



## Article

# Single-Molecule Magnets Based on Heteroleptic Terbium(III) Trisphthalocyaninate in Solvent-Free and Solvent-Containing Forms

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**Abstract:** Binuclear heteroleptic triple-decker terbium(III) phthalocyaninate (Pc)Tb[(15C5)<sub>4</sub>Pc]Tb(Pc), where Pc<sup>2−</sup> is phthalocyaninate dianion and 15C5 is a 15-crown-5 moiety, has been synthesized as a solvent-free powder (**1**) and a well-defined crystal solvate with *o*-dichlorobenzene (Pc)Tb[(15C5)<sub>4</sub>Pc]Tb(Pc)·6C<sub>6</sub>H<sub>4</sub>Cl<sub>2</sub> (**2**). In the crystal structure of **2**, the Tb–N(Pc) distances to the nitrogen atoms in the outer and inner decks are 2.350–2.367(4) and 2.583–2.598(4) Å, respectively, and the Tb–Tb distance is 3.4667(3) Å. The twist angle between the outer and the inner decks is 42.6°. The magnetic properties were studied for both **1** and **2**. The  $\chi_M T$  magnitude of 23.3 emu·K/mol at 300 K indicates a contribution of two Tb<sup>III</sup> centers with the <sup>7</sup>F<sub>6</sub> ground state. The  $\chi_M T$  product increases with decreasing temperature to reach 38.5 emu·K/mol at 2 K. This is indicative of ferromagnetic coupling between Tb<sup>III</sup> spins in accordance with previous data for triple-decker lanthanide phthalocyaninates of a dipolar nature. Both forms show a single-molecule magnet (SMM) behavior manifesting the in-phase ( $\chi'$ ) and out-of-phase ( $\chi''$ ) AC susceptibility signals in an oscillating field of 3 Oe with estimated effective spin-reversal energy barriers ( $U_{\text{eff}}$ ) of 222(9) and 93(7) cm<sup>−1</sup> for **1** and **2**, respectively. The compounds show narrow hysteresis loops in the −1 – +1 kOe range, and the splitting between the zero-field-cooling and field-cooling curves is observed below 6 K. Thus, in spite of similar static magnetic characteristics, each form of the Tb(III) complex shows a different dynamic SMM behavior.

**Keywords:** terbium; binuclear complex; phthalocyanine; single-molecule magnet; ferromagnetic coupling; spin-reversal energy barriers; solvate; crystal structure

## 1. Introduction

Single-molecule magnets (SMMs) can show a slow relaxation of magnetization below blocking temperatures. Great progress has been made in this field as increasingly higher spin-reversal barriers ( $U_{\text{eff}}$ ) have been achieved, and several synthetic strategies have been offered to increase the blocking temperatures for these SMMs [1–4]. SMMs can potentially find application in molecular electronics, for example, for high-density information storage, spintronics, quantum computers and other devices due to blocked magnetic moment and essential quantum effects [5–10]. Among different SMMs, lanthanides are promising candidates due to high unquenched orbital moments and significant inherent spin-orbit coupling, which can lead to strong single-ion anisotropy [11–14].

In spite of the maximal barriers and blocking temperatures found for substituted metallocene Dy(III) derivatives [4,15], terbium(III) phthalocyanine complexes also attract great attention due to the possibility of the chemical modification of their structure and properties [16], as well as their high air stability and the relative ease of fabricating films to be used in different devices [14]. The SMM properties of double-decker phthalocyanine complexes were first reported by Ishikawa for the Tb<sup>III</sup>Pc<sub>2</sub> complexes with a  $U_{\text{eff}}$  of 230 and 410 cm<sup>−1</sup> [1,17]. After that, the barriers were increased to 642–652 cm<sup>−1</sup> for heteroleptic Tb<sup>III</sup>Pc<sub>2</sub> derivatives with eight electron-rich NBu<sub>2</sub> or *p*-tBuPhO substituents on the periphery of one of the Pc macrocycles [18,19].

Triple-decker phthalocyanines can also show properties of SMMs [20–26]. All these systems also have  $D_{4d}$  axial symmetry, giving a possibility for a significant orbital contribution from the Tb<sup>III</sup> ions. This can provide a large separation between the states and, as a result, high  $U_{\text{eff}}$  values, which, however, are lower than the barriers for the double-decker complexes [27] because of the nonequivalence of the bond lengths between Tb<sup>III</sup> and the outer/inner Pc ligands. Nevertheless, triple-decker complexes provide wider possibilities to study the influence of structural and electronic factors on SMM behavior [14], as these scaffolds show a higher conformational flexibility in comparison with double-decker sandwiches [28,29].

In this work, we have synthesized triple-decker Tb<sup>III</sup> phthalocyaninate with the inner 15-crown-5-substituted deck (Pc)Tb[(15C5)<sub>4</sub>Pc]Tb(Pc) and have studied its magnetic properties. The (Pc)Tb[(15C5)<sub>4</sub>Pc]Tb(Pc) complex has been isolated as a solvent-free powder (1) and single crystals of solvate with *o*-dichlorobenzene (Pc)Tb[(15C5)<sub>4</sub>Pc]Tb(Pc)·6C<sub>6</sub>H<sub>4</sub>Cl<sub>2</sub> (2). Its crystal structure has been solved for the first time and discussed. Magnetic properties studied for both the powder and crystal solvate have revealed ferromagnetic coupling of the spins in the binuclear units. Both forms show SMM behavior with different effective spin-reversal barriers.

