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A white-light-emitting LnMOF with color properties improved *via* Eu^{3+} doping: an alternative approach to a rational design for solid-state lighting†

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The intrinsic white-light-emitting properties of a lanthanide metal–organic framework that approach requirements for solid-state lighting are easily improved by incorporating minute quantities of red-emitting Eu^{3+} into the host framework by virtue of the iso-structural character of the La^{3+} and Eu^{3+} compounds and efficient sensitization of ligands toward Eu^{3+} ions.

White-light-emitting diodes (WLEDs) have broad applications in solid-state lighting (SSL) for the purpose of conserving energy and miniaturization of equipment.[1] At the present time, commercially available WLEDs are based on the blue InGdN/GaN LEDs encapsulated with a yellow-emitting phosphor (YAG:Ce^{3+}) coating.[2] But the WLEDs have drawbacks such as poor color rendering index (CRI) and high correlated color temperature (CCT) which limit their widespread commercialization in general lighting market. With the development of LED chip technology, the shift of emission bands of LED chips from blue light to near-UV light can offer higher energy to pump the phosphor. There has been great interest shown in the employment of near-UV InGaN LEDs with triple-wavelength RGB phosphors to produce WLEDs.[3] Unfortunately, the combination of different phosphors brings difficulties in the integration of individual materials and may not give rise to uniformly disperse and thermodynamically stable compositions. Thus, generating white light from a single phosphor to avoid the mixing problems is one of the current academic interests.[4]

Tremendous efforts have been dedicated to the search for white-light-emitting materials including metal-doped or hybrid inorganic materials,[5] nanomaterials,[6] organic molecules,[7] and metal compounds.[8] Due to the exceptional tenability, structural diversity and very rich luminescent emitting sources of metal–organic frameworks (MOFs),[9] there has been great interest devoted to white-light-emitting MOFs in recent years. But it is still difficult to target white-light-emitting MOFs because the blue and yellow light emitters or blue, green and red light emitters should compensate exactly through the dichromatic and trichromatic approaches, respectively. Single-phase white light emitters based on MOFs have seldom been achieved.[10] On the other hand, a few known examples show good color rendering properties and high luminous efficiency to meet the criteria for SSL use.[11] High-quality white light illumination requires a source with the CIE (the Commission International ed'Eclairage) coordinate approaching the ideal value (0.333, 0.333), CRI above 80, and CCT between 2500 and 6500 K.[1,12] To design a white-light-emitting MOF material according to high-quality illumination requirements is a great challenge for chemists. In this study, we present a novel lanthanide metal–organic framework (LnMOF) material featuring intense white emission, with color properties improved by incorporation of minute quantities of red-emitting Eu^{3+} into the host framework solid.

The material was obtained by the hydrothermal reaction of $La(NO_3)_3$, H_2MBDC (isophthalic acid), NaSTP (sodium 4-(2,2′:6′,2″-terpyridin-4′-yl)benzenesulfonate) with a molar ratio of 1 : 1 : 1 at 180 °C for 4 days. Good agreement between the calculated and experimental powder X-ray diffraction (XRD) patterns verifies the purity of the as-synthesized sample. Thermogravimetric analysis (TGA) measurements showed that the title material has excellent thermal stability as no strictly clean weight loss step occurred below 450 °C. The structure was determined using single crystal X-ray crystallography, studied as [La(MBDC)(STP)] featuring a 3D polymeric structure.‡ The La^{3+} center is in a monocapped square antiprismatic environment and nine-coordinated to three terpyridyl nitrogen atoms, one oxygen atom from the sulfonic group of ligand STP and five oxygen atoms from carboxylate groups of ligands MBDC. The two metal centers are connected by four carboxylate groups exhibiting two types of coordination modes (bidentate bridging and chelating bridging), forming a dimer building block. As shown in Fig. 1C and D, each dimer building block as a 6-connected node is linked by ligands MBDC to four blocks with

