Electronic Supplementary Material (ESI) for Chemical Communications

Electronic Supplementary Information

Twist Angle Perturbation on Mixed (Phthalocyaninato)(porphyrinato) Dysprosium(III) Double-decker SMMs

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Experimental Section

General Remarks. All the reagents and solvents were used as received. The compounds Dy(Pc)(TClPP) (**1a**), Dy{Pc(α-$OC_5H_{11})_4$}(TClPP) (**2a**), and DyH{Pc(α-$OC_5H_{11})_4$}(TClPP) (**2b**) were prepared and isolated following the reported procedures mentioned in the text.

Electronic absorption spectra were recorded on a Hitachi U-4100 spectrophotometer. 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 analyses were performed on an Elementar Vavio El III. Electrochemical measurements were carried out with a BAS CV-50W voltammetric analyser.

Satisfactory elemental analysis results were obtained for all the newly prepared double-decker complexes in particular **1a**, **2a**, and **2b** after repeatedly column chromatographic purification followed by recrystallization from chloroform and methanol, Table S3 (Supporting Information). The MALDI-TOF mass spectra of these complexes showed an intense cluster corresponding to the molecular ion **$[M+H]^+$**, Table S3 (Supporting Information). These sandwich double-decker compounds were also characterized with electronic absorption spectroscopy, Fig. S12†. Single crystals of all three mixed ring double-decker compounds suitable for X-ray diffraction analysis were obtained by diffusion of methanol onto the solution of corresponding compounds in chloroform.

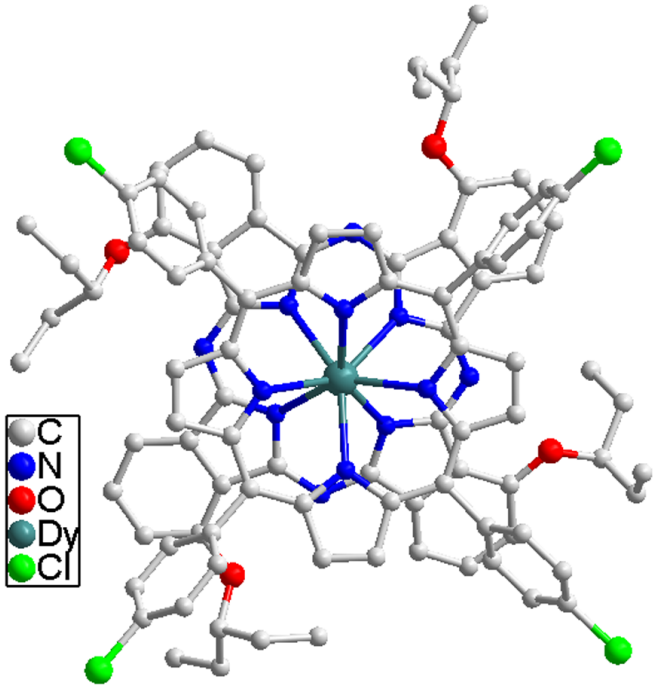

Figure S1. Molecular structure of Dy[Pc(α-OC_5H_{11})$_4$](TClPP) (**2a**) in a top view with all hydrogen atoms and solvent molecules omitted for clarity.

