Electronic Supporting Information

Thiacalix[4]arene-supported mononuclear lanthanide compounds: slow magnetic relaxation in dysprosium and erbium analogues

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Table S1 Selected bond angles (deg) for **1**–**4**

	1 (Tb)	**2 (Dy)**	**3 (Ho)**	**4 (Er)**
O2-Ln1-O4	103.38 (11)	103.69 (11)	103.3 (2)	103.82 (9)
O2-Ln1-O7	111.66 (12)	111.38 (11)	121.9 (2)	113.68 (10)
O4-Ln1-O7	122.80 (11)	122.39 (11)	111.6 (2)	120.01 (10)
O2-Ln1-O6	159.99 (13)	160.11 (12)	149.4 (2)	157.94 (10)
O4-Ln1-O6	84.59 (10)	84.43 (10)	86.9 (2)	84.05 (9)
O7-Ln1-O6	77.55 (11)	77.73 (11)	78.7 (2)	78.16 (9)
O2-Ln1-O5	87.41 (11)	87.35 (11)	84.5 (2)	85.69 (9)
O4-Ln1-O5	148.14 (12)	148.38 (11)	160.1 (2)	150.47 (9)
O7-Ln1-O5	78.37 (11)	78.51 (11)	78.0 (2)	79.23 (9)
O6-Ln1-O5	76.87 (11)	76.98 (11)	77.8 (2)	78.17 (9)
O2-Ln1-O1	82.34 (10)	82.56 (10)	78.30 (19)	82.14 (9)
O4-Ln1-O1	77.44 (10)	77.87 (9)	82.51 (19)	78.70 (9)
O7-Ln1-O1	148.75 (10)	148.78 (10)	148.90 (17)	148.58 (8)
O6-Ln1-O1	81.56 (10)	81.46 (10)	74.51 (19)	79.24 (9)
O5-Ln1-O1	74.40 (10)	74.28 (10)	81.2 (2)	74.98 (8)
O2-Ln1-O3	77.48 (10)	77.37 (9)	78.42 (18)	77.76 (9)
O4-Ln1-O3	79.11 (9)	79.05 (9)	77.64 (18)	78.72 (8)
O7-Ln1-O3	66.79 (9)	66.47 (9)	66.22 (17)	66.39 (8)
O6-Ln1-O3	122.36 (11)	122.33 (11)	132.16 (19)	124.24 (9)
O5-Ln1-O3	132.74 (10)	132.55 (10)	122.1 (2)	130.81 (8)
O1-Ln1-O3	144.40 (8)	144.68 (8)	144.84 (15)	145.03 (7)

Table S2. Shape analysis for the metal centers of **1**–**4**

ML7	PBPY-7	COC-7	CTPR-7	JPBPY-7
Tb1	5.667	**1.501**	1.623	8.035
Dy1	5.713	**1.512**	1.655	8.056
Ho1	5.720	**1.524**	1.611	8.131
Er1	6.271	**1.297**	1.426	8.737
Dy1′[S1]	6.598	**1.095**	1.616	8.994
Tb1′[S1]	6.536	**1.064**	1.596	9.028

PBPY-7 (D_{5h}): Pentagonal bipyramid COC-7 (C_{3v}): Capped octahedron

CTPR-7 (C_{2v}): Capped trigonal prism JPBPY-7 (D_{5h}): Johnson pentagonal bipyramid J13

Table S3. Fitting of the Cole-Cole plots for **2** with an extended Debye model under 1 kOe dc field

T / K	χ_s / cm^3 mol^{-1}	χ_t / cm^3 mol^{-1}	τ_1 / s	α_1	τ_2 / s	α_2
1.9	1.79E-01	6.38E+00	1.09E-01	2.28E-01		
2.1	1.49E-01	5.59E+00	5.12E-02	2.32E-01		
2.3	8.07E-02	5.35E+00	2.95E-02	2.82E-01		
2.5	1.91E-01	4.87E+00	6.66E-03	9.87E-02	6.73E-02	1.75E-02
2.7	2.06E-01	4.27E+00	1.88E-03	6.08E-02	2.25E-02	8.60E-02
2.9	2.42E-01	3.89E+00	8.10E-04	1.49E-02	9.54E-03	1.39E-01
3.2	2.87E-01	3.57E+00	4.15E-04	2.81E-04	4.97E-03	1.39E-01
3.5	3.70E-01	1.64E+00			1.94E-03	1.42E-01
4	1.14E+00	1.49E+00			8.74E-04	1.45E-01
4.5	1.14E+00	2.55E+00			3.74E-04	1.81E-01

