### Supporting information

# Proton-Controlled Synthesis of Unprecedented Diol Functionalized Anderson-type POMs

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#### **Experimental Section**

#### General methods and materials

All syntheses and manipulations were performed in the open air, all other chemicals, including solvents, were commercially available as reagent grade and used as received without further purification from Adamas-beta®.  $[NH_4]_3[CrMo_6O_{18}(OH)_6]$  were synthesized according to literature methods<sup>1</sup>. IR spectra were measured by using KBr pellets and recorded on a Perkin Elmer FT-IR spectrometer. UV-Vis spectra were measured in acetonitrile with UV2100s spectrophotometer. The mass spectra were obtained by using an ion trap mass spectrometer (Thermofisher LTQ). Negative mode was chosen for the experiments (capillary voltage 33 V). Sample solution (in acetonitrile) was infused into the ESI source at a flow rate of 300 µL min<sup>-1</sup>. Elemental analyses were performed by Elementar Analysensysteme GmbH (vario EL). <sup>13</sup>C NMR spectra were obtained on a JOEL JNM-ECA400 spectrometer and reported in ppm applying [D<sub>6</sub>]DMSO as sovlent.

#### Synthesis and Crystallization process

The synthesis of [TBA]<sub>3</sub> {[NH<sub>2</sub>C(CH<sub>2</sub>OH)(CH<sub>2</sub>O)<sub>2</sub>] CrMo<sub>6</sub>O<sub>18</sub>(OH)<sub>4</sub>}, compound 1:

 $3.213g [NH_4]_3[CrMo_6O_{18}(OH)_6]$  were dissolve in 30ml H<sub>2</sub>O,  $0.363g (HOCH_2)_3CNH_2(L_1)$  were dissolve in 9ml 1M HCl. Then these two solutions was mixed together and refluxing at 100 °C for 3 h forming  $[NH_4]_3\{[NH_2C(CH_2OH)(CH_2O)_2] CrMo_6O_{18}(OH)_4\}$ . Then it was precipitated from the aqueous by adding equivalent amount of 2.898g [TBA]Br to substitute the  $NH_4^+$  cation. The title compound could be obtained as pink crystalline products (75% yields based on Mo)

Compound 1 can be obtained  $C_{52}H_{122}CrMo_6N_4O_2 M_r = 1831.17$ , H 6.69 C 34.08 N 3.08 while calcd H 6.72 C 34.11 N 3.06. IR (KBr pellet, major absorbances, cm<sup>-1</sup>): 3335, 2961, 2984, 2874, 1681, 1601, 1512, 1464, 1382, 1251, 1161, 1053, 1028, 914, 886, 836, 783, 688.UV-Vis (in MeCN, nm):  $\lambda_{LMCT} = 230(c=10^{-5} \text{ L·mol}^{-1}, \epsilon_{LMCT}=4.72\times10^5 \text{ L·mol}^{-1}\text{cm}^{-1}$ ),  $\lambda_{d-d} = 530(c=10^{-3} \text{ L·mol}^{-1}, \epsilon_{d-d}=5.73 \times 10^2 \text{ L·mol}^{-1}\text{cm}^{-1}$ ). ESI mass spectrometry (MeCN): calcd m/z=1588.70 {(TBA)<sub>2</sub>{[NH<sub>2</sub>C(CH<sub>2</sub>OH)(CH<sub>2</sub>O)<sub>2</sub>] CrMo<sub>6</sub>O<sub>18</sub>(OH)<sub>4</sub>}<sup>-</sup>, 1105.76 {[H<sup>+</sup>]{[NH<sub>2</sub>C(CH<sub>2</sub>OH)(CH<sub>2</sub>O)<sub>2</sub>] CrMo<sub>6</sub>O<sub>18</sub>(OH)<sub>4</sub>}<sup>-</sup>, 552.38 {[H<sup>+</sup>]<sub>2</sub>{[NH<sub>2</sub>C(CH<sub>2</sub>OH)(CH<sub>2</sub>O)<sub>2</sub>] CrMo<sub>6</sub>O<sub>18</sub>(OH)<sub>4</sub>}<sup>-</sup>, 573.9, 552.67, 367.88 respectively. <sup>13</sup>C NMR (400 MHz, [D<sub>6</sub>]DMSO, ppm):  $\delta = 13.8$  (C<sub>a</sub>), 19.0 (C<sub>β</sub>), 23.5 (C<sub>γ</sub>), 57.8 (C<sub>ε</sub>), 59.6 (C<sub>a</sub>), 64.9 (C<sub>b</sub>), 65.5 (C<sub>c</sub>).

