

A Series of Carboxylic-Functionalized Ionic Liquids and their Solubility for Lanthanide Oxides

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Abstract: Herein we report the synthesis of propanoic acid functionalized ionic liquids (ILs) with various lengths of alkyl chain on the imidazole ring. The synthesized propanoic acid functionalized ILs were used to dissolve Eu₂O₃ (or Tb₄O₇) due to the formation of europium(III) (or terbium(III)) car-

boxylate, aimed to get soft luminescent materials combining the properties of ILs and attractive luminescent proper-

Keywords: europium · ionic liquids · lanthanides · luminescence · terbium

ties of lanthanide ions. The luminescent behavior of Eu³⁺ and Tb³⁺ in the ILs were investigated by luminescence spectroscopy. The affect of the alkyl chain on the luminescent behavior (the asymmetry parameter (*R*), the lifetime of ⁵D₀, and the ⁵D₀ quantum efficiency) of Eu³⁺ has been discussed.

Introduction

Room temperature ionic liquids (RTILs) are a new class of solvents that are entirely constituted of large organic cations, such as imidazolium, pyridinium, and tetraalkylammonium, appended with alkyl groups and combined with various anions.^[1] RTILs 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. The appropriate combination of the anion/cation allows tuning of ionic liquids, such as dissolving ability, polarity, viscosity, and density. RTILs are, therefore, often considered as designer solvents and are showing promising perspectives in various application fields of synthesis, catalysis, materials science, electrochemistry, and separation technology both at the laboratory level and on the industrial scale.^[2–8]

Recently, increased efforts have been directed towards the exploration of the functionalized ionic liquids that are ionic liquids with a functional group covalently tethered to the cationic or anionic part.^[9] Up to date, a variety of functional groups, such as amino,^[10] terpyridine,^[11] carboxylic acid,^[12] thioether,^[13] and others^[14] have been incorporated

into the cations of ionic liquids for specific applications, such as catalysis, electrochemistry, organic synthesis, metal-ion separation, and the synthesis of nanomaterials and functional materials.^[15]

Lanthanide-containing ILs are highly attractive as they might be used as advanced catalysts and as promising soft luminescent materials.^[15–24] Furthermore, special interest for f elements in ILs comes from actinide and Ln separation and extraction as well as nuclear fuel reprocessing and waste treatment.^[25,26] Nevertheless, the low solubility of Ln compounds hampers the possible applications of ionic ILs that require high concentrations of dissolved metal, such as the electrodeposition of metals or solvents for the synthesis of nanoparticles. Incorporating Ln ions as an anion endows a promising way to increase the concentration.^[27–29] An alternative approach to increase the solubility of metal salts in ILs is to use TSILs (TSIL = task-specific ionic liquids) in which a complexing moiety is grafted onto the cation skeleton.^[30–35] This method has opened new routes for liquid–liquid extraction purposes.^[36]

Among these functional groups, the carboxylic functional groups seem to be the most useful for dissolving lanthanide compounds. For example, Binnemans and co-workers have reported on the TSIL bearing a carboxyl group that has a selective solubilizing ability for metal oxides in the presence of water.^[30–32] We have obtained highly luminescent materials through directly dissolving lanthanide oxide and organic ligands with TSILs bearing carboxyl functional groups.^[33–35] However, Tb₄O₇ could not be dissolved by the carboxyl-functionalized TSIL under the conditions described in the literature.^[33,34]

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Herein, we report the synthesis of carboxylic-acid-functionalized ILs with linear alkyl chains of various length on the cations ([Carb- C_n minm]Br, $n=8, 12, 16$). We also test the solubilizing ability for Eu_2O_3 and Tb_4O_7 of the synthesized ILs that lead to soft luminescent materials combined of Ln^{3+} ions and ILs, and the luminescent properties of the obtained soft materials were investigated in detail. We also discussed the affect of alkyl chains on the luminescent behavior of Eu^{3+} or Tb^{3+} ions in the ILs in detail.

