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Highly selective detection of Palladium and Picric acid by a Luminescent MOF: A Dual functional fluorescent sensor

Suresh Sanda,[a] Srinivasulu Parshamoni,[a]† Soumava Biswas[a]† and Sanjit Konar *[a]

A Zn(II) based luminescent Metal Organic Framework is synthesized which acts as dual functional fluorescent sensor to detect picric acid and palladium(II) selectively.

Currently, the sensitive and selective detection of nitro explosives has been attracted an immense attention due to their broad range of applications in security operations, environmental protection, forensic investigations and mine-field analysis.[1] Among the common nitro explosives such as 2,6-dinitrotoluene (2,6-DNT), 2,4-dinitrotoluene (2,4-DNT), 2,4,6-trinitrotoluene (TNT), 2,4,6-trinitrophenol (TNP or Picric acid (PA)) and nitrobenzene (NB), PA is extremely hazardous and strong explosive. However, little attention has been paid for the sensitive and selective detection of PA.[2] Besides, PA is also commonly used in leather and pharmaceutical industries, dyes, fireworks and can be easily contaminated into ground water and soil once it released to the environment.[3] Furthermore, contamination of PA in ground water and soil can creates severe health problems like anemia, male infertility, respiratory organs damage etc.[4] Thus the selective, rapid and convenient detection of PA is on high demand for preventing environmental pollution and tracing buried explosives. On the other hand, as a rare transition metal, Palladium (Pd^{2+}) has wide spectrum of applications in materials, electronics and heterogeneous catalysis.[5] However, the presence of palladium even in extreme low concentration can create very serious health complexity such as cytotoxic effects, skin and eye allergies.[6] Apart from this, Pd^{2+} ions can bind to biomolecules such as amino acids, DNA and RNA, proteins and regulate a variety of cellular processes.[7] In order to restrict such hazards, environmental agencies proposed that, the maximum dietary intake of Palladium is <1.5-15 µg day^{-1} per person and its threshold in drugs is 5-10 ppm.[8] Therefore, the highly selective and sensitive detection of trace amounts of Pd^{2+} is also very important in environmental as well as human health concerns.

Although various spectroscopic and analytical techniques are known for the detection of nitroaromatics and hazardous metals but many of them are expensive, less sensitive and have portability issues during in-

field use.[9] Recently, Fluorescence-based chemosensors for the detection of nitroaromatics or metal ions have attracted great attention because of their high sensitivity, portability, rapid response time and convenient visual detection.[10] Among the several fluorescence based sensors, Metal Organic Frameworks (MOFs) have emerged as a new generation sensors for explosives and metal ions due to their designable architectures and tunable chemical and physical properties.[1, 11] MOFs have already been proved as an intriguing class of materials owing to their tremendous potential for diverse applications.[12] In particular, luminescent MOFs provide several advantages over conventional fluorophores.[1] It has been reported that, introduction of electron rich π-conjugated ligands for the construction of MOFs could give an efficient luminescent sensory material for the detection of nitroaromatic explosives.[1]

In this work, we have chosen a highly conjugated, rigid bpeb linker (bpeb = 1,4-bis [2-(4-pyridyl)ethenyl] benzene) in combination with π-electron-rich tetra-topic carboxylate ligand (H4tcpb = 1,2,4,5,-Tetrakis(4-carboxyphenyl)benzene) and synthesized a new luminescent MOF ($\{[Zn(C_{34}H_{18}O_8)_{0.5}(C_{20}N_2H_{16})_{0.5}]\cdot 0.5(C_{20}N_2H_{16}).2H_2O]\}_n$ (**1**) with $Zn(NO_3)_2\cdot 6H_2O$. Although several Luminescent MOFs have been reported for the sensing of nitroaromatics and metal ions, but there is only one report available in the literature on specific sensing of Palladium by MOF material[13] and there is no report on the dual sensing property of any MOFs for the selective detection of PA and Pd^{2+}. The present compound shows the sensitive and selective detection of trace amounts of PA or Pd^{2+} even in presence of other competing analogues and works as an efficient dual sensor.

