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ORIGINAL PAPER

Amino-functionalized MIL-101(Fe) metal-organic framework as a viable fluorescent probe for nitroaromatic compounds

Peramaiah Karthik[1] · **Alagarsamy Pandikumar**[1] · **Mani Preeyanghaa**[2] · **Mariyappan Kowsalya**[2] · **Bernaurdshaw Neppolian**[1]

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Abstract A highly luminescent iron(III)-based amino-functionalized metal-organic framework (MOF) of type NH_2-MIL-101(Fe) was synthesized by a solvothermal method. Its structure and morphology were studied by X-ray diffraction, scanning electron microscopy, and FTIR. The strong fluorescence of the electron-rich MOF is shown to be quenched by electron-deficient nitroaromatic compounds. Compared to solvents such as water and other organic solvents, quenching by the nitroaromatic compounds nitrobenzene (NB), 4-nitrophenol (4-NP), 4-nitrotoluene (4-NT) and 1,3-dinitrobenzene (1,3-DNB) is particularly strong. The detection limits for NB, 4-NP, 4-NT and 1,3-DNB are 32 ppm, 17 ppm, 9.8 ppm and 11.5 ppm.

Keywords Photoluminescence · Optical probe · Stern-Volmer plot · Guest-host interaction · XRD · Scanning electron microscopy

Introduction

Selective and precise detection of explosive substances have gained much attention due to their obvious value to security efforts. Most commonly, nitroaromatic compounds such as 2,4,6-trinitrotoluene (TNT), 1,3,5-trinitrobenzene (TNB), 1,3-dinitrobenzene (DNB), 2,4-dinitrotoluene (DNT), and others [1] are used as ingredients in explosives and hence numerous sensing methods have been developed for the selective and accurate detection of nitroaromatics [2, 3]. However, existing methods such as gas chromatography coupled with mass spectrometry, surface enhanced Raman spectroscopy and nuclear quadrupole resonance, etc. [4], requires highly sophisticated instrumentation, a trained technician, lengthy sample preparation and time consuming procedures. Alternatively, turn-off or turn-on fluorescence based chemosensor methods for the detection of explosives have several advantages, such as high sensitivity, selectivity and ease of handling, when compared with the other conventional analytical methods. A variety of florescence sensor materials, such as transition metal complexes [5], supramolecular polymers [6], carbon nanotubes [7], quantum dots [8], dendrimers [8] and long chain conjugated polymer etc. [8] were more often used for the detection of nitroaromatics. On the other hand, stability, toxicity, lower sensitivity, lower selectivity and non-biodegradability of existing fluorescence sensor materials limit their application.

Metal-Organic frameworks (MOFs) are a class of porous hybrid materials constructed by organic linkers, transitions and non-transition metal cluster. Their distinctive properties such as tunable architecture, multi-functional sites, high porosity, large surface area etc. widens their applications in a variety of ways [9–12]. Among these, multi-functional sites including catalytically active sites, open metal sites and photo-responsive sites look promising for application in fluorescence chemical sensors [13]. Furthermore, different fluorescence emissions of MOFs can be synthesized by changing the organic linkers. Various novel metal-organic frameworks have been utilized as a fluorescence sensor material for the detection of nitroaromatic compounds. Qu et al. synthesized a Cd-

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✉ Bernaurdshaw Neppolian
neppolian.b@res.srmuniv.ac.in

[1] SRM Research Institute and Department of Chemistry, SRM University, Kattankulathur, Chennai, Tamil Nadu 603203, India

[2] Department of Nanotechnology, SRM University, Kattankulathur, Chennai, Tamil Nadu 603203, India

based metal-organic framework for nitrobenzene detection [14]. Gole et al. fabricated a novel Zn-based electron deficient MOF for the selective fluorescence detection of nitroaromatic compounds [15]. Sun and his research group developed pentiptycene-based luminescent Cu (II) MOF for a highly sensitive and selective detection of electron deficient compounds [16]. Moreover, Su and co-workers synthesized the Cd–based 2D stable MOF for detection of -NO_2 groups containing electron deficient species [17]. Generally, the sensing phenomena of fluorescent MOFs followed the oxidative quenching mechanism. Moreover, the fluorescent MOFs act as electron donors and nitroaromatics act as electron acceptors due to the presence of the electron-withdrawing -NO_2 group.

A few studies reported that amine functionalized MOFs have excellent selectivity and sensitivity for the detection of nitroaromatic compounds compared to other MOFs, due to the Lewis basic sites of amine [18]. Lewis basic amine functionality of MOFs can lead to the binding of analyte molecules through hydrogen bonding and induce electron transfer between MOFs and analytes. In this report, amine functionalized Fe-based metal-organic framework NH_2-MIL-101(Fe) was synthesized using 2-aminoterephthalic acid as an organic linker by means of a simple hydrothermal method. Notably, the photoluminescence quenching studies demonstrated that the prepared MOF is highly selective for electron deficient nitroaromatic compounds such as nitrobenzene, dinitrobenzene, 4-nitrophenol and 4-nitrotoluene. A quenching mechanism between guest and Lewis basic amine functionalities of MOF is also proposed. To the best of our knowledge, no reports exist concerning the ‘turn off’ fluorescence detection of nitroaromatic compounds using an NH_2-MIL-101(Fe) metal-organic framework.

Experimental section

Chemical requirements

Nitroaromatic compounds such as nitrobenzene (NB), nitrotoluene (4-NT), nitrophenol (4-NP), 1, 3-dinitrobenzene (1,3-DNB) and 2-amino terephthalic acid were purchased from Alfa Aesar (https://www.alfa.com/en/catalog/A10293/). All the solvents were purchased from SRL chemicals Pvt. Ltd. India (http://www.srlchem.com/) and used without any further purification. Metal salts, such as $CaCl_2$, Co $(NO_3)_2$, $FeCl_3$, $FeCl_2$, KCl, $MnCl_2$, NaCl and $NiCl_2$ were purchased form Sigma Aldrich (https://www.sigmaaldrich.com/), Loba Chemicals, India and SRL chemicals Pvt. Ltd. India (http://www.srlchem.com/).

