Supporting information for

Step-By-Step Covalent Modification of Cr-templated Anderson-type Polyoxometalates

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Experimental Section

General: All of the chemicals used were analytical grade purchased from Alfa Aesar and used without further purification. Single-crystal X-ray diffraction (single-crystal XRD) data were collected at 150 (2) K on an Oxford Diffraction Gemini S Ultra diffractometer (λ ($Mo_{k\alpha}$) = 0.7107 Å) equipped with a graphite monochromator. Structure solution and refinement was carried out with SHELXS-97[1] and SHELXL-97[1] using WinGX.[2] The electrospray mass spectra (ESI-MS) of compounds **1**, **3** and **5** were recorded on Bruker cryospray microTOF Q mass spectrometer, while the ESI-MS spectra of compounds **2** and **4** were carried out on a Bruker APEX IV FTMS, and all experiments were performed in negative mode using acetonitrile as solvent. Fourier transform infrared (FT-IR) spectra were carried out on a Bruker Vector 22 infrared spectrometer using KBr pellet method; intensities donated as br = broad, vs = very strong, s = strong, m = medium, w = weak. Elemental Analyses were completed by using varioEL cube from Elementar An alysensysteme GmbH. $Na_3[Cr(OH)_6Mo_6O_{18}]$ was prepared and characterized according to the literature method.[3]

Synthesis of $[(C_4H_9)_4N]_3\{Cr(OH)_3Mo_6O_{18}[(OCH_2)_3CCH_2OH]\}\cdot 12H_2O$ (1): $Na_3[Cr(OH)_6Mo_6O_{18}]$ (2.18 g, 2 mmol) and pentareythriol (0.27 g, 2 mmol) were dissolved in 60 mL deionized water to form a clear purple solution. Then the resulting solution was sealed in a 100-mL stainless steel reactor with a teflon liner and heated at 140 ºC for 24 hours. After the reaction mixture was cooled down to room temperature, tetrabutylammonium bromide (abbreviated as TBA-Br, 2.0 g) was added into the solution and stirred for 5 min, a small amount of precipitation was filtered off, and the filtrate was sealed to give crystals of compound **1** within 3 days. Yield: 2.0 g (50.0 %, based on Mo). ESI-MS (negative mode, MeCN): 1585.67 ($\{(TBA)_4[Cr(OH)_3Mo_6O_{18}\{(OCH_2)_3C\text{-}CH_2OH\}_2]\}^{2-}$). FT-IR (KBr, cm^{-1}): 3397 (br), 2961 (s), 2874 (s), 1670 (m), 1484 (s), 1381 (m), 1117 (m), 1077 (w), 1020 (m), 940 (vs), 918 (vs), 654 (vs), 565 (w), 488 (w), 417 (m).

Synthesis of $[(C_4H_9)_4N]_3\{Cr(OH)_3Mo_6O_{18}[(OCH_2)_3CCH_3]\}\cdot 11H_2O$ (2): The synthesis of compound **2** is similar to that of compound **1**, except the use of 1,1,1-tris(hydroxymethyl)ethane (Tris-CH_3) instead of pentareythriol. Yield: 1.86 g (46.5 %, based on Mo). ESI-MS (negative mode, MeCN): 1568.99 ($\{(TBA)_4[Cr(OH)_3Mo_6O_{18}\text{-}\{(OCH_2)_3CCH_3\}]_2\}^{2-}$). FT-IR (KBr, cm^{-1}): 3422 (br), 2960 (s), 2873 (s), 1653 (m), 1483 (s), 1381 (m), 1132 (m), 1041 (m), 941 (vs), 916 (vs), 654 (vs), 565 (w), 492 (w), 419 (m).

