Soft material with intense photoluminescence obtained by dissolving Eu_2O_3 and organic ligand into a task-specific ionic liquid†

Huanrong Li,* Huifang Shao, Yige Wang,* Dashan Qin, Binyuan Liu, Wenjun Zhang and Weidong Yan

Received (in Cambridge, UK) 23rd June 2008, Accepted 1st August 2008
First published as an Advance Article on the web 10th September 2008
DOI: 10.1039/b810631b

A task-specific ionic liquid containing a carboxylate group with the ability to dissolve metal oxide and organic ligands has been used as the solvent to prepare lanthanide complexes without the addition of extra solvent; thus a soft material with intense photoluminescence has been obtained by directly dissolving Eu_2O_3, 2-thenoyltrifluoroacetone (TTA) and 1,10-phenanthroline (Phen) into the task-specific ionic liquid.

Ionic liquids have attracted considerable attention during the past few years due to their very low vapor pressure, their wide liquid range, their good electric conductivity, their large electrochemical window, and their potential as solvents for liquid–liquid extraction.[1] Furthermore, many ionic liquids are colorless or have only a slight (yellowish) color and are transparent through almost the whole visible and near-infrared spectral regions.[2] This, together with their excellent stability, makes them very interesting as optical solvents. Therefore, it would be an interesting topic to investigate the spectroscopic behavior of lanthanide complexes, and whether lanthanide-doped ionic liquids can be regarded as new luminescent 'soft' materials.[3] Lanthanide complexes show intense luminescence in the visible and near-infrared regions with many favorable properties such as narrow emission bands, long decay times, and a large Stokes' shift. Actually, lanthanide compounds have gained widespread attention as potential materials for light-emitting diodes, medical and biological applications.[4] Some recent studies demonstrate the use of room-temperature ionic liquids (RTILs) in photochemistry and spectroscopy.[2,3,5]

Despite the wealth of literature on the use of ionic liquids as 'green solvents' for organic reactions, as catalysts, and as unique solvents for the IL/aqueous extractions, there are relatively few studies on the luminescence properties of trivalent lanthanide ions in IL. [2,3,5] In addition, most of lanthanide complex-containing ionic liquids to date were prepared by dissolving the lanthanide complexes in the corresponding ionic liquid. Nevertheless, this always requires the preparation of lanthanide complexes in advance. It would be very interesting and attractive if one can obtain luminescent lanthanide complex/ionic liquid by directly dissolving lanthanide oxide and organic ligand into ionic liquid without the addition of extra solvents. Recently, Binnemans and co-workers have reported the dissolution of metal oxides in a task-specific ionic liquid (TSIL) containing carboxylate.[6] This encouraged us to try an alternative way to obtain lanthanide complex-containing ionic liquids by directly co-dissolving lanthanide oxides and organic ligands into a task-specific ionic liquid.

In the present work, we report an original method to introducing a highly luminescent lanthanide complex into ionic liquid by directly dissolving Eu_2O_3 and the organic ligands TTA and Phen into the task-specific ionic liquid 3-(5-carboxypropyl)-1-methylimidazolium bromide. To the best of our knowledge, this is the first report in this regard.

3-(5-Carboxypropyl)-1-methylimidazolium bromide was prepared according the previously reported procedure.[7] An interesting property of the ionic liquid is its ability to dissolve Eu_2O_3 because the europium oxide can react with the carboxylic acid from the ionic liquid to form carboxylate complexes and water.[6] IL-Eu was obtained by dissolving an appropriate amount of Eu_2O_3 into the synthesized ionic liquid; IL–Eu–TTA was prepared by dissolving TTA into IL–Eu, and IL–Eu–TTA–Phen was synthesized by dissolving Phen into IL–Eu–TTA. Both IL–Eu–TTA and IL–Eu–TTA–Phen are highly transparent and luminescent as shown in Fig. 1. However, irradiating IL–Eu with UV-lamp (365 nm) produces no obvious emission.