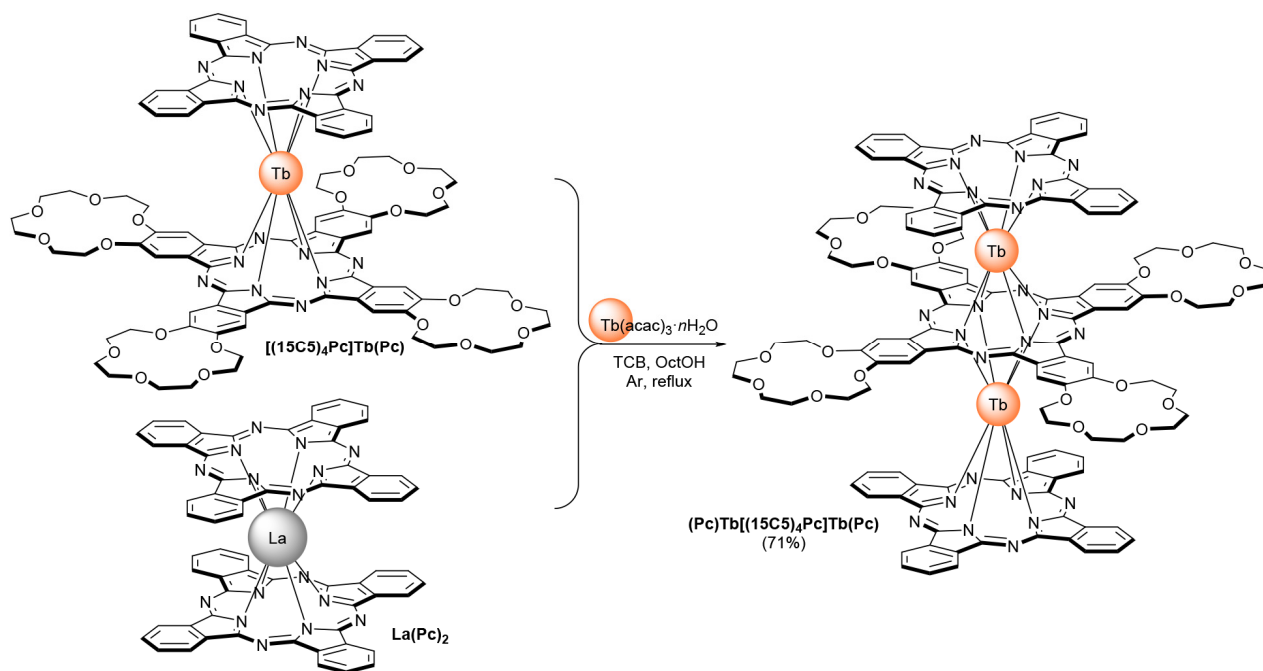
## 2. Results and Discussion

The choice of the ligand surrounding for the studied complex is based on our previous experience in SMM studies of crown-substituted heteronuclear triple-decker complexes [(15C5)<sub>4</sub>Pc]M\*[(15C5)<sub>4</sub>Pc]M(Pc), where M and M\* is Tb or Y [26]. The Tb(III) ion placed in the homoleptic position M\* has smaller  $U_{\text{eff}}$  (90 cm<sup>−1</sup>) in comparison with the heteroleptic position M (117 cm<sup>−1</sup>). Thus, (Pc)Tb[(15C5)<sub>4</sub>Pc]Tb(Pc) studied herein has both metal centers in an asymmetric heteroleptic position, which expectedly can provide better SMM properties. Whereas the synthesis of (Pc)Tb[(15C5)<sub>4</sub>Pc]Tb(Pc) has been reported elsewhere [30], we have made an attempt to improve its preparation. Previously, this complex was isolated in 19% yield by the reaction of tetra-15-crown-5-phthalocyanine with lanthanum bisphthalocyaninate La(Pc)<sub>2</sub> and terbium(III) acetylacetonate in refluxing 1-chloronaphthalene. A lanthanum (III) complex was used as a convenient source of Pc<sup>2−</sup> species via transmetalation reaction. The modest yield of (Pc)Tb[(15C5)<sub>4</sub>Pc]Tb(Pc) is explained by the statistical nature of this reaction, while in the present work, we aim at making it more selective towards the target complex. Therefore, we use the “raise-by-one-story” approach which implies the addition of one more deck to the double-decker complex [(15C5)<sub>4</sub>Pc]Tb(Pc) to give a triple-decker sandwich (Scheme 1).

Starting [(15C5)<sub>4</sub>Pc]Tb(Pc) was synthesized as described earlier [31]. The synthesis of another precursor—La(Pc)<sub>2</sub>—was also reported previously. It was isolated in 47% yield after the reaction of H<sub>2</sub>(Pc) with La(acac)<sub>3</sub> *n*H<sub>2</sub>O in refluxing 1-chloronaphthalene in the presence of 1,8-diazabicyclo [5.4.0]undec-7-ene (DBU) [32]. Herein, we show that the addition of *n*-octanol (OctOH) to the reaction mixture allows one to decrease the reaction time from 3 h to 30 min and increase the yield of La(Pc)<sub>2</sub> to 85%.

The reaction between [(15C5)<sub>4</sub>Pc]Tb(Pc) and La(Pc)<sub>2</sub> in the presence of Tb(acac)<sub>3</sub> *n*H<sub>2</sub>O proceeded in a refluxing mixture of 1,2,4-trichlorobenzene (TCB) and OctOH. Monitoring the consumption of starting reagents using UV-vis indicated an exceptionally high reaction rate affording the formation of the target complex within 3–5 min; the latter was isolated in

80% yield using column chromatography with a mixture of chloroform and 0.5–1 vol.% methanol. The evaporation of these solvents from the fractions afforded the powdered form of complex **1**, and the absence of solvent molecules was confirmed using elemental analysis. According to the X-ray powder diffraction pattern for **1** (Figure S1), its crystal structure is similar to that of the known (Pc)Sm[(15C5)<sub>4</sub>Pc]Sm(Pc)·8CHCl<sub>3</sub> complex [30], with the doubling of the unit cell along the *c* direction and a slightly smaller unit cell volume.



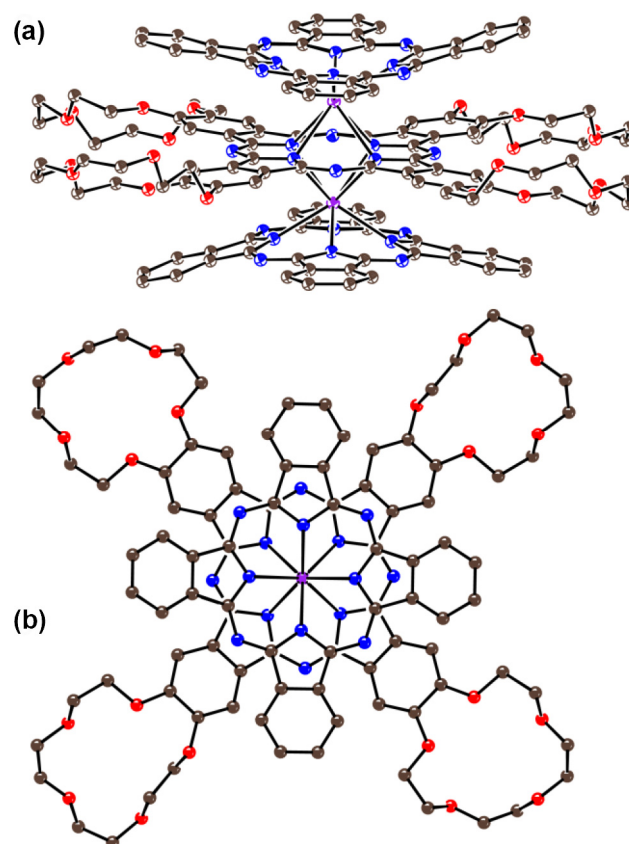
**Scheme 1.** Synthesis of (Pc)Tb[(15C5)<sub>4</sub>Pc]Tb(Pc).

