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A Bifunctional Europium–Organic Framework with Chemical Fixation of CO₂ and Luminescent Detection of Al³⁺

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Supporting Information

ABSTRACT: A novel three-dimensional lanthanide–organic framework {[Eu(BTB)(phen)]·4.5DMF·2H₂O}_n (1) has been synthesized. Structural characterization suggests that framework 1 possesses one-dimensional channels with potential pore volume, and the large channels in the framework can capture CO₂. Interestingly, investigations on the cycloaddition reaction of CO₂ and epoxides reveal that compound 1 can be considered as an efficient catalyst for CO₂ fixation with epoxides under 1 atm pressure. Importantly, 1 can be reused at least five times without any obvious loss in catalytic activity. Furthermore, the luminescent explorations of 1 reveal that 1 can act as a recyclable sensor of Al³⁺, and the corresponding detection limit can reach 5 × 10⁻⁸ M (1.35 ppb), which is



obviously lower than the United States Environmental Protection Agency's recommended level of Al^{3+} in drinking water (200 ppb). These results show that 1 has a level of sensitivity higher than that of other reported MOF-based sensors of Al^{3+} .

INTRODUCTION

As an emerging class of porous materials, lanthanide-supported metal-organic frameworks (Ln-MOFs) are receiving extensive attention owing to not only their diversified structures and topologies¹ but also their promising applications in gas storage/ separation,² optical properties,³ magnetism,⁴ heterogeneous catalysis,⁵ chemical sensing,^{6–8} etc.⁹ In these types of applications, the catalytic reaction for CO₂ conversion is gradually becoming a hot issue as the excess emission of CO₂ causes a series of environmental problems such as global warming and ocean acidification.¹⁰ Until now, guite a lot of effort has been focused on converting CO₂ into high value added products,¹¹ and the coupling reaction of CO₂ with epoxides to provide cyclic carbonates is considered as one of the best strategies for CO2 conversion due to not only its excellent reactivity and high atom efficiency but also the significant and extensive applications of cyclic carbonates as aprotic polar solvents, precursors for affording polycarbonates, and chemical intermediates in organic synthesis.¹² In terms of cycloaddition reaction with CO₂ and epoxides, many catalysts have been developed and exhibit fine activity, but comparably, only a few MOF-based catalysts have been reported,¹² and porous Ln-MOFs are considered as ideal candidates for CO2 conversion with epoxides for following reasons: (1) porous Ln-MOFs can significantly adsorb CO_{2} (2) large-sized porosity in Ln-MOFs may enrich epoxides to increase the substrate concentration, (3) Ln³⁺ ions act as Lewis acidic sites to enhance catalytic activities, ^{5e-g} and (4) stable Ln-MOFs, as heterogeneous catalysts, can be reused to reduce the cost. Therefore, it is necessary to explore Ln-MOF-based catalysts for chemical fixation of CO_2 with epoxides.

On the other hand, as luminescent materials, many Ln-MOFs as chemical sensors have been investigated, and those chemical sensors mainly focused on the detection of Cu²⁺, Fe³⁺, Zn^{2+} , F⁻, PO₄³⁻, explosives, acetone, etc.⁶⁻⁸ However, in these studies, just three examples are associated with the detection of Al^{3+,8} which is the most abundant metallic element in the earth's crust and can be accumulated in human body to damage nervous system, leading to Alzheimer's disease and Parkinson's syndrome, and other issues.⁸ Nowadays, with the casual discarding of aluminum products and the erosion of acid rain, the environment is directly exposed to more and more Al³⁺, which poses a serious threat to human health. Therefore, effective detection of Al³⁺ is urgent to prevent Al³⁺ from harming human health, and it is necessary to develop new Ln-MOFs as recyclable luminescent sensors to detect Al³⁺ with high sensitivity.

