Electronic Supplementary Information

(Part 2)

Combination of single-molecule magnet behaviour and luminescence properties in a new series of lanthanide complexes with tris(pyrazolyl)borate and oligo(β-diketonate) ligands

Elena A. Mikhalyova,[a] Matthias Zeller,[b] Jerry P. Jasinski,[c] Raymond J. Butcher,[d] Luca M. Carrella,[e] Alexander E. Sedykh,[f,g] Konstantin S. Gavrilenko,[h,i] Sergey S. Smola,[j] Michael Frasso,[k] Sebastian C. Cazorla,[b] Kuluni Perera,[b] Anni Shi,[b] Habib G. Ranjbar,[b] Casey Smith,[b] Alexandru Deac,[b] Youlin Liu,[b] Sean M. McGee,[l] Vladimir P. Dotsenko,[j] Michael U. Kumke,[l] Klaus Müller-Buschbaum,[f,g] Eva Rentschler,[e] Anthony W. Addison,*[m] & Vitaly V. Pavlishchuk*[a]

[a] *L. V. Pisarzhevskii Institute of Physical Chemistry of the National Academy of Sciences of the Ukraine, Prospekt Nauki 31, Kiev, 03028, Ukraine, tel. (38 044) 525 42 28, fax (38 044) 525 62 16, e-mail: shchuk@inphyschem-nas.kiev.ua;*

[b] *Department of Chemistry, Purdue University, 560 Oval Drive, West Lafayette, IN, 47907, U.S.A., e-mail: zeller4@purdue.edu;*

[c] *Department of Chemistry, Keene State College, Keene, NH 03435, USA*

[d] *Chemistry Department Howard University, 525 College St. N.W., Washington, DC 20059, USA*

[e] *Institute of Inorganic and Analytical Chemistry, Johannes Gutenberg University Mainz, Duesbergweg 10-14, D-55128 Mainz, Germany*

[f] *Institute of Inorganic and Analytical Chemistry, Justus-Liebig-Universität Giessen, Heinrich-Buff-Ring 17, 35392 Giessen, Germany*

[g] *Institute of Inorganic Chemistry, Julius-Maximilians-Universität Würzburg, Am Hubland, 97074 Würzburg, Germany*

[h] *Chembiocenter of Taras Shevchenko National University of Kiev, 67 Chervonotkatska St., 02094, Kiev, Ukraine*

[i] *Enamine Ltd, 78 Chervonotkatska St., 02094, Kiev, Ukraine*

[j] *A.V. Bogatsky Physico-Chemical Institute of the National Academy of Sciences of the Ukraine, 86 Lustdorfskaya doroga, 65080 Odessa, Ukraine;*

[k] *Department of Chemistry, 217 Clark Hall West Virginia University, Morgantown, WV, 26508*

[l] *University of Potsdam, Institute of Chemistry, Karl-Liebknecht-Str. 24-25, 14476 Potsdam, Germany*

[m] *Department of Chemistry, Drexel University, Philadelphia, PA 19104-2816, U.S.A., e-mail: addisona@drexel.edu.*

Magnetic data

Tp_2DyPhm (1Dy)

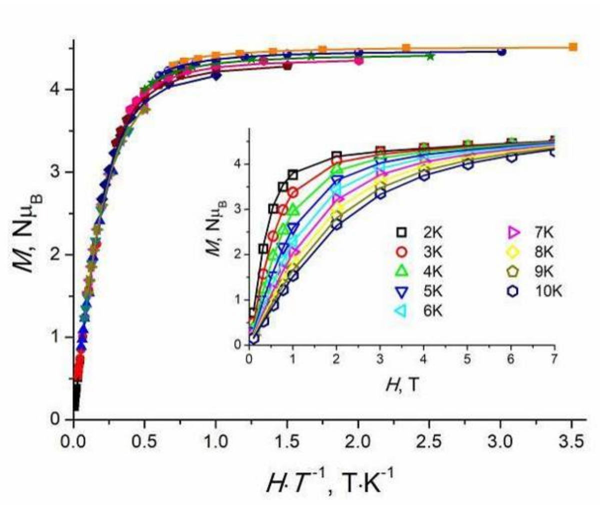

Fig. S7. *M vs. H/T* and *M vs. H* dependences for **1Dy**. Solid lines represent the best fits to eqn. 1 (from the main text) using the program PHI.[1]

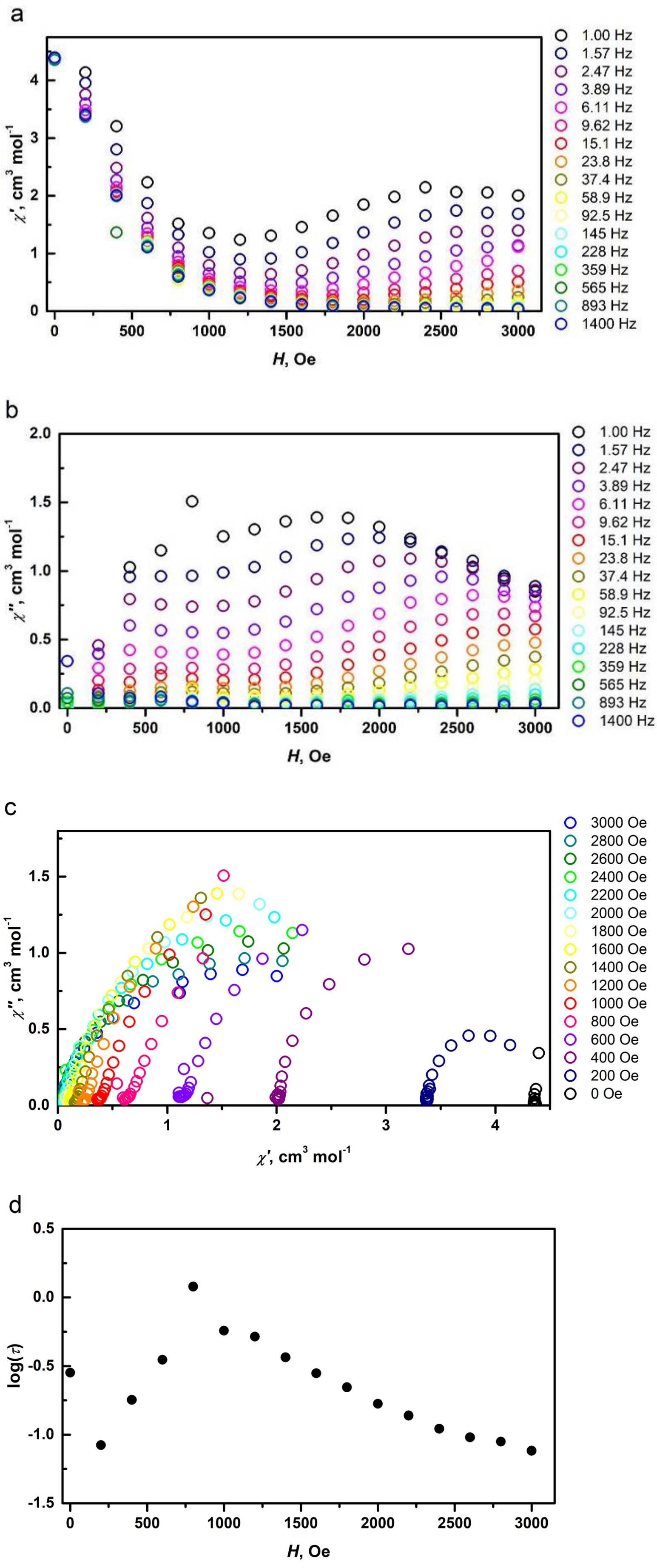

Fig. S8. Field dependences of in-phase (χ'), out-of-phase (χ'') magnetic susceptibilities and log(τ) (T = 2 K) for **1Dy**.

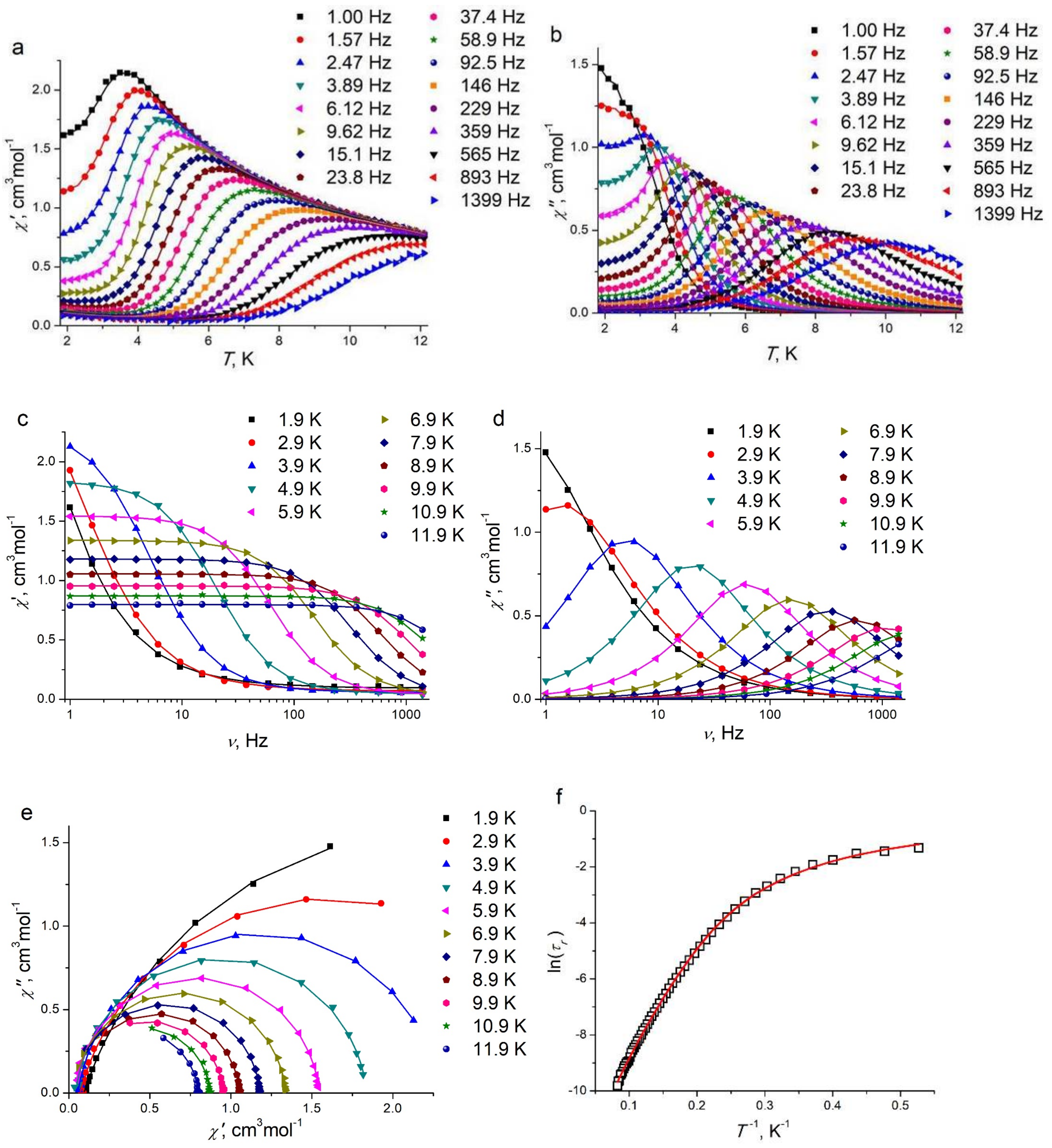

Fig. S9. Temperature and frequency dependences of in-phase (χ') and out-of-phase (χ'') magnetic susceptibilities ($H = 0.18$ T) for **1Dy**. Solid lines represent the best fits to a generalized Debye model, using the program *cc-fit*[2] (a-e) or to eqn. 2 (from the main text) (f).

$(Tp_2Dy)_2Tae$ (2Dy)

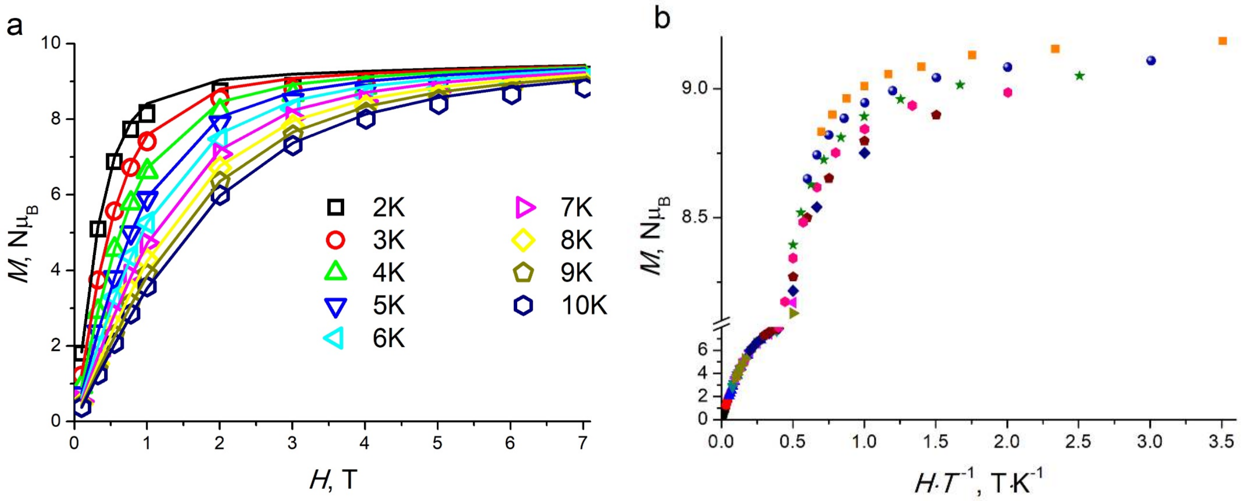

Fig. S10. *M vs. H* (a) and *M vs. H/T* (b) dependences for **2Dy**. Solid lines represent the best fits to eqn. 1 (from the main text) using the program PHI.[1]

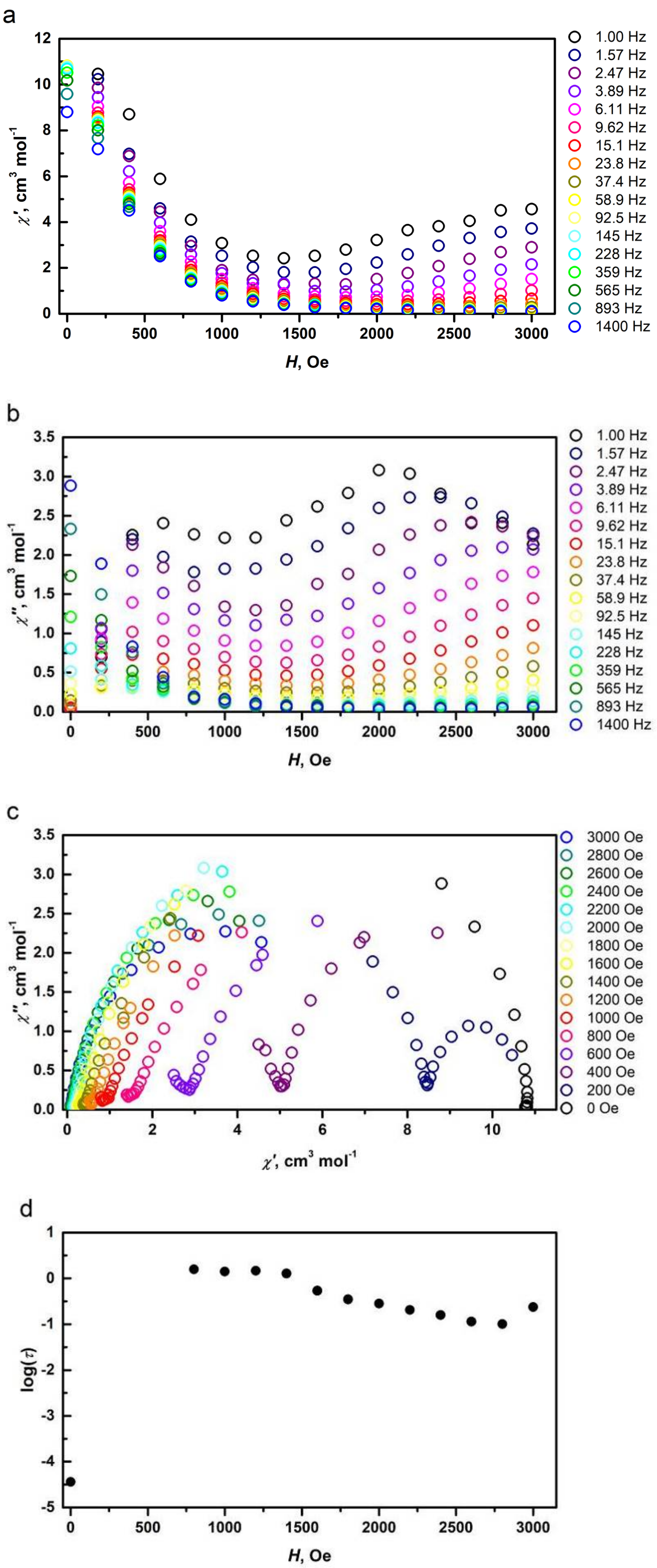

Fig. S11. Field dependences of in-phase (χ'), out-of-phase (χ'') magnetic susceptibilities and log(τ) (T = 2 K) for **2Dy**.