Synthesis of NH_2-MIL-101(Fe) metal-organic framework

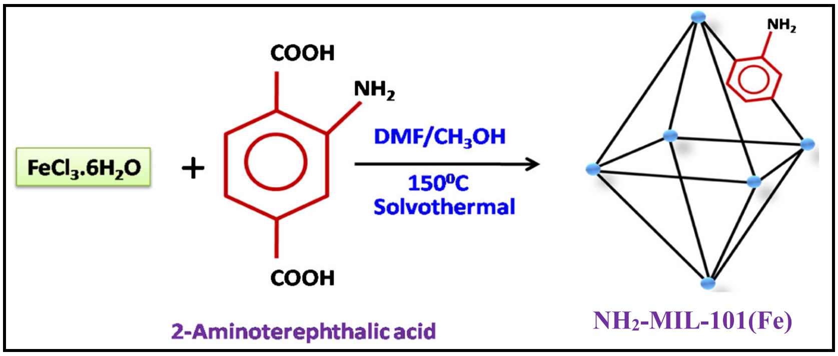
The amine functionalized-NH_2-MIL-101(Fe) was synthesized by following a previously reported method [19] with some modifications (Scheme 1). In a typical procedure, 1.6 g of $FeCl_3.H_2O$ and 1.4 g of 2-aminoterephthalic acid were dissolved in DMF and the resulting solution was transferred into a 100 mL Teflon-lined autoclave and then heated at 150 °C for 12 h. After the hydrothermal treatment, the brown amine functionalized metal-organic framework was separated by centrifugation and washed with DMF and methanol and dried at 60 °C overnight. Furthermore, the resultant powder was suspended in 100 mL of methanol and stirred for 2 days to remove the residual DMF. Finally, the MOF was separated and dried at 150 °C for 12 h.

Fluorescence studies

For the fluorescence titration experiment, 5 mg of NH_2-MIL-101(Fe) MOF was dispersed in 10 mL de-ionized water and 2 mL was poured into a quartz cuvette. The photoluminescence was measured by excitation at 360 nm (λ_{ex} = 360 nm) and emission was observed at 430 nm. Similarly, all the photoluminescence titration experiments were carried out through the gradual incremental increase of analyte concentration in the ppm scale. The homogeneity of the reaction solution was maintained by magnetic stirring.

Choice of materials

Metal − organic frameworks (MOFs) are a class of porous materials composed of metal nodes/clusters and organic



Scheme 1 A schematic illustration of NH_2-MIL-101(Fe) MOF synthesis

linkers. A variety of luminescent metal-organic frameworks have been used for sensing applications. Compared to quantum dots, conjugated conductive polymers, carbon nanotubes, MOFs are considered to be a good sensing platform in analytical science due to their unique properties such as high surface area, versatile framework compositions, and exposed active sites. Fe-based MOF are considered as simple material for the nitroaromatic compounds sensing. The synthesis process and precursor which is used for Fe-MOF synthesis is cost effective compared to all other MOFs, such as those based on Ti, La and Cd. To date, many strategies have been used in the attempt to apply MOFs in the fluorescent detection of nitroaromatic compounds. However, most of the reported MOFs are used for fluorescent detection in the organic or gas phases as MOFs have poor hydrolytic stability. In this study, an iron-based MOF was synthesized by a simple hydrothermal method and, importantly, the prepared MOF was used for the detection of nitroaromatic compounds in the aqueous-phase.

In addition, unlike other MOFs, light absorption of amine functionalized MOFs lies in the visible region. The organic linker such as 2- amino terephthalic acid can effectively harvest the light and transfer the photo-generated electrons to the Fe-oxo cluster. Moreover, the amine group of MOF facilitates H-bond formation with nitroaromatic compounds and thereby enhances quenching. Thus, a facile synthesis process, greater light absorption, the possibility of H-bond formation, water stability and low-cost precursors, makes NH_2-MIL-101(Fe) a potential fluorescent probe for sensing applications.

Characterization techniques

Powder X-ray diffraction (PXRD) patterns were recorded with a PAN analytical X'pert powder diffractometer using Cu Kα radiation. The morphology of the synthesized MOFs was studied using field emission-scanning electron microscopy (FEI Quanta FEG 200 HR-SEM). Fourier Transform Infrared (FTIR) spectra were obtained using PerkinElmer (FTIR) spectrometer (Perkin-Elmer, USA). The photoluminescence studies were carried out using a spectrofluorometer FluoroMax (Horiba. Scientific Instrument Inc., USA). The time resolved spectroscopy and TGA measurements were recorded using DAS6 HORIBA instrument from Jobin Yvon - Japan and NETZSCH STA 449 F3 from Jupiter-India.

Results and discussion

The phase purity and crystalline nature of synthesized NH_2-MIL-101(Fe) MOFs was analyzed by X-ray powder diffraction (XRD). Figure S1 shows that the characteristic diffraction peaks of the prepared samples are analogous to those previously reported for NH_2-MIL-101(Fe) and no peaks corresponding to Fe_2O_3 were observed [19]. These peaks indicate the formation of phase pure NH_2-MIL-101(Fe) MOF without any oxide impurities [20]. Moreover, the fact that there is no difference between the synthesized and the activated sample (i.e., the synthesized sample stirred in methanol for 3 days to remove the DMF solvent) demonstrates that, during the activation process, the structure of MOF is not changed or affected by the long period of mechanical stirring (Fig. S1).

