Research Article

# Novel Luminescent Soft Materials of Terpyridine-Containing Ionic Liquids and Europium(III)

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S *Supporting Information*

ABSTRACT: Herein, we describe novel luminescent soft materials via reaction of Eu^{3+}-coordinated carboxyl functionalized ionic liquids with terpyridine-functionalized imidazolium salts that are built from an imidazolium ring substituted on one side with a terpyridine derivative and, on the opposite side, a paraffin chain of various lengths. The obtained materials are either pastelike substances or viscous fluids, depending on the anions of the carboxyl functionalized ionic liquids. The soft luminescent materials were investigated by Fourier transform infrared spectroscopy (FT-IR), X-ray diffraction (XRD), thermogravimetry (TG), and luminescence spectroscopy. The soft materials show bright red emission irradiated with UV light, because of the energy transfer from terpyridine-functionalized imidazolium salts to the Eu^{3+} ions. The absolute quantum yields of the materials were determined and the energy transfer efficiency was estimated according to the reported method.

KEYWORDS: *Ionic liquid, soft materials, terpyridine, europium(III), energy transfer, luminescent properties*
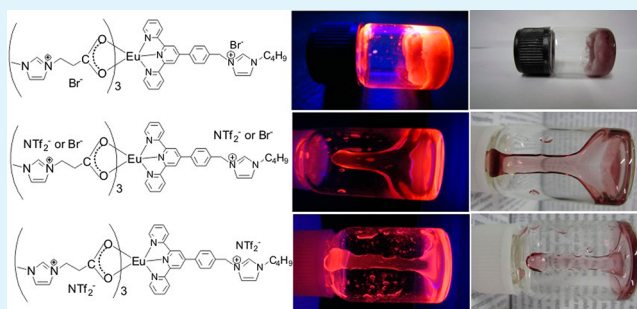
1. INTRODUCTION

Ionic liquids (ILs) have been under intense scrutiny, because of their unique properties, such as their negligible vapor pressures, wide liquid ranges, good thermal stabilities, good electric conductivity, wide electrochemical windows, and good solubility for various substances, which render them suitable for various applications.[1−3] One of the most distinguished features of ILs is the tunability of their chemical and physical properties through the appropriate selection of anion/combination. Currently, the applications of ILs under intensive investigation include uses as solvents for organic reactions,[2,4] separations,[5−10] electrodeposition,[11,12] electrolyte in photovoltaic devices,[13,14] and as template and/or reaction media for nonmaterial.[15−21] Recently, a host of investigations on the combination of ILs with lanthanide compounds as potential new optical materials have been reported.[22−29] Improved luminescence performances as well as enhanced photochemical stability of some lanthanide complexes dissolved in ILs are observed.[30] Most of them can be regarded as luminescent soft materials, which show obvious advantages in fabricating soft optical devices.[31,32] We have prepared such materials by directly dissolving lanthanide oxide and organic sensitizer in carboxyl-functionalized ILs.[33,34] Luminescent ionogels prepared from lanthanide-containing ILs have also been reported by us and other groups.[27,28,35−41]

Specific functional groups have been introduced in the cations or anions of ILs, leading to a novel type of so-called "task-specific ionic liquids" (TSILs, or functionalized

ILs),[10,42−46] which was first reported by Rogers et al.[47] TSILs containing functional groups toward metal complexation have been used in metal separation and extraction process,[10,42,43] as well as in catalysis.[48] Moreover, the presence of complexing moeties in TSILs can increase the solubility of lanthanide compounds in ILs, e.g., carboxyl groups.[44,45] Terpyridine moeties also have been incorporated into the cations of TSIL by Ziessel and co-workers,[43] the importance of which is that terpyridine easily forms complexes with various metal ions that can find interesting application in sensing, extraction, and supramolecular chemistry.[49−54] The obtained TSIL was also tested for biphasic extraction of Fe^{2+} from water solutions. As well-known, terpyridine can form molecular luminescent materials upon complexing with lanthanide ions due to the energy transfer, which is the so-called "antenna effect".[51,52,55] However, the luminescent behaviors of terpyridine-carrying TSIL complexed with lanthanide ions have never been investigated, to the best of our knowledge. Herein, we report the synthesis of novel terpyridine-carrying TSILs (Terpy-TSILs) by functionalization of the imidazolium cations with a terpyridine substituent. As well, luminescent soft materials with intense red-emitting color have also been prepared by mixing Terpy-TSIL with carboxyl-functionalized IL([Carb-C_1mim]Br and [Carb-C_1mim]NTf_2 (NTf_2 = bis(trifluoromethane-

sulfonyl)imide)) in which Eu^{3+} ions are coordinated with the carboxyl group. The resulting luminescent soft materials display intense red-emitting colors when irradiated with an ultraviolet (UV) lamp (λ_{max} = 365 nm), some of which can be coated on a large area.

2. EXPERIMENTAL SECTION

Materials. 3-Bromopropanoic acid (98%, Aldrich), 1-methylimidazole (98%, Aldrich), lithium bis(trifluoromethanesulfonyl)imide (98%, Aldrich), 1-butylimidazole (99%, Aldrich), N-bromosuccinimide (99%, Acros), 2-acetylpyridine (98%, Aldrich), p-tolualdehyde (98%, Aldrich) were used as-received. Benzoyl peroxide (98%, Guoyaojituan Chemical Reagent Co.) was crystallized from the methyl alcohol. Eu$_2$O$_3$ was purchased from Shanghai Yuelong. Carboxyl-functionalized IL([Carb-C$_1$mim]Br) was synthesized according to the reported procedure.[56] 4′-(p-Tolyl)-2,2′:6′,2″-terpyridine and 4′-(4-(bromomethyl)phenyl)-2,2′:6′,2″-terpyridine (**1**) were synthesized by the modified method previously reported.[54,57,58] 1-Hexadecylimidazole was synthesized according to the method reported elsewhere.[59]

General Synthesis Procedure for [C$_n$terpyim]Br (n = 1, 4, 16). **1** (402.0 mg, 1 mmol) was added to a solution of alkylimidazole (1.2 mmol) in 20 mL of dried acetonitrile. The mixture was subsequently refluxed for 36 h at 80 °C. Evaporation of the solvent under vacuum yielded the crude product, which was purified by repeated washing with appropriate solvents. The resulting solid was centrifuged and dried under vacuum.

