SUPPLEMENTARY INFORMATION

FOR THE MANUSCRIPT

Single-molecule magnets based on heteroleptic terbium(III) trisphthalocyaninate in solvent-free and solvent-containing forms

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Spectral and structural characteristics of (Pc)Tb[(15C5)$_4$Pc]Tb(Pc)

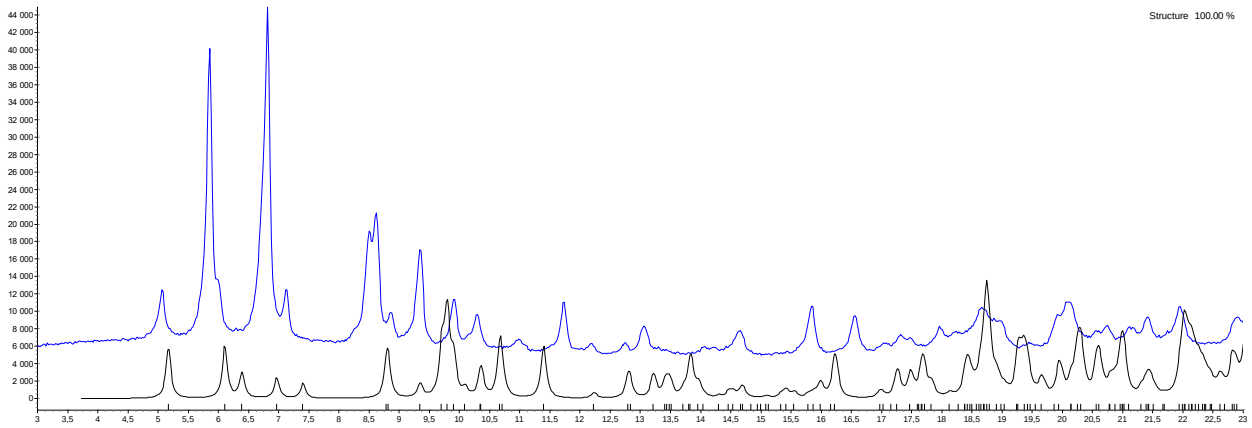

Figure S1. Powder diffraction pattern of the compound (Pc)Tb[(15C5)$_4$Pc]Tb(Pc) (**1**) (blue curve) taken in Bragg-Brentano scheme for flat packed sample using SmartLab diffractometer with CuKa radiation. Black curve shows powder diffraction pattern of the compound (Pc)Sm[(15C5)$_4$Pc]Sm(Pc)·8CHCl$_3$ generated from its CIF file**.**

Indexing of powder diffraction spectrum of **1** (Fig.S5) gives as possible solution the following lattice parameters:

a = 13.037, b = 15.323, c = 38.456 Å, α = 102.80, β = 109.70, γ = 96.36°, V = 6907.5 Å^3. These parameters are close to those for the double unit cell of the known crystal structure of (Pc)Sm[(15C5)$_4$Pc]Sm(Pc)·8CHCl$_3$ [Martynov, A. G.; Zubareva, O. V.; Gorbunova, Y. G.; Sakharov, S. G.; Nefedov, S. E.; Dolgushin, F. M.; Tsivadze, A. Y. Diphthalocyaninatolanthanum as a New Phthalocyaninato-Dianion Donor for the Synthesis of Heteroleptic Triple-Decker Rare Earth Element Crown-Phthalocyaninato Complexes. *Eur. J. Inorg. Chem.* **2007**, 4800–4807, doi:10.1002/ejic.200700489].

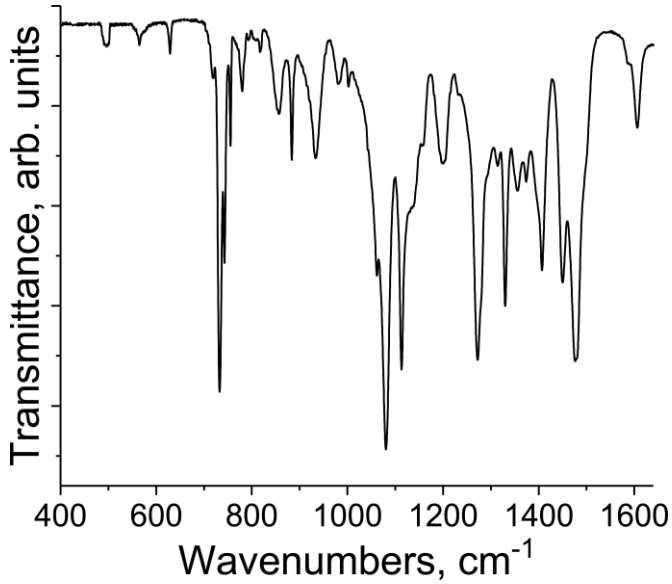

Figure S2. IR-spectrum of (Pc)Tb[(15C5)$_4$Pc]Tb(Pc)·6C$_6$H$_4$Cl$_2$ **2** measured in KBr pellet prepared in anaerobic conditions.

