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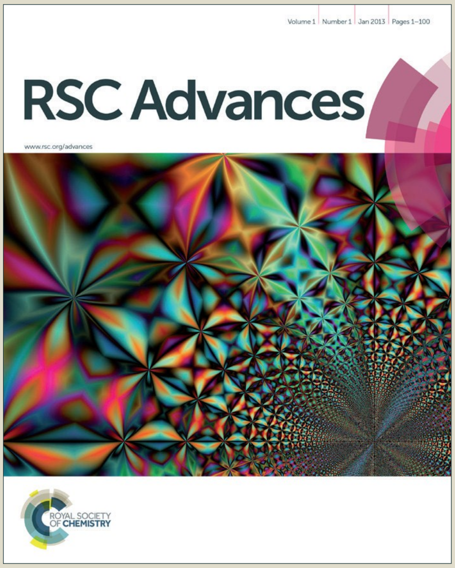

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3D lanthanide metal organic frameworks constructed from lanthanide formate skeleton and 3,5-bis(4’-carboxy-phenyl)-1,2,4-triazole connector: synthesis, structure and luminescence

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Three isomorphic lanthanide metal-organic frameworks (Ln-MOFs) have been constructed from lanthanide formate skeletons and 3,5-bis(4’-carboxy-phenyl)-1,2,4-triazole) (H_2bct) connectors. Further, by adjusting the co-doping ratio of different Ln^{3+} ions into the framework, two doped Ln-MOFs are synthesized and show tunable luminescent emission including white-light emission.

Metal organic frameworks (MOFs) as functional materials are of interest owing to their impressive structural diversity and variety of actual or potential applications.[1] Among them, lanthanide-based MOFs (Ln-MOFs) have received great attention due to their unique luminescence and catalytic properties.[2-5] On the one hand, Ln-MOFs as the luminescent materials exhibit high photoluminescence efficiency, unique narrow-band, and long luminescence lifetimes emissions.[3] Moreover, the lanthanide based color-tunable and white light-emitting materials can be achieved by incorporating Eu^{3+}, Tb^{3+} and Gd^{3+} /Ce^{3+} into the isostructural frameworks, and their luminescence can be effectively tuned by varying the stoichiometric ratio of Ln^{3+} ions or the excitation wavelengths.[4,5] However, in comparison with transition metal ions, Ln^{3+} ions possess higher coordination numbers and more flexible coordination geometries, thus to rationally design and construct Ln-MOFs with desired geometries and properties is still a challenge.

As well known, several factors have great influence on the design and synthesis of Ln-MOFs, such as the choice of organic ligands, the metal/ligand ratio and anions etc. Lanthanide ions have a high affinity and prefer to bond to oxygen atoms, thus, the selection or design of ligands containing appropriate oxygen atom coordination sites is crucial to construct Ln-MOFs.[6] So far, many carboxylic acids, such as benzenepolycarboxylates,[7] pyridinecarboxylates,[8] imidazolecarboxylates[9] and pyrazolecarboxylates[10] have been widely employed to construct Ln-MOFs. More recently, base on mixed organic or inorganic anion ligands, such as carboxylate–oxalate, [11] carboxylate–isonicotinate[12] and carboxylate–sulfate[13], carboxylate–acetate[14], various Ln-MOFs have been prepared, in which anions as bridges incorporated in inorganic lattices. Thus, anion not only acts as a contributor to increase complexity but also exerts a synergistic influence in the structural control for self-assembly of Ln-MOFs. [15] Especially, formate anion can be in situ generated by the hydrolysis of dimethylformamide (DMF) solvent under solvothermal conditions.[16] It provides a new strategy for constructing functional Ln-MOFs.