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† Electronic supplementary information (ESI) available: Details about the preparation of NaSTP and its ^1H NMR (DMSO), study on the charge transfer properties and corresponding quantum chemical calculations, calculation of photophysical parameters for the Eu(III) compound, XRD, PL. CCDC 969324, 969325 and 974705. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c3cc48344d

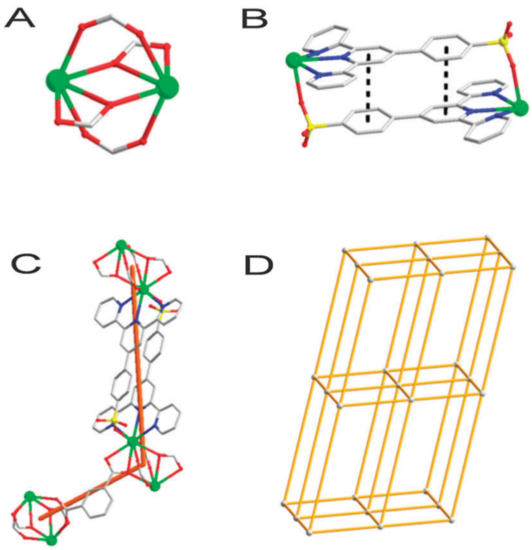

Fig. 1 Crystal structure of [La(MBDC)(STP)]: (A) dimer building block, (B) π–π attractions between the parallel ligands STP, (C) two types of linking modes between the building blocks, (D) topological representation.

a separation of 10.007 Å, forming a 2D planar structure, and further linked by parallel ligands STP to another two blocks with a separation of 16.490 Å, resulting in the dense three-periodic structure featuring a PCU topology. It is notable that there are strong π–π attractions between the parallel ligands STP (Fig. 1B). The outer phenyl rings stack with the central pyridyl rings in face to face mode (3.639 Å centroid–centroid). The phenyl ring is twisted with respect to the adjacent pyridyl ring about the interannular C–C bond by 10°, smaller than that observed in related systems.[13]

PL emission spectra were collected on the as-synthesized solid. It is remarkable that the title material appears as intense white light to the naked eye when irradiated with the whole near-UV (350–400 nm) light, while some of the coordination compounds show only white emission when excited at certain wavelengths.[8a,10b] As shown in the measured emissions (Fig. 2), the title compound shows broad linker-based emission with two peaks located at around 430 nm and 550 nm. In addition, the temperature-dependent emission spectra (Fig. S4, ESI†) showed that the emission intensity becomes weaker with increase in temperature, but returns to the initial state when the sample is cooled to room temperature. The stability is attributed to the dense 3D polymeric structure of the title material.

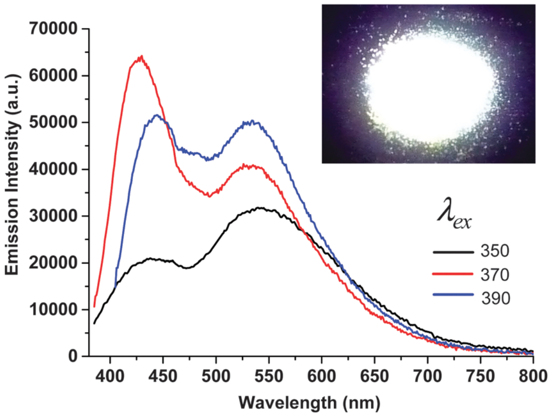

Fig. 2 Emission spectra of [La(MBDC)(STP)] excited between 350 and 390 nm; inset: optical image of the white light emission in the powder sample upon excitation at 370 nm.

