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Europium Metal-Organic Frameworks as Recyclable and Selective Turn-off Fluorescence Sensors for Aniline Detection

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Accepted 00th January 20xx DOI: 10.1039/x0xx00000x www.rsc.org/ Hui-Jun Feng^{a,b}, Ling Xu^{a*}, Bing Liu^c, HuanJiao^{a*} Seven Eu-(H)BDC compounds, [RMI][Eu₂(BDC)₃CI] (R = ethyl (1), propyl (2), butyl (3), H₂BDC = 1,4-benzendicarboxylic acid), [EMI]₂[Eu₂(BDC)₃(H₂BDC)Cl₂] (4), [Eu(BDC)(HCOO)] (5), [Eu(BDC)Cl(H₂O)] (6) and [Eu₃(BDC)₄Cl(H₂O)₆] (7), were synthesized under ionothermal conditions. Compounds 4 and 6 behave as potential high selective turn-off fluorescence sensors to aniline, which can be detected in the mixtures of aniline with contrast organic amides or alkylbenzenes. Fluorescence quenchings can be observed when compounds 4 and 6 mix with the samples containing aniline. Compounds 4 and 6 show

basically unchanged emission intensities and rapid response to aniline after ten recycling tests, suggesting the compounds

Introduction

In recent years, amines have been widely used in chemical, pharmaceutical, food and military industries.^{1,2} Most of them are severe destroyers of environmental ecological equilibrium and carcinogen via breathing or skin contact.3,4 Aniline exists in cigarette smoke, some foods and industrial emissions,⁵ and is the main indicator of potential lung cancer.⁶ At present, the sensing systems of aniline have a long way to overcome their defects of low sensitivity and poor selectivity. Especially, the selective detection of aniline from mixed amines is not practically feasible, which is still a challenge.^{7,8} Therefore, it becomes necessary to develop a new method to selectively detect aniline from mixed amines. Lanthanide metal-organic frameworks (Ln-MOFs) as luminescent functional MOFs have received remarkable attention in the latest decade with wide applications in chemical sensors,^{9,10} light-emitting devices,^{11,12} and biomedicine¹³ owing to their advantages, such as high sensitivity, short response time, and convenience.¹⁴ Numerous effort has been exerted into this filed, including detecting various

have high stable recycle repeatabilities.

metal ions, anions, and small organic molecules.^{15,16} Generally, the luminescence of Ln-MOFs contains ligand-to-metal energy transfer.¹⁰ Therefore, the energy level of ligand is a crucial factor to target the lanthanide cations. H₂BDC (1,4-benzendicarboxylic acid), easy to excite intraligand charge-transfer (ILCT), is a suitable organic moiety to absorb photons.¹³ Its excited electrons can be transferred to Eu³⁺ cation, thus to target the characteristic emissions of Eu³⁺ cation.¹⁷ Moreover, the simple structure configuration of H₂BDC can effectively eliminate the effect of ligands on the structure, which should be helpful to explore the factors that affect the structure and property. We selected H₂BDC and EuCl₃·6H₂O as starting materials to search luminescent Eu-MOFs with ionothermal method by using ionic liquids (ILs) as reaction media. It will utilize their advantages of high ionic conductivity, non-flammability and negligible vapor pressure,¹⁸⁻²⁰ which will offer significantly different reaction environment for new type MOF materials.²¹⁻²³

Herein, H₂BDC reacted with EuCl₃·6H₂O at different ratios with three kinds of nine 1-methyl-3-alkylimidazolium halides [RMI]X (R = ethyl to butyl; MI = imidazolium; X = Cl⁻, Br⁻, l⁻) to give seven compounds: [RMI][Eu₂(BDC)₃Cl] (R = ethyl (1), propyl (2), butyl (3)), [EMI]₂[Eu₂(BDC)₃(H₂BDC)Cl₂] (4), [Eu(BDC)(HCOO)] (5). $[Eu(BDC)Cl(H_2O)]$ (6) and $[Eu_3(BDC)_4Cl(H_2O)_6]$ (7). These compounds are characterized by single crystal X-ray diffraction, powder X-ray diffraction (PXRD), thermogravimetric analysis (TGA), fluorescence and FT-IR. Compounds 4 and 6 were selected as turn-off fluorescent sensory materials, which can selectively detect aniline from the solutions of contrast organic amines and alkylbenzenes. Compounds 4 and 6 exhibit high selective recyclable detection for aniline, which can be potential turn-off fluorescence sensors for aniline detection.

Experimental

Materials and physical measurements

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[†]Electronic Supplementary Information (ESI) available: crystal date; the coordination fashions of BDC²⁻ ligands; the coordination spheres of Eu(III) centers in compounds 1-7; the 2D layersof compounds 1-7; PXRD patterns; IR characteristic absorption peaks; TG; temperature-dependent emission intensities; photoluminescent spectra; UV-Vis spectra; additional emission spectra; the compaund6 to aniline; the luminescence intensity of compounds vs. aniline concentration. CCDC numbers 1455818-1455824. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/x0xx0000x

