

## Regular Article

## Multi-component hybrid soft ionogels for photoluminescence tuning and sensing organic solvent vapors

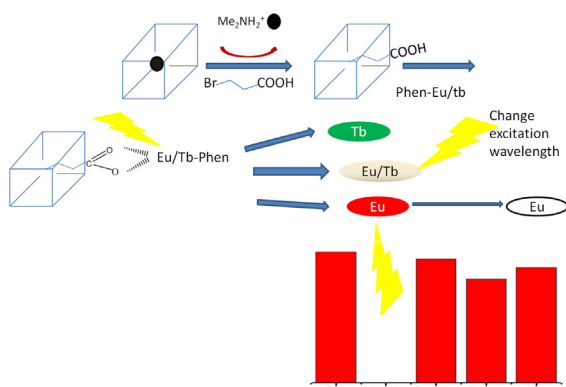


Jing Ma, Bing Yan\*

School of Chemical Science and Engineering, Tongji University, Shanghai 200092, China

## GRAPHICAL ABSTRACT

Soft iono-gels through the carboxyl ion liquid connecting with Bio-MOF-1 and rare earth complexes by cation exchange and rare earth ions coordinating with carboxyl of  $\text{IM}^+\text{Br}^-$ . Choose the Phen-Eu- $\text{IM}^+\text{Br}^-$  to sense volatile substances. Ammonia vapors luminescence quenching.



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## ABSTRACT

This paper tries to prepare soft ionogels through the carboxyl ion liquid ( $\text{IM}^+\text{Br}^-$ ) as double chemical linker connecting both Bio-MOF-1 ( $\text{Zn}_8(\text{ad})_4(\text{BPDC})_6\text{O}\cdot 2\text{Me}_2\text{NH}_2$ , BPDC = biphenyl-4,4'-dicarboxylate, Ad = adeninate) and lanthanide complexes. Among anionic Bio-MOF-1 interacts with  $\text{IM}^+\text{Br}^-$  through cation exchange ( $\text{IM}^+$ ) to form BMOF-IM and lanthanide ions are further introduced through the coordination to the carboxylic group of  $\text{IM}^+$  together with Phen (1,10-phenanthroline) as assistant ligand for  $\text{Ln}^{3+}$  ( $\text{Ln} = \text{Eu}, \text{Tb}$  or  $\text{Eu}/\text{Tb}$ ). The resulting multi-component hybrid ionogels (Phen- $\text{Ln}$ - $\text{IM}$ @BMOF) are prepared and characterized by PXRD, FTIR, TGA and mechanical properties by compression experiment, respectively. The photophysical properties of these hybrid systems are studied in details. By controlling the composition of different  $\text{Ln}^{3+}$  cations in  $\text{IM}$ @BMOF, the luminescent color of them can be tuned and the white light output can be realized. Furthermore, with careful adjustment of the excitation wavelength, the color of the luminescence can be modulated. Eventually we obtain luminescence trichromatic (Phen-Eu/Tb- $\text{IM}$ @BMOF) white-light-emitting materials. Moreover, we try to choose Phen-Eu- $\text{IM}$ @BMOF hybrid system for the detection of organic volatile substances, which shows the apparent luminescence quenching effect on ammonia for high sensitivity of sensing.

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\* Corresponding author.

E-mail address: [byan@tongji.edu.cn](mailto:byan@tongji.edu.cn) (B. Yan).

## 1. Introduction

Lanthanide ion luminescence is due to the lining 4f electrons transition between its different energy levels. Trivalent lanthanide ions have unique optical properties, such as high color purity of narrow emission spectrum [1,2], wide range from visible to near infrared region (NIR), broad lifetimes and high quantum efficiency [3,4]. However, due to the f-f transition prohibition, to generate effective emission light is difficult to obtain through the direct excitation of lanthanide ions for their very little molar absorption coefficients. To solve this problem, lanthanide ions are usually introduced into some special hosts or coordinated to organic ligands. Lanthanide complexes are limited in the practical application for their poor thermal stability and machinability [5,6]. In order to overcome these problems, people begin to look for a variety of excellent substrate carrier to develop hybrid materials [7–10].

Metal organic frameworks (MOFs) belong to important inorganic-organic hybrid material [11,12] consisting of a variety of metal ion and organic ligand [13]. The changeable choice of metal ion and organic ligand makes it has many advantages [14], such as a wide variety of skeleton, function, the porosity and specific surface area, etc. As a result, MOFs can behave as the host of lanthanide ions, from which lanthanide ions are encapsulated to form the hybrid systems. These lanthanide ions functionalized MOFs hybrid materials display the benefit luminescence performance of both into MOFs themselves and lanthanide ions [15–18]. Subsequently, the introduction of lanthanide ions can make whole color adjustable of luminous system, even realizing the white light output [19–22].

Ionic liquid is molten salt in the form of liquid at room temperature or near room temperature (melting point less than 100 °C) [23], usually by large organic cation (1-alkyl halide-3-methyl imidazole) and inorganic anion (halogen ions, six fluoride phosphate ions, etc.). Ionic liquid is a kind of green, sustainable chemicals as solvent has the following several advantages, which can dissolve a variety of organic inorganic matter and set a number of different components in the same phase. For a variety of chemical reactions, positive and negative charges are adjustable [24]. Functionalized ionic liquid refers to the structure of ionic liquids containing character of active functional groups, such as amino [25], sulphur [26], terpyridine [27], carboxyl [28], alkoxy [29] and so on. Based ionic liquid as chemical linkers, some lanthanide hybrid materials can be prepared and even hybrid ionogels can be further obtained [30–32].

