

A europium(III) based metal–organic framework: bifunctional properties related to sensing and electronic conductivity†

Cite this: *J. Mater. Chem. A*, 2014, 2, 237

Zhaomin Hao,^{ab} Guocheng Yang,^c Xuezhi Song,^{ab} Min Zhu,^{ab} Xing Meng,^{ab} Shuna Zhao,^{ab} Shuyan Song^a and Hongjie Zhang^{*a}

The accessible interspace of [Eu₄(BPT)₄(DMF)₂(H₂O)₈] (EuL) metal–organic framework (MOF) based host materials can serve as good candidates for loading of a variety of guest molecules. In this regard, two functional properties, sensing and electronic conductivity of EuL MOF were systematically studied in this contribution. The photoluminescent properties reveal that the EuL exhibits characteristic red emission of Eu³⁺ ion, and presents highly detectable luminescence responses for Cu²⁺ ions and acetone molecules in DMF solution. For the studies of electrical properties, they were focused on the electronic conductivities of I₂-incorporated EuL in anhydrous media and at different temperatures. With the increase of temperature from 25 to 80 °C, the I₂-incorporated EuL showed significant changes in conductivities from 8.27 × 10⁻⁷ S cm⁻¹ to 2.71 × 10⁻⁵ S cm⁻¹. Meanwhile, the activation energy (*E_a*) was for the first time estimated for iodine-element-incorporated MOF with the help of Arrhenius plots. The successful achievements of the impedance measurements and analyses for I₂-incorporated EuL prove for the first time that iodine-element-incorporated MOF can also be used for studies of conductivity under anhydrous conditions and at moderate temperature.

Received 13th August 2013
Accepted 17th October 2013

DOI: 10.1039/c3ta13179c

www.rsc.org/MaterialsA

1. Introduction

The combination of multiple functions belonging to the distinguishable features of various materials into a single compound or micro/nano-composite system could be very attractive for a broad range of applications as compared to homogeneous functional materials.¹ For example, the bifunctional organic catalyst has emerged at the forefront of research in the field of asymmetric catalysis and it provides enormous opportunities for development of organic chemistry and physical chemistry.² Bifunctional materials in possession of both magnetic and luminescent properties have drawn much attention because of their great potential applications, especially in biological research such as bioimaging³ and cell labeling,⁴ etc.

Since the recognition of “metal–organic frameworks” (MOFs) in 1995, they have been extensively studied because of their

unique properties among the various types of microporous and mesoporous materials.⁵ Recent studies on MOFs have shown that their designable framework architectures and specific pore surfaces are of great interest to chemists studying various applications of solid-state materials, such as selective gas sorption,⁶ heterogeneous catalysis,⁷ magnetism,⁸ electrical and sensing applications.^{9,10} Among the various kinds of MOFs, lanthanide metal–organic frameworks (LnMOFs) are well investigated due to their unique optical properties,^{11,12} such as large Stokes' shifts, high color purity, and relatively long luminescence lifetimes, which originate from f–f transitions *via* an “antenna effect”.¹³ However, design and synthesis of such compounds remains a challenge. This is because lanthanide ions have higher coordination numbers of typically more than six, thus the *in situ* formed open lanthanide sites during activation/de-solvation prefer to bind back with the oxygen and/nitrogen donors from the organic linkers, leading to condensed frameworks.

In the past few years, our group has been pursuing the recognition and sensing of small molecules and metal ions.¹⁴ In the meanwhile, it is surprising that relatively little progress has been made in using LnMOFs as the host materials for electrical applications. So it leads us to the synthesis of a bifunctional LnMOF material for both sensing and electrical applications. In this context, we present a synthesis of [Eu₄(BPT)₄(DMF)₂(H₂O)₈] (EuL) MOF, which presents not only highly detectable luminescence responses for Cu²⁺ ions and acetone molecules, but

^aState Key Laboratory of Rare Earth Resource Utilization, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, People's Republic of China. E-mail: hongjie@ciac.jl.cn; Fax: +86 43185685653; Tel: +86 43185262127

^bGraduate School of Chinese Academy of Sciences, Beijing, 100049, People's Republic of China

^cSchool of Chemistry and Life Science, Changchun University of Technology, Changchun 130012, People's Republic of China

† Electronic supplementary information (ESI) available. CCDC reference number 955403. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c3ta13179c

also possesses good electronic conductivity when I₂ molecules were incorporated into the channels of the host skeleton. To the best of our knowledge, the reports which can achieve the above two applications in one MOF material were still rather rare. The electronic conductivities of I₂-incorporated microporous materials have been reported,¹⁵ but all of them were investigated under room temperature and a LnMOF material has never been reported in this respect.

2. Experimental section

Materials and measurements

All reagents were purchased commercially and used without further purification. The **EuL** was synthesized following the method reported by Cao *et al.*,¹⁶ which used a large excess amount of Eu(NO₃)₃·6H₂O and H₃BPT as starting materials. Herein, we used a moderate ratio to obtain the same material with higher purity and yield. Furthermore, the crystal structure of **EuL** was not discussed in detail previously. XRD data were collected on a D8 Focus (Bruker) diffractometer at 40 kV and 30 mA with monochromated Cu K α radiation ($\lambda = 1.5405 \text{ \AA}$) with a scan speed of 5° min^{-1} and a step size of 0.02° in 2 theta. Inductively coupled plasma (ICP) analyses of Eu and I, and elemental analyses of C, H, and N were conducted on a Perkin-Elmer Optima 3300DV spectrometer and a Perkin-Elmer 2400 elemental analyzer, respectively. Thermogravimetric (TG) data were recorded on a Thermal Analysis Instrument (SDT 2960, TA Instruments, New Castle, DE) from room temperature to 900 °C with a heating rate of $10^\circ \text{ C min}^{-1}$ under an air atmosphere. The photoluminescence (PL) excitation and emission spectra were performed on a Hitachi F-4500 spectrophotometer equipped with a 150 W xenon lamp as the excitation source. The measurements of nitrogen adsorption were carried out on ASAP 2020 and Autosorb MP-1 apparatuses. The measurements of electronic conductivity were carried out using an impedance and gain-phase analyzer (PARSTAT 2273, Ametek, USA), in the frequency range 1 Hz to 1 MHz, with a four-probe electrochemical cell and an applied ac voltage of 300 mV. Single crystal X-ray diffraction data for compound **EuL** was collected on a Bruker Apex CCD diffractometer with graphite-monochromated Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$) at 273 K. The crystal structures were solved by means of direct methods and refined employing full-matrix least squares on F^2 (SHELXTL-97).¹⁷ All the hydrogen atoms except for one disordered DMF molecule (related to C67 and C68) were generated geometrically and refined isotropically using the riding model. All non-hydrogen atoms were refined with anisotropic displacement parameters. The guest molecules in channels were removed using the SQUEEZE routine of PLATON.

