Electronic Supplementary Material (ESI) for RSC Advances.

Electronic Supplementary Information

Influence of Porphyrin Meso-attached Substituent on the SMM Behavior of Dysprosium(III) Double-deckers with Mixed Tetrapyrrole Ligands

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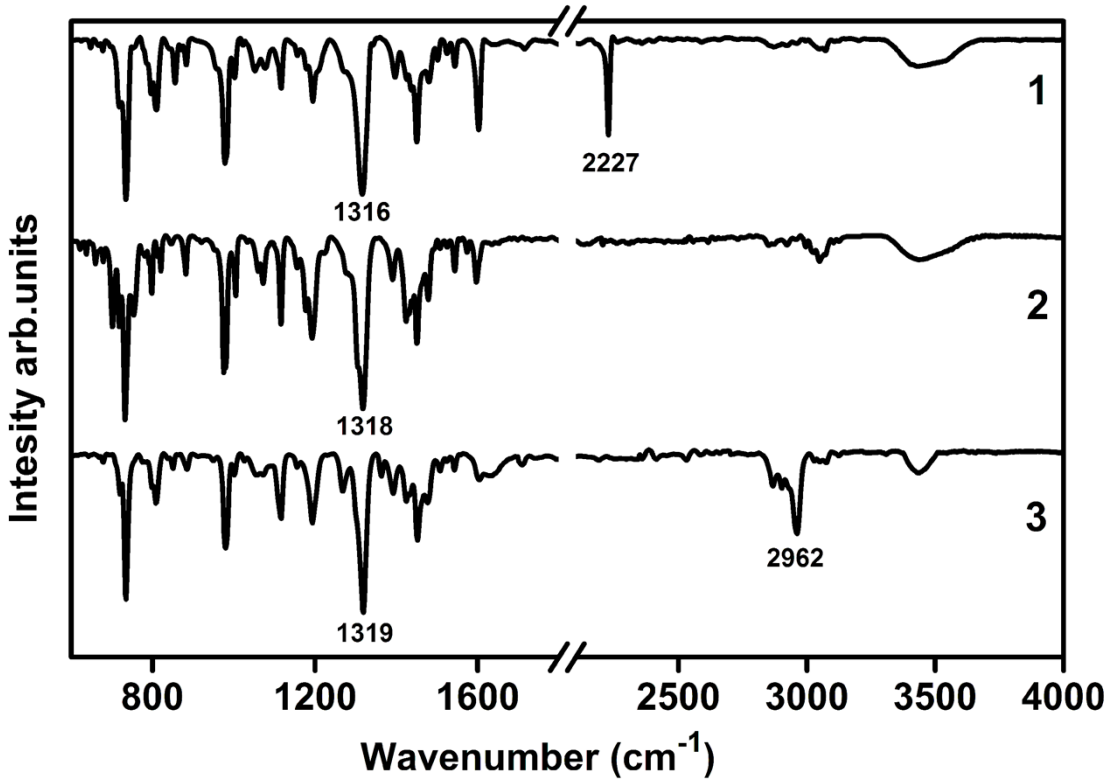

Figure S1. IR spectra of **1**-**3** in the region of 600-1800 and 2100-4000 cm^{-1}.

