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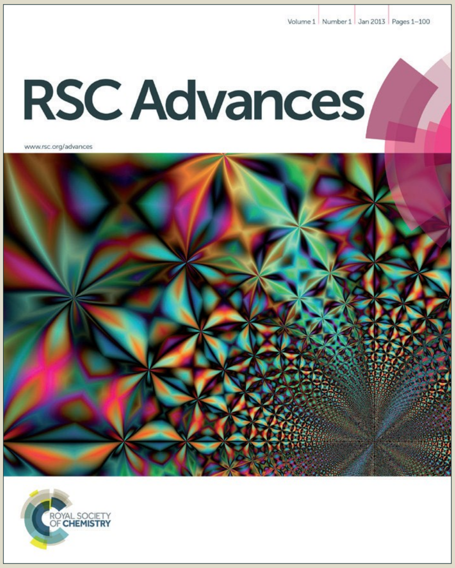

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A dual-functional Cd(II)-organic-framework demonstrating selective sensing of Zn^{2+} and Fe^{3+} ions exclusively and size-selective catalysis towards cyanosilylation

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A dual-functional complex with the formula $Cd_2(L)(DMF)_2(H_2O)_2$ (L = 2,3′,5,5′-biphenyl tetracarboxylic acid) has been successfully synthesized under solvothermal conditions and characterized by thermogravimetric analyses, IR spectroscopy, X-ray powder diffraction and single crystal X-ray diffraction. This material can selectively sense Zn^{2+} and Fe^{3+} ions over mixed metal ions through fluorescence enhancement and quenching, respectively. The cyanosilylation of aldehydes reactionhas been studied used activated complex as catalyst; the results showed that this complex with Lewis acid sites can act as stable heterogeneous catalyst.

Introduction

Over the past decade, functional metal-organic frameworks (MOFs) have attracted much attention, not only for their compositional and structural diversities, but also for their potential applications in the areas of catalysis,[1] luminescence,[2] gas adsorption and separation,[3] ion exchanging,[4] magnetism[5] and so on. It should be noted that study on MOFs as chemosensors is one of the hot topics.[6-7] Most probes are sensitive to certain metal ions such as Zn^{2+}, Al^{3+} and Fe^{3+},[8-9] which follow the principle that there exists coordination sites in the structure to postsynthetically interact with the special metal ions, and then exert an effect on the luminescent intensity of the material.[10]

Zn^{2+} and Fe^{3+} are widely used in many areas such as industry, agriculture and especially in the medical. However, they have different influences on the human body and other biological tissues. Fe^{3+} ion plays an essential part in many vital cell functions such as hemoglobin formation, muscle and brain function, electron transfer processes in DNA and RNA synthesis.[11] But excess amounts of Fe^{3+} in a living cell may cause damage to nucleic acids and proteins through catalyzing the production of reactive oxygen species.[12] Zn^{2+} ion is the second most abundant transition metal essential for the human body with a concentration ranging from sub-nM to ~ 0.3 mM.[13] Recent work showed that Zn^{2+} is closely associated with severe pathological disease, such as Alzheimer's disease and familial amyotrophic lateral sclerosis,[14] and its intracellular concentration is under tight control.[15] Hence, selective detection or sensing of Fe^{3+} and Zn^{2+} over other mixed metal ions seems to be very important for human health.

The studies on MOFs as catalysts have also caused considerable attention due to their potential properties including porosity, extraordinarily robust and high internal surface area.[16] The catalyticmechanismof MOFs results from the metal center in the structure, or the catalytically-active functional organic sites of the organic ligand.[17] However, MOFs with Lewis acid sites could also serve as size- and shape-selective heterogeneous catalysts, which is one of the hot topics.[18]

In this work, we report the synthesis, structural characterization and applications of a unique porous MOF with the formula $Cd_2(L)(DMF)_2(H_2O)_2$ (**1**) using L ligand (L = 2,3′,5,5′-biphenyl tetracarboxylic acid) as organic linker. Complex **1** is sensitive to Zn^{2+} and Fe^{3+} ions without the interference of other mixed ions. More interestingly, activated **1** with Lewis acid sites shows size-selective catalytic activity toward the cyanosilylation of aldehydes.