Slow mixing of a solution of the powder in *o*-dichlorobenzene (prepared under anaerobic conditions) with *n*-hexane produced the high-quality large single crystals of **2**. All crystals had the same color and shape, and the testing of several crystals from the synthesis showed that only one crystal phase was formed with the same unit cell parameters. The content of C<sub>6</sub>H<sub>4</sub>Cl<sub>2</sub> was supported using elemental analysis. Crystals were additionally characterized with IR and UV-Vis-NIR spectra in KBr pellets (Figures S2 and S3).

The molecular structure of complex **2** is shown in Figure 1. The asymmetric unit contains only a half of the triple-decker phthalocyanine and three solvent *o*-dichlorobenzene molecules, one of which is disordered over three orientations. Therefore, the composition of **2** is (Pc)Tb[(15C5)<sub>4</sub>Pc]Tb(Pc)·6C<sub>6</sub>H<sub>4</sub>Cl<sub>2</sub>. Several parts of the 15-crown-5 rings also show the conformational disorder of the -CH<sub>2</sub>-CH<sub>2</sub>- moieties, but this disorder cannot be described well by two positions for each fragment. The Tb–N(Pc) distances with the nitrogen atoms of the outer and inner decks are different, being 2.350–2.367(4) and 2.583–2.598(4) Å, respectively. The Tb–Tb distance of 3.4667(3) Å is shorter than the sum of the van der Waals radii of the two terbium atoms, 4.74 Å. The twist angle between the outer and inner decks is 42.6°. This angle is close to 45°, which corresponds to the *D*<sub>4d</sub> axial symmetry. The skew angle in **2** is close to those observed for double-decker terbium(III) phthalocyanines showing SMM behavior. In general, the structural characteristics of the triple-decker molecules in **2** are similar to the structure of the (Pc)Sm[(15C5)<sub>4</sub>Pc]Sm(Pc)·8CHCl<sub>3</sub> solvate [30].

The triple-decker phthalocyanines form chains arranged along the *a* axis. They are positioned in such a way that two 15C5 rings of one molecule are positioned over two such rings from the neighboring molecules (Figure S4). The hydrogen atoms of one 15C5 ring are directed to the oxygen atoms of the neighboring ring and form several H...O hydrogen bonds 2.57–2.69 Å in length indicating that hydrogen bonding is a driving force for the packing of (Pc)Tb[(15C5)<sub>4</sub>Pc]Tb(Pc) molecules into chains. There are two types of chains

directed along the *a* axis. These chains are arranged in such a way that the phthalocyanine planes belonging to two different chains form an angle of  $59.6^\circ$  (see Figure S4).



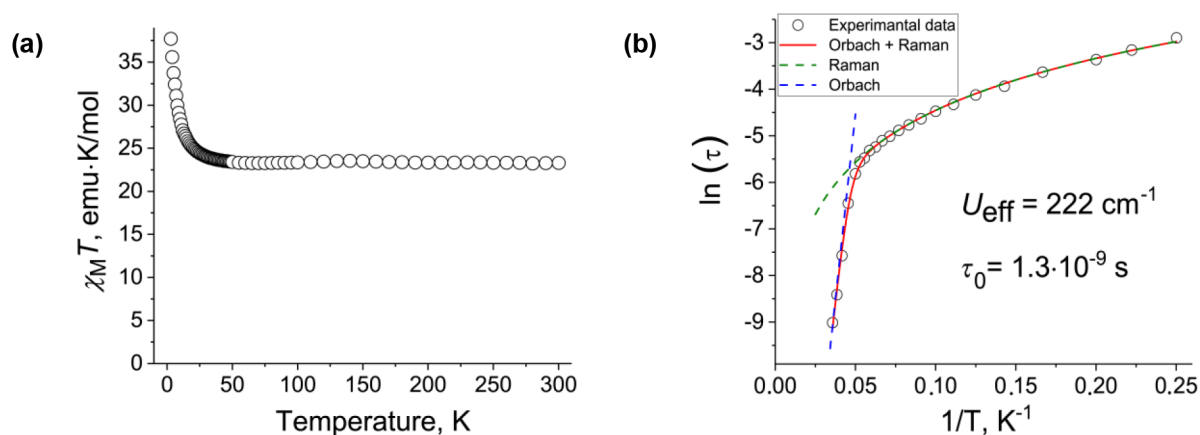
**Figure 1.** Molecular structure of triple-decker phthalocyanine— $(\text{Pc})\text{Tb}[(15\text{C}5)_4\text{Pc}]\text{Tb}(\text{Pc}) \cdot 6\text{C}_6\text{H}_4\text{Cl}_2$  2—viewed approximately along the Pc planes (a) and along two terbium atoms (b).

The  $(\text{Pc})\text{Tb}[(15\text{C}5)_4\text{Pc}]\text{Tb}(\text{Pc})$  molecules are surrounded by *o*-dichlorobenzene molecules that occupy cavities in their packing. Ordered molecules are positioned mainly between the 15C5 rings and above and below the 15C5 rings. The solvent molecules are also positioned above and below the outer Pc macrocycles separating the triple-decker phthalocyanine chains (Figure S5). As a result, multiple shortened  $\text{Cl}(\text{C}_6\text{H}_4\text{Cl}_2) \dots \text{H}(\text{Pc})$  and  $\text{O}(15\text{C}5) \dots \text{H}(\text{C}_6\text{H}_4\text{Cl}_2)$  contacts are formed.

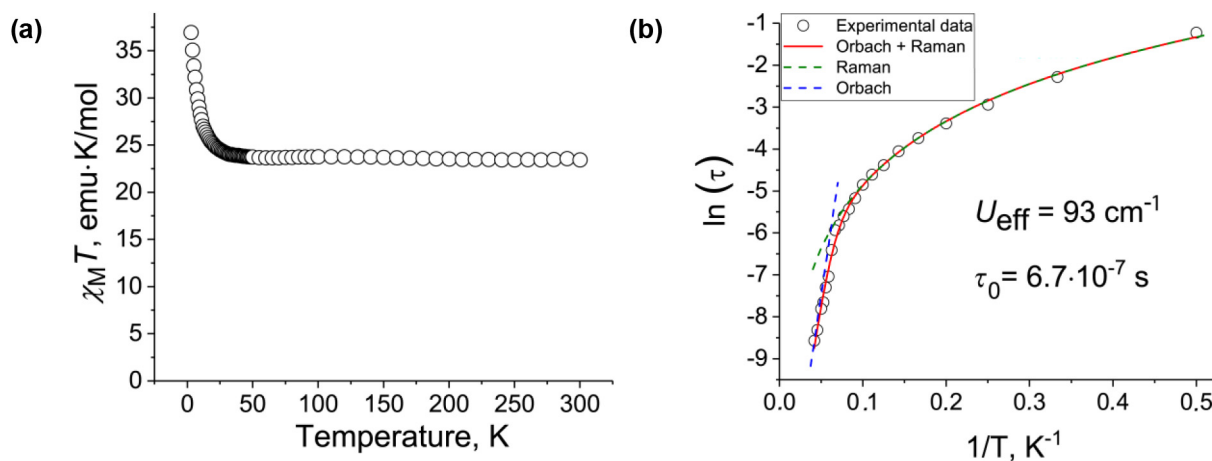
Static and dynamic magnetic susceptibilities were studied for powdered **1** (Figures S6–S11) and crystalline **2** (Figures S12–S15) sealed in quartz tubes on a SQUID magnetometer. Both complexes are EPR silent in the whole studied temperature range (4.2–295 K) for X-band EPR in the 70–700 mT magnetic field.