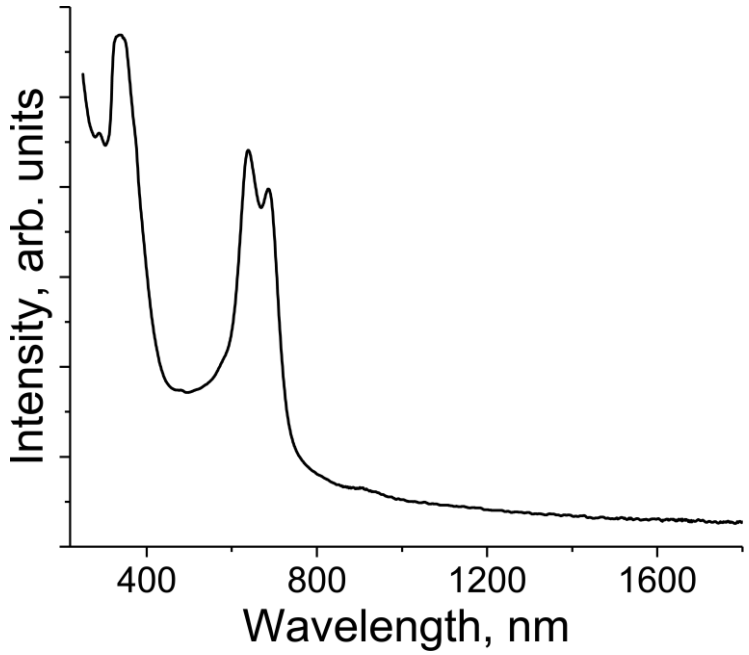

Figure S3. UV-visible-NIR spectrum of (Pc)Tb[(15C5)$_4$Pc]Tb(Pc)·6$C_6H_4Cl_2$ **2** in the 220-1800 nm range. Spectrum is measured in KBr pellet prepared in anaerobic conditions.

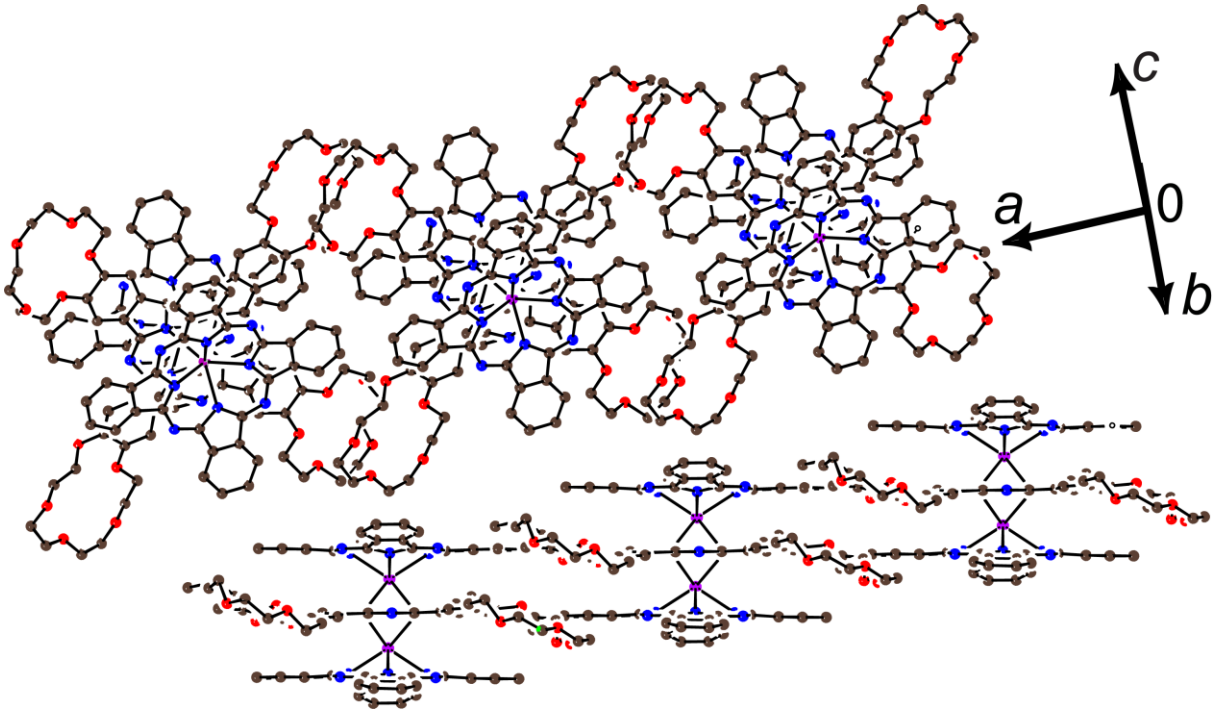

Figure S4. View on two chains from the (Pc)Tb[(15C5)$_4$Pc]Tb(Pc) molecules in **2** arranged along the *a* axis and having van der Waals contacts between two 15-crown-5 fragments. Phthalocyanine planes in two neighboring chains are positioned at an angle of 59.6°.