Synthesis of **EuL**

The molar ratio of ligand and metal ions was confined to 1 : 1.6. Biphenyl-3,4',5-tricarboxylate (H₃BPT, 0.07 mmol, 20 mg), Eu(NO₃)₃·6H₂O (0.112 mmol, 50 mg), DMF (1.0 mL) and H₂O (1.0 mL) were charged in a 10 mL glass vial, which was sealed and heated to 80 °C for 24 h, and then cooled down to room

temperature. The colorless crystals were collected and air-dried (yield, 87%, based on H₃BPT). Elemental analysis (%) calcd for **EuL**: Eu 24.82; C 39.70; H 4.07; N 4.00. Found: Eu 24.46; C, 39.55; H, 4.09; N, 3.84.

Synthesis of I₂-incorporated **EuL**

The **EuL** crystals were immersed in dry methanol for 3 days in a 25 mL glass bottle with renewal of the methanol repeatedly three times a day. Then the crystals (200 mg) were outgassed at 120 °C for 12 h, followed by immersion in a dry hexane solution of I₂ ($2 \times 10^{-2} \text{ mol L}^{-1}$) for 2 days. Finally, the obtained sample was washed by hexane 4–6 times to remove the residual I₂ molecules on the surface.

3. Results and discussion

Structure for **EuL**

The X-ray crystallographic analysis reveals that the **EuL** MOF crystallizes as the space group of $P\bar{1}$. There are two distinct Eu coordination environments in **EuL**. The Eu1 is nine coordinated with nine oxygen atoms, forming a distorted monocapped square antiprism; while Eu2, Eu3 and Eu4 are eight coordinated (Fig. S1[†]), forming three distorted square antiprisms where four oxygen atoms create a local square plane, and four other oxygen atoms form the other distorted square plane in each polyhedron. The bond angles for O–Eu–O are in the range of $48.76(8)$ – $153.96(12)^\circ$, while the Eu–O bond length ranges from $2.293(3)$ to $2.503(3) \text{ \AA}$ (Table S1[†]). All O–Eu–O bond angles and Eu–O bond lengths are within the expected ranges.¹⁸

One of the most notable structural features of **EuL** is its two types of channels (A and B), as revealed by single crystal X-ray analysis, with the approximate sizes of $9.5 \times 8.4 \text{ \AA}$ and $7.8 \times 9.2 \text{ \AA}$ without taking the van der Waals radius into consideration (Fig. 1). Channel A, which accommodates the free guest molecules (DMF and H₂O), has an approximately elliptical shape in which the BPT groups define the planes of the ellipsoid, and Eu atoms are located at the vertices. Channel B provides a rectangular space, but the coordinated DMF

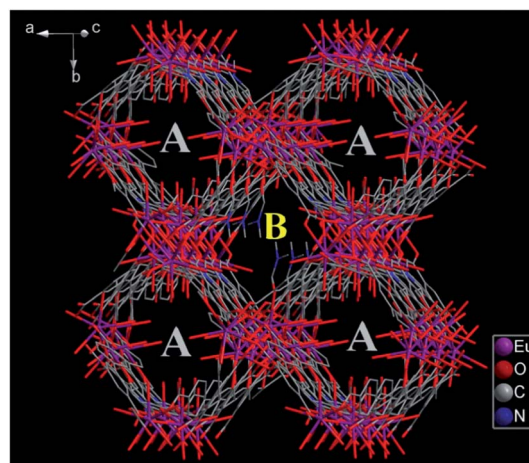


Fig. 1 Two types of channels (A and B) in **EuL**.

molecules on Eu sites point toward the inside of the channels, and as a result, this distribution pattern reduces the space of channel B. The total solvent-accessible volume is 1717.9 Å³, which corresponds to 35.9% (4784 Å³) of desolvated **EuL** according to the PLATON calculations. The high-solvent-accessible space of this microporous structure can serve as good sites for various guest molecules. In this regard, two applications, sensing properties and electronic conductivity of **EuL** are systematically studied in the following sections.

General characterization

To study the thermal stability and the incorporation percentage of guest molecules in the I₂-incorporated MOF, the TG curves of **EuL**, outgassed **EuL**, and I₂-incorporated **EuL** were measured under air atmosphere (Fig. 2). The TG curve of **EuL** shows that the first weight loss is 28.49% in the temperature range 65–450 °C, corresponding to the loss of guest molecules (DMF and H₂O) in channels. The second weight loss is due to the collapse of host structure from 462 to 566 °C. For outgassed **EuL**, there is no significant weight loss observed before 460 °C, after which an abrupt decomposition weight loss takes place. For I₂-incorporated **EuL**, the TG curve shows that the first weight loss is 17.03%, which fits well with the amount of I₂ weight loss calculated by ICP results (17.41% for iodine) in the temperature range 74–280 °C. The second weight loss is 44.9% from 465 to 618 °C, also due to the skeleton collapse of host. Quite significantly, the TG curve of I₂-incorporated **EuL** shows a hysteresis for the loss of the iodine as the complete weight loss for solid I₂ was observed before 126 °C (Fig. S3†), hinting that there are some interactions between the iodine and the framework.