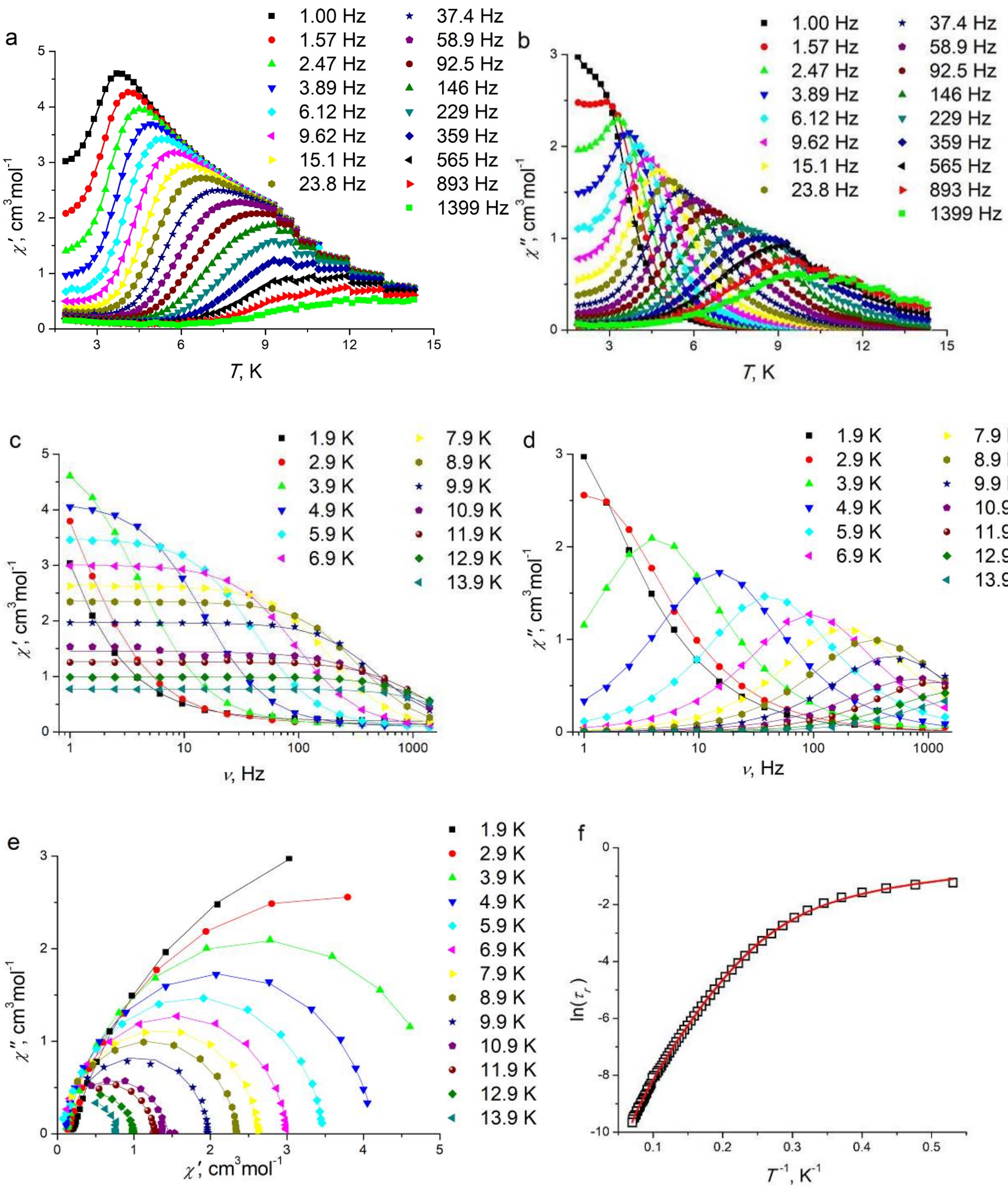

Fig. S12. Temperature and frequency dependences of in-phase (χ') and out-of-phase (χ'') magnetic susceptibilities (H = 0.2 T) for **2Dy**. Solid lines represent the best fits to a generalized Debye model, using the program *cc-fit*[2] (a-e) or to eqn. 2 (from the main text) (f).

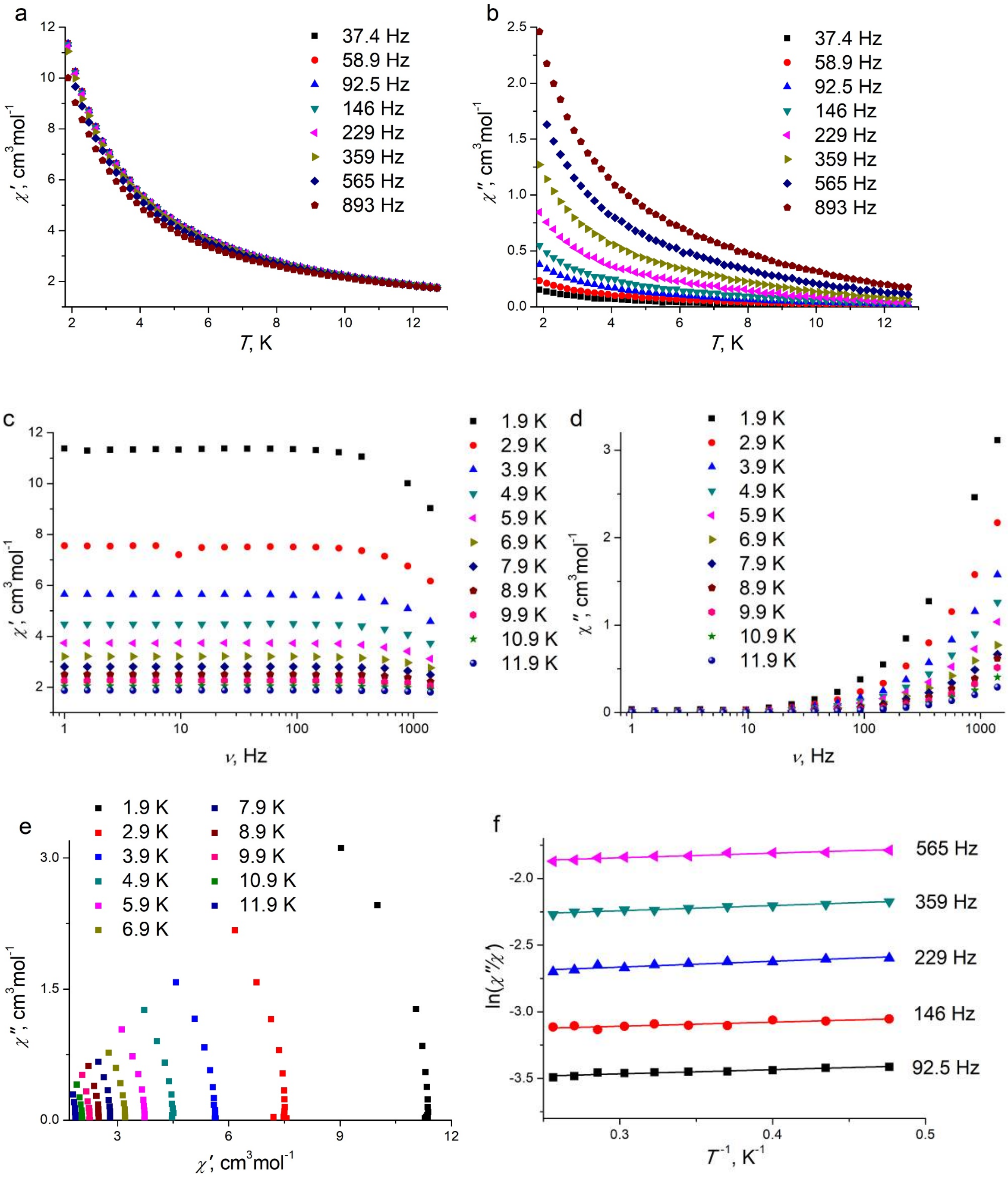

Fig. S13. Temperature and frequency dependences of in-phase (χ') and out-of-phase (χ'') magnetic susceptibilities in zero *dc* field for **2Dy**. Solid lines (d) represent the best fits to eqn. 3 (from the main text) (f).

($Tp_2Dy)_2$pPhd (3Dy)

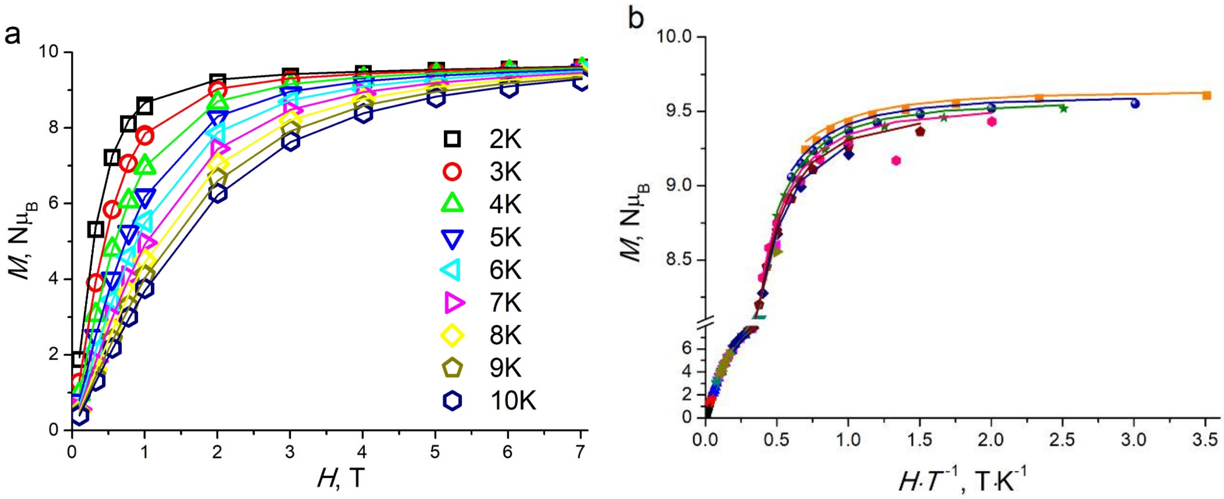

Fig. S14. *M vs*. *H* (a) and *M vs. H/T* (b) dependences for **3Dy**. Solid lines represent the best fits to eqn. 1 (from the main text) using the program PHI.[1]

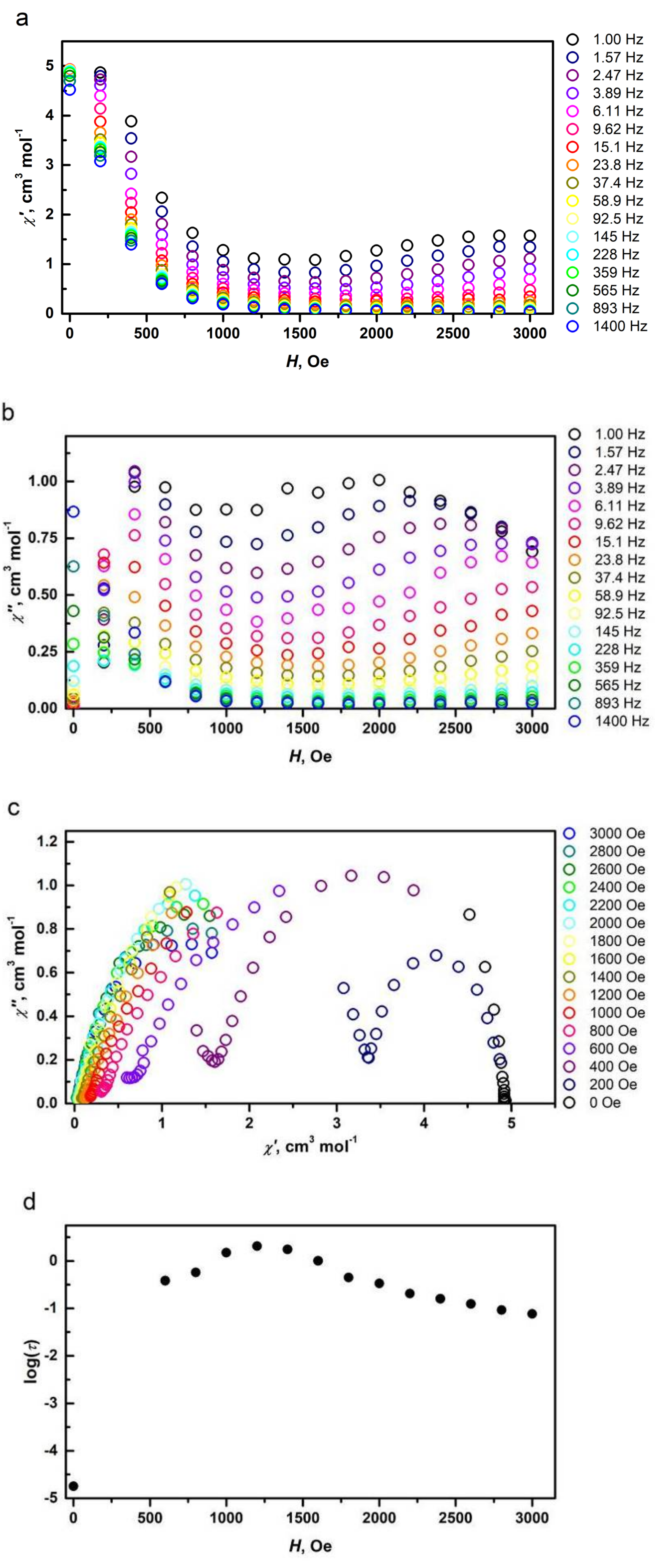

Fig. S15. Field dependences of in-phase (χ'), out-of-phase (χ'') magnetic susceptibilities and log(τ) (T = 2 K) for **3Dy**.

