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Designing a new type of magnetic ionic liquid: a strategy to improve the magnetic susceptibility†

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A new type of magnetic ionic liquid (MIL) with the general formula $[\text{Ln}(\text{TODGA})_3][\text{Ln}(\text{hfa})_4]_3$ ($\text{Ln} = \text{Tb}, \text{Dy}, \text{Ho}, \text{Er}, \text{Tm}, \text{Yb}$; $\text{TODGA} = N,N,N',N'$ -tetra(*n*-octyl)diglycolamide; $\text{hfa} = 1,1,1,5,5,5$ -hexafluoroacetylacetonate) named as MILs 1–6, containing the same lanthanide ions in the cation and anion has been synthesized and characterized. The values of $\chi_M T$ ($T = 300 \text{ K}$) for MILs 1–6 are 46.7, 54.2, 52.2, 43.9, 26.7, and $8.7 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$, respectively, four times higher than those of MILs containing single corresponding lanthanide ions. The magnetic properties of these MILs indicate that it is an effective strategy to improve the magnetic susceptibility by incorporating lanthanide ions in both the cation and anion of ionic liquids.

Ionic liquids (ILs) are a class of molten salts exhibiting melting points at or below 373 K. Following their discovery, ILs have attracted great attention in many fields such as catalysis, synthesis, energy production and solvent extraction due to their advantageous physicochemical properties including negligible vapor pressure at ambient temperature, high thermal stability, wide electrochemical window, strong ability to dissolve compounds and tunable solvation properties.^{1–3}

Recently, magnetic ionic liquids (MILs) produced by incorporating a paramagnetic component in either the cation or anion of the IL structure has been a center of attention of materials research.^{4–6} 1-Butyl-3-methylimidazolium tetrachloroferrate(III) ($[\text{C}_4\text{mim}][\text{FeCl}_4]$) was the first example of MILs.⁷ Since then, a variety of transition and rare earth ions have been used as paramagnetic centers in the preparation of MILs.⁵ Lan *et al.*⁸ synthesized a MIL containing Ni(II) that exhibited thermochromic properties and a concomitant change in magnetic properties. An electrochromic MIL based on a cobalt(III) complex was also investigated.⁹ Li *et al.* studied magnetic chiral ILs derived from amino acids.¹⁰ Nockemann *et al.*¹¹ incorporated the rare earth ions(III) for the first time into

ILs forming low-melting MILs with the general formula $[\text{C}_4\text{mim}]_{x-3}[\text{RE}(\text{NCS})_x(\text{H}_2\text{O})_y]$ ($x = 6-8, y = 0-2, \text{RE} = \text{Y}, \text{La}, \text{Pr}, \text{Nd}, \text{Sm}, \text{Eu}, \text{Gd}, \text{Tb}, \text{Ho}, \text{Er}, \text{Yb}$). Recently they have reported dimeric lanthanide(III)-containing ILs and developed an innovative approach to study the speciation of metals in the liquid state by using the magnetic interactions within the dimeric structure.¹² The anomalous magnetic behavior of lanthanide halides and slow relaxation of magnetization in dysprosium-based ionic liquids have been studied.^{13,14} The introduction of rare earth ions provides not only a new approach for solving the problem of low saturation magnetization of MILs containing transition metal ions but also a good scheme for the design of fluorescogenic magnetofluids. Therefore, various MILs containing rare earth ions such as $[\text{C}_3\text{mim}][\text{Eu}(\text{NTf}_2)_4]$, $[\text{C}_6\text{mim}]_{5-x}[\text{Dy}(\text{SCN})_{8-x}(\text{H}_2\text{O})_x]$ ($x = 0-2$), $[\text{P}_{66614}]_3[\text{RECl}_6]$ ($\text{RE} = \text{La}, \text{Ce}, \text{Pr}, \text{Nd}, \text{Sm}, \text{Eu}, \text{Gd}, \text{Tb}, \text{Dy}, \text{Ho}, \text{Er}, \text{Tm}, \text{Yb}, \text{Lu}, \text{Y}, \text{Sc}$), $[\text{P}_{66614}][\text{Ln}(\text{III})(\text{hfa})_4]$ ($\text{Ln} = \text{Gd}, \text{Dy}, \text{Nd}$), $[\text{R}_{C_n}\text{mim}]_2[\text{Ln}(\text{NO}_3)_5]$ ($\text{R} = \text{H}$ or methyl; $\text{C}_n\text{mim} = 1$ -alkyl-3-methylimidazolium; $\text{Ln} = \text{Gd}, \text{Tb}, \text{Dy}$), and $[\text{C}_n\text{mim}]_2[\text{Eu}(\text{NO}_3)_5]$ ($n = 1, 2, 4, 6, 8$) have been reported.^{15–20} To improve magnetism, MILs containing five lanthanides(III) in the cation with the general formula $[\text{Ln}_5(\text{C}_2\text{H}_5-\text{C}_3\text{H}_3\text{N}_2-\text{CH}_2\text{COO})_{16}(\text{H}_2\text{O})_8](\text{NTf}_2)_{15}$ ($\text{Ln} = \text{Er}, \text{Ho}, \text{Tm}$; $\text{C}_3\text{H}_3\text{N}_2 =$ imidazolium moiety) were synthesized.²¹ Besides, tricationic MILs have been synthesized to improve magnetism.²² Another kind of MIL is a metal-free magnetic ionic liquid by the inclusion of a sulfate group to a neutral 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) radical moiety.^{23,24}

