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COMMUNICATION

## Chemodosimetric cyanide sensing in 5,15-porphodimethene Pd(II) Complex

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**Pd(II) complex of 5,15-porphodimethene is shown as a chemodosimetric sensor where it selectively senses cyanide ion, monitored through electronic spectral analysis and identified by naked eye. The possible binding mechanism is also proposed based on the <sup>1</sup>H NMR analyses. Two polymorphs of the mentioned complex are obtained by different polar solvents and further confirmed by single crystal X-ray analyses.**

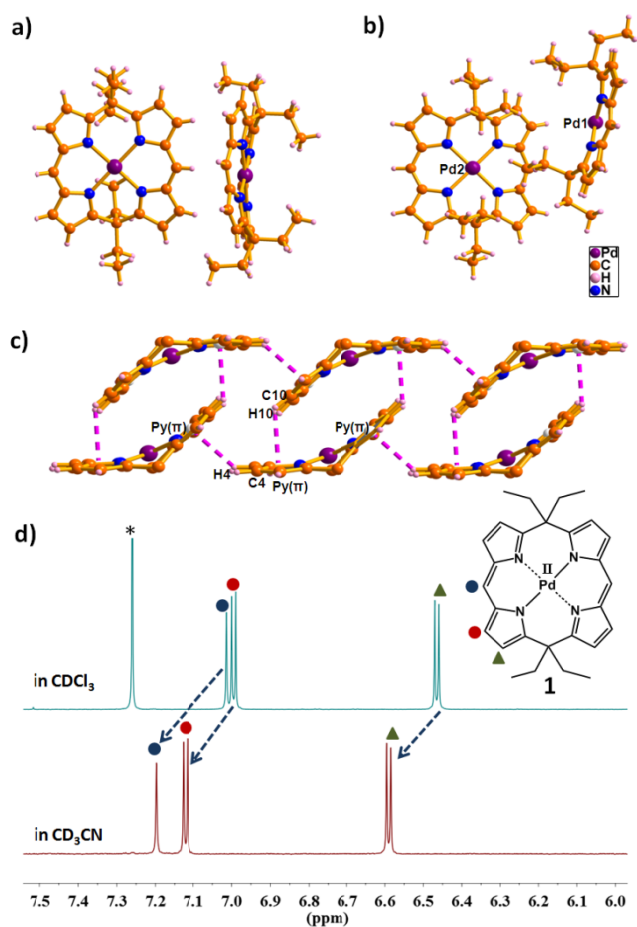
Cyanide is of particular interest, because it is widely used in various industrial applications like metallurgy, mining, electroplating, polymer synthesis, and also involved in separating metal ions like, gold, silver and copper from platinum.<sup>1</sup> However, cyanide is one among the toxic anions; even a trace amount can affect the living cells, where it binds with cytochrome *c* and enters into mitochondrial electron transport chain, thus inhibiting cellular respiration.<sup>2</sup> The cyanide ion can be detected through various instrumental techniques like electronic absorption, emission, electrochemical and mass spectrometric techniques; however, the initial two methods are often used to detect trace amount of cyanide ions.<sup>3</sup> Three different approaches are utilized to design optical sensors for various anions; (a) both the signalling subunits and binding sites are linked covalently; (b) displacement assay and (c) chemodosimetric method.<sup>4</sup> The last approach involves an irreversible chemical reaction, is more specific and minimizes the effect of interfering anions. Due to nucleophilic nature, cyanide ion has strong affinity towards carbonyl carbon, electrophilic carbon and boron, which leads to cyanide imparting absorption and emission spectral changes.<sup>4,5</sup> Hence, the chemodosimeters utilizing visible color change are highly useful for naked eye detection of cyanide ion.

Calixphyrin, a structural hybrid of porphyrin and calixpyrrole, binds effectively with cation;<sup>6</sup> however, the anion binding abilities are rare.<sup>7</sup> The chemosensor for cyanide ion is well known among porphyrin and phthalocyanine derivatives,<sup>3c,8</sup> however, only two methods<sup>9</sup> are known as chemodosimetric sensor; (i) Chang-Hee Lee and co-workers recently reported the synthesis of new calix[4]pyrrole derivative which is used as a cyanide selective indicator.<sup>9a</sup> (ii) The boron incorporated subphthalocyanine dye was reported by Palomares and Torres et al, which selectively detect the cyanide ion by colorimetric and fluorimetric technique.<sup>9b</sup> However, the calixphyrin based chemodosimetric sensors are not known in the literature. Herein, we report two important observations of calixphyrin derivative

such as 5,15-porphodimethene Pd(II) complex (**1**); in the first part, we highlight the polymorphic nature of **1** and in the second part, we describe, how this complex might be used as a chemodosimetric sensor.

