Inorganic Chemistry

Assembly of Two Self-Interpenetrating Metal–Organic Frameworks Based on a Trigonal Ligand: Syntheses, Crystal Structures, and **Properties**

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ABSTRACT: Two self-interpenetrating metal-organic frameworks (MOFs) 1 and 2 were designed and constructed through the coordination self-assembly of transition metal nodes and a trigonal ligand. They both exhibit interesting three-dimensional constructions with the 1 + 2 self-locked mode. Because of the outstanding moisture susceptibility and luminescence property, MOF 1 has a potential detectability toward nitrofurantoin (NFT) in water. More importantly, MOF 1 can efficiently monitor NFT in bovine serum. Taking into account of Lewis basic sites in the skeleton, MOF 2 can be implemented as an outstanding heterogeneous catalyst for the Knoevenagel reaction. Furthermore, they both reveal excellent circularity and an application effect for five cycles.

INTRODUCTION

Metal-organic frameworks (MOFs) have been widely investigated and used as interesting and diversiform crystals. MOFs have captured the focus of many scientists because of their rich compositional and structural diversity¹⁻⁶ and their applicability in gas sorption, catalysis, sensors, and so on.⁷⁻¹² MOFs can be well designed and constructed by tuning organic linkers and inorganic metal nodes.^{13–15} Hence, the functional properties of MOFs are able to be affected by various components in MOFs. Various organic linkers have been widely synthesized and used to construct MOFs, such as linkers with only carboxylic acid, only an N-heterocyclic fragment, as well as both N-heterocyclic and carboxylic acid; meanwhile, the same organic ligand can generate totally different MOFs by the self-assembly with different metal ions to endow various application properties. Among all organic ligands, N-heterocyclic ligands have diversiform coordination modes with metal nodes and great potential application as Lewis basic catalysts for the Knoevenagel reaction.¹⁶⁻¹⁸ In addition, organic linkers with luminophores always have been employed to assemble with metal ions with the d¹⁰ outer electron to construct luminescent MOFs, which can preserve the luminescent properties in MOFs, such as Cd^{II}- and Zn^{II}based MOFs.¹⁹⁻²¹ These luminescent MOFs can served as highly efficient sensors to detect contaminants, including heavy metals, strong oxidants, explosives, pesticides, and volatile organic compounds.²²⁻²⁵ Nonetheless, the weak stability of MOFs greatly confines their usability in the detection



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pollutants in water. Efficient strategies have been widely explored and implemented to strengthen the MOFs' water stability to expand their applications.²²⁻²⁵ Construction of stable MOFs is still a remarkable challenge for detecting target objects in water.

Among common contaminants, antibiotics have been widely applied in a large variety of systems for a long time, because antibiotics have excellent effects for a variety of bacterial infections in the treatment of various bacterial contaminations in people, livestock, poultry, and aquaculture.^{26,27} Nevertheless, the overuse of antibiotics causes lots of serious problems because residual antibiotics can be observed in drinking water, milk, and food to increase the antibiotic resistance of bacteria.^{28–30} Many developed countries and governments limit the use of antibiotics to reduce their harmfulness, but various antibiotics have still been found in many places to penetrate into the human body. Therefore, the highly efficient detection of antibiotics has become the most important and urgent challenge to today. Several MOFs were prepared and employed to test antibiotics, but the poor water stability of MOFs restricts the detectable system to only

Received: February 24, 2020



nonaqueous systems. Thus, it is an urgent task to design and synthesize highly stable MOFs in the luminescent detection of antibiotics in water.

In this work, two self-interpenetrating MOFs, $[CdL(NO_3)_2]$. $4H_2O_{n}$ (namely, MOF 1) and $\{[CoL(H_2O)_3] \cdot 2NO_3\}_n$ (namely, MOF 2) can be prepared based on a trigonal ligand tris(4-(4H-1,2,4-triazol-4-yl)phenyl)amine (namely, L). They both exhibit interesting three-dimensional (3D) constructions with the 1 + 2 self-locked mode. This ligand does not merely have various N-donors as Lewis basic catalytic sites but also exhibits an obvious luminescent property. MOF 1 possesses luminescent properties from the ligand because of Cd^{II} with the d¹⁰ outer electron and exhibits excellent water stability, resulting in that it can be implemented as a sensor in the detection of nitrofurantoin (NFT) in aqueous solution with favorable recyclability, selectivity, and sensitivity. MOF 2, as a Lewis basic catalyst, displays a superior catalytic ability for the Knoevenagel reaction with excellent reusability for at least five cycles.