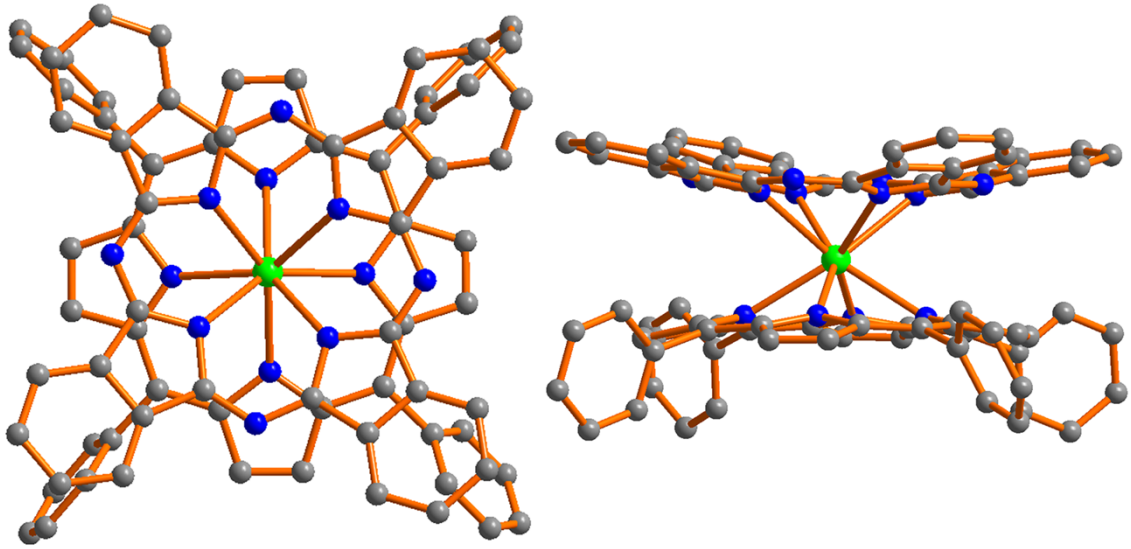

Figure S2. Molecular structure of Dy^{III}(Pc)(TPP) (**2**) in top and side views with the hydrogen atoms omitted for clarity.

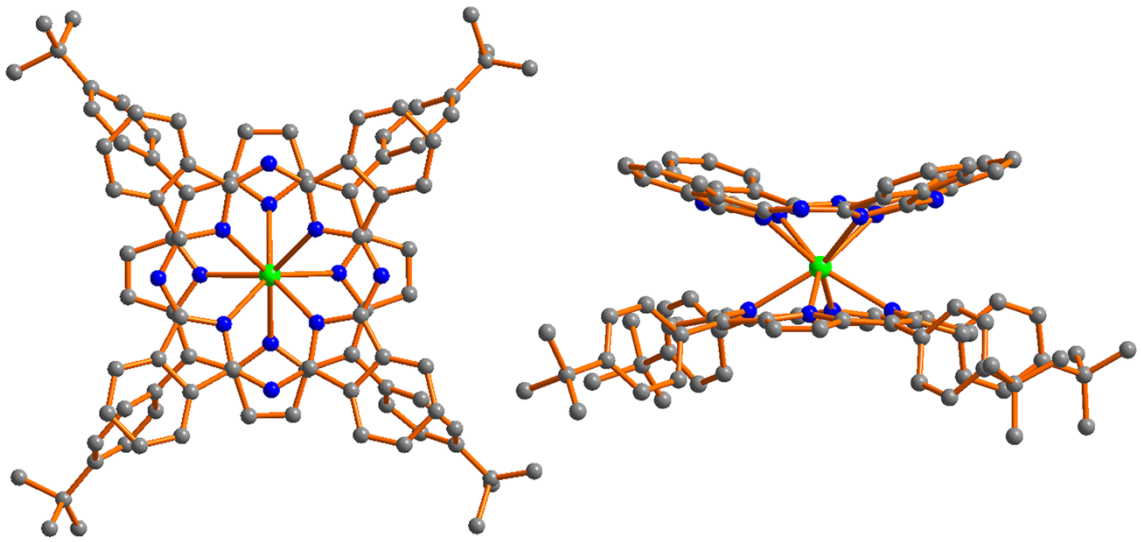

Figure S3. Molecular structure of Dy^{III}(Pc)(TBPP) (**3**) in top and side views with the hydrogen atoms omitted for clarity.

