# **Electronic Supporting Information**

Reagents were used as received from commercial suppliers. High purity solvents were obtained from a SPS 800 (MBraun) solvent purification system.

### **1 - Instrumentation**

NMR experiments were performed on a Bruker Advance 600 MHz NMR spectrometer equipped with a CryoProbe Prodigy. Electrospray mass spectra (ESI-MS) were performed using a hybrid linear ion trap FTICR mass spectrometer LTQFT UltraTM (Thermo Fisher Scientific, Bremen, Germany). EA, ESI HRMS and NMR analyses were performed by the Central Institute of Engineering and Analytics (ZEA-3), Forschungszentrum Jülich GmbH (52425, Jülich, Germany). UV-Vis experiments were performed on a Shimadzu UV-3600 plus spectrophotometer using 10 mm quartz glass cuvettes. IR spectra were collected on a Bruker Vertex 70 FT-IR spectrometer on KBr disks. CV experiments were performed with a Biologic SP-150 potentiostat using EC-Lab software V.11.12. The operational framework consists of a 20 mL onecompartment cell, glassy carbon working electrode (disk, 3.0 mm) and two Pt wires. Plotted data were corrected for ohmic drop (PEIS method) and referenced vs. [Cp<sub>2</sub>Fe]/[Cp<sub>2</sub>Fe]<sup>+</sup>. Sweeping direction is from negative to positive potentials. Unless otherwise stated, the second cycle is shown. Magnetic properties were determined using a Quantum Design MPMS-5XL SQUID magnetometer for direct current (dc) and alternating current (ac) measurements. Powder samples of 2 and microcrystalline sample of 3 were compacted and immobilised into cylindrical PTFE sample holders. Experimental dc data were recorded at 0.1 T and 1.0 T in the temperature range 2.0 - 290 K and at 2.0 K in the field range 0 - 5.0 T. Experimental (ac) data were collected at various static bias fields between 0 and 1000 Oe in the temperature range 1.9 -50 K and frequency range 3 – 937 Hz using an amplitude of  $B_{ac}$  = 3 G. All data were corrected for the sample holder contributions and intrinsic diamagnetic contributions that were determined from  $(NBu_4)_4H_2[Y^{III}Pc(PW_{11}O_{39})]$ . Single-crystal X-ray diffraction data were collected on beamline I-19 at Diamond Light Source.

# 2 - Synthesis and analytical characterisation

The tetra-*n*-butylammonium salt of monolacunary Keggin phosphotungstate  $(NBu_4)_4H_3[PW_{11}O_{39}]$  and the lanthanide(III) single-decker phthalocyanine complexes [LnPc(OAc)] were synthesised as described in the literature.<sup>[1-3]</sup>

### Synthesis of (NBu<sub>4</sub>)<sub>4</sub>H<sub>2</sub>[Y<sup>III</sup>Pc(PW<sub>11</sub>O<sub>39</sub>)] (1)

A solution of  $(NBu_4)_4H_3[PW_{11}O_{39}]$  (0.1 mmol),  $(N(nBu)_4)Br$  (0.2 mmol) and triethylamine (1.0 mmol) in 10 mL acetonitrile was added dropwise to a flask containing [Y(Pc)(OAc)] (0.1 mmol) in a 20 mL mixture of dichloromethane (DCM)/methanol (1:1) and heated overnight at 50 °C. The reaction mixture was filtered to remove any unreacted species. The filtrate was evaporated under reduced pressure to obtain a green product. Precipitation of the dissolved crude product in DCM with hexane renders a green powder, which is purified by column chromatography using a mixture of DCM/acetone as eluent.

<sup>1</sup>**H NMR** (600 MHz, CD<sub>3</sub>CN):  $\delta = 9.52$  (bs, 8H, *H-a*), 8.21 (bs, 8H, *H-β*), 3.03–3.00 (m, 45H, *CH*<sub>2*TBA*</sub>), 1.54–1.49 (m, 45H, *CH*<sub>2*TBA*</sub>), 1.31–1.28 (m, 45H, *CH*<sub>2*TBA*</sub>), 0.92–0.89 (t, 67H, *CH*<sub>3*TBA*</sub>) ppm.