Inspired by above research, we choose an anionic MOF (Bio-MOF-1,  $Zn_8(ad)_4(BPDC)_6O \cdot 2Me_2NH_2$ , BPDC = biphenyl-4,4'-dicarboxylate, Ad = adeninate)) where the cationic guest molecules or ions can undergo exchange with other species exogenous cationic [33]. Carboxyl ionic liquid (IMBr) is a kind of positively charged viscous liquid, which connects with anionic Bio-MOF-1 by electrostatic interactions to form a transparent blue colloid. On the other hand, lanthanide ions are introduced to coordinate to the carboxylic group of IMBr, resulting in the final multi-component hybrid soft ionogels. The photoluminescence tuning and chemical sensing of some solvent molecules are studied.

## 2. Experimental section

### 2.1. Chemicals

All of the chemicals were commercially available and used without further purification. 3-Bromine propionic acid, 1-methyl imidazole and anhydrous ethanol were used to synthesize compound carboxyl ion liquid (IMBr). Adenine (Ad), diphenyl

dicarboxylic acid (BPDC),  $Zn(Ac)_2 \cdot 2H_2O$ , and nitric acid were used to synthesize compound Bio-MOF-1. Lanthanide chlorides  $LnCl_3 \cdot xH_2O$  ( $Ln = Eu$  and  $Tb$ ) were synthesized by dissolving their oxides ( $Eu_2O_3$  and  $Tb_4O_7$ ) into the concentrated nitric acid along with heating and stirring to accelerate the rate of reactions till the crystal film appeared.

### 2.2. Instrumentation

Powder X-ray diffraction patterns (PXRD) were recorded with a Bruker D8 diffractometer using  $CuK\alpha$  radiation with 40 mA and 40 kV and the data were collected within the  $2\theta$  range of 3–50°. Thermal gravimetric analysis (TGA) was carried out on a Netzsch STA 449C system at a heating rate of 5 K  $min^{-1}$  from 40 °C to 800 °C temperature under nitrogen atmosphere in the  $Al_2O_3$  crucibles. Fourier transform infrared (FTIR) spectra were recorded in the range 4000–400  $cm^{-1}$  on a Nexus 912 AO446 spectrophotometer using KBr pellets. Stress-strain curves were obtained on Sansizongheng UTM6000 electronic universal testing machine. Luminescence excitation and emission spectra of the samples were obtained on Edinburgh FLS920 spectrophotometer using a 450 W xenon lamp as excitation source.

### 2.3. Synthesis of Bio-MOF-1(BMOF)

Bio-MOF-1 was synthesized according to the synthesis method and conditions (molar ratio, time and temperature) in the literature [33]. Adenine (Ad, 0.125 mmol), diphenyl dicarboxylic acid (BPDC, 0.25 mmol), the hydrated zinc acetate ( $Zn(Ac)_2 \cdot 2H_2O$ , 0.375 mmol), nitric acid (1 mmol) were dissolved in 13.5 mL of DMF and 1 mL of distilled water. The mixed solution was put to 20 mL reaction tube. After reaction at 130 °C for 24 h, the products were obtained by centrifugation, washed with DMF for several times and finally were dried at 80 °C in vacuum.

### 2.4. Synthesis of carboxyl ion liquid ( $IM^+Br^-$ )

Carboxyl ion liquid was synthesized according to the literature [28]. 3-Bromine propionic acid was dissolved in anhydrous ethanol, and then added 1-methyl imidazole. Reflux after ultrasonic mixing, a viscous crude product was obtained. After washing with ether, steaming, pale yellow viscous acid ionic liquid was prepared for  $IM^+Br^-$ .

### 2.5. Synthesis of $IM@BMOF$

Appropriate Bio-MOF-1 was dissolved in suitable amount DMF solution, and suitable carboxyl ion liquid was added. After ultrasonic mixing, condensation reaction was kept 24 h at 65 °C. The soft ionogels with Bio-MOF-1 and  $IM^+Br^-$  were prepared.

### 2.6. Synthesis of $Phen-Ln-IM@BMOF$

Appropriate Bio-MOF-1 was dissolved in suitable amount DMF solution and suitable carboxyl ion liquid was added. After ultrasonic mixing, lanthanide complexes ( $Eu^{3+}$ ,  $Tb^{3+}$ , and  $Eu^{3+}/Tb^{3+}$ ) condensation reaction was kept 24 h at 65 °C. The soft ionogels with Bio-MOF-1,  $IM^+Br^-$  and lanthanide complexes were obtained.

### 2.7. Fluorescence sensing vapor of $Phen-Eu-IM@BMOF$

The films were used for vapor sensing experiments, which was fabricated with luminescent  $Phen-Eu-IM@BMOF$ . For each experiment, before exposure to various organic solvent vapors (acetone, methanol, cyclohexane, and ammonia), the luminescent spectra of the  $Phen-Eu-IM@BMOF$  films were measured. Then the film was

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