3,5-bis(4’-carboxy-phenyl)-1,2,4-triazole) (H_2bct) endowed with two carboxylate groups and a triazole ring, is a versatile bridging ligand for the construction of multi-dimensional MOFs[17] and has conjugated system possess good energy-transfer ability, which can magnify the luminescence of the f–f transitions of Ln^{3+} ions. In this work, using DMF and H_2O as solvents, a new family of isomorphic Ln-MOFs, namely, $[Ln_2(HCOO)_2(bct)_2]\cdot H_2O$ (Ln = Tb, Eu, Gd) have been constructed from lanthanide formate skeletons and bct^{2-} connectors, exhibiting a 3D framework with 1D oval channels. Luminescence investigation reveals that **1-Tb** and **2-Eu** show characteristic green and red emissions of the corresponding Tb^{3+} and Eu^{3+} ions, respectively, while **3-Gd** exhibits blue emission arising from the bct^{2-} ligand. Then based on their luminescent properties, we have successfully designed and constructed two novel doped Ln-MOFs, Eu^{3+}-doped **1-Tb** and Eu^{3+}, Tb^{3+}-doped **3-Gd** by adjusting the co-doping ratio of different Ln^{3+} ions into the same framework as that of **1**-**3**. The emission colors of Eu^{3+}-doped **1**-**Tb** can be tuned from red to green by varying the molar ratios of Eu^{3+} ion from 10% to 0.02%, while that of Eu^{3+}, Tb^{3+}-doped **3-Gd** can be tuned from yellow to white by changing excitation length.

Solvothermal reaction of H_2bct with $Ln(NO_3)_3$ in a mixed solvent DMF and H_2O yields isomorphic Ln-MOFs, $[Ln_2(HCOO)_2(bct)_2]\cdot H_2O$ (Ln = Tb (1), Eu (2) and Gd (3)). The corresponding mixed-lanthanide MOF, Eu^{3+}-doped **1-Tb** and Eu^{3+}, Tb^{3+}-doped **3-Gd**, can be readily synthesized by using mixed lanthanide salts following the same procedure applied to **1-3**.

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Electronic Supplementary Information (ESI) available: Additional structural figures, PXRD patterns, TGA and luminescent decay curves, IR, excitation spectra of 1-3 and H_2bct and energy levels of H_2bct, Eu^{3+} and Tb^{3+}. CCDC 1011116 and 1428248. See DOI: 10.1039/x0xx00000x

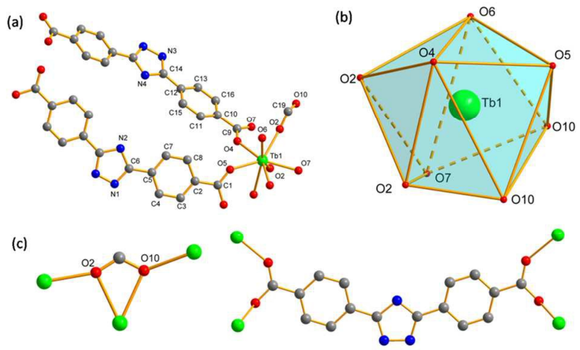

Fig. 1 (a) The coordination environment of Tb(III) center in **1-Tb**. (b) Schematic representation of the distorted TbO_8 dicapped trigonal prismatic coordination polyhedron presents in **1-Tb**. (c) The coordination modes of formate anion and the bct^{2-} ligand.

X-ray analyses of **1-Tb**, **2-Eu** and **3-Gd** reveals that they are isomorphous and exhibit a 3D framework with 1D oval channels constructed via dense $[Ln_2(HCOO)_2]_\infty$ 2D layers and bct^{2-} bridging ligands. Hence, only the crystal structure of **1-Tb** is described herein as a representative example. **1-Tb** crystallizes in the orthorhombic space group *P*nma and there are one unique Tb^{3+} ion, one bct^{2-} ligand, one formate anion, and one lattice water molecule in the asymmetrical unit of **1-Tb**. As shown in Fig.1, the central Tb^{3+} ion is eight-coordinated and described as a slightly distorted dicapped trigonal prism coordination mode: four oxygen atoms from the carboxylate moiety of four bct^{2-} anions and four carboxylate oxygen atoms from two formate anions. The Tb–O bond lengths range from 2.279(7) to 2.589(7) Å which are comparable to those reported in the related Tb^{3+} compounds.[18] The bond angles of O-Tb-O are in the range of 50.5(2) to 157.3(2) °. The formate anions adopt the chelating and bridging coordination modes, while bct^{2-} anions exhibit the bis(monodentate) coordination fashion as depicted in Fig.1c. All carboxyl groups of these ligands are deprotonated, in agreement with the IR data (Fig. S1) in which no strong absorption peaks around 1700 cm^{-1} (-COOH) are observed.[19]

