Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Electronic Supplementary Information

Designing A New Type of Magnetic Ionic Liquids: A Strategy to Improve Magnetic Susceptibility

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Experimental

Materials

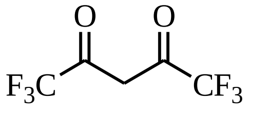
All chemicals were obtained commercially from China. N,N,N’,N’,-tetra(n-octyl)diglycolamide (TODGA, 98%) and 1,1,1,5,5,5-hexafluoroacetylacetone (99%) were purchased from Shanghai YuDuo-biological science & Technology and J & K Scientific, respectively. Terbium (III) chloride hexahydrate (99.99%), dysprosium (III) chloride hexahydrate (99.99%) and thulium (III) chloride hexahydrate (99.99%) were obtained from Shanghai Xianding Biological Science & Technology. Holmium (III) chloride hexahydrate (99.99%) and erbium (III) chloride hexahydrate (99.99%) were received from Shanghai Sun Chemical Technology. Ytterbium (III) chloride hexahydrate (99.99%) was purchased from Shanghai D&B Biological Science and Technology. Ammonium hydroxide, 1,2-dichloroethane, ethanol, acetonitrile and ethyl ether were of analytical grade. All solvents and reagents were used as received without any additional drying or purification. Ultra-pure water (18.2 MΩ cm) was used throughout the experiments.

Instruments

ESI-MS was done on a Fourier transform ion cyclotron resonance mass spectrometer, Solarix XR (Bruker, Germany). EA were measured on an elemental analyzer, vario EL (Elementar Analysensysteme GmbH, Germany). IR spectra of MILs **1-6** were recorded on a nicolet is50 spectrometer (ThermoFisher). TGA were accomplished on a Q600 TGA-DSC-DTA (Q600 SDT, TA) under N_2 atmosphere with the temperature ranging from room temperature to 873 K at a heating rate of 10 K / min. DSC were carried out on a Q100 Differential Scanning Calorimeter (Q100DSC, TA). A cooling and heating ramp of 10 K / min was used within the temperature ranging from 203 to 303 K, and three scans were carried out for each sample. Luminescent Measurements were recorded on a lifetime and steady state spectrometer (FLS920, Edinburgh Instruments Ltd.). Magnetic Measurements were preformed on a Quantum Design MPMS3 magnetometer. Temperature dependence of magnetization (M-T) was measured under an applied field of 10000 Oe in the temperature range of 2-300 K. Diamagnetic corrections were calculated from Pascal’s constants (G. A. Bain and J. F. Berry, *J. Chem. Educ.*, 2008, **85**, 532-536) and applied to all data. Field dependence of magnetization (M-H) for $[Dy(TODGA)_3][Dy(hfa)_4]_3$ was measured at 2, 5 and 300 K in the magnetic field range -6 T to 6 T.

Preparation of $[Ln(TODGA)_3][Ln(hfa)_4]_3$

$$\text{TODGA} + \text{LnCl}_3\ 6\text{H}_2\text{O} \longrightarrow \text{Ln(TODGA)}_3\text{Cl}_3 \tag{1}$$



$$+\ \text{LnCl}_3\ 6\text{H}_2\text{O} \longrightarrow \text{NH}_4[\text{Ln(hfa)}_4] \tag{2}$$

$$\text{Ln(TODGA)}_3\text{Cl}_3 + \text{NH}_4[\text{Ln(hfa)}_4] \longrightarrow [\text{Ln(TODGA)}_3][\text{Ln(hfa)}_4]_3 \tag{3}$$

Synthesis of $Ln(TODGA)_3Cl_3$ (Ln = Tb, Dy, Ho, Er, Tm, Yb). $LnCl_3$ $6H_2O$ (1 equiv.) was added to a solution of TODGA (3 equiv.) in 1,2-dichloroethanein. The reaction was stirred overnight at room temperature and then the solution was filtered to remove any insoluble compound. A viscous liquid was obtained upon slow evaporation of 1,2-dichloroethanein. The compound was then dried overnight under high vacuum at 333 K.