In order to further confirm the formation and bonding of NH_2-MIL-101(Fe) MOF, FTIR analysis was carried out. The results are depicted in supplementary information (Fig. S2). The characteristic stretching and bending vibrations of O-C-O bonds in the NH_2-MIL-101(Fe) appeared in the region of 1600–1400 cm^{-1} [21]. The peaks appearing at 3249 and 3329 cm^{-1} can be attributed to N-H stretching vibrations. In addition, the aromatic ring C = C bond frequency was observed in the region of 1500 to 1600 cm^{-1} [22]. The peak identified at 545 cm^{-1} can mainly be attributed to Fe-O bonding of MOF (Fig. S2 inset) [19]. These FTIR results reveal the formation of metal-organic framework with 2-aminoterephthalic acid utilized as an organic linker, similar to previous reports [23]. Moreover, the FTIR spectra of synthesized MOF are analogous to those of activated NH_2-MIL-101(Fe) MOF; indicating that the structure of MOF did not collapse during the simulation process and remained the same.

The morphology and elemental compositions of NH_2-MIL-101(Fe) MOF were determined by means of FESEM and EDX analysis. FESEM images with different magnifications of MOF are shown in Fig. S3a–d. As showed in Fig. S3, the synthesized NH_2-MIL-101(Fe) MOF shows hexagonal micro-spindle morphology with uniform particle distribution. Based on statistical histogram analysis (Fig. S3) the average particle size of NH_2-MIL-101(Fe) was calculated to be 42.9 nm. Moreover, the elemental composition result shows the presence of elements including C, N, O and Fe. These observations clearly indicates that the MOF particles formed are discrete and not in an aggregated state, and also indicate the purity of the NH_2-MIL-101(Fe) MOF prepared.

The absorption and emission spectra of NH_2-MIL-101(Fe) MOF and organic linker (2-aminoterephthalic acid) were recorded and compared in order to further confirm MOF formation. The UV-visible absorption and emission spectra of both the free linker and NH_2-MIL-101(Fe) MOF are depicted in Fig.1a, b. A sharp absorption peak appearing at 350 nm for the free organic linker may be due to π-π* and n- π* transitions. In contast, the absorption spectrum of NH_2-MIL-101(Fe) completely deviated from that of the free organic linker and a broad absorption peak was observed. The broadening of UV-vis spectra may have been caused by greater electron transfer between the Fe-oxo cluster and 2-aminoterephthalic acid. In addition, along with π –π*, n –π* transition of organic linker, LCCT transition may also have

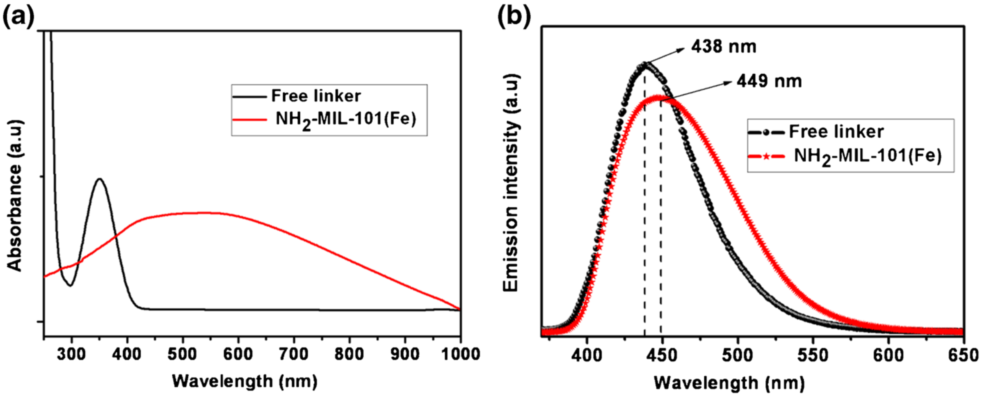


Fig. 1 **a** UV-vis absorption spectra and **b** photoluminescence (PL) spectra (λ_{ex} = 360 nm) of free organic linker and NH_2-MIL-101(Fe) MOF

occurred due to strong interactions between organic linkers and Fe-oxo clusters, resulting in a broadening of the the absorption spectra of NH_2-MIL-101(Fe). This suggests that organic linkers interact strongly with Fe-oxo clusters and take part in MOF formation. Similarly, the PL spectra of the free organic linker and NH_2-MIL-101(Fe) MOF were recorded at room temperature (excitation wavelength (λex) = 360 nm). The free organic linker and NH_2-MIL-101(Fe) MOF exhibit emission peaks at 438 and 449 nm, respectively. The emission peak of NH_2-MIL-101(Fe) MOF shifted to a higher wavelength compared to the linker. It is worth mentioning that the red shift in the emission peak reflects strong coordination between the metal cluster and the organic linker [24].

Fluorescence sensing of nitroaromatic compounds with NH_2-MIL-101 (Fe) MOF

In order to analyze the influence of solvents on fluorescence quenching of synthesized MOF, various solvents were used to record photoluminescence. As can be seen from Fig. 2, the fluorescence intensity of MOF depended considerably on the solvents in question. The relative order of % of quenching of luminescence with respect to different solvents is NB (96%) > CB (30%) > Toluene (29%) > Ethanol (17%) > IPA (14%) > DMF (9%) > water (0%). A drastic fluorescence quenching was observed upon the addition of nitrobenzene. Thus, the physical interaction of solvent molecules with MOF plays the vital role in influencing fluorescence intensity. This observation clearly demonstrated that in the case of MOF, the fluorescence intensity was "turned off" in the presence of electron deficient nitroaromatic compounds. To evaluate the selective sensing behavior of MOF towards nitrobenzene (NB), a series of fluorescence titrations were carried out with gradually increasing NB concentration whilst monitoring the emission response. The luminescence intensity gradually decreased with increasing NB concentration. However, 100% quenching was observed with 120 ppm of NB. This indicates that NB is closely attached to the MOF surface and facilitates much host-guest interaction [15, 25]. Hence, electron transfer reactions between electron donating MOF and electron deficient NB can take place during excitation, resulting in fluorescence quenching.