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The reagents, solvents and [EMI]CI IL were used directly as supplied commercially without further purification except other eight 1methyl-3-alkylimidazolium halide ILs synthesized from the reactions of 1-alkyl halides with 1-methylimidazole according to the literature processes.²⁴ Degassed alkyl halides (alkyl = ethyl to butyl; X = Cl, Br, I) were refluxed with the distilled 1-methylimidazole to give the eight kinds of ILs. The ILs were washed with ethyl acetate, and then dried under a vacuum at least for 10 h to give [PMI]Cl as a colorless oil, [BMI]Cl as a white solid, [EMI]Br as a white solid, [PMI]Br as a colorless oil, [BMI]Br as a white solid, [EMI]I as a yellow solid, [PMI]I and [BMI]I as yellow oils. Elemental analysis of C, H and N was carried out on a Vario EL III elemental analyzer. FT-IR spectra were collected from KBr pellets (Aldrich, >99%, FT-IR grade) with a Bruker Tensor 27 FT-IR spectrometer in the range of 4000-400 cm⁻¹. TGA were carried out in N2 atmosphere on a SDT Q600 V8.3 Build 101 instrument with a heating rate of 10 °C·min⁻¹ and a N₂ flow rate of 20 cm³·min⁻¹. PXRD data for the materials were collected at ambient temperature with a Rigaku D/Max-3c (Japan) diffractometer (Cu-K $\alpha_{1,2}$ X-radiation, λ_1 = 1.540598 Å and λ_2 = 1.544426 Å), equipped with an X'Celerator detector and a flatplate sample holder in a Bragg-Brentano para-focusing optics configuration (40 kV, 50 mA). Intensity data were collected by the step counting method (step being 0.02°) in continuous mode in the 2ϑ range of 5-60°. Solid state fluorescence spectra were acquired on a Hitachi F-4600 fluorescence spectrophotometer with the excitation and emission slits setted to 2.5 nm. UV-Vis spectra were acquired on a UV-6000PC spectrophotometer.

Aniline Detection

Aniline or the contrast organic amides/alkylbenzenes (Triethanolamine, N,N-dimethylformamide, methanamide, nbutylamine, ethylenediamine, methylbenzene, ethylbenzene, and propylbenzene) were added into a 3 mL HEPES aqueous buffer (pH = 6.5) to prepare HEPES aqueous buffer with a certain concentration. 3 mg powder compound **4** or **6** was added into the above HEPES aqueous buffer through 30 min ultrasonic processing to obtain a suspension for determination.

The similar processes were carried out under DMF solution. $^{\ensuremath{\text{27}}\xspace}$

The selective detection of aniline

 1×10^{-2} mol·L⁻¹ aniline mixed with the contrast organic amides of 1×10^{-2} mol·L⁻¹ one by one in a HEPES aqueous buffer (pH = 6.5) to prepare HEPES aqueous buffer. 3 mg powder compound **4** or **6** was added into the above HEPES aqueous buffer through 30 min ultrasonic processing to obtain a suspension for fluorescence characterization.

The similar process was carried out with all contrast organic amides of 1×10^{-2} mol·L⁻¹ together for selective detection of aniline. The recycle repeatability of compounds 4 and 6 for aniline detection

Compound **4** or **6** pasted to a slide glass was dipped in 1 cm colorimetric utensil containing 1×10^{-2} mol·L⁻¹ aniline aqueous solution, then the fluorescence spectrum was characterized. The slide glass with compound **4** or **6** was renewed by dried at 50 °C for 1h for the next fluorescence characterization. The process was carried out for 10 times.

Synthetic procedures

Synthesis of [EMI][Eu₂(BDC)₃Cl] (1)

0.5 mmol, 0.1833 g EuCl₃·6H₂O and 0.5 mmol, 0.0834 g H₂BDC mixed with 0.8009 g [EMI]Br were placed in a crystallisation vial placed in a 25 mL teflon-lined stainless-steel autoclave. The mixture was kept inside the furnace at 180 °C for 5 days, and then cooled to ambient temperature. The colorless crystals of **1** suitable for X-ray diffraction were collected after clearing with acetone. Yield based on H₂BDC: 0.0629 g, 39.5%. Elemental analysis (%), Found (calcd): C, 38.05(38.21); H, 2.31(2.45); N, 2.75(2.97). IR data (in KBr, cm⁻¹) for **1**: 3458(m), 3153(w), 3103(w), 3084(w), 2979(w), 2928(w), 1625(s), 1596(s), 1504(s), 1404(s), 1305(m), 1168(m), 1103(w), 1022(m), 941(w), 885(w), 829(m), 754(s), 590(m), 507(s), 435(w).

Compound 1 was also synthesized via the molar ratio (1:2) of EuCl₃·6H₂O to H₂BDC in 1.0011 g [EMI]I at 170 °C.

Synthesis of [PMI][Eu2(BDC)3CI] (2)

0.5 mmol, 0.1830 g EuCl₃·6H₂O and 0.5 mmol, 0.0829 g H₂BDC mixed with ca. 0.8 mL [PMI]Br were placed in a crystallisation vial placed in a 25 mL teflon-lined stainless-steel autoclave. The mixture was kept inside the furnace at 180 °C for 5 days, and then cooled to ambient temperature. The colorless crystals of **2** suitable for X-ray diffraction were collected after clearing with acetone. Yield based on H₂BDC: 0.0543 g, 33.6%. Elemental analysis (%), Found (calcd): C, 38.25(38.91); H, 2.63(2.63); N, 2.75(2.93). IR data (in KBr, cm⁻¹) for **2**: 3390(w), 3168(w), 3116(w), 3062(w), 2993(w), 2949(w), 2758(w), 2617(w), 2489(w), 1679(s), 1610(s), 1546(s), 1504(s), 1386(s), 1321(m), 1249(m), 1172(m), 1136(m), 1091(w), 1014(m), 879(w), 867(m), 833(m), 752(s), 622(m), 518(s), 437(w).