The **EuL** (activated at 120 °C under vacuum for 12 h) was further analyzed by N₂ sorption isotherm at 77 K, which displays typical type-I sorption behavior (Fig. S4†) with a limited adsorption capacity, confirming the permanent porosity of the activated **EuL**. Calculated from the nitrogen adsorption data, the estimated Langmuir and BET surface areas are 114.2 and 69.6 m² g⁻¹, and the estimated pore volume is 0.048 cm³ g⁻¹. These values are lower than our previous compound using the

same organic ligand and ytterbium ions,^{14a} indicating that the pores are quite different even though the chemical properties of Ln ions are similar.

Luminescence properties

The fascinating optical properties of LnMOFs make them especially attractive for potential applications such as fluorescence probes and luminescence bioassays.^{19,20} The pioneering work has focused on various LnMOF materials for the sensing of various cations, anions and small molecules, showing that different LnMOFs have different sensing properties.^{21–23} It is necessary to further investigate the influence of different structural features on luminescence properties.

The luminescence spectrum of the **EuL** suspension (5 mg of sample dispersed in 5 mL DMF) is shown in Fig. 3. The **EuL** compound exhibits characteristic electronic transitions of Eu³⁺ ion at 579, 591, 615, 651, and 696 nm, which are attributed to the ⁵D₀ → ⁷F₀, ⁵D₀ → ⁷F₁, ⁵D₀ → ⁷F₂, ⁵D₀ → ⁷F₃ and ⁵D₀ → ⁷F₄ transitions, respectively.

The as-synthesized **EuL** sample was dispersed in 0.01 mol L⁻¹ DMF solution containing M(NO₃)_x (M = Na⁺, Mg²⁺, Ni²⁺, Zn²⁺, Gd³⁺, Co²⁺ and Cu²⁺) for the sensing studies. The luminescence spectra of the metal ions incorporated in **EuL** suspensions exhibit similar transitions of Eu³⁺ ion, but the luminescence intensities of the Eu³⁺ in different suspensions are quite different and are mostly quenched by the added metal ions. Different metal ions exhibit different level of quenching of the luminescence intensity, especially the Cu²⁺ ions (Fig. 4), which show the highest quenching effect. To examine the sensing sensitivity toward Cu²⁺ ions, **EuL** dispersed in DMF solutions with gradually increased Cu²⁺ concentration were prepared to monitor the emission response. As seen in Fig. S5,† the **EuL** still has a good sensing performance when the Cu²⁺ concentration is as low as 10⁻⁵ mol L⁻¹. It is very remarkable that this material features such highly detectable luminescence responses for Cu²⁺ ions in DMF solution. For the possible sensing mechanisms, we speculate that the quenching effect of

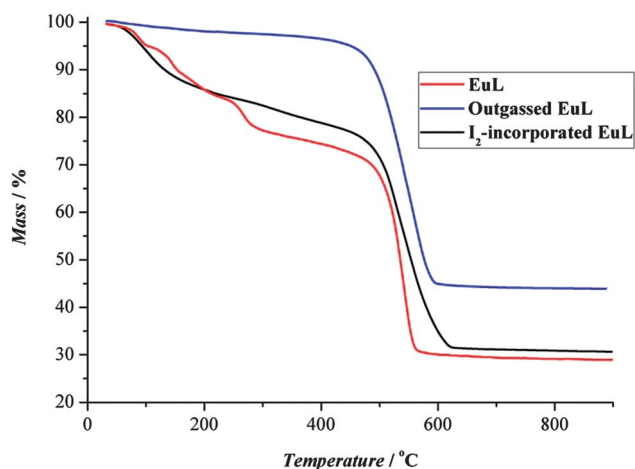


Fig. 2 TG curves of **EuL**, outgassed **EuL**, and I₂-incorporated **EuL**.

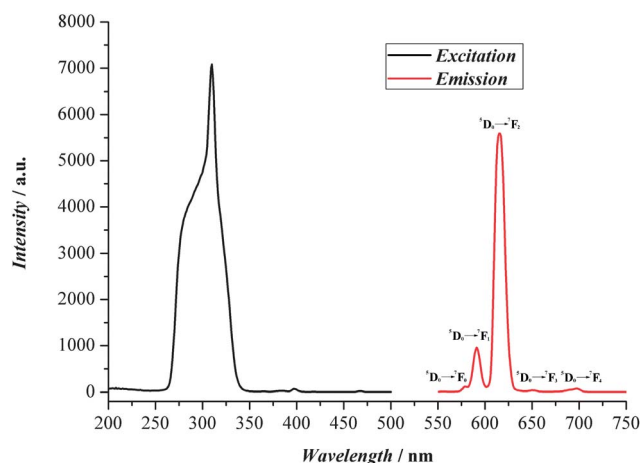


Fig. 3 The excitation ($\lambda_{em} = 615$ nm) and emission spectra ($\lambda_{ex} = 321$ nm) of **EuL** in DMF solution.

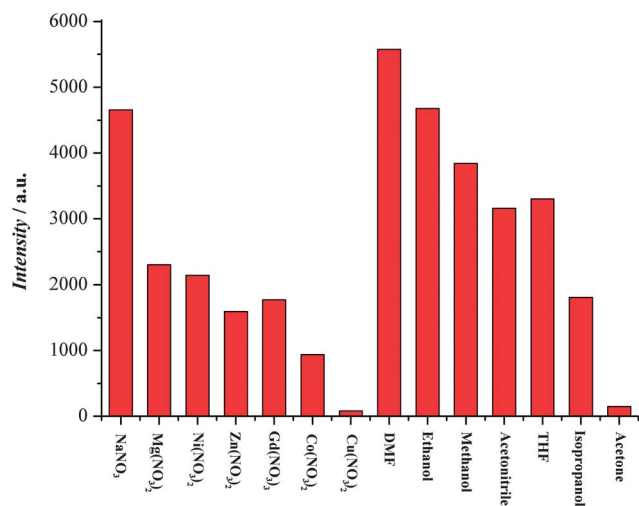


Fig. 4 Comparison of the ${}^5D_0 \rightarrow {}^7F_2$ luminescence intensity of **EuL** in DMF solutions incorporating different metal ions and small organic molecules.

