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Cluster-based metal–organic framework as sensitive and selective luminescent probes for sensing nitro explosives

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One new cluster-based metal–organic frameworks, namely, [Cd$_{2.5}$Na(NTB)$_3$(DMF)$_3$]·3DMF (1) ((NTB = 4,4′,4″-nitrolotrisbenzoic acid; DMF = N, N-dimethylformamide) have been successfully obtained by employing a C3 symmetric ligand. In 1, the NTB links two different metal centers (single metal and Cd$_3$ cluster) to form two kinds of 1D chains, which linked through carboxylate O atom of the NTB ligand to give rise to a 3D framework. Moreover, desolvated 1 can be well dispersed in different solvents, 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 and selectivity.

Introduction

The design and synthesis of novel metal–organic frameworks (MOFs) have attracted considerable attention owing to their fascinating structural topologies, as well as the realization of their potential for use in magnetism, catalysis, gas storage, molecular recognition and optical properties, etc.\(^1\)\(^,\)\(^2\) Compared with single metal ions, the coordination geometry and positions of polynuclear clusters have more directionality and selectivity. Moreover, MOFs based on metal cluster as SBU are generally more robust because they can maintain the framework integrity after the removal of guest molecules. Therefore, the utilization of metal clusters as secondary building blocks (SBUs) has proved to be a feasible method to construct unusual coordination polymers with unique network topologies and desirable properties.\(^3\)\(^,\)\(^4\) More efforts have therefore been made on this field: for example, higher nuclearity clusters, octahedral Zn$_4$(µ$_4$-O)(CO$_2$)$_6$ clusters and cuboctahedral Zr$_6$O$_4$(OH)$_4$(CO$_2$)$_{12}$ clusters, can be used as nodes by linking linear bridging organic ligands to form [Zn$_4$(µ$_4$-O)(bdc)$_3$] (MOF-5) and Zr$_6$O$_4$(OH)$_4$(bdc)$_{12}$ \(_{12}$ (UIO-66).\(^5\)

In the past two decades, the detection of nitro compounds has drawn great interest due to its importance in homeland security and environmental safety.\(^6\) The most commonly nitro aromatics are nitrobenzene (NB), 1,3-dinitrobenzene (1,3-DNT), 2,4,6-Trinitrotoluene (TNT) and 2,4,6-trinitrophenol (TNP), and so on, and they are also categorized as plastic explosives.\(^7\) During commercial production and use, TNT is released into the environment, leading to the contamination of soil and aquatic systems. During mammalian metabolic processes, TNT transforms into picramic acid (2-amino-4,6-dinitrophenol), which has ten times more mutagenic activity than TNP.\(^8\) Detection of explosives by fluorescence quenching methods employing suitable chemical sensors has been proven to be very effective. Metal organic frameworks (MOFs) have been shown to have high sensitivity and selectivity towards nitro explosives due to their high binding strength to the nitroaromatic compounds as electron donors.\(^9\) Considering the above, there is an urgent need to develop sensitive and reliable MOF sensors for nitro explosives, especially for TNP.

Following the above consideration, we report one new MOFs based on polynuclear cadmium cluster SBUs, namely, [Cd$_{2.5}$Na(NTB)$_3$(DMF)$_3$]·3DMF (1), which is structurally characterized by single-crystal X-ray diffraction. In compound 1, the NTB links two different metal centers (single metal and Cd$_3$ cluster) to form two 1D chains (A and B chain), which linked through O atom of the NTB, to give rise to a 3D framework. Considering metal-organic frameworks constructed from d\(^0\) 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 $2.8 \times 10^4$ 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
Crystal structure determination

Single-crystal X-ray diffraction data for 1 were collected on a Bruker Apex CCD II area-detector diffractometer with graphitemonochromated Mo-Kα radiation (λ = 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 The crystal data and structure refinement results of 1 are summarized in Table S1. CCDC 1056264 (I) contain the supplementary crystallographic data for this paper.

