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## Water-Soluble Tb<sup>3+</sup> and Eu<sup>3+</sup> Complexes Based on Task-Specific Ionic Liquid Ligand and Their Application in Luminescent Poly(vinyl alcohol) Films

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Novel water-soluble lanthanide complexes (Ln(IMI-DPA)<sub>3</sub>) have been synthesized using the task-specific ionic liquid consisting of a dipicolinic acid motif as the sensitizer of lanthanide luminescence. In Ln(IMI-DPA)<sub>3</sub>, Ln<sup>3+</sup> ions are in 9-fold coordination through six carboxylate oxygen atoms and three nitrogen atoms in pyridine units, and water molecular is excluded from the coordination sphere of the lanthanides. It is found that Ln(IMI-DPA)<sub>3</sub> possess bright luminescence, long luminescence lifetime in aqueous solution, high thermal stability and good water solubility. Furthermore, these complexes can be incorporated in water-soluble poly(vinyl alcohol) (PVA) matrixes to obtain the highly luminescent, transparent and flexible PVA composite films. The emission colors of the films can be tuned from red, orange, yellow, light green, green to white light by regulating the concentration of the various luminescence components.

#### Introduction

Task-specific ionic liquids (TSILs), especially imidazolium cationbased ionic liquids are commonly used as solvents, ion conductive materials or organic ligands for metallic complexes which are widely used in heterogeneous or homogeneous catalysis.<sup>1-4</sup> One of the most stunning features of TSILs is their easily tailable properties through the chemical modification of both cations and anions.<sup>5</sup> Considering the attractive feature of TSILs, specific functional groups designed for selective complexation of lanthanide metal ions have been covalently conjugated either to the cation or to the anion of TSILs, aiming at improving thephysicochemical properties and water-solubility of TSILs.<sup>6-9</sup> Indeed, some well-designed TSILs are used as the ionophilic ligands for the preparation of novel luminescence complexes.  $^{\rm 10\cdot12}$  For instance, Rodrigues and coworkers reported two water-soluble lanthanide complexes with aromatic carboxylic acid grafted ionic liquid as the ligand, which could be acted as a fluorescence imaging probe for invasive mammal cancer cells.<sup>13</sup> Currently, the introduction of a hydrophilic group such as imidazolium salts into lanthanide complexes seems to be one of the effective ways to improve their water solubility. However, the design and synthesis of water-soluble lanthanides complexes with excellent luminescence properties in aqueous

solution still remains an open issue for developing this kind of materials. The primary question needed to be addressed is the very low luminescence efficiency of the lanthanide complexes since the luminescence is likely quenched by the solvent molecule such as water molecule.

Lanthanides complexes containing one or more N, O-chelating ligands usually exhibit sharp and intense emission lines, long lifetimes and high quantum efficiency of luminescence under the excitation of ultraviolet (UV) light, because of the effective intramolecular energy transfer from the ligands to the lanthanide ions<sup>14-21</sup>. Some of the water-soluble lanthanide complexes demonstrate potential applications in time-resolved fluoroimmunoassay, fluorescence imaging, metal ion detection and protein labelling.<sup>22-25</sup> Among them, dipicolinic acid (DPA) has shown to be an efficient N, O-chelating ligand for sensitizing the luminescence of Tb<sup>3+</sup> and Eu<sup>3+</sup> ions.<sup>26-30</sup> The ligands are capable of forming stable  $[Ln(DPA)_3]^{3-}$  complexes with the lanthanides, in which the coordination number of the central Ln<sup>3+</sup> reaches its coordination-saturated state.<sup>31,32</sup> Therefore, the nonradiative deactivation of lanthanides luminescence due to the coupled O-H vibrations is greatly reduced because water molecule is excluded from the coordination sphere of the lanthanides. Hence, it is reasonable to envisage the combination of a DPA-functionalized ionic liquid with lanthanide ions to afford new water-soluble luminescence complexes. Herein, we report the synthesis of novel water-soluble lanthanide complexes based on an ionophilic ligand by functionalizing the imidazolium ionic liquid with a DPA substituent. The introduction of imidazolium cations can improve the water-solubility of the luminescence complexes as well as intersolubility with the water-soluble and full-biodegradable

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#### ARTICLE

poly(vinyl alcohol) (PVA). Therefore, the transparent and flexible phosphor films are readily obtained by casting the water-soluble luminescence complexes with the aqueous solution of PVA. Moreover, the obtained PVA films exhibit various emission colors simply by changing the concentration of the various luminescence components.