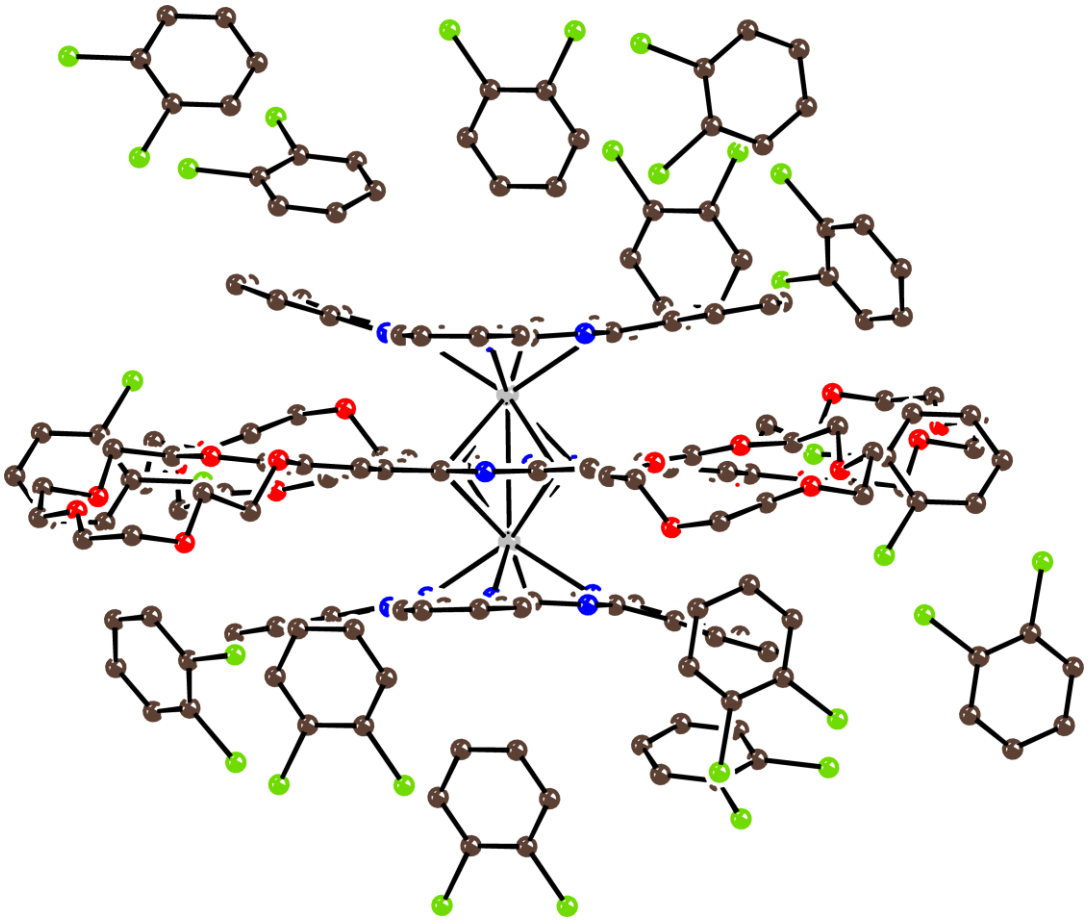

Figure S5. Surrounding of one (Pc)Tb[(15C5)$_4$Pc]Tb(Pc) molecule by 14 solvent *o*-dichlorobenzene molecules in the crystal structure of **2**. One most occupied orientation only is shown for one of three solvent molecules which is disordered between three orientations.