In this contribution, a Ln-MOF {[Eu(BTB)(phen)]· 4.5DMF·2H₂O}_n (1) was obtained based on a high C_3 symmetric ligand, 1,3,5-benzenetribenzoate (H₃BTB), and framework 1 exhibits one-dimensional (1D) open channels with potential pore volume of 56.1% and high thermal stability. In terms of CO₂ conversion, compound 1 can effective catalyze

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the cycloaddition reaction with CO₂ and epoxides under 1 atm pressure of CO₂, and investigations of the recycling performance suggest that 1 as catalyst can be reused at least five times without any obvious loss in catalytic activity. On the other hand, luminescent investigations of compound 1 reveal that 1 can act as a recyclable luminescent sensor for detecting Al³⁺ with 5×10^{-8} M (1.35 ppb), which is far lower than the United States Environmental Protection Agency's recommended level of Al³⁺ in drinking water (200 ppb) and represents the lowest detection limit among MOF-based sensors so far.⁸

EXPERIMENTAL SECTION

Preparation of {[Eu(BTB)(phen)]·4.5DMF·2H₂O}_n (1). A mixture of Eu(NO₃)₃·6H₂O (0.1 mmol, 44.6 mg), H₃BTB (0.1 mmol, 43.8 mg), and 1,10-phen (0.2 mmol, 36.0 mg) in DMF (4 mL) and H₂O (2 mL) was sealed in a 15 mL Teflon-lined stainless steel autoclave. The autoclave was heated at 100 °C for 3 days under autogenous pressure and then cooled to room temperature at a rate of 2 °C/h under ambient conditions. The crystals were obtained and washed with DMF. Yield: 85%, based on Eu(NO₃)₃·6H₂O. Elemental analysis (%) Calcd for compound 1: C 55.68, H 5.17, N 8.04. Found: C 55.53, H 5.20, N 7.99.

RESULTS AND DISCUSSION

Structure. Single crystal X-ray diffraction analysis revealed that compound 1 crystallizes in the monoclinic system with space group C2/c, and the asymmetric unit contains an eight coordinated Eu^{3+} ion into square antiprism geometry (Figure 1b), which is achieved by six carboxylic oxygen atoms and two nitrogen atoms from 1,10-phenanthroline. Two crystallographically equivalent Eu^{3+} ions are bridged by four carboxyl groups into a binuclear unit as secondary unit buildings (SUBs), which are further linked by BTB³⁻ into a three-dimensional (3D) framework exhibiting atypical 1D open channels (Figure 1c). Additionally, the total potential pore



Figure 1. (a) Coordinated environments of BTB³⁻. (b) Coordinated environments of Eu³⁺. (c) 3D framework of 1 along the *c* direction. (d) Simplified *flu*-3 topology network of 1.

volume of **1** is as high as 56.1%, calculated by the PLATON program. From the topological point of view, each dinuclear $[Eu_2]$ unit is coordinated by six BTB³⁻ anions; thus, the $[Eu_2]$ unit can be considered as a 6-connected node. Each BTB³⁻ anion is bridging three $[Eu_2]$ units; thus, it can be regarded as a 3-connected node. According to this simplification, the structure of compound **1** can be simplified as a (3,6)-connected 3D framework with topology symbol of *flu*-3 (Figure 1d).¹³

Powder X-ray Diffraction Analyses (PXRD) and Thermogravimetric Analyses (TGA). The powder XRD diffraction (PXRD) of compound 1 is recorded in Figure S1, and the synthesized PXRD of 1 is almost identical to the simulated one, suggesting that the purity of compound 1 is high.

To study the stability of compound 1, thermogravimetric analyses (TGA) were measured under N_2 atmosphere. As shown in Figure S2, from room temperature to 165 °C, a weight loss of 32.12% can be observed, which corresponds to the loss of H₂O and DMF molecules (calcd: 32.21%). Subsequently, TGA curves show a weight loss of 15.93% between 265 and 421 °C, corresponding to the loss of coordinated phen molecules (calcd: 15.91%). Then, compound 1 starts to decompose above 521 °C. The high thermostability of structures is possibly attributed to the robust BTB ligands.