Table S4. Fitting of the Cole-Cole plots for **4** with a generalized Debye model under 1 kOe dc field

T / K	χ_s / cm^3 mol^{-1}	χ_t / cm^3 mol^{-1}	τ / s	α
1.9	2.68E-01	3.86E+00	2.07E-02	2.20E-01
2.1	2.58E-01	3.44E+00	1.14E-02	1.67E-01
2.3	2.39E-01	3.13E+00	6.14E-03	1.28E-01
2.5	2.16E-01	2.87E+00	3.29E-03	1.01E-01
2.7	2.01E-01	2.66E+00	1.74E-03	8.05E-02
2.9	1.94E-01	2.48E+00	9.83E-04	5.83E-02
3.1	1.84E-01	2.27E+00	5.58E-04	3.51E-02
3.5	3.36E-01	2.09E+00	2.16E-04	2.86E-02

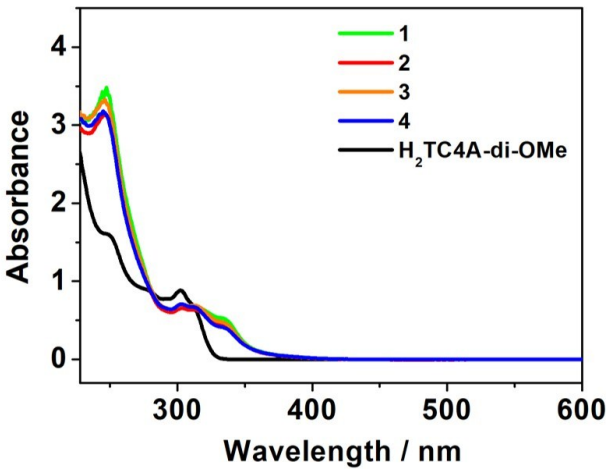

Fig. S1 UV-vis absorption spectra for compounds **1**–**4** in CH_2Cl_2.

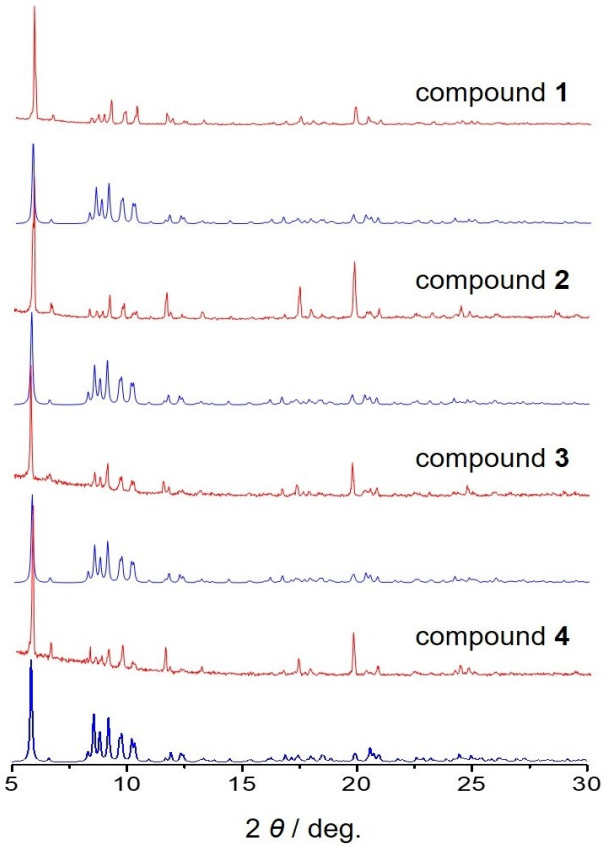

Fig. S2 The PXRD patterns obtained from the as-synthesized solids (red lines) and the simulated ones (blue lines) from the single crystal data of compounds **1**–**4**.