EXPERIMENTAL SECTION

Materials and Analysis. Chemicals in this work were purchased directly. Tris(4-(4H-1,2,4-triazol-4-yl)phenyl)amine was prepared according to a previous report.³¹ Thermogravimetric (TGA) curves were collected on a SDT-Q600 analyzer. Powder X-ray diffraction (PXRD) profiles were obtained on a Siemens Bruker D5000 X-ray powder diffractometer. The luminescent spectra were implemented on a Horiba FluoroMax 4 spectrometer. UV–Vis adsorption spectra were acquired on a Shimadzu UV–2450 spectrophotometer. Catalytic data were calculated on a GC-6890B gas chromatograph machine. Elemental analyses were carried out on a PerkinElmer 240 analyzer.

Preparation of [CdL(NO₃)₂·4H₂O]_n (MOF 1). Cd(NO₃)₂·4H₂O (0.03 g) and L (0.015 g) were both mixed in a mixed solution of H₂O (1.2 mL) and ethanol (3.8 mL) in a Teflon-lined autoclave, which was still heated in an oven at 165 °C for 1 week. After it slowly cooled to room temperature at 10 °C h⁻¹, the light yellow crystals were collected and dried in air. The yield was ~59% based on this ligand. Element analysis of C, H, and N (%): H, 4.21; C, 37.89; N, 22.11; Found: H, 4.27; C, 37.94; N, 22.06.

Preparation of {[CoL(H₂O)₃]·2NO₃} (MOF 2). Co(NO₃)₂·6H₂O (0.03 g) and L (0.015 g) were putted in ethanol (4 mL) and H₂O (1 mL), which was all added in a Teflon-lined autoclave. The system was heated in an oven at 165 °C for a 1 week. After this autoclave was cooled down to room temperature at a decreasing temperature rate of 10 °C h⁻¹, violet crystals were generated and dried in air. The yield is ~64% based on this ligand. Element analysis of C, H, and N (%): H, 4.35; C, 41.80; N, 24.38; Found: H, 4.41; C, 41.72; N, 24.32.

Sensing Experiments of MOF 1. Before these luminescence sensing trials, as-synthesized crystals were gradually ground to reduce their sizes in a mortar before luminescent sensing experiments, which can directly enhance the dispersity of MOF 1 in water. The suspension of ground samples in water (0.3 mg mL⁻¹) was successfully obtained by adding 9 mg of ground crystals into 30 mL of water, which was continuously stirred for 20 min and then treated by ultrasonication for 20 min. All luminescent experiments of MOF 1 were measured under the excitation of 348 nm. Luminescent signals were collected with or without antibiotics in water for 2 min at 0.05 mM, including nitrofurantoin (NFT), dimetridazole (DTZ), sulfamethazine (SMZ), florfenicol (FFC), penicillin (PCL), chloramphenicol (CAP), and thiamphenicol (THI). The relationship between spectral intensities and concentrations were performed and analyzed by gradually adding antibiotics into the detectable system. The recyclability was measured and investigated by detecting antibiotics at 0.05 mM. After each sensing experiment, MOF 1 was able to be centrifugally obtained and regenerated by washing with water.

Catalysis Experiments of MOF 2. MOF 2 was first immersed in toluene for 30 min before the catalytic reaction to remove other solvents on the surface of MOFs. Then these samples were filtered and directly dried in air. Various substrates (1.0 mmol), malononitrile (1.1 mol), and MOF 2 were all mixed in a bottle glass containing toluene (6 mL) and heated at 80 °C for 4 h. The yield can be well determined by GC with biphenyl as the internal standard. The recyclability of MOF 2 was continuously reused after each catalytic reaction.

