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Introduction

How paramagnetic and diamagnetic LMOCs detect picric acid from surface water and the intracellular environment: a combined experimental and DFT-D3 study†‡

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Diamagnetic and Paramagnetic Luminescent Metal Organic Complexes (LMOCs) have been reported for Explosive and Pollutant Nitro Aromatic (epNAC) recognition. The diamagnetic complex shows a highly intense AIE induced by NEt₃H⁺, which disappears after picric acid recognition and subsequently RET will quench the emission intensity. Radical stabilized paramagnetic LMOCs seem to be active but show lower sensing efficiency in comparison with diamagnetic LMOCs. Solution and solid state spectroscopy studies along with DFT-D3 have been executed to enlighten the host guest interaction. Limit of PA detection is ~250 ppb with a binding constant of $1.2 \times 10^5 \text{ M}^{-1}$. Time-stepping, *i.e.* intervening in the problem of picric acid recognition from surface water collected from several places of West Bengal, India, has been performed. Mutagenic picric acid has been successfully detected in an aqueous medium inside both prokaryotic and eukaryotic cells at a ppm level using fluorescence microscopy.

In recent days, Luminescent Metal Organic Complexes (LMOCs) are attracting much attention due to their vibrant and potential application in selective catalysis, sensing several sensational properties which are also similarly produced by other multifunctional materials.¹ Incorporation of suitable metal ions along with the selective luminescent organic skeleton could be a perfect choice in preparing LMOCs as a chemosensor. In very recent times, Prof. Li *et al.*, Prof. Mukherjee *et al.* and Prof. Ghosh *et al.* have reported the use of Luminescent Metal Organic Frameworks (LMOFs) as an explosive (such as picric acid or nitro benzoic acid *etc.*) chemosensor.²

Supramolecular LMOCs can be sub-categorised under LMOFs and the difference between MOFs and MOCs is that MOFs are

coordination polymers whereas MOCs are mostly supramolecular polymers. In comparison to MOFs, MOCs are easier to prepare, less expensive and posses a comparatively greener way of synthesis. With these added advantages and in the house handling experience of LMOFs as an explosive sensor, these researchers are compelled to focus on the development of LMOCs for rapid detection of such explosives concerning their wide application in forensic and criminal investigations. Homeland security is one of our major concerns as terrorist groups most commonly use IEDs (improvised explosive devices) in mostly crowded places as it is their calling card towards exposure of their ideology. Surprisingly, to date most of the devices and attention for explosive detection have been focused only on 2,4,6-trinitro toluene (TNT). There are several other such nitro explosives specially 2,4,6-trinitro phenol or picric acid (PA) whose explosion power is even more lethal than that of 2,4,6-trinitro toluene (TNT).^{2e} In between, deadly impacts are occurring one after another in our homeland where terrorists have used picric acid as one of the explosive materials.³

Apart from being used as an explosive, picric acid is well known due to its high toxicity when it is metabolized to picramic acid in the mammalian digestive cycle. Picric acid is under the category of nitro phenols which are known to be hematotoxic, hepatotoxic and promote mutagenesis and carcinogenesis inside human cells and other living organisms. It is an important key maker of several fungicides, analytical reagents, staining agents, fireworks, germicides, matches, glasses and leather industries.^{4a} It can be produced as a by-product of nitrobenzene synthesis. Therefore there is a huge possibility of incautious release of

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 $[\]dagger$ Dedicated to the martyrs of Pathankot, India who lost their lives in a terrorist attack in January, 2016.

[‡] Electronic supplementary information (ESI) available: ESI-MS, FT-IR data of both the ligand **dtHBAP** and Co metallated complex **PP**; X-ray crystallographic data of **PP**; UV-Vis spectra; CV; ESI-MS of the **PP**...TNP adduct; coordinates used in the DFT and DFT-D3 study; bond distances related to quinoidal distortion and the Stern Volmer plot; limit of detection calculation. CCDC 1430015 (**PP**). For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c6cp01620k

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epNACs like picric acid from industry to the environment, which may eventually cause serious detrimental impact to soil or the aquatic ecosystem equilibrium. Another possibility of picric acid contamination to ground water is unexploded land mines. These are found to contain unused nitro derivatives.⁴ With time there is a large possibility that these nitro explosives might contaminate the ground water and cause several pernicious effects to aquatic life. Therefore, detection of picric acid is vital, concerning its major impact on environmental and health-related issues, and significantly from the view of homeland security.

To date, the detection of epNACs is mainly dependent on canine's efficacy or other several sophisticated instrumental techniques. These techniques for epNAC sensing are not only expensive but also difficult to carry due to poor portability. In this regard, development of fluorescent MOCs for epNAC detection is nowadays drawing more attention for its unique features like safety, portability, high sensitivity, quick response time, cost effectiveness in preparation and detection. Prof. Mukherjee *et al.*, Prof. Ajayaghosh *et al.* and Prof. Ghosh *et al.* have recently reported several interesting imidazolium, carbazole, self assembled cage, pentafluoro unit base organogel molecules or Schiff base type compounds for detection of picric acid or tri nitrotoluene.⁵

In this connection, it will be very interesting to work with both diamagnetic and paramagnetic LMOCs as there is no such report of working with LMOCs as a supramolecular host for detection of epNACs. Diamagnetic MOCs normally interact with possible epNACs through strong hydrogen bonding. Precise modification in the backbone of MOCs makes them electrochemically sound for easy oxidation in the ligand centre, which will eventually produce a radical stabilized paramagnetic complex. The main reason for working with paramagnetic MOCs is the behavior of the loosely bound unpaired electron towards a guest like epNACs.