Data of magnetic measurements for the powdered sample of 1

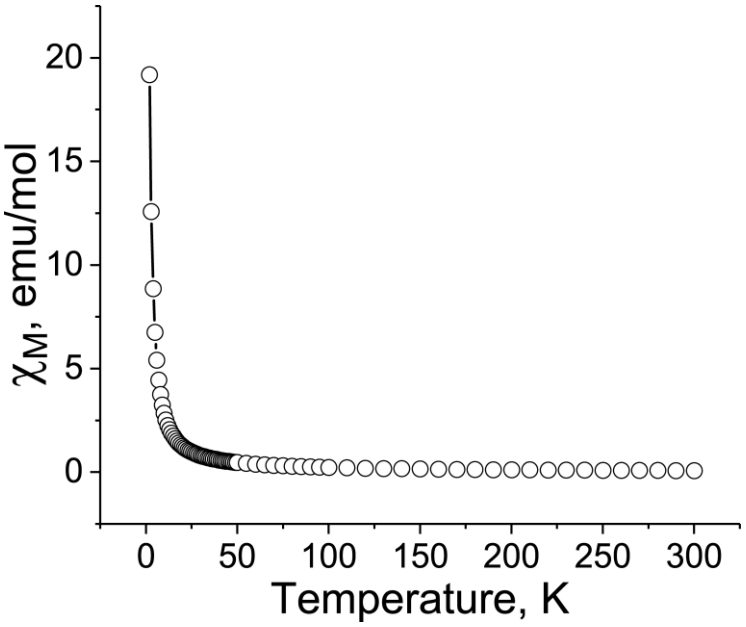

Figure S6. Temperature dependence of molar magnetic susceptibility for powdered sample of (Pc)Tb[(15C5)$_4$Pc]Tb(Pc) **1** measured in 1 kOe magnetic field after subtraction of the temperature independent part.

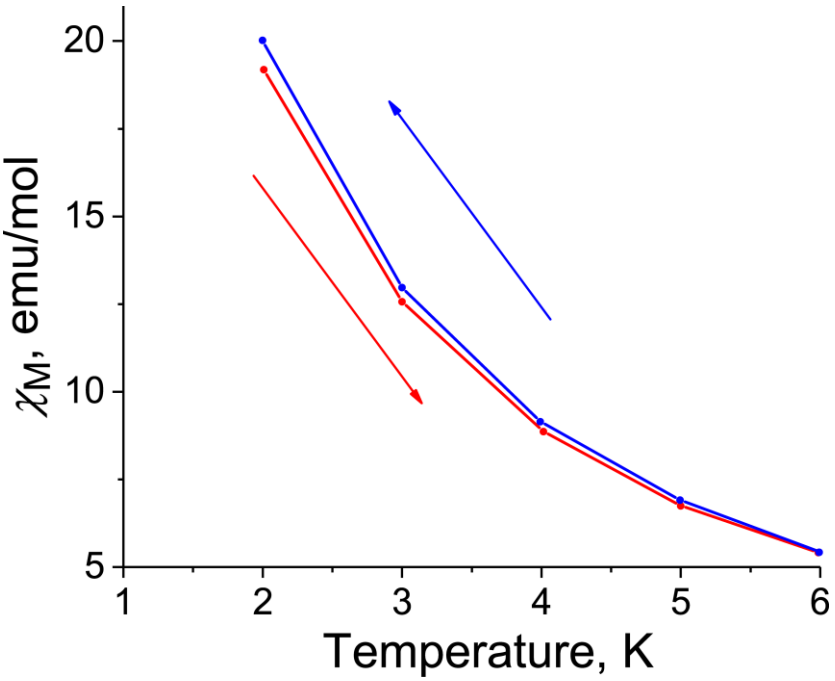

Figure S7. Temperature dependence of molar magnetic susceptibility in zero-field (ZF, red curve) and field cooling conditions (FC, blue curve) for the powdered sample of (Pc)Tb[(15C5)$_4$Pc]Tb(Pc) **1**. Splitting between two curves is observed below ~6 K.

