Electronic Supporting Information

Synthesis, Structures and Magnetic studies of Hexanuclear Lanthanide Complexes: SMM behavior in Dy^{III} analogue and MCE properties in Gd^{III} analogue

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Table S1. Details of solvent mask

Sl. No.	Volume/ Formula Unit ($Å^3$)	Electron Count/ Formula Unit	Contents/Formula Unit
1 (AJ1860)	180	36	2 CH_3OH
2 (AJ1863)	302	80	2 CH_3OH, 4 H_2O
3 (AJ1920)	252	40	4 H_2O
4 (AJ1851)	238	70	4 CH_3OH

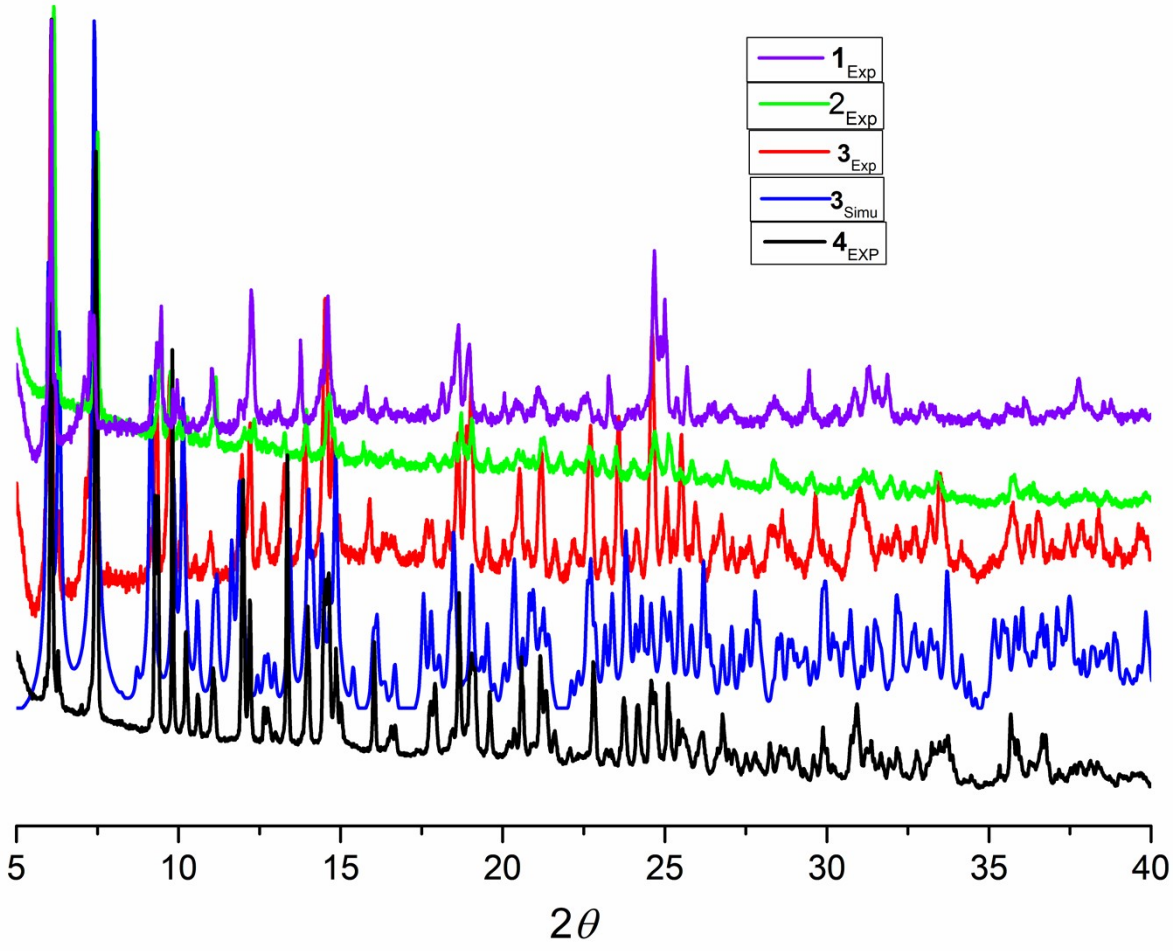


Figure S1. Experimental powder XRD patterns of **1**(in violet), **2**(in green), **3**(in red), **4**(in black) with the simulated powder XRD from single crystal data for **3**(in blue).

