

Transition metal decorated soft nanomaterials through modular self-assembly of an asymmetric hybrid polyoxometalate

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Supporting Information

Table of Contents

Methods	2
Syntheses and Materials.....	3
NMR Characterisation of Pt-1.....	4
Mass Spectrometry of Pt-1	6
UV-Vis Absorption Spectroscopy	7
FTIR Analysis	8
DLS and TEM of assemblies of Pt-1	9
Electrochemistry of Pt-1	11

Methods

^1H NMR and ^{31}P NMR-spectra were obtained using a Bruker Ascend™ 400 MHz spectrometer.

Infra-red spectra were measured using a Bruker Alpha FTIR spectrometer with a platinum ATR module.

UV/Vis absorption spectroscopy was performed on a Cary 5000 UV/VIS NIR spectrophotometer.

Electrospray ionisation mass spectrometry (ESI-MS) was performed on a Bruker MicroTOF spectrometer operating in negative mode. The sample was prepared as an acetonitrile solution (ca. 0.1 mg mL^{-1}) and introduced to the spectrometer *via* an autosampler which injected $20 \mu\text{L}$ of the sample into a stream of 70:30 v/v MeOH/H₂O. Data was analysed using the Bruker Daltonics Data Analysis software suite.

CHN microanalysis was carried out using an Exeter Analytical CE-440 Elemental Analyser.

Dynamic Light Scattering (DLS) measurements were acquired using a Malvern Instrument Nano-ZS Zetasizer at room temperature.

Cryo-TEM samples were vitrified using a Gatan CP3 cryoplunge and imaged with a JEOL 2100 Plus TEM operating at 200 kV. Samples ($3 \mu\text{L}$) were deposited onto a graphene oxide / holey carbon copper 300 mesh grid, in a controlled environment ($20 \text{ }^\circ\text{C}$, 78% humidity) and blotted (1.5s), before plunging into liquid ethane ($-172 \text{ }^\circ\text{C}$). The sample was maintained under liquid nitrogen ($-196 \text{ }^\circ\text{C}$) during transfer (Gatan 926 cryo sample holder) to the TEM, with the temperature held around $-176 \text{ }^\circ\text{C}$ throughout imaging (Gatan Smartset model 900 cold stage controller). Images were recorded using a Gatan Ultrascan 100XP camera, with a nominal underfocus value of 3-6 μm and a 60 μm objective aperture to enhance phase contrast. Sizes were measured using ImageJ 2.0.0 64-bit software.

Electrochemical measurements were performed on a CHI600e (CH Instruments) workstation. Cyclic voltammetry (CV) experiments were performed using a three-electrode arrangement; working electrode (glassy carbon, $d=3 \text{ mm}$), reference electrode (Ag wire) and a counter electrode (Pt wire). Experiments were performed in TBA.PF₆ (0.1 M) as the supporting electrolyte in dry DMF. All potentials with ferrocene as an internal standard, are quoted relative to the $E_{1/2}$ of the ferrocene redox couple. Solutions were purged with nitrogen for 10 mins and kept under a positive pressure of N₂ for the duration of the experiment. All measurements were performed at a scan rate of 100 mVs^{-1} .

Syntheses and Materials

All reagents and solvents were obtained from commercial sources and were used without further purification.

$K_4(C_2H_8N)_2[P_2W_{17}O_{57}(PO_3C_{21}H_{14}N_3)(PO_4C_{24}H_{41})].3H_2O$ (**1**):

The asymmetric POM hybrid **1** was prepared according to the synthetic procedure previously reported by our group.^[1]

$K(C_2H_8N)_3[P_2W_{17}O_{57}(PO_3C_{21}H_{14}N_3Pt(C_3H_7ON))(PO_4C_{24}H_{41})].C_3H_7ON$ (**Pt-1**):

Pt(COD)Cl₂ (30.5 mg, 0.0814 mmol) and AgBF₄ (31.7 mg, 0.163 mmol) were dissolved in acetone (14 mL) and stirred at room temperature for 15 mins. The white precipitate was removed by centrifugation before the colourless filtrate was added to a solution of **1** (400 mg, 0.0775 mmol) in CH₃CN-DMF (1:1 v/v, 14 mL) and stirred for 72 hours at room temperature. The yellow-orange solution was then centrifuged to remove any insoluble material before the solvent was decanted and then removed *in vacuo*. The remaining yellow-green solid was then sonicated in ether, and the suspension was centrifuged. The solvent was then decanted and the retained solid was allowed to dry in air before it was re-dissolved in minimum DMF. An excess of ether was then added to cause precipitation and the cloudy mixture was centrifuged before the filtrate was decanted to leave a green solid. The process of sonicating the solid in ether, centrifuging and decanting the solvent was then repeated a few times (as necessary, checking purity by NMR) in order to wash the solid product before it was finally dried in air with gentle heating (393 mg, 90%).