Herein, we report on the preparation of MILs by incorporating lanthanide ions in both the cation and anion of the ILs. A series of MILs with the general formula $[\text{Ln}(\text{TODGA})_3][\text{Ln}(\text{hfa})_4]_3$ ($\text{Ln} = \text{Tb}, \text{Dy}, \text{Ho}, \text{Er}, \text{Tm}, \text{Yb}$), containing the same lanthanide ions in the cation and anion, were studied (Fig. 1). For convenience, these MILs containing Tb, Dy, Ho, Er, Tm, and Yb are named MILs 1, 2, 3, 4, 5 and 6, respectively.

The syntheses of MILs 1–6 were achieved by three steps (see the ESI†). Firstly, TODGA coordinated with Ln^{3+} to form $\text{Ln}(\text{TODGA})_3\text{Cl}_3$. And then, hfa coordinated with Ln^{3+} to form $\text{NH}_4[\text{Ln}(\text{hfa})_4]$.¹⁸ Finally, $[\text{Ln}(\text{TODGA})_3][\text{Ln}(\text{hfa})_4]_3$ was obtained

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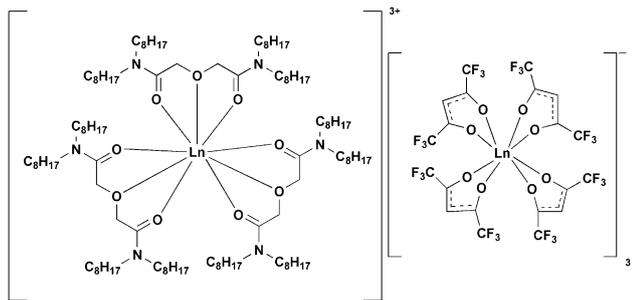


Fig. 1 The structure of $[\text{Ln}(\text{TODGA})_3][\text{Ln}(\text{hfa})_4]_3$ ($\text{Ln} = \text{Tb}, \text{Dy}, \text{Ho}, \text{Er}, \text{Tm}, \text{Yb}$).

by reaction of $\text{Ln}(\text{TODGA})_3\text{Cl}_3$ with $\text{NH}_4[\text{Ln}(\text{hfa})_4]$. $\text{Ln}(\text{TODGA})_3\text{Cl}_3$ and $\text{NH}_4[\text{Ln}(\text{hfa})_4]$ were characterized by mass spectrometry along with electrospray ionization (ESI-MS). The peaks in the positive mode appear at m/z 968.4, 970.3, 971.3, 972.4, 973.4 and 975.3 that are attributed to $[\text{Ln}(\text{TODGA})_3\text{Cl}]^{2+}$ ($\text{Ln} = \text{Tb}, \text{Dy}, \text{Ho}, \text{Er}, \text{Tm}, \text{Yb}$), respectively (Fig. S1, ESI[†]). Peaks at m/z 986.9, 991.9, 992.9, 995.9, 996.9 and 1001.9 in the negative mode represent $[\text{Ln}(\text{hfa})_4]^-$ ($\text{Ln} = \text{Tb}, \text{Dy}, \text{Ho}, \text{Er}, \text{Tm}, \text{Yb}$), respectively (Fig. S2, ESI[†]). $[\text{Ln}(\text{TODGA})_3][\text{Ln}(\text{hfa})_4]_3$ was characterized by ESI-MS, elemental analysis (EA) and infrared spectroscopy (IR). Peaks displayed at m/z 1153.5, 1158.5, 1159.6, 1162.5, 1163.5 and 1168.5 in the positive mode are attributable to $[\text{Ln}(\text{TODGA})_2][\text{Ln}(\text{hfa})_4]^{2+}$ ($\text{Ln} = \text{Tb}, \text{Dy}, \text{Ho}, \text{Er}, \text{Tm}, \text{Yb}$), respectively (Fig. S3, ESI[†]). As for EA, the experimental values of the percentage for carbon, hydrogen and nitrogen are close to those of theoretical values (Table S1, ESI[†]). In addition, no absorption peaks of water and NH_4^+ appear in the IR spectra of these MILs, which further confirms their purity (Fig. S4, ESI[†]). The above characterization shows that MILs 1–6 were successfully synthesized.