Analysis of Single Crystal Structure. Single crystals with high quality were selected to measure their structures on a Bruker SMART APEX II with Cu K_{α} radiation. Single data were corrected by the multiscan absorption in the application of *SADABS*.³² Then they were determined by the direct method and refined through the *SHELXTL* program.³³ All non-hydrogen atoms were ensured and refined by the anisotropic approach. The *PLATON/SQUEEZE* method can be used to wipe off the poor independent reflections from solvents.^{34,35} All data are shown in Table 1.

Table	1.	Crystal	Data	of	MOFs	1	and	2
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1	2
$C_{24}H_{26}O_{10}N_{12}Cd$	$C_{24}H_{18}O_3N_{10}Co$
755	553.41
monoclinic	monoclinic
C2y	C2y
27.6524(9)	26.668(4)
15.3074(4)	14.944(2)
9.0504(3)	9.1400(15)
90	90.00
103.559(3)	100.944(14)
90	90.00
3724.1(2)	3576.4(10)
4	4
1.218	1.028
5.109	4.050
6950	4885
1368.0	1132.0
0.028	0.0564
1.010	1.127
0.0396, 0.1072	0.1185, 0.3004
0.0409, 0.1093	0.1322, 0.3309
	$\frac{1}{C_{24}H_{26}O_{10}N_{12}Cd} \\ 755 \\ monoclinic \\ C2y \\ 27.6524(9) \\ 15.3074(4) \\ 9.0504(3) \\ 90 \\ 103.559(3) \\ 90 \\ 103.559(3) \\ 90 \\ 3724.1(2) \\ 4 \\ 1.218 \\ 5.109 \\ 6950 \\ 1368.0 \\ 0.028 \\ 1.010 \\ 0.0396, 0.1072 \\ 0.0409, 0.1093 \\ \end{bmatrix}$

RESULTS AND DISCUSSION

Structure of $[CdL(NO_3)_2 \cdot 4H_2O]_n$ (MOF 1). MOF 1 is the C2y space group and the monoclinic crystal system. There is one Cd atom, one L, and two coordinated NO3- ions in the asymmetrical unit. The Cd atom is connected with three Ndonors in three ligands and four O-donors atoms from two NO₃⁻ ions; meanwhile, the organic linker is linked with three Cd atoms through the Cd–O coordination bond with the bind mode of μ_3 - η^1 : η^1 : η^1 (Figure 1a). Only one N atom in the fivering of the linker is connected with one Cd atom, resulting in another N atom free in the five-ring motif. The mononuclear Cd is connected with the bridging linkers to construct a twodimensional (2D) network with hexagonal pores with a length of ~9.7 Å (Figure 1b). The Cd…Cd distance in MOF 1 in this 2D layer is ~16.5 Å. Because of the large pore size, an 1 + 2self-locked structure can be found to construct a threedimensional (3D) network (Figure 1c-e).

Structure of $\{[CoL(H_2O)_3] \cdot 2NO_3\}_n$ (MOF 2). The single crystal data show that MOF 2 crystallizes in the C2y space group and the monoclinic system. The asymmetrical unit of MOF 2 contains one Co atom, one linker, and three



Figure 1. (a) Coordination modes of mononuclear Cd and linker; (b) the 2D single layer; (c-e) the self-interpenetrating framework.

coordinated water molecules. The coordination mode of Co atom illustrates that each Co center connects with six atoms, including three N-donors from three linkers and another three O-donors from three coordinated water molecules (Figure 2a). One coordination mode of linker exists in MOF 2 by adopting μ_3 - η^1 : η^1 : η^1 to connect with three Co atoms (Figure 2a). A 2D layer with hexagonal pores can be seen in MOF 2 by the coordination assembly between Co centers and bridging



Figure 2. (a) Coordination modes of Co^{II} and linker; (b) the 2D single network in MOF 2; and (c-e) the 3D self-interpenetrating structure.

linkers, which is similar to that in MOF 1 (Figure 2b). More importantly, these 2D layers are self-interpenetrated by a 1 + 2 self-locked fashion to generate a 3D structure (Figure 2c-e).