Synthesis of $NH_4[Ln(hfa)_4]$ (Ln = Tb, Dy, Ho, Er, Tm, Yb). The reaction of ammonium hexafluoroacetylacetonate ($[NH_4][hfa]$) with various rare earth metal centers was referred to the literature (S. A. Pierson, O. Nacham, K. D. Clark, H. Nan, Y. Mudryk and J. L. Anderson, *New J. Chem.*, 2017, **41**, 5498-5505).

Synthesis of $[Ln(TODGA)_3][Ln(hfa)_4]_3$ (Ln = Tb, Dy, Ho, Er, Tm, Yb). $Ln(TODGA)_3Cl_3$ (1 equiv.) and $NH_4[Ln(hfa)_4]$ (3 equiv.) were dissolved in acetonitrile. The solution was allowed to stir at room temperature for 24 hours. The solvent was removed under reduced pressure and the crude product was redissolved in a certain volume of diethyl ether and washed several times with ultra-pure water until the aqueous fraction yielded no precipitate during a $AgNO_3$ test. A viscous liquid was obtained upon slow evaporation of diethyl ether. The compound was then dried overnight under high vacuum at 333 K.

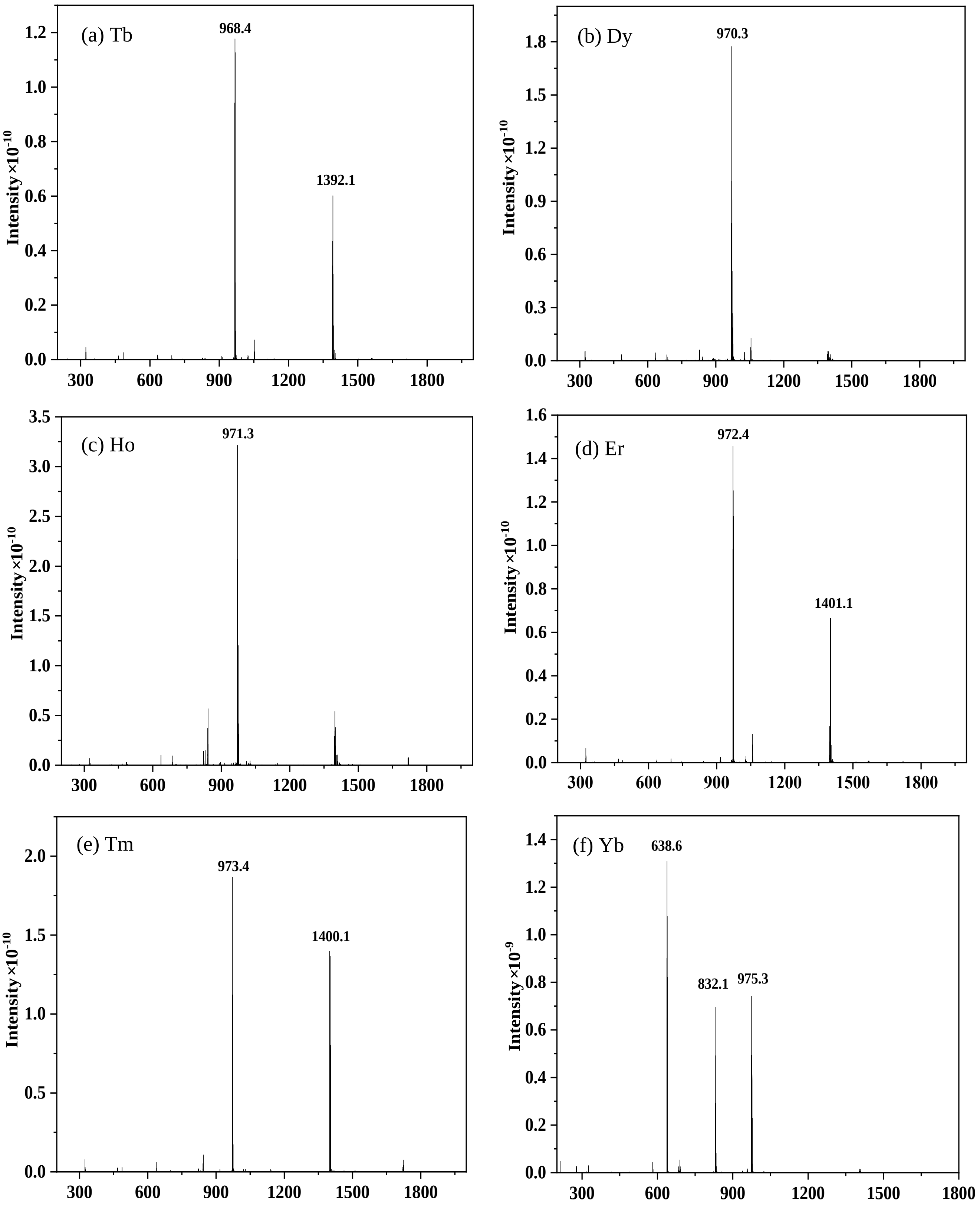


Figure S1. Positive mode mass spectra of $Ln(TODGA)_3Cl_3$ (Ln = Tb, Dy, Ho, Er, Tm, Yb).

