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Novel metal–organic framework with tunable fluorescence property: supramolecular signaling platform for polynitrophenolics†

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With the aid of a rotational C_3-symmetric tricarboxytriphenylamine based ligand, a new Cd-MOF was synthesized and characterized by various spectroscopic techniques as well as by single-crystal X-ray diffraction analysis. The structural investigation of the crystalline Cd-MOF complex revealed the existence of unique three symmetry independent coordination environments of Cd(II) ions with common octahedral and pentagonal bipyramidal geometries. Small cavities with dimensions 6.40 Å × 6.41 Å were present in the crystal system. The tunable fluorescence property of the complex was explored to detect selectively polynitrophenol based explosive materials in the presence of other nitro explosives such as RDX, HMX, TNT and so on. Thermogravimetric analysis and powder X-ray diffraction data support the high thermal stability and crystallinity of the complex.

Among the various types of solid crystalline materials being developed for practical applications, the self-assembly of metal–organic frameworks (MOF) with emerging engineered architectures, has attracted considerable interest in various scientific arenas that include gas storage, separation, sensing, drug delivery, optical properties, catalysis, molecular magnetism and too many more to mention.[1] Introducing further the luminescent properties with the help of structurally engineered ligands and accessible porosity with high surface area within MOF materials have demonstrated them to be promising candidates for chemical sensing.[2] While developing sensing materials is one of the fastest growing research fields as these materials ensure the requirements of many areas starting from quality control to environmental concerns, chemical sensors for rapid and selective recognition of explosive materials have attracted increasing attention owing to their versatile application in homeland security, anti-terrorism, forensic investigation, mine-field and humanitarian implications.[3] The nitroaromatic compounds such as 2,4,6-trinitrotoluene (TNT) and 2,4,6-trinitrophenol (TNP) are used as principle ingredients in the explosives industry and are also found in unexploded landmines worldwide.[3b,4] Thus, a selective and sensitive sensor for nitro explosives is very much desirable. Various methods such as high-pressure liquid chromatography, electrochemical methods and surfaced-enhanced Raman spectrometry have been developed over the years for their detection and quantification at trace levels.[5] However, these techniques suffer from several drawbacks including their expense and poor portability; they are also highly time consuming. In order to overcome these difficulties, recently fluorescent materials which render different optical signals while interacting with explosive materials have being widely used as easy, sensitive and inexpensive optical sensing platforms. On the other hand, MOF materials have proved to be excellent candidates for the efficient detection of explosives.[6] The key is the large surface area of MOFs which makes them novel sensing platforms as they can accommodate a large number of analytes onto their surfaces. Though literature reports witness the existence of various MOFs for the detection of different explosive materials, MOFs for selective detection of aromatic polynitrophenol based explosives have rarely been reported.[6a,b,o,p,q,r] Moreover, and to the best of our knowledge, no MOF has been reported to date which is capable of distinguishing polynitrophenols and polynitroalcohols. Because of their high negative oxygen balance as compared to polynitrophenols, polynitroalcohols are inferior as explosives compared with polynitrophenols.

The present study describes the development of a novel 3D luminescent supramolecular framework Cd-MOF, $[Cd_5(TCA)_4(H_2O)_2]$, and its application in selective and sensitive detection of polynitrophenolic explosives over other nitroaromatics.

The present material has the potential to distinguish nitrophenol from nitroalcohols.

The present luminescent metal–organic framework of pentanuclear cadmium complex, $[Cd_5(TCA)_4(H_2O)_2]$, was

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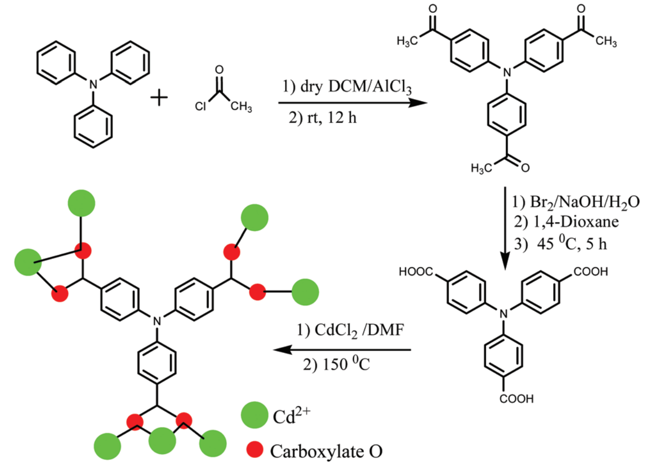

Scheme 1 Synthetic methodology for TCA ligand and Cd-complex.

