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In Situ Formed White-Light-Emitting Lanthanide–Zinc–Organic Frameworks

Shu-Mu Li,[†] Xiang-Jun Zheng,*[,†] Da-Qiang Yuan,[‡] Ayjamal Ablet,[†] and Lin-Pei Jin[†]

[†]College of Chemistry, Beijing Normal University, Beijing 100875, People's Republic of China

[‡]State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou, Fujian, 350002, People's Republic of China

Supporting Information

ABSTRACT: Five novel 3D heterometallic lanthanide–zinc–organic frameworks, $[H(H_2O)_8][LnZn_4(imdc)_4(Him)_4]$ [Ln = La (**1**), Pr (**2**), Eu (**3**), Gd (**4**), Tb (**5**); H_3imdc = 4,5-imidazoledicarboxylic acid; Him = imidazole], were synthesized via an in situ hydrothermal reaction, and tunable luminescence from yellow to white was obtained through the doping of Eu and Tb ions in the La–Zn framework.

White-light-emitting diodes (WLEDs) have attracted considerable attention because of their application in displays and lighting.[1] They are on track to replace mercury-containing fluorescent lights for environmental concerns. Different approaches have been reported to obtain efficient WLEDs. The reported WLED materials mainly focus on metal-doped or hybrid inorganic materials,[2] organic molecules,[3] polymers,[4] nanomaterials,[5] and metal complexes.[6] Generally, white light can be obtained through three methods: a single component emitting in the whole visible region, a two-chromophore-containing component emitting blue and yellow or orange, a three-chromophore-containing component emitting primary colors.[7] The most reported one is the combination of different chromophores. However, blending brings difficulties in the integration of individual materials and may not give rise to uniformly disperse and thermodynamically stable compositions. In recent years, metal–organic frameworks (MOFs) have attracted considerable attention because of their novel topological structure and their potential application in gas storage, separation, catalysis, drug delivery, and magnetism.[8] As to the WLED study of MOFs, few works have been reported.[9]

Lanthanide ions are widely used in luminescent materials because of their excellent luminescence feature: long lifetime, large Stokes shift, and narrow-band emission to give rise to pure light.[10] 4,5-Imidazoledicarboxylate is a rigid and conjugated multidentate N,O-containing ligand and has been widely used to construct 3d, 4f, or 3d–4f MOFs.[11] In its lanthanide complexes,[11c,d] water molecules are involved in coordination to meet the high coordination number, which leads to fluorescence quenching. As is known, 3d transition-metal ions usually have small coordination numbers, which helps to decrease the steric hindrance around the Ln^{3+} ion in the 3d–4f heterometallic complexes, preventing the water molecule from coordinating to the Ln^{3+} ion and accordingly enhancing the photoluminescence intensity.

Herein, we report a series of heterometallic Ln–Zn (Ln = La, Pr, Eu, Gd, Tb) MOFs with $imdc^{3-}$ and Him obtained in a buffer solution under hydrothermal conditions. Their notable feature is that they are isomorphous, which makes it feasible to codope as a uniform compound, resolving some of the critical integration problem. Therefore, tunable luminescence from yellow to white was achieved by the doping of Eu^{3+} and Tb^{3+} ions into La–Zn MOFs excited by different lights.

Rod-shaped crystals of $[H(H_2O)_8][LnZn_4(imdc)_4(Him)_4]$ [Ln = La (**1**), Pr (**2**), Eu (**3**), Gd (**4**), Tb (**5**)] were obtained by the hydrothermal reaction of $LnCl_3$, $Zn(Ac)_2$, and H_3imdc in a HAc–NaAc buffer solution at 180 °C for 4 days. The phase purity was confirmed by powder X-ray diffraction, as shown in Figure S1 in the Supporting Information (SI). Interestingly, the Him ligand derived from the in situ decarboxylation of H_3imdc, which is different from the reported decarboxylation of H_3imdc to 4-imidazolecarboxylic acid.[11c,f] The single-crystal X-ray structure analyses[12] revealed that **1**–**5** are isomorphous and possess a 3d–4f heterometallic framework with 1D channels, in which protonated lattice water molecules are located. Therefore, only the structure of **3** is described in detail. In the asymmetrical unit, there are two Zn^{II} ions, half of a Eu^{III} ion, two $imdc^{3-}$ anions, two Him, and half-protonated water clusters. The Eu^{3+} ion (Eu1) in the framework is eight-coordinated in a triangular dodecahedron environment with eight O atoms from four $imdc^{3-}$ anions (Figure 1a). Two Zn^{2+} (Zn1 and Zn2) ions present similar configurations: both of them are five-coordinated with an Him N atom, two N atoms, and two O atoms from two $imdc^{3-}$ anions, making up a distorted trigonal-bipyramidal geometry with two O atoms in the axial direction. The $imdc^{3-}$ ligand adopts only one coordination mode: each $imdc^{3-}$ connects two Zn^{2+} ions and one Eu^{3+} ion all in a bidentate mode (Figure 1b).

