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ARTICLE

A 2D bilayer metal-organic framework as fluorescence sensor for highly selective sensing of nitro explosives

Cite this: DOI: 10.1039/x0xx00000x

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Received 00th January 2012

Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

www.rsc.org/

A novel Cd-MOF (metal organic framework) $[\text{Cd}_3(\text{NTB})_2(\text{DMA})_3] \cdot 2\text{DMA}$ (H_3NTB = 4,4',4''-nitriлотrisbenzoic acid; DMA = N,N-dimethylacetamide) (**1**) was obtained under solvothermal condition. The resulted MOF exhibits a novel (2D→3D) interdigitated architecture that is obtained from bilayer motif with hexagonal grids. Luminescent properties of activate phase **1a** well dispersed in different solvents have also been investigated systematically, which demonstrate distinct solvent-dependent luminescent spectra with emission intensities significantly quenched toward nitrobenzene (NB) and 2,4,6-trinitrophenol (TNP). The results reveal that **1** could be applied as a fluorescence sensor for TNP with high sensitivity, selectivity, and recyclability.

Introduction

Rapid and selective detection of explosives has become one of the most pressing issues concerning homeland security, military applications, forensic investigations, and mine-field analysis.¹ Nitro aromatics such as nitrobenzene (NB), 1,3-dinitrobenzene (1,3-DNT), 2,4,6-Trinitrotoluene (TNT) and 2,4,6-trinitrophenol (TNP), are common ingredients of industrial explosives and found in many unexploded land mines worldwide.² Amongst these nitro explosives TNP shows superior explosive power than TNT.^{3a} TNP is released into the environment during commercial production and use, leading to the contamination of soil and aquatic systems. Moreover, picramic acid (2-amino-4,6-dinitrophenol), which is the by-products of metabolism, has ten times more mutagenic activity than TNP.³ Thus it is very important for the selective and sensitive detection of TNP present in soil and ground water for security screening, homeland security and environmental monitoring. However, the materials usually used for detection of explosives are still defective in the respects of stability, toxicity, sensitivity, and recyclability. It is a challenge to synthesize novel materials for fluorescence detection of explosives.

Metal organic frameworks (MOFs) are well known for their applications in molecular storage, separation, drug delivery, and catalysis.^{4,5} MOFs in principle can serve as the excellent candidate for chemical sensors to detect trace amounts of nitroaromatic compounds, because the detectable changes of fluorescence response could be easily achieved by a photo induced electron-transfer mechanism (from π -electron-rich MOFs to π -electron-deficient nitroaromatic compounds).^{6,7} Li et al. reported the first highly luminescent MOF that is able to detect trace nitroaromatic explosives 2,4-dinitrotoluene (DNT) and 2,3-dimethyl-2,3-dinitrobutane (DMNB) in the vapor

phase.⁸ Chang et al. reported a high sensitivity luminescent MOF $[\text{NH}_2(\text{CH}_3)_2]_2[\text{Cd}_{17}(\text{L})_{12}(\mu_3\text{-H}_2\text{O})_4(\text{DMF})_2(\text{H}_2\text{O})_2] \cdot \text{solvent}$ (H_3L =2,4,6-tri[1-(3-carboxylphenoxy)ylmethyl]mesitylene and DMF = N, N-dimethylformamide), which quenched at 100 ppm with a high quenching efficiency of 92.5%.⁹ These MOF materials exhibit fast, highly sensitive, reversible sensing and selective detection of nitro explosives. Considering the above excellent works, there is an urgent need to develop sensitive and reliable MOF sensors for nitro explosives, especially for TNP.

Here, we report the synthesis of a novel Cd(II) MOF, $[\text{Cd}_3(\text{NTB})_2(\text{DMA})_3] \cdot 2\text{DMA}$ (**1**), which defines a 3D interdigitated architecture assembled by bilayer motifs with hexagonal grids. The phase purities of bulk products were confirmed using X-ray powder diffraction (XRPD). Considering metal-organic frameworks constructed from d^{10} metal ions and conjugated organic linkers are promising candidates for potential photoactive materials, luminescent properties of activated **1a** dispersed in different solvents have been investigated systematically. Notably, it exhibits high sensitivity for 2,4,6-trinitrophenol (TNP) with K_{sv} constant $2.0 \times 10^4 \text{ M}^{-1}$ through luminescence quenching experiments.