Results and Discussion

The carboxylic-functionalized ILs can be easily obtained from 3-bromopropanoic acid and the corresponding alkylimidazole in EtOH under reflux, which were purified by repeated washing with Et_2O . [Carb- C_n minm]Br ($n=8$) are viscous liquids with a slight orange color at room temperature and [Carb- C_{12} minm]Br and [Carb- C_{16} minm]Br are waxlike and white solids at room temperature, respectively (Figure 1). One of the interesting and useful properties of the ILs is the ability to dissolve lanthanide oxide in an aqueous solution. Eu_2O_3 is found to be soluble in [Carb- C_n minm]Br under heating at 90°C for less than half an hour. Except for [Carb- C_{16} minm]Br, which is a waxlike solid upon reaction with Eu_2O_3 , all the compounds are transparent and highly viscous solids with a slightly yellowish color at room temperature. Tb_4O_7 is insoluble in this ionic liquid under the identical experimental conditions used to dissolve Eu_2O_3 . However, it can be solubilized in [Carb- C_n minm]Br by heating the mixture in a Teflon-lined stainless steel autoclave at 120°C .

The formation of the carboxylate complexes can be verified by FTIR spectra (Figure 2). As shown in Figure 2a, the vibration band in the range of $3100\text{--}2800\text{ cm}^{-1}$ can be ascribed to the C–H stretching of the ring and of the aliphatic chain, whereas absorption bands at 1633, 1570, 1455, and 1172 cm^{-1} can be ascribed to ring stretching of the imidazolium ring. The strong and sharp absorption band at 1729 cm^{-1} is due to the stretching vibration of C=O of COOH groups. Upon reaction with Eu_2O_3 , the band at 1729 cm^{-1} disappears and two strong bands at 1570 and 1437 cm^{-1} can be observed (Figure 2c), which can be assigned to the asymmetric and symmetric stretching vibration of the carboxylate group, respectively.

Figure 3 shows the luminescence data of europium(III) in [Carb- C_n minm]Br. The excitation spectra were obtained by monitoring the $\text{Eu}^{3+} \ ^5\text{D}_0 \rightarrow \ ^7\text{F}_2$ transition at 615 nm, and the emission spectra were measured by excitation into the $\text{Eu}^{3+} \ ^7\text{F}_0 \rightarrow \ ^5\text{L}_6$ absorption line at 394 nm. All of the samples show similar excitation spectra composed of a weak broad band ranging from 200 to 400 nm and several discrete linelike f–f transitions of Eu^{3+} ions at 320 ($\ ^7\text{F}_0 \rightarrow \ ^7\text{H}_6$), 362 ($\ ^7\text{F}_0 \rightarrow \ ^5\text{D}_4$), 380 ($\ ^7\text{F}_0 \rightarrow \ ^5\text{G}_2$), 395 ($\ ^7\text{F}_0 \rightarrow \ ^5\text{L}_6$), 415 ($\ ^7\text{F}_0 \rightarrow \ ^5\text{D}_3$), and 465 nm ($\ ^7\text{F}_0 \rightarrow \ ^5\text{D}_2$) with the most efficient excitation length being 395 nm,^[37] which is much stronger than the broad band as revealed in Figure 3. Excitation into the $\ ^7\text{F}_0 \rightarrow \ ^5\text{L}_6$ absorption