The crystallization of compound 1: [TBA]<sub>4</sub> {[NH<sub>3</sub>C(CH<sub>2</sub>OH)(CH<sub>2</sub>O)<sub>2</sub>] CrMo<sub>6</sub>O<sub>18</sub>(OH)<sub>4</sub>}<sub>2.4</sub>[TBA]Br.

#### 2[NH<sub>4</sub>]Br.15H<sub>2</sub>O

 $C_{136}H_{354}Br_6Cr_2Mo_{12}N_{12}O_{65}, M_r = 4933.00$ 

 $1.831 \text{ g} [\text{TBA}]_3 \{[\text{NH}_2\text{C}(\text{CH}_2\text{OH})(\text{CH}_2\text{O})_2] \text{ CrMo}_6\text{O}_{18}(\text{OH})_4\}$  were redissolved in 10 mL MeCN. Additional 0.2 g of [TBA]Br and 0.2g [NH<sub>4</sub>]Br were added into the crystallization solution to accelerate crystallization process. Suitable single crystals for X-ray diffraction were grown by slow evaporation. After crystallization, compound 1 was obtained as pink crystalline products.

#### The synthesis of $[TBA]_3 \{ [NH_2CCH_3(CH_2O)_2] CrMo_6O_{18}(OH)_4 \}$ , compound 2:

3.213g  $[NH_4]_3[CrMo_6O_{18}(OH)_6]$  were dissolve in 30ml H<sub>2</sub>O, 0.357g NH<sub>2</sub>CCH<sub>3</sub>(CH<sub>2</sub>OH)<sub>2</sub> (L<sub>2</sub>) were dissolve in 9ml 1M HCl. Then these two solutions was mixed together and refluxing at 100 °C for 3 h forming  $[NH_4]_3\{[NH_2CCH_3(CH_2O)_2] CrMo_6O_{18}(OH)_4\}$ . Then it was precipitated from the aqueous by adding equivalent amount of 2.898g [TBA]Br to substitute the NH<sub>4</sub><sup>+</sup> cation. The title compound could be obtained as pink crystalline products (71% yields based on Mo)

Compound 2 can be obtained  $C_{52}H_{122}CrMo_6N_4O_{24}M_r = 1815.17374$ , H 6.81 C 34.44 N 3.07 while calcd H 6.77 C 34.41 N 3.09. IR (KBr pellet, major absorbances, cm<sup>-1</sup>): 3391 2961 2984 2874 1673 1480 1384 1126 1023 938 918 899 661.UV-Vis (in MeCN, nm):  $\lambda_{LMCT} = 229(c=10^{-5} \text{ L} \cdot \text{mol}^{-1}, \epsilon_{LMCT} = 4.69 \times 10^{5} \text{ L} \cdot \text{mol}^{-1}, \lambda_{d-d} = 531(c=10^{-3} \text{ L} \cdot \text{mol}^{-1})$ L·mol<sup>-1</sup>,  $\varepsilon_{d-d}=5.67 \times 10^2$  L·mol<sup>-1</sup>·cm<sup>-1</sup>). ESI mass spectrometry (MeCN): calcd m/z=1572.71  $\{(TBA)_2\{[NH_2CCH_3(CH_2O)_2]\}$  $CrMo_6O_{18}(OH)_4\}\}^-,$ 1331.23 {[NH<sub>2</sub>CCH<sub>3</sub>(CH<sub>2</sub>O)<sub>2</sub>] {(TBA) [H<sup>+</sup>]  $CrMo_6O_{18}(OH)_4\}\}^-,$  $CrMo_6O_{18}(OH)_4\}\}^{2-}$ 665.12 {(TBA)  $\{[NH_2CCH_3(CH_2O)_2]\}$ 544.38  $\{[H^+]_2 \{[NH_2CCH_3(CH_2O)_2] CrMo_6O_{18}(OH)_4\}\}^2, 362.59 \{[NH_2CCH_3(CH_2O)_2] CrMo_6O_{18}(OH)_4\}^3; found$ 

1572.66, 1331.32, 665.29, 544.47, 362.97 respectively. <sup>13</sup>C NMR (400 MHz, [D<sub>6</sub>]DMSO, ppm):  $\delta$  = 13.8 (C<sub>α</sub>), 19.0 (C<sub>β</sub>), 23.5 (C<sub>γ</sub>), 57.8 (C<sub>ε</sub>), 8.8 (C<sub>α</sub>), 25.4 (C<sub>b</sub>), 58.9 (C<sub>c</sub>), 67.6 (C<sub>d</sub>).