As a continuation of our ongoing research activity in coordination⁶ and supramolecular chemistry,⁷ in this report emphasis has been given towards preparation of an easy to make LMOCs in its both diamagnetic (**PP**) as well as paramagnetic (**PP**_{ox}) state. Paramagnetic **PP**_{ox} is a ligand centred phenoxyl radical complex, produced from the diamagnetic complex **PP** by both a chemical and electrochemical pathway. The phenoxyl radical stabilised ligand has been synthesized due to precise modification of the ligand by tertiary butyl group substitution. Tertiary butyl group functionalisation in the ligand **dtHBAP** has added advantages over the others:

(i) It makes the LMOCs electron rich and eventually highly emissive by improved charge transfer

(ii) Phenoxyl radical stabilized paramagnetic LMOC generation

Both diamagnetic and paramagnetic LMOCs can selectively detect picric acid by a spectrofluorimetric technique. Though **dtHBAP** has been previously explored,⁸ its diamagnetic and paramagnetic cobalt complex possibility has not been reported for sensing epNACs like picric acid. The reason behind choosing cobalt is that cobalt metallated complexes with a redox non-innocent multidentate Schiff base ligand mimics cobalamin (vitamin B_{12}), a metal complex in our body with a C—N linkage.⁹ In this perspective generation of a redox active and biologically

relevant phenoxyl radical metalloligand and its sensing and recognition property for picric acid like guest analyte will always be of interest. Herein authors briefly discuss the preparation of dia- and paramagnetic LMOCs (PP and PPox) confirmed by several characteristic studies like UV-Vis, EPR, and room temperature magnetic measurements and finally density functional theory (DFT) as supportive evidence in favour of paramagnetic LMOC generation. Detection of epNACs with both diamagnetic PP and paramagnetic PPox has been carried out. Thorough characterisation (both in solid and solution state) in support of their detection has been performed. Interestingly, a very strong supportive tool [e.g.; modern DFT (DFT-D3)] has also been carried out to investigate the sensing of picric acid by the host receptor.^{7c} DFT-D3 concerns about the polarisation factor of hydrogen make the outcome more accurate and effective. Resonance energy transfer (RET) has been found to be the best mechanism in explaining epNAC sensing.⁴ Moreover, detection has been performed not only from organic solvents but also from several surface water specimens too (collected from various parts of West Bengal, India) where commonly interfering agents like Na^+ , K^+ , Ca^{2+} , Mg^{2+} , Cl^- , HCO_3^- , SO_4^{2-} and gases O_2 , N_2 and CO_2 may be present and interfere with the fluorescence of the host. Still, the presence of those interfering agents has no way affected the quenching event even in a subtle amount. It is well known that picric acid is highly toxic to aquatic life and obviously to mankind. Therefore in vitro detection is highly necessary in line with saving aquatic life and for human health-related concerns. In line with this thought, in vitro detection of picric acid has been performed from both eukaryotic and prokaryotic cells through fluorescence microscopy.7a-d

Results and discussion

Synthesis and characterization

The ligand **dtHBAP** and its corresponding dia and paramagnetic cobalt coordination complexes (**PP** and **PP**_{ox}) are characterized by FT-IR, ESI-MS, UV-Vis, CV, EPR and single crystal X-ray study. In connection with the experimental evidences, density functional theory (DFT) has been carried out as a theoretical support for **PP**_{ox} formation. Modern DFT or DFT-D3 has been carried out in order to investigate the details of the PA sensing pathway with both **PP** and its oxidized product **PP**_{ox}. Significantly, the outcome of DFT-D3 is in line with fluorescence spectroscopy outcomes.

Crystallographic description of diamagnetic LMOCs

The synthesized Co complex **PP** (Scheme 1) crystallizes in a monoclinic space group P21/n (no. 14) (see Table S1, ESI‡) and shows distorted octahedral geometry. Two tridentate O,N,O donor Schiff base ligands are ligated with a central metal atom of cobalt and the overall charge of the complex is balanced by a counter cation NEt₃H⁺. Geometrically the complex is meridional and the relative orientations are *cis*[O1–O3], *trans*[N1–N2] and *cis*[O2–O5] respectively (Table S2, ESI‡). Two ligands are situated in a 90° fashion towards each other. In between two coordinated ligands, one is participating in a weak interaction with NEt₃H⁺



Scheme 1 Schematic representation of complex PP preparation.



Fig. 1 Zig-zag view of PP (green arrow shows the direction).

while the other doesn't (Fig. 1). An oxygen atom O(1) from the amino phenol unit of the participating ligand is weakly interacting with the N(3) atom of the counter cation NEt₃H⁺. Eventually, a weak interaction of the mononuclear complex makes a 1D zigzag supramolecular structure. The extensive hydrogen bonding makes a π - π interaction between tertiary butyl substituted units of one ligand with the amino phenol unit of the other ligand (bond distances are 4.2 Å). It shows a unique T shaped π - π interaction which results in a better fluorescence property of the complex **PP** (Fig. 2).¹⁰

In the crystal structure of **PP** no quinoidal distortions (reflecting two shorter C=C double bonds and four longer C-C bonds in a six member aromatic ring) have been observed. The chelate bite angle average of O2-Co1-N1 or O5-Co1-N2 (95.2°) is larger than the average chelate bite angle of O1-Co1-N2 and O3-Co1-N1 (86.2°), which is quite evident due to the difference



Fig. 2 Segmented polyhedral view of the supramolecular network of PP.

in their consecutive chelate ring size (Table S3, ESI‡). O2–Co1–N1 or O5–Co1–N2 is forming a six membered chelate ring, on the contrary for O1–Co1–N2 and O3–Co1–N1, the chelate ring is only five membered.

