

Supporting Information

A Tetravalent Praseodymium Complex with Field-Induced Slow Magnetic Relaxation

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1. Experimental Section

General Considerations and Methods. All manipulations were carried out with standard Schlenk techniques or in a glovebox under an argon atmosphere. Glassware was dried overnight at 120 °C before use. Toluene and n-hexane were dried over activated alumina and stored over potassium mirror before use. All other reagents including solvents were purchased from Energy-Chemical and used without further purification. Anhydrous PrCl₃ was synthesized by adopting a literature procedure [1]. Elemental analyses were recorded on a Carlo Erba EA1110 simultaneous CHN elemental analyzer. Thermal gravimetric analysis (TGA) was performed on a METTLER TOLEDO (TGA2) instrument under an argon atmosphere with a heating rate of 10 °C min⁻¹ to 800 °C. Powder X-ray diffraction (XRD) measurements were performed using a Smartlab (9 kW) instrument with Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$, $2\theta = 5\text{--}50^\circ$, scan rate = 10° min⁻¹).

Cyclic Voltammetry experiments were performed using the CHI 760E Electrochemical. All experiments were performed using electrochemical cells consisting of a sealed 50 mL vial filled with Ar atmosphere, a glassy carbon (1 mm diameter) working electrode, a platinum wire counter electrode, and a silver wire for the pseudo reference electrode. The working electrode surface was polished prior to each experiment. Solutions used contained 1.2 mM analyte (40 mg **1** dissolved in 20 mL CH₂Cl₂) and 100 mM [NBu₄][PF₆] in dichloromethane. Ferrocene was added as an internal standard for calibration at the end of each run.

The UV-Vis spectra were recorded as 0.15 mM solutions in dichloromethane using 1 mm cuvettes and a Perkin Elmer Lambda 365 spectrometer. To ensure reliable photophysical data and avoid decomposition, the solutions of samples were prepared and stored in the glovebox.

Pr(OSiPh₃)₃(THF)₃. This compound was prepared via similar procedure as the analogue Tb(III) complexes by following literature procedure [2]. To a solution of Pr(N(SiMe₃)₂)₃ (5.08 mmol, 3.16 g) in THF (5 mL) at room temperature was added Ph₃SiOH (15.42 mmol, 4.26 g) in THF (5 mL). The solution was intensely stirred and white product precipitated immediately with exothermic phenomenon. Supernatants

were removed by filtration, and the solid product was rinsed with hexane (20 mL) and vacuum-dried (4.27 g, 67% yield).

Pr(OSiPh₃)₄(L) (1). A solution of [N(C₆H₄Br)₃][SbCl₆] (0.082 g, 0.1 mmol, 1 equiv.) in MeCN (2 mL) was added at room temperature to a slurry solution of Pr(OSiPh₃)₃(THF)₃ (0.12 g, 0.1 mmol, 1 equiv.) and KOSiPh₃ (0.03 g, 0.1 mmol, 1 equiv.) in MeCN (1 mL). The colorless suspension changed to dark blue immediately. After stirring for 2 h, deep reddish brown precipitates were formed in a red supernatant. The reddish brown solid was filtered and washed with MeCN (1 mL) for three times. The residue was extracted with 3 mL toluene, and the deep reddish brown solution was filtered. A colorless solution of 4,4'-dimethoxy-2,2'-bipyridine (L, 0.02 g, 0.1 mmol, 1 equiv.) in toluene (1 mL) was added at room temperature to the previous toluene solution of residue. Layering of the concentrated solution with n-hexane resulted in the dark red crystalline solid (**1·2Tol**) at -30 °C after 2 days. **1·2Tol** loses one of the toluene molecules during the filtration and drying process to isolated the solid sample **1·Tol** (131 mg, 80%). IR: ν [cm⁻¹] = 3062 (w), 3023 (w), 2962 (w), 2927 (w), 2873 (w), 1959 (w), 1893 (w), 1824 (w), 1774 (w), 1608 (m), 1562 (w), 1492 (m), 1427 (m), 1319 (w), 1249 (m), 1184 (w), 1106 (s), 1029 (m), 998 (m), 883 (s), 732 (m), 698 (s). Anal. Calc. for **1·Tol** (1550.87 g mol⁻¹): C₉₁H₈₀N₂O₆PrSi₄: C, 70.47; H, 5.20; N, 1.81. Found: C, 70.11; H, 5.29; N, 1.76.