Fig. 2 shows the excitation and emission of IL–Eu. Several discrete f–f transitions can be observed at 362 ($^7F_0 \rightarrow {}^5D_4$), 380 ($^7F_0 \rightarrow {}^5G_2$), 395 ($^7F_0 \rightarrow {}^5L_6$), 415 ($^7F_0 \rightarrow {}^5D_3$) and 465 nm ($^7F_0 \rightarrow {}^5D_2$), the most efficient excitation wavelength being at 395 nm.[8] After excitation at 395 nm, the emission spectrum of IL–Eu clearly shows the emission bands centered at 579, 592, 615, 650 and 697 nm, corresponding to $^5D_0 \rightarrow {}^7F_{0-4}$

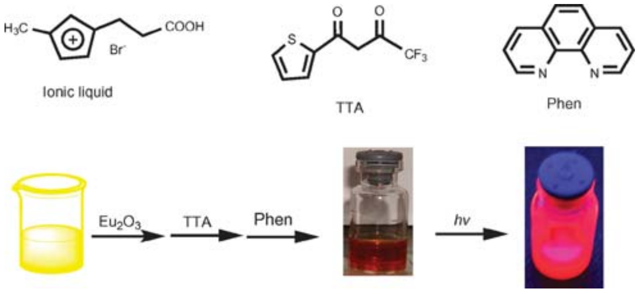

Fig. 1 Ionic liquid and organic ligand used in this study (top) and the procedure for obtaining lanthanide complex in ionic liquid (bottom).

School of Chemical Engineering and Technology, Hebei University of Technology, Tianjin, 300130, ChinaE-mail: lihuanrong@hebut.edu.cn; E-mail: wangyige@hebut.edu.cn; Fax: 0086225264294; Tel: 00862260200441

† Electronic supplementary information (ESI) available: ESI1: Decay curve of IL–Eu. ESI2: Excitation and emission spectra of $Eu(TTA)_3$Phen in the solid state and in IL. ESI3: Decay curve of IL–Eu–TTA–Phen. See DOI: 10.1039/b810631b

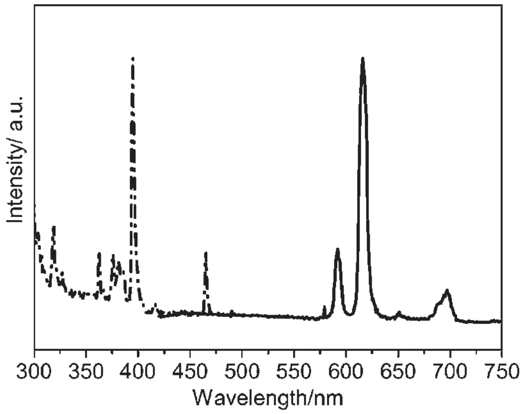

Fig. 2 Excitation (---) and emission (—) spectra of IL–Eu.

transitions, respectively. The luminescence decay curve is found to be mono-exponential and the luminescence decay time of the $^5D_0$ level is 0.136 ms (see ESI†).

The ionic liquid shows an intense red photoluminescence when irradiated with UV radiation upon dissolving the organic ligands TTA and Phen into the europium(III) ion-containing ionic liquid (Fig. 1). The excitation and emission spectra of IL–Eu–TTA–Phen are shown in Fig. 3. The excitation spectrum obtained by monitoring the $^5D_0 \rightarrow {}^7F_2$ transition at 612 nm displays a broad excitation band peaking at 377 nm, which may result from the $\pi \rightarrow \pi^*$ transitions of the organic ligands. The absence of negligible intensity of the intra-4f^6 transitions in the excitation spectrum indicates that an energy transfer occurs from the ligands to the central Eu^{3+} ions. Excitation of the ligands (337 nm) leads to sharp emission peaks arising from transitions between $^5D_0 \rightarrow {}^7F_J$ crystal-field components (J = 0, 1, 2, 3, 4) while no broad emission band resulting from organic ligand molecules in the blue region can be observed. The typical red color of europium emission is mostly attributed to the strongest transition $^5D_0 \rightarrow {}^7F_2$ centered at 613 nm. The fine splitting of the $^5D_0 \rightarrow {}^7F_2$ europium peak into distinct crystal field components points to a 'crystalline' lanthanide ion environment, rather than an amorphous one and indicates that in fact a europium complex is formed in the ionic liquid.[9] The excitation and emission spectral features are very similar to that of the ternary complex (Eu(TTA)$_3$Phen) both as solid and dissolved in the IL (see ESI†), which further proves that both TTA and Phen are coordinated to the metal ions. In addition, the non-observation of Eu^{3+} intra-4f^6 lines in the excitation spectrum of IL–Eu–TTA–Phen compared with those of the ternary complex (Eu(TTA)$_3$Phen) both as solid and dissolved in the IL suggests that the IL contributes to enhance the Eu^{3+} sensitization process with respect to direct excitation into the 4f lines.[10] Furthermore, the detection of a single line for the $^5D_0 \rightarrow {}^7F_0$ transition, the local-field splitting of the $^7F_{1,2}$ levels and the higher intensity of the $^5D_0 \rightarrow {}^7F_2$ transition indicate that the Eu^{3+} local coordination site has a low symmetry without an inversion center.[11] The $^5D_0$ emission decay curve was monitored within the $^5D_0 \rightarrow {}^7F_2$ transition under the excitation wavelength maximizing the emission intensity. The decay curve is well-reproduced by means of a single-exponential function, yielding a $^5D_0$ lifetime value of 0.793 ms. IL–Eu–TTA displays similar luminescence behavior to IL–Eu–TTA–Phen except for its much shorter lifetime (τ = 0.34 ms) and lower splitting of the $^5D_0 \rightarrow {}^7F_2$ transition. The prolonged lifetime compared with IL–Eu could be ascribed to the removal of water molecules from the first coordination sphere of Eu^{3+} ions by the organic ligands (Phen).[12]