Synthesis of $[(C_4H_9)_4N]_3\{CrMo_6O_{18}[(OCH_2)_3CCH_2OH][(OCH_2)_3CCH_3]\}$ (3): compound **1** (3.65 g, 2 mmol), Tris-CH_3 (0.24 g, 2 mmol) was added into H_2O/MecN (v/v, 1:1) dilute solution and stirred for a while to give a clear solution. Then the resulting solution was sealed in the 100-mL stainless steel reactor again and heated at 140 ºC for 2 days. After cooled down to room temperature, the solution was evaporated under reduce pressure. The residue was collected, washed with hot water to remove the starting materials, and dried in the air to give compound **3**. The crystals could be obtained by vapor diffusion of ether into the acetonitrile solution of compound **3** for 2 days. Yield: 2.15 g (56.8 %, based on Mo). ESI-MS (negative mode, MeCN): 1653.08 ($\{(TBA)_2\{CrMo_6O_{18}[(OCH_2)_3CCH_3][(OCH_2)_3CCH_2OH]\}\}^{-}$). FT-IR (KBr, cm^{-1}): 3421 (br), 2961 (s), 2873 (s), 1655 (m), 1480 (s), 1381 (m), 1120 (m), 1071 (w), 1021 (m), 940 (vs), 920 (vs), 665 (vs), 565 (m), 513 (m), 460 (m), 418 (m). Elemental analysis cald (%) for $C_{58}H_{126}CrMo_6N_3O_{25}$ (1893.26 g mol^{-1}): C 36.76, H 6.66, N 2.22; found: C 36.31, H 7.02, N 2.23.

Synthesis of $[(C_4H_9)_4N]_3\{CrMo_6O_{18}[(OCH_2)_3CCH_2OH]_2\}\cdot 2DMF$ (4): $Na_3[Cr(OH)_6Mo_6O_{18}]$ (2.18 g, 2 mmol) and pentareythriol (0.81 g, 6 mmol) were dissolved in 60 mL deionized water to form a clear purple solution and the resulting solution was sealed in a 100-mL stainless steel reactor with a Teflon liner and heated at 140 ºC for 24 hours. After cooled down to room temperature, TBA-Br (2.0 g) was added into the solution and light purple precipitation began to form immediately. The precipitation was filtered off and dried in the air to give compound **4**. The crystals could be obtained by ether diffusion into DMF for 2 days. Yield: 2.80 g (73.7 %, based on Mo). ESI-MS (negative mode, MeCN): 1667.05 ($\{(TBA)_2\{CrMo_6O_{18}[(OCH_2)_3CCH_2OH]_2\}\}^-$). FT-IR (KBr, cm^{-1}): 3397 (br), 2961 (s), 2873 (s), 1660 (s), 1480 (s), 1382 (m), 1115 (m), 1073 (w), 1014 (m), 940 (vs), 919 (vs), 663 (vs), 565 (m), 513 (m), 459 (m), 415 (m). Elemental analysis cald (%) for $C_{64}H_{140}CrMo_6N_5O_{28}$ (2055.57 g mol^{-1}): C 37.36, H 6.81, N 3.41; found: C 36.94, H 7.19, N 3.35.

Synthesis of $[(C_4H_9)_4N]_3\{CrMo_6O_{18}[(OCH_2)_3CCH_3]_2\}$ (5): The synthesis of compound **5** is similar to that of compound **4**, except the use of Tris-CH_3 instead of pentareythriol. Yield: 1.98 g (52.8 %, based on Mo). ESI-MS (negative mode, MeCN): 1635.03 ($\{(TBA)_2\{CrMo_6O_{18}[(OCH_2)_3CCH_3]_2\}\}^-$). FT-IR (KBr, cm^{-1}): 3448 (br), 2959 (s), 2874 (s), 1649 (w), 1479 (s), 1382 (m), 1127 (m), 1026 (s), 941 (vs), 921 (vs), 665 (vs), 564 (m), 511 (m), 460 (m), 418 (m). Elemental analysis cald (%) for $C_{58}H_{126}CrMo_6N_3O_{24}$ (1877.26 g mol^{-1}): C 37.07, H 6.71, N 2.24; found: C 37.01, H 7.07, N 2.25.

