Synthesis of Copper Metal Organic Framework Based on Schiff Base Tricarboxylate Ligand for Highly Selective and Sensitive Detection of 2,4,6-Trinitrophenol in Aqueous Medium

Manpreet Kaur1 · M. Yusuf1 · Ashok Kumar Malik1

Received: 22 July 2021 / Accepted: 8 September 2021 / Published online: 25 September 2021
© The Author(s), under exclusive licence to Springer Science+Business Media, LLC, part of Springer Nature 2021

Abstract
By using Schiff base tricarboxylate ligand 5-(4-carboxybenzylideneamino)isophthalic acid (H3CIP), a new imine functionalized copper metal organic framework (MOF) has been synthesized solvothermally. It was fully characterized by Fourier Transform Infrared (FTIR) Spectroscopy, Powder X-Ray Diffraction (PXRD), Scanning Electron Microscopy (SEM), Energy Dispersive X-Ray Spectroscopy (EDS), and elemental mapping techniques. The as-synthesized MOF has been utilized as fluorescent probe for detection of nitro aromatic explosives (NAEs). The results show that the copper MOF can be developed into highly selective and sensitive sensor for detection of TNP in the aqueous medium via the “turn-off” quenching response. The linear fitting of the Stern-Volmer plot for TNP offered large quenching constant of $1.07 \times 10^4$ M$^{-1}$ for Cu-MOF indicating the high sensitivity of the sensing process. Outstanding sensitivity of prepared material towards TNP detection was further validated by the low detection limit of 80 ppb (0.35 µM). The detailed mechanistic studies for their mode of action and density functional theory (DFT) calculations reveals that photo-induced electron transfer (PET) and fluorescence resonance energy transfer (FRET) processes, as well as electrostatic interactions (i.e. H-bonding) are the key factors for the turn-off response toward TNP by this fluorescent sensor. Thus, this new LMOF owing to their high water stability and remarkable functional features are potential candidates which can be developed into selective and sensitive TNP detection devices.

Keywords Schiff base · Metal-organic framework (MOF) · Fluorescent sensor · Density functional theory (DFT) · 2,4,6-Trinitrophenol (TNP) · Photo-induced electron transfer (PET) · Fluorescence resonance energy transfer (FRET)

Highlight
- A Schiff base tricarboxylate ligand, 5-(4-carboxybenzylideneamino)isophthalic acid (H3CIP), has been synthesized using one step condensation method
- Schiff base ligand has been utilized for the preparation of an imine functionalized copper MOF
- Experiment showed that copper MOF showed excellent fluorescent properties
- A fluorescent sensor showed the turn-off sensing response towards 2,4,6-trinitrophenol
- Fluorescence quenching of the host in the presence of guest like TNP can be explained through PET and FRET mechanisms
- Experimental results are well supported by theoretical calculations

Introduction
Development of highly selective and sensitive sensing materials for the detection of hazardous nitro explosives (NEs) has become one of the most critical concerns all over the world because of ever increasing terrorist activities and unpredicted industrial disasters [1]. Both aromatic and aliphatic nitro compounds such as 2,4,6-trinitrotoluene (TNT), nitrobenzene (NB), 2,6-dinitrotoluene (2,6-DNT), 3,4-dinitrotoluene (3,4-DNT), 1,3-dinitrobenzene (1,3-DNB), 2,4,6-trinitrophenol (TNP; also known as picric acid, PA), and nitro methane etc. are hazardous and/or explosive in nature. Among these NEs, picric acid is highly toxic and difficult to degrade. It is commonly used in various industries including dyes, polymers, plastics, pharmaceuticals, etc. [2]. The effluent released from these industries contains high concentration of TNP which gets easily accumulated in the soil and agricultural land owing to its high solubility in water [3]. Moreover, exposure to the high concentration of...
TNP can cause many health issues such as lung disorders, liver damage, asphyxiation, skin irritation, and even death [4]. Hence, precise, efficient, and selective detection of hazardous TNP in industrial waste, groundwater and soil is a significantly important [5]. Diverse analytical techniques e.g. mass spectrometry [6], high performance liquid chromatography (HPLC) [7], ion-mobility spectroscopy (IMS) [8], electrochemical methods [9], and fluorescence spectroscopy [10] have been employed for the detection of TNP. However, among these fluorescence spectroscopy have gained tremendous attraction of the researchers because of its easy operation, low cost, good sensitivity/selectivity, and quick response time, etc. [11].

Till date, various types of fluorescent materials such as carbon dots [12], conjugated polymers [13], nanoparticles [14], and covalent organic frameworks [15] etc. have been developed for the detection of TNP. Thus, search on new materials for the selective and sensitive detection of TNP is still in high demand to solve the critical health and environmental issues.