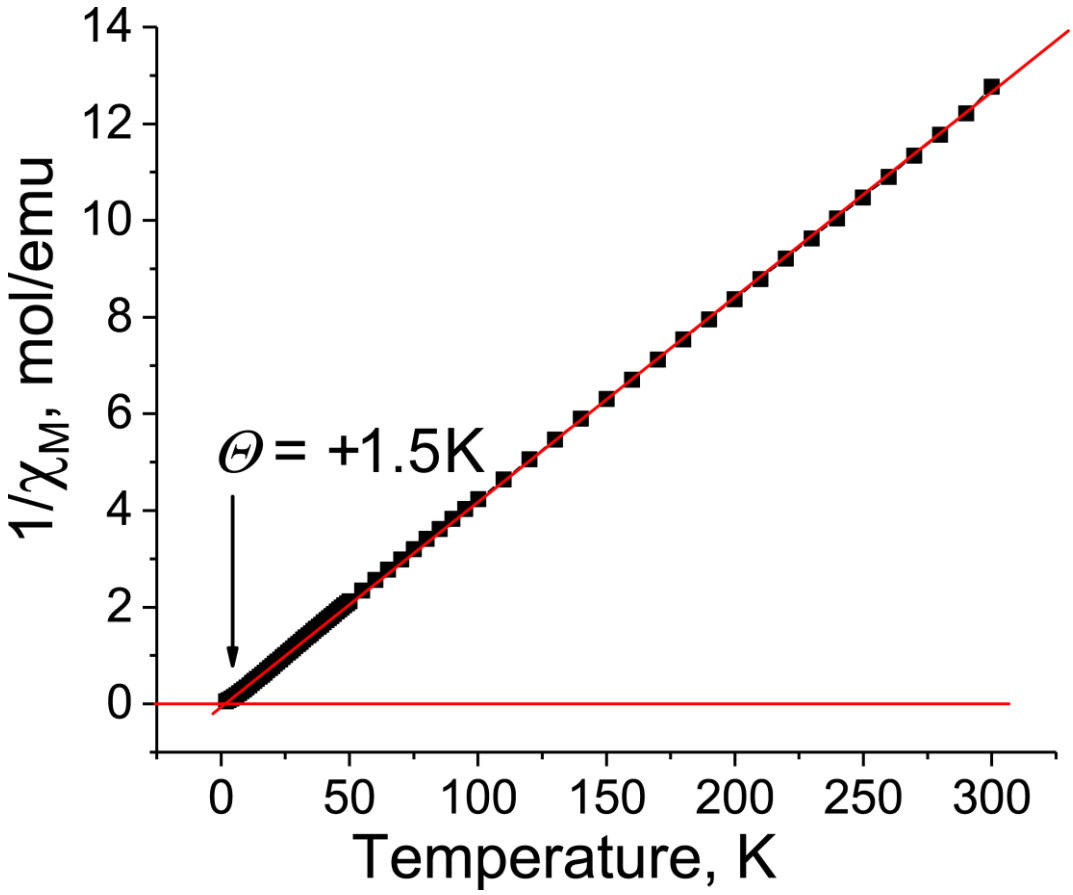

Figure S8. Temperature dependence of reciprocal molar magnetic susceptibility of **1** allowing to determine Weiss temperature of +1.5 K.

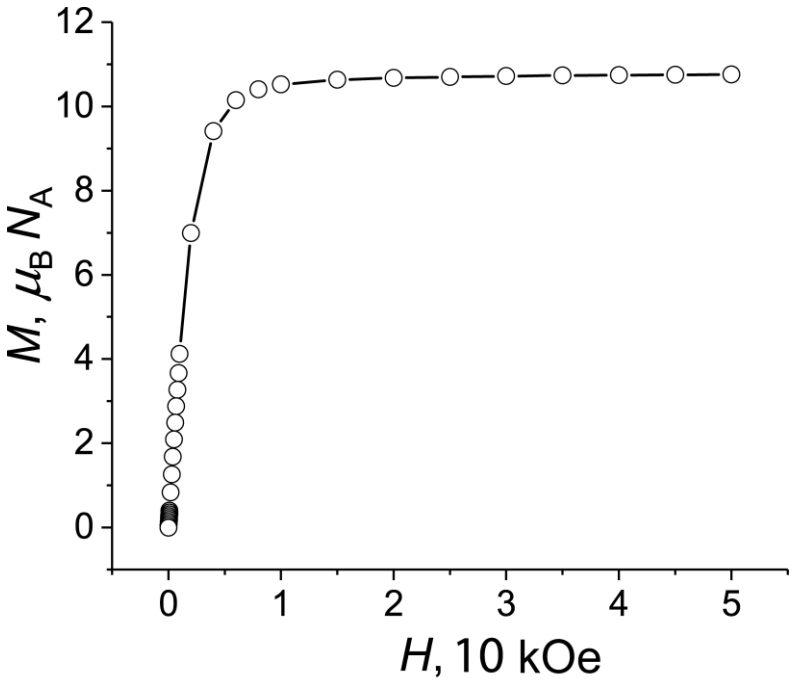

Figure S9. Dependence of magnetization *vs* magnetic field up to 50 kOe at 2K (black line is a guide to the eye) for the powdered sample of (Pc)Tb[(15C5)$_4$Pc]Tb(Pc) **1**.

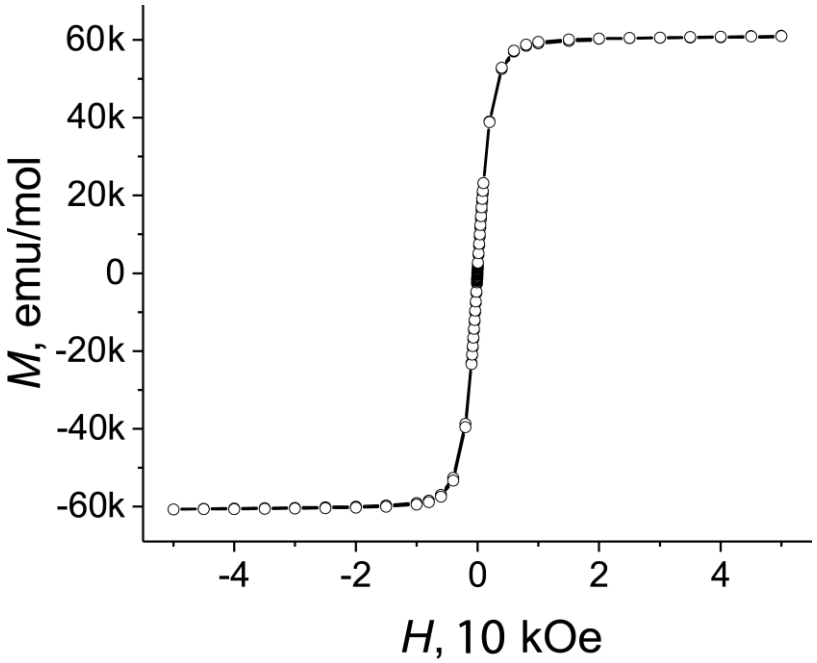

Figure S10. Hysteresis loop at 2K observed in magnetic field between -50 and 5o kOe for the powdered sample of (Pc)Tb[(15C5)$_4$Pc]Tb(Pc) **1**.