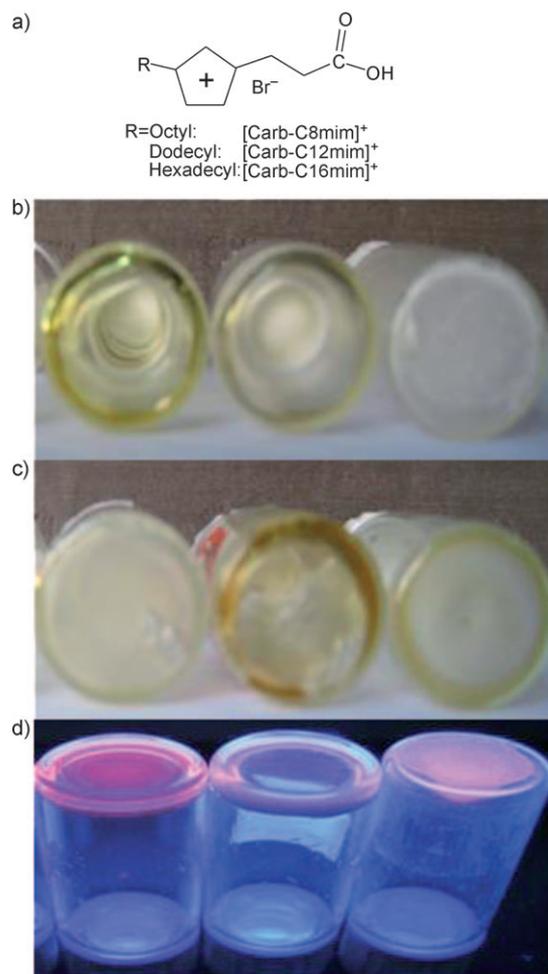


Figure 1. a) Carboxylic-functionalized ILs synthesized in this study. b,c) Photographs of the ILs upon dissolving Eu_2O_3 (b), Tb_4O_7 (c), and Eu_2O_3 with irradiation under a UV lamp (d).

line at 394 nm leads to sharp emission peaks arising from the transition between $\ ^5\text{D}_0 \rightarrow \ ^7\text{F}_J$ ($J=0\text{--}4$) emission bands located at 579, 590, 614, 653, and 703 nm, respectively, with

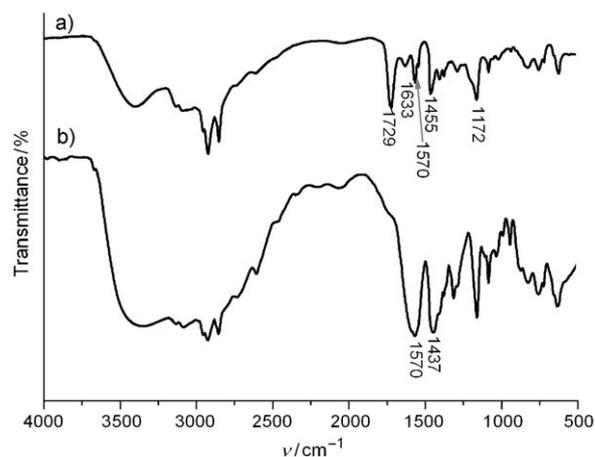


Figure 2. FTIR spectrum of [Carb- C_{12} minm]Br (a) and upon dissolving Eu_2O_3 (b). t_{dec} = decay time.