In recent years, metal-organic frameworks (MOFs) draws special attention of researchers as fluorescence sensor for detection of TNP owing to their high porosity, high surface area, high surface to volume ratio, chemical functionalities, features of pore surface, well-defined crystalline structure, predictable interaction such as hydrogen bonding, π–π stacking interactions, and coordination bonds between the guest species and MOF host [16]. Metal-organic frameworks (MOFs) are crystalline organic-inorganic hybrid materials constructed from the metal ions stitched together by the organic linker [17]. Such a kind of periodic porous crystal materials are considered to be promising candidates for many emerging applications such as gas storage/separation [18], heterogeneous catalysis [19], chemical sensing [20], drug delivery [21], and bio-imaging [22]. Particularly, the luminescent MOFs are tremendously attractive owing to their potential applications in chemical sensors and light-emitting devices [23]. The luminescent properties of MOF fluorescent sensors mainly depend upon the metal ions and organic ligands. A broad diversity of di- or multi-topic N- and O-donor organic ligands have been widely utilized for the synthesis of MOFs. These ligands have significant influence on the chemical and physical properties of MOFs. Typically, the synthesis of di- or multi-topic N- and O-donor organic ligands involve multi-step organic reactions, which could be costly and time consuming. With the increasing demand of time saving protocols and cheap starting reagents, different organic ligands have been searched in past few years. Schiff base ligands have gained enormous attention from the researchers due to cheap and readily available starting reagents (aldehyde/ ketones), less number of steps for their synthesis, typically one-step reaction, high yield, easy tuning of its properties by judicious selection of the reactants, stability, etc. [24]. The essential criteria for designing Schiff base ligand suitable for synthesis of MOF sensors for the detection of electron-deficient NEs are as follows: (i) the presence of π-electron-rich moiety in the molecule which can offer effective π–π interactions with the electron-poor NEs, (ii) the presence of Lewis basic sites that can further form H-bonding interactions with the nitrophenol derivatives.

Herein, considering these criteria, we have designed and synthesized Schiff base ligand 5-(4-carboxybenzylideneamino) isophthalic acid (H₃CIP) with hydrophobic pendant moiety, namely, aromatic ring (benzene) and Lewis basic imine groups. In our design, the benzene ring provide effective π–π stacking with the NAEs while the imine groups act as the Lewis basic recognition sites for the acidic NEs via the hydrogen bonding interactions (H-bonding). Interestingly, H₃CIP has been utilized for preparation of copper MOF. This MOF has been found to show selective detection of TNP through a turn-off response with low detection limit of 80 ppb (0.35 µM).

Experimental

Materials and Reagents

4-Formylbenzoic acid (4-FBA), 5-aminoisophthalic acid (5-AIP), copper nitrate trihydrate (Cu(NO₃)₂·3H₂O), silica gel G, and N,N’-dimethylformamide (DMF) were purchased from Sigma Aldrich. NAEs: 4-nitrotoluene (4-NT), 2,4-dinitrotoluene (2,4-DNT), 2,6-dinitrotoluene (2,6-DNT), 1,3-dinitrobenzene (1,3-DNB), 2,4-dinitrophenol (2,4-DNP), 4-nitrophenol (4-NP), nitrobenzene (NB), and 2,4,6-trinitrophenol (TNP) were purchased from Avra synthesis Pvt. Ltd. All materials mentioned above were of analytical reagent grade and used without further purification.

Measurements

Fourier transform infrared spectra of the synthesized Schiff base ligand and copper MOF were scanned in the range 400–4000 cm⁻¹ on a Perkin Elmer FT-IR Spectrophotometer. The progress of the aldime condensation reaction was monitored by Thin-Layer Chromatography (TLC) using silica gel G (Sigma Aldrich). The spots on TLC plates were cautiously visualized by their exposure to the I₂ fumes in the iodine chamber. Powder X-ray diffraction (XRD) diffractograms for crystal structure determination were recorded using XPERT PRO Powder X-ray Diffractometer [CuKα X-ray(λ=1.5406Å), 1800W (45 kV, 40 mA)] in 2θ range 2° to 50° keeping step size of 0.026°. JEOL, JSM-6510LV scanning electron microscope (SEM) was used for morphological and topographical analyses of synthesized MOF. Electron micrographs of gold coated...
sample were recorded at accelerating voltage of 15kV at a working distance of 11mm. EDS spectrum of gold coated sample rigidly mounted on the specimen stub was recorded using Oxford instrument (INCA X-act) EDS spectrometer equipped as an additional accessory to SEM. UV-Vis. spectrophotometer (Shimadzu UV-Vis 1600) was used for absorption studies. Shimadzu RF-5301PC spectrofluorometer was opted for photoluminescence studies. The theoretical studies were carried out using Gaussian 09 software.

Methods

Synthesis of 5-(4-Carboxybenzylideneamino)isophthalic Acid (H3CIP)

In order to synthesize the copper MOF, an organic ligand 5-(4-carboxybenzylideneamino)isophthalic acid (H3CIP) was first prepared by the aldimine condensation reaction of 5-aminoisophthalic acid (5-AIP) and 4-formylbenzoic acid (4-FBA) according to the synthesis method and conditions reported in literature [25]. The 5-AIP (1 mmol, 0.181 g) and 4-FBA (1 mmol, 0.150 g) were added to a round bottom flask (100 mL) containing 30 mL ethanol and slowly refluxed at 55 °C for 3 h. The white precipitation with a Schiff base structure was filtered and washed by ethanol and diethyl ether several times, and then vacuum-dried.