Synthesis of [Cd$_{2.5}$Na(NTB)$_3$(DMF)$_4$]·3DMF (1)

The mixture of CdCl$_2$·6H$_2$O (45 mg, 0.2 mmol), and NTB (18mg, 0.05 mmol) in 3 mL of N,N-Dimethylformamide (DMF) and 2 drops of NaOH (2M) was sealed in a 15 mL vial and heated to 100 °C for 24 h, and the extracts were decanted. Fresh CH$_2$Cl$_2$ was subsequently added, and the crystals were allowed to stay for an additional 24 h to remove the nonvolatile dimethylformamide (DMF). 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 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

The crystal structure of [Cd$_{2.5}$Na(NTB)$_3$(DMF)$_4$]·3DMF (I) single-crystal X-ray determination reveals that compound I contains paddle-wheel trinuclear {Cd$_6$(CO$_2$)$_6$} secondary building units, which are further connected via O atoms from NTB to result in a 3D coordination framework. Compound I crystallizes in the monoclinic space group P21/c with the asymmetric unit consisting of two and a half Cd(II) ions, one Na ion and two NTB ligands and four coordinated DMF molecules. As shown in Fig. 1, the Cd(II) cations exhibit three different coordination geometries: Cd1 is six-coordinated by four oxygen atoms (O1, O6) from four individual NTB ligands, leaving the remaining coordination sites occupied by two DMF molecules (Cd-O = 2.301(10)- 2.283(11) Å). Each of the two symmetry-related terminal Cd2 ions is bound to five carboxylate O atoms (O1, O2, O3, O4, O5) from three NTB ligands, one oxygen atom (O02) from DMF to form a distorted octahedral geometry. The Cd-O bond distances range from 2.199(12) to 2.459(10) Å. Cd3, different to other two Cd ions, six-coordinated by five carboxylate O atoms (O7, O9, O10, O11, O12) from three NTB ligands and one O atom from DMF molecule (Cd-O = 2.263(11)-2.384(12) Å). The three Cd...
atoms in the sequence of Cd2-Cd1-Cd2, are bridged by six carboxylate groups to form a trinuclear \{ Cd3(CO2)6\} SBU with 
the paddle-wheel structure, and the adjacent Cd1-Cd2 distance is 3.95 Å. In 1, the NTB ligands show two different coordination modes. \(L^b\) adopts \(\mu^2-\eta^1:\eta^1:\eta^1:\eta^1:\eta^1\) chelating bidentate coordination mode to connect three Cd^{II} ions; 
meanwhile \(L^b\) adopts \(\mu^2-\eta^1:\eta^2:\eta^1:\eta^1:\eta^1\) coordination mode to connect five Cd^{II} ions (Fig. S3). The NTB links single metal center Cd3 into a 1-D chain (A chain), two of which forming a square-shaped cavity (Fig. 1b). The Cd3 cluster units are connected by carboxylate O of NTB to form a 1D chain that extends along the b axis (B chain). The B chains containing 
\{ Cd3(CO2)6\} SBUs are linked infinitely through O atom of the NTB (Fig. 1c), in the sequential order of AAB, which gives rise 
to a 3D “vase” framework (Fig. 1e). Meanwhile, the total solvent-accessible volume in this noninterpenetrated framework 
accounts for approximately 25.9 % of the whole crystal volume as estimated by PLATON.11

From the viewpoint of structural topology, the NTB ligand linked with three \{ Cd3(CO2)6\} SBUs as 3-connected node, and the trinuclear \{ Cd3(CO2)6\} SBUs act as 6-connected nodes, the whole 3D structure exhibits a (3, 3, 3, 6)-connected net with the point symbol of \(\{4.8^2;4.8^2,10^1;8^2.10^1;8^1\}\) (Fig. 2).12

**Powder XRD patterns and Thermal properties**

In order to confirm the phase purity of 1, we measured the powder X-ray diffraction at room temperature (Fig. S5). The experimental X-ray diffraction patterns compared to the corresponding simulated patterns calculated based on single crystal diffraction data, which indicates that all the samples were in a pure phase. To study the thermal stability of the compound, thermogravimetric analyses (TGA) were performed on polycrystalline samples under nitrogen atmosphere with a heating rate of 10 °C min\(^{-1}\) (Fig. S6). The TGA curve of 1 reveals the first weight loss 14.0 % is from 25 to 263 °C and 
corresponds to the loss of three DMF molecules, then starts to decompose after 263 °C. The architectural stability and 
permanent porosity of 1a were confirmed by measuring the N\(_2\) adsorption experiments at 77 K, the N\(_2\) adsorption amount

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**Luminescence behaviors and sensing properties**

To examine the luminescence properties of MOFs, the photoluminescence spectra of 1 and the free ligand in the solid state 
were investigated. The NTB ligand presents blue luminescence with emission maxima at 450 nm (\(\lambda_{ex}=379\) nm), this may be assigned to the \(\pi^* \rightarrow \pi\) or \(\pi^* \rightarrow \pi^*\) transition. Compounds 1 exhibits one broad band with the maximum emission peaks a centered at ca. 445 nm 
(\(\lambda_{ex} = 370\) nm) (Fig. S8). Such fluorescent emissions may be tentatively assigned to the intraligand \(\pi^*\)-\(\pi\) emission, since similar emission at 448 nm (\(\lambda_{ex} = 366\) nm) was observed for the free NTB ligand.