¹H NMR (DMSO-d₆, 400.1 MHz) δ = 9.12 (m, 2H; Ar-H), 8.93 (m, 4H; Ar-H), 8.57 (t, 2H; Ar-H, *J* = 7.8 Hz), 8.42- 8.22 (m, 4H; Ar-H), 8.22-8.02 (br, 6H; NH₂(CH₃)₂⁺), 7.95 (s, 7H; HCON(CH₃)₂), 7.94-7.87 (m, 4H; Ar-H), 7.03 (d, 2H; Ar-H, *J* = 8.7 Hz), 4.03 (t, 2H; O-CH₂-, *J* = 6.1 Hz), 2.89 (s, 21H; HCON(CH₃)₂), 2.73 (s, 21H; HCON(CH₃)₂), 2.56 (t, 18H; NH₂(CH₃)₂⁺, *J* = 5.5 Hz), 1.73 (m, 2H; CH₂-CH₃), 1.47-1.18 (m, 30H; -CH₂-), 0.85 (t, 3H; -CH₃, *J* = 6.6 Hz) ppm; **³¹P NMR** (DMSO-d₆, 162 MHz) δ = 17.00, 12.55, -11.32, -12.93 ppm; **IR** (ATR): 471 (s), 523 (s), 580 (s), 727 (br, vs), 906 (s), 953 (s), 1085 (s), 1136 (w), 1251 (w), 1295 (w), 1385 (m), 1412-1432 (w), 1463 (m), 1504 (w), 1601 (m), 1651 (s), 2850 (m), 2920 (m) cm⁻¹; **Elemental Analysis** calcd (%) for KP₄W₁₇O₆₆C₅₇H₉₃N₈Pt: C 12.61, H 1.73, N 2.06, found: C 12.50, H 1.79, N 2.11; **UV/Vis (DMF)**: λ_{max} (ε, mol⁻¹Lcm⁻¹) = 285 nm (76,120), 386 nm (9640), 408 nm (10,110).

NMR Characterisation of Pt-1

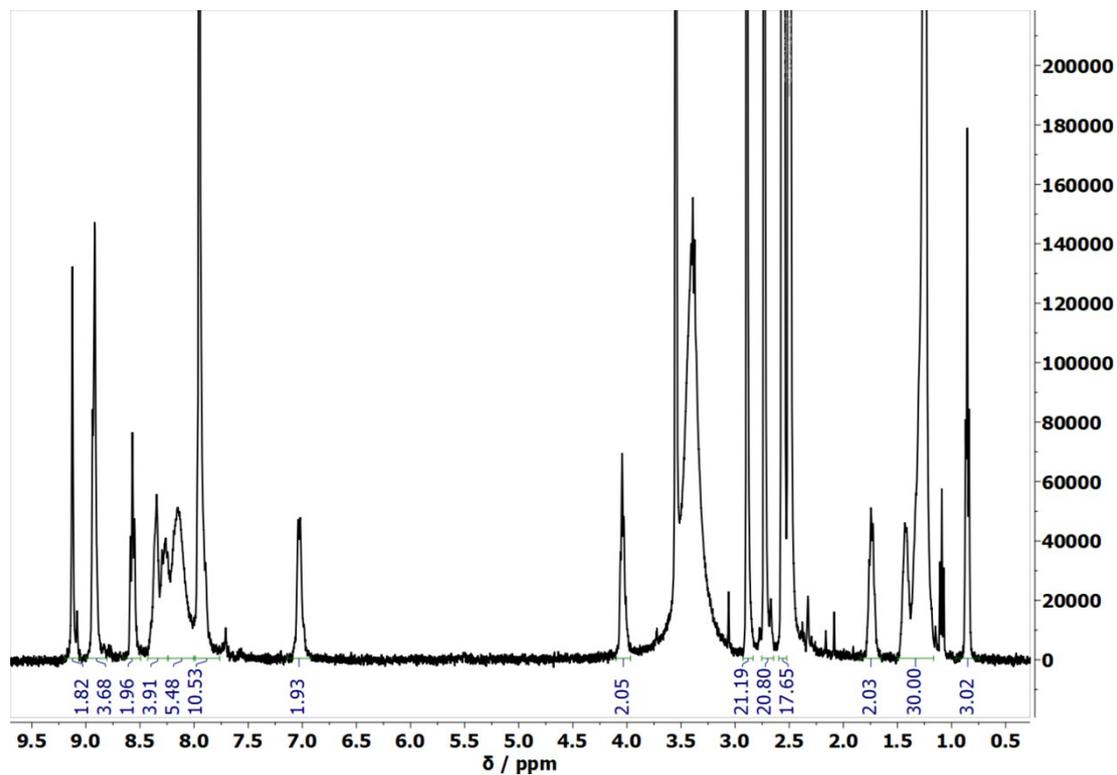


Figure S1. ^1H NMR spectrum of **Pt-1** in DMSO-d_6 . The peaks at 2.73, 2.89 and 7.95 arise from the inclusion of 7 DMF molecules per cluster. DMA (dimethylammonium) cations (peak at 2.56) arise from the decomposition of the solvent (DMF) under our reaction conditions as observed previously.^[1]

