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# Luminescent Materials of Europium(III) Coordinated by a Terpyridine-Functionalized Poly(Ionic Liquid)

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A new poly(ionic liquid) (Terpy-PIL) carrying a terpyridine group in each repeating unit of the polymer architecture was readily prepared by polymerization of the monomer (Terpy-IL), which was initiated by azobis(isobutyronitrile) (AIBN). The obtained poly(ionic liquid) can coordinate and sensitize europium(III) ions through numerous chelating terpyridine moieties, which are linked to the polymer chains. A red-emitting luminescent material was obtained by the complexation

### Introduction

Ionic liquids (ILs) are organic salts that are composed of large organic cations combined with various anions.<sup>[1-3]</sup> Because of their intrinsic unique properties, such as very low vapor pressures, a wide liquid range, good electric conductivity, large electrochemical windows, and good solubility for a wide range of substances, ILs have recently been widely used in materials science and technology as lubricants,<sup>[4]</sup> composite materials,<sup>[5]</sup> media for the synthesis of nanomaterials,<sup>[6-10]</sup> luminescent soft materials,<sup>[11]</sup> electrolytes in devices, and so forth.<sup>[12]</sup> Furthermore, both the cationic and anionic components of ILs can be easily changed, and they can therefore be tailored for particular applications or be designed to have a specific set of properties.<sup>[13]</sup> Specific functional groups were introduced in the cations or anions of ILs, which led to the so-called task-specific ionic liquids (TSILs).<sup>[14-18]</sup> However, there is currently a challenging need to immobilize ILs in solid devices and at the same time retain their unique properties from the viewpoint of material applications. Confining ILs within silica matrices through sol-gel processing is a promising way to immobilize ILs, which can give access to transparent, crack-free silica monoliths.<sup>[19-24]</sup> Another strategy involves the immo-

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of europium(III) salts with Terpy-PIL, and the luminescence is due to an energy transfer from the terpyridine moieties to  $Eu^{3+}$  ions. The luminescence performance of the luminescent material based on Terpy-PIL, for example the  ${}^{5}D_{0}$  quantum efficiency and the decay time, is much higher than that of the luminescent material prepared from the monomer Terpy-IL, which can be ascribed to the confinement of the europium(III)–terpyridine complexes to the polymer architecture.

bilization of ILs within polymers.<sup>[25-39]</sup> Among such polymers, poly(ionic liquid)s (PILs) have attracted considerable attention in the field of polymer chemistry and materials science, because they combine the unique properties of ILs with a macromolecular architecture. PILs are a special kind of electrolytes synthesized by polymerization of monomeric ILs, and they combine the functionality of ILs with the spatial control of IL moieties, which is provided by the polymer architectures.<sup>[26]</sup> PILs show obvious advantages, such as enhanced mechanical stability, improved processability, durability, etc.,<sup>[37,40]</sup> which make them suitable for various applications as solid ion conductors,<sup>[41]</sup> carbon precursors,<sup>[38]</sup> porous materials,<sup>[42]</sup> CO<sub>2</sub> sorbents,<sup>[43,44]</sup> and dispersants.<sup>[37]</sup> The self-assembly of PILs is highly interesting, because they can find potential application as nanostructured functional materials.[45-47]

So far, there are no reports about PILs carrying a ligating moiety in each of the repeating units of the polymers, although TSILs carrying complexing groups have already been reported and have been employed in metal separation and extraction processes<sup>[14,16,48]</sup> and in catalysis after metal complexation.<sup>[49]</sup> In the present contribution, we report for the first time a new PIL with terpyridine moieties incorporated into the polymer chain. The resulting PIL, a terpyridine-functionalized poly(ionic liquid) (Terpy-PIL), is obtained by the polymerization of terpyridine-functionalized IL monomers (Terpy-IL). Compared with the previously reported PILs, one obvious advantage of the new Terpy-PIL reported by us is the availability of terpyridine groups in the repeating units of the polymer, as shown in Figure 1.

