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X-ray Crystallographic Analysis of a Tailor-Made Bis(phthalocyaninato)-Tb^{III} Single-Molecule Magnet as a Fundamental Unit for Supramolecular Spintronic Devices

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The single-crystal X-ray diffraction analysis of the title compound, the pyrene-substituted unsymmetrical bis(phthalocyaninato)terbium(III) Single-Molecule Magnet (SMM) [Pc–Tb–Pc*]^0 (**1**) (Pc = dianion of phthalocyanine, P* = dianion of phthalocyanine decorated with six flexible hexyl chains and one 4-pyren-1yl-butoxy group), was carried out. Both phthalocyaninato ligands in **1** are distorted from planarity and, therefore, adopt a biconcave shape. Effective π–π interactions between the molecules lead to the formation of head-to-tail π dimers. These dimers are stacked in the crystal, forming adjacent, parallel columns, the axes of which are tilted by 30° with respect to the C_4 axes of the macrocycles. Herein, we also report the synthesis and characterization of the new isostructural Dy (compound **2**) and Ho (compound **3**) analogues of **1**.

Introduction

The bis(phthalocyaninato)terbium(III) complexes $[TbPc_2]^{-/0/+}$ (Pc = dianion of phthalocyanine) as well as the isostructural dysprosium(III) and holmium(III) compounds, discovered by Ishikawa and co-workers,[1–6] are the first examples of mononuclear metal complexes behaving like single-molecule magnets (SMMs). They exhibit large magnetic anisotropies, slow relaxation, and quantum tunneling of magnetization (QTM) in a temperature range significantly higher than that of all other known SMMs, which provides an unique quantum fingerprint of the molecule on the magnetic-reversal mechanism.[7] For the terbium complexes, the out-of-phase component of the dynamic magnetic susceptibility appears well above 40 K because of the unusually high energy barrier ΔE for the reversal of the magnetization.[8]

These striking magnetic properties and their robust monoatomic structure (unlike in most d-metal cluster SMMs) provided the possibility to chemically tune the molecular properties of these systems and, at the same time, to maintain their metallic core and, hence, their SMM behavior.[9] Moreover, the properties of this molecule remain unchanged when it is grafted onto different substrates including non-magnetic substrates, such as HOPG (highly ordered pyrolytic graphite),[10,11] Au(111), Cu(111), Cu(100)[12–15], and magnetic substrates, such as Ni films,[16] ultrathin Co and Ni films,[17] a perovskite manganite of LSMO (lanthanum strontium manganite)[18], and substrates with antiferromagnetic Mn and CoO layers.[19] Therefore, bis(phthalocyaninato)lanthanide(III) complexes could serve as the fundamental units in single-molecule devices, which includes the possibility to electrically read out the spin state of a single nuclear spin, which could be of great importance for a wide range of applications, from nanospintronics to quantum computing.[20] Indeed, this molecule has been successfully fabricated into different spintronic devices by direct coupling in molecular junctions,[21,22] by indirect coupling within double magnetic quantum dots (QD) based on sp^2-carbon materials, such as SWNT and graphene,[23–28] and by supramolecular self-assembly of the custom-made complex [Pc–Tb–Pc*]^0 (**1**),[9] which shows promising applications.

Results and Discussion

Because of the flexibility of long hydrocarbon chains and similar substituents, single crystals of phthalocyanine derivatives with long flexible chains (such as alkyl and alkoxy) are not easy to obtain and X-ray diffraction analyses of substituted compounds remain few.[29] Nevertheless, there are exceptions, and these include a number of examples of octasubstituted derivatives, where alkyl,[30,31] alkoxy,[32–34] or crown-ether[35] groups are located at peripheral and non-peripheral positions. To the best of our knowledge, there is

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no X-ray diffraction analysis of bis(phthalocianinato) derivatives bearing one unsymmetrical phthalocyanine ligand (Pc*).