It is noticeable that the free ligand NaSTP only shows one emission in solution, but double emission in solid state (Fig. S5, ESI†). By analysis of the crystal structure of the title compound and the results of electronic structure calculations (ESI†), we could deduce that the high-energy emission was due to intraligand charge transfer (ILCT) of STP and low-energy emission should be relative to π–π attractions between the parallel ligands STP. The absolute luminescence quantum yields (QY) of the title compound and the free ligand in solid state measured upon excitation at 370 nm are 11% and 0.8%, respectively. The enhancement of emission could be attributed to the planar character *via* coordination of STP to metal ions which increases the rigidity of the ligand and thus reduces the loss of energy by radiationless decay of the intraligand emission excited state.[9]

Assessment of the white light property for the as-synthesized material revealed a low CRI, which does not approach the set target CRI of ∼90% for SSL use.[1] The low CRI is due to the red region missing in the emission spectra. In order to improve the intrinsic color properties, we introduced a narrow-band, red emission component into the LnMOF system *via* Eu^{3+} doping. The notable feature is that the La^{3+} and Eu^{3+} compounds are isostructural, which makes it feasible to codope them as a uniform compound, resolving some of the critical integration problems.

The pure Eu^{3+} compound [Eu(MBDC)(STP)] exhibits bright red photoluminescence emission due to the internal 4f–4f transitions in Eu^{3+} (Fig. 3). The narrow-band peaks of Eu^{3+} at around 590, 614, 650 and 696 nm are attributed to transitions from $^5D_0$ to ^7F_J ($J = 1, 2, 3, 4$) respectively. The absence of emissions of ligands MBDC and STP was evident from the emission spectrum, which is typically diagnostic of sensitization of ligands toward Eu^{3+} ions. Calculations showed that the efficiency of sensitization η_{sens} is up to 73% (Table 1).[14]

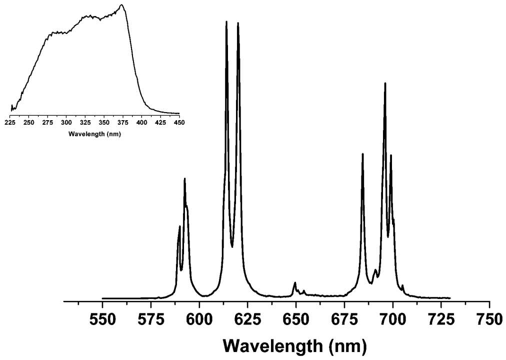

Fig. 3 Emission spectrum of [Eu(MBDC)(STP)]; inset: excitation spectrum measured at 614 nm emission.

Table 1 Photophysical parameters of [Eu(MBDC)(STP)] in the solid state under ligand excitation (373 nm)

τ_{obs} (ms)	QY (%)	τ_{rad} (ms)	Φ_{Ln} (%)	η_{sens} (%)
1.65	41	2.92	56	73

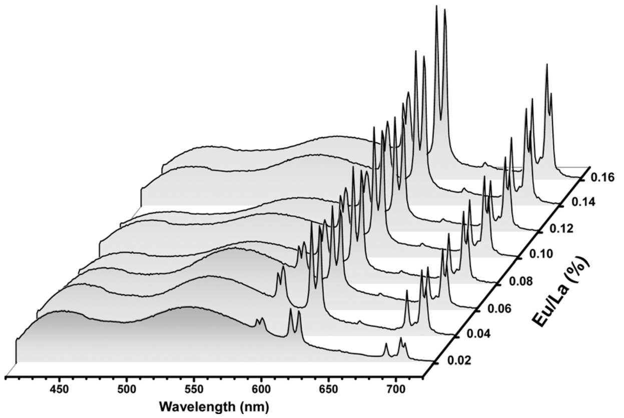

Fig. 4 Emission spectra of target concentrations of the Eu-doped LnMOF upon excitation at 390 nm.

The absolute luminescence quantum yield (QY) measured under an excitation of 373 nm is 41%, which is higher than that of the normal Eu^{3+} compounds.[9] It is well known that water molecules are often involved in coordination to meet the high coordination number of lanthanide ions, which leads to fluorescence quenching.[15] The bright photoluminescence of the Eu^{3+} compound could be attributed to beneficial effect of the ancillary ligand MBDC: not only are high-energy vibrations removed from the inner coordination sphere, increasing observed lifetime, but the symmetry around the Eu^{3+} ion is decreased, rendering the f–f transitions less forbidden, and a better positioning of the excited state with one of the first ligand STP increases the efficiency of energy transfer.[16]