Complexes **1** and **2** show similar temperature dependencies of molar magnetic susceptibility. The  $\chi_M T$  value is 23.3 emu K/mol at 300 K (Figures 2a and 3a). The  $\text{Tb}^{\text{III}}$  ions have the  $^7F_6$  ground state [ $S = 3$ ,  $L = 3$ ,  $g = 3/2$ ], whereas the phthalocyanine macrocycles are diamagnetic. The calculated value for two independent spins with such configuration is 23.62 emu K/mol. This value is close to the experimentally observed one. The  $\chi_M T$  product increases with decreasing temperature in both samples (Figures 2a and 3a), indicating the ferromagnetic coupling of the spins between two terbium atoms within nearly isolated triple-decker phthalocyanine molecules. This is supported by positive Weiss temperatures, which are +1.5 and +1.7 K, respectively, for **1** and **2** (Figures S8 and S14). The highest value of  $\chi_M T$  of 38.5 emu K/mol is attained at 2 K (Figures 2a and 3a). This value is only slightly lower than 43.8 emu K/mol calculated for the system where spins of both terbium(III) atoms are arranged parallel to each other, and correspondingly, the system has  $S = 12$  spin state. Previously, the magnetic properties of triple-decker phthalocyanines with different

metal atoms have been studied. It has been demonstrated that terbium, dysprosium and holmium show ferromagnetic coupling; according to the calculations, this interaction has mainly a dipole nature, whereas the contribution from the exchange between two Tb<sup>III</sup> spins is negligible [33]. Clearly, intermolecular coupling gives no essential contribution to the magnetic properties of this compound as the shortest distances between the Tb<sup>III</sup> pairs separated by diamagnetic macrocycles are 15.3–16.6 Å. In both samples, the spins of the Tb<sup>III</sup> atoms are arranged parallel to each other at 2 K, and clearly, this state coexists with the SMM behavior discussed below and observed in the same temperature range.



**Figure 2.** (a) Temperature dependence of  $\chi_M T$  for powdered sample of (Pc)Tb[(15C5)<sub>4</sub>Pc]Tb(Pc) **1** in the 300–1.9 K range. (b) The plot of  $\ln(\tau)$  vs.  $1/T$  for powdered sample **1**, which allows the  $U_{\text{eff}}$  value to be determined.



**Figure 3.** (a) Temperature dependence of  $\chi_M T$  for polycrystalline solvate **2** in the 300–1.9 K range. (b) The plot of  $\ln(\tau)$  vs.  $1/T$  for **2**, which allows the  $U_{\text{eff}}$  value to be determined.

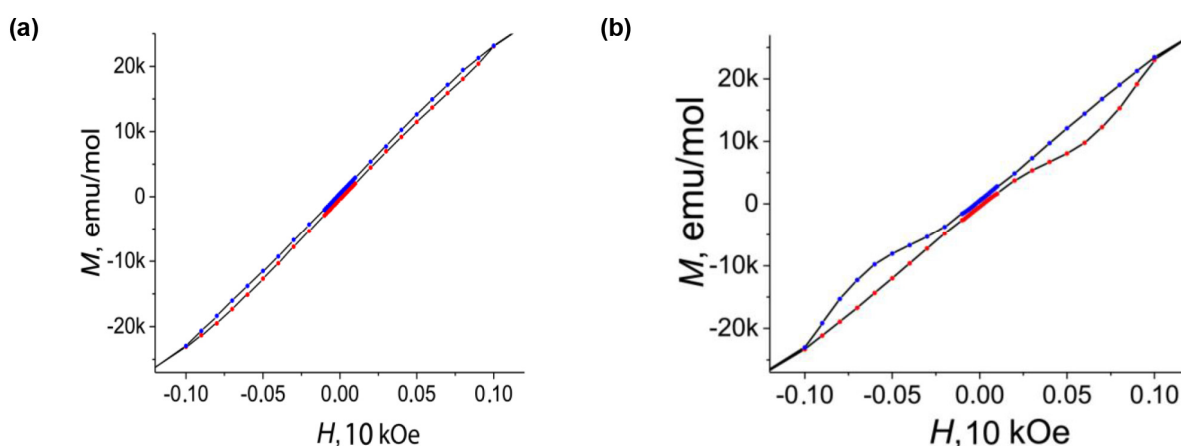
Both samples manifest the in-phase ( $\chi'$ ) and out-of-phase ( $\chi''$ ) AC susceptibility signals when measured in a zero DC field and an oscillating field of 3 Oe (Figures S11 and S15). It is seen that both compounds show a frequency-dependent character of  $\chi'$  and  $\chi''$ , revealing their slow magnetic relaxation and SMM behavior without the need for an external DC field. The temperature dependences of the relaxation times for **1** and **2** show the absence of any temperature-independent regimes even at low temperatures (Figures 2b and 3b). This allows one to fit the data of  $\ln(\tau)$  vs.  $1/T$  without a QTM term. Fitting the data was made with Equation (1).

$$\tau^{-1} = \tau_0^{-1} e^{-U_{\text{eff}}/k_B T} + C T^n \quad (1)$$

Here,  $\tau_0$  and  $U_{\text{eff}}$  are parameters of the Orbach process, and  $C$  and  $n$  denote the Raman parameters. The fitting gave the energy barrier  $U_{\text{eff}} = 222(9) \text{ cm}^{-1}$  (319(13) K) with  $\tau_0 = 1.3(2) \cdot 10^{-9} \text{ s}$  and the Raman parameters  $C = 2.1(2) \text{ s}^{-1} \text{ K}^{-n}$  and  $n = 1.61(4)$  for the powdered sample **1** ( $R = 0.998$ ) (Figure 2b). For the crystal solvate **2**, an adequate fitting to the experimental data was achieved at  $U_{\text{eff}} = 93(7) \text{ cm}^{-1}$  (134(10) K) with  $\tau_0 = 6.7(3) \cdot 10^{-7} \text{ s}$  and the Raman parameters  $C = 0.8(1) \text{ s}^{-1} \text{ K}^{-n}$  and  $n = 2.18(7)$  ( $R = 0.997$ ) (Figure 3b). It has been demonstrated that two relaxation processes are possible for diterbium triple-decker phthalocyanines, and one process can be observed at higher frequencies and temperatures [23,24]. An essential increase in the  $\chi''$  values was observed in **2** when the frequency increased above 400 Hz (Figure S15). However, if maxima were present, they would be observed above a frequency of 1500 Hz, which was the maximum for the SQUID used in this work. As a result, no information on the possible maxima in the high-frequency range could be obtained.