This paper describes a single-crystal X-ray diffraction study of the unsymmetrical bis(phthalocyaninato)terbium(III) complex **1**. Single crystals suitable for X-ray diffraction analysis were obtained as fine dark green needles by slow diffusion of EtOH into a solution of complex **1** in a hexane/$CHCl_3$ mixture. A view of the molecular structure of **1** is depicted in Figure 1. Compound **1** crystallizes in the triclinic space group $P\bar{1}$ with two molecules per unit cell (Table 1). The terbium ion occupies a central position in the complex and is eightfold coordinated by the isoindole nitrogen atoms (N_{iso}) of the phthalocyaninato ligands [N1–N4 (Pc) and N5–N8 (Pc*)]. The central terbium ion lies 1.425 Å from the N_{iso} mean plane of the Pc ligand and 1.378 Å from the N_{iso} mean plane of the Pc* ligand bearing peripheral substituents. The calculated distance between the two N_{iso} mean planes is 2.824 Å. This value is slightly larger than that reported for other terbium bis(phthalocyanine) materials (2.67–2.70 Å).[36–38]

Unlike the previously described unsubstituted lanthanide phthalocyanine structures,[8,12,39,40] both phthalocyaninato ligands of **1** are distorted from planarity and, therefore, adopt a biconcave shape. Nevertheless, the distortions of the Pc and Pc* ligands are not equal and more pronounced

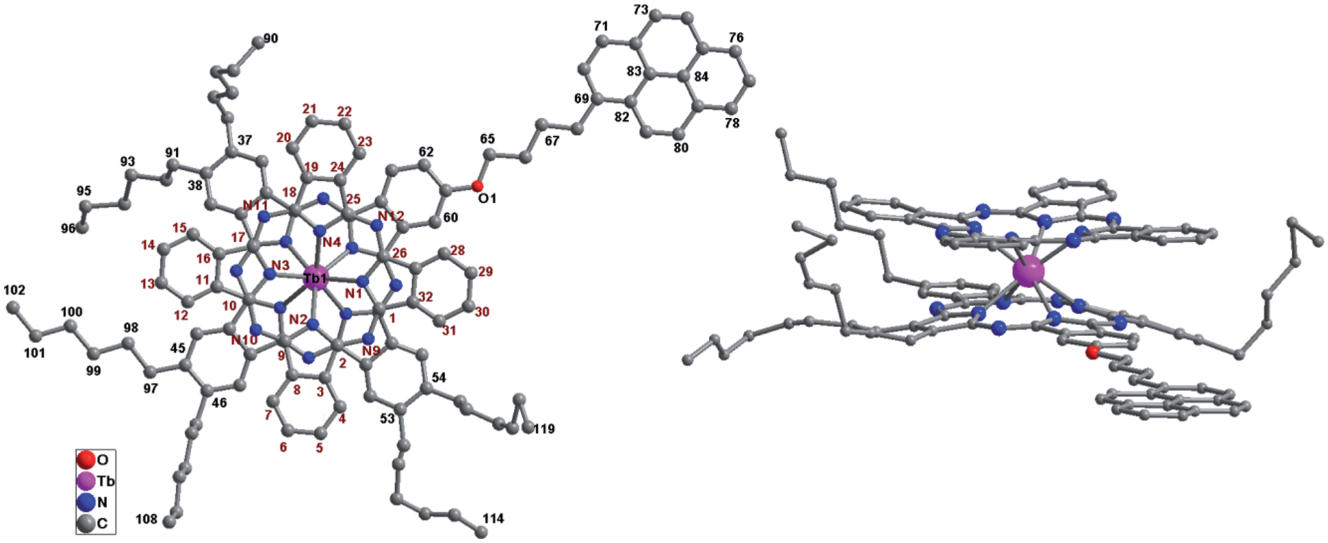


Figure 1. ORTEP plot of one molecule of **1** with ellipsoids drawn at the 50% probability level for all non-hydrogen atoms. Top view (left) indicating the numbering scheme. Atoms labelled *n* represent the carbon atoms C*n*. Side view (right): the chains at C46 and C38 have been omitted for clarity. There is disorder in the hexyl chains at C53 and C54. The disorder model and the positions of the hydrogen atoms are omitted for clarity.

