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Syntheses, structures and tunable luminescence of lanthanide metal-organic frameworks based on azole-containing carboxylic acid ligand

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A B S T R A C T

Design and synthesis of a series of isostructural lanthanide metal-organic frameworks (LnMOFs) serving as phosphors by coordinate the H_2TIPA (5-(1*H*-tetrazol-5-yl)isophthalic acid) ligands and lanthanide ions is reported. The color of the luminescence can be tuned by adjusting the relative concentration of the lanthanide ions in the host framework **GdTIPA**, and near-pure-white light emission can be achieved.

1. Introduction

White light emitting diodes (WLEDs) are of low energy consumption, high efficiency, and have long lifetimes and wide applications in solid-state lighting, displays, and other photonic devices [1–3]. For decades, many solid state materials have been explored and developed as white light emitting sources. These include inorganic oxide, inorganic quantum dots, nitride, organic molecules, polymers, and metal complexes [4–12]. Common approaches, such as dichromatic, tri-chromatic, and tetra-chromatic methods are often used to generate white light [13–15]. However, tri-chromatic white light emitting materials have recently been attracting much attention due to their excellent color rendering properties and color stability, as well as high efficiency [16–19].

Metal-organic frameworks (MOFs) have been widely investigated in view of their structural diversity and porosity. They are promising as light emitting materials with a wide range of colors provided by inorganic metal centers, organic linkers, guest solvent molecules, as well as metal-organic charge transfer [20–36]. In addition, the emitted color can also be readily modulated by different lanthanide ions and their concentrations, guest species, and excitation wavelengths [37–41]. These advantages support the MOF approach for constructing white light emitting MOFs.

To date, several examples of white light emitting MOFs have been reported [42–49]. These MOF materials can incorporate lanthanide dopants (for example, Eu^{3+}, Tb^{3+}, Dy^{3+}) into the host framework and lead to white light emission when excited at given wavelengths [42–49]. Lanthanides metal-organic frameworks (LnMOFs), by comparison, are excellent candidates for designing light emitting materials because of their high photoluminescence efficiency, narrow bandwidth, and wide range of lifetimes [50]. Furthermore, isostructural mixed LnMOFs could be synthesized via in situ doping because of the comparability in the chemical reactivity and coordination behavior of the lanthanide ions. As a consequence, the color of the emitted light can be modulated by the constituent lanthanide ions and their relative concentrations [16–19].

It is well known that the RGB (red, green, blue) light emitters should mix properly to generate pure white light. But, it is still a challenging task to explore suitable LnMOFs with white light emission. Here we report the design and synthesis of a LnMOF **GdTIPA**:Tb^{3+}, Eu^{3+} as the phosphor which can emit white light. A reference schematic representation for the sensitization process is shown in Scheme 1. The Gd^{3+} MOFs usually exhibit ligand-centered visible emission in the blue light region because of the high energy of the lowest-lying emission level (32,150 cm^{-1}) of Gd^{3+} ion [50]. The Tb^{3+} and Eu^{3+} ions can display the characteristic $^5D_4 \rightarrow {}^7F_4$ and $^5D_0 \rightarrow {}^7F_2$ emissions, which correspond to the green and red light, respectively. Therefore, the emission color can be tuned through incorporating the Tb^{3+} and Eu^{3+} ions into the

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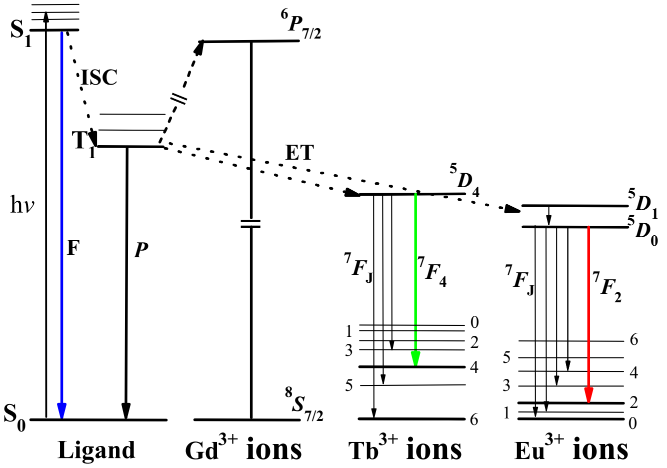