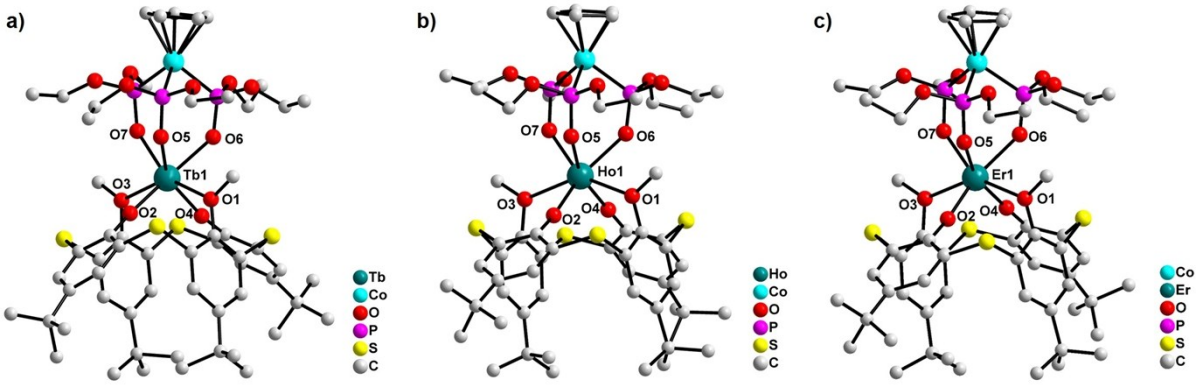

Fig. S3 Crystal structure of compound [Tb(TC4A-di-OMe)(L_{OEt})] (**1**) (a), [Ho(TC4A-di-OMe)(L_{OEt})] (**3**) (b), and [Er(TC4A-di-OMe)(L_{OEt})] (**4**) (c).

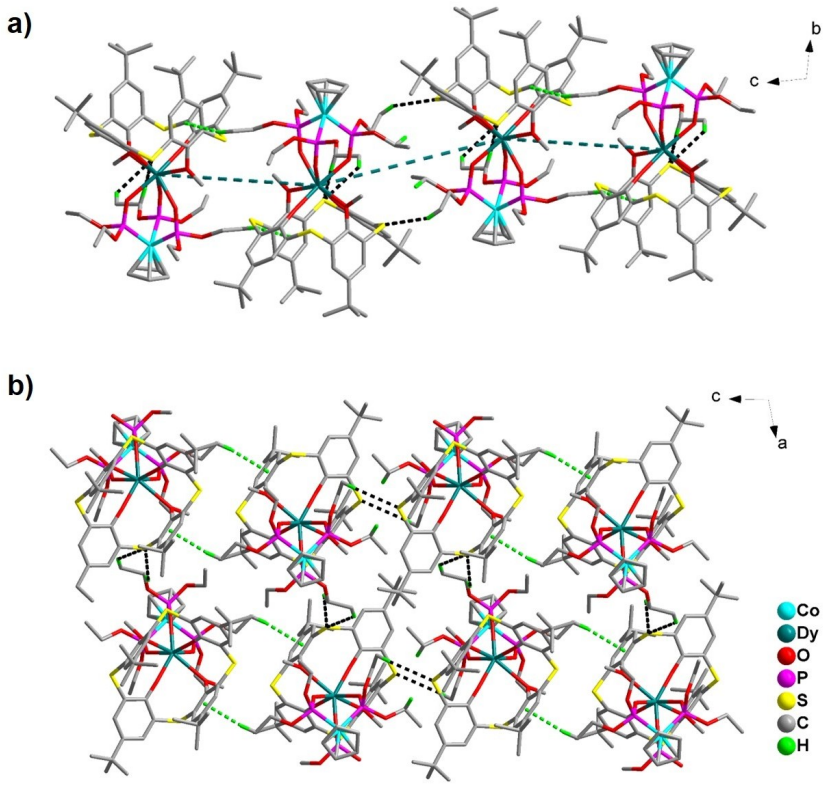

Fig. S4 The extended structure of compound **2** in the *bc* plane (a) and *ac* plane (b), showing various C−H···S (black dashed line) and C−H···π (green dashed line) interactions between the neighboring molecules.

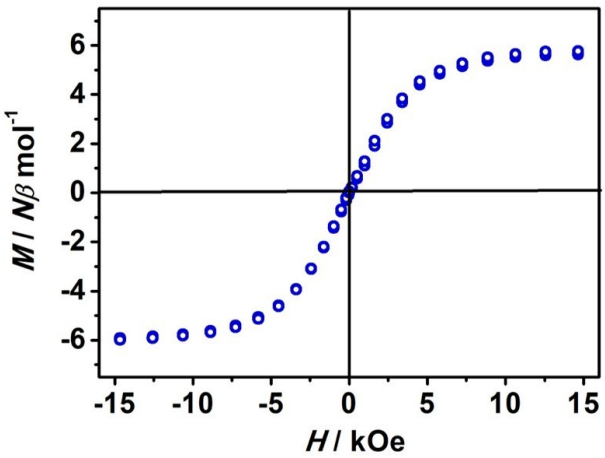

Fig. S5 Plots of *M* versus *H* at 2 K from -15 to 15 kOe for **2**.