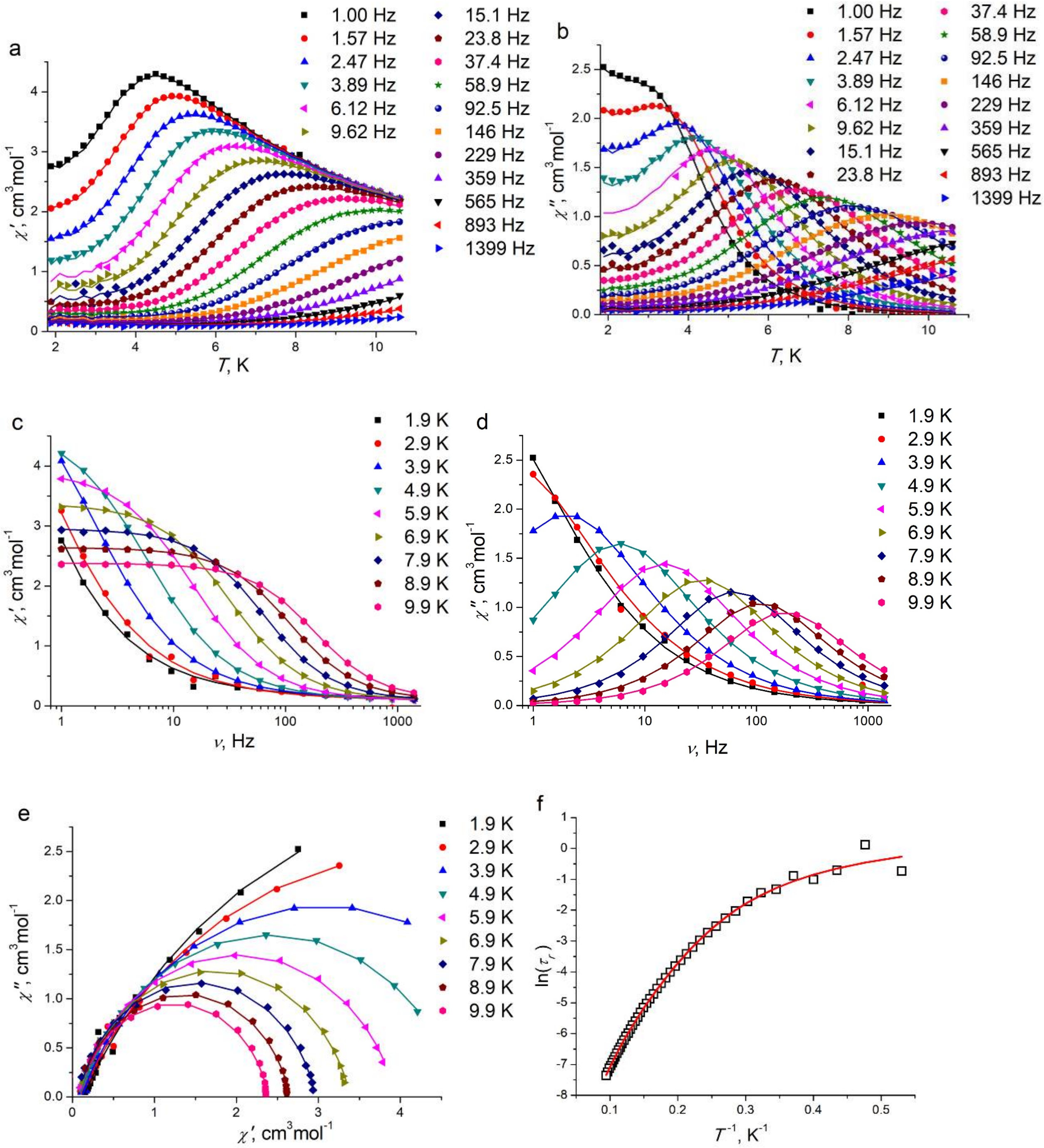

Fig. S16. Temperature and frequency dependences of in-phase (χ') and out-of-phase (χ'') magnetic susceptibilities (H = 0.18 T) for **3Dy**. Solid lines represent the best fits to a generalized Debye model, using the program *cc-fit*[2] (a-e) or to eqn. 2 (from the main text) (f).

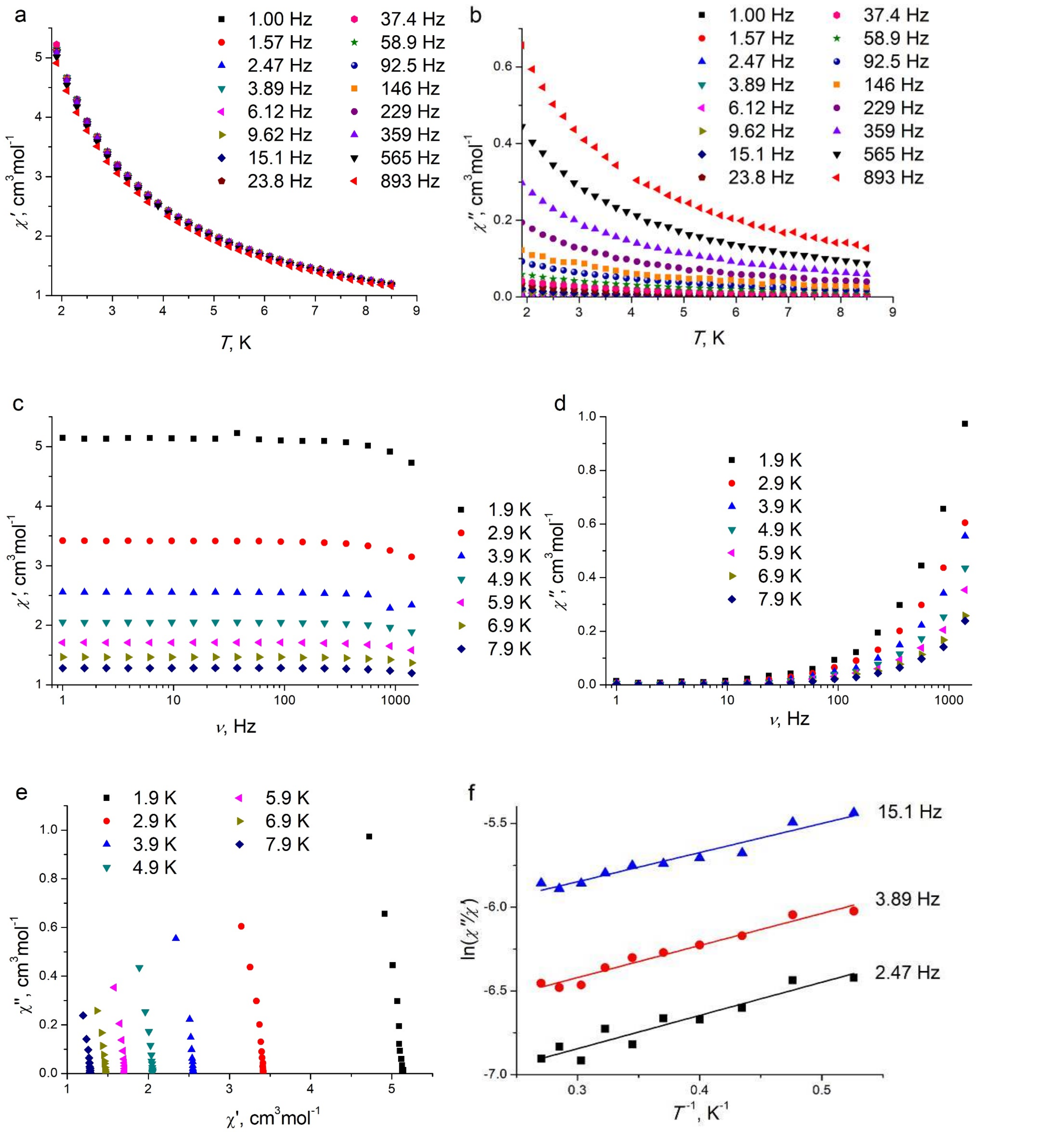

Fig. S17. Temperature and frequency dependences of in-phase (*χ'*) and out-of-phase (*χ''*) magnetic susceptibilities in zero *dc* field for **3Dy**. Solid lines (d) represent the best fits to eqn. 3 (from the main text) (f).

$(Tp_2Dy)_2mPhd$ (4Dy)

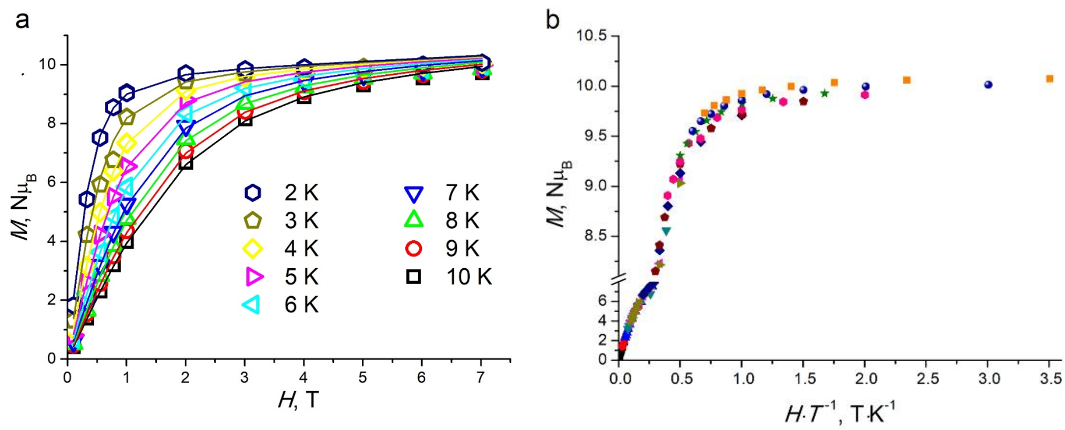

Fig. S18. *M vs. H* (a) and *M vs. H/T* (b) dependences for **4Dy**. Solid lines represent the best fits to eqn. 1 (from the main text) using the program PHI.[1]

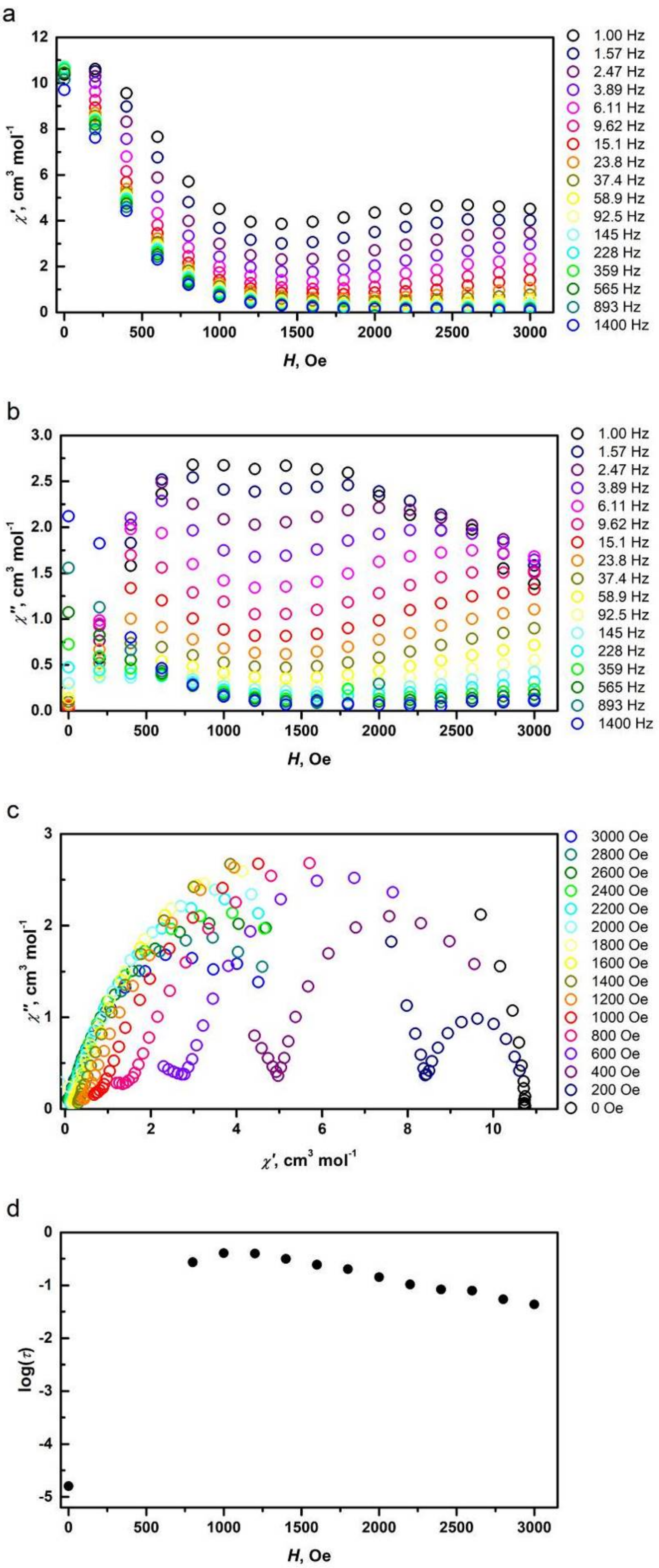

Fig. S19. Field dependences of in-phase (χ'), out-of-phase (χ'') magnetic susceptibilities and log(τ) (T = 2 K) for **4Dy**.

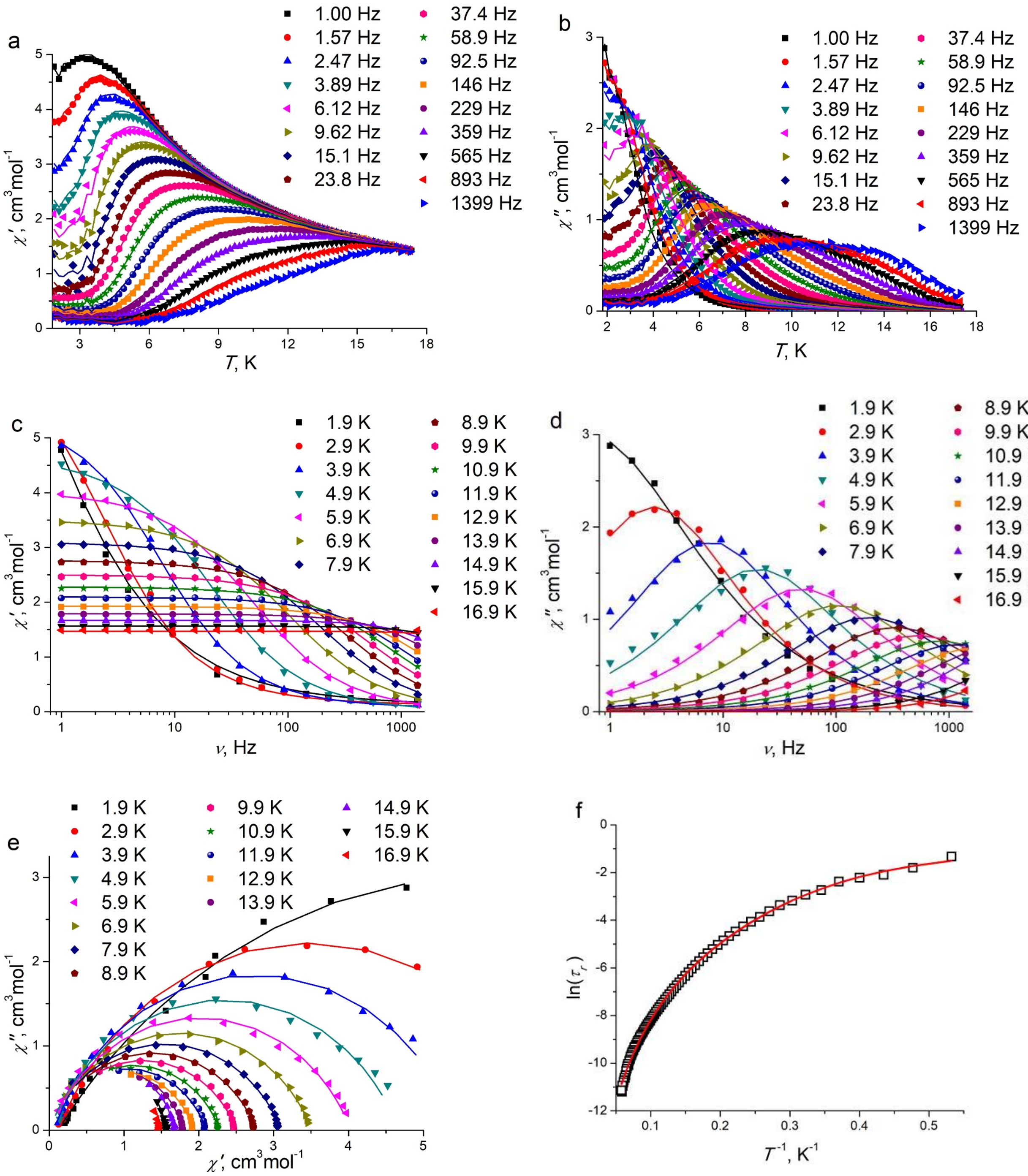

Fig. S20. Temperature and frequency dependences of in-phase (χ') and out-of-phase (χ'') magnetic susceptibilities ($H = 0.18$ T) for **4Dy**. Solid lines represent the best fits to a generalized Debye model, using the program *cc-fit*[2] (a-e) or to eqn. 2 (from the main text) (f).

