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Pure white-light and yellow-to-blue emission tuning in single crystals of Dy(III) metal–organic frameworks†

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Direct white-light emission was first achieved in a single phase material of a Dy(III) metal–organic framework, which also shows tunable yellow-to-blue photoluminescence upon variation of excitation wavelengths.

White-light-emitting diodes (WLEDs) have wide applications in lasers, indicators, backlights, displays, *etc.*[1,2] Apart from the traditional method of blending multi-LEDs (for example, mixing LEDs with three primary colors red, green and blue, *i.e.* RGB), single component (SC) white-light-emitting materials provide an alternative approach to fabricate WLEDs characteristic of uniform and well-balanced color, as well as easy-manipulation and low-cost.[3–6] In recent years, lanthanide containing metal–organic frameworks (Ln-MOFs) have aroused special interest in the design of SC white-light and color-tunable materials, taking advantages of the intrinsic multiple-colored f–f emissions of Ln atoms with efficient antenna effect, sharp band and long lifetime.

To reach this goal, Ln atoms that could emit pure visible lights, *e.g.* red Eu(III) and green Tb(III) emissions, have been most frequently applied. In principle, if these two primary colors are further combined with blue luminescence, which is often contributed by the ligand-based emission, white-light emitting phosphor can be achieved in a single phase Ln-MOF containing mixed Eu and Tb centers.[7–10] So far, most of the white-light emitting Ln-MOFs are constructed on the basis of such trichromatic RGB strategy; however, studies on the white-light emission of Ln-MOFs with other Ln(III) centers remain quite rare.[11] This is probably due to the fact that visible color emissions from other Ln atoms, such as Sm(III) and Dy(III), are usually rather weak. Dy(III) possesses appropriate f–f transitions which are able to emit colors in blue (480 nm), yellow (573 nm) and red (661 nm) regions upon adequate excitation. Usually yellow emission dominates over the other two emissive colors. Therefore, if a Dy-MOF can be designed to emit yellow (Dy-based) and blue (ligand-based) colors simultaneously, white-light emission can be achieved through a BY dichromatic strategy on the balance of the blue (B) and yellow (Y) colors. This will provide an alternative way to utilize Ln-MOFs as potential candidates of single-phase white phosphors. Nevertheless, due to the less efficient luminescence in most Dy-MOFs compared with the Eu/Tb counterparts,[12] little attention has been paid to the photoluminescence (PL) of Dy-MOFs, especially SC white-light emitting and color tuning properties.

We herein report a multiple-color photoluminescent Dy-MOF, [Dy(TETP)(NO₃)₃]·4H₂O (**1**·4H₂O, **TETP** = 1,1′,1″-((2,4,6-triethylbenzene-1,3,5-triyl)tris(methylene))tris(pyridin-4(1H)-one)), in which the ligand **TETP** can play dual functions. On one hand, it can effectively sensitize Dy centers to produce yellow light; on the other hand, it is strongly blue luminescent with its blue emission in Dy-MOF being sufficient to balance yellow emission of Dy to generate white-light, offering a Commission Internationale de l'Eclairage (CIE) chromaticity coordinate of (0.33, 0.35). Moreover, by varying the excitation wavelengths, yellow-to-blue PL color-tuning can be readily accomplished depending on the variation of the intensity ratios between the characteristic yellow emission of Dy atoms and the blue luminescence of the **TETP** ligand.

Complex **1**·4H₂O was prepared through a simple wet chemical method by reaction of **TETP** ligand and Dy(NO₃)₃·6H₂O salt in a water–acetone solvent system, affording colorless crystals in reasonable yield (58%). The phase purity of the bulky sample of **1**·4H₂O has been confirmed by powder X-ray diffraction in comparison with its single-crystal data simulation (Fig. S1, ESI†). Complex **1** crystallizes in the space group *Pna*2₁ with the asymmetric unit consisting of one Dy(III), one **TETP** and three coordinating NO₃⁻ groups. The Dy(III) centers lie in a tricapped trigonal prismatic geometry, coordinated by three **TETP** through terminal O and three NO₃⁻ groups in chelating mode (Fig. 1a). Meanwhile, each tripodal **TETP** connects

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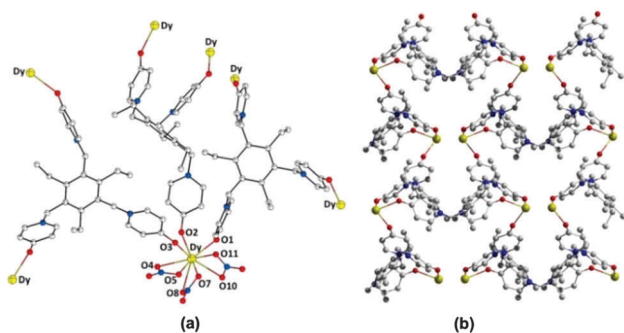
Fig. 1 Crystal structure of complex **1**: (a) coordination environment of the central Dy(III) atom and surrounding ligands, and (b) 3D framework along the *a* axis, the solvent molecules, counter anions and H atoms are omitted for clarity (yellow for Dy, blue for N, red for O, and gray for C atoms, respectively).