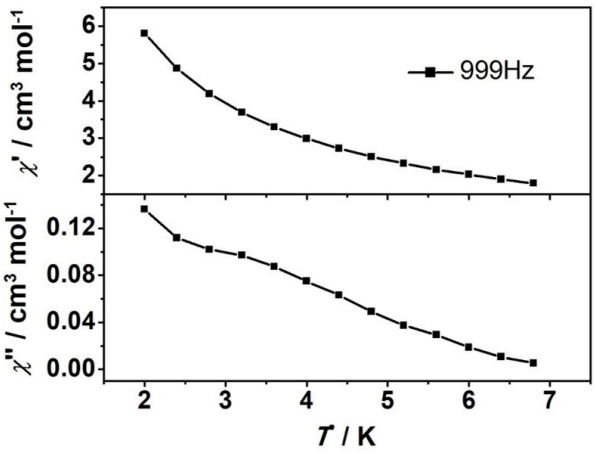

Fig. S6 Temperature-dependent in-phase χ' and out-of-phase χ'' ac susceptibility signals for **2** at the frequency of 999 Hz under zero dc field.

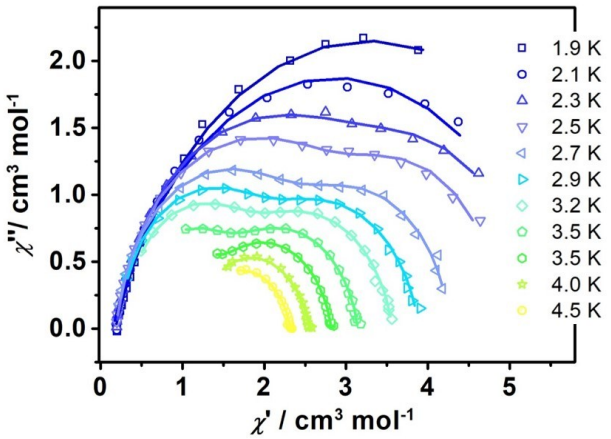

Fig. S7 Cole−Cole plots for **2** under a 1 kOe dc field. The solid lines represent the fit to the extended Debye model at the indicated temperatures.

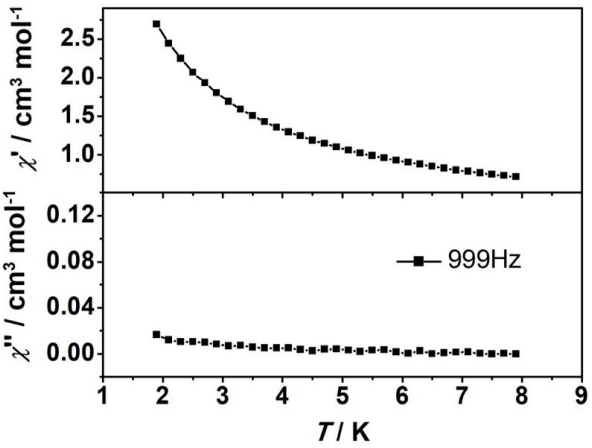

Fig. S8 Temperature-dependent in-phase χ' and out-of-phase χ'' ac susceptibility signals for **4** at the frequency of 999 Hz under zero dc field.