A comparison of the zero-field-cooling and field-cooling curves (Figures S7 and S13) demonstrates that the difference between these curves is observed below 6 K, which allows one to evaluate the blocking temperature ( $T_b$ ) for both samples. It turns out that **1** and **2** have the same blocking temperatures, though the  $U_{\text{eff}}$  values differ more than twice. The magnetization curve for **1** is shown in Figure S9. Magnetization is quickly saturated in a magnetic field of 8–10 kOe, and then it is temperature-independent up to 50 kOe. The maximal value attained at high magnetic fields is only  $10.8 \mu_B N_A$ . This value is nearly two times lower than the  $18.2 \mu_B N_A$  value expected for the isolated pairs with a parallel arrangement of  $\text{Tb}^{\text{III}}$  spins. Previously, it has been shown that the magnetization in triple-decker phthalocyanines is strongly anisotropic, and the maximal value can be attained when a crystal is oriented in such a way that the Tb–Tb pair is aligned exactly with the magnetic field direction, while for the perpendicular orientation, the magnetization decreases several times [21]. Therefore, the maximal available magnetization cannot be attained for randomly oriented polycrystals of **2**.

The compounds show a rather narrow hysteresis loop in the magnetic field of 20 Oe/s, as demonstrated in Figure 4. This loop is observed in the  $-1 - +1$  kOe magnetic field range. The magnetic hysteresis width for crystals is larger than for the powder (Figure 4). It is likely that the wider hysteresis loop for the powder can be observed only at temperatures essentially lower than 1.9 K. For example, a hysteresis loop is not observed for  $\text{Tb}_2[(\text{BuO})_8\text{Pc}]_3$  above 1.5 K, and a wider hysteresis loop is found only at very low temperatures ( $T = 0.04 \text{ K}$ ) [21].



**Figure 4.** Hysteresis loops for powdered  $(\text{Pc})\text{Tb}[(15\text{C}5)_4\text{Pc}]\text{Tb}(\text{Pc})$  **1** (a) and polycrystalline sample of  $(\text{Pc})\text{Tb}[(15\text{C}5)_4\text{Pc}]\text{Tb}(\text{Pc}) \cdot 6\text{C}_6\text{H}_4\text{Cl}_2$  **2** (b) measured at 2 K in 20 Oe/s magnetic field.

Thus, in spite of the similar magnetic characteristics of both forms of  $(\text{Pc})\text{Tb}[(15\text{C}5)_4\text{Pc}]\text{Tb}(\text{Pc})$ , they show different dynamic behavior, which is manifested in a more than two times higher  $U_{\text{eff}}$  value for powder **1** ( $222 \text{ cm}^{-1}$ ) in comparison with crystal solvate **2** ( $93 \text{ cm}^{-1}$ ). It is seen

that the formation of well-defined crystals and the presence of solvent ( $\text{C}_6\text{H}_4\text{Cl}_2$ ) molecules, which isolate and surround triple-decker  $(\text{Pc})\text{Tb}[(15\text{C}5)_4\text{Pc}]\text{Tb}(\text{Pc})$  phthalocyanines, do not increase the barrier compared to the solvent-free powdered phase. Unfortunately, the exact crystal structure of **1** is unknown, which prevents the determination of the difference in the geometry of the  $\text{Tb}^{\text{III}}$  environment in both forms. We can only suppose that the appearance of the solvent molecules can affect the dihedral angle between the Pc planes or some other parameters.

Previously, it has been elucidated that the twist angle between the Pc macrocycles can affect the  $D_{4d}$  symmetry of  $\text{Tb}^{\text{III}}$  and, hence, the dynamic magnetic properties of SMMs [14]. Thus, the different packing and arrangement of the surrounding cations and solvent molecules can affect the geometry and properties of double- and triple-decker complexes. For example, the cationic surrounding of the double-decker  $\text{Tb}^{\text{III}}(\text{Pc})_2$  anions changes when  $\text{PPN}^+$  (bis(triphenylphosphoranylidene)ammonium) cations are replaced by the  $\{\text{Cryptand}(\text{Na}^+)\}$  cations. This leads to a change in the twist angle from  $41.2$  to  $38.8^\circ$  and, as a result, the first compound is an SMM with a high  $U_{\text{eff}} = 538 \text{ cm}^{-1}$ , whereas the second compound shows no signs of SMM behavior [34]. There are several examples of different SMM behaviour depending on the nature of the solvent molecules in the crystal lattice. In particular,  $\text{Tb}(\text{Pc})_2$  can be crystallized from either  $\text{CH}_2\text{Cl}_2/\text{MeOH}$  or  $\text{CHCl}_3/\text{MeOH}$ , affording the solvate  $\text{Tb}(\text{Pc})_2 \cdot \text{CH}_2\text{Cl}_2$  or solvent-free crystals, respectively [35]. In spite of only a subtle difference in the geometries of the complex itself in both samples, a butterfly-shaped hysteresis loop is observed up to 10 K only in the case of the solvate, while solvent-free crystals show almost no opening even at 2 K. Binuclear monophthalocyaninate  $(\mu\text{-Pc})[\text{Er}(\text{dpm})_2]_2$  ( $\text{dpm}^-$ —dipivaloylmethanate anion) can be solvated either with  $\text{C}_6\text{H}_6$  or  $\text{CH}_2\text{Cl}_2$  in the course of “crystal-to-crystal” transformation [36]. Fast relaxation with a  $U_{\text{eff}} = 2.6 \text{ cm}^{-1}$  under a 600 Oe dc field is observed for the benzene solvate, while the dichloromethane solvate behaves as a field-induced SMM with a higher  $U_{\text{eff}} = 34.3 \text{ cm}^{-1}$ .