Experimental section

General information

All chemical materials were purchased from commercial sources and used without further purification. The FT-IR spectra were recorded from KBr pellets in the range 4000–400 cm^{-1} on a Mattson Alpha-Centauri spectrometer. XRPD patterns were recorded on a Siemens D5005 diffractometer with Cu $K\alpha$ ($\lambda = 1.5418 \text{ \AA}$) radiation in the range of 3–60° at a rate of 5°/min. The C, H, and N elemental analyses were conducted

on a Perkin-Elmer 2400CHN elemental analyzer. TG curves were performed on a Perkin-Elmer TG-7 analyzer heated from room temperature to 1000 °C at a ramp rate of 5 °C/min under nitrogen. The photoluminescence spectra were measured on a Perkin-Elmer FLS-920 Edinburgh Fluorescence Spectrometer.

Crystal structure determination

Single-crystal X-ray diffraction data for **1** were recorded on a Bruker Apex CCD II area-detector diffractometer with graphite-monochromated Mo-K α radiation ($\lambda = 0.71073$ Å) at 296(2) K. Absorption corrections were applied using multi-scan technique. Their structures were solved by the direct method of SHELXS-97 and refined by full-matrix least-square techniques with the SHELXL-97 program.¹⁰ Non-hydrogen atoms were refined with anisotropic temperature parameters. The crystal data and structure refinement results of **1** are summarized in Table S1.

Synthesis of [Cd₃(NTB)₂(DMA)₃]·2DMA (**1**)

The mixture of Cd(NO₃)₂·4H₂O (60 mg, 0.2 mmol), and H₃NTB (18 mg, 0.05 mmol) in 3 mL of N,N-dimethylacetamide (DMA) was sealed in a 15 mL vial and heated to 130 °C for 3 days, and then cooled to room temperature. The light yellow crystals were obtained, washed with ethanol, and dried at room temperature (Yield: 60%). Anal. Calcd for C₆₂H₆₉N₇O₁₇Cd₃: C, 48.94; H, 4.57; N, 6.44. Found: C 48.57; H 4.38; N 6.02. IR (KBr, cm⁻¹): 594.65 (w), 441.51 (w), 1105.23 (w), 714.72 (w), 1140.31 (w), 2931.75 (w), 536.46 (w), 676.89 (w), 3420.78 (w), 1015.01 (m), 851.56 (m), 1175.73 (m), 783.48 (m), 1268.95 (m), 1536.03 (s), 1506.51 (s), 1314.80 (s), 1594.09 (s), 1392.13 (s).

Activation of **1a**

The samples **1** were immersed in CH₂Cl₂ for 24 h, and the extracts were decanted. Fresh CH₂Cl₂ was subsequently added, and the crystals were allowed to stay for an additional 24 h to remove the nonvolatile dimethylacetamide (DMA). After the removal of dichloromethane by decanting, the activated samples **1a** were obtained by drying under a dynamic vacuum at 80 °C overnight.

The solvent sensing experiment

The solvent sensing experiment has been performed as follows: finely ground samples of activated **1a** was immersed in different organic solvents (3 mL), treated by ultrasonication for 30 minutes, and then aged to form stable emulsions before fluorescence was measured.

Results and discussion

Crystal structure description

Single-crystal X-ray diffraction study reveals that **1** is a 2D bilayer structure and crystallizes in the triclinic space group P $\bar{1}$. The asymmetric unit contains three independent Cd atoms, two H₃NTB

ligands and three DMA molecules. Cd1 atom is coordinated by six O atoms (O4, O5, O7, O9, O10, O13) from five H₃NTB ligands, showing a distorted octahedral geometry (Cd-O = 2.234(4)-2.436(5) Å). The Cd2 ion has a six-coordinated octahedral geometry which is defined by four O atoms (O5, O6, O8, O9) from three H₃NTB ligands and two O atoms (O1, O3) from two coordinated DMA molecules (Cd-O = 2.198(5)-2.572(5) Å). While Cd3, similar to Cd2, exhibits an octahedral geometry which is formed by five O atoms (O2, O11, O12, O13, O14) from three H₃NTB ligands and one O atom (O15) from one coordinated DMA molecule (Cd-O = 2.193(5)-2.531(5) Å). Cd1, Cd2 and Cd3 are associated together by six carboxylate groups of six NTB³⁻ ligands to form a {Cd₃} SBU [Cd₃(CO₂)₆], with the distance of Cd1-Cd2 3.467(2) Å, Cd1-Cd3 3.779(2) Å (Fig. 1 and Fig. S1). It is interesting to note that the H₃NTB ligands show two different coordination modes (L^a and L^b). L^a adopts $\mu^6-\eta^1:\eta^1:\eta^1:\eta^2:\eta^1:\eta^2$ bridging coordination mode to connect six Cd^{II} ions; meanwhile L^b adopts $\mu^5-\eta^1:\eta^1:\eta^1:\eta^1:\eta^1:\eta^2$ coordination mode to connect five Cd^{II} ions (Fig. 2).