4. Crystallographic Data

Single-crystal X-ray diffraction studies were carried out with the use of a Bruker D8 VENTURE diffractometer with Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$) at 100 K. Using Olex2 [3], the structures were solved with the SHELXT structure solution program using Intrinsic Phasing [4] and refined with the SHELXL refinement package using Least Squares minimization [5]. All hydrogen atom positions were generated geometrically and refined with isotropic temperature factors. Cambridge Crystallographic Data Centre contains the crystal structure with the following CCDC number 2323641 (Pr(OSiPh₃)₃(THF)₃), 2323639 (**1·2Tol**) and 2334474 (**1·Tol**).

Table S1. Crystallographic Data of Pr(OSiPh₃)₃(THF)₃, **1·2Tol**, and **1·Tol**.

	Pr(OSiPh ₃) ₃ (THF) ₃	1·2Tol	1·Tol
Formula	C ₇₀ H ₇₆ O ₇ PrSi ₃	C ₉₈ H ₈₈ N ₂ O ₆ PrSi ₄	C ₉₁ H ₈₀ N ₂ O ₆ PrSi ₄
F.w.	1254.48	1642.97	1550.84
<i>T</i> (K)	100.01	100.0	101.15
cell	monoclinic	monoclinic	monoclinic
Space group	<i>P</i> 2 ₁	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> (Å)	14.6493(5)	19.0038(11)	17.1044(19)
<i>b</i> (Å)	16.2996(5)	18.2175(9)	18.958(2)
<i>c</i> (Å)	14.6770(5)	24.5942(12)	24.198(2)
α (°)	90	90	90
β (°)	115.0839(13)	102.266(2)	99.729(4)
γ (°)	90	90	90
<i>V</i> (Å ³)	3174.02(18)	8320.2(8)	7733.7(13)
<i>Z</i>	2	4	4
F(000)	1306.0	3412.0	3212.0
<i>D</i> _c (g cm ⁻³)	1.313	1.312	1.332
μ (mm ⁻¹)	0.876	0.700	0.748
Data collected/unique	35982/14102	47907/18418	93734/13655
<i>R</i> 1 (>2 σ /all data)	0.0447/0.0533	0.0522/0.0752	0.0652/0.1305
<i>wR</i> 2 (>2 σ /all data)	0.1053/0.1112	0.1071/0.1179	0.1216/0.1474
GOF	1.040	1.060	1.096
Residues (e Å ⁻³)	1.48/-1.44	1.71/-1.47	0.95/-1.17

Table S2. Selected bond lengths (Å) and angles (°) for Pr (III or IV) ions in Pr(OSiPh₃)₃(THF)₃, **1·2Tol**, and **1·Tol**.