The luminescence property of 1a in different solvent emulsions 
was investigated. The solvents used are CH\(_2\)Cl, CH\(_3\)Cl, N, N-dimethylformamide (DMF), N, N-dimethylacetamide (DMA), 
acetonitrile, ethanol, methanol, acetone, n-propanol, n-butyl alcohol, and nitrobenzene (NB). The most interesting feature is that its PL spectrum is largely dependent on the solvent molecules. The intensity of 1a in DMA/DMF is almost unchanged, and diminished 
in other solvents. Particularly in the case of nitrobenzene, the luminescence property exhibits the most significant quenching 
effects (Fig. 3). Such solvent-dependent luminescence properties are of interest for the sensing of nitrobenzene solvent molecules. To 
examine the sensitivity of fluorescence quenching by NB, a batch of 
emulsions of 1a in DMF with gradually increased nitrobenzene 
concentration. As seen in Fig. 4, the luminescence intensity of 
the emulsions significantly decreased with increasing addition of 
nitrobenzene. The intensity of 1a standard emulsion decreased to 43 % at 400 ppm and 17 % at 500 ppm, which allowed us to detect 
small amounts of nitrobenzene in solution. The possibility of quenching mechanism is assumed to originate from the electron-
withdrawing property of the nitro groups in the analytes, which

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**Fig. 2** The (3, 3, 3, 6)-connected network with the point symbol of 
\(\{4.8^2;4.8^2.10^1;8^2.10^1;8^1\}\).

**Fig. 3** Comparisons of the luminescence intensity of 1a-solvent emulsions at 
room temperature (excited at 369 nm) (solvent = CH\(_2\)Cl, DMA, CH\(_3\)Cl, DMF, n-propanol, EtOH, n-butyl alcohol, Acetonitrile, MeOH, Acetone and Nitrobenzene).

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results in a significant donor–acceptor electron transfer from the ligands to the electron-donating MOF structures.\textsuperscript{13}

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 a DMF solution. As shown in Fig. 5, the fluorescent intensity clearly decreased with increasing TNP amount. The quenching efficiency was estimated to be 8.5\% for 1 ppm of TNP, 51\% for 10 ppm of TNP, and 93\% for 50 ppm of TNP.

The fluorescence quenching efficiency was further analyzed using the Stern–Volmer (SV) equation: \(\frac{I}{I_0} = K_{sv}[A] + 1\), 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\(^{-1}\)).\textsuperscript{14} The SV plot for TNP was nearly linear at low concentrations and subsequently deviated from linearity, bending upwards at higher concentrations. The nonlinear nature of the SV plot of TNP may be ascribed to a self-absorption or energy transfer process.\textsuperscript{15} The quenching constant \((K_{sv})\) of 1 for TNP is \(2.8 \times 10^4\) M\(^{-1}\) (Fig. 6). These observations clearly demonstrate the potential of 1 as a highly selective sensor for TNP.

The luminescence quenching may be due to the photoinduced electron-transfer (PET) mechanism. The electron-transfer progress can be interpreted by inductive effect. The nitrobenzene/2,4,6-trinitrophenol with electron-deficient property can obtain an electron from excited ligand,\textsuperscript{16} which has been confirmed by molecular orbital theory.\textsuperscript{17} The frontier molecular orbitals of nitrobenzene, TNP and the ligand are calculated by density functional theory at the level of B3LYP/6-31G*.\textsuperscript{17} The LUMO of analytes (nitrobenzene and 2,4,6-trinitrophenol) are low-lying \(\pi^*\) -type orbital stabilized by the -NO\(_2\) through conjugation, so it is lower than LUMO of ligand (Fig. 7). Therefore, the excited state electrons can transfer from MOF to nitrobenzene, which leads to luminescence quenching.

Conclusions

One new cadmium metal–organic frameworks constructed from C\(_3\) symmetric NTB ligand have been successfully obtained under solvothermal conditions. Compounds 1 display diverse structural features including a (3, 3, 3, 6)-connected net with the point symbol of \(\{4.8^1\}_2\{4^2.8.10^3\}_2\{8^8.10^5\}_2\{8^1\}_2\) constructed from \([\text{Cd}_6(\text{CO}_3)_6\] SBU. Especially, 1 can display distinct solvent-dependent PL emissions and detect TNP with high selectivity and sensitivity. 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.

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Notes and references

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