Electronic spectra and emission property of diamagnetic LMOCs

Electronic spectra of **dtHBAP** and **PP** have been recorded in a dichloromethane solvent $[1 \times 10^{-4} \text{ (M) conc.}]$ in the UV/Vis region (250–800 nm). The ligand (**dtHBAP**) exhibits one intense absorption peak at 290 nm and another transition around 385 nm, which can be assigned as phenolate $\pi \to \pi^*$ and $n \to \pi^*$ type transitions respectively.^{6*m*,11} A broad response around 480 nm can be assigned to intramolecular charge transfer. In the metal complex (**PP**) a new broad peak is again appearing at 520 nm apart from peaks at 275 and 390 nm (sh), which can be assigned as LMCT transitions (phenolate–Co^{III} charge transfer).^{6*m*,11}

Fluorescence experimentation for **PP** has been carried out in a 1×10^{-5} (M) concentration in acetonitrile (*vide supra*). It shows high emission of the receptor **PP**. The possible reasons of this high emission are as follows:

(a) Inhibition of the C=N bond rotation

(b) Extensive intramolecular charge transfer (ICT) inside the complex $\ensuremath{\textbf{PP}}$

(c) NEt₃H⁺ driven closely packed supramolecular entity for T shaped π - π interaction results in better charge transfer: in short it is an example of NEt₃H⁺ induced aggregation for better emission intensity.

Electrochemical study of diamagnetic LMOCs

Cyclic voltammetry study for **PP** [conc. 5 mM, scan rate 25 mV s⁻¹, temperature: 298 K, working electrode: platinum, supporting electrolyte: TBAPF₆ (0.10 mol dm^{-3})] has been executed in dichloromethane. The current vs. voltage curve shows one reversible and another quasi reversible response in the potential range \pm 1.2 V vs. saturated calomel electrode (SCE). In the oxidation region the reversible response at ~ 0.45 V can be attributed to ligand based oxidation of one of the schiff base ligands $(L)^{2-}$ to its corresponding phenoxyl radical species $(L^{\bullet})^{1-}$ (furthermore supported by EPR, spectroelectrochemistry and DFT; ESI‡) as there is hardly any scope for further oxidisation of the Co^{III} centre. The oxidative response is mainly reversible but the reductive one is not. In particular, when the tertiary butyl (-tBu) group having a high +I effect is present in a molecule, it makes the molecule electron rich and thus it becomes prone to oxidation and obviously difficult to reduce (Fig. S5a, ESI‡). The reversibility of the oxidation peak is verified under the domain of a mathematical perspective. In cyclic voltammetry, the Randles-Sevcik (R-S) equation is used to understand the effect of the scan rate on the peak current i_p (Fig. S5b, ESI‡).

Diamagnetic to paramagnetic LMOC preparation

Oxidised complexes are active due to the unpaired electron and several enzymatic pathways are known to proceed through a radical pathway. To the best of our knowledge, to date there is no direct evidence of working with a radical stabilised complex

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as a host for detection of picric acid like epNACs. It would be of enormous interest if a radical complex can be stabilised and investigated for epNAC sensing. A cyclic voltammetry study reveals that the Co-complex **PP** has a single reversible oxidative response at 0.45 V. Under an argon blanketing glove box the oxidation process of **PP** with AgNO₃ in a suitable potential range was executed in dry dichloromethane.¹² The X-band EPR study of the product obtained from the reaction has been executed in a dichloromethane–toluene (1:1) solution at liquid nitrogen (77 K) temperature. A single line curve suggests the presence of an organic radical in the chemically generated complex (Fig. S6, ESI‡). The room temperature (298 K) magnetic study supports the one electron paramagnetic nature of the complex ($\mu \sim 1.78$ BM).

A coulometric study in controlled potential for PP was executed in dichloromethane at required potentials for 1e⁻ oxidation under an argon blanketing atmosphere in order to produce the oxidized species by an electrochemical way. The species has also shown a similar nature as chemically generated species in EPR and the room temperature magnetic study. At this stage it is confirmed that **PP** is oxidized to an organic radical based complex (**PP**_{ox}) both chemically and electrochemically, but it is not yet confirmed whether the radical is azomethine or phenoxyl based. At this juncture spectroelectrochemistry helps regarding its radical feature. It has been noticed that a chemically and electrochemically oxidised complex shows a similar nature in the UV-Visible spectrum. In UV-Vis the changes at 390 and 680 nm can be treated as a marker of generation of phenoxyl radical species during oxidation of diamagnetic PP at a constant potential of 0.8 V (see ESI[‡] for details). The 390 nm peak gradually diminishes and a low energy band at 680 nm has concomitantly been generated.^{6m} Therefore, from a chemical and electrochemical perspective one can conclude that the 1e⁻ oxidised product is a paramagnetic Co^{III}-phenoxyl radical species (**PP**_{ox}).¹³

Density functional theory (DFT) calculations could be helpful as supportive evidence to further confirm the radical nature. Spin unrestricted Kohn–Sham (UKS) calculation with a B3LYP hybrid functional was executed for geometry optimization of the diamagnetic **PP** complex. Spin distributions along with the geometry optimization of paramagnetic **PP**_{ox} was also carried out with the same UKS and B3LYP functional.^{6a,d,e,m}

The diamagnetic complex **PP** shows no unpaired electron in the Loewdin spin density plot (Fig. 3a). In case of **PP**_{ox}, the spin density plot shows the presence of one unpaired electron over one **dtHBAP** ligand (Fig. 3b).