Pr(OSiPh ₃) ₃ (THF) ₃		1·2Tol		1·Tol	
Pr-X bond length (Å)		Pr-X bond length (Å)		Pr-X bond length (Å)	
Pr1-O1	2.193(4)	Pr1-O1	2.151(3)	Pr1-O1	2.129(5)
Pr1-O2	2.209(4)	Pr1-O2	2.106(3)	Pr1-O2	2.111(4)
Pr1-O3	2.228(4)	Pr1-O3	2.115(2)	Pr1-O3	2.098(4)
Pr1-O4	2.577(5)	Pr1-O4	2.130(3)	Pr1-O4	2.122(4)
Pr1-O5	2.565(4)	Pr1-N1	2.567(3)	Pr1-N1	2.532(5)
Pr1-O6	2.563(6)	Pr1-N2	2.536(3)	Pr1-N2	2.570(5)
X-Pr-X angle(°)		X-Pr-X angle(°)		X-Pr-X angle(°)	
O3- Pr1-O5	87.55(16)	O2- Pr1-O1	99.22(10)	O2- Pr1-O1	93.36(17)
O3- Pr1-O4	87.11(18)	O2- Pr1-O4	96.85(10)	O2- Pr1-O4	95.34(17)
O3- Pr1-O6	161.2(2)	O2- Pr1-O3	102.38(10)	O2- Pr1-O3	103.85(16)
O2- Pr1-O3	101.37(18)	O2- Pr1-N2	148.80(10)	O2- Pr1-N2	168.69(16)
O2- Pr1-O5	166.29(16)	O2- Pr1-N1	85.46(10)	O2- Pr1-N1	106.23(16)
O2- Pr1-O4	87.36(17)	O1- Pr1-N2	79.80(10)	O1- Pr1-N2	88.31(16)
O2- Pr1-O6	88.73(19)	O3- Pr1-N2	108.81(10)	O3- Pr1-N2	87.08(16)
O5- Pr1-O4	82.67(16)	O3- Pr1-N1	171.96(10)	O3- Pr1-N1	149.76(15)
O1- Pr1-O3	102.85(18)	O1- Pr1-N1	86.68(10)	O1- Pr1-N1	85.30(17)
O1- Pr1-O2	100.58(18)	O4- Pr1-O1	161.26(11)	O4- Pr1-O1	163.67(16)
O1- Pr1-O5	87.36(16)	O4- Pr1-N2	81.45(10)	O4- Pr1-N2	80.53(16)
O1- Pr1-O4	165.62(18)	O4- Pr1-N1	85.04(10)	O4- Pr1-N1	79.01(17)
O1- Pr1-O6	90.6(2)	O3- Pr1-O1	93.71(10)	O3- Pr1-O1	96.10(17)
O6- Pr1-O5	79.96(18)	O3- Pr1-O4	92.19(10)	O3- Pr1-O4	95.20(17)
O6- Pr1-O4	77.5(2)	N2- Pr1-N1	63.34(9)	N2- Pr1-N1	62.73(15)

Table S3. Continuous Shape Measures (CShM) calculations [6] for the complex unit **1**.

Structure [ML6] ^a	HP-6	PPY-6	OC-6	TPR-6	JPPY-6
1 2Tol	30.740	23.063	2.152	12.356	26.108
1 Tol	30.735	25.299	1.886	13.433	28.088

^a HP-6 = Hexagon (D_{6h}); PPY-6 = Pentagonal pyramid (C_{5v}); OC-6 = Octahedron (O_h); TPR-6 = Trigonal prism (D_{3h}); JPPY-6 = Johnson pentagonal pyramid J2 (C_{5v})