Compound **2** was also synthesized via the molar ratio (1:2) of $EuCl_3 \cdot 6H_2O$ to H_2BDC in ca. 0.8 mL [PMI]I or through the different molar ratios (including 1:2, 1:1, 2:1 and 3:1) of $EuCl_3 \cdot 6H_2O$ to H_2BDC in ca. 0.8 mL [PMI]Cl at 170 °C.

Synthesis of [BMI][Eu2(BDC)3CI] (3)

0.5 mmol, 0.1835 g EuCl₃·6H₂O and 0.5 mmol, 0.0836 g H₂BDC mixed with 0.7996 g [BMI]Br were placed in a crystallisation vial placed in a 25 mL teflon-lined stainless-steel autoclave. The mixture was kept inside the furnace at 170 °C for 5 days, and then cooled to ambient temperature. The colorless crystals of **3** suitable for X-ray diffraction were collected after clearing with acetone. Yield based on H₂BDC: 0.0590 g, 36.0%. Elemental analysis (%), Found (calcd): C, 39.13(39.58); H, 2.65(2.80); N, 2.74(2.89). IR data (in KBr, cm⁻¹) for **3**: 3523(w), 3145(m), 3105(m), 3072(m), 3020(w), 2949(m), 2871(m), 2837m), 1674(s), 1610(s), 1587(s), 1546, 1506(s), 1396(s), 1311(m), 1247(m), 1164(m), 1134(m), 950(w), 887(m), 854(w), 829(s), 754(s), 659(m), 626(m), 513(s), 437(w).

Compound **3** was also synthesized via the molar ratio (1:2) of $EuCl_3 \cdot 6H_2O$ to H_2BDC in ca. 0.8 mL [BMI]I or through the different molar ratios (including 1:2, 1:1, 2:1 and 3:1) of $EuCl_3 \cdot 6H_2O$ to H_2BDC in 0.8011 g [BMI]Cl at 170 °C.

Synthesis of $[EMI]_2[Eu_2(BDC)_3(H_2BDC)CI_2]$ (4)

0.5 mmol, 0.1834 g EuCl₃· GH_2O and 0.5 mmol, 0.0829 g H_2BDC mixed with 1.0005 g [EMI]Br were placed in a crystallisation vial placed in a 25 mL teflon-lined stainless-steel autoclave. The mixture was kept inside the furnace at 170 °C for 5 days, and then cooled to ambient temperature. The colorless crystals of **4** suitable for X-ray diffraction were collected after clearing with acetone. Yield based

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on H₂BDC: 0.0536 g, 33.8%. Elemental analysis (%), Found (calcd): C, 42.01(42.16); H, 3.24(3.06); N, 4.38(4.47). IR data (in KBr, cm⁻¹) for 4: 3361(w), 3161(w), 3111(w), 3062(w), 2965(w), 2954(w), 2748(m), 2619m), 2482(m), 1687(s), 1616(s), 1589(s), 1552, 1504(s), 1396(s), 1317(m), 1296(m), 1269(m), 1247(m), 1174(m), 1136(w), 1105(w), 1085(w), 1014(m), 891(m), 869(m), 837(m), 827(m), 754(s), 732(m), 622(m), 568(w), 518(s), 441(w).

Compound **4** was also synthesized via the molar ratio (1:1) of $EuCl_3 \cdot 6H_2O$ to H_2BDC in ca. 0.8011 g [EMI]I or through the different molar ratios (including 1:2, 1:1, 2:1 and 3:1) of $EuCl_3 \cdot 6H_2O$ to H_2BDC in ca. 0.80 g [EMI]Cl at 170 °C.

Synthesis of Eu(BDC)(CO₂) (5)

1.5 mmol, 0.5498 g EuCl₃· $6H_2O$ and 0.5 mmol, 0.0827 g H₂BDC mixed with 0.8006 g [EMI]Br were placed in a crystallisation vial placed in a 25 mL teflon-lined stainless-steel autoclave. The mixture was kept inside the furnace at 180 °C for 5 days, and then cooled to ambient temperature. The colorless crystals of **5** suitable for X-ray diffraction were collected after clearing with acetone. Yield based on H₂BDC: 0.0672 g, 36.7%. Elemental analysis (%), Found (calcd): C, 29.75(30.02); H, 1.52(1.12). IR data (in KBr, cm⁻¹) for **5**: 3406(s), 2970(w), 2956(w), 1633(s), 1614(s), 1591(s), 1568, 1506(s), 1438 (m), 1404(s), 1377(m), 1303(m), 1161(w), 1153(w), 1136(w), 1107(w), 1091(w), 1018(m),891(w), 881(w), 821(m), 750(s), 673(w), 516(s).

Synthesis of $Eu(BDC)Cl(H_2O)$ (6)

1.5 mmol, 0.5492 g EuCl₃·6H₂O and 0.5 mmol, 0.0828 g H₂BDC mixed with 0.8004 g [EMI]I were placed in a crystallisation vial placed in a 25 mL teflon-lined stainless-steel autoclave. The mixture was kept inside the furnace at 170 °C for 5 days, and then cooled to ambient temperature. The colorless crystals of **6** suitable for X-ray diffraction were collected after clearing with acetone. Yield based on H₂BDC: 0.1246 g, 66.5%. Elemental analysis (%), Found (calcd): C, 26.15(26.00); H, 1.53(1.64). IR data (in KBr, cm⁻¹) for **6**: 3330(s), 2995(w), 2950(w), 1630(m), 1592(s), 1566(m), 1504(m), 1442(m), 1404(s), 1377(m), 1161(w), 1109(w), 1016(m), 883(m), 827(m), 748(s), 597(m), 511(s).