SC-XRD analysis revealed that compound **1** crystallizes in triclinic system with *P*-1 space group and the asymmetric unit contains a Zn(II) cation, half of a tcpb ligand and one bpeb linker (Fig. S3). Each Zn(II) center adopts a square pyramidal geometry with four oxygen atoms from four different tcpb ligands and one nitrogen atom from bpeb linker (Fig. S4). The structure of compound **1** consists a paddle wheel type SBU ($[Zn_2(1,2,3,4-tcpb)_4(bpeb)_2]$) with two Zn(II) centers, four tcpb ligands and two bpeb linkers (Fig. 1a). Each tcpb ligand holds four

SBUs and forms a 2D layer on the *bc*-plane (Fig. 1b, Fig. S5). These layers are further pillared by bpeb linkers resulting a 3D interpenetrated framework with one dimensional channels along the *b*-direction (Fig. 1c). It is interesting to notice that, compound **1** contains two types of bpeb linkers, one is co-ordinated to two Zn(II) centers in bi-dentate fashion and the other one remains uncoordinated and resides in the channels (Fig. 1c). The free bpeb ligands are stabilized by noncovalent interactions (such as localized and semilocalized C-H···π [C56-H56···C6 = 2.835(4) Å], [C52-H52···C3/C4 = 2.614 Å], C-H···N [C39-H39···N3 = 2.689(4) Å] respectively) (Fig. S6). It is noteworthy to mention that, the 1D channels in the framework are occupied by bpeb ligands with coplanar π-conjugated arrangement and the walls are lined with π-electron-rich benzene moieties of tcpb making overall framework electron rich in nature.
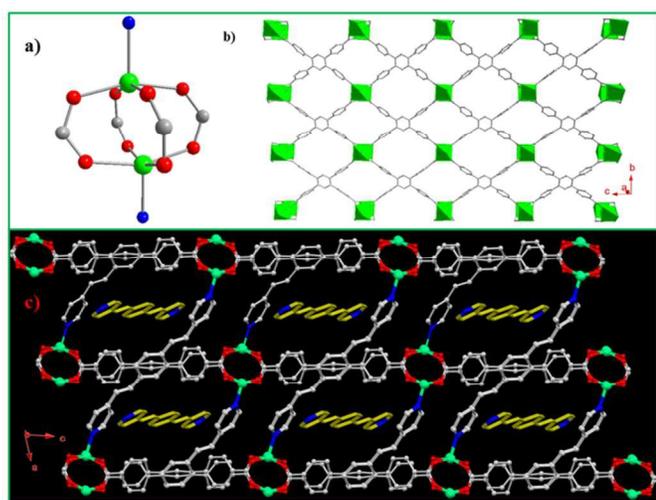

Fig. 1. a) SBU of compound **1,** b) illustration of 2D layer along the *a*-axis, c) 3D view of compound **1.** Color code**:** Zinc (green), Oxygen (red), Nitrogen (blue), Carbon (grey).

The ligand arrangement as well as the π-electron rich environment in the entire framework stimulated us to investigate the sensing behavior of compound **1** towards nitroaromatic explosives. The photoluminescence spectrum of compound **1** dispersed in DMF exhibits a strong fluorescence band at 415 nm with a small shoulder at 393 nm upon excitation at 340 nm (Fig. S9). The shoulder is due to the inter-ligand charge transitions (LLCT) between free bpeb and co-ordinated bpeb ligands.[14] To check the sensing ability of compound **1** towards different nitro aromatics, the fluorescence titration experiments have been carried out with the dispersed compound **1** by gradual addition of 1 mM stock solutions of various nitroaromatics such as NB, 1,2-DNB (1,2-dinitrobenzene), 1,3-DNB (1,3-dinitrobenzene), 1,4-DNB (1,4-dinitrobenzene), 4-NT (4-nitro toluene), 2,4-DNT, 2,6-DNT and PA. As shown in Fig. S10-S16 incremental addition of NB, 2,6-DNT, 2,4-DNT had minor effect on fluorescence intensity of compound **1** whereas 4-NT, 1,2-DNB, 1,3-DNB, 1,4-DNB shown negligible effect. Interestingly, compound **1** shows very good sensing behavior towards PA by quenching the initial fluorescence intensity by 94% (calculations in ESI) after adding 15.2 ppm of PA (Fig. 2a, c). The major fluorescence quenching of 26% can be clearly observed even at very low concentration of PA (1.5 ppm). The quenching efficiency of

