



Enhancing luminescence in lanthanide coordination polymers through dilution of emissive centers

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ABSTRACT

A Ln-adipate metal-organic framework templated with 4,4'-bipyridine (GWMOF-6) was synthesized with Eu(III) or Tb(III) ions with various concentrations of optically inert Gd(III) ion in order to evaluate the effects of diluting the emissive metal center on the efficiency of luminescence. The doping ratios of Ln:Gd (Ln = Eu or Tb) showed that of the ratios studied, the 50:50 system had among the highest quantum yields (Eu = 3.9%, Tb = 7.6%) with increasing lifetimes as Gd(III) concentration increased. A 50:50 Eu:Tb system was also synthesized and showed to be more efficient than the Eu:Gd systems ($\Phi = 15.3\%$), with an exceptionally high energy transfer efficiency (80%) from the 5D_4 state of the Tb(III) ion to the 5D_1 and 5D_0 energy levels of the Eu(III) ion.

1. Introduction

Coordination polymers (CPs) and metal-organic frameworks (MOFs) have had a great surge of interest over the past decade with applications ranging from cancer detection and drug delivery [1–3] to separations, sensing, and catalysis [4–7]. The wide range of applications of these materials can be attributed to their large pore sizes, high surface areas, and thermal and chemical stabilities [8–12]. These, and the ability to design MOFs by changing the metal center or organic linker for desired applications have made them ideal candidates for a myriad of applications.

Lanthanides (Ln(III)), when incorporated in MOFs, can invoke interesting properties due to the unique nature of the Ln ion. With radially contracted f-orbitals, these metals commonly exhibit large coordination numbers, giving rise to unique structures not obtainable by their transition metal counterparts. Since lanthanides do not vary considerably in size, the ability to interchange Ln ions for tailoring the behavior of MOFs is advantageous, particularly in the field of luminescent MOFs [13–18]. Our group focuses on the luminescent properties of these ions and their roles when incorporated into extended network solids such as MOFs [19–22].

Unfortunately luminescence in Ln ions is inefficient, which is attributed to symmetry and often spin forbidden processes [23,24]. To address this challenge, the antenna effect can be employed to transfer energy from the absorbing organic species to the Ln ion [25,26]. During the process of the antenna effect, energy is absorbed by an organic moiety and is transferred to the Ln ion through a series of energy transfer processes, where emission occurs as sensitized luminescence.

Heteronuclear lanthanide coordination polymers have shown great promise in numerous applications, particularly in color tuning, multimodal imaging, and photonic devices [27–29]. By adjusting the ratio of Tb/Yb ions, groups have produced NIR emissive materials, where the Tb transfers the energy received from the organic antenna to the energy level of the lower lying emissive species [30–32]. In a similar manner, the Tb ion can act as a bridge between the excited state of an antenna and Eu in mixed Eu/Tb systems [33–37].

In these aggregated compounds, Ln centers are often in close proximity. This can induce a non-radiative energy transfer mechanism via an intermetallic energy transfer process, and has been noted in CP and MOF systems [29]. At distances less than approximately 10 Å between Ln centers, the emission of one Ln can be re-absorbed by a neighboring Ln, resulting in an overall reduction of the luminescence efficiency [38]. Investigations into the luminescent behavior of Eu and Tb ions within MOFs by doping them within an optically inert Ln matrix can be used to produce highly luminescent materials by spacing out emissive centers to achieve the distance required to reduce intermetallic energy transfer [39]. Understanding Ln/Ln' interactions and aggregation effects is crucial for exploiting CPs and MOFs for luminescent applications.