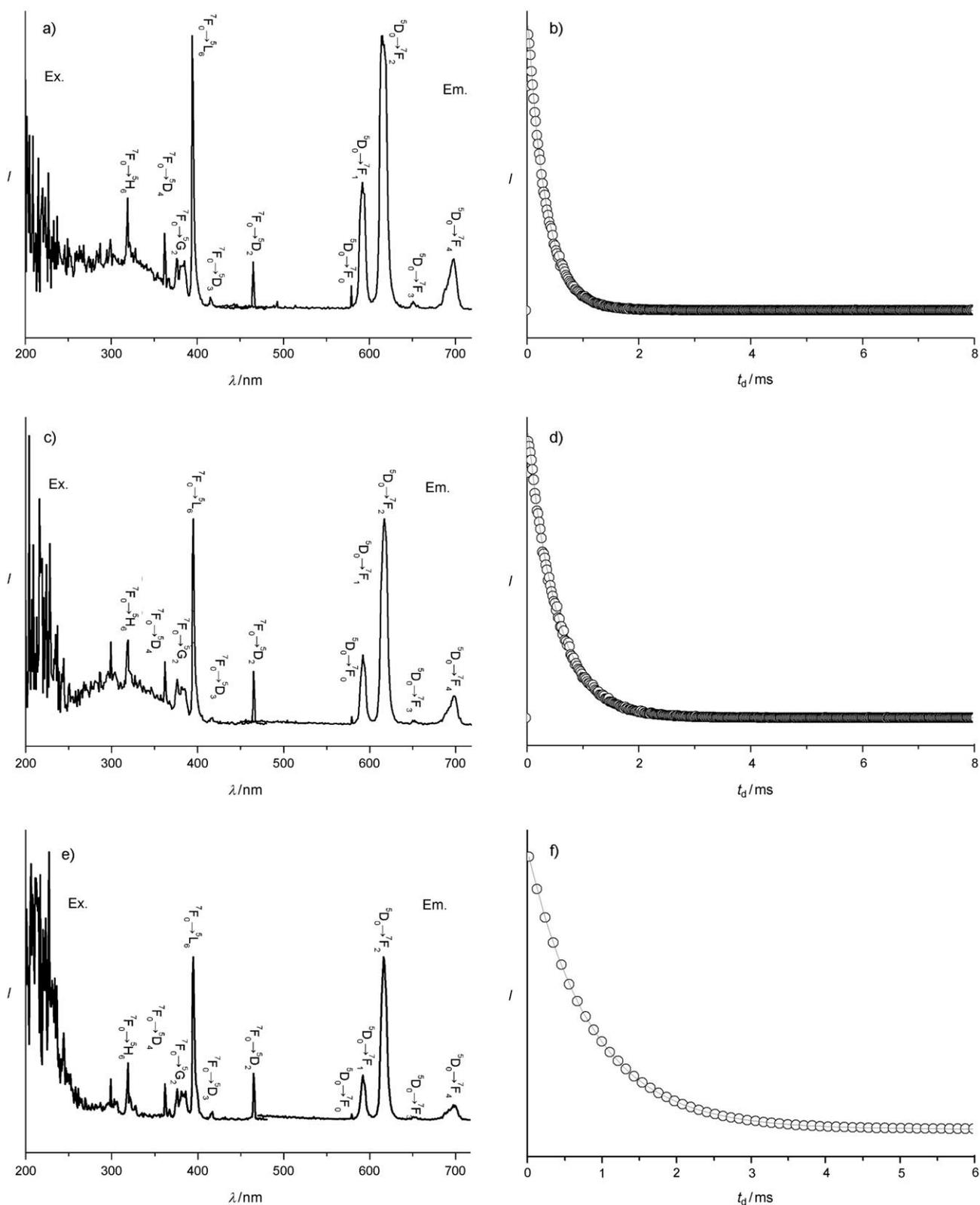


Figure 3. Excitation (.....) and emission spectra (—) of the ILs upon dissolving Eu_2O_3 in a) [Carb-C₈minm]Br, c) [Carb-C₁₂minm]Br, and e) [Carb-C₁₆minm]Br. Decay curve of $\text{Eu}^{3+} {}^5D_0$ in b) [Carb-C₈minm]Br, d) [Carb-C₁₂minm]Br, and f) [Carb-C₁₆minm]Br. \circ : experimental data; —: fitted according to $I = I_0 + A \exp[-(t - t_0)/\tau]$. Excitation wavelength was at 395 nm.

the hypersensitive transition ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$ as the most prominent line, which suggests that Eu^{3+} sites are indeed without a center of inversion.^[38] The ${}^5\text{D}_0 \rightarrow {}^7\text{F}_1$ transition is allowed as a magnetic dipole transition and its intensity is not affected by the host environment; therefore, it can be used for the normalization.^[39] The ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$ transition is hypersensitive and thus strongly changes with the local surrounding around the Eu^{3+} ions. The intensity ratios (R) of the ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$ and ${}^5\text{D}_0 \rightarrow {}^7\text{F}_1$ transitions can be taken as a measure of the asymmetry of the Eu^{3+} sites.^[40] It is believed that the value of R becomes larger as the interaction of Eu^{3+} with its neighbors becomes stronger and the Eu^{3+} site symmetry becomes lower.^[28] From the emission spectra, we found that the value of R increases from 2.71 to 4.21 as the carbon number of linear alkyl increases from 8 to 16 (Table 1), which implies a

Table 1. Intensity ratios (R) of $I({}^5\text{D}_0 \rightarrow {}^7\text{F}_2)/I({}^5\text{D}_0 \rightarrow {}^7\text{F}_1)$, lifetimes, calculated radiative and nonradiative ${}^5\text{D}_0$ decay rate, ${}^5\text{D}_0$ quantum efficiency value (Q), and the number of H_2O molecules coordinated to Eu^{3+} ions in TSILs.