#### **Results and discussion**

#### Preparation

The synthesis procedure of IMI-DPA and corresponding lanthanide complexes is illustrated in Scheme 1. 4-(hydroxylmethyl)pyridine-2, 6-dicarboxylate (compound 2), 4-(chloromethyl)pyridine-2, 6-dicarboxylate (compound 3) were synthesized as described in the literature.<sup>33</sup> Compound 4 was obtained by a simple nucleophilic substitution reaction of 4-(chloromethyl)pyridine-2, 6-dicarboxylate with 1-methylimidazole in anhydrous acetonitrile, and then hydrolyzed under acidic aqueous conditions to yield the target compound (IMI-DPA) as a white powder. The designed organic ligand has been characterized by <sup>1</sup>H-NMR, <sup>13</sup>C-NMR (Fig. S1 and S2) and mass spectrometry. The crystals of the lanthanide complexes were obtained by the conventional solvent evaporation method.



Scheme 1 Synthesis procedure for IMI-DPA and corresponding lanthanide complexes

#### Single-crystal X-ray diffraction

Single-crystal X-ray diffraction analysis reveals that  $Eu(IMI-DPA)_3$ and Tb(IMI-DPA)<sub>3</sub> are isostructural, crystallizing in the triclinic space group *P*/-1. As for Eu(IMI-DPA)<sub>3</sub>, and the Eu<sup>3+</sup> ions is ninecoordinated with three nitrogen atoms of pyridine units and six oxygen atoms of carboxyl groups from three different IMI-DPA ligands (Fig. 1). The coordination sphere of Eu<sup>3+</sup> is saturated by three IMI-DPA ligands, leaving no coordination site for water or other solvent molecules, and this kind of complex usually exhibits excellent luminescence properties and long luminescent lifetime in aqueous solution.



Fig. 1 The crystal structure of Eu(IMI-DPA)<sub>3</sub>

#### FT-IR spectrum

The FT-IR spectra of IMI-DPA, Tb(IMI-DPA)<sub>3</sub> and Eu(IMI-DPA)<sub>3</sub> are displayed in Fig. 2. The absorption bands located at 1735, 1237, 3518 and 1431 cm<sup>-1</sup> observed in Fig. 2a can be ascribed to stretching vibrations of the C=O (1735 cm<sup>-1</sup>), C-O (1237 cm<sup>-1</sup>), O-H (3518 cm<sup>-1</sup>) and bending vibrations of O-H (1431 cm<sup>-1</sup>), respectively.<sup>11</sup> The bands at 1602, 1555, 1431 cm<sup>-1</sup> correspond to the skeleton vibration of imidazole and pyridine ring, and the unsaturated C-H stretching vibration modes appear at 3149, 3092 and 3072 cm<sup>-1</sup>.<sup>34,35</sup> However, the absence of the absorption band at 1735 cm<sup>-1</sup> ascribed to C=O of the free carboxylic acid suggests the coordination of Ln<sup>3+</sup> to oxygen atoms of IMI-DPA (Fig. 2b and 2c). In fact, the asymmetric and symmetric stretching vibration of the COO<sup>-</sup> group in Tb(IMI-DPA)<sub>3</sub> or Eu(IMI-DPA)<sub>3</sub> can be detected at 1640 and 1406 cm<sup>-1</sup>, respectively. This finding is consistent with previous reports on Ln<sup>3+</sup> coordinated to the carboxylate groups.<sup>11</sup>



Fig. 2 FT-IR spectra of IMI-DPA (a), Eu(IMI-DPA)<sub>3</sub> (b) and Tb(IMI-DPA)<sub>3</sub> (c)

