Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information

Constructing Bis(porphyrinato) Rare Earth Double-Decker Complexes Involving N-Confused Porphyrin

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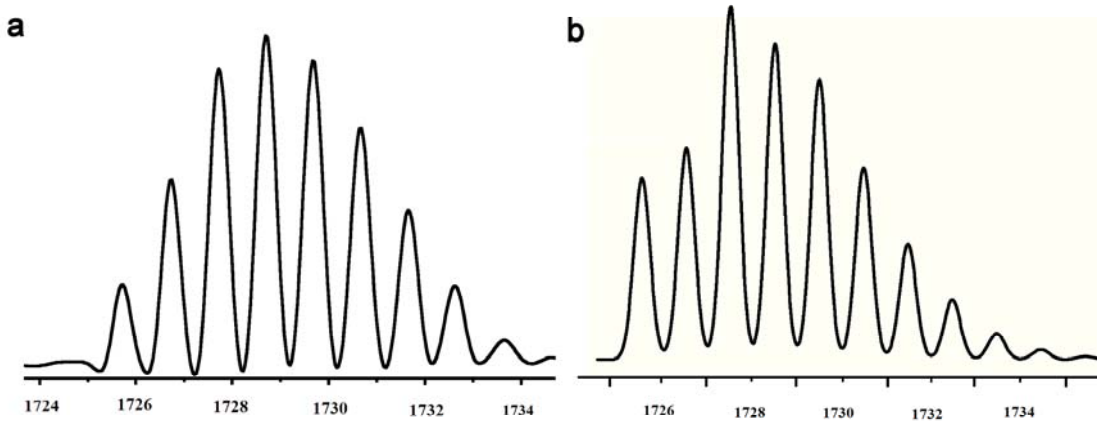

Fig. S1. Experimental (a) and simulated isotopic (b) pattern for the protonated molecular ion of La^{III}(HNTClPP)(TBPP) (**1**).