Scheme 1. Schematic representation for the sensitization process in luminescent LnMOFs (selected levels displayed). Abbreviations: S=singlet; T=Triplet; *hv*=energy absorption; ISC=intersystem crossing; ET=energy transfer; F=fluorescence; P=phosphorescence. The green and red arrows are represent the characteristic $^5D_4 \rightarrow {}^7F_4$ (Tb^{3+} ions) and $^5D_0 \rightarrow {}^7F_2$ (Eu^{3+} ions) transitions. (For interpretation of the references to color in this figure, the reader is referred to the web version of this article.)

Gd^{3+} MOFs host framework, and white light emission can be realized with reasonable doping ratios [48,50]. It is worth noting that with this scheme, the organic ligand as the blue light emitter is closely related to the emission color of the as-synthesized MOFs, and its antenna effect for the Ln^{3+} ions is extremely important. This is strongly associated with the lowest triplet energy state of ligand due to the interactions between the ligands and Ln^{3+} ions, including radiation, nonradiative energy transfer and decay, quench etc [38].

In this study, we chose H_2TIPA (5-(1*H*-tetrazol-5-yl)isophthalic acid) as the organic linker, which results in blue emission under UV excitation, to construct the LnMOFs. Its triplet excited state energy is 25,257 cm^{-1} (calculated with the time-dependent density function theory, Fig. S11), which located in the range of 22,000 to 27,000 cm^{-1} that can sensitize the Eu^{3+} and Tb^{3+} ions simultaneously [36,38,41]. H_2TIPA is then used to construct a new family of LnMOFs, $Ln(TIPA)(H_2O)_5$ (we name these MOFs as **LnTIPA**; Ln=Sm^{3+}, Eu^{3+}, Gd^{3+}, Tb^{3+}, Dy^{3+}) with the 1D structure, where white light is emitted. By controlling the relative concentration of the Eu^{3+} and Tb^{3+} ions in the host framework, the color of the luminescence of **GdTIPA**:Tb^{3+}, Eu^{3+} can be modulated, and white light-emission can indeed be achieved.

2. Experimental section

2.1. Materials and measurements

All the solvents and regents were commercially available and can be used directly. The 5-(1*H*-tetrazol-5-yl)isophthalic acid was purchased from Jinan Henghua Sci. & Tec. Co., Ltd. and used without further purification. Thermogravimetric analyses (TGA) were obtained using a Netzsch TG209F3 at a heating rate of 5 °C/min in nitrogen atmosphere. Infrared spectrum (IR) was measured at a Thermo Fisher Nicolet iS10 spectrometer with KBr pallets. Elemental analyses were carried out on an EA1112 microelemental analyzer for C, H, and N. Powder X-ray diffraction (PXRD) patterns were performed on a X'Pert PRO diffractometer with Cu Kα (λ=1.542 Å) radiation and collected in the $2\theta = 5-60°$ range at room temperature. All the luminescence spectra for the solid-state samples were measured by a Hitachi F4600 fluorescence spectrometer at 750 V for the photomultiplier tube voltage, with a scan speed of 240 nm/min, and the slit widths were 2.5 nm and 1.0 nm, corresponding to the excitation and emission spectra of LnTIPA (Ln=Eu, Tb), and 2.5 nm and 2.5 nm for the other samples, respectively. The luminescence decay curve were obtained using an Edinburgh Instrument F920 spectrometer at 2.0 nm for both the excitation and emission slits, and the peak count and the channel are 2000 and 1000, respectively. The quantum yields of the samples were measured by an Edinburgh Instrument F920 spectrometer with an integrating sphere of 150 mm diameter and $BaSO_4$ coating, and calculated with the formula

$$\Phi_{\text{overall}} = \frac{A_H}{R_{ST} - R_H} \tag{1}$$

where A_H is the integral area of emission spectrum of the sample, and R_{ST} and R_H are the diffuse-reflectances corresponding to the reference standard and the sample, respectively. The estimated errors are within 5% for both the quantum yields and luminescent lifetimes.