<sup>31</sup>**P NMR** (243 MHz, CD<sub>3</sub>CN):  $\delta = -14.74$  ppm.

**ESI HRMS**, *m/z*: found: 1093.7730 [M + 3H]<sup>3-</sup> (55%), calculated for  $[C_{32}H_{19}N_8O_{39}PW_{11}Y]^{3-}$ : 1093.7733; found: 1174.5303 [M + NBu<sub>4</sub> + 2H]<sup>3-</sup> (100% relative abundance), calculated for  $[C_{48}H_{54}N_9O_{39}PW_{11}Y]^{3-}$ : 1174.5328. M =  $[Y^{III}(Pc)(PW_{11}O_{39})]^{6-}$ .

**UV-Vis**, solution in CH<sub>2</sub>Cl<sub>2</sub>,  $\lambda / \text{nm}$  ( $\epsilon / 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ ): 258 (5.0), 351 (3.3), 692.5 (7.49) and 710 (5.8).

**IR**, KBr disk, *v*/cm<sup>-1</sup>: 2959 (m), 2930 (w), 2871 (m), 1630 (s), 1459 (m), 1379 (w), 1327 (m), 1280 (w), 1158 (w), 1101 (m), 1057 (s), 952 (s), 890 (m), 802 (s), 732 (s), and 515 (w).

**Elemental analysis**, calculated for  $C_{96}H_{162}N_{12}O_{39}PW_{11}Y$ : C 27.13, H 3.84, N 3.95%. Found: C 27.42, H 4.07, N 4.01%.

#### Synthesis of $(NBu_4)_4H_2[Dy^{III}(Pc)(PW_{11}O_{39})]$ (2)

The same synthetic procedure used for  $(NBu_4)_4H_2[Y^{III}Pc(PW_{11}O_{39})]$  has been followed for the preparation of  $(NBu_4)_4H_2[Dy^{III}(Pc)(PW_{11}O_{39})]$  (2), using [Dy(Pc)(OAc)] in place of [Y(Pc)(OAc)].

**ESI-HRMS**, m/z: found: 1198.8733 [M + NBu<sub>4</sub> + 2H]<sup>3-</sup> (100% relative abundance), calculated for  $[C_{48}H_{54}N_9O_{39}PW_{11}Dy]^{3-}$ : 1198.8732; found: 1279.9644 [M + 2NBu<sub>4</sub> + 1H]<sup>3-</sup> (90%), calculated for  $[C_{64}H_{89}N_{10}O_{39}PW_{11}Dy]^{3-}$ : 1279.9649. M =  $[Dy^{III}(Pc)(PW_{11}O_{39})]^{6-}$ .

**UV-Vis**, solution in CH<sub>2</sub>Cl<sub>2</sub>,  $\lambda / \text{nm} (\epsilon / 10^4 \text{ M}^{-1} \text{ cm}^{-1})$ : 259 (5.1), 352.5 (3.4), 693 (7.45), 711 (6.0).

**IR**, KBr disk, *v*/cm<sup>-1</sup>: 2959 (w), 2925 (m), 2856 (w), 1632 (m), 1458 (m), 1379 (w), 1326 (m), 1280 (w), 1164 (w), 1095 (m), 1056 (m), 953 (s), 886 (m), 800 (s), 730 (s), and 514 (w).

**Elemental analysis**, calculated for C<sub>96</sub>H<sub>162</sub>N<sub>12</sub>O<sub>39</sub>PW<sub>11</sub>Dy: C 26.67, H 3.78, N 3.89%. Found: C 26.90, H 3.86, N 3.64%.

#### Synthesis of (NBu<sub>4</sub>)<sub>4</sub>H<sub>2</sub>[Tb<sup>III</sup>(Pc)(PW<sub>11</sub>O<sub>39</sub>)] (3)

The same synthetic procedure used for  $(NBu_4)_4H_2[Y^{III}Pc(PW_{11}O_{39})]$  has been followed for the preparation of  $(NBu_4)_4H_2[Tb^{III}(Pc)(PW_{11}O_{39})]$  (3), using [Tb(Pc)(OAc)] in place of [Y(Pc)(OAc)].

