

Supporting Information

Sandwich-type Tetrakis(phthalocyaninato) Dysprosium-cadmium

Quadruple-decker SMM

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Experimental Section

General Remarks. All the reagents and solvents were used as received. The compound $\{[\text{Pc}(\text{OC}_4\text{H}_9)_8]\text{Dy}[\text{Pc}(\text{OC}_4\text{H}_9)_8]\}$ was prepared referring to the published procedure.¹

¹H NMR spectrum was recorded on a Bruker DPX 400 spectrometer in CDCl₃. Spectrum was referenced internally using the residual solvent resonances ($\delta = 7.24$ for ¹H NMR). Electronic absorption spectra were recorded on a Hitachi U-4100 spectrophotometer. IR spectrum was recorded as KBr pellets using a Bruker Tensor 37 spectrometer with 2 cm⁻¹ resolution. MALDI-TOF mass spectra were taken on a Bruker BIFLEX III ultrahighresolution Fourier transform ion cyclotron resonance (FT-ICR) mass spectrometer with alpha-cyano-4-hydroxycinnamic acid as matrix. Elemental analysis was performed on an Elementar Vavio EI III. The crystallographical data of **1** has been determined by X-ray diffraction analysis at 120 K using Oxford Diffraction Gemini E system with Cu_{K α} radiation $\lambda = 1.5418$ Å. The EQIV, EADP DFIX, ISOR, PART (for disordered butoxy side chains) and SIMU (for all atoms) commands have been used. The DAMP command has been utilized to replace many constraints. Magnetic measurements were performed on a Quantum Design MPMS XL-5 SQUID magnetometer on polycrystalline samples. Data were corrected for the diamagnetism of the samples using Pascal constants and of the sample holder by measurement. The hysteresis loops at 0.5 K were measured on the *i*Helium Measurement Console in coordination with MPMS MultiVu, and the samples

were fixed by eicosane to avoid movement during the measurement.

The synthesis of
 $\{[\text{Pc}(\text{OC}_4\text{H}_9)_8]\text{Dy}[\text{Pc}(\text{OC}_4\text{H}_9)_8]\text{Cd}[\text{Pc}(\text{OC}_4\text{H}_9)_8]\text{Dy}[\text{Pc}(\text{OC}_4\text{H}_9)_8]\}$ (1): A mixture of $\text{Cd}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ (5.3 mg, 0.02 mmol) and neutral bis[2,3,9,10,16,17,23,24-octa(butyloxy)phthalocyaninato] dysprosium double-decker compound $\{[\text{Pc}(\text{OC}_4\text{H}_9)_8]\text{Dy}[\text{Pc}(\text{OC}_4\text{H}_9)_8]\}$ (23.5 mg, 0.01 mmol) in TCB (4 mL) was heated to reflux under nitrogen for 2.5 h. After being cooled to room temperature, the volatiles were removed under reduced pressure. The residue was chromatographed on a silica gel column using CHCl_3 as the eluent to give a green band, which contained mainly the unreacted $\{[\text{Pc}(\text{OC}_4\text{H}_9)_8]\text{Dy}[\text{Pc}(\text{OC}_4\text{H}_9)_8]\}$. Further elution with CHCl_3 gave a blue band containing the target quadruple-decker complex $\{[\text{Pc}(\text{OC}_4\text{H}_9)_8]\text{Dy}[\text{Pc}(\text{OC}_4\text{H}_9)_8]\text{Cd}[\text{Pc}(\text{OC}_4\text{H}_9)_8]\text{Dy}[\text{Pc}(\text{OC}_4\text{H}_9)_8]\}$ (1). Repeated chromatography followed by recrystallization from chloroform and methanol gave the pure sandwich-type homoleptic tetrakis[2,3,9,10,16,17,23,24-octa(butyloxy)phthalocyaninato] dysprosium-cadmium quadruple-decker complex $\{[\text{Pc}(\text{OC}_4\text{H}_9)_8]\text{Dy}[\text{Pc}(\text{OC}_4\text{H}_9)_8]\text{Cd}[\text{Pc}(\text{OC}_4\text{H}_9)_8]\text{Dy}[\text{Pc}(\text{OC}_4\text{H}_9)_8]\}$ (1) in the yield of 10.2 mg (43%). Single crystals of quadruple-decker compound **1** suitable for X-ray diffraction analysis have been obtained by diffusion of methanol into a solution of this complex in chloroform. ^1H NMR (400 MHz, CDCl_3) for **1**, $\delta = -3.21$ (48 H), -4.05 (16 H), -4.26 (32 H), -5.53 (32 H), -11.56 (48 H), -11.67 (16 H), -14.30 (32 H), -15.56 (32