Eu^{3+} in	R	τ [ms]	k_r [ms^{-1}]	k_{nr} [ms^{-1}]	Q [%]	n_w
[Carb- C_8 minm]Br	2.71	0.33	0.24	2.56	7.76	3.07
[Carb- C_{12} minm]Br	3.57	0.51	0.29	1.67	14.80	1.52
[Carb- C_{16} minm]Br	4.21	0.85	0.34	0.86	26.70	0.84

lower site symmetry and a larger europium–ligand interaction in [Carb- C_{16} minm]Br than in [Carb- C_8 minm]Br and [Carb- C_{12} minm]Br. A monoexponential intensity decay can be detected for all samples (Figure 3b,d,f), which indicates that only one Eu^{3+} species is present. The Eu^{3+} (${}^5\text{D}_0$) lifetime in [Carb- C_8 minm]Br, [Carb- C_{12} minm]Br, and [Carb- C_{16} minm]Br can be determined to be 0.33, 0.51, and 0.85 ms, respectively (Table 1). The longer lifetime of Eu^{3+} in [Carb- C_{16} minm]Br than in [Carb- C_8 minm]Br and [Carb- C_{12} minm]Br implies that the number of H_2O molecules in the Eu^{3+} primary coordination sphere in [Carb- C_{16} minm]Br is less than that in [Carb- C_8 minm]Br and [Carb- C_{12} minm]Br since the presence of H_2O molecules contributes to nonradiative de-excitation and a reduced quantum yield for europium(III) luminescence. We therefore roughly estimated the ${}^5\text{D}_0$ quantum efficiency (Q) and the number (n_w) of H_2O molecules in the primary coordination sphere based on the emission spectra and the lifetime of the ${}^5\text{D}_0$ state by using the following equations as described in the literature.^[41]

The radiative contribution may be calculated from the relative intensities of the ${}^5\text{D}_0 \rightarrow {}^7\text{F}_J$ ($J=0-4$) transitions (the transitions ${}^5\text{D}_0 \rightarrow {}^7\text{F}_J$ with $J=5$ and 6 are either not observed or are very weak) and can be expressed as

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

in which A_{0-1} is Einstein's coefficient of spontaneous emission between the ${}^5\text{D}_0$ and ${}^7\text{F}_1$ level, usually considered to be

equal to 50 s^{-1} when an average index of refraction n equal to 1.5 was considered for both samples, and E_{0-J} and S_{0-J} are the energy and the integrated intensity of the ${}^5\text{D}_0 \rightarrow {}^7\text{F}_J$ transitions, respectively.

On the basis of the empirical formula suggested by Supkowski and De Horrocks Jr.,^[42] we can estimate the number of water molecules (n_w) coordinated to the metal ions in the material, which can be written as

$$n_w = 1.1(k_{\text{exp}} - k_r - 0.31) \quad (2)$$

in which k_{exp} is the reciprocal value of the ${}^5\text{D}_0$ lifetime. The obtained data are summarized in Table 1.

It was found from Table 1 that the Q value increases and the number of H_2O molecules in the primary coordination sphere decreases as the alkyl chain length increases; the increase in the Q value maybe attributed to a decrease in the k_{nr} value. The decrease of k_{nr} might be due to the decreased H_2O molecules in the primary coordination sphere of Eu^{3+} as shown in Table 1.

Figure 4 shows the luminescence data of terbium(III) in [Carb- C_n minm]Br ($n=8, 12, 16$). The excitation spectra were obtained by monitoring $\text{Tb}^{3+}{}^5\text{D}_4 \rightarrow {}^7\text{F}_5$ transitions at 544 nm, and the emission spectra were measured by excitation at 300 nm. The excitation spectra are consisted of a strong and broad band ranging from 220 to 400 nm with a maximum at 305 nm overlapped with a weak and narrow band. The origin of the broad band is as yet unclear. However, one possible assignment would be that it could be a bromide to terbium(III) charge transfer. In addition, a chloride to Eu^{3+} charge transfer has recently been reported in ionic liquids.^[43] The narrow band is obviously ascribed to the f–f transition of Tb^{3+} ions. Upon excitation into the broad absorption at 300 nm, the emission spectra contain four sharp emission lines peaking at 487, 543, 583, and 620 nm, which can be ascribed to the f–f transitions of Tb^{3+} (${}^5\text{D}_4 \rightarrow {}^7\text{F}_J$, $J=6,5,4,3$) with ${}^5\text{D}_4 \rightarrow {}^7\text{F}_5$ transition (green emission) as the dominant feature. A monoexponential intensity decay can be detected for all samples (Figure 4b,d,f), the ${}^5\text{D}_4$ lifetime of the green emission of Tb^{3+} in [Carb- C_n minm]Br was determined by single-exponential fitting of the decay curve to be 0.85, 0.88, and 1.16 for [Carb- C_8 minm]Br, [Carb- C_{12} minm]Br, and [Carb- C_{16} minm]Br, respectively.

