Electronic Supplementary Material (ESI) for Chemical Communications

Rational addition of capping groups to the phosphomolybdate Keggin anion $[PMo_{12}O_{40}]^{3-}$ by mild, non-aqueous reductive aggregation

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Electronic Supplementary Information

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General Experimental

All reactions and manipulations were carried out under an atmosphere of dry, oxygen-free nitrogen in screw-top flasks fitted with PTFE screw valves using Schlenk and dry-box techniques.[1] Diethyl ether was dried over and distilled from sodium benzophenone ketyl, acetonitrile was dried over and distilled from calcium hydride. ^{31}P NMR spectra were recorded on a JEOL 500 MHz Lambda/Eclipse spectrometer operating at 202.47 MHz and chemical shifts are quoted in ppm relative to external 85 % phosphoric. FTIR spectra were recorded from powders on a Varian 800 FT-IR spectrometer fitted with an ATR attachment. Cyclic voltammetry was carried out using an e-DAQ potentiostat and e-corder with eChem and Mac OS X software in a mini (2 mL volume) three-electrode cell using glassy carbon working electrode, Pt wire counter electrode and a Ag/AgCl quasi reference electrode. Potentiometric redox titrations were carried out using a home-made voltmeter and an e-DAQ e-corder with Chart and Mac OS X software in a mini (2 mL volume) cell using a Pt wire electrode and a Ag/AgCl quasi reference electrode. Elemental analyses were performed by Newcastle University Chemical Analysis Service.

Preparation of (^{n}Bu$_4$N)$_3$[PMo$_{12}$O$_{40}${Co(MeCN)$_2$}], (^{n}Bu$_4$N)$_3$**1.**

(^{n}Bu$_4$N)$_3$[PMo$_{12}$O$_{40}$] (0.81 g, 0.32 mmol) and $CoCl_2$ (0.04 g, 0.32 mmol) were dissolved in MeCN (30 mL) with warming. The resulting solution was transferred via cannula onto sodium-mercury amalgam (0.4 %, 3.65 g, 0.64 mmol) and the mixture was stirred for 12 h, during which time the solution changed from green to deep blue. After filtration, volatiles were removed under reduced pressure and the residual solid was washed with diethyl ether (2 20 mL) then dried in vacuo to give a blue-black powder. Yield 0.81 g, 94 %. Pure material was obtained by low temperature (–20 °C) recrystallization from MeCN-Et_2O and single crystal for X-ray diffraction were obtained by diffusion of a diethyl ether layer into a MeCN solution of (^{n}Bu$_4$N)$_3$**1**.

Calculated for (^{n}Bu$_4$N)$_3$[PMo$_{12}$O$_{40}$Co(MeCN)$_{1.64}$] ($C_{51.28}H_{112.92}N_{4.64}CoMo_{12}O_{40}P$) C, 23.0; H, 4.3; N, 2.4 %. Found C, 22.8; H, 4.5; N, 2.4 %.

^{31}P NMR (202.47 MHz, CH_3CN) δ_P 20.6, $w_{1/2}$ ~85 Hz.

IR 2963 m, 2927 m, 2874 w, 2282 w, 1483 m, 1380 w, 1363 w, 1058 m, 941 s, 875 m, 782 s, br cm^{-1}.

Preparation of (^{n}Bu$_4$N)$_3$[PMo$_{12}$O$_{40}$(VO)$_2$], (^{n}Bu$_4$N)$_3$**2.**

(^{n}Bu$_4$N)$_3$[PMo$_{12}$O$_{40}$] (1.09 g, 0.43 mmol) was dissolved in MeCN (30 mL) with warming and transferred via cannula onto sodium-mercury amalgam (0.4 %, 14.73 g, 2.56 mmol) with stirring. After 10 min. a solution of [$VOCl_3$(dme)] (0.23 g, 0.85 mmol) in MeCN (10 mL) was added and the mixture was stirred for 19 h. After filtration, the volume of the deep blue solution was reduced by ~30 % and diethyl ether (10 mL) was added. After warming to dissolve any solid, the solution was stored at –20 °C to give dark blue crystals, which were separated and pumped dry. Yield 0.56 g, 48 %.