H), -22.12 (16 H), -23.02 (16 H), -24.29 (16 H), and -36.51 (16 H), Fig. S6 (ESI[†]). MS (MALDI-TOF) for **1**: an isotopic cluster peaking at m/z 4795.21 (Calcd. for M^+ 4795.21). Anal. Calcd. for $C_{256}H_{320}CdDy_2N_{32}O_{32}$: C 64.13, H 6.73, N 9.35; Found: C 63.76, H 6.28, N 9.39. The electronic absorption data for **1** in $CHCl_3$ λ_{max} (log ϵ): 357 (5.35), 580 (4.88), and 657 nm (5.08).

The synthesis of [(Pc)Dy(Pc)Cd(Pc)Dy(Pc)]: Homoleptic sandwich-type phthalocyaninato dysprosium-cadmium quadruple-decker complex [(Pc)Dy(Pc)Cd(Pc)Dy(Pc)] was also synthesized as detailed below: A mixture of $Cd(OAc)_2 \cdot 2H_2O$ (26.5 mg, 0.1 mmol) and neutral bis(phthalocyaninato) dysprosium compound [(Pc)Dy(III)(Pc)] (119 mg, 0.1 mmol) in TCB (10 mL) was heated to reflux under nitrogen for 7 h. After being cooled to room temperature, the volatiles were removed under reduced pressure. The residue was chromatographed on a silica gel column using $CHCl_3$ as the eluent to give a green band, which contained the unreacted bis(phthalocyaninato) dysprosium double-decker [(Pc)Dy(Pc)]. After collecting this band, the column was further eluted with $CHCl_3:CH_3OH$ (95:5) to give a blue band containing the homoleptic sandwich-type phthalocyaninato dysprosium-cadmium quadruple-decker complex [(Pc)Dy(III)(Pc)Cd(II)(Pc)Dy(III)(Pc)]. Repeated chromatography followed by recrystallization from chloroform and methanol gave the pure target quadruple-decker complex, 45 mg (36%). MALDI-TOF mass spectrum was taken on a Bruker Daltonics BIFLEX IIITM MALDI-TOF mass spectrometer with

α -cyano-4-hydroxycinnamic acid as matrix on Dec. 25, 2009: MS (MALDI-TOF): an isotopic cluster peaking at m/z 2487.78 (Calcd. for M^+ 2487.36), Fig. S5 (ESI[†]).

References

- (1) Wang, R.; Li, R.; Bian, Y.; Choi, C.-F.; Ng, D. K. P.; Dou, J.; Wang, D.; Zhu, P.; Ma, C.; Hartnell, R. D.; Arnold, D. P.; Jiang, J. *Chem. Eur. J.* 2005, **11**, 7351-7357.

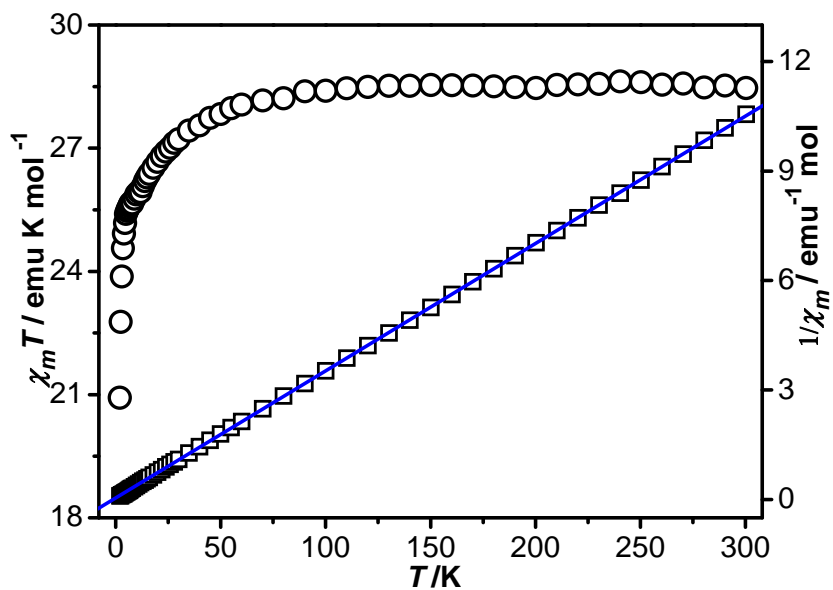


Fig. S1 Temperature dependence of $\chi_m T$ for **1** (the blue solid line represents the best fitting for the complex of 2–300 K).