Experimental Section

Materials and Methods

All reagents and solvents employed were commercially available and used without further purification. The C, H, and N microanalyses were carried out with Perkin-Elmer 240 elemental analyzer. Thermogravimetric analyses (TGA) were taken on a Perkin-Elmer Pyrisl (25-800 °C, 10 °C min^{-1}, flowing N_2 (g)). The FT-IR spectra were recorded from KBr pellets in the range 4000-400 cm^{-1} on a Nicolet 5DX spectrometer. X-ray powder diffraction was recorded with a Bruker AXS D8advanced automated diffractometer with Cu-Kα radiation. Luminescencespectra for the solid samples and liquid samples were investigated with a HitachiF-4500 fluorescence spectrophotometer and Varian Cary Eclipse Fluorescencespectrophotometer, respectively. The products of catalysis reaction are monitored byGas chromatography with a SP-2100A Gas chromatograph.

Solvothermal Synthesis

$Cd_2(L)(DMF)_2(H_2O)_2$ (**1**).

$Cd(NO_3)_2 \cdot 4H_2O$ (25 mg, 0.26 mmol) was added to the $DMF/CH_3CH_2OH/H_2O$(3:3:2, 4 ml) solution of H_4L (15 mg, 0.45 mmol), and the mixture was stirred for *ca.* 20 min in air. Then it was heated at 75 °C for 2 days, followed by slow cooling (5 °C h^{-1}). The resulting light yellow crystals were washed with distilled water and dried in air (yield: *ca.* 60%).Elemental analysis calcd (%) for

1$C_{22}H_{24}Cd_2N_2O_{12}$ (%): C: 36.01; H: 3.27; N: 3.82; found: C: 35.96; H: 3.34; N: 3.86. IR (KBr, cm^{-1}): 3400(s), 1652 (s), 1574(s), 1385 (vs), 1242(w), 1108(w), 828(w), 773(w), 724(w).

X-ray Crystallography

Crystallographic data of **1** were collected at 173 K with a Bruker Apex CCD II diffractometer with Mo-Kα radiation (λ = 0.71073 Å) and graphite monochromator using ω-scan mode. The structure was solved by direct methods and refined on F^2 by full-matrix least squares using SHELXTL.[19] This was a twinned structure and The values of Rint, provided by TWINABS, are 0.0351 and 0.0400 corresponding to the two crystal domains. Crystallographic data and experimental details for structural analyses are summarized in Table 1. The CCDC reference number 1014278 for **1**. Copy of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: int code +44(1223)336-033; E-mail: deposit@ccdc.cam.ac.uk].

Table 1. Crystallographic Data for 1.

Empirical formula	$C_{22}H_{24}Cd_2N_2O_{12}$
Formula weight	733.23
Wavelength/ Å	0.71073
Crystal system	Monoclinic
Space group	$P2_1$
a/ Å	9.7549(13)
b/ Å	13.1891(17)
c/ Å	10.5080(13)
□/ °	109.603(4)
V/ $Å^3$	1273.6(3)
Z	2
Dc/mg m^{-3}	1.912
μ/ mm^{-1}	1.736
F(000)	724
Range for data collection/°	2.06-26.00
Reflections collected	4702
Max., min. transmission	0.7931, 0.7012
T/ K	173(2)
Data/restraints/parameters	4702 / 43 / 320
Final R indices[$I > 2\sigma(I)$]^a	$R_1 = 0.0431$, $wR_2 = 0.0735$
R indices(all data)	R_1=0.0495, $wR_2 = 0.0746$
Largest diff. peak and hole /e $Å^{-3}$	0.924, -1.057