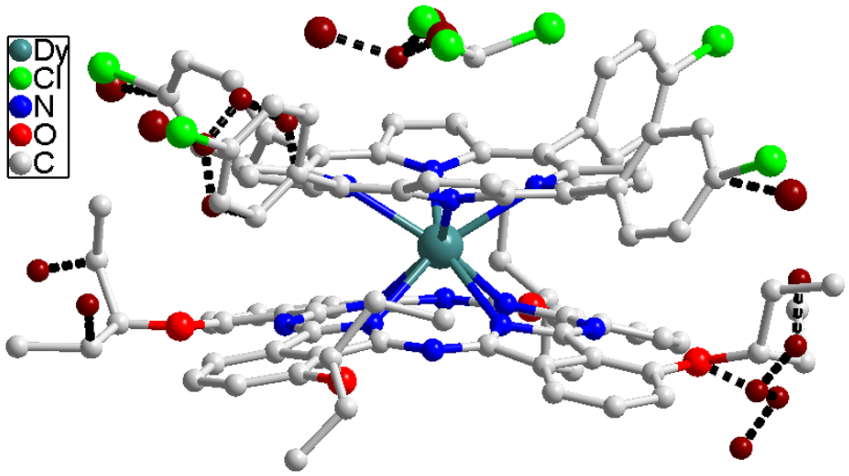

Figure S2. Molecular structure of DyH[Pc(α-OC_5H_{11})$_4$](TClPP) (**2b**) in a side view with all disorder atoms drawn in dark red colour and corresponding bond drawn in black dash line (all hydrogen atoms omitted for clarity).

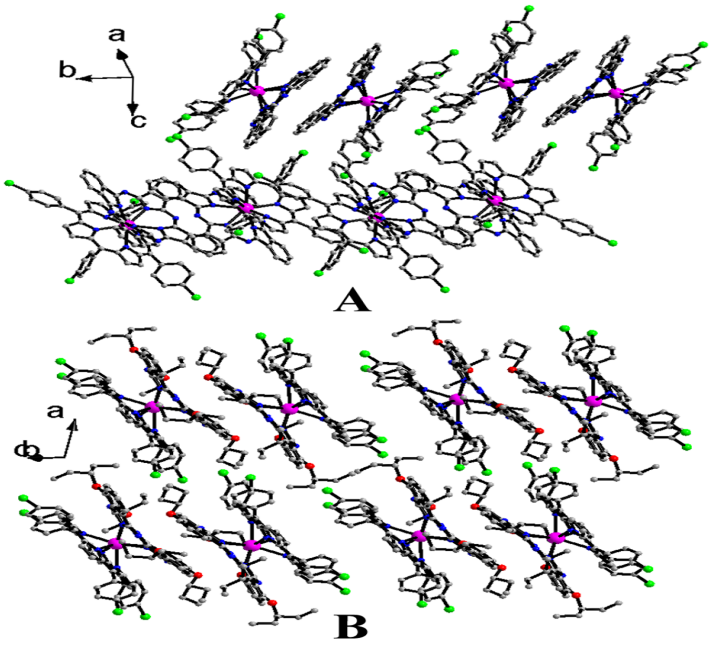

Figure S3. Molecular packing in single crystals of **1a** (A) and **2a** (B) with hydrogen atoms and solvent molecules omitted for clarity.

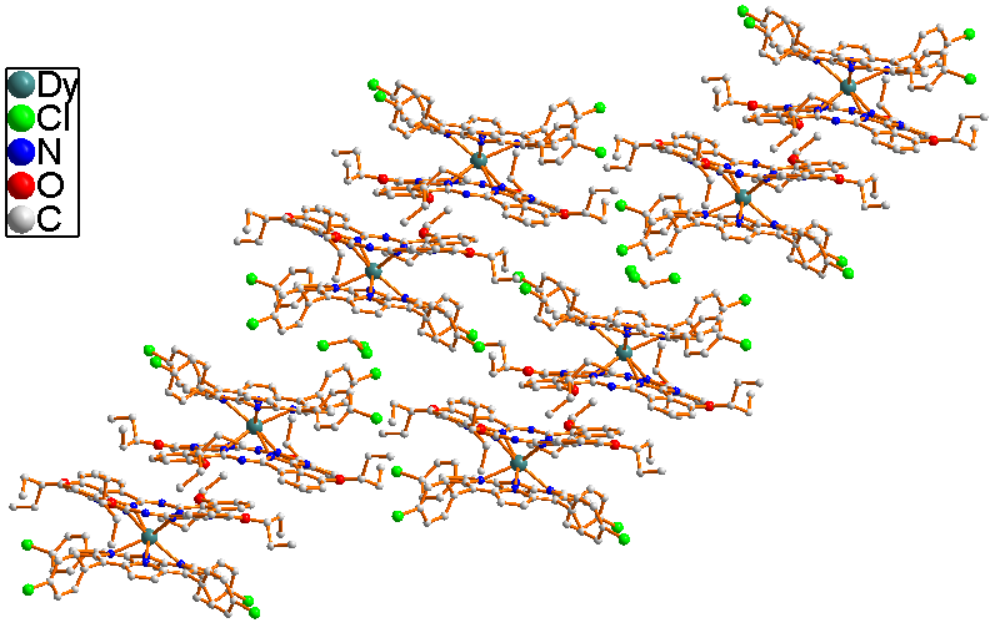

Figure S4. Molecular packing in single crystal of DyH[Pc(α-$OC_5H_{11})_4$](TClPP) (**2b**) (B) with hydrogen atoms and solvent molecules omitted for clarity.

