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# Metal–Organic Frameworks

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# An Ideal Detector Composed of Two-Dimensional Cd(II)–Triazole Frameworks for Nitro-Compound Explosives and Potassium Dichromate

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Dedicated to Professor Dr. Xiao-Jun Zhao on the occasion of his 60th birthday

**Abstract:** The two-dimensional (2D) metal–organic framework (MOF) [Cd(TPTZ)(H<sub>2</sub>O)<sub>2</sub>(HCOOH)(IPA)<sub>2</sub>]<sub>n</sub> (1; TPTZ = {4-[4-(1*H*-1,2,4-triazol-1-yl)phenyl]phenyl]-1*H*-1,2,4-triazole, IPA = isophthalic acid) has been constructed with the  $\pi$ -electronrich aromatic ligand TPTZ, auxiliary ligand IPA, and the metal Cd<sup>2+</sup> ion with a d<sup>10</sup> configuration under solvothermal conditions. Complex 1 exhibits a strong ligand-originated photoluminescence emission, which is selectively sensitive toward electron-deficient nitroaromatic compounds, such as nitrobenzene (NB), 1,3-dinitrobenzene (*m*-DNB), and 1,4-dinitrobenzene (*p*-DNB), and nitro-aliphatic compounds, such as nitromethane (NM) and tris(hydroxymethyl)nitromethane. This property makes complex **1** a potential fluorescence sensor for these chemicals. Single-crystal X-ray diffraction studies revealed that dinuclear cadmium building units were further bridged by TPTZ ligands to give a four-connected uninodal net with the Schläfli symbol of [4.6<sub>3</sub>.4.6<sub>3</sub>.6<sub>2</sub>.6<sub>4</sub>].

# Introduction

The assembly of porous materials from organic molecules and metal-ion building blocks is an emerging area that yields new generations of open supramolecular architectures.<sup>[1]</sup> One of the most promising applications for such open metal-organic frameworks (MOFs)<sup>[2]</sup> is their use as porous materials for storage, separation, purification, catalysis, and sensing.<sup>[3-5]</sup> The recent upsurge in MOFs reflects their application in the storage and separation of gases such as hydrogen, methane, and carbon dioxide.<sup>[6]</sup> In contrast, fluorescence sensing based on luminescent MOFs is of great interest due to the quick response, reversibility, operability, and high selectivity of these materials.<sup>[7]</sup> Among various applications, a wide range of luminescent MOFs for the sensing of cations,<sup>[8]</sup> anions,<sup>[9]</sup> small molecules,<sup>[10]</sup> vapors,<sup>[11]</sup> and biomolecules<sup>[12]</sup> have been reported. For example, Allendorf and co-workers reported a luminescent complex that is sensitive to solvent exchange.<sup>[9a]</sup> Chen and co-workers reported the detection of C<sub>2</sub>H<sub>2</sub>, CH<sub>3</sub>OH, and DMF with a robust near-infrared luminescent ytterbium complex [Yb(BPT)-

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 $(H_2O) \cdot (dmf)_{1.5}(H_2O)_{1.25}$ ] (BPT = biphenyl-3,4,5-tricarboxylate).<sup>[10e]</sup> However, up to now, several MOF-based fluorescence sensors have been developed for the detection of nitroaromatic explosives.<sup>[13]</sup>

Among various nitroaromatic compounds, nitrobenzene (NB) is the simplest and is a basic constituent of explosives. Furthermore, NB is also a highly toxic environmental pollutant that could cause serious health problems.<sup>[14]</sup> Therefore, the development of the detection of NB vapor is very important for environmental and safety considerations. Besides, the application of MOFs for the sensing of nitroaromatic explosives is limited because most porous MOFs used for the detection of nitroaromatic explosives must be activated to evacuate the pores before sensing as the presence of solvent or other guest molecules diminish the performance of the MOFs.<sup>[13]</sup> On the other hand, the introduction of electron-rich aromatic ligands could improve sensor performances effectively because as the quenching sensing is generally realized by the electron transfer of the photoexcited electrons from the MOFs to the electrondeficient analytes.[15]

Based on the above considerations, we chose a bidentate triazole ligand {4-[4-(1*H*-1,2,4-triazol-1-yl)phenyl]phenyl}-1*H*-1,2,4-triazole (TPTZ; Scheme 1) and the auxiliary ligand iso-



Scheme 1. Structure of {4-[4-(1*H*-1,2,4-triazol-1-yl)phenyl]phenyl}-1*H*-1,2,4-triazole (TPTZ).