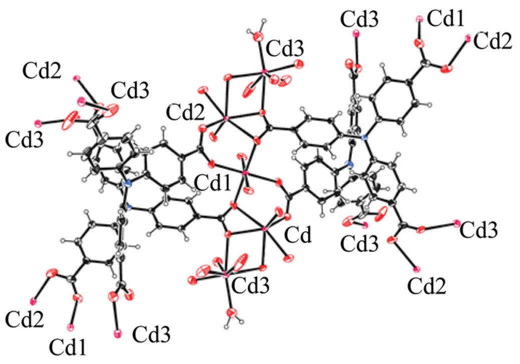

Fig. 1 ORTEP (Oak Ridge Thermal Ellipsoid) plot of Cd–TCA complex. Thermal ellipsoids are set at the 50% probability level; [Symmetry code: *x*, *y*, *z*, −*x*, *y* + 1/2, −*z* + 1/2, −*x*, −*y*, −*z*, *x*, −*y* − 1/2, *z* − 1/2].

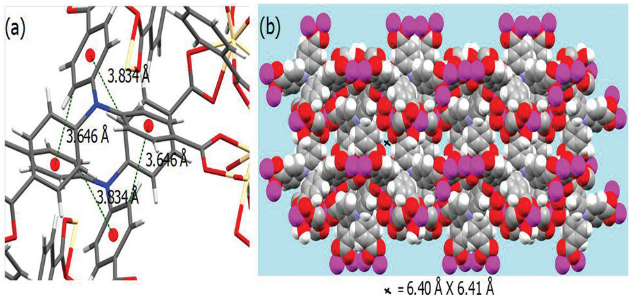

Fig. 2 (a) C–H⋯π non-covalent interactions of aromatic centroids with C–H moieties in Cd$_5$ complex and other atoms are omitted for clarity. (b) Three dimensional packing view of the Cd–TCA^{3-} complex contains a small porous cavity with dimensions, 6.40 Å × 6.41 Å.

synthesized at high temperature (150 °C) upon addition of tricarboxytriphenylamine (TCA) into CdCl$_2$ in DMF–ethanol solvent mixture (Scheme 1 and see the ESI†). Structural analysis revealed that the TCA^{3-}–Cd complex crystallized in monoclinic $P2_1/c$ space group (Fig. 1) where three symmetry independent coordination environments of Cd(ɪɪ) were present in the crystal system.[7]

Two types of Cd(ɪɪ) (Cd$_1$ and Cd$_2$) are coordinated distorted octahedrally with four pairs of carboxylate groups of TCA^{3-} ligand in *syn* ± *syn*, and *syn* ± *anti* (O,O′) bridging modes (Fig. 1 and Fig. S1†),[8] whereas Cd$_3$(ɪɪ) is tightly held with one water molecule and three pairs of TCA ions to show a hepta-coordinated pentagonal bipyramidal geometry. The intrametallic distances between adjacent Cd$_1$(ɪɪ)⋯Cd$_2$(ɪɪ) and Cd$_2$(ɪɪ)⋯Cd$_3$(ɪɪ) are 3.57 Å and 3.61 Å, respectively. Within a complex, the phenyl rings of TCA^{3-} ligand are almost perpendicular to each other and are stacked with other phenyl groups *via* C–H⋯π interactions (C–H⋯π 3.84 Å, C–H⋯π 3.64 Å) (Fig. 2a).[9] One disordered ethanol solvent molecule which was present outside of the metal coordination environment but in the unit cell of the crystal system was removed using the SQUEEZE function of the PLATON analysis and viewing software package. The three dimensional space-filling view of the metal–organic framework (Fig. 2b) illustrates a porous 1D channel with a cavity dimension, 6.405 Å × 6.405 Å along the *c* axis.

The photophysical properties of Cd-MOF were measured in the solution state. The Cd-MOF exhibited strong fluorescence at 417 nm (λ_{em}) upon excitation at 352 nm while dispersed in DMF. The addition of TNP (600 μL) to MOF solution (1.25 mg/3 mL, 1.98 × 10^{-4} M) resulted in quenching of the fluorescence emission (Fig. 3). Similarly, fluorescence quenching was observed when a solution of 2,4-DNP was added to the MOF solution (Fig. S2†). But, the quenching was not found significant while mono nitrophenols were added to MOF solution (Fig. S3 and S4†).