#### Thermal analysis

In order to investigate the thermal stability of the obtained lanthanide complexes, the thermogravimetric analysis (TGA) of

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Tb(IMI-DPA)<sub>3</sub> and Eu(IMI-DPA)<sub>3</sub> is carried out in N<sub>2</sub> atmosphere from 30 to 900 °C at a heating rate of 10 °C min<sup>-1</sup> (Fig. 3). The weight loss observed for both samples is occured at three temperature regimes. The first weight loss at temperature lower than 120 °C is mostly attributed to the loss of small amount of physically adsorbed water molecules. While the relatively large weight loss occurs quickly at about 340 °C in the temperature range of 340-800 °C (approximately 65 % for Tb(IMI-DPA)<sub>3</sub> and 63.7% for Eu(IMI-DPA)<sub>3</sub>), which can be ascribed to the thermal decomposition of organic components. At temperatures higher than 800 °C, the weight loss is not obvious. The results of TGA show that the prepared complexes exhibit high thermal stability, which makes them promising for application in optical device.



Fig. 3 TGA curves of Eu(IMI-DPA)<sub>3</sub> (a) and Tb(IMI-DPA)<sub>3</sub> (b)

#### **Optical properties**

The optical properties of Tb(IMI-DPA)<sub>3</sub> and Eu(IMI-DPA)<sub>3</sub> solution were investigated by UV-vis absorption and photoluminescence (PL) spectra. The UV-vis absorption spectrum of IMI-DPA exhibits a broad band with maxima at 273 nm ( $\epsilon = 8.2 \times 10^3 \text{ L} \cdot \text{ moL}^{-1} \cdot \text{ cm}^{-1}$ ) (Fig. S3), which is ascribed to the typical absorption of the  $\pi \rightarrow \pi^{-1}$ transition of aromatic ring. In addition, the absorption spectra of  $Tb(IMI-DPA)_3$  and  $Eu(IMI-DPA)_3$  revealed two peaks at 273  $(\epsilon=1.68\times10^4$  L· moL<sup>-1</sup> · cm<sup>-1</sup> for Tb(IMI-DPA)<sub>3</sub> and  $\epsilon=1.48\times10^4$  $L \cdot moL^{-1} \cdot cm^{-1}$  for Eu(IMI-DPA)<sub>3</sub>) and 281 nm, attributable to the  $\pi \rightarrow \pi^*$  transition of the complexes (Fig. S3). Usually, for lanthanide complexes with three  $\beta$ -diketone derivatives as the ligands, the molar absorption coefficient (ɛ) value of the complexes are about three times higher than that of the ligand.<sup>36,37</sup> However, For lanthanide complexes with three dipicolinic acid derivatives as the ligands, the  $\varepsilon$  value of the complexes are only a little higher or lower than that of the ligand.<sup>38</sup> As for Ln(IMI-DPA)<sub>3</sub>, the  $\varepsilon$  value of the complexes are less than two times than that of IMI-DPA. It seems that the relative  $\varepsilon$  value of complex is dependent on the structure of the ligand or complex. The PL excitation and emission spectra of Tb(IMI-DPA)<sub>3</sub> and Eu(IMI-DPA)<sub>3</sub> in aqueous solution are shown in Fig. 4. It is evident that the Tb(IMI-DPA)<sub>3</sub> and Eu(IMI-DPA)<sub>3</sub> solution show bright green and red characteristic emissions under UV light (254 nm) excitation (insets of Fig. 4b and d). The excitation spectra of Tb(IMI-DPA)<sub>3</sub> and Eu(IMI-DPA)<sub>3</sub> solution monitored at 543 nm for  $\text{Tb}^{3+}$  and 615 nm for  $\text{Eu}^{3+}$  possess a similar excitation band with a maximum at about 290 nm which can be assigned to