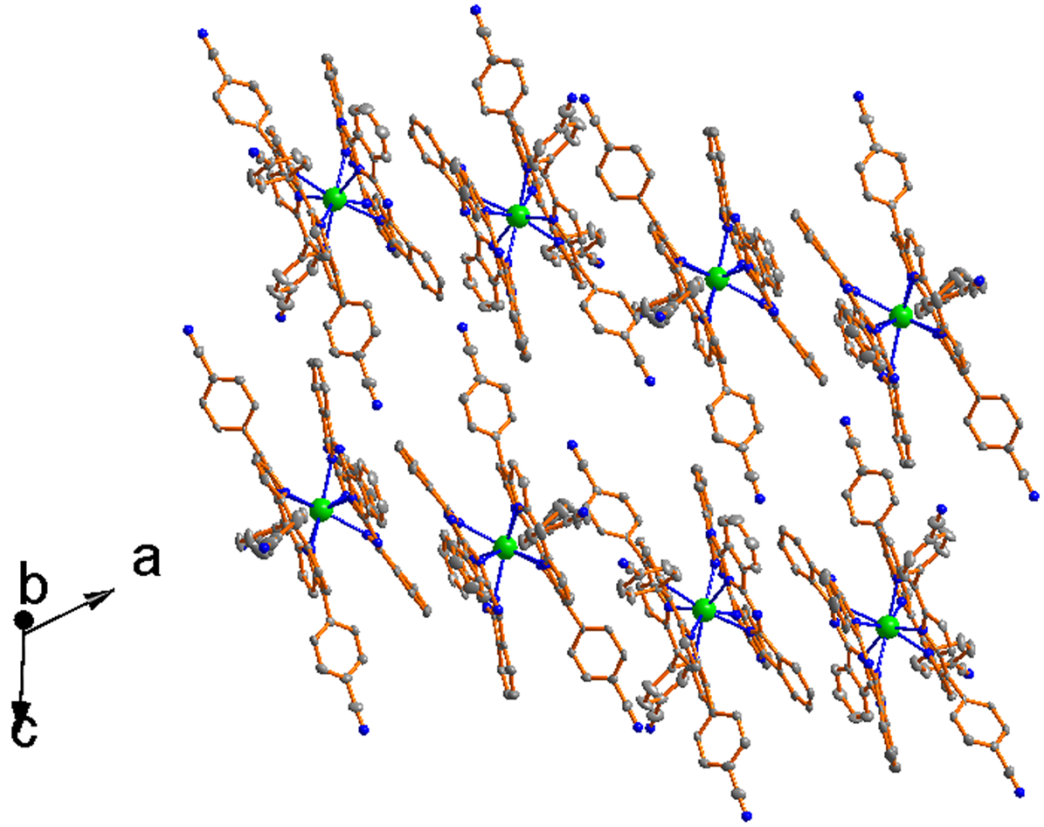

Figure S4. Molecular packing in single crystals of **1** with hydrogen atoms and solvent molecules omitted for clarity.

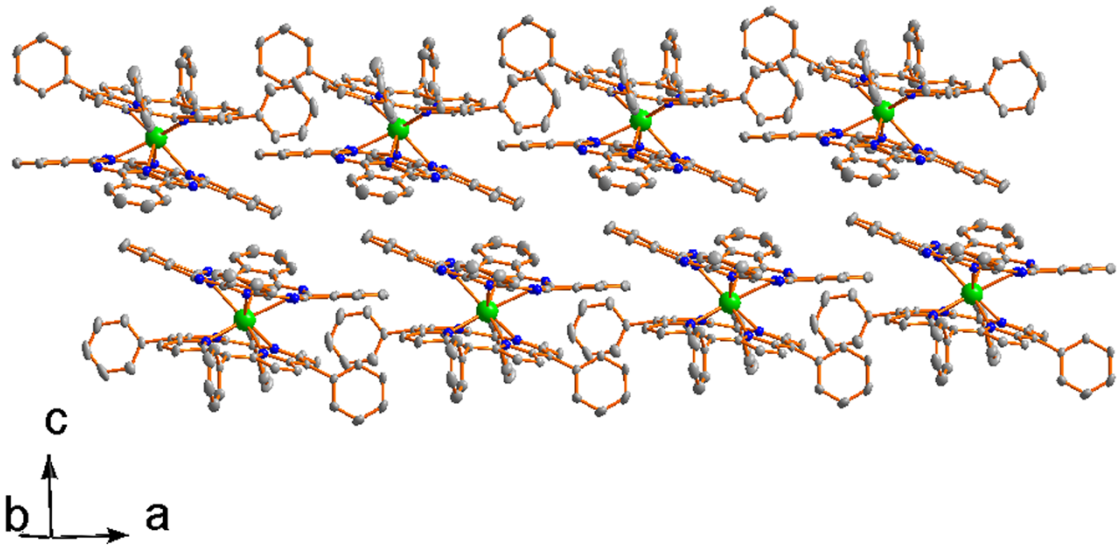

Figure S5. Molecular packing in single crystals of **2** with hydrogen atoms and solvent molecules omitted for clarity.