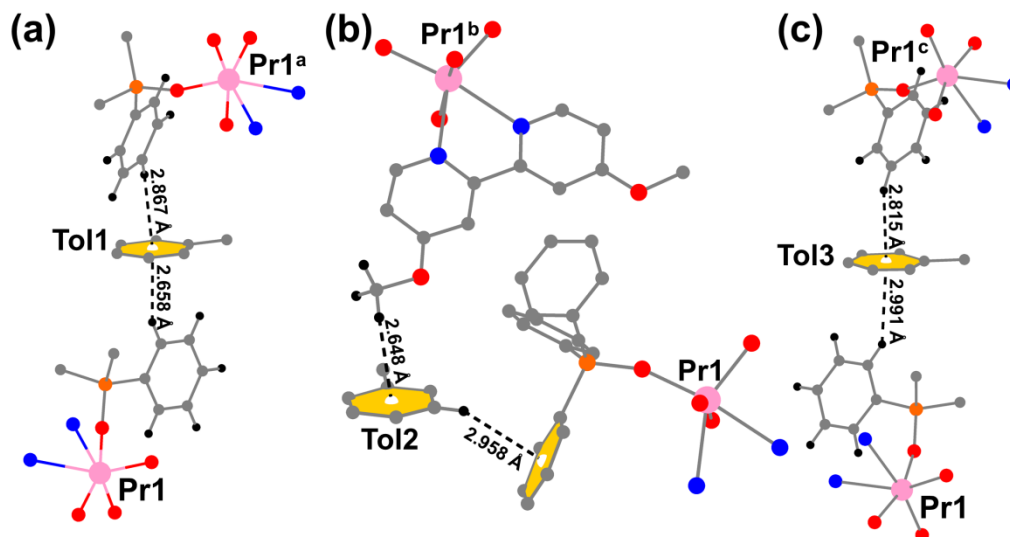


Figure S1 Illustration of the C-H... π stacking interactions of the toluene molecules with the phenyl group and the methyl group of (a-b) $1 \cdot 2\text{Tol}$ and (c) $1 \cdot \text{Tol}$. ^a 1-x, 2-y, 1-z; ^b x, 1.5-y, -0.5+z. ^c -x, 1-y, -z. Color code: pink (Pr), red (O), orange (Si), gray (C), blue (N), black (H).

2. Thermogravimetric Analysis

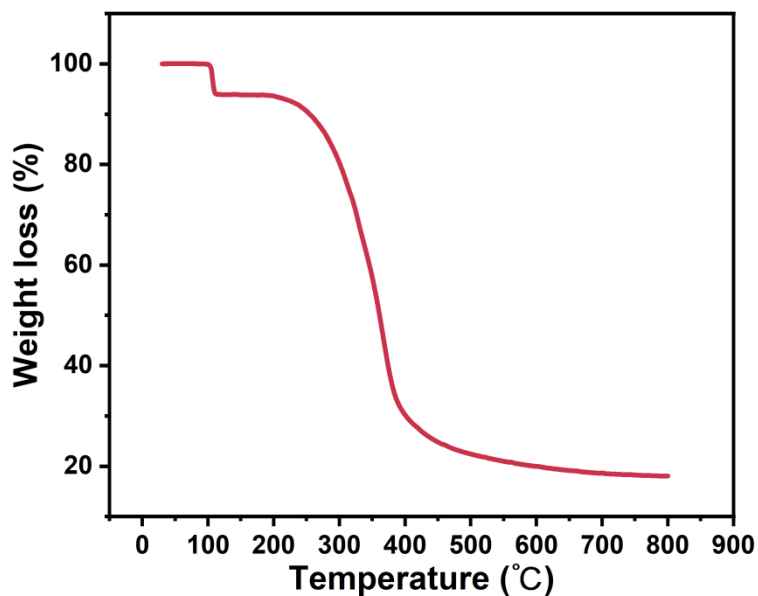


Figure S2 TGA profile diagram of 1·Tol.

The thermal stability of 1·Tol under an argon atmosphere was investigated by thermogravimetric analysis (TGA) with a heating rate of 10 °C min⁻¹ to 800 °C. (Figure S1). The first weight loss at 97 °C was due to evaporation of the crystallization solvent toluene. As the temperature continues to rise to 195°C, the mass remains relatively constant, indicating that 1·Tol is stable up to 195°C. The complex decomposes rapidly as the temperature continues to rise up to 400°C. From 400°C to 800°C, the decomposition gradually slows down towards completion. At 800°C, 18% of the mass was still retained, presumably a mixture of residual praseodymium oxide and silica.