The crystallization of compound **2**:  $[TBA]_4 \{ [NH_3CCH_3(CH_2O)_2] CrMo_6O_{18}(OH)_4 \}_2.4 [TBA]Br. 2[NH_4]Br. 14H_2O C_{136}H_{352}Br_6Cr_2Mo_{12}N_{12}O_{62}, M_r = 4882.98$ 

1.815 g  $[TBA]_3 \{[NH_2C(CH_2OH)(CH_2O)_2] CrMo_6O_{18}(OH)_4\}$  were redissolved in 10 mL MeCN. Additional 0.1 g of [TBA]Br and 0.1g  $[NH_4]Br$  were added into the crystallization solution to accelerate crystallization process. Suitable single crystals for X-ray diffraction were grown by slow evaporation. After crystallization, compound 2 was obtained as pink crystalline products.

The synthesis of [TBA]<sub>3</sub> {[CHOH(CH<sub>2</sub>O)<sub>2</sub>] CrMo<sub>6</sub>O<sub>18</sub>(OH)<sub>4</sub>}, compound **3**:

 $3.213g [NH_4]_3[CrMo_6O_{18}(OH)_6]$  were dissolve in 30ml H<sub>2</sub>O, 0.276g CHOH(CH<sub>2</sub>OH)<sub>2</sub> (L<sub>3</sub>) were dissolve in 9ml 1M HCl. Then these two solutions was mixed together and refluxing at 100 °C for 3 h forming [NH<sub>4</sub>]<sub>3</sub>{[CHOH(CH<sub>2</sub>O)<sub>2</sub>] CrMo<sub>6</sub>O<sub>18</sub>(OH)<sub>4</sub>}. Then it was precipitated from the aqueous by adding equivalent amount of 2.898g [TBA]Br to substitute the NH<sub>4</sub><sup>+</sup> cation. The title compound could be obtained as pink crystalline products (66% yields based on Mo)

Compound **3** can be obtained  $C_{51}H_{119}CrMo_6N_3O_{25} M_r = 1802.13$ , H 6.69 C 34.04 N 2.30 while calcd H 6.66 C 33.99 N 2.33. IR (KBr pellet, major absorbances, cm<sup>-1</sup>): 3399 2961 2874 1641 1485 1384 1117 1027 937 916 897 790 737 661.UV-Vis (in MeCN, nm):  $\lambda_{LMCT} = 231(c=10^{-5} \text{ L} \cdot \text{mol}^{-1}, \epsilon_{LMCT}=4.59 \times 10^5 \text{ L} \cdot \text{mol}^{-1}, cm^{-1}), \lambda_{d-d} = 531(c=10^{-3} \text{ L} \cdot \text{mol}^{-1}, \epsilon_{d-d} = 5.57 \times 10^2 \text{ L} \cdot \text{mol}^{-1} \text{ cm}^{-1})$ . ESI mass spectrometry (MeCN): calcd m/z=1559.66 {(TBA)<sub>2</sub>{[CHOH(CH<sub>2</sub>O)<sub>2</sub>] CrMo<sub>6</sub>O<sub>18</sub>(OH)<sub>4</sub>}<sup>2-</sup>, 537.86 {[H<sup>+</sup>]<sub>2</sub>{[CHOH(CH<sub>2</sub>O)<sub>2</sub>] CrMo<sub>6</sub>O<sub>18</sub>(OH)<sub>4</sub>}<sup>2-</sup>, 358.24 {[CHOH(CH<sub>2</sub>O)<sub>2</sub>] CrMo<sub>6</sub>O<sub>18</sub>(OH)<sub>4</sub>}<sup>2-</sup>; found 1559.61, 658.64, 537.89, 358.21 respectively. <sup>13</sup>C NMR (400 MHz, [D<sub>6</sub>]DMSO, ppm):  $\delta = 13.8 (C_{\alpha})$ , 19.0 (C<sub>β</sub>), 23.5 (C<sub>γ</sub>), 57.8 (C<sub>ε</sub>), 66.9 (C<sub>a</sub>), 73.8 (C<sub>b</sub>).

