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Article

# Robust Anionic Ln<sup>III</sup>–Organic Frameworks: Chemical Fixation of CO<sub>2</sub>, Tunable Light Emission, and Fluorescence Recognition of Fe<sup>3+</sup>

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**ABSTRACT:** With the aim of exploring and enriching nanocaged functional platforms of lanthanide–organic frameworks, the subtle combination of  $[Ln_2(CO_2)_8]$  secondary building units and  $[Ln(CO_2)_4]$  units by employing the hexacarboxylic acid of 4,4',4"-(pyridine-2,4,6-triyl)tris(1,3-benzenedicarboxylic acid) (H<sub>6</sub>PTTBA) successfully realized the self-assembly of highly robust multifunctional  $\{Ln^{III}_2\}Ln^{III}$ –organic anionic skeletons of  $\{(Me_2NH_2)[Ln_3(PTTBA)_2]\cdot xDMF \cdot yH_2O\}_n$  (1-Ln), which had remarkable intrinsic nature of high thermal and water stability, large permanent porosity, interconnected nanocaged void volume, and high specific surface area. Here, only the Eu-based framework of 1-Eu was taken as one representative to discuss in detail. Gassorption experiments showed that the activated solvent-free 1-Eu



framework possessed the outstanding ability to separate the mixed gases of  $CO_2/CH_4$  (50:50, v/v) with an ideal adsorbed solution theory selectivity of 14. Furthermore, **1-Eu** was an efficient and recycled catalyst for the chemical cycloaddition of  $CO_2$  and epoxides into their corresponding carbonates, which possessed a better catalytic performance than the documented unique  $Eu^{3+}$ -organic framework of [Eu(BTB)(phen)] and could be widely applied in industry because of its simple synthetic conditions and high yield. In the meantime, adjustable emission colors devoted by the efficient  $Tb^{3+} \rightarrow Eu^{3+}$  energy transfer confirmed that  $Eu_x/Tb_{1-x}$ -organic framework could be taken as a good substitute for barcode materials by changing the ratio of  $Eu^{3+}$  and  $Tb^{3+}$ . Moreover, quantitative luminescence titration experiments exhibited that **1-Eu** possessed good selectivity for the identification of Fe<sup>3+</sup> in aqueous solution by fluorescence quenching with a low limit of detection value of  $6.32 \times 10^{-6}$  M.

#### INTRODUCTION

In recent years, porous metal-organic frameworks (MOFs) with high specific surface area and ordered passageway distribution have attracted special attention because of a wide range of potential applications, including excellent selective adsorption and storage of volatile gases, fluorescence recognition of specific molecules, catalytic properties for specific chemical reactions, drug delivery, and release, etc.,1-10 whereas, recently, the promising subclass of Ln-MOFs has been paid great attention because of its special structural features and good performance.<sup>11-16</sup> During the selfassembly process under different environments, the synergistic effect of the Ln<sup>3+</sup> coordination diversities and applied various functional organic ligands resulted in massive MOFs with infinitely structural adjustability, Whereas, as for most Ln-MOFs, although the Ln<sup>3+</sup> cations usually are octa- or nonacoordinated to form polar covalent bonds by devotion of nine empty electronic orbitals of 6s, 6p, and 5d, the highest coordination number could reach 12 with the advantage of 4f space orbitals when coordinated with smaller molecular ligands, such as  $NO_3^-$  with low charge and repulsion.<sup>1'</sup> Thus, octa- or nonacoordinated Ln<sup>3+</sup> cations in Ln-MOFs do not reach the saturated coordination state and could serve as

Lewis and Brønsted acidic sites, which render porous Ln-MOFs as an ideal heterogeneous catalyst for various chemical reactions, such as the synthesis of cyclic carbonates from the cycloaddition of epoxides and carbon dioxide  $(CO_2)$ .<sup>21–24</sup>

Moreover,  $CO_2$ , a huge greenhouse gas devoted to the consumption of fossil fuels, vehicle emissions, industrial discharge, and straw combustion, has gradually become a focus of global concern and could cause devastation with regard to global pestilence diseases and sea-level rise.<sup>25–32</sup> Thereby, the unconquered technology of reducing the amount of  $CO_2$  through consumption poses a challenge to global scientific researchers. So far, tentative and purposeful operations, including selective adsorption and storage and chemical conversion, have been widely launched with the help of consensus graphene, zeolite sieves, inorganic metal oxide or

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clusters, activated MOFs, etc.<sup>33-36</sup> At this time, catalytic cycloaddition of CO<sub>2</sub> under wild conditions is the most economic and convenient treatment method by the transformation of epoxides into cyclic carbonates, which could be further economically applied in the industrial fields of nontoxic aprotic solvent, raw material of polymer, pharmaceutical and pesticide intermediates, battery electrolyte, etc.<sup>37-39</sup> Among all porous MOF materials, Ln-MOFs are one of the most efficient and sustainable heterogeneous catalysts because Ln<sup>3+</sup> cations own rich empty electronic orbitals and a strong affinity for large dipole-moment  $CO_2$  molecules,<sup>40–42</sup> whereas, hitherto, most of the reported Ln-MOFs were usually self-assembled from mixed ligands and lack solvent-accessible voids and structural stability. Therefore, in order to pursue the applicability of Ln-MOFs in a comparatively complicated environment, the strict demand for strong skeletons is necessary. Moreover, with an increase in the length of ligands, for the class of Ln-MOFs, it is almost inevitable that a decrease of the skeleton stability or a decrease of the porosity is caused by interpenetration. Thus, so far, optimization research on the catalytic platform of Ln-MOFs with respect to the surface area, porosity, pore size, and adsorption capacity is still relatively scarce compared to all reported MOFs, which may be attributed to the laborious crystallization and related structure characterization due to the highly pluralistic coordination number and equivocal directionality of Ln<sup>3+</sup>.43,44