3. Powder X-ray diffraction

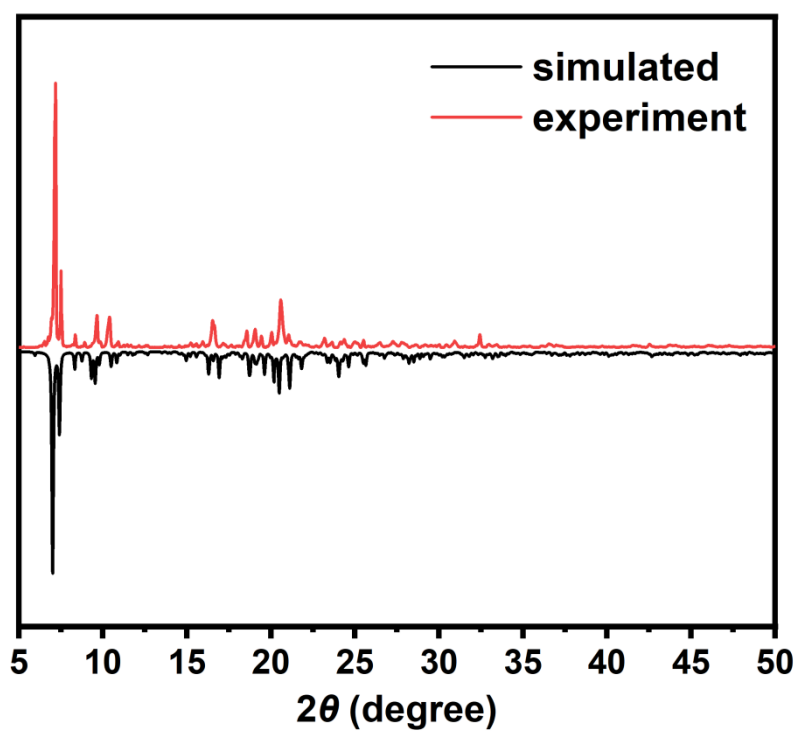


Figure S3 PXRD patterns of 1·Tol.

Table S4. π - π stacking interactions in **1** (distance (Å), angles: (°)). Cg-Cg: Distance between ring centroids. Angle: Dihedral angle between planes *I* and *J*. Distance 1: Distance between plane *I* and centroid of Cg(*J*). α : Angle between Cg(*I*)-Cg(*J*) vector and normal to plane *I*. Distance 2: Distance between plane *J* and centroid of Cg(*I*). β : Angle between Cg(*J*)-Cg(*I*) vector and normal to plane *J*.

Entry	π - π interactions	Cg-Cg	Angle	Distance 1	α	Distance 2	β
1	Cg1-Cg3	4.771(2)	62.11(12)	4.723(2)	8.13	2.614(7)	56.78
2	Cg1-Cg5	3.593(2)	6.18(12)	-3.281(3)	24.05	3.419(3)	17.90
3	Cg2-Cg4	3.761(2)	10.48(13)	3.242(4)	30.46	-3.534(3)	20.01
4	Cg2-Cg6	4.401(2)	50.32(16)	-4.391(3)	3.86	-2.583(8)	54.06

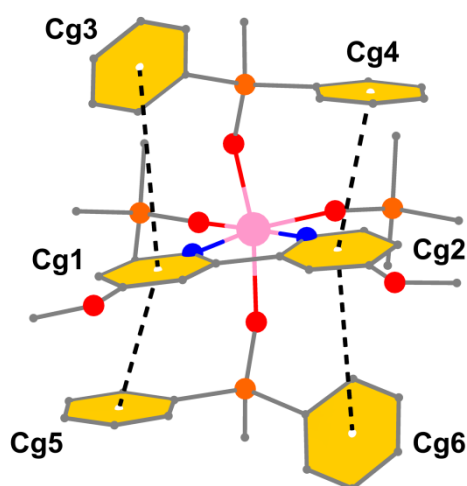


Figure S4 Illustration of the π - π stacking interaction of the phenyl group with the pyridine group of **1**. The yellow hexagon indicates the π -conjugate plane and the black dashed line indicates the π - π stacking interaction. The lighting effect was removed for clarity. Color code: pink (Pr), red (O), orange (Si), gray (C), blue (N).

5. Magnetism

Magnetic susceptibility measurements were carried out with a Quantum Design MPMS-3 SQUID magnetometer, with polycrystalline samples sealed with melted eicosane in NMR tubes under a vacuum. Static magnetic susceptibilities were measured under an applied DC field of 1 T upon cooling from 300 K to 2 K. Field-dependent magnetizations were measured at low temperatures with field up to a maximum field of 7 T.