**ESI-HRMS**, *m/z*: found: 1197.8721 [M + NBu<sub>4</sub> + 2H]<sup>3-</sup> (100% relative abundance), calculated for  $[C_{48}H_{54}N_9O_{39}PW_{11}Tb]^{3-}$ : 1197.8726; found: 1278.2987 [M + 2NBu<sub>4</sub> + 1H]<sup>3-</sup> (20%), calculated for  $[C_{64}H_{89}N_{10}O_{39}PW_{11}Tb]^{3-}$ : 1278.2983; found: 1917.9501 [M + 2NBu<sub>4</sub> + 2H]<sup>2-</sup> (50 %), calculated for  $[C_{64}H_{90}N_{10}O_{39}PW_{11}Tb]^{2-}$ : 1917.9511. M =  $[Tb^{III}(Pc)(PW_{11}O_{39})]^{6-}$ .

**UV-Vis**, solution in CH<sub>2</sub>Cl<sub>2</sub>,  $\lambda / \text{nm} (\epsilon / 10^4 \text{ M}^{-1} \text{ cm}^{-1})$ : 258.5 (4.9), 350 (3.5), 692 (7.26) and 713 (5.98).

**IR**, KBr disk, *v*/cm<sup>-1</sup>: 2959 (s), 2923 (m), 2853 (m), 1633 (m), 1457 (m), 1379 (w), 1326 (m), 1280 (w), 1164 (w), 1094 (m), 1056 (m), 952 (s), 888 (m), 799 (s), 730 (s), and 514 (w).

**Elemental analysis**, calculated for  $C_{96}H_{162}N_{12}O_{39}PW_{11}Tb$ : C 26.69, H 3.78, N 3.89%. Found: C 26.70, H 3.84, N 3.68%.



**Figure S1.** Cyclic voltammograms of a 0.33 mM solution of **1** in 0.1 M NBu<sub>4</sub>PF<sub>6</sub> in DCM, from -2.10 to -0.24 V (left) and from -0.25 to +0.94 V (right). Values are corrected for ohmic drop and referenced *versus* [Cp<sub>2</sub>Fe]/[Cp<sub>2</sub>Fe]<sup>+</sup>. Second cycle shown.



**Figure S2.** Cyclic voltammogram of a 0.5 mM solution of  $(NBu_4)_4H_3[PW_{11}O_{39}]$  in 0.1 M NBu<sub>4</sub>PF<sub>6</sub> in CH<sub>3</sub>CN at 100 mV (scan window: +1.0 to -1.5 V). Values are corrected for ohmic drop and referenced *versus* [Cp<sub>2</sub>Fe]/[Cp<sub>2</sub>Fe]<sup>+</sup>. Second cycle shown.



**Figure S3.** Cyclic voltammograms of a 0.5 mM solution of  $(NBu_4)_4H_2[Y^{III}(Pc)(PW_{11}O_{39})]$  (1, left)/ (NBu<sub>4</sub>)<sub>4</sub>H<sub>2</sub>[Tb<sup>III</sup>(Pc)(PW\_{11}O\_{39})] (3, right) in 0.1 M NBu<sub>4</sub>PF<sub>6</sub> in DCM at 100 mV. Values are corrected for ohmic drop and referenced *versus* [Cp<sub>2</sub>Fe]/[Cp<sub>2</sub>Fe]<sup>+</sup>.