Calculated for (^{n}Bu$_4$N)$_3$[PMo$_{12}$O$_{40}$(VO)$_2$]•MeCN ($C_{50}H_{111}N_4Mo_{12}O_{42}PV_2$) C, 22.0; H, 4.1; N, 2.1 %. Found C, 22.0; H, 4.6; N, 1.9 %.

^{31}P NMR (202.47 MHz, CH_3CN) δ_P –6.5, $w_{1/2}$ ~30 Hz.

IR 2963 m, 2934 m, 2877 m, 1483 m, 1380 w, 1153 w, 1056 m, 974 s, 947 s, 876 m, 793 s, br, 642 m, 590 w cm^{-1}.

Preparation of (^{n}Bu$_4$N)$_3$[PMo$_{12}$O$_{40}$Sb$_2$], (^{n}Bu$_4$N)$_3$3.

(^{n}Bu$_4$N)$_3$[PMo$_{12}$O$_{40}$] (0.92 g, 0.36 mmol) was dissolved in MeCN (30 mL) with warming and transferred via cannula onto sodium-mercury amalgam (0.4 %, 12.47 g, 2.17 mmol) with stirring. After 10 min. a solution of $SbCl_3$ (0.17 g, 0.72 mmol) in MeCN (10 mL) was added and the mixture was stirred for 30 h. After filtration, a layer of diethyl ether was added to the deep blue solution and single crystals were formed upon diffusion. Yield 0.43 g, 42 %.

Calculated for (^{n}Bu$_4$N)$_3$[PMo$_{12}$O$_{40}$Sb$_2$]•(MeCN)$_{0.7}$ ($C_{49.40}H_{110.10}N_{3.70}Mo_{12}O_{40}PSb_2$) C, 21.0; H, 3.9; N, 1.8 %. Found C, 20.6; H, 4.2; N, 2.0 %.

^{31}P NMR (202.47 MHz, CH_3CN) δ_P –5.3, $w_{1/2}$ ~35 Hz.

IR 2963 m, 2934 m, 2877 m, 1467 m, 1380 w, 1166 w, 1070 w, 1065 w, 1034 w, 954 s, 941 s, 880 m, 797 w, 727 s, 643 m, 605 w, 589 w cm^{-1}.

References

1 R. J. Errington, *Advanced Practical Inorganic and Metalorganic Chemistry*, Blackie Academic & Professional, London, **1997**.