Based on the above observation, the quenching of fluorescence is mainly attributed to the electron deficient nature of nitroaromatic compounds. Hence, the detection ability of NH_2-MIL-101(Fe) MOF towards the electron deficient nitroaromatic compounds 4-nitrophenol, 1,3-dinitrobenzene and 4-nitrotoluene was investigated with identical experimental conditions. The results are given in Fig. 3. Interestingly, all nitroaromatic compounds showed significant quenching in

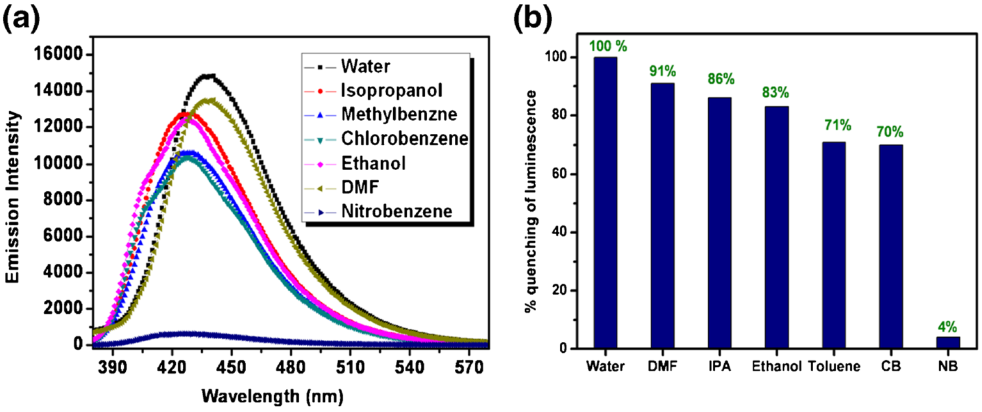


Fig. 2 **a** Fluorescence spectra of NH_2-MIL-101(Fe) MOF in the presence of various solvents (λ_{ex} was 360 nm), **b** Plot of fluorescence quenching % with respect to different solvents obtained for NH_2-MIL-101(Fe) MOF

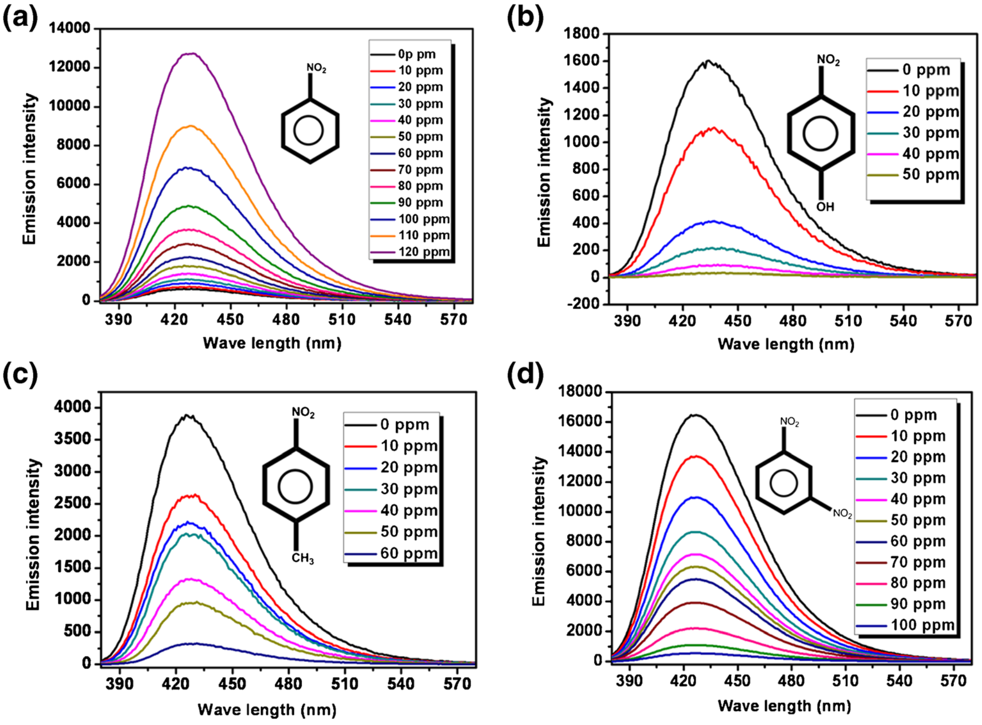
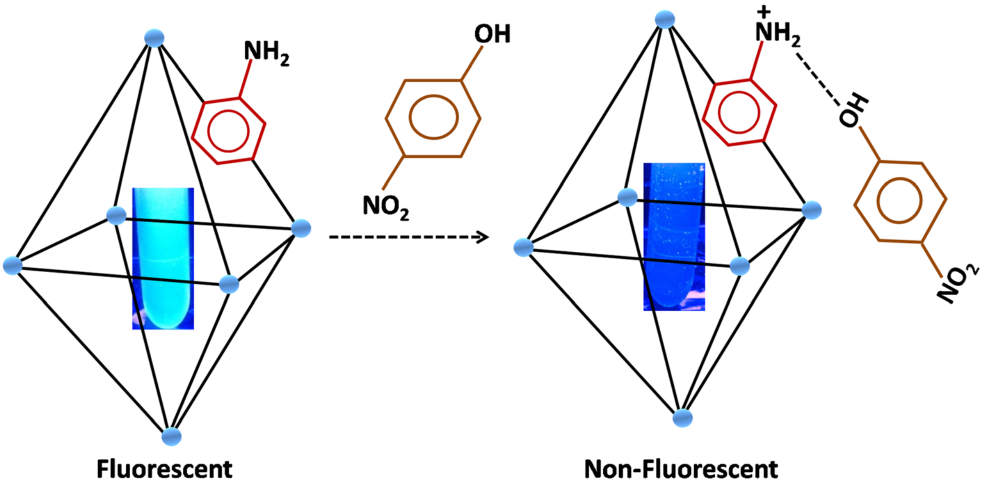