Results and discussion

Crystal structure

The Single-crystal X-ray analysis reveals that **1** crystallizes in a chiral space group $P2_1$. The asymmetric unit of **1** contains two crystallographically unique Cd(II) ions, one L ligand, two coordinated DMF molecules and two aqua ligands. As shown in Fig. 1a, the Cd1 atom is six-coordinate with five carboxylate oxygen atoms from four individual L ligands and one oxygen atom from one coordinated DMF molecule, Like Cd1, Cd2 atom is also six-coordinate with three carboxylate oxygen atoms from three individual L ligands and one oxygen atoms from one coordinated DMF molecule and two aqua ligands, respectively. Cd1 is linked to Cd2 via two μ_2-η^2:η^1 bidentate carboxylate groups and one μ_2-η^1:η^1carboxylate group to form a dinuclear Cd cluster. The Cd clusters are bridged by L ligands to form a three-dimensional (3D) framework. It is noted that four carboxylate groups in the L ligand exhibit three kinds of connection modes: monodentate, bidentate bridging and chelating/bridging mode and all the carboxylate groups are deprotonated (Fig. 1b). It is worth mentioning that regardless of the coordinated solvent molecules, it showed 1D channelswith the size of *ca.*11.4 × 9.7 $Å^2$along the *b* axis (Fig. 1c and Fig. 1d).With omitting the coordinated solvent molecules, PLATON analysis[20]revealed that the 3D framework was composed of voids of562.2 $Å^3$, which represent 44.1% per unit cell volume.

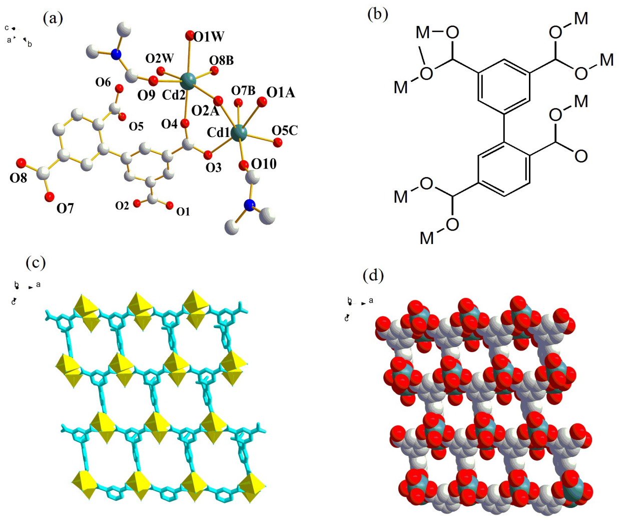


Fig. 1. (a) Coordination environments of Cd(II) in **1.** Symmetry mode:A: x-1, y, z; B: x-1, y, z-1; C: -x, 0.5+y, -z+1. (b) The coordination modes of L ligand in **1**. (c) 3D single network of **1** with removing coordinated DMF molecule. (d) space-filling representation of 3D structure of **1** along the *b*-axis (DMF molecules were omitted for clarify).

Thermal Stability

The simulated and experimental PXRD patterns of **1** are shown in Fig. S1a.Their peak positions are in good agreement with each other, indicating the phase purity of the products. The differences in the intensity may be due to the preferred orientation of the powder sample.

The TGA curve (Fig. S2) of **1** shows the first weight loss of 4.94 % from ca. 29.0 °C to 118.0 °C, corresponding to the loss of two coordinated water molecules (calculated 4.91 %). The weight loss of 20.44 % from 118 °C to 330 °C, which corresponds to the loss of two coordinated DMF molecules (calculated 19.91 %). The residue was CdO (experimental: 35.36 % and calculated: 35.02 %).

Photoluminescence properties

Previous studies have shown that Cd(II) coordination polymersexhibitphotoluminescent properties.[21-22] So we investigated the luminescentproperties of **1**in the solid state and in methanolsuspension at room temperature.

As expected, **1**exhibits anintense emission band at *ca.*420 nm uponexcitation at 368 nm (Fig. S3a). It should be noted that there is a emission band at 420 nm for free L ligand under thesame experimental conditions (Fig. S3b). Thus the emission may be assigned to the ligand-centered π–π* transition because their fluorescentemission bands are same to that of the free ligand.[23]