Cu^{2+} ions might be related to the interaction between the Cu^{2+} ions and the carboxylate and/or terminal water Lewis basic sites on the **EuL**, which reduces the energy transfer efficiency from BPT to Eu^{3+} ions within **EuL**, thus decreasing the luminescent intensity.^{14c}

Furthermore, an energy-dispersive X-ray spectroscopy (EDS) line scan was also employed to investigate if the Cu^{2+} ions entered the channels of **EuL**. According to the literature, an equal-height of EDS line-scan signals indicates an even distribution of the investigated element in the three-dimensional sample. The signals of the EDS line scan show a saddle-pattern with a low central portion and two high edges if the measured element is mainly located on the surface of the sample, because the edge of the sample contains a higher surface area than the

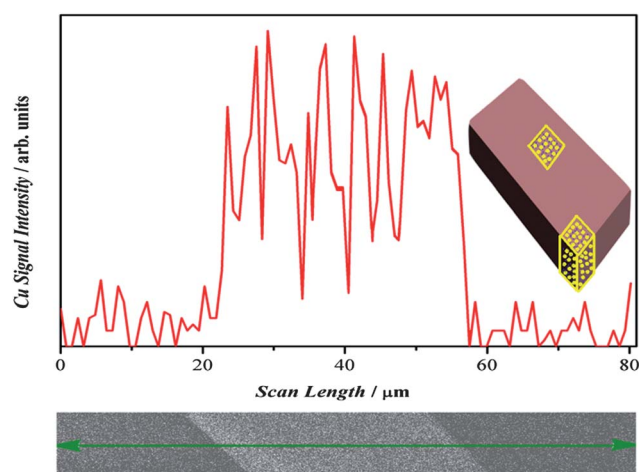


Fig. 5 The energy-dispersive X-ray spectroscopy (EDS) line scan across a single crystal of Cu^{2+} -incorporated **EuL** for Cu, and the colored inset is the schematic illustration for the difference in surface area between the edge and the central portion when they have an equal volume.

central portion when they have an equal volume (as shown in the schematic illustration of the colored inset in Fig. 5).²⁴ In Fig. 5, the line scan for the single crystal of Cu^{2+} -incorporated **EuL** shows that the Cu signals are approximately equal in height, excluding the possibility of surface absorption of the Cu^{2+} ions on the surface of **EuL**, and indicating that the sensing sites of Cu^{2+} are in the channels.

The sensing of small organic molecules by **EuL** was also examined, with 0.01 mol L^{-1} methanol, ethanol, isopropanol, acetonitrile, THF and acetone in DMF solutions for testing. In a typical experiment, **EuL** was dispersed in DMF and used as the standard suspension, while the investigated solvent was gradually added and the response of the Eu^{3+} emission from **EuL** was *in situ* monitored. As shown in Fig. 4, the photoluminescence intensity is quite sensing organic molecule dependent, especially in the case of acetone, which shows a significant quenching effect. The luminescence intensity of the **EuL** suspension significantly decreases with the addition of acetone, as shown in Fig. 6, and almost disappears at an acetone concentration level of 5.0 vol%. Quantitatively, this quenching effect can be rationalized by the Stern–Volmer equation: $I_0/I = 1 + K_{\text{sv}} \times [\text{M}]$. The values I_0 and I are the luminescence intensity of **EuL** suspension without and with addition of acetone, respectively. $[\text{M}]$ is the molarity of acetone, and K_{sv} is the quenching coefficient of acetone. K_{sv} was calculated by the experimental data fitting from the known acetone concentration. The K_{sv} value is calculated as 48.7 L mol^{-1} for acetone, indicating a strong quenching effect on the luminescence intensity of **EuL**.^{10d} The absorption band of H_3BPT ligand is located between 250 and 325 nm, which is overlapped with the absorption band of acetone. Other solvents have no significant absorption band between 250 and 325 nm. From the results of the absorption and luminescent spectra, it is strongly suggested that the energy absorbed by BPT is transferred to the acetone molecules, resulting in a decrease in luminescence intensity of **EuL**, consistent with the quenching mechanism reported in the literature.²⁵

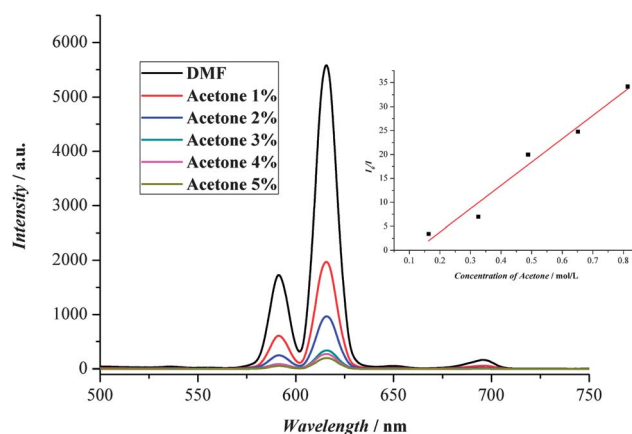


Fig. 6 The luminescence spectra of **EuL** in DMF solution with different added acetone-concentrations. The inset is the Stern–Volmer plot for the quenching of **EuL** by acetone.