Furthermore, as for Ln-MOFs, the luminescence performance could be effectively enhanced by the "antenna effect" of aromatic ligands with energy transfer (ET) of  $\pi - \pi^*$  and  $n - \pi^*$ , by which the disadvantageous of the outer-electron distribution features of Ln<sup>3+</sup> ions could be overcome. In recent years, with the application of favorably designed  $\pi$ -conjugated polycarboxyl acids as illuminants, a lot of bimetallic doped Eu<sub>x</sub>Tb<sub>1-x</sub> MOFs were reported because modulation of the ET by adjustments to the Tb<sup>3+</sup> and Eu<sup>3+</sup> contents could offer new single-molecule white materials and probes for guest molecules or metal cations baseed on the principle of light switching.

In view of the comparisons of documented MOFs built from separate organic ligands of 1,3-bis(2,4-dicarboxylphenyl)benzene, 2,6-bis(2,4-dicarboxylphenyl)pyridine, 1,3,5-benzenetricarboxylic acid, and 1,3,5-(4-carboxylphenyl)benzene, the large sizes of the organic ligands could increase the MOF characteristics of surface area, porosity, pore size, and adsorption capacity, and more carboxyl groups could enhance the MOF stability.45,46 When the advantages of the abovementioned four organic ligands were combined, the hexacarboxylic acid of 4.4',4"-(pyridine-2,4,6-triyl)tris(1,3benzenedicarboxylic acid) (H<sub>6</sub>PTTBA) was successfully synthesized by our research group for the first time. On the basis of the considerations of the above-mentioned application, the acidic solvothermal reaction of Ln<sub>2</sub>O<sub>3</sub> and H<sub>6</sub>PTTBA in the mixed solvent of N,N-dimethylformamide (DMF)/H<sub>2</sub>O generated a series of 3D nanoporous Ln<sup>III</sup>-organic frameworks:  $\{(Me_2NH_2)[Ln_3(PTTBA)_2]\cdot xDMF\cdot yH_2O\}_n$ , which proved that H<sub>6</sub>PTTBA was an excellent organic linker for the construction of MOFs with large surface area, high porosity, and pore size and anticipated adsorption capacity under convenient hydrothermal conditions. Herein, the Eubased framework of {(Me2NH2)[Ln3(PTTBA)2]·4DMF·  $3H_2O_{n}^{1}$  (1-Eu) was taken as one representative to discuss in detail. Structural analysis of 1-Eu confirmed that H<sub>6</sub>PTTBA had the following several characteristics: (i) enriched carboxyl groups could catch enough cations/secondary building units

(SBUs) to form a wall of nanotubes or nanocages; (ii) the torsion angle between aromatic planes among one  $H_6PTTBA$  could range from 0 to 90° and further facilitate the SBU-based framework construction; (iii) under certain suitable conditions, the N-heterocycle could serve as a negative charge compensator to reduce the electronegativity of the MOF by the protonation of a nitrogen atom or as a Lewis basic site to prompt the special catalytic reaction.

# EXPERIMENTAL SECTION

Materials and General Methods. All of the starting reagents and solvents were commercially available without further purification. Elemental analyses were performed using a CE instruments (model EA 1110 elemental analyzer). Powder X-ray diffraction (PXRD) data were collected on a Panalytical X-Pert Pro diffractometer working in Bragg–Brentano geometry with Cu K $\alpha$  radiation. Thermogravimetric analysis (TGA) was carried out on a PerkinElmer TGA-7 thermogravimetric analyzer under an air atmosphere. Emission and excitation spectra were carried out on an Edinburgh FLS920 spectrophotometer with an nF900 flash lamp. The luminescence lifetime was measured on an Edinburgh FLS920 phosphorimeter with a microsecond lamp (100 mW). The quantum efficiency was measured using the integrating sphere on a FluoroMax-4 spectrophotometer. Single-component gas sorption was tested on an ASAP 2020 analyzer at 273 and 298 K. The catalytic yield was measured and calculated on a Thermo Fisher Trace ISQ gas chromatography (GC)/ mass spectrometry (MS) instrument. <sup>1</sup>H NMR spectra were recorded on a JEOL-ECX 500 FT instrument in CDCl<sub>3</sub> or dimethyl- $d_6$ sulfoxide with n-dodecane as the internal standard. Inductively coupled plasma (ICP) was analyzed on a IRIS Advantage spectrometer.

**Preparation of 1-Eu.** A mixture of  $Eu_2O_3$  (0.08 mmol, 32.0 mg), 1 mL of 10% HNO<sub>3</sub>, and H<sub>6</sub>PTTBA (0.10 mmol, 57.1 mg) was dissolved in a 8 mL mixed solution of DMF and H<sub>2</sub>O (7:1, v/v) and stirred for 30 min to generate a homogeneous solution, which was further transferred into a 25 mL Teflon-lined autoclave at 110 °C for 2 days. Colorless block crystals were obtained upon slow cooling to room temperature at a rate of 10 °C h<sup>-1</sup>, followed by washing with DMF/acetone. Yield: 95% based on H<sub>6</sub>PTTBA. Anal. Calcd for **1-Eu** (C<sub>72</sub>H<sub>66</sub>N<sub>7</sub>O<sub>31</sub>Eu<sub>3</sub>): C, 43.80; H, 3.34; N, 4.96. Found: C, 43.56; H, 3.58; N, 4.47. IR (KBr pellet, cm<sup>-1</sup>): 3405 (vs), 1596 (vs), 1394 (vs), 1113 (w), 1017 (w), 783 (s), 705 (w), 516 (w).