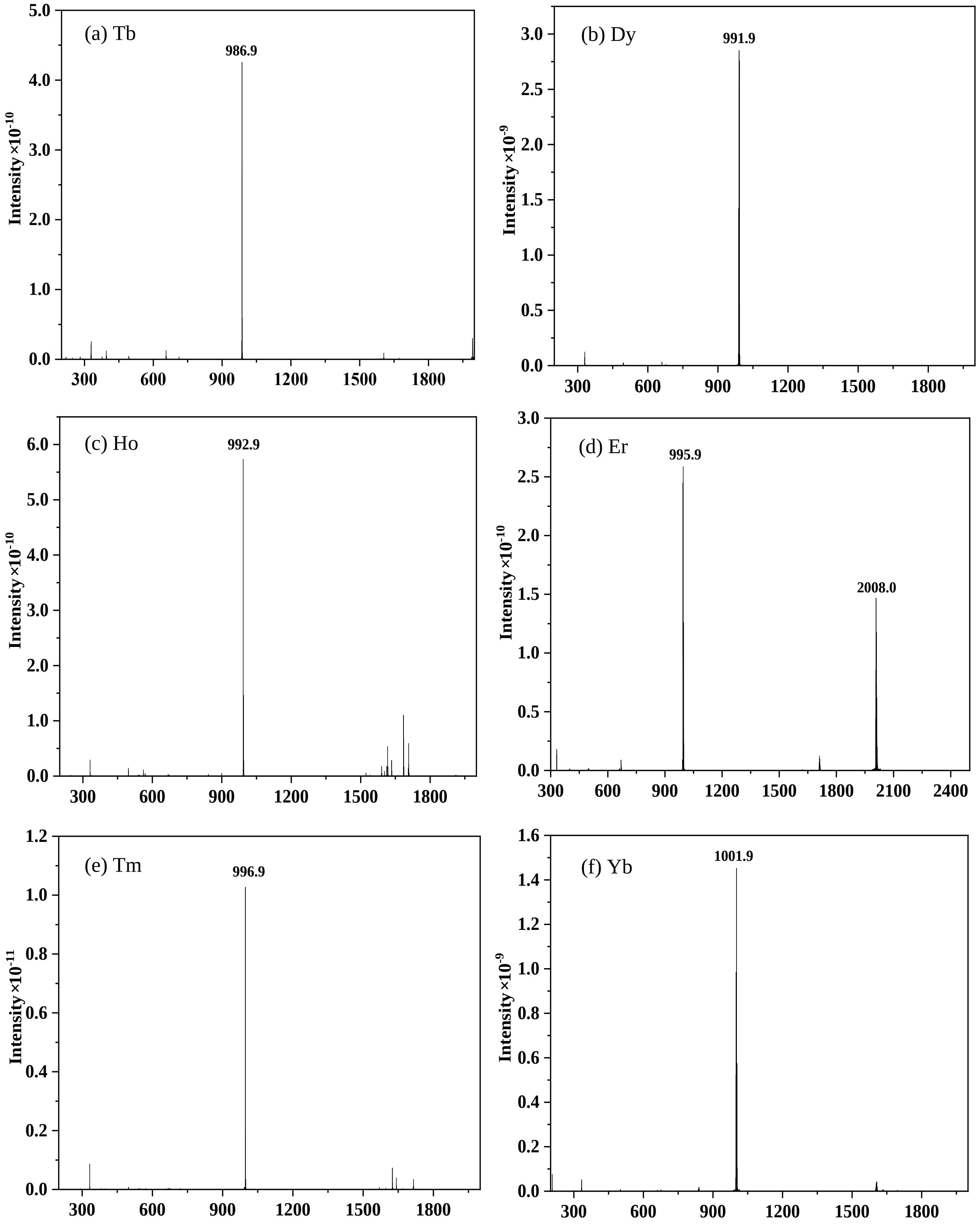


Figure S2. Negative mode mass spectra of $NH_4[Ln(hfa)_4]$ (Ln = Tb, Dy, Ho, Er, Tm, Yb).