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phthalic acid (IPA) to construct a two-dimensional (2D) cadmium(II) MOF [Cd(TPTZ)(H<sub>2</sub>O)<sub>2</sub>(HCOOH)(IPA)<sub>2</sub>]<sub>n</sub> (1) with sensing properties in this study. The obtained luminescent MOF reveals selective enhancement or quenching of luminescence from different analytes. The luminescence of 1 shows a high sensitivity and quick response toward the presence of trace amounts of NB in solution, behavior that might be employed for NB sensing applications. Meanwhile, 1 can also detect trace amounts of other nitroaromatic compounds, such as 1,3-dinitrobenzene (*m*-DNB) and 1,4-dinitrobenzene (*p*-DNB), and nitroaliphatic compounds, such as nitromethane (NM) and tris(hydroxymethyl)nitromethane.

# **Results and Discussion**

### Structure of 1

Single-crystal structural analysis reveals that complex 1 crystallizes in the monoclinic space group C2m and possesses a 2D layered structure. The asymmetric unit consists of two crystallographically independent Cd<sup>II</sup> ions, one-and-a-half protonated IPA molecules, one TPTZ ligand, and one formate anion (Figure 1). The Cd1 ion is situated in the center of a distorted



**Figure 1.** Coordination environment around the Cd<sup>II</sup> centers in **1**. C gray, O dark gray, Cd black, N medium gray.

octahedral environment with two axial oxygen atoms ( $O_{ax}$ ), one of which is from a water molecule and the other from an IPA ligand. Four equatorial atoms are composed of two  $N_{triazole}$  atoms and two oxygen atoms from an IPA ligand and a formate anion. However, Cd2 adopts a slightly distorted tetragonal pyramidal geometry and coordinates with two  $N_{triazole}$  atoms and three oxygen atoms from one IPA ligand and one formate anion. The Cd–N distances are in the range 2.275(7)–2.336(7) Å and the Cd–O bond lengths are 2.230(6)–2.401(8) Å, which are in the normal range of those observed in cadmium compounds.<sup>[16]</sup>

One triazole group of TPTZ connects two Cd<sup>II</sup> centers through two N<sub>triazole</sub> atoms and the other triazole group links to Cd2 (Figure 2). Two IPA moieties act as bridging ligands to link two Cd<sup>II</sup> center ions, thus presenting coordination modes I and II, respectively. The carboxylate groups adopt the bidentate chelate mode with Cd2 in mode I, whereas one of the carboxylate groups adopts a  $\mu$ - $\eta^1$ : $\eta^1$  fashion and the other adopts  $\mu$ - $\eta^1$ : $\eta^0$  fashion in mode II. The Cd1 and Cd2 centers are connect-



**Figure 2.** a) View of the coordination environment of TPTZ. The coordination of IPA: b) mode I and c) mode II. C gray, O dark gray, Cd black, N medium gray.



Figure 3. a) View of the wavy chain constructed from  $\{Cd_2\}$  units and IPA ligands. b) View of the 2D layer with large rings. c) The topological layer in 1. C gray, O red, Cd green, N blue.

ed through the TPTZ moiety to form a dinuclear unit {Cd<sub>2</sub>} with a Cd--Cd distance of 3.7016(2) Å. A closed ring can be described as a {Cd<sub>2</sub>} unit and the neighboring {Cd<sub>2</sub>} units are alternatively bridged by two IPA ligands in mode II to form a wave chain (Figure 3a). TPTZ ligands connect these wave chains in turn to give rise to a 2D layer with a cavity dimension of  $1.8 \times 2.8 \text{ Å}^2$  (Figure 3 b). To obtain better insight into such a layer, the {Cd<sub>2</sub>} units can be considered to be nodes, the two types of ligand serve as linkers, and each {Cd<sub>2</sub>} unit links four adjacent {Cd<sub>2</sub>} units. Therefore, the combination of the nodes and linkers suggests a four-connected uninodal net with a Schläfli symbol of {4<sup>2</sup>.6<sup>4</sup>} and extended point symbol of [4.6<sub>3</sub>.4.6<sub>3</sub>.6<sub>2</sub>.6<sub>4</sub>] (Figure 3 c). The 2D sheetlike layers are stacked by translation (Figure 4). The benzene rings of TPTZ ligands from adjacent layers overlap parallel to each other and show a suitable space for  $\pi \cdot \cdot \pi$  stacking interactions. The corresponding dihedral angles between the benzene rings and triazole moieties in TPTZ in 1 are 62 and 78.1°, respectively, thus indicating a strong spatial-distortion effect from coordination with the Cd<sup>II</sup> ions.