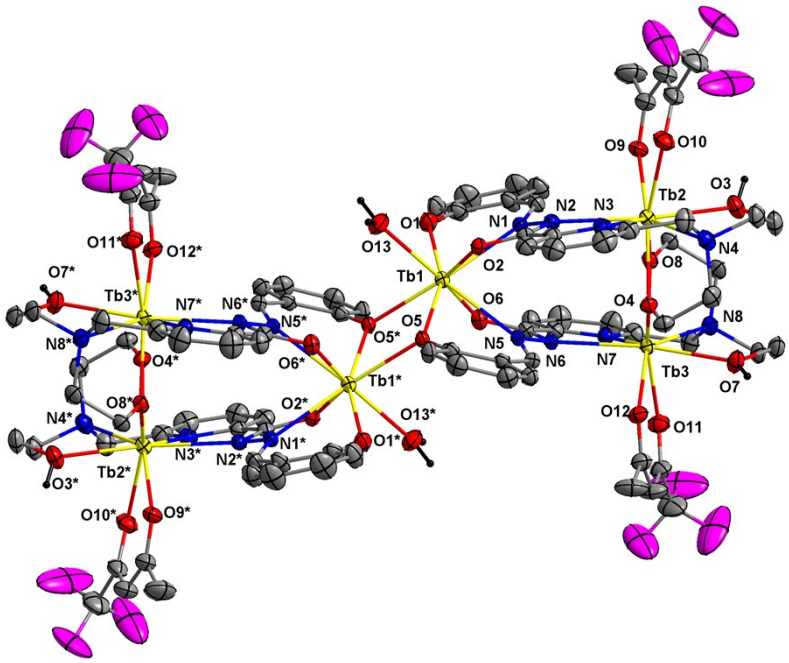


Figure S2. Molecular structure of **2** (selected hydrogen atoms and the solvent molecules have been omitted for clarity). Thermal ellipsoids at 30% probability level are shown. Color codes: N = blue; O = red; C = grey; Tb= yellow; H = black, and F = pink). Selected bond lengths (Å) for **2**: for Tb1; Tb1–O1, Tb1–O2, Tb1–O5, Tb1–O5*, Tb1–O6, Tb1–O13, Tb1–N1, Tb1–N5, are 2.304(4), 2.332(4), 2.380(4), 2.368(3), 2.351(4), 2.417(5), 2.519(4), 2.538(4), respectively, for Tb2; Tb2–O3, Tb2–O4, Tb2–O8, Tb2–O9, Tb2–O10, Tb2–N2, Tb2–N3, Tb2–N4, are 2.410(4), 2.305(4), 2.291(4), 2.359(4), 2.382(4), 2.525(4), 2.526(5), 2.615(5), respectively, for Tb3; . Tb3–O4, Tb3–O7, Tb3–O8, Tb3–O11, Tb3–O12, Tb3–N6, Tb3–N7, Tb3–N8, are 2.307(4), 2.435(4), 2.288(4), 2.398(4), 2.342(4), 2.536(4), 2.523(5), 2.600(4), respectively, and selected bond angles (°) for **2**: Tb1–O5–Tb1*, Tb3–O8–Tb2, Tb3–O4–Tb2, 108.37(14)°, 110.81(14)° , 109.62(15)°, respectively.