Redox titrations

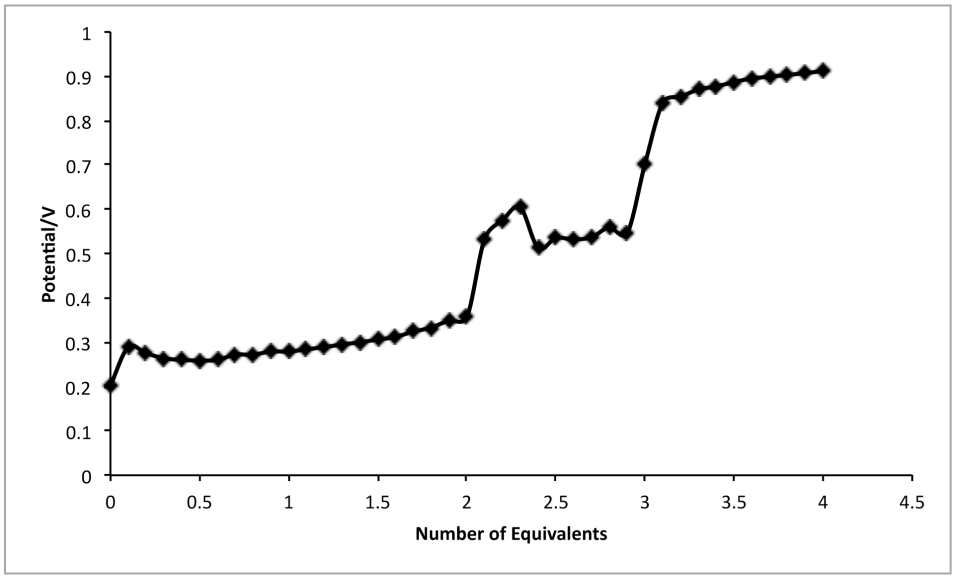

Fig. S1 Potentiometric redox titration of (^{n}Bu$_4$N)$_3$**1** with ammonium cerium(IV) nitrate in MeCN.

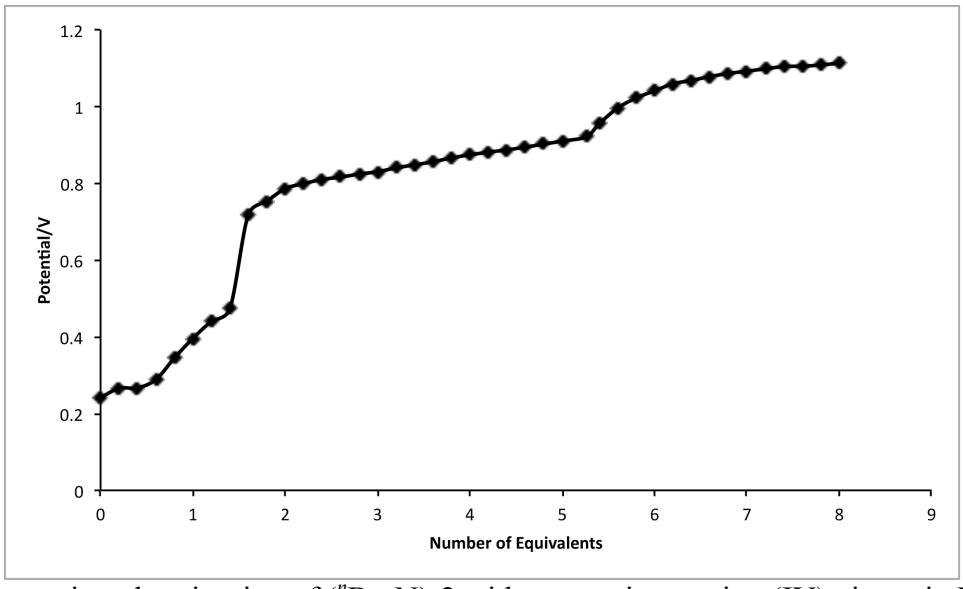

Fig. S2 Potentiometric redox titration of (^{n}Bu$_4$N)$_3$**2** with ammonium cerium(IV) nitrate in MeCN.

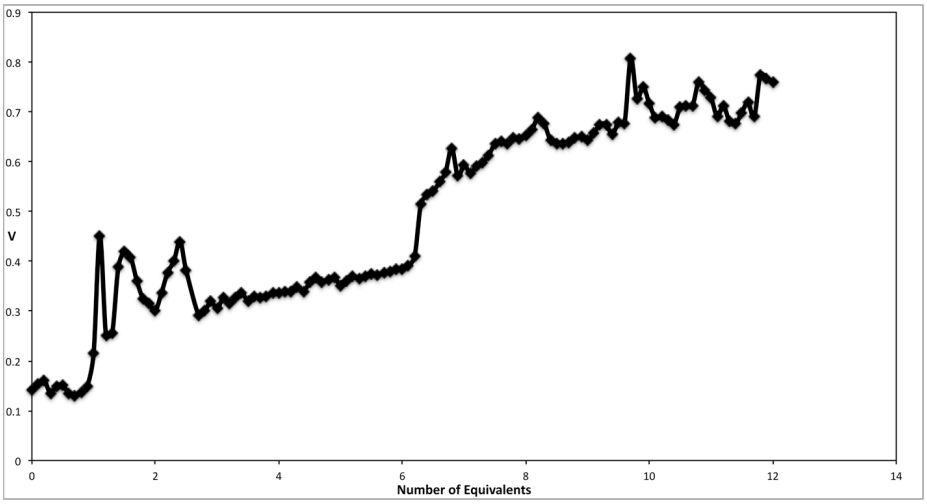

Fig. S3 Potentiometric redox titration of (^{n}Bu$_4$N)$_3$**3** with ammonium cerium(IV) nitrate in MeCN. Note that some precipitation occurred during this titration, which accounts for the less smooth variation in potential.