N-Methyl-N′-(4′-(p-tolyl)-2,2′:2″,6′-terpyridyl)imidazolium bromide([C$_1$terpyim]Br). The procedure was followed using 1-methylimidazole (98.50 mg,1.2 mmol), and the crude product was purified by repeated washing with acetone. The product was obtained as a pale yellow solid (363 mg, 0.75 mmol, 75%).

^{1}H NMR (400 MHz, CDCl$_3$, ppm), δ_H: ^{1}H NMR (CDCl$_3$, ppm). 10.99 (s, 1H), 8.69 (t, 6H), 7.90 (t, 4H), 7.61 (d, 2H), 7.38 (t, 2H), 7.21 (d, 2H), 5.70 (s, 2H), 4.12 (s, 3H); ^{13}C NMR (100 Hz, CDCl$_3$, ppm), δ_C: ^{13}C NMR (CDCl$_3$, ppm). 155.85, 149.00, 139.66, 137.85, 133.58, 129.65, 128.30, 124.03, 123.36, 121.81, 121.42, 118.79, 77.25, 52.99, 36.86; EI-MS m/z: 404.4 ([M−Br], 100); Anal. Calcd for C$_{26}$H$_{22}$N$_5$Br (484.11): C 64.41, H 4.54, N 14.45. Found: C 64.18, H 4.72, N 14.02. IR (KBr): v = 3417 (vOH), 3058 (v_{as}CH$_3$), 2933 (v_{as}CH$_2$), 1587, 1460, 1394, 1267, 1153, 844, 796, 742.

N-Butyl-N′-(4′-(p-tolyl)-2,2′:2″,6′-terpyridyl)imidazolium bromide([C$_4$terpyim]Br). The procedure was followed using 1-butylimidazole (149.0 mg, 1.2 mmol) and the crude product was purified by repeated washing with CH$_2$Cl$_2$/Et$_2$O mixtures. The product was obtained as a pale yellow solid (407 mg, 0.77 mmol, 77%).

^{1}H NMR (400 MHz, CDCl$_3$, ppm), δ_H: ^{1}H NMR (CDCl$_3$, ppm). 10.88 (s, 1H), 8.74 (t, 6H), 7.95 (t, 4H), 7.65 (d, 2H), 7.41 (t, 2H), 7.35 (d, 2H), 5.76 (s, 2H), 4.33(t, J = 7.6 Hz, 2H), 1.93 (m, J = 15.2 Hz, 7.6 Hz, 2H), 1.41 (m, J = 7.6 Hz, 2H), 0.98 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 Hz, CDCl$_3$, ppm), δ_C: ^{13}C NMR (CDCl$_3$, ppm). 155.85, 149.01, 139.59, 139.27, 137.20, 137.06, 133.90, 129.71, 128.25, 123.96, 122.06, 121.42, 118.82, 77.40, 76.77, 52.89, 50.07, 32.06, 19.53, 13.45; EI-MS m/z: 446.3 ([M−Br], 100); Anal. Calcd for C$_{29}$H$_{28}$N$_5$Br (526.50): C 66.14, H 5.32, N 13.30. Found: C 65.65, H 5.53, N 12.93. IR (KBr): v = 3150 (v_{as}CH$_3$), 2968 (v_{as} CH$_2$), 1607, 1587, 1563, 1473, 1394, 1163, 790 (vC−C).

N-Hexadecyl-N′-(4′-(p-Tolyl)-2,2′:2″,6′-terpyridyl)-imidazolium bromide([C$_{16}$terpyim]Br). The procedure was followed using 1-hexadecylimidazole (351.0 mg, 1.2 mmol) and the crude product was purified by repeated washing with CH$_2$Cl$_2$/Et$_2$O mixtures. The product was obtained as a pale yellow solid (479 mg, 0.69 mmol, 69%).

^{1}H NMR (400 MHz, CDCl$_3$, ppm), δ_H: ^{1}H NMR (CDCl$_3$, ppm). 10.64 (s, 1H), 8.71 (t, 6H), 7.91 (t, 4H), 7.64 (d, 2H), 7.38 (t, 2H), 7.20 (d, 2H), 5.75 (s, 2H), 4.32 (t, J = 7.2 Hz, 2H), 1.93 (m, J = 7.6 Hz, 6.8 Hz, 2H), 1.29 (m, 26H), 0.87 (t, J = 6.8 Hz, 3H); ^{13}C NMR (100 Hz, CDCl$_3$, ppm), δ_C: ^{13}C NMR (CDCl$_3$, ppm). 155.61, 149.08, 139.47, 137.32, 133.96, 129.74, 128.28, 124.08, 122.05, 121.87, 121.57,

118.95, 77.29, 52.88, 50.35, 31.92, 30.24, 29.50, 28.98, 26.32, 22.69, 14.12; EI-MS m/z: 614.5 ([M−Br], 100); Anal. Calcd for C$_{29}$H$_{28}$N$_5$Br: C 70.83, H 7.49, N 10.08. Found: C 70.47, H 8.01, N 9.87. IR (KBr): v = 3148 (vOH), 3125 (v_{as}CH$_3$), 3062 (v_sCH$_3$), 3922 (v_{as}CH$_2$), 2581 (v_sCH$_2$), 1585, 1567, 1467, 1390, 1154, 857, 790, 738.

General Procedure for the Metathesis of Anions. To a solution of lithium bis(trifluoromethanesulfonyl)imide (344.5 mg, 1.2 mmol) dissolved in ethanol (8 mL) was added 0.6 mmol of [C$_n$terpyim]Br. The mixture was refluxed at 78 °C for 36 h, and the solvent was removed under vacuum. The crude product was dissolved in CHCl$_3$ (3 mL) and was washed with a H$_2$O/acetone mixture several times. Evaporation of the solvent resulted in a yellow-brown oil that was dried at 65 °C under vacuum overnight.