the  $\pi \rightarrow \pi^*$  electronic transition of the complexes (Fig. 4a and c), respectively. This indicates that these two kinds of different lanthanide complexes can be excited by the UV light with the same wavelength and exhibit different color emissions caused by the different central lanthanide ions. As expected, under the excitation with the same wavelength (290 nm), the Tb(IMI-DPA)<sub>3</sub> solution gives the characteristic emission of Tb<sup>3+</sup> with the peaks centered at 492, 543, 582, 622 nm, corresponding to the transitions from the  ${}^{5}D_{4}$  level to  ${}^{7}F_{1}$  (J=6, 5, 4, 3) levels of Tb ${}^{3+}$ , respectively, of which the  ${}^{5}\text{D}_{4} {\rightarrow} {}^{7}\text{F}_{5}$  emission is the most prominent one (Fig. 4b).  $^{13,38\cdot40}$  While, the Eu(IMI-DPA)<sub>3</sub> solution reveals the characteristic Eu<sup>3+</sup> emission peaks centered at 592, 615, 649 and 695 nm, corresponding to the  ${}^{5}D_{0} \rightarrow {}^{7}F_{J}$  (J=1, 2, 3, 4) transitions, respectively.  ${}^{30,41\cdot44}$  Among these transitions, the  ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$  transition shows the strongest emission, resulting in the red luminescence. No broad emission band from the organic ligand in both  $Tb(IMI-DPA)_3$  and  $Eu(IMI-DPA)_3$  complexes can be observed in the region, which demonstrates that the energy transfer occurs from the ligand to the central  $Ln^{3+}$  (Ln =Tb or Eu).<sup>2</sup>

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ARTICLE



**Fig. 4** PL excitation and emission spectra of  $Tb(IMI-DPA)_3$  (a, b) and  $Eu(IMI-DPA)_3$  (c, d) in aqueous solution, and the insets of Fig. 4b and d are photos of  $Tb(IMI-DPA)_3$  (green) and  $Eu(IMI-DPA)_3$  (red) solution excited by UV light (254 nm)

The lifetime values of the excited state  ${}^{5}D_{4}$  (Tb<sup>3+</sup>) in Tb(IMI-DPA)<sub>3</sub> solution and  ${}^{5}D_{0}$  (Eu<sup>3+</sup>) in Eu(IMI-DPA)<sub>3</sub> solution can be determined by the luminescent decay curves. As shown in Fig. 5, both the luminescence decay curves are well fitted into a singleexponential function of I = I<sub>0</sub> exp  $(-t/\tau)$ , where I<sub>0</sub> is the initial intensity at t = 0,  $\tau$  is the 1/e lifetime of the lanthanide ions. The result implies the presence of single luminescence center. According to the fitting results, the lifetime values of Tb(IMI-DPA)<sub>3</sub> and Eu(IMI-DPA)<sub>3</sub> are determined to be 1.73 and 1.56 ms, respectively. The quantum efficiencies of the Tb(IMI-DPA)<sub>3</sub> and  $Eu(IMI-DPA)_3$  are about 21.6% and 49.0%, respectively. The optical data like molar absorptivity ( $\epsilon$ ), excitation wavelength ( $\lambda_{ex}$ ), emission wavelength ( $\lambda_{em}$ ), lifetime ( $\tau$ ) and luminescence quantum efficiency ( $\eta$ ) of our samples and  $[Ln(DPA)_3]^{3-}$  (Ln = Tb or Eu) are listed in Table 1. It appears that the quantum efficiency of Eu(IMI-DPA)<sub>3</sub> is higher than that in  $[Eu(DPA)_3]^{3-}$ , while as for Tb(IMI-DPA)3, the quantum efficiency is lower than that in  $[Tb(DPA)_3]^{3-}$ , and other

#### ARTICLE

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optical data for our samples are very similar to that obtained in  ${\rm [Ln(DPA)_3]^{3^{-}}}$  (Ln = Tb or Eu).

Table 1 The optical data including molar absorptivity ( $\epsilon$ ), excitation wavelength ( $\lambda_{ex}$ ), emission wavelength ( $\lambda_{em}$ ), lifetime ( $\tau$ ) and luminescence quantum efficiency ( $\eta$ ) of the Ln(IMI-DPA)<sub>3</sub> (Ln = Tb, Eu) and previously reported [Ln(DPA)<sub>3</sub>]<sup>3</sup>.