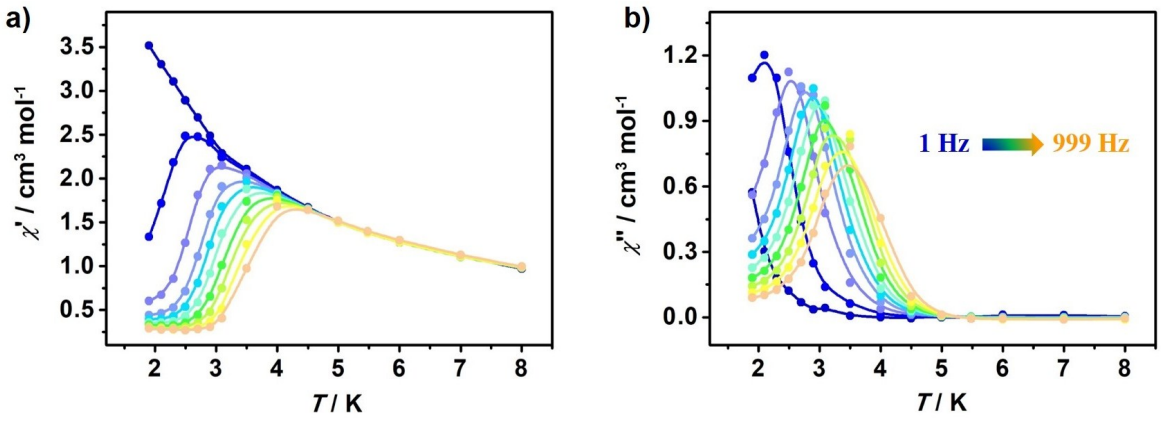

Fig. S9 Temperature-dependent in-phase χ' (a) and out-of-phase χ'' (b) ac susceptibilities under 1 kOe dc field for **4**.

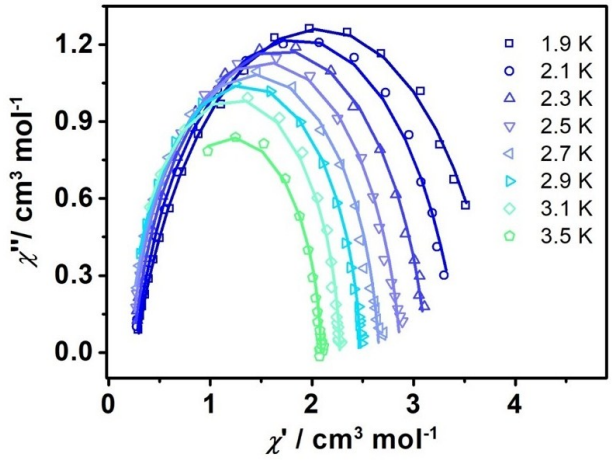

Fig. S10 Cole-Cole plots for **4** under a 1 kOe dc field. The solid lines represent the fit to the generalized Debye model at the indicated temperatures.

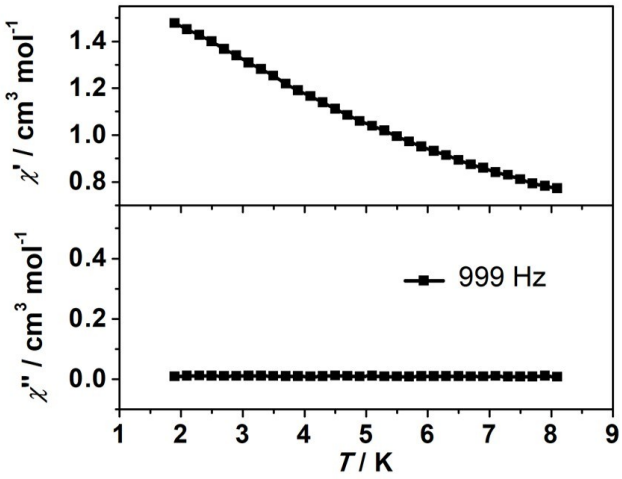

Fig. S11 Temperature-dependent in-phase χ' and out-of-phase χ'' ac susceptibility signals for **1** at the frequency of 999 Hz under 1 kOe dc field.

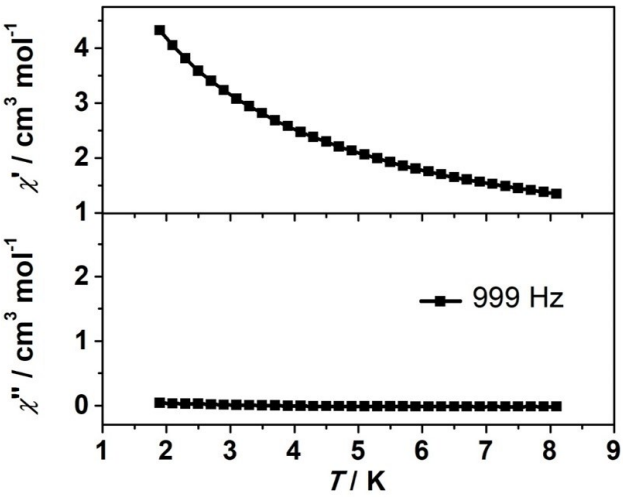

Fig. S12 Temperature-dependent in-phase χ' and out-of-phase χ'' ac susceptibility signals for **3** at the frequency of 999 Hz under 1 kOe dc field.

[S1] F. Gao, L. Cui, Y. Song, Y. Z. Li and J. L. Zuo, *Inorg. Chem.*, 2014, **53**, 562-567.