Because the Cd2 and Cd3 are terminated by DMA molecules, the trinuclear units in a *ab* plane are linked by six H₃NTB ligands, forming a unique 2D bilayer framework.¹¹ In this 2D framework, each H₃NTB ligands are approximately parallel to each other, with the distance of N-N is 5.01 Å. Simply, three [Cd₃(CO₂)₆] SBU are linked by six NTB³⁻ to form a unique 2D bilayer framework containing hexagonal grids of approximate dimension of 16.8 Å (Fig. 1b). The adjacent bilayers adopt an ABAB stacking mode, further packing into a 3D supramolecular structure (Fig. 1c). It is noteworthy that weak intramolecular C-H...O hydrogen bonding interactions formed between the coordinated DMA molecules and the carboxyl groups in adjacent bilayer stabilize the coordination structure (C...O = 3.13-3.59Å).

To get deep insight into the structure of **1**, the topological analysis was carried out. The Cd atom is treated as four-connected nodes, and the H₃NTB ligands are defined as the three-connected nodes; the sheet can be simplified as a bi-nodal (3, 4)-coordinated net with the

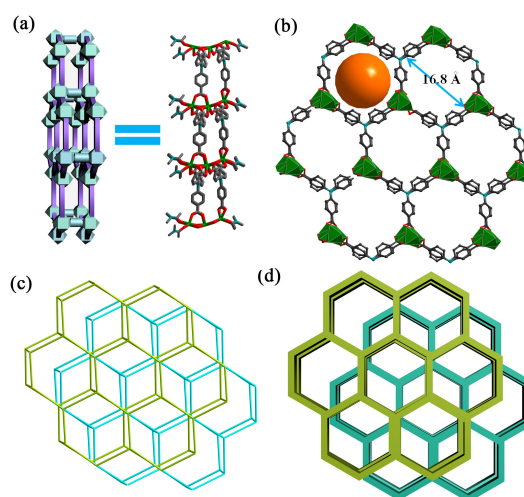


Fig. 1 (a) View of the 2D bilayer framework along *a* axis. (b) View of the 2D structure along the *c* axis. (c) The representation of the AB packing of the 2D sheet-like structure. (d) Schematic view of the 3D supramolecular architecture. All the hydrogen atoms are omitted for clarity

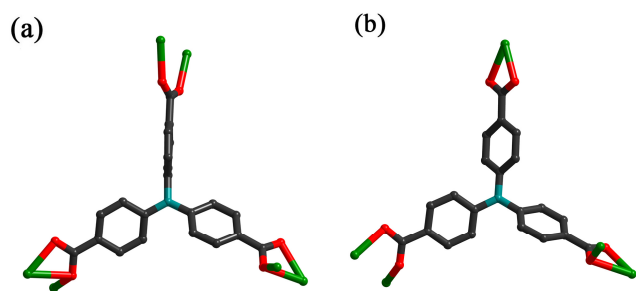


Fig. 2 Coordination modes of the carboxylate groups of H_3NTB ligand: (a) L^a , (b) L^b .

point symbol is $(6^3)-(6^6)$. The total accessible volume in desolvated compound **1** after removal of guest solvent is 28.3% using the PLATON/VOID routine.¹²

The purity of the as-synthesized MOF **1** is confirmed by similarities between simulated and experimental X-ray powder diffraction (XRPD) patterns (Fig. S4). Thermal stability of MOF **1** is also examined. Compound **1** shows a gradual weight loss of ~11.7% (calculated = 11.5%) up to 235 °C that corresponds to loss of 2 DMA molecules in the lattice. The frameworks collapsed in the temperature around 340°C (Fig. S5)

Luminescence behaviors and sensing properties

Considering that MOFs constructed by d^{10} metal ions and various π -conjugated organic ligands have been proposed as promising candidates for photoactive materials,¹³ the photoluminescence spectra of **1** and the free ligand in the solid state were investigated. The H_3NTB ligand presents blue luminescence with emission maxima at 450 nm (λ_{ex} = 371 nm), which could probably be attributed to the π^* - π transitions (Fig. S6). Upon excitation at 366 nm, the emission spectra of **1** are observed with a maximum at 443 nm, which makes it ideal to be employed as fluorescence sensor materials for detection of chemical reagents (Fig. S7).