Table S1. Summary of crystal data for compounds **1**, **2**, and **4**

	1	**2**	**4**
Formula	$C_{53}H_{144}CrMo_6N_3O_{37}$	$C_{53}H_{142}CrMo_6N_3O_{35}$	$C_{64}H_{140}CrMo_6N_5O_{28}$
F.W.	2043.35	2009.34	2055.45
Cryst. Syst.	orthorhombic	orthorhombic	monoclinic
Space group	$P2_12_12_1$	$P2_12_12_1$	$P2_1/c$
a/ Å	14.924 (3)	15.164 (3)	25.2904 (16)
b/ Å	21.749 (4)	21.818 (4)	13.8087 (9)
c/ Å	25.646 (5)	25.095 (5)	24.6841 (16)
α (°)	90	90	90
β (°)	90	90	90.966 (4)
γ (°)	90	90	90
V/ Å^3	8324 (3)	8303 (3)	8556.7 (10)
Z	4	4	4
ρ	1.630	1.607	1.596
R_1	0.0396	0.0403	0.0814
$wR2$	0.0910	0.0979	0.2300

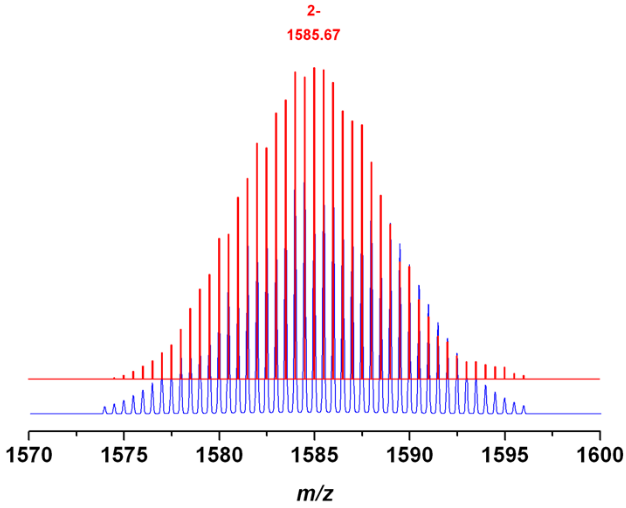
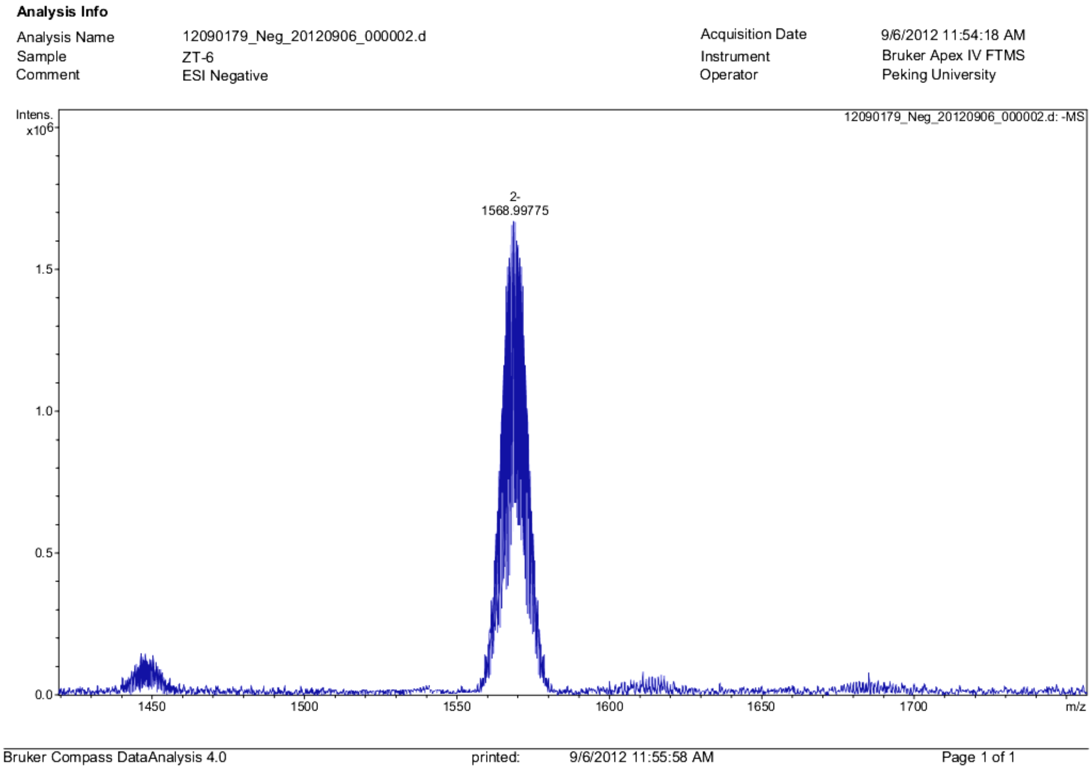