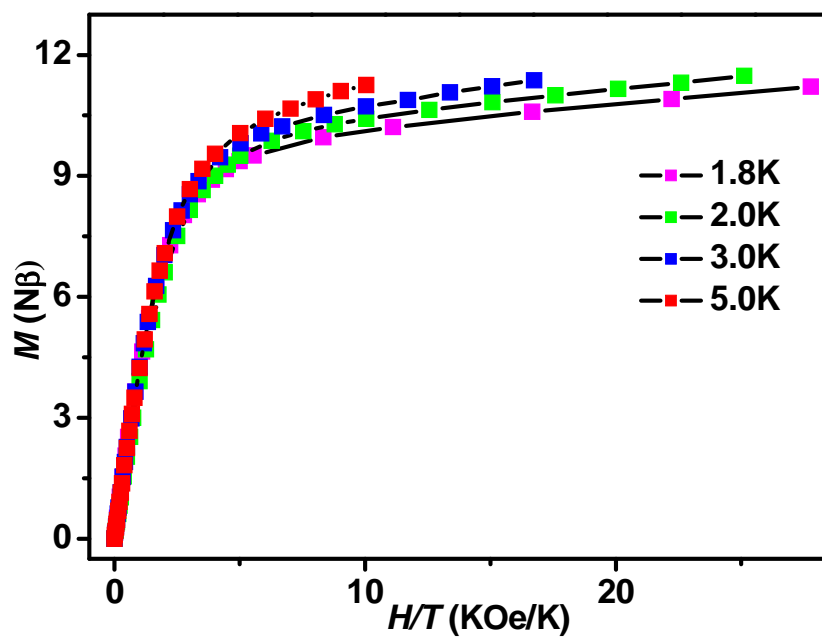


Fig. S2 The M vs H/T curves for **1** at different temperature.

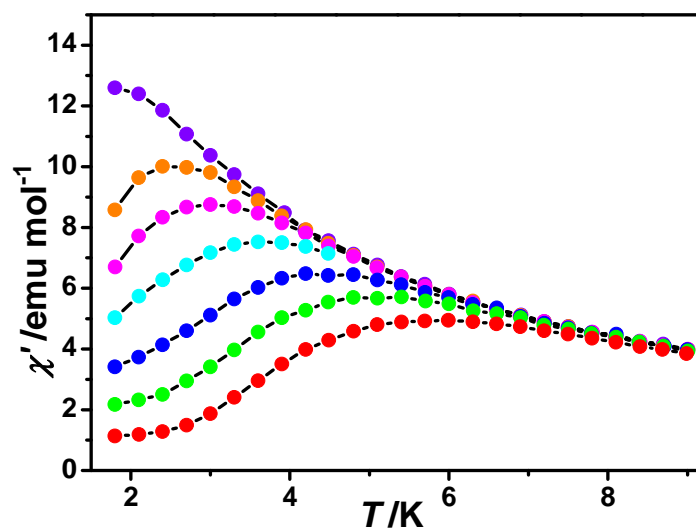


Fig. S3 Temperature dependence of the in-phase χ' ac susceptibility of **1** under 2000 Oe applied dc fields.