Terpyridine can bind various metal ions, which impart many properties including luminescence and electrochemical, photochemical, or catalytic activity.<sup>[50–56]</sup> For instance,



Figure 1. Synthesis procedure for Terpy-PIL.

luminescent materials of polymer covalently grafted with terpyridine–lanthanide(III) complexes in the side chains have already been reported.<sup>[57,58]</sup> However, no luminescent materials derived from the incorporation of lanthanide complexes in the side chains of PILs have been reported up to now. We therefore also report the first luminescent PIL obtained by the complexation of Terpy-PIL with europium(III) ions. To the best of our knowledge, this is the first PIL, in which terpyridine–europium(III) complexes are linked in the polymer chains. A luminescent material resulting from the coordination of europium(III) to the terpyridine-functionalized IL monomer (Terpy-IL) was also prepared to investigate the effect of polymerization on the luminescence behavior of the luminescent materials.

### **Results and Discussion**

The Terpy-PIL was prepared by polymerization of 4'-(1vinylimidazolyl)-2,2':6',2''- terpyridine (Terpy-IL) in methanol at 65 °C for 24 h, which was initialized with AIBN, as shown in Figure 1. Terpyridines are well-known ligands for transition-metal and lanthanide complexes, which find wide applications in supramolecular chemistry, in dye sensitization of solar cells, in luminescent materials, in catalysis, and in extraction. We investigate the applications of Terpy-PIL in the preparation of luminescent materials, because terpyridine moieties linked to the polymer chain have the ability to coordinate to and sensitize Eu<sup>3+</sup> ions. A luminescent material was prepared by stirring a mixture of EuCl<sub>3</sub>·6H<sub>2</sub>O and Terpy-PIL (molar ratio 1:2) in EtOH/DMF at 70 °C for 5 h. The product was precipitated by addition of diethyl ether and washed with EtOH several times, and it is referred to as Terpy-PIL@Eu. The obtained materials are highly luminescent when they are irradiated with UV light, as shown in Figure 2. The amount of Eu<sup>3+</sup> in Terpy-PIL@Eu was determined to be 13.07% by using the EDTA titration method. Moreover, the luminescent material Terpy-IL@Eu was prepared similarly by reaction of EuCl<sub>3</sub>·6H<sub>2</sub>O with Terpy-IL. The amount of Eu<sup>3+</sup> in Terpy-IL@Eu was determined to be 12.16% by the same titration method.

The polymerization of the monomers can be simply verified by FTIR spectra. The band at 1649 cm<sup>-1</sup> shown in the FTIR spectrum of Terpy-IL (Figure 3a) is assigned to the vibration of the vinyl groups. The bands in the range 1610–1450 cm<sup>-1</sup> are ascribed to the terpyridine and imidazolium



**FULL PAPER** 

Figure 2. Possible structure of Terpy-PIL@Eu, which shows the coordination of the terpyridine moieties to Eu<sup>3+</sup> ions and the energy transfer as well as a digital photo taken under UV light ( $\lambda_{max} =$  365 nm).

rings. The strong band at 790 cm<sup>-1</sup> is due to the C–C bond between the pyridine rings.<sup>[59,60]</sup> As revealed in Figure 3b, similar absorption bands can be observed for the FTIR spectrum of Terpy-PIL except for the band of the vinyl group at 1649 cm<sup>-1</sup>, which has disappeared, and this indicates the completion of the polymerization of Terpy-IL under the experimental conditions.



Figure 3. FTIR spectrum of Terpy-IL (a) and the obtained PIL Terpy-PIL (b).

The polymerization can be further confirmed by <sup>1</sup>H NMR spectra. Comparative <sup>1</sup>H NMR spectra of the obtained PIL and the Terpy-IL together with an assignment of the resonances are shown in Figure 4. The absence of the vinyl hydrogen signals and the presence of sp<sup>3</sup>-hydrogen signals in the spectrum of the PIL indicate the complete polymerization of Terpy-IL. The relative broadening in the NMR spectra of the polymers has been observed previously and can be attributed to the lack of solution mobility of the bulky polymer chains.<sup>[61]</sup> The molecular weight distributions of Terpy-PIL were determined by gel-permeation chromatography (GPC) [ $M_n$ (GPC) = 63939 g/mol,  $M_w/M_n$  = 1.75]. All obtained data were based on a calibration curve [log  $M_w$  vs V (V = retention volume)] constructed by using narrow-molecular-weight-range polystyrene standards.



Figure 4. <sup>1</sup>H NMR spectrum of Terpy-IL (a) and Terpy-PIL (b).