The $imdc^{3-}$ ligands have good coplanarity with mean deviations of 0.0272 and 0.0692 Å from the plane, respectively. Also, the Zn^{2+} ions are almost coplanar with the imdc plane, while the Eu^{3+} ion has a large deviation (0.4064 and 0.6420 Å) from the $imdc^{3-}$ plane. The Him ligand as a terminal ligand only coordinates with one Zn^{2+} ion through one N atom. Every Zn^{2+} ion coordinates with two imdc anions, and every imdc links two Zn ions (Zn1 and Zn2). The imdc anions link the

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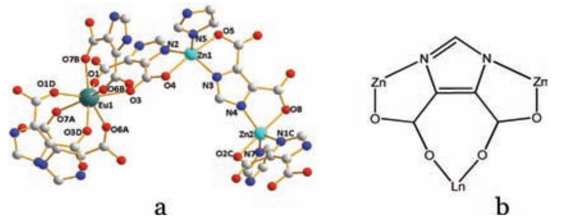

Figure 1. (a) Coordination environment of Eu^{3+} and Zn^{2+} in **1**. Symmetry operation: A, $1.5 - x, 0.5 + y, -z$; B, $-0.5 + x, 1.5 - y, -z$; C, $x, y, -1 + z$; D, $1 - x, 2 - y, z$. (b) Coordination mode of the $imdc^{3-}$ ligand.

Zn^{2+} ion into a 1D helical chain along the *c*-axis direction (Figure 2a). The dihedral angle between the adjacent $imdc^{3-}$ planes in the chain is 58.9°. Every Eu^{3+} coordinates with four imdc ligands. Therefore, around every Eu^{3+}, there are four zigzag chains, forming a butterflylike structure viewed along the *c*-axis direction (Figure 2b). In order to simplify the structure of complex **3**, Him was eliminated because it is a terminal ligand, and the $imdc^{3-}$ ligand can be expressed as a three-connect pink ball. Every Eu^{3+} ion is described as a dark-green ball, around which there are four $imdc^{3-}$ ligands. Every Zn^{2+} ion is expressed as a blue ball, around which there are two $imdc^{3-}$ ligands. Therefore, the simplified 3D structure for complex **3** is shown in Figure S2a in the SI. It is worth noting that the Zn^{2+} ion and $imdc^{3-}$ ligand form left-handed helical chains, as shown in Figure S2b in the SI.

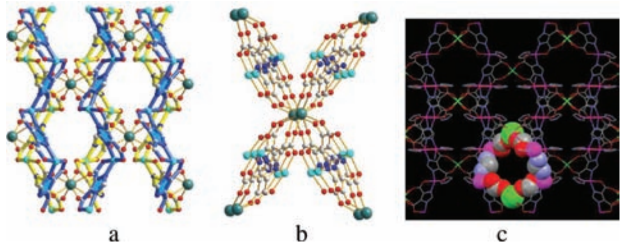

Figure 2. (a) Connection between the Eu^{3+} ions and Zn^{2+} chains. The chains of different color (yellow and blue) showing the zigzag chains formed by the Zn^{2+} ion and $imdc^{3-}$ ligand along the *c* axis. (b) Butterflylike structure formed by Eu^{3+} and the connected helical chains. Color scheme: cyan, Zn^{2+}; gray, C; blue, N; red, O; teal blue, Eu^{3+}. (c) 3D MOFs of **3** viewed along the *a*-axis direction. The 24-membered ring shown in the space-filling model indicates the position of the 1D channel. Color scheme: Eu^{3+}, green; C, gray; N, blue; O, red; Zn^{2+}, pink.