The crystallization of compound 3: [TBA]<sub>3</sub> {[CHOH(CH<sub>2</sub>O)<sub>2</sub>] CrMo<sub>6</sub>O<sub>18</sub>(OH)<sub>4</sub>}<sub>2</sub>. [TBA]Br.3H<sub>2</sub>O

 $C_{67}H_{161}BrCrMo_6N_4O_{28}, M_r = 2178.55$ 

1.802 g  $[TBA]_3 \{[CHOH(CH_2O)_2] CrMo_6O_{18}(OH)_4\}$  were redissolved in 10 mL MeCN. Additional 0.2 g of [TBA]Br and 0.1g  $[NH_4]Br$  were added into the crystallization solution to accelerate crystallization process. Suitable single crystals for X-ray diffraction were grown by slow evaporation. After crystallization, compound 2 was obtained as pink crystalline products.

#### The synthesis of [TBA]<sub>2</sub>[H]{[HOH<sub>2</sub>CC(CH<sub>2</sub>O)<sub>3</sub>] CrMo<sub>6</sub>O<sub>18</sub>(OH)<sub>3</sub>}, compound 4:

 $3.213g [NH_4]_3[CrMo_6O_{18}(OH)_6]$  were dissolve in 30ml H<sub>2</sub>O, 0.408g (HOCH<sub>2</sub>)<sub>4</sub>C (L<sub>4</sub>) were dissolve in 9ml 1M HCl. Then these two solutions was mixed together and refluxing at 100 °C for 3 h forming [NH<sub>4</sub>]<sub>2</sub>[H]{[HOH<sub>2</sub>CC(CH<sub>2</sub>O)<sub>3</sub>] CrMo<sub>6</sub>O<sub>18</sub>(OH)<sub>3</sub>}. Then it was precipitated from the aqueous by adding equivalent amount of 2.898g [TBA]Br to substitute the NH<sub>4</sub><sup>+</sup> cation. The title compound could be obtained as pink crystalline products (76% yields based on Mo)

The crystallization of compound 4: [TBA]<sub>2</sub>[H] {[HOH<sub>2</sub>CC(CH<sub>2</sub>O)<sub>3</sub>] CrMo<sub>6</sub>O<sub>18</sub>(OH)<sub>3</sub>}.3DMF.H<sub>2</sub>O

 $C_{46}H_{108}N_5CrMo_6O_{28}, M_r = 1807.00$ 

 $1.58 \text{ g} [TBA]_2[H] \{[HOH_2CC(CH_2O)_3] CrMo_6O_{18}(OH)_3\}$  were redissolved in 5 mL DMF. Additional 0.2 g of [TBA]Br is added into the crystallization solution to accelerate crystallization process. Suitable single crystals for X-ray diffraction were grown by slow evaporation After crystallization, compound 4 was obtained as pink crystalline products.

## The proton-controlled transformation cycling among $\psi$ , $\delta$ and $\chi$ isomer and the ultimate proton tolerance of Anderson cluster