compound **1** is amongst the highest values reported for MOFs.[1, 2a, 4a] In addition to this, upon gradual addition of PA to the solution of compound **1**, an immediate color change from colorless to pale yellow was observed which signifies a naked eye detection. However, in presence of other analytes no considerable color change in the solution of **1** was noticed (Fig. 2b). To verify the fluorescence response of **1** towards other aromatic substituents we have also performed the sensing experiments with Dimethyl benzene (DMB), Bromobenzene (BB) and 1,2-diamino benzene (1,2-DAB) but negligible quenching was observed (Fig. S17-S19). This indicates that, there is a strong interaction between PA and compound **1** which helps to show the high selective sensing behavior towards PA.
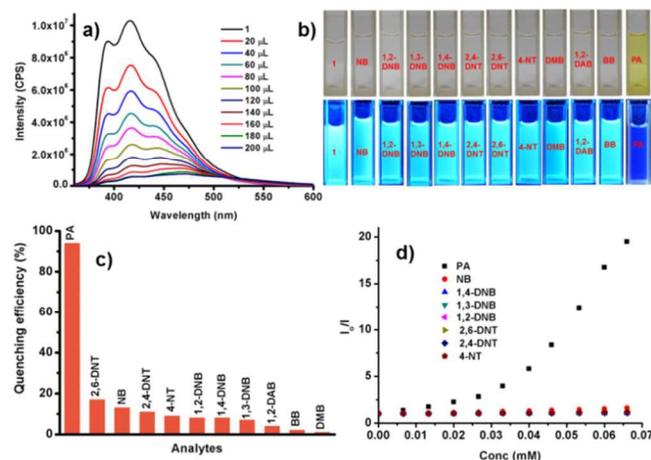

Fig. 2. a) The change in fluorescence intensity of compound **1** with incremental addition of PA. b) Digital photographs of solutions of compound **1** in the presence of different nitroaromatic analytes under normal light (top) and under portable UV light (bottom), c) The fluorescence quenching efficiencies of different analytes, d) Stern-Volmer plot for various nitro analytes.

To investigate reason behind the selective sensing of PA as well as the quenching mechanism, we analyzed the quenching efficiencies of all the analytes by using Stern-Volmer equation[15] (Details in ESI). The plot with PA shows a linear increase at low concentrations which upon deviates from linearity and turns to upward direction with increasing concentrations whereas the other nitro analytes showed only linear trend in S-V plots (Fig. 2d). From the linear fitting of the plot, the quenching constant for PA was found to be 8.1 x 10^4 M^{-1} which indicates the super quenching ability of compound **1** towards PA. To the best of our knowledge, this is the highest quenching constant value among the reported MOFs for selective sensing of PA to date.[1] The nonlinear trend in the S-V plot is indicative of the energy transfer between PA and the framework or due to the combination of static and dynamic quenching mechanisms.[15] These two mechanisms can be differentiated by measuring the life time of sensor in the presence and absence of the quencher. In the static mechanism the life time of the sensor will remain unchanged due to the formation of non-emissive ground state complex through the bonding between fluorophore and quencher. In dynamic quenching mechanism, the life time will be reduced due to the electron transfer between the excited state sensor and quencher through diffusion controlled collisions.[15] To explore the quenching mechanism, we measured the fluorescence life time of compound **1** before and after the addition of PA. The average life time

remain unchanged even after the addition of PA suggesting that the quenching process follows static mechanism (Fig. S20). To get deeper insight, we have recorded the UV-vis spectrum of compound **1** in presence of PA (Fig. S21) and found that, upon gradual addition, a new band at 423 nm was appeared which confirms the formation of non-emissive ground state complex and also supporting the static mechanism.[2a] In case of other nitroanalytes no considerable change was observed in the spectral pattern (Fig. S22). From the above spectroscopic results it is very clear that there is a strong interaction between PA and compound **1** in the ground state. As PA contains two types of functional groups, to verify whether the hydroxyl group plays any role in sensing, we have done some experiments with hydroxyl substituted aromatic molecules but without nitro groups like catechol, 4-iodo phenol, 4-methoxy phenol, phloroglucinol. As shown in Fig S23-S26, no considerable quenching was observed in the emission spectrum with incremental addition of analytes which confirms that the whole PA molecule is playing the role in sensing.
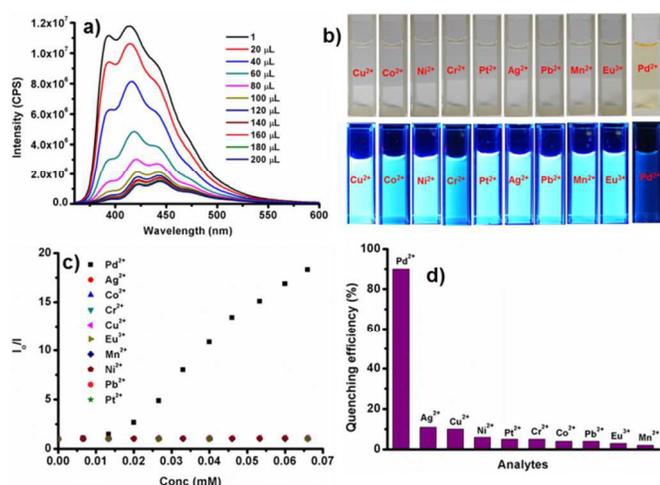

Fig. 3. a) The change in fluorescence intensity of compound **1** with incremental addition of Pd[2+] solution. b) Digital photographs of solutions of compound **1** in the presence of different metal ions under normal light (top) and under portable UV light (bottom), c) Stern-Volmer plot for various metal ions. d) The fluorescence quenching efficiencies of different metal ions.