Fig. 3 Spin density population of (a) PP and (b) PPox.

Expectedly, quinoidal distortions for **PP**_{ox} have been observed. The ligand on which the electron density is delocalized has shown quinoidal distortion (*i.e.*; two shorter C==C double bonds and four longer C-C bonds in the six membered aromatic ring of paramagnetic **PP**_{ox} in comparison to diamagnetic **PP**). Other ligands have no such effect. This finding supports the existence of the one electron oxidized phenoxyl radical based species **PP**_{ox} (see Table S7, ESI‡).¹³

The proposed chemical formula of the complex PP after oxidation (PP_{ox}) is as follows:

$$[\mathrm{Co}^{\mathrm{III}}(\mathrm{L}^{2-})(\mathrm{L}^{2-})]^{1-} (S=0) \rightarrow [\mathrm{Co}^{\mathrm{III}}(\mathrm{L}^{\bullet 1-})(\mathrm{L}^{2-})]^0 (S=1/2)$$

(PP, colour: brown) (PP_{ox}, colour: reddish brown)

Picric acid recognition: analytical application of LMOCs

It is always important to explore the functional property of an easy to synthesize and economically viable ligand and its suitable metal complexes in the dia- as well as paramagnetic state. The same group has reported similar type of organic compounds as corrosion inhibitor.¹⁴ Herein, both the ligand and its Co metal complex are explored well in an emergent area of chemistry: picric acid recognition.

Picric acid is a very well known pollutant and it converts to mutagenic picramic acid during the mammalian metabolic process. It is also purposefully used as an explosive in several military applications. Several deadly impacts have taken place many times in recent years by terrorists where the use of picric acid was observed. Therefore selective detection of picric acid as an organic explosive and pollutant has become highly essential.

Keeping all these factors in mind, we have investigated the recognition of several epNACs such as 2,6-DNT (2,6-dinitro toluene), NB (nitro benzene), 1,3-DNB (1,3-dinitro benzene), 3,4-DNT (3,4-dinitro toluene), 3,5-dinitro benzoic acid (DNBA) and PA in a 5×10^{-4} (M) concentration in an acetonitrile : water (2 : 1, v/v) solution for titrating **PP** and **dtHBAP**. In case of titration with **PP**_{ox} the epNAC solution has been prepared in acetonitrile at the same concentration.

The 1×10^{-5} M acetonitrile solution of the host (ligand **dtHBAP** and complex **PP** and **PP**_{ox}) was used for the fluorescence titration study. **dtHBAP** shows emission at 560 nm at room temperature. Emission of **dtHBAP** actually remained unaltered after addition of picric acid. On the other hand, **PP** shows an intense emission at 430 nm, and upon gradual addition of picric acid (up to 2 equivalents) solution, the emission intensity was rapidly quenched (Fig. 4a). Other epNACs (upto 2.5 equivalents) like 2,6-DNT, NB, 1,3-DNB, 3,4-DNT and 3,5-DNBA didn't show any detectable influence on the emission of **PP** (Fig. 4a inset).

In the case of a radical stabilized complex the emission peak is more or less same in its position, but the nature is a bit different. Actually fluorescence is related with the electronic distribution of the complex, so if the distribution is altered then obviously it will influence the emission property of the complex. That's why the difference in the emission peak nature has been observed in the radical complex PP_{ox} . It is generally found that the unpaired electrons are loosely bounded. There must be chances of better



Fig. 4 Fluorescence response of (a) PP [inset: response of PP with other epNACs] (b) PPox with PA.

picric acid sensitivity by that unpaired electron. But, when picric acid [as of **PP**, *i.e.*; 2 equivalents] was added gradually it shows a comparatively weaker response in comparison with **PP**. Perhaps electron deficiency of the paramagnetic complex **PP**_{ox} is responsible for this anomaly (Fig. 4b). In addition, **PP** has been tested with nitrophenol and di nitrophenol (ESI,‡ Fig. S7).

Jobs plot

In order to measure the stoichiometric ratio of diamagnetic **PP** a series of solutions of picric acid and **PP** $(4 \times 10^{-5} \text{ M})$ have been prepared in acetonitrile solution. The fluorescence at 430 nm has been plotted against the mole fraction of picric acid. The curve indicates a 1:2 binding stoichiometry phenomenon between host **PP** and picric acid (Fig. 5a).

FT-IR study

In the solution state study it has been found that **PP** can recognise PA. Thus to investigate the recognition capability of **PP** in a solid state condition, a sophisticated tool like FT-IR has been purposefully used. It has been noticed that after interaction with **PP** the stretching frequency of PA has been shifted to a higher energy. The stretching at 1250 cm^{-1} responsible for C–N stretching has now been shifted to 1270 cm^{-1} . C–O bond stretching at 1145 cm^{-1} has swung to 1165 cm^{-1} . Symmetric stretching of –NO₂ group at 1340 cm^{-1} and asymmetric stretching at 1525 cm^{-1} have been moved to 1365 cm^{-1} and 1555 cm^{-1}



Fig. 5 (a) Jobs plot of host **PP** with guest PA, (b) FT-IR study of **PP** and PA complexation (blue: **PP**; cyan: PA; red: **PP** and PA mixture).

respectively (Fig. 5b). In every case the PA stretching has been moved to a higher wavenumber suggesting lowering of the bond length and enhancement of the bond order, which is basically the reflection of the withdrawing effect of the electron from **PP** to picric acid.¹⁵ This stretching event fully supports the formation of a supramolecular entity between **PP** and picric acid in a solid state too.