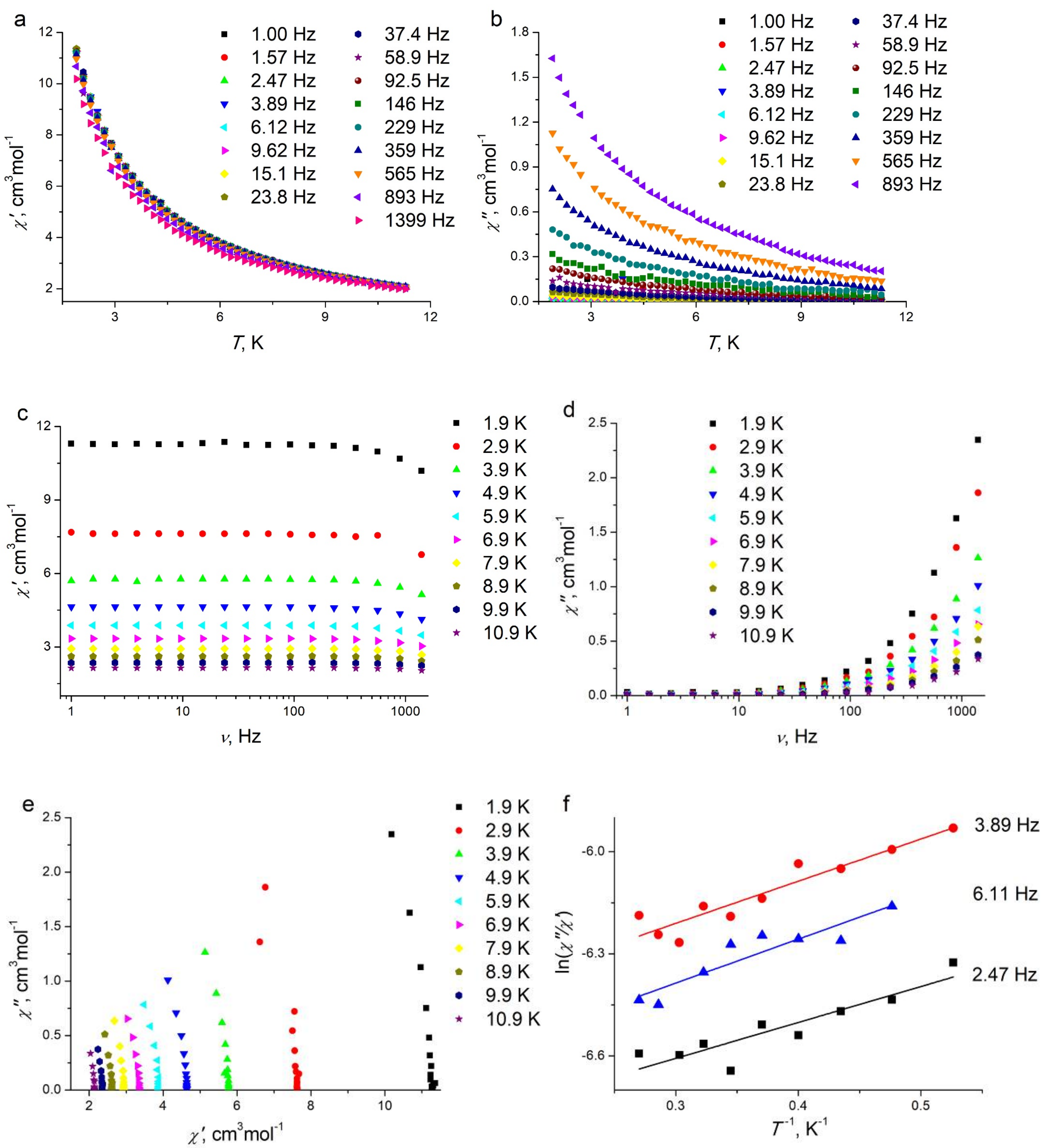

Fig. S21. Temperature and frequency dependences of in-phase (χ') and out-of-phase (χ'') magnetic susceptibilities in zero *dc* field for **4Dy**. Solid lines (d) represent the best fits to eqn. 3 (from the main text) (f).

(Tp$_2$Dy)$_3$Pht (5Dy)

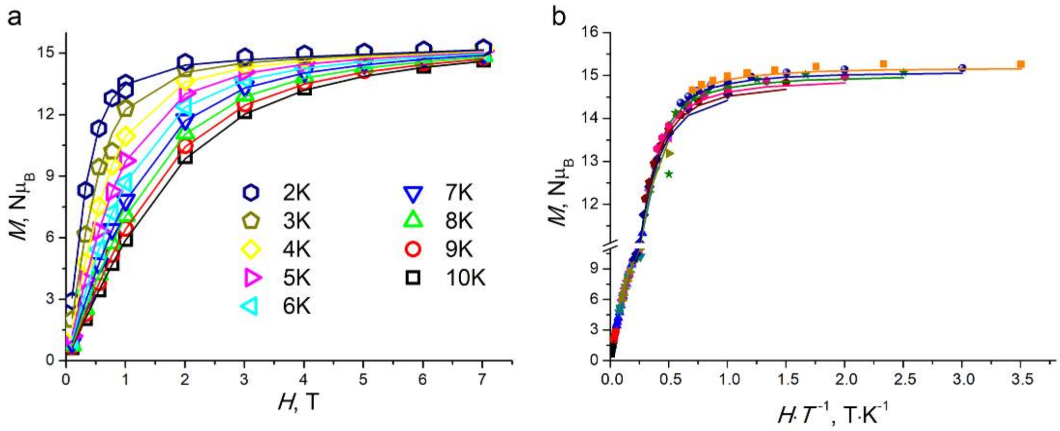

Fig. S22. *M vs*. *H* (a) and *M vs. H/T* (b) dependences for **5Dy**. Solid lines represent the best fits to eqn. 1 (from the main text) using the program PHI.[1]

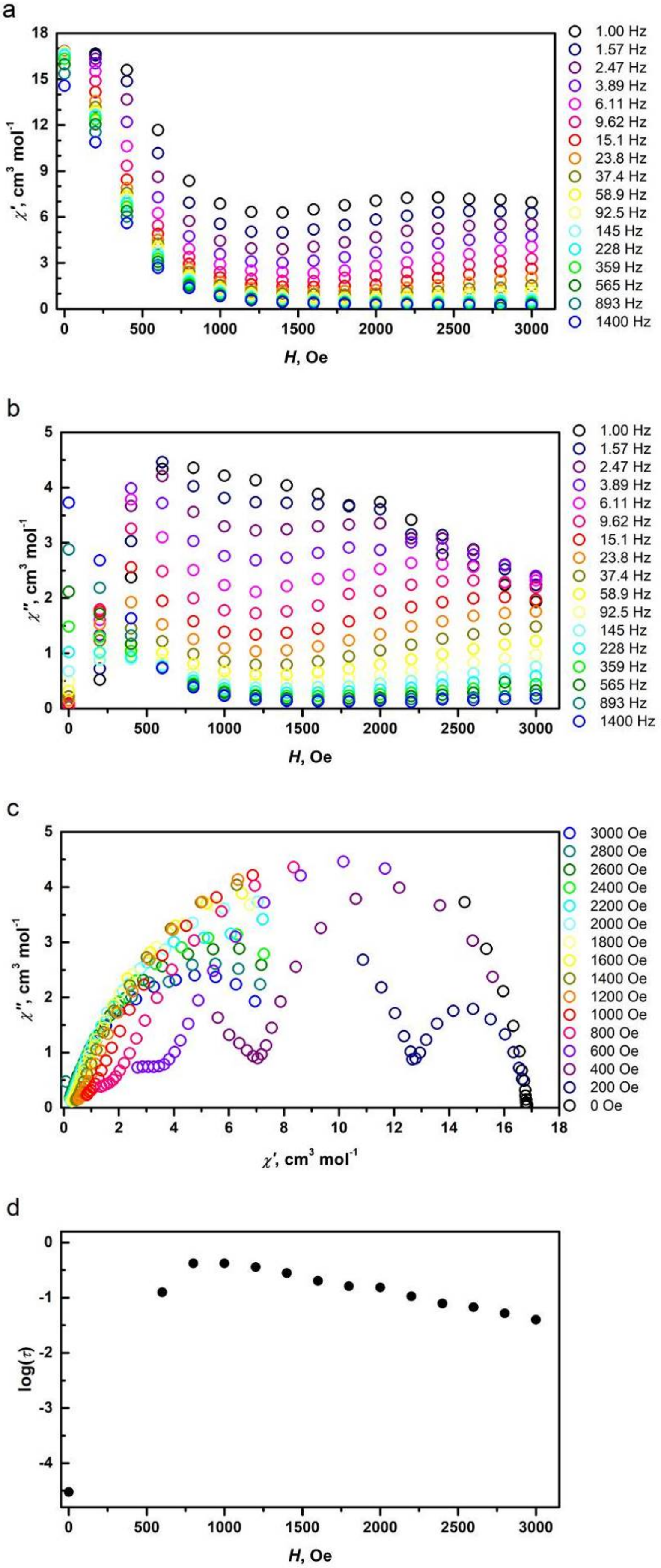

Fig. S23. Field dependences of in-phase (χ'), out-of-phase (χ'') magnetic susceptibilities and log(τ) (T = 2 K) for **5Dy**.

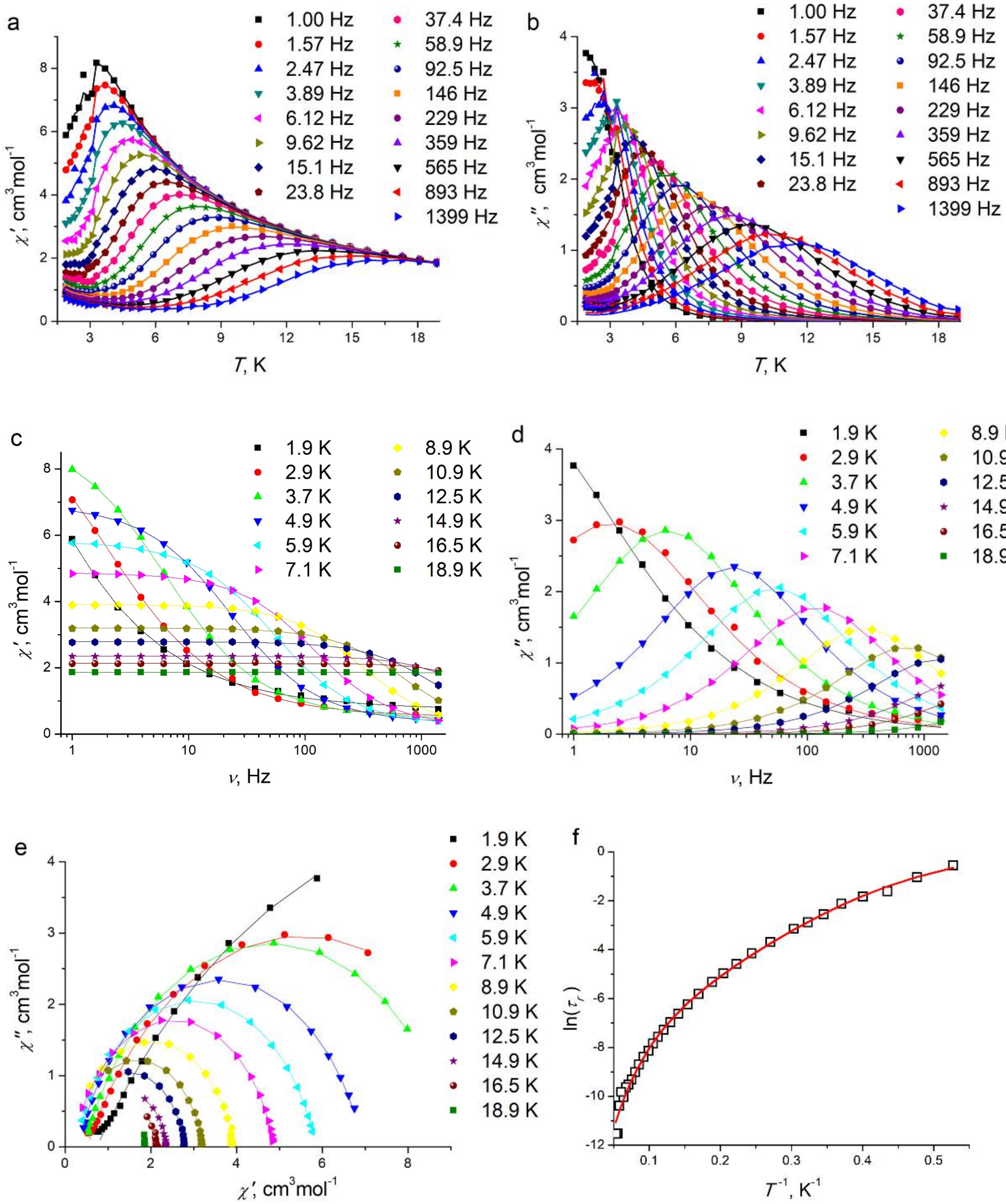

Fig. S24. Temperature and frequency dependences of in-phase (χ') and out-of-phase (χ'') magnetic susceptibilities (H = 0.1 T) for **5Dy**. Solid lines represent the best fits to a generalized Debye model, using the program *cc-fit*[2] (a-e) or to eqn. 2 (from the main text) (f).

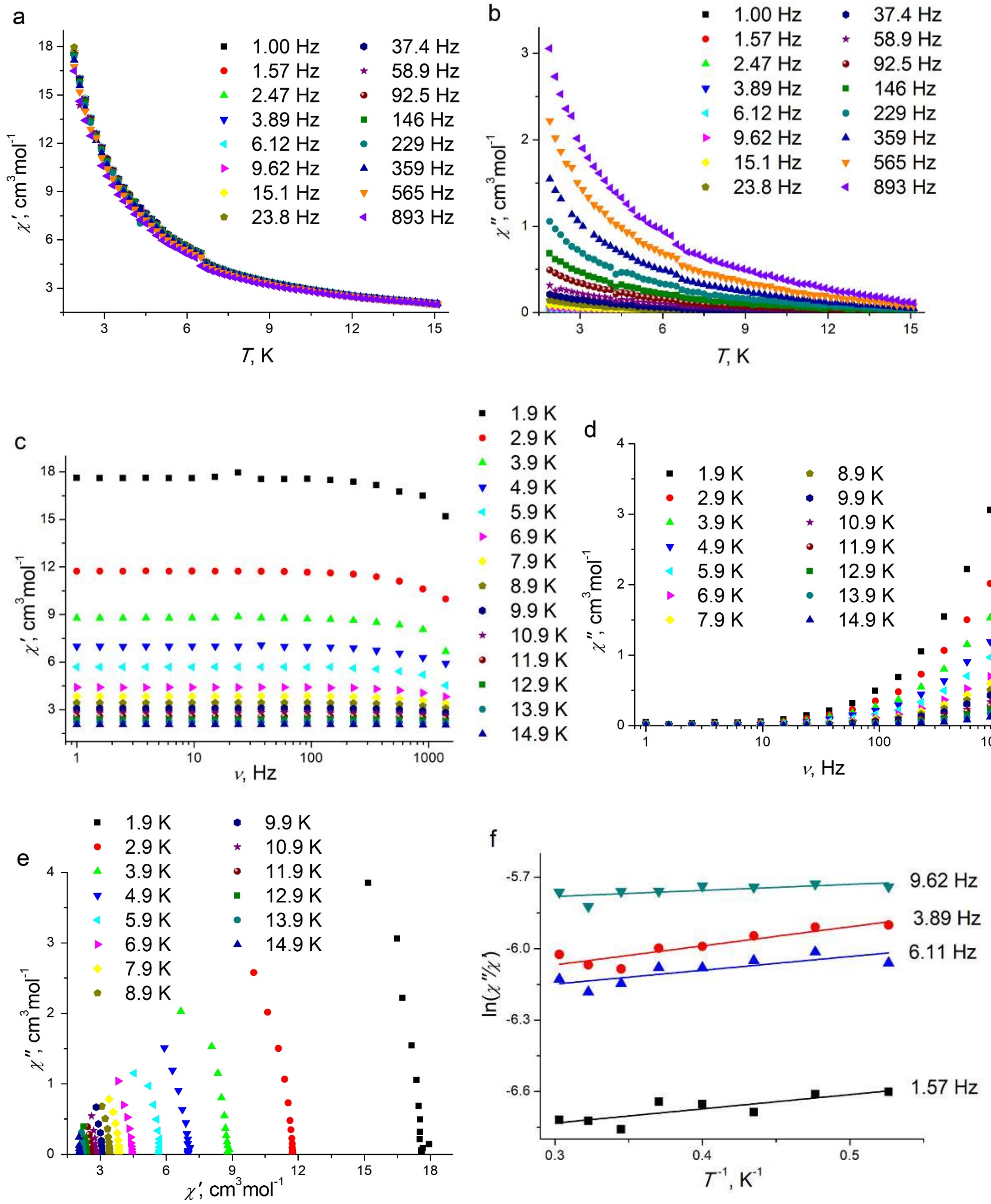

Fig. S25. Temperature and frequency dependences of in-phase (χ') and out-of-phase (χ'') magnetic susceptibilities in zero *dc* field for **5Dy**. Solid lines (d) represent the best fits to eqn. 3 (from the main text) (f).