Figure S1. ESI-MS spectrum of **1** with and peaks at *m/z* 1585.67 attributed to $\{(TBA)_4[Cr(OH)_3Mo_6O_{18}\{(OCH_2)_3C\text{- }CH_2OH\}_2]\}^{2-}$. Red line: experimental data; blue line: simulated isotopic patterns.



Analysis Info

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Sample ZT-6
Comment ESI Negative

Acquisition Date 9/6/2012 11:54:18 AM
Instrument Bruker Apex IV FTMS
Operator Peking University

Bruker Compass DataAnalysis 4.0 printed: 9/6/2012 11:55:58 AM Page 1 of 1

Figure S2. ESI-MS spectrum of **2** with and peaks at *m/z* 1568.99 attributed to $\{(TBA)_4[Cr(OH)_3Mo_6O_{18}\{(OCH_2)_3C\text{- }CH_3\}_2]\}^{2-}$.

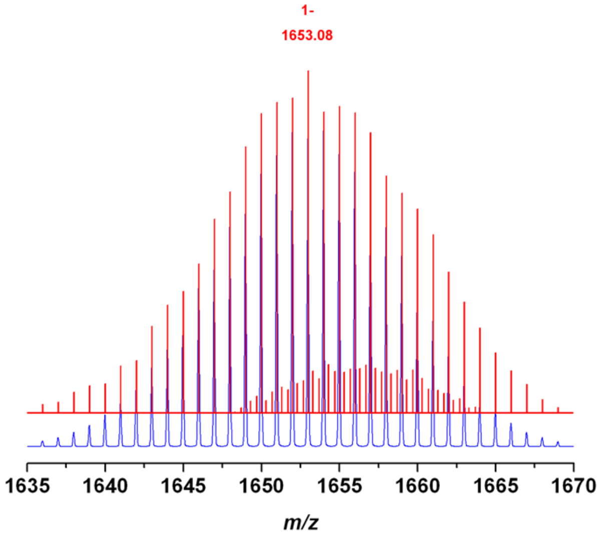


Figure S3. ESI-MS spectrum of **3** with and peaks at *m/z* 1653.08 attributed to $\{(TBA)_2\{CrMo_6O_{18}[(OCH_2)_3CCH_3]\text{- }[(OCH_2)_3CCH_2OH]\}\}^-$. Red line: experimental data, blue line: simulated isotopic patterns.