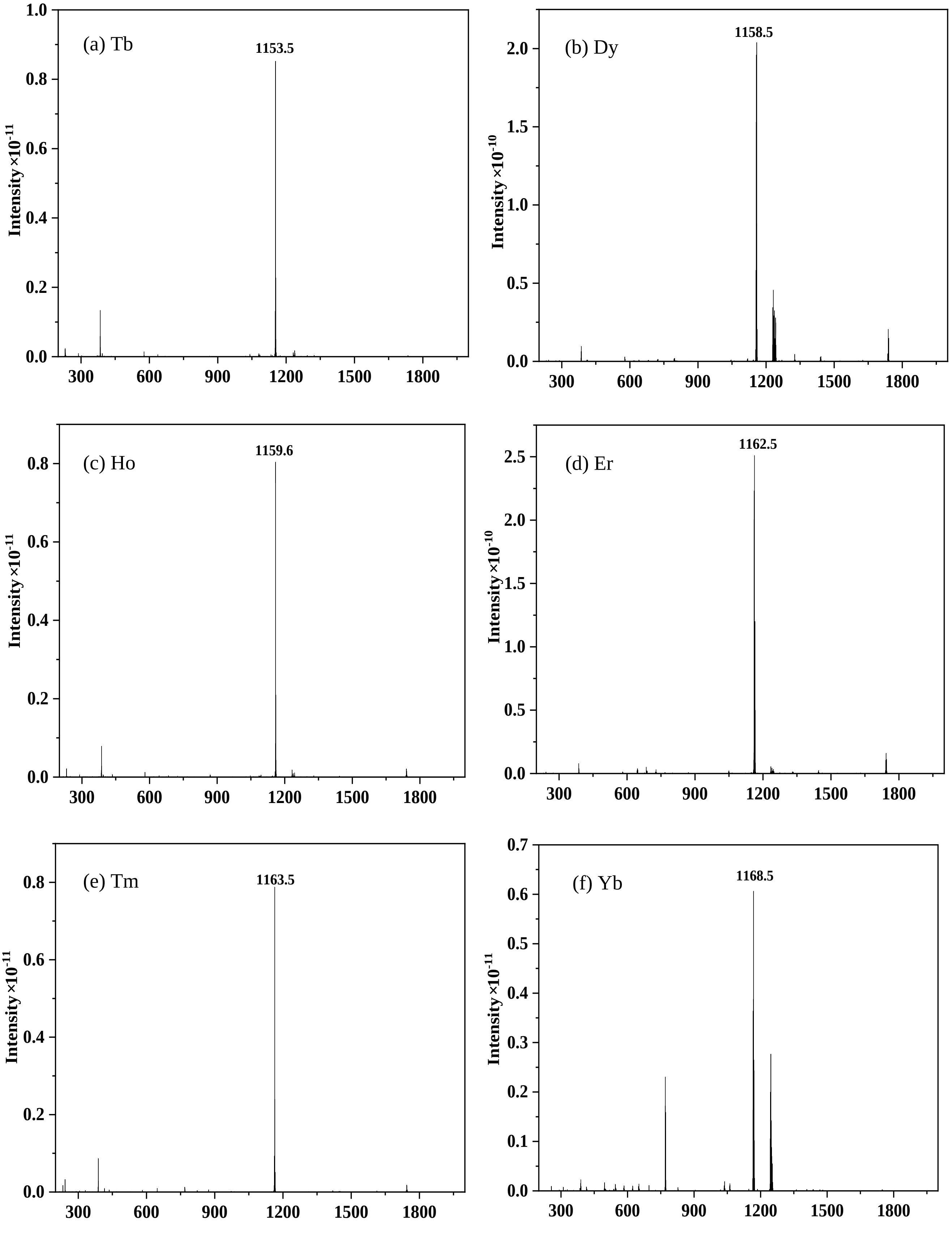


Figure S3. Positive mode mass spectra of $[Ln(TODGA)_3][Ln(hfa)_4]_3$ (Ln = Tb, Dy, Ho, Er, Tm, Yb).