Thermogravimetric analyses were performed to determine the thermal stability of the Terpy-PILs, and the TG curves are shown in Figure 5. Three steps of weight loss can be observed in the TG curve of Terpy-PIL. The first one with approximately 4% weight loss below 230 °C is attributed to the desorption of physically adsorbed water and residual solvents. The second weight loss (ca. 43%) in the range 230-510 °C can be ascribed to backbone degradation. The last one starts at 510 °C and is complete at 650 °C, and the observed weight loss is approximately 48%, which can be attributed to the decomposition of terpyridine moieties attached to the polymer chains. A horizontal thermal curve was observed above 650 °C. Similarly, three decomposition steps can also be observed in the TG curve of Terpy-PI-L@Eu, and they can be assigned to the removal of the residual solvents, to the decomposition of the polymer chains, and to the decomposition of the terpyridine moieties, respectively. Finally, a horizontal thermal curve was observed at temperatures exceeding 650 °C, which is due to the formation of the thermally stable product Eu<sub>2</sub>O<sub>3</sub> (13.95%). The amount of the chelated europium(III) ions was determined from the TG curve of the luminescent material to be 12.05%, and this value roughly corresponds to a molar ratio of 2:1 between Terpy-PIL and Eu<sup>3+</sup>. The coordination of Eu<sup>3+</sup> ions to terpyridine moieties in the PIL can be confirmed by the luminescence data of the luminescent material Terpy-PIL@Eu, which are shown in Figure 6.



Figure 5. TG curve of Terpy-PIL and Terpy-PIL@Eu.

The luminescence data of Terpy-PIL@Eu and Terpy-IL@Eu are shown in Figure 6. The excitation spectrum of Terpy-PIL@Eu, recorded in the range 200-470 nm and monitored at the  ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$  hypersensitive transition at 612 nm, displays a large broad band ascribed to the excited states of the terpyridine moieties in the polymer, which largely overlaps with the absorption bands of the poly(ionic liquid) Terpy-PIL (Figure S1). This is diagnostic of the typical sensitization by the terpyridine moieties of the Terpy-PIL and therefore confirms that Eu<sup>3+</sup> ions are surrounded by terpyridine moieties in Terpy-PIL@Eu. The emission spectrum excited at 340 nm shows characteristics of the Eu<sup>3+</sup> emissions in the 570–725 nm region, and it exhibits well-resolved, sharp peaks, which are due to the transitions from the metal-centered  ${}^{5}D_{0}$  excited state to the  ${}^{7}F_{I}$ ground state multiplet. Maximum peak intensities at 579, 590, 612, 652, and 702 nm are observed for the J = 0, 1, 2, 1, 13, and 4 transitions, respectively, and the so-called "hypersensitive" J = 2 transition is the most prominent feature, which is responsible for the brilliant red emission of the luminescent materials, which is shown in Figure 2. The intensity of the  ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$  transition is much higher than that of the  ${}^{5}D_{0} \rightarrow {}^{7}F_{1}$  transition, and the intensity ratio of the  ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$  and  ${}^{5}D_{0} \rightarrow {}^{7}F_{1}$  transitions is 5.42, which implies that the coordination environment of the Eu<sup>3+</sup> ions is devoid of an inversion center.<sup>[21]</sup> In fact, the ratio is approximately 0.63 for a hydrated Eu<sup>3+</sup> species.<sup>[62]</sup> The coordination of terpyridine in the polymer to Eu<sup>3+</sup> ions results in the repulsion of water molecules from the coordination sphere, and, as a consequence, this causes the remarkable changes in the intensity ratio of the  ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$  and  ${}^{5}D_{0} \rightarrow {}^{7}F_{1}$ transitions. The presence of water molecules in the coordination sphere of the oxophilic lanthanide center has long been recognized to influence the luminescence properties of lanthanide ions, and it normally leads to reduced lifetimes for the excited state and to the quenching of any emissions. No broad emission band of the polymer can be observed



Figure 6. Luminescence data of the luminescent material Terpy-PIL@Eu: (a) Excitation spectra, (b) emission spectra, and (c) decay curves. Excitation spectra were observed at 612 nm, and emission spectra were obtained upon excitation at 340 nm. Decay curves were measured at an excitation wavelength of 340 nm and an emission wavelength of 612 nm.