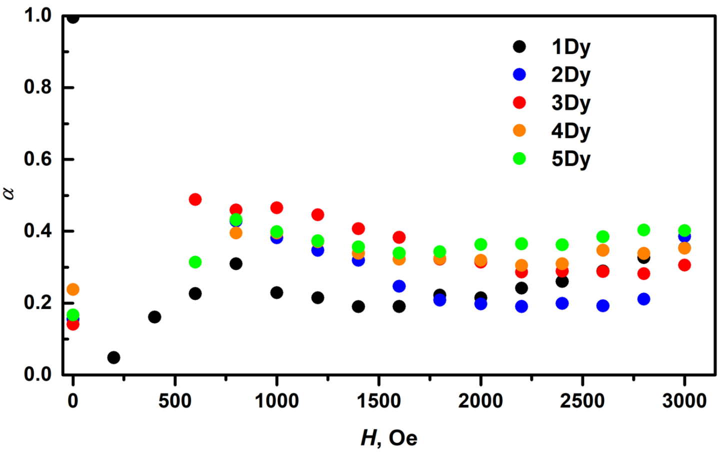

Fig. S26. Field dependences of α for **1Dy-5Dy** compounds.

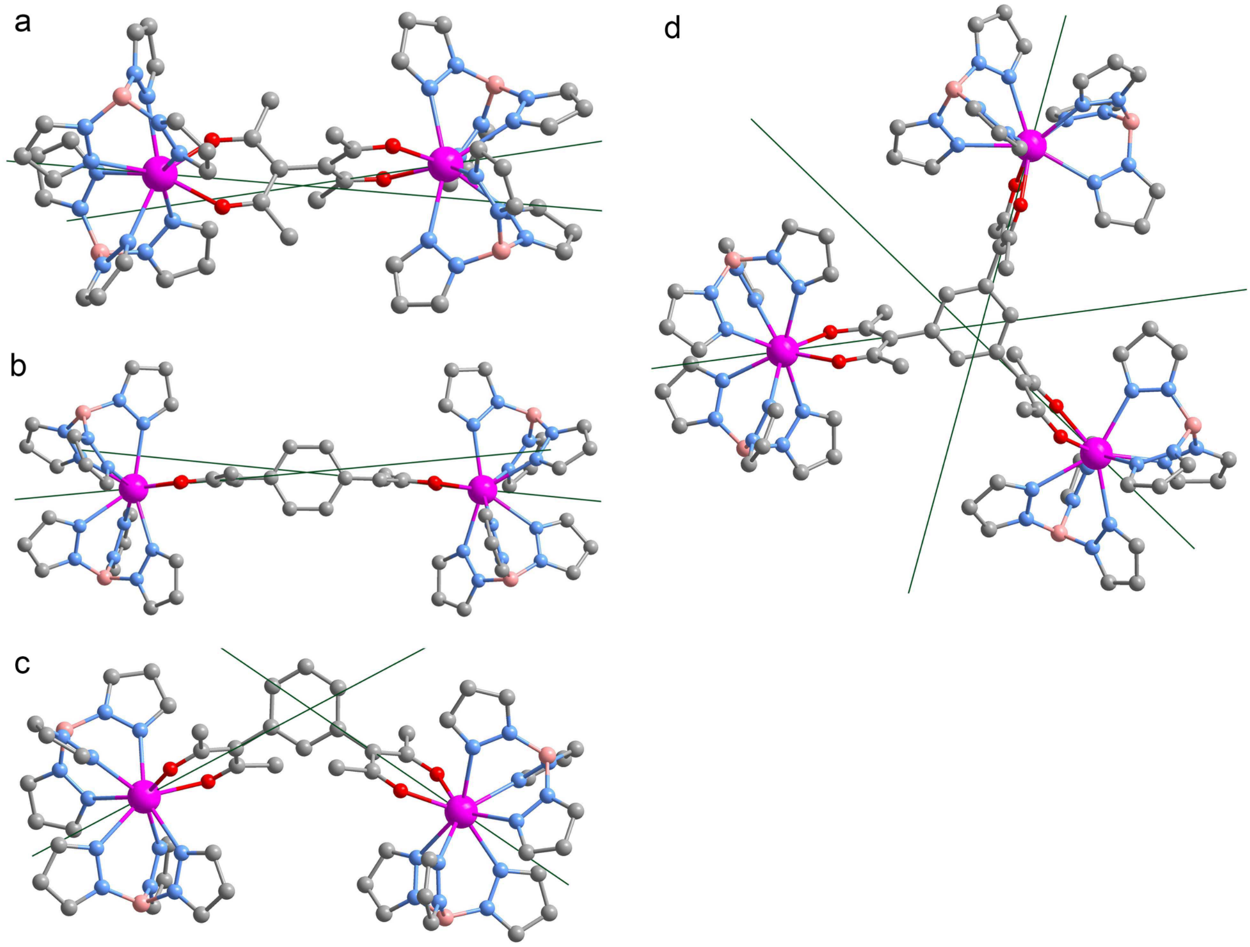

Fig. S27. The directions of the anisotropy axes in **2Dy** (a), **3Dy** (b), **4Dy** (c), **5Dy** (d) estimated by an electrostatic model using *MAGELLAN*.[3]

Table S5. Estimated from eqn. 3: U_{eff} and τ_0 for Dy^{3+} complexes displaying no maxima for their temperature dependence of χ'' in zero *dc* field

	U_{eff} (cm^{-1})	τ_0 (s)
1Dy	-	-
2Dy	0.5(2)	$2.4(1)\cdot10^{-4}$
3Dy	1.0±0.5	$1.5(3)\cdot10^{-4}$
4Dy	1.0±0.5	$2.1(2)\cdot10^{-4}$
5Dy	0.5(3)	$3.2(1)\cdot10^{-4}$

Tp_2TbPhm (1Tb)

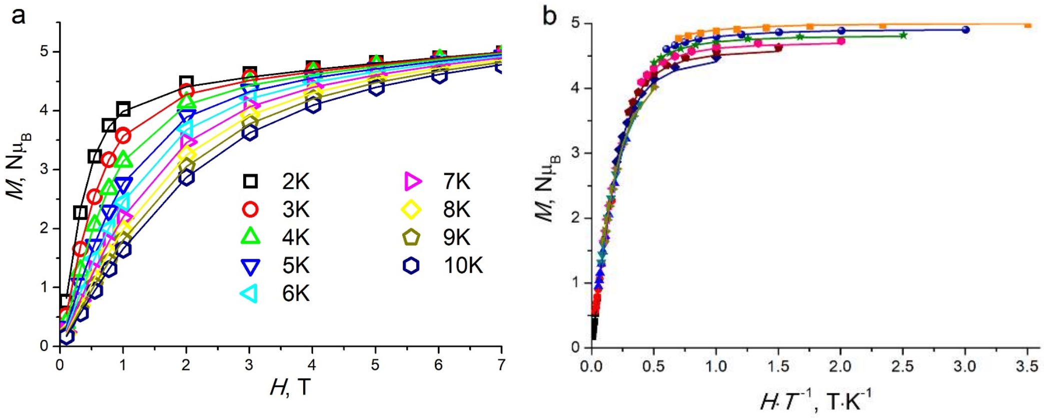

Fig. S28. *M vs*. *H* (a) and *M vs. H/T* (b) dependences for **1Tb**. Solid lines represent the best fits to eqn. 1 (from the main text) using the program PHI.[1]

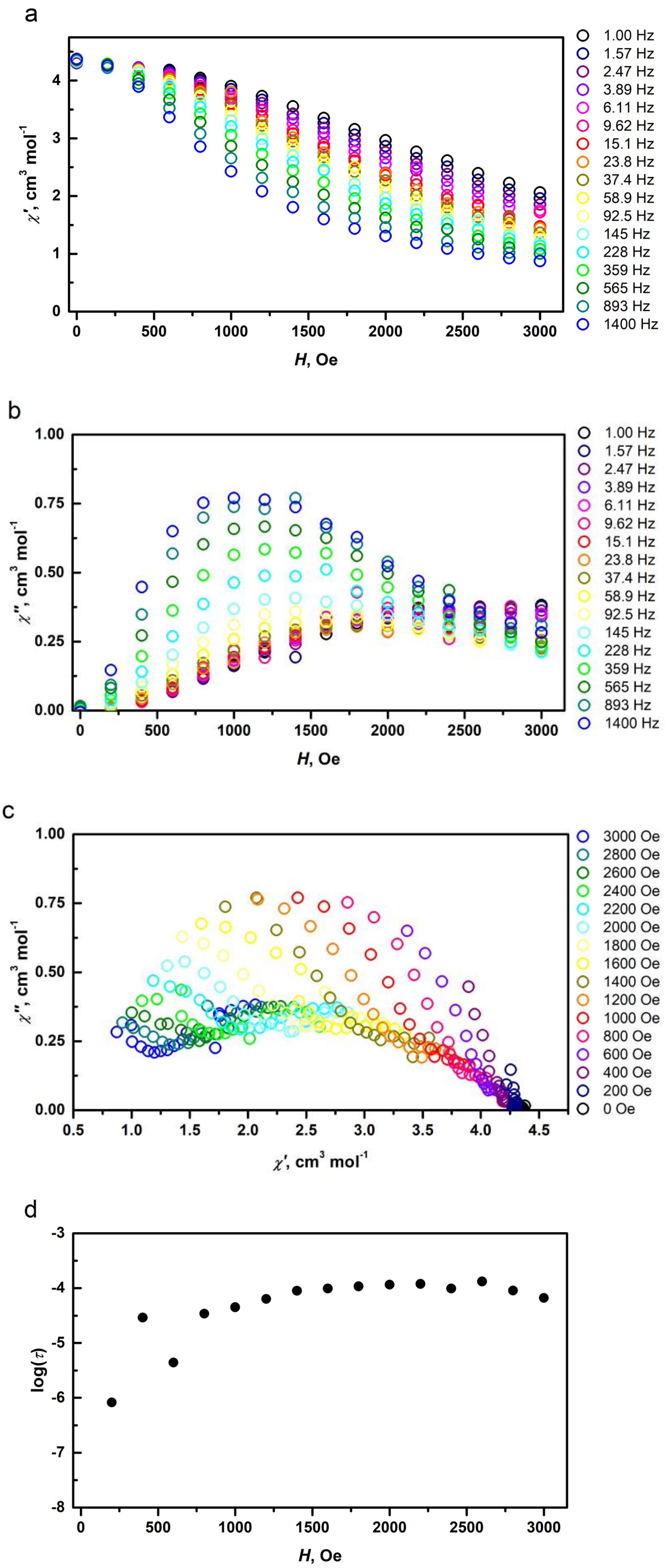

Fig. S29. Field dependences of in-phase (χ'), out-of-phase (χ'') magnetic susceptibilities and log(τ) (T = 2 K) for **1Tb**.

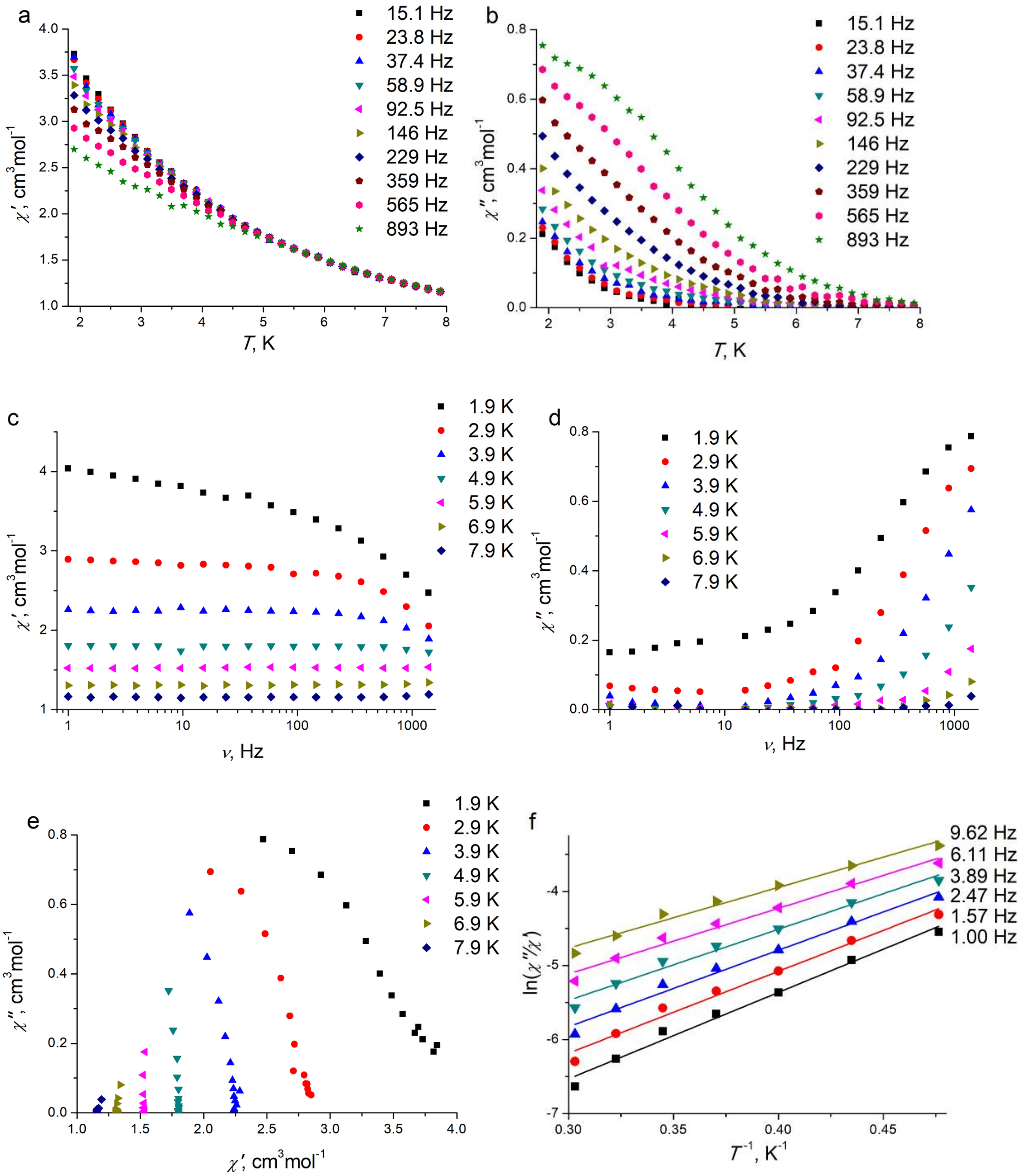

Fig. S30. Temperature and frequency dependences of in-phase (χ') and out-of-phase (χ'') magnetic susceptibilities (H = 0.1 T) for **1Tb**. Solid lines (d) represent the best fits to eqn. 3 (from the main text) (f).