**Preparation of other 1-Ln Complexes.** Other **1-Ln** (Ln = Yb, Ho, Er, Tb, Dy, Lu, and Gd) complexes were prepared under conditions similar to those of **1-Eu** except that  $Eu_2O_3$  was replaced by the corresponding lanthanide oxides.

**Preparation of 1-Eu**<sub>x</sub>**Tb**<sub>1-x</sub>. The doped 1-Eu<sub>x</sub>**Tb**<sub>1-x</sub> complexes were prepared in a manner similar to that of 1-Eu except that Eu<sub>2</sub>O<sub>3</sub> was replaced by equal mixed lanthanide oxides. The Eu<sup>3+</sup>/Tb<sup>3+</sup> molar ratio for as-synthesized samples of 1-Eu<sub>x</sub>**Tb**<sub>1-x</sub> was determined by ICP analysis (Table S4), which confirmed that the ratio of Eu<sup>3+</sup>/Tb<sup>3+</sup> was equal to the one added for the reaction.

X-ray Crystallography. The diffraction data of 1-Ln were collected on a Bruker Smart-APEX II CCD area detector equipped with graphite-monochromated Mo K $\alpha$  radiation ( $\lambda = 0.071073$  nm) at 296(2) K. The structures were solved by direct methods and refined by full matrix least-squares using the SHELXL and SHELXT packages. All non-hydrogen atoms were refined anisotropic displacement parameters, and hydrogen atoms except those on water molecules were generated geometrically with fixed isotropic thermal parameters and refined in the structure factor calculations. The block of SQUEEZE in PLATON was carried out to remove the disordered solvent molecules. The solvent content of 1-Eu was concluded from TGA (Figure S1) and elemental analysis. The crystallographic data and refinement parameters are shown in Table S1. Selected bond lengths and angles are listed in Table S2. Furthermore, the crystals deposited as CCDC 1997911 and 2008436-2008442 could be downloaded from the Cambridge Crystallographic Data Centre.

# RESULT AND DISCUSSION

**Crystal Structure Description.** As shown in Figure 1, single-crystal X-ray diffraction (SCXRD) analysis showed that



**Figure 1.** Porous framework of **1-Eu**: (a) coordination mode of a PTTBA<sup>6-</sup> ligand; (b) 3D framework of **1-Eu** viewed along the [100] axis; (c) structural detail of interpenetrating channels viewed along the [010] axis; (d) 3D framework featured by interspersed channels with dimensions of  $5.2 \times 4.6$  and  $10.6 \times 9.2$  Å<sup>2</sup>, respectively. All hydrogen atoms were removed for visual clarity.

**1-Eu** crystallized in the monoclinic space group C12/c1 and displayed one nanocaged { $[Eu^{II}_2]Eu^{III}$ }-organic 3D host framework with a void volume of 51.2% derived from *PLATON* calculations. In **1-Eu**, the Eu<sup>III</sup>-organic coordination skeleton of  $[Eu_3(PTTBA)_2]$  was negatively charged and electron-balanced by the  $H_2N(CH_3)_2^+$  cation dwelling in the tunnels, which was created from acidic hydrolysis of DMF under solvothermal conditions and confirmed by <sup>1</sup>H NMR spectroscopy. Moreover, the disordered solvent constituents were ascertained by the recognized means of *SQUEEZE*, TGA, and elemental analysis. For all we know, **1-Eu** was the scarcely reported Ln-MOF model self-assembled from two kinds of Eu<sup>III</sup>-centered SBUs bridged by one unique hexacarboxyl ligand.