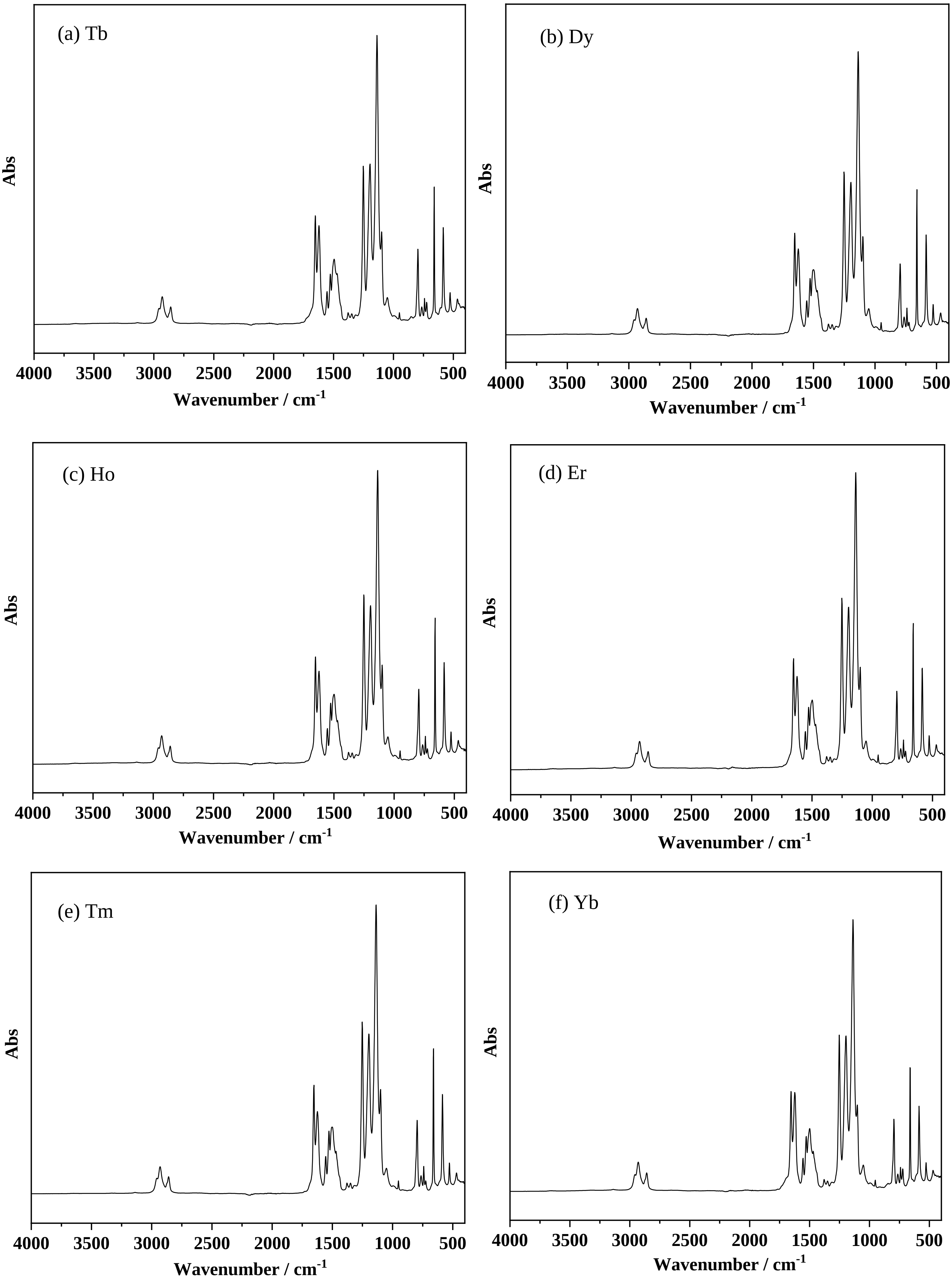


Figure S4. IR spectra of $[Ln(TODGA)_3][Ln(hfa)_4]_3$ (Ln = Tb, Dy, Ho, Er, Tm, Yb).