in the emission spectrum, which implies that the polymer transfers the absorbed energy effectively to the emitting level of the Eu<sup>3+</sup> ions. The Terpy-IL@Eu material shows spectral features, which are very similar to those of the polymer material Terpy-PIL@Eu. The decay curves of Terpy-PIL@Eu and Terpy-IL@Eu are well-fitted by means of a single-exponential function (Figure 6c), which indicates the presence of only one emissive Eu<sup>3+</sup> center. The lifetimes  $\tau$  are (0.863 ± 0.003) and (0.522 ± 0.002) ms for Terpy-IL@Eu and Terpy-IL@Eu, respectively. This result shows that the lifetime is significantly prolonged after the polymerization, which might be due to the confinement of the terpyridine-europium(III) complexes within the rigid chains of the polymer architecture. In fact, the grafting of lanthanide complexes to conventional polymers has been frequently reported. In those cases, an increase in the lifetime was also observed.<sup>[63,64]</sup> Terpyridine was frequently used as the sensitizer for lanthanide ions in polymers,<sup>[52,57]</sup> organosilica,<sup>[59,65]</sup> and ionic liquids<sup>[48]</sup>. The luminescence features of these materials are similar to those of the PILs reported in this work. Interestingly, luminescent materials based on

the coordination of Eu<sup>3+</sup> and Tb<sup>3+</sup> to polymers containing terpyridine show obvious reversible thermochromism.<sup>[57]</sup> Furthermore, all the aforementiond materials containing terpyridine–europium(III) complexes show a relatively low intensity ratio of  $I({}^{5}D_{0} \rightarrow {}^{7}F_{2})/I({}^{5}D_{0} \rightarrow {}^{7}F_{1})$  compared to those of europium(III) β-diketonate complexes, which typically show values higher than  $10^{[66,67]}$  (even higher than 20 for some cases).<sup>[68]</sup> The coordination of the PIL to europium(III) tris(2-thenoyltrifluoroacetonate) dehydrate through a nitrogen atom from the terpyridine can increase the value of the intensity ratio of  $I({}^{5}D_{0} \rightarrow {}^{7}F_{2})/I({}^{5}D_{0} \rightarrow {}^{7}F_{1})$ .<sup>[42]</sup> This work is in progress in our laboratory.

To further compare the luminescence performances of Terpy-PIL@Eu and Terpy-IL@Eu, the <sup>5</sup>D<sub>0</sub> radiative  $(k_r)$  and the non-radiative  $(k_{nr})$  transition probabilities and the <sup>5</sup>D<sub>0</sub> quantum efficiencies of both samples were estimated according to a reported method by using the following equations, which are based on the emission spectra and the lifetime of the <sup>5</sup>D<sub>0</sub> state of the Eu<sup>3+</sup> ions.<sup>[69]</sup> By assuming that only non-radiative and radiative processes are involved in the depopulation of the <sup>5</sup>D<sub>0</sub> state, *q* can be defined as shown in Equation (1).

$$q = k_{\rm r}/(k_{\rm r} + k_{\rm nr}) \tag{1}$$

Here  $k_r$  and  $k_{nr}$  represent the radiative and non-radiative probabilities, respectively. The radiative contribution can be obtained 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 very weak) and can be expressed by Equation (2).

$$k_{\rm r} = \frac{A_{0-1}E_{0-1}}{S_{0-1}} \sum_{J=0}^{4} \frac{S_{0-J}}{E_{0-J}}$$
(2)

Here,  $A_{0-1}$  represents the Einstein coefficient of the spontaneous emission between the  ${}^5D_0$  and  ${}^7F_1$  level and is considered to be 50 s<sup>-1</sup>.  $E_{0-J}$  and  $S_{0-J}$  are the energy and the integrated intensity of the  ${}^5D_0-{}^7F_J$  transitions, respectively. The resulting data are shown in Table 1. The higher value of quantum efficiency (*q*) for Terpy-PIL@Eu compared to that of Terpy-IL@Eu can be attributed to a decrease in the  $k_{nr}$  value in the polymer (0.71 ms<sup>-1</sup>) with respect to that of Terpy-IL@Eu (1.49 ms<sup>-1</sup>), as shown in Table 1.