As shown in Figure 1b, the asymmetric unit included three  $Eu^{3+}$  ions [Eu(1) and Eu(2)] as well as two PTTBA<sup>6-</sup> ligands. Two  $\mu_1$ - $\eta^1$ : $\eta^1$  carboxyl groups residing on the 2 position of two phenyl rings located on both sides of the nitrogen atom named as the 2 and 6 positions of the N-heterocycle in one PTTBA<sup>6-</sup> ligand first chelated the europium center of Eu(1), which was then connected by one chelated + bridged  $\mu_2$ - $\eta^2$ : $\eta^1$  carboxyl group arranged on the 4 position of the phenyl ring residing in the 4 position of pyridine from another PTTBA6- ligand and bridged by two 4-position  $\mu_2 - \eta^1 : \eta^1$  carboxyl groups of two phenyl rings residing in the 2 position of pyridine devoted by two other  $PTTBA^{6-}$  ligands. Thus, in brief, the Eu(1) cation and its commensurable symmetrically generated  $Eu(1^{\#})$  were spanned together to generate one  $[Eu_2(CO_2)_8]$  SBU with the aid of two  $\mu_2 - \eta^2 : \eta^1$  and two  $\mu_2 - \eta^1 : \eta^1$  carboxylic groups from four separate PTTBA<sup>6-</sup> ligands. Thus, the Eu(1) ion was nonacoordinated by nine oxygen atoms from six carboxyl groups offered by five  $PTTBA^{6-}$  ligands with  $Eu(1)-O_{carboxyl}$ bond distances in the range of 2.319-2.851 Å, which was shorter than the documented Eu–O distance.<sup>47</sup> Moreover, it is worth mentioning that the separated  $Eu(1)\cdots Eu(1^{\#})$  distance of 4.004 Å was much smaller than those of the reported dinuclear paddlewheel  $\{Eu_2\}$  SBUs,<sup>47</sup> which may be attributed to the effects of rigidity and nonarbitrary torsion among aromatic cycles in one PTTBA<sup>6-</sup> ligand. As shown in Figure 1b, the great distortion between three separately branched phenyl rings and the central N-heterocycle pyridine plane took place with the respective dihedral angles of 46.91°, 46.98°, and 71.15°, which could be ascribed to the synergistic effect of  $[Eu(1)_2(CO_2)_8]$  SBUs and  $[Eu(2)(CO_2)_4]$  units. Moreover, although six carboxyl groups of H<sub>6</sub>PTTBA were thoroughly deprotonated, a proton was grasped by the N-heterocycle pyridine to reduce the electronegativity of the host skeleton, whereas the Eu(2) ion was chelated by four spare carboxyl groups from four PTTBA<sup>6-</sup> ligands with  $\mu_1$ - $\eta^1$ : $\eta^1$  coordination mode, leaving one dodecahedron geometry (Figure 1a). The carboxyl groups connected to the Eu(2) ion were called spares because the host framework could be established from  $[Eu(1)_2(CO_2)_8]$  SBUs and PTTBA<sup>6-</sup> ligands with neglect of the Eu(2) ions, which all-in-all played a role in reinforcing the overall framework by installing the Eu(2) cations in the negative central area embraced by four carboxyl groups. In addition, it is worth mentioning that PTTBA<sup>6-</sup> exhibited an extremely strong affinity to coordinating with seven metal cations under acidic solvothermal conditions with three types of coordination modes of  $\mu_1$ - $\eta^1$ : $\eta^1$ ,  $\mu_2$ - $\eta^1$ : $\eta^1$ , and  $\mu_2$ - $\eta^1$ : $\eta^1$  and thus easily prompted the formation of one dual-channel 3D framework enriched with nanovoid cages, as shown in Figure 1e

Finally, the disassembly analysis of the porous 1-Eu framework showed that four  $[Eu(2)(CO_2)_4]$  units and eight  $[Eu(1)_2(CO_2)_8]$  SBUs were intermittently linked through eight PTTBA<sup>6-</sup> ligands to create one large solvent-residing cagelike space with an aperture of around 13.8 Å (Figure 1c), which were further infinitely propagated by edge-sharing the organic tetracycle carbon skeleton, leaving the 3D interspersed channels with minimum and maximum open-node windows of  $5.2 \times 4.6$  and  $10.6 \times 9.2$  Å<sup>2</sup>, respectively, as shown in parts c and d of Figure 1. In detail, two  $[Eu(1)_2(CO_2)_8]$  SBUs and one  $[Eu(2)(CO_2)_4]$  unit were interlinked via an organic carbon skeleton to form the small triangular window, whereas two  $[Eu(1)_2(CO_2)_8]$  SBUs and two  $[Eu(2)(CO_2)_4]$  units formed the slightly larger one. Finally, from the topological view,  $[Eu(1)_2(CO_2)_8]$  SBUs,  $[Eu(2)(CO_2)_4]$  units, and one PTTBA<sup>6-</sup> ligand could be simplified as 4-, 4-, and 5-connected nodes, generating an undocumented 3D TAYZIC topology with a Schläfli symbol of  $\{4^4.6^2\}\{4^5.6^5\}_2\{4^6.6^8.8\}$  (Figure 1f).

**Thermal and Water Stability.** Considering the practical application, verification for the robustness of the **1-Eu** framework was essential. TGA of **1-Eu** was carried out under an air atmosphere from room temperature to 800 °C, as shown in Figure S2. Below 400 °C, the weight loss of 18.7% (calcd 19.6%) was in accordance with the loss of aqueous molecules, DMF, and dimethylamine cations. With rising temperature, the host framework of **1-Eu** began to break down. The final white products with a residual weight of ca. 34.0% should be  $Eu_2O_3$ , which was roughly consistent with a calculated value of 31.4%. Moreover, the PXRD patterns of the fresh **1-Eu** samples immersed in water for 2 weeks or even boiling water for 72 h proved that the original framework maintained good integrity

(Figure S3). This unusual heat- and water-resisting behavior could be attributed to the strong linking mode between binuclear SBUs and single polycarboxylic ligands, which was further reinforced by  $[Eu_2(COO)_4]$  units.

**Gas-Adsorption Studies.** In view of the superior nanochannel environment and appropriate pore size (7.2-10.4 Å)in **1-Eu**, which were elucidated from the SCXRD analysis, the sorption studies for CO<sub>2</sub> and CH<sub>4</sub> were fulfilled. Prior to the sorption experiment, the crystalline sample of **1-Eu** was activated by the solvent exchange with acetone for 3 days and evacuation at 150 °C under vacuum for 12 h, and further checked by the PXRD pattern (Figure S9). As shown in Figure S4, the N<sub>2</sub> adsorption–desorption results tested at 77 K manifested that the Brunauer–Emmett–Teller specific surface area and pore volume were 1735 m<sup>2</sup> g<sup>-1</sup> and 0.49 cm<sup>3</sup> g<sup>-1</sup>, respectively, which was in accordance with the structural data. Furthermore, the adsorption capacity of fully activated **1-Eu** samples for CO<sub>2</sub> could reach 81.1 and 54.8 cm<sup>3</sup> g<sup>-1</sup> at 273 and 298 K under 1 bar (Figure 2). The impressive enhanced uptake



Figure 2. CO<sub>2</sub>and CH<sub>4</sub> sorption isotherm of 1-Eu at 273 and 298 K.