Synthesis of Imine Functionalized Copper MOF

The Schiff base tricarboxylate ligand 5-(4-carboxybenzylideneamino)isophthalic acid (H3CIP) (0.1 mmol, 0.0313g) was dissolved (after sonication for 3 minutes) in 5 mL DMF in a 20 mL glass vial and solid Cu(NO3)2 ·3H2 O (0.1mmol, 0.0241g) was added to this solution. The mixture was sonicated for 3 min, sealed and then, heated in hot air oven at 100 °C for 24 h. During this period, light green crystalline material of copper MOF was formed. They were isolated by filtration, washed several times with DMF and diethylether followed by solvent exchange with methanol, and dried under vacuum.

Luminescent Sensing

For luminescence sensing studies a stock solution was prepared by dissolving 1 mg of finely grounded Cu-MOF in 3 ml water followed by sonication for 30 min. The photoluminescent studies of above prepared stock solution was performed at room temperature. Inspired by its interesting fluorescent behavior, the potential applications of Cu-MOF as a fluorescence sensor was investigated for the detection of various NAEs. 20 µM aqueous solution of each NAE (4-NT, NB, 2,4-DNT, 2,6-DNT, 1,3-DNB, 4-DNP, 4-NP, TNP) were prepared in water. For the selective studies, 1mg of MOF was added in 3 mL of stock solution of NAEs to produce the stable suspension. Resulting suspension was sonicated for 30 min before the photoluminescent (PL) studies. For the thorough study of selective luminescent (PL) synthesis process was depicted in Scheme 1.

Result and Discussion

Synthesis and Characterization of Copper MOF

In the present work, 5-(4-carboxybenzylideneamino)isophthalic acid (H3CIP) was synthesized by the aldimine condensation reaction of an equimolar amount of 5-aminoisophthalic acid and 4-formylbenzoic acid. H3CIP, a Schiff base ligand, was then heated with Cu(NO3)2 ·3H2 O in DMF at 100 °C for 24 h to synthesize the copper MOF. The overall synthesis process was depicted in Scheme 1.

FTIR determinations were performed to establish the formation of Schiff base ligand, H3CIP. The band observed around 1683 and 1688 cm⁻¹ for 5-AIP to 767 cm⁻¹ in the FTIR spectrum of H3CIP disappear in the copper MOF (Fig. 1b). The new strong stretch absorption of carbonyl of –COOH group, present in the H3CIP ligand (Fig. 1a). Meanwhile, the C–H vibration peak at 1624 cm⁻¹ which corresponding to the characteristic absorption of an imine group (–CH=N-) can confirmed the formation of H3CIP ligand. FTIR analysis was further utilized to provide the conclusive evidence of formation of copper MOF from H3CIP. The strong peak at 1725 cm⁻¹ which corresponding to the characteristic antisymmetric stretch absorption of carbonyl of –COOH group, present in the H3CIP disappear in the copper MOF (Fig. 1b).
of the copper MOF can be regarded as the symmetric and antisymmetric stretching modes of the coordinated (–COO) group, respectively. It indicates that –COOH of H₃CIP involved in the coordination with copper. It should be noted that the values of Δν (Δν = νₘₐ(COO) − νₛ(COO)) for metal carboxylates are useful tool for distinguish the coordination modes. According to this, the carboxylate group coordinates in a bidentate chelating fashion if Δν(COO) is significantly less compared to that of the ligand; a monodentate fashion if Δν(COO) of the complex is much larger compared to that of the ligand; and bridging can be reflected when near to the ionic values [27]. Therefore, the observed difference in antisymmetric and symmetric carbonyl stretching frequencies Δν for Cu-MOF was 251 (Δν = 1637− 1379 = 250) significantly less than H₃CIP (Δν = 1725 − 1288 = 378), indicating the chelating bidentate coordination mode of carboxylate moieties in copper MOF. The peak at 1590 cm⁻¹ peak can be attributed to aromatic rings C = C stretching vibration in the copper MOF. The vibrations associated with metal linker bond are present below 600 cm⁻¹. These vibrational modes are difficult to observe with IR method. The bonding between Cu-O appears at 491 cm⁻¹, which is another conclusive evidence of coordination between Schiff base ligand and Cu²⁺ [28]. The absence of peaks at 410, 500, 610, and 615 cm⁻¹ indicates that synthesized material is free from CuO and Cu₂O during the nucleation of copper MOF. These results indicated that high purity copper MOF was synthesized successfully.