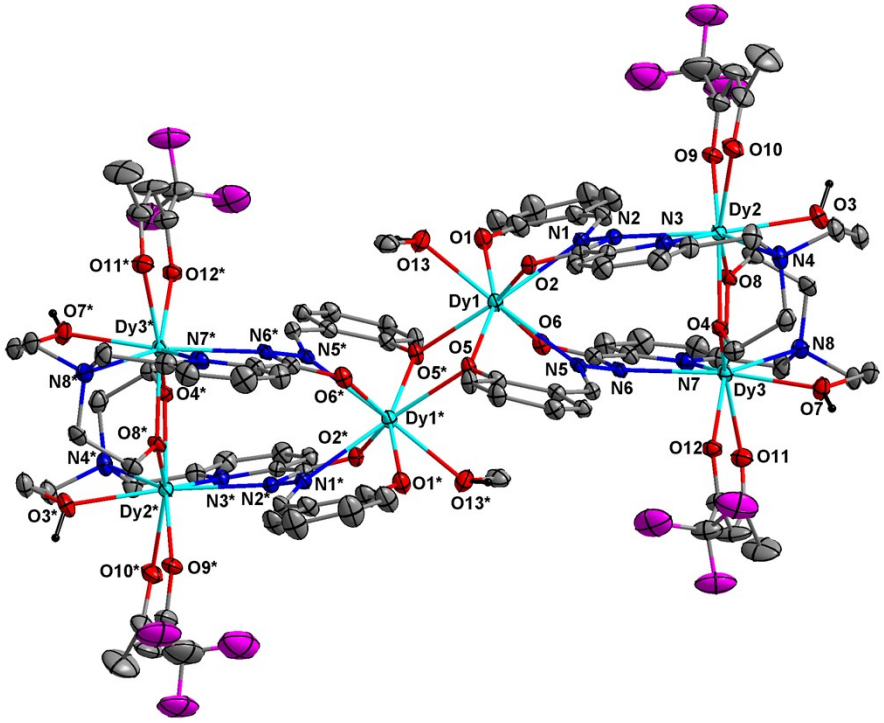


Figure S3. Molecular structure of **3** (selected hydrogen atoms and the solvent molecules have been omitted for clarity). Thermal ellipsoids at 30% probability level are shown. Color codes: N = blue; O = red; C = grey; Dy = cyan, H = black; and F = pink). Selected bond lengths (Å) for **3**: for Dy1; Dy1–O1, Dy1–O2, Dy1–O5, Dy1–O5*, Dy1–O6, Dy1–O13, Dy1–N1, Dy1–N5, are 2.278(5), 2.311(4), 2.345(4), 2.362(4), 2.331(4), 2.412(5), 2.507(5), 2.512(5), respectively, for Dy2; Dy2–O3, Dy2–O4, Dy2–O8, Dy2–O9, Dy2–O10, Dy2–N2, Dy2–N3, Dy2–N4, are 2.413(4), 2.474(4), 2.283(4), 2.334(4), 2.366(5), 2.503(5), 2.513(5), 2.605(5), respectively, for Dy3; . Dy3–O4, Dy3–O7, Dy3–O8, Dy3–O11, Dy3–O12, Dy3–N6, Dy3–N7, Dy3–N8, are 2.303(4), 2.422(4), 2.267(4), 2.369(4), 2.314(5), 2.504(5), 2.509(5), 2.597(5), respectively, and selected bond angles (°) for **3**: Dy1–O5– Dy1*, Dy3–O4– Dy2, Dy3–O8– Dy2, 108.93(15) °, 110.01(16)°, 110.97(16)°, respectively.