**Figure S4.** Left: Full ESI-HRMS spectrum of  $(NBu_4)_4H_2[Y^{III}(Pc)(PW_{11}O_{39})]$  (1); *m/z*, found: 1093.7730 [M + 3H]<sup>3-</sup> (55%), calculated for  $[C_{32}H_{19}N_8O_{39}PW_{11}Y]^{3-}$ : 1093.7733; found: 1174.5303 [M + NBu<sub>4</sub> + 2H]<sup>3-</sup> (100% relative abundance), calculated for  $[C_{48}H_{54}N_9O_{39}PW_{11}Y]^{3-}$ : 1174.5328. Right: Partial ESI-HRMS corresponding to  $[M + NBu_4 + 2H]^{3-}$ .  $M = [Y^{III}(Pc)(PW_{11}O_{39})]^{6-}$ .



Figure S5. Left: Full ESI-HRMS spectrum of 3 ( $M = [Tb^{III}(Pc)(PW_{11}O_{39})]^{6-}$ ); *m/z*, found: 1197.8721 [M + NBu<sub>4</sub> + 2H]<sup>3-</sup> (100% relative abundance), calculated for  $[C_{48}H_{54}N_9O_{39}PW_{11}Tb]^{3-}$ : 1197.8726; found: 1917.9501 [M + 2NBu<sub>4</sub> + 2H]<sup>2-</sup> (50 %), calculated for  $[C_{64}H_{90}N_{10}O_{39}PW_{11}Tb]^{2-}$ : 1917.9511. Right: partial ESI-HRMS corresponding to  $[M + NBu_4 + 2H]^{3-}$ .



**Figure S6.** IR spectra of  $(NBu_4)_4H_2[Y^{III}(Pc)(PW_{11}O_{39})]$  (1, red graph) and the synthesis precursors [YPc(OAc)] (blue graph) and  $(NBu_4)_4H_3[PW_{11}O_{39}]$  (green graph).



Figure S7. IR spectra of 2 (left) and 3 (right).



**Figure S8.** Left: UV/Vis/NIR spectra of DCM solutions of  $(NBu_4)_4H_2[Y^{III}(Pc)(PW_{11}O_{39})]$  (1) and the starting materials  $(NBu_4)_4H_3[PW_{11}O_{39}]$  and  $[Y^{III}(Pc)(OAc)]$ . Right: Molar extinction graphs for  $(NBu_4)_4H_2[Y^{III}(Pc)(PW_{11}O_{39})]$  (1),  $(NBu_4)_4H_2[Dy^{III}(Pc)(PW_{11}O_{39})]$  (2) and  $(NBu_4)_4H_2[Tb^{III}(Pc)(PW_{11}O_{39})]$  (3).



Figure S9. Thermogravimetric analysis (TGA) of 1 (top) 2 (bottom left) and 3 (bottom right). Both compounds exhibit significant thermal stability up to ~400 °C. The mass loss of ~22 % corresponds to the loss of four NBu<sub>4</sub> units.



Figure S10. <sup>31</sup>P NMR (243 MHz, CD<sub>3</sub>CN) spectrum of the precursor  $(NBu_4)_4H_3[PW_{11}O_{39}]$ .



Figure S11. <sup>1</sup>H NMR (600 MHz, 300 K) spectrum of the precursor [Y<sup>III</sup>(Pc)(OAc)] in DMSO-d6.



**Figure S12.** <sup>1</sup>H NMR (600 MHz, 300 K) spectrum of  $(NBu_4)_4H_2[Y^{III}(Pc)(PW_{11}O_{39})]$  (1) in CD<sub>3</sub>CN. Solvent signals corresponding to residual solvents (CD<sub>3</sub>CN and water) have been removed for clarity.



Figure S13. <sup>31</sup>P NMR (243 MHz, 300 K) spectrum of (NBu<sub>4</sub>)<sub>4</sub>H<sub>2</sub>[Y<sup>III</sup>(Pc)(PW<sub>11</sub>O<sub>39</sub>)] (1) in CD<sub>3</sub>CN.

### 3 - Magnetochemistry



**Figure S14.** Molar magnetic ac susceptibility components of **2** in a static bias field of 500 Oe. Left: Inphase molar magnetic susceptibility  $\chi_m'$  vs. frequency *f*. Right: Out-of-phase molar magnetic susceptibility  $\chi_m''$  vs. *f* (symbols: data, lines: fits to generalised Debye expression).