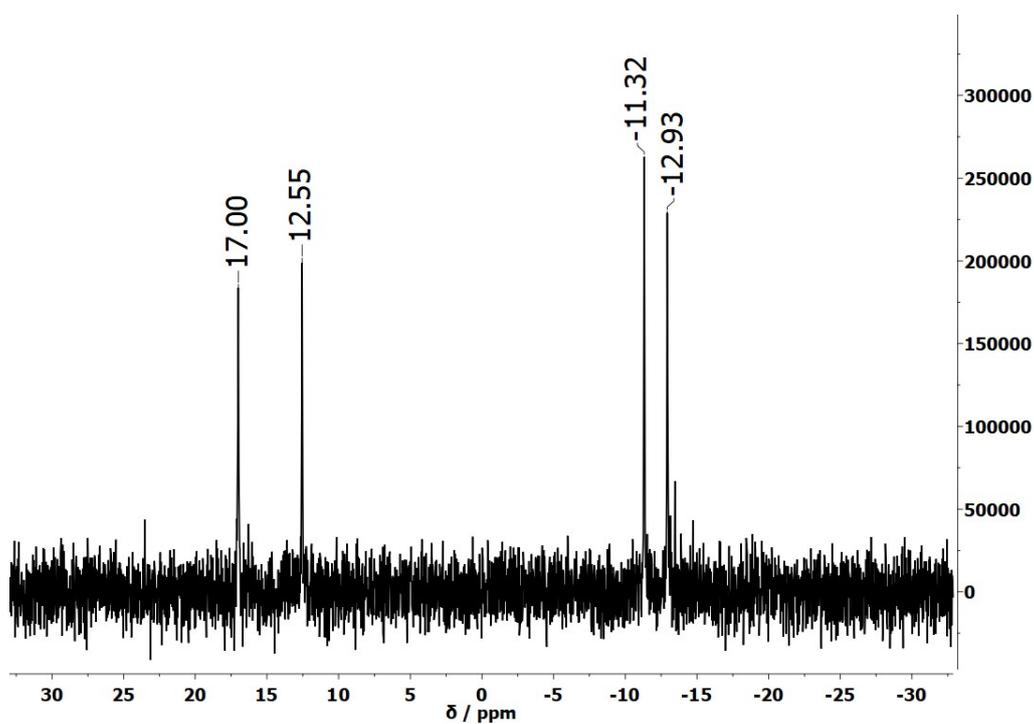


Figure S2. ^{31}P NMR spectrum of **Pt-1** in DMSO-d_6 .

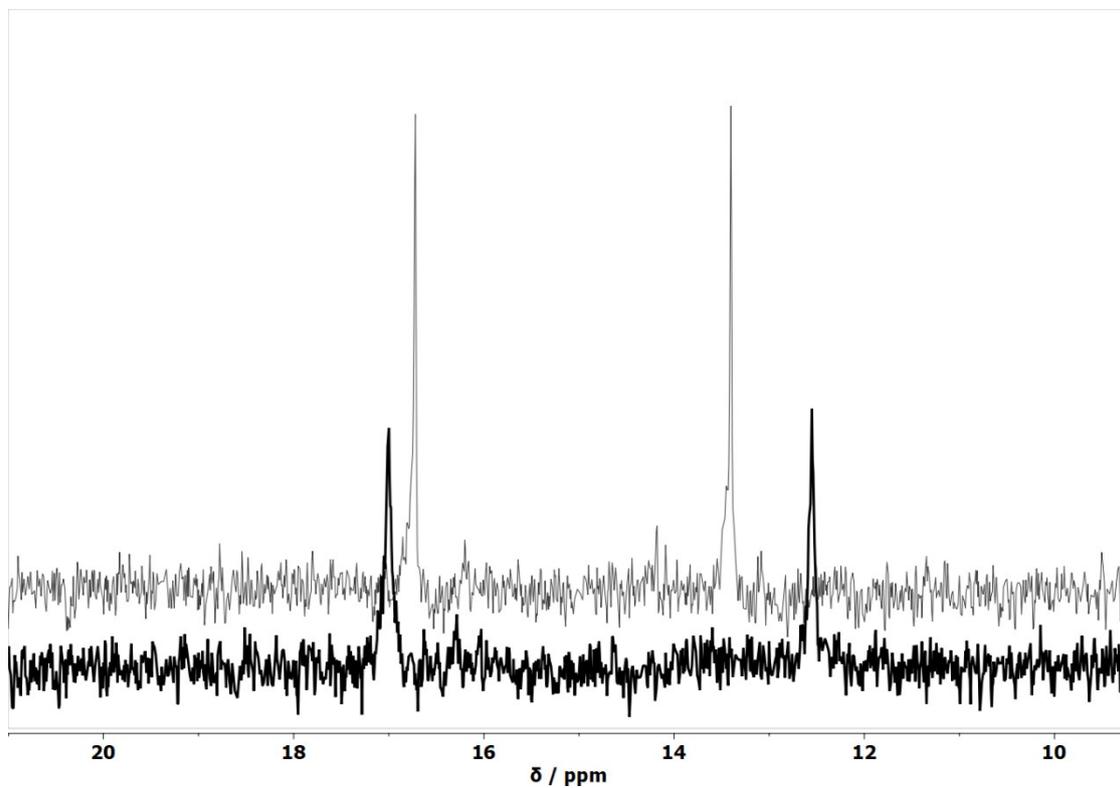


Figure S3. Overlaid ^{31}P NMR spectra of **Pt-1** (below) and **1** (above) in DMSO-d_6 , focused on the organophosphonate signals.