Recently, we reported series of 5,15-porphodimethene metal complexes through metal templated synthesis and explored anagostic interaction in the Ni(II) and Zn(II) complexes.<sup>10</sup> However such interactions were not found in the Pd(II) complex. Initially, the crystals of **1** were obtained by slow evaporation of CH<sub>2</sub>Cl<sub>2</sub> solution in *n*-hexane and the compound crystallized in monoclinic lattice with *P*2<sub>1</sub>/*n* space group. There were two metal complexes present in the unit cell and the distance between the two metal centers were 7.07 Å. The *meso*-ethyl units were oriented away from the metal centers and both the units were almost perpendicular (~ 80°) to each other and connected by strong intermolecular hydrogen bonding interactions (Fig. S7, ESI†). To our surprise, when we crystallized **1** by slow evaporation of CH<sub>3</sub>CN solution in hexane, we observed that the complex crystallizes in triclinic lattice with space group of *P*-1 (Fig. 1a). The structural features of the polymorphic crystal are largely different from the one we observed in CH<sub>2</sub>Cl<sub>2</sub>. As observed earlier, two metal complexes are present in one unit cell. The distance between the two metal centers (Pd1 and Pd2) is 7.56 Å, where one of the *meso*-ethyl units is in between the metal centers and widens the distance between them. The intermolecular hydrogen bonding interactions, as observed in the case of CH<sub>2</sub>Cl<sub>2</sub>, are absent in CH<sub>3</sub>CN. However, out of two metal centers, one of the complex present in the unit cell (Pd1) forms self-assembled dimer and 1-D array. There are two π-clouds generated in Pd1 unit, where the pyrrolic β-CH (C10-H10) and *meso* CH (C4-H4) of the second units interacts with the pyrrolic π-clouds through hydrogen bonding interactions (Fig. S8, ESI†). The distances and angles of C10-H10...Py(π) and C4-H4...Py(π) are 2.86 Å, 132° and 2.80 Å, 135° respectively. The self-assembled dimer and array combine together to generate 1-D supramolecular assembly in the solid state (Fig. 1c). Similar hydrogen bonding interactions are absent in other complex present in the unit cell (Pd2).

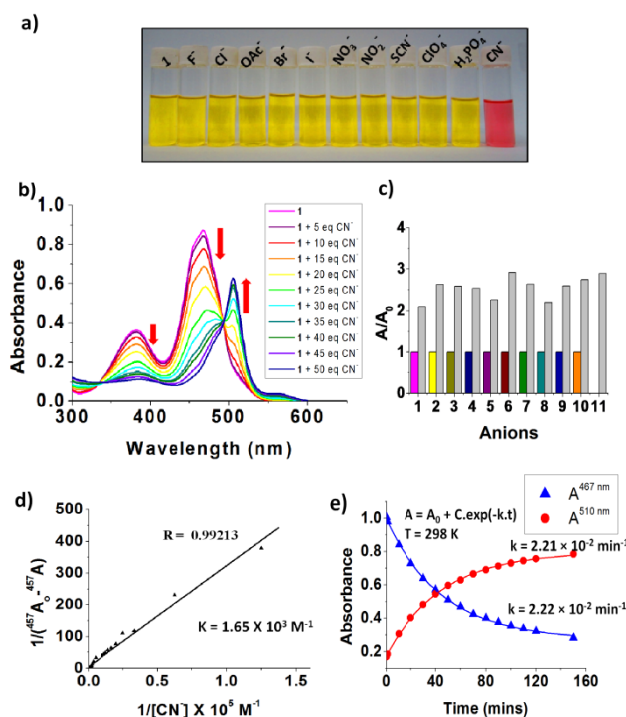
The <sup>1</sup>H NMR spectrum of the Pd(II) complex (**1**) is recorded in CDCl<sub>3</sub> and CD<sub>3</sub>CN at room temperature and are shown in Fig. 1d. The results fully agree with the single crystal data of the two complexes and throws light on the effect of solvent polarity of the polymorphs. In CDCl<sub>3</sub>, the aromatic region consists of three set of peaks, where two *meso* protons were observed as singlet at