The determined barriers are attributed to the energy gap between the ground and first-excited Stark sublevels. The barrier for powder **1** is higher than that for the powdered heteroleptic triple-decker terbium(III) phthalocyanine with two  $(15\text{C}5)_4\text{Pc}$  decks— $159 \text{ cm}^{-1}$ . Therefore, when both terbium atoms are bound in an asymmetric heteroleptic environment, this can increase the barrier in comparison with the situation when the terbium atoms are in hetero- and homoleptic positions as in  $[(15\text{C}5)_4\text{Pc}]\text{Tb}[(15\text{C}5)_4\text{Pc}]\text{Tb}(\text{Pc})$  [26]. Nevertheless, the homoleptic phthalocyanine with three octa(butoxy)phthalocyanine decks has nearly the same barrier [21]. At the same time, the  $U_{\text{eff}}$  barrier determined for the crystals of **2** is one of the lowest among triple-decker terbium(III) phthalocyanines. Previously, it has been demonstrated that the dynamic characteristics of SMMs based on triple-decker complexes depend mainly on the twist angle between Pc planes, and a dipolar term can affect the dynamic properties.<sup>14</sup> The twist angle of  $42.6^\circ$  in **2** is close to  $45^\circ$ , which is favorable for manifestation of high  $U_{\text{eff}}$ . The f-f dipole interaction generally acts as exchange bias, suppressing the quantum tunneling. As a result, triple-decker complexes showing the f-f interaction generally manifest higher  $U_{\text{eff}}$  barriers in comparison with similar phthalocyanines but containing only one  $\text{Tb}^{\text{III}}$  atom and another diamagnetic lanthanide. For example, the barrier for triple-decker  $(\text{Tb}, \text{Tb})$  phthalocyanine with two  $(15\text{C}5)_4\text{Pc}$  decks is  $159 \text{ cm}^{-1}$ , whereas such barriers for triple-decker phthalocyanines with the  $(\text{Tb}, \text{Y})$  and  $(\text{Y}, \text{Tb})$  combinations are only 90 and  $117 \text{ cm}^{-1}$ , respectively [26]. The dipolar term depends substantially on the distance between two terbium ions proportionally to  $1/R^3$ , where  $R$  is the distance between two terbium atoms [33]. Information on the effect of these distances on the barrier can be obtained only from the oxidation of  $\text{Tb}_2[(\text{BuO})_8\text{Pc}]_3$ . It shows the SMM behavior with  $U_{\text{eff}} = 230 \text{ cm}^{-1}$  at a dihedral angle of only  $32^\circ$  and the Tb–Tb distance of  $3.517 \text{ \AA}$  [21]. As the HOMO of this molecule is antibonding relative to the Tb–N bonds, oxidation depopulates the HOMO, decreasing the Tb–Tb distance in  $\{\text{Tb}_2[(\text{BuO})_8\text{Pc}]_3\}^{2+}(\text{SbCl}_6^-)_2$  to  $3.435 \text{ \AA}$  [37]. As a result, the  $U_{\text{eff}}$  value decreases to  $167 \text{ cm}^{-1}$  despite the fact that the dihedral angle in this complex,  $44.2^\circ$ , is close to  $45^\circ$ , which should provide a higher  $U_{\text{eff}}$ . It should be noted that both compounds show the

f-f interactions with an increase in  $\chi_M T$  values at 2 K (this increase is higher for the oxidized dicationic sample). Therefore, a decrease in the Tb-Tb distance can enhance the f-f interactions and decrease  $U_{\text{eff}}$ . The Tb-Tb distance of 3.4667(3) Å in **2** is one of the shortest distances among neutral triple-decker terbium(III) phthalocyanines. Therefore, the contribution of the dipole term is rather high in **2** and can be one of the reasons for the decrease of  $U_{\text{eff}}$ .

Some of the crystallographic and magnetic data for **1** and **2** are summarized in Table 1.

**Table 1.** Summary of selected structural and magnetic characteristics of samples **1** and **2**.

| Compound                                         | 1             | 2             |
|--------------------------------------------------|---------------|---------------|
| The Tb-Tb distance, Å                            | -             | 3.4667 (3)    |
| Twist angle between inner and outer planes, °    | -             | 42.6          |
| $U_{\text{eff}}$ , cm <sup>-1</sup>              | 222           | 93            |
| Blocking temperature, K                          | ~6            | ~6            |
| Type of coupling between Tb <sup>III</sup> spins | ferromagnetic | ferromagnetic |

### 3. Materials and Methods

#### 3.1. Synthesis

Starting phthalocyanines were synthesized according to the previously reported procedures [31,38]. *o*-dichlorobenzene (C<sub>6</sub>H<sub>4</sub>Cl<sub>2</sub>) was distilled over CaH<sub>2</sub> under reduced pressure, and *n*-hexane was distilled over Na/benzophenone. The solvents were degassed and stored in a glove box. Chloroform was distilled over CaH<sub>2</sub>. All other solvents were used as received from commercial suppliers.

All manipulations for the isolation of solvate **2** were carried out in an MBraun 150B-G glove box with controlled atmosphere and a content of H<sub>2</sub>O and O<sub>2</sub> less than 1 ppm. The crystals were stored in the glove box and sealed in 2 mm quartz tubes under ambient pressure in argon for EPR and SQUID measurements. KBr pellets for the IR- and UV-visible-NIR measurements were prepared in the glove box.

##### 3.1.1. Improved Procedure for the Synthesis of the La(Pc)<sub>2</sub> Complex

Unsubstituted phthalocyanine (257 mg, 0.5 mmol) was suspended in a mixture of 4 mL of 1-chloronaphthalene and 2 mL of octanol, and DBU (152 mg, 1 mmol, 2 equiv.) was added. The reaction mixture was brought to reflux under an argon atmosphere, and lanthanum acetylacetonate (133 mg, 0.3 mmol, 0.6 equiv.) was added. After half an hour, the reaction mixture was cooled down to room temperature, and a mixture of *n*-hexane and ethyl acetate (4:1 *v/v*) was added. The precipitate was filtered off, washed with the same solvent mixture and washed off with a mixture of chloroform and methanol, and the solution was evaporated under reduced pressure. The resulting solid was dissolved in chloroform, and 500 mg of manganese dioxide was added; the resulting mixture was sonicated in an ultrasonic bath for 30 min. The resulting suspension was transferred to a chromatographic column packed with neutral alumina in chloroform, and lanthanum bisphthalocyanate was eluted with a mixture of chloroform with 0 → 4 vol.% methanol. The resulting fractions were combined and evaporated under reduced pressure. The resulting black powder was washed with *n*-hexane, and the complex was dried overnight at 80 °C. The yield was 245 mg (85%). MALDI TOF: *m/z* calcd. for C<sub>64</sub>H<sub>32</sub>LaN<sub>16</sub> 1163.2 found 1163.2—[M]<sup>+</sup>. UV-vis (CHCl<sub>3</sub>)  $\lambda_{\text{max}}$ , nm (*A*<sub>norm</sub>) 691 (0.87), 614 (0.34), 490 (0.21), 450 (0.17), 326 (1.00), 278 (0.43). The analytical characteristics of the complex are consistent with previously reported data [32].