ESI-MS study

An appreciably strong hydrogen bonding interaction occurring between **PP** and picric acid is obviously reflected from the desired supramolecular aggregation between π electron rich **PP** and electron deficient picric acid. In order to investigate the stoichiometry of the adduct formed in between **PP** and picric acid, ESI-MS has been executed in a methanolic medium. In ESI-MS it was observed that at the most abundant peak around ~1165 amu reflects a 1:2 adduct (**PP**...picric acid) formation in between the formed adduct (ESI,‡ Fig. S8).

DFT-D3 study

The pathway through which the receptor **PP** is sensing PA needs to be explored for more vivid studies and for better insight into this current endeavour. In this connection, density functional theoretical calculation with dispersion factor can enlighten us to understand the interaction occurring between the host **PP** and guest analytes. The dispersion as well as polarization factor of the hydrogen atom have to be considered in this sort of interaction because PA or 3,5-DNBA contains dissociable protons. Modern DFT or DFT-D3 has been used herein, for correlation of the experimental and theoretical findings for **PP** with the guest analytes and thus to firmly establish a general methodology for using it which will be easier for predicting the receptor level of sensitivity and selectivity towards epNAC recognition before doing experiments.

In the host–guest interaction strategy, to find out whether the recognition pathway is based on a supramolecular domain or something else, DFT-D3 has been successfully executed. In the fluorescence titration study, the quenching is only observed with PA whereas other epNACs do not have any detectable influence on **PP** emission. In view of the above, to understand the host

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guest interaction of PP with analytes, a detailed computational analysis using ORCA (version 3.0.3, developed by Prof. Dr Frank Neese, Department of Molecular Theory and Spectroscopy, MPI für chemische Energiekonversion for ORCA)¹⁶ and version 6.5 for Turbomole has been carried out. The Becke-Johnson damping parameter has also been included during the calculation.^{7c} The coordinates and subsequent geometry of PP have been obtained from single crystal X-ray structural analysis data. After geometry optimization of PP, the converged geometry was taken for further study of the weak interaction between PP and guest analytes. During calculation, picric acid has been considered in a 1:2 ratio with PP. As a consequence, other analyte recognition events have been considered in a similar fashion (see Tables S8-S15, ESI[‡]). In the case of **PP**_{ox} a similar procedure for calculation is followed. dtHBAP is segmented from CIF of PP for execution of the DFT-D3 calculation.

An energy minimized geometry optimized structure leads to the conclusion that PA is no way interacting with the ligand **dtHBAP** (Fig. 6a), which is also quite evident from the fluorescence titration experiment. It is found that PA is positioned at around a 3 Å distance from the sensor **PP**. It is due to steric hindrance possessed by a bulky tertiary butyl group and coulombic repulsion ($\delta^+ \cdots \delta^+$) of phenolic protons between the receptor **dtHBAP** and guest analyte picric acid. In the case of **PP**, the phenolic hydrogen of PA is interacting strongly with the host



Fig. 6 PA complexation with (a) dtHBAP, (b) PP and (c) PP_{ox} in the DFT-D3 study.

phenolic oxygen unit/sidearm in the amino phenol part of the ligand [O1 (guest)-H1···O2 (host): 1.13 Å and 1.29 Å/ O1' (guest)–H1'···O2' (host): 1.12 Å and 1.30 Å] (Fig. 6b). PA is interacting with the host through its phenolic proton and thereafter facilitating the electron transfer from the host PP to the guest PA leading to fluorescence quenching. In the case of another acidic guest molecule, i.e.; 3,5-DNBA there is no such indication of an interaction. Picric acid, which is one of the important members of the epNAC family, is highly electron deficient and will obviously interact in better way with an electron rich receptor like **PP.** In this connection PP_{ox} is electron deficient in comparison with PP and thus after experimentation it was found that fluorescence quenching of PPox with PA is less efficient than PP as expected. In the DFT-D3 calculation, the distance between phenolic hydrogen of the PA unit and the host phenolic oxygen unit of the amino phenol part [O1 (guest)-H1···O2 (host): 1.03 Å and 1.56 Å/O1' (guest)–H1'···O2' (host): 1.04 Å and 1.52 Å] supports a comparatively weak bonding of PPox ··· picric acid (Fig. 6c). From the spin density calculation it was found that in one electron oxidised system (*i.e.*; **PP**_{ox}) the unpaired electron is predominantly residing particularly on one of the ligand sides only. Therefore it is expected that in between two host oxygen centres (amino phenol unit) of PPox, the one which is oxidised will interact less in comparison with the other centre where electron density remains unaltered. Significantly, in the geometry optimized convergent calculation it was found that PA spatially resided at about 1.56 Å from the oxidised ligand and to the level of our satisfaction it is residing at a decreased distance *i.e.*, 1.52 Å from the other ligand which is not that much affected after 1e⁻ oxidation. Herein PP has a higher electron density than PPox and thus it forms a stronger bond with guest electron deficient picric acid (newly formed bond distance: 1.30 Å).