Fig. 3 Fluorescence spectra obtained for the NH_2-MIL-101(Fe) MOF upon addition of various concentrations of **a** nitrobenzene (a) nitrobenzene, (b) 4-nitrophenol, (c) 4-nitrotoluene and (d) 1,3-dinitrobenzene (λex was 360 nm)

fluorescence luminescence intensity. The order of quenching was as follows: 4-nitrophenol >4-nitrotoluene >1,3-dinitrobenzene > nitrobenzene. Complete fluorescence quenching was observed for 4-nitrophenol at 50 ppm. Whereas, 4-nitrotoluene, 1,3-dinitrobenzene and nitrobenzene showed complete quenching at 60 ppm, 100 ppm and 120 ppm respectively. These results clearly indicate that quenching intensity is not only dependent on the electron deficient nature of aromatic compounds but also on host-guest interactions. Among the different nitro aromatics, 4-nitrophenol shows 100% fluorescence quenching even at the low concentration of 50 ppm. This can be explained by the possibility for H-bond formation between guest (MOF) and host molecules (nitroaromatics) (Scheme 2) [26]. The H-atom present in the phenolic group of 4-nitrophenol can form an H-bond with NH_2-MIL-101(Fe) MOF, resulting in rapid electron transfer between guest and host molecules, thereby decreasing the 60 ppm intensity. Besides 4-nitrophenol, 4-nitrotoluene also exhibits complete fluorescence quenching. The limit of detection for all the analytes was calculated from calibration plots (ESM; Fig. S6–S9) by means of the following formula [27]:

$$\text{LoD (ppm)} = 3\sigma/\text{m},$$

where σ is standard deviation and m is slope. The LoDs of NB, 4-NP, 4-NT and 1,3-NB were calculated to be 32.2 ppm,



Scheme 2 Mechanism for the interaction for nitroaromatic compound with fluorescent NH_2-MIL-101 (Fe) MOF

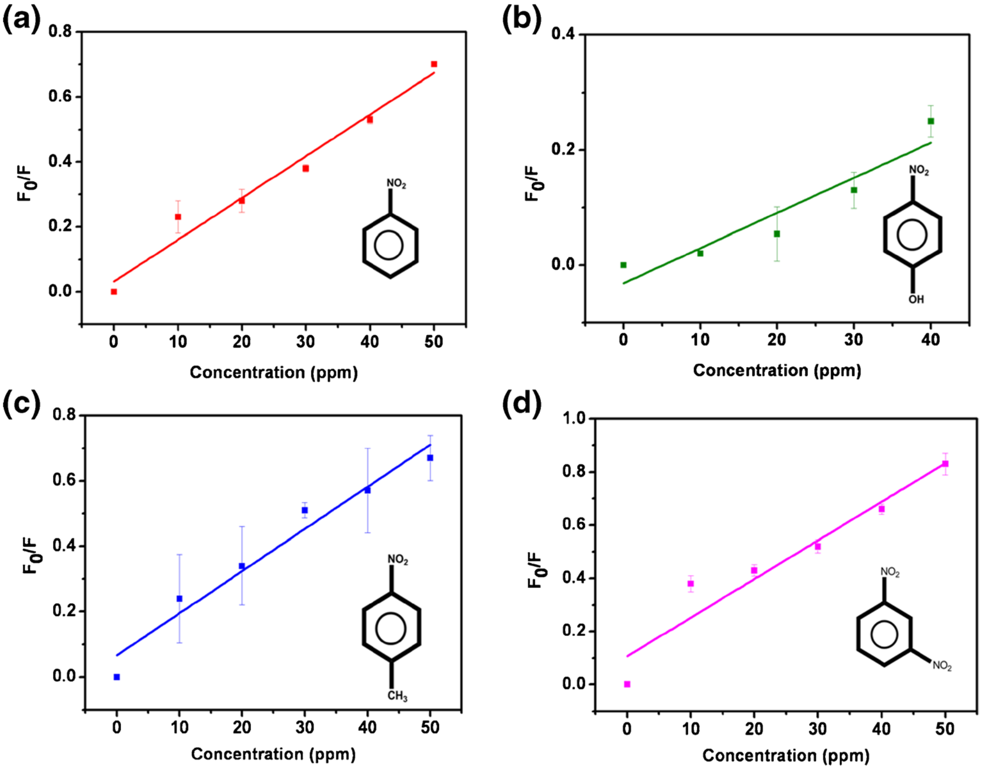


Fig. 4 Stern–Volmer plots for the quenching of the luminescence of NH_2-MIL-101(Fe) MOF upon addition of various concentrations of (a) nitrobenzene, (b) 4-nitrophenol, (c) 4-nitrotoluene and (d) 1,3-di-nitrobenzene (λex was 360 nm)

17.3 ppm, 9.8 ppm and 11.5 ppm, respectively, which further supports the high sensitivity of MOF towards electron deficient nitroaromatic compounds.