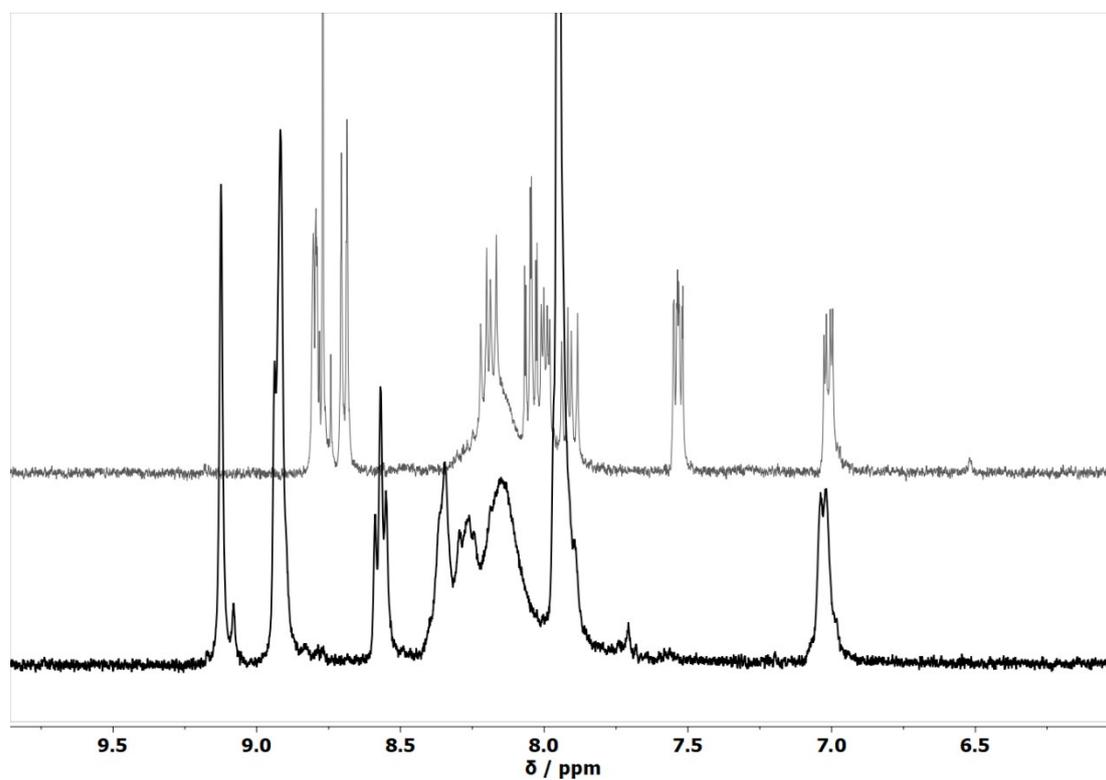


Figure S4. Overlaid ^1H NMR spectra of **Pt-1** (below) and **1** (above) in DMSO-d_6

Mass Spectrometry of Pt-1

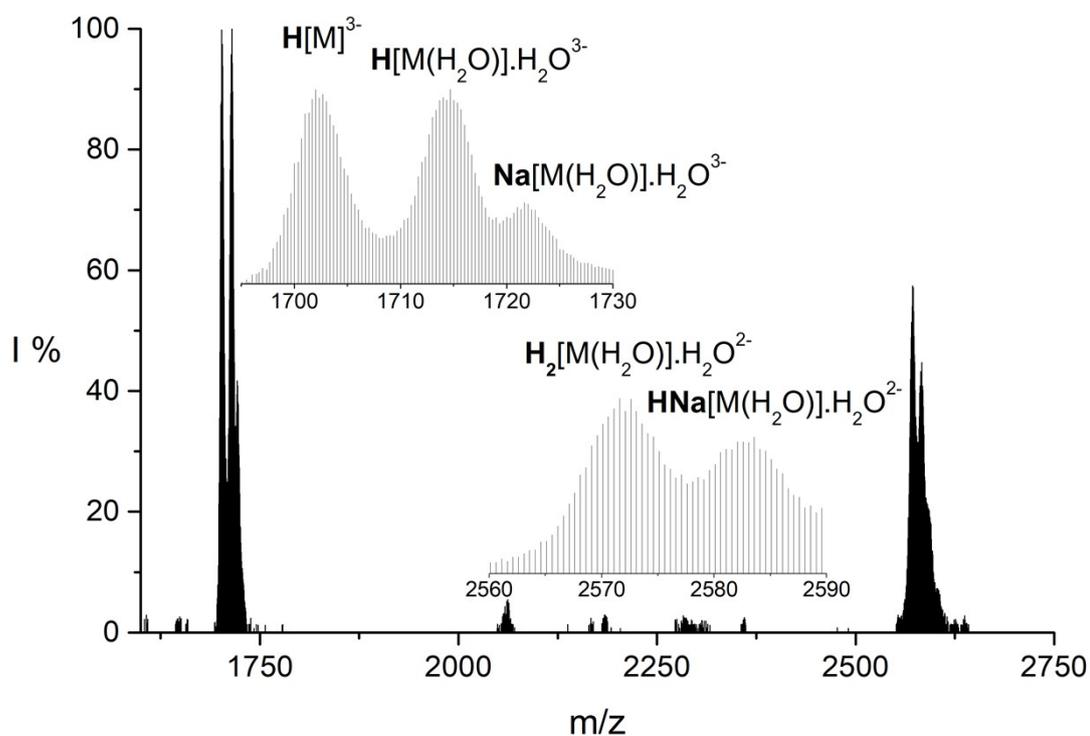


Figure S5. Negative mode ESI mass spectrum of **Pt-1** in acetonitrile.