value at 298 K was comparable to some famous MOF-based adsorbents, such as BUT-11 (53.5 cm<sup>3</sup>/g),<sup>48</sup> MIL-100(Fe) (50.2 cm<sup>3</sup> g<sup>-1</sup>),<sup>49</sup> etc. Moreover, the CO<sub>2</sub> isosteric heat of adsorption  $(Q_{st})$  fitted by using the virial equation (Figure S5) for the CO<sub>2</sub> isotherms measured at 273 and 293 K was 26.75 kJ mol<sup>-1</sup> at zero loading and equivalent to the values of MAF-25 (26.3 kJ mol<sup>-1</sup>),<sup>50</sup> InOF-1 (29 kJ mol<sup>-1</sup>),<sup>51</sup> etc. It should be noted that the strong charge-density cations of  $Eu^{III}$  in **1-Eu** serving as the Lewis acidic sites will play an important role in host-guest interaction, as discussed by Zhao et al.52 Meanwhile, there was evidence that the exposed coordinated oxygen atoms as unorthodox Lewis basic sites also could form stronger dipole-dipole interactions with the CO2 quadrupole. 53-57 However, there was an indispensable fact that the comparatively low amount of CH4 also could be adsorbed with the values of 17.3 and 9.8  $\rm cm^3~g^{-1}$  at 273 and 298 K, respectively. In order to check the adsorption selectivity between CO<sub>2</sub> and CH<sub>4</sub>, the ideal adsorbed solution theory (IAST) calculation by the dual-site Langmuir-Freundlich equation for fitting the single-component adsorption isotherm parameters determined that the selectivity coefficient of CO<sub>2</sub>/  $CH_4$  (50:50, v/v) was 14 in at 100 kPa under 298 K, which proved that the separation of CO<sub>2</sub> from natural gas was quite straightforward and feasible (Figure S6).

**Catalytic Performance for the Cycloaddition of CO<sub>2</sub> with Epoxide.** In our preliminary study on the catalytic reaction of  $CO_2$  with epoxides, the optimal reaction conditions were explored by taking styrene oxide as the model substrate, and the obtained data along with the varied conditions are listed in Table 1. First of all, referring to the traditional dosage

Table 1. Cycloaddition Reaction of  $CO_2$  with Styrene Oxide under Various Conditions<sup>*a*</sup>

	<u>}</u> _	Catalyst (1-Eu), CO <sub>2</sub> TBAB, 1 atm	• 07	
entry	<b>1-Eu</b> (mg)	TBAB (mol %)	$T(^{\circ}C)$	yield (%) <sup>b</sup>
1	40	2.5	60	39
2	40	2.5	70	60
3	40	2.5	80	72
4	40	5	60	75
5	40	5	70	99
6	0	5	80	38
7	40	0	80	5

<sup>&</sup>lt;sup>*a*</sup>Reaction conditions: 20 mmol of styrene oxide, 40 mg of 1-Eu catalyst, solvent-free,  $CO_2$  (1 atm), 24 h. <sup>*b*</sup>Checked by <sup>1</sup>H NMR and GC–MS with *n*-dodecane as the internal standard.

with slight modifications, solvent-free phenylethylene carbonate was collected with a yield of 39% from the starting reactant of styrene oxide under the conditions of 1 atm of  $CO_{2}$ , 40 mg (1.26 mol %) of activated 1-Eu catalyst, and a 2.5 mol % (16 mg) cocatalyst of tetrabutylammonium bromide (TBAB) at 333 K (60 °C) (entry 1, Table 1). Then, with an increase of the temperature, the yield ascended gradually (entries 2 and 3) and reached 72% at 353 K (80 °C). Therefore, in order to avoid excessive energy consumption at high temperature, the quantity of the cocatalyst TBAB was doubled in the following reaction. As exhibited in entries 4 and 6, the transformation of styrene oxide to phenylethylene carbonate could rise to 75% at 333 K and be nearly stopped with a yield of 99% at 353 K (entry 5). For comparison, other reaction conditions were the same as that of entry 6 except for the absence of catalyst 1-Eu, and the yield was only 38%, indicating that 1-Eu had an essential catalytic role in the cycloaddition reaction of CO<sub>2</sub> and epoxides. Therefore, the optimal dosages of 1-Eu and TBAB were set at 40 mg (1.26 mol %) and 5 mol % (32 mg), respectively, along with the conditions of 1 atm of CO<sub>2</sub>, 353 K (70 °C), and 24 h. It is worth mentioning that cycloaddition reactions catalyzed by Ln-MOFs have been comparatively scarcely covered so far.<sup>58</sup>

To test the catalytic universality of 1-Eu, a series of industrialized cycloaddition reactions from the typical epoxide substrates were carried out by employing the concluded optimal conditions. As shown in Table 2, the catalytic generality of the activated 1-Eu framework was confirmed by the high yields of the cycloaddition transformation for six selected epoxide regents. Moreover, it is worth discussing that the high polarity of the substituents had a greatly adverse influence on the reaction rate and yield, which was confirmed by two sets of experimental comparisons including entries 1 and 2 and entries 3 and 4. Meanwhile, the larger substituents were not conducive to the reaction, which could be verified by entries 1 and 3 and entries 5 and 6. In short, the catalytic pubs.acs.org/IC

Table 2. Cycloaddition Reaction of  $CO_2$  and Various Epoxides with 1-Eu as the Catalyst<sup>*a*</sup>



<sup>*a*</sup>Reaction conditions: substrates (20 mmol), NBu<sub>4</sub>Br (5 mol %), 1-Eu catalyst (40 mg), CO<sub>2</sub> (1 atm), 70 °C, 24 h. <sup>*b*</sup>Determined by GC– MS with *n*-dodecane as the internal standard.

activities of activated porous MOFs for the transformation of epoxides were affected by the electron-withdrawing altitude of the polar substituents, steric hindrance of the substrates, and reaction conditions.