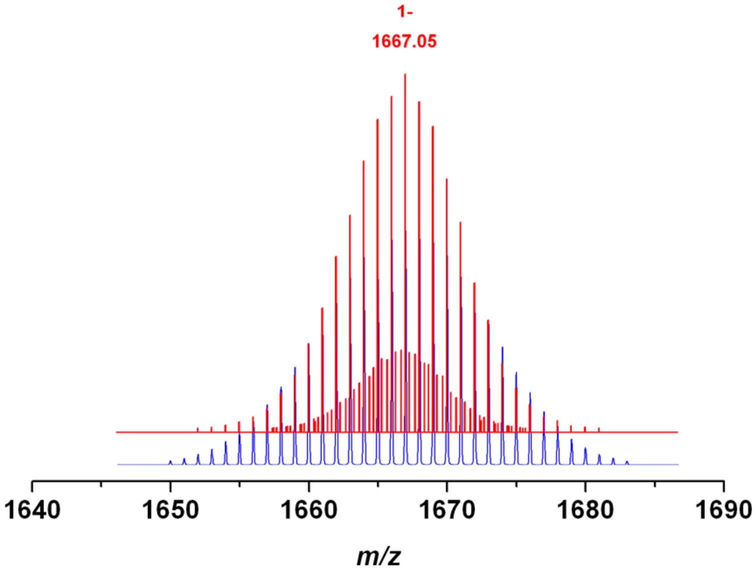
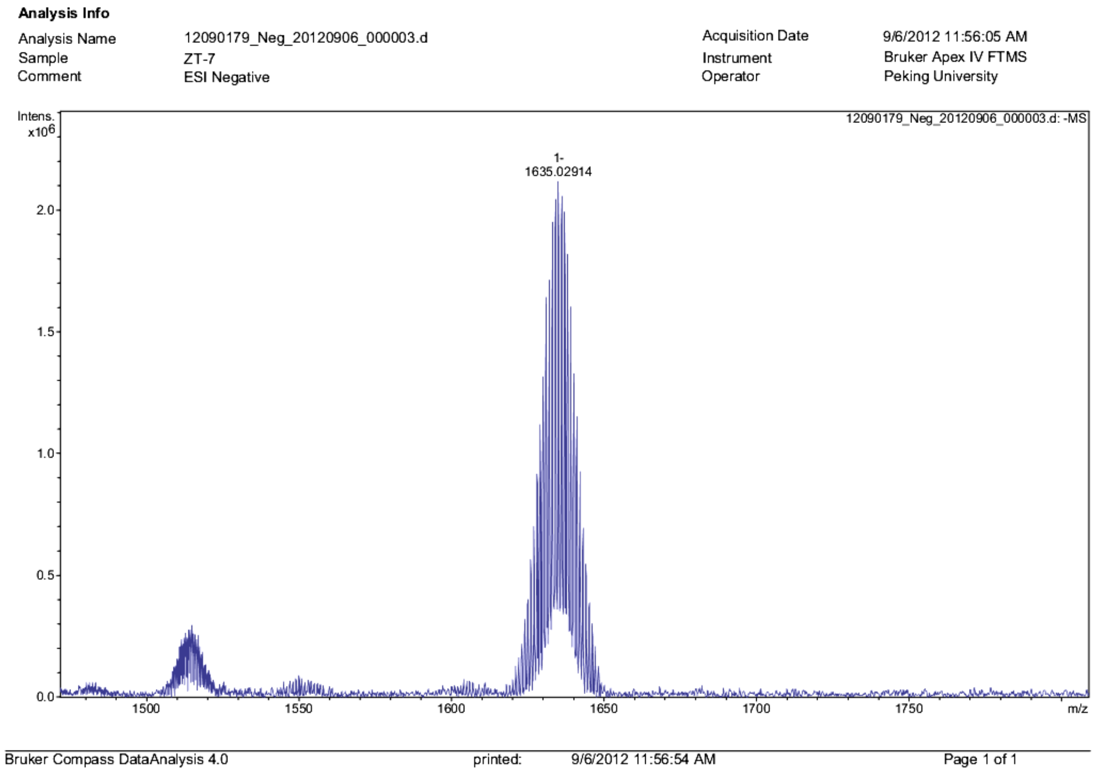


Figure S4. ESI-MS spectrum of **4** with and peaks at *m/z* 1667.05 attributed to $\{(TBA)_2\{CrMo_6O_{18}[(OCH_2)_3C\text{-}CH_2OH]_2\}\}^-$. Red line: experimental data, blue line: simulated isotopic patterns.



