Supporting Information for:

Bright Solvent-Free Luminescent Liquid with Magnetism

Composed of a Thiocyanate Complex of Ce(III)

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Synthesis of 1-hexyl-3-methylimidazolium thiocyanate ([C₆mim]SCN). [C₆mim]Cl (Tokyo Chemical Industry) was degassed using an oil-diffusion vacuum pump. To a round-bottom flask containing degassed [C₆mim]Cl (4.5 g) in a glove box filled with N₂ gas, two equivalents of KSCN (Junsei Chemical, 4.4 g) were added and dissolved in 47 mL of acetone. The solution was stirred for 48 h, and the precipitate was removed by filtration with a filter paper. The acetone in the filtrate was removed in a rotary evaporator. 40 mL of dichloromethane was then added to the resultant material and placed in a refrigerator overnight. The precipitate in the solution was removed by filtration with a filter paper, and dichloromethane was then removed using a rotary evaporator. The resultant material was dried using a rotary pump with a liquid N₂ trap for one night. 30 mL of dehydrated dichloromethane (Wako Pure Chemical Industry) was added to the dried material, which was then cooled at -25 °C overnight. The solution was filtered using a filter paper, followed by a polytetrafluoroethylene (PTFE) membrane filter (0.22 µm pore size). The dichloromethane was removed from the filtrate in a rotary evaporator. The resultant material was dried with a rotary pump, dissolved in 100 mL of ethanol, and mixed with activated charcoal (Norit® SX Plus) under stirring for 2-3 days. The activated charcoal was then removed by filtration, and the ethanol was removed from the filtrate using a rotary evaporator. The resultant material was dried with an oildiffusion vacuum pump. The final product was obtained as a faint-yellow transparent liquid. The purity of the [C₆mim]SCN product was examined using NMR (JEOL, JNM-ECA500) and electrospray ionization-mass spectrometry (ESI-MS) measurements.

Figure S1 shows the ¹H-NMR spectrum for [C₆mim]SCN. ¹H-NMR δ H (500 MHz; CD₂Cl₂; Me₄Si) 0.915 (3H, t, CH₂CH₃), 1.356 (6H, m, CH₂CH₂CH₂CH₂CH₃), 1.946 (2H, m,

NCH₂CH₂CH₂), 4.081 (3H, s, NCH₃), 4.300 (2H, t, NCH₂CH₂), 5.356 (solvent), 7.415 (1H, m, NCHCHN), 7.454 (1H, m, NCHCHN), and 9.437 (1H, s, NCHN). The observed δ were in good agreement with the reported values.¹

Figure S2 shows the ¹³C-NMR spectrum for [C₆mim]SCN. ¹³C-NMR ∂ C (500 MHz; CD₂Cl₂): 13.777, 22.471, 25.943, 30.183, 31.142, 36.726, 50.476, 122.261, 123.682, 131.165, and 137.136. The solvent signals appeared at δ = 53.1–54.0. The observed δ were in good agreement with the reported values.¹

The ESI-MS spectrum was recorded by dissolving [C₆mim]SCN in methanol (Applied Biosystems, API2000LC/MS/MS). Positive: m/z 83.3 (fragment daughter ion of [C₆mim]⁺), and 167.3 ([C₆mim]⁺). Negative: m/z 58.2 (SCN⁻).



Fig. S1. ¹H-NMR spectrum of [C₆mim]SCN.



Fig. S2. ¹³C-NMR spectrum of [C₆mim]SCN.

Measurement of emission quantum yield (QY). The emission QY was measured relative to a fluorescence standard. Quinine sulphate dissolved in 0.1 mol L⁻¹ H₂SO₄ was used as a standard solution. The standard solution was contained in a stoppered quartz cell with a 10 mm optical path length. The emission QY of $[C_6mim]_4[Ce(SCN)_7(H_2O)_1]$ (Φ_{Ce}) was calculated using Eq. (1):

$$\Phi_{\rm Ce} = \Phi_{\rm st} \frac{F_{\rm Ce}}{F_{\rm st}} \frac{A_{\rm st}}{A_{\rm Ce}} \frac{n_{\rm Ce}^2}{n_{\rm st}^2} \tag{1}$$

where Φ_{st} is the literature value of the fluorescence QY (0.577),² F_{st} is the integral of the fluorescence spectrum excited at 346 nm, and A_{st} is the absorbance of the standard solution (0.05) at 346 nm. The refractive index of the standard solution n_{st} , was approximated to be that of water (1.34). The value of the refractive index (n_{Ce}) for [C₆mim]₄[Ce(SCN)₇(H₂O)₁] was approximated to be unity. A_{Ce} is the absorbance taken from the observed spectrum of the film, and F_{Ce} is the integral of the emission spectrum excited at 355 nm. A similar procedure was used to calculate the emission QY in acetonitrile.



(Left) **S3**. Fig. Geometry of $[La(SCN)_7(H_2O)]^{4-}$ reproduced from the X-ray crystal structure data reported in Ref. 3. (Right) Initial geometry of $[Ce(SCN)_7(H_2O)_1]^{4-}$ for calculation of the optimized geometry. (Top) Schematic presentation of the almost SAP coordination of the lanthanoid ions.



Fig. S4. (Left) Geometry of $[Ce(SCN)_7(H_2O)_1]^{4-}$ optimized using DFT calculations. The same structure is shown in Fig. 2. (Right) Schematic presentation of a distorted trigonal dodecahedral coordination of the cerium ion.