Electrical properties

Recently the electronic/ion-conductive MOFs materials, which have potential applications in the electrolyte of fuel cells, have received much attention.²⁶ Currently the electronic/ion conductivity in MOFs materials under damp conditions is not difficult to achieve and several works on the conductivity of MOFs under high-humidity conditions have been reported.²⁷ However, the reports on the electronic/ion conductivity of MOFs materials under anhydrous conditions were rather rare.²⁷ Under high-humidity conditions, the composites always show a remarkable drop of conductivity when dehydrated, so it would be unwise to use these kinds of material for practical systems. In the limited examples under anhydrous conditions, the incorporated molecules in MOFs frameworks were always confined to limited options, such as imidazole or its derivatives.²⁸

Herein, we focused on the electric properties of I₂-incorporated **EuL** with iodine element as the charge-carrier medium. The electrochemical impedance spectroscopy of the pellet of I₂-incorporated **EuL** with 0.8 cm diameter and 0.12 cm thickness was performed under anhydrous conditions. As shown in Fig. 7, the impedance plots of the I₂-incorporated **EuL** are typical of materials with predominant ionic conductivity. From 25 to 80 °C under anhydrous conditions, I₂-incorporated **EuL** shows conductivities (σ) of approximately $8.27 \times 10^{-7} \text{ S cm}^{-1}$ to $2.71 \times 10^{-5} \text{ S cm}^{-1}$ (Fig. 8a). In 2012, Zeng and coworkers have stated that the iodine element is scattered in the MOF framework in

the form of polyiodide ions (I₅⁻ or I₇⁻) when the concentration of I₂ is at a high level.^{15b} At room temperature, the electronic conductivity of Zeng's material is $8.11 \times 10^{-7} \text{ S cm}^{-1}$, which is pretty similar to our I₂-incorporated **EuL**. Providing that there is no other charge-carrier medium except iodide ions in I₂-incorporated **EuL**, we speculate that our charge-carrier medium is similar to Zeng's. The electronic conductivity of solid I₂ is $7.69 \times 10^{-8} \text{ S cm}^{-1}$, which is one tenth of I₂-incorporated **EuL**. The significant increase compared to solid I₂ can be attributed to the restriction of polyiodide ions within well-regulated aromatic nanochannels, inducing a high efficiency of $n \rightarrow \sigma^*$ charge-transfer (CT).^{15a,15b,29}

Moreover, the conductivity of I₂-incorporated **EuL** is improved significantly as the temperature increases and reaches $2.71 \times 10^{-5} \text{ S cm}^{-1}$ at 80 °C. Note that there is a significant loss of I₂ after 80 °C, as revealed in the TG curve, above which temperature the Nyquist plot (Z'' versus Z') measurement was stopped. Fig. 7 shows the Nyquist plots of the conductivity of I₂-incorporated **EuL** in the temperature range 25 to 80 °C under anhydrous conditions. Such a temperature dependent impedance study might allow the quantification of the activation energy charge transfer related to the two kinds of channels on the basis of an Arrhenius relationship. The $\ln \sigma T$ increases almost linearly within the temperature range from 25 to 80 °C, and the corresponding activation energy (E_a) for the conductivity was estimated to be 0.602 eV (Fig. 8b). The activation energy of I₂-incorporated **EuL** is very similar to other anhydrous

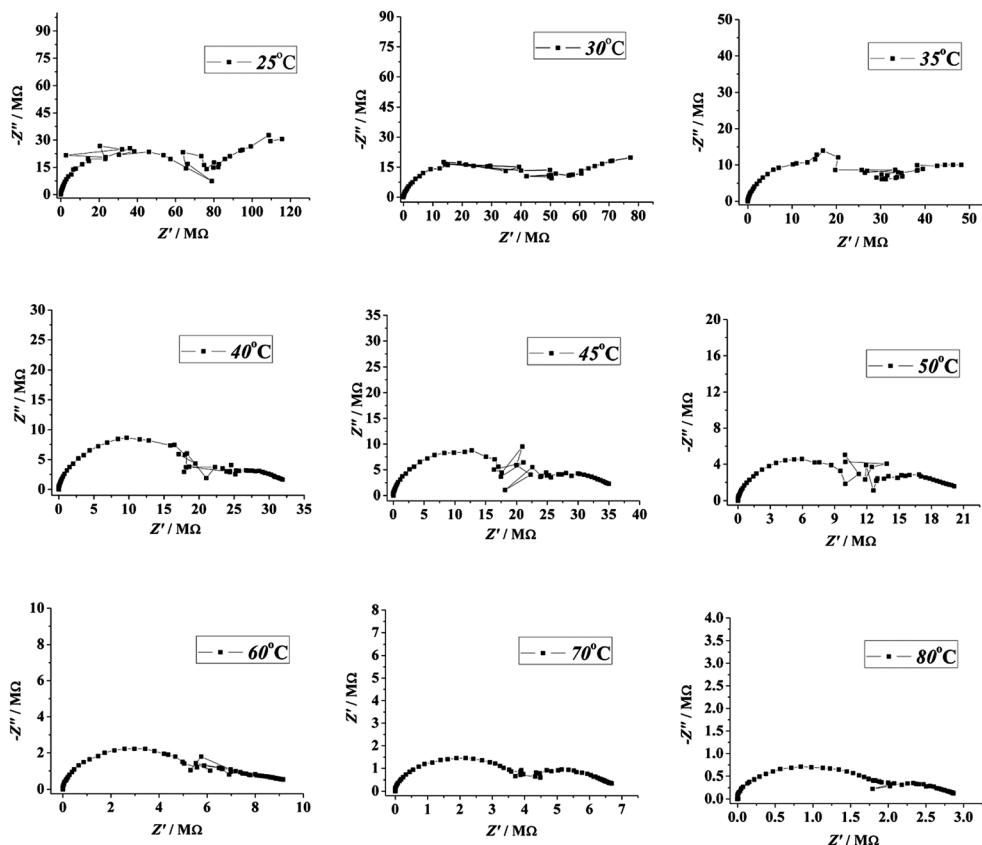


Fig. 7 Nyquist plots for I₂-incorporated **EuL** at different temperatures under anhydrous conditions.