Compound **6** was also synthesized via the molar ratio (3:1) of EuCl₃·6H₂O to H₂BDC in ca. 0.8 mL [PMI]I or ca. 0.8 mL [BMI]I at 170 °C.

Synthesis of $Eu_3(BDC)_4Cl(H_2O)_6(7)$

1.5 mmol, 0.5498 g EuCl₃·6H₂O and 0.5 mmol, 0.0835 g H₂BDC mixed with 0.8012 g [EMI]Br were placed in a crystallisation vial placed in a 25 mL teflon-lined stainless-steel autoclave. The mixture was kept inside the furnace at 170 °C for 5 days, and then cooled to ambient temperature. The colorless crystals of **7** suitable for X-ray diffraction were collected after soak clearing with acetone. Yield based on H₂BDC: 0.0519 g, 32.0%. Elemental analysis (%), Found (calcd): C, 30.25(30.04); H, 1.43(1.26). IR data (in KBr, cm⁻¹) for **7**: 3462(m), 3195(w), 3066(w), 2980(w), 2939(w), 1635(m), 1596(s), 1564(m), 1510(m), 1442(m), 1406(s), 1301(m), 1151(w), 1101(w), 1010(w), 945(w), 887(w), 825(m), 754(s), 671(w), 507(s).

Compound **7** was also synthesized via the molar ratio (3:1) of EuCl₃·6H₂O to H₂BDC in ca. 0.8 mL [PMI]Br or 1.0006 g [BMI]Br at 170 °C.

Single Crystal X-ray Diffraction

Single crystals of compounds 1-7 were manually harvested from crystallisation vials and mounted on Hampton Research CryoLoops using FOMBLIN Y perfluoropolyether vacuum oil (LVAC 25/6, purchased from Aldrich)²⁸ with the help of a Stemi 2000 stereomicroscope equipped with Carl Zeiss lenses. Data were collected on a Rigaku Mercury CCD diffractometer equipped with a graphite-monochromated Mo-K α radiation (λ = 0.71073 Å) at 293(2) K. The intensity data were collected by the ω scan technique and were reduced using CrystalClear program.²⁹ The crystal structures of compounds 1-7 were solved by direct method using SHELXTL[™] version 5 package of crystallographic software³⁰ and refined by full-matrix least-squares technique on F^2 . All nonhydrogen atoms were refined anisotropically. Hydrogen atoms were located at geometrically calculated positions to their carrier atoms and refined with isotropic thermal parameters included in the final stage of the refinement. The summaries of the structural determination and refinement for compounds 1-7 are listed in Supporting Information (Tables S1-S2, ESI+). The selected bond distance and angles are listed in ESI⁺ (Tables S3-S4).

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Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre (the deposition CCDC numbers 1455818-1455824 for compounds **1-7** respectively). These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data request/cif.

Results and discussion

Synthesis

The summary of the synthetic conditions is listed in Table 1. By the analysis of the table, we can find some approximate trends in the products formed. When X⁻ fixed as Cl⁻, the single type of the compounds 4, 2 and 3 appeared respectively, indicating [RMI]⁺ plays the critical role in the structure construction. In the case of Br and I, the products display structure diversity depending on the Eu:H₂BDC ratios, especially in the situations using [EMI]Br. If Eu:H₂BDC ratios fixed at 1:1 to 1:2, the products remain unchanged under [PMI]X/[BMI]X situations, also indicating the template role of [RMI]⁺ cations. However, as the Eu:H₂BDC ratio increasing to 3:1, compounds 2 and 3 transfer into 7 and 6 respectively, which concerns with the higher Eu:H2BDC ratios. Despite the different ratios in the case of [EMI]⁺, with Cl⁻ changing to I⁻, the products gradually transform from 4 to 1, indicating the effect of X^{-} in the structure construction. However, at higher Eu:H₂BDC ratios, compounds 7 and 6 appear under [EMI]Br and [EMI]I respectively. The observation suggests that higher reaction temperature and lower Eu:H₂BDC ratio prefer to compound 1; higher Eu:H₂BDC ratio is apt to compounds 7 and 6 under [RMI]Br and [RMI]I respectively. Structure descriptions of compounds 1-7

Compound **1** features a 3D architecture $[EMI][Eu_2(BDC)_3CI]$, possessing a negative $[Eu_2(BDC)_3CI]^-$ skeleton with $[EMI]^+$ cations locating in the framework. Because the structure of compound **1** has been reported in the literature, ³¹ its structure will be discussed in brief. The asymmetric unit of **1** comprises of two Eu(III) cations,

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templates anchoring in the channels. (2) Fig. 1 The structure constructions of compounds 1-3

Fig. 2 The structure construction of compound 4

Table 1. Summary of the synthetic conditions of compounds **1–7**, including Eu:H₃BDC ratios and reaction temperature.