Table 1. Crystallographic data for compound (**1**).

	$\mathbf{1}\cdot 1.4CHCl_3\cdot 0.5C_2H_5OH$
Elemental formula[a]	$C_{119.40}H_{116.90}Cl_{4.20}N_{16}O_{1.50}Tb$
Formula weight [g/mol]	2107.80
Crystal system	triclinic
Space group	$P\bar{1}$
Unit cell dimensions	
a, *b*, *c* [Å]	14.249(3), 18.994(4), 23.114(5)
α, *β*, *γ* [°]	72.30(3), 78.81(3), 75.53(3)
Cell volume, *V* [Å^3]	5723(2)
Number of formula units/cell, *Z*	2
Absorption coefficient, $\mu(\lambda)$ [mm^{-1}]	0.771
Temperature [K]	150(2)
Total number of reflections measured	62627
Number of unique reflections measured	22040
R_{int} for equivalents	0.0537
Number of "observed" reflections, $I > 2\sigma_I$	17247
Final *R* indices, R_1 ("observed" data)[b], wR_2 (all data)[c]	0.0514, 0.1422

[a] Non-integer numbers of atoms result from partial disorder of the hexyl groups, which could not be completely modeled. [b] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [c] $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$.

for the substituted ligand. In the Pc ligand, the angle between the N_{iso} plane and the planes of benzene rings are about 7°. In the Pc* ligand, the angle between the N_{iso} plane and the planes of two alternating benzene rings with hexyl substituents is 18°, whereas the other set bearing a pyren-1-yl-butoxy group lies in plane. This suggests that the long alkyl chains and the 4-pyren-1yl-butoxy group on the benzene rings have a significant effect on the geometry of the phthalocyanine molecular plane. Only two of the six hexyl chains, those attached to atoms C45 and C53, lie within the plane of the Pc ring. The chain bound to atom C39 is pointing down relative to the Pc ligand, whereas the chains attached to C37, C46, and C54 are facing up. The skew angel, determined as the rotational angle of the N_{iso} mean planes with respect to each other, is 41.2°, and it is in good agreement with published values for Tb bis(phthalocyaninato) complexes.[12] On the basis of the distance between two hydrogen atoms at hexyl and pyrenyl groups (H121/H85), the width of one molecule of **1** was estimated to be approximately 3.4 nm , and the height of the bis(phthalocyaninato) core was estimated to be 0.5 nm on the basis of the distance between the hydrogen atoms H8 and H53 of the Pc and Pc* rings, respectively.

Phthalocyanines and their derivatives typically have a large conjugated molecular electronic structure. The dominant π–π interactions between phthalocyanine molecules usually lead to 1D nanostructures.[40] Nevertheless, tuning the intermolecular interaction towards more complex self-assembled nanostructures can be achieved by incorporating functional groups into the phthalocyanine framework.[41] Thus, the presence of a 4-pyren-1yl-butoxy group in the molecular structure of **1** with its large conjugated electronic structure is expected to induce complexity in the internal crystal packing. The crystal packing of $[Pc–Tb–Pc^*]^0$ (**1**) is depicted in Figure 2. There are two principal features of the packing. Firstly, despite the deformed molecular structure and the saucer conformation adopted by the Pc and Pc* rings, effective π–π interactions exist between the molecules of **1**. Thus, pairs of complex molecules form head-to-tail π dimers, which is evidenced by the overlap of the pyrenyl group and the Pc* ring of a second molecule with a shortest intermolecular distance of 3.345–3.369 Å (Figure 2, Figure S1), which is in a good agreement with the general values observed for π–π stacking.[42–44] Secondly, the dimers translate in the crystal with an offset, which leads to the formation of columns parallel to the *b* axis (Figure 2). The column axis is tilted by 30° with respect to the C4 axis of the Pc macrocycle, which is similar to the solvated YPc_2 compound.[39] The adjacent columns are intercalated with shortest distances of 3.617 Å between benzene rings of Pc ligands from two different columns (Figures S2 and S3).