To this end, a series of isostructural MOFs (the previously reported GWMOF-6 [33,40]) were synthesized with adipic acid, 4,4'-bipyridine, and varying Ln ion mixtures with the general formula $[Ln_xLn_y(C_6H_8O_4)_3(H_2O)_2] \cdot 4,4'$ -bipy (where $Ln_x = Eu$ or Tb , and $Ln_y = Gd$) to investigate the effects of concentration quenching with an optically inert Ln ion. Gd(III) was selected as the optically inert host matrix since its emissive level ($^6P_{7/2}$) lies too high in energy to typically

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be populated by organic antennae and since its ionic radius is very similar to that of trivalent Eu and Tb.

Further investigation with an optically active spacing ion in an isostructural Tb/Eu system was employed to give insight into the role of Ln-Ln sensitization. These systems were characterized with powder X-ray diffraction and photophysical measurements.

2. Experimental

2.1. Synthesis

In a typical synthesis, a mixture of $\text{Eu}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (207 mg, 0.60 mmol), 4,4'-bipyridine (95 mg, 0.60 mmol), and adipic acid (86 mg, 0.60 mmol) was added to 1.7 mL of water. Ammonium hydroxide (aqueous, concentrated) was then added (60 μL) to adjust the pH to ~ 9 . The vessel was then tightly sealed and heated autogenously at 180 $^\circ\text{C}$ for 3 days (72 h). After naturally cooling to room temperature, the white cloudy liquid was decanted from crystalline solids. These solids were thoroughly washed with water and ethanol and left to air dry. Isostructural compounds with varying lanthanide ion concentrations were synthesized in an otherwise identical manner.

2.2. Powder X-ray diffraction characterization

Powder X-ray diffraction experiments were performed with an Olympus BTX II Benchtop XRD using $\text{Co K}\alpha$ ($\lambda = 1.79 \text{ \AA}$) radiation from a range of $5\text{--}55^\circ 2\theta$. PXRD patterns were compared to those calculated from single crystal data to confirm phase identification (Figs. 1, 2, and 6).

2.3. Photophysical characterization

Emission spectra along with quantum yield and lifetime measurements were measured using a Perkin Elmer LS55 Fluorescence Spectrometer with a Xe pulsed lamp source at room temperature ($23 \pm 2^\circ\text{C}$). All spectra were measured with a 5.0/5.0 nm excitation and emission slit widths in phosphorescence mode at zero delay time and with a scan speed of 100 nm/min. Samples were ground with poly (methyl methacrylate) (PMMA) to reduce the possibility of self-absorbance. Solid-state reflectance values were measured using a 60 mm integrating sphere on a Perkin Elmer Lambda 850 UV/Vis Spectrometer by scanning the emission monochromator through a specific excitation

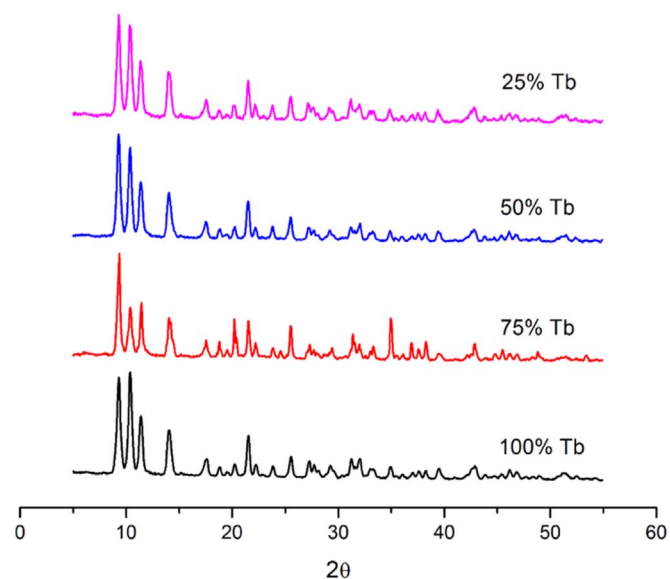


Fig. 2. Powder X-ray diffraction pattern of Tb:Gd GWMOF-6 analogs at 100:0, 75:25, 50:50, and 25:75 doping ratios.