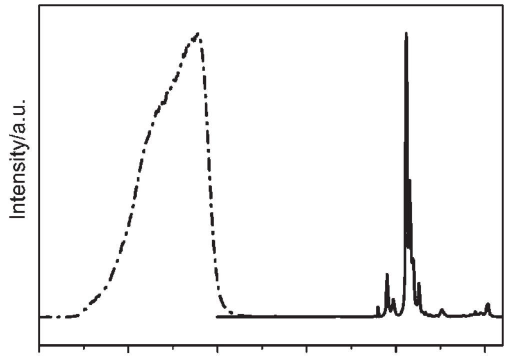

Fig. 3 Excitation (---) and emission (—) spectra of IL–Eu–TTA–Phen.

The $^5D_0$ quantum efficiency (q) and the number of the water molecules, n_w, coordinated to the Eu^{3+} ion can be estimated on the basis of emission spectrum and lifetime of $^5D_0$ state by using the following equations according to ref. 13. Assuming that only nonradiative and radiative processes are involved in the depopulation of the $^5D_0$ state, q may be defined as:

$$q = k_r/(k_r + k_{nr}) \qquad (1)$$

where k_r and k_{nr} are the radiative and nonradiative probabilities, respectively. The radiative contribution maybe calculated from the relative intensities of the $^5D_0$–^7F_J (J = 0–4) transitions (the transitions $^5D_0$–^7F_J with J = 5 and 6 are either not observed or are very weak) and can be expressed as:

$$k_r = \frac{A_{0-1}E_{0-1}}{S_{0-1}} \sum_{J=0}^{4} \frac{S_{0-J}}{E_{0-J}} \qquad (2)$$

where A_{0-1} is the Einstein coefficient of spontaneous emission between the $^5D_0$ and $^7F_1$ level, usually considered to be equal to 50 s^{-1}, and E_{0-J} and S_{0-J} are the energy and the integrated intensity of the $^5D_0$–^7F_J transitions, respectively.

On the basis of the empirical formula suggested by Supkowski and De Horrocks Jr,[14] we can estimate the number of water molecules (n_w) coordinated to the metal ions in the material, which can be written as:[13]

$$n_w = 1.1\,(k_{exp} - k_r - 0.31) \qquad (3)$$

where k_{exp} is the reciprocal value of the $^5D_0$ lifetime. The data obtained are summarized in Table 1. From the result, it is

Table 1 Experimental $^5D_0$ lifetime, calculated radiative and non-radiative $^5D_0$ decay rate, $^5D_0$ quantum efficiency value, experimental quantum yield and number of waters coordinated to Eu $^{3+}$ ion in IL–Eu–TTA–Phen

τ/ms	0.793
k_r/ms^{-1}	0.491
k_{nr}/ms^{-1}	0.770
q (%)	39
n_w	0.5

reasonable to assume that most of the water molecules have been expelled from the first coordination sphere of Eu^{3+} ions.

In summary, 3-(5-carboxypropyl)-1-methylimidazolium bromide is a useful task-specific ionic liquid that can be used for dissolving europium oxide and organic ligand. Consequently, a soft material has been obtained by directly dissolving Eu_2O_3 and TTA as well as Phen into the task-specific ionic liquid. The obtained soft material shows high luminescence and could find potential applications in emission displays and laser dyes despite the low concentration of lanthanide complexes in the ionic liquid (*ca.* 3 mol%). We are currently improving our method by adding water to the ionic liquid to increase the concentration of lanthanide ions and lanthanide complexes.[6] Our preliminary results indicate the concentration of lanthanide ions in the ionic liquid can reach 33 mol%. The extension of this method to lanthanide complexes other than those of europium are being done in our lab.

This work is financially supported by Hebei University of Technology, the Key Project of Chinese Ministry of Education (208016), Ministry of Personal, People's Republic of China and Department of Personal, Hebei Province, the Scientific Program launched in 2008 by Hebei province (08965110D) and National Natural Science Foundation of China (No. 20636030).