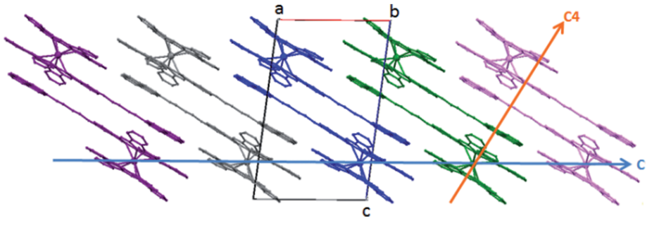
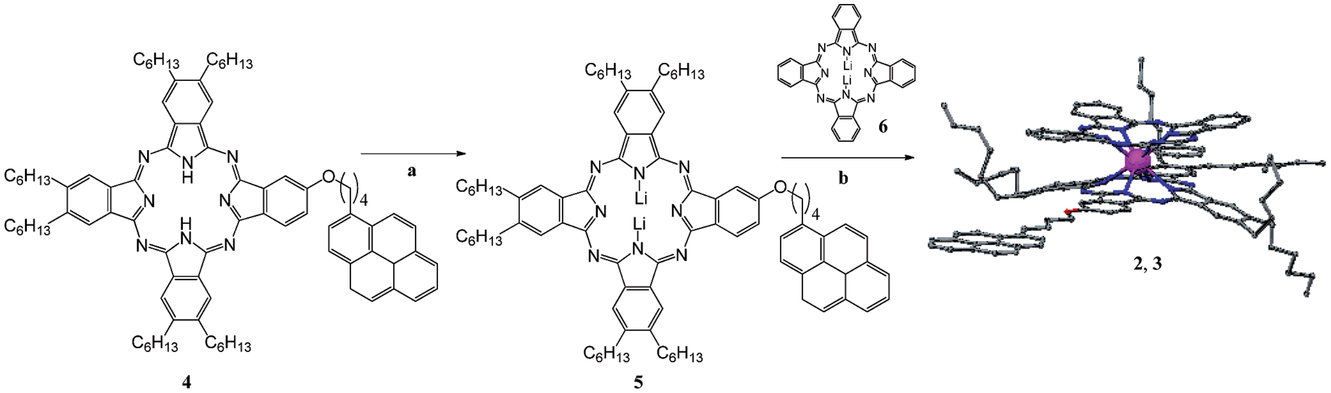


Figure 2. View of the packing in **1** along the *b* axis. All H atoms and $–C_6H_{13}$ groups are omitted for clarity. Different color codes are indicating π dimers.

The shortest intermetallic Tb–Tb distance of 13.084 Å was found between adjacent, parallel columns, whereas the Tb–Tb distance is much larger (16.976 Å) within the π dimer. Complex **1** crystallizes with molecules of ethanol and chloroform in the crystal lattice. Each π dimer is surrounded by two EtOH and four $CHCl_3$ molecules. Chloroform molecules indicate the formation of hydrogen bonds with N and H atoms ($Cl_3C–H\cdots N$; $CHCl_2–Cl\cdots H$) of the phthalocyanine macrocycles (Figure S4).

Herein, we also report the synthesis of new isostructural pyrene-substituted bis(phthalocyaninato)-Ln^{III} complexes [Ln = Dy (compound **2**), Ho (compound **3**)] (Scheme 1). The complexes **2** and **3** were synthesized according to a published procedure[9] from two different phthalocyaninato lithium salts (**5** and **6**) and $Ln(acac)_3$ hydrate (Ln = Dy or Ho) in a 1:1:1 ratio. The synthesis of 4,5-dihexylbenzene (**9**) was significantly improved by using the Pd/Cu-catalyzed Sonogashira cross coupling of dichlorophthalonitrile (**7**)



Scheme 1. Synthesis of $[Pc–Ln–Pc^*]^0$ complexes, where Ln = Dy (for **2**), Ho (for **3**). (a) Li/MeOH; (b) 1-chloronaphthalene, reflux.