**Fig. 1** Single crystal X-ray structure of **1**. From  $\text{CHCl}_3/n$ -Hexane (a) and  $\text{CH}_3\text{CN}/n$ -Hexane (b). (c) 1-D array. (d)  $^1\text{H}$  NMR spectrum of **1** in  $\text{CDCl}_3$  and  $\text{CD}_3\text{CN}$ . \*corresponds to solvent proton.

6.98 ppm, while the pyrrolic  $\beta$ -CH as doublets at 6.96-6.95 ppm and 6.46-6.45 ppm respectively. When the solvent is changed from  $\text{CDCl}_3$  to  $\text{CD}_3\text{CN}$ , in contrast to the above observations, all the peaks in the aromatic region are shifted downfield. In particular, the *meso* CH proton in  $\text{CD}_3\text{CN}$  is shifted more downfield, as compared to the pyrrolic  $\beta$ -CH protons, where the *meso* CH protons are resonated at 7.2 ppm and shifted by 0.22 ppm, as compared to **1** in  $\text{CDCl}_3$ . The pyrrolic  $\beta$ -CH protons are observed as doublets at 7.13-7.12 ppm and 6.58-6.57 ppm, respectively. However, there is not much change in the aliphatic proton signals as the solvent changed from  $\text{CDCl}_3$  to  $\text{CD}_3\text{CN}$ , where the methyl protons are resonated as triplet at 0.82 ppm, while the methylene protons are observed as a quartet at 2.09-2.03 ppm. In the electronic spectral analysis, we do not find any drastic spectral variations by changing the solvent from  $\text{CHCl}_3$  to  $\text{CH}_3\text{CN}$ .

In order to investigate the anion binding ability, the preliminary qualitative experiment was performed by using dilute  $\text{CH}_3\text{CN}$  solution of **1** with 10 equiv. of various anions such as  $\text{F}^-$ ,  $\text{Cl}^-$ ,  $\text{NO}_3^-$ ,  $\text{OAc}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$ ,  $\text{NO}_2^-$ ,  $\text{SCN}^-$ ,  $\text{ClO}_4^-$ ,  $\text{H}_2\text{PO}_4^-$ ,  $\text{CN}^-$  in the form of tetrabutylammonium (TBA) salts. Out of 11 anions used, no noticeable color change was observed in the case 10 anions (Fig. 2a). However, the color of the solution changes from yellow to red upon addition of  $\text{CN}^-$ . The electronic spectral analysis of **1**



**Fig. 2** Anion receptor properties of **1**. (a) Color of  $\text{CH}_3\text{CN}$  solution of **1** (20  $\mu\text{M}$ ) without and with addition of different anions, as seen through naked eye. (b) Absorption spectral analysis of **1** (20  $\mu\text{M}$ ) in  $\text{CH}_3\text{CN}$  with increasing concentration of  $\text{CN}^-$ . (c) Competitive binding studies between  $\text{CN}^-$  over 100 equiv. of other anions. The color bars represent the change in absorption intensity of **1** (20  $\mu\text{M}$ ) at 510 nm upon addition of 100 equiv. of anions: 1)  $\text{Br}^-$ , 2)  $\text{Cl}^-$ , 3)  $\text{ClO}_4^-$ , 4)  $\text{F}^-$ , 5)  $\text{H}_2\text{PO}_4^-$ , 6)  $\text{I}^-$ , 7)  $\text{NO}_3^-$ , 8)  $\text{NO}_2^-$ , 9)  $\text{OAc}^-$ , 10)  $\text{SCN}^-$  and 11)  $\text{CN}^-$ . Corresponding grey bars represent the change in absorption intensity at 510 nm upon addition of 25 equiv. of  $\text{CN}^-$  in the presence of anion. Spectra were recorded after 10 min of addition. (d) Benesi-Hildebrand plot for the absorption spectral changes of **1** upon addition of  $\text{CN}^-$ . (e) Plot between changes in the intensity of absorption of **1** solution at 467 nm and 510 nm, after addition of 25 equiv. of  $\text{CN}^-$ , and time interval.