The number of water molecules  $(n_w)$  in the coordination sphere of Eu<sup>3+</sup> ions can be estimated on the basis of the empirical formula suggested by Supkowski and De Horrocks Jr. by using Equation (3).<sup>[70]</sup>

$$n_{\rm w} = 1.1(k_{\rm exp} - k_{\rm r} - 0.31) \tag{3}$$

Here,  $k_{exp}$  is the reciprocal value of the <sup>5</sup>D<sub>0</sub> lifetime. The numbers of estimated water molecules in the coordination sphere of Eu<sup>3+</sup> ions in Terpy-PIL@Eu and Terpy-IL@Eu are listed in Table 1. The number of water molecules in the polymer is 0.44, which indicates that most of the water molecules coordinated to Eu<sup>3+</sup> ions in europium(III) chloride hexahydrate have been displaced from the coordination sphere by the terpyridine in the polymer, as shown in Fig-



ure 2. The number of water molecules coordinated to each  $Eu^{3+}$  ion in the monomeric Terpy-IL@Eu is 1.3, which indicates that less water molecules are coordinated to  $Eu^{3+}$  ions in the polymer than in Terpy-IL@Eu.

Table 1. Experimental  ${}^{5}D_{0}$  lifetime ( $\tau$ ), calculated radiative ( $k_{r}$ ) and nonradiative ( $k_{nr}$ ) transition probabilities, quantum efficiency (q), and the number of coordinated water molecules ( $n_{w}$ ).

Sample	$\tau$ [ms]	$k_{\rm r}  [{\rm ms}^{-1}]$	$k_{\rm nr}~[{\rm ms}^{-1}]$	q [%]	$n_{\rm w}$
Terpy-PIL@Eu	0.86	0.45	0.71	38.79	0.44
Terpy-IL@Eu	0.52	0.43	1.49	22.39	1.3

# Conclusions

A new poly(ionic liquid) with terpyridine moieties grafted in each of the repeating units of the polymer was designed and synthesized for the first time in this work. The obtained terpyridine-carrying poly(ionic liquid) might find potential applications in various fields, such as molecular electronics, sensing, extraction, catalysis, optics, supramolecular chemistry, and so on, which is due to the presence of numerous terpyridine moieties, which can bind various metal ions. The binding of europium(III) ions to the poly(ionic liquid) was used as an example to illustrate the utilization of these PILs as luminescent materials. The luminescent material resulting from the coordination of europium(III) to the new poly(ionic liquid) shows a bright red emission when it is irradiated by UV light, which makes them suitable for combinations with UV-light-emitting LEDs, because they can be excited in the near-UV region.

## **Experimental Section**

**Materials:** 1-Vinylimidazole (Aldrich 99%), 2-acetylpyridine (Aldrich 98%), *p*-tolualdehyde (Aldrich 98%), and azobis(isobutyronitrile) (AIBN) initiator (Aldrich 99%) were purchased and used as received. 4'-(Methylphenyl)-2,2':6',2''-terpyridine was synthesized according to a reported procedure.<sup>[71]</sup> EuCl<sub>3</sub>·6H<sub>2</sub>O was obtained by dissolving Eu<sub>2</sub>O<sub>3</sub> in hydrochloric acid (37%), and the excess of the acid was removed by the addition of water and the subsequent evaporation of the solvent, and this process was repeated several times.

Synthesis of 4'-[4-(Bromomethyl)phenyl]-2,2':6',2''-terpyridine (1): A mixture of 4'-(methylphenyl)-2,2':6',2''-terpyridine (0.4 g, 1.2 mM), *N*-bromsuccinimide (NBS, 0.3 g, 1.6 mmol), and benzoyl peroxide (BPO) (0.16 g, 0.6 mM) in dry ethyl acetate (40 mL) was heated at 78 °C for 3 h. The warm reaction mixture was filtered to remove the succinimide, and the solvent was evaporated. The crude product was recrystallized from ethanol to afford a pale-yellow solid (yield: 0.458 g, 90%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta_{\rm H} = 8.73$  (t, 4 H), 8.67 (d, J = 8.0 Hz, 2 H), 7.89 (t, 4 H), 7.53 (t, 2 H), 7.34 (t, 2 H), 4.59 (d, J = 8.0 Hz, 2 H) ppm. C<sub>22</sub>H<sub>16</sub>BrN<sub>3</sub> (402.12): calcd. C 65.71, H 3.97, N 10.44; found C 66.36, H 3.52, N 9.75.