Assignment	z	m/z (obs.)	m/z (calcd.)
$\text{H}[\text{P}_2\text{W}_{17}\text{O}_{61}(\text{POC}_{21}\text{H}_{14}\text{N}_3\text{Pt})(\text{PO}_2\text{C}_{24}\text{H}_{41})]$	3-	1702.37	1702.38
$\text{H}[\text{P}_2\text{W}_{17}\text{O}_{61}(\text{POC}_{21}\text{H}_{14}\text{N}_3\text{Pt}(\text{H}_2\text{O}))(\text{PO}_2\text{C}_{24}\text{H}_{41})]\cdot\text{H}_2\text{O}$	3-	1714.35	1714.39
$\text{Na}[\text{P}_2\text{W}_{17}\text{O}_{61}(\text{POC}_{21}\text{H}_{14}\text{N}_3\text{Pt}(\text{H}_2\text{O}))(\text{PO}_2\text{C}_{24}\text{H}_{41})]\cdot\text{H}_2\text{O}$	3-	1721.67	1721.72
$\text{H}_2[\text{P}_2\text{W}_{17}\text{O}_{61}(\text{POC}_{21}\text{H}_{14}\text{N}_3\text{Pt}(\text{H}_2\text{O}))(\text{PO}_2\text{C}_{24}\text{H}_{41})]\cdot\text{H}_2\text{O}$	2-	§	2572.09
$\text{HNa}[\text{P}_2\text{W}_{17}\text{O}_{61}(\text{POC}_{21}\text{H}_{14}\text{N}_3\text{Pt}(\text{H}_2\text{O}))(\text{PO}_2\text{C}_{24}\text{H}_{41})]\cdot\text{H}_2\text{O}$	2-	2583.07	2583.08

Table S5. Selected peak assignments for **Pt-1**. $[\text{M}] = [\text{P}_2\text{W}_{17}\text{O}_{61}(\text{POC}_{21}\text{H}_{14}\text{N}_3\text{Pt})(\text{PO}_2\text{C}_{24}\text{H}_{41})]^{4-}$

UV-Vis Absorption Spectroscopy

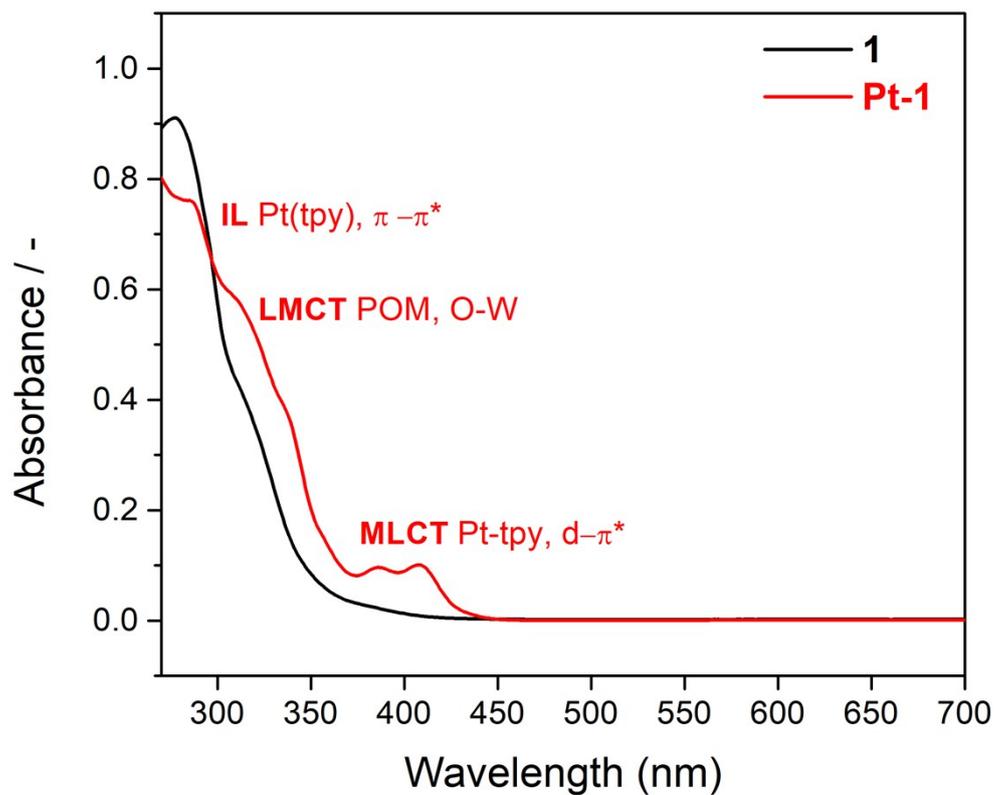


Figure S6. Absorption spectra of **Pt-1** and **1** in DMF (10 μ M). Assignment of bands for **Pt-1**: 285- \sim 350 cm^{-1} = IL Pt(tpy) ($\pi-\pi^*$), LMCT POM (O-W) bands also overlap this region, 386- 408 cm^{-1} = MLCT Pt-tpy ($d-\pi^*$).^[2]