Atom	Initial geometry			Optimized geometry		
C	-3.07108	2.10129	0.519698	-3.31813	1.672778	1.068159
С	1.2309	1.94697	-2.95448	1.640722	1.986276	-3.02029
С	-2.29424	0.037986	-2.94402	-2.58222	-0.24771	-3.03388
С	1.27665	-2.98196	-1.88042	1.43838	-2.84215	-2.29698
С	-1.77148	-3.07347	1.22745	-1.70397	-2.97314	1.33134
С	3.52517	-0.50566	1.13123	3.293045	-0.66216	1.42709
С	0.544361	3.51103	1.12082	0.960482	3.523971	1.247986
Ce	0	0	0	-0.00612	-0.01904	-0.30185
Ν	-2.21669	1.30995	0.487342	-2.32596	1.169223	0.671889
Ν	1.06675	1.25274	-2.05017	1.121477	1.366606	-2.16177
Ν	-1.61336	-0.27748	-2.0418	-1.78013	-0.17111	-2.17315
Ν	0.959102	-2.02994	-1.28273	0.980998	-1.94741	-1.68062
Ν	-1.3392	-2.0544	0.859964	-1.1994	-2.06957	0.766866
Ν	2.47019	-0.27967	0.762261	2.292863	-0.4488	0.840711
Ν	0.696935	2.39638	0.744738	0.67286	2.468092	0.803883
0	0	0	2.55409	-0.2478	0.338892	2.385051
S	-4.28015	3.21443	0.564953	-4.70492	2.380698	1.64204
S	1.50003	2.93629	-4.23624	2.369969	2.858937	-4.22629
S	-3.28031	0.454139	-4.2032	-3.71146	-0.35354	-4.24398
S	1.73044	-4.30287	-2.73167	2.082719	-4.10099	-3.16345
S	-2.3679	-4.52618	1.70339	-2.41542	-4.24237	2.129748
S	5.05001	-0.79126	1.68292	4.699405	-0.95945	2.256567
S	0.359266	5.06172	1.58247	1.35897	5.002763	1.888696
Н	-0.70142	-0.25506	2.91476	-1.1807	0.588069	2.222041
Н	0.488574	0.361723	3.11415	0.22688	1.187839	2.265681

Table S1. Cartesian coordinates of the initial and optimized geometries of $[Ce(SCN)_7(H_2O)_1]^{4-}$.



Fig. S5. Magnetization per unit mass (M) as a function of magnetic field (H) at 298 K for $[C_6 mim]$ SCN.

Absorption and emission spectra in acetonitrile. $[C_6mim]_4[Ce(SCN)_7(H_2O)_1]$ was dissolved in acetonitrile (Wako Pure Chemical Industry, Spectroscopy Analytical Grade). A 10 mm quartz cell was used to measure the absorption and emission spectra (Fig. S6). The concentration of $[C_6mim]_4[Ce(SCN)_7(H_2O)_1]$ was 6×10^{-5} mol L⁻¹. The emission QY was calculated with the procedure described previously.



Fig. S6. Absorption spectrum, emission spectrum with an excitation wavelength of 345 nm, and excitation spectrum monitoring 447 nm for $[C_6mim]_4$ [Ce(SCN)₇(H₂O)₁] in acetonitrile.

Fig. S7. Absorption and emission spectra measured with excitation at 348 nm, and emission excitation spectrum monitored at 452 nm for the $[C_6 mim]_{x-3}[Ce(SCN)_x (H_2O)_y]$ thin film.



Fig. S8. (Dashed line) Semi-log plot of the emission intensity decay recorded in the solvent-free liquid of $[C_6 \text{mim}]_{x-3}[\text{Ce}(\text{SCN})_x$ $(\text{H}_2\text{O})_y]$. The instrument response function (IRF) and the fit to a single exponential decay are also shown. Excitation wavelength was 355 nm.

Fig. S9. (a) Magnetization per unit mass (*M*) as a function of magnetic field (*H*) at 298 K. (b) Inverse of the molar susceptibility χ_{mol} at H = 5000 Oe as a function of temperature for $[C_6 mim]_{x-3} [Ce(SCN)_x(H_2O)_y].$



Fig. S10. Absorption spectrum, emission spectrum with an excitation wavelength of 339 nm, and excitation spectrum monitoring 447 nm for $[C_6mim]_{x-3}[Ce(SCN)_x(H_2O)_y]$ in acetonitrile.

Fig. S11. DSC curve of $[C_6 mim]_{x-3}$ $_3[Ce(SCN)_x(H_2O)_y]$. Blue line, first cooling cycle; red line, subsequent heating cycle.

Morphological change in response to methanol vapor. A drop of dichloromethane, in which the $[C_6 mim]_{x-3}[Ce(SCN)_x (H_2O)_y]$ ionic liquid was dissolved, was placed onto the center of a ca. 15 mm diameter quartz dish. The solvent was evaporated in the air and a film of the ionic liquid was obtained. A small amount of methanol was poured into a glass petri dish with a diameter of 55 mm and a depth of 13 mm. The methanol was allowed to vaporize for a while, so that the glass petri dish contained the methanol vapour mixed with air inside. The surface coverage of the ionic liquid on the quartz dish was visualized by watching the emission of the ionic liquid excited at 365 nm. The quartz dish with the ionic liquid was transferred to the inside of the glass petri dish. When the quartz dish was placed in the glass petri dish containing the methanol vapor, the ionic liquid absorbed methanol molecules, spontaneously contracted, and formed a droplet. When the quartz dish was then removed from the glass petri dish and placed in the air, the droplet began to spread out as the methanol molecules evaporated. The change in the morphology was recorded by repeating this procedure and is shown in Movie S1.

Movie S1. Change in the morphology of the $[C_6 mim]_{x-3}[Ce(SCN)_x (H_2O)_y]$ ionic liquid in the air and in methanol vapor. The ionic liquid was excited at 365 nm.

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