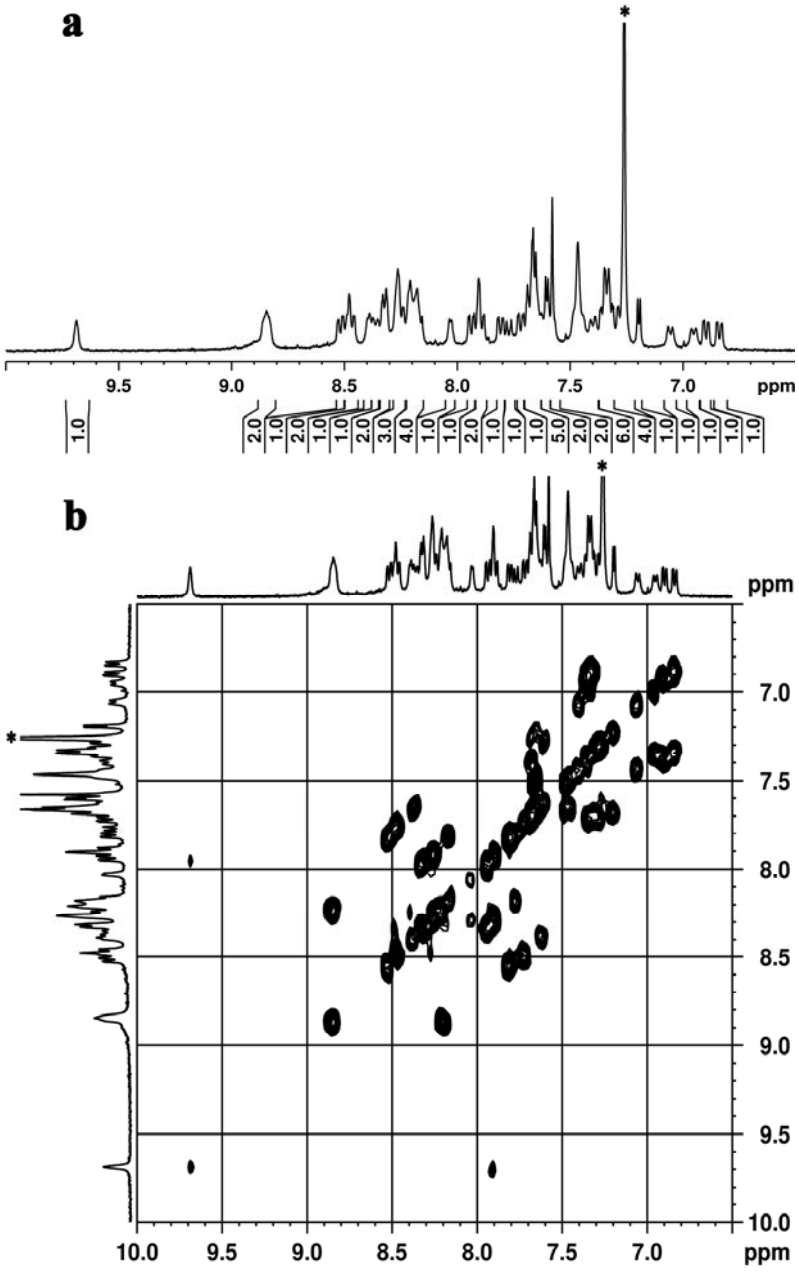

Fig. S2. (a) ^{1}H NMR and (b) ^{1}H-^{1}H COSY spectra of La^{III}(HNTClPP)(TBPP) (**1**) in $CDCl_3$ in the region from δ 6.5-10.0 ppm at 263K. * indicates the signals of residual solvent.

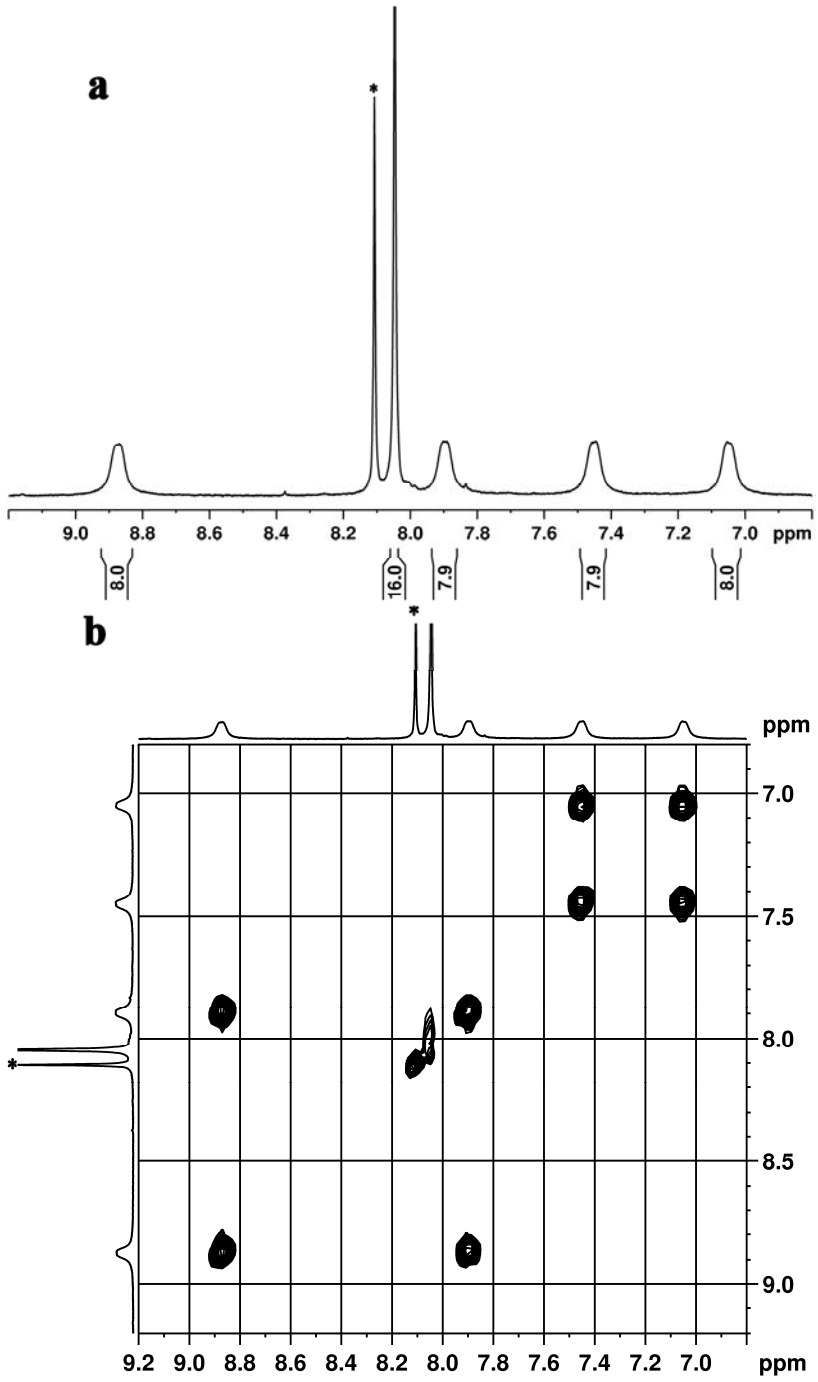

Fig. S3. (a) ^{1}H NMR and (b) ^{1}H-^{1}H COSY spectra of $HLa^{III}(TBPP)_2$ (**3**) in $CDCl_3$/[D_6]DMSO (1:1) in the presence of approximately 1% hydrazine hydrate in the region from δ 6.8-9.2 ppm at 298K. * indicates the signals of residual solvent.