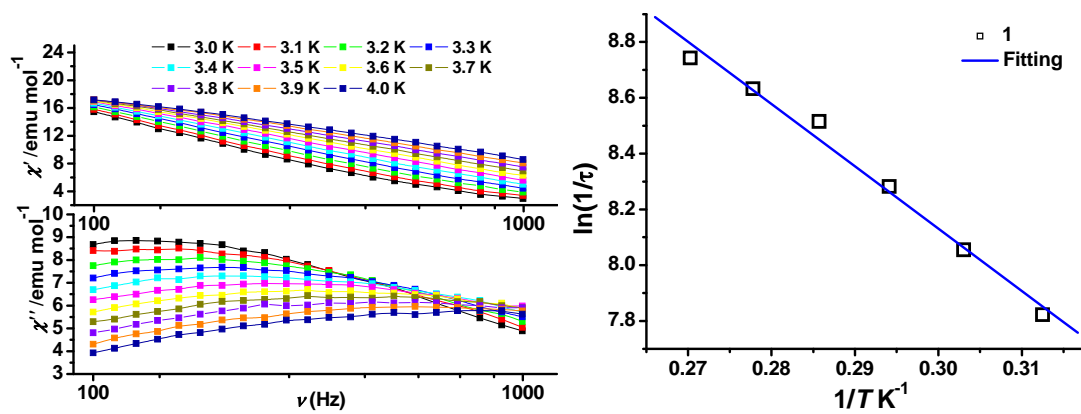


Fig. S4 Frequency dependence of in-phase (χ' top) and out-of phase (χ'' bottom) ac susceptibility of **1** under zero applied dc fields (left) and the plot of $\ln(1/\tau)$ vs. $1/T$ (right).

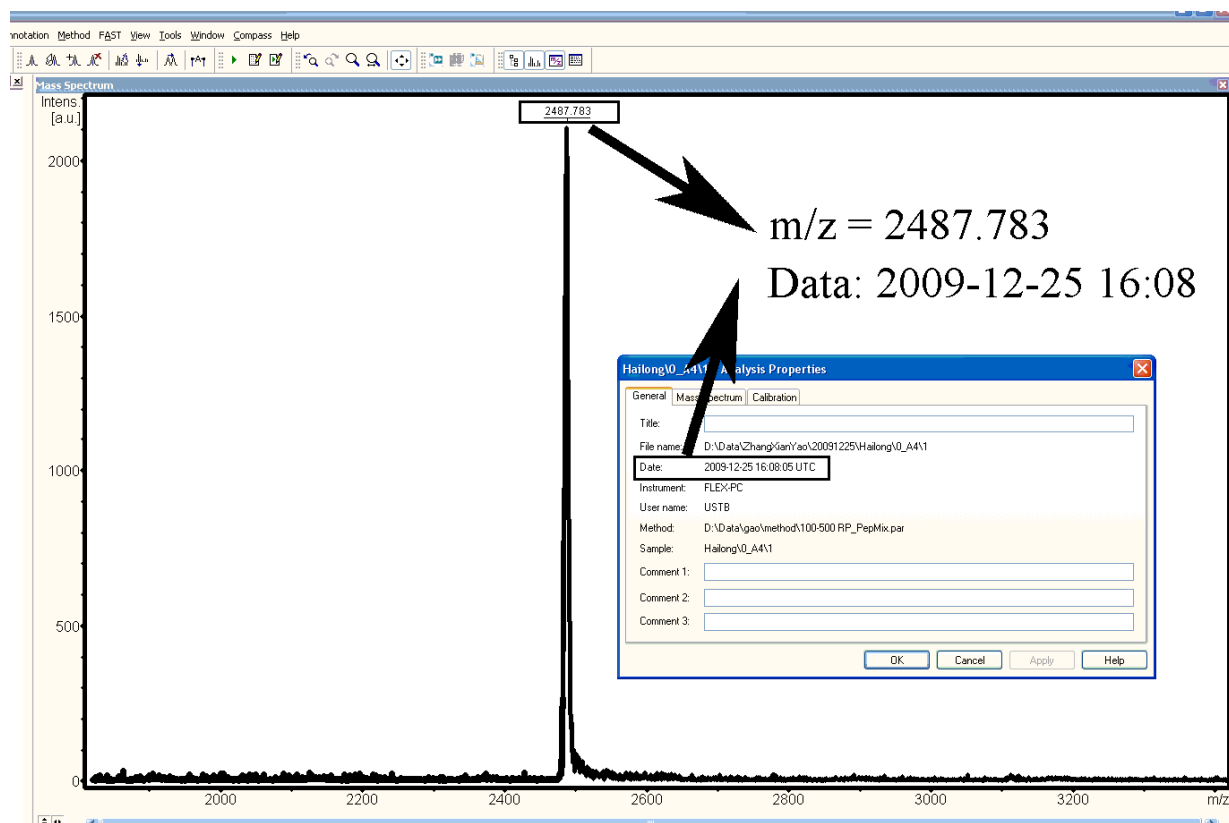


Fig. S5 Experimental isotopic pattern for the molecular ion of $[(Pc)Dy(Pc)Cd(Pc)Dy(Pc)]$.