To get more perception in to the selective sensing behavior of **1** towards PA in presence of other interfering nitro analytes, we performed some competition experiments by sequential addition of different nitroaromatics followed by PA into compound **1** and the corresponding emission spectra were recorded. As shown in Fig. S27-S33, the initial addition of different analytes show negligible intensity quenching but an effective quenching was observed after addition of PA solution. The similar trend was observed for almost all the nitroanalytes even in high concentrations which demonstrates the exceptional selectivity of compound **1** for PA.

From the crystal structure, it can be seen that the pores are almost occupied by the free bpeb linkers and there is no chance for encapsulation of the nitroanalytes in to the pores. The adsorption isotherm of **1** with N_2 further suggests that the fluorescence quenching due to the encapsulation of analytes is ruled out here (Fig. S34). The mechanism behind the fluorescence quenching might be due to the photo induced electron transfer between the electron rich framework

and electron deficient analyte adsorbed on the surface[4a] as compound **1** has plenty electron rich components such as highly conjugated carboxylic acid ligands and two different types of long delocalized neutral spacers in the pores (Fig. 1C, Fig. S6). To get more insight into this mechanism, we have calculated the HOMO-LUMO energies of the employed nitroanalytes by DFT at the B3LYP/6-31G* level as shown in the Fig. S35 and from the results it can be anticipated that the observed maximum fluorescence intensity quenching is due to easy electron transfer from framework to the lowest LUMO energy level of PA compared to the other nitroanalytes (Table S3).[1a, 9, 10a] However, the order of observed quenching efficiency is not in full agreement with the corresponding LUMO energies of other nitroanalytes which indicates that, electron transfer is not the sole mechanism for intensity quenching.[9,3b, 10a] To investigate this, we have recorded the UV-vis spectrum for all the nitroaromatics (Fig. S36). Among all, only PA shows the maximum spectral overlap with the emission spectrum of compound **1** whereas for other nitroanalytes it is negligible. From the non-linearity in the S-V plot and the spectral overlap of PA with **1** it is quite clear that the resonance energy transfer mechanism along with the electron transfer mechanism is responsible for selective fluorescence quenching with PA whereas for other nitroanalytes the fluorescence quenching is happening only through electron transfer mechanism.[1, 10a]

As we mentioned earlier, the crystal structure of compound **1** possess two different types of bpeb linkers in the pores as well as on the walls and thus it is expected that the alkene (-CH=CH-) moieties in the bpeb linkers could facilitate the selective sensing behavior towards Pd[2+] ions. In the typical experiment, the fluorescence spectra of **1** were recorded upon incremental addition of Pd(NO$_3$)$_2$·xH$_2$O solution in DMF (1 mM). As expected, the gradual addition of Pd[2+] solution into **1** resulted in fast and high fluorescence quenching (90%) with the significant spectroscopic variation (Fig. 3a). Compound **1** also displays selective chromogenic behavior towards Pd[2+] with a color change from colorless to grey, which was observed by naked eye (Fig. 3b). Specifically, compound **1** could detect Pd[2+] even in the concentrations of as low as 0.03 ppm. It is worth mentioning that, the calculated detection limit of 0.03 ppm is much below the permissible limit of 5-10 ppm set by the World Health Organization (WHO) for Pd[2+] in drug chemicals and this value fall in the range of reported fluorescence probes for selective Pd[2+] sensing via fluorescence quenching mechanism.[5,8] Moreover, the stability of framework has been confirmed by the comparative PXRD patterns of **1**, before and after soaking in the solution of Pd[2+] for 24 h (Fig.S37). The Stern-Volmer plot (Stern-Volmer constant, K_{SV} = 3.6 x 10^{4} M^{-1}) (Details in ESI) obtained from the fluorescence quenching of compound **1** with increasing Pd[2+] concentration showed a good linear response in the low concentrations (Fig. 3c). As the concentration increased, the plot deviates from linearity, demonstrating the simultaneous presence of both static and dynamic mechanisms. Once again the fluorescence life time measurement proved that, in the case of Pd[2+] also the fluorescence quenching follows static mechanism (Fig. S38).