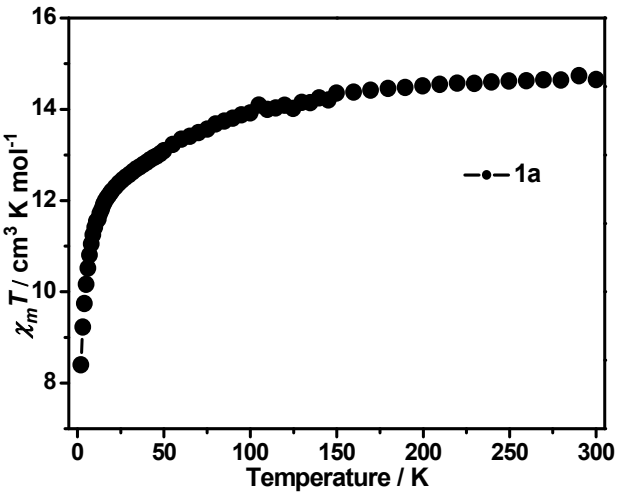

Figure S5. Temperature dependence of $\chi_m T$ for **1a**.

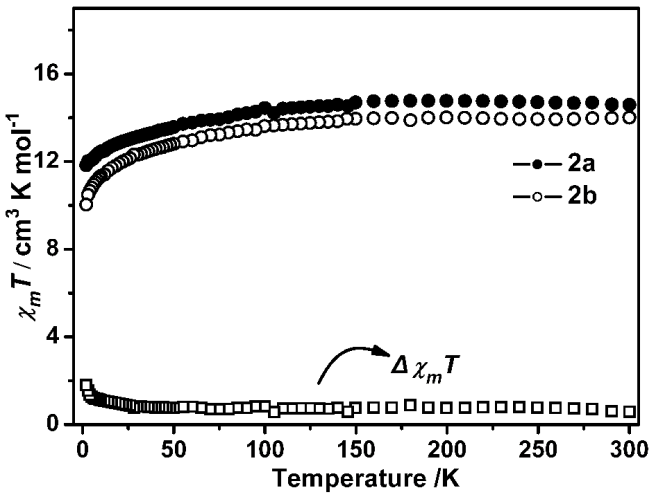

Figure S6. Temperature dependence of $\chi_m T$ for **2a** and **2b** as well as $\Delta\chi_m T$ ($\Delta\chi_m T = \chi_m T_{2a} - \chi_m T_{2b}$).

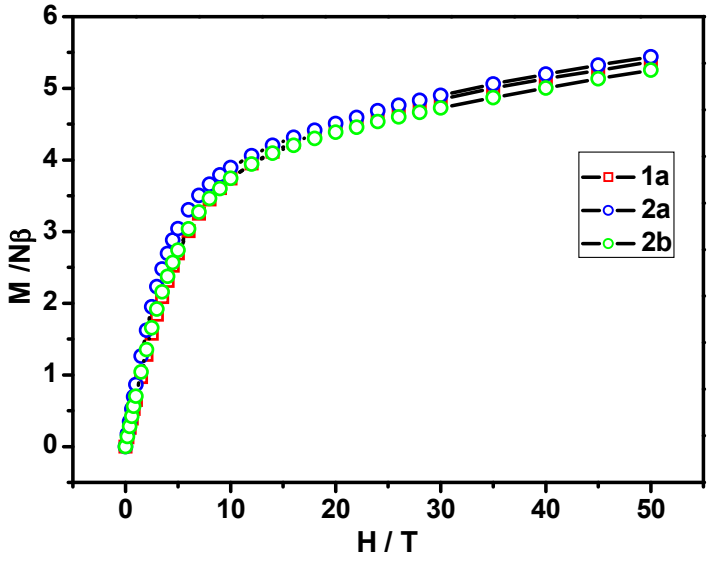

Figure S7. The *M vs H*/T curves for **1a**, **2a**, and **2b** at 2.0 K.