Figure 4. The stacking of the topological layers. Cd represented by black spheres; TPTZ ligand: black lines.

### Luminescence behavior and sensing properties

With the development of modern society and industry, hazardous chemicals, such as toxic ions and organic small molecules, are increasingly released from industrial facilities and other anthropogenic activities, thus causing adverse effects on human health and the environment. Environmental pollutants, such as poisonous gases, organic solvent vapors, heavy-metal species, and anions, have acute and chronic effects on human health and consequently can lead to heart attacks, lung cancer, hepatosis, and other serious diseases.<sup>[17]</sup> It is of great challenge and significance to identify and monitor these environmental pollutants directly by detection through the development of advanced materials. Considering the intense luminescent signal and visible luminescent colors, cadmium MOFs could be good candidates as luminescent sensing materials for environmental pollutants. To explore the luminescent properties of cadmium MOFs in sensing, luminescent Cd<sup>2+</sup> centers and judiciously selected ligands are key to obtaining luminescent cadmium MOFs with proper porosity and functional groups to provide potential open Lewis acid or base sites for specific host-guest interactions that can tune the luminescent properties. There are several reported cadmium MOFs for sensing functions that highlight the significance of the luminescent MOFs (Table 1). Importantly, a series of  $G_n \subset CdL_2$  (L=4-amino-3,5-bis(4-pyridyl-3-phenyl)-1,2,4-triazole; n = 1, 2) host-guest complexes reported by the Dong and co-workers<sup>[18]</sup> and the Cd<sup>II</sup>–guanazole (3,5diamino-1,2,4-triazole) hybrid family reported by Yao and coworkers<sup>[19]</sup> exhibit interesting sensing properties for organic small-molecule solvents and anions, respectively. The porosity and potential open metal-center/organic-group sites within cadmium MOFs have played a significant role in their sensing functionality, such as open Cd<sup>2+</sup> sites for small-molecule sensing, hydrogen-bonding interactions for X<sup>-</sup> ions, and open Lewis basic triazole sites for  $Cd^{2+}$  ions.

Aromatic organic molecules and inorganic–organic hybrid coordination complexes were investigated for their photoluminescent properties and for potential applications as luminescent materials, such as light-emitting diodes (LEDs).<sup>[20]</sup> The construction of inorganic-organic coordination complexes through the judicious incorporation of transition-metal centers and conjugated organic spacers can be an efficient strategy for the synthesis of new types of photoluminescent material because the emission strength and wavelength of organic materials can be adjusted. As we know, a double bond is composed of  $\sigma$  and  $\pi$  bonds, and the emissions of organic ligands are usually ascribed to the  $\pi^* \rightarrow n$  or  $\pi \rightarrow \pi^*$  transitions.<sup>[21]</sup> Therefore, it is expected that the double-bond-based ligand TPTZ would exhibit photoluminescence. Previous research also confirms that coordination polymers can affect the emission strength and wavelength of organic materials through the judicious incorporation of different central metal ions.<sup>[22-24]</sup> Because MOFs constructed from d<sup>10</sup> metal ions and conjugated organic linkers are promising candidates for potential photoactive materials,<sup>[25]</sup> the emission spectrum of complex 1 was investigated first.