Hysteresis can be resolved between -1 - and 1 kOe (see manuscript) and is not resolved in this figure.

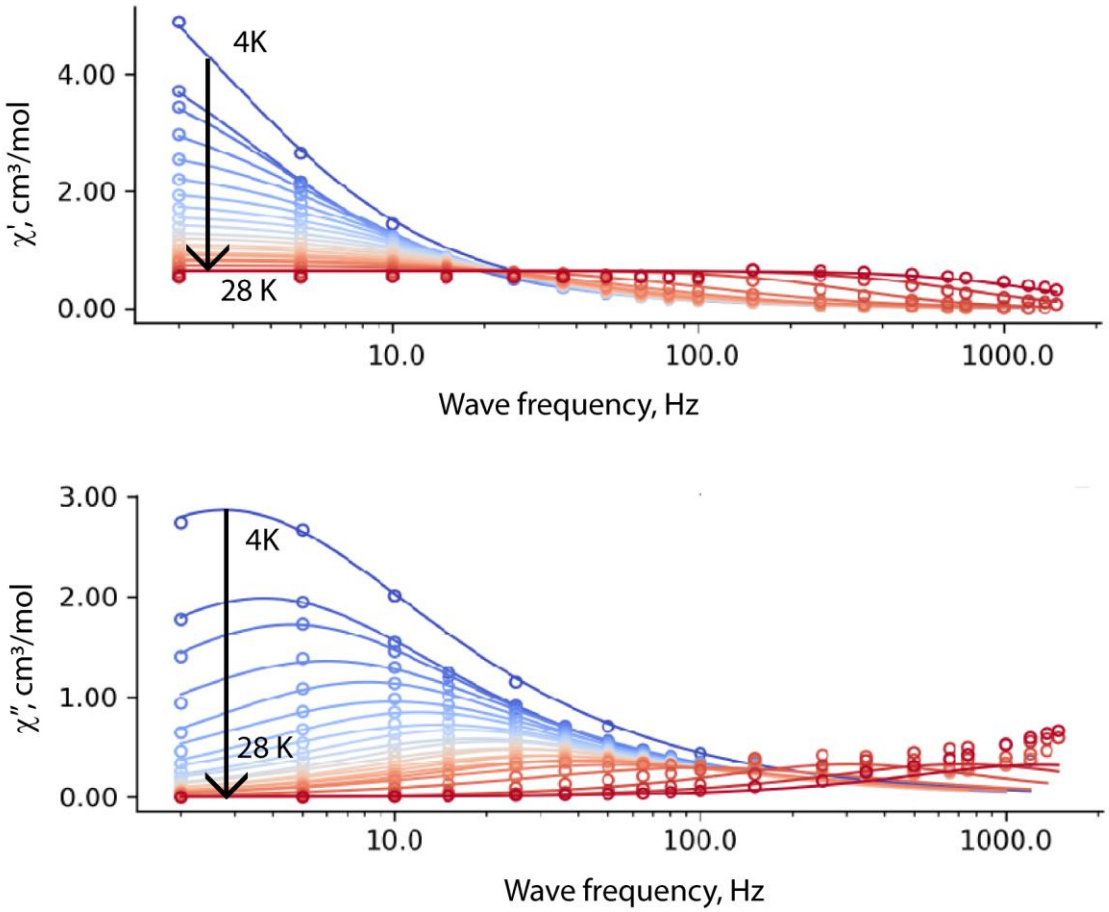

Figure S11. Frequency dependence of: (a) in-phase (χ') and (b) out-of-phase (χ'') ac magnetic susceptibility of powdered sample of (Pc)Tb[(15C5)$_4$Pc]Tb(Pc) **1**. Solid lines represent the fit of the data by the generalized Debye model.