Viewed along the *a* axis, two Eu^{3+} ions with a distance of 10.621 Å along the *c* axis, four Zn^{2+}, and four COO, two NCN form a 24-membered ring (the ring in the space-filling model as shown in Figure 2c), which further induces the 1D channel in **3**. In the 1D channels are located cationic guests $[H(H_2O)_8]^+$. For the cation $[H(H_2O)_8]^+$, the O atoms are disordered and a protonated water cluster is obtained by charge balancing. The total void volume, V_{void}, within the complex without water molecules is 12% per unit volume determined by *PLATON*.[13]

The luminescent properties of the MOFs are of interest for solid-state lighting applications, in particular in structures where the ligand itself is luminescent. The photoluminescence properties of complexes **1**, **3**, and **5** were investigated at room temperature, as shown in Figure 3. The excitation (Figure S3 in the SI) and emission spectra (Figure 3a) of complex **1** are both similar to those of the ligand (Figure S4 in the SI), which is in accordance with the fact that there is no f–f transition for the La^{3+} ion. When excited at 354 nm, a broad emission centered at 430 nm was obtained, which can be attributed to the $\pi-\pi^*$ transition of the ligand. Its lifetime was measured from the decay profile (Figure S5a in the SI) by fitting with biexponential decay curves with $\tau_1 = 0.85 \pm 0.01$ ns and $\tau_2 = 6.04 \pm 0.04$ ns. It is in accordance with the existence of two ligands (Him and imdc), which both can emit at 425 nm. Complex **3** displays intense red luminescence. Its emission spectrum (Figure 3b) excited at 289 nm exhibited the characteristic narrow bands (594, 612, 650, and 700 nm) arising from the $^5D_0 \rightarrow {}^7F_J$ ($J = 1-4$) transitions of the Eu^{3+} ion. Among the peaks, the emission at 612 nm from the $^5D_0 \rightarrow {}^7F_2$ transition is the strongest, suggesting that the Eu^{3+} ion does not locate on an inversion center. The emission spectrum of the Tb^{3+} complex (Figure 3c) excited at 292 nm also exhibited the characteristic narrow bands (491, 545, 587, and 623 nm) arising from the $^5D_4 \rightarrow {}^7F_J$ ($J = 3-6$) transitions of the Tb^{3+} ion. The absence of the ligand-based emission in the fluorescence spectra of **3** and **5** suggests that the energy transfer from the ligand to the lanthanide center is very effective. The luminescent lifetimes of complexes **3** and **5** were measured from their respective decay profiles (Figure S5b,c in the SI) by fitting with monoexponential decay curves to be 1.956 ± 0.002 and 1.751 ± 0.003 ms, respectively. The longer lifetimes of **3** and **5** than the reported Eu^{3+} or Tb^{3+} complexes[11b,e] are indicative of our successful synthetic strategy because no water molecules are involved in coordination. The monoexponential fitting also indicates that the Eu^{3+} or Tb^{3+} ion possesses one single chemical environment in these complexes. Also, the intrinsic quantum yield (η) of the $^5D_0$ Eu^{3+} excited state could be estimated to be 41% based on the emission spectra and lifetime of complex **3**.[14] Considering that complexes **1**, **3**, and **5** emit the primary colors (blue, red, and green) and that they are isostructural, we expect to obtain white-light emission through the doping of Eu^{3+} and Tb^{3+} ions in the La^{3+} complex. A series of codoped complexes with different doping ratios were obtained. It was found that two excitation peaks (centered at 294 and 350 nm, respectively) appear in the excitation spectra of the codoped materials when the maximum intensity of the characteristic emission line of Eu^{3+} (612 nm) or Tb^{3+} (545 nm) was monitored (see Figure 4, inset), while only one broad peak centered at 350 nm was obtained when the blue emission based on the ligand (425 nm) was monitored. All of these facts show that when excited at 294 nm, the ligand can sensitize Eu^{3+}/Tb^{3+} emission effectively, and that when excited at 350 nm, the energy was only partially transferred to the emission level of Eu^{3+}/Tb^{3+}. This leads to residual emission due to the ligand. So, the partial self-emission from ligands, in combination with

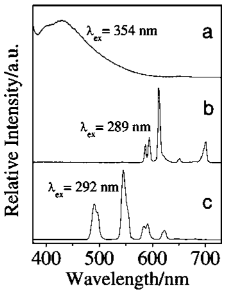

Figure 3. Emission spectra of complexes **1** (a), **3** (b), and **5** (c) in the solid state at room temperature.