The luminescence property of **1a** in different solvent emulsions was investigated. The solvents used are N, N-dimethylacetamide (DMA), N, N-dimethylformamid (DMF), methanol (MeOH), *n*-propanol, trichloromethane (CH_2Cl), ethanol (EtOH), *n*-butyl alcohol, acetonitrile, acetone, dichloromethane (CH_2Cl_2), and nitrobenzene (NB). The most interesting feature is that its PL spectrum is largely dependent on the solvent molecules, particularly in the case of nitrobenzene, which exhibit the most significant quenching effects (Fig. 3). The possibility of quenching mechanism of nitrobenzenes is assumed to originate from the electron-withdrawing property of the nitro groups in the analytes, which results in a significant donor-acceptor electron transfer from the ligands to the electron-donating MOF structures. Such solvent-dependent luminescence properties are of interest for the sensing of nitrobenzene solvent molecules. To examine the sensitivity of fluorescence quenching by NB, the fluorescence spectra were recorded with addition of increasing concentration of NB. As can be seen from Fig. 4, the luminescent intensity of the emulsions

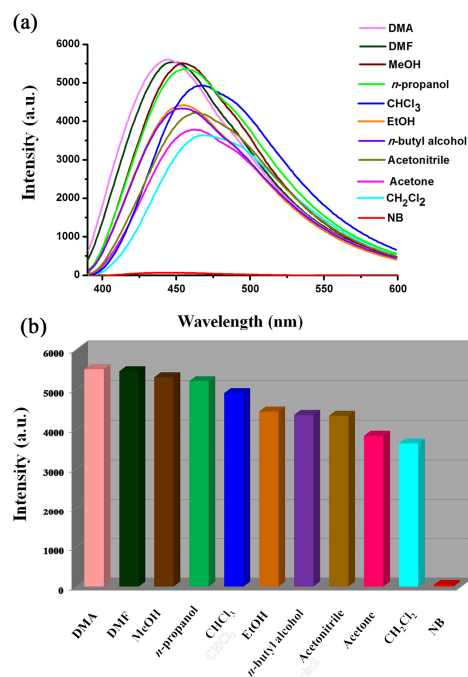


Fig. 3 Comparisons of the luminescence intensity of **1a**-solvent emulsions at room temperature (excited at 366 nm) (solvent = DMA, DMF, MeOH, *n*-propanol, CH_2Cl , EtOH, *n*-butyl alcohol, Acetonitrile, Acetone, CH_2Cl_2 , and Nitrobenzene).

significantly decreased with increasing addition of nitrobenzene. The intensity of **1a** standard emulsion decreased to 21% at 600 ppm, the quenching efficiency is considerably higher than some reported MOFs.¹⁴ The results allowed us to detect small amounts of nitrobenzene in solution.

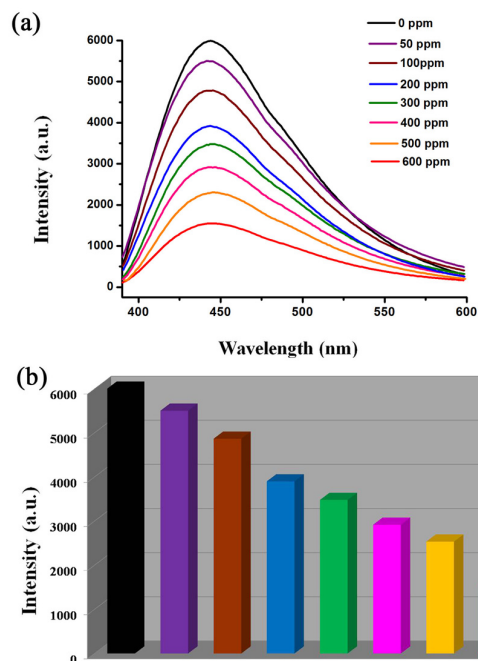


Fig. 4 Emission spectra of **1a** at different nitrobenzene (NB) concentrations in DMA.