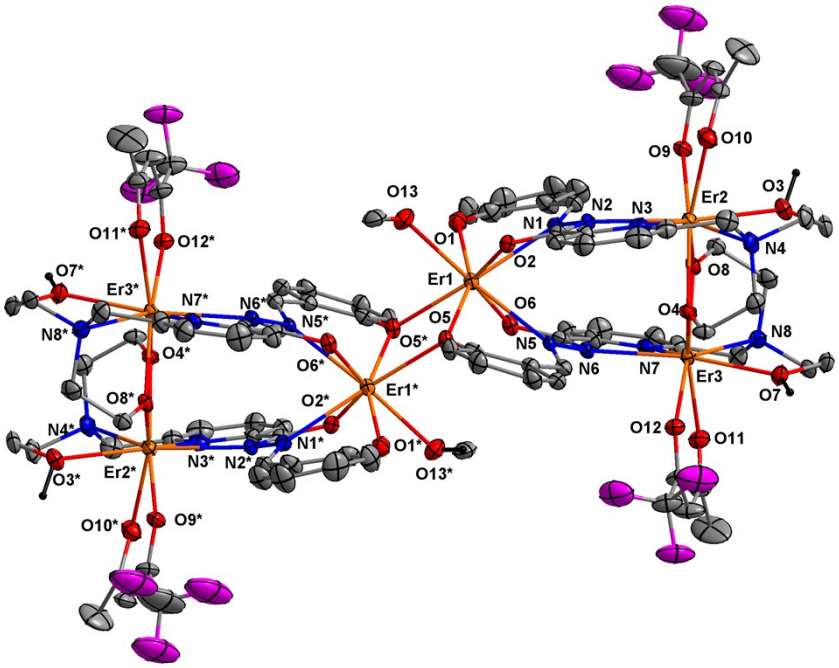


Figure S4. Molecular structure of **4** (selected hydrogen atoms and the solvent molecules have been omitted for clarity). Thermal ellipsoids at 30% probability level are shown. Color codes: N = blue; O = red; C = grey; Er = orange; H = black; and F = pink) Selected bond lengths (Å) for **4**: for Er1; Er1–O1, Er1–O2, Er1–O5, Er1–O5*, Er1–O6, Er1–O13, Er1–N1, Er1–N5, are 2.293(7), 2.294(7), 2.342(7), 2.337(6), 2.303(7), 2.375(7), 2.496(8), 2.491(7), respectively, for Er2; Er2–O3, Er2–O4, Er2–O8, Er2–O9, Er2–O10, Er2–N2, Er2–N3, Er2–N4, are 2.382(7), 2.274(6), 2.269(6), 2.317(7), 2.370(7), 2.489(7), 2.498(8), 2.594(8), respectively, for Er3; Er3–O4, Er3–O7, Er3–O8, Er3–O11, Er3–O12, Er3–N6, Er3–N7, Er3–N8, are 2.270(6), 2.392(7), 2.260(6), 2.365(7), 2.313(6), 2.489(7), 2.503(8), 2.576(8), respectively, and selected bond angles for **4**: Er1–O5– Er1*, Er3–O4– Er2, Er3–O8– Er2, 108.5(3) °, 110.2(2)°, 110.7(3)°, respectively.

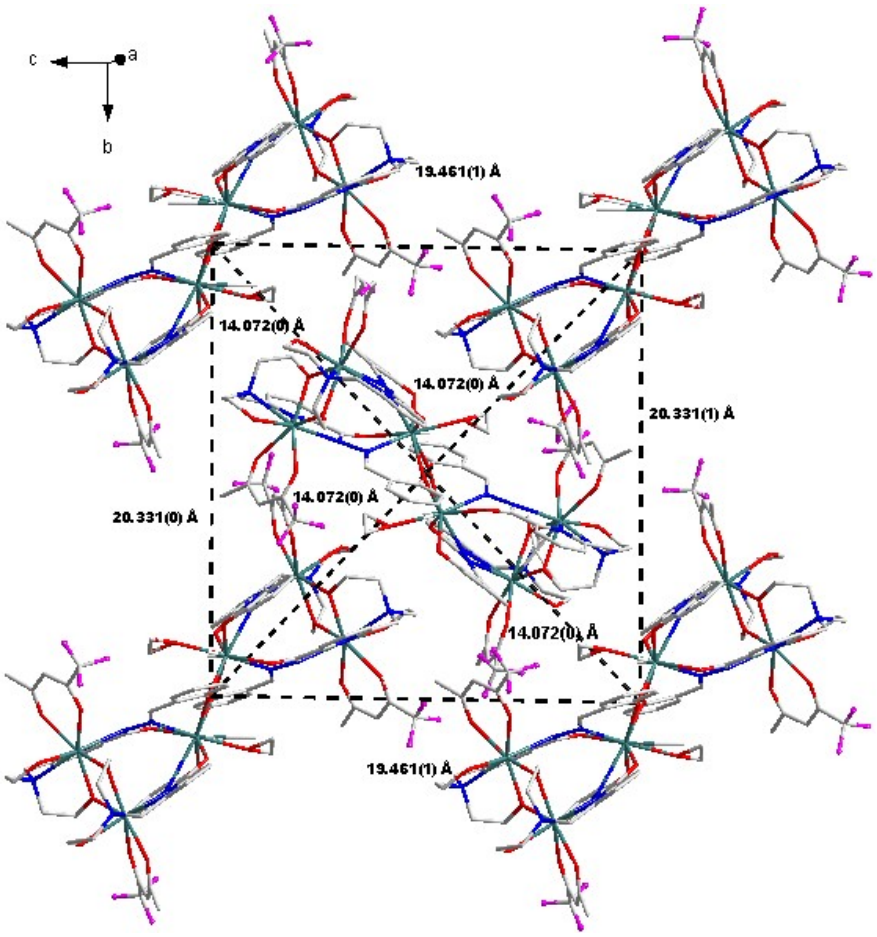


Figure S5. 2D supramolecular structure of complex **1** (selected carbon, hydrogen is omitted for clarity). Color codes: N = blue; O = red; C = grey; Gd= dark green; and F = pink)

Table S2. Continuous Shape Measures (CShM) calculations for **1**.

