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Surfactant-thermal method to synthesize a new Zn(II)-trimesic MOF with confined $Ru(bpy)_3^{2+}$ complex

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ABSTRACT

A surfactant-thermal method was used to prepare a new zinc-1,3,5-benzentricarboxylate-based metal-organic framework (ZJU-100) with confined $Ru(bpy)_3^{2+}$ (RuBpy) complex by using surfactant PEG 400 as reaction medium. The RuBpy molecules were encapsulated between the 2-D sheets in ZJU-100. ZJU-100 showed bathochromic shift in the steady-state emission spectrum and increased emission lifetimes relative to RuBpy molecules. The extended lifetime is attributed to the reduced nonradiative decay rate due to the stabilization of RuBpy within the rigid MOF framework. These results represent the first example of MOF with confined complex synthesized by surfactant, indicating that the surfactant-thermal method could offer exciting opportunities for preparing new MOFs host/guest materials with novel structures and interesting luminescent properties.

1. Introduction

Metal-Organic Frameworks (MOFs) have attracted great attention due to their promising applications in gas storage, separation, catalysis and sensors [1–15]. In particular, the regular pores/channels of MOF materials make them excellent platforms to incorporate fluorescent guest molecules towards potential applications in solid-state emission devices [16–21]. Compared with individual counterparts, MOF host/guest materials offer several advantages. The homogeneous distribution of the fluorescent molecules within MOF matrices can avoid high concentration chromophores induced self-absorption and thus enhance the fluorescent performance [20,22,23]. In addition, MOF host matrices offer higher mechanical, thermal and chemical stability for the guest molecules [24]. Moreover, the immobilization of guest complex in the MOF matrices reduces the environment pollution and operation risk.

On the other hand, the surfactant-thermal method, using surfactant instead of tranditional organic solvents as the reaction media, has been emerging as a new type of unique strategy for growing crystalline materials, such as zeolites and oxochalcogenides [25–30]. Recently, Zhang's group has reported the application of surfactants in controllable synthesis of crystalline MOFs with diverse structures, which initiated the very promise of surfactant-thermal method in growing crystalline MOF materials [31–34]. Compared with traditional organic solvents, the surfactants not only have higher chemical stability and lower vapor pressure, but also show multifunctional properties such as acidic, basic, neutral, anionic, cationic, etc. [35,36]. In addition, the diverse structure of surfactant contains both hydrophilic and hydrophobic groups, which could efficiently increase the interactions with MOFs, leading to a variety of different MOF structures. More importantly, the surfactants are low cost, environmentally friendly and readily accessible, making them ideal media for growing MOFs. However, surfactant-thermal method has not been manipulated to synthesize crystalline fluorescent MOF host/guest materials.

Herein, we report the first example of a fluorescent Ru(II)tris(2,2'-bipyridine) (RuBpy) complex confined within a new zinc-1,3,5-benzenetricarboxylate (**ZJU-100**) MOF prepared in surfactant PEG as reaction media. The fluorescent properties of RuBpy@**ZJU-100** are studied in detail. Polyethylene glycol (PEG) is used in growing RuBpy@**ZJU-100** as reaction media for its low toxicity, biodegradability and tunable melting point [37,38].

2. Experimental section

2.1. Materials and general methods

All chemicals were purchased from Alfa Aesar, TCI chemical and Aldrich and used without further purification. Polyethylene glycol

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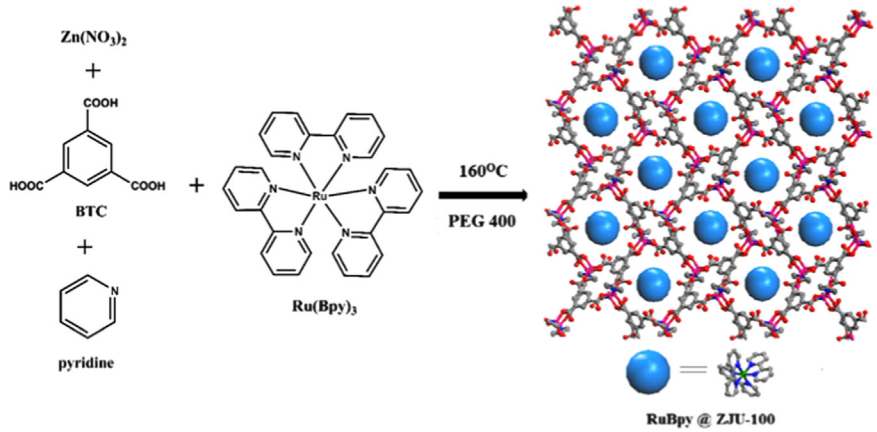

Scheme 1. Scheme diagram shows the preparation of RuBpy@ZJU-100 .

Table 1
Summary of crystal and structure refinement data for RuBpy@ZJU-100.