The emissions of TPTZ and 1 as a suspension and in solution were tested. DMF was utilized as the dispersion medium because complex 1 was synthesized in DMF and showed good stability in this solvent. Before recording of the spectrum, finely ground samples of TPTZ and 1 were immersed in DMF, treated by ultrasonication for half an hour, and aged for three days to form a stable suspension and solution, respectively. TPTZ in DMF at ambient temperature is luminescent and exhibits a narrow emission maximum at  $\lambda_{em,max} =$  450 nm ( $\lambda_{ex} =$ 360 nm; Figure 5). Relative to TPTZ, complex 1 exhibits a redshifted and relatively strong green fluorescent emission band at  $\lambda = 505$  nm. The main emission bands of TPTZ and **1** exhibit almost the same band shape, which are neither metal-toligand charge transfer (MLCT) nor ligand-to-metal charge transfer (LMCT) in nature and probably can be ascribed to the intraligand fluorescent emission because similar behaviors are also observed for the free TPTZ ligand in DMF.<sup>[26]</sup> In the solid state, both TPTZ and 1 exhibit strong blue and green emissions at  $\lambda_{max} = 450$  and 550 nm, respectively, whereas excitations are located at  $\lambda = 350 \pm 5$  nm (Figure 6). In comparison with the fluorescent emissions of the free ligand TPTZ and its complex 1 in solution, the emission is blue-shifted and narrow. The chromophores of TPTZ are the aromatic rings, and the observed emission is due to the  $\pi{\rightarrow}\pi^*$  transition. The strong emissions of complex 1 in the solid state and as a suspension pave the way for its application in fluorescence detection.

Table 1. Selected luminescent cadmium MOF materials for sensing.					
Cd MOF luminescent materials	Luminescent substrates	Ref.			
$ \begin{array}{l} CdL_2^{[a]} \\ [Cd(NDC)_{0.5}(PCA)]\cdotG_x^{[b]} \\ [NH_2(CH_3)_2]_2[Cd_{17}(L)_{12}(\mu_3\text{-}H_2O)_4(DMF)_2(H_2O)_2]\cdotsolvent^{[c]} \\ [Cd_5(datrz)_4X_4(OH)_2]^{[d]} \end{array} $	organic small molecules 2,4,6-trinitrophenol derivatives of NB <sup>(e)</sup> anions	[18] [13c] [13e] [16c]			
$ \begin{tabular}{lllllllllllllllllllllllllllllllllll$					

The fluorescence sensing ability of 1 was first examined with the addition of different organic molecules to the suspension of the complex. The addition of nitro compounds at 4000 ppm could almost quench the emission of 1 (Figure 7), whereas the maximum change in the emission intensity was no more than 21% with the addition of the same amount of other organic

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Figure 5. Emission spectra of solutions of TPTZ and 1 in DMF at room temperature  $(1 \times 10^{-4} \text{ mol } L^{-1})$ .



Figure 6. Emission spectra of TPTZ and 1 in the solid state at room temperature.



Figure 7. Emission spectra of 1 dispersed in DMF with the addition of different organic molecules (4000 ppm).



Figure 8. Fluorescence titration of complex 1 dispersed in DMF with the addition of different concentrations of NB.

molecules, including alcohols (methanol, ethanol, 1-propanol, and 2-propanol), amides (*N*,*N*-dimethylacetamide (DMA), diethylmethylchitosan (DEMC)), chloroalkanes ( $CH_2CI_2$ ),  $CH_3CN$ , and even other aromatic complexes (benzene and toluene). These results indicate that **1** has a selective response to nitro-compound explosives.

To investigate the sensing properties of 1 further, the emissive response was monitored by gradually increasing the NB content of emulsions of 1 dispersed in DMF. The emission intensity decreased upon the addition of 5 ppm of NB and was nearly completely quenched at a concentration of 100 ppm, with a high quenching efficiency of 99.2% which is higher than or comparable to other MOF sensors for NB (Figure 8).<sup>[7b, 13d,e, 25]</sup> The photoluminescent intensity decreased to concentration of only 50% at а 200 ppm for  $[Zn_2(TIB)(HL^1)(H^2L^1)_{0.5}] \cdot 2H_2O$ (TIB = 1,3,5-tris(1-imidazolyl)benzene,  $H^4L^1$  = biphenyl-3,3',4,4'-tetracarboxylic acid),<sup>[7b]</sup> thus allowing us to detect small amounts of NB in solution. Another 2D zinc(II) complex  $[Zn_2(L)(bipy)(H_2O)_2] \cdot 3H_2O \cdot 2DMF$  (H<sub>4</sub>L = bis(3,5-dicarboxyphenyl) terephthalamide, bipy = 4,4'-bipyridine) reported by Bu and co-workers group could selectively detect NB through a redox fluorescence quenching mechanism.<sup>[13d]</sup> When the additional amount of NB was only 2000 ppm, the fluorescence intensity of the suspension of this zinc(II) complex at  $\lambda = 450$  nm was decreased by 90%. Furthermore, the 3D luminescent MOF  $[NH_2(CH_3)_2]_2[Cd_{17}(L)_{12}(\mu_3 - \mu_3)_2]_2[Cd_{17}(L)_{12}(\mu_3 - \mu_3)_2]_2[Cd_{17}(\mu_3 -$ H<sub>2</sub>O)<sub>4</sub>(DMF)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>]-solvent showed high sensitivity and a quick response toward the presence of a trace amount of NB in solution or the vapor state, which might be used for a NB-sensing application.<sup>[13e]</sup> Meanwhile, such a 3D cadmium(II) complex can also detect trace amounts of derivatives of NB, such as 4-nitrotoluene (NT), m-DNB, and p-DNB; furthermore, the emission in-