PXRD analysis was done to examine the crystallinity and phase purity of synthesized copper MOF. It has been already reported in literature that when the ligands possessing the isophthalic acid moiety are employed in Cu²⁺ chemistry, they often afford structures which are similar to that of HKUST-1 [29]. Herein, Cu-MOF has been prepared using H₃CIP ligand which is significantly extended ligand compared to other commonly used tricarboxylic acids (for example, trimesic acid which was used for the preparation of Cu-BTC or HKUST-1 MOF) and possesses the semi-rigid
 Furthermore, the H$_3$CIP ligand is similar to the PEIPH$_2$ Schiff base ligand but contains benzoic acid moiety in place of pyridyl group [29]. Thus, it was found that the PXRD pattern of as-synthesized Cu-MOF was very similar to the simulated pattern reported for the Cu-BTC (HKUST-1) as well as Cu-PEIP (whose structure similar to HKUST-1) confirming the formation of isostructural MOF [28]. The PXRD pattern of the synthesized sample is shown in Fig. 2 which displays the main diffraction peaks of Cu-MOF at 2θ = 5.912°, 7.121°, 9.811°, 11.904°, 12.414°, 15.411°, 16.908°, 18.021°, 19.615°, 26.578°, and 29.573° corresponding to the Miller indices (111), (200), (220), (222), (400), (331), (422), (511), (440), (731), and (751), respectively [28]. The characteristic diffraction peaks of Cu$_2$O at 2θ = 36.4°, 42.3°, and 43.3° are not observed in the PXRD pattern of the synthesized sample indicates the high purity of synthesized copper MOF product [30]. The crystalline nature of the synthesized material is indicated from the sharp observed PXRD peaks. Unfortunately, all efforts used for the preparation of single crystal of copper MOF from H$_3$CIP ligand such as use of series of modulators (like acetic acid, benzoic acid) in varying concentrations and mixture of solvents has been failed. Based on the FTIR and PXRD analysis, the structure of as-synthesized imine functionalized MOF has been proposed which resembles the structure of HKUST-1 and Cu-PEIP MOF as shown in Fig. 3.

SEM images were taken to reveal the surface morphology of the synthesized Cu-MOF. SEM image of copper MOF are shown in Fig. 4. The SEM of copper MOF displayed the flake like morphology (Fig. 4a, b). Zoomed images indicated uniform sphere like particles (Fig. 4c). EDS was carried out to investigate the elemental composition of copper MOF. EDS of spectra of copper MOF are shown in Fig. 5. Compositional analysis carried from EDS spectra reveal the presence of carbon (C), nitrogen (N), oxygen (O), and copper (Cu) with detected weights (atomic ratios) to be 44.82% (60.40%), 6.36% (7.35%) and 22.63% (5.76%), respectively. In the recorded EDS spectra an extra peak at 2.2 keV is also observed due to coating of sample by gold for conductive SEM analysis. Presence and distribution of these elements was further confirmed with the elemental maps of Cu, C, N, and O in the Fig. 6a-d. EDS analysis confirms the formation

---

Fig. 1 (a) FTIR spectra of the 4-FBA, 5-AIP, and product Schiff base ligand (H$_3$CIP), (b) FTIR spectra of the imine functionalized copper MOF
of high purity copper MOF by illustrating the presence of elements (C, O, N, and Cu) of the organic ligand and metal in the final structure of MOF.

**Water Stability**

For the successful in-field applications, the stability of MOFs towards water, moisture, and humidity is crucial. Thus, we have assessed the impact of water on the structural integrity of synthesized Cu-MOF. Typically, Cu-MOF was soaked in water for a period of 24 h and then analyzed by PXRD analysis. Furthermore, to understand the impact of TNP on the stability of Cu-MOF, it was also soaked in aqueous TNP solutions for 24 h. PXRD analyses indicated that the crystallinity of Cu-MOF was not destroyed even after soaking in water or aqueous TNP solution for 24 h.

**Photoluminescent Properties**

Luminescent properties of H$_3$CIP and Cu-MOF was explored in water at room temperature. As shown in Fig. 7, the excitation spectrum of ligand H$_3$CIP presents a broad peak centered at 355 nm. Upon excitation at 355 nm, H$_3$CIP display a broad emission peak centered at 423 nm, which may arise from a π–π* or n–π* electron transition within the ligand. However, as seen from Fig. 7, the emission spectrum of Cu-MOF displays a maximum emission at 450 nm upon excitation at 340 nm, a significant red shift in comparison with the H$_3$CIP ligand. This may be due to the coordination interactions within the framework, which may increase the rigidity of the ligands, decrease the energy loss, and in this manner effect the electron transition.

**Detection of TNP**

To investigate the sensing properties of Cu-MOF toward different NAEs, water was selected as the solvent because Cu-MOF shows high stability, good dispersion, and excellent luminescent properties in water. Figure 8a shows the emission spectra of Cu-MOF dispersed in water at different excitation wavelengths from 260 nm to 360 nm with maximum emission intensity observed at 757 nm at $\lambda_{ex}$=340 nm. Thus, 340 nm excitation wavelength has been selected as appropriate excitation wavelength for the further PL studies to detect NAEs. A 1 mg of powdered sample of as-synthesized Cu-MOF was ground and introduced into the 3 mL aqueous solutions of 20 µM of different NAEs (TNP, NB, 4-NT, 4-NP, 2,4-DNP, 2,4-DNT, 2,6-DNT, and 1,3-DNB) to form stable suspension after ultrasonication for 30 min. The luminescent response of suspensions were recorded and compared in Fig. 8b. The results revealed that all examined NAEs quenched the luminescent intensity of Cu-MOF. It is worth mentioning that the contacting between TNP and Cu-MOF leads to the significant suppression effect on the luminescence, while other NAEs perform slight influence on the emission intensity of the Cu-MOF. As depicted from Fig. 8c, the histogram of luminescence intensity of Cu-MOF around 450 nm shows that after immersing into 20 µM aqueous solution of TNP, the seven fold quenching of emission intensity was observed compared to original one. The fluorescence quenching efficiency was calculated by $[(I_0 − I)/I_0] \times 100\%$, where $I_0$ and $I$ are the fluorescence intensities before and after addition of the analyte. In particular, it has been observed that TNP addition into Cu-MOF aqueous suspensions shows highest fluorescence quenching efficiency amounting to 86.12 % compared to 2,4-DNP (∼38.04 %), 4-NP (∼23.64 %), 1,3-DNB (∼19.2 %), 2,4-DNT (∼14.13 %), 2,6-DNT (∼11.36 %), NB (∼7.52 %), and 4-NT (∼2.24 %) as shown in Fig. 8d. These outcomes implied that the Cu-MOF could operate as a “turn-off” fluorescent sensor for TNP.