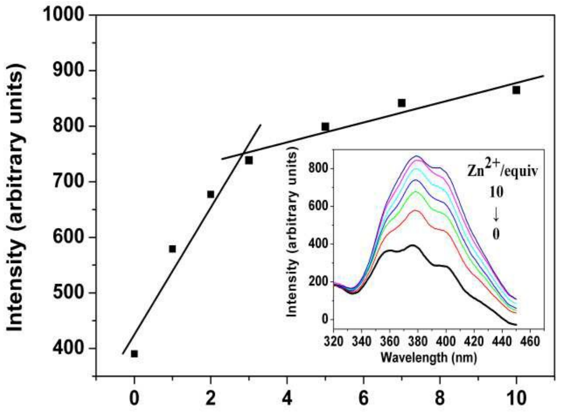


Fig. 2. Emission spectra of the complex **1** in methanol at room temperature in the presence of different equiv of Zn^{2+} ions with respect to **1**, respectively, excited at 250 nm.

We also investigated the effects of the metal ions such as K^+, Ca^{2+}, Na^+, Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Pb^{2+}, Mg^{2+}, Cr^{3+}, Ag^+, Mn^{2+}, $Hg^{2+}$and Cd^{2+} on the fluorescent intensity of **1** in methanol suspension at room temperature. The emission intensity of **1** enhanced distinctly with Zn^{2+} doping in**.**More remarkably, with increasing Zn^{2+} concentration, the emission intensities of **1** increased gradually upon addition of different equiv of Zn^{2+} with respect to **1** (Fig. 2). When adding 10 equiv of Zn^{2+}, the highest peak at 378 nm is more than twice as intense as the corresponding band in the solution without Zn^{2+}, whereas adding Fe^{3+} can almost quench the fluorescence intensity of **1** and others had no evident effect on the emission intensity of **1**(Fig. 3). In order to check the high sensitivity to Zn^{2+} and Fe^{3+} over other metal ions, the experiments were performed for the introduction of other metal ions (K^+, Ca^{2+}, Na^+, Co^{2+}, Ni^{2+}, Mg^{2+}, Ag^+, Mn^{2+}, Hg^{2+}) into the system. More importantly, the selectivity to Zn^{2+} and Fe^{3+} is not interfered by some other metal ions (Fig. 4 and Fig. S4-S5).

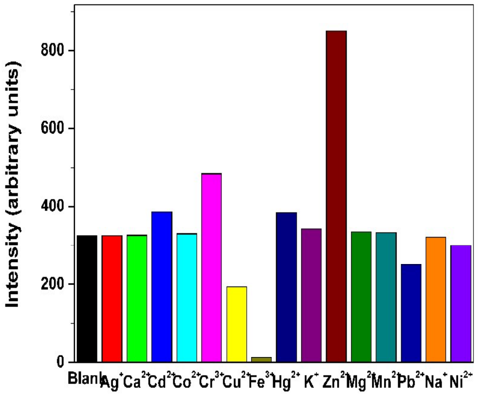
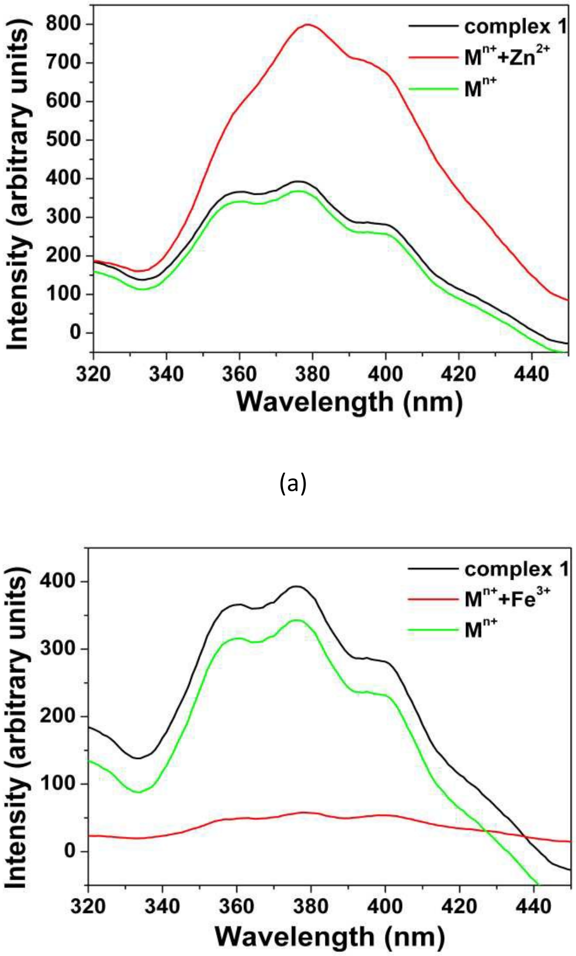


Fig. 3. Room-temperature luminescent intensity of **1**at 378 nm in methanol uponaddition of 10 equiv of various metal ions (excited at 250 nm).