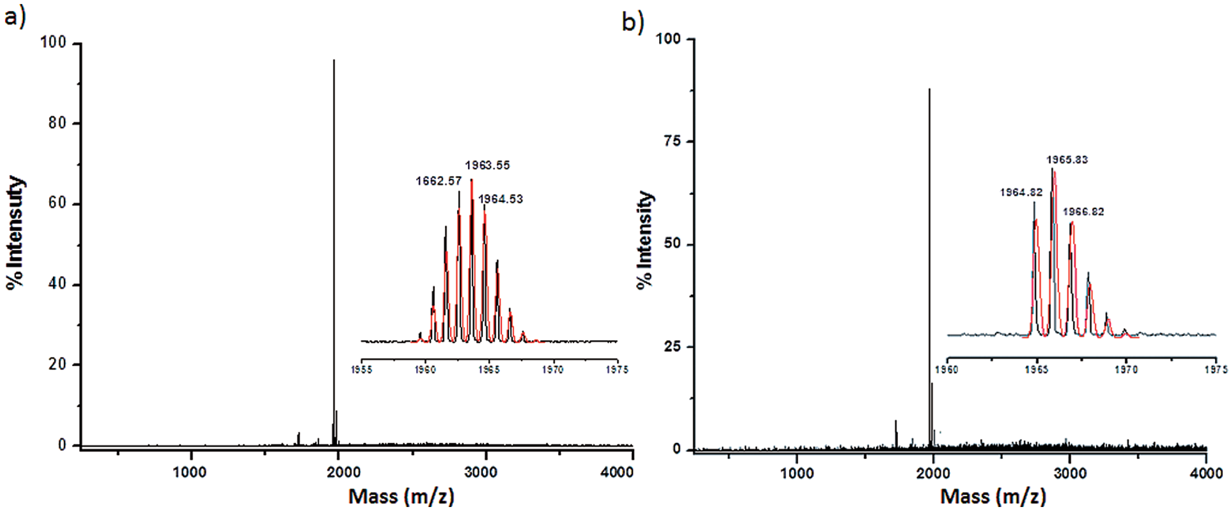


Figure 3. MALDI-TOF spectra of complexes **2** (a) and **3** (b); here, the experimental and calculated (red lines) values of the relative abundances of the isotopic ions are summarized.

with hex-1-yne, which was followed by catalytic hydrogenation with gaseous H_2 (Scheme S1). This approach allowed us to increase the total yield of the key building block **4** from 10%[9] to 60%. The MALDI-TOF mass spectra of **2** and **3** both showed intense signals for the molecular ion $[M - H^+]$ at m/z = 1963 and m/z = 1965, respectively, and this proves their unsymmetrical nature. In both cases, the molecular ion was the most abundant high-mass ion with a distinct isotopic distribution. The relative abundances of the isotopic ions are in good agreement with the simulated spectra, as depicted in Figure 3, where the experimental and calculated values are summarized.

The nature of complexes **2** and **3** was further confirmed by UV/Vis–NIR and NMR spectroscopy. The complexes have a one-electron-oxidized-ligand "sandwich" structure, in which the unpaired electron is delocalized on both phthalocyanine ligands.[45,46] Similar to the parent Tb complex **1**, the lanthanide bis(phthalocyaninato) complexes **2** and **3** exhibit two bands at 490 and 922 nm (the $e_g \rightarrow a_{1u}$ transitions), which are characteristic of a Pc π radical, as well as another broad band in the range 1200–1700 nm, which corresponds to intramolecular-charge-transfer (ICT) (Figure S5). The two absorption bands at 673 and 328 nm were assigned to the Q band and the Soret band, respectively. The weak shoulder attached to the Q band (605 nm) has been reported to be due to weak π–π interactions occurring between the two Pc/Pc* ligands. All the NIR bands disappear upon reduction of **2** and **3** with hydrazine hydrate (1%, v/v). Moreover, good NMR spectroscopic data in $CDCl_3$ could only be obtained after reduction, which supports the assumption that a radical form of the complexes **2** and **3** is present. The ^1H NMR spectra are quite complex and show many superimposed multiplets, which confirms the unsymmetrical nature of **2** and **3**, whereas the unsubstituted $LnPc_2$ complexes[8,47] are symmetrical and have rather simple NMR spectra.