In addition, as one negative heterogeneous catalytic platform, **1-Eu** could be easily recycled by the processing operation of centrifugal precipitation, filtration, DMF/MeOH cleansing, and drying. As displayed in Figure S7, there was no obvious decrease in the catalytic efficiency for the cycloaddition reaction of styrene oxide and  $CO_2$  after **1-Eu** was reused many times. The characteristics peaks of PXRD for the purified **1-Eu** sample were nearly in accordance with the simulation results from the single-crystal structure data (Figure S9), confirming that the catalyst of **1-Eu** possessed a renewable performance without damage to the integrity of the framework.

In view of the structure characteristics of 1-Eu and related works documented so far, the catalytic mechanism for the cycloaddition of epoxides with  $CO_2$  was speculated, as exhibited in Figure S8. First,  $CO_2$  and epoxides could easily get into the 1D channels and concentrate the cagelike void volume of 1-Eu. Second, epoxide molecules were slightly constrained by the bare electron-free orbitals of the Eu<sup>3+</sup> cations by way of van der Waals while the polarized epoxy ring was activated. Finally, the nucleophilic anion of Br<sup>-</sup> offered by the cocatalyst of TBAB assaulted the less-hindered carbon atom to result in the intermediate alkylcarbonate anion, which preferably attacked the closest carbon atom of the polarized  $CO_2$  molecule, generating the salts of alkylcarbonate.  $^{59,60}$  Thus, along with the successive liberation of the cyclic carbonate, the catalysts of **1-Eu** and TBAB returned to the original state.

It is worth mentioning that the activated 1-Eu displayed a better catalytic performance than the documented  $Eu^{3+}$ organic framework of [Eu(BTB)(phen)] (phen = 1,10phenanthroline), which was constructed from the single SBUs of  $[Eu_2(phen)(CO_2)_6]$  and 1,3,5-benzenetricarboxylic acid.<sup>52</sup> We speculated that this may be attributed to the adverse effect of steric hindrance from phen, which in the meantime reduced the polarization ability of Eu<sup>3+</sup> as the Brønsted acid to CO<sub>2</sub> molecule.<sup>61</sup> Furthermore, the content of Eu<sup>3+</sup> in the activated **1-Eu** sample was 28.8% and much higher than that in [Eu(BTB)(phen)] (15.3%). Furthermore, the catalytic performance displayed by 1-Eu was better than that of some of the known porous MOFs self-assembled from 3d series metal ions, as listed in Table S3. Thus, an excellent catalytic platform should not only have high porosity and large specific surface area but also possess smaller steric hindrance around active open metal sites and high metal content. So, we sincerely hope that keeping these factors in mind can make us more effective at constructing porous catalytic MOFs in the future.

Fluorescence Characteristics. Ln-MOFs endowed with partial filling of the 4f shells of Ln<sup>3+</sup> were proven to own excellent luminescent properties including large Stokes shifts, long luminescence lifetimes, and sharp characteristic emissions, especially for Eu/Tb-MOFs. Therefore, the solid-state luminescence spectra of 1-Eu and 1-Tb were investigated at room temperature. The emission spectra of 1-Eu excited at 320 nm exhibited four distinct characteristic peaks of 591, 613, 651, and 700 nm (Figure S10b), which should be assigned to the  ${}^{5}D_{0} \rightarrow {}^{7}F_{1}$ ,  ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ ,  ${}^{5}D_{0} \rightarrow {}^{7}F_{3}$ , and  ${}^{5}D_{0} \rightarrow {}^{7}F_{4}$  transitions of the Eu<sup>3+</sup> ion. The high ( ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ )/( ${}^{5}D_{0} \rightarrow {}^{7}F_{1}$ ) luminescence intensity ratio confirmed that Eu<sup>3+</sup> cations were located at nonconversion coordination centers, consistent with the SCXRD data. However, for 1-Tb, the emission spectra of 1-Tb excited at 320 nm displayed four completely different characteristic peaks of 489, 546, 585, and 621 nm (Figure S10c), which caustically corresponded to  ${}^{5}D_{4} \rightarrow {}^{7}F_{I}$  (J = 6, 5, 4, and 3) diagnostic transitions of  $Tb^{3+}$  cations. The strongest emission peak at 617 nm induced from the  ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ electronic transition enabled 1-Tb to emit bright-green luminescence upon UV-light irradiation. In order to further explore the photophysical behavior of 1-Eu and 1-Tb, the luminescence lifetimes  $(\tau)$  were estimated from the luminescent decay curve. As shown in Figure S11, the decay curves of both 1-Eu and 1-Tb could be well fitted by the singleexponential function as  $I(t) = I_0 \exp(-t/\tau)$ , with lifetimes of 854 and 135  $\mu$ s (Ex = 300 nm), respectively, which were comparable to those of the documented Eu<sup>III</sup>/Tb<sup>III</sup>-MOFs. Furthermore, the absolute quantum yields ( $\Phi$ ) were calculated as 82.32% and 18.95%, respectively. As far as we know, 1-Eu exhibited the highest quantum yield in the solid state compared to all documented Eu<sup>III</sup>-MOF materials,<sup>62-</sup> which could partly confirm the highly effective ET from the PTTBA<sup>6-</sup> ligand to Eu<sup>3+</sup> ions in the nanocaged architecture of 1-Eu. Meanwhile, the missing characteristic emission peak of free H<sub>6</sub>PTTBA (450 nm; Figure S10a) in 1-Eu and 1-Tb proved that the effective ET process increased from organic ligands to  $Ln^{3+}$  cations rather than intraligand  $n-\pi$  or  $\pi-\pi^*$ electron transitions. The triplet  $(T_1)$  energy for the H<sub>6</sub>PTTBA ligand derived from the phosphorescence spectra (Figure S12)