FTIR Analysis

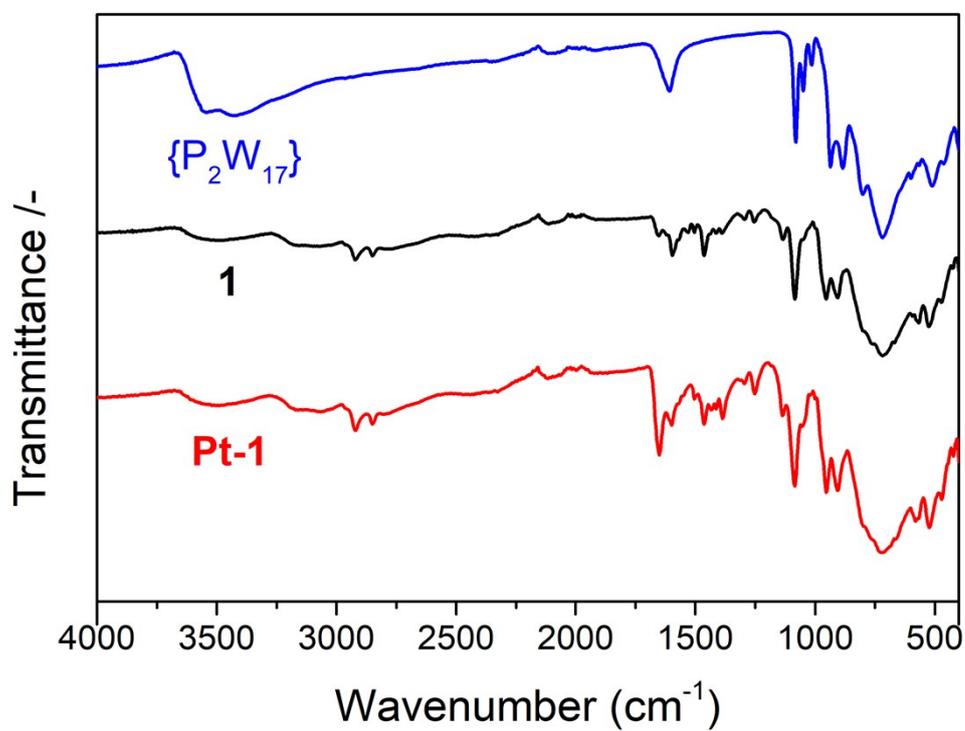


Figure S7. Overlaid FTIR (ATR) spectra of **Pt-1**, the asymmetric hybrid POM precursor **1**, and the parent lacunary POM $K_{10}[P_2W_{17}O_{61}]$.

DLS and TEM of assemblies of Pt-1

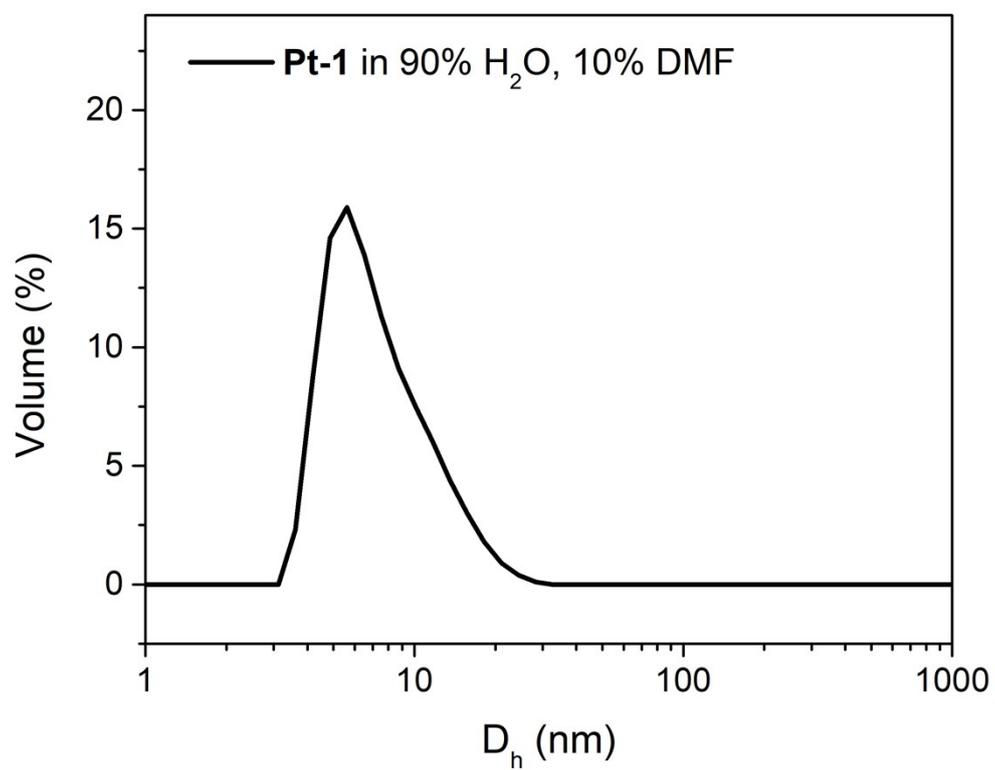


Figure S8. Particle-size distribution curve determined by DLS of **Pt-1** (1.4 mM) in water-DMF (9:1 v/v) solution. D_h maximum is at 5.6 nm.