The electrochemical behavior of the complexes **2** and **3** was studied by cyclic voltammetry (CV) with a platinum working electrode and solutions in dichloromethane containing 0.1 M $[nBu_4N][ClO_4]$. The cyclic voltammograms of **2** and **3** are very similar to those of the unsymmetrical Tb bis(phthalocyanine) **1**,[9] and three quasi-reversible one-electron redox processes appear near +0.64, –0.19, and –0.61 V (Figure S6). Thus, the neutral forms of the sandwich complexes **2** and **3** undergo one oxidation and two reduction steps as well.

The SMM behavior of **1** was reported before,[9] whereas the SMM behavior of complexes **2** and **3** is evidenced by the opening of hysteresis cycles in the subkelvin temperature range (Figure 4), as acquired with a micro-SQUID magnetometer.[48] The hysteresis behavior was investigated

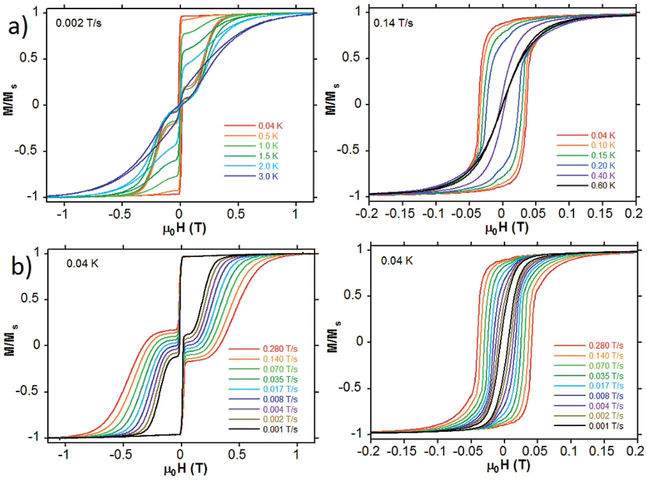


Figure 4. Micro-SQUID hysteresis cycles of **2** (left) and **3** (right), recorded at different temperatures (a) and scan rates (b). The applied magnetic field was aligned along the easy axis of magnetization.

as a function of temperature and field sweeping rate. The hysteresis loops exhibit increasing hysteresis with decreasing temperature at a constant sweep rate (Figure 4, a) and increasing hysteresis with increasing field sweep rate at a constant temperature (Figure 4, b), as expected for the superparamagnet-like properties of a SMM.

Conclusions

The molecular structure of the SMM [Pc–Tb–Pc*] (**1**), which was intensively studied over the last years, as it is the active unit in spintronic devices,[21–28] was determined by means of single-crystal X-ray diffraction analysis. The crystallographic analysis revealed that both phthalocyaninato ligands are slightly distorted from planarity. Despite this, effective π–π interactions exist between the molecules, which lead to the formation of head-to-tail π dimers. A homologous series of the new unsymmetrical mononuclear pyrenyl-containing bis(phthalocyaninato)-based SMMs, [Pc–Ln–Pc*] with Ln = Dy (**2**), Ho (**3**) was successfully synthesized. Their spectroscopic and electrochemical properties are almost identical to the parent Tb complex **1**, and their SMM behavior is evidenced by the appearance of hysteresis cycles for both compounds in the subkelvin temperature range, which is similar to their parent compound **1**.[5,6] These results revealed the outstanding robustness of the SMM behavior in this series of modified bis(phthalocyaninato)lanthanide(III) complexes.