Interestingly, the addition of other nitroaromatics and nitro-explosives [2-nitrophenol (2-NP), 4-nitrophenol (4-NP), 4-nitrotoluene (4-NT), 2,4,6-trinitrotoluene (TNT), nitrobenzene (NB), 1,4-dinitrobenzene (1,4-DNB), RDX, HMX, nitromethane (NM) and 2,4-dinitrotoluene (DNT)] in DMF solution of Cd-MOF caused no significant changes in fluorescence signal which indicates the specificity of the present MOF towards polynitrophenolic compounds (Fig. S5–S8†). While investigating the fluorescence emission of the MOF in different common organic solvents including acetonitrile, pyridine, propylamine and chloroform, we observed the highest fluorescence intensity in DMF (Fig. S9†). Most importantly, this

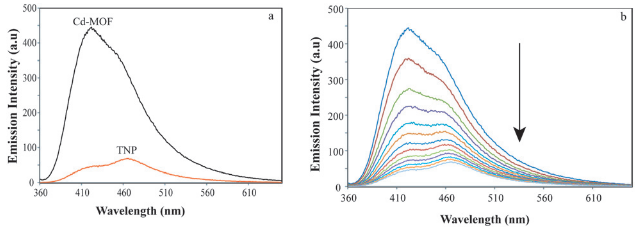

Fig. 3 Change in fluorescence intensity of (a) Cd-MOF in the presence of TNP and (b) upon incremental addition of TNP solution (0 to 600 μL) in DMF. (λ_{ex} = 352,Cd-MOF = 1.25 mg/3 ml, 1.98 × 10^{-4} M).

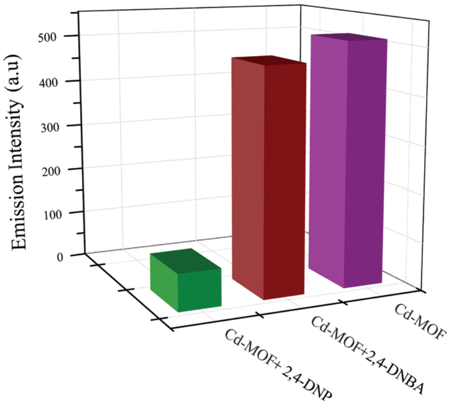

Fig. 4 The change in fluorescence intensity of Cd-MOF in DMF upon addition of 2,4-DNP and 2,4-DNBA solutions (λ_{ex} = 352 nm, λ_{em} = 415 nm).

supramolecular platform can efficiently differentiate polynitrophenols from polynitroalcohols through their optical signal. For example, the addition of 2,4-DNP resulted in a drastic quenching of the fluorescence signal of the MOF while the addition of 2,4-dinitrobenzyl alcohol (2,4-DNBA) did not cause any effect on the fluorescence property of the MOF (Fig. 4). To check the sensitivity of the MOF towards TNP, fluorescence titrations were performed. The gradual decrease in fluorescence intensity of the MOF was observed upon incremental addition of TNP (600 µl) to MOF solution (Fig. 3b).

The quenching efficiency of all the explosive materials was calculated and plotted (Fig. 5). It was observed that the presence of TNP and 2,4-DNP caused maximum quenching (91.78% and 82%) within 1 minute of addition (Fig. S10 and 11†). On the other hand, only 1–10% quenching was observed upon addition of much higher amounts (1200 µl) of other nitroaromatic compounds (Fig. S12†).

Next we investigated the potential of Cd-MOF as a selective sensor for polynitrophenolics, particularly TNP. The addition of an excess amount of a large number of various nitroaromatics to Cd-MOF dispersed in DMF did not show any fluorescence quenching although high affinity binding sites of Cd-MOF were available for these nitroaromatics, whereas the addition of TNP to the same solution resulted in a drastic decrease in the fluorescence intensity (Fig. S12†). These results suggested that the Cd-MOF could be used as efficient sensing platforms for polynitrophenols even in complicated systems. To investigate its practical applicability in more benign solvents such as water, fluorescence titrations were performed in DMF–H_2O (80 : 20) medium. Interestingly, a much higher and faster quenching efficiency of TNP was observed in the presence of mixed aqueous media (Fig. S13 and S14†). Further, competitive experiments were also performed to examine the selectivity of Cd-MOF for TNP in the presence of other nitroaromatics in mixed aqueous media. In these experiments an excess amount of nitroaromatics were added to the aqueous medium of Cd-MOF followed by addition of an aqueous solution of TNP to the same solution. Surprisingly, Cd-MOF showed a higher sensitivity in mixed aqueous medium. Thus, Cd-MOF showed unprecedented selectivity and sensitivity for TNP in both DMF and in 20% aqueous medium.

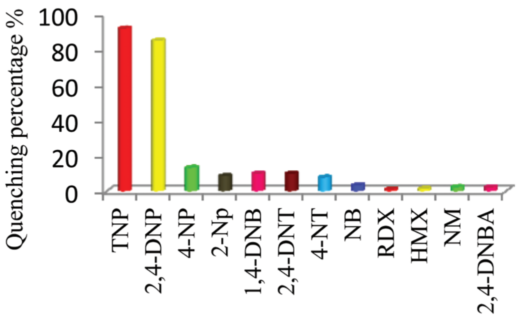

Fig. 5 The quenching percentage of Cd-MOF in DMF upon incremental addition of TNP, 2,4-DNP,4-NP, 2,4-NP, 1,4-DNB, 2,4-DNT, 4-NT, NB, RDX, HMX, NM and 2,4-DNBA solutions. (λ_{ex} = 352 nm, λ_{em} = 415 nm).