$(Tp_2Tb)_2Tae$ (2Tb)

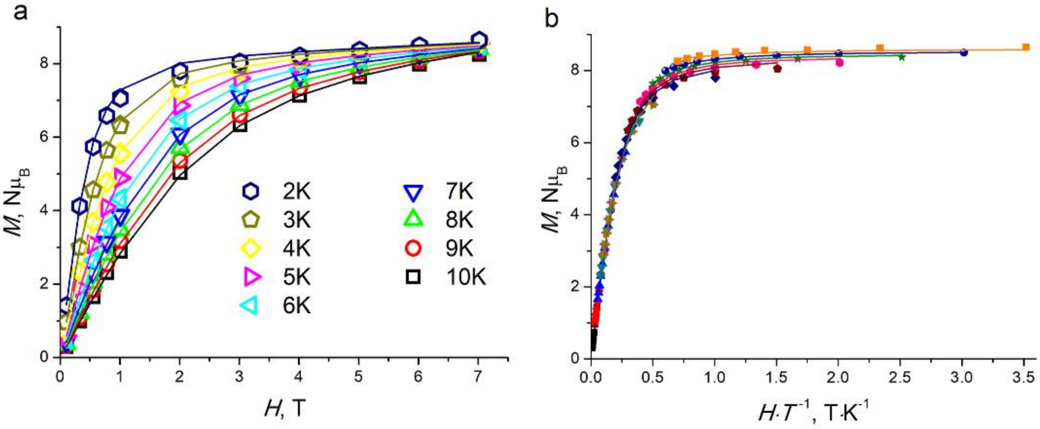

Fig. S31. *M vs*. *H* (a) and *M vs. H/T* (b) dependences for **2Tb**. Solid lines represent the best fits to eqn. 1 (from the main text) using the program PHI.[1]

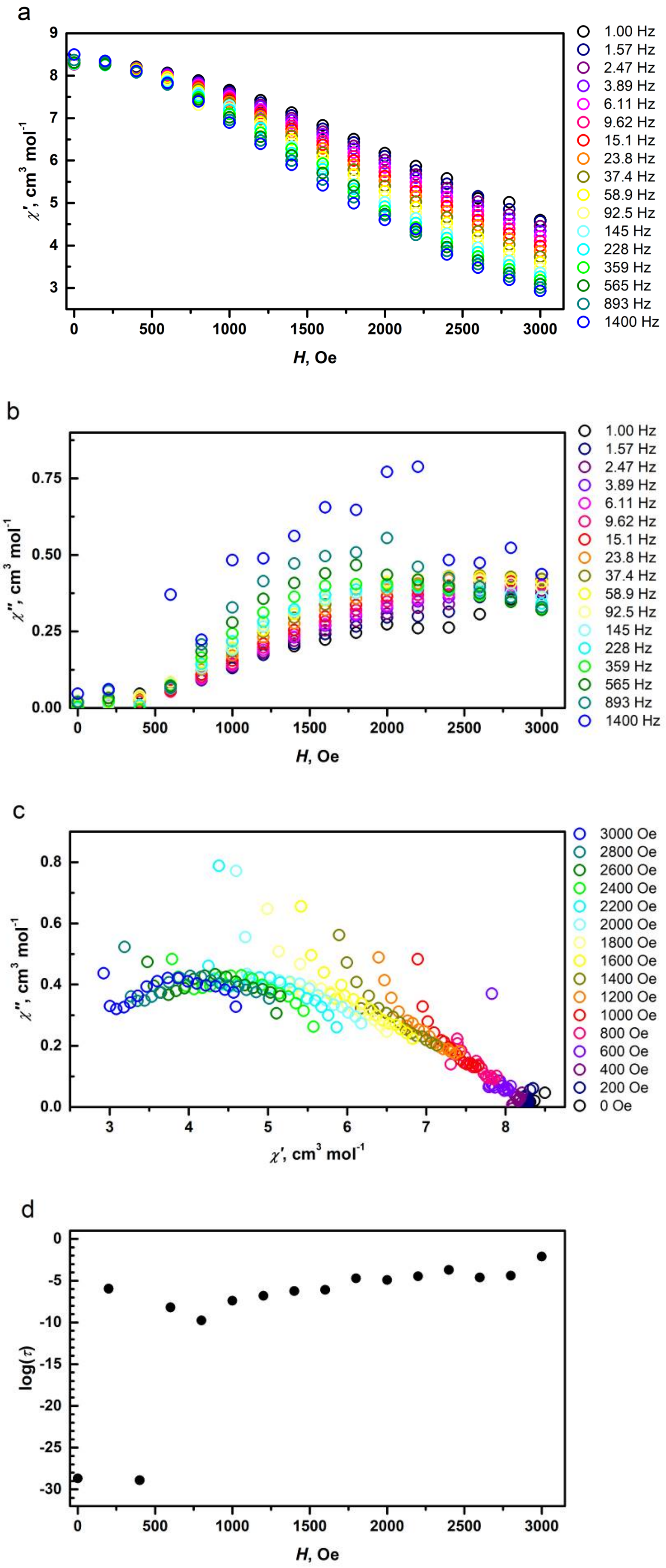

Fig. S32. Field dependences of in-phase (χ'), out-of-phase (χ'') magnetic susceptibilities and $\log(\tau)$ ($T = 2$ K) for **2Tb**.

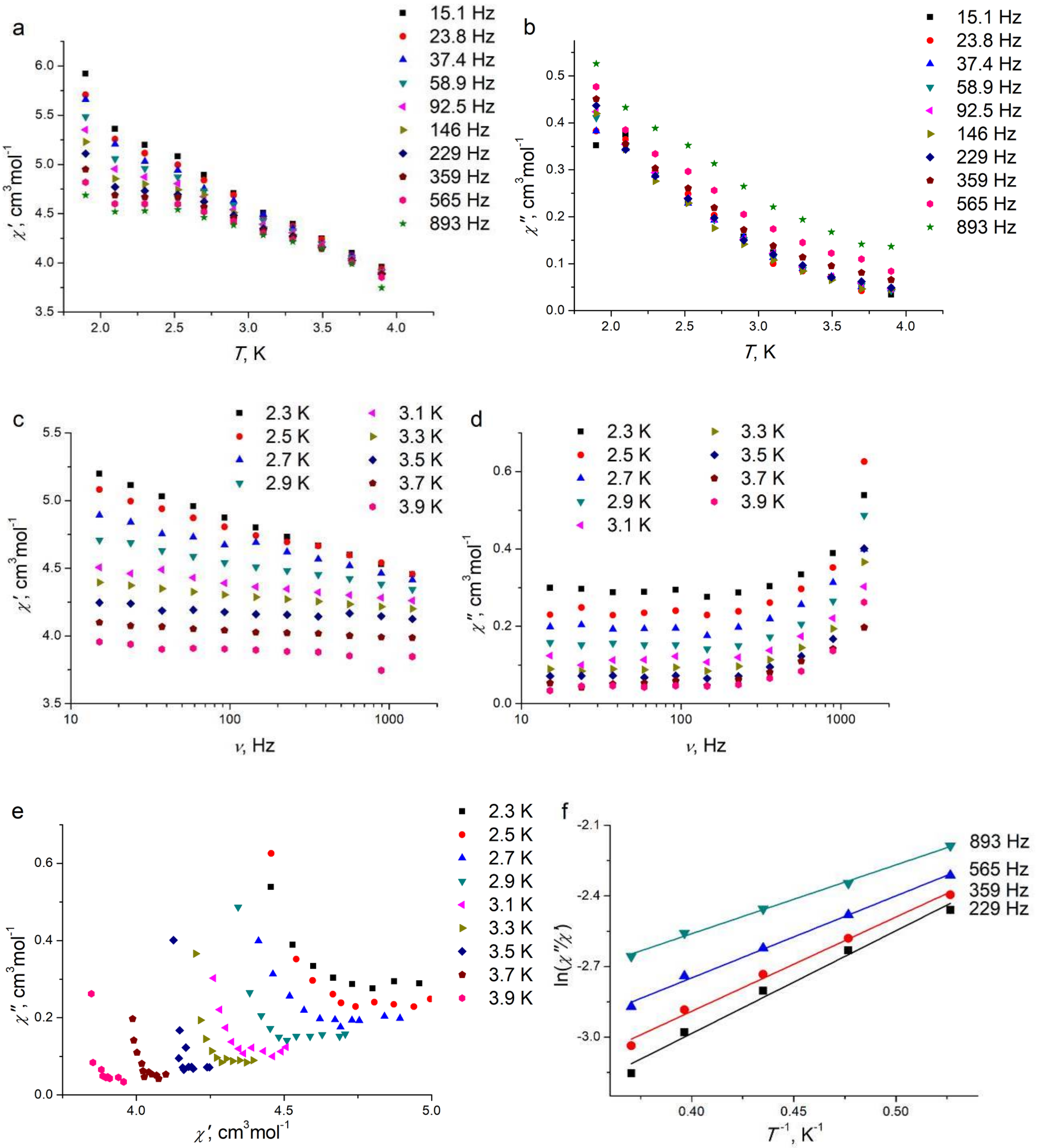

Fig. S33. Temperature and frequency dependences of in-phase (χ') and out-of-phase (χ'') magnetic susceptibilities (H = 0.2 T) for **2Tb**. Solid lines (d) represent the best fits to eqn. 3 (from the main text) (f).

$(Tp_2Tb)_2pPhd$ (3Tb)

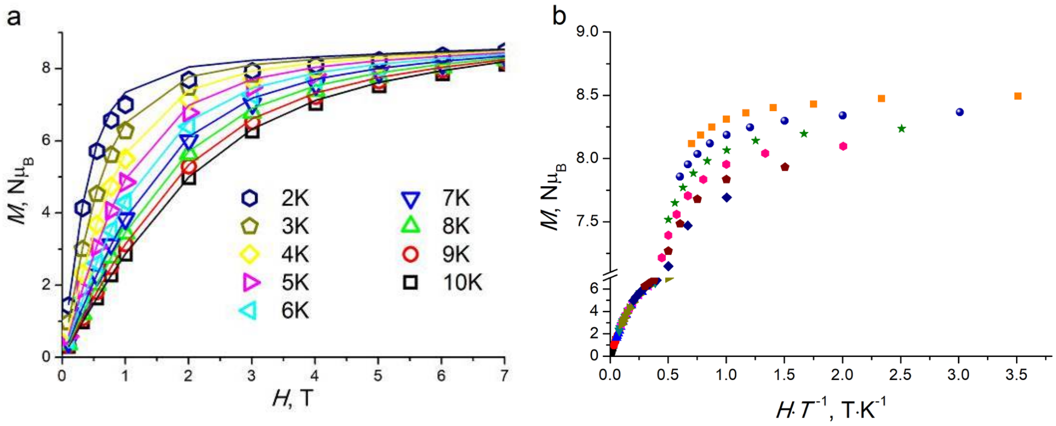

Fig. S34. *M vs. H* (a) and *M vs. H/T* (b) dependences for **3Tb**. Solid lines represent the best fits to eqn. 1 (from the main text) using the program PHI.[1]

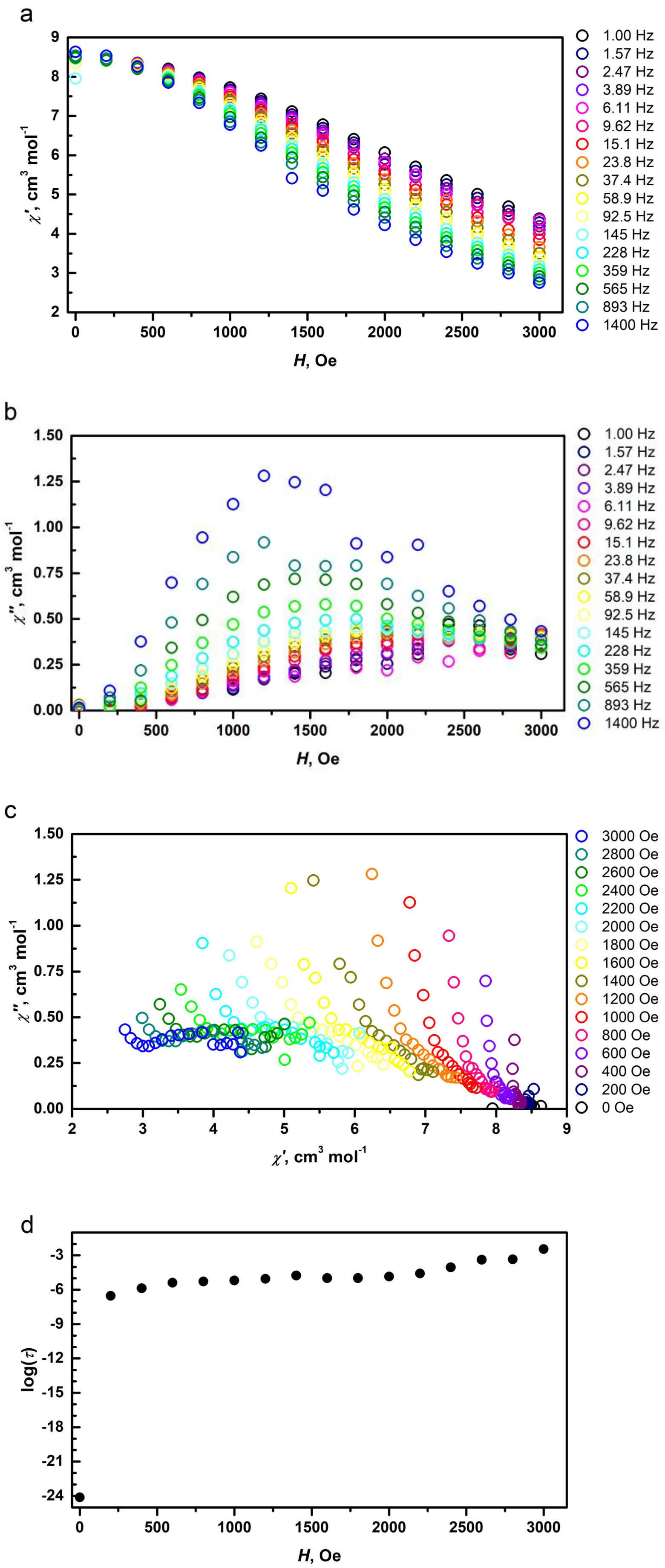

Fig. S35. Field dependences of in-phase (χ'), out-of-phase (χ'') magnetic susceptibilities and log(τ) ($T = 2$ K) for **3Tb**.