	Cl	Br	Ι
EMI	4 (1:2; 1:1; 2:1;3:1,	1 (1:1, 180 °C)	1 (1:2, 170 °C)
	170 °C)	4 (1:1, 170 °C)	4 (1:1, 170 °C)
		5 (3:1, 180 °C)	6 (3:1, 170 °C)
		7 (3:1, 170 °C)	
PMI	2 (1:2; 1:1; 2:1;3:1,	2 (1:1, 180 °C)	2 (1:2, 170 °C)
	170 °C)	7 (3:1, 170 °C)	6 (3:1, 170 °C)
BMI	3 (1:2; 1:1; 2:1; 3:1,	3 (1:1, 170 °C)	3 (1:2, 170 °C)
	170 °C)	7 (3:1, 170 °C)	6 (3:1, 170 °C)

two full-occupied BDC²⁻ and two half-occupied BDC²⁻ ligands, one μ_2 -Cl⁻anion, and one [EMI]⁺ template (Fig. S1, ESI⁺). The seven positive charges on Eu(III) cations and [EMI]⁺template are balanced by total three BDC²⁻ligands and Cl⁻ anion. Eu1 and Eu2 centers exhibit the same coordination geometries: Eu1 and Eu2 are surrounded by seven carboxylic oxygen atoms and one Cl⁻ anion to shape distorted trigonal dodecahedra. BDC²⁻ ligands show three kinds of connectivity modes: μ_3 -chelating and monodentate bridging/chelating, μ_4 -bis-bidentate bridging, and μ_4 -chelating and monodentate bridging/chelating (Scheme S1a, S1b, and S1c, ESI⁺). Eu1 and Eu2 are connected by μ_2 -Cl⁻ bridge into a [Eu₂(μ_2 -Cl)] SBU with Eu1…Eu2 separations of 4.1335(6) Å. The $[Eu_2(\mu_2-CI)]$ SBUs are connected by BDC²⁻ (the one connects with O11) ligands into a lattice 2D layer along the *ab*-plane, or by those containing O31, O41 into lattice 2D layer along the ac-plane (Fig. S2, ESI⁺). A 3D architecture is constructed through the BDC2- ligands containing O21 along the *c*-direction based on the 2D layers (Fig. 1) with [EMI]⁺

Compound 2, [PMI][Eu2(BDC)3CI], shows independent eightcoordinated Eu1 and Eu2 with the same coordination geometries of bicapped trigonal prism. Eu1 and Eu2 both are surrounded by one chelating COO⁻, five COO⁻ and one μ_2 -Cl⁻anion (Fig. S1, ESI⁺). Eu1 and Eu2 units are connected by one μ_2 -Cl⁻ into a [Eu₂(μ_2 -Cl)] SBU as

compound **1**, which is further linked by the BDC^{2-} ligands with O21, O22, O23 and O24 into a lattice 2D layer along the ac-plane (Fig. S3a, ESI^{\dagger}), or the BDC²⁻ ligands with O11, O12, O13 and O14 or O41 and O42 into a 2D layer along the *bc*-plane (Fig.S3b and S3c, ESI⁺). The 2D layers grow into a 3D framework through the linkage of the BDC²⁻ ligands with O31 and O32 (Fig. 1).

Though compound 3 exhibits similar empirical formulas with compounds 1 and 2, the structural details are different. Eightcoordinated Eu1 shows a square antiprism geometry and sevencoordinated Eu2 locates in a monocapped trigonal prism (Fig. S1, ESI⁺). The Eu1 and Eu2 units are also connected by one μ_2 -Cl⁻ into a $[Eu_2(\mu_2-CI)]$ SBU (Fig. 1). The SBUs are linked by the BDC²⁻ ligands with O11, O12, O13 and O14 to form a 1D chain along the bdirection (Fig. S4a, ESI⁺), and further grow into a 2D layer along the *ab*-plane by the linkage of the BDC^{2-} ligands with O41 and O42 along the [110]-direction (Fig. S4b, ESI⁺), or only through the BDC² ligands with O21, O22, O23 and O24 to form 2D layer along the abplane (Fig. S4c, ESI⁺). Based on two double layers, a 3D framework is constructed via the BDC^{2-} ligands with O31 and O32 (Fig. 1).

Compound 4, [EMI]₂[Eu₂(BDC)₃(H₂BDC)Cl₂], comprises of ninecoordinated Eu1 in a tricapped trigonal prism (Fig. S1, ESI⁺). The Eu1 unit and its symmetrical unit connect through two pairs of bidentate bridging COO⁻ groups and two pairs of chelating/monodentate bridging COO⁻ groups into a [Eu₂Cl₂(COO)₈] SBU (Fig. 2). A 2D (4,4) lattice along the bc-plane can be shaped via the SBU connecting with the benzene rings with C11. The benzene rings with C21 locate in the (4,4) lattice making the (4,4) lattice into a (3,6) layer (Fig.S5a, ESI⁺). The benzene rings with C31 fabricate with the (3,6) lattice along the *c*-direction into a 3D architecture with 1D open triangular aperture (Fig. 2).

Eight-coordinated Eu1 in compound 5, Eu(BDC)(HCOO), is surrounded by one chelating and six monodentate COO⁻ groups, shaping a [Eu(COO)₇] bicapped trigonal prism. Eu1 and its symmetrical atom connect each other through one pair of bidentate bridging COO⁻ groups to form a [Eu₂(COO)₂] SBU, which grow into a 2D layer along the bc-plane via the connection of HCOO⁻ (decarboxylication product, Fig. S5b, ESI⁺) and further into a 3D framework with bis-bidentate bridging BDC^{2-} ligand (Fig. 3).



Fig. 4 The structure construction of compound 6



Eu1 in compound **6** [Eu(BDC)Cl(H₂O)] is surrounded by four monodentate COO⁻ groups, two μ_2 -Cl⁻ and one water into a [Eu(COO)₄Cl₂(H₂O)] monocapped trigonal prism. Eu1 atoms are connected via one pair of bidentate bridging COO⁻ groups into a [Eu₂(COO)₂(H₂O)₂] SBU, which is surrounded by four Cl⁻ ligands and the residual parts of six BDC²⁻ ligand. The [Eu₂(COO)₂(H₂O)₂] SBUs bridge μ_2 -Cl⁻ into a 2D layer along the *bc*-plane (Fig. S6a, ESI⁺), and further fabricate with BDC²⁻ ligands along the *a*-direction into a 3D framework (Fig. 4).