To check selective sensing behavior of **1** towards Pd[2+], we performed the fluorescence experiments with other metal ions such as Cr^{2+}, Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Ag^{2+}, Pt[2+], Pb^{2+} and Eu^{3+} (Fig. S39-47). All these metal ions had no significant effect on the fluorescence intensity under identical experimental conditions which suggests the selective sensing behavior of **1** towards Pd[2+] (Fig 3d). To examine the selectivity of Pd[2+]

in the presence of other metal ions we have also performed some competition experiments. When we added different metal ions to compound **1**, the fluorescence intensities were not affected much even in high concentrations but an impressive quenching was observed after adding Pd^{2+} solution which confirms the remarkable selectivity (Fig. S48-S56).

The mechanism behind the Pd^{2+} selectivity was analyzed by emission and absorption spectra. In the emission spectrum of **1** with Pd^{2+}, In addition to the intensity quenching, a slight red shift was observed in the band (~5 nm) upon adding an appropriate quantity of Pd^{2+} solution that suggests the presence of significant interactions between the framework and Pd^{2+} (Fig. 3a).[16] From the selective chromogenic behavior towards Pd^{2+} and the significant variation in fluorescence spectrum, we anticipated that, the observed selective sensing behavior of compound **1** for Pd^{2+} over other metal ions is due to the interaction between the unsaturated alkene moieties (-CH=CH-) of bpeb linkers and Pd^{2+} as it is a well-known fact that the π-philic metal ions like Pd^{2+} could co-ordinate with alkenes through the $(\pi \rightarrow d)$ transitions.[17] To get more insight into the interactions between Pd^{2+} and compound **1**, we recorded the UV-vis spectrum by progressively adding Pd^{2+} solution into a solution **1** (Fig. S57). The addition of Pd^{2+} solution caused an enhancement in the absorbance of excitation band with a red shift from 340 nm to 362 nm, meanwhile a new peak was appeared at 270 nm confirming the interaction between Pd^{2+} and alkene moieties of bpeb in compound **1** and also suggesting the possibility of Pd^{2+} and alkene complex formation.[17] In the presence of other metal ions no such change was observed in UV-vis spectral pattern (Fig. S58). For better understanding, the stoichiometry between Pd^{2+} and compound **1** was verified by Job's method (Fig. S59).[7a,8b,5c] The plot shows 1:2 stoichiometric complex formation between compound **1** and Pd^{2+} solution. These spectroscopic results proved that the selective sensing behavior of compound **1** is due to the Palladium-alkene complex formation.

In conclusion, we have successfully synthesized a new luminescent MOF that shows highly selective and sensitive detection of PA and Pd^{2+} even in the concurrent presence of other competing nitroanalytes and metal ions. The mutual existence of energy and electron transfer mechanisms amplified the selectivity towards PA and the presence of unsaturated alkene moieties (-CH=CH-) of bpeb linkers in the framework helped for the selective detection of Pd^{2+}. The Stern-Volmer plot of compound **1** gives the highest quenching constant value among the reported MOFs for selective PA sensing as well as it could detect Pd^{2+} below the permissible limits set by WHO. The present work demonstrates the potential of a dual sensing fluorescent MOF for practical detection of nitroaromatic explosives as well as hazardous metal ions for environmental and security concerns.

Notes and references

[a]Department of Chemistry, Indian Institute of Science Education and Research (IISER), Indore By-pass Road, Bhauri, Bhopal-462066, India. E-mail: skonar@iiserb.ac.in; Fax: +91-755-6692392; Tel: +91-755-6692339.

† These authors equally contributed to this work.

Electronic Supplementary Information (ESI) available: Synthetic procedure, PXRD pattern, TGA, fluorescence plots, CIF files, and additional figures. See DOI: 10.1039/c000000x/

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Graphical Abstract
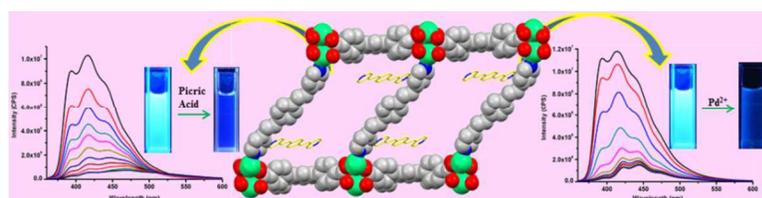
A new luminescent Metal-Organic Framework has been synthesized and explored as a dual functional fluorescent sensor to detect picric acid and Pd^{2+}.

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