N-Methyl-N′-(4′-(p-tolyl)-2,2′:2″,6′-terpyridyl)imidazolium bis(trifluoromethane sulfonyl)imide([C$_1$terpyim] NTf$_2$). ^{1}H NMR (400 MHz, CDCl$_3$, ppm), δ_H: ^{1}H NMR (CDCl$_3$, ppm). 8.92 (s, 1H), 8.66 (t, 6H), 7.86 (m, 4H), 7.45 (d, 2H), 7.35 (d, 2H), 7.31 (m, 4H), 5.37 (s, 2H), 3.93 (s, 2H); ^{13}C NMR (100 Hz, CDCl$_3$, ppm), δ_C: ^{13}C NMR (CDCl$_3$, ppm). 155.73, 148.99, 139.75, 137.22, 136.32, 133.07, 129.52, 128.37, 124.63, 123.86, 121.46, 118.82, 115.06, 77.25, 53.14, 36.45. IR (ATR): v = 3151 (v_{as}CH$_3$), 2972 (v_{as}CH$_2$), 1579, 1463, 1394, 1348 (v_{as}S=O), 1188 (v_sS=O2), 1130 (v_sS=O$_2$), 1055 (v_sC−F), 835, 783(C−C), 736.

N-Butyl-N′-(4′-(p-tolyl)-2,2′:2″,6′-terpyridyl)imidazolium bis(trifluoromethanesulfonyl)imide([C$_4$terpyim]NTf$_2$). ^{1}H NMR (400 MHz, CDCl$_3$, ppm), δ_H: ^{1}H NMR (CDCl$_3$, ppm). 9.016 (s, 1H), 8.69 (t, 6H), 7.89 (t, 4H), 7.51 (d, 2H), 7.36 (t, 2H), 7.34 (d, 2H), 5.42 (s, 2H), 4.22 (t, J = 7.6 Hz, 2H), 1.88 (m, J = 15.2 Hz, 7.6 Hz, 2H), 1.39 (m, J = 7.6 Hz, 2H), 0.97 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 Hz, CDCl$_3$, ppm), δ_C: ^{13}C NMR (CDCl$_3$, ppm). 155.89, 149.04, 139.88, 137.08, 135.61, 133.14, 129.49, 124.07, 122.49, 121.47, 118.81, 77.36, 76.73, 53.18, 50.14, 31.90, 19.37, 13.23. IR (ATR): v = 3150 (v_{as}CH$_3$), 2968 (v_{as}CH$_2$), 1581, 1489, 1388, 1346 (v_{as} S=O), 1188, 1139 (v_sS=O$_2$), 1047 (v_s C−F), 889, 819, 790 (C−C).

N-Hexadecyl-N′-(4′-(p-tolyl)-2,2′:2″,6′-terpyridyl)-imidazolium bis(trifluoromethanesulfonyl)imide([C$_{16}$terpyim]-NTf$_2$). ^{1}H NMR (400 MHz, CDCl$_3$, ppm), δ_H: ^{1}H NMR (CDCl$_3$, ppm). 9.25 (s, 1H), 8.73 (t, 6H), 7.96 (t, 4H), 7.54 (d, 2H) 7.42 (t, 2H), 7.28 (d, 2H), 5.48 (s, 2H), 4.23 (t, J = 7.2 Hz, 2H), 1.91 (m, J = 7.6 Hz, 6.8 Hz, 2H), 1.33 (m, 28H), 0.88 (t, J = 6.8 Hz, 3H); ^{13}C NMR (100 Hz, CDCl$_3$, ppm), δ_C: ^{13}C NMR (CDCl$_3$, ppm). 156.00, 149.09, 140.02, 137.02, 135.76, 133.06, 129.54, 128.48, 124.66, 122.35, 121.47, 118.81, 77.29, 53.25, 50.44, 31.92, 30.07, 29.47, 28.87, 26.17, 22.69, 14.12. IR (ATR): v = 3064 (v_sCH$_3$), 2927 (v_{as}CH$_2$), 2852 (v_sCH$_2$), 1579, 1467, 1380, 1352 (v_{as}S=O), 1184 (v_sS=O2), 1136 (v_sS=O$_2$), 1049 (v_sC−F), 825, 777, 734.

Dissolution of Eu$_2$O$_3$ in [Carb-C$_1$mim]X(Eu/[Carb-C$_1$minm]X (X = Br$^-$ and NTF$_2^-$). Eu$_2$O$_3$ (176.0 mg, 0.5 mmol) was introduced into [Carb-C$_1$minm]X (9 mmol) dissolved in ethanol (9 mL) and deionized water (1 mL). The mixture was heated at 80 °C with stirring until the complete dissolution of Eu$_2$O$_3$. The solvent was removed under vacuum and viscous light yellow oil was obtained, which was dried at 65 °C under vacuum overnight.

Preparation of the Soft Luminescent Materials. Eu/([Carb-C$_1$mim]Br-[C$_n$terpyim]Br) (n = 1, 4, 16). [C$_n$terpyim]Br (1 mmol) was introduced into the prepared Eu/[Carb-C$_1$minm]Br (2.2647 g) dissolved in ethanol (10 mL) and the mixture was heated at 80 °C with stirring for 24 h. Evaporation of the solvents under vacuum resulted in pastelike materials that were further dried at 65 °C under vacuum overnight.

Eu/([Carb-C$_1$mim]NTf$_2$-[C$_4$terpyim]Br). [C$_4$terpyim]Br (1 mmol) was introduced into the prepared Eu/[Carb-C$_1$minm]NTf$_2$ (4.0669 g) dissolved in ethanol (10 mL) and the mixture was heated at 80 °C with stirring for 24 h. Evaporation of the solvents under vacuum resulted in a viscous wine-red oil that was further dried at 65 °C under vacuum overnight. IR(ATR): v = 3155 (v_{as}CH$_3$), 2976 (v_{as}CH$_2$), 1726 (vC=O), 1569, 1438, 1346 (v_{as}S=O), 1178 (v_sS=O$_2$), 1132 (v_sS=O$_2$), 1045 (vC−F), 954, 833, 786 (vC−C), 734.