As mentioned above, the exoteric Zn^{2+} can sensitize theluminescence of **1**. The enhancement of luminescent intensity may result from more effective intramolecular energy transfer between the L ligand and the Cd^{2+}. With the addition of Zn^{2+} and Fe^{3+}, the results indicate that the energy transfer from the organic ligands to metal ions is changed, and the energy transfer is not interfered by some other metal ions.



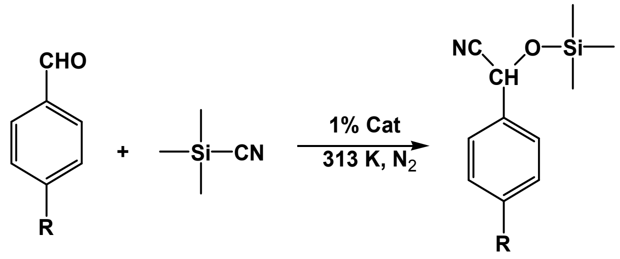
(a)

(b)

Fig. 4. Comparison of the photoluminescence intensity of **1** in methanol suspension with theintroduction of other metal ions (K^+, Ca^{2+}, Na^+, Co^{2+}, Ni^{2+}, Mg^{2+}, Ag^+, Mn^{2+}, Hg^{2+}) in the absence and presence of 5 equiv (a**)** Zn^{2+} (b) Fe^{3+}.

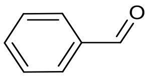
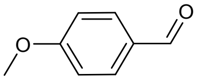
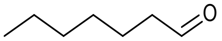
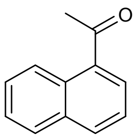
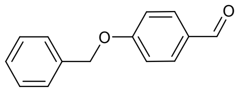
Catalysis properties

Scheme 1. Cyanosilylation of Aldehydes Reaction Catalyzed by **1**.



Metal-organic frameworks as catalysts with Lewis acid sites have caused much attention due to their metallic components, which either provide the coordinatively unsaturated nodes or form the active metal complexes incorporated into the linker ligand.[24]In order to probe the Lewis acid catalytical activity of complex **1** thecyanosilylation reaction was chosen. This reaction provides a convenient route to cyanohydrins, which are key derivatives in the synthesis of fine chemicals and pharmaceuticals.[25]To expose the active metal sites, the coordinated molecules of complex **1** have been removed by heating to 150 °C in vacuum condition, and the block shape of the crystal did not change (See Fig. S1a). In order to investigate the size selective catalysis of **1**,we took a systematic approach by varying the size and shape of the substrates. So, five different sizes of aldehydes were performed in the cyanosilylation reaction.

Table 2. Cyanosilylation Reaction Catalyzed by **1**.

run	substrate	Time (h)	Conversion (%)[a]	TOF (h^{-1})[b]]]
1		1.5 h	97.44	64.96
2		2 h	94.52	47.26
3		2 h	96.36	48.18
4		3 h	81.41	27.14
5		3 h	34.22	11.41

[a]Conversion determined by GC.[b]TOF: % conversion (mmol ofsubstrate/mmol of cat. h)