Data of magnetic measurements for the polycrystalline sample of 2

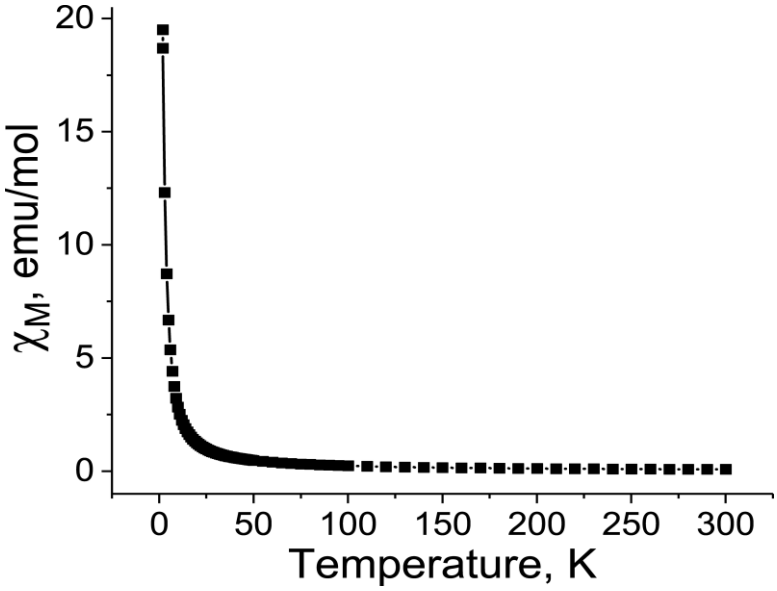

Figure S12. Temperature dependence of molar magnetic susceptibility for polycrystalline sample of (Pc)Tb[(15C5)$_4$Pc]Tb(Pc)·6C$_6$H$_4$Cl$_2$ (**2**) measured in 1 kOe magnetic field after subtraction of the temperature independent part.

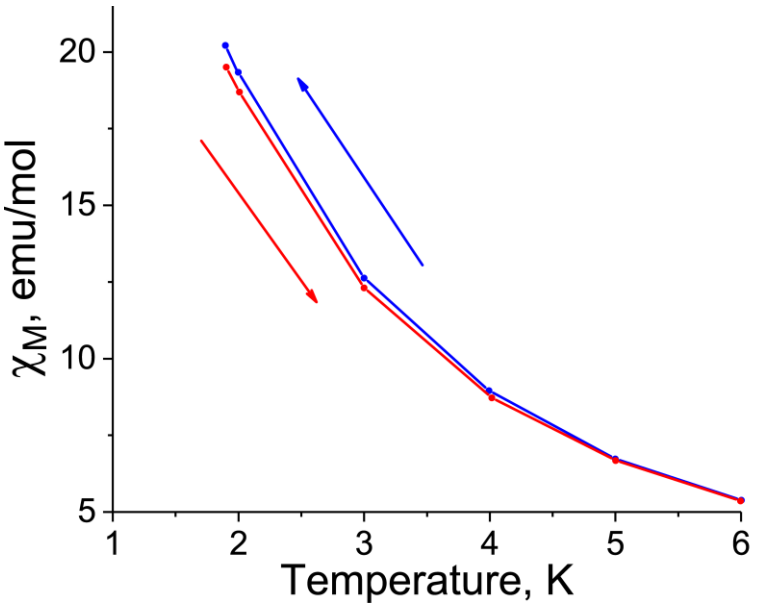

Figure S13. Temperature dependence of molar magnetic susceptibility in zero-field (ZF, red curve) and field cooling conditions (FC, blue curve) for polycrystalline sample of (Pc)Tb[(15C5)$_4$Pc]Tb(Pc)·6C$_6$H$_4$Cl$_2$ (**2**). Splitting between two curves is observed below ~6 K.