Eu/([Carb-C$_1$mim]NTf$_2$-[C$_4$terpyim]NTf$_2$). [C$_4$terpyim]NTf$_2$(0.7267g, 1 mmol) was introduced into the prepared Eu/[Carb-

Scheme 1. Procedure for the Synthesis of the Terpy-TSILs and the Possible Structure of Europium(III) Complexes Formed in the Soft Materials
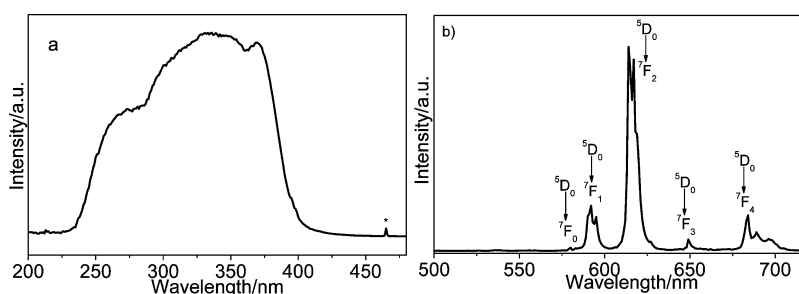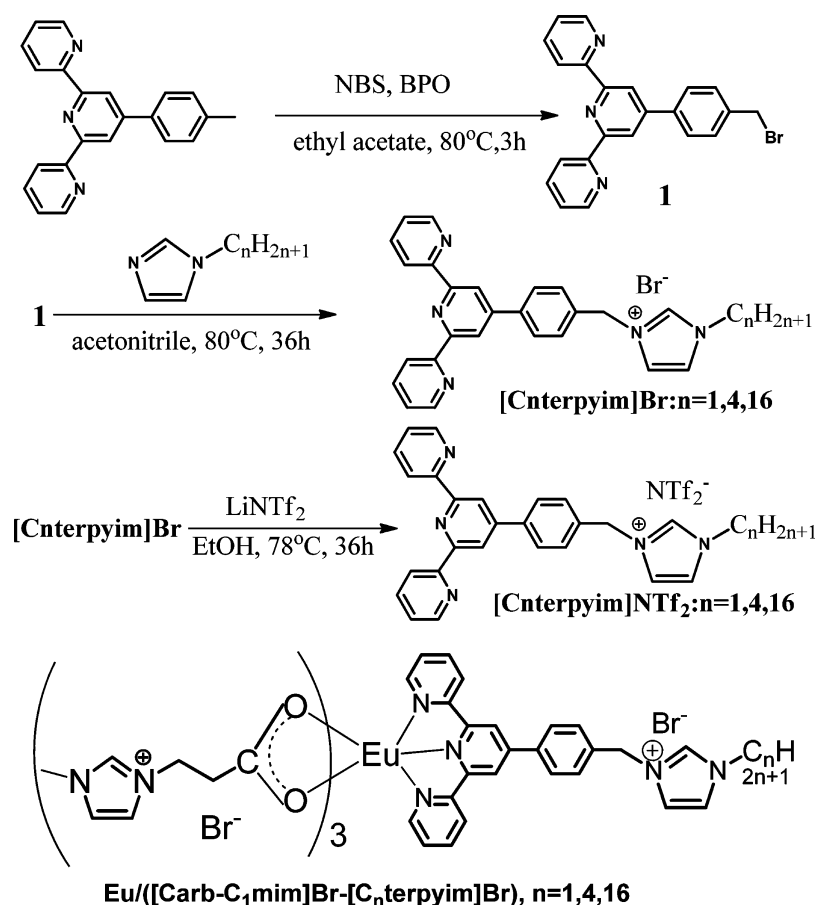

Figure 1. (a) Excitation spectrum and (b) emission spectrum of the complex formed between [C$_1$terpyim]Br and Eu(NO$_3$)$_3$·6H$_2$O. Excitation spectrum was observed at 613 nm, while the emission spectrum was obtained upon excitation at 340 nm.

C$_1$minm]NTf$_2$ (4.0669 g) dissolved in ethanol (10 mL) and the mixture was heated at 80 °C with stirring for 24 h. Evaporation of the solvents under vacuum resulted in a viscous wine-red oil that was further dried at 65 °C under vacuum overnight. IR (ATR): v = 3155 (v_{as}CH$_3$), 2970 (v_{as}CH$_2$), 1726 (vC=O), 1569 (v_{as}C=O), 1433 (v_sC=O), 1350 (v_{as}S=O), 1136, 1178 (v_sS=O$_2$), 1047 (v_sC−F), 956, 840, 786 (vC−C), 742.

Characterization. ^{1}H and ^{13}C NMR spectra were recorded at room temperature, using perpetuated solvents as internal standards. Elemental analysis was performed on an Elementar Vario EI system. UV/vis spectra were recorded on a Varian Cary Model 50 UV/vis spectrophotometer. Infrared (IR) spectra were obtained on a Bruker Vector 22 spectrometer in the range of 400−4000 cm^{-1} at a resolution of 4 cm^{-1} (16 scans were collected). Samples for thermogravimetry (TG) studies were transferred to open platinum crucibles and analyzed using a TA Instruments Model SDT-TG Q 600 system at a heating rate of 5 °C min^{-1}. The steady-state luminescence spectra and the lifetimes were measured on an Edinburgh Instruments Model FLS920P 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 semiconductor-cooled Hamamatsu Model RMP928 photomultiplier tube. The absolute quantum yields of solid samples were determined by standard procedures using a spectrofluorometer (Model FLS920P) equipped with an integrating sphere coated with BaSO$_4$.

3. RESULTS AND DISCUSSION

Terpy-TSILs [C$_n$terpyim]X (n = 1, 4, 16; X = Br, NTf$_2$) were synthesized as outlined in Scheme 1. 4′-(4-(Bromomethyl)-phenyl)-2,2′:6′,2″-terpyridine (**1**) was synthesized via the bromination of 4′-(p-tolyl)-2,2′:6′,2″-terpyridine using N-bromosuccinimide (NBS) and benzoyl peroxide (BPO) in ethyl acetate. The synthesis of 4′-(p-tolyl)-2,2′:6′,2″-terpyridine