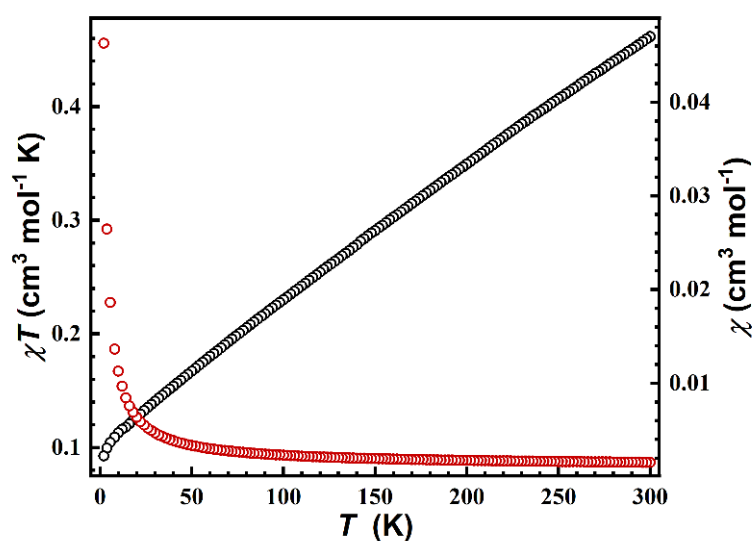


Figure S5 The χT (black) and χ (red) versus T plot of $1 \cdot \text{Tol}$ under a DC field of 1 T.

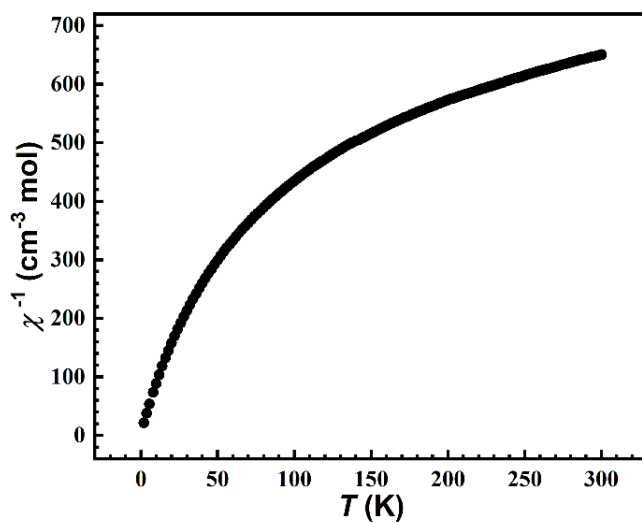


Figure S6 The χ^{-1} versus T plot of $1 \cdot \text{Tol}$ under a DC field of 1 T.

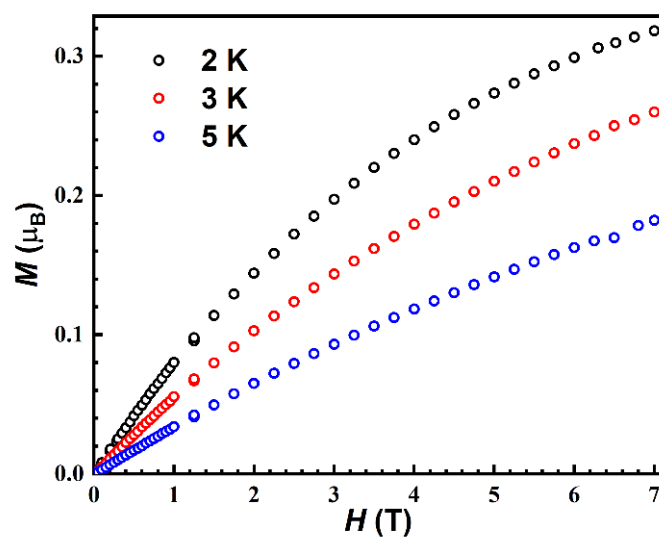


Figure S7 The field-dependent magnetization plots at indicated temperatures for **1·Tol**.