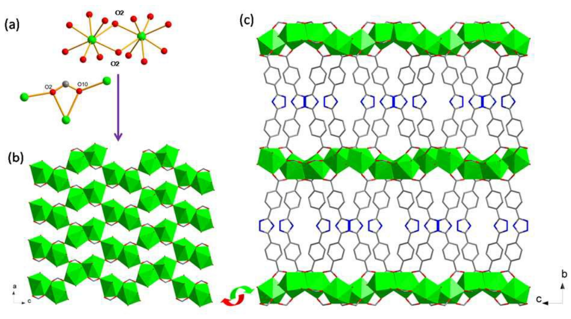

Fig. 2 (a) The $[Tb_2O_2]$ rhombic SBU in **1-Tb**. (b) The dense $[Tb_2(HCOO)_2]\infty$ 2D layer built by $[Tb_2O_2]$ rhombic SBUs and formate anions in **1-Tb**. (c) The 3D open-framework constructed by dense $[Tb_2(HCOO)_2]\infty$ 2D layers and bridging bct^{2-} ligands in **1-Tb**.

In the structure of **1-Tb**, two Tb^{3+} centers, Tb1 and Tb1A (A = symmetry code: -x,-y+2,-z+1) are directly bridged by two μ_2-O(4) atoms from two formate anions to form a $[Tb_2O_2]$ rhombic SBU with a Tb···Tb distance of 3.8948(9) Å as shown in Fig. 2a. These dinuclear SBUs are connected to each other via O(6) atoms from formate anions forming a dense $[Tb_2(HCOO)_2]_\infty$ 2D network in the *ac* plane (Fig. 2b). As viewed along the *a* axis, the bct^{2-} ligands further bridge the adjacent layers in a μ_2-O coordination mode to result in a 3D framework with 1D oval channels (Fig.2c).

The luminescent properties of **1-Tb**, **2-Eu** and **3-Gd** and H_2bct ligand in the solid state were investigated at room temperature. As shown Fig. 3, upon excitation with 350 nm, the free H_2bct ligands show a blue emission band centered around 410 nm, which is assigned to the π-π* transition. Upon excitation at 307 nm, **1-Tb** exhibits characteristic emission bands of Tb^{3+} ions at 488, 546, 582, and 620 nm, associated with the $^5D_4$-^7F_J (J= 6–3) transitions. **2-Eu** emits red light when excited at 382 nm. The emission peaks at 579, 590, 616, 653, and 700 nm originate from the $^5D_0$-^7F_J (J=0–4) transitions. The characteristic emission from H_2bct ligand around 410 nm disappears, indicating that there exists energy transfer from H_2bct ligands to Ln^{3+} ions that "magnifies" the luminescence of the f–f transitions. Under excitation at 380 nm, **3-Gd** presents a blue emission with a broad band centered at 430 nm, which is quite similar to that of the free H_2bct ligand, except for a slight red shift. As the lowest excited state of the Gd^{3+} $^6P_{7/2}$ is too high to accept energy from the ligand, its characteristic 4f–4f transition at 311 nm is not visible. Therefore, it is reasonable to assign this emission to the intra ligand π-π* charge transfer. This phenomenon is similar to that previously reported. [20]

The characteristics of luminescent emission in **1-Tb** and **2-Eu** indicate that the antenna effect occurs, that is, energy migration takes place upon H_2bct ligand absorption, followed by intersystem crossing $S_1 \rightarrow T_1$ and antenna $T_1 \rightarrow$f transfer, and then generating f–f emissions of Tb^{3+} and Eu^{3+} ions as shown in Fig.S2. According to Latva's empirical rule, a Ligand-to-metal transfer process requires an energy gap of 2500–4500 cm^{-1} for Tb^{3+} and 2500–4000 cm^{-1} for Eu^{3+}. [21,22] Therefore, the H_2bct ligand can effectively sensitize Tb^{3+} emission, but is not an ideal situation for the sensitization of Eu^{3+}