To understand the fluorescence quenching response of Cu-MOF towards TNP, we measured the luminescent responses of 1 mg of Cu-MOF immersed in TNP aqueous solutions with different concentrations. It is obvious that the luminescence intensity of Cu-MOF incorporated with TNP shows a strong dependence on the concentration of TNP. As depicted from Fig. 9a, the emission intensity of Cu-MOF decreases gradually with the increase of TNP concentration in the range from 1 to 10 µM. Quantitatively, the quenching effect of TNP can be analyzed and calculated by the Stern-Volmer equation:
where, $I_0$ and $I$ are the luminescent intensity of the Cu-MOF suspension at 450 nm in the presence and absence of TNP, $K_{SV}$ is the Stern-Volmer quenching constant (M$^{-1}$), and [TNP] is the concentration of TNP. As seen from Fig. 9b, there is a good linear relationship (correlation coefficient $R^2 = 0.9962$) between $I/I_0$ and [TNP] at a low concentration range of 0-10 µM, indicating that the quenching effect of TNP on the luminescence of Cu-MOF agrees the Stern-Volmer mode well. The Stern-Volmer quenching constant value is calculated to be $1.07 \times 10^4$ M$^{-1}$, which reveals a strong quenching effect on the Cu-MOF luminescence (Fig. 9c). The limit of detection (LOD) of Cu-MOF towards TNP was calculated using the equation $LOD = 3.3\sigma/m$, where $\sigma$ = standard deviation and $m$ = slope of the linear curve plotted at lower concentration for DL calculations. The LOD values for TNP was found to be 80 ppb (0.35 µM). The $K_{SV}$ and LOD values demonstrate H$_2$L are good fluorescent sensor for detection of TNP.

In order to perform the time dependent detection of TNP, 1 mg of Cu-MOF was introduced into the 3 mL of 20 µM TNP aqueous solution and emission spectra were recorded with 1 min intervals up to 10 min upon excitation at 340 nm.
It can be noticed from Fig. 10a, the luminescence emission reached a constant value after 1 min. Along with the contact time between TNP and Cu-MOF, the emission intensity of the suspension remains almost unchanged, which tells that TNP induced fluorescence weaken reaction is relatively fast. Hence, the presented material could be utilized for the rapid detection of TNP.

Inspired by the highest fluorescence quenching efficiency of TNP among the selected NAEs, the specificity of Cu-MOF towards TNP in the co-existence of other NAEs was examined to analyze the competing effect of NAEs. In such an experiment, the fluorescence intensity of Cu-MOF was recorded by the 3 mL addition of a 20 µM aqueous solution of particular nitro analyte followed by the 3 mL addition of 20 µM aqueous solution of TNP. As shown in Fig. 10b, the insignificant change in the intensity was observed in the presence of other NAEs followed by tremendous decrease in intensity after the TNP addition, whereas in the presence of 2,4-DNP and 4-NP, significant decrease was observed followed by moderate change after the TNP addition. These experimental results proved that the existence of other explosives would not disturb the detection of TNP. Hence, it becomes obvious that the presented material has remarkable selectivity towards TNP over other congeners.

**Fig. 6** Elemental mapping of Cu-MOF showing (a) Carbon (C); (b) Nitrogen (N); (c) Oxygen (O); (d) Copper (Cu)
Possible Mechanism for the TNP Detection

For understanding the high selectivity of Cu-MOF towards TNP, the sensing mechanism was examined. The possible mechanisms of turn-off quenching between electron-rich Cu-MOF and electron-deficient TNP are: (1) Destruction of crystalline structure of MOF; (2) Photo-induced electron transfer (PET); (3) Fluorescence resonance energy transfer (FRET); and (4) Molecular interactions (such as electrostatic and \( \pi-\pi \) interactions). The PXRD pattern, and FTIR of copper MOF (Fig. 11) still maintained intact before and after quenched by TNP. These results confirmed that the interactions between TNP and copper MOF could result in the quench phenomenon, but it was not strong enough to destroy the crystalline structure of copper MOF.

