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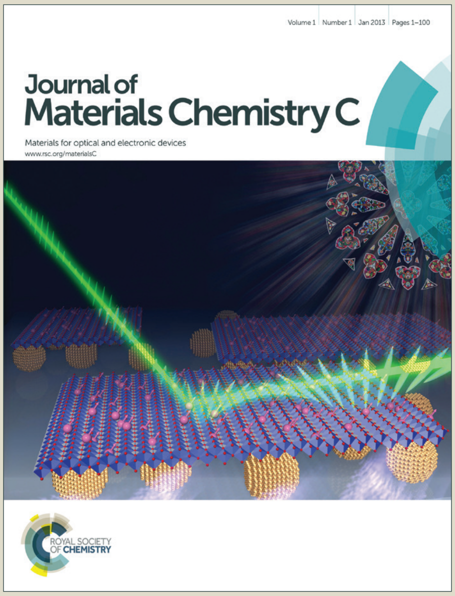

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High-efficiency white light-emitting lanthanide −organic framework assembled from 4,4′-oxybis(benzoic acid), 1,10-phenanthroline and oxalate

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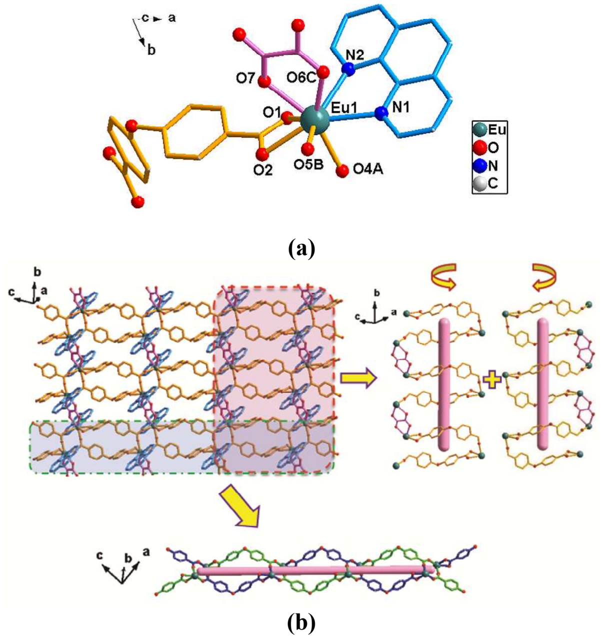
The metal−organic frameworks, [Ln(oba)phen(ox)$_{0.5}$]$_n$ (H_2oba = 4,4′-oxybis(benzoic acid), phen = 1,10-phenanthroline and ox = oxalate), have been designed and synthesized. The Eu(III)/Tb(III)- frameworks display highly efficient red / green emissions, respectively. A high-efficiency white light emission was realized through the doping of the Gd(III) framework with Eu(III)/Tb(III).

White-light-emitting diodes (WLED) have attracted extensive attention because of their potential applications in general lighting applications and display backlighting.[1] Generally, white light emission can be obtained by adjusting the ratio of red, green and blue (RGB) light-emitting components in the material.[1a] Metal−organic frameworks (MOFs) offer a unique platform for the development of white-light-emitting materials.[2] A variety of combinations of metal centers and organic ligands lead to the formation of MOFs with different structural characteristics and physical properties.[3,4] Lanthanide-based metal-organic frameworks (LnOFs) showed high luminescence efficiency, narrow bandwidth, and long luminescence lifetime. Therefore, LnOFs became good candidates in luminescence devices, fluoroimmunoassays, optical displays, including white-light-emitting materials.[2a-h, 4] Lanthanide luminescence is usually sensitized through the ‘‘antenna effect’’ from the light harvesting organic ligands.[5] In fact, the number of reported Ln(III) complexes with high luminescence quantum yields, is limited.[6] It is known that the emissive states of Ln(III) ions could readily be deactivated through nonradiative O–H, N–H and C–H vibrations from organic ligands and water or other solvent molecules, resulting in a remarkablely lower luminescence intensity for Ln(III) centres.[7] Thus, a suitable strategy to design and synthesize a high-efficiency emitting Ln(III) complexes still remain a great challenge to chemists. The choice of the proper ligands is crucial for the success of a rational design. The ligand that binds to Ln(III), can itself act as a high absorption, light-harvesting ligand for efficient emission sensitization.[4a]