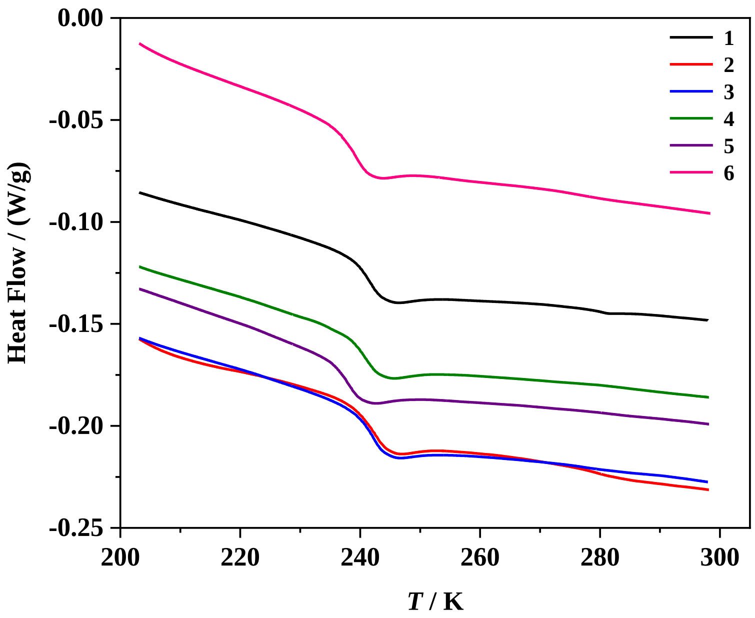


Figure S5. DSC curves of [Ln(TODGA)$_3$][Ln(hfa)$_4$]$_3$. (1) Tb, (2) Dy, (3) Ho, (4) Er, (5) Tm and (6) Yb.