As proposed for many other MOFs, the PET might govern the highly selective detection of NAEs by the Cu-MOF. Generally, the LUMOs of the electron-deficient NAEs are situated between the conduction band (CB) and valence band (VB) of the MOFs [31]. Therefore, an electron transfer process can easily take place from the CB of Cu-MOF to the LUMO of electron-deficient NAEs. This process can cause quenching of the fluorescence intensity of Cu-MOF upon excitation. To validate the PET mechanism relevant for this turn-off quenching, the \( E_{\text{HOMO}} \) and \( E_{\text{LUMO}} \) energies of the Schiff base tricarboxylate ligand (H₃CIP) and NAEs were calculated using DFT with the basis set B3LYP/6-311G and the Gaussian 09 package program (Fig. 12). The existence of easy electron transition between \( E_{\text{HOMO}} \) and \( E_{\text{LUMO}} \) of reacting species was established by the popular Frontier Molecular Orbital (FMO) theory. According to FMO theory, the quenching efficiency of analyte species is a function of its \( E_{\text{HOMO}} \) and \( E_{\text{LUMO}} \). It is well known that the species with high energy HOMO are more capable to donate electrons than those with lower energy HOMO. On the other hand, species with low-lying LUMO are more capable to accept electrons than those with higher energy LUMO and thus will show higher quenching efficiency. From the HOMO–LUMO energy gaps, it is inferred that PET takes place from the HOMO of the Cu-MOF to the LUMO of electron-deficient TNP compared to other NAEs. This agrees well with the observed maximum quenching efficiency for TNP. It was observed that TNP molecule has the lowest LUMO energy value (~4.730 eV). Thus, it is concluded that the higher quenching efficiency of TNP. The HOMO and LUMO orbital energies for the NAEs are presented in Fig. 12. The ascending order for the calculated LUMO energy values of the NAEs is: TNP < 1,3-DNB < 2,4-DNT < 2,6-DNT < 2,4-DNP < NB < 4-NT < 4-NP. The ease of electron transfer from the electron-rich Cu-MOF to the electron-deficient NAEs should follow reverse of this sequence. Therefore, the highest quenching efficiency of TNP agrees well with its lowest LUMO energy value. Moreover, the trend of quenching efficiencies (i.e., TNP > 2,4-DNP > 4-NP > 1,3-DNB > 2,4-DNT > 2,6-DNT > NB > 4-NT) is not fully in accordance with the LUMO energy values of other analytes. These theoretical results are not in good correlation in our experimental results. These results suggest that only PET mechanism cannot completely account for the observed quenching behavior. Moreover, FRET mechanism might be recognized for the quenching process.

In order for FRET to take place, there should be an efficient spectral overlap between the emission spectrum of the fluorophore and the absorption spectrum of the analyte. As presented in Fig. 13, TNP shows a strong absorption band at 353 nm and copper MOF exhibits a strong fluorescence emission band at 471 nm. There is a large overlap between the absorption spectrum of TNP and the emission spectrum of copper MOF. On the other hand, other analytes have almost no such spectral overlap. The largest spectral overlap for TNP is in accordance with its highest quenching efficiency. The spectral overlap supports the fact that the fluorescence quenching by TNP takes place by an energy transfer mechanism.

In addition, the fluorescence quenching might be ascribed to some molecular interactions such as electrostatic (between the hydroxyl group of electron-deficient TNP and the basic sites i.e. imine group of electron-rich copper MOF) and \( \pi-\pi \) interactions (between the benzene rings of TNP and copper MOF) (Scheme 2). In order to verify that the electrostatic interactions are involved in the fluorescence quenching process, the quenching efficiencies of some NAEs containing one hydroxyl group, such as TNP, 2,4-DNP and PNP were compared. The quenching efficiencies decreased in the sequence: TNP > 2,4-DNP > PNP, which is in accordance with the acidity of the phenolic protons. A decrease in the quenching efficiency with the reduction in the acidity can also be
Fig. 8 (a) Fluorescence emission spectra (excitation wavelength (λex) from 250 to 360 nm) of Cu-MOF (1 mg) in aqueous solution (3 mL). (b) Suspension-state fluorescence spectra for Cu-MOF (1 mg) dispersed in aqueous solution containing different nitro explosives (20 µM, 3 mL) when excited at 340 nm; (c) The relative intensities of emission peak monitored at 450 nm for Cu-MOF dispersed in different nitro explosives aqueous solutions (20 µM, 3 mL) when excited at 340 nm. (d) Quenching efficiency of Cu-MOF (1 mg) in the presence of aqueous solutions of various nitro explosives with the concentration of (20 µM, 3 mL).

Fig. 9 (a) Decrease in fluorescence emission of Cu-MOF upon continuous addition of 0-10 µM solution of TNP in aqueous medium. (b) Stern–Volmer plots of $I_0/I$ versus TNP concentration in the range 0-10 µM showing linear relationship and the fitting line in aqueous medium ($R^2 = 0.9962$; $K_{SV} = 1.07 \times 10^4$ M$^{-1}$).
ascribed to the presence of imine groups where the imine
groups can form H-bonding interactions with the phenolic
protons of the nitrophenol derivatives, which are absent
in the other NAE analytes. A probable mechanism for
the selective sensing of TNP from these observations has
been illustrated in Scheme 2, where an energy transfer
of Cu-MOF in the presence of (20 µM, 3 mL) aqueous solution of
NAEs. The sky blue bars represent the change of the emission that
occurs upon the subsequent addition of (20 µM, 3 mL) aqueous solution
of TNP to a solution containing of Cu-MOF and 20 µM NAEs
via π−π interactions between TNP and benzene moieties
and the above mentioned H-bonding with the more acidic
phenolic proton of TNP play important roles. This sug-
ests that electron and energy transfer processes as well as
H-bonding processes interplay together for the observed
quenching response.