wavelength. The solid-state quantum yields were determined against pyrene ($\Phi_{\text{ST}} = 61\%$ at 313 nm) in PMMA as described by Brill [41], with

$$\Phi_x = \frac{1 - R_{\text{ST}}}{1 - R_x} \times \frac{I_x}{I_{\text{ST}}} \times \Phi_{\text{ST}} \quad (1)$$

where Φ is the quantum yield, R is the diffuse reflectance, and I is the integrated emission spectrum of sample (x) and standard (ST). Integrations were performed using OriginPro 8.1 software. The quantum yield of anthracene ($\Phi = 23\%$) was determined congruently against the pyrene standard with all Ln samples at an excitation of 313 nm to ensure validity of the quantum yields. Lifetime measurements were collected at 617 nm for Eu(III) and 545 for Tb(III) systems ($\lambda_{\text{ex}} = 285 \text{ nm}$) using the BioLight Fluorescence Application software and analyzed using OriginPro 8.1.

3. Results and discussion

3.1. PXRD and elemental analysis

A series of isostructural GWMOF-6 compounds were successfully synthesized with Eu:Gd and Tb:Gd with approximate ratios of 25:75, 50:50, 75:25, and 100:0, and phase identity was confirmed with PXRD (Figs. 1 and 2). These ratios and phase purity were further confirmed with elemental analysis (ICP, Galbraith Laboratories, Knoxville, TN; see Tables 1–3). Attempts to synthesize compounds with other optically inert lanthanide ions (La(III), Ce(III), and Lu(III)) were unsuccessful. We speculate that the ionic radii of these compounds may not be suitable to incorporate into this particular structure [13].

3.2. Photophysical results

For emission spectra, all samples were in equimolar concentrations and excited at a wavelength of 285 nm (Figs. 3 and 4) [42]. In the doped Eu:Gd system, the compound with the highest intensity was the 50:50, followed by the 25:75, 75:25, and the system with the lowest emission intensity was the pure Eu(III) compound. In the Tb:Gd system, the 50:50 ratio also showed higher emission intensities than the other systems, followed by the 75:25, 25:75, and 100:0. This trend is slightly different than that of the Eu system, where the 25:75 was the second highest in intensity. This difference can be attributed to the energy level of the Eu(III) ion ($17,270 \text{ cm}^{-1}$) residing at a lower energy than the Tb(III) ion ($20,460 \text{ cm}^{-1}$) [43], which may make the Eu(III) ion more

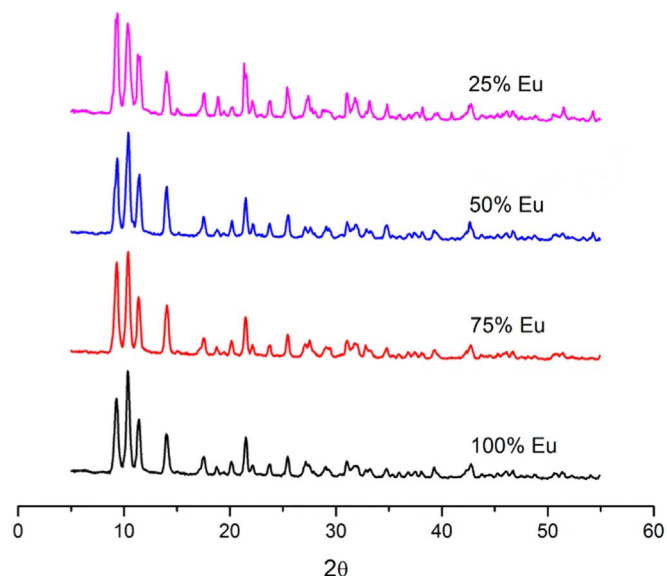


Fig. 1. Powder X-ray diffraction pattern of Eu:Gd GWMOF-6 analogs at 100:0, 75:25, 50:50, and 25:75 doping ratios.

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