**Figure S15.** Molar magnetic ac susceptibility components of **2** at a static bias field of 500 Oe. Left: Inphase molar magnetic susceptibility  $\chi_m'$  vs. temperature *T*. Right: Out-of-phase molar magnetic susceptibility  $\chi_m''$  vs. *T*.



**Figure S16.** Cole-Cole plots of the molar magnetic ac susceptibility data. Top left:  $\chi_m''$  vs.  $\chi_m'$  for **2** at zero static bias field. Top right:  $\chi_m''$  vs.  $\chi_m'$  for **3** at zero static bias field. Bottom left:  $\chi_m''$  vs.  $\chi_m'$  for **3** at a static bias field of 500 Oe. Bottom right:  $\chi_m''$  vs.  $\chi_m'$  for **3** at a static bias field of 1000 Oe.

**Table S1.** Summary of structural parameters of  $[Tb^{III}Pc_2]^-$ ,  $Tb^{III}(PW_{11}O_{39})_2]^{11-}$  and  $[Tb^{III}Pc(PW_{11}O_{39})]^{6-}$  relevant to the distortion of the  $Tb^{III}N_4$ ,  $Tb^{III}O_4$  and  $Tb^{III}N_4O_4$  fragments compared to a  $D_{4d}$ -symmetric ligand field.

Complex	<b>d</b> <sub>Tb-O</sub> ª <b>/</b> Å	<b>d</b> <sub>ть-N</sub> ь / Å	φ <sup>c</sup> /°	<b>d</b> <sub>pp</sub> <sup>g</sup> / Å	<b>d</b> <sub>in(O-O)</sub> <sup>h</sup> / Å	d <sub>in(N-N)</sub> <sup>i</sup> / Å	<b>Ø</b> <sup>f</sup> / °
[Tb <sup>III</sup> Pc₂] <sup>−</sup>		2.434	45.00 <sup>d</sup>	2.824		2.803	0.80
Tb <sup>III</sup> (PW <sub>11</sub> O <sub>39</sub> ) <sub>2</sub> ] <sup>11–</sup>	2.389		45.03 <sup>e</sup>	2.595	2.825		3.25
[Tb <sup>III</sup> Pc(PW <sub>11</sub> O <sub>39</sub> )] <sup>6–</sup>	2.375	2.462	45.26 <sup>f</sup>	2.672	2.861	2.833	5.24

<sup>a</sup> Average Tb–O bond distance. <sup>b</sup> Average Tb–N bond distance. <sup>c</sup> Average skew angle relative to an eclipsed geometry (for an ideal  $D_{4d}$  symmetry  $\varphi = 45^{\circ}$ ). <sup>d</sup> Average  $\varphi$  value of 44.84°, 46.49°, 43.37° and 45.31°. <sup>e</sup> Average  $\varphi$  value of 55.24°, 36.18°, 35.16° and 53.55°. <sup>f</sup> Average  $\varphi$  value of 44.53° and 45.96°. <sup>g</sup> Interplanar distances between the upper and lower planes containing four coordinating O or N atoms taken at the centroids. <sup>h, i</sup> Average distance between four neighbouring O or N atoms placed in each plane. <sup>f</sup> Angle between the upper and lower planes.

#### **Discussion of magnetostructural aspects (Table S1)**

The Tb<sup>3+</sup> compound **3** does not exhibit out-of-phase frequency dependence signals above 2 K. Compound **2**,  $(N(nBu)_4)_4H_2[Dy^{III}Pc(PW_{11}O_{39})]$ , shows maxima in the  $\chi_m''$  vs. *f* plots and pronounced curvatures in the Cole-Cole representation, characteristic of SMM behaviour under an applied dc field (500 Oe). Fitting of the magnetic data yields  $U_{eff} = (33.7\pm1.5) \text{ cm}^{-1}$  and  $\tau_0 = (1.08\pm0.31)\times10^{-7}$  s. This is the first communicated SMM behaviour for such  $Ln^{III}$ -Pc-POM hybrid species. Although complex **2** does not surpass the  $U_{eff}$  barrier of the homoleptic double-decker complex  $[Dy^{III}(Pc)_2]^-$ , a comparison to  $[Dy^{III}(PW_{11}O_{39})_2]^{11-}$  shows the necessity of applying a smaller bias field (500 Oe *vs.* 3000 Oe) to reach maximal out-of-phase components, and a four orders of magnitude larger relaxation time ( $\tau_0 = (1.08\pm0.31)\times10^{-7}$  s *vs.* 9.6× 10<sup>-12</sup> s). The lack of a single-crystal structure of **2** limits any comparative explanation based on single-crystal structural determination.