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tensity decreased upon the addition of 5 ppm of NB and was nearly completely quenched at a concentration of 100 ppm, with a high quenching efficiency of 92.5% which is higher than or comparable to other MOF sensors for NB.<sup>[7b, 13d, 25]</sup>

Among the five nitro compounds (Supporting Information, Figure S1), complex 1 is more sensitive to p-DNB relative to other four nitro compounds at room temperature. Complex 1 exhibits extremely high detection sensitivity toward p-DNB explosives, with a high guenching efficiency of 99.998%. Also, the quenching phenomenon of 1 in the solid state is consistent with that realized in the liquid-sensing process, thus indicating that the quenching mechanism should be based on the nature of the complex rather than the testing environments. Up to now, several MOF-based fluorescence sensors have been developed for the detection of nitroaromatic explosives. For example, Li and co-workers reported the highly luminescent MOFs<sup>[13a, 27a]</sup> [Zn<sub>2</sub>(oba)<sub>2</sub>(bpy)]·3 DMA (H<sub>2</sub>oba = 4,4'-oxybis(benzoic acid), bpy = 4,4'-bipyridine, DMA = dimethylacetamide) and  $[Zn_2(bpdc)_2(bpee)] \cdot 2 DMF$ (bpdc = 4,4'-biphenyldicarboxylate,bpee = 1,2-bipyridylethene), which exhibit unique selectivity in the detection of nitroaromatic compounds with different groups and high explosives. The excellent fluorescence quenching response to 2,3-dimethyl-2,3-dinitrobutane (DMNB, a taggant required by law in all commercial plastic explosives) can be further attributed to the pore confinement of the analyte inside the molecule-sized cavities of such a zinc(II) complex, thus facilitating stronger interactions between the DMNB molecule and the host framework, as reflected by the relatively small difference in the quenching percentages for NB, which exhibits only 10% higher sensitivity (94% quenching at 10 s) relative to DMNB. However, NB in [Zn<sub>2</sub>(oba)<sub>2</sub>(bpy)]·3 DMA quenches the emission by as much as 84%, and the order of quenching efficiency for the selected nitroaromatic compounds is NB > m-DNB  $> NT \approx p$ -DNB > dinitrotoluene (DNT). Notably, this order is not fully in accordance with the trend of electron-withdrawing groups, but it is fully consistent when the vapor pressure of each analyte is also taken into consideration.