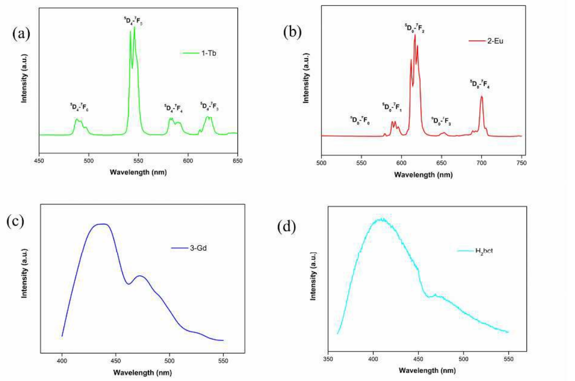

Fig. 3 Emission spectra of **1-Tb** (a), **2-Eu** (b), **3-Gd** (c) and H_2bct ligand (d) in the solid state at room temperature.

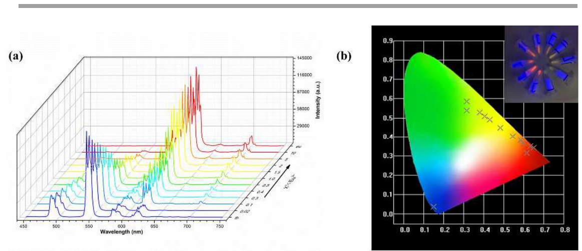

Fig. 4 (a) Emission spectra of Eu^{3+}-doped with different Eu^{3+} molar ratios. (b) CIE chromaticity diagram for Eu^{3+}-doped **1-Tb** when excited at 307 nm. Inset: The optical photographs of Eu^{3+}-doped **1-Tb** products with different Eu^{3+} molar ratios under irradiation of UV light.

luminescence, due to the energy gap between T_1 and $^5D_4$ state of Tb^{3+} is 2765 cm^{-1} while the energy gap between T_1 and $^5D_0$ state of Eu^{3+} being 5985 cm^{-1}. The quantum yields of **1**-Tb and **2**-Eu, measured at room temperature upon excitation at 307 nm and 382 nm respectively, are 19.85% and 17.10%.

Considering that the emissions of **1**-**3** consist of three primary colors and they are isostructural, we expect to obtain tunable luminescent emission including white-light emission by doping different Ln^{3+} ions into one framework. By carefully choosing the starting lanthanide salts and optimizing the molar ratio of different Ln^{3+} ions, we successfully designed and constructed two novel doped Ln-MOFs, Eu^{3+}-doped **1**-**Tb** and Eu^{3+}, Tb^{3+}-doped **3-Gd**. As shown in Fig.4, the luminescent behaviors of a series of Eu^{3+}-doped **1**-**Tb** with different doping molar ratios were investigated when excited at 307 nm. It was found that their emission colors can be tuned from red to green by varying the molar ratios of Eu^{3+} ion from 10% to 0.02%. Indeed, the luminescent intensities of Tb^{3+} characteristic peak decrease abruptly as soon as some Eu^{3+} ions are present. Moreover, the red component to the color emission keeps strong even for low Eu^{3+}/Tb^{3+} ratios. It indicates the emission of the Eu^{3+} ions in Eu^{3+}-doped **1**-**Tb** is further sensitized by the Tb^{3+} ions within the same frameworks. In addition, the luminescent decay test shows the values of lifetime for **1**-**Tb** and **2**-**Eu** are 0.57(1) ms and 0.56(1) ms, while $^5D_4$ (Tb^{3+}) and $^5D_0$ (Eu^{3+}) lifetime values in Eu^{3+}-doped **1**-**Tb** being 0.16(01) ms and 1.28(3) ms, respectively (Fig.S3). This further approves the phenomenon of Tb^{3+} to Eu^{3+} energy transfer in Eu^{3+}-doped **1**-**Tb**.