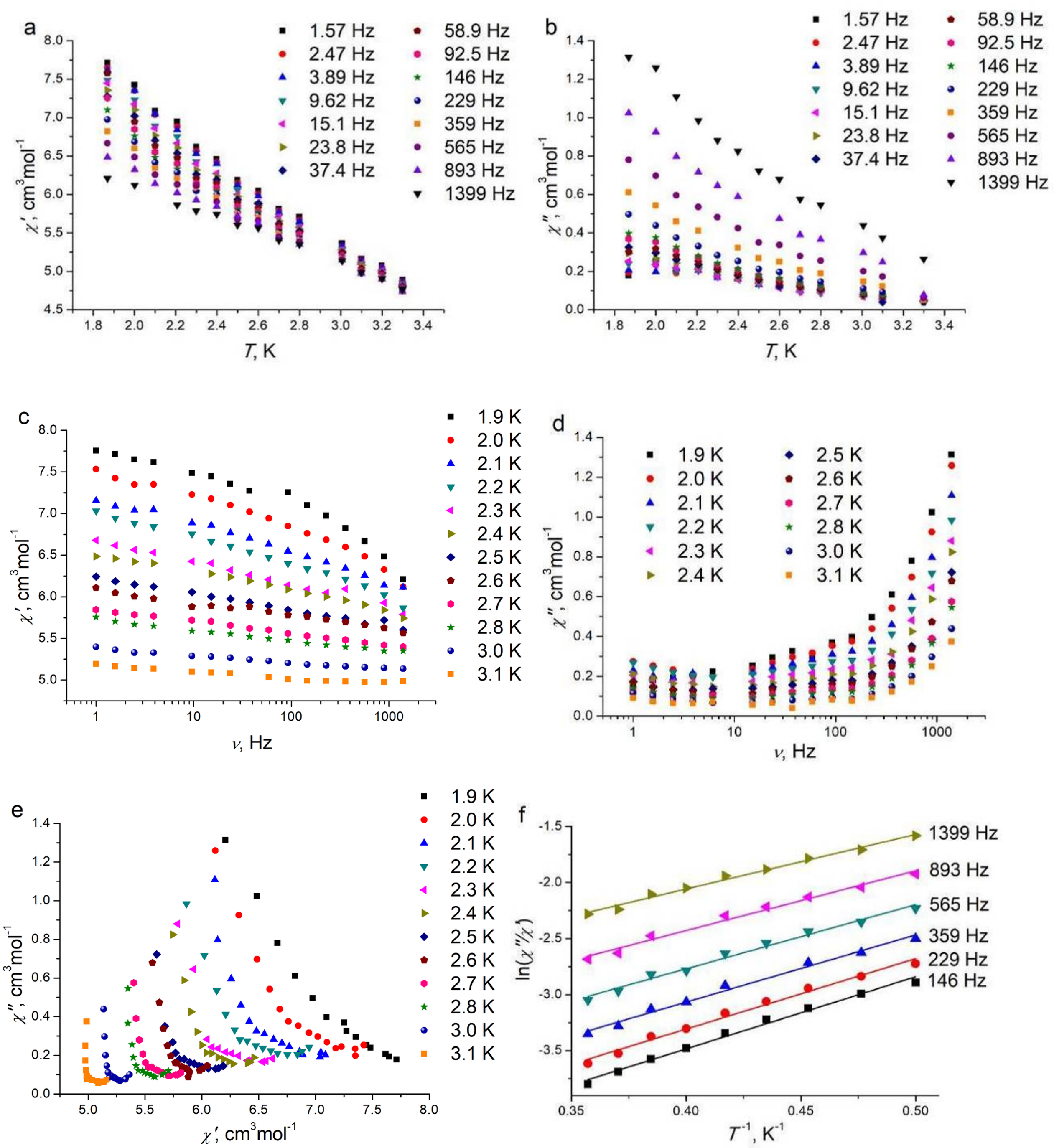

Fig. S36. Temperature and frequency dependences of in-phase (χ') and out-of-phase (χ'') magnetic susceptibilities (H = 0.12 T) for **3Tb**. Solid lines (d) represent the best fits to eqn. 3 (from the main text) (f).

$(Tp_2Tb)_2mPhd$ (4Tb)

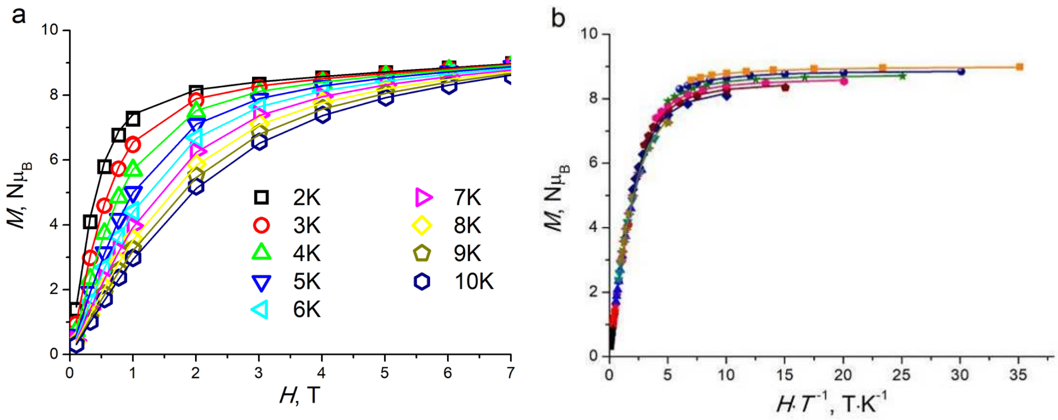

Fig. S37. *M vs. H* (a) and *M vs. H/T* (b) dependences for **4Tb**. Solid lines represent the best fits to eqn. 1 (from the main text) using the program PHI.[1]

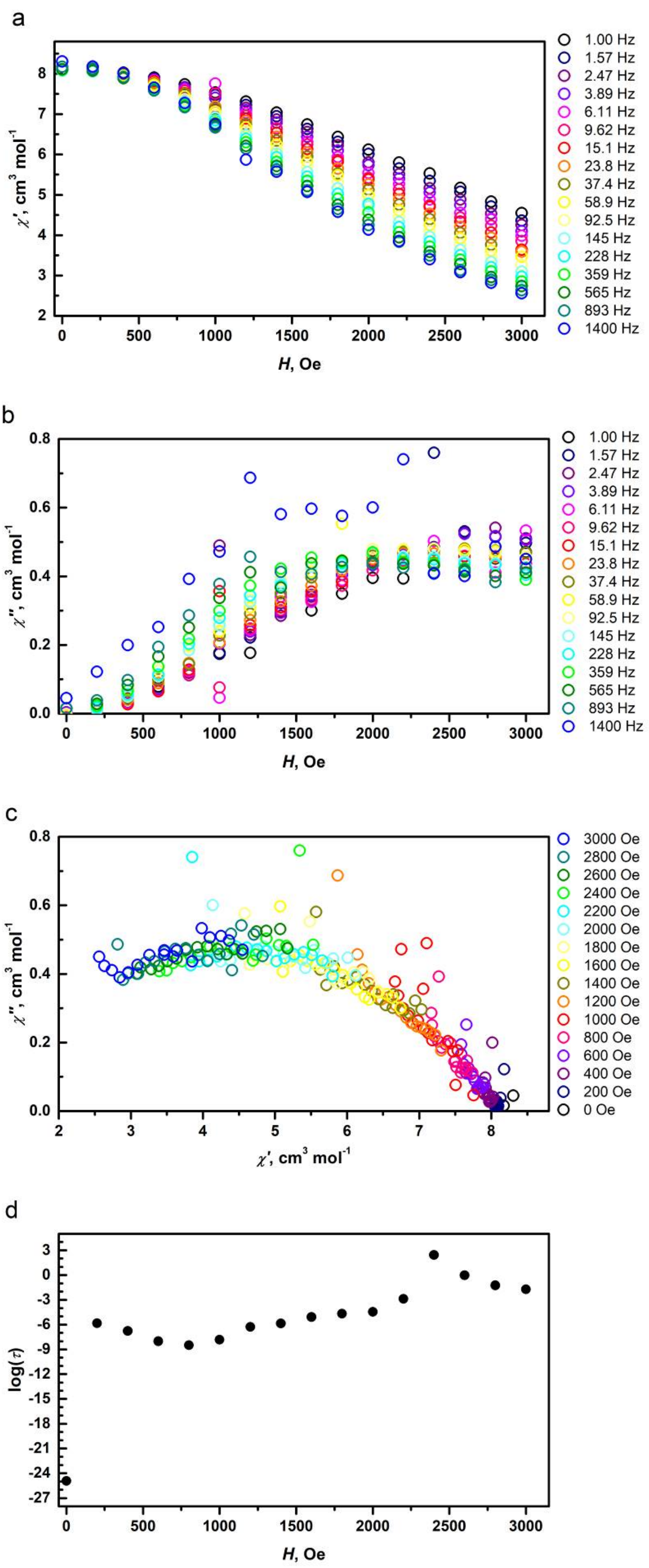

Fig. S38. Field dependences of in-phase (χ'), out-of-phase (χ'') magnetic susceptibilities and log(τ) ($T = 2$ K) for **4Tb**.

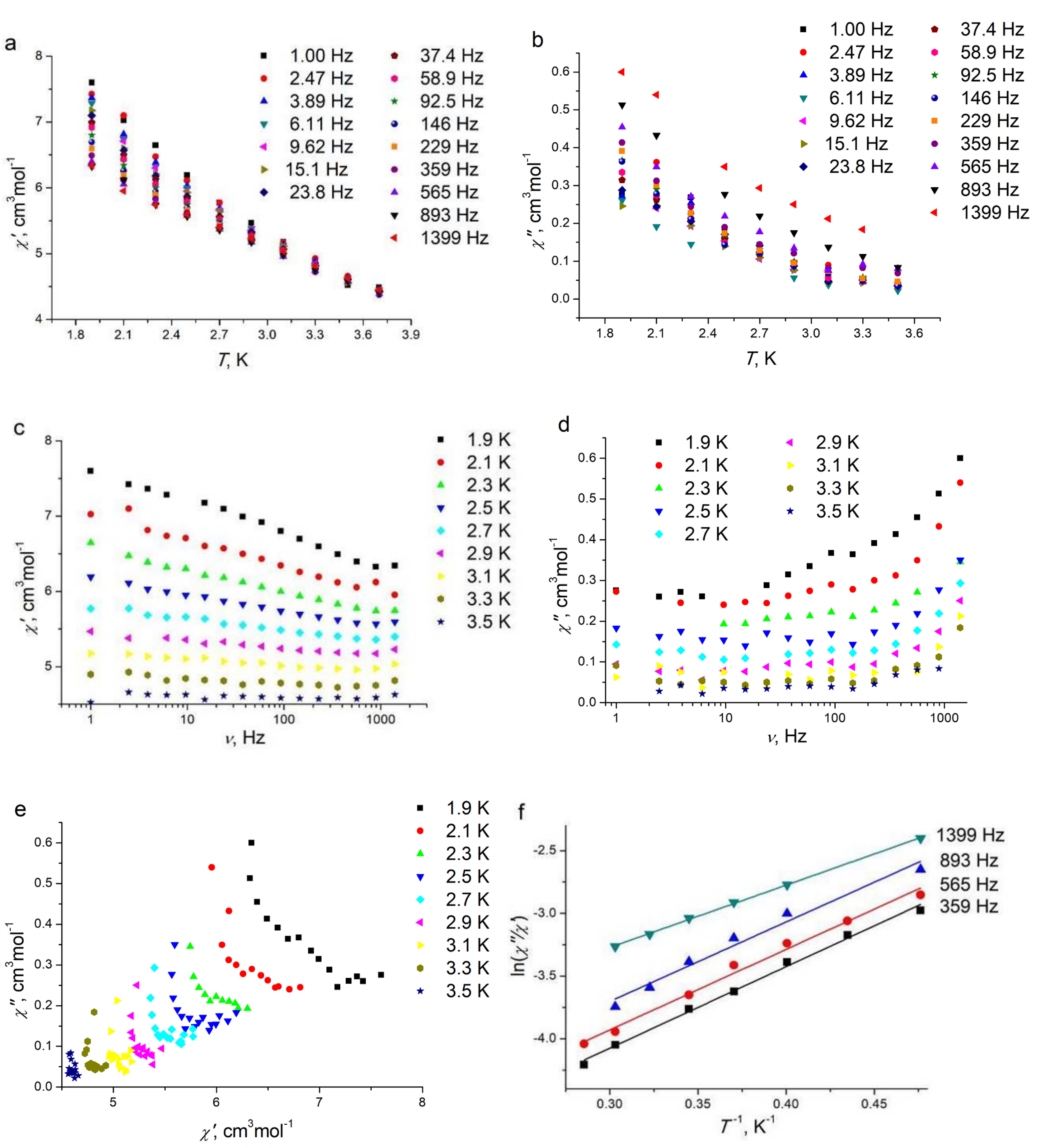

Fig. S39. Temperature and frequency dependences of in-phase (χ') and out-of-phase (χ'') magnetic susceptibilities (H = 0.12 T) for **4Tb**. Solid lines (d) represent the best fits to eqn. 3 (from the main text) (f).

$(Tp_2Tb)_3Pht$ (5Tb)

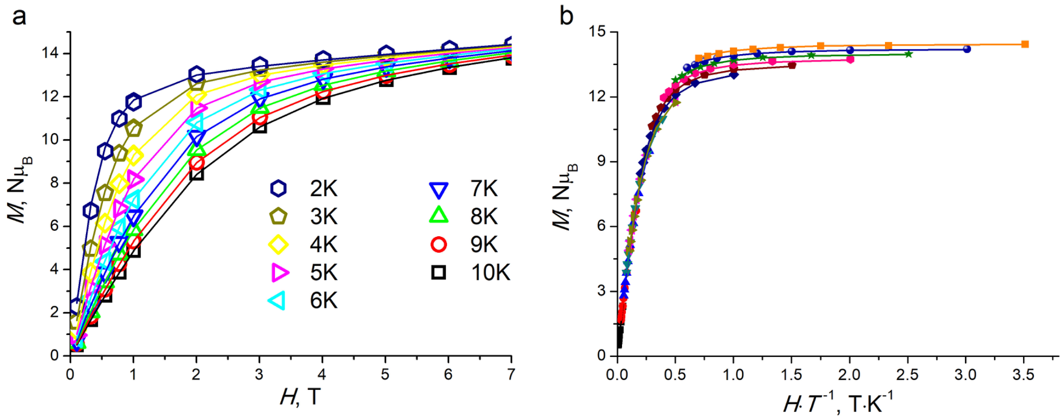

Fig. S40. *M vs. H* (a) and *M vs. H/T* (b) dependences for **5Tb**. Solid lines represent the best fits to eqn. 1 (from the main text) using the program PHI.[1]

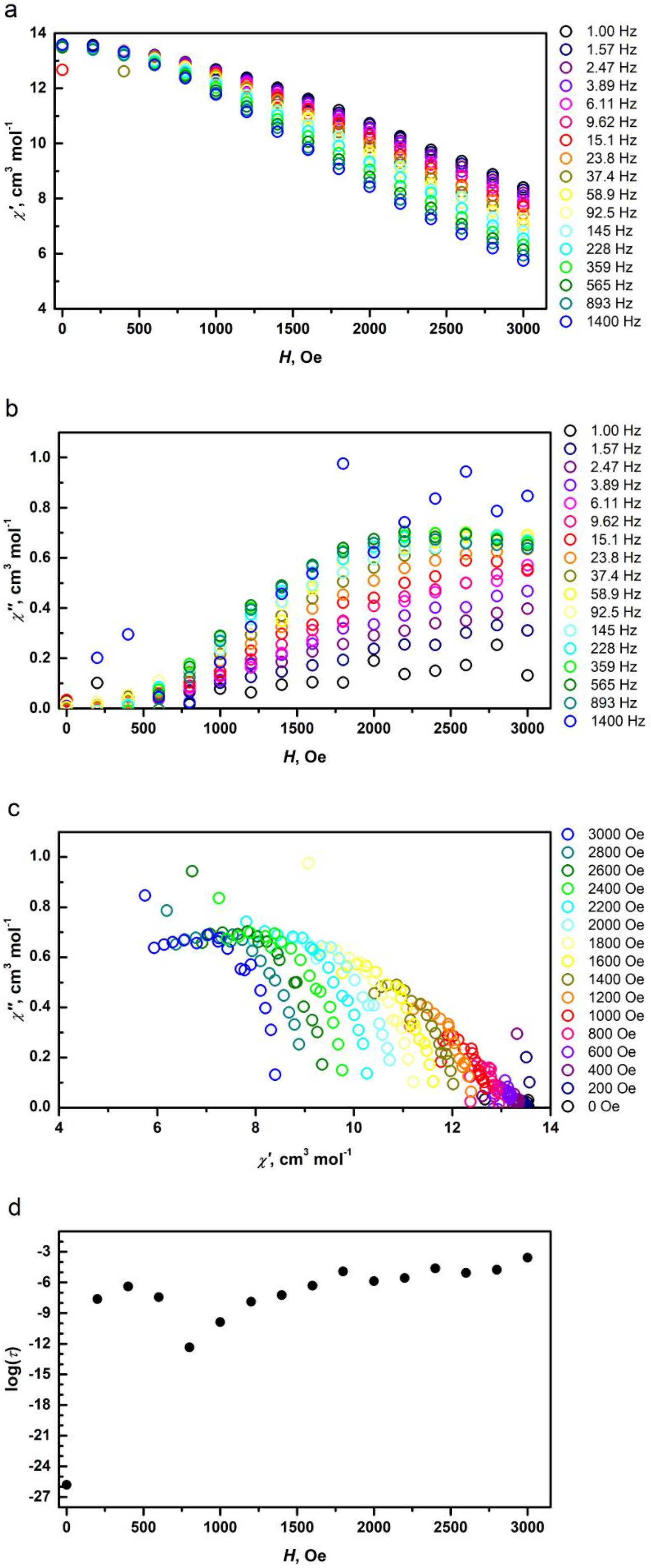

Fig. S41. Field dependences of in-phase (χ'), out-of-phase (χ'') magnetic susceptibilities and log(τ) (T = 2 K) for **5Tb**.