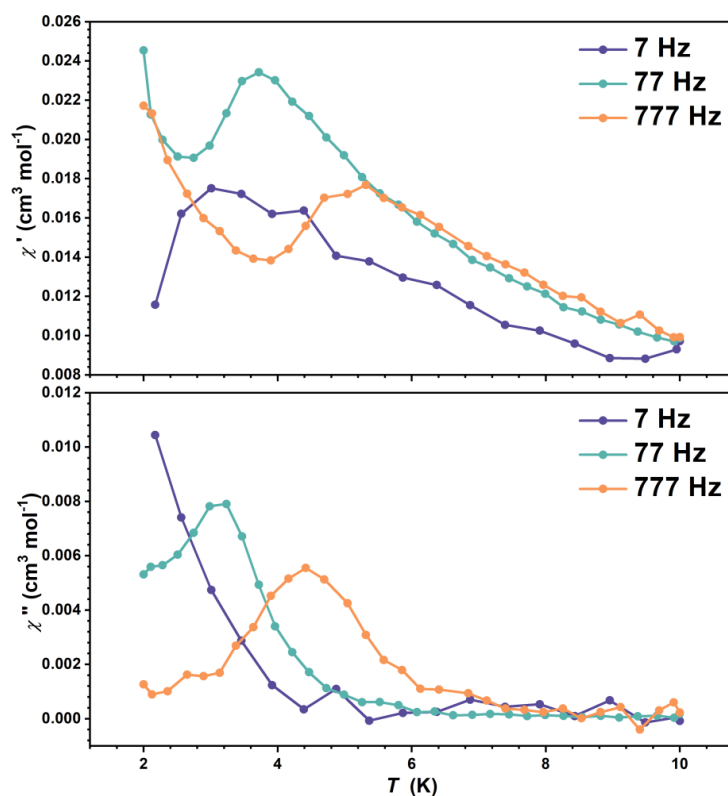


Figure S8 Temperature-dependence of the in-phase (χ' , top) and out-of-phase (χ'' , bottom) AC susceptibility signals under 4 kOe DC field by standard AC susceptibility measurements for **1·Tol**. Solid lines are guide for vision.

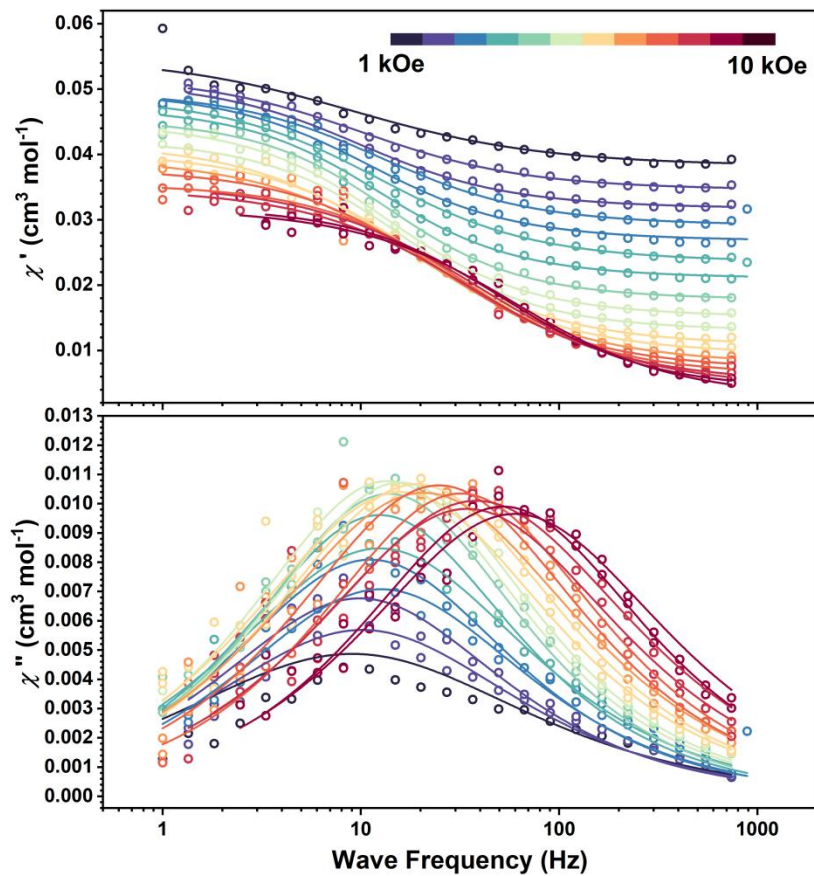


Figure S9 Frequency-dependence of the in-phase (χ' , top) and out-of-phase (χ'' , bottom) AC susceptibility signals at 2 K from 1 kOe to 10 kOe applied DC field for **1·Tol**. Solid lines are best fits with a generalized Debye model.