The fact that NB exhibits the strongest quenching effect can be attributed to two factors: high vapor pressure and the strongly electron-withdrawing NO<sub>2</sub> group. Although the vapor pressure of NT is comparable to that of NB, the quenching efficiency (29%) is significantly less because of the presence of the electron-donating CH<sub>3</sub> group. Similarly, although *m*- and *p*-DNB have two strongly electron-withdrawing NO<sub>2</sub> groups, both have very low vapor pressures at room temperature. Interestingly, Ghosh and co-workers demonstrated the luminescent 3D MOF  $[Cd(NDC)_{0.5}(PCA)] \cdot G_x$  (G = guest molecules, NDC = 2,6-napthalenedicarboxylic acid, PCA = 4-pyridinecaboxylic acid) for the highly selective detection of 2,4,6-trinitrophenol (TNP).<sup>[27b]</sup> To explore the ability of such a cadmium(II) complex to sense a trace quantity of nitro explosives, fluorescencequenching titrations were performed with the incremental addition of analytes to such a cadmium(II) complex dispersed in MeCN. Fast and high fluorescence guenching was observed upon incremental addition of a solution of TNP in MeCN (1 mm). The visible bright-blue emission of such a cadmium(II) complex in UV light vanished upon the addition of the solution of TNP, which quenched nearly 78% of the initial fluorescence intensity. The fluorescence quenching by TNP could be easily discerned at low concentration (4  $\mu$ M). Fluorescence quenching titrations were also performed with nitroaromatic compounds, such as 2,4,6-trinitrotoluene (TNT), 2,4-DNT, 2,6-DNT, *m*-DNB, NB, and nitroaliphatic compounds, such as DMNB, NM, and 1,3,5-trinitro-1,3,5-triazacyclohexane. All other nitro compounds showed little effect on the fluorescence intensity. These results demonstrate that such a cadmium(II) compound has a high selectivity for TNP relative to other nitro compounds.

Among the tested aromatic organic molecules (toluene, benzene, and nitro compounds), the emission of 1 can only be quenched by nitro-compound explosives (Figure 7). Therefore, the fluorescence response of 1 to nitro-compound explosives was attributed to the electron-transfer quenching mechanism; that is, in the presence of nitro compounds, the excited electron of complex 1 undergoes a transfer to the nitro compound instead of relaxation to the ground state with fluorescence emission. Because the photoluminescence of 1 originated from the ligand, the sensitive response of 1 to nitro-compound explosives could be attributed to the electron-rich property of the ligand, which facilitates the excited-state electron-transfer process. Though there are cavities in the framework of 1, the absence of an accessible path excludes the possibility of analyte encapsulation during the sensing process. Therefore, the sensing mechanism of 1 should not be based on guest-induced quenching,<sup>[13]</sup> in which analyte molecules are included in the pores as a guest and interact directly with the fluorophore. The particles of 1 could be dispersed well in solution with DMF, which enables the nitroaromatic explosive molecules to be closely adsorbed on the surface of the particles and facilitates possible electron transfer.<sup>[28]</sup> A similar solvent-dependent fluorescence quenching of MOFs has also been reported by Chen, Qian, Sun, and Mukherjee.[5a,b,7b,29] Therefore, luminescence quenching behavior observed in 1 is not only the result of the electron-deficient nature of nitroaromatic compounds and the highly electron-rich conjugated framework structure, but also the highly dispersible nature of the MOF particles.

Simultaneously, various anions were selected to carry out the anion-sensing function in view of the cationic framework and porosity of 1. Different aqueous solutions of anions (that is, F<sup>-</sup>, Cl<sup>-</sup>, Br<sup>-</sup>, l<sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, ClO<sub>4</sub><sup>-</sup>, CO<sub>3</sub><sup>2-</sup>, BF<sub>4</sub><sup>-</sup>, NO<sub>3</sub><sup>-</sup>, Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup>,  $\mathrm{NO}_2^{-},$  and  $\mathrm{OAc}^{-})$  were used to soak complex 1. The luminescent measurements illustrate that the different anions have a great influence on the luminescent intensity of 1. Remarkably, the  $Cr_2O_7^{2-}$  ion has the largest quenching effect on the luminescent emission (Figure 9). The toxic  $Cr_2O_7^{2-}$  ion is very harmful to human health and the environment and can be accumulated in living organisms, thus leading to serious diseases.<sup>[30]</sup> Although there are several reports on the exchange of anions based on MOFs, it is still rare to explore the exchange and capture of pollutant anions by using a cadmium(II) luminescent cationic framework.[31] Therefore, the exchange and capture capacity of **1** regarding the  $Cr_2O_7^{2-}$  ion was further





**Figure 9.** Photoluminescent spectra of 1 in the solid state treated with aqueous solutions  $(10^{-2} \text{ M})$  of the anions F<sup>-</sup>, Cl<sup>-</sup>, Br<sup>-</sup>, l<sup>-</sup>, SO<sub>4</sub><sup>-2</sup>, CO<sub>3</sub><sup>-2</sup>, BF<sub>4</sub><sup>-</sup>, ClO<sub>4</sub><sup>-</sup>, NO<sub>3</sub><sup>-</sup>, Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup>, and OAc<sup>-</sup>.