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was first reported by Spahni and Calzagerri.[57] The first luminescent complexes based on such *p*-substituted phenyl-terpy was also reported by this group.[60] [C*n*terpyim]Br salts were synthesized from **1** and the corresponding alkylimidazole in acetonitrile under heating for 36 h, which were purified by repeated washing with the mixture of Et$_2$O and CH$_2$Cl$_2$. All the [C*n*terpyim]Br salts were pale yellow solids. Anion exchange was performed in EtOH using LiNTf$_2$ to obtain [C*n*terpyim]-NTf$_2$, which are yellow-brown oils at room temperature. Similar to terpyridine, both [C*n*terpyim]Br and [C*n*terpyim] NTf$_2$ can form luminescent europium(III) complexes, because of the energy transfer to Eu^{3+} ions, which can simply be demonstrated by the fact that the complexes of Terpy-TSILs with Eu(NO$_3$)$_3$·6H$_2$O (molar ratio = 2:1) display an intense red emission color irradiated under a UV lamp (λ_{max} = 365 nm). The luminescence data of the complex of [C$_1$terpyim]Br with Eu(NO$_3$)$_3$·6H$_2$O are shown in Figure 1. The excitation spectrum obtained by monitoring $^5D_0 \rightarrow {}^7F_2$ line at 613 nm shows a broad band, ranging from 200 to 400 nm, which is overlapped with the absorption spectrum (see Figure S1 in the Supporting Information) and can be ascribed to the absorption of the terpyridine moieties. This indicates the occurrence of energy transfer from [C$_1$terpyim]Br to Eu^{3+} ions. Upon excitation of the [C$_1$terpyim]Br at 340 nm gives rise to characteristic metal-centered Eu^{3+} emission at 579, 613, 655, and 703 nm attributed to the $^5D_0 \rightarrow {}^7F_{0-4}$ transition, respectively. The lifetime of Eu^{3+} is determined to be 0.48 ± 0.01 ms from the decay curve, which can be well-fitted by monoexponential function (see Figure S2 in the Supporting Information). However, our aim in this work is to prepare soft luminescent materials rather than a powder sample. Therefore, we adopt another strategy to utilize Terpy-TSILs to prepare soft materials with intense red luminescence via the introduction of the Terpy-TSILs into the [Carb-C$_1$mim]Br, where an appropriate amount of Eu^{3+} ions are coordinated with the carboxyl group (Scheme 1).[34] The prepared soft material is Eu/([Carb-C$_1$mim]Br-[C$_1$terpyim]Br), Eu/([Carb-C$_1$mim]Br-[C$_4$terpyim]Br), and Eu/([Carb-C$_1$mim]Br-[C$_{16}$terpyim]Br), respectively. It is observed that the anions of the carboxyl-functionalized ILs can influence the physical state of the obtained soft materials. Typically, soft luminescent materials obtained from [Carb-C$_1$mim]Br are pastelike samples, while substitution of [Carb-C$_1$mim]Br with [Carb-C$_1$mim]NTf$_2$ leads to viscous transparent soft luminescent materials which are fluid at room temperature, regardless of the anions used for Terpy-TSILs. Luminescent, transparent soft material is obtained when [Carb-C$_1$mim]NTf$_2$ was used for preparing the luminescent materials, which is called Eu/([Carb-C$_1$mim]NTf$_2$-[C$_4$terpyim]Br). Furthermore, soft luminescent material (Eu/([Carb-C$_1$mim]NTf$_2$-[C$_4$terpyim]NTf$_2$)) was also prepared via the combination of [Carb-C$_1$mim]NTf$_2$ and [C$_4$terpyim] NTf$_2$. Both samples are viscous and transparent at room temperature and show bright red emissions under UV light (see Scheme 2). They can be used as paint to coat large areas of various surfaces, as exemplified in Scheme 2.

FT-IR spectra were first employed to investigate the soft materials (see Figure S3 in the Supporting Information). The reaction of Eu$_2$O$_3$ with the carboxyl groups of carboxyl-functionalized IL can be verified by the presence of absorption bands at 1558 and 1443 cm^{-1}, as shown in Figure S3a in the Supporting Information, which is assigned to the aymmetric and the symmetric stretch of the carboxylate group, respectively.[34] The absorption band at 1730 cm^{-1} in Figure

Scheme 2. Digital Photos of the Soft Materials: (A) Eu/([Carb-C$_1$mim]Br-[C$_1$terpyim]Br), (B) Eu/([Carb-C$_1$mim]Br-[C$_4$terpyim]Br), (C) Eu/([Carb-C$_1$mim]Br-[C$_{16}$terpyim]Br), (D) Eu/([Carb-C$_1$mim]NTf$_2$-[C$_4$terpyim]Br), (E) Eu/([Carb-C$_1$mim]NTf$_2$-[C$_4$terpyim]NTf$_2$), and (F) a Glass Slide Coated with Eu/([Carb-C$_1$mim]NTf$_2$-[C$_4$terpyim]NTf$_2$)

