared as of **1** using 2-formyl-*meso*-tetrakis-(3',5'-di-*tert*-butyl-4'-hydroxyphenyl)porphyrinato Nickel(II) **(Ni-TDtBHPP-CHO)**.Yield was found to be 79%.

Ni-TDtBHPP-MN (2): UV/Vis (CH_2Cl_2): λ_{max} (nm) 393, 462, 554, 613. ^{1}H NMR in $CDCl_3$ (500 MHz): δ_H (ppm) 9.47 (s, 1H, β-H), 8.875 (d, 1H, J = 5Hz, β-H), 8.794-8.766 (m, 4H, β-H), 8.735 (d, 1H, J = 5Hz, β-H), 7.803 (s, 2H, *meso*-*o*-phenyl-H), 7.778-7.776 (m, 4H, *meso*-*o*-phenyl-H), 7.70 (s, 2H, *meso*-*o*-phenyl-H), 7.282 (s, 1H, -CH=C$(CN)_2$), 5.68 (s, 1H, -OH), 5.539 (s, 1H, -OH), 5.498 (s, 2H, -OH), 1.574-1.586 (m, 72H); MALDI-TOF-MS (m/z): found 1260.73, [M+], calcd. 1260.31. Anal. Calcd for $C_{80}H_{92}NiN_6O_4$: C, 76.24; H, 7.36; N, 6.67%. Found: C, 76.56; H, 7.60; N, 6.42%.

Synthesis of H_2-TDtBHPP-MN (3): **Cu-TDtBHPP-MN (1)** or **Ni-TDtBHPP-MN (2)** (0.06 g) was taken in 15 mL of $CHCl_3$ and to it was added 0.1 mL of conc. H_2SO_4 dropwise, stirred vigorously at 0°C for 1 hour. At the end of this period, distilled water (40 mL) was added. The organic layer was separated and neutralized using 25% aqueous ammonia solution. The organic layer was dried over anhydrous Na_2SO_4 and concentrated to small volume. This was purified by silica gel chromatography using $CHCl_3$ as eluent and the yield of the product was found to be 0.025 g (44%).

H_2-TDtBHPP-MN (3): UV/Vis (CH_2Cl_2): λ_{max} (nm) 415, 464, 541, 625, 689. ^{1}H NMR in $CDCl_3$ (500 MHz): δ_H (ppm) 9.472 (s, 1H, β-H), 9.05 (s, 2H, β-H), 8.99 (s, 2H, β-H), 8.82 (s, 2H, β-H), 8.07 (s, 2H, *meso*-*o*-phenyl-H), 8.01 (m, 4H, *meso*-*o*-phenyl-H), 7.94 (s, 2H, *meso*-*o*-phenyl-H), 7.29 (s, 1H, -CH=C$(CN)_2$), 5.77 (s, 1H, -OH), 5.63 (s, 1H, -OH), 5.57 (s, 2H, -OH), 1.63-1.65 (m, 72H,), -2.42 (s, 2H, inner NH); MALDI-TOF-MS (m/z): found 1204.83, [M+], calcd. 1203.64. Anal. Calcd for $C_{80}H_{94}N_6O_4$: C, 79.83; H, 7.87; N, 6.98%. Found: C, 79.56; H, 7.69; N, 6.52%.

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