Due to the similarity of ionic radius of Tb<sup>III</sup> and Dy<sup>III</sup> (0.092 vs. 0.091 nm) we are going to explain some structural differences amongst complex **2** [Tb<sup>III</sup>Pc(PW<sub>11</sub>O<sub>39</sub>)]<sup>6-</sup>, [Tb<sup>III</sup>Pc<sub>2</sub>]<sup>-</sup> <sup>[4]</sup> and [Tb<sup>III</sup>(PW<sub>11</sub>O<sub>39</sub>)<sub>2</sub>]<sup>11-.[5]</sup> Ishikawa *et al.*, in double-decker [Ln<sup>III</sup>Pc<sub>2</sub>]<sup>-</sup> complexes, reported the placement of a large  $|J_z|$  value at the lowest energy arising from the splitting of the *J* ground state of the Ln<sup>III</sup> ion in a  $D_{4d}$ -symmetric ligand field (LF) and assigned this as the origin of the slow relaxation of the magnetisation.<sup>[6]</sup> Coronado *et al.* in a magnetic study of [Ln<sup>III</sup>(SiW<sub>11</sub>O<sub>39</sub>)<sub>2</sub>]<sup>13-</sup>, compared their complexes with the phthalocyanine complexes of Ishikawa *et al.*, stating that the disparity in magnetic properties originate from the different LF splitting as a consequence of structural distortions from the  $D_{4d}$  symmetry.<sup>[7]</sup> While Ln<sup>III</sup>(POM)<sub>2</sub> complexes show an axial compression of the lanthanide coordination site, the [Ln<sup>III</sup>Pc<sub>2</sub>]<sup>-</sup> family displayed an elongation; furthermore, the two coordinating planes are not parallel for [Ln<sup>III</sup>(SiW<sub>11</sub>O<sub>39</sub>)<sub>2</sub>]<sup>13-</sup> complexes. This structural difference should account for the different alignment of the  $M_J$  states *vs.* energy and the energy separation between the ground state and low-lying states.

Our  $[Tb^{III}Pc(PW_{11}O_{39})]^{6-}$ , although holds a bigger  $\varphi$  angle than  $[Tb^{III}(PW_{11}O_{39})_2]^{11-}$ , suffers a lesser axial compression and has a consistency in the  $\varphi$  skew angles (44.53° and 45.96°) not exhibited by  $[Tb^{III}(PW_{11}O_{39})_2]^{11-}$  (55.24°, 36.18°, 35.16° and 53.55°), representing a smaller distortion of the  $D_{4d}$  symmetry.

### 4 - Crystallographic analysis details

**Crystal data of 3.**  $C_{76}H_{122}N_{12}O_{39}PW_{11}Tb.6(CH_2Cl_2)$ ,  $M_r = 4549.64 \text{ g mol}^{-1}$ , monoclinic, C2/m (No. 12), a = 22.5917(14) Å, b = 21.7413(12) Å, c = 26.2648(15) Å,  $\beta = 95.3550(10)^{\circ}$ ,  $\alpha = \gamma = 90^{\circ}$ , V = 12844.3(13) Å<sup>3</sup>, T = 100.15 K, Z = 4, Z' = 0.5,  $\mu$ (Synchrotron) = 9.767, 53920 reflections measured, 7102 unique ( $R_{int} = 0.0833$ ), which were used in all calculations. The final  $wR_2$  was 0.1507 (all data) and  $R_1 = 5.09$  % ( $I > 2\sigma(I)$ ).