Catalytic Properties. In our initial investigations on the reaction of CO_2 with epoxides, styrene oxide (1a) was selected as a model substrate to explore the optimized reaction conditions, and the corresponding results are recorded in Table 1. First, the reaction was conducted using 3.5 mol %

Table 1. Cycloaddition Reaction of CO_2 with Styrene Oxide under Various Conditions^{*a*}

	0 	Cat.		0 ((2 a
entry	catalyst 1 (mol %)	TBAB (mol %)	$T(^{\circ}C)$	yield (%) ^b
1	3.5	2.5	60	36.38
2	3.5	2.5	70	57.13
3	3.5	2.5	80	68.25
4	3.5	5	60	70.75
5	3.5	5	70	>99
6	0	5	70	38.61
7	3.5	0	70	<1

^{*a*}Reaction conditions: styrene oxide (1a, 240.3 mg, 2.0 mmol), solvent-free, catalyst 1, CO_2 (0.1 MPa), 12 h, 40 mg catalyst 1 loading (based on metal center, about 3.5 mol %). ^{*b*}Total yield of 1b determined by ¹H NMR spectroscopy using 1,3,5-trimethoxybenzene as an internal standard.

compound 1 and 2.5 mol % cocatalyst (tetrabutylammonium bromide, TBAB) under solvent-free conditions and 0.1 MPa CO_2 , and the corresponding cyclic carbonate was obtained in 36.38% yield at 60 °C (entry 1, Table 1). Then, the yield gradually enhanced as the temperature was increased (entries 2 and 3), but the yield was still no more than 70% until 80 °C. Therefore, to avoid higher temperatures consuming too much energy, cocatalyst TBAB was added to 5 mol % in this reaction. As shown in entries 4 and 5, the yield can reach 70.75% at 60 °C, and over 99% yield can be obtained at 70 °C. Comparably,

only 38.61% yield was obtained under 5% TBAB without compound 1, suggesting that 1 plays an important role in this reaction. Therefore, the optimized reaction conditions should be loaded 3.5 mol % catalyst 1 and 5 mol % TBAB at 70 °C. Importantly, cycloaddition reactions under atmospheric pressure of CO₂ to afford cyclic carbonates is still rarely reported.^{12a}

To further explore the catalytic generality of compound 1, several typical epoxides substrates were examined for this cycloaddition reaction. Under the optimized conditions, all of the corresponding cyclic carbonates were obtained in excellent yields (68.66–99%, Table 2). The results clearly show that compound 1 possesses the capacity of catalyzing a cycloaddition reaction with extensive epoxides.

Table 2. Synthesis of Various Cyclic Carbonates from CO_2 and Epoxides with Catalyst 1^a



^{*a*}Reaction conditions: epoxides (2.0 mmol), solvent-free, 40 mg catalyst 1 loading (based on metal center, about 3.5 mol %), TBAB (32.4 mg, 0.1 mmol, 5 mol %), CO₂ (0.1 MPa), 70 °C, 12 h. ^{*b*}Determined by ¹H NMR spectroscopy using 1,3,5-trimethoxyben-zene as an internal standard.

As a stable heterogeneous catalyst, compound 1 can be simply separated from the reaction mixture through centrifugation and filtration. Hence, the recycle performance of 1 as a catalyst was explored, and the corresponding results are recorded in Figure 2. To our excitement, excellent catalytic activity of 1 still could be observed after being employed five times, indicative that 1 can be reused at least five times. Then, the PXRD patterns and inductively coupled plasma (ICP) results were further obtained (Figure S4 and Table S2), and the results remain consistent with the simulated results of 1, revealing that used 1 is still stable and only trace amounts of



Figure 2. Recycle tests with 1 for the cycloaddition reaction of CO_2 with styrene oxide.

leakage from the robust framework occurred, resulting in high recoverable performance.