A solution of equivalent amounts of cyanotrimethylsilane (4 mmol) and aldehyde(4 mmol) wasmixed in CH_2Cl_2. This solution was added at 40°C to suspension of activated **1**in CH_2Cl_2 (Scheme 1) and the progress of the reaction was monitored by using gaschromatography (See Fig. S7).As shown in Table 2 and Fig. 5,benzaldehyde (8.9 × 6.7 Å^2) had high sensitive to the catalyst. After 1.5 h, a yield of 97.44% (isolated yield: 88.65%) and a TOF value of 64.96 h^{-1} was achieved. Compared to the MOF Lewis catalyst, the complex **1** exhibited obvious performance(Table S1).[26] After 2 hours, n-heptaldehyde and p-anisaldehyde (10.4 × 6.1 Å^2) had a yield of 96.36% (TOF: 48.18 h^{-1}) and 94.52% (TOF: 47.26 h^{-1}), respectively. However, for the larger size aromatic aldehydes, for example, 1-naphthaldehyde (9.6×8.6 Å^2) and 4-benzyloxybenzaldehyde (16.1×6.1 Å^2), only a relative low yield of 81.41% (TOF: 27.14 h^{-1}) and 34.22% (TOF: 11.41 h^{-1}) was achieved after 3 hours. A control filtration test was carried out to demonstrate whether the catalytic activity of the Cd metal sites is due to active sites in the solid phase or to any active species leaching into the liquid phase (Fig. S8). Only small increase of the conversion after filtration could be attributed to a thermally activated slow reaction. We have also carried out the reaction(benzaldehyde) using $Cd(NO_3)_2$or H_4L as catalyst, respectively. The yield of 64.32% was achieved when using $Cd(NO_3)_2$ as catalyst, which is higher than the control filtration test. No activity was observed when using H_4Las catalyst (Fig. S11). This demonstrates that no homogeneous catalyst species exists in the reaction solution.

The catalytical activity differences among the five reactions may be two reasons below: First, the reactants could access into the inside of the catalyst through the channels (11.4 ×9.7 Å^2) of **1**. Therefore, larger size of aldehydes were difficult to access into the channel and results in the relative low conversion and TOF value such as 4-benzyloxybenzaldehyde. Second, there were considerable active sites on the surface of the activated catalyst. So even the relative large size aldehydes, for example, 1-naphthaldehyde also performed high conversion.It should be noted that complex **1**as catalyst is easily isolatedfrom the reaction suspension by a simple filtration. The PXRD (powder X-ray diffraction) pattern of **1** after the reactions werecollected and examined, which is complete to the one before the reaction (see Fig. S1b), indicating the stability of the catalyst.And the activity of the catalyst didn't loss after 5 cycles' reactions (Fig. S9).

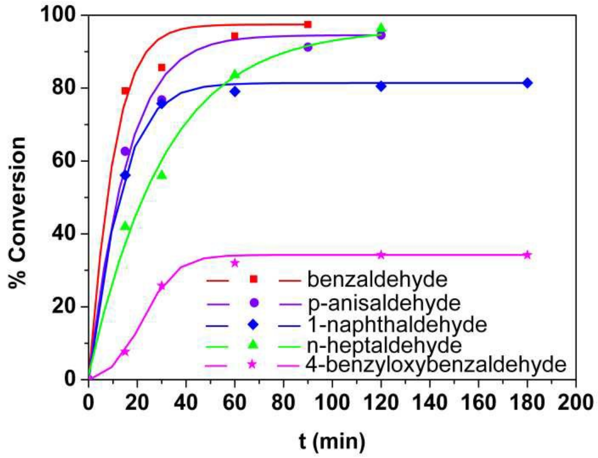


Fig. 5. Conversion (%) versus time (min) for cyanosilylation for different aldehydes for **1**.

Conclusions

In summary, a new MOF based on L ligand has been successfully designed and synthesized. It exhibits strong fluroescent emission in the solid state and in methanol suspension at room temperature. **1** displayed high performance selectivity for Zn^{2+} and Fe^{3+} over other metal ions, which implies that it may be used as luminescent probes of Zn^{2+} and Fe^{3+}. After removing the coordinated solvent molecules, the Lewis acid sites in the activated **1** were used as catalyst for cyanosilylation both on the surface and inside the channel of complex **1**. These results will bring more attention on the potential properties of metal-organic-framework.

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Supporting Information Available: Experimental procedures, structure figures, a TGA plot, simulated and experimental X-ray powder diffraction patterns, fluorescence studies, catalysisstudies and crystallographic data (CIF) for **1** are available free of charge *via* the internet at http://pubs.acs.org.

Notes and references

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