Electronic Supplementary Material (ESI) for Chemical Communications

Supporting Information

Dinuclear single-molecule magnet with porphyrin-phthalocyanine mixed triple-decker ligand system giving SAP and SP coordination polyhedra

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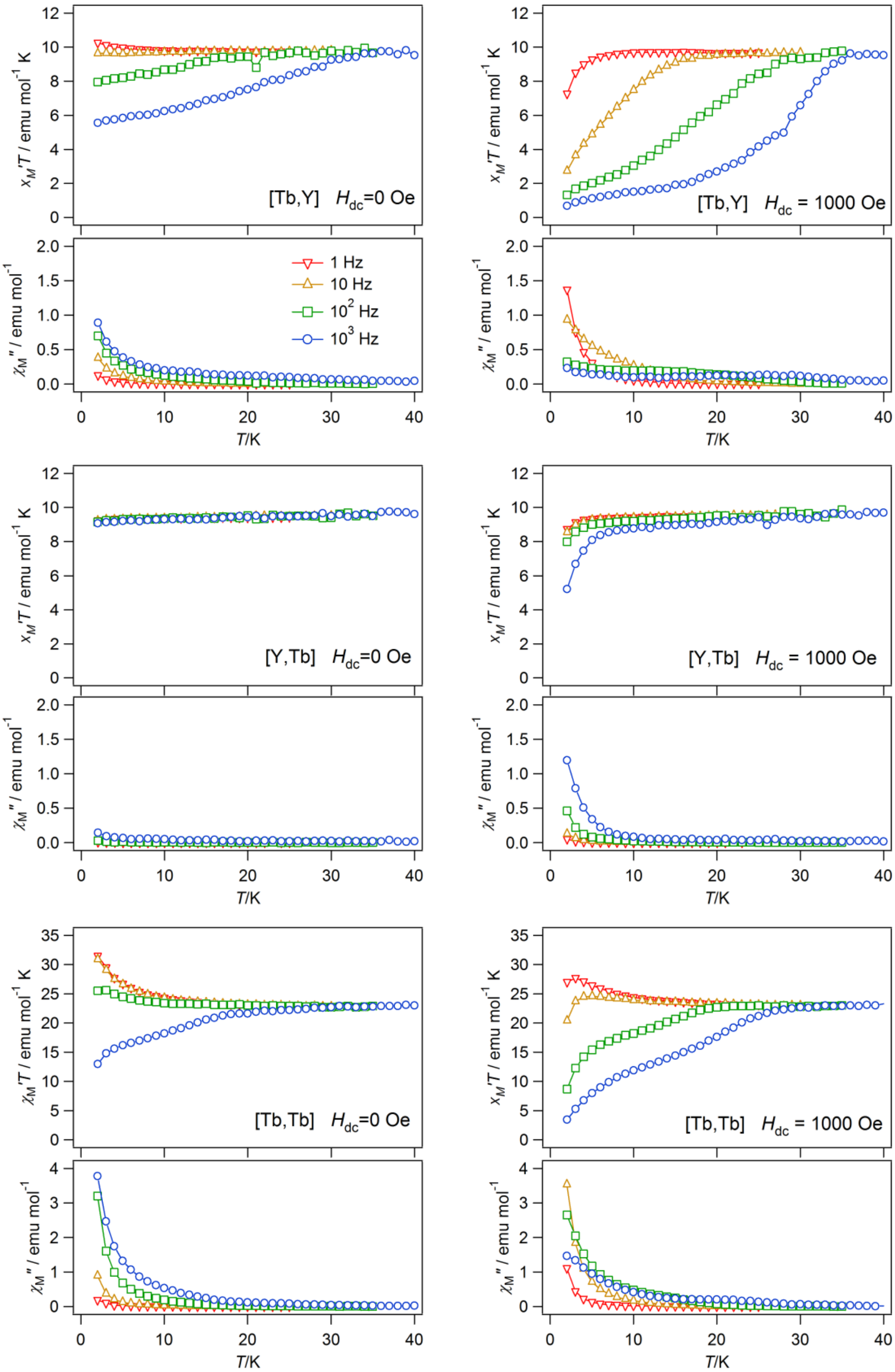
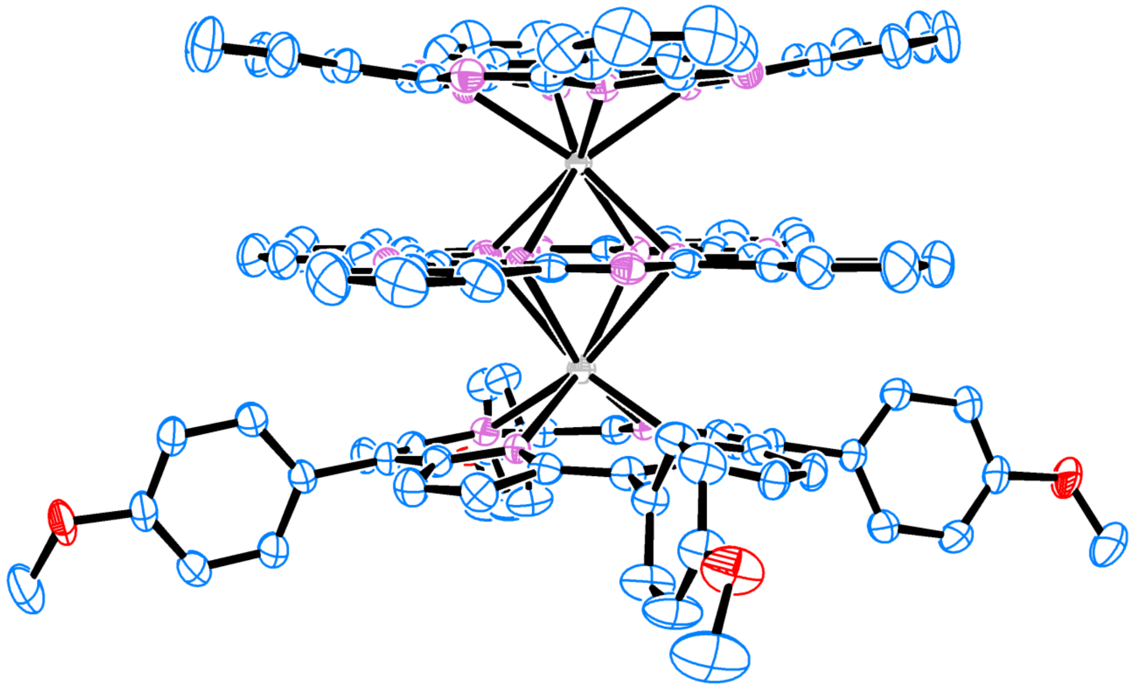


