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Coordination Modulation Induced Synthesis of Nanoscale Eu$_{1-x}$Tb$_x$–Metal-Organic Frameworks for Luminescent Thin Films

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Metal organic frameworks (MOFs) or porous coordination polymers (PCPs) are hybrid inorganic-organic materials made from an assembly of metal ions with organic linkers.[1–3] Their well-defined porosity and tunable chemical functionality make them extremely attractive for applications in gas storage,[4,5] catalysis,[6] and separation.[7] Apart from their use as bulk materials, MOFs are also potential candidates for thin film applications. Pioneering studies on MOF films or membranes have already been reported in the literature.[8–13] However, the reported approaches are either highly complex in preparation routes or ineffective in producing smooth and dense MOF thin films.[14] Therefore, developing a scalable method for MOF film preparation is definitely needed.

Recently, lanthanide metal–organic frameworks (Ln-MOFs) have received special attention due to their unusual coordination characteristics and exceptional optical and magnetic properties arising from 4f electrons.[15–21] Their specific applications in thin film devices, however, depend greatly on the ability to control the size and shape of individual Ln-MOFs crystallites as well as their assembly on various supporting surfaces. Thus, it is very important to synthesize individual nanoscale Ln-MOFs crystallites that are useful for Ln-MOFs film preparation. To date, however, only a few approaches for the fabrication of nanometer-sized metal organic frameworks (NMOFs) are developed. These include reverse microemulsion,[22,23] microwave-assisted synthesis[24] and the use of capping agents.[25,26] Here, we report an easily scalable method using carboxylate salts as capping reagent for the synthesis of nanosized Ln-MOFs crystals. We also show that these particles are well suited to make Eu$_{1-x}$Tb$_x$-MOF films using the spin-coating deposition method. These films exhibited fascinating luminescence properties and efficient Tb^{3+}-to-Eu^{3+} energy transferability.

Our strategy for reducing the size of Ln-MOFs crystals to diameters of around 100 nm uses the addition of capping reagents with the same chemical functionality as the linkers. Typically, nanoscale Ln(BTC)(H$_2$O),[19] hereafter denoted as Ln-MOFs, where Ln = Dy^{3+}, Eu^{3+}, or Tb^{3+} and BTC = 1,3,5-benzenetricarboxylate, were prepared by heating a solution containing LnNO$_3$·xH$_2$O (0.1 mol), BTC (0.1 mol), sodium carboxylate (0-0.3 mol), DMF (8 mL) and H$_2$O (4 mL) in a sealed beaker at 60 °C for 12-72 h. Sodium carboxylates (sodium formate, sodium acetate, or sodium oxalate) were used as capping reagent to control the resulting crystal size and morphology. After synthesis, the particles were isolated by centrifugation and washed several times with DMF and ethanol. The XRD diffraction patterns of all samples agree well with literature suggesting phase purity and an unaffected MOF structure (see Supporting Information, Figure S1). Moreover, the diffraction peaks are sharper with addition of sodium formate and sodium acetate, implying that these two capping reagents can also improve the crystallinity of Ln-MOFs. Similar effects have also been observed by Kitagawa et al.[26] In the absence of a capping reagent, Ln-MOFs are pillar-like rods with a length of 60 ± 10 μm (**Figure 1a**). With the addition of the capping reagent, both the shape and size of Ln-MOFs are drastically changed. Addition of sodium formate results in fairly uniform bean-shaped nanocrystals with a length and width of 125 ± 25 nm and 100 ± 15 nm, respectively (Figure 1c, d). Smaller crystals, 90 ± 15 nm in length and 75 ± 10 nm in width, are obtained, when sodium acetate is used as additive (Figure 1e, f). However, sodium oxalate, leads to the needle-shaped crystals (Figure 1b) and the length of the crystals with lengths between 30–60 μm.