In compound **7**, $[Eu_3(BDC)_4Cl(H_2O)_6]$, Eu1 and Eu2, though the coordination atoms are different, are in the same bicapped trigonal prisms (Fig. S1, ESI⁺). There exist two SBUs for Eu1 and Eu2 respectively: Eu(H_2O)_2 and Eu(H_2O)_2Cl. The BDC²⁻ ligands containing O11 bind Eu(H_2O)_2 and Eu(H_2O)_2Cl SBUs through one group of bidentate bridging COO⁻ along the *c*-direction to form 1D lattice chains, the two chains alternately grow along the *b*-direction into a 2D grid (Fig. S6b, ESI⁺), which is further connected by the other BDC²⁻ ligands into a 3D framework (Fig. 5).

Characterization

PXRD

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The experimental PXRD patterns for compounds **1–7** match well with those simulated from single crystal structure data, indicating that bulk samples of compounds **1–7** were isolated as single crystal pure phases (Fig.S7, ESI⁺).

FT-IR spectra

The characteristic absorption peaks of the main functional groups for compounds 1-7 are listed in Table S5 (ESI⁺). The asymmetric stretching vibrations $\upsilon_{as}(\text{COO}^{-})$ are observed in the range 1546– 1635 cm^{-1} and symmetric stretching vibrations $\upsilon_s(\text{COO}^-)$ in the range 1386–1510 cm⁻¹. The asymmetric stretching vibrations of free $\rm H_2BDC$ ligand are 1680 $\rm cm^{-1}$ and 1575 $\rm cm^{-1}$ and symmetric stretching vibrations of free H₂BDC ligand are 1510 cm⁻¹ and 1420 cm⁻¹. The stretchings of the seven compounds are shifted to lower wave numbers, compared to the carbonyl frequencies of free H₂BDC ligands. The differences of $\Delta(v_{as}(COO^{-})-v_{s}(COO^{-}))$ were beyond 200 cm⁻¹, showing carboxylic groups in coordination status.³² The C–N stretching of the imidazolium ring around 1160 cm⁻¹ and C–H stretching of the imidazolium ring from 3062 to 3168 cm^{-1} are observed in compounds **1–4**. While, the above stretchings are absent in compounds 5–7, demonstrating no RMI⁺ templates. TG analysis

The very small weight losses of 1.1-5.3% in compounds 1, 2, 5 and 6 under 140 °C may come from the loss of the water absorbed by the MOFs or combining with $[RMI]^+$ templates. Compounds 1–3 start to decompose at 350 °C for 1, 300 °C for 2, and 270 °C for 3 (Fig. S8a, ESI⁺). The decomposition temperatures decrease depending on the increased alkyl chains in the $[RMI]^+$ templates. The decreased trend of the decomposition temperatures with the increased alkyl chains

relates with the electrostatic interactions between the negative skeletons and positive $\left[\mathsf{RMI}\right]^+$ templates. The stronger the electrostatic interaction is, the more stable framework will be. In the case of our work, the electrostatic interactions are relevant to the inductive effect between the positive imidazole ring and the alkyl chains. As well known, alkyls are electron-releasing groups, exhibiting +I inductive effect. Therefore, the positive charge in the imidazole ring becomes 'de-amplified' and the electrostatic interactions will be decreased with the alkyl chains, thus to make less stable frameworks. This observation suggests the effect of the [RMI]⁺ templates on the thermal behaviors. The decomposition temperatures of compounds 4-7 are 280, 250, 260 and 150 °C respectively (Fig. S8b-e, ESI⁺). Generally, the compounds containing [RMI]⁺ templates show higher decomposition temperatures than those without [RMI]⁺ templates, indicating the electrostatic interactions between the negative skeletons and [RMI]⁺ templates reinforce the final structures. All steps of weight losses after decomposition temperature can be assigned to the synchronous oxidation of the organic components including ILs and BDC^{2-1} ligands.

Fluorescence

The solid state emission spectra of compounds 1-7 and free H₂BDC ligand were recorded at ambient temperature. Free H₂BDC ligand shows a broad emission at 378 nm with the excitation at 271 nm, which is related with the intraligand $n \cdot \cdot \pi^*$ and $\pi \cdot \cdot \pi^*$ transfer respectively. Compounds 1-7 exhibit similar emissions at ca. 382(weak), 580(very weak), 590(middle), 615(strong), 650(very weak) and 699(weak) nm excited at ca. 275 nm (Fig. 6). Compared to that of free H₂BDC ligand, the emissions at ca. 382 nm assigned to ILCT. While, those at 580, 590, 615 and 650 nm are revealed as the characteristic emission peaks of Eu³⁺ cation, which are assigned to ${}^{5}D_{0} \rightarrow {}^{7}F_{0}$, ${}^{5}D_{0} \rightarrow {}^{7}F_{1}$, ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$, ${}^{5}D_{0} \rightarrow {}^{7}F_{3}$ and ${}^{5}D_{0} \rightarrow {}^{7}F_{4}$ transitions, respectively.^{33,34} The emissions also concern with the process of ligand-to-metal energy transfer.^{10,13} The (H)BDC ligand absorbs the photon from ultraviolet light and then targets the characteristic emission of Eu³⁺ by intramolecular energy transfer. Therefore, the emission intensity at 382 nm becomes very weak.