The quenching effect for NB inspired us to further investigate the possibility of sensing other nitro explosives in detail. The fluorescence signals of **1a**-containing suspensions in different nitro explosives, including NB, *o*-DNB (1,2-dinitrobenzene), *m*-DNB (1,3-dinitrobenzene), *p*-DNB (1,4-dinitrobenzene) and TNP (2,4,6-trinitrophenol) were measured. As shown in Fig. 5, upon the addition of an identical amount of analytes (50 ppm), different degrees of fluorescence quenching of the suspension were recorded. The quenching efficiency, defined by $(I_0 - I)/I_0 \times 100\%$, where I_0 and I are the luminescence intensities of **1** before and after the addition of analyte. To a certain extent, all the analytes can weaken the emission of **1** with the quenching efficiency in the following order: TNP > *p*-DNB > *m*-DNB > *o*-DNB > NB. On further study into the PL spectra, we have found the spectrum of TNP is obviously red-shifted by 37 nm as compared with that of other nitro explosives.

To further investigate the sensing ability of **1** for TNP, the emission spectra are recorded by the gradual addition of TNP solution into a suspension of 0.3 mg of **1** dispersed in 3 mL of DMA solution. As shown in Fig. 6, the fluorescent intensity clearly decreased with increasing TNP amount. The quenching efficiency was estimated to be 8.8 % for 1 ppm of TNP, 56.2 % for 20 ppm of TNP, and 89 % for 50 ppm of TNP. The differences in quenching efficiency can be quantitatively treated with the Stern-Volmer (SV) equation: $(I_0/I) = K_{sv}[A] + 1$, in which I_0 is the initial fluorescence intensity without analyte, I represents the fluorescence intensity with added analyte of the molar concentration $[A]$, and K_{sv} is the quenching constant (M^{-1}).¹⁵ The SV plot for TNP was nearly linear at low concentrations and subsequently deviated from linearity, bending upwards at higher concentrations (Fig. 7). The nonlinear nature of the SV plot of TNP can be ascribed to a self-absorption or

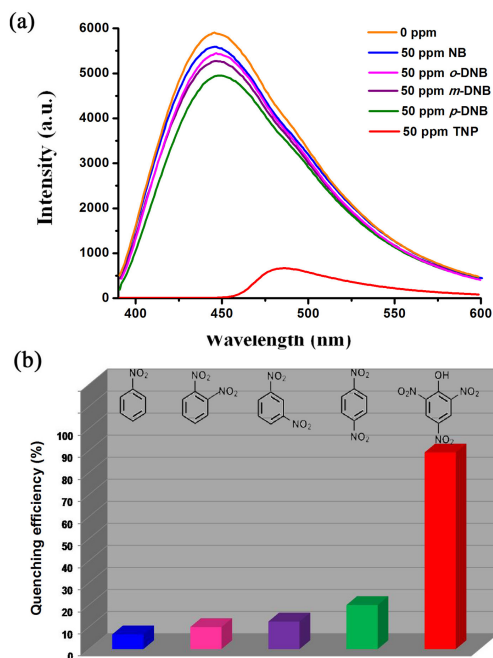


Fig. 5 Reduction of fluorescent intensity (plotted as quenching efficiency) upon the addition of several analyte ([analyte] = 50 ppm).

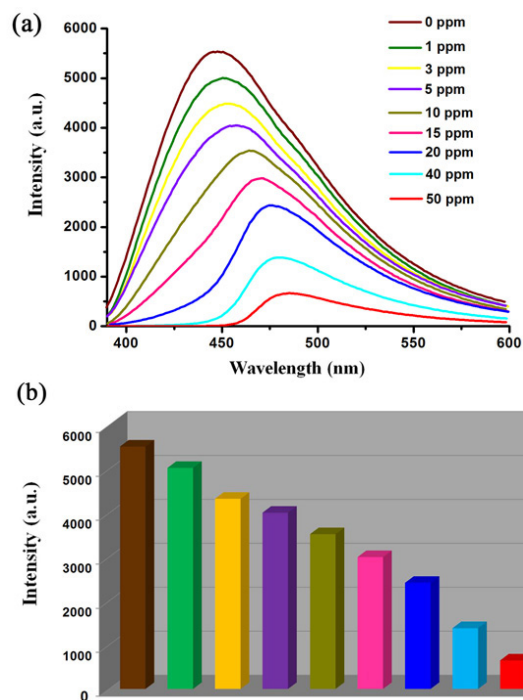


Fig. 6 Emission spectra of **1a** dispersed in DMA upon incremental addition of a TNP (excited at 366 nm).