The role of carboxylic salts in reducing the particle size is attributed to its modulating effect on the coordinating interactions between the metal ions and organic linkers. In the initial stage of synthesis, Ln cations coordinate to carboxylic groups, which are not only from organic linker BTC but also from carboxylic salt added. The crystal growth is, therefore, impeded in a very early stage allowing more nuclei to be formed. Moreover, the competitive coordination of the capping reagent is speculated to regulate the rate of crystal growth.[26] In the case of sodium acetate and sodium formate, their appropriate interactions with Ln cations slow down the rate of crystal growth leading to smaller and relatively uniform nanoparticles.

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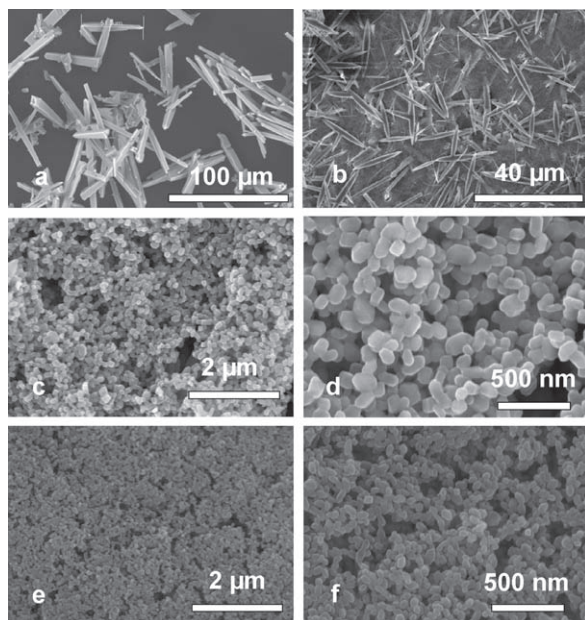www.advmat.de

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Figure 1. SEM images of Ln-MOFs crystals synthesized: (a) without capping reagent; with addition of (b) sodium oxalate, (c,d) sodium formate and (e,f) sodium acetate.

Figure 2. SEM images of $Tb_{0.5}Eu_{0.5}$-MOF film viewed from: (a) the surface and (b) the cross section.

However, sodium oxalate presents a minor effect on the size of crystals. This is because oxalic acid is a dicarboxylate acid that can be an organic linker for MOFs. The growth of Ln-MOF crystals may continue even when the oxalate terminates the Ln-MOF crystals. When more sodium oxalate was added, we did observe the appearance of another phase from both scanning electron microscopy (SEM) images and XRD diffraction patterns.

Using sodium acetate as capping reagent, we have also successfully synthesized bimetallic $Eu_{1-x}Tb_x$-MOF nanocrystals by replacing $LnNO_3 \cdot xH_2O$ in the synthesis precursor with a mixture of $Tb(NO_3)_3 \cdot 5H_2O$ and $Eu(NO_3)_3 \cdot 5H_2O$. The resulting nanocrystals have a similar size and morphology as single metallic Ln-MOFs, and the XRD diffraction patterns (Supporting Information, Figure S2) are nearly identical, indicating the unchanged morphology and structure.

Following the successful preparation of the nanocrystals, glass-supported luminescent $Eu_{1-x}Tb_x$ -MOF films were prepared by spin-coating. Typically, nanocrystals of $Eu_{1-x}Tb_x$ -MOF were redispersed in DMF. The concentration of nanocrystals was in the range of 10-25 mg/mL. The suspension was then centrifuged at 4000 rpm for 10 min to remove big particles before it was spun onto a precleaned 2 cm × 2 cm ITO glass. A Laurell spin-coater was used and the spin rate was 1000 rpm for 60 s. The solvent adsorbed was removed by heating films at 100 °C for 12 h after spin-coating. The film thickness could be controlled by the nanocrystal concentration in the suspension and the spin-coating rate.