Samples	$\epsilon \; (L \cdot \; moL^{\cdot 1} \cdot \; cm^{\cdot 1})$	$\lambda_{ex} \ (nm)$	$\lambda_{em} \; (nm)$	$\tau \ (ms)$	η (%)
[Tb(DPA) <sub>3</sub> ] <sup>3</sup> ·	9.63×10 <sup>3</sup> (279nm)	286	492, 543, 582, 622	2.01	39.9
[Eu(DPA)3]3-	8.95×10 <sup>3</sup> (279nm)	286	594, 615, 649, 694	1.58	34.6
Tb(IMI-DPA)3	1.68×10 <sup>4</sup> (273nm)	290	492, 543, 582, 622	1.73	21.6
Eu(IMI-DPA) <sub>3</sub>	1.48×10 <sup>4</sup> (273nm)	290	592, 615, 649, 695	1.56	49.0

The luminescence lifetime of  $Ln^{3+}$  is greatly affected by the vibration of the solvent molecules which are known to be deactivators of the vibrationally excited states of the  $Ln^{3+}$  ions.<sup>46</sup> However, as for our complexes, the coordination sphere of  $Ln^{3+}$  is saturated by the ligands, leaving no coordination site for water molecules, resulting in long luminescence lifetimes of  $Ln^{3+}$  in aqueous solution. The chromaticity diagram (CIE) indicates that the emission of the complexes lie in green and red region with the chromaticity coordinates (x = 0.36, y = 0.59) for Tb(IMI-DPA)<sub>3</sub> and (x = 0.66, y = 0.33) for Eu(IMI-DPA)<sub>3</sub>, respectively (Fig. S4). Moreover, the chromaticity coordinate of the Eu(IMI-DPA)<sub>3</sub> is very close to the edge of the CIE diagram, showing the high color purity of this sample.



Fig. 5 Luminescence decay curves of  $Tb(IMI-DPA)_3$  (a) and  $Eu(IMI-DPA)_3$  (b) in aqueous solution

As mentioned above,  $Tb(IMI-DPA)_3$  and  $Eu(IMI-DPA)_3$  complexes have well water-soluble, prominent luminescent properties and multi-color emission under the excitation of a single

wavelength UV light, hence these complexes might be formed homogeneously mutual solubility with some hydrophilic or watersoluble substances to obtain the luminescent materials with different states such as liquid, film and powders. Moreover, the luminescent color of these homogeneous composites only could be adjusted through changing the relative component of Tb(IMI-DPA)<sub>3</sub> and Eu(IMI-DPA)<sub>3</sub> complexes. It is well known that Poly(vinyl alcohol) (PVA) is a water-soluble, nontoxic and full-biodegradable organic polymer. This material has excellent film-forming ability, high tensile strength and bending flexibility, which make it an attractive material for a wide range of applications.<sup>47</sup> It has been confirmed in this work that the obtained water-soluble lanthanide complexes can be readily well-dispersed into PVA aqueous solution to form a transparent film, and the representative PVA and Eu(IMI-DPA)<sub>3</sub> film is shown in Fig. 6 (2)f, clearly showing the transparent and flexible characteristic.



**Fig. 6** (1) Chromaticity diagram (CIE) of the luminescent films under 290 nm UV illumination (a) PVA-Eu, (b) PVA-Eu<sub>1</sub>Tb<sub>1</sub>, (c) PVA-Eu<sub>1</sub>Tb<sub>3</sub>, (d) PVA-Eu<sub>1</sub>Tb<sub>5</sub>, (e) PVA-Tb; (2) Photos of the corresponding luminescence films on glass substrate under 254 nm (a-e) UV illumination, and (f) photo of PVA-Eu film under daylight