In this work, we aim to design and synthesize new LnOFs to achieve high-efficiency white-light emissions. So, the new LnOFs, [Ln(oba)phen(ox)$_{0.5}$]$_n$ (Ln = Eu **1**, Gd **2**, Tb **3;** H_2oba = 4,4′- oxybis(benzoic acid); phen = 1,10-phenanthroline; and ox = oxalate), have been designed and synthesized. The notable feature is that these LnOFs do not contain solvent molecules. Among all the ligands in the complexes, H_2oba is a good ligand to construct various LnOFs with versatile bridging modes and is an efficient chromophore for the sensitization of Ln(III) luminescence.[8] Phen has rigidity, aromaticity and chelating capability. It acts as light harvesting antenna to sensitize metal cations.[9] The ox anion is utilized to prevent water molecules from binding to the Ln(III) ions, hence to improve the luminescence efficiency. The resulted Eu(III) and Tb(III) – complexes exhibit bright red and green emissions with high quantum yields of 50.91% for **1** and 41.7% for **3**, respectively. Notably, when the Eu(III) and Tb(III) are doped into the Gd(III) framework with appropriate ratios, significant white light emission with quantum yields up to 38.74% was achieved. However, high-efficiency white light emitting materials of MOFs have been rarely reported.[2a]

The complexes [Ln(oba)phen(ox)$_{0.5}$]$_n$ (Ln = Eu **1**, Gd **2**, Tb **3**) are isostructural (Table S1). Their phase purity was verified by elemental analysis, IR spectrum, powder X-ray diffraction (PXRD) determination (Fig. S1), and thermogravimetric analysis (TGA) (Fig. S2). The TGA result shows that the complexes are thermally stable up to about 248 °C under air atmosphere. The structures of **1**-**3** are significantly different from those of the previously reported oba complexes. [8] The notable feature is that the complexes do not contain solvent molecules. The comparison of crystal data (Table S2) in **1**-**3** shows that the corresponding distances of the Ln-O, Ln-N, and Ln…Ln decrease as the ionic radius of the metal becomes smaller in the order Eu(III) > Gd(III) > Tb(III), which is consistent with the lanthanide contraction. Herein only the structure of **1** is discussed in details here. Complex **1** has a 2D structure with one Eu(III) ion, one oba ligand, a half of ox ligand and one phen ligand in an asymmetric unit (Fig. 1). Each Eu(III) ion has a distorted square antiprism geometry (EuO_6N_2) formed by four oxygen atoms from three oba ligands, two oxygen atoms from ox and two nitrogen atoms from phen molecule (Fig. 1a). The bond lengths of Eu-O and Eu-N range from 2.315(4) to 2.469(4) Å and 2.562(5) to 2.568(5) Å, respectively. The ox ligands act as tetradentate bridges linking two



(a)

(b)

Fig. 1 (a) Coordination environment of complex **1**. (b) 2D structure by Eu-oba-ox or Eu-oba helical stranded helices. Symmetry codes: A: 1-x, 1-y, 1-z; B: 1+x, y, -1+z; C: 2-x, -y, -z.

different Eu(III) centers through the four oxygen atoms. The oba ligand displays an inter-ring twist of 83.32° and its two carboxylate groups are twisted relative to their benzene rings by 5.3° and 12.4°, respectatively. The two carboxylate groups of oba adopt μ_2:$\eta^1\eta^1$ and μ_1:$\eta^1\eta^1$ bridging coordination modes, connecting three Eu(III) ions. It is notable that the left- and right- double stranded helices are formed in a layer structure. The Eu-oba-ox helical strand is built with EuO_6N_2 units connected by oba and ox ligands, and it has a repeat unit consisting of three Eu(III) centers, one ox ligand and two oba ligands with a pitch of 10.787 Å along b axis (Fig. 1b). Thus, the structure can be described as the Eu-oba-ox double helices paralleling to the crystallographic b axis. Interestingly, the Eu-oba right- and left-handed double helices are observed along c axis. The Eu-oba helical motif is built from EuO_6N_2 units connected by oba likages. So, the 2D structure may also be described as the Eu- oba double helices via ox bridges along b axis. The distances between Eu(III) centres separated by oba ligands, double COO groups and ox anions are 14.859(8), 5.441(3) and 6.272(3)Å, respectively. The phen ligands occupy the coordination sites of the Eu(III) ions at both sides of the layer, preventing the structures from extending into higher dimensions. The resulted layers are stacked into the 3D architecture through C-H…O and π…π stacking noncovalent interactions (Fig. S3).