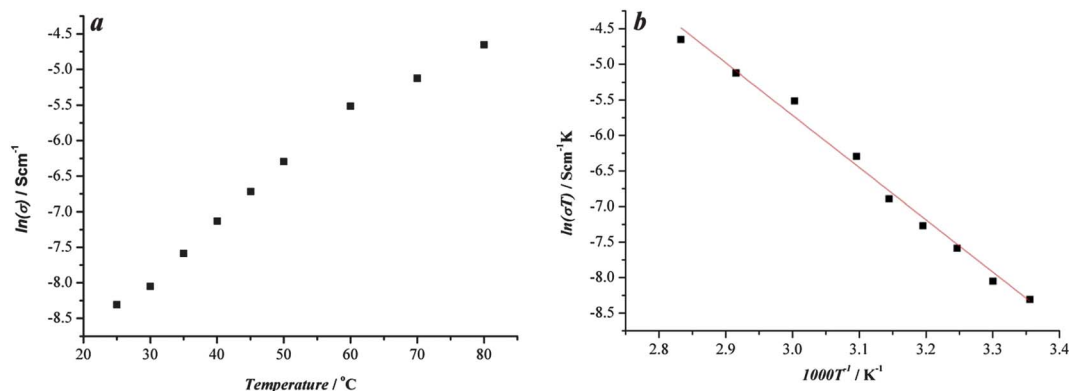


Fig. 8 (a) $\ln \sigma$ versus temperature plot of I_2 -incorporated EuL from 25 to 80 °C under anhydrous conditions; (b) Arrhenius plot of the conductivities of I_2 -incorporated EuL at different temperatures.

conditions, such as an imidazole-incorporated porous coordination polymer reported by Kitagawa (0.6 eV).^{28b} The powder X-ray diffraction data in the supporting information (Fig. S6†) suggest that the powder samples after the conductivity measurement preserve their structures. Thus, the structural descriptions of the two kinds of channels in EuL are valid for the electronic/ion-conductive MOF material under anhydrous conditions. The successful achievements of the impedance measurements and analyses for I_2 -incorporated EuL prove for the first time that iodine-element-incorporated MOF can also be used for the studies of conductivity under anhydrous conditions and at moderate temperature.

4. Conclusion

In summary, we have constructed a bifunctional EuMOF material which exhibits excellent sensing properties and electronic conductivity. The luminescence properties suggest that the EuL have highly detectable luminescence responses for Cu^{2+} ions and acetone molecules. Furthermore, we investigated anhydrous and moderate temperature electronic/ion-conductive MOF material after a comprehensive and systematic study for I_2 -incorporated EuL. Inspired by the present work, it is envisaged that more bifunctional LnMOFs will be developed in the future.

Acknowledgements

The authors are grateful to the financial aid from the National Natural Science Foundation of China (Grant no. 21071140), National Natural Science Foundation of China Major Project (Grant no. 91122030), '863'-National High Technology Research and Development Program of China (Grant no. 2011AA03A407) and National Natural Science Foundation for Creative Research Group (Grant no. 20921002).

Notes and references

- 1 (a) O. Sato, *Acc. Chem. Res.*, 2003, **36**, 9692; (b) J. R. Long and O. M. Yaghi, *Chem. Soc. Rev.*, 2009, **38**, 1213; (c) E. Pardo,

- C. Train, G. Gontard, K. Boubekeur, O. Fabelo, H. Liu, B. Dkhil, F. Lloret, K. Nakagawa, H. Tokoro, S. I. Ohkoshi and M. Verdager, *J. Am. Chem. Soc.*, 2011, **133**, 15328; (d) J. Ferrando-Soria, P. Serra-Crespo, M. de Lange, J. Gascon, F. Kapteijn, M. Julve, J. Cano, F. Lloret, J. Pasán, C. Ruiz-Pérez, Y. Journaux and E. Pardo, *J. Am. Chem. Soc.*, 2012, **134**, 15301; (e) J. Ferrando-Soria, H. Khajavi, P. Serra-Crespo, J. Gascon, F. Kapteijn, M. Julve, F. Lloret, J. Pasán, C. Ruiz-Pérez, Y. Journaux and E. Pardo, *Adv. Mater.*, 2012, **24**, 5625.
- 2 (a) R. Noyori, *Angew. Chem., Int. Ed.*, 2002, **41**, 2008; (b) A. G. Doyle and E. N. Jacobsen, *Chem. Rev.*, 2007, **107**, 5713.
- 3 F. Erogbogbo, K. T. Yong, R. Hu, W. C. Law, H. Ding, C. W. Chang, P. N. Prasad and M. T. Swihart, *ACS Nano*, 2010, **4**, 5131.
- 4 I. L. Medintz, H. Mattoussi and A. R. Clapp, *Int. J. Nanomed.*, 2008, **3**, 151.
- 5 O. M. Yaghi and H. L. Li, *J. Am. Chem. Soc.*, 1995, **117**, 10401.
- 6 (a) J. R. Li, J. Sculley and H. C. Zhou, *Chem. Rev.*, 2012, **112**, 869; (b) J. R. Li, R. J. Kuppler and H. C. Zhou, *Chem. Soc. Rev.*, 2009, **38**, 1477; (c) R. Matsuda, R. Kitaura, S. Kitagawa, Y. Kubota, R. V. Belosludov, T. C. Kobayashi, H. Sakamoto, T. Chiba, M. Takata, Y. Kawazoe and Y. Mita, *Nature*, 2005, **436**, 238; (d) S. Shimomura, M. Higuchi, R. Matsuda, K. Yoneda, Y. Hijikata, Y. Kubota, Y. Mita, J. Kim, M. Takata and S. Kitagawa, *Nat. Chem.*, 2010, **2**, 633; (e) S. Bourrelly, P. L. Llewellyn, C. Serre, F. Millange, T. Loiseau and G. Férey, *J. Am. Chem. Soc.*, 2005, **127**, 13519; (f) M. Sadakiyo, T. Yamada and H. Kitagawa, *J. Am. Chem. Soc.*, 2011, **133**, 11050.
- 7 (a) J. Y. Lee, O. K. Farha, J. Roberts, K. A. Scheidt, S. T. Nguyen and J. T. Hupp, *Chem. Soc. Rev.*, 2009, **38**, 1450; (b) J. Song, Z. Luo, D. K. Britt, H. Furukawa, O. M. Yaghi, K. I. Hardcastle and C. L. Hill, *J. Am. Chem. Soc.*, 2011, **133**, 16839; (c) J. S. Seo, D. Whang, H. Lee, S. I. Jun, J. Oh, Y. J. Jeon and K. Kim, *Nature*, 2000, **404**, 982; (d) C. D. Wu, A. Hu, L. Zhang and W. Lin, *J. Am. Chem. Soc.*, 2005, **127**, 8940; (e) R. Q. Zou, H. Sakurai and Q. Xu, *Angew. Chem., Int. Ed.*, 2006, **45**, 2542; (f) S. Hasegawa, S. Horike, R. Matsuda, S. Furukawa,