The transparent, flexible and luminescence PVA films embedded with Eu(IMI-DPA)<sub>3</sub> or Tb(IMI-DPA)<sub>3</sub>, denoted as PVA-Eu or PVA-Tb were prepared simply by dropping the PVA solution of Eu(IMI-DPA)<sub>3</sub> or Tb(IMI-DPA)<sub>3</sub> onto a glass substrate, followed by drying at 50 °C. The same procedure afforded the mixed systems

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described above, with Eu/Tb molar ratios of 1:1, 1:3 and 1:5, yielding PVA-Eu<sub>1</sub>Tb<sub>1</sub>, PVA-Eu<sub>1</sub>Tb<sub>3</sub>, PVA-Eu<sub>1</sub>Tb<sub>5</sub> films, respectively. The metal compositions of the designed films were confirmed by energy dispersive X-ray (EDX) analysis and found to be matching with that of the nominal one in each sample (Table 2 and Fig. S6).<sup>48</sup>

Table 2 Molar ratios of Eu/Tb for designed films by EDX analysis, <sup>a</sup> Relative mass percentage, <sup>b</sup> measured by EDX

Luminescent	Stoichiometric	Weight % <sup>a</sup>		Eu/Tb molar	
materials	Ratio (Eu/Tb)	Eu	Tb	ratios <sup>b</sup>	
PVA-Eu <sub>1</sub> Tb <sub>1</sub>	1:1	47.0	53.0	1:1.07	
PVA-Eu1Tb3	1:3	24.8	75.2	1:2.90	
PVA-Eu1Tb5	1:5	16.3	83.7	1:4.91	
PVA-Na- BTC-Eu <sub>1</sub> Tb <sub>1</sub>	1:1	46.4	53.6	1:1.10	

The emission colors of the films can be tuned from red to green by doping the required amounts of luminophor as displayed in CIE (1) and luminescence photos (2) in Fig. 6a to e. The emission spectra of the films are shown in Fig. S5. We observe the sharp characteristic emission peaks of the  $Eu^{3+}$  ions at 592, 615, 649 and 695 nm and  $Tb^{3+}$  ions at 492, 543, 582 and 622 nm, respectively. Moreover, the intensity ratio of the red to green emission decreases obviously with increasing the  $Tb^{3+}$  concentrations, and the emission colors of the films thus varied from red, orange, yellow, light green to green correspondingly. However, according to the equation (1) as follow:<sup>49,50</sup>

$$\eta = 1 - \tau_1 / \tau_0$$

where  $\tau_1$  and  $\tau_0$  are the excited state lifetimes of the donor in the presence and absence of the acceptor, the energy transfer from Tb^{3+} to Eu^{3+} is not obviously observed in the films at room temperature.

(1)



Fig. 7 The emission spectrum of the luminescence PVA-Na-BTC-Eu1Tb1 film upon excitation at 305 nm, and the inset of Fig. 7 is the photo of PVA-Na-BTC-Eu<sub>1</sub>Tb<sub>1</sub> film excited by UV light (305 nm)

White-light emitting materials have attracted considerable interest over the past years due to their practical applications in full-color flat panel display and general lighting.<sup>51-54</sup> Sodium 1,2,4,5-benzenetetracarboxylate (Na-BTC), as a kind of blue light emitting

organic salt, usually used to regulate the white light emission of the luminescence materials.<sup>55</sup> In principle, the obtained prominent luminescence Eu(IMI-DPA)<sub>3</sub> (red) and Tb(IMI-DPA)<sub>3</sub> (green) complexes can be mixed with Na-BTC (blue), thus white-light emission might be realized only through altering the relatively ratio of Eu(IMI-DPA)<sub>3</sub>, Tb(IMI-DPA)<sub>3</sub> and Na-BTC. To prove the hypothesis, Eu(IMI-DPA)<sub>3</sub>, Tb(IMI-DPA)<sub>3</sub> and Na-BTC were dispersed into PVA solution with a molar ratio of 1:1:77 (The metal compositions of the designed films was also confirmed by energy dispersive X-ray (EDX) analysis (Table 2 and Fig. S6)), and a novel luminescence PVA-Na-BTC-Eu<sub>1</sub>Tb<sub>1</sub> film was made. Upon the excitation of UV light at 305 nm, PVA-Na-BTC-Eu1Tb1 shows a broad emission band in the blue region from Na-BTC, the green emission lines from Tb(IMI-DPA)<sub>3</sub> complex and red emission lines from Eu(IMI-DPA)<sub>3</sub> complex, as shown in Fig. 7. Incorporation of blue emission component in the presence of Eu<sup>3+</sup> and Tb<sup>3+</sup> result in white emission (Fig. 7 inset) with CIE co-ordinates of (0.31, 0.31) (Fig. S7), which is close to the coordinate of standard white light (0.33, 0.33).