studied. When 0.01 mmol of 1 was placed into an aqueous solution containing 0.005 mmol of K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>, the exchange process was carried out at room temperature with slow stirring. The exchanged solution was detected by liquid UV/Vis spectroscopic analysis at intervals. The absorption intensity of the main characteristic band of the Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup> ion in the solution of K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> at around  $\lambda = 350$  nm distinctly decreased with time,<sup>[32]</sup> thus demonstrating that Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup> ions in solution were gradually included into the channels of 1. By soaking 1 for 12 h in a solution of K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>, the UV/Vis absorption intensity of the Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup> ions in solution almost kept unchanged, and the corresponding concentration decreased by about 43% (Figure 10). With the guest-inclusion process, the luminescent intensity of 1 gradually decreased, which coincided with the quenching effect of the Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup> ion (Figure 11).



**Figure 10.** UV/Vis spectra of the inclusion of an aqueous solution of  $K_2Cr_2O_7$ in the channels of 1 at room temperature (1/K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> = 2:1 mol/mol).



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Figure 11. Photoluminescent spectra of 1 during the  $K_2Cr_2O_7$ -inclusion process within the cavity at room temperature.

#### Thermogravimetric analysis

The thermal stability of 1 was investigated by employing thermogravimetric analysis (TGA) in an air atmosphere, with a heating rate of  $10 \,^\circ$ C min<sup>-1</sup>. The coordination network of complex 1 begins to decompose at about 240  $\,^\circ$ C (Supporting Information, Figure S2). A slight weight decrease corresponds to the loss of two coordinated water molecules and formic acid (observed: 10.4%; calcd: 9.8%). The organic framework collapsed in the range 240–600  $\,^\circ$ C. Powder X-ray diffraction studies of activated samples at 80, 120, 160, and 240  $\,^\circ$ C were carried out to confirm the stability of 1 further (Supporting Information, Figure S3).

## Conclusion

A 2D Cd<sup>II</sup>-based MOF has been synthesized with a  $C_3$ -symmetric multicarboxylate ligand. The luminescent emission of this MOF could be quenched by trace amounts of nitro compounds and  $K_2Cr_2O_7$ . The quenching mechanism is attributed to electron transfer from the excited-state electron-donating MOF framework to electron-withdrawing nitroaromatic explosives and the highly dispersible nature of the MOF particles.

### **Experimental Section**

**General**: All of the reagents are commercially available and were used without further purification. Elemental analysis was measured on a PerkinElmer 240 elemental analyzer. Powder X-ray diffraction studies were performed on a D/Max-2500 X-ray diffractometer with CuK $\alpha$  radiation. The photoluminescence spectra were recorded by a MPF-4 fluorescence spectrophotometer with a xenon arc lamp as the light source. The TGA experiments were performed on a NETZSCH TG 209 instrument with a heating rate of 10 °C min<sup>-1</sup>. <sup>1</sup>H NMR spectroscopic data were measured on a Bruker Avance 400 MHz spectrometer. Chemical shifts  $\delta$  are reported in ppm relative to tetramethylsilane.

Synthesis of {4-[4-(1*H*-1,2,4-triazol-1-yl)phenyl]phenyl]-1*H*-1,2,4-triazole (TPTZ): 4,4'-Diiodobiphenyl (1.11 g, 2.74 mmol), 1*H*-1,2,4-

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triazole (0.38 g, 5.48 mmol), K<sub>2</sub>CO<sub>3</sub> (0.76 g, 5.48 mmol), and CuO (0.01 g, 0.125 mmol) were mixed and heated while stirring in DMSO (15 mL) at 150 °C for 2 days. The resulting suspension was cooled to 25 °C, and the solids were removed by filtration. Further filtrate was removed by vacuum distillation. Dichloromethane (30 mL) was added to the remaining filtrate. The resulting mixture was washed with deionized water, stored under vacuum overnight, and the dichloromethane was removed. The products were crystallized from methanol and deionized water and to yield a light-yellow solid. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  = 7.89 (d, 4H), 7.96 (d, 4H), 8.27 (s, 2 H), 9.37 ppm (s, 2 H) (Supporting Information, Figure S4); elemental analysis calcd (%) for C<sub>16</sub>N<sub>6</sub>H<sub>12</sub> (TPTZ): C 66.66, H 4.20, N 29.15; found: C 66.62, H 4.15, N 29.21.