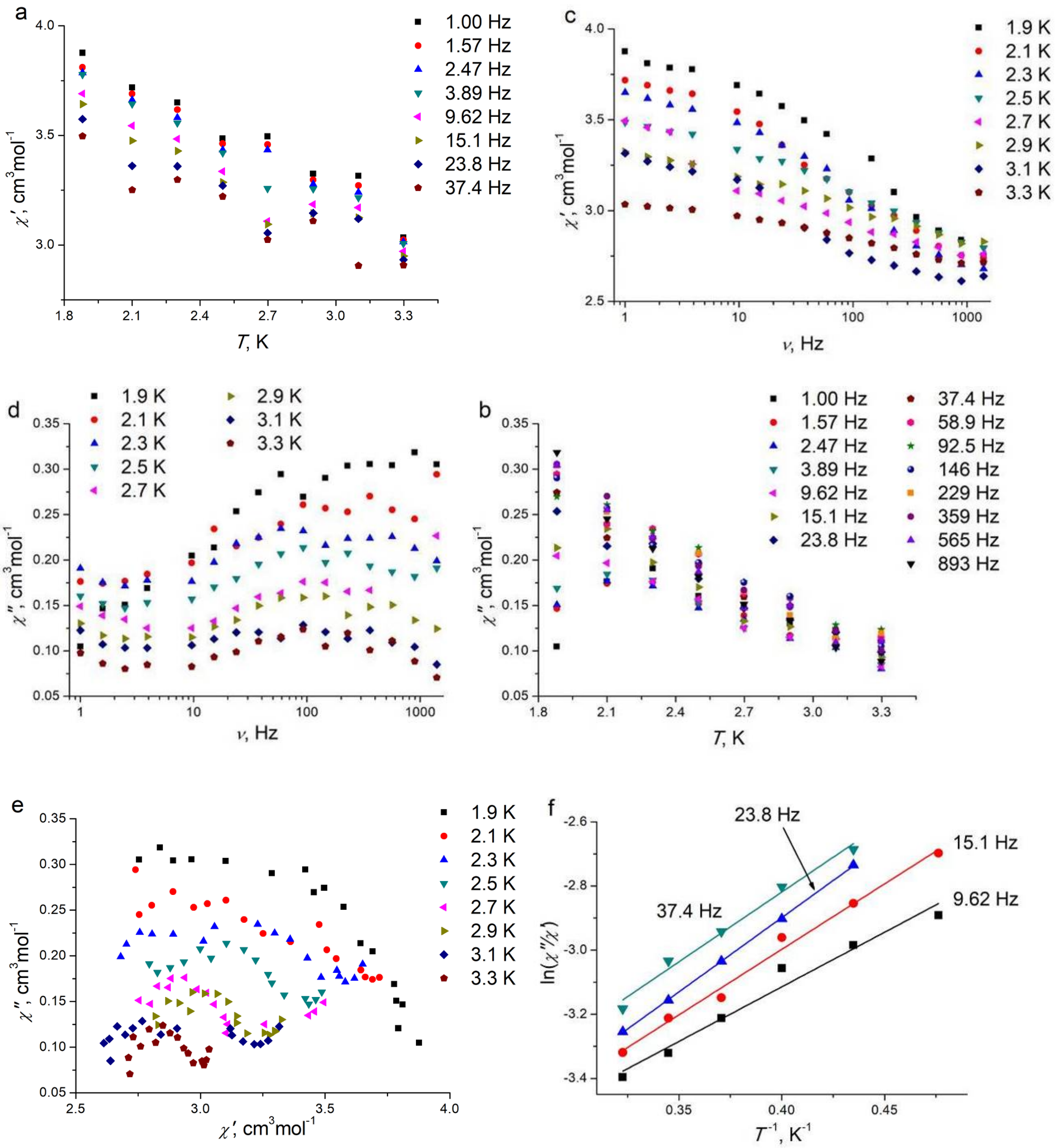

Fig. S42. Temperature and frequency dependences of in-phase (χ') and out-of-phase (χ'') magnetic susceptibilities (H = 0.26 T) for **5Tb**. Solid lines (d) represent the best fits to eqn. 3 (from the main text) (f).

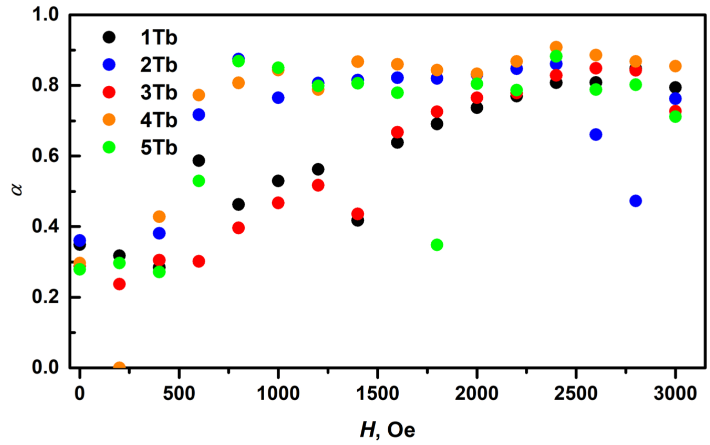

Fig. S43. Field dependences of α for compounds **1Tb-5Tb**.

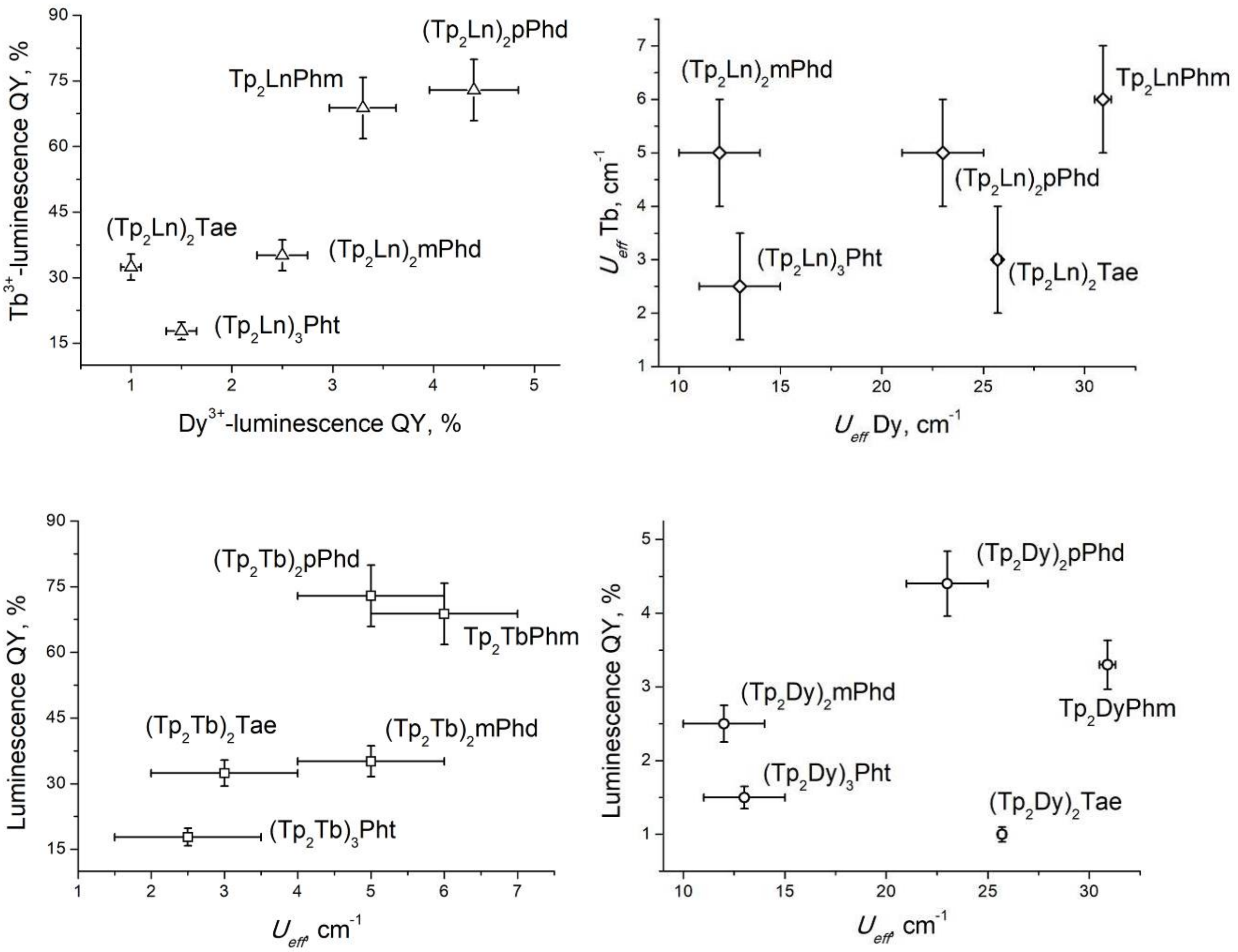

Fig. S44. Maps illustrating comparisons of U_{eff} and QY values for the complexes **1Ln – 5Ln** (Ln = Tb, Dy).

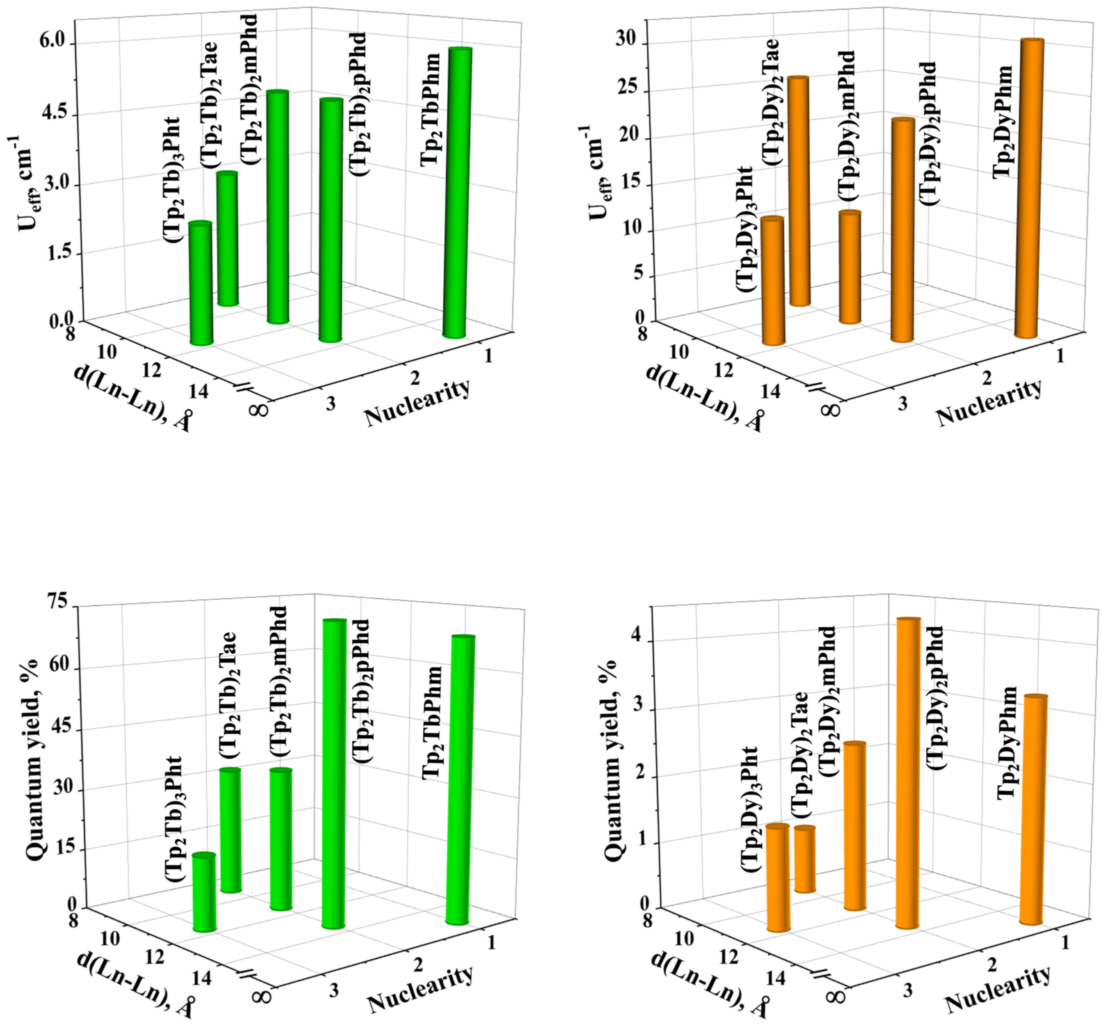

Fig. S45. Changes in U_{eff} and quantum yield values for **1Ln** – **5Ln** (Ln = Tb, Dy) complexes, depending on the nuclearities of the compounds and their intramolecular Ln-Ln distances

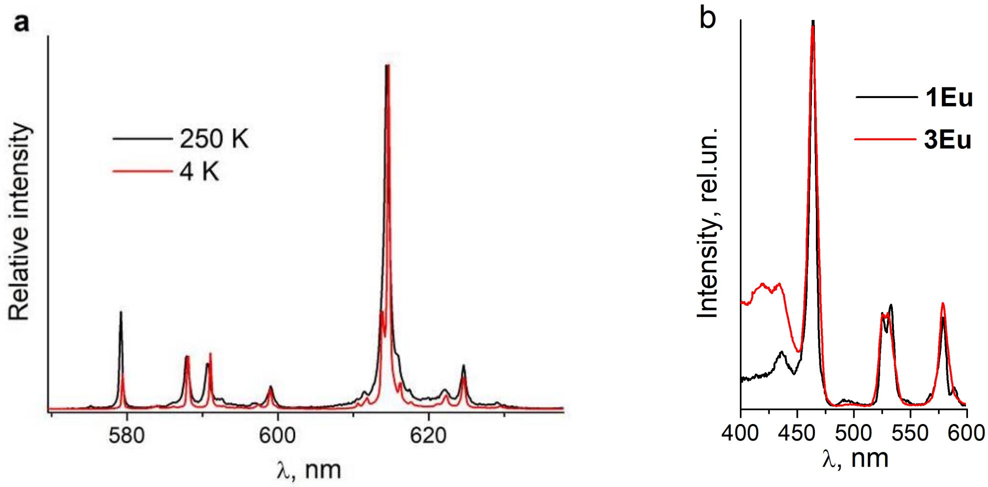

Fig. S46. a) Emission spectra of **1Eu** at 250 K and 4 K. b) Excitation spectra (RT, λ_{em} = 617 nm) of **1Eu** and **3Eu**. The spectra are normalized with respect to maximum intensity.

References

1. N. F. Chilton, R. P. Anderson, L. D. Turner, A. Soncini and K. S. Murray, *J. Comput. Chem.*, 2013, **34(13)**, 1164–1175.
2. Y.-N. Guo, G.-F. Xu, Y. Guo and J. Tang, *Dalton Trans.*, 2011, **40(39)**, 9953–9963.
3. N. F. Chilton, D. Collison, E. J. L. McInnes, R. E. P. Winpenny and A. Soncini, *Nat. Commun.*, 2013, **4**, 2551.