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ARTICLE

#### Conclusions

A new type of water-soluble luminescence complexes of terbium and europium has been prepared with DPA-functionalized ionic liquid (IMI-DPA) as the ligand. The complexes display intenseluminescence, long luminescence lifetime and high luminescence quantum efficiency in aqueous solution irradiated with the same wavelength. The resulting water-soluble and prominent luminescence lanthanide complexes as well as sodium 1,2,4,5-benzenetetracarboxylate can be used as building blocks for fabricating luminescence PVA composite films, where various emission colors ranging from red, orange, yellow, light green, green to white light can be tuned by modulating the concentration of the various luminescence components. Such tunable phosphor films are promising in the use of optical systems, sustainable energy devices and biological applications.<sup>56,57</sup>

#### **Experimental section**

#### Materials

1-Methylimidazole (99%, Energy chemical), Terbium (III) chloride hexahydrate (99.99%, Energy chemical), Europium (III) chloride hexahydrate (99.99%, Energy chemical) were used without further purification.

#### 3-((2,6-bis(methoxycarbonyl)pyridin-4-yl)methyl)-1methylimidazolium chloride (4)

4-(chloromethyl)pyridine-2, 6-dicarboxylate (3.65g, 0.015mol) was dissolved in anhydrous acetonitrile (40mL) and then 1-methylimidazole (2.46g, 0.03mol) was added to the above mixture under an atmosphere of argon. The mixture was stirred at 80 °C for about 16 h, and then cooled down to room temperature. The resulting white suspension was filtered, washed with acetonitrile and dried under vacuum at 40 °C for 8 h (3.74g, 76.3%). <sup>1</sup>H-NMR (400MHz, D<sub>2</sub>O)  $\delta$  ppm: 8.90 (1H, s), 8.07 (2H, s), 7.47 (2H, d), 5.57 (2H, s), 3.85 (9H, s). <sup>13</sup>C-NMR(100MHz, D<sub>2</sub>O)  $\delta$  ppm: 165.3, 148.0,

#### ARTICLE

147.1, 137.1, 127.1, 124.5, 122.7, 53.5, 50.9, 36.2. ESI-MS: M/Z calcd for  $C_{14}H_{16}N_{3}O_{4}^{\ +}:$  290.2945,  $M^{\ +}:$  found: 290.1143.

# 3-((2,6-dicarboxypyridin-4-yl)methyl)-1-methylimidazolium chloride (IMI-DPA)

A mixture of the compound 4 (3.26g, 0.01mol) and hydrochloric acid (6mol/L, 35mL) was refluxed under stirring for about 24 h, and then cooled down to room temperature. The solvent was removed under reduced pressure, and the slurry residue was recrystallizated with ethanol to give 3-((2, 6-dicarboxypyridin-4-yl)methyl)-1-methylimidazolium chloride as white solid (2.71g, 90.9%). <sup>1</sup>H-NMR (400MHz, D<sub>2</sub>O)  $\delta$  ppm: 8.88 (1H, s), 7.96 (2H, s), 7.46 (2H, d), 5.59 (2H, s), 3.86 (3H, s). <sup>13</sup>C-NMR(100MHz, D<sub>2</sub>O)  $\delta$  ppm: 166.6, 148.8, 148.6, 137.3, 126.1, 124.6, 122.9, 51.0, 36.0. ESI-MS: M/Z calcd for C<sub>12</sub>H<sub>12</sub>N<sub>3</sub>O<sub>4</sub><sup>+</sup> : 262.2414, M<sup>+</sup>: found: 262.0816. Anal. Calcd for IMI-DPA : C, 48.41; H, 4.06; N, 14.12; found C, 47.78; H, 4.51; N, 13.57.