Table S5 Relaxation fitting parameters obtained using a generalized Debye model for **1·Tol** at 2 K from 1 kOe to 10 kOe applied DC field.

H / Oe	τ / s	τ_{err}	α
1000	0.01757	0.00348	0.33815
1500	0.01562	8.61997E-4	0.27266
2000	0.01607	7.97366E-4	0.2309
2500	0.01257	5.86477E-4	0.23697
3000	0.01423	9.87765E-4	0.21991
3500	0.01281	4.66453E-4	0.2536
4000	0.01278	5.97695E-4	0.19697
4500	0.01148	3.20442E-4	0.18534
5000	0.0117	3.34649E-4	0.20527
5500	0.01003	3.4231E-4	0.19851
6000	0.00996	4.84448E-4	0.25495
6500	0.0083	3.27985E-4	0.23563
7000	0.00768	4.40505E-4	0.26636
7500	0.00642	3.6909E-4	0.23556
8000	0.00499	2.98787E-4	0.22042
8500	0.00463	3.36999E-4	0.26196
9000	0.00416	2.16449E-4	0.27704
9500	0.00305	1.41852E-4	0.22388
10000	0.00266	1.7588E-4	0.2591

Table S6 Relaxation fitting parameters obtained using a generalized Debye model for **1·Tol** from 2 K to 4.8 K under 4 kOe applied DC field.

T/K	τ/s	τ_{err}	α
2	0.01423	0.00195	0.25835
2.2	0.00982	9.33484E-4	0.18021
2.4	0.00901	7.00126E-4	0.13872
2.6	0.00641	3.98948E-4	0.1663
2.8	0.00429	2.794E-4	0.10754
3	0.00308	1.44984E-4	0.09842
3.2	0.00206	1.34287E-4	0.06146
3.4	0.00131	7.21029E-5	0.10093
3.6	9.95149E-4	5.8223E-5	0.009
3.8	6.86883E-4	9.20337E-6	0.05257
4	4.63707E-4	8.66201E-6	0.08614
4.2	3.26763E-4	1.05997E-5	0.09051
4.3	2.71113E-4	1.17557E-5	0.0994
4.4	2.11017E-4	1.06787E-5	0.1213
4.5	1.61168E-4	1.29552E-5	0.15591

6. Infrared spectra

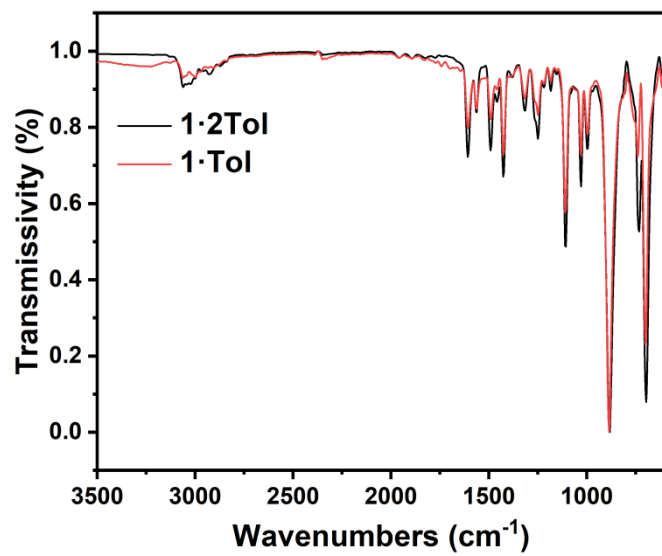


Figure S10 Infrared spectra of 1·Tol and 1·2Tol.

7. Reference

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