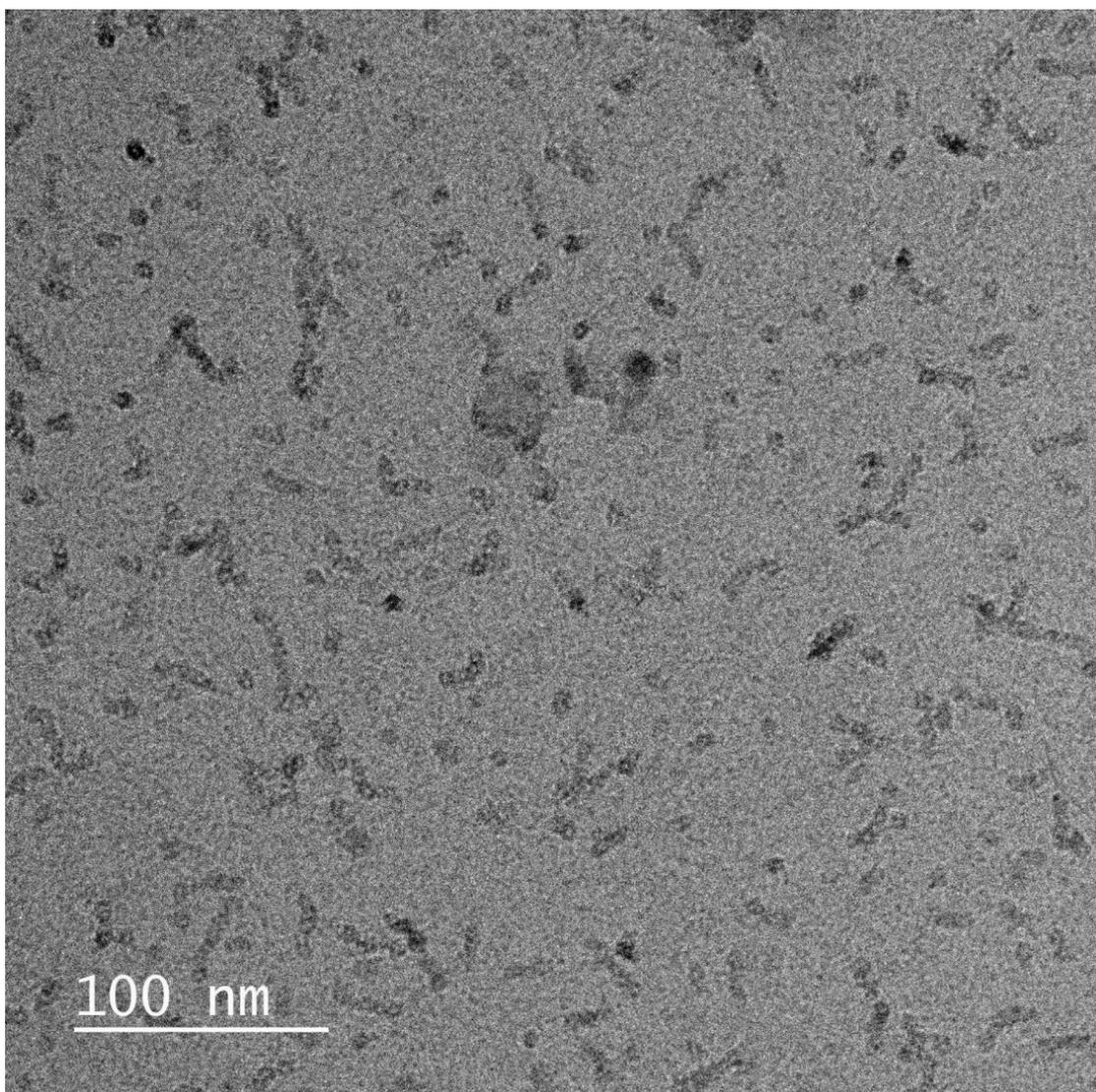


Figure S9. Cryo-TEM imaging of micellar assemblies of **Pt-1** formed in 1.4 mM water-DMF (9:1 v/v) solution.