In order to assess the thermal stabilities of the MILs, the decomposition temperatures were determined using thermogravimetric analysis (TGA). These MILs possess good thermal stability up to nearly 573 K (Fig. 2). The TGA curves of these MILs show similar one-step weight loss profiles due to a similar chemical structure. In the temperature range from 523 to 623 K, the MILs decompose. The glass transition temperatures (T_g) of these compounds were determined by differential scanning

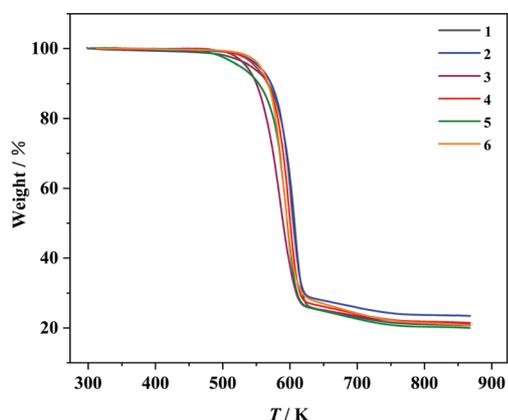


Fig. 2 TGA curves of MILs 1–6.

calorimetry (DSC). The T_g values of MILs 1–6 are 242.1, 243.0, 242.3, 240.6, 237.9, and 239.1 K, respectively (Fig. S5, ESI[†]). Therefore, all of the MILs are in liquid states at room temperature.

Nearly all substances are diamagnetic and only the substances with unpaired electrons are paramagnetic such as some transition and rare earth ions. In the absence of an external magnetic field, the magnetic moment is randomly orientated due to thermal motion resulting in a loss of magnetization. When there is an external magnetic field, the magnetic moment has a tendency to be oriented along the direction of the magnetic field because of the spin alignment of unpaired electrons in the 4f orbital for rare earth ions. The configurations of $4f^8$, $4f^9$, $4f^{10}$, $4f^{11}$, $4f^{12}$ and $4f^{13}$ of Tb^{3+} , Dy^{3+} , Ho^{3+} , Er^{3+} , Tm^{3+} and Yb^{3+} contribute to the extraordinary electron-spin magnetic moments. The magnetic property for all samples displays simple paramagnetic behavior over the studied temperature range and constant $\chi_M T$ values are achieved in a high temperature region (Fig. 3). In addition, it is worth noting that as the temperature decreases, especially at lower temperatures, $\chi_M T$ values decrease dramatically suggesting the occurrence of antiferromagnetic coupling.¹⁹ Whereas at room temperature, the interactions between lanthanide ions are negligible because of thermal motion. The $\chi_M T$ values at room temperature for MILs 1–5 are 46.7, 54.2, 52.2, 43.9 and 26.7 $\text{cm}^3 \text{mol}^{-1} \text{K}$, respectively, four times higher than those of MILs containing single corresponding lanthanide ions because of high concentrations of magnetic centers in MILs, but lower than MILs containing five lanthanide ions in the cation (Table 1). For MIL 6, the $\chi_M T$ value at room temperature is 8.7 $\text{cm}^3 \text{mol}^{-1} \text{K}$, which is nearly four times higher than the theoretical value of Yb^{3+} (2.57 $\text{cm}^3 \text{mol}^{-1} \text{K}$).²⁵

MILs have been widely used in the field of extraction and separation due to their exhibition of a certain response toward external magnetic fields.^{4,5,26–32} MILs were used as the extraction phase and a magnet was applied to remove the complex of the analyte and the MIL from the solution at extraction equilibrium. The improvement of magnetic susceptibility may help achieve fast magnetic separation.