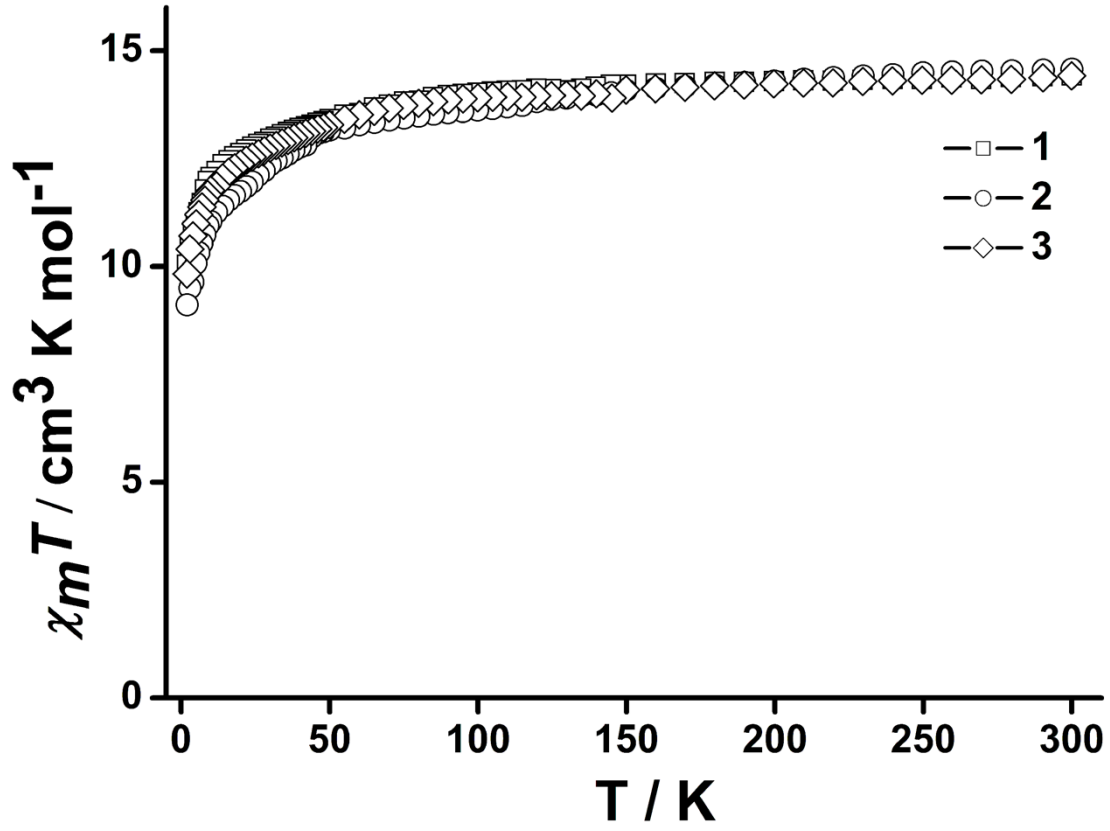

Figure S6. Temperature dependence of $\chi_m T$ for **1-3**.