2.2. Synthesis of LnTIPA materials

The identical procedure was used for the preparation of all the compounds including the mixed-lanthanide ones except for the different starting lanthanide salts. The synthesis of $Eu(C_9H_4O_4N_4)(H_2O)_5$ (**EuTIPA**) is thus presented here in detail as a representative: 5-(1*H*-tetrazol-5-yl)isophthalic acid (H_2TIPA, 24.0 mg, 0.1 mmol), $Eu(NO_3)_3(H_2O)_6$ (45.5 mg, 0.1 mmol), 1 M NaOH (0.2 mL) and water (8 mL) were sealed into a 25 mL Teflon cup, and the resulting solution had been kept at 160 °C for 2 days and cooled it to room temperature slowly. After that, colorless rod-like crystals were grown and can be collected by filtration and washed with DMF and H_2O (35.6 mg, 75% based on H_2TIPA). **EuTIPA**, Anal. calcd for $C_9H_{14}N_4O_9Eu$ (%): C, 22.80; H, 2.95; N, 11.82; found: C, 23.15; H, 2.66; N, 11.85. IR (KBr pallet, cm^{-1}): 3608(w), 3469(s), 2289(w), 1625(s), 1606(s), 1550(s), 1501(m), 1443(s), 1391(s), 1345(s), 1231(s), 1194(m), 1148(m), 1102(w), 953(m), 914(m), 788(s), 757(w), 701(m), 565(w), 487(m). **SmTIPA**, Anal. calcd for $C_9H_{14}N_4O_9Sm$ (%): C, 22.87; H, 2.99; N, 11.86; found: C, 23.24; H, 2.69; N, 11.78. IR (KBr pallet, cm^{-1}): 3609(w), 3470(s), 2288(w), 1624(s), 1606(s), 1550(s), 1502(m), 1444(s), 1392(s), 1346(s), 1232(s), 1195(m), 1148(m), 1102(w), 954(m), 913(m), 789(s), 756(w), 700(m), 563(w), 485(m). **GdTIPA**, Anal. calcd for $C_9H_{14}N_4O_9Gd$ (%): C, 22.55; H, 2.94; N, 11.69; found: C, 22.84; H, 2.75; N, 11.76. IR (KBr pallet, cm^{-1}): 3606(w), 3467(s), 2287(w), 1626(s), 1607(s), 1551(s), 1500(m), 1444(s), 1390(s), 1346(s), 1232(s), 1193(m), 1149(m), 1103(w), 955(m), 916(m), 786(s), 758(w), 703(m), 563(w), 488(m). **TbTIPA**, Anal. calcd for $C_9H_{14}N_4O_9Tb$ (%): C, 22.47; H, 2.93; N, 11.64; found: C, 22.82; H, 2.56; N, 11.72. IR (KBr pallet, cm^{-1}): 3606(w), 3469(s), 2285(w), 1627(s), 1604(s), 1550(s), 1500(m), 1443(s), 1392(s), 1344(s), 1232(s), 1193(m), 1149(m), 1101(w), 954(m), 915(m), 787(s), 756(w), 701(m), 565(w), 486(m). **DyTIPA**, Anal. calcd for $C_9H_{14}N_4O_9Dy$ (%): C, 22.30; H, 2.91; N, 11.56; found: C, 22.75; H, 2.46; N, 11.46. IR (KBr pallet, cm^{-1}): 3606(w), 3469(s), 2287(w), 1625(s), 1608(s), 1552(s), 1503(m), 1443(s), 1390(s), 1342(s), 1234(s), 1194(m), 1149(m), 1103(w), 954(m), 912(m), 785(s), 757(w), 699(m), 565(w), 485(m).

Compounds containing mixed lanthanide ions, these include **GdTIPA**:Tb^{3+}, **GdTIPA**:Eu^{3+} and **GdTIPA**:Tb^{3+}, Eu^{3+} were synthesized similarly to **GdTIPA** except for using a mixture containing the desired lanthanide nitrate.

2.3. X-ray collection and structure determination

Single-crystal data of **EuTIPA** was measured with a Bruker