Daylight   UV-light
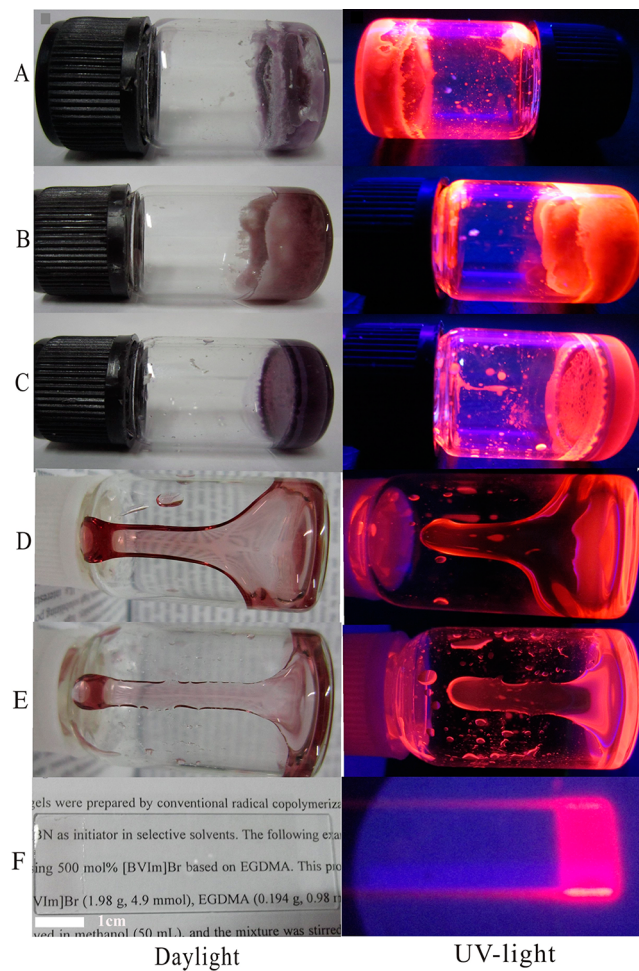
S3a in the Supporting Information is assigned to the unreacted νC=O for COOH of carboxyl-functionalized IL, since an excess of IL is used in this study. Figure S3b in the Supporting Information shows the FT-IR spectrum of the [C$_4$terpyim]Br salt, the bands at 1607, 1587, and 1563 cm^{-1} are assigned to the imidazole ring and the pyridine ring, the strong band at 790 cm^{-1} can be ascribed to the C−C bond between the pyridine rings.[55,61] Upon addition of the [C$_4$terpyim]Br salt into the Eu^{3+}-containing carboxyl-functionalized IL, the shift of absorption bands corresponding to the terpyridine moeties can be observed and is due to the coordination of Eu^{3+} ions (Figure S3c in the Supporting Information). The coordination of Eu^{3+} ions with terpyridine in the organic salts can be further confirmed by the luminescence data, which will be discussed later. In addition, the presence of NTf$_2^-$ can be easily evidenced by the observation of the absorption band at 1350 cm^{-1} attributed to the asymmetric stretching mode of −S=O in NTf$_2^-$, as shown in Figure S3d in the Supporting Information,[38] the ν_s(SO$_2$) bands occur at 1178 and 1136 cm^{-1}, which undergo no obvious shifts, compared to the FT-IR spectrum of [C$_4$terpyim]NTf$_2$ shown in Figure S3e, implying
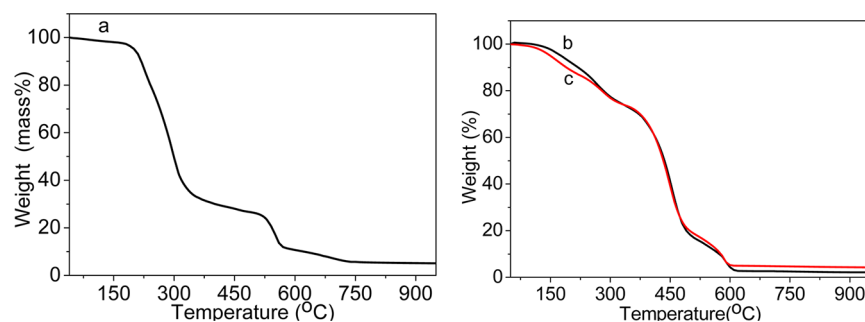
Figure 2. Thermogravimetry (TG) curves of the luminescent soft materials: (a) Eu/([Carb-C$_1$mim]Br-[C$_4$terpyim]Br), (b) Eu/([Carb-C$_1$mim]NTf$_2$-[C$_4$terpyim]Br), and (c) Eu/([Carb-C$_1$mim]NTf$_2$-[C$_4$terpyim]NTf$_2$).
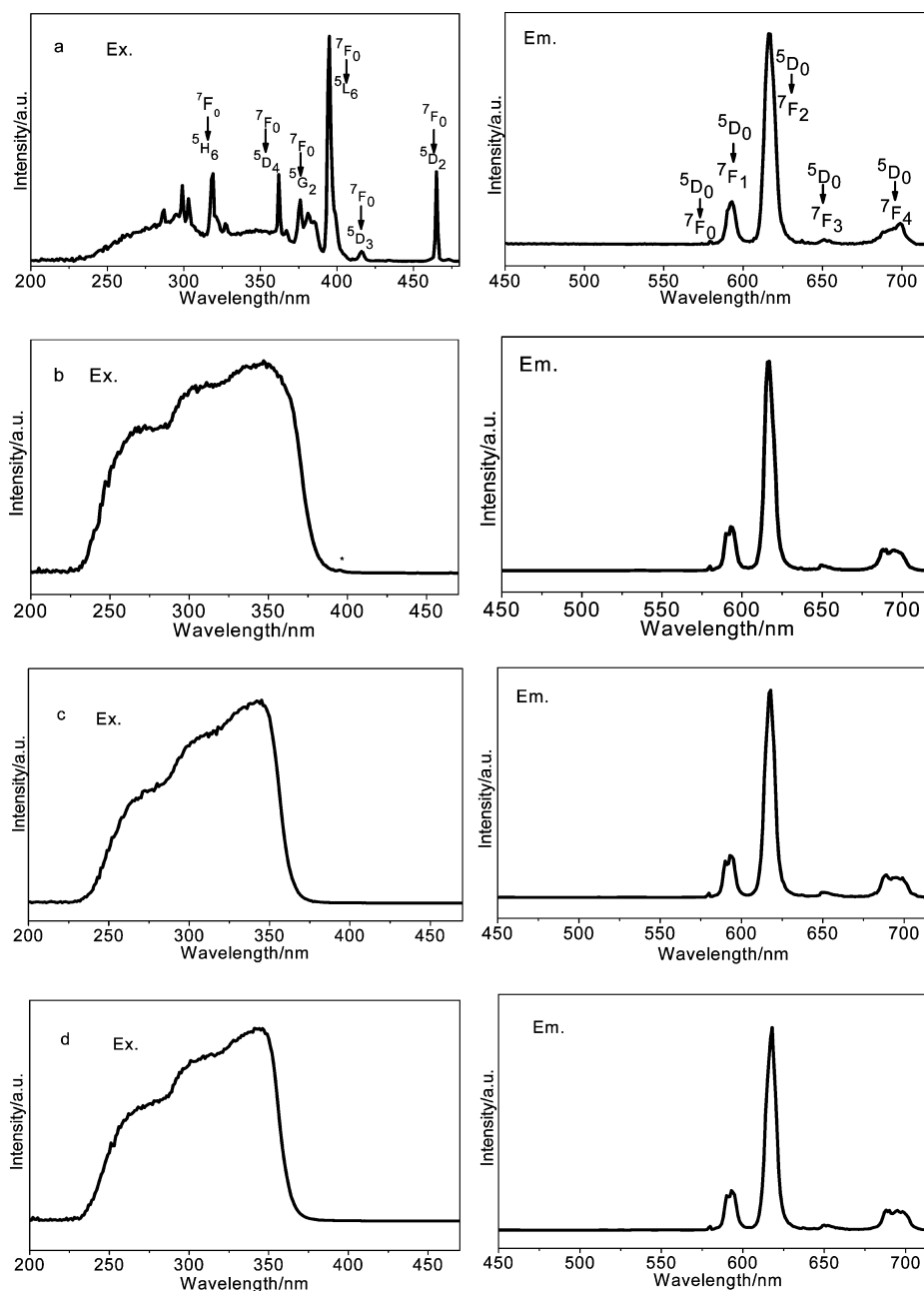