Fig. 2 Solid-state PL spectrum of **1** (λ_{ex} = 365 nm). The emission curve is superimposed on the white-light spectrum. Inset: photograph of white emissive Dy-MOF in a sample vial and CIE chromaticity coordinates.

three different Dy(III) with metal and ligand centers as nodes and pyridone arms as linkers, thus generating an intricate three-dimensional (3D) framework in (10, 3)-d (or **utp**) topology[13] as seen in Fig. 1b.

The UV-adsorption of ligand **TETP** in solution shows a strong $\pi\pi^*$ band at around 265 nm, and relatively weak intra-ligand charge transfer (ILCT)[10] above 300 nm originating from pyridone donors. These ligand transitions are merged and even expanded beyond 400 nm in the solid-state (Fig. S2, ESI†). The solid-state emission spectrum of **TETP** displays a broad asymmetric emission band at around 430 nm with decay lifetimes τ = 1.2 and 2.2 ns (Fig. S3, ESI†), revealing the blue nature of the ligand-centered (LC) luminescence which can only be excited above 300 nm, thereof, dominated by ILCT. Upon excitation at 365 nm at room temperature, the solid sample of **1** displays multiple emission peaks at 430, 480, 573 and 661 nm. The first broad band centered at 430 nm is attributable to the reserved ILCT emission of **TETP**, while the three narrow peaks originate from f–f transitions between the Dy(III) lowest emitting state $^4F_{9/2}$ and ground levels of $^6H_{15/2}$, $^6H_{13/2}$ and $^6H_{11/2}$. The nature of these emissions has been confirmed by the measurement of their decay dynamics. The 430 nm peak has a decay feature with τ = 0.8 and 3.2 ns, typical of LC emission. And the main peak at 573 nm has a decay lifetime of 31 μs, characteristic of Dy-centered emission (Fig. S4, ESI†). Remarkably, combination of these four emissions in complex **1** is properly balanced to result in white-light output, offering a CIE coordinate of (0.33, 0.35) which is close to that of pure white light (0.33, 0.33). The collected emissions of **1** (λ_{ex} = 365 nm, detection span: 400–800 nm) give an absolute quantum yield of ~7%, which is among the highest value for the Dy(III) complex.[14] The white-light can also be directly detected by the naked eye (Fig. 2, inset).

The PL mechanism and energy transfer (ET) processes involved in this Dy-MOF may be complicated as illustrated in Scheme 1. The PL spectrum of isostructural Gd-MOF (Fig. S1 and S5, ESI†) indicates a triplet energy level of **TETP** at ~23 000 cm^{-1} (T = 77 K, τ = 0.7 and 6.9 μs), which is adequate for ET to the $^4F_{9/2}$ level of Dy (~21 500 cm^{-1}).[14] Therefore, after **TETP** absorbs the UV light at either $\pi\pi^*$ (singlet transition, <300 nm) or ILCT (300–400 nm) bands, it can transfer the energy directly[15] or *via* its triplet state to the Dy center to generate the metal-centered (MC) emission;
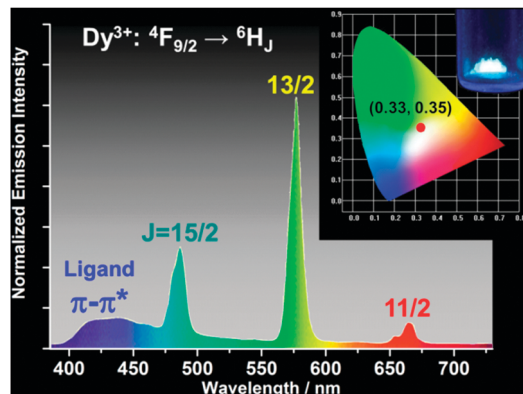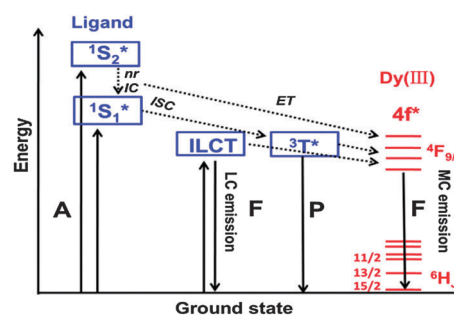