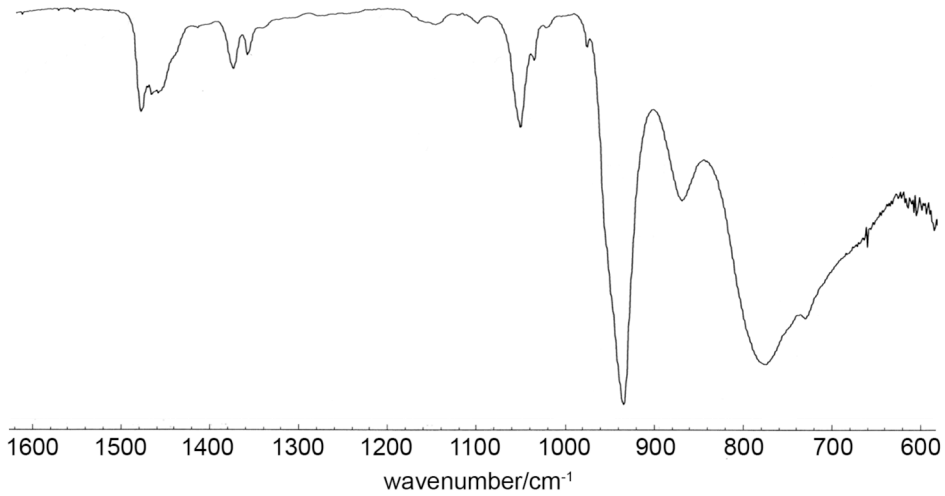

Fig. S4 FTIR spectrum of $(^{n}Bu_4N)_3$**1** in the range 600-1600 cm^{-1}

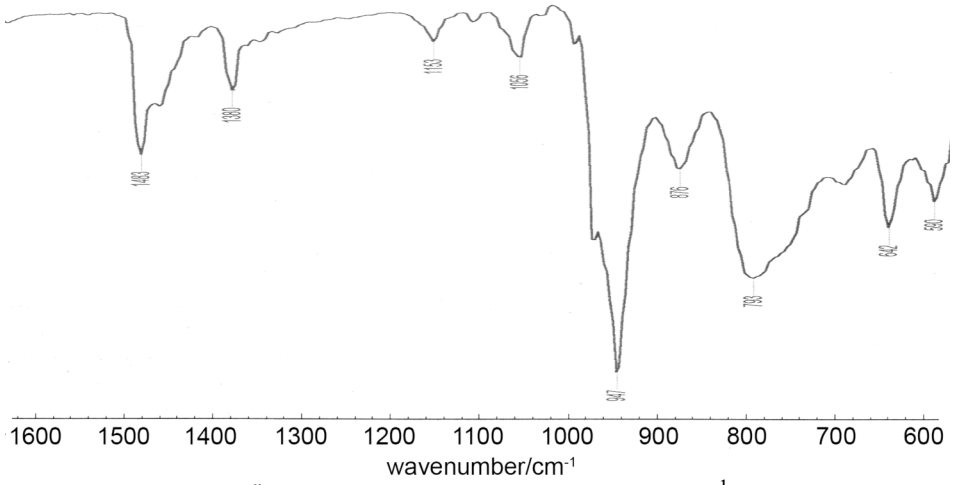

Fig. S5 FTIR spectrum of $(^{n}Bu_4N)_3$**2** in the range 600-1600 cm^{-1}

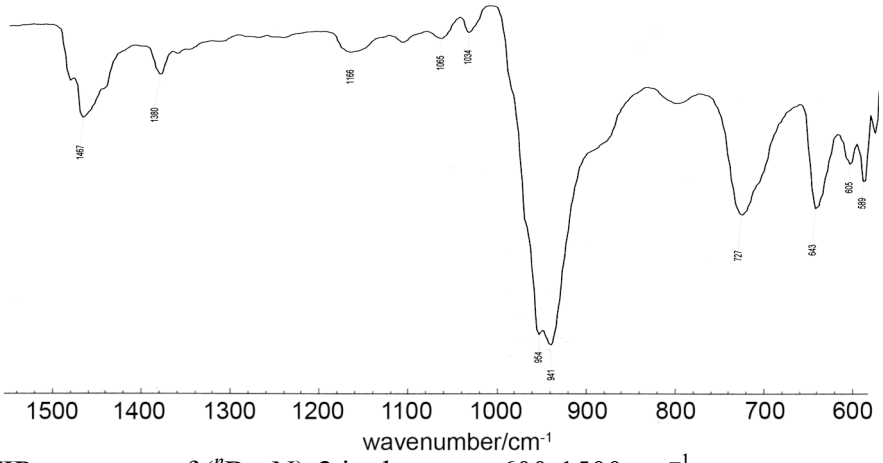

Fig. S6 FTIR spectrum of $(^{n}Bu_4N)_3$**3** in the range 600-1500 cm^{-1}

Table S1 Crystal data and structure refinement for (^{n}Bu$_4$N)$_3$**1**.MeCN

Chemical formula (moiety)	$3C_{16}H_{36}N^+ \cdot C_4H_6CoMo_{12}N_2O_{40}P^{3-} \cdot C_2H_3N$	
Chemical formula (total)	$C_{54}H_{117}CoMo_{12}N_6O_{40}P$	
Formula weight	2731.72	
Temperature	150(2) K	
Radiation, wavelength	MoKα, 0.71073 Å	
Crystal system, space group	orthorhombic, Cmca	
Unit cell parameters	a = 17.975(4) Å	α = 90°
	b = 22.382(9) Å	β = 90°
	c = 44.296(16) Å	γ = 90°
Cell volume	17821(10) Å^3	
Z	8	
Calculated density	2.036 g/cm^3	
Absorption coefficient μ	1.909 mm^{-1}	
F(000)	10792	
Crystal colour and size	blue, 0.34 0.30 0.30 mm^3	
Reflections for cell refinement	185 (θ range 2.5 to 27.5°)	
Data collection method	Nonius KappaCCD diffractometer	
	ϕ and ω scans	
θ range for data collection	4.0 to 25.0°	
Index ranges	h 21 to 21, k 26 to 26, l 52 to 52	
Completeness to θ = 25.0°	97.1 %	
Reflections collected	48140	
Independent reflections	7887 (R_{int} = 0.0717)	
Reflections with $F^2>2\sigma$	6224	
Absorption correction	semi-empirical from equivalents	
Min. and max. transmission	0.563 and 0.598	
Structure solution	direct methods	
Refinement method	Full-matrix least-squares on F^2	
Weighting parameters a, b	0.0000, 186.6674	
Data / restraints / parameters	7887 / 1005 / 794	
Final R indices [$F^2>2\sigma$]	R1 = 0.0409, wR2 = 0.0782	
R indices (all data)	R1 = 0.0607, wR2 = 0.0870	
Goodness-of-fit on F^2	1.089	
Largest and mean shift/su	0.003 and 0.000	
Largest diff. peak and hole	0.90 and 1.53 e Å^3	