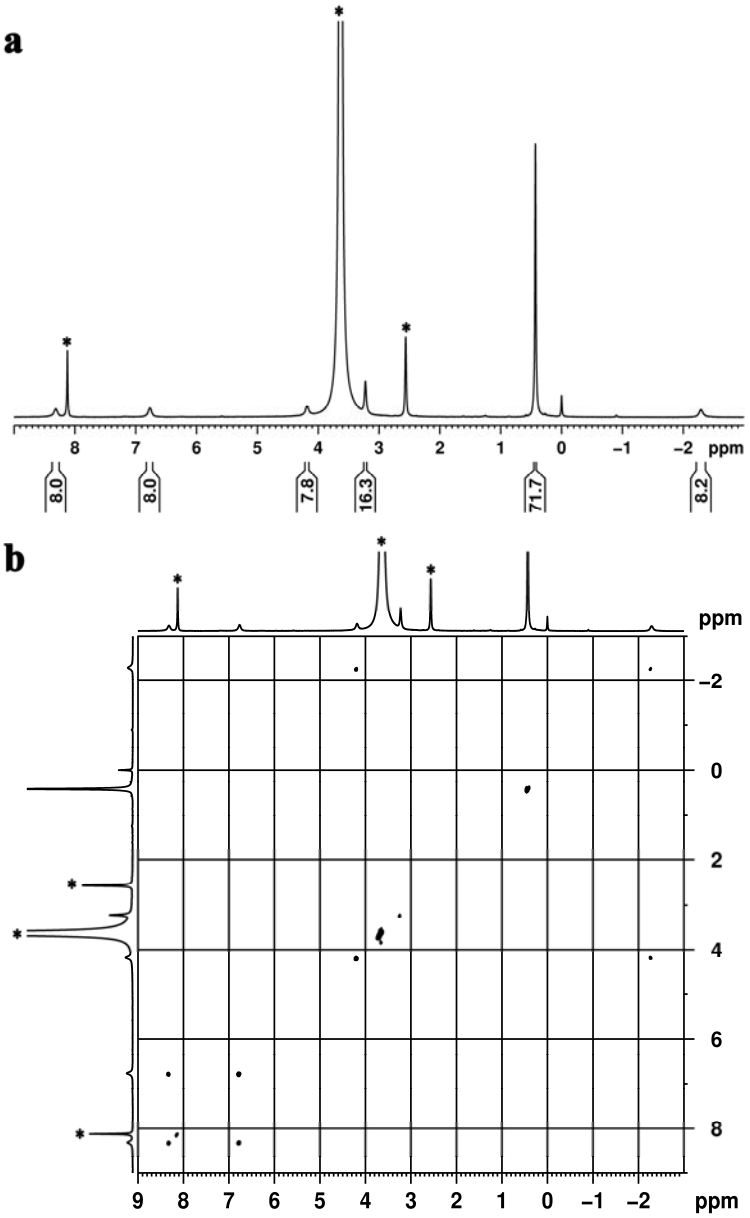

Fig. S4. (a) ^{1}H NMR and (b) ^{1}H-^{1}H COSY spectra of $HPr^{III}(TBPP)_2$ (**4**) in $CDCl_3$/[D_6]DMSO (1:1) in the presence of approximately 1% hydrazine hydrate in the region from δ -3.0-9.0 ppm at 298K. * indicates the signals of residual solvents and water.