#### Preparation of lanthanide complexes

IMI-DPA (0.597g, 2mmol) and LnCl<sub>3</sub>·6H<sub>2</sub>O (Ln= Tb or Eu, 0.66mmol) were dissolved in 30mL distilled water, and the pH value of the mixture was adjusted to 7.0. After evaporating the solvent at 50  $^{\circ}$ C for about 12h, the mixture was slowly cooled to room temperature, and the colorless bulk-like crystals, denoted as Tb(IMI-DPA)<sub>3</sub> or Eu(IMI-DPA)<sub>3</sub> were obtained in 65% yield based on IMI-DPA. Anal. calcd for Eu(IMI-DPA)<sub>3</sub> : C, 46.36; H, 3.24; N, 13.52; found C, 46.81; H, 3.13; N, 13.06, Anal. calcd for Tb(IMI-DPA)<sub>3</sub> : C, 46.06; H, 3.22; N, 13.42; found C, 46.28; H, 3.41; N, 13.58.

#### Preparation of luminescent films

A desired amount of Tb(IMI-DPA)<sub>3</sub> and Eu(IMI-DPA)<sub>3</sub> were dissolved in the PVA solution (2% (wt)) and then the solution was sonicated for 30 min. The luminescent films were formed by dropping the above mixture on slide glass, followed by drying in an oven at 50 °C for overnight.

#### Characterization

Single crystal X-ray diffraction data were collected on a Bruker SMART APEX II diffractometer. Data reductions and absorption corrections were performed with the SAINT and SADABS programs, respectively. The structures were solved by direct methods and refined with full-matrix least squares on F2 using the SHELXS-97 program. Fourier transform infrared (FT-IR) spectrum was measured using a Nicolet 5700 infrared spectrometer by the KBr tablet method. The thermogravimetric (TG) curves were measured on a PerkinElmer STA 6000 thermal analyzer at a heating rate of 10 <sup>o</sup>C min<sup>-1</sup> under N<sub>2</sub> atmosphere. Ultraviolet-visible (UV-vis) absorption spectra were recorded on a PerkinElmer Lambda 25 UVvis spectrophotometer. The micro analysis (EDX) of designed films was recorded on a JEOL JSM-6335F electron microscope equipped with energy-dispersive X-ray spectrometer. <sup>1</sup>H-NMR and <sup>13</sup>C-NMR spectra were acquired on a Bruker AV400 NMR spectrometer. Mass spectrometry was obtained on an Agilent 6520 Q-TOF mass spectrometer. Photoluminescence and luminescence lifetime measurements were performed using an Edinburgh FLS920P instruments apparatus equipped with a 450 W xenon lamp and a

high-energy micro-second flash lamp as the excitation sources. The quantum efficiencies were determined using an integrating sphere whose inner face was coated with BenFlect from FLS920P Edinburgh spectrofluorometer. The quantum yield described by R. H. Friend <sup>58</sup> can be represented in the equation below:

$$\eta = \frac{\int L_{emission}}{\int E_{solvent} - \int E_{sample}}$$

Where  $\eta$  is the quantum yield,  $L_{emission}$  is the luminescence emission spectrum of the sample, collected using the sphere,  $E_{solvent}$  is the spectrum of the light used for excitation with only the solvent in the sphere, collected using the sphere,  $E_{sample}$  is the spectrum of the light used to excite the sample, collected using the sphere.

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## Water-Soluble Tb<sup>3+</sup> and Eu<sup>3+</sup> Complexes Based on Task-Specific Ionic Liquid Ligand and Their Application in Luminescent Poly(vinyl alcohol) Films

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Synthesis of water-soluble  $Tb^{3+}$  and  $Eu^{3+}$  complexes based on TSILs ligand and their application in luminescent poly(vinyl alcohol) films



TOC Figure