- K. Mochizuki, Y. Kinoshita and S. Kitagawa, *J. Am. Chem. Soc.*, 2007, **129**, 2607.
- 8 (a) M. Kurmoo, *Chem. Soc. Rev.*, 2009, **38**, 1353; (b) H. Tamaki, Z. J. Zhong, N. Matsumoto, S. Kida, M. Koikawa, N. Achiwa, Y. Hashimoto and H. Ōkawa, *J. Am. Chem. Soc.*, 1992, **114**, 6974; (c) M. Ohba and H. Ōkawa, *Coord. Chem. Rev.*, 2000, **198**, 313; (d) W. Kaneko, M. Ohba and S. Kitagawa, *J. Am. Chem. Soc.*, 2007, **129**, 13706; (e) R. Ohtani, K. Yoneda, S. Furukawa, N. Horike, S. Kitagawa, A. B. Gaspar, M. C. Munoz, J. A. Real and M. Ohba, *J. Am. Chem. Soc.*, 2011, **133**, 8600; (f) K. Tomono, Y. Tsunobuchi, K. Nakabayashi and S. Ohkoshi, *Inorg. Chem.*, 2010, **49**, 1298.
- 9 (a) S. Takaishi, M. Hosoda, T. Kajiwara, H. Miyasaka, M. Yamashita, Y. Nakanishi, Y. Kitagawa, K. Yamaguchi, A. Kobayashi and H. Kitagawa, *Inorg. Chem.*, 2009, **48**, 9048; (b) Y. Kobayashi, B. Jacobs, M. D. Allendorf and J. R. Long, *Chem. Mater.*, 2010, **22**, 4120; (c) H. Kitagawa, N. Onodera, T. Sonoyama, M. Yamamoto, T. Fukuwa, T. Mitani, M. Seto and Y. Maeda, *J. Am. Chem. Soc.*, 1999, **121**, 10068; (d) K. Otsubo, A. Kobayashi, H. Kitagawa, M. Hedo, Y. Uwatoko, H. Sagayama, Y. Wakabayashi and H. Sawa, *J. Am. Chem. Soc.*, 2006, **128**, 8140; (e) Y. Fuma, M. Ebihara, S. Kutsumizu and T. Kawamura, *J. Am. Chem. Soc.*, 2004, **126**, 12238.
- 10 (a) B. Zhao, X. Y. Chen, P. Cheng, D. Z. Liao, S. P. Yan and Z. H. Jiang, *J. Am. Chem. Soc.*, 2004, **126**, 15394; (b) W. Liu, T. Jiao, Y. Li, Q. Liu, M. Tan, H. Wang and L. Wang, *J. Am. Chem. Soc.*, 2004, **126**, 2280; (c) B. Chen, L. Wang, F. Zapata, G. Qian and E. B. Lobkovsky, *J. Am. Chem. Soc.*, 2008, **130**, 6718; (d) B. Chen, L. Wang, Y. Xiao, F. R. Fronczek, M. Xue, Y. Cui and G. Qian, *Angew. Chem., Int. Ed.*, 2009, **48**, 500; (e) B. V. Harbuzaru, A. Corma, F. Rey, P. Atienzar, J. L. Jordá, H. García, D. Ananias, L. D. Carlos and J. Rocha, *Angew. Chem., Int. Ed.*, 2008, **47**, 1080; (f) B. Chen, Y. Yang, F. Zapata, G. Lin, G. Qian and E. B. Lobkovsky, *Adv. Mater.*, 2007, **19**, 1693; (g) Y. Qiu, H. Deng, J. Mou, S. Yang, M. Zeller, S. R. Batten, H. Wu and J. Li, *Chem. Commun.*, 2009, 5415; (h) H. Kozłowski, A. Janicka-Kłós, J. Brasun, E. Gaggelli, D. Valensin and G. Valensin, *Coord. Chem. Rev.*, 2009, **253**, 2665; (i) E. L. Que, D. W. Domaille and C. J. Chang, *Chem. Rev.*, 2008, **108**, 1517.
- 11 (a) M. D. Allendorf, C. A. Bauer, R. K. Bhakta and R. J. T. Houk, *Chem. Soc. Rev.*, 2009, **38**, 1330; (b) Y. J. Cui, Y. F. Yue, G. D. Qian and B. L. Chen, *Chem. Rev.*, 2012, **112**, 1126; (c) J. Rocha, L. D. Carlos, F. A. A. Paz and D. Ananias, *Chem. Soc. Rev.*, 2011, **40**, 926; (d) L. D. Carlos, R. A. S. Ferreira and S. J. L. Ribeiro, *Adv. Mater.*, 2009, **21**, 509; (e) K. Binnemans, *Chem. Rev.*, 2009, **109**, 4283; (f) H. L. Jiang and Q. Xu, *Chem. Commun.*, 2011, **47**, 3351.
- 12 (a) K. A. White, D. A. Chengelis, M. Zeller, S. J. Geib, J. Szakos, S. Petoud and N. L. Rosi, *Chem. Commun.*, 2009, 4506; (b) K. A. White, D. A. Chengelis, K. A. Gogick, J. Stehman, N. L. Rosi and S. Petoud, *J. Am. Chem. Soc.*, 2009, **131**, 18069; (c) H. L. Jiang, N. Tsumori and Q. Xu, *Inorg. Chem.*, 2010, **49**, 10001; (d) W. J. Rieter, K. M. L. Taylor, H. An, W. Lin and W. Lin, *J. Am. Chem. Soc.*, 2006, **128**, 9024; (e) Q. G. Meng, R. J. Witte, Y. J. Gong, E. L. Day, J. C. Chen, P. S. May and M. T. Berry, *Chem. Mater.*, 2010, **22**, 6056; (f) H. L. Guo, Y. Z. Zhu, S. L. Qiu, J. A. Lercher and H. J. Zhang, *Adv. Mater.*, 2010, **22**, 4190; (g) Y. J. Cui, G. D. Qian and B. L. Chen, *J. Am. Chem. Soc.*, 2012, **134**, 3979.