Notes and references

1 (*a*) T. Welton, *Chem. Rev.*, 1999, **99**, 2071; (*b*) *Ionic Liquids in Synthesis*, ed. P. Wasserscheid and P. T. Welton, Wiley-VCH, Weinheim, Germany, 2003; (*c*) A. E. Visser and R. D. Rogers, *J. Solid State Chem.*, 2003, **171**, 109; (*d*) G. H. Tao, L. He, W. S. Liu, L. Xu, W. Xing, T. Wang and Y. Kou, *Green Chem.*, 2006, **8**, 639; (*e*) M. Antonietti, D. B. Kuang, B. Smarsly and Y. Zhou, *Angew. Chem., Int. Ed.*, 2004, **43**, 4988; (*f*) M. Antonietti, D. B. Kuang, B. Smarsly and Y. Zhou, *Chem. Commun.*, 2001, 135.

2 K. Driesen, P. Nockemann and K. Binnemans, *Chem. Phys. Lett.*, 2004, **395**, 306.

3 P. Nockemann, E. Beurer, K. Driesen, R. Van Deun, K. Van Hecke, L. Van Meervelt and K. Binnemans, *Chem. Commun.*, 2005, 4354.

4 (*a*) J. Kido and Y. Okamoto, *Chem. Rev.*, 2002, **102**, 2357; (*b*) D. Parker, *Coord. Chem. Rev.*, 2000, **205**, 109; (*c*) V. W. W. Yam and K. K. W. Lo, *Coord. Chem. Rev.*, 1999, **184**, 157; (*d*) N. Sabbatini, M. Guardigli and J.-M. Lehn, *Coord. Chem. Rev.*, 1993, **123**, 201.

5 (*a*) P. Nockemann, B. Thijs, N. Postelmans, K. Van Hecke, L. Van Meerveltand and K. Binnemans, *J. Am. Chem. Soc.*, 2006, **128**, 13658; (*b*) E. Guillet, D. Scopelliti and J.-C. G. Buenzil, *Chem. Mater.*, 2004, **16**, 4063; (*c*) K. Lunstroot, K. Driesen, P. Nockemann, C. Goerller-Walrand, K. Binnemans, S. Bellayer, J. Le Bideau and A. Vioux, *Chem. Mater.*, 2006, **18**, 5711; (*d*) A. Babai and A.-V. Mudring, *Chem. Mater.*, 2005, **17**, 6230; (*e*) C. Gaillard, I. Billard, A. Chaumont, S. Mekki, A. Quadi, M. A. Denecke, G. Moutiers and G. Wipff, *Inorg. Chem.*, 2005, **44**, 8355; (*f*) S. Samikkanu, K. Mellem, M. Berry and P. S. May, *Inorg. Chem.*, 2007, **46**, 7121.

6 P. Nockemann, B. Thijs, S. Pittois, J. Thoen, C. Glorieux, K. Van Hecke, L. Van Meervelt, B. Kirchner and K. Binnemans, *J. Phys. Chem. B*, 2006, **110**, 20978.

7 J. F. Dubreuil and J. P. Bazureau, *Tetrahedron Lett.*, 2000, **41**, 7351.

8 P. P. Yang, Z. W. Quan, C. X. Li, J. Yang, H. Wang, X. M. Liu and J. Lin, *J. Solid State Chem.*, 2008, in press.

9 M. H. Bartl, B. J. Scott, H. C. Huang, G. Wirnsberger, A. Popitsch, B. F. Chmelka and G. D. Stucky, *Chem. Commun.*, 2002, 2474.

10 P. P. Lima, R. A. Sá Ferreira, R. O. Freire, F. A. Almeida Paz, L. S. Fu, S. Alves, Jr, L. D. Carlos and O. L. Malta, *ChemPhysChem*, 2006, **7**, 735.

11 L. S. Fu, R. A. S. Ferreira, N. J. O. Silva, A. J. Fernandes, P. Ribeiro-Claro, I. S. Gonçalves, V. de Z. Bermudez and L. D. Carlos, *J. Mater. Chem.*, 2005, **15**, 3117.

12 K. Binnemans, P. Lenaerts, K. Driesen and C. Görller-Walrand, *J. Mater. Chem.*, 2004, **14**, 191.

13 M. Fernandes, V. de Zea Bermudez, R. A. Sá Ferreira, L. D. Carlos, A. Charas, J. Morgado, M. M. Silva and M. J. Smith, *Chem. Mater.*, 2007, **19**, 3892.

14 R. M. Supkowski and W. De Horrocks, Jr, *Inorg. Chim. Acta*, 2002, **340**, 44.