3.468g [NH<sub>4</sub>]<sub>3</sub>{[NH<sub>2</sub>C(CH<sub>2</sub>OH)(CH<sub>2</sub>O)<sub>2</sub>] CrMo<sub>6</sub>O<sub>18</sub>(OH)<sub>4</sub>} was obtained following protocol in Scheme 1. Then it was redissolve in 30ml H<sub>2</sub>O, 9 ml 1M NaOH was added. The solutions was refluxing at 100 °C for 2 h. Then it was precipitated from the aqueous by adding equivalent amount of 2.898g [TBA]Br to substitute the NH4<sup>+</sup> cation. The pink crystalline products were redissolved in the V% ratio of 60/40 in DMF/MeCN mix solvent of 9 mL DMF and 6mL MeCN. Additional 0.2 g of [TBA]Br was added into the crystallization solution to accelerate recrystallization process. After crystallization the  $\delta$  isomer structure of {[H<sub>2</sub>NC(CH<sub>2</sub>O)<sub>3</sub>]CrMo<sub>6</sub>O<sub>18</sub>(OH)<sub>3</sub>]<sup>3-</sup> was definitely confirmed as [TBA]<sub>3</sub>{[H<sub>2</sub>NC(CH<sub>2</sub>O)<sub>3</sub>]CrMo<sub>6</sub>O<sub>18</sub>(OH)<sub>3</sub>}[TBA]Br·2H<sub>2</sub>O (compound **5**). Following the similar process while 6ml 1M NaOH was added instead. Then it was precipitated from the aqueous by adding equivalent amount of 2.898g [TBA]Br to substitute the NH4+ cation. The pink crystalline products were redissolved in 9 mL DMF and 2ml  $H_2O$  mix solvent. After crystallization the  $\chi$  isomer structure of  ${[H_2NC(CH_2O)_3]CrMo_6O_{18}(OH)_3}^{3-}$ definitely was confirmed  $[TBA]_{2}[H]_{\{H_{2}NC(CH_{2}O)_{3}]}CrMo_{6}O_{18}(OH)_{3}\}.3DMF.2H_{2}O$  (compound 6). 3.414g  $\delta$   $[NH_{4}]_{3}\{[NH_{2}C (CH_{2}O)_{3}]$ CrMo<sub>6</sub>O<sub>18</sub>(OH)<sub>3</sub> was obtained following our previous reported protocol. Then it was redissolve in 24 ml 1M HCl

solution. The solutions was refluxing at 100 °C for 2 h. Then it was precipitated from the aqueous by adding equivalent amount of 2.898g [TBA]Br to substitute the NH4<sup>+</sup> cation. The pink crystalline products were redissolved in in 10 mL MeCN. Additional 0.2 g of [TBA]Br and 0.2g [NH<sub>4</sub>]Br were added into the crystallization solution to accelerate crystallization process. After crystallization the  $\psi$  isomer structure of  $\{ [NH_2C(CH_2OH)(CH_2O)_2] CrMo_6O_{18}(OH)_4 \}^{3-} was definitely confirmed as [TBA]_4 \{ [NH_3C(CH_2OH)(CH_2O)_2] (CH_2O)_2 \} \}$ CrMo<sub>6</sub>O<sub>18</sub>(OH)<sub>4</sub><sup>2</sup>.4[TBA]Br (compound 1). While redissolve in 36 ml 1M HCl solution instead. The colour of solution turned to yellow from pink. Then it was precipitated from the aqueous by adding equivalent amount of 2.898g [TBA]Br to substitute the NH4<sup>+</sup> cation. The yellow precipitate was obtained and further conducted ESI-MS characterization with the confirmation of  $[Mo_6O_{19}]^{2-}$  anion formation. 3.363g  $\chi[NH_4]_2\{[NH_2C (CH_2O)_3]\}$ CrMo<sub>6</sub>O<sub>17</sub>(OH)<sub>4</sub>} was obtained following our previous reported protocol. Then it was redissolve in 21 ml 1M HCl solution. The solutions was refluxing at 100 °C for 2 h. Then it was precipitated from the aqueous by adding equivalent amount of 2.898g [TBA]Br to substitute the NH4<sup>+</sup> cation. The pink crystalline products were redissolved in in 10 mL MeCN. Additional 0.2 g of [TBA]Br and 0.2g [NH<sub>4</sub>]Br were added into the crystallization solution to accelerate crystallization process. After crystallization the  $\psi$  isomer structure of {[NH<sub>2</sub>C(CH<sub>2</sub>OH)(CH<sub>2</sub>O)<sub>2</sub>] CrMo<sub>6</sub>O<sub>18</sub>(OH)<sub>4</sub>}<sup>3-</sup> was definitely confirmed as [TBA]<sub>4</sub> {[NH<sub>3</sub>C(CH<sub>2</sub>OH)(CH<sub>2</sub>O)<sub>2</sub>] CrMo<sub>6</sub>O<sub>18</sub>(OH)<sub>4</sub><sup>2</sup>,24[TBA]Br (compound 1). While redissolve in 33 ml 1M HCl solution instead. The colour of solution turned to yellow from pink. Then it was precipitated from the aqueous by adding equivalent amount of 2.898g [TBA]Br to substitute the NH4<sup>+</sup> cation. The yellow precipitate was obtained and further conducted ESI-MS characterization with the confirmation of [Mo<sub>6</sub>O<sub>19</sub>]<sup>2-</sup> anion formation.