Solid-state photoluminescence property of complexes **1**-**3** and free ligands were investigated. Complex **2** displays a broad emission spectrum centered at 432 nm in the blue spectral region (380–520 nm) ascribed to the ligands (Fig. S4). The luminescent quantum yield of complex **2** is 4.77%. Because the first excited level of Gd(III) ion is at the high energy level (around 32150 cm^{-1}), energy transfer from the ligand to Gd(III) is not possible.[4b,c] The emission spectrum of the Gd(III) complex is not the characteristic f–f emission of Gd(III) in the visible range. However, complexes **1** and **3** emit red and green light, respectively, under UV light. The emission intensities of **1** and **3** are controlled by excitation wavelengths. The luminescent properties of **1** and **3** were investigated at the maximum excitations of the ligands (350 nm for **1** and 356 nm for **3**) and at f–f absorption (395 nm for **1** and 379 nm for **3)** (Fig. S5). Their emission spectra are essentially identical except for the intensity. However, the intensity at f–f absorption is less than that at the ligand excitation maxima, indicating an efficient ligand-to-metal energy transfer process. This is also confirmed by the excitation spectra of **1** and **3** (Fig. S5, insert). The emission spectrum of **1** consists of characteristic $^5D_0 \rightarrow {}^7F_J$ (J = 0−4) transitions of Eu(III) at 579, 591, 613, 650, and 698 nm, respectively. The emission at 613 nm from the $^5D_0 \rightarrow {}^7F_2$ induced in the electric dipole transition is the strongest, suggesting that the chemical environment around Eu(III) ion does not locate on an inversion center. Complex **3** shows the characteristic narrow emission peaks at 490, 544, 584 and 619 nm, corresponding to the $^5D_4 \rightarrow {}^7F_J$ (J = 6−3) transitions of Tb(III). The $^5D_4 \rightarrow {}^7F_5$ emission at 544 nm is the most prominent one. The $^5D_0$ Eu(III) and $^5D_4$ Tb(III) lifetime values are 0.88 ± 0.06 ms for **1** and 0.69 ± 0.03 ms for **3** from their luminescent decay profiles by fitting the data with a monoexponential curve (Fig. S6), indicating that Eu(III)/Tb(III) ions have one kind of symmetrical site of Ln(III) ion in the complexes.[7f] Notably, complexes **1** and **3** exhibit high fluorescence quantum yields of 50.91% and 41.7% respectively. Furthermore, the blue light emission from ligands in **1** and **3** completely disappears, which indicates the ligands as light-harvesting chromophores effectively transfer energy to Eu(III)/Tb(III) ions. The result indicates that the oba and phen are good antenna ligands.[8a,9] Furthermore, the coordination sphere of Ln(III) ion is fully occupied by the ligands, preventing the quenching effects of solvent water molecules, which proves that the luminescence intensity of **1** and **3** can be further enhanced by eliminating the solvents' quenching effect. The quantum yield is an important parameter to characterize the Ln(III) luminescence. Hence those complexes can be used as promising fluorescent materials.