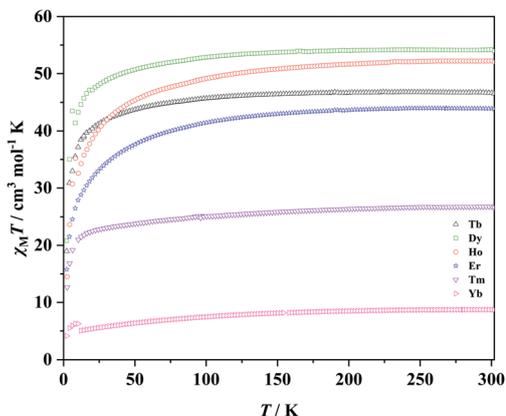


Fig. 3 Susceptibility multiplied by the temperature as a function of temperature.

Table 1 $\chi_M T$ values of some selected MILs containing lanthanide ions at 300 K

MIL	$\chi_M T / \text{cm}^3 \text{ mol}^{-1} \text{ K}$	θ / K	Ref.
[Tb(TODGA) ₃][Tb(hfa) ₄] ₃	46.7	-3.6	This work
[Dy(TODGA) ₃][Dy(hfa) ₄] ₃	54.2	-3.6	This work
[Ho(TODGA) ₃][Ho(hfa) ₄] ₃	52.2	-8.7	This work
[Er(TODGA) ₃][Er(hfa) ₄] ₃	43.9	-9.1	This work
[Tm(TODGA) ₃][Tm(hfa) ₄] ₃	26.7	-7.3	This work
[Yb(TODGA) ₃][Yb(hfa) ₄] ₃	8.7	-20.3	This work
[CH ₃ C ₁ mim][Gd(NO ₃) ₅]	7.54	0.32	19
[CH ₃ C ₁ mim][Tb(NO ₃) ₅]	11.76	-1.13	19
[CH ₃ C ₁ mim][Dy(NO ₃) ₅]	13.65	-7.97	19
[P ₆₆₆₁₄] ₃ [GdCl ₆]	7.3 ± 0.4	-1.5 ± 42.8	17
[P ₆₆₆₁₄] ₃ [TbCl ₆]	10.8 ± 0.5	2.7 ± 38.6	17
[P ₆₆₆₁₄] ₃ [DyCl ₆]	12.9 ± 0.6	0 ± 43.8	17
[P ₆₆₆₁₄] ₃ [HoCl ₆]	12.4 ± 0.6	-3.8 ± 45.0	17
[P ₆₆₆₁₄] ₃ [ErCl ₆]	11.0 ± 0.6	-6.2 ± 44.7	17
[P ₆₆₆₁₄] ₃ [Gd(hfa) ₄]	7.4	—	18
[P ₆₆₆₁₄] ₃ [Dy(hfa) ₄]	11.8	—	18
{Er ₅ } ^a	56.2	-9.0	21
{Ho ₅ }	67.9	-6.0	21
{Tm ₅ }	32.9	-13.0	21

^a [Ln₅(C₂H₅-C₃H₃N₂-CH₂COO)₁₆(H₂O)₈](Tf₂N)₁₅ (Ln = Er, Ho, Tm).

The inverse relationship between the magnetic susceptibility and temperature of paramagnetic compounds is defined as the Curie–Weiss law (eqn (1)).

$$\chi = \frac{C}{T - \theta} \quad (1)$$

where C is the Curie constant, T is the temperature in kelvin and θ is the Weiss constant.

The θ values for MILs 1–6 extrapolated from the temperature region of 2–300 K are -3.6, -3.6, -8.7, -9.1, -7.3 and -20.3 K, respectively, indicating the existence of antiferromagnetic coupling at low temperatures (Fig. S6, ESI[†]). The θ values of MILs 1–4 are smaller than those of [P₆₆₆₁₄]₃[LnCl₆] (Ln = Tb, Dy, Ho, Er), respectively, suggesting that the antiferromagnetic coupling is stronger in MILs 1–4 (see Table 1).

The field dependent magnetization of MIL 2 at 2, 5 and 300 K shows different trends (Fig. 4). At 2 K, magnetic hysteresis is observed. The value of the magnetization in the descending path from 60 000 Oe to 0 is greater than the corresponding value in the ascending path from 0 to 60 000 Oe. And no magnetic hysteresis is observed with magnetic field scanning at 5 and 300 K. At 5 K, the magnetization increases logarithmically and the slope of the magnetization curve decreases with the gradually increasing external magnetic field. At a low temperature, electronic spins of Ln³⁺ are gradually redirected from chaotic states to directional states with the increasing magnetic field. However, due to weak thermal motion and indirect interactions between Ln³⁺, the spin orientation driven by the magnetic field becomes more and more difficult.¹⁹ At 2 and 5 K, the appearance of magnetic relaxation suggests that it should be a single molecule magnet. At 300 K, it shows typical paramagnetic behaviour: the magnetization linearly increases with increasing magnetic field for no interactions between Ln³⁺ caused by thermal motion.