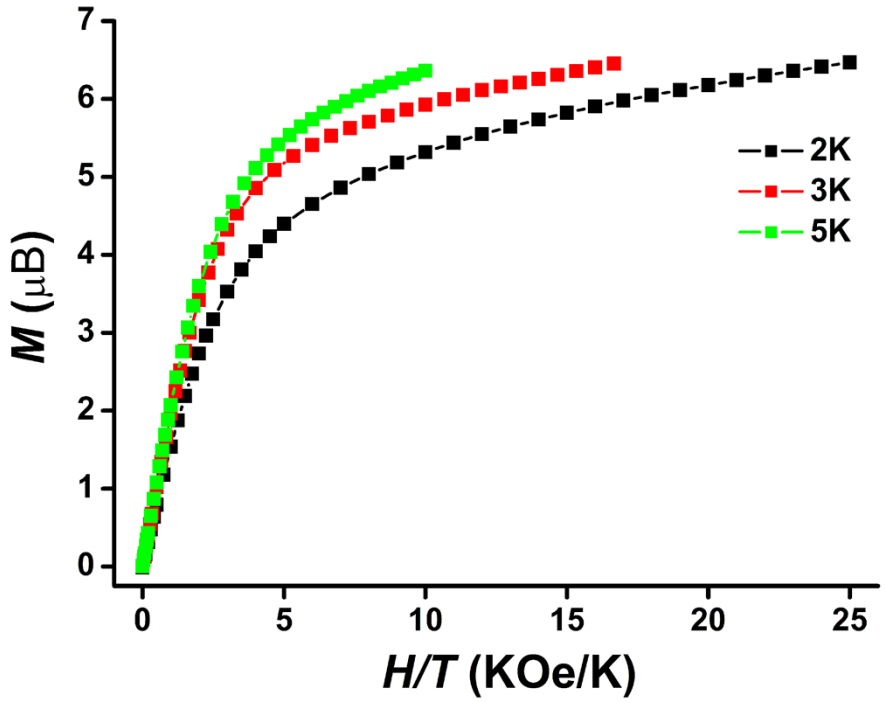

Figure S7. The *M vs H*/T curves for **2** at 2.0 K, 3.0 K and 5.0 K.

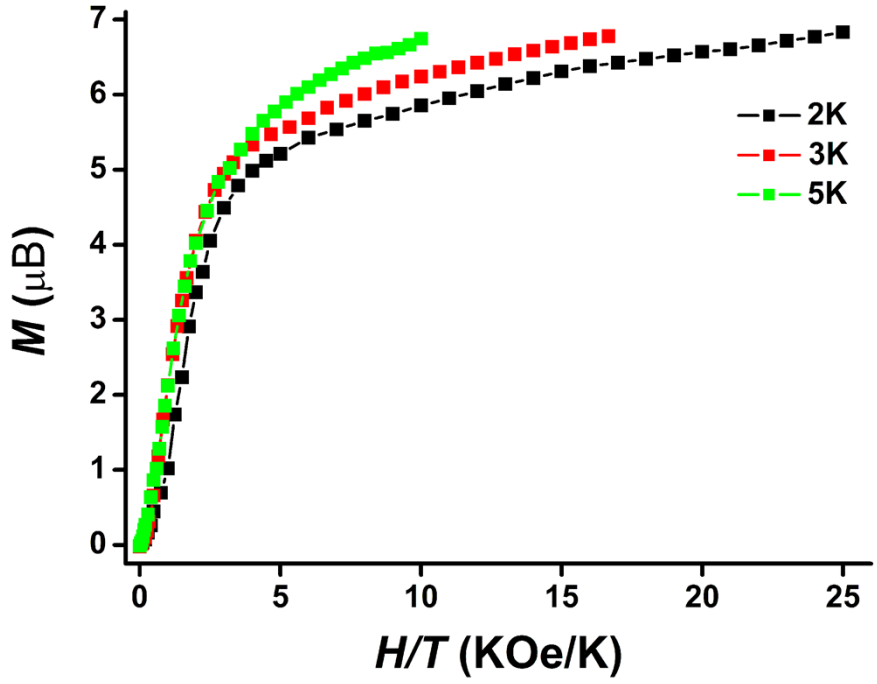

Figure S8. The *M vs H*/T curves for **1** at 2.0 K, 3.0 K and 5.0 K.