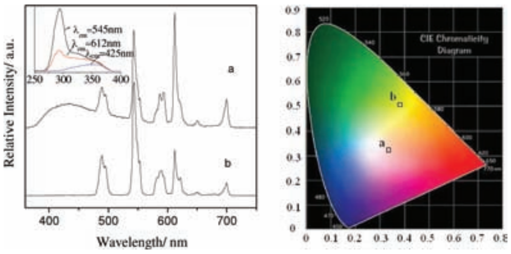

Figure 4. Emission spectra and the CIE chromaticity diagram of the codoped complex with a La, Eu, and Tb doping ratio of 50:22:28 excited at 350 nm (a) and 294 nm (b).

Eu^{3+} and Tb^{3+}, was utilized to obtain a pure white-light-emitting material. The CIE chromaticity coordinates for the La−Zn heterometallic compounds doped with Eu and Tb of different molar ratios excited at different wavelengths are listed in Table S1 in the SI. It can be seen that the MOF emission color can be fine-tuned by varying the codoping ratio and that when La^{3+}, Eu^{3+}, and Tb^{3+} were codoped in the molar ratio of 50:22:28, pure white-light emission (Figure 4) was obtained with CIE chromaticity coordinates (0.3285, 0.3306) upon excitation at 350 nm. However, by a shift of the excitation wavelength from 350 to 294 nm, a yellow-light emission was obtained with CIE chromaticity coordinates (0.3736, 0.5096). The codoped materials may therefore provide a promising and convenient approach to obtain uniform white-light-emitting or tunable luminescent MOF.

In summary, we have successfully synthesized five novel isomorphous heterometallic Ln−Zn MOFs under hydrothermal conditions in which decarboxylation of partial H_3imdc occurred. Eu^{3+} and Tb^{3+} ions were doped in the La−imdc−Zn skeleton to obtain a uniform pure white-light-emitting material. Also, yellow emission can also be obtained by shifting of the excitation wavelength.

■ ASSOCIATED CONTENT

S Supporting Information

Experimental procedures, additional figures, table of CIE chromaticity coordinates, and crystallographic data (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: xjzheng@bnu.edu.cn.

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(12) Crystal data for **1**: $C_{64}H_{74}La_2Zn_8N_{32}O_{48}$, M_r = 2860.54, orthorhombic, space group $P2_12_12$, a = 12.4243(5) Å, b = 18.9943(7) Å, c = 10.4978(5) Å, V = 2477.39(18) Å^3, Z = 1, D_c = 1.918 g cm^{-3}, μ = 2.852 mm^{-1}, F(000) = 1420, R_1 = 0.0665, wR_2 = 0.1403. Crystal data for **2**: $C_{64}H_{74}Pr_2Zn_8N_{32}O_{48}$, M_r = 2864.55, orthorhombic, space group $P2_12_12$, a = 12.3868(2) Å, b = 18.8433(3) Å, c = 10.6414(2) Å, V = 2483.79(7) Å^3, Z = 1, D_c = 1.916 g cm^{-3}, μ = 2.965 mm^{-1}, F(000) = 1411, R_1 = 0.0473, wR_2 = 0.0975. Crystal data for **3**: $C_{64}H_{74}Eu_2Zn_8N_{32}O_{48}$, M_r = 2886.66, orthorhombic, space group $P2_12_12$, a = 12.3030(4) Å, b = 18.5769(7) Å, c = 10.6212(4) Å, V = 2427.49(15) Å^3, Z = 1, D_c = 1.975 g cm^{-3}, μ = 3.322 mm^{-1}, F(000) = 1432, R_1 = 0.0537, wR_2 = 0.0966. Crystal data for **4**: $C_{64}H_{74}Gd_2Zn_8N_{32}O_{48}$, M_r = 2897.23, orthorhombic, space group $P2_12_12$, a = 12.2981(2) Å, b = 18.5449(3) Å, c = 10.6409(2) Å, V = 2426.84(7) Å^3, Z = 1, D_c = 1.983 g cm^{-3}, μ = 3.397 mm^{-1}, F(000) = 1434, R_1 = 0.0467, wR_2 = 0.0917. Crystal data for **5**: $C_{64}H_{74}Tb_2Zn_8N_{32}O_{48}$, M_r = 2900.58, orthorhombic, space group $P2_12_12$, a = 12.3365(1) Å, b = 18.4776(2) Å, c = 10.6822(1) Å, V = 2435.00(4) Å^3, Z = 1, D_c = 1.979 g cm^{-3}, μ = 3.476 mm^{-1}, F(000) = 1436, R_1 = 0.0303, wR_2 = 0.0782.

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