The reusability of the Cd-MOF has been checked and it has been observed that the Cd-MOF can be reused many times as ~89% quenching efficiency was observed even after five cycles (Fig. S15†). The limit of detection was calculated using (3σ/slope) method and found to be in the nanomolar range.[10] The MOF could detect as low as 2.3 and 1.7 nM of 2,4 DNP and TNP, respectively (Fig. S16 and S17†).

The reason for the maximum quenching in fluorescence emission of Cd-MOF solution in the presence of polynitrophenols may be ascribed to the energy transfer from fluorophore to the analyte.[6a,f] The energy transfer depends on the extent of overlap between the absorption band of the analyte and the emission band of the fluorophore. It has been observed that the absorption spectrum of polynitrophenol shows 41.2% overlap with the emission spectrum of Cd-MOF, while no overlap was observed with other explosive materials (Fig. S18†). The fluorescence quenching efficiency was also investigated by the Stern–Volmer equation: ($I_0/I = K_{sv}[A] + 1$, where I_0 and I are the fluorescence intensities before and after addition of the analyte respectively, K_{sv} is the quenching constant (M^{-1}), [A] is the molar concentration of analyte. As shown in (Fig. S19–S21†), the SV plot for MOF with TNP appeared linear at low concentration and lost its linearity at higher concentration. This non-linear nature of the plot may be attributed to self-absorption or energy transfer.[11] The quenching constants of all explosive materials were calculated and the quenching constant of TNP was found to be 5.9×10^4 which is *ca.* 11 times greater than for RDX, NB and TNT. It was also observed that the quenching constant value for TNP is comparable with the reported MOF and common organic polymers.[12]

In general, nitroaromatic based explosive detection by MOFs largely depends on the electronic structure of the ligand and the electron-donor/electron-acceptor orbital overlap where the MOF acts as an electron donor and the nitroaromatic acts as an electron acceptor. In the case of the present MOF, the ligand contains basic nitrogen which possibly induces strong electrostatic interaction with the highly acidic OH functionality of TNP. This effect helps to bring TNP closer to the MOF resulting in a better confinement of TNP into the MOF which in turn helps in effective energy transfer from MOF to TNP (Förster type strut-to-strut energy transfer).[1k,6a]

In order to characterize the thermal stability of the complex, thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were performed. As shown in Fig. S22,† the Cd-MOF exhibited weight loss at the temperature ~180 °C and ~300 °C. TGA and DSC analyses also show that the major weight loss occurred at ~380 °C and ~475 °C, which can be attributed to the decomposition and combustion of the complex. The formation of Cd-MOF complex as well as its stability during explosive sensing was investigated with the help of powder X-ray diffraction (PXRD) studies. A comparative study on PXRD patterns of the Cd-MOF powder, reusable Cd-MOF powder (obtained after one round of the sensing experiment) and simulated Cd-MOF complex has been shown in Fig. S23.† The PXRD pattern of Cd-MOF powder was found to be similar to that of the simulated pattern. These results support our conclusion that the present MOF maintains its crystalline property even in the bulk phase. Moreover, the similarity in PXRD patterns between unused MOF and reused MOF powder indicated that the MOF is stable in the dispersion. These results were further supported by FT-IR studies (Fig. S24†).

In conclusion, the development and importance of a new Cd-MOF have been demonstrated. The results suggest that the present MOF can act as a novel sensing platform for the highly sensitive and selective detection of polynitrophenol-based explosive materials. Besides, the Cd-MOF was found to be an interesting candidate for selective detection of TNP in the presence of other nitroaromatic materials in environmental conditions which may offer a broad range of applications in the field of detection of explosive materials. The selective detection of polynitrophenols over polynitroalcohols is quite interesting and a useful application of this newly developed MOF.

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7 Crystal data for $C_{84}H_{52}Cd_5N_4O_{26}$, M = 2095.35, CCD = 736670, T = 298(2) K, monoclinic, space group $P2(1)/c$, a = 14.6163(3) Å, b = 23.1639(4) Å, c = 15.7113(4) Å, β = 108.061(3)°, V = 5057.28 Å^3, Z = 2, μ = 1.100 mm^{-1}, 10 323 reflections, 8303 unique, (R_{int} = 0.0447), $R(F)$ = 0.0574 ($I > 2\sigma(I)$, $wR(F^2)$ = 0.1358 (all data).

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