We utilized oba, phen and ox ligands to obtain Eu(III) and Tb(III)-complexes with highly efficient red and green luminescence, respectively. With an appropriate ratio, it is possible to obtain high-efficiency white light emission using complexes **1, 2** and **3** as red, blue and green emitter components. The $Gd_{0.91}Eu_{0.05}Tb_{0.04}(oba)phen(ox)_{0.5}$ doped complex has thus been synthesized, and its X-ray spectrum has been recorded. The emission spectra of the doped complex were memorized. The metal-centered red emissions at 592 and 613 nm from Eu(III), green emissions at 490 and 544 nm from Tb(III) and the blue emission centered at 420 nm from the ligands are observed (Fig. 2). Noteworthy, the luminescent intensity at 613 nm corresponding to the $^5D_0 \rightarrow {}^7F_2$ transition of Eu(III) is lower (1.2-fold) in this doped complex than that in complex **1** (Fig. S7). This is mainly due to the lower concentration of the Eu(III) ion. However, the emission at 545 nm corresponding to the $^5D_0 \rightarrow {}^7F_2$ transition of Tb(III) in this doped complex shows a 10.3-fold lower intensity compared to that in complex **3** (Fig. S7), indicating the Tb(III) to Eu(III) energy transfer. Furthermore, the lifetimes of Eu(III) and Tb(III) emissions in the doped complex are 0.93 ± 0.05 ms and 0.41 ± 0.03 ms, respectively (Fig. S6). Compared to the pure Eu(III)/Tb(III)- complexes **1** and **3**, the doped complex has shorter emission lifetime of the Tb(III) but longer emission lifetime of the Eu(III), further proving that the energy transfer from the Tb(III) to Eu(III) centers indeed takes place. This type of intermetallic energy transfer mechanism has been reported.[2e,8a,10] The emission intensities of the doped complex are determined by the excitation wavelength (Fig. S8). Interestingly, when excited at 370 nm, the complex emits white light. The CIE chromaticity coordinate (Fig. 2, insert) A(0.333, 0.335) is close to the standard white light (0.333, 0.333) according to 1931 CIE coordinate diagram. The color rendering index (CRI) and corresponding color temperature (CCT)

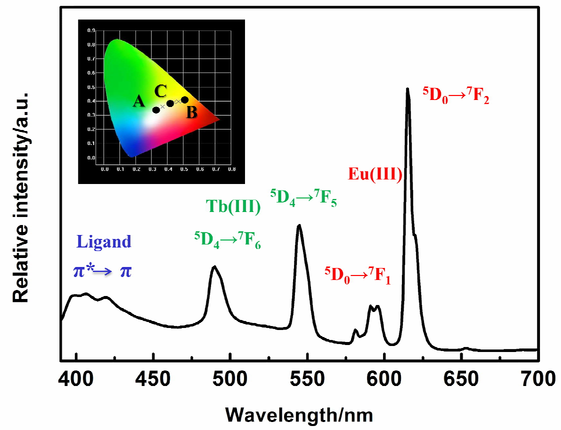


Fig. 2 Emission spectra of the Gd$_{0.91}$Eu$_{0.05}$Tb$_{0.04}$(oba)phen(ox)$_{0.5}$doped complex excited at 370nm (Insert: The CIE chromaticity diagram).

are 84 and 5454K, respectively. The white light emission has high quantum yield of 38.74%. Nevertheless, only one example of white light emission of MOFs with the high quantum yield was reported so far.[2a] High-quality white-light illumination requires a source with CIE coordinates at (0.333; 0.333), CCT in the range of 2500–6500 K, and CRI above 80.[4b,c] Therefore, we provide a promising high-quality white light emitting material based on the MOFs. In addition, under excitation wavelengths of 330 - 360 nm, the CIE coordinates change from B(0.506, 0.403) to C(0.415, 0.382), falling within the yellow light region. Therefore, the luminescence of the LnOF can be tuned from yellow to white with the change of excitation wavelength.

In summary, we have developed a rational design strategy to construct new LnOFs utilizing the oba, phen and ox ligands. The Eu(III)- /Tb(III)- containing complexes show good photoluminescence properties. Tunable yellow-to white light emission has been obtained by co-doping Eu(III) and Tb(III) ions into the Gd(III) framework and by adjusting the excitation wavelength. Notably, a significant white light emission with quantum yield of 38.74% is realized.

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High-efficiency white light-emitting lanthanide –organic frameworks assembled from 4,4′-oxybis(benzoic acid), 1,10-phenanthroline and oxalate

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High-efficiency white light emission was developed through the Gd(III)/ Eu(III)/Tb(III) doped complex with 4,4′-oxybis(benzoic acid), 1,10-phenanthroline and oxalate.