It is noticeable that DFT-D3 in the present study supports the experimental findings very nicely and it can be corroborated that the PA recognition process solely belongs to the realm of the supramolecular chemistry world. In particular, the main driving force of sensing is the strong interaction between the guest and host through phenolic hydrogen sites of the arm of the receptor. To maintain the resemblance, a DFT-D3 study with other analytes has also been carried out. In line with experimental outcomes, herein also, other than picric acid, no other analytes participate in such a recognition event with the host **PP**. 3,5-Dinitro benzoic acid doesn't even show interaction through its acidic proton with the host **PP** (see Fig. S9–S13, ESI‡).

Insight into fluorescence quenching phenomena

The fluorescence quenching process of receptor **PP** with picric acid can be explained through resonance energy transfer (RET) and also in presence of NEt_3H^+ driven π - π interaction related phenomena. RET is a well acclaimed methodology for explaining fluorescence quenching. This phenomenon is mainly concerned about energy transfer occurring from an electronically excited donor chromophore to the acceptor (Fig. 7a). Selective sensing of picric acid in the presence of the complex **PP** by a fluorescence quenching phenomenon lead us to explore the chemistry behind it.



Fig. 7 Overlap zone of epNAC absorption spectra with fluorescence spectra of **PP** (blue: absorption spectra of epNACs and red: emission spectrum of **PP**).

RET can be said to have an effect in fluorescence quenching. The S-V plot for **PP** (Fig. 7b) suggests a resonance energy transfer between PA and **PP** in this present case, [where $(I_0/I) = K_{sv}(A) + 1$; I_0 = initial fluorescence intensity of **PP** and I = fluorescence intensity of **PP** in the presence of epNACs, {A} = molar concentration of epNACs and K_{sv} = quenching constant (M^{-1})].⁴ The non linear characteristic in the S–V plot of **PP** depicts that the quenching phenomenon basically relies on an energy transfer pathway. The calculated K_{sv} value is $1.2 \times 10^5 M^{-1}$. The PA detection limit calculated for **PP** is 250 ppb (see ESI‡).

In the resonance energy transfer process, the resonance energy can be easily transferred from an excited fluorophore to electron deficient analytes if an overlap persists between the absorption band of analytes with the emission band of the fluorophore (**PP**). It is noteworthy to mention that the level of energy transfer depends on the extent of spectral overlap between the analyte absorption band and the emission band of **PP**.

It could be noticed (Fig. 8) that among the investigated epNACs, picric acid shows the maximum spectral overlap with **PP** while for other epNACs the extent of overlap is significantly less. Therefore RET is certainly the responsible route for explaining the fast and rapid fluorescence quenching of **PP** with picric acid.

In case of **PP**, it is a supramolecular host and shows high emission due to a NEt₃H⁺ driven closely packed T shaped π - π interaction in the complex; AIE (aggregation induced emission). When picric acid comes in closer vicinity it forms a strong hydrogen bond with the host **PP**. Therefore the π - π interaction is reduced and the supramolecular building block collapsed as, due to steric hindrance, it is not possible to form further supramolecular networks in the presence of picric acid. Eventually, the emission quenched, *i.e.* NEt₃H⁺ induced aggregation for emission (AIE) disappears and RET comes into the scenario for quenching



Fig. 8 Selectivity of PP over picric acid compared to other epNACs.

the emission. On the other hand, in the case of **PP**_{ox}, it is a neutral complex and thus has no chance of becoming a supramolecular host by a NEt₃H⁺ driven pathway as with **PP**. Thus no chance of a π - π interaction is there which results in a lower fluorescence intensity of the complex **PP**_{ox}. RET is the only reason for emission quenching for paramagnetic **PP**_{ox} with picric acid.

Selectivity of picric acid sensing over other epNACs

It has been already discussed that paramagnetic $\mathbf{PP_{ox}}$ is less sensitive and diamagnetic \mathbf{PP} shows better selectivity (*vide supra*). To establish \mathbf{PP} as a universal sensor, *i.e.* \mathbf{PP} can detect picric acid in the presence of other epNACs, an interference study has been performed by the following steps:

(I) The emission of PP in MeCN has shown appreciable emission intensity ($\sim\!980$ a.u.).

(II) A concentrated solution of epNACs like 2,6-DNT (10^{-2} M) has been added in the **PP** solution and the corresponding emission has been monitored. 2,6-DNT has been added to check the affinity towards **PP**, which shows negligible impact on **PP** emission. A more or less similar trend was observed with other epNACs like; NB, 1,3-DNB, 3,4-DNT, and 3,5-DNBA, where epNACs (other than PA) have shown almost negligible influence on **PP** emission. So, it can be concluded that, other than PA, all epNACs have more or less no effect on **PP** emission.

(III) Addition of a PA aqueous solution to epNACs (2,6-DNT, NB, 1,3-DNB, 3,4-DNT and 3,5-DNBA) containing **PP**, resulted in appreciable quenching of emission (high degree of fluorescence quenching \sim 96%).

These results establish the selective sensitivity of picric acid by **PP** in the presence of several other epNACs (Fig. 8).

Picric acid detection from an environmental surface water specimen collected throughout various parts of West Bengal, India

Picric acid is an explosive and toxic organic pollutant, which can be converted to mutagenic picramic acid during the mammalian metabolic process. Selective detection of picric acid as an organic explosive as well as pollutant is highly essential not only from an organic medium but also from natural surface water resources where several interfering agents are present. We have collected several surface water specimens throughout West Bengal, India (see ESI‡ for complete details). It was found that **PP** showed a better response than **PP**_{ox}. Therefore a picric acid response study in the surface water has been performed with **PP**.

Specimen I: rural area, central-western area of West Bengal, India (Bardhaman development authority supplied water).