PXRD and TG Curves. The PXRD patterns of as-synthesized **1** and **2** were both measured. As shown in Figure 3a, diffraction peaks of prepared samples are matched well with those of simulated data, illustrating that bulk samples are pure phases. The TG curves of as-synthesized samples are displayed in Figure 3b. The first weight losses of 9.71% and 9.85% for MOFs **1** and **2** are similar to the calculated values of 9.54% (MOF **1**) and 9.76% (MOF **2**); meanwhile, the second weight losses are 16.37% for MOF **1** (calculated 16.42%) and 22.42% for MOF **2** (calculated 22.61%), respectively.

Luminescence Sensing Properties. Luminescence signals of the free ligand and MOF 1 were collected and discussed in detail. As seen in Figure 4a, the emission spectra of the linker and MOF 1 were excited under 366 nm. The maximum peaks are 414 nm for MOF 1 and 422 nm for this free linker, respectively. It clearly found that the luminescence behavior of MOF 1 is similar to that of this linker, but a slight blue-shift phenomenon was mainly attributed to the metal-coordination interaction to enhance the ligand rigidity and decrease the energy loss by radiationless decay.³⁶⁻³⁸ Antibiotics are easily dissolved in water, so water was selected as the detectable system. From the previous reports, some MOFs have been implemented as luminescent sensors to monitor antibiotics.³⁹⁻⁵⁰ In addition, MOF 1 can preserve the luminescent behavior in water after 1 day (Figure 4b). This encouraged us to explore the detectability of MOF 1 to antibiotics in aqueous solutions. As displayed in Figure 4c, luminescent properties of MOF 1 (~0.3 mg mL⁻¹) were detected in frequently used antibiotics at 0.05 mM, including NFT, SMZ, FFC, DTZ, CAP, THI, and PCL. The luminescence intensities of MOF 1 can keep very well after immersion in CAP, THI, PCL, and FFC; meanwhile, the signals of as-synthesized 1 show a little decrease in SMZ and DTZ aqueous solutions. More importantly, an obvious luminescence quenching can be found after immersing MOF 1 in the NFT aqueous solution.

It is clearly found that the quenching order of MOF 1 toward antibiotics is NFT > DTZ > SMZ > FFC > PCL > THI > CAP, illustrating that it can discern NFT by the quenching performance. To estimate the ability of MOF 1, titration experiments were performed by adding NFT. Emission spectra were collected at different NFT aqueous concentrations. Figure 5a shows that the signal intensity is significantly weakened after increasing the NFT concentration, which can be estimated by calculating the K_{sv} value, the Stern-Volmer constant, from the value of $I_0/I - 1$ and the NFT concentration from the Stern-Volmer equation. Figure 5b shows the linear relationship of the values of $I_0/I - 1$ and the NFT concentrations in the full detection concentration range. The calculated K_{sv} value of NFT is as high as 4.64 \times 10⁴ M⁻¹, and the corresponding R^2 value is obtained as 0.9981, which shows that MOF 1 is the most sensitive sensor material.^{39–50} The selectivity of MOF 1 is a very significant factor for sensors in real applications, which can be studied and proven by the selective trials. It is found that all emission spectra almost disappeared only after adding NFT in the detected system (Figure 5c), proving that MOF 1 has excellent selectivity toward NFT even in other disturbed antibiotics. The recollected samples were washed and regenerated by fresh water to further detect NFT in the water system again. Figure 5d evidently shows that MOF 1 not only can restore the



Figure 3. (a) PXRD patterns and (b) TG curves of both samples.



Figure 4. (a) Emission bands of linker and MOF 1; (b) the luminescent signal of MOF 1 after immersing in water; and (c) corresponding intensities of MOF 1 toward different antibiotics in water.

original luminescence spectra but also preserve its sensing ability toward NFT at least five times. The result exhibits that MOF 1 possesses outstanding reusability during the detecting process.