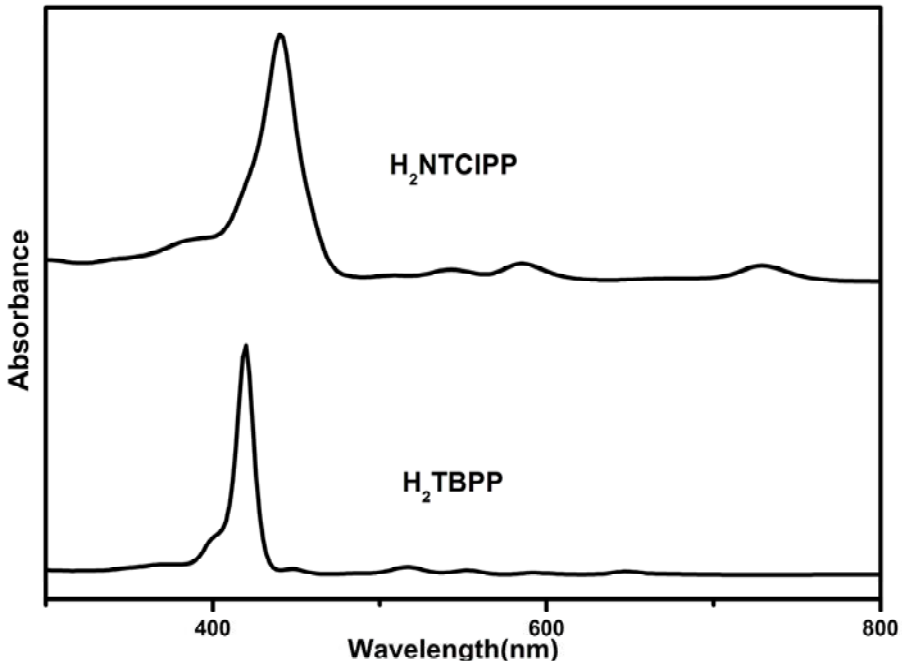

Fig. S5. Electronic absorption spectra of H_2NTClPP and H_2TBPP.

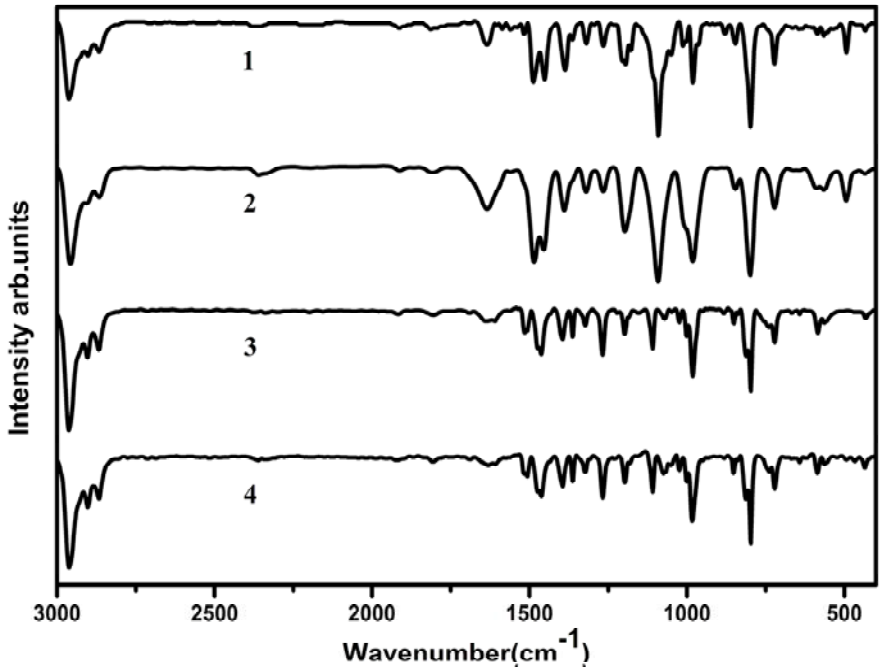

Fig. S6. IR spectra of **1-4** in the region of 400-3000 cm^{-1}.