Figure 3. Excitation and emission spectra of the luminescent soft materials: (a) carboxyl-functionalized IL, where an appropriate amount of Eu^{3+} ions are coordinated with carboxyl groups; (b) Eu/([Carb-C$_1$mim]Br-[C$_4$terpyim]Br); (c) Eu/([Carb-C$_1$mim]NTf$_2$-[C$_4$terpyim]Br); and (d) Eu/([Carb-C$_1$mim]NTf$_2$-[C$_4$terpyim]NTf$_2$). Excitation spectrum was observed at 617 nm for all the samples. Emission spectrum was obtained upon excitation at 395 nm for panel (a) and at 350 nm for panels (b–d).

Table 1. Photophysical Data for the Samples[a]

sample	radiative lifetime, τ_{RAD} [ms]	experimental lifetime, τ_{obs} [ms]	intrinsic quantum yield, Φ_{Ln} [%]	efficiency of energy transfer, Φ_{sen} [%]	overall quantum yield, $\Phi_{overall}$ [%][b]
Eu/([Carb-C_1mim]Br-[C_4terpyim]Br)	2.86	1.05 ± 0.01	36.7	40.05	14.7
Eu/([Carb-C_1mim]NTf$_2$-[C_4terpyim]Br)	2.17	0.90 ± 0.02	41.6	25.24	10.9
Eu/([Carb-C_1mim]NTf$_2$-[C_4terpyim]NTf$_2$)	2.00	0.86 ± 0.01	42.9	20.41	8.8

[a]The excitation wavelength for measuring the decay curve and the overall quantum yield for all the samples is 350 nm. [b]Average value of three measurements under the same experimental conditions. The experimental error is 10%.

that Eu^{3+} ions in the soft materials do not coordinate with NTf$_2$.[62] The XRD pattern (Figure S4 in the Supporting Information) for all the samples show a broad band at $2\theta = 21°$, indicating the amorphous characteristic of the soft materials.

The thermal stability of the soft materials were investigated by thermogravimetry (TG) analysis. Figure 2 shows the TG profiles of the soft materials. Three decomposition stages can be clearly observed in the TG curve of Eu/([Carb-C_1mim]Br-[C_4terpyim]Br) shown in Figure 2a. The first weight loss below 200 °C is attributed to the release of solvents molecules, which is determined to be ca. 2.70%. The second weight loss, from 200 to 400 °C, correspondes to the decomposition of the carboxyl-functionalized IL,[34] the amount of which is ca. 70.58%. The wieght loss during the temperature range of 400−700 °C can be due to the decoposition of [C_4terpyim]Br (21.66%). Above 700 °C, there is a plateau, which corresponds to the formation of the stable Eu_2O_3 (5.62%). However, TG curves of Eu/([Carb-C_1mim]NTf$_2$-[C_4terpyim]Br) and Eu/([Carb-C_1mim]NTf$_2$-[C_4terpyim]NTf$_2$) show less obvious decomposition stage (see Figures 2b and 2c) compared with that of Eu/([Carb-C_1mim]Br-[C_4terpyim]Br), which reveal that a gradual decomposition occurs from ca. 100 °C and ends at ca. 600 °C, corresponding to the slowly release of solvent molecules and the decomposition of the ILs, the total weight loss during the decomposition for Eu/([Carb-C_1mim]NTf$_2$-[C_4terpyim]Br) and Eu/([Carb-C_1mim]NTf$_2$-[C_4terpyim]-NTf$_2$) is 97.7% and 94.7%, respectively. A plateau is developed above 600 °C, implying the formation of stable Eu_2O_3, the amount of which is 2.3% and 5.3%, respectively. Therefore, the amount of Eu^{3+} in Eu/([Carb-C_1mim]Br-[C_4terpyim]Br), Eu/([Carb-C_1mim]NTf$_2$-[C_4terpyim]Br), and Eu/([Carb-C_1mim]NTf$_2$-[C_4terpyim]NTf$_2$) is calculated to be 4.85, 1.73 and 4.57, respectively. An excess amount of [Carb-C_1mim]Br-[C_4terpyim]Br) was used to prepare the luminescent materials. As a consequence, the luminescent soft materials are composed of europium(III) complexes (a possible structure is shown in Scheme 1) and the carboxyl functional ILs. It is worth noting that the samples have been dried under vacuum at 60 °C for months. The TG curves shown in Figures 2b and 2c indicate that the removal of trace amounts of solvent molecules confined in the viscous fluids is not an easy task.

The soft materials show intense red emissions when irradiated with a UV lamp, as shown in Scheme 2. The luminescence data of the soft materials are shown in Figure 3, and the excitation and emission spectra of Eu^{3+}-containing carboxyl-functionalized IL sample are also shown in Figure 3 for comparison. In good agreement with the previously reported results,[33] the excitation spectrum of Eu/[Carb-C_1mim]Br consists of a series of sharp absorption lines that can be attributed to the transitions within $4f^6$configurations of Eu^{3+} ions. Its emission spectrum, obtained with a excitation