PL spectra were collected for all concentrations of the Eu-doped LnMOF (Fig. 4). In a typical doping experiment, the amount of La was kept the same as that for the pristine material. Because of efficient sensitization of ligands toward Eu^{3+} ions, emission of the Eu-doped sample shows red photoluminescence of Eu^{3+} ions and has almost no characteristic double emission peaks of the host framework when the molar ratio Eu/La is more than 0.2%. Table 2 and Table S1 (ESI†) exhibit color properties of the 0.02–0.16% Eu-doped samples upon the excitations at 390 nm and 370 nm, respectively. Apart from the double emissions of the host framework, narrow-band emissions of Eu^{3+} are seen, which become stronger with the increase of Eu^{3+} concentration. All of the 0.02–0.16% Eu-doped samples appear as white light to the naked eye and the color properties are easily improved to approach requirements for SSL application. In general, the Eu-doped samples exhibit better chromaticity coordinates, higher CRI and cooler CCT compared with that of the pure La^{3+} compound, accordingly with high-quality white light illumination requirements. Moreover, the Eu-doped samples show good emission efficiency. For example, the absolute luminescence quantum yield of the 0.10% Eu-doped sample measured under an excitation of 390 nm is 12%, higher than the most of reported white-light-emitting coordination compounds.[10,11a]

Table 2 Color properties of targeted concentrations of the Eu-doped LnMOFs upon excitation at 390 nm

Eu/La (%)	CRI	CCT (K)	*x*	*y*
0	71	10 068	0.265	0.317
0.02	77	7423	0.293	0.346
0.04	84	6209	0.316	0.353
0.06	80	5580	0.330	0.378
0.08	89	5144	0.342	0.368
0.10	93	5404	0.334	0.355
0.12	91	5016	0.345	0.364
0.14	88	4266	0.373	0.387
0.16	94	4411	0.364	0.364

In the end, it needs to be mentioned that Nenoff *et al.* have recently reported broad-band direct white light originating from an indium compound SMOF-1 and the color properties approaching requirements for SSL were optimized *via* Eu^{3+} doping, opening a new path for the rational design of alternative materials for SSL applications.[11a] Herein, we report a white-light-emitting LnMOF material with higher luminous efficiency. The intrinsic white-light-emitting properties can be easily improved by incorporating minute quantities of red-emitting Eu^{3+} into the host framework by virtue of the isostructural character of the La^{3+} and Eu^{3+} compounds and efficient sensitization of ligands toward Eu^{3+} ions.

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Notes and references

‡ Crystal data for [Eu(MBDC)(STP)]: $C_{29}H_{18}N_3O_7SEu$, M_r = 704.48, monoclinic, space group $P2_1/c$, a = 16.365(4) Å, b = 11.123(3) Å, c = 16.421(4) Å, β = 119.828(3)°, V = 2592.9(10) Å^3, Z = 4, D_c = 1.805 g cm^{-1}, μ(Mo-Kα) = 2.555 mm^{-1}, T = 293(2) K, 20 079 observed reflections, 5886 (R_{int} = 0.0327) unique reflections and 370 parameters yielded wR_2 = 0.1341 and R_1 = 0.0408 based on 4896 reflections with $I > 2\sigma(I)$, GOF = 1.050, CCDC 969324; crystal data for [La(MBDC)(STP)]: $C_{29}H_{18}N_3O_7SLa$, M_r = 691.44, monoclinic, space group $P2_1/c$, a = 16.490(5) Å, b = 11.144(3) Å, c = 16.625(4) Å, β = 120.16(2)°, V = 2641.5(12) Å^3, Z = 4, D_c = 1.739 g cm^{-1}, μ(Mo-Kα) = 1.751 mm^{-1}, T = 293(2) K, 20 273 observed reflections, 5950 (R_{int} = 0.1036) unique reflections and 370 parameters yielded wR_2 = 0.1518 and R_1 = 0.0460 based on 3957 reflections with $I > 2\sigma(I)$, GOF = 1.053, CCDC 969325.

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