of 1-Gd at 77 K was calculated to be 20858 cm<sup>-1</sup> (480 nm), whereas for 1-Eu, the energy gap  $\Delta E(T_1-{}^5D_0)$  of 3558 cm<sup>-1</sup> was in the range of 2500–4000 cm<sup>-1</sup>, which confirmed that 1-Eu possessed the ideal limit value according to Latva's empirical rule. Furthermore, the energy difference of 1-Tb  $[\Delta E (T_1-{}^5D_4)]$  isolated from the ideal limit area was calculated as 358 cm<sup>-1</sup>, which showed that the H<sub>6</sub>PTTBA ligand could sensitize the ion of Eu<sup>3+</sup> far more sufficiently than the ion of Tb<sup>3+</sup>. Thus, the higher quantum yield of 1-Eu relative to that of 1-Tb should be attributed to the more effective ET process.<sup>64</sup>

Tuning of the Luminescent Color for Bimetallic Doped 1-Eu<sub>x</sub>Tb<sub>1-x</sub>. Isomorphic features of 1-Eu and 1-Tb prompted us to investigate the tunable luminous characteristics of 1-Eu<sub>x</sub>Tb<sub>1-x</sub>. Samples of 1-Eu<sub>x</sub>Tb<sub>1-x</sub> synthesized from the incremental ratio of Eu<sub>2</sub>O<sub>3</sub>/Tb<sub>2</sub>O<sub>3</sub> under similar hydrothermal reaction conditions were determined by the ICP measurements, as listed in Table S4. Furthermore, the PXRD patterns confirmed that the obtained crystalline samples of doped 1-Eu<sub>x</sub>Tb<sub>1-x</sub> were well consistent with 1-Eu and 1-Tb (Figure S13), indicating that the coordination behavior transmitted smoothly from a monometallic structure to a doped bimetallic structure. A gradient color change with the increasing ratio of Eu<sup>3+</sup>/Tb<sup>3+</sup> irradiated at 268 nm from light green to orange to red occurred, as shown in Figure S14. As shown in Figure 3,



**Figure 3.** Luminescence spectra of doped  $1-\text{Eu}_x\text{Tb}_{1-x}$  ( $x = \text{ratio of Eu}^{3+}$ ;  $\lambda_{ex} = 320 \text{ nm}$ ).

with a gradual increase in the emission intensity of the Eu<sup>3+</sup> ion at 617 nm determined by the transition of  ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ , the  $Tb^{3+}$ -dominated  ${}^{5}D_{4} \rightarrow {}^{7}F_{5}$  peak at 547 nm consequently receded, which proved that the systematically modulated characteristic emission could be realized by adjusting different ratios of the  $Eu^{3+}$  and  $Tb^{3+}$  contents within a range of 7–37%. On the basis of documented mixed  $Eu^{3+}/Tb^{3+}$ -organic platforms, the disproportionate and rapid change of the dominated emission peak with the enhanced ratio of Eu<sup>3+</sup> was ascribed to ET from Tb<sup>3+</sup> to Eu<sup>3+</sup>, whose ET efficiency  $(\eta_{\rm ET})$  was well in accordance with the classical equation  $\eta_{\rm ET}$  =  $1 - \tau/\tau_0$ , where  $\tau$  and  $\tau_0$  were the  ${}^5D_4$  lifetime of Tb<sup>3+</sup> ions in the presence and absence of doped Eu<sup>3+</sup> ions. Moreover, as shown in Table S4, there is a linear correlation between the ET efficiency ( $\eta_{\rm ET}$ ) increase and the contents of the Eu<sup>3+</sup> ions with the molar ratio in the range of 15.56-45.93%, which confirmed that doped  $Eu^{3+}/Tb^{3+}$  frameworks with adjustable emission colors could be taken as one good substitute for barcode materials.

**Luminescence Sensing.** In order to explore the fluorescence applications of the high robust platform of 1-Eu, the sensitive response to a series of some guest cations was fulfilled and the detailed manipulations were carried out as follows: 2 mg of the 1-Eu sample was uniformly dispersed in 3 mL of a  $M(NO_3)_x$  aqueous solution (M = Li<sup>+</sup>, K<sup>+</sup>, Na<sup>+</sup>, Ca<sup>2+</sup>, Mg<sup>2+</sup>, Mn<sup>2+</sup>, Ba<sup>2+</sup>, Cd<sup>2+</sup>, Zn<sup>2+</sup>, Hg<sup>2+</sup>, Cu<sup>2+</sup>, Co<sup>2+</sup>, Ni<sup>2+</sup>, Cr<sup>3+</sup>, Al<sup>3+</sup>, and Fe<sup>3+</sup>) and ultrasonicated for 30 min. Under the interfere of metal cations, the recorded luminescence intensities of the above resultant M@1-Eu suspensions showed that only the dominant emission peak (613 nm) was observed, as shown in Figure 4. With the addition of alkali-metal cations



Figure 4. Luminescence intensity of 1-Eu for different metal ions.