Compound	**RuBpy@ZJU-100**
Empirical formula	$C_{58}H_{42}N_8O_{14}RuZn_2$
Formula weight	1306.81
T (K)	103(2)
λ	1.54178
Crystal system	Monoclinic
Space group	$P2(1)/n$
a	17.7510(9)
b	17.5007(11)
c	18.0280(9)
α	90.00
β	108.1077(19)
γ	90.00
V	5323.1(5)
Z	4
D_c (g/cm^3)	1.631
GOF on F2	1.038
$R1a$ $[I > 2\sigma(I)]$	0.0610
$\omega R2b[I > 2\sigma(I)]$	0.1272

400 (PEG 200) were purchased from Alfa Aesar. Powder X-ray diffraction data were recorded on a Bruker D8 Advance diffractometer with a graphite-monochromatized Cu$K\alpha$ radiation. Thermogravimetric analysis (TGA) was carried out on a TA Instrument Q500 Thermogravimetric Analyzer at a heating rate of 10 °C/min up to 800 °C under N_2 atmosphere. FTIR spectra were recorded from KBr pellets by using a Perkin Elmer FTIR SpectrumGX spectrometer. Elemental analyses were obtained from a Thermo Finnigan Instruments Flash EA1112 microelemental analyser. The optical diffuse reflectance spectra were measured on a Perkin Elmer Lambda 750 s UV–vis–NIR spectrometer equipped with an integrating sphere. $BaSO_4$was used as the reference materials, and the polycrystalline samples were ground well before the measurement. The absorption (α/S) data were calculated from the reflectance using the Kubelka–Munk function: $\alpha/S=(1-R)_2/2R$, in which R is the reflectance at a given wavelength, α is the absorption coefficient, and S is the scattering coefficient.

2.2. Synthesis

2.2.1. Synthesis of $Zn_2(BTC)_2py_2\cdot(RuBpy)\cdot 2H_2O$ (RuBpy@ZJU-100)

A mixture of anhydrous $Zn(OAc)_2$ (1.5 mmol, 0.27 g), H_3BTC (1 mmol, 0.21 g), pyridine (py) (0.5 mL), $Ru(bpy)_3Cl_2\cdot 6H_2O$ (0.2 mmol, 0.15 g) and 3 mL PEG-400 was put into a 25 mL Teflon-lined stainless-steel autoclave and heated at 160 °C for 6 days. Then, the mixture was naturally cooled to room temperature and washed with methanol to give orange-red crystals of RuBpy@**ZJU-100**. Yield: 53% (based on $Ru(bpy)_3Cl_2$).

2.3. Single-crystal structure determination

Data collection of crystals was carried out on a Bruker APEX II CCD diffractometer equipped with a graphite-monochromatized Mo$K\alpha$ radiation source ($\lambda=0.71073$ Å). Empirical absorption was performed, and the structure was solved by direct methods and refined with the aid of a SHELXTL program package. All hydrogen atoms were calculated and refined using a riding model. The CCDC number for **RuBpy@ZJU100** is 1049558.

2.4. PL spectra

PL spectra were taken on a Hitachi F4600 fluorescence spectrometer. The photomultiplier tube (PMT) voltage was 700 V, the scan speed was 240 nm min^{-1}, the excitation and the emission slit width were 5 and 2.5 nm, respectively. The PL lifetime was taken on an Edinburgh Instrument F900, both the excitation and emission slits are 1.5 nm. The excitation wavelengths are 370 nm.

3. Results and discussion

The reaction between $Zn(OAc)_2$, pyridine(py), trimesic acid (H_3BTC) and Ru(II)tris(2,2'-bipyridine) (RuBpy) in PEG 400 produced a new MOF host/guest crystalline material RuBpy@**ZJU-100** (Scheme 1). The structure was characterized by single-crystal X-ray diffraction studies, and the phase purity of the bulk material was independently confirmed by powder X-ray diffraction (PXRD) (Fig. S1). The crystal-lineproduct is insoluble in most of the common organic solvents.

Single crystal XRD analysis shows that RuBpy@**ZJU-100** crystallizes in the space group $P2(1)/n$ with framework formula$Zn_2(BTC)_2py_2\cdot(RuBpy)\cdot 2H_2O$ (Table 1). **ZJU-100** is a 2-D framework comprising zinc-BTC 2-D sheets, which were further coordinated to pyridine via one pyridine sites. All the zinc atoms displayed tetrahedral geometry through coordination to three oxygen atoms from the carboxylate groups and one pyridine molecules, as shown in Fig. 1a. **ZJU-100** has one-dimensional pores along the a axis of about 9.6 Å, as shown in Fig. 1c. The most interesting thing is that **ZJU-100** is an ionic MOF with the anionic 2-D sheet-type skeleton, which is further fulfilled with charge-balance cationic RuBpy (Fig. 1d). The RuBpy molecules are arrayed between the Zn-BTC sheets in a sandwich type, and the distance between two Ru cores inside one sheet is 12.0 Å. The total loading amount of RuBpy in **ZJU-100** is about 43.6 wt%. The experimental powder XRD pattern for RuBpy@**ZJU-100** matched very well with the simulated one that are generated from single crystal