Conclusions

The carboxylic-functionalized ILs with various lengths of alkyl chain on the imidazole ring can be easily obtained from 3-bromopropanoic acid and the corresponding alkyl-imidazole in EtOH under reflux and purified by repeating washing with Et_2O . Eu_2O_3 can be easily dissolved by simply heating the mixture of Eu_2O_3 and the carboxylic-functionalized IL dissolved in solvents due to the formation of europium carboxylate complexes, whereas the realization of dissolution of Tb_4O_7 in the same ILs have to be done under much more harsh conditions. It has been found that the lu-

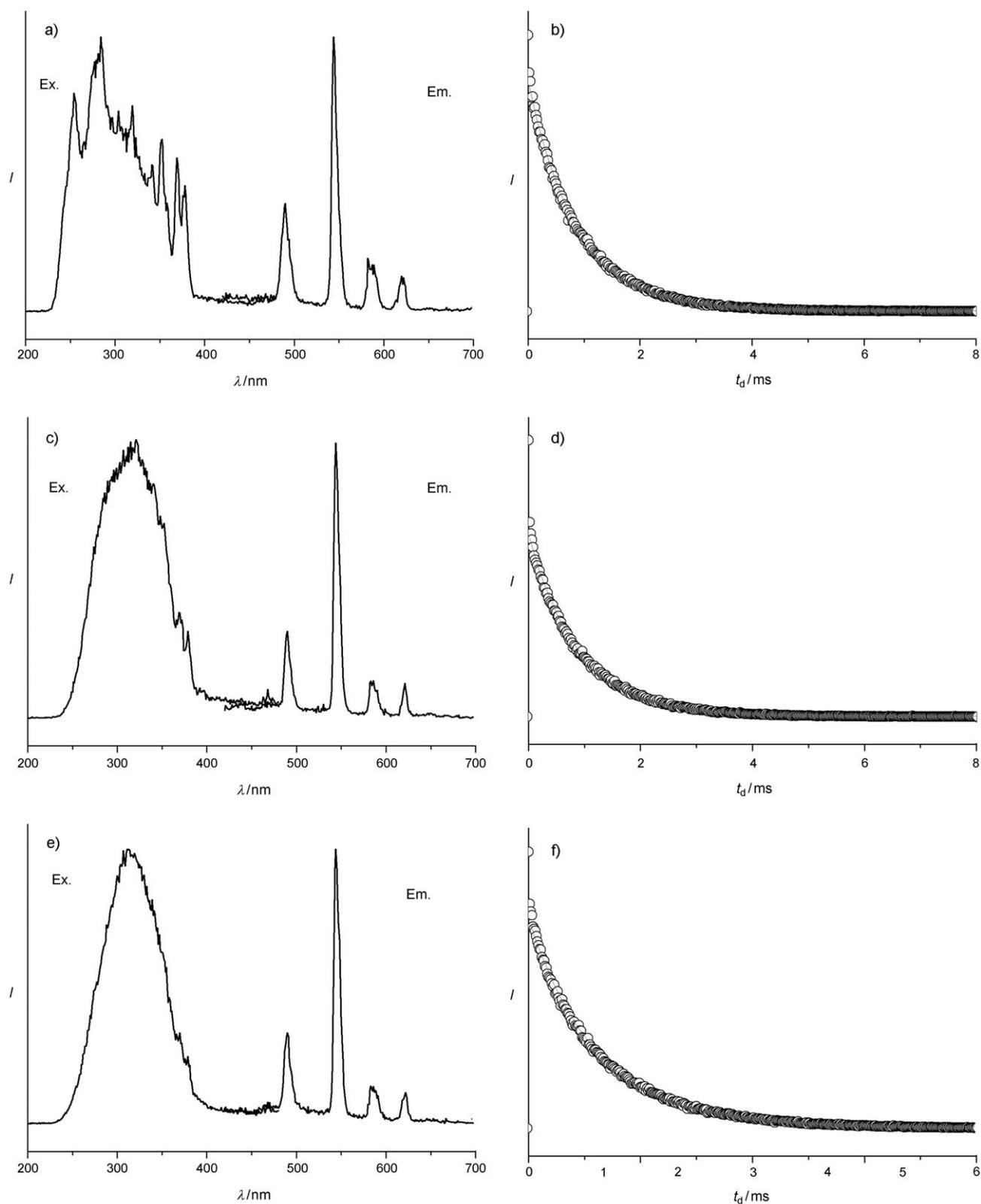


Figure 4. Excitation (.....) and emission spectra (—) of the ILs upon dissolving Tb_2O_3 . a) [Carb- C_8 minm]Br, c) [Carb- C_{12} minm]Br, and e) [Carb- C_{16} minm]Br. Decay curve of $Tb^{3+} \ ^5D_4$ in b) [Carb- C_8 minm]Br, d) [Carb- C_{12} minm]Br, and f) [Carb- C_{16} minm]Br. \circ : experimental data; —: fitted according to $I = I_0 + A \exp[-(t - t_0)/\tau]$. Excitation wavelength was at 310 nm.

minescent behavior of Eu^{3+} ions in the carboxylic-functionalized ILs, such as the asymmetry parameter (R), the life-

time of 5D_0 , and the 5D_0 quantum efficiency increases with increasing length of the alkyl chain. The properties of the