energy transfer process.¹⁶ The quenching constant (K_{sv}) of **1** for TNP is $2.0 \times 10^4 M^{-1}$ (Fig. 7). These observations clearly demonstrate the potential of MOF **1** as a highly selective sensor for TNP. Furthermore, the detection ability of MOF can be restored and it can be recycled for significant number of cycles by centrifuging the dispersed solution after use and washing several times with DMA.¹⁷ Remarkably, the initial fluorescence intensity was almost regained even after five cycles suggesting a high photostability and reversibility of **1** for detection applications (Fig. 8). The PXRD patterns of the initial sample and recovered sample after 5 cycles of quenching and recovery also indicate the high stability of this compound (Fig. S8). These results reveal that **1** could be applied as a

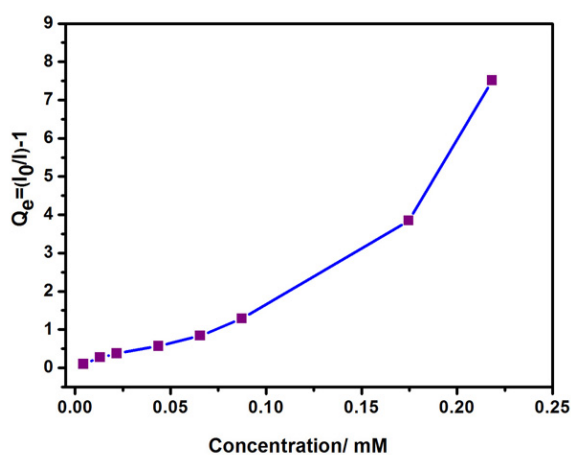


Fig. 7 The Stern-Volmer plot for TNP.

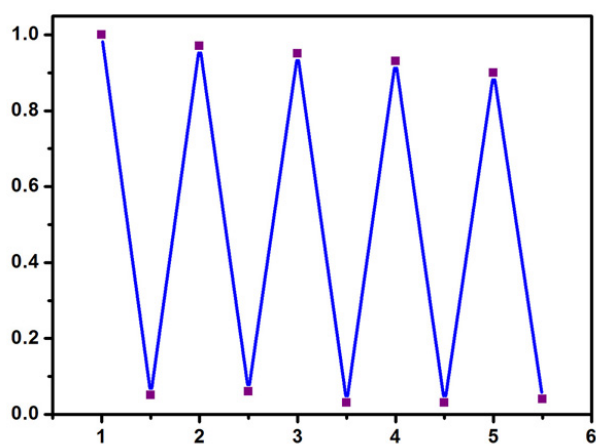


Fig. 8 The quenching and recyclability test of **1**, the upper dots represent the initial luminescence intensity and the lower dots represent the intensity upon addition of 50 ppm of DMA solution of TNP.

fluorescence sensor for TNP with high sensitivity, selectivity, and recyclability.

The excellent fluorescence quenching response to TNP can be attributed to the photo-induced electron-transfer mechanism. The electron transfer from the electron-donating framework with rich π -electron to the highly electron-deficient TNP molecule adsorbed by the surface of MOF particles can take place upon excitation, resulting in fluorescence quenching.¹⁸

Conclusions

In summary, we have obtained a novel Cd-MOF which defines a 3D supramolecular architecture assembled by bilayer motifs with ABAB packing mode. Especially, **1** can display distinct solvent-dependent PL emissions and detect TNP with high selectivity, sensitivity, recyclability. The fluorescence quenching mechanism is in consequence of photoinduced electron transfer from electron-rich MOF framework to electron-withdrawing 2,4,6-trinitrophenol. This work provides a new perspective into the design of highly sensitive sensor with multifunction applications.

Acknowledgements

This work was financially supported by the NSFC of China (No. 21471027, 21171033, 21131001, 21222105), National Key Basic Research Program of China (No. 2013CB834802), Changbai mountain scholars of Jilin Province and FangWu distinguished young scholar of NENU.

Notes and references

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Electronic Supplementary Information (ESI) available: Experimental details, XRPD, TG, IR, solid photoluminescence (PL) spectra and additional figures. CCDC 1047289 (1). For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/x0xx00000x

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