Fig. 10 (a) Effect of response time on the fluorescent intensities upon
the addition of aqueous solution of TNP (20 µM, 3 mL) into the Cu-
MOF suspension. (b) Comparison of the luminescence intensity of
Cu-MOF (1 mg) upon the addition of TNP in the presence of other
NAEs in aqueous solvent. The orange bars represent the emission

Fig. 11 (A) FT-IR (B) PXRD pattern of (a) fresh Cu-MOF and (b) after TNP sensing in the aqueous medium
Fig. 12  HOMO and LUMO plots and energy values (in eV) of various nitro explosives and Schiff base fluorescent ligand (H₃CIP)

Fig. 13  Spectral overlap of emission spectra of Cu-MOF and absorption spectra of TNP
Scheme 2 Probable mechanism for TNP sensing by the imine functionalized MOF
Conclusions

In summary, we have successfully synthesized a luminescent MOF (Cu-MOF) with an imine functionalized tricarboxylate ligand. Cu-MOF show outstanding photoluminescent properties and remarkable water stability even when soaked in water for 24 h. These features of Cu-MOF have been exploited to develop an excellent approach for water based fluorescence quenching detection of TNP. Results showed LODs is as low as 80 ppb (0.35 µM) and Stern-Volmer quenching constants as high as 1.07 × 10^4 M^-1 for aqueous phase detection of TNP. The as-synthesized Cu-MOF exhibited outstanding sensitivity, and high selectivity toward TNP without suffering from the interference of other NAEs. The highest quenching efficiency of TNP among several other NAEs can be related to the existence of electron and energy transfer processes as well as molecular interactions (π-π and electrostatic) between the MOF and TNP. Eventually, the present study provides the new insight into the design of water stable LMOF-based explosive sensors, which may be useful under more realistic conditions for the detection of TNP which has relevance to homeland security and ecological concerns.

Authors’ Contributions Manpreet Kaur has collected the data, performed the experiments and compiled the paper. M. Yusuf and Ashok Kumar Malik has edited the data of this paper.

Funding One of the Miss Manpreet Kaur is thankful to the CSIR, New Delhi for the grant of research fellowship.

Availability of Data and Material Data will be provided later on.

Declarations

Ethics Approval All authors approve ethics for the publication.

Consent to Participate Yes.

Consent for Publication Yes, all authors agree for the publication.

Conflicts of Interest/Competing Interests The authors declare no conflict of interest.