- 13 (a) S. I. Weissman, *J. Chem. Phys.*, 1942, **10**, 214; (b) F. J. Steemers, W. Verboom, D. N. Reinhoudt, E. B. van der Tol and J. W. Verhoeven, *J. Am. Chem. Soc.*, 1995, **117**, 9408.
- 14 (a) Z. Y. Guo, H. Xu, S. Q. Su, J. F. Cai, S. Dang, S. C. Xiang, G. D. Qian, H. J. Zhang, M. O'Keefe and B. L. Chen, *Chem. Commun.*, 2011, **47**, 5551; (b) S. Dang, E. Ma, Z. M. Sun and H. J. Zhang, *J. Mater. Chem.*, 2012, **22**, 16920; (c) W. T. Yang, J. Feng and H. J. Zhang, *J. Mater. Chem.*, 2012, **22**, 6819; (d) S. Dang, J. H. Zhang, Z. M. Sun and H. J. Zhang, *Chem. Commun.*, 2012, **48**, 11139.
- 15 (a) M. H. Zeng, Q. X. Wang, Y. X. Tan, S. Hu, H. X. Zhao, L. S. Long and M. Kurmoo, *J. Am. Chem. Soc.*, 2010, **132**, 2561; (b) Z. Yin, Q. X. Wang and M. H. Zeng, *J. Am. Chem. Soc.*, 2012, **134**, 4857; (c) Y. C. He, J. Yang, G. C. Yang, W. Q. Kan and J. F. Ma, *Chem. Commun.*, 2012, **48**, 7859.
- 16 Z. J. Lin, B. Xu, T. F. Liu, M. N. Cao, J. Lü and R. Cao, *Eur. J. Inorg. Chem.*, 2010, **2010**, 3842.
- 17 G. M. Sheldrick, *SHELXL-97, Program for refinement of crystal structures*, University of Göttingen, Germany, 1997.
- 18 Z. M. Hao, S. Y. Song, S. Q. Su, X. Z. Song, M. Zhu, S. N. Zhao, X. Meng and H. J. Zhang, *Cryst. Growth Des.*, 2013, **13**, 976.
- 19 K. L. Wong, G. L. Law, Y. Y. Yang and W. T. Wong, *Adv. Mater.*, 2006, **18**, 1051.
- 20 W. G. Lu, L. Jiang, X. L. Feng and T. B. Lu, *Inorg. Chem.*, 2009, **48**, 6997.
- 21 B. Zhao, P. Cheng, X. Y. Chen, C. Cheng, W. Shi, D. Z. Liao, S. P. Yan and Z. H. Jiang, *J. Am. Chem. Soc.*, 2004, **126**, 3012.
- 22 B. V. Harbuzaru, A. Corma, F. Rey, J. L. Jorda, D. Ananias, L. D. Carlos and J. Rocha, *Angew. Chem., Int. Ed.*, 2009, **48**, 6476.
- 23 W. Lin, W. J. Rieter and K. M. L. Taylor, *Angew. Chem., Int. Ed.*, 2009, **48**, 650.
- 24 (a) F. Wang, R. R. Deng, J. Wang, Q. X. Wang, Y. Han, H. M. Zhu, X. Y. Chen and X. G. Liu, *Nat. Mater.*, 2011, **10**, 968; (b) K. A. Abel, J. C. Boyer, C. M. Andrei and F. C. J. M. van Veggel, *J. Phys. Chem. Lett.*, 2011, **2**, 18.
- 25 (a) W. T. Yang, J. Feng, S. Y. Song and H. J. Zhang, *ChemPhysChem*, 2012, **13**, 2734; (b) X. Q. Xiao, L. B. Wang, Y. J. Cui, B. L. Chen, F. Zapata and G. D. Qian, *J. Alloys Compd.*, 2009, **484**, 601.
- 26 (a) Z. W. Chen, B. Holmberg, W. Z. Li, X. Wang, W. Q. Deng, R. Munoz and Y. S. Yan, *Chem. Mater.*, 2006, **18**, 5669; (b) X. Li, E. P. L. Roberts, S. M. Holmes and V. Zholobenko, *Solid State Ionics*, 2007, **178**, 1248; (c) R. Marschall, I. Bannat, A. Feldhoff, L. Z. Wang, G. Q. Lu and M. Wark, *Small*, 2009, **5**, 854; (d) S. Sanghi, M. Tuominen and E. B. Coughlin, *Solid State Ionics*, 2010, **181**, 1183.
- 27 (a) J. A. Hurd, R. Vaidhyanathan, V. Thangadurai, C. I. Ratcliffe, I. L. Moudrakovski and G. K. H. Shimizu, *Nat. Chem.*, 2009, **1**, 705; (b) S. Bureekaew, S. Horike,

- M. Higuchi, M. Mizuno, T. Kawamura, D. Tanaka, N. Yanai and S. Kitagawa, *Nat. Mater.*, 2009, **8**, 831.
- 28 (a) H. Kitagawa, Y. Nagao, M. Fujishima, R. Ikeda and S. Kanda, *Inorg. Chem. Commun.*, 2003, **6**, 346; (b) T. Yamada, M. Sadakiyo and H. Kitagawa, *J. Am. Chem. Soc.*, 2009, **131**, 3144; (c) S. Ohkoshi, K. Nakagawa, K. Tomono, K. Imoto, Y. Tsunobuchi and H. Tokoro, *J. Am. Chem. Soc.*, 2010, **132**, 6620.
- 29 S. T. Meek, J. A. Greathouse and M. D. Allendorf, *Adv. Mater.*, 2011, **23**, 249.