Scheme 1 Schematic representation of energy absorption, migration, emission (plain arrows) and dissipation (dotted arrows) processes in complex **1**. LC, ligand-centered; MC, metal-centered; ILCT, intra-ligand charge transfer; S, singlet state; T, triplet state; A, absorption; F, fluorescence; P, phosphorescence; nr, nonradiative; ISC, intersystem crossing; ET, energy transfer.[10b]

however, the blue LC emission can only be excited in the ILCT spectral region. These ETs are subject to influence of excitation energy. As shown in excitation spectra of **1** (Fig. S6, ESI†), MC emission (573 nm) can be effectively sensitized *via* ligand singlet adsorption (<300 nm), or moderately by ILCT and hypersensitized f–f transitions (300–400 nm), while this ILCT excitation in the 300–400 nm region also generates LC emission. Monitoring at 430 nm reveals a wide excitation band resembling that of pure **TETP**, and shows a structured profile with a few troughs corresponding to f–f adsorptions of Dy(III). This implies that ILCT excitation has no efficient antenna effect as singlet transition of **TETP**, leading to LC emission accompanied with f–f emissions. Therefore, fine color-tuning is achievable through a dichromatic approach upon variation of excitation wavelengths. At proper wavelength, the relative intensity between MC and LC emissions can be balanced to give white-light output directly from the single phase of Dy-MOF.

Based on the above discussion, this Dy-MOF can be considered to contain two kinds of emissive centers, *i.e.* Dy atoms emitting mainly yellow (573 nm) color and **TETP** components emitting blue color (430 nm), of which the luminescent intensities depend on the ET efficiency at varied excitation wavelengths. As a consequence,
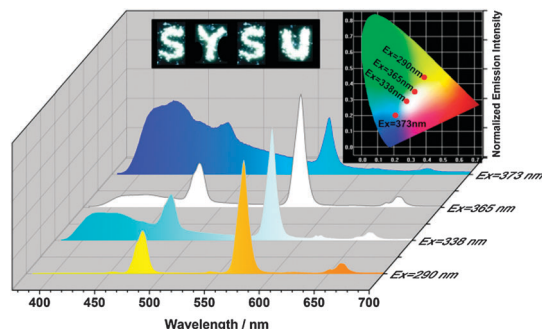
Fig. 3 Emission spectra of **1** excited at different λ_{ex}. Insets: chromaticity coordinates of **1** at different excitation wavelengths (λ_{ex} = 290, 338, 365 and 373 nm; CIE = (0.39, 0.44), (0.28, 0.29), (0.33, 0.35) and (0.21, 0.20)) and photographs of the name of our University SYSU written with the white-light emitting **1**.

the PL of **1** is tunable from yellow to blue according to variation of excitation wavelengths. As seen in Fig. 3 and Fig. S6 (ESI†), when excited at 265 or 290 nm, the LC blue emission is negligible, while f–f emissions of Dy dominate. This denotes an effective ET from ligand antenna to Dy centers at ligand singlet excitation, resulting in a CIE coordinate of (0.39, 0.44) in the yellow region. In contrast, at an excitation of 373 nm, the ligand-to-metal ET becomes less efficient, while LC blue emission predominates over Dy emission. The resulting CIE coordinate is (0.21, 0.20), falling in the blue region. In between these two wavelengths, the excitation at 338 nm leads to bluish-white emission with a CIE coordinate of (0.28, 0.29), while the excitation at 365 nm brings pure white-light emission at (0.33, 0.35) as mentioned before. When excited at 77 K, a similar emission feature and color-tuning property can be achieved for this Dy-MOF (Fig. S7, ESI†), and the short lifetimes (0.9 and 5.5 ns) at 430 nm indicate that the nature of LC emission at this temperature is similar to the fluorescence at room temperature, other than phosphorescence as in Gd-MOF.

In summary, we have successfully synthesized a 3D Dy-MOF showing tunable yellow-to-blue PL by variation of excitation wavelengths. It is noteworthy that pure white-light emission has been realized by this Dy-MOF in a single phase for the first time. In contrast to the common strategy to utilize mixed-metal Ln-MOFs (*e.g.* Eu and Tb) for white-light emission, this provides an alternative way to use homogeneous Ln-MOFs as single-phase white-light phosphors, which will make the preparation and manipulation even easier.

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