For the better understanding and quantification of the fluorescence quenching efficiency, the Stern-Volmer graph was plotted for all quenching studies (Fig. 4) using the equation:

$$(F_0/F) = K_{sv}[A] + 1$$

Where F_0 and F are the fluorescence intensities before and after addition of the analyte, respectively, Ksv is the quenching constant (m^{-1}), [A] is the concentration of the analyte. The Stern-Volmer plots for all analytes are linear at lower concentration levels. This linearity of Stern-Volmer plots reveals that the quenching occurred due to the static energy transfer process and not through dynamic mechanisms [28, 29]. The fluorescence quenching occurred due to photo-induced electron transfer (PET) between guest and host molecules. When, NH_2-MIL-101(Fe) MOF was irradiated with light, the photo-excited electrons migrated to the lowest unoccupied molecular orbital (LUMO) of nitroaromatic compounds which is the low-lying π*-orbital and is stabilized by the -NO_2 group through conjugation [30]. This stimulates electron transfer from the CB of MOF to the LUMO level of the analytes, thereby quenching the fluorescence intensity during excitation.

In order to confirm the quenching mechanism for the detection of 4-NP, the fluorescence lifetime measurement was carried out by monitoring fluorescence life time decay with the gradual addition of 4-NP to the MOF (Fig. 5). As can be seen from Fig. 5, the gradual addition of 4-NP to MOF resulted in only nominal change in the lifetime decay values. The average life time (τ) values of excited state carriers of MOF suspension at different concentration of 4-NP added MOF suspensions 0, 20, 40 and 60 μL of 4-NP were found to be 2.3, 2.2, 2.2 and 1.7 ns, respectively. The average life time of excited state carriers essentially remain unchanged after and before the addition of 4-NP. Thus, no change in the lifetime values of carriers strongly suggests that the fluorescence quenching follows static process rather than dynamic quenching process [31, 32].

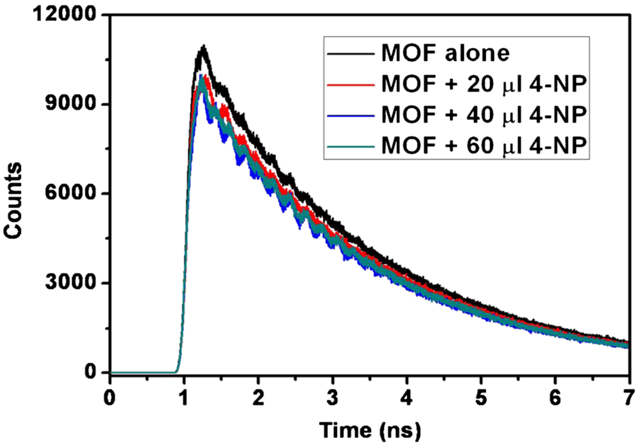


Fig. 5 Lifetime decay profile of fluorescence spectra obtained for the NH_2-MIL-101(Fe) MOF upon addition of various concentration of 4-NP

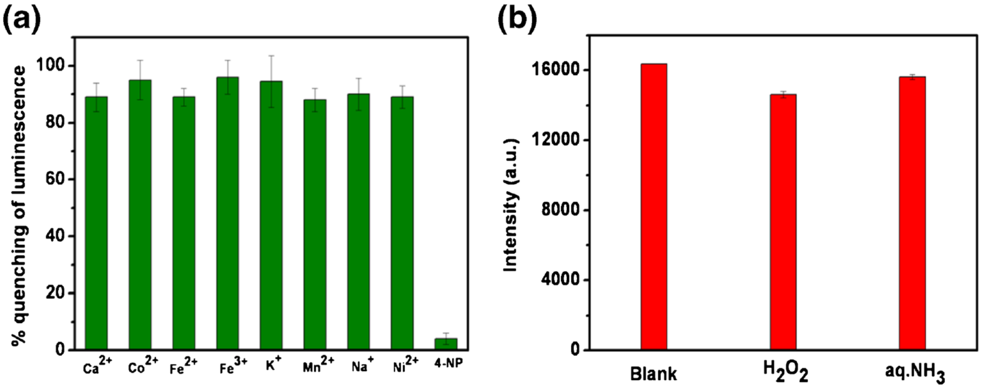


Fig. 6 **a** PL responses of NH_2-MIL-101(Fe) MOF upon the addition of 1000 ppm of Ca^{2+}, Co^{2+}, Fe^{2+}, Fe^{3+}, K^{+}, Mn^{2+} Na^{+} and Ni^{2}; **b** 50 μM of H_2O_2 and aq NH_3 (all the experiments were carried out three times ($n = 3$) and *Error bars* indicate standard deviations)

Interference study

In order to test the selectivity of this method, interference studies were carried out with H_2O_2, NH_3 and metal ions such as Ca^{2+}, Co^{2+}, Fe^{2+}, Fe^{3+}, K^{+}, Mn^{2+} Na^{+} and Ni^{2+}. The results are shown in Fig. 6. It can observed that no significant quenching was observed when adding high concentrations (50 μL: 1000 ppm) of metal ions, clearly indicating the good selectivity of MOF for the sensing process. Similarly, with H_2O_2 and NH_3 the fluorescence intensity also remains unchanged. These results further confirm the selectivity of NH_2-MIL-101(Fe) MOF. The efficiency of the present method was compared with that of the recently reported fluorescence based probes for nitroaromatic compounds. Table 1 shows the K_{sv} (Stern-Volmer constant) of each reported fluorescence detection method.