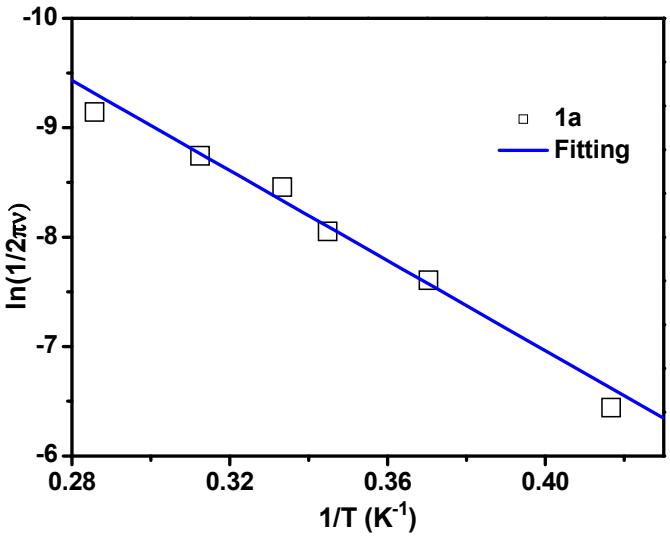

Figure S8. The plot of ln(τ) vs. 1/T for **1a** under zero applied field.

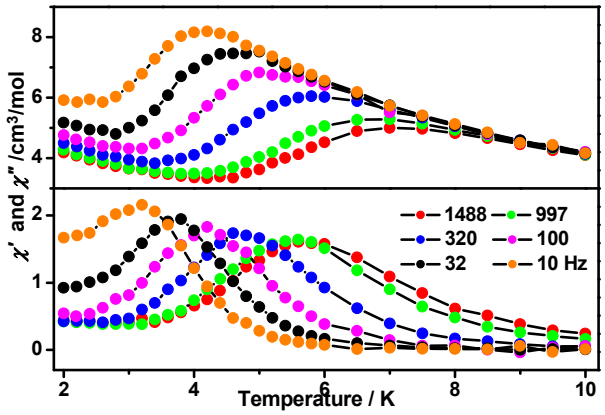

Figure S9. Temperature dependence of the in-phase (χ′) and out-of-phase (χ″) ac susceptibility of **2a** (top and bottom).

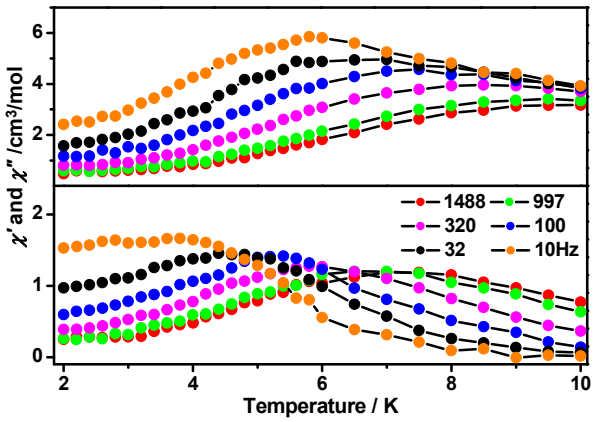

Figure S10. Temperature dependence of the in-phase (χ′) and out-of-phase (χ″) ac susceptibility of **2b** (top and bottom).