Cation exchange by using NHEt<sub>3</sub><sup>+</sup> was needed in order to obtain X-ray quality crystals. Akin to the Y complex, green rod-like crystals were obtained in a concentrated DCM solution of  $(NBu_4)_2(NHEt_3)_2H_2[Tb^{III}(Pc)(PW_{11}O_{39})]$ . Compound **3** was provided as intense turquoise-blue crystals. Paratone oil was used to coat a selection of crystals which were then mounted on MiTeGen kapton loops and frozen in liquid nitrogen. The loops were stored in a MiTeGen Unipuck and transported to Diamond Light Source. Data were collected remotely at beam line I-19 of Diamond Light Source (award CY22240).<sup>[8]</sup>

**Experimental.** Single blue-plate crystals of **3** were recrystallised from dichloromethane by slow evaporation. A suitable crystal with dimensions  $0.05 \times 0.02 \times 0.02$  mm<sup>3</sup> was selected and mounted on a MITIGEN holder in Paratone oil on a Diamond Light Source I-19 EH1 diffractometer. The crystal was kept at a steady T = 100.0 K during data collection. The structure was solved with the ShelXT<sup>[9]</sup> programme using dual methods and by using Olex2<sup>[10]</sup> as the graphical interface. The model was refined with ShelXL 2018/3<sup>[11]</sup> using full matrix least squares minimisation on  $F^2$ .

*Refine\_special\_details*: The resolution of the data set was cut a 1 Å during integration due to rapidly rising values of R(int) at higher resolution. Two of the methyl C atoms were modelled with disordered H due to close contacts with symmetry related atoms. One triethyammonium cation lies on a symmetry element, the second is quite badly disordered across a symmetry element. In modelling this second triethylammonium a best faith effort was made to model ethyl groups with occupancies linked using SUMP in ShelXL such that the total number of C atoms added up correctly. Hydrogen atoms were added and occupancies adjusted so that they sum correctly. Some free refinement was carried out and then the U(ij) values of the disordered C atoms were fixed. Two additional positive charges, identified as two H atoms by elemental analysis, are needed. These could not be located from a difference map in any chemically reasonable location and so are not included in the model. They are, however, included in the total chemical formula (as are molecules of dichloromethane handled with solvent masking); this triggers checkCIF alerts which should be ignored. Geometric restraints and constraints were used to control the phthalocyanine shape, as was a global restraint on displacement ellipsoids.

#### **Compound 3**

Formula	C <sub>76</sub> H <sub>122</sub> N <sub>12</sub> O <sub>39</sub> PW <sub>11</sub> Tb·6 (DCM)
$D_{calc.}$ / g cm <sup>-3</sup>	2.353
$\mu$ / mm <sup>-1</sup>	9.767
Formula Weight / g mol <sup>-1</sup>	4549.64
Colour	blue
Shape	plate

Size / mm <sup>3</sup>	0.05×0.02×0.02
T/K	100.15
Crystal System	monoclinic
Space Group	C2/m
a / Å	22.5917(14)
b / Å	21.7413(12)
<i>c</i> / Å	26.2648(15)
α	90°
β	95.3550(10)°
γ	90°
$V/Å^3$	12844.3(13)
Ζ	4
Ζ'	0.5
Wavelength / Å	0.6889
Radiation type	Synchrotron
$\Theta_{min}$	1.263°
$\Theta_{max}$	20.294°
Measured Refl's.	53920
Ind't Refl's	7102
Refl's with $I > 2\sigma(I)$	5609
R <sub>int</sub>	0.0833
Parameters	585
Restraints	931
Largest Peak	1.798
Deepest Hole	-0.814
GooF	1.110
$wR_2$ (all data)	0.1507
$wR_2$	0.1470
$R_1$ (all data)	0.0595
$R_1$	0.0509