References

1. Shyamal M, Mazumdar P, Maity S, Samanta S, Sahoo GP, Misra A (2016) Highly selective turn-on fluorogenic chemosensor for robust quantification of Zn (II) based on aggregation induced emission enhancement feature. ACS Sensors 1(6):739–747
2. Parmar B, Rachuri Y, Bisht KK, Laiya R, Suresh E (2017) Mechanochemical and conventional synthesis of Zn (II)/Cd (II) luminescent coordination polymers: dual sensing probe for selective detection of chromate anions and TNP in aqueous phase. Inorganic Chemistry 56(5):2627–2638
3. Chakraborty G, Mandal SK (2018) Design and development of fluorescent sensors with mixed aromatic bicyclic fused rings and pyridyl groups: solid mediated selective detection of 2, 4, 6-trinitrophenol in water. ACS Omega 3(3):3248–3256
4. Maity S, Shyamal M, Das D, Mazumdar P, Sahoo GP, Misra A (2017) Aggregation induced emission enhancement from antipyridine-based Schiff base and its selective sensing towards picric acid. Sensors and Actuators B: Chemical 248:223–233
5. Parmar B, Rachuri Y, Bisht KK, Suresh E (2016) Syntheses and structural analyses of new 3D isosstructural Zn (II) and Cd (II) luminescent MOFs and their application towards detection of nitroaromatics in aqueous media. ChemistrySelect 1(19):6308–6315
6. Barron L, Gilchrist E (2014) Ion chromatography-mass spectrometry: a review of recent technologies and applications in forensic and environmental explosives analysis. Analytica Chimica Acta 806:27–54
7. Rahimi-Nasrabadi M, Zahedi MM, Pourmortazavi SM, Heydari R, Rai H, Jazayeri J, Javidan A (2012) Simultaneous determination of carbazole-based explosives in environmental waters by dispersive liquid—liquid microextraction coupled to HPLC with UV-Vis detection. Microchimica Acta 177(1):145–152
8. Guerra-Diaz P, Gura S, Almirall JR (2010) Dynamic planar solid phase microextraction–ion mobility spectrometry for rapid field air sampling and analysis of illicit drugs and explosives. Anal Chem 82(7):2826–2835
9. Yan F, He Y, Ding L, Su B (2015) Highly ordered binary assembly of silica mesochannels and surfactant micelles for extraction and electrochemical analysis of trace nitroaromatic explosives and pesticides. Anal Chem 87(8):4436–4441
10. D Jawale Patil P, D Ingle R, M Wagalgave S, S Bhosale R, V Bhosale S, P Pawar R, V Bhosale S (2019) A naphthalimide-benzothiazole conjugate as colorimetric and fluorescent sensor for selective trinitrophenol detection. Chemosensors 7(3):38
11. Wang W, Li H, Yin M, Wang K, Deng Q, Wang S, Zhang Y (2018) Highly selective and sensitive sensing of 2, 4, 6-trinitrophenol in beverages based on guanidine functionalized upconversion fluorescent nanoparticles. Sensors and Actuators B: Chemical 255:1422–1429
12. Siddique AB, Pramanick AK, Chatterjee S, Ray M (2018) Amorphous carbon dots and their remarkable ability to detect 2, 4, 6-trinitrophenol. Sci Rep 8(1):1–10
13. Jiang S, Meng L, Ma W, Qi Q, Zhang W, Xu B, Liu L, Tian W (2021) Morphology controllable conjugated network polymers based on AIE-active building block for TNP detection. Chinese Chemical Letters 32(3):1037–1040
14. Rong M, Lin L, Song X, Zhao T, Zhong Y, Yan J, Wang Y, Chen X (2015) A label-free fluorescence sensing approach for selective and sensitive detection of 2, 4, 6-trinitrophenol (TNP) in aqueous solution using graphitic carbon nitride nanosheets. Analytical Chemistry 87(2):1288–1296
15. Zhu M-W, Xu S-Q, Wang X-Z, Chen Y, Dai L, Zhao X (2018) The construction of fluorescent heteropore covalent organic frameworks and their applications in spectroscopic and visual detection of trinitrophenol with high selectivity and sensitivity. Chem Commun 54(18):2308–2311
16. Nandi S, Biswas S (2019) A recyclable post-synthetically modified Al (iii) based metal–organic framework for fast and selective fluorogenic recognition of bilirubin in human biofluids. Dalton Trans 48(25):9266–9275
17. Zhao D, Cui Y, Yang Y, Qian G (2016) Sensing-functional luminescent metal–organic frameworks. CrystEngComm 18(21):3746–3759
18. Li H, Li L, Lin RB, Zhou W, Zhang Z, Xiang S, Chen B (2019) Porous metal-organic frameworks for gas storage and separation: Status and challenges. EnergyChem 1(1):100006
19. Kang Y-S, Lu Y, Chen K, Zhao Y, Wang P, Sun W-Y (2019) Metal–organic frameworks with catalytic centers: From synthesis to catalytic application. Coor Chem Rev 378:262–280
20. Hu Z, Deibert BJ, Li J (2014) Luminescent metal–organic frameworks for chemical sensing and explosive detection. Chem Soc Rev 43(16):5815–5840
21. Sun C-Y, Qin C, Wang X-L, Su Z-M (2013) Metal–organic frameworks as potential drug delivery systems. Expert Opinion on Drug Delivery 10(1):89–101
22. Wang H-S (2017) Metal–organic frameworks for biosensing and bioimaging applications. Coor Chem Rev 349:139–155
23. Zhu S-Y, Yan B (2018) A novel sensitive fluorescent probe of $\text{S}_2\text{O}_8^{2-}$ and $\text{Fe}^{3+}$ based on covalent post-functionalization of a zirconium (iv) metal–organic framework. Dalton Trans 47(33):11586–11592
24. Halder S, Ghosh P, Hazra A, Banerjee P, Roy P (2018) A quinoline-based compound for explosive 2, 4, 6-trinitrophenol sensing: experimental and DFT-D3 studies. New J Chem 42(11):8408–8414
25. Manos MJ, Kyprianidou EJ, Papaefstathiou GS, Tasiopoulos AJ (2012) Insertion of Functional Groups into a Nd3+ Metal–Organic Framework via Single-Crystal-to-Single-Crystal Coordinating Solvent Exchange. Inorganic Chemistry 51(11):6308–6314
26. Zhang L-J, Qi L, Chen X-Y, Liu F, Liu L-J, Ding W-L, Li D-L, Yuan G-C, Tong J-Z, Chen F-Y (2019) Synthesis, crystal structure and photophysical properties of two reduced Schiff bases derived from 5-Aminoisophthalic acid. Journal of Chemical Crystallography 49(4):260–266
27. Aryanejad S, Bagherzade G, Farrokhi A (2018) Efficient and recyclable novel Ni-based metal–organic framework nanostructure as catalyst for the cascade reaction of alcohol oxidation–Knoevenagel condensation. Appl Organomet Chem 32(2):e3995
28. Rani R, Deep A, Mizaikoff B, Singh S (2019) Enhanced hydrothermal stability of Cu MOF by post synthetic modification with amino acids. Vacuum 164:449–457
29. Kourtellaris A, Moushi EE, Spanopoulos I, Tampaxis C, Charalambopoulou G, Steriotis TA, Papaefstathiou GS, Trikalitis PN, Tasiopoulos AJ (2016) A microporous Cu 2+ MOF based on a pyridyl isophthalic acid Schiff base ligand with high CO 2 uptake. Inorg Chem Front 3(12):1527–1535
30. Cheng J, Xuan X, Yang X, Zhou J, Cen K (2018) Preparation of a Cu (BTC)-rGO catalyst loaded on a Pt deposited Cu foam cathode to reduce CO 2 in a photoelectrochemical cell. RSC Advances 8(56):32296–32303
31. Pramanik S, Zheng C, Zhang X, Emge TJ, Li J (2011) New microporous metal–organic framework demonstrating unique selectivity for detection of high explosives and aromatic compounds. J Am Chem Soc 133(12):4153–4155

Publisher's Note Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.