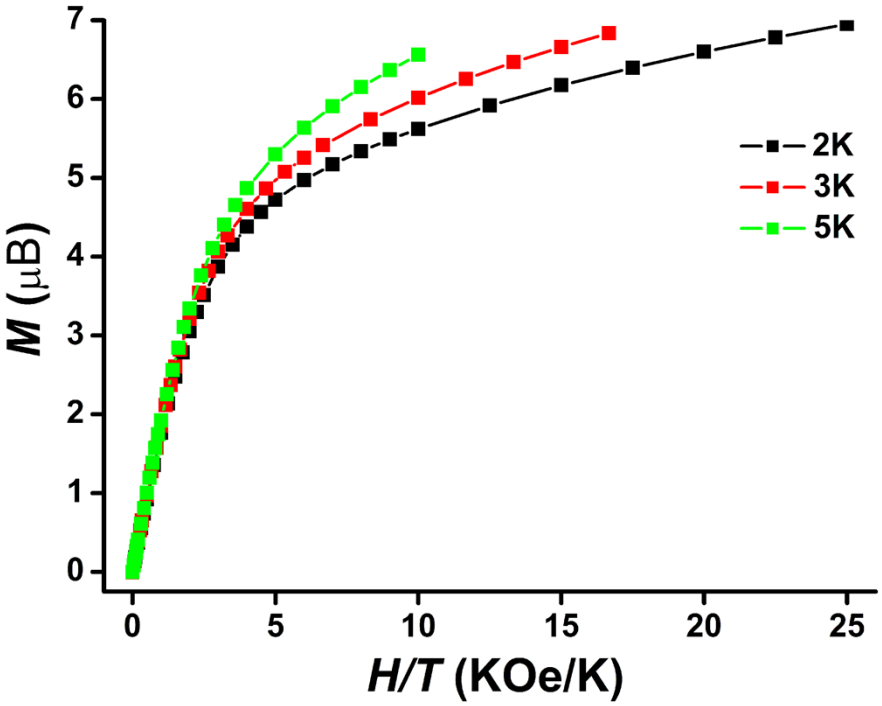

Figure S9. The *M vs H*/T curves for **3** at 2.0 K, 3.0 K and 5.0 K.

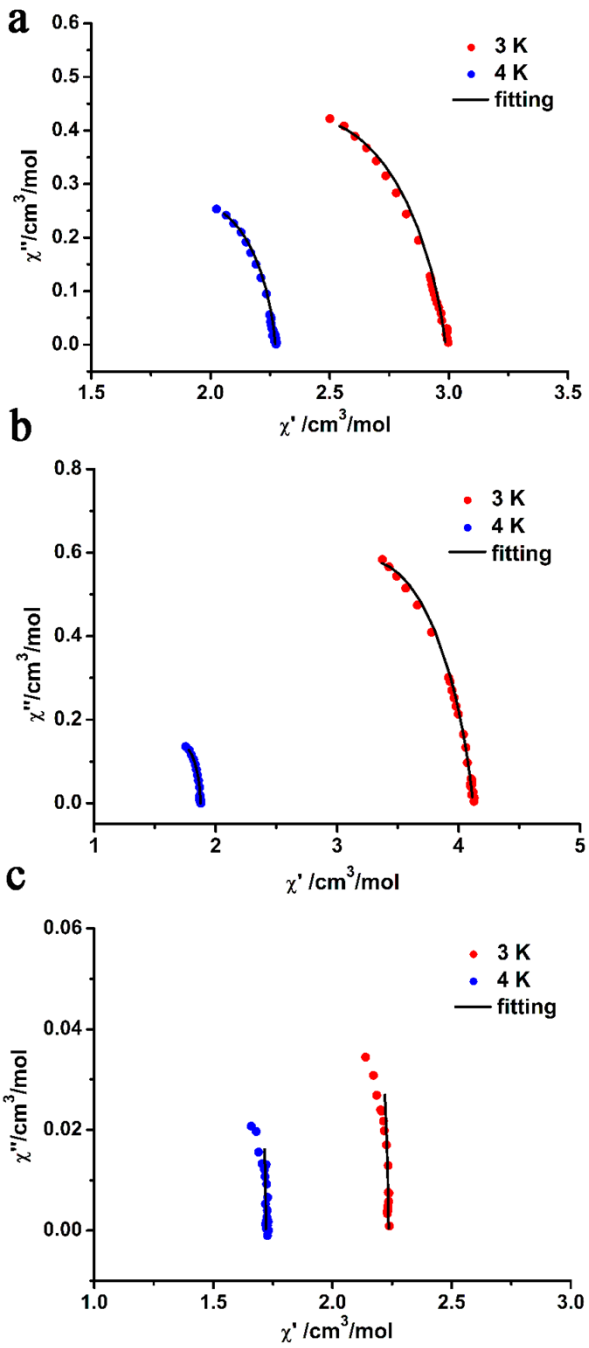

Figure S10. Cole-Cole diagrams of **1** (a), **2** (b) and **3** (c) with the ac susceptibility data under a zero applied dc field.