#### X-ray Crystallographic Structural Determinations

Suitable single crystals were selected. Data collections were performed for compound 1-5 respectively, by using graphite-monochromated Mo-K $\alpha$  radiation ( $\lambda = 0.71073$  Å). Data reduction, cell refinement and experimental absorption correction were performed with the software package of Rigaku RAPID AUTO (Rigaku, 1998, ver 2.30). Structures were solved by direct methods and refined against F<sup>2</sup> by full-matrix least-squares. All non-hydrogen atoms were refined anisotropically. All calculations were carried out by the program package of SHELXTL ver 5.1<sup>2</sup> and Olex2 ver 1.2.7<sup>3</sup>.

#### **DFT** calculations

All of the calculations presented herein were carried out with Gaussian09 program package. The structures of each stationary point were fully optimized by using the B3LYP method, in combination with the LANL2DZ basis set for molybdate and chromium atoms and the 6-31+G(d) basis set for main group elements. Configuration optimized before Mülliken charge analysis. The calculations were completed on the "Explorer 100" cluster system of Tsinghua National Laboratory for Information Science and Technology.

The solid state IR spectra of compounds 1-3 were similar to each other and they were all in agreement with the typical Anderson-type structures. Herein, we took compound 1 as example, the characteristic peaks at 914, 886 and 836 cm<sup>-1</sup> were assigned to the vibrations of terminal Mo=O units and those ones at 783 and 688 cm<sup>-1</sup> were belonged to the vibrations of the Mo-O-Mo groups. One obvious difference in this single-side triol functionalized  $\psi$  isomer distinguish  $\delta$  and  $\chi$  isomer was the vibration peak of the C-O bonds which demonstrated the grafting of triol onto the surface of POMs at different positions. In  $\delta$  isomer of {[H<sub>2</sub>NC(CH<sub>2</sub>O)<sub>3</sub>]CrMo<sub>6</sub>O<sub>18</sub>(OH)<sub>3</sub>}<sup>3</sup>, only one C-O vibration band was detected at 1050 cm<sup>-1</sup>, while in  $\psi$  isomer, peak of C-O bonds obviously split into two peaks 1053 and 1028 cm<sup>-1</sup> as in  $\chi$  isomer. However, the reason of such split was quite different for  $\psi$  and  $\chi$  isomer. In  $\chi$  isomer this was because there existed two type of C-O bonds: C-( $\mu_2$ -O) and C-( $\mu_3$ -O) while in  $\psi$  isomer because one foot of triol ligand pending, the peak at 1053 was the reserved C-O vibration in CH<sub>2</sub>OH group as in triol ligand. Another peak at 1028 was the C-( $\mu_3$ -O) vibration indicated that the other two feet anchored on Anderson cluster in diol functionalized mode (Fig. S4).

The LMCT and d-d bands of compounds 1-3 were similar to each other. Hypsochromic shift observed in LMCT and d-d bands as our previous reported. Herein we take compound 1 as example. Compared with the LMCT absorption band of the parent POM cluster,  $[Cr(OH)_6Mo_6O_{18}]^{3-}$ , locating around 238 nm, which corresponds to ligand center  $\mu_3$ -OH  $\pi$   $t_{2g}$  to metal-center Mo<sup>6+</sup>  $t_{2g}$ \* charge transfer transition (LMCT). The LMCT band of compound 1 shows slight hypsochromic shift to 230 nm (Fig. S5a), the *d-d* transition absorption band of the parent  $[Cr(OH)_6Mo_6O_{18}]^{3-}$  locating around 540 nm is assigned to the metal center lowest energy electronic transition from HOMO  $t_{2g}$ \* to LUMO  $e_g$ \* transition of Cr<sup>3+</sup> which resulting in the forming of pink colour. Similar hypsochromic shift phenomenon is observed at 530 nm (see Fig. S5b).