According to reported work,^{12a} a possible mechanism for the cycloaddition reaction with CO₂ and epoxides was proposed. First, framework 1 with 1D channels can enrich CO₂ and the substrate. Second, as shown in Figure S5, the coupling reaction starts to bind with the Lewis acidic Eu³⁺ site through the oxygen atom of epoxide, which activates an epoxy ring. Finally, the nucleophilic Br⁻ attacks the less-hindered carbon atom to open the epoxy ring. In the next step, the interaction between CO₂ and the oxygen anion of the opened epoxy ring occurs to form an alkylcarbonate salt, and the corresponding cyclic carbonate is obtained through intramolecular ring closure. Thus, the corresponding cyclic carbonate is successfully obtained in a high yield.

Luminescent Behaviors and Sensing Properties. Under excitation at 300 nm, five characteristic emission peaks of compound 1 appear at 535, 591, 614, 655, and 697 nm (Figure S6),^{7c,8c} which are attributed to ${}^{5}D_{1} \rightarrow {}^{7}F_{1}$ and ${}^{5}D_{0} \rightarrow$ ${}^{7}F_{J}$ (J = 1, 2, 3, or 4) transitions of Eu³⁺ ions, respectively. On the basis of the transition rules of Eu³⁺ ions, when Eu³⁺ ions locate at an inversion center, the magnetic dipole transitions (${}^{5}D_{0} \rightarrow {}^{7}F_{1}$) are regnant, emitting orange light; when Eu³⁺ ions locate at a noninversion center, the electric dipole transitions (${}^{5}D_{0} \rightarrow {}^{7}F_{2}$) are dominant, emitting red light. As shown in Figure S6, the emission intensities at 591 nm are weaker than those at ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ transitions (614 nm), which is indicative that Eu³⁺ ions locate at noninversion center sites, agreeing with the structural analyses.^{7c,8c}

Generally, luminescent MOF-supported materials may be sensitive to some guest cations. Hence, the luminescent investigations of 1 were further carried out as follows: 4 mg samples of 1 were dispersed in 3.8 mL of ethanol solution into suspension by the ultrasound method for 40 min, and then 0.2 mL of an $M(NO_3)_x$ ethanol solution $(1 \times 10^{-2} \text{ M})$ (M = Al³⁺, Li⁺, Na⁺, K⁺, Cs⁺, Mg²⁺, Ca²⁺, Sr²⁺, Ba²⁺, Ag⁺, Mn²⁺, Cr³⁺, Fe²⁺, Co²⁺, Ni²⁺, Zn²⁺, Cu²⁺, or Fe³⁺, respectively) were slowly added into the above solutions into 1-M suspensions (5 × 10⁻⁴ M). Under the perturbation of the above cations, the luminescence intensities of resultant suspensions were recorded by a fluorescence spectrophotometer, and only regnant emission transitions (614 nm) were shown in Figure 3. Obviously, Al³⁺



Figure 3. Luminescence intensity of the ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ transitions (614 nm) of 1-M in 5 × 10⁻⁴ M different cations.

of 1, while other cations have a negligible effect on the emission or decrease the luminescent intensity. However, the luminescent change between Al^{3+} and other quenchable cations can be clearly observed as the much stronger quenching effect of Al^{3+} on the emission. Furthermore, mixed cations were also tested for luminescence (Figure S7), and the emission was still quenched after mixed cations were added, indicating that the quenching effect of Al^{3+} on the emission is not significantly influenced by other introduced cations. The different behavior between Al^{3+} and other cations on the emission are clearly observed, revealing that 1 is a promising luminescent sensor of Al^{3+} .

In addition, to study the detection limit of the Al³⁺ sensor, we prepared a series of ethanol suspensions of 1-Al³⁺. As shown in Figure 4, the luminescence intensity of 1 gradually decreases as



Figure 4. Emission spectra of 1 with different concentrations of Al^{3+} ions and the luminescence intensity vs the Al^{3+} concentration plot.