Conclusion

In this study, we have reported on the detection of nitroaromatic compounds with NH_2-MIL-101(Fe) MOF based on fluorescence quenching. The quenching in the fluorescence is mainly attributed to photo-induced electron transfer between guest and host molecules. Moreover, rapid quenching was observed for 4-nitrophenol due to inter-molecular H-bond formation; facilitating the rapid electron transfer reaction. The present work will stimulate interest towards developing Fe-

Table 1 An overview on recently reported nanomaterial-based fluorometric methods for the determination of nitroaromatic compounds

Material	Figures of merit K_{sv}/M^{-1}	Ref
(4-(2-hydroxyethyl) 1piperazineethanesulfonic acid (HEPES) buffer containing DMSO (2%)	NB- 2.2×10^{2}	[33]
2,6-diamino pyridine functionalized graphene oxide (DAP-RGO)-Fluorescence method	NB- 1.89×10^{3}	[34]
1,3,5-Tris(4-bromophenyl)benzene (TBB) covalent organic framework – Fluorescence method	NB-4.13×10^{3}	[35]
Fe3O4@Tb-BTC magnetic metal–organic framework (MOF) - Fluorescence method	NB-9.5×10^{2}	[36]
This work	NB- 9.5×10^{7}	This work
Lanthanide based metal–organic frameworks- Fluorescence method	4-NP- 2.2×10^{4}	[37]
This work	4-NP- 1.3×10^{6}	This work
Pyrene based Luminescent compound – Fluorescence method	1,3-DNB- 5.6×10^{3}	[38]
1,3-di(4-carboxyphenyl)benzene-Zn MOF- Fluorescence method	1,3-DNB- 1.5×10^{3}	[39]
Pentiptycene-Based Luminescent Cu (II) MOF- Fluorescence method	1,3-DNB- 1.4×10^{5}	[16]
This work	1,3-DNB- 1.6×10^{6}	This work
Zn–PDA- Metal–organic framework (MOF)- Fluorescence method	4-NT- 511.4×10^{4}	[40]
This work	4-NT- 1.04×10^{6}	This work

based simple MOF materials for the selective and sensitive detection of nitroaromatics.

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Compliance with ethical standards The author(s) declare that they have no competing interests.

References

1. Toal SJ, Trogler WC (2006) Polymer sensors for nitroaromatic explosives detection. J Mater Chem A 16(28):2871–2883
2. Forzani ES, Lu D, Leright MJ, Aguilar AD, Tsow F, Iglesias RA, Zhang Q, Lu J, Li J, Tao N (2009) A hybrid electrochemical–colorimetric sensing platform for detection of explosives. J Am Chem Soc 131(4):1390–1391
3. Dorozhkin L, Nefedov V, Sabelnikov AG, Sevastjanov V (2004) Detection of trace amounts of explosives and/or explosive related compounds on various surfaces by a new sensing technique/material. Sens Actuator B Chem 99(2):568–570
4. Wong JM, Li QX, Hammock BD, Seiber JN (1991) Method for the analysis of 4-nitrophenol and parathion in soil using supercritical fluid extraction and immunoassay. J Agric Food Chem 39(10):1802–1807
5. Shanmugaraju S, Jadhav H, Patil YP, Mukherjee PS (2012) Self-assembly of an Octanuclear platinum (II) tetragonal prism from a new PtII4 organometallic star-shaped acceptor and its Nitroaromatic sensing study. Inorg Chem 51(24):13072–13074
6. Shanmugaraju S, Jadhav H, Karthik R, Mukherjee PS (2013) Electron rich supramolecular polymers as fluorescent sensors for nitroaromatics. RSC Adv 3(15):4940–4950
7. Thomas SW, Joly GD, Swager TM (2007) Chemical sensors based on amplifying fluorescent conjugated polymers. Chem Rev 107(4):1339–1386
8. Cavaye H, Smith AR, James M, Nelson A, Burn PL, Gentle IR, Lo S-C, Meredith P (2009) Solid-state dendrimer sensors: probing the diffusion of an explosive analogue using neutron reflectometry. Langmuir 25(21):12800–12805
9. Long JR, Yaghi OM (2009) The pervasive chemistry of metal–organic frameworks. Chem Soc Rev 38(5):1213–1214
10. Yang X, Xia Y (2016) Urea-modified metal-organic framework of type MIL-101 (Cr) for the preconcentration of phosphorylated peptides. Microchim Acta 183(7):2235–2240
11. Jin D, Xu Q, Yu L, Hu X (2015) Photoelectrochemical detection of the herbicide clethodim by using the modified metal-organic framework amino-MIL-125 (Ti)/TiO2. Microchim Acta 182(11–12):1885–1892
12. Das MC, Xiang S, Zhang Z, Chen B (2011) Funktionelle Gemischtmetall-organische Gerüste mit Metalloliganden. Angew Chem 123(45):10696–10107
13. Yu H, Long D (2016) Highly chemiluminescent metal-organic framework of type MIL-101 (Cr) for detection of hydrogen peroxide and pyrophosphate ions. Microchim Acta 183(12):3151–3157
14. Qu XL, Gui D, Zheng XL, Li R, Han HL, Li X, Li PZ (2016) A cd (ii)-based metal–organic framework as a luminance sensor to nitrobenzene and Tb (iii) ion. Dalton Trans 45(16):6983–6989
15. Gole B, Bar AK, Mukherjee PS (2014) Modification of extended open frameworks with fluorescent tags for sensing explosives: competition between size selectivity and electron deficiency. Chem Eur J 20(8):2276–2291
16. Zhang M, Zhang L, Xiao Z, Zhang Q, Wang R, Dai F, Sun D (2016) Pentiptycene-based luminescent cu (II) MOF exhibiting selective gas adsorption and unprecedentedly high-sensitivity detection of Nitroaromatic compounds (NACs). Sci Report 6:20672–20681
17. Zhang SR, Du DY, Qin JS, Bao SJ, Li SL, He WW, Lan YQ, Shen P, Su ZM (2014) A fluorescent sensor for highly selective detection of Nitroaromatic explosives based on a 2D, extremely stable, metal–organic framework. Chem Eur J 20(13):3589–3594
18. Baron A, Brown MR, Jones CR (2010) Chemosensory receptor ligand-based therapies. Google patents, U.S. patent application 12/763, 926
19. Zhang Z, Li X, Liu B, Zhao Q, Chen G (2016) Hexagonal microspindle of NH 2-MIL-101 (Fe) metal–organic frameworks with visible-light-induced photocatalytic activity for the degradation of toluene. RSC Adv 6(6):4289–4295
20. Ghorbani-Kalhor E (2016) A metal-organic framework nanocomposite made from functionalized magnetite nanoparticles and HKUST-1 (MOF-199) for preconcentration of cd (II), Pb (II), and Ni (II). Microchim Acta 183(9):2639–2647
21. Vu TA, Le GH, Dao CD, Dang LQ, Nguyen KT, Dang PT, Tran HT, Duong QT, Nguyen TV, Lee GD (2014) Isomorphous substitution of Cr by Fe in MIL-101 framework and its application as a novel heterogeneous photo-Fenton catalyst for reactive dye degradation. RSC Adv 4(78):41185–41194
22. Modrow A, Zargarani D, Herges R, Stock N (2012) Introducing a photo-switchable azo-functionality inside Cr-MIL-101-NH 2 by covalent post-synthetic modification. Dalton Trans 41(28):8690–8696
23. Shen L, Liang S, Wu W, Liang R, Wu L (2013) Multifunctional NH_2-mediated zirconium metal–organic framework as an efficient visible-light-driven photocatalyst for selective oxidation of alcohols and reduction of aqueous Cr (vi). Dalton Trans 42(37):13649–13657
24. Yang J, Liu X, Wang X, Dai F, Zhou Y, Dong B, Zhang L, Liu Y, Sun D (2015) Syntheses, crystal structures, and properties of four metal–organic complexes based on 1, 4, 5, 6, 7, 7-Hexachlorobicyclo [2.2. 1] hept-5-ene-2, 3-dicarboxylic acid. Cryst Growth Des 15(9):4198–4205
25. Shanmugaraju S, Mukherjee PS (2015) π-electron rich small molecule sensors for the recognition of nitroaromatics. Chem Commun 51(89):16014–16032
26. Barman N, Singha D, Sahu K (2013) Fluorescence quenching of hydrogen-bonded coumarin 102-phenol complex: effect of excited-state hydrogen bonding strength. J Phys Chem A 117(19):3945–3953
27. Yusoff N, Pandikumar A, Ramaraj R, Lim HN, Huang NM (2015) Gold nanoparticle based optical and electrochemical sensing of dopamine. Microch Acta 182(13–14):2091–2114
28. Li Y, Liu K, Li W-J, Guo A, Zhao F-Y, Liu H, Ruan W-J (2015) Coordination polymer Nanoarchitecture for Nitroaromatic sensing by static quenching mechanism. J Phys Chem C 119(51):28544–28550
29. Sanda S, Parshamoni S, Biswas S, Konar S (2015) Highly selective detection of palladium and picric acid by a luminescent MOF: a dual functional fluorescent sensor. Chem Commun 51(30):6576–6579
30. Meaney MS, McGuffin VL (2008) Luminescence-based methods for sensing and detection of explosives. Anal Bioanal Chem 391(7):2557–2576
31. Mostakim SK, Shyam Biswas S (2016) A thiadiazole-functionalized Zr (IV)-based metal-organic framework as highly fluorescent probe for the selective detection of picric acid. Cryst EngComm 18:3104–3113