Synthesis of [Cd(TPTZ)(H<sub>2</sub>O)<sub>2</sub>(HCOOH)(IPA)<sub>2</sub>I<sub>n</sub> (1): A mixture of TPTZ (0.0576 g, 0.2 mmol), Cd(NO<sub>3</sub>)<sub>2</sub> (0.0617 g, 0.2 mmol), IPA (0.0332 g, 0.2 mmol), DMF (6 mL), and H<sub>2</sub>O (2 mL) were put in a 20 mL acid-digestion bomb and heated at 90 °C for 3 days. The crystal products for single-crystal X-ray diffraction studies were collected after washing with H<sub>2</sub>O (2×5 mL) and diethyl ether (2×5 mL). Yield: 60%. Elemental analysis calcd (%) for  $C_{30}H_{27}Cd_2N_6O_9$ : C 42.88, H 3.24, N 10.01; found: C 42.96, H 3.30, N 10.12.

### **Crystallographic studies**

Single-crystal X-ray diffraction studies of complex **1** were carried out on an APEX II CCD area detector. A graphite crystal monochromator was equipped with an incident beam for data collection at 293(2) K. The  $\omega$ - $\phi$  scan technique was applied. Direct methods were applied to solve the structures. Full-matrix least-squares methods that used the SHELXL-97 and SHELXS-97 programs were to refine the crystal structures.<sup>[33,34]</sup> For all of the coordination complexes, anisotropic thermal parameters were applied to the nonhydrogen atoms. Anomalous dispersion corrections were incorporated and analytical expressions of neutral-atom scattering factors were also used. The crystallographic data and selected bond distances and angles of these complexes are listed in Tables 2 and 3, respectively. CCDC 1056556 (1) contains the supplementary crystal-

Table 2. Crystallographic data and details of refinements for complex 1.			
	1		
formula	C <sub>30</sub> H <sub>27</sub> Cd <sub>2</sub> N <sub>6</sub> O <sub>9</sub>		
$M [gmol^{-1}]$	840.38		
crystal system	monoclinic		
space group	C2/m		
<i>T</i> [°C]	293(2)		
a [Å]	23.5151(14)		
b [Å]	38.646(3)		
c [Å Å	10.6197(4)		
α [°]	90		
β [°]	106.299(4)		
γ [°]	90		
V [Å <sup>3</sup> ]	9262.9(10)		
Z	8		
F(000)	3336		
$ ho_{ m calcd}  [ m Mg  m^{-3}]$	1.205		
$\mu \text{ [mm^{-1}]}$	0.601		
Data/restraints/params	8907/6/427		
GOF on F <sup>2</sup>	1.075		
$R_1^{[a]}(l=2\sigma(l))$	0.0797		
$\omega R_2^{[b]}$ (all data)	0.2349		
[a] $R_1 = \sum   F_0  -  F_c   /  F_0 $ , [b] $\omega R_2 = [$	$\sum w( F_0 ^2 -  F_c^2 ^2/w F_0^2 ^2)^{1/2}$		

Table 3. Selected bond lengths [Å] and angles [°] for $1.^{[a]}$						
Cu1-N4 Cu1-N1 Cu1-O1 N4-Cu1-N1 N4-Cu1-O1 N4A-Cu1-N1	2.018(2) 2.032(2) 2.3983(19) 88.37(8) 83.38(8) 91.63(8)	N1-Cu1-N1#1 N1-Cu1-O1 N4#1-Cu1-N4 N4#1-Cu1-N1 N4-Cu1-O1#1 N1-Cu1-O1#1	180.00(11) 97.79(8) 179.999(2) 91.63(8) 96.62(8) 82.21(8)			
[a] Symmetry transformations used to generate equivalent atoms for 1: #1 $-x+1/2$ , $-y+1/2$ , $-z+1$ ; #2 $x-1/2$ , $-y+1/2$ , $z+1$ ; #3 $x$ , $-y$ , $z$ ; #4 $x+1/2$ , $-y+1/2$ , $z-1$ .						

lographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

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frameworks • N ligands	• ser	nsors		

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