The temperature-dependent emission intensities of compounds **1**, **4**, **6** and **7** were investigated between 25 and 200 °C (Fig. S9, ESI⁺) .The fluorescence intensity of compound **1** decreases with temperature increasing, about 42% fluorescenceintensity is quenched at 200 °C. When the temperature is back to 25 °C from 200 °C, the fluorescence intensity can be recovered. The similar phenomena can be observed in compounds **4**, **6** and **7** and **7**. At 200 °C, the fluorescenceintensities of compounds **4**, **6** and **7** quench 31, 58 and 56% respectively, which suggests the frameworks including RMI⁺ have the better fluorescent stability in the higher temperature.





Fig. 7. Suspension-state photoluminescent spectra of ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ at 615 nm for compound 4 dispersed in aniline and contrast organic amines and alkylbenzene aqueous solutions.

Aniline detection

Compounds 1-7 show fluorescence quenchings when mixed with aniline. Due to the consideration on the yields and possible effect of [RMI]⁺, compounds **4** and **6** were selected for aniline detection. Compound **4** was immersed in the 1×10^{-2} mol·L⁻¹ aniline HEPES aqueous buffer (pH = 6.5) to be a homogeneous suspension solution via ultrasonic oscillation, whose emission spectrum was recorded at ambient temperature. A very obvious fluorescence quenching was observed. In order to find out the selectivity of aniline detection, several representative types of organic amines were chosen as contrast samples: alkylol amine (triethanolamine), acid amides (N,N-dimethylformamide), primary amine (methanamide and n-butylamine), and diamine (ethylenediamine); to eliminate the possible effect of benzene ring, three kinds of alkylbenzenes (methylbenzene, ethylbenzene, and propylbenzene) were used as comparison. The selected contrast organic amines and alkylbenzenes indicate the almost same emission features as the



Fig. 8. The comparison offluorescence intensities of ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ emissions at 615 nm for compound 4 dispersed in aniline mixed with contrast organic amines one by one or all together (mixed amindes) and alkylbenzene samples.



blank sample in water, which emit strong red light (assigned to ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ transition of Eu³⁺ at 615 nm); while, the aniline sample exhibits very obvious fluorescence quenching in all the emission peaks (Fig. 7). It suggests that compound 4 can behave as a potential high selective turn-off fluorescence sensor to aniline detection. To check the detection selectivity, we mixed aniline with other contrast samples one by one, or with all five contrast organic amides together (Fig. 8), compound 4 still exhibited obvious fluorescence quenching, showing very excellent selectivity to aniline. The recycle repeatability of compound 4 detecting aniline was checked (Fig. 9). Compound 4 was pasted to a slide glass, which was further inserted to the colormietric utensil containing aniline, then to test fluorescence. After 10 times recycling, compound 4 still remains basically unchanged emission intensity and rapid response to aniline, indicating compound 4 has a high stable recycle repeatability.

For expanding application range, the similar tests were performed when mixed with compound **4** under DMF media (Fig. S10, ESI[†]). The same phenomena can be observed: aniline shows fluorescence quenching and other eight contrast samples show strong red light, which indicates compound **4** also have high effectiveness for aniline detection in DMF solutions.

Based on the above observations, compared to alkylbenzenes, compound 4 does not determine the existence of benzene ring. Similarly, compared to the selected contrast samples, alkylol amine, acid amides, primary amine and diamine cannot be detected. Also, aniline belongs to primary amine. Therefore, we infer the synergistic action of benzene and amine group leads to the strong fluorescence quenching of aniline. The UV-Vis spectra of aniline and other eight contrast samples suggest that UV-Vis peak of aniline covers those of compounds 4 and 6, indicating the energy of aniline matches with that of compounds 4 and 6 (Fig.S11, ESI⁺). By the fluorescence comparison of free H₂BDC, free aniline and the mixture of H₂BDC and aniline, the broad emission of free H₂BDC was weaken greatly after mixed with aniline, whose mixture shows the similar emission to aniline (Fig. S12, ESI⁺). It can be inferred that with the existence of aniline, the fluorescence of H₂BDC is inhibited, thus to inhibit the ligand-to-metal transfer, that is, aniline makes H₂BDC a linear decline in effectiveness for targeting the emissions of Eu³⁺.

The concentration-dependent fluorescence quenching of aniline mixed with compound **4** in water or DMF suspension were

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determined. Both show very similar trends in water (Fig. 10) or DMF (Fig. S13, ESI⁺): the fluorescence intensities gently increase from 1×10^{-2} to 5×10^{-3} mol·L⁻¹, then rapidly climb up until 1×10^{-4} mol·L⁻¹, relatively mildly increase at 1×10^{-5} mol·L⁻¹. As the aniline concentration locating in 1×10^{-4} – 5×10^{-3} mol·L⁻¹, the relationships [*I*-(-lgc)] (*I*: the fluorescence intensity; *c*: the aniline concentrations follow the similar linear equations y = 2783.4x - 5733.9 ($R^2 = 0.9894$) (Fig. S14, ESI⁺) in water and y = 3332.38x - 7499.2 ($R^2 = 0.9899$) in DMF (Fig. S15, ESI⁺), indicating water and DMF have negligible effect on the fluorescence quenching of aniline on compound **4**. The concentration-dependent fluorescence indicates the detection limit of compound **4** is 6.8×10^{-6} mol·L⁻¹ in WATE.