europium(III) (or terbium(III)) carboxylate complexes including high concentrations of Ln³⁺ ions, narrow linewidth and high color purity make them greatly interesting from both an academic viewpoint and for various applications. Further studies are being carried out to get the crystals of the europium(III) carboxylate complexes and to elucidate the exact origin of the broad band absorption in the excitation spectra of the samples.

Experimental Section

Materials

3-Bromopropanoic acid (98%, ALDRICH), (1*H*)-imidazole (98%, ALDRICH), 1-bromoalkane, and Bu₄NI were used as received. Alkyl-(1*H*)-imidazolium was synthesized and characterized according to the reported procedure.^[44]

Preparation of [Carb-C_nminm]Br (n = 8, 12, 16)

Alkyl-(1*H*)-imidazolium (10 mmol) was dissolved in ethanol (10 mL) and an appropriate amount of 3-bromopropionic acid was added. Then the mixture was refluxed for 5 h at 75 °C. Evaporation of the solvent under vacuum yielded the crude ionic liquid, which was purified by repeated washing with Et₂O. The obtained ionic liquids were characterized by ¹H, ¹³C NMR and FTIR spectroscopy and the purity of the ionic liquids have been verified by ¹H NMR spectroscopy.

[Carb-C₈minm]Br: ¹H NMR (400 MHz, CDCl₃): δ_H = 0.865 (t, 3H; CH₃), 1.252–1.329 (d, 10H; 5CH₂), 1.915 (t, 2H; CH₂), 3.138 (t, 2H; CH₂-COOH), 4.295 (t, 2H; N-CH₂), 4.697 (t, 2H; N-CH₂), 7.433 (s, 1H, Ring-CH), 7.878 (s, 1H; Ring-CH), 9.896 ppm (s, 1H; Ring-CH); ¹³C NMR: (400 MHz, CDCl₃): δ_C = 14.142 (CH₃), 22.467 (CH₂), 26.187 (CH₂), 30.183–30.275 (CH₂), 30.398 (CH₂), 31.492 (CH₂), 34.819 (CH₂), 45.499 (N-CH₂), 50.239 (N-CH₂), 121.173 (Ring-CH), 123.440 (Ring-CH), 136.780 (Ring-CH), 171.804 ppm (COOH).