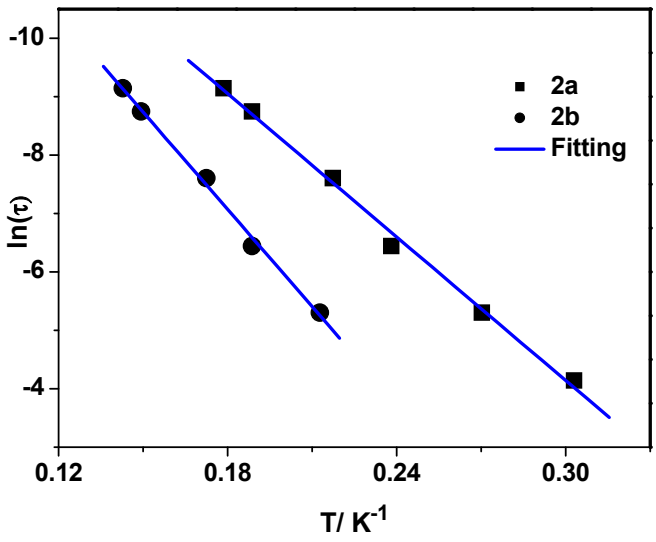

Figure S11. The plot of ln(τ) vs. 1/T for **2a** and **2b** under 2000 Oe.

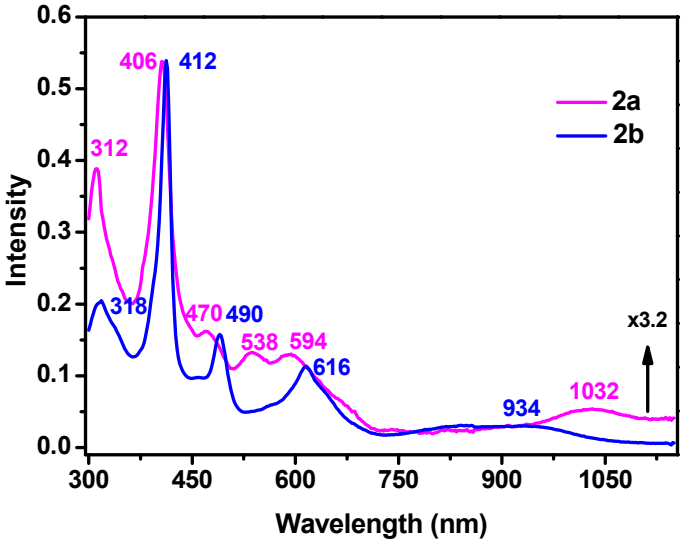

Figure S12. Electronic absorption spectra of double-decker **2a** and **2b** in $CHCl_3$.

Table S1. Crystallographic data and selected structural information for **1a**, **2a**, and **2b**.

	1a	**2a**	**2b**
Molecular formula	$C_{79}H_{54}Cl_{10}DyN_{12}O_5$	$C_{97}H_{81}Cl_7DyN_{12}O_4$	$C_{97}H_{82}Cl_7DyN_{12}O_4$
M	1768.38	1889.39	1890.44
Temperature /K	293	120	150
Crystal system	Monoclinic	Triclinic	Triclinic
Space group	*C2/c*	*P-1*	*P-1*
a/Å	38.436(5)	14.0680(5)	14.0969(4)
b/Å	19.024(2)	17.6605(7)	17.6251(5)
c/Å	26.273(3)	18.6659(7)	18.9482(5)
α/°	90	112.931(4)	111.959(2)
/°	127.986(3)	96.166(3)	97.403(2)
γ°	90	97.426(3)	97.046(2)
V/Å^3	15141	4171.5(3)	4254.5(2)
Z	8	2	2
F(000)	7040	1928	1928
D_c/Mg m^{-3}	1.551	1.504	1.475
Data collection range/°	1.56 to 25.00	2.90 to 25.00	2.98 to 25.00
Reflections collected	36641	29700	30362
Independent reflections	13255	14580	14890
R_1 [$I>2\sigma(I)$]	0.0487	0.0668	0.0510
wR_2 [$I>2\sigma(I)$]	0.1398	0.1387	0.1167
R_1 [*for all*]	0.0634	0.0969	0.0672
wR_2 [*for all*]	0.1506	0.1527	0.1238
Goodness of fit	1.092	1.025	1.029
separation of Dy and two N_4 planes (Å)	2.76	2.794	2.794
separation of Dy and N_4 planes of Pc' (Å)	1.483	1.484	1.484
skew angle φ (°)	43.60	38.02	38.02