#### Details and results of the DFT calculations

Anderson-Evans- $\psi$ -{[NH<sub>2</sub>C(CH<sub>2</sub>OH)(CH<sub>2</sub>O)<sub>2</sub>] CrMo<sub>6</sub>O<sub>18</sub>OH)<sub>4</sub>}<sup>3-</sup>

# b3lyp/gen opt freq pop=full int=grid=ultrafine

C N O H 0 6-31+G(d) \*\*\*\* Mo Cr 0 LANL2DZ \*\*\*\* Calculation Type = FREQ Calculation Method = UB3LYP Basis Set = Gen Charge = -3 Spin = Quartet E(UB3LYP) = -2428.61559975 a.u. RMS Gradient Norm = 0.00008743 a.u. Imaginary Freq = 0 Dipole Moment = 2.7804 Debye

Optimization completed Atomic coordinates

Мо	-0.91501400	-3.24511200	-0.13586200
Мо	2.23726600	-2.28076200	-0.52042600
Мо	-2.60055000	2.26361100	0.02488100
Мо	0.56937700	3.33149400	-0.15628800
Cr	-0.11767000	0.02762800	-0.22241300
Mo	-3.30362500	-0.97155300	-0.01791600
Мо	3.01907700	1.11198200	-0.54136300
0	-2.26387100	-2.36260900	0.87001400
0	2.69432900	-3.34311400	0.73853400
0	-3.01385600	3.48411800	-1.09268400
0	2.00075900	2.49139100	-1.25330100
0	-0.35148900	-4.34613400	1.04293800
0	1.48605700	-0.33576500	-1.34299400
Н	1.34221500	-0.31054400	-2.31152900
0	0.48955900	-1.55559700	0.76525200
0	-1.67653200	0.37830600	0.92702700
0	0.16208800	4.55710200	-1.25632000
0	-4.12735200	-1.88680100	-1.19626700
0	-4.42678000	-0.70997400	1.23936600
0	0.73177600	-3.10224300	-1.24223900
0	-1.02953500	3.08996400	0.83647900
0	3.93080300	1.86828700	0.68594200
0	3.10001000	-0.67996800	0.51986100
0	-1.30973100	-1.22232200	-1.14881700
Н	-1.33098100	-1.19550600	-2.12765400
0	-3.69267600	2.44345000	1.31988800
0	1.53874100	4.07767100	1.03319400
0	-1.81675000	-4.16507600	-1.24219000
0	-3.32974200	0.74112900	-0.90941800
0	4.11389700	0.73211600	-1.78400600
0	1.11166800	1.21692000	0.75058100
0	-0.65044200	1.66720800	-1.18921300

Н	-0.68971300	1.64754100	-2.16781600
0	3.40814500	-2.45427200	-1.73831200
С	3.09762100	-0.65595100	1.96992700
Н	3.72567900	0.01882700	2.27547000
Н	3.40319800	-1.51496400	2.30046400
С	0.71044300	-1.44941100	2.18411300
Н	1.02968400	-2.30366400	2.51703300
Н	-0.13507200	-1.26062600	2.61987600
С	1.72099900	-0.35706000	2.56311100
Ν	1.84181400	-0.37412200	4.09903500
Н	2.21360000	-1.37985900	4.44217500
Н	2.59654100	0.37838800	4.51361100
С	1.24075200	1.04427200	2.17828400
Н	0.38104900	1.21024700	2.59555700
Н	1.86943000	1.69882900	2.52123900

Mulliken charges with hydrogens summed into heavy atoms:

IKCI	i chaig	ges with flydloge
1	Мо	9.229511
2	Мо	10.140739
3	Мо	10.179190
4	Мо	9.675233
5	Cr	3.767344
6	Мо	9.951467
7	Мо	10.059528
8	0	-6.739819
9	0	-3.991844
10	0	-4.441049
11	0	-5.311376
12	0	-4.864917
13	0	4.905962
15	0	3.365466
16	0	1.877979
17	0	-4.321822
18	0	-4.866717
19	0	-4.734865
20	0	-5.287436
21	0	-6.983303
22	0	-3.938882
23	0	-5.070156
24	0	5.774089
26	0	-5.128104
27	0	-5.017648
28	0	-4.329845
29	0	-6.124490
30	0	-4.506545