Complex_Metal Centre	Structure†			
	SAPR-8	TDD-8	JBTPR-8	BTPR-8
1_Gd1 CShM	**1.351**	2.079	2.608	3.716
1_Gd2 CShM	1.810	**1.680**	2.031	2.594
1_Gd3 CShM	2.069	**1.516**	2.330	2.826

† *SAPR-8 = Square antiprism (D_{4d}); TDD-8 = Triangular dodecahedron (D_{2d}); JBTPR-8 = Biaugmented trigonal prism J50 (C_{2v}); BTPR-8 = Biaugmented trigonal prism (C_{2v})*

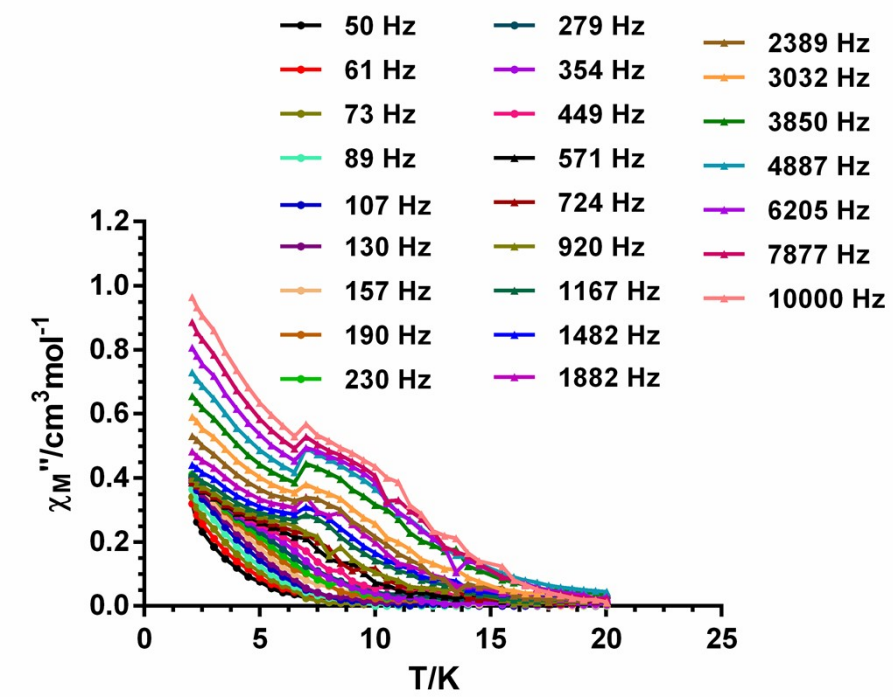


Figure S6. Temperature dependence of out-of-phase signals (χ''_M) for **3** at zero field and at the indicated frequencies.