Table S2. Selected bond distances (Å) and bond angles (°) for **1a**, **2a**, and **2b**.

bond and angle	**1a**	**2a**	**2b**
N(1)-Dy(1)	2.468(4)	2.441(5)	2.479(4)
N(3)-Dy(1)	2.466(4)	2.450(5)	2.494(4)
N(5)-Dy(1)	2.461(4)	2.467(5)	2.453(4)
N(7)-Dy(1)	2.463(4)	2.462(5)	2.459(4)
N(9)-Dy(1)	2.420(4)	2.454(5)	2.444(3)
N(10)-Dy(1)	2.429(4)	2.442(5)	2.446(4)
N(11)-Dy(1)	2.427(4)	2.444(5)	2.450(4)
N(12)-Dy(1)	2.438(4)	2.456(5)	2.439(4)
shortest Dy…Dy ions distance	8.928	8.937	9.077
N(1)-Dy(1)-N(10)	144.30(12)	137.92(17)	137.40(12)
N(1)-Dy(1)-N(11)	142.11(12)	148.44(17)	149.38(13)
N(10)-Dy(1)-N(11)	73.31(13)	72.84(17)	72.63(12)
N(1)-Dy(1)-N(3)	68.81(12)	69.98(17)	69.02(12)
N(10)-Dy(1)-N(3)	141.16(12)	148.07(17)	148.31(12)
N(11)-Dy(1)-N(3)	79.83(12)	83.67(17)	85.43(12)
N(1)-Dy(1)-N(9)	82.23(11)	77.64(17)	77.59(12)
N(10)-Dy(1)-N(9)	74.19(12)	73.51(17)	73.72(12)
N(11)-Dy(1)-N(9)	115.44(12)	114.30(17)	114.66(12)
N(3)-Dy(1)-N(9)	144.02(12)	137.34(17)	137.48(12)
N(1)-Dy(1)-N(12)	79.47(12)	83.52(17)	84.71(14)
N(10)-Dy(1)-N(12)	117.65(12)	115.08(17)	115.28(13)
N(11)-Dy(1)-N(12)	74.61(12)	73.62(17)	73.45(13)
N(3)-Dy(1)-N(12)	80.24(12)	77.03(17)	78.30(13)
N(9)-Dy(1)-N(12)	73.69(12)	72.33(17)	73.02(12)
N(1)-Dy(1)-N(7)	68.24(12)	69.03(17)	68.27(13)
N(10)-Dy(1)-N(7)	81.70(12)	78.84(17)	77.92(12)
N(11)-Dy(1)-N(7)	143.89(12)	137.81(17)	137.97(13)
N(3)-Dy(1)-N(7)	106.12(12)	106.80(17)	106.21(12)
N(9)-Dy(1)-N(7)	80.98(12)	85.83(17)	84.01(12)
N(12)-Dy(1)-N(7)	141.22(12)	148.13(17)	147.82(13)
N(1)-Dy(1)-N(5)	105.89(12)	107.10(16)	106.10(12)
N(10)-Dy(1)-N(5)	79.30(12)	84.80(17)	84.67(12)
N(11)-Dy(1)-N(5)	80.88(12)	77.77(17)	78.13(12)
N(3)-Dy(1)-N(5)	69.03(12)	69.02(17)	68.31(12)
N(9)-Dy(1)-N(5)	142.35(13)	149.62(18)	149.08(12)
N(12)-Dy(1)-N(5)	143.51(13)	137.45(18)	137.41(12)
N(7)-Dy(1)-N(5)	69.01(12)	68.99(17)	69.78(12)

Table S3. Analytical and mass spectroscopic data for the (**1a**, **2a**, and **2b**).

	Molecular formula	$[M+H]^+$ (*m/z*)	computed/found(%)		
			C	H	N
2a	$C_{96}H_{80}Cl_4DyN_{12}O_4 \bullet CHCl_3$	1771.23	61.66/62.03	4.32/4.64	8.90/8.56
2b	$C_{96}H_{81}Cl_4DyN_{12}O_4 \bullet CHCl_3$	1772.06	61.63/61.64	4.37/4.81	8.89/8.59