Fig. S1 Plots for temperature dependence of $\chi_M'T$ and χ_M'' of [Tb,Y] (top), [Y,Tb] (middle) and [Tb,Tb] (bottom) measured in the absence of external dc magnetic field (H_{dc} = 0, left column) and in the presence of H_{dc} set at 1000 Oe (right colmn) with indicated ac magnetic field frequencies.

Crystallographic data for [Tb,Tb] : $C_{128}H_{68}Cl_4N_{20}O_4Tb_2$, M = 2409.74, tetragonal, a = 20.2591(7) Å, c = 12.8252(4) Å, V = 5263.8(3) Å^3, T = 200 K, Space group = P4/n, Z = 2, Number of reflections measured = 68247, Number of independent reflections = 6053, R_{int} = 0.0405, Final R values : $R1$ = 0.0648; $wR2$ = 0.1653, Crystal color = dark-red, Habit = Platelet, Crystal size = 0.20mm×0.17mm×0.01mm. CCDC deposition number 866895.



ORTEP plot (ellipsoids at 50% probability level) for [Tb,Tb]

General information.

All chemicals and solvents were of reagent grade and used without further purification. The dc and ac magnetic susceptibility measurements were carried out on a Quantum Design MPMS-XL7AC SQUID magnetometer. X-ray structure determination was conducted on a Rigaku R-AXIS VII / FR-E system with $Mo_{K\alpha}$ radiation. In all cases, the structure was solved by direct methods (SHELXS-97) [1] and refined by full-matrix least-squares techniques on F^2 (SHELXL-97).[2]

Synthesis of [Tb,Tb], (Pc)Tb(Pc)Tb(T(p-OMe)PP).

5,10,15,20-tetra(p-methoxyphenyl)porphyrin (H_2T(p-OMe)PP) was prepared using a literature method.[3] [Tb,Tb] was prepared according to a literature procedure for corresponding neodymium complex with some modifications.[4] H_2T(p-OMe)PP (76.5 mg) and $Tb^{III}(acac)_3 \cdot xH_2O$ (336 mg) were treated at 230 ˚C for 4 h in 1,2,4-trichlorobenzene (5 ml), followed by addition of Li_2Pc and treatment at 200 ˚C for 12 h under argon atmosphere. The obtained residue was purified by passing it through an alumina column (CH_2Cl_2) to give a dark red solid (9.1 mg, 4.2%). Single crystal used for crystallographic measurement was obtained by slow evaporation of dichloroehane solution of [Tb,Tb]. MALDI-TOF MS (m/z): M^+ calcd for $C_{112}H_{72}N_{20}O_4Tb_2$, 2078.46; found 2079.

Synthesis of [Tb,Y], (Pc)Tb(Pc)Y(T(p-OMe)PP).

[Tb,Y] was prepared by treating H_2T(p-OMe)PP (153 mg), $Tb(Pc)_2$ (260 mg) and $Y^{III}(acac)_3 \cdot xH_2O$ (424 mg) were treated at 180 ˚C for 1.5 h in 1,2,4-trichlorobenzene (4 ml) under argon atmosphere. The obtained residue was purified by passing it through an alumina column (CH_2Cl_2) to give a dark red solid (9.08 mg, 2.3%). MALDI-TOF MS (m/z): M^+ calcd for $C_{112}H_{72}$ $N_{20}O_4TbY$, 2008.44; found 2008.

Synthesis of [Y,Tb], (Pc)Y(Pc)Tb(T(p-OMe)PP).

[Y,Tb] was prepared by treating H_2T(p-OMe)PP (150 mg), $Y(Pc)_2$ (220 mg) and $Tb^{III}(acac)_3 \cdot xH_2O$ (456 mg) were treated at 180 ˚C for 1.5 h in 1,2,4-trichlorobenzene (4 ml) under argon atmosphere. The obtained residue was purified by passing it through an alumina column (CH_2Cl_2) to give a dark red solid (13.6 mg, 3.4%). MALDI-TOF MS (m/z): M^+ calcd for $C_{112}H_{72}$ $N_{20}O_4TbY$, 2008.44; found 2008.

(1) Sheldrick, G. M. *SHELXS-97*, Universität-Gottingen, 1997
(2) Sheldrick, G. M. *SHELXL-97*, Universität-Gottingen, 1997.
(3) Lindsey, J. S.; Schreiman, I. C.; Hsu, H. C.; Kearney, P. C.; Marguerettaz, A. M. *J Org Chem* **1987**, *52*, 827.
(4) M. Moussavi, A. De Cian, J. Fischer, R. Weiss, *Inorg. Chem.* 1986, **25**, 2107.