shows intense absorption bands at 467 nm and 386 nm. Upon addition of different anions other than  $\text{CN}^-$ , there was no observable change in the absorption spectra. However, upon the addition of  $\text{CN}^-$ , the absorption maxima was red-shifted by about 43 nm and observed at 510 nm (Figure S2, ESI $^\dagger$ ). To get a quantitative idea of the sensing, the experiment was further performed by using  $\text{CN}^-$  alone. Upon increasing concentrations of  $\text{CN}^-$  in **1** (20  $\mu\text{M}$ ), the intensity of band at 467 nm and 386 nm gradually decreased and a new band was formed at 510 nm, with two isosbestic points at 330 and 490 nm. The isosbestic points suggest the presence of equilibrium between the **1** and **1**.anion complex (Fig. 2b). The binding constant value is found to be  $1.65 \times 10^3 \text{ M}^{-1}$  from the Benesi-Hildebrand plot (Fig. 2d). Further, the competitive binding of cyanide ion over the other anions was tested and found that **1** selectively senses cyanide ion even in presence of 100 equiv. of other anions (Fig. 2c). The detection limit was found to be 0.3 ppm, which is higher as compared to other porphyrin derivatives.<sup>9</sup>

The spectral changes, upon addition of 25 equiv. of  $\text{CN}^-$  to **1** (20  $\mu\text{M}$ ) in  $\text{CH}_3\text{CN}$ , were also monitored over time (Fig. S3, ESI $^\dagger$ ). Though there is no immediate color change, over period of

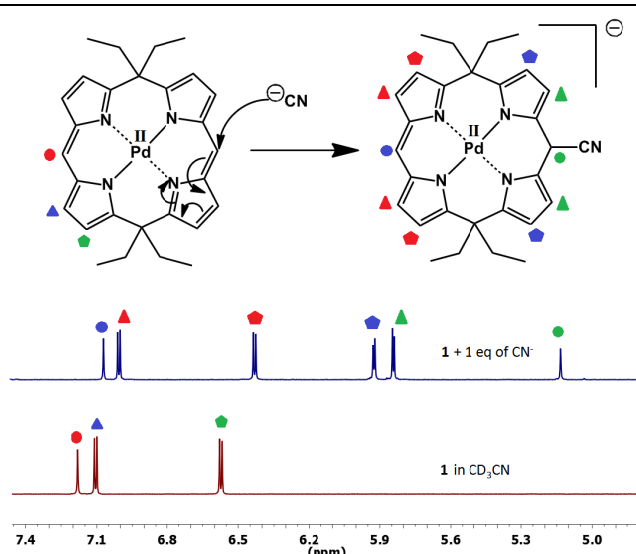


Fig. 3 Proposed mechanism of formation of  $[1.CN]^-$  adduct.

time the color of the solution gradually changes from yellow to red. The overall outcome is depicted in Fig. 2e where the band at 467 nm and 510 nm is monitored at different time intervals. The saturation was observed after 150 min. The changes in the absorption intensity at 467 nm and 510 nm could be fitted perfectly considering a pseudo first order kinetics with respect to the concentration of **1**. The rate constant for the conversion was calculated to be  $2.2 \times 10^{-2} \text{ min}^{-1}$ .

In order to get a clear insight about the binding mechanism and the interaction of  $CN^-$  with **1**, the  $^1H$  NMR titration experiments were conducted by gradual addition of tetrabutylammonium cyanide salt with 2.5 mM of **1** in  $CD_3CN$  (ESI†). The three set of peaks initially observed in **1** at 7.2 ppm, 7.1 ppm and 6.58 ppm, gradually decreased upon increasing the concentration of  $CN^-$ . At 1 equiv. of  $CN^-$ , the respective signals disappeared and six new peaks were observed between 5.1 ppm to 7.1 ppm, which suggests formation of a 1:1 adduct. Further increasing  $CN^-$  concentration, no appreciable change in the spectra was observed (Fig. S1, ESI†).