wavelength of 395 nm, contains sharpen emission lines assigned to $^5D_0 \rightarrow {}^7F_J$ ($J = 0−4$) transitions. Upon the addition of [C_4terpyim]Br, notable changes can be observed for the excitation spectra that show a broad band in the range of 200−400 nm, which result from the absorption of terpyridine moieties. This indicates that an energy transfer occurs from [C_4terpyim]Br to the central Eu^{3+}. Similar emission spectra are obtained upon excitation with a wavelength of 350 nm, five sharp emission lines at 579, 593, 617, 650, and 696 nm arising from the transitions between $^5D_0 \rightarrow {}^7F_J$ crystal-field components ($J = 0, 1, 2, 3, 4$) are clearly seen, which also means the coordination of Eu^{3+} to terpyridine moieties grafted in [C_4terpyim]Br.[52] The lifetime of Eu^{3+} for the soft material Eu/([Carb-C_1mim]Br-[C_4terpyim]Br) is determined to be 1.05 ± 0.01 ms from the corresponding decay curve that can be well-fitted with monoexponential function. The absolute quantum yield of the soft materials is determined using the integrated sphere coated with $BaSO_4$[35] and is listed in Table 1, which shows the determined absolute quantum yield to be 14.7%. The viscous transparent soft materials Eu/([Carb-C_1mim]NTf$_2$-[C_4terpyim]Br) and Eu/(Carb-C_1mim]NTf$_2$-[C_4tarpyim]-NTf$_2$) display similar excitation and emission spectra to that of Eu/([Carb-C_1mim]Br-[C_4terpyim]Br). The lifetime of Eu^{3+} is determined to be 0.90 ± 0.02 and 0.86 ms, respectively, from the corresponding decay curve (see Figure 4). The absolute quantum yield is 10.9% and 8.8%, respectively, as shown in Table 1.
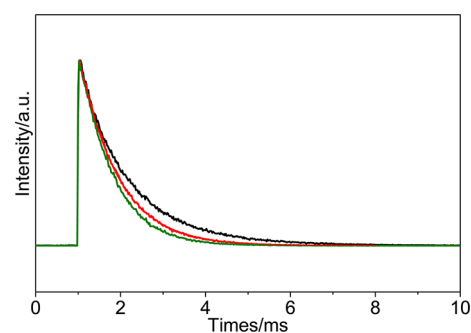

Figure 4. Decay curves of the soft materials: Eu/([Carb-C_1mim]Br-[C_4terpyim]Br) (black trace), Eu/([Carb-C_1mim]NTf$_2$-[C_4terpyim]-Br) (red trace), and Eu/([Carb-C_1mim]NTf$_2$-[C_4terpyim]NTf$_2$) (green trace). The decay curves were measured at 350 nm.

We also calculated the efficiency of energy transfer from [C_4terpyim]$^+$ to Eu^{3+} ions in the soft materials based on the emission spectrum, the lifetime of the $^5D_0$ state, and the quantum yield of the samples, according to the reported method.[63,64] The overall quantum yield of the sample can be defined as follows when one excites the ligand:

$$\Phi_{overall} = \Phi_{sen}\Phi_{Ln} \tag{1}$$

where Φ_{sen} is the efficiency of energy transfer and Φ_{Ln} is the intrinsic quantum yield of the Ln^{3+} ions, which can be obtained by the following equation:

$$\Phi_{Ln} = \left(\frac{A_{RAD}}{A_{RAD} + A_{NR}}\right) = \frac{\tau_{obs}}{\tau_{RAD}} \tag{2}$$

The radiative lifetime (τ_{RAD}) of an Eu^{3+} compound can be calculated using eq 3,[63,64] assuming that the energy of the $^5D_0 \rightarrow {}^7F_1$ transition (MD) and its oscillator strength are constant.

$$A_{RAD} = \frac{1}{\tau_{RAD}} = A_{MD,0}n^3\left(\frac{I_{TOT}}{I_{MD}}\right) \tag{3}$$

Here, $A_{MD,0}$ is the spontaneous emission probability of the $^5D_0 \rightarrow {}^7F_1$ transition in vacuo and its value is ca. 14.65 s^{-1}. I_{TOT}/I_{MD} represents the ratio of the total area of the corrected Eu^{3+} emission spectrum to that of the $^5D_0 \rightarrow {}^7F_1$ band and n is the refractive index of the medium, which is usually considered to be equal to 1.5.[64] The obtained values of energy transfer efficiency are listed in Table 1, which is 40.05%, 25.24%, and 20.41%, respectively, for Eu/([Carb-C_1mim]Br-[C_1terpyim]-Br), Eu/([Carb-C_1mim]NTf$_2$-[C_4terpyim]Br), and Eu/([Carb-C_1mim]NTf$_2$-[C_4terpyim]NTf$_2$).

It is revealed that the luminescence performances (e.g., lifetime, absolute quantum yield, and energy transfer efficiency) of the creamlike material are better than that of the viscous fluids materials. A possible explanation is that it is easier to excite vibrations in the liquid state than in the pastelike state; similar results have been reported previously by Mudring, who observed that the lifetime of Eu^{3+} is shorter in liquid than in solid state.[30]

4. CONCLUSION

The first luminescent soft materials based on the coordination of Eu^{3+} with task-specific ionic liquids (ILs) in which the terpyridine moieties with the ability to coordinate and sensitize Eu^{3+} ions are linked to imidazolium rings have been achieved in this study. The physical state of obtained soft luminescent materials is largely dependent on the anions of the carboxyl-functionalized ILs. Pastelike luminescent soft materials are obtained when the carboxyl-functionalized IL with Br$^-$ as the anion, with substitution of Br$^-$ in the carboxyl-functionalized IL with NTf$_2^-$, leads to viscous, transparent, and luminescent fluid, regardless of the anions used for Terpy-TSILs. The content of the ionic liquid in the soft materials can be up to 97% by weight. Depending on the anions used in the ILs, the lifetime of Eu^{3+} in the soft materials is in the range of 0.8−1.1 ms, the absolut quantum yield is determined to be ranging from 8.8% to 14.7%, and the energy transfer effiency from Terpy-TSIL to Eu^{3+} is calculated to be in the range of 36.7%−42.9%. The interesting features of these soft materials, such as a high content of ILs, easy coating on surfaces, and excellent luminescence properties (e.g., long lifetime, high color purity) might render them extremely valuable for varous optical applications such flexible displays. Moreover, the europium(III) content in soft materials is relativly low(<5% by weight) in this work, the results reported by us previously show that the luminescencent behaviors of soft materials are dependent on the concentration of lanthanide to some extent.[34] Therefore, it is necessary to study the effect of Eu^{3+} concentrations on the

luminescent behaviors and the physical state of these novel soft materials, which are being carried out in our laboratory.

■ ASSOCIATED CONTENT

ⓢ Supporting Information

UV/vis absorption spectrum of [C_1terpyim] Br in EtOH, decay curve of complex formed between [C_1terpyim]Br and Eu-(NO$_3$)$_3$·6H$_2$O, FT-IR spectra, and XRD pattern. This information is available free of charge via the Internet at http://pubs.acs.org.

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Notes
The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

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