 $C_{192}H_{324}N_{24}O_{78}P_2W_{22}Y \cdot 3.5(CH_2Cl_2), M_r = 8798.43 \text{ g mol}^{-1}$ , monoclinic,  $P2_1/c$  (No. 14), a = 29.676(4) Å, b = 30.709(4) Å, c = 29.725(4) Å,  $\beta = 91.830(2)^\circ$ ,  $\alpha = \gamma = 90^\circ$ , V = 27074(5) Å<sup>3</sup>, T = 100.0 K, Z = 4, Z' = 1,  $\mu$ (Synchrotron) = 9.036, 213327 reflections measured, 28548 unique ( $R_{int} = 0.1538$ ) which were used in all calculations. The final  $wR_2$  was 0.2344 (all data) and  $R_1$  was 0.0869 ( $I > 2\sigma(I)$ ).

Crystal

data

of

1.

 $(NBu_4)_4H_2[Y^{III}(Pc)(PW_{11}O_{39})]$  (1) was provided as green plate-shaped crystals. Paratone oil was used to coat a selection of crystals which were then mounted on MiTeGen kapton loops and frozen in liquid nitrogen. The loops were stored in a MiTeGen Unipuck and transported to Diamond Light Source. Data were collected remotely at beam line I-19 of Diamond Light Source (award CY22240).<sup>[8]</sup>

**Experimental.** Single green plate crystals of **1** were recrystallised from dichloromethane by slow evaporation. A suitable crystal with dimensions  $0.04 \times 0.04 \times 0.02$  mm<sup>3</sup> was selected and mounted on a MITIGEN holder in Paratone oil. on a Fluid Film Devices diffractometer. The crystal was kept at a steady T = 100.0 K during data collection. The structure was solved with the ShelXT 2018/2<sup>[9]</sup> solution programme using dual methods and by using Olex2<sup>[10]</sup> as the graphical interface. The model was refined with ShelXL 2018/3<sup>[11]</sup> using full matrix least squares minimisation on  $F^2$ .

*Refine special details*: The model is based on a weak data set collected using synchrotron radiation with 5% beam transmission. The crystals proved to be very susceptible to radiation damage. A data set measured using 10% beam transmission resulted in destructive radiation damage before the end of the first of four runs. No more crystals remained for testing (data were measured by remote access, only two crystals had been prepared for testing). Despite this, the majority of the structure was determined easily. Seven out of a necessary eight tetrabutylammonium cations were identified. The eighth could not be modelled satisfactorily using discrete atoms, although the void occupied by the cation can be seen. The fragment database of Olex2 was used to help model the cations, with some changes made to the geometry of the butyl groups depending on peaks in a difference map. The remaining  $(nBu_4N)^+$  was handled using the solvent masking procedure in Olex2. This also accounted for 3.5 molecules of dichloromethane solvent per asymmetric unit. A further two hydrogen atoms per Y complex (four per asymmetric unit) are indicated by elemental analysis and other methods. Two of these are included as N-bound H atoms, deduced by the presence of likely N-H…O hydrogen bonds (the N…O distance would otherwise be unreasonably short). The second two H atoms could not be located even by hydrogen bond interaction deduction and so are not included in the model. They are, however, included in the total chemical formula. This, and the use of solvent masking, triggers a lot of checkCIF alerts and these should be ignored. Displacement ellipsoid restraints were applied globally and geometric restraints were applied to the cations. One O atom (O12) was modelled isotropically as it became non-positive definite when refined using an anisotropic model. There is no chemically obvious reason for this as the site cannot be anything other than oxygen. The resolution of the data set was cut at 1 Å during integration, consistent with the weakness of the data set.

## Compound 1

$C_{195.5}H_{331}N_{24}O_{78}P_2W_{22}Y_2Cl_7$
2.159
9.036
8798.43
green
plate
0.04×0.04×0.02
100.0
monoclinic
$P2_{1}/c$
29.676(4)
30.709(4)
29.725(4)
90°
91.830(2)°
90°
27074(5)
4
1
0.6889
Synchrotron
0.665°
20.222°
213327
28548
18075
0.1538
2727
4697
2.249
-1.590
1.028
0.2344
0.2095
0.1264
0.0869

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