As shown in Figure 6a, UV-vis data of all selected antibiotics and MOF 1's excitation spectrum clearly show that only NFT possesses an overlap performance with the excitation band of MOF 1. On the basis of previous reports, the most probable quenching mechanism is deduced as the energy competition between NFT and MOF 1 in water. In addition, the PXRD pattern of MOF 1 after five cycles is well preserved to illustrate its high stability (Figure 6b). Because of the residue NFT in our lives, we tried to monitor NFT in bovine serum by adding a certain amount of NFT. Table 2 shows that MOF 1 has a favorable detection ability toward NFT with a relative standard deviation (RSD) under \sim 5.1%. All results illustrate that MOF 1 has a potential application in the detection of NFT.

Catalysis Properties. By virtue of abundant N atoms as Lewis basic sites in the framework, MOF 2 can be investigated and implemented to catalyze the Knoevenagel condensation reaction. $^{51-65}$ The prepared block crystals were soaked in fresh toluene for 30 min and further dried in air for 2 h. In a typical reaction, malononitrile (1.1 mol) and substrates with various functional groups (1.0 mmol) were dissolved in 6 mL of toluene in the presence of MOF 2 (100 mg), which was continually heated at 80 °C for 4 h under slow stirring. The catalytic resultant was measured and calculated by the GC method. All catalytic results are provided in Table 3 based on various aldehyde substrates. The catalytic yield of targeted



Figure 5. (a) The emission intensities of MOF 1 toward NFT at different concentrations; (b) their Stern–Volmer plots; (c) the selectivity; and (d) the recyclability of MOF 1.



Figure 6. (a) UV-vis data of selected antibiotics and the excitation spectrum of MOF 1; (b) the PXRD result of MOF 1 after five cycles.

Table 2. Detecting NFT in Bovine Serum Samples ($n = -$	4)
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sample	added (μM)	found (μM)	recovery (%)	RSD (%)
1	50	51.7	103	3.2
2	75	73.2	98	4.2
3	100	103.1	103	3.7
4	125	127.9	102	3.5
5	150	158.7	106	5.1

product 2-benzylidenemalononitrile is as high as \sim 98% after reaction 4 h in entry 1 of Table 3. The benzaldehyde was used as a substrate model not only to investigate the kinetic rate but also to prove the necessity of MOF **2**. The result shows that this reaction can be almost transformed into the targeted product 2-benzylidenemalononitrile within 4 h with the catalysis of MOF 2 (Figure 7a), but the reaction immediately stopped after filtering MOF 2 in the reaction system. More importantly, the catalytic product almost cannot be found without MOF 2 with a yield of ~6% in entry 2 of Table 3. Various substrates with different functional groups were implemented to explore the relationship between catalytic yields and functional groups. When the functional groups in aldehyde substrates are the electron-withdrawing -F and $-NO_2$, the corresponding results are both significantly higher than >99% (entries 3 and 4 of Table 3). However, the catalytic yields remarkably decrease to 89% of one electron donor -OMe group (entry 5) and 81% (entry 6) of two -OMegroups, respectively. The catalytic result clearly proves that the different electron effects will affect the catalytic yields. In addition, the recyclability is a vitally important element for

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Table 3. Catalytic Yields of the Knoevenagel Condensations



heterogeneous catalysts. MOF **2** was further reused for the Knoevenagel condensation. As seen in Figure 7b, MOF **2** can well preserve the original catalytic performance even after continuously recycling five runs by using benzaldehyde.

CONCLUSION

In conclusion, we successfully designed and constructed two interpenetrating MOFs based on Cd^{II} and Co^{II}. By virtue of different structural characteristics, MOF 1 and MOF 2 exhibit completely different properties in sensing and catalytic fields. MOF 1 can be used as a sensor material toward NFT with high selectivity and stability; meanwhile, MOF 2 is implemented as a Lewis basic heterogeneous catalyst for Knoevenagel condensation with outstanding recyclability. Further work is ongoing in our laboratories to prepare and investigate such functional MOFs.

ASSOCIATED CONTENT

Accession Codes

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CCDC 1888298 and 1910143 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.



Figure 7. (a) The kinetic catalytic yields and (b) the reusable capability of MOF 2.

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