Al³⁺ increases, and the decreased luminescence still can be clearly observed under the concentration of Al³⁺ at about 5 \times 10⁻⁸ M, which is indicative that the detection limit of this Al³⁺ sensor can reach 5 \times 10⁻⁸ M (1.35 ppb), which is lower than the United States Environmental Protection Agency's recommended level of Al³⁺ in drinking water (200 ppb). Therefore, 1 displays the lowest detection limit compared to those of the

reported MOF-based sensors of Al³⁺ (Table S3). To further explore the quenching effect of Al³⁺ on the emission, a luminescence intensity vs Al³⁺ concentration chart was made (Figure 4), which can be linearly fitted by the equation $I_0/I =$ $1.04 + K_{sv}[Al^{3+}]$ (I_0 and I represent the luminescent intensity of 1 before and after dropping Al³⁺, respectively; [Al³⁺] represents the concentration of Al³⁺, and K_{sv} represents quenching rate constant), which is close to the Stern–Volmer equation $I_0/I =$ $1 + K_{sv}[Al^{3+}]$. The K_{sv} value was calculated to be 1.59×10^4 L/ mol, revealing that Al³⁺ displays a high quenching efficiency on the emission of compound 1.

Most luminescent sensors are not widely used in practical applications because they are costly and can be difficult to recycle. Hence, fast and simple recycling methods are important research topics for luminescent probes. In view of recyclable performance, we washed the used 1 with ethanol several times, and recycled samples were tested using luminescence and PXRD. As shown in Figures 5 and S4, the resultant luminescence and PXRD results are still in accord with the original results after being recycled five times, which is indicative that compound 1 as an Al³⁺ sensor can be reused at least five times without an obvious loss in luminescence response. Additionally, the corresponding ICP reveals that recycled samples do not contain Al³⁺ (Table S2), indicating that recovered luminescence is attributed to removal of Al³⁺ on the surface.

Next, the possible mechanism is discussed. Generally, there are the following reasons to quench the emission: first, collapse of the framework is a common way to quench the luminescence. For compound 1, the well-matched PXRD results (Figure S8) reveal that the framework is still intact after the introduction of Al³⁺, suggesting that luminescence quenching is not caused by collapse of the framework. Second, the BTB^{3–} ligand in compound $\hat{1}$ can efficiently absorb energy from the UV spectrum and transfer energy to Eu³⁺, resulting in the characteristic luminescence spectrum of compound 1. Comparably, Al³⁺ shows negligible photon-absorption at 300 nm (excitation wavelength), suggesting that the introduction of Al^{3+} ions have no obvious effect on the energy absorption of the ligand to further influence the emission. Third, the collision interaction between structure 1 and free Al³⁺ ions may consume the energy and reduce the luminescent intensity.¹⁴ In addition, the concentration of Al³⁺ and the luminescent intensity can be



Figure 5. Emission intensity of 1 after being recycled five times (dominant emission under the excitation wavelength of 300 nm).

fitted well into the Stern–Volmer equation, indicating that the quenching process can be attributed to the dynamic process mechanism (namely, the collision interaction). Thus, a possible quenching mechanism is proposed as follows: the introduction of Al^{3+} may consume the energy through the collision interaction and further decrease the energy transfer from BTB to Eu³⁺ centers, resulting in the luminescence quenching of compound 1.

CONCLUSIONS

In summary, a novel 3D lanthanide–organic framework $\{[Eu(BTB)(phen)]\cdot 4.5DMF\cdot 2H_2O\}_n$ was obtained based on a carboxylate ligand (H_3BTB) with C_3 symmetry. The characterization of structures showed that compound 1 has 1D channels with potential pore volume as high as 56.1%, and 1 with large pores can adsorb CO_2 . Interestingly, compound 1 can be demonstrated as an effective and recoverable catalyst for cycloaddition reaction with CO_2 and epoxides, and the recycling number can reach at least five. Additionally, as a luminescent MOF, 1 could detect Al^{3+} after being recycled with high selectivity and high sensitivity with the lowest detection limit among other MOF-based Al^{3+} sensors of 5×10^{-8} M (1.35 ppb).

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorg-chem.6b01407.

PXRD, TGA, ICP, and luminescent spectra (PDF)

Crystallographic information for 1 (CIF)

Additional crystallographic information for 1, CCDC: 1414991 (PDF)

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Notes

The authors declare no competing financial interest.

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