SUPPORTING INFORMATION FOR:

Programming the Assembly of Carboxylic Acid-Functionalised
Hybrid Polyoxometalates

Marie Hutin, Carine Yvon, Jun Yan, Andrew Macdonell, De-Liang Long and Leroy Cronin*

School of Chemistry, WestCHEM, Joseph Black Building, University of Glasgow, Glasgow, G12 8QQ, United Kingdom. Email: Lee.Cronin@glasgow.ac.uk; web: http://www.croninlab.com

Materials: all starting material has been purchased from the highest grade of purity and used as received.

The glass slides used for AFM pictures were microscope slides purchased from Thermo Scientific Menzel-Gläser, 1.0-1.2mm, ca 76 × 26 mm

AFM: AFM pictures were taken in semi-contact mode with a NT-MDT spectrometer on the NTEGRA Spectra platform. The probes used were the NSG10 purchased from the same company. The scanning head used incorporates a 650 nm laser.

ESI-MS: All spectra were recorded from MeCN solutions in the negative mode on a MicroTOF-Q Bruker quadrupole spectrometer.

Microanalysis: Carbon, nitrogen and hydrogen content were determined by the microanalysis services within the Department of Chemistry, University of Glasgow using an EA 1110 CHN, CE-440 Elemental Analyser
I. NMR spectra

Figure S1 NMR spectrum of [MnMo₇]₂⁺, DMSO-d₆, 400 MHz

Figure S2 NMR of spectrum of [MnMo₇]₂⁺, DMSO-d₆, 400 MHz
**Figure S 3** NMR spectrum of $\{\text{MnMo}_6\}_4^2$, DMSO-$d_6$, 400 MHz

**Figure S 4** NMR spectrum of $\{\text{MnMo}_6\}_5^2$, DMSO-$d_5$, 400 MHz
Figure S 5 NMR spectrum of \( [\text{MnMo}_6]_2 \), DMSO-\( d_6 \), 500 MHz

Figure S 6 NMR spectrum of \( [\text{MnMo}_6]_7 \), DMSO-\( d_6 \), 400 MHz
II. ESI-MS Spectra

Figure S 7 Top: ESI-MS spectrum of \([\text{MnMo}_6\text{I}_2]\) (MeCN, negative mode), bottom: simulated spectrum

Figure S 8 Top: ESI-MS spectrum of \([\text{MnMo}_6\text{I}_2]\) (MeCN, negative mode), bottom: simulated spectrum
Figure S 9 Top: ESI-MS spectrum of \{\text{MnMo}_6\}_2^2 (\text{MeCN}, \text{negative mode}), bottom: simulated spectrum

Figure S 10 Top: ESI-MS spectrum of \{\text{MnMo}_6\}_5^2 (\text{MeCN}, \text{negative mode}), bottom: simulated spectrum
**Figure S 11** Top: ESI-MS spectrum of \( \text{[MnMo}_6 \text{]}_2 \) (MeCN, negative mode), bottom: simulated spectrum

**Figure S 12** Top: ESI-MS spectrum of \( \text{[MnMo}_6 \text{]}_7 \) (MeCN, negative mode), middle: simulated spectrum of \( \text{[MnMo}_6 \text{]}_7 \) with a free acid group and a closed phthalimide group, bottom: simulated spectrum of \( \text{[MnMo}_6 \text{]}_7 \)
III. Packing diagrams

Figure S 13 Structure of (a)-[MnMo₆]₆²⁻ obtained from DMF / Et₂O. A) Crystal structure of (a)-[MnMo₆]₆²⁻; B) Packing diagram of (a)-[MnMo₆]₆²⁻ in the (xz) plan and C) evidence of the H-bonding network in the (xy) plan; bond lengths are 2.70 and 2.71 Å. Colour scheme: O (red), Mo (dark blue), Mn (orange), N (light blue), C (dark grey) and H (light grey). The TBA cations and the solvent molecules are removed from the packing diagrams for clarity reasons.

Figure S 14 Packing diagrams of [MnMo₆]₄₂. Colour scheme: O (red), Mo (dark blue), Mn (orange), N (light blue), C (dark grey) and H (light grey). The TBA cations and the solvent molecules are removed from the packing diagrams for clarity reasons.
Figure S 15 Packing diagram of [MnMo₆]₇₂. Colour scheme: O (red), Mo (dark blue), Mn (orange), N (light blue), C (dark grey) and H (light grey). The TBA cations and the solvent molecules are removed from the packing diagrams for clarity reasons.

IV. AFM height pictures

Figure S 16 AFM height picture in semi-contact mode of [MnMo₆]₄₂ drop cast on a glass surface previously plunged for 10 min in a solution 3:1 H₂SO₄/H₂O₂ and thoroughly washed with deionised water.

Figure S 17 AFM height picture in semi-contact mode of [MnMo₆]₄₂ drop cast on a glass surface previously plunged for 10 min in a solution 5:1 H₂SO₄/H₂O₂ and thoroughly washed with deionised water.
Figure S 18 AFM height picture in semi-contact mode of \( \{\text{MnMo}_6\}_4 \) drop cast on a glass surface previously plunged for 10 min in a solution \( 7:1 \text{H}_2\text{SO}_4/\text{H}_2\text{O}_2 \) and thoroughly washed with deionised water

Note. All glass slides were treated the same way prior to use: they were plunged in a solution \( \text{H}_2\text{SO}_4/\text{H}_2\text{O}_2 \) of ratio 3:1, 5:1, 7:1 for 10 min at room temperature, then plunged in deionised water and washed with plenty of deionised water. They were dried with compressed air afterwards. 10μl (measured with a Gilson pipette) of the 1mg/mL MeCN solution of \( \{\text{MnMo}_6\} \text{R}_2 \) were then drop cast on the freshly cleaned surface, and the solvent was allowed to evaporate under air.

V. Profile extracts from AFM height pictures

Figure S 19 Profile of a 25 × 25 μm height picture of \( \{\text{MnMo}_6\}_4 \) drop cast on glass cleaned for 10 min in a solution \( \text{H}_2\text{SO}_4/\text{H}_2\text{O}_2 \) 7:1
**Figure S 20** Profile of a $10 \times 10 \, \mu m$ height picture of $\{\text{MnMo}_6\}_4$ drop cast on glass cleaned for 10 min in a solution $\text{H}_2\text{SO}_4 / \text{H}_2\text{O}_2$ 7:1

**Figure S 21** Profile of a $5 \times 5 \, \mu m$ height picture of $\{\text{MnMo}_6\}_7$ drop cast on glass cleaned for 10 min in a solution $\text{H}_2\text{SO}_4 / \text{H}_2\text{O}_2$ 7:1