##### 3.1.2. Improved Procedure for the Synthesis of (Pc)Tb[(15C5)<sub>4</sub>Pc]Tb(Pc)

A mixture of complexes [(15C5)<sub>4</sub>Pc]Tb(Pc) (37 mg, 19.0 µmol [31]) and La(Pc)<sub>2</sub> (22 mg, 19.0 µmol) with terbium acetylacetonate hydrate (27 mg, 57.1 µmol) was refluxed in a mixture of 1,2,4-trichlorobenzene (2.15 mL) with *n*-octanol (0.23 mL) for 7 min under

argon. The reaction mixture was poured into *n*-hexane and filtered. The solid was washed with *n*-hexane and dissolved in chloroform, and the target complex (Pc)Tb[(15C5)<sub>4</sub>Pc]Tb(Pc) was isolated in 71% yield (35.3 mg) using column chromatography on neutral alumina (CHCl<sub>3</sub> + 0.75% vol MeOH), followed by drying overnight at 80 °C, thus affording a powder sample of **1**. MALDI TOF: *m/z* calcd. for C<sub>128</sub>H<sub>104</sub>N<sub>24</sub>O<sub>20</sub>Tb<sub>2</sub> 2615.6 found 2615.9—[M]<sup>+</sup>. UV-vis (CHCl<sub>3</sub>) λ<sub>max</sub>, nm (A<sub>norm</sub>) 696 (0.17), 642 (1.00), 332 (0.63), 294 (0.40). Anal. calc. for C<sub>128</sub>H<sub>104</sub>N<sub>24</sub>O<sub>20</sub>Tb<sub>2</sub>: C 58.76, H 4.01, Tb 12.15 found C 57.76, H 4.16, Tb 11.82. Chlorine was not found in the samples, suggesting complete removal of chloroform upon sample drying. The analytical characteristics of the complex are consistent with reported data [30].

### 3.1.3. Preparation of Single Crystals of (Pc)Tb[(15C5)<sub>4</sub>Pc]Tb(Pc)·6C<sub>6</sub>H<sub>4</sub>Cl<sub>2</sub> (**2**)

First, 25 mg of (Pc)Tb[(15C5)<sub>4</sub>Pc]Tb(Pc) (0.0095 mmol) was dissolved in 17 mL of *o*-dichlorobenzene during 24 hours at 50 °C. Obtained green solution was cooled down to room temperature and filtered into a glass tube of 46 ml volume, and *n*-hexane (26 mL) was layered onto the obtained solution. Slow diffusion of *n*-hexane during 1 month yielded crystals on the walls of the tube suitable for X-ray diffraction analysis. The solvent was decanted from the crystals, and they were washed with *n*-hexane to give black blocks of **2** with 62% yield. The composition of the crystals determined from the X-ray diffraction was (Pc)Tb[(15C5)<sub>4</sub>Pc]Tb(Pc)·6C<sub>6</sub>H<sub>4</sub>Cl<sub>2</sub> (**2**). All crystals had the same shape and color. Several crystals tested from the synthesis gave the same unit cell parameters indicating that only one crystal phase was formed. Anal. calc. for C<sub>164</sub>H<sub>128</sub>Cl<sub>12</sub>N<sub>24</sub>O<sub>20</sub>Tb<sub>2</sub>: Cl 12.18, found Cl 11.94.

IR-spectrum of **2**: 492 w, 565 w, 630 w, 719 w, 732 s, 743 s, 756 w, 780 w, 856 w, 883 m, 934 m, 981 w, 1002 w, 1061 m, 1081 s, 1113 s, 1199 w, 1273 s, 1315 w, 1329 m, 1356 w, 1374 w, 1407 m, 1450 m, 1478 s, 1607 w, 2867 w, 2921 w, 3047 w, 3077 w cm<sup>−1</sup> (w: weak; m: medium; s: strong intensity). IR- and optical spectra are shown in Figures S1 and S2, respectively.

Crystal data for **2** at 100(1) K: C<sub>164</sub>H<sub>128</sub>Cl<sub>12</sub>N<sub>24</sub>O<sub>20</sub>Tb<sub>2</sub>, F.W. 3498.14, black prism, 0.400 × 0.190 × 0.080 mm, monoclinic, space group *P*2<sub>1</sub>/*n*, *a* = 15.6657(3), *b* = 23.5878(6), *c* = 20.3168(6) Å, β = 96.146(2)°, *V* = 7464.3(3) Å<sup>3</sup>, *Z* = 2, *d*<sub>calcd</sub> = 1.556 M gm<sup>−3</sup>, μ = 1.233 mm<sup>−1</sup>, *F*(000) = 3548, 2θ<sub>max</sub> = 54.206°; 50,991 reflections collected, 15,290 independent; *R*<sub>1</sub> = 0.0428 for 11,779 observed data [*>2σ*(*F*)] with 698 restraints and 1090 parameters; *wR*<sub>2</sub> = 0.1050 (all data); final GoF = 1.049. CCDC 2225666.

### 3.2. General

UV-visible-NIR spectra were recorded as KBr pellets on a Perkin Elmer Lambda 1050 spectrophotometer in the 250–2500 nm range. FT-IR spectra were recorded as KBr pellets on a Perkin-Elmer Spectrum 400 spectrophotometer (400–7800 cm<sup>−1</sup>). A Quantum Design MPMS-XL SQUID magnetometer was used to measure the static magnetic susceptibility of **1** and **2** under a magnetic field of 100 mT, under cooling and heating conditions in the 300–1.9 K range. The sample-holder contribution and core temperature-independent diamagnetic susceptibility (χ<sub>d</sub>) were subtracted from the experimental values. The χ<sub>d</sub> values were estimated from the extrapolation of the data in the high-temperature range by fitting the data with the following expression: χ<sub>M</sub> = *C*/(*T* − Θ) + χ<sub>d</sub>, where *C* is the Curie constant and Θ is the Weiss temperature. The dynamic magnetic properties of **1** and **2** were studied at 3.0 Oe ac field at the 1–1500 Hz frequencies using a Quantum Design MPMS-5S SQUID magnetometer.