**Synthesis of 4'-(1-Vinylimidazolyl)-2,2':6',2''-terpyridine[Br]** (Terpy-IL): A mixture of 1 (0.8528 g, 1.2 mM) and 1-vinylimidazole (0.1694 g, 1.8 mM) in acetonitrile (18 mL) was heated at reflux at 80 °C for 24 h. The crude product was washed with acetonitrile several times and dried at 80 °C until its weight remained constant. The product is a white solid (yield: 0.5957 g, 82%). <sup>1</sup>H NMR (400 MHz, [D<sub>6</sub>]DMSO):  $\delta_{\rm H}$  = 9.68 (t, 1 H), 8.76 (t, 4 H), 8.68 (d, J = 8.0 Hz, 2 H), 8.29 (s, 1 H), 8.06 (t, 4 H), 8.03 (s, 1 H), 7.70 (t, 2 H), 7.56 (t, 2 H), 7.34 (m,1 H),6.03 (d,1 H), 5.59 (s, 2 H), 5.46 (d, 1 H) ppm. C<sub>27</sub>H<sub>22</sub>BrN<sub>5</sub> (496.17): calcd. C 65.35, H 4.43, N 14.10; found C 64.65, H 5.30, N 13.98.

**Synthesis of Terpy-PIL:** In a Schlenk flask (50 mL), **2** (0.6 g), AIBN (0.03 g), and dry methanol (12 mL) were mixed. The mixture was completely deoxygenated by three cycles of a freeze–pump–thaw procedure and was backfilled with nitrogen. The mixture was then stirred, and the flask was thermostated in an oil bath at 65 °C for 28 h. After cooling to room temperature, the crude product was washed with diethyl ether and methanol several times to give Terpy-PIL as a yellow solid.  $(C_{27}H_{22}BrN_5)_n$  (496.4): calcd. C 65.35, H 4.43, N 14.10; found: C 66.38, H 4.95, N 14.25. IR (KBr):  $\tilde{v} = 1610-1450 [v(C=N)]$ , 790  $[v(C-C)] \text{ cm}^{-1}$ .  $M_n(\text{GPC}) = 63939 \text{ g/mol}$ ,  $M_w = 111893 \text{ g/mol}$ ,  $M_w/M_n = 1.75$ .

**Preparation of Terpy-PIL@Eu:** Independent solutions of europium(III) chloride (typically 2 mL, 0.05 mM), and Terpy-PIL (2 mL, 0.1 mM) were first prepared in an EtOH/DMF mixture. The solutions were then mixed, and the mixture was stirred in an oil bath thermostated at 70 °C for 5 h. The product was precipitated by the addition of diethyl ether and washed with EtOH several times.

Characterization Methods: <sup>1</sup>H NMR spectra were recorded with a Bruker ARX 300 spectrometer. IR spectra were recorded with a Bruker Vector 22 spectrometer in the range 400-4000 cm<sup>-1</sup> at a resolution of 4 cm<sup>-1</sup> (16 scans were collected). Gel-permeation chromatography (GPC) was measured with a PL-GPC220 apparatus (Agilent Technologies) by using DMF as an eluent and polystyrene as the standard sample, and the concentration of the sample was 1 mg/mL, the flow rate was 1.0 mL/min, and the test temperature was 40 °C. Samples for thermogravimetric studies were transferred to open platinum crucibles and analyzed by using an SDT-TG Q 600 TA instrument at a heating rate of 5 °C/min<sup>-1</sup>. The steady-state luminescence spectra and the lifetimes were measured with an Edinburgh Instrument FS920P spectrometer with a 450 W xenon lamp as the steady-state excitation source, a double excitation monochromator (1800 lines/mm<sup>-1</sup>), an emission monochromator (600 lines/mm $^{\!-\!1}$ ), and a semiconductor cooled Hamamatsu RMP928 photomultiplier tube.

**Supporting Information** (see footnote on the first page of this article): Absorption spectrum of Terpy-PIL in DMF.

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