Table S2 Crystal data and structure refinement for (^{n}Bu$_4$N)$_3$**2**.MeCN

Chemical formula (moiety)	$3C_{16}H_{36}N^+ \cdot Mo_{12}V_2PO_{42}^{3-} \cdot C_2H_3N$	
Chemical formula (total)	$C_{50}H_{111}Mo_{12}N_4O_{42}PV_2$	
Formula weight	2724.56	
Temperature	120(2) K	
Radiation, wavelength	synchrotron, 0.6393 Å	
Crystal system, space group	monoclinic, I2/a	
Unit cell parameters	a = 23.8622(17) Å	α = 90°
	b = 14.4740(17) Å	β = 95.462(7)°
	c = 49.226(4) Å	γ = 90°
Cell volume	16925(3) Å^3	
Z	8	
Calculated density	2.139 g/cm^3	
Absorption coefficient μ	1.420 mm^{-1}	
F(000)	10720	
Crystal colour and size	black, 0.10 0.03 0.02 mm^3	
Reflections for cell refinement	979 (θ range 2.2 to 25.0°)	
Data collection method	Bruker APEX2 CCD diffractometer	
	thin-slice ω scans	
θ range for data collection	2.0 to 25.3°	
Index ranges	h 29 to 31, k 19 to 9, l 55 to 65	
Completeness to θ = 25.3°	96.9 %	
Reflections collected	37547	
Independent reflections	20469 (R_{int} = 0.0743)	
Reflections with $F^2>2\sigma$	11207	
Absorption correction	semi-empirical from equivalents	
Min. and max. transmission	0.871 and 0.972	
Structure solution	direct methods	
Refinement method	Full-matrix least-squares on F^2	
Weighting parameters a, b	0.0429, 0.0000	
Data / restraints / parameters	20469 / 980 / 1010	
Final R indices [$F^2>2\sigma$]	R1 = 0.0588, wR2 = 0.1209	
R indices (all data)	R1 = 0.1175, wR2 = 0.1485	
Goodness-of-fit on F^2	0.930	
Largest and mean shift/su	0.001 and 0.000	
Largest diff. peak and hole	0.80 and 0.98 e Å^3	

Table S3 Crystal data and structure refinement for $(^{n}Bu_4N)_3$**3**

Chemical formula (moiety)	$3C_{16}H_{36}N^{+}\cdot Mo_{12}O_{40}PSb_2^{3-}$	
Chemical formula (total)	$C_{48}H_{108}Mo_{12}N_3O_{40}PSb_2$	
Formula weight	2793.12	
Temperature	150(2) K	
Radiation, wavelength	MoKα, 0.71073 Å	
Crystal system, space group	monoclinic, C2	
Unit cell parameters	a = 26.922(10) Å	α = 90°
	b = 14.066(4) Å	β = 96.447(16)°
	c = 11.8345(11) Å	γ = 90°
Cell volume	4453(2) Å^3	
Z	2	
Calculated density	2.083 g/cm^3	
Absorption coefficient μ	2.319 mm^{-1}	
F(000)	2716	
Crystal colour and size	blue, 0.40 0.35 0.30 mm^3	
Reflections for cell refinement	27116 (θ range 2.5 to 27.5°)	
Data collection method	Nonius KappaCCD diffractometer	
	θ and ω scans	
θ range for data collection	3.9 to 27.5°	
Index ranges	h 34 to 34, k 18 to 18, l 15 to 15	
Completeness to θ = 25.0°	99.3 %	
Reflections collected	27110	
Independent reflections	9548 (R_{int} = 0.0265)	
Reflections with $F^2>2\sigma$	8182	
Absorption correction	semi-empirical from equivalents	
Min. and max. transmission	0.457 and 0.543	
Structure solution	direct methods	
Refinement method	Full-matrix least-squares on F^2	
Weighting parameters a, b	0.0353, 58.2558	
Data / restraints / parameters	9548 / 326 / 461	
Final R indices [$F^2>2\sigma$]	R1 = 0.0468, wR2 = 0.1042	
R indices (all data)	R1 = 0.0585, wR2 = 0.1102	
Goodness-of-fit on F^2	1.050	
Absolute structure parameter	0.47(5)	
Extinction coefficient	0.00015(3)	
Largest and mean shift/su	0.068 and 0.002	
Largest diff. peak and hole	1.02 and 1.39 e Å^3	