[Carb-C₁₂minm]Br: ¹H NMR (400 MHz, CDCl₃): δ_H = 0.876 (t, 3H; CH₃), 1.248–1.325 (d, 18H; 9CH₂), 1.900 (t, 2H; CH₂), 3.134 (t, 2H; CH₂-COOH), 4.279 (t, 2H; N-CH₂), 4.681 (t, 2H; N-CH₂), 7.361 (s, 1H; Ring-CH), 7.799 (s, 1H; Ring-CH), 9.827 ppm (s, 1H; Ring-CH); ¹³C NMR: (400 MHz, CDCl₃): δ_C = 14.131 (CH₃), 22.688 (CH₂), 26.374 (CH₂), 29.102–29.653 (CH₂), 30.264 (CH₂), 31.916 (CH₂), 34.825 (CH₂), 45.498 (N-CH₂), 50.188 (N-CH₂), 121.946 (Ring-CH), 123.532 (Ring-CH), 136.651 (Ring-CH), 171.714 ppm (COOH).

[Carb-C₁₆minm]Br: ¹H NMR (400 MHz, CDCl₃): δ_H = 0.896 (t, 3H; CH₃), 1.246–1.321 (d, 26H; 13CH₂), 1.879–1.913 (t, 2H; CH₂), 3.122 (t, 2H; CH₂-COOH), 4.283 (t, 2H; N-CH₂), 4.609 (t, 2H; N-CH₂), 7.421 (s, 1H; Ring-CH), 7.843 (s, 1H; Ring-CH), 9.753 ppm (s, 1H; Ring-CH); ¹³C NMR: (400 MHz, CDCl₃): δ_C = 14.137 (CH₃), 22.707 (CH₂), 26.394 (CH₂), 29.127–29.746 (CH₂), 30.273 (CH₂), 31.946 (CH₂), 34.834 (CH₂), 45.507 (N-CH₂), 50.185 (N-CH₂), 121.889 (Ring-CH), 123.525 (Ring-CH), 136.644 (Ring-CH), 171.676 ppm (COOH).

Dissolution of Eu₂O₃

Eu₂O₃ (0.198 g, 0.565 mmol) was introduced into [Carb-C_nminm]Br (n = 8, 12, 16) (3.38 mmol) dissolved in alcohol (4 mL) and deionized water (1 mL) and the mixture was refluxed at 90 °C with stirring for 5 h until most of the added Eu₂O₃ was dissolved and the orange color of [Carb-C_nminm]Br (n = 8, 12) became lighter. The excess of Eu₂O₃ was removed by filtration and the solvents were removed under vacuum and the obtained samples were dried at 80 °C under vacuum overnight.

Dissolution of Tb₄O₇

Tb₄O₇ (0.209 g, 0.277 mmol) was introduced into [Carb-C_nminm]Br (n = 8, 12, 16) (3.324 mmol) dissolved in alcohol (4 mL) and deionized water (1 mL) and Tb₄O₇ ((0.209 g, 0.277 mmol) was added. Then the mixture was heated in a 25 mL capacity stainless-steel reactor with Teflon liner at

120 °C for 6 days. All of the added brown-colored Tb₄O₇ was dissolved. The solvent was removed under vacuum and the gel-like samples obtained were dried at 80 °C under vacuum overnight.

Characterization

IR spectra were obtained on a Bruker Vector 22 spectrometer by using KBr pellets for solid samples, from 500–4000 cm⁻¹ at a resolution of 4 cm⁻¹ (16 scans collected). The steady-state luminescence spectra and the lifetime measurements were measured on an Edinburgh Instruments FS920P spectrometer with a 450 W xenon lamp as the steady-state excitation source, a double excitation monochromator (1800 lines mm⁻¹), an emission monochromator (600 lines mm⁻¹), and a Hamamatsu RMP928 photomultiplier tube. All spectra were obtained at room temperature.

Acknowledgements

This work is financially supported by the National Natural Science Foundation of China (no. 20871040, no.20901022), the Program for New Century Excellent Talents in University (NCET-09-0113), the Tianjin Natural Science Foundation (09JCYBJC05700), the Hebei Province Natural Science Foundation for Distinguished Young Scholars (no.B2010000034, no. 2009000013), and the State Key Laboratory of Rare Earth Resource Utilization, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences (RERU2011007).

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Received: December 6, 2010
Published online: April 20, 2011