Efforts to crystallize the  $[1.CN]^-$  adduct have been unsuccessful. Nevertheless, the observations from the  $^1H$  NMR titrations have been rationalized and a possible mechanism of formation of the adduct is depicted in Fig. 3. The splitting of the aromatic peaks indicate a lowering of symmetry by the addition of cyanide to either of the *meso* carbon of **1** forming the  $[1.CN]^-$  adduct. As a result one of the *meso*-CH is converted to a saturated carbon and the corresponding  $^1H$  NMR signal is shifted upfield, where the *meso*-CH ( $sp^2$ ) signal resonates at 7.1 ppm, while the *meso*-CH ( $sp^3$ ) is observed at 5.1 ppm. The remaining four pyrrolic  $\beta$ -CH protons are resonated as doublet between 5.8 ppm to 7.0 ppm, respectively. The 1:1 adduct is further confirmed by ESI mass spectrometry analysis, where the adduct shows the molecular ion signal at  $m/z = 554.1665$  (calculated = 554.15) in the negative mode (Fig. S6, ESI†).

In summary, we have discussed the polymorphism observed in 5,15-porphodimethene Pd(II) complex. We have also successfully demonstrated the selective binding of  $CN^-$  at the *meso*-position of calixphyrin skeleton and justified the chemodosimetric sensor property of the mentioned complex. To the best of our

knowledge, such type of cyano adduct formation is hitherto unknown in calixphyrin chemistry. Moreover the nucleophilic attack at the unsubstituted *meso* position of the porphodimethene paves a new methodology for synthesis of functionalized unsymmetrical porphomethenes and calixpyrroles.

#### Notes and references

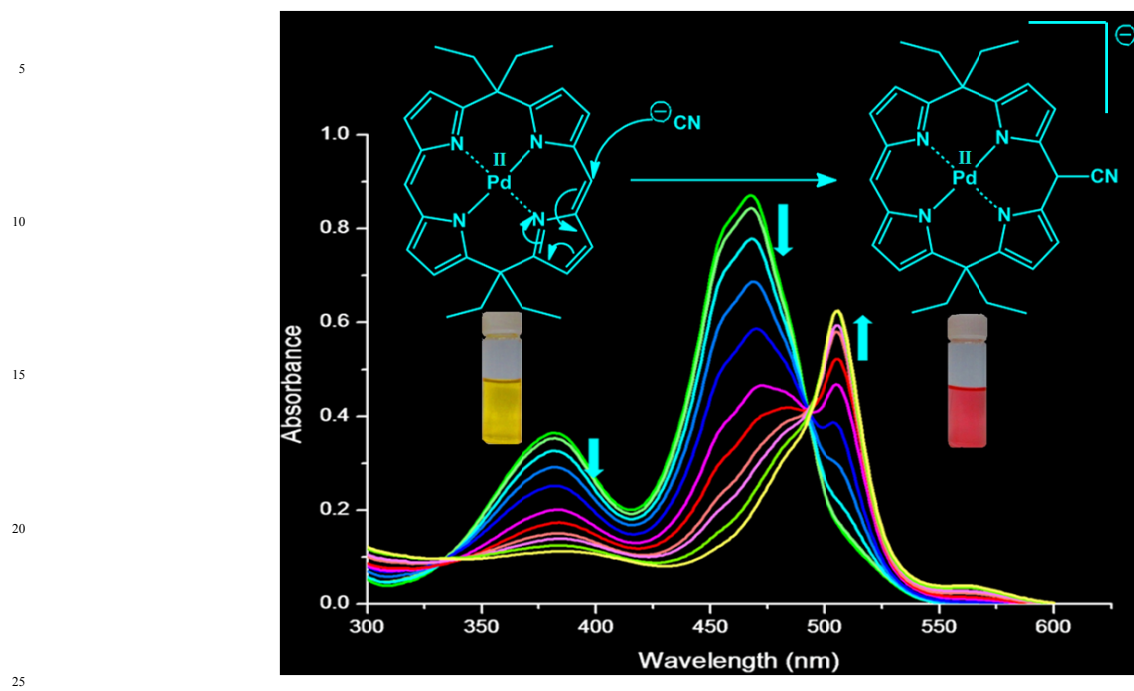
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†Electronic Supplementary Information (ESI) available: Spectral, structural characterization and anion binding studies of **1**. See DOI: 10.1039/b000000x/

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## TOC Graphic



The calixphyrin derivative, 5,15-porphodimethene Pd(II) complex has been demonstrated as a chemodosimetric cyanide sensor.