Experimental Section

X-ray Crystallography: Crystals suitable for single-crystal X-ray diffraction were obtained by slow diffusion of EtOH into a solution of complex **1** in a hexane/$CHCl_3$ mixture, and they were then selected in perfluoroalkyl ether oil. Single-crystal X-ray diffraction data of **1** were collected by using graphite-monochromatized Mo-K_α radiation (λ = 0.71073 Å) with a STOE STADI Vari (Pilatus Hybrid Pixel Detector). Raw intensity data were collected and treated with the STOE X-Area software version 1.64. The data were corrected for Lorentz and polarization effects. Interframe scaling was done with the implemented program LANA.

The structure was solved with the direct-methods program SHELXS of the SHELXTL PC suite programs,[49] and it was refined by using the full-matrix-least-squares program SHELXL. Crystal data and the results of the refinement are collected in Table 1. Molecular diagrams were prepared by using Diamond.[50]

In **1**, Tb and all C, O, and N atoms were refined with anisotropic displacement parameters. Two of the hexyl groups (C109–C114 and C115–C120) showed strong disorder, which was modelled by using partial-occupancy carbon atoms. For one of these chains (C115–C120), one carbon atom could not be localized in the difference Fourier map. For two other hexyl groups, four carbon atoms, which are situated at the end of the chains (C88, C89, C90, and C96) could only be refined with half occupancy. Disordered C atoms were refined isotropically. H atoms were placed in fixed positions. $CHCl_3$ and C_2H_5OH solvent molecules were also refined with partial occupancy. Further residual electron density identified within the crystal lattice of **1** could not be adequately refined. The data were therefore corrected for the residual electron density by using the SQUEEZE option within the PLATON[51] program package, and a total number of 84 electrons were found in a potential solvent-accessible area of 280 Å^3.

An attempt to improve the quality of the model by recording a dataset for **1** at the synchrotron facility ANKA (KIT, Germany) with a stronger X-ray source resulted only in comparable data.

CCDC-912132 (for **1**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Magnetic Measurements: Hysteresis cycles were acquired with a homemade micro-SQUID setup.

General Synthetic Remarks: Reactions requiring an inert gas atmosphere were conducted under argon, and the glassware was oven dried (140 °C). All reagents were purchased from commercial sources and used as received. Radial chromatography was performed with a Chromatotron 7924 T, with plates prepared from Silica gel $60PF_{254}$ containing gypsum. The asymmetrically substituted phthalocyanine Pc^*H_2 (compound **4**), its lithium salt (compound **5**), and 4-(4-pyren-1-yl-butoxy)phthalonitrile (**10**) were prepared according to literature procedures.[9]

4,5-Bis(hex-1-yn-1-yl)phthalonitrile (8): To a solution of dichlorophthalonitrile (**7**) (5.81 g, 30 mmol) in dry Et_3N (300 mL), $Pd(PPh_3)_4$ (200 mg) and CuI (80 mg) were added, and the reaction mixture was heated to 80 °C. A solution of hex-1-yne (7.3 g, 90 mmol) in 30 mL of Et_3N was added dropwise over 20 min. After the addition was complete, the reaction mixture was heated at reflux until **7** had fully reacted (1.5 h, TLC control). The mixture was poured into ice water (200 mL) and then extracted with diethyl ether (3×100 mL). The combined organic layers were washed twice with water and dried with magnesium sulfate. The solvent was removed under reduced pressure, and the residue was purified by chromatography on SiO_2 to afford compound **8** (5.2 g, 65% yield). ^{1}H NMR ($CDCl_3$): δ = 0.96 (t, J = 7 Hz, 6 H), 1.41–1.52 (m, 4 H), 1.60–1.64 (m, 4 H), 2.50 (t, J = 7 Hz, 4 H), 7.72 (s, 2 H) ppm. ^{13}C NMR ($CDCl_3$): δ = 13.60, 19.49, 21.96, 30.30, 102.30, 113.39, 114.86, 131.74, 136.39 ppm. NIR–IR (KBr): $\tilde{\nu}$ = 2104 (C≡C) cm^{-1}. $C_{20}H_{20}N_2$ (288.39): calcd. C 83.30, H 6.99, N 9.71; found C 83.35, H 7.08, N 9.80.