The same processes were repeated with aniline mixed with compound 6. The same phenomena appeared: a very obvious fluorescence quenching was observed in the presence of aniline compared to strong red light in the contrast organic amines and alkylbenzenes (Fig. S16 and S17, ESI⁺). Obvious fluorescence quenchings were observed when compound 6 was immersed in samples of aniline with other contrast samples one by one, or with all five contrast organic amides together (Fig. S18, ESI⁺), indicating high selective aniline detection. High recycle repeatability for compound 6 is confirmed that the fluorescence intensity remain stable (Fig. S19, ESI⁺). The concentration-dependent fluorescence quenching of aniline mixed with compound 6 in water or DMF suspension solutions also exhibits similar trends: generally, the fluorescence intensities increase with the decreased aniline concentrations (Fig. S20 and S21, ESI⁺). When the aniline concentration ranging $5 \times 10^{-4} - 1 \times 10^{-2}$ mol·L⁻¹ in water, the fluorescence intensity l vs (-lgc) satisfies the linear equations y =4413.9x - 8796.4 (R² = 0.9961) (Fig. S22, ESI⁺), and the relationship $[I-(-\lg c)]$ in aniline concentration range of $1 \times 10^{-5} - 5 \times 10^{-3}$ mol·L⁻¹ in case of DMF situation complies with the linear equations y =999.34x – 2305 (R^2 = 0.9815) (Fig. S23, ESI⁺). The detection limit of compound **6** is 9×10^{-6} mol·L⁻¹ in water and 7×10^{-6} mol·L⁻¹ in DMF respectively.

The exploration of the determination on organic amides focuses on aliphatic amines, including diamide (1,2-Ethanediamine and 1,3-Propanediamine), diammonium phosphate, butylamine, n-propylamine and ethanolamine.³⁵ Relatively, aniline vapour

detection is common.³⁶ Compared to those reported methods of aniline detection, the presented method that uses Eu-(H)BDC compounds as detection agent behaves high selectivity, stable recycle repeatability, rapid response and low detection limit. Especially, MOF materials are rare reported in aniline detection.

Conclusions

Herein, we ionothermally synthesized seven Eu-(H)BDC compounds with three kinds of nine 1-alkyl-3-methyl imidazolium halides [RMI]X (R = ethyl to butyl; MI = imidazolium; X = CI, Br, I), $[RMI][Eu_2(BDC)_3CI]$ (R = ethyl (1), propyl (2), butyl (3)), $[EMI]_2[Eu_2(BDC)_3(H_2BDC)Cl_2]$ [Eu(BDC)(HCOO)] (4), (5), $[Eu(BDC)Cl(H_2O)]$ (6) and $[Eu_3(BDC)_4Cl(H_2O)_6]$ (7). The crystal structures and phase purities of compounds 1-7 were characterized by single crystal X-ray diffraction and PXRD respectively. TGA indicate decomposition temperatures of compounds 1-3 decrease with the increased alkyl chains in the [RMI]⁺ templates, which concerns with stronger +I inductive effect of longer alkyl groups decreasing the positive density on imidazole rings, thus to decrease the electrostatic interactions and lead to less stable frameworks. Additionally, compounds 1-4 with [RMI]⁺ templates show higher decomposition temperatures than compounds 5-7 without [RMI]⁺ templates. Compounds 1-7 exhibit similar emissions at ca. 382, 580, 590, 615, 650 and 699 nm excited at ca. 275 nm, among which the emissions at 382 nm are assigned to ILCT, and those at 580, 590, 615 and 650 nm are relevant to Eu^{3+} , assigned to ${}^{5}D_{0} \rightarrow {}^{7}F_{0}$, ${}^{5}D_{0} \rightarrow {}^{7}F_{1}$, ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$, ${}^{5}D_{0} \rightarrow {}^{7}F_{3}$ and ${}^{5}D_{0} \rightarrow {}^{7}F_{4}$ transitions respectively. The temperature-dependent emissions of compounds 1, 4, 6 and 7 exhibit ca. 42, 31, 58, and 56% fluorescence quenching respectively with temperature increasing to 200 °C. As temperatures reverse to ambient temperature, the fluorescenceintensity can be recovered.

Obvious fluorescence quenchings can be observed when compounds 4 and 6 mix with aniline HEPES aqueous buffers: the strong red emissions assigned to ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ transition of Eu³⁺ at 615 nm were quenched. Compounds 4 and 6 can behave as potential high selective turn-off fluorescence sensors to aniline detection. Compounds 4 and 6 can detect aniline in the mixtures of aniline with five contrast organic amines one by one or all together. The fluorescence quenching come from aniline can block the photon transfer from H₂BDC to Eu³⁺. After 10 times recycling of aniline test, compounds 4 and 6 show basically unchanged emission intensity and rapid response to aniline, which suggests that compounds 4 and 6 have high stable recycle repeatability. The similar results can be also obtained in DMF solutions. The concentration-dependent fluorescence quenchings of aniline mixed with compounds 4 and 6 show linear [I-(-lgc)] relationships in $1 \times 10^{-4} - 5 \times 10^{-3}$ mol·L⁻¹ and $5 \times 10^{-4} - 1 \times 10^{-2}$ mol·L⁻¹ aniline in water respectively. The detection limits of compounds 4 and 6 in water are 6.8×10^{-6} and 9×10^{-6} mol·L⁻¹ respectively.

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Europium Metal-Organic Frameworks as Recyclable and Selective

Turn-off Fluorescence Sensors for Aniline Detection

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Seven Eu(III) compounds are ionothermally synthesized and well characterized, among which compounds 4 and 6 exhibit as high selective turn-off fluorescence sensors for aniline detection with stable recyclable repeatability.