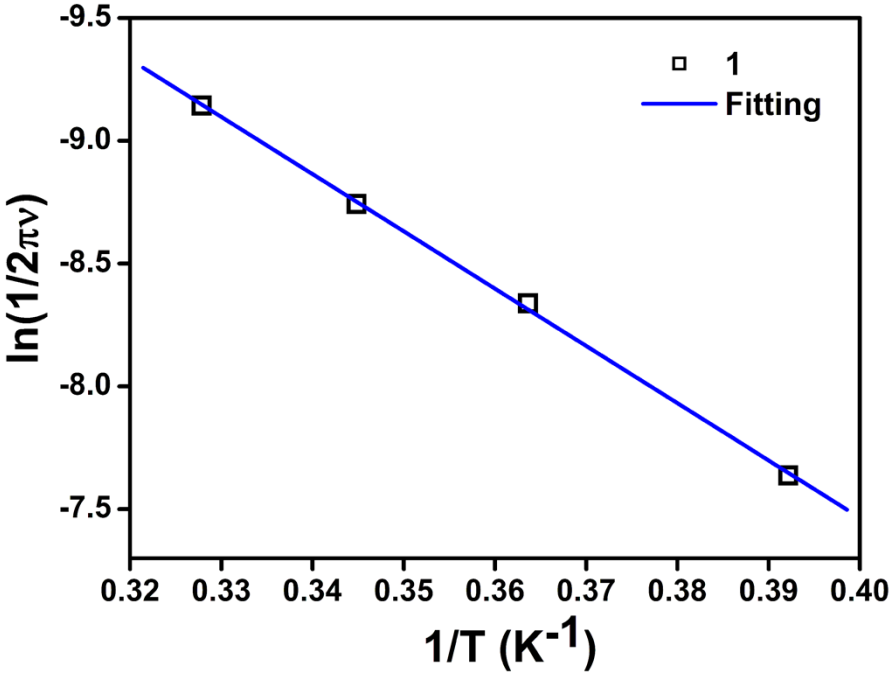

Figure S11. The plot of ln(τ) vs. 1/T for **1** under 2000 Oe.

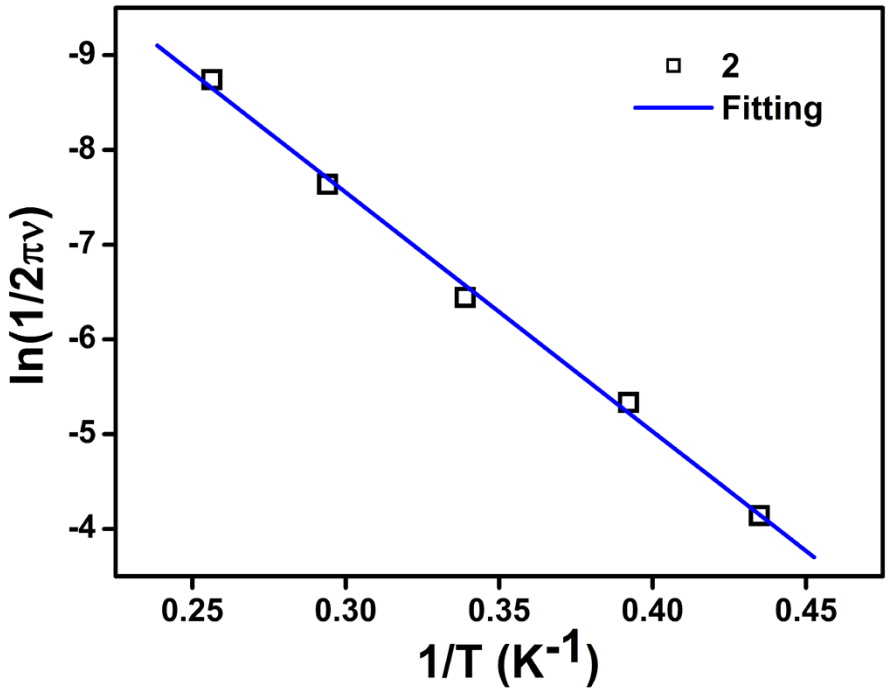

Figure S12. The plot of ln(τ) vs. 1/T for **2** under 2000 Oe.

Table S1. Analytical and mass spectroscopic data for the mixed double-deckers **1**-**3**.