4,5-Dihexylbenzene (9): To a solution of 1,5-bis(hex-1-yn-1-yl)-phthalonitrile (**8**) (2.88 g, 10 mmol) in EtOH (150 mL), Pd black/C (2 g) was added. The reaction was kept at room temperature, and gaseous H_2 was bubbled through the mixture until **8** had fully reacted (2.5 h, TLC control). The solids were filtered off, and the solvent was removed from the filtrate under reduced pressure. The residue was purified by chromatography on SiO_2 to afford compound **9** (2.7 g, 93% yield), which was recrystallized from light petroleum (m.p. 85–89 °C). ^{1}H NMR ($CDCl_3$): δ = 0.90 (t, J = 7 Hz, 6 H), 1.31–1.33 (m, 8 H), 1.36–1.39 (m, 4 H), 1.54–1.60 (m, 4 H), 2.67 (t, J = 7 Hz, 4 H), 7.55 (s, 2 H) ppm. ^{13}C NMR ($CDCl_3$): δ = 13.61, 19.47, 21.94, 22.17, 30.30, 30.75, 113.56, 114.98, 131.70, 136.79 ppm. NIR–IR (KBr): no band corresponding to (C≡C). $C_{20}H_{18}N_2$ (286.38): calcd. C 81.03, H 9.52, N 9.45; found C 81.15, H 9.08, N 9.39.

Synthesis of the Bis(phthalocyaninato)Ln^{III} Complexes 2 and 3: Under a slow stream of Ar, a mixture of $PcLi_2$ (**6**) (68 mg, 0.13 mmol) and $Ln(acac)_3·2H_2O$ (0.13 mmol) in 1-chloronaphthalene (5 mL), which was percolated through a basic alumina column just before being used, was heated at 185–195 °C for 1 h until **6** had fully reacted. The resulting dark blue solution was cooled down, and **5** (160 mg, 0.11 mmol) was added. The mixture was again heated up to 200–210 °C for 1 h until **5** had fully reacted (MALDI-TOF control). The mixture was then subjected to column chromatography (basic aluminum oxide, 60 g) with CH_2Cl_2/hexane (7:4 v/v) as the eluent. 1-Chloronaphthalene was eluted first. Then, a greenish-blue band was collected and concentrated to yield a product mixture {according to MALDI-TOF, the main components are $[Pc–Ln–Pc^*]^{0/–}$ and [Pc*–Ln–Pc–Ln–Pc); minor components are $[Pc^*–Ln–Pc^*]^{0/–}$, $[Pc–Ln–Pc]^{0/–}$} as a dark blue-green powder.

Ln = Dy (compound 2): Complex **2** was separated from the crude mixture by column chromatography (basic aluminum oxide) with CH_2Cl_2/MeOH (10:1 v/v) as the eluent, which was followed by reprecipitation from a hexane/CH_2Cl_2 mixture to afford a deep green solid of neutral **2** (87 mg, 24% with respect to **5**; R_f = 0.38; CH_2Cl_2). MALDI-TOF: calcd. for $C_{120}H_{120}N_{16}ODy$ $[M – H]^+$ 1963.9143; found 1963.5697 (M^+, 100%).

Ln = Ho (compound 3): Complex **3** was separated from the crude mixture by column chromatography (basic aluminum oxide) with CH_2Cl_2/MeOH (10:1 v/v) as the eluent, which was followed by reprecipitation from a hexane/CH_2Cl_2 mixture to afford a deep green solid of neutral **3** (74 mg, 20% with respect to **5**; R_f = 0.38; CH_2Cl_2). MALDI-TOF: calculated for $C_{120}H_{120}N_{16}OHo$ $[M – H]^+$ 1965.9160; found 1965.6942 (M^+, 100%).

Supporting Information (see footnote on the first page of this article): UV/Vis–NIR–IR spectra and CV data of the complexes **2** and **3**. Additional packing diagrams, scheme of synthesis of phthalocyanine base **4**.

Acknowledgments

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