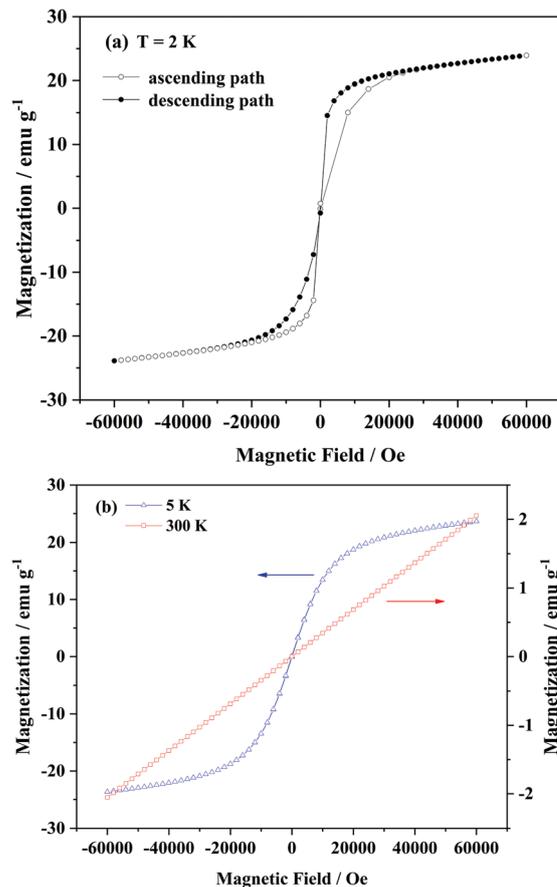


Fig. 4 Field dependence of magnetization ($M-H$) at 2, 5 and 300 K for MIL 2.

Lanthanides have intrinsic luminescence properties due to f-f transitions. The luminescence properties of MIL 1 were investigated. MIL 1 shows visible-light luminescence (Fig. 5). Upon excitation at 352 nm, the sample shows typical narrow Tb³⁺ emission peaks. The sharp bands at 488, 543, 582, and 617 nm were assigned to the ⁵D₄ → ⁷F₆, ⁵D₄ → ⁷F₅, ⁵D₄ → ⁷F₄, and ⁵D₄ → ⁷F₄ electronic transitions, respectively. Furthermore, the luminescence properties

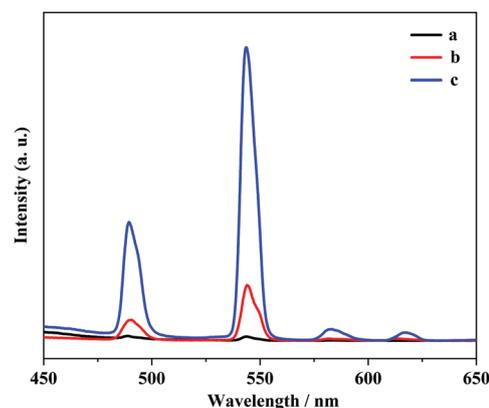


Fig. 5 Emission spectra of (a) Tb(TODGA)₃Cl₃, (b) NH₄[Tb(hfa)₄], and (c) MIL 1 at 1 mM in acetonitrile.

of Tb(TODGA)₃Cl₃, NH₄[Tb(hfa)₄] and MIL **1** were compared (Fig. 5). The lowest luminescence emission is from Tb(TODGA)₃Cl₃, nearly no emission, while the highest is from MIL **1** for higher concentrations of luminescence emission centers. The above results show that the luminescence emission of MIL **1** is mainly derived from the anion moiety, indicating that hfa is more effective than TODGA in sensitizing Tb³⁺.

Conclusions

We have synthesized a new type of magnetic ionic liquid. The χ_{MT} values of MILs **1–6** at room temperature are nearly four times higher than those of MILs containing single corresponding lanthanide ions because of high concentrations of magnetic centers in MILs. The magnetic properties of these MILs indicate that it is an effective strategy to improve the magnetic susceptibility by incorporating rare earth ions in both the cation and anion of ILs. The appearance of magnetic relaxation at low temperature suggests that it should be a single molecule magnet.

Experimental

The experimental section is shown in the ESI.†

Conflicts of interest

There are no conflicts to declare.

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