32. Xiao Y, Jin-Long C, Meng-Xiang S, Fang Y, Bo L, Bin D (2014) Phosphate-containing metabolites switch on phosphorescence of ferric ion engineered carbon dots in aqueous solution. RSC Adv 4:22318
33. Kumar R, Sandhu S, Singh P, Hundal G, Hundal MS, Kumar S (2014) Tripodal fluorescent sensor for encapsulation-based detection of picric acid in water. Asian J Org Chem 3(7):805–813
34. Liu T, Ding L, He G, Yang Y, Wang W, Fang Y (2011) Photochemical stabilization of terthiophene and its utilization as a new sensing element in the fabrication of monolayer-chemistry-based fluorescent sensing films. ACS Appl Mater Interfaces 3(4): 1245–1253
35. Dinda D, Gupta A, Shaw BK, Sadhu S, Saha SK (2014) Highly sensitive and selective detection of 2,4,6-Trinitrophenol using covalent-organic polymer luminescent probes. Appl Mater Interfaces 6:10722–10728
36. Qian J-J, Qiu L-G, Wang Y-M, Yuan Y-P, Xie A-J, Shen Y-H (2014) Fabrication of magnetically separable fluorescent terbium-based MOF nanospheres for highly selective trace-level detection of TNT. Dalton Trans 43(10):3978–3983
37. Wang XQ et al (2015) Lanthanide metal-organic frameworks containing a novel flexible ligand for luminescence sensing of small organic molecules and selective adsorption. J Mater Chem A 3: 12777–12785
38. Ding L, Liu Y, Cao Y, Wang L, Xin Y, Fang Y (2012) A single fluorescent self-assembled monolayer film sensor with discriminatory power. J Mater Chem 22(23):11574–11582
39. He H, Song Y, Sun F, Bian Z, Gao L, Zhu G (2015) A porous metal–organic framework formed by a V-shaped ligand and Zn (ii) ion with highly selective sensing for nitroaromatic explosives. J Mater Chem A 3(32):16598–16603
40. Jiang X, Liu Y, Wu P, Wang L, Wang Q, Zhu G, X-l L, Wang J (2014) A metal-organic framework with a 9-phenylcarbazole moiety as a fluorescent tag for picric acid explosive detection: collaboration of electron transfer, hydrogen bonding and size matching. RSC Adv 4(88):47357–47360