31	0	3.812207
32	0	6.048103
34	0	-4.505075
35	С	-3.524930
38	С	-1.535322
41	С	4.529612
42	Ν	0.281512
45	С	-1.373797

Sum of Mulliken charges with hydrogens summed into heavy atoms = -3.00000

bond lengths (Å)					
Mo <sub>1</sub> -(µ <sub>2</sub> -O <sub>7</sub> ) 1.943	Mo <sub>3</sub> -(µ <sub>2</sub> -O <sub>9</sub> ) 1.847	Mo <sub>5</sub> -(µ <sub>2</sub> -O <sub>11</sub> ) 1.981	N <sub>1</sub> -H <sub>1A</sub> 0.89		
Mo <sub>2</sub> -(µ <sub>2</sub> -O <sub>7</sub> ) 1.958	Mo <sub>4</sub> -(µ <sub>2</sub> -O <sub>9</sub> ) 1.992	Mo <sub>6</sub> -(µ <sub>2</sub> -O <sub>11</sub> ) 1.922	H <sub>1A</sub> -(μ <sub>2</sub> -Ο <sub>7</sub> ) 1.803		
Mo <sub>2</sub> -(µ <sub>2</sub> -O <sub>8</sub> ) 1.890	Mo <sub>4</sub> -(µ <sub>2</sub> -O <sub>10</sub> ) 1.885	Mo <sub>6</sub> -(µ <sub>2</sub> -O <sub>12</sub> ) 1.990			
Mo <sub>3</sub> -(µ <sub>2</sub> -O <sub>8</sub> ) 1.941	Mo <sub>5</sub> -(µ <sub>2</sub> -O <sub>10</sub> ) 1.973	Mo <sub>1</sub> -(µ <sub>2</sub> -O <sub>12</sub> ) 1.848			

Table S1. Selected bond lengths (Å) of the cluster anion for compound  $\boldsymbol{1}$ 



Fig. S1 The single crystals of compound 1



Fig. S2 ORTEP drawings of cluster anions of  $\chi$  isomer compounds 4(left),  $\delta$  isomer compounds 5 (middle) and  $\chi$  isomer compounds 6 (right) in the proton-controlled transformation cycling among  $\psi$ ,  $\delta$  and  $\chi$  isomer. Thermal ellipsoids are drawn at the 30% probability level



**Fig. S3**. ESI mass spectra of substance obtained from  $\delta$  [NH<sub>4</sub>]<sub>3</sub>{[NH<sub>2</sub>C (CH<sub>2</sub>O)<sub>3</sub>] CrMo<sub>6</sub>O<sub>18</sub>(OH)<sub>3</sub>} refluxing in 12 times stoichiometric ratio of 1M HCl solution at 100 °C for 2 h and precipitated by 3 times stoichiometric ratio of [TBA]Br



Fig. S4a IR spectrum of compound 1



Fig. S4b IR spectrum of compound 2



Fig. S4c IR spectrum of compound 3



Fig. S4d IR spectrum of compound 4:  $\delta$  isomers of {[H<sub>2</sub>NC(CH<sub>2</sub>O)<sub>3</sub>]CrMo<sub>6</sub>O<sub>18</sub>(OH)<sub>3</sub>}<sup>3-</sup>



Fig. S4e IR spectrum of compound 5:  $\chi$  isomers of {[H<sub>2</sub>NC(CH<sub>2</sub>O)<sub>3</sub>]CrMo<sub>6</sub>O<sub>18</sub>(OH)<sub>3</sub>}<sup>3-</sup>



Fig. S5a UV/Vis LMCT spectra of [TBA]<sub>3</sub>[CrMo<sub>6</sub>O<sub>18</sub>(OH)<sub>6</sub>] and compound 1



Fig. S5b UV/Vis d-d transition spectra of [TBA]<sub>3</sub>[CrMo<sub>6</sub>O<sub>18</sub>(OH)<sub>6</sub>] and compound 1



Fig. S6a The <sup>13</sup>C NMR spectra of compound 1



Fig. S6b The <sup>13</sup>C NMR spectra of compound 2



Fig. S6c The <sup>13</sup>C NMR spectra of compound 3



Fig. S7a ESI mass spectrometry of compound 1



Fig. S7b ESI-MS of compound 1(100% intensity peak in original size)



Fig. S7c ESI mass spectrometry of compound 2



Fig. S7d.ESI-MS of compound 2(100% intensity peak in original size)







Fig. S7f ESI-MS of compound 3(100% intensity peak in original size)



Fig S.9 The stoichiometric ratio proton introduced served as a key option to control whether the  $\psi$ ,  $\delta$ , or  $\chi$  isomer will be generated

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