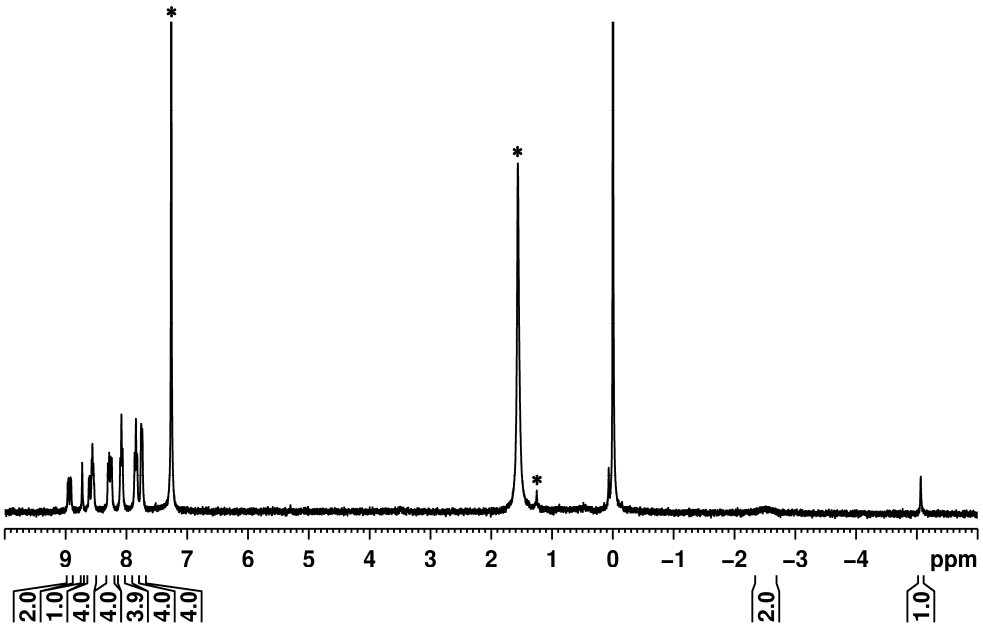

Fig. S7. ^{1}H NMR spectra of $H_2NTClPP$ in $CDCl_3$. * indicates the signals for residue solvent and impurities.

Table S1. ^{1}H NMR data (δ) for the heteroleptic double-decker **1** in $CDCl_3$ at 263K.

Compound	H_a[a]	H_b[a]	H_c[a]	H_β	H_{aryl}	$H_{t\text{-}butyl}$
1	9.69(s, 1 H)	7.94(d, 1 H)	-4.18 (s, 1 H)	8.84 (br s, 2H)[b], 8.40 - 8.32 (m, 4H)[b], 8.26 - 8.16 (m, 7 H)[b], 7.90 - 7.88 (m, 2 H)[b], 7.77 (d, 1 H), 7.69 - 7.65 (m, 6H)[b], 7.60 (d, 1 H), 7.58 (s, 2 H), 7.35 - 7.29 (m, 4H)[b], 7.20 (d, 1 H)	8.84 (br s, 2H)[b], 8.53 - 8.46(m, 3H), 8.40 - 8.32 (m, 4H)[b], 8.26 - 8.16 (m, 7 H)[b], 8.03 (d, 1 H), 7.90 - 7.88 (m, 2 H)[b], 7.81 (d, 1 H), 7.72 (d, 1 H), 7.69 - 7.65 (m, 6H)[b], 7.47 - 7.36 (m, 6H), 7.35 - 7.29 (m, 4H)[b], 7.06 (d, 1H), 6.95 (d, 1H), 6.90 (d, 1H), 6.84 (d, 1H)	1.77 (s, 18 H), 1.53 (s, 18H)

[a] H_a and H_b stand for the NH proton and CH proton, respectively, on the inverted pyrrole, while H_c stands for the proton attached to C(21) in HNTClPP ligand. [b] Some of the H_β and H_{aryl} protons' signals were partially overlapped.

Table S2. ^{1}H NMR data for the homoleptic double-deckers **3** and **4** in $CDCl_3$/[D_6]DMSO (1:1) in the presence of approximately 1% hydrazine hydrate at 298 K.

Compound	H_{aryl}	H_{β}	$H_{t\text{-}butyl}$
3	8.87 (s, 8H), 7.90 (s, 8H), 7.45 (s, 8H), 7.05 (s, 8H)	8.05 (s, 16H)	1.67 (s, 72H)
4	8.32 (s, 8H), 6.76 (s, 8H), 4.18 (s, 8H), -2.29 (s, 8H)	3.22 (s, 16H)	0.43 (s, 72H)

Table S3. Electronic absorption data for the double-deckers **1**-**4** in $CHCl_3$.

Compound	λ_{max}/nm (log ε)				
1	320(4.69)	356(4.68)	420 (5.49)	574 (3.99)	846 (4.00)
2	325(4.57)	358(4.60)	420 (5.44)	562 (3.89)	849 (3.80)
3	--	--	416 (5.63)	559 (4.05)	--
4	--	--	415 (5.56)	556 (4.04)	--

Table S4. Crystallographic data for the heteroleptic double-decker **2**.

	2
Molecular formula	$C_{104}H_{85}Cl_4N_8Pr$
M	1729.51
Crystal system	Monoclinic
Space group	*P 21/n*
a/Å	21.9573(8)
b/Å	31.7949(7)
c/Å	32.7974(13)
α/°	90
β/°	108.506(4)
γ/°	90
U/Å^3	21712.9(13)
Z	8
D_c/Mg m^{-3}	1.058
μ/mm^{-1}	4.677
Data collection range/°	3.12 to 62.50
Reflections measured	61304
Independent reflections	34233 (R_{int} = 0.0872)
Parameters	1915
R_1 [$I>2\sigma(I)$]	0.0755
wR_2 [$I>2\sigma(I)$]	0.1627
Goodness of fit	0.987