Specimen II: north western part of West Bengal, India (Dubrajpur hand pump water).

Picric acid solution (1 mM) has been prepared with the collected natural water specimens (Specimen I–VI) and their effect was monitored on **PP** emission. An appreciable quenching in fluorescence emission was observed for each and every case study (Fig. 9).

It is worth mentioning that the blank water samples (without picric acid) don't have any detectable effect on **PP** emission. Therefore, it can be concluded that, irrespective of water





Fig. 9 Recognition of picric acid from surface water specimens by fluorescence quenching of $\ensuremath{\text{PP}}$.

resources, the **PP** emission quenching can happen in the presence of a PA solution. The outcome firmly establishes the ability of **PP** as a universal fluorescent sensor of PA like an organic nitroaromatic explosive and mutagenic water pollutant.

In vitro detection of picric acid

Paper

As picric acid is a highly toxic water pollutant and may affect all the soft tissues and organs of the human body, *in vitro* picric acid detection is very urgent for quick and easy identification of this contaminant in natural bodies water. To date there are no such reports found where *in vitro* picric acid detection is reported. We have chosen this highly emissive complex **PP** in order to detect picric acid inside cells. In West Bengal, Durgapur is an industrial belt and the surface water in most cases is polluted with several toxic substances or other elements as well. To establish **PP** as a universal sensor of picric acid, we have performed biological detection of picric acid inside cells grown in the surface water collected from Durgapur (see ESI‡ for details).

For the *in vitro* detection study two different types of living cells *viz. Candida albicans* (IMTECH no. 3018) (Fig. 10a and b) and pollen grains of *Techoma stans* (Fig. 10c and d) have been used. *Candida albicans* is prokaryotic and pollen grains are eukaryotic cells. During the fluorescence titration study, it was noticed that the emission of **PP** is quenched with gradual addition of picric acid. Herein, first of all, the cells were incubated in a **PP**



Fig. 10 In vitro picric acid detection by **PP** in both prokaryotic (a and b) and eukaryotic cells (c and d).

solution and after a forty five minute interval those cells were again incubated in a picric acid solution for thirty minutes. The control cells are obtained by staining with **PP** only (see Experimental section for details about the preparation of cells and procedure of cell imaging). Noticeably, the blue-green emission of the **PP** stained cells is quenched with incubation in picric acid contaminated water.

Conclusions

Diamagnetic as well as paramagnetic Luminescent Metal Organic Complexes (LMOCs) have been synthesized and thoroughly characterized for Explosive and Pollutant Nitro Aromatic (epNAC) recognition. A tertiary butyl substituted diamagnetic complex has been oxidized to a paramagnetic complex by both chemical and electrochemical pathways. The diamagnetic complex has NEt₃H⁺ induced AIE and shows a highly intense emission. AIE disappears after picric acid recognition due to the positional change of NEt_3H^+ by picric acid. Due to a steric effect of picric acid there is no chance of a π - π interaction between two adjacent benzene rings of the host complex. In addition, resonance energy transfer is also coming into action, which together results in the quenching of emission. Paramagnetic LMOCs seem to be more active than diamagnetic LMOCs, showing lower emission intensity and sensing efficiency in comparison with diamagnetic LMOCs. Insightful solution as well as solid state analytical tools along with DFT-D3 have been carried out to enlighten the host guest interaction. The binding constant is $1.2 \times 10^5 \text{ M}^{-1}$ and the PA detection limit is 250 ppb. As a daily life application, detection of picric acid from surface water collected within West Bengal, India has been successful. Being toxic and mutagenic, picric acid is always harmful to the living organism; diamagnetic LMOCs can detect picric acid inside both eukaryotic (pollen grains of Techoma stans) and prokaryotic cells (Candida albicans, a diploid fungus) using fluorescence microscopy in an aqueous medium. Several research projects with variable LMOCs as explosive sensors are under active progress in our laboratory.

Experimental section

Materials

All chemicals used for synthesis are of analytical grade. Precursor metal salt $CoCl_2 \cdot 6H_2O$ and other chemicals *e.g.*, 3,5-ditertbutyl salicylaldehyde, 2-amino phenol, and triethyl amine were purchased from Merck India Pvt. Ltd, S.D. Fine Chemicals and used without any further purification. AgNO₃ was purchased from Merck India. Picric acid was obtained from Lobachemie, India. Nitro benzene was purchased from Merck India. 2,6-Dinitro toluene, 1,3-dinitro benzene, and 3,4-dinitro toluene were procured from Sigma Aldrich. 3,5-Dinitro benzoic acid was obtained from Nice chemicals, Kerala, India. Solvents such as dichloromethane (DCM), tetrahydrofuran (THF) and diethyl ether were purchased from Merck India Pvt. Ltd and dried over activated molecular sieves and fused calcium chloride then finally distilled before use. Other solvents *e.g.*, methanol, hexane

(**Caution**: since PA is highly explosive and toxic in nature, care should be taken during use!!)