Figure 2 shows SEM images of a typical $Eu_{1-x}Tb_x$ -MOF film (~15mg/mL, spin-coated 2 times). The film surface is smooth, continuous, and defect-free over a large area (Figure 2a). From the cross-sectional view shown in Figure 2b it can be seen that the film is dense and compact with a thickness of ~8 μm.
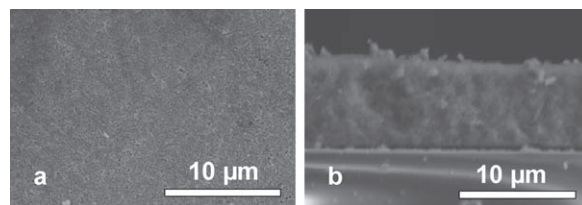
Exposure of the films in an ultrasonic bath in de-ionized water for 5 min did not result in visible detachment of the film from the ITO glass support indicating strong interactions between the film and the support and among the nanocrystals. It has to be noted that cracks are formed on MOF films coated on normal glass (Supporting Information, S3). Formation of cracks on normal glass is due to the relative rough surface and the lack of strong chemical bonds between Ln-MOFs and normal glass. Energy-dispersive X-ray (EDX) analysis of $Eu_{1-x}Tb_x$-MOF films confirmed the presence of europium and terbium in the samples. The EDX spectra also revealed that the atomic ratios of Tb/Eu are 2.75, 2.44, 1.95, 1.46, 1.02, 0.40, and 0.30, which agrees well with the original ratio (3.0, 2.7, 2.0, 1.5, 1.0, 0.4, and 0.26) in the precursor solution.

The photoluminescent (PL) spectra of $Eu_{1-x}Tb_x$-MOF films are compiled in **Figure 3**. The photoluminescence peak located at 540 nm corresponds to the $^5D_4 \rightarrow {}^7F_5$ transition of the Tb^{3+} ions in the green region.[17] The two main peaks at ca. 589 and 615 nm are assigned to the $^5D_0 \rightarrow {}^7F_1$ and $^5D_0 \rightarrow {}^7F_2$ transitions of the Eu^{3+} ions, respectively. The intensity of the peak at 540 nm changes with Tb^{3+}/Eu^{3+} ratio, suggesting the existence of Tb^{3+}-to-Eu^{3+} energy transfer and the typical emission peaks of Tb^{3+} disappear completely at $Tb^{3+}/Eu^{3+} = 1$ (Figure 3e), indicating the highest efficiency of Tb^{3+}-to-Eu^{3+} energy transfer. Furthermore, the colors in the fluorescent images of films are consistent with calculated results (Supporting Information, S4).
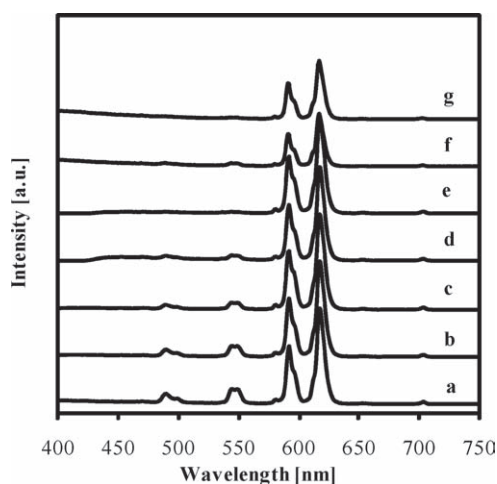

Figure 3. Photoluminescent spectra of as-prepared $Eu_{1-x}Tb_x$-MOF films with Tb^{3+}/Eu^{3+} mol ratio of: (a) 2.75, (b) 2.44, (c) 1.95 (d) 1.46, (e) 1.02, (f) 0.40 and (g) 0.30.

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In summary, the presented capping method with moderately strong coordinating carboxylates presents a general method using carboxylate salts as a capping agent for the synthesis of single or bimetallic Ln-MOFs nanocrystals. The small crystals can be used to synthesize continuous, smooth $Eu_{1-x}Tb_x$-MOF films with high mechanical stability via spin-coating deposition. This indicates sufficient open coordination to facilitate strong bonding between MOF crystals. The films have strong luminescent properties and efficient Tb^{3+}-to-Eu^{3+} energy transferability and hence are potential candidates for applications in the field of color displays, luminescence sensors, and structural probes. The generality and simplicity of both NMOFs synthesis and MOFs film preparation approaches should allow the design of other MOFs films for various application purposes.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements

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