Due to the blue emission of the bct^{2-} ligand in **1**-**Tb** and **2**-**Eu** is almost completely suppressed by the strong green and red luminescence of the Tb^{3+} and Eu^{3+} ions, an excess amount of non-luminescent Gd^{3+} ion is required to dilute these two Ln^{3+} ions in the solid state. By optimizing the molar ratio of Eu^{3+}, Tb^{3+} and Gd^{3+} ions being 0.0006: 0.2: 0.7994, Eu^{3+}, Tb^{3+}-doped **3**-**Gd** is synthesized, which can simultaneously show the characteristic emissions of the Eu^{3+} and Tb^{3+} ions, as well as the broad blue emission of the ligand. The emission spectra changes of Eu^{3+}, Tb^{3+}-doped **3**-**Gd** as a function of the excitation wavelength were investigated (Fig. 5). As the excitation wavelength increases from 307 nm to 393 nm, the emission intensities of the red and blue components gradually increase, while the emission intensity of green component decreases, thus the emission color of Eu^{3+}, Tb^{3+}-doped **3**-**Gd** can be tuned from yellow to white. A white emission with CIE coordinates of (0.313, 0.312), which fall within the white-light region, emerges upon excitation at 377 nm. The quantum yield of Eu^{3+}, Tb^{3+}-doped **3**-**Gd** is 10.7%, which is measured under λ$_{ex}$ = 377 nm at room temperature.

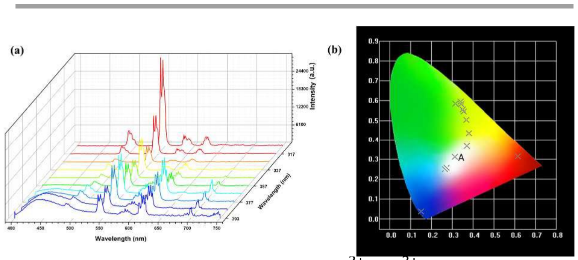

Fig.5 (a) The Emission spectra of Eu^{3+}, Tb^{3+}-doped **3-Gd** by changing the excitation wavelength. (b) CIE chromaticity diagram showing the emission of Eu^{3+}, Tb^{3+}-doped **3-Gd** varying from yellow to white by changing different excitation wavelength. x = 0.313 and y = 0.312 for A.

Conclusions

In summary, by reacting H$_2$bct ligand with lanthanide ions, three isostructural Ln-MOFs **1**-**Tb**, **2**-**Eu** and **3**-**Gd** have been synthesized under the solvothermal conditions. They present 3D framework with 1D oval channels built by dense lanthanide formate skeletons and bridging bct^{2-} ligands. Based on their luminescent properties, two novel doped Ln-MOFs, Eu^{3+}-doped **1**-**Tb** and Eu^{3+}, Tb^{3+}-doped **3-Gd** have been successfully prepared by adjusting the co-doping ratio of different Ln^{3+} ions into the same framework as that of **1**–**3**. The emission colors of Eu^{3+}-doped **1**-**Tb** can be tuned from red to green by varying the molar ratios of Eu^{3+} ion from 10% to 0.02%, while Eu^{3+}, Tb^{3+}-doped **3-Gd** displays white light emission upon excitation at 377 nm and its emission can be tuned from yellow to white by the change of excitation wavelength. Further studies will focus on investigating the differences arising upon exchange of H$_2$bct ligand for other *N*-heterlcyclic carboxylate ligands toward the synthesis of novel functional Ln-MOFs.

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Graphical abstract

3D lanthanide metal organic frameworks constructed from lanthanide formate skeleton and 3,5-bis(4'-carboxy-phenyl)-1,2,4-triazole connector: synthesis, structure and luminescence

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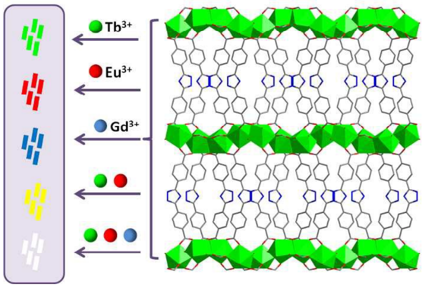

3D Ln-MOFs constructed from lanthanide formate skeletons and 3,5-bis(4'-carboxy-phenyl)-1,2,4-triazole connectors show tuning luminescence emission including white light emitting.