### 3.3. X-ray Crystal Structure Determination

X-ray diffraction data for **2** were collected on an Oxford diffraction “Gemini-R” CCD diffractometer with graphite monochromated MoK<sub>α</sub> radiation using an Oxford Instrument Cryojet system. Raw data reduction to *F*<sup>2</sup> was carried out using CrysAlisPro, Oxford Diffraction Ltd. (Abingdon, UK). The structures were solved using direct methods and refined using the full-matrix least-squares method on *F*<sup>2</sup> with SHELX-2018/3.[39] Non-hydrogen atoms were refined anisotropically. Positions of hydrogen atoms were

included into refinement in a riding model. Crystal structure of **2** contains half independent  $(\text{Pc})\text{Tb}[(15\text{C}5)_4\text{Pc}]\text{Tb}(\text{Pc})$  unit which is ordered and has full occupancy. In addition, there are three positions of solvent  $\text{C}_6\text{H}_4\text{Cl}_2$  molecules. Two molecules are ordered, but the third molecule is disordered over three orientations with the 0.422(2)/0.419(2)/0.159(2) occupancies. To keep anisotropic thermal parameters of the disordered fragments, the displacement components were restrained using SHELXL instructions of ISOR, SIMU and DELU. That resulted in the use of 698 restraints for the refinement of crystal structure of **2**.

#### 4. Conclusions

We have obtained solvent-free (**1**) and solvent-containing (**2**) forms of triple-decker phthalocyanine  $(\text{Pc})\text{Tb}[(15\text{C}5)_4\text{Pc}]\text{Tb}(\text{Pc})$  with the inner 15-crown-5-substituted deck and studied the crystal structure of the *o*-dichlorobenzene solvated form. These forms also have different crystallinity as **2** was obtained as well-defined single crystals in contrast to powdered **1**. Both forms have similar static magnetic properties manifesting ferromagnetic coupling between  $\text{Tb}^{\text{III}}$  spins. Such behavior is typical of triple-decker terbium(III) phthalocyanines, and this coupling has mainly a dipolar nature [33]. In spite of similar static magnetic properties, the solvent-free form shows more than two times higher  $U_{\text{eff}}$  ( $222\text{ cm}^{-1}$ ) in comparison with the *o*-dichlorobenzene crystal solvate ( $93\text{ cm}^{-1}$ ). Most probably, this difference is explained by the effect of the solvent molecules on the skew angle between the Pc planes and/or some other parameters. As the shortening of the Tb–Tb distance can enhance the f–f coupling and decrease the  $U_{\text{eff}}$  barrier, we suppose that the Tb–Tb distance in **2** is minimal among the described neutral triple-decker  $\text{Tb}^{\text{III}}$  complexes, which can be one of the reasons for a low  $U_{\text{eff}}$  barrier. Information on the dynamic properties of structurally characterized triple-decker terbium(III) complexes is still rather limited, and only additional studies will be able to shed light onto the exact correlations between the dynamic properties of SMMs and their geometric parameters.

**Supplementary Materials:** The following are available online at <https://www.mdpi.com/article/10.3390/magnetochemistry9020036/s1>, Figure S1: Powder diffraction pattern of the compound  $(\text{Pc})\text{Tb}[(15\text{C}5)_4\text{Pc}]\text{Tb}(\text{Pc})$  **1**. Figure S2: IR-spectrum of  $(\text{Pc})\text{Tb}[(15\text{C}5)_4\text{Pc}]\text{Tb}(\text{Pc}) \cdot 6\text{C}_6\text{H}_4\text{Cl}_2$  **2** measured in KBr pellet. Figure S3: UV-visible-NIR spectrum of  $(\text{Pc})\text{Tb}[(15\text{C}5)_4\text{Pc}]\text{Tb}(\text{Pc}) \cdot 6\text{C}_6\text{H}_4\text{Cl}_2$  **2** in the 220–1800 nm range. Figure S4: View on two chains from the  $(\text{Pc})\text{Tb}[(15\text{C}5)_4\text{Pc}]\text{Tb}(\text{Pc})$  molecules in **2** arranged along the *a* axis. Figure S5: Surrounding of one  $(\text{Pc})\text{Tb}[(15\text{C}5)_4\text{Pc}]\text{Tb}(\text{Pc})$  molecule by 14 solvent *o*-dichlorobenzene molecules in the crystal structure of **2**. Figure S6: Temperature dependence of molar magnetic susceptibility for powdered sample of  $(\text{Pc})\text{Tb}[(15\text{C}5)_4\text{Pc}]\text{Tb}(\text{Pc})$  **1**. Figure S7: Temperature dependence of molar magnetic susceptibility in zero-field and field-cooling conditions for the powdered sample of  $(\text{Pc})\text{Tb}[(15\text{C}5)_4\text{Pc}]\text{Tb}(\text{Pc})$  **1**. Figure S8: Temperature dependence of reciprocal molar magnetic susceptibility of **1** allowing us to determine Weiss temperature of  $-1.5\text{ K}$ . Figure S9: Dependence of magnetization vs. magnetic field up to 50 kOe at 2 K for the powdered sample of  $(\text{Pc})\text{Tb}[(15\text{C}5)_4\text{Pc}]\text{Tb}(\text{Pc})$  **1**. Figure S10: Hysteresis loop at 2 K observed in magnetic field between  $-50$  and  $50\text{ kOe}$  for the powdered sample of  $(\text{Pc})\text{Tb}[(15\text{C}5)_4\text{Pc}]\text{Tb}(\text{Pc})$  **1**. Figure S11: Frequency dependence of in-phase ( $\chi'$ ) and out-of-phase ( $\chi''$ ) ac magnetic susceptibility of powdered sample of  $(\text{Pc})\text{Tb}[(15\text{C}5)_4\text{Pc}]\text{Tb}(\text{Pc})$  **1**. Figure S12: Temperature dependence of molar magnetic susceptibility for polycrystalline sample of  $(\text{Pc})\text{Tb}[(15\text{C}5)_4\text{Pc}]\text{Tb}(\text{Pc}) \cdot 6\text{C}_6\text{H}_4\text{Cl}_2$  **2** measured in 1 kOe magnetic field. Figure S13: Temperature dependence of molar magnetic susceptibility in zero-field and field-cooling conditions for polycrystalline sample of  $(\text{Pc})\text{Tb}[(15\text{C}5)_4\text{Pc}]\text{Tb}(\text{Pc}) \cdot 6\text{C}_6\text{H}_4\text{Cl}_2$  **2**. Splitting between two curves is observed below  $\sim 6\text{ K}$ . Figure S14: Temperature dependence of reciprocal molar magnetic susceptibility of **2** allowing us to determine Weiss temperature of  $-1.7\text{ K}$ . Figure S15: Frequency dependence of in-phase ( $\chi'$ ) and out-of-phase ( $\chi''$ ) ac magnetic susceptibility of polycrystalline sample of **2**.

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