Electrochemistry of Pt-1

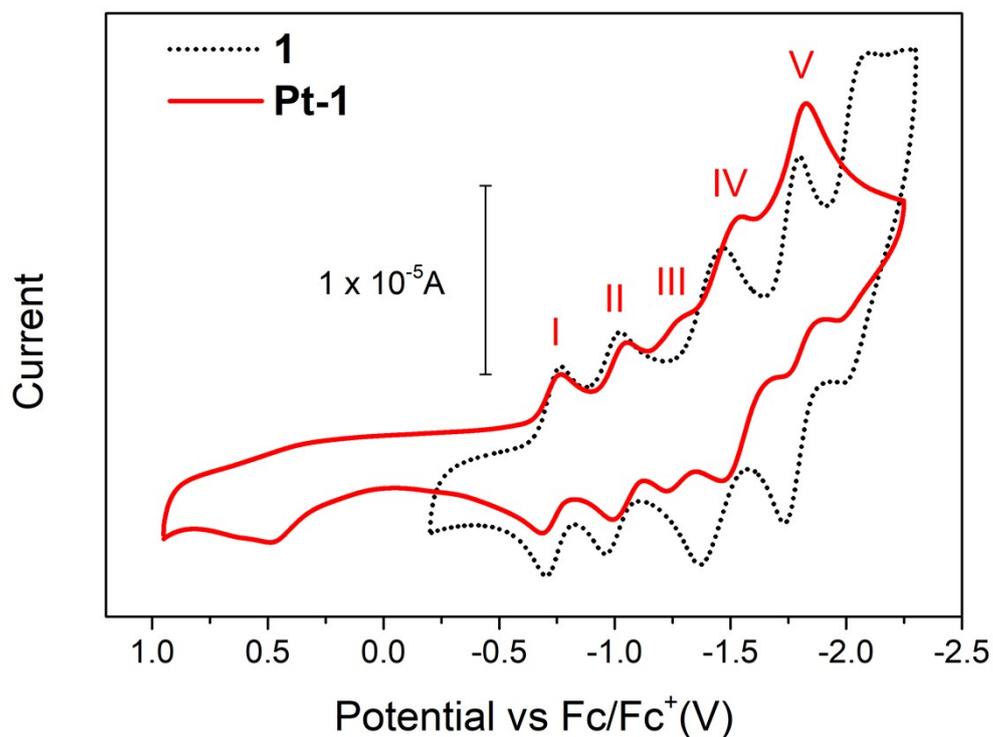


Figure S10. Cyclic voltammograms of **Pt-1** and **1** (0.5 mM) in DMF, with 0.1M TBAPF₆ as electrolyte. Scan rate: 0.1 V/s. Ferrocene is used as an internal standard.

Redox potentials vs Fc/Fc ⁺ (V)	Pt ^{2+/3+}	I	II	III	IV	V
E _{red}	-	-0.764	-1.050	-1.295	-1.541	-1.826
E _{ox}	+0.476	-0.688	-0.998	-1.227	-1.475	-1.737
E _{1/2}	-	-0.726	-1.024	-1.261	-1.508	-1.782

Table S10. Redox potentials of **Pt-1** in DMF

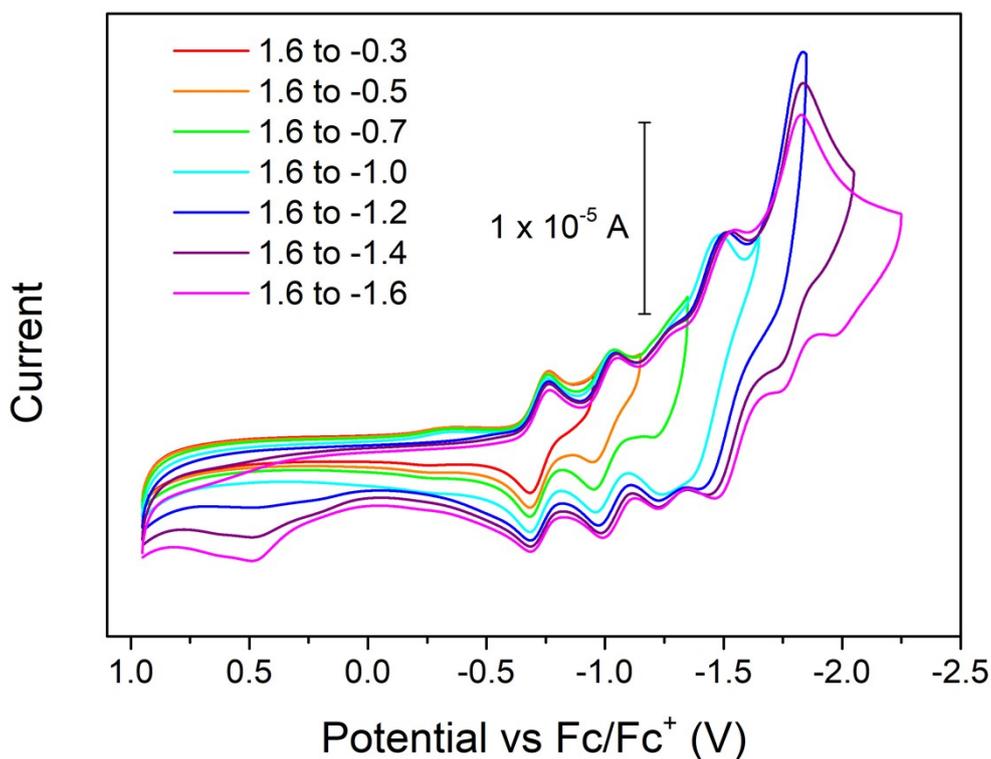


Figure S11. Sequential cyclic voltammograms of **Pt-1** (0.5 mM) in DMF on increasing potential windows, starting from +1.6 to -0.3 V (vs Ag/Ag⁺) (red line) and scanning to more negative potentials from +1.6 V down to -1.6 V (vs Ag/Ag⁺) (magenta line). Scan rate: 0.1 V/s, with 0.1M TBA.PF₆ as electrolyte. Data plotted vs. ferrocene as an internal standard (Fc/Fc⁺ E_{1/2} = +0.649 V vs Ag/Ag⁺).

- [1] E. Hampson, J. M. Cameron, S. Amin, J. Kyo, J. A. Watts, H. Oshio, G. N. Newton, *Angew. Chem. Int. Ed.*, 2019, **58**, 18281-18285.
- [2] a) J. A. Bailey, M. G. Hill, R. E. Marsh, V. M. Miskowski, W. P. Schaefer, H. B. Gray, *Inorg. Chem.*, 1995, **34**, 4591-4599; b) D. R. McMillin, J. J. Moore, *Coord. Chem. Rev.*, 2002, **229**, 113-121.