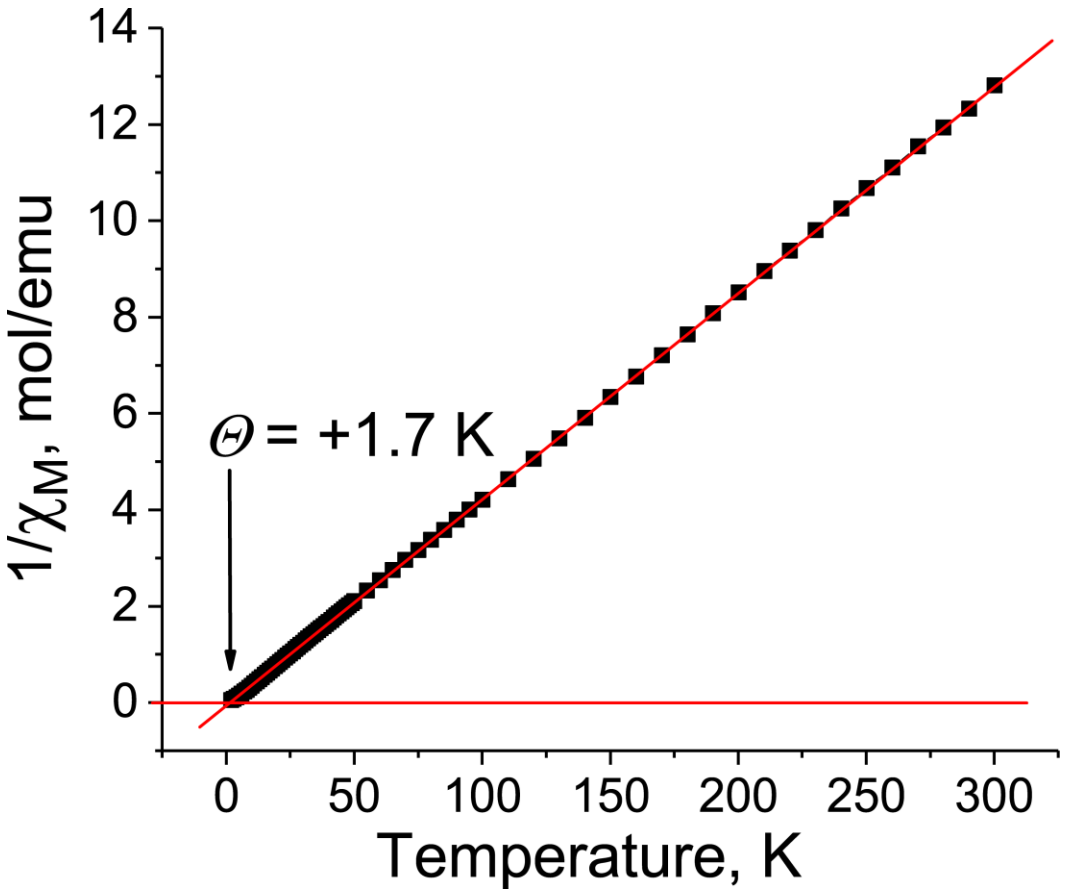

Figure S14. Temperature dependence of reciprocal molar magnetic susceptibility of **2** allowing to determine Weiss temperature of +1.7 K.

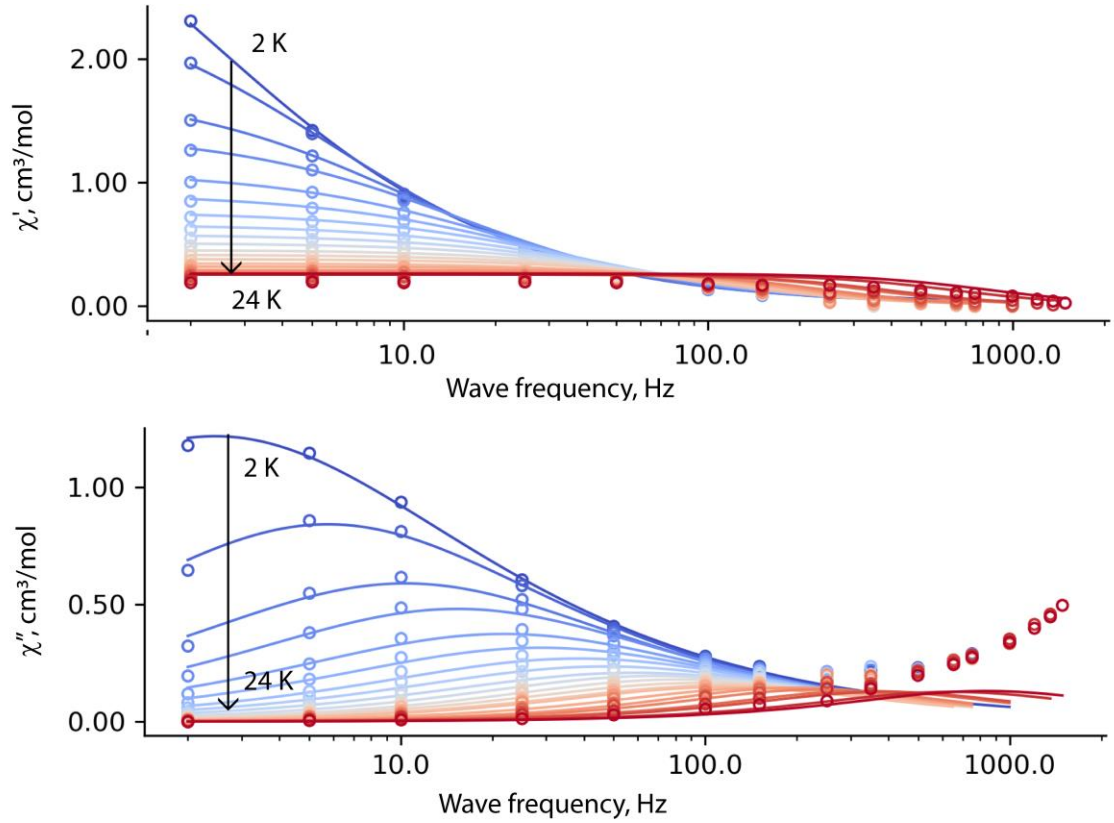

Figure S15. Frequency dependence of: (a) in-phase (χ') and (b) out-of-phase (χ'') ac magnetic susceptibility of polycrystalline sample of **2**. Solid lines represent the fit of the data by the generalized Debye model.