of Li<sup>+</sup>, Na<sup>+</sup>, and K<sup>+</sup>, it was obvious that only negligible changes of the luminescence intensity could be traced. As for the alkaline-earth cations (Mg<sup>2+</sup> and Ca<sup>2+</sup>), transition-metal ions (Cd<sup>2+</sup>, Mn<sup>2+</sup>, Co<sup>2+</sup>, Zn<sup>2+</sup>, Ni<sup>2+</sup>, Hg<sup>2+</sup>, and Cu<sup>2+</sup>), and trivalent ions (Cr<sup>3+</sup> and Al<sup>3+</sup>), a comparatively slight fluorescence quenching rate could be observed. Comparatively speaking, the cations of Fe<sup>3+</sup> caused almost complete luminescence quenching to the red emission peak of 613 nm devoted by **1-Eu**. Furthermore, competitive experiments in equal proportion for the above-mentioned cations to Fe<sup>3+</sup> ions were performed and showed that other metal ions had no significant effect on the Fe<sup>3+</sup>-induced luminescence response, which revealed that **1-Eu** could efficiently sense Fe<sup>3+</sup> ions in a water solution without interference (Figure S15).

Consequently, quantitative luminescence titration experiments were fulfilled to explore the sensing sensitivity of 1-Eu toward Fe<sup>3+</sup> ions in an aqueous solution. As illustrated in Figure S16, the fluorescent intensity of 1-Eu decreased gradually with an increased concentration of Fe<sup>3+</sup> ions in an aqueous solution. Fluorescent intensity changes were recorded along with the  ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$  emission variations, and the fluorescence quenching efficiency was quantitatively analyzed by using the Stern–Volmer equation. As shown in Figure S17, the global relationship between  $I_0/I$  ( $I_0$  and I were the luminescence intensities before and after the addition of an analyte, respectively) and the concentration of the Fe<sup>3+</sup> ion  $([Fe^{3+}])$  could not match the Stern–Volmer equation, as explained by the coexistence of a static and dynamic quenching process, but was well fitted with the following equation:  $I_0/I =$  $0.871 \exp([Fe^{3+}]/0.039) + 0.412$ . Meanwhile, a good linear correlation was observed for the plot of  $I_0/I = 1 + K_{SV} [Fe^{3+}]$  in the range of 0–0.4 mM, with the  $K_{SV}$  value of 1-EU for Fe<sup>3+</sup> ions being  $4.75 \times 10^4$  M<sup>-1</sup>, which should be attributed to selfabsorption or an ET process, as shown in Figure S18. On the basis of the  $K_{sv}$  value and standard deviation ( $\delta$ ), the limit of

detection for Fe<sup>3+</sup> ions was estimated to be  $6.32 \times 10^{-6}$  M by the ratio of  $3\delta/K_{SV}$  and much lower than most of the reported Eu<sup>III</sup>-MOFs for Fe<sup>3+</sup> detection.<sup>65–67</sup> In the meantime, PXRD analysis of the samples soaking in a Fe<sup>3+</sup> aqueous solution confirmed that the fluorescence quenching could not be attributed to the framework collapse of 1-Eu, as shown in Figure S9. Meanwhile, elemental analysis showed that there was no obvious change for the proportion of the Eu<sup>III</sup> content, which confirmed that the fluorescent quenching was not caused by ion exchange. On the basis of the documented devotions, the fluorescent quenching mechanism should be attributed to the fact that the strong competitive UV-vis absorption of Fe<sup>III</sup> ions in the range of 320-400 nm led to the luminescence quenching effect (Figure S19).<sup>68-70</sup> By the way, Ru<sup>3+</sup> ion with an outer electronic configuration similar to that of Fe<sup>3+</sup> ion in a aqueous solution also played an adverse influence on the luminescence intensity of 1-Eu but considerably lower than that of Fe<sup>3+</sup> ion, as shown in Figure S20.

# CONCLUSIONS

In conclusion, the acidic solvothermal self-assembly of Ln<sub>2</sub>O<sub>3</sub> and 4,4',4"-(pyridine-2,4,6-triyl)tris(1,3-benzenedicarboxylic acid) (H<sub>6</sub>PTTBA) in a mixed solvent of DMF and H<sub>2</sub>O generated a highly robust multifunctional {Ln<sup>III</sup><sub>2</sub>}Ln<sup>III</sup>-organic framework, which featured the intrinsic characteristics of interconnected nanocaged void volume, large permanent porosity, high specific surface area, and high thermal and water stability. Performance analyses exhibited that the representative of Eu-based 1-Eu could efficiently separate the mixed gases of  $CO_2/CH_4$  (50:50, v/v) and catalyze the chemical transformation of epoxides and CO2 into the corresponding carbonates. In the meantime, adjustable emission colors devoted by the efficient  $Tb^{3+} \rightarrow Eu^{3+} \ ET$ confirmed that the  $Eu_x/Tb_{1-x}$ -organic framework could be taken as a good substitute for barcode materials by changing the ratio of Eu<sup>3+</sup> and Tb<sup>3+</sup>. Moreover, 1-Eu could be taken as one fluorescent probe for Fe<sup>3+</sup> in an aqueous solution by fluorescence quenching.

# ASSOCIATED CONTENT

#### **Supporting Information**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.inorgchem.0c01782.

Crystallographic data and refinement parameters, comparison of catalytic cycloadditions of  $CO_2$ , TGA curves, PXRD patterns,  $N_2$  absorption/desorption isotherms, recyclability study, catalytic mechanism, luminescence emissions and decay curves, emission intensity and spectra, and UV–vis absorption (PDF)

#### Accession Codes

CCDC 1997911 and 2008436–2008442 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.

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