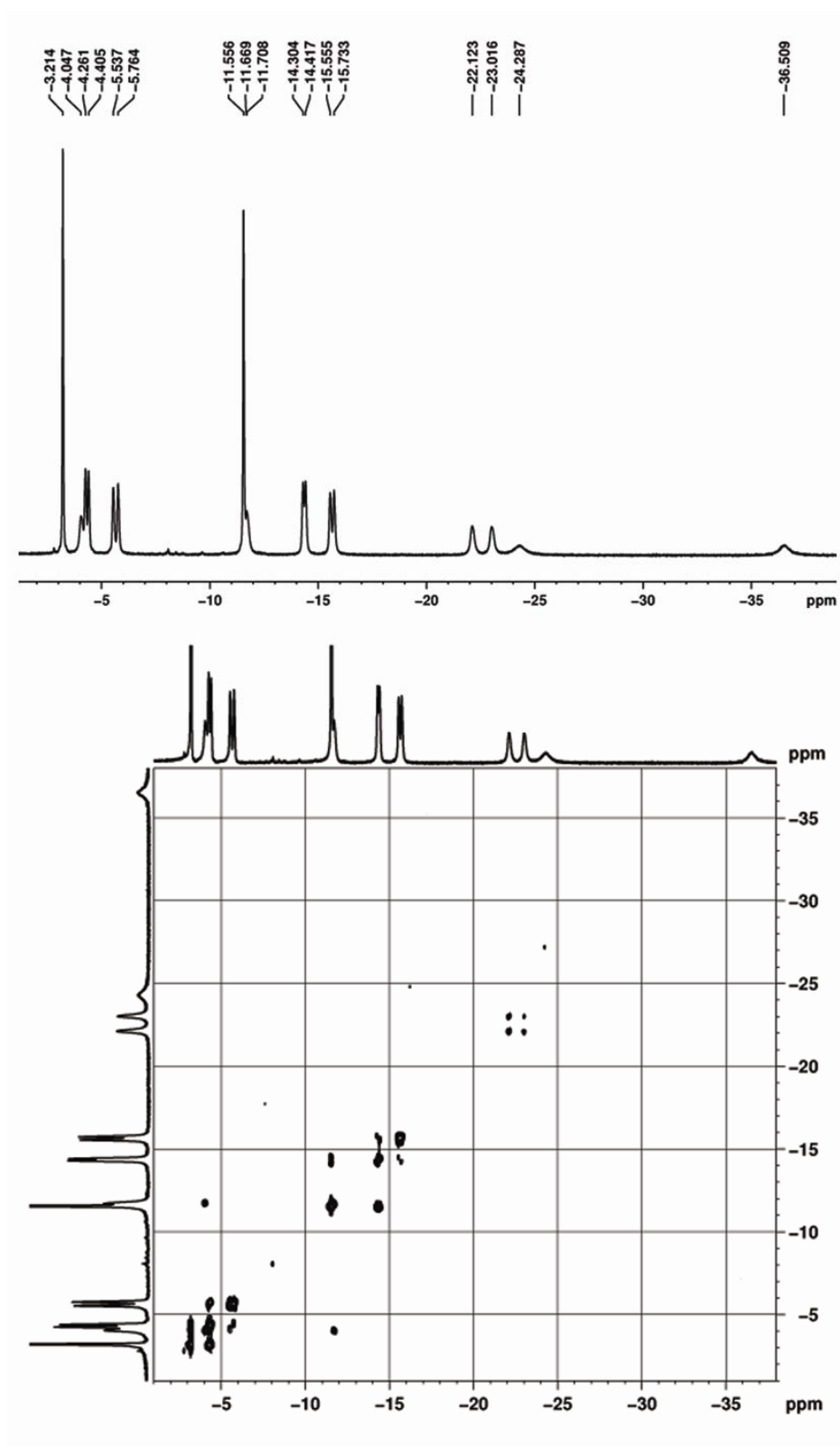


Fig. S6 ¹H NMR and ¹H-¹H COSY spectra of $\{[\text{Pc}(\text{OC}_4\text{H}_9)_8]\text{Dy}[\text{Pc}(\text{OC}_4\text{H}_9)_8]\text{Cd}[\text{Pc}(\text{OC}_4\text{H}_9)_8]\text{Dy}[\text{Pc}(\text{OC}_4\text{H}_9)_8]\}$ (**1**) in CDCl₃.