Compound	Yield (%)	$[M+H]^+$ (*m/z*)[a,b]	Analysis (%)[a]		
			C	H	N
Dy^{III}(Pc)(TCPP) (**1**)[c]	16	1389.7 (1388.3)	67.01 (66.64)	5.54 (5.86)	12.82 (13.04)
Dy^{III}(Pc)(TPP) (**2**)[d]	20	1288.6 (1287.7)	68.97 (68.85)	3.64 (3.80)	12.57 (12.68)
Dy^{III}(Pc)(TBPP) (**3**)[e]	22	1513.1 (1512.6)	70.17 (69.94)	5.38 (4.93)	10.91 (10.52)

[a] Calculated values given in parentheses. [b] By MALDI-TOF mass spectrometry. The value corresponds to the most abundant isotopic peak of the protonated molecular ion $[M+H]^+$. [c] Contain 3 equiv. of solvated H_2O. [d] Contain 2 equiv. of solvated H_2O. [e] Contain 1 equiv. of solvated CH_2Cl_2.

Table S2. Electronic absorption data for the mixed double-deckers **1**-**3** in $CHCl_3$.

Compound	λ_{max}/nm (log ε)					
1	330 (4.95)	404 (5.08)	466 (4.74)	732 (3.62)	1024 (3.82)	1184 (3.80)
2	332 (4.96)	402 (5.10)	474 (4.71)	726 (3.56)	1050 (3.80)	1296 (4.02)
3	328 (4.93)	404 (5.09)	476 (4.71)	728 (3.56)	1060 (3.78)	1320 (4.01)

Table S3. Electrochemical data for the mixed double-deckers **1**-**3**.[a]

Compound	$\mathbf{Oxd_2}$	$\mathbf{Oxd_1}$	$\mathbf{Red_1}$	$\mathbf{Red_2}$	$\mathbf{\Delta E^o_{1/2}}$[b]	$\mathbf{\Delta E^{o\prime}_{1/2}}$[c]
1	1.52	0.77	0.19	-1.24	0.75	1.45
2	1.37	0.64	0.14	-1.30	0.73	1.44
3	1.28	0.56	0.11	-1.33	0.72	1.44

[a] Recorded with $[Bu_4N][ClO_4]$ as electrolyte in CH_2Cl_2 (0.1 mol dm^{-3}) at ambient temperature. Potentials were obtained by CV with a scan rate of 50 mV s^{-1} and are expressed as half-wave potentials ($E_{1/2}$) in V relative to ferrocenium/ferrocene (Fe^+/Fe) couple [$E_{1/2}$ (Fe^+/Fe) = 0.50 V vs. SCE] unless otherwise stated. [b] $\Delta E^o_{1/2}$ is the potential difference between the second oxidation and the first oxidation processes: $\Delta E^o_{1/2} = Oxd_2 - Oxd_1$. [c] $\Delta E\,^{o\prime}_{1/2}$ is the potential difference between the first reduction and the second reduction processes: $\Delta E\,^{o\prime}_{1/2} = Red_1 - Red_2$

Table S4. Crystallographic data for the mixed double-deckers **1-3**.

	1·6$CHCl_3$	**1**·3$CHCl_3$	**3**·3C_{60}
Molecular formula	$C_{86}H_{46}N_{16}Cl_{18}Dy$	$C_{79}H_{47}N_{12}Cl_9Dy$	$C_{272}H_{76}N_{12}Dy$
M	2103.99	1645.84	3673.95
Crystal system	Monoclinic	Triclinic	Orthorhombic
Space group	*C 2/c*	*P -1*	*P n m a*
a/Å	41.811(2)	12.7919(3)	35.7514(8)
b/Å	16.9262(5)	13.0670(3)	19.3317(3)
c/Å	27.4218(15)	20.6488(6)	27.1223(3)
α/°	90	81.461(2)	90
β/°	119.425(7)	87.235(2)	90
γ/°	90	89.539(2)	90
U/Å^3	16902.8(14)	3409.25(15)	18745.2(6)
Z	8	2	4
F(000)	8368	1648	7432
D_c/Mg m^{-3}	1.654	1.603	1.302
μ/mm^{-1}	10.438	1.506	2.652
Data collection range/°	3.08 to 63.00	3.00 to 25.00	3.07 to 63.00
Reflections measured	24694	21395	48039
Independent reflections	13535 (R_{int} = 0.0375)	11959 (R_{int} = 0.0337)	15577 (R_{int} = 0.0820)
Parameters	1042	910	1357
R_1 [$I>2\sigma(I)$]	0.0913	0.0563	0.0943
wR_2 [$I>2\sigma(I)$]	0.2508	0.1398	0.2521
Goodness of fit	1.037	1.041	1.053