Analysis Info

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Sample	ZT-7	Instrument	Bruker Apex IV FTMS
Comment	ESI Negative	Operator	Peking University

Bruker Compass DataAnalysis 4.0 printed: 9/6/2012 11:56:54 AM Page 1 of 1

Figure S5. ESI-MS spectrum of **5** with and peaks at *m/z* 1635.03 attributed to $\{(TBA)_2\{CrMo_6O_{18}[(OCH_2)_3C\text{-}CH_3]_2\}\}^-$.

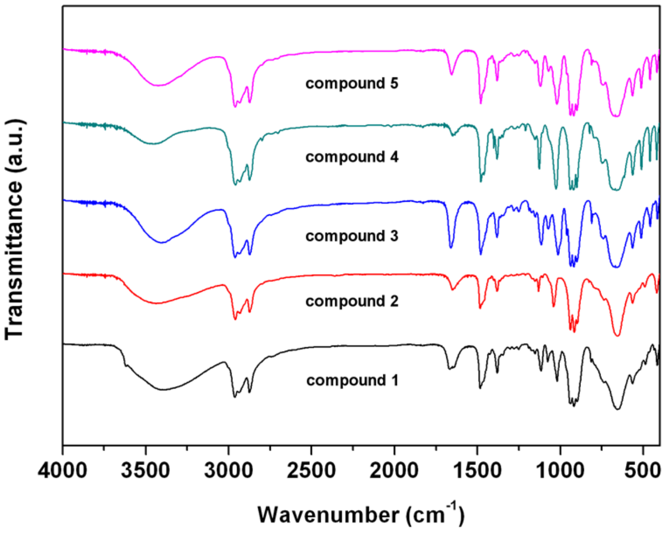

Figure S6. FT-IR spectra of compound **1**-**5**.

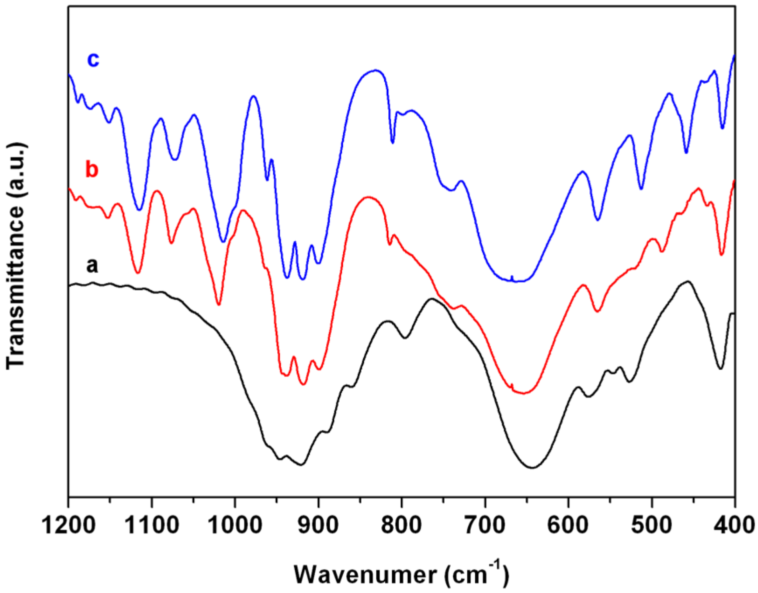

Figure S7. FT-IR spectra of chromium Anderson (a), compound **1** (b) and compound **3** (c).

References

1. G. M. Sheldrick, *Acta Crystallogr., Sect. A* **2008**, *64*, 112-122.
2. L. J. Farrugia, *J. Appl. Crystallogr.* **1999**, *32*, 837-838.
3. A. Perloff, *Inorg. Chem.,* 1970, **9**, 2228.