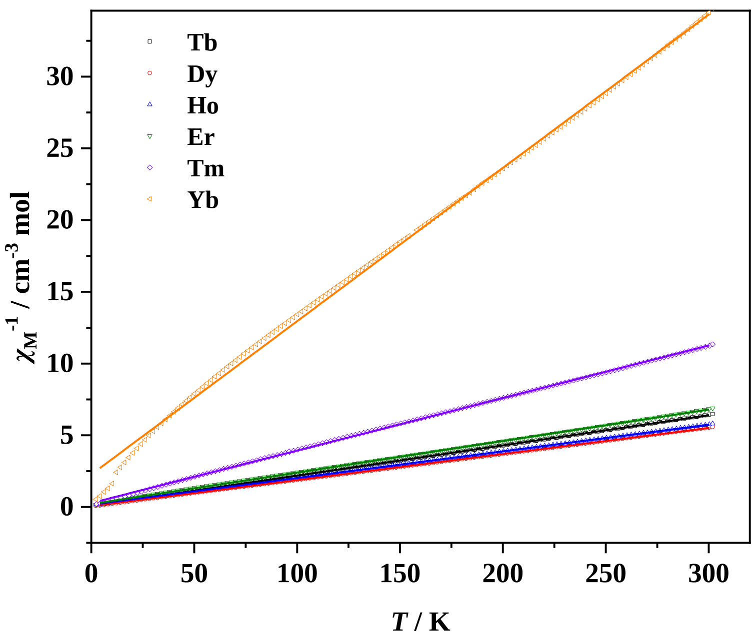


Figure S6. Temperature dependence of 1/ χ_M measured under 10000 Oe for MILs **1-6**.

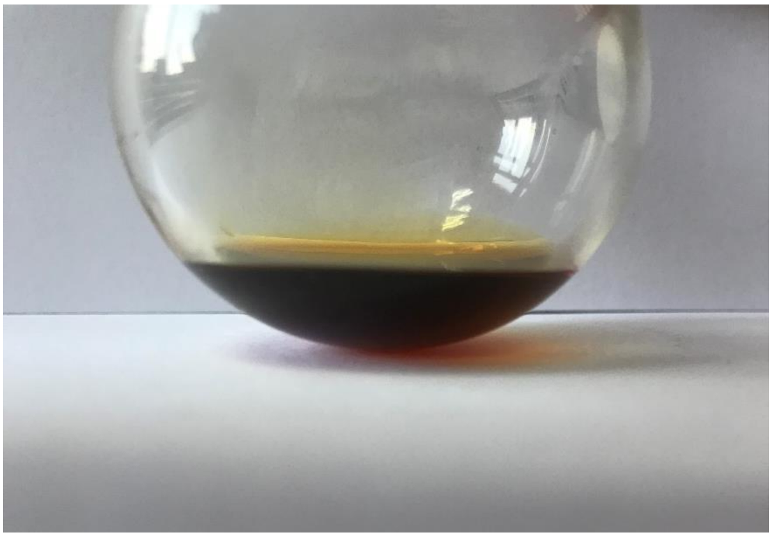


Figure S7. The photograph of MIL **1**.

Table S1. Element analyses of MILs **1-6**.

MIL	C / % (calcd / found)	H / % (calcd / found)	N / % (calcd / found)
Tb	41.49 / 41.22	4.73 / 4.63	1.73 / 1.71
Dy	41.37 / 41.34	4.71 / 4.76	1.72 / 1.62
Ho	41.29 / 41.44	4.70 / 4.76	1.72 / 1.77
Er	41.21 / 40.95	4.69 / 4.57	1.72 / 1.58
Tm	41.15 / 40.98	4.69 / 4.60	1.71 / 1.63
Yb	41.01 / 40.74	4.67 / 4.65	1.71 / 1.71