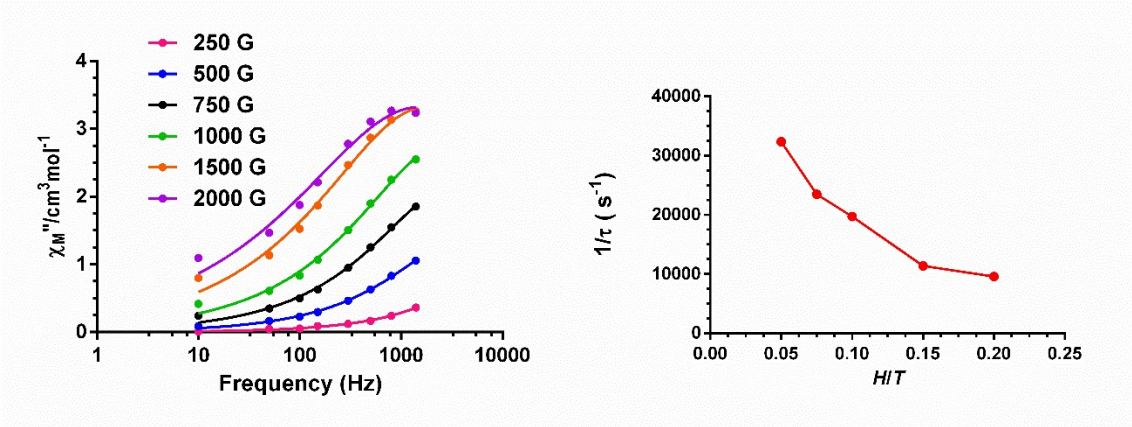
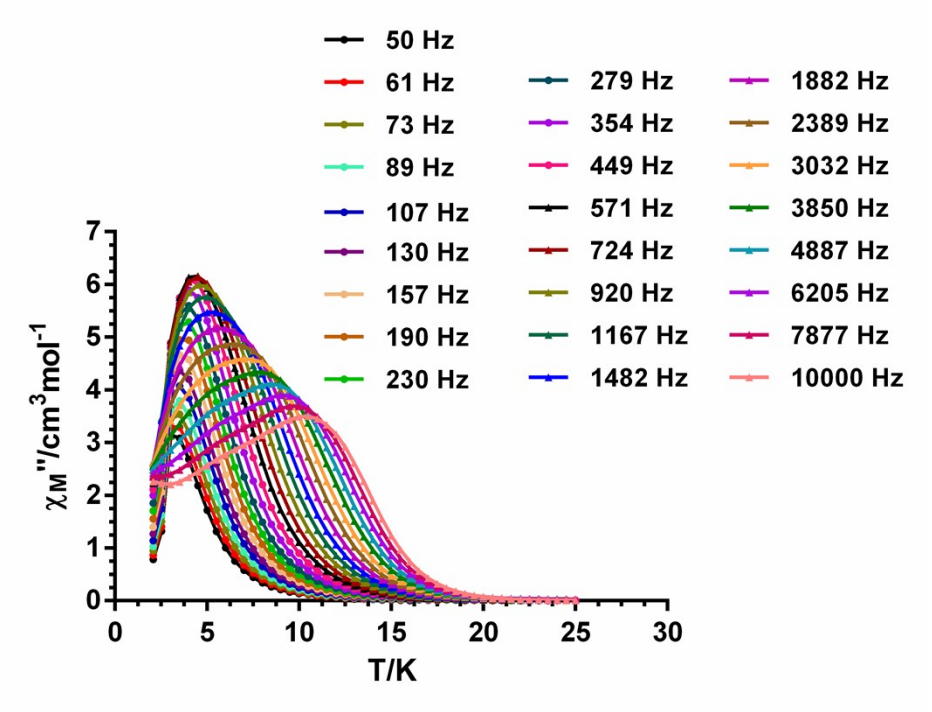


Figure S7. Frequency dependence of the of out-of-phase signals (χ''_M) for **3** at the indicated fields (*left*). Field dependence of the inverse of the relaxation times (*right*). Solid red line is a guide for the eye.



Temperature dependence of out-of-phase signals (χ''_M) for **3** at H_{dc} = 0.2 T and at the indicated frequencies.

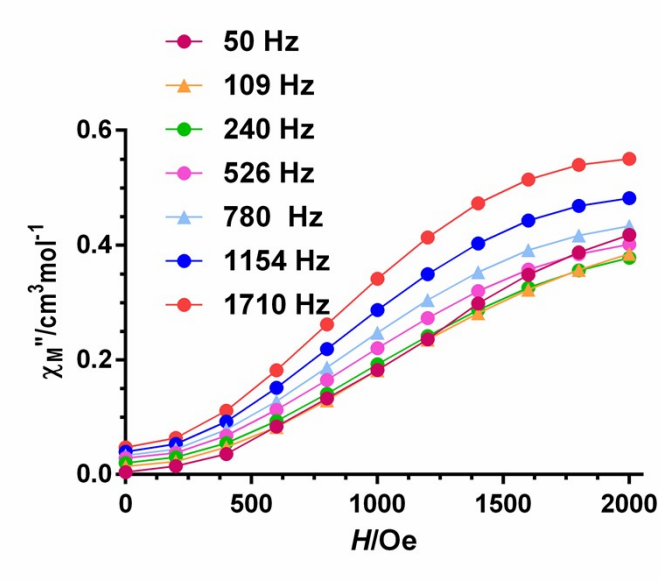


Figure S9. Field dependence of out-of-phase signals (χ''_M) for **4** at the indicated frequencies and at a temperature of 2.5 K.