Instrumentation

A Perkin Elmer 2400C elemental analyzer was used to collect the micro analytical (C, H, N) data. UV-Visible spectroscopy was done on an ALS-SEC2000 spectrophotometer. A FT-IR spectrometer (spectrum 65, Perkin Elmer) instrument was used for FT-IR studies (with KBr pellets). A CMS (compact mass spectrometer, Serial no.: 3013-0140, Advion) was used for ESI-MS. The magnetic susceptibility experiment was carried out at room temperature (298 K) on a Sherwood Magnetic Susceptibility Balance. SP-150 Biologic, France made the Potentiostat-galvanostat used for electrochemical measurements. Cyclic voltammetry (CV) was performed in dichloromethane solution under an Argon medium containing tetrabutylammonium hexafluorophosphate (TBAPF₆) $(0.10 \text{ mol } \text{dm}^{-3})$ as the supporting electrolyte. The CV experimentation was done in a three electrode configured system with a varied scan rate of $\sim 25-170$ mV s⁻¹. A platinum electrode (6 mm diameter) was used as the working electrode. A platinum wire was used as the counter electrode, and saturated calomel electrode (SCE) was used as the reference electrode. SEC-C05 thin layer Quartz glass spectroelectrochemical cell kit (light pass length of 1 mm) with a SEC-C05 platinum gauze working electrode (80 mesh) and SEC-C05 platinum counter electrode were used for spectroelectrochemical measurements. A Ferrocenium/ferrocene (Fc⁺/Fc) couple (0.38 eV) was the reference internal standard to all potentials. Varian, USA made E-112, ESR spectrometer was used for electron paramagnetic resonance (EPR) spectroscopy. Density functional theory (DFT) and DFT-D3 calculations were carried out in a Z-200 workstation with the help of the ORCA program package (version 3.0.3) and Turbomole software. The argon blanketing M-Braun glove box was used to perform the oxidation reaction of the Co complex PP to PPox.

Synthesis of dtHBAP

Ligand **dtHBAP** was prepared by simple condensation of 3,5ditertbutyl salicylaldehyde and 2-amino phenol in methanolic medium at a 1 : 1 ratio at room temperature. The yellow colored product thus obtained was dried under vacuum. Anal. calc. $C_{21}H_{27}NO_2$: C, 77.50; H, 8.36; N, 4.30%. Found: C, 77.30; H, 8.16; N, 4.38%. ESI-MS (*m*/*z*, -ve mode): calc. 325.2, found: 324.2 (Fig. S1, ESI‡). FT-IR (ν , cm⁻¹, KBr disk): 3540(s), 2950(s), 1615(s), 1580(s), 1490(s), 1422(s), 1250(s), 1170(s), 970(s) (Fig. S2, ESI‡).

Synthesis of diamagnetic LMOCs

Ligand (**dtHBAP**) (650 mg, 2 mmol) was taken in 30 mL of methanol. Triethyl amine as a base (560 μ L, 4 mmol) was added. A methanolic solution of the metal [Co^{II}Cl₂·6H₂O (238 mg, 1 mmol)] was added at a time to the ligand solution. An immediate color change from reddish orange to brown was noticed (Scheme 1). Aerial oxidation lead to the +3 oxidation state of the cobalt center from +2. At room temperature, after

6 h of stirring, excess solvent was removed under vacuum to get complex **PP**. A microcrystalline brown colored product thus obtained was re-dissolved in dichloromethane and layered with hexane to get single crystals of **PP** suitable for X-ray analysis. Anal. calc. for C₄₈H₆₆CoN₃O₄: C, 71.35; H, 8.23; N, 5.20%. Found: C, 71.29; H, 8.21; N, 5.21%. ESI-MS (*m*/*z*, –ve mode): calc. 706.4, found: 705.9 (Fig. S3, ESI‡). FT-IR (ν , cm⁻¹, KBr disk): 2945(s), 1605(s), 1515(s), 1470(s), 1420(s), 1305(s), 1160(s), 1020(s) (Fig. S4, ESI‡).

Synthesis of paramagnetic LMOCs

AgNO₃ (17 mg, 0.1 mmol) as an oxidizing agent was added to the stirring solution of **PP** (~71 mg, 0.1 mmol) in dry dichloromethane (5 mL) under an argon blanketing glove box. The brown color of **PP** changed to reddish brown after 5 h of the reaction. The reaction mixture was filtered through celite and excess solvent was removed under pressure. **PP**_{ox} thus obtained was taken for further study. The room temperature magnetic susceptibility measurement shows that **PP**_{ox} is paramagnetic ($\mu \sim 1.78$ BM). Anal. calc. for C₄₂H₅₀CoN₂O₄ calc.: C, 71.47; H, 7.14; N, 3.97%. Found: C, 71.25; H, 7.07; N, 3.89%. FT-IR (ν , cm⁻¹, KBr disk): 2980(s), 1615(s), 1550(s), 1475(s), 1445(s), 1350(s), 1250(s), 1145(s).

DFT study

DFT calculations have been carried out for $[Co^{III}(dtHBAP)_2]$ $[NHEt_3]$ (**PP**) in its different plausible oxidation states [0 or -1]with the ORCA programme package (version 3.0.3).^{16,17} Geometry optimizations were performed with the B3LYP functional. All electron Gaussian basis sets were developed by the Ahlrichs group.¹⁸ In the calculation, TZV(P) triple- ζ quality basis sets were used with one set of polarization functions on a central metal and also on other atoms which are directly coordinated to the central metal. In case of atoms like carbon and hydrogens, slightly smaller polarized split-valence SV(P) basis sets were used which were of double- ζ quality in the valence region and have a polarizing set of d functions on the nonhydrogen atoms. SCF calculations were converged tightly $(1 \times 10^{-8} \text{ Eh in energy},$ 1×10^{-7} Eh in the density change, and 1×10^{-7} in maximum element of the DIIS error vector).19 The geometry searches for PP were carried out in their redundant internal coordinates without imposing any constraints in their geometry. Corresponding²⁰ orbital and density plots were performed using Molekel.²¹

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