Supporting information

Unprecedented χ Isomers of Single-Side Triol-Functionalized Anderson Polyoxometalates and Their Proton-Controlled Isomer Transformation

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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®. $[NH_4]_3[CrMo_6O_{18}(OH)_6]$ and $[NH_4]_3[MnMo_6O_{18}(OH)_6]$ were synthesized according to modified literature methods[1]. 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^{-1}. Elemental analyses were performed by Elementar Analysensysteme GmbH (vario EL). ^{13}C NMR spectra were obtained on a JOEL JNM-ECA400 spectrometer and reported in ppm.

Synthesis and Crystallization process

The synthesis of $[TBA]_2[H]\{[H_2NC(CH_2O)_3]CrMo_6O_{18}(OH)_3\}$, compound **1**:

Method A:3.213g $[NH_4]_3[CrMo_6O_{18}(OH)_6]$ and 0.471g hydrochloride salt of $(HOCH_2)_3CNH_2$ were dissolve in 50ml H_2O then the solution was refluxing at 100 °C for 3 h forming $[NH_4]_2[H]\{[H_2NC(CH_2O)_3]CrMo_6O_{18}(OH)_3\}$. Then it was precipitated from the aqueous by adding equivalent amount of 2.898g [TBA]Br to substitute the $NH4^+$ cation. The title compounds could be obtained as pink crystalline products (85% yields based on Mo)

Method B: 3.213g $[NH_4]_3[CrMo_6O_{18}(OH)_6]$ and 3ml 1M HCl were synchronously dissolved in 50ml H_2O then the solution was refluxing at 100 °C for 0.5 h forming $[NH_4]_2[CrMo_6O_{17}(\mu_3\text{-}OH)_6(\mu_2\text{-}OH)]$.Then 0.363g $(HOCH_2)_3CNH_2$ were added into this refluxing solution for another 3h. Then it was precipitated from the aqueous by adding equivalent amount of 2.898g [TBA]Br to substitute the $NH4^+$ cation. The title compounds could be obtained as pink crystalline products (82% yields based on Mo)

Both method A and B, compound 1 can be obtained $C_{36}H_{84}N_3CrMo_6O_{24}$ M_r =1570.70, H 5.42 C 27.48 N 2.71 while calcd H 5.39 C 27.53 N 2.68. IR (KBr pellet, major absorbances, cm^{-1}): 3458, 2960, 2935, 2874, 1647, 1468, 1384, 1118, 1057, 939, 912, 901, 723, 670, 568.UV-Vis (MeCN, nm): λ_{LMCT} = 229 (ε_{LMCT}=4.62×10^5 L·mol^{-1}·cm^{-1}), $\lambda_{d\text{-}d}$ =531 ($\varepsilon_{d\text{-}d}$=5.61×10^2 L·mol^{-1}·cm^{-1}). ESI mass spectrometry (MeCN): calcd m/z=1569.70 $\{(TBA)_2[NH_2C(CH_2O)_3]CrMo_6O_{18}(OH)_3\}^-$,1328.23 $\{(TBA)[NH_2C(CH_2O)_3]CrMo_6O_{17}(OH)_4\}^-$, $C_{20}H_{48}N_2CrMo_6O_{24}$,663.61 $\{(TBA)[NH_2C(CH_2O)_3]CrMo_6O_{18}(OH)_3\}^{2-}$, 1086.76 $\{[H^+][NH_2C(CH_2O)_3]CrMo_6O_{17}(OH)_4\}^-$, 542.88 $\{NH_2C(CH_2O)_3]CrMo_6O_{17}(OH)_4\}^{2-}$, 361.59 $\{[NH_2C(CH_2O)_3]CrMo_6O_{18}(OH)_3\}^{3-}$; found 1569.37,1328.36,1086.63,663.39,542.69,361.65 respectively. ^{13}C NMR (400 MHz, $[D_6]$DMSO, ppm): δ = 13.8 (C_α), 19.0 (C_β), 23.5 (C_γ), 57.8 (C_ε), 61.6 (C_a), 65.8 (C_b), 75.6 (C_c).

The crystallization of compound **1**: $[TBA]_2[H]\{[H_2NC(CH_2O)_3]CrMo_6O_{18}(OH)_3\}.3DMF.2H_2O$

$C_{45}H_{109}N_6CrMo_6O_{29}$, M_r = 1826.00

1.57 g $[TBA]_2[H]\{[H_2NC(CH_2O)_3]CrMo_6O_{18}(OH)_3\}$ were redissolved in 5 mL DMF and further filtrated to remove some insoluble precipitate. Suitable single crystals for X-ray diffraction were grown by ether vapor diffusion into the solution containing the product. After crystallization, compound 1 was obtained as pink crystalline products.

The synthesis of $[TBA]_2[H]\{[H_3CC(CH_2O)_3]\ CrMo_6O_{18}(OH)_3\}$, compound **2**:

3.213g $[NH_4]_3[CrMo_6O_{18}(OH)_6]$ and 0.363g $(HOCH_2)_3CCH_3$ were dissolve in 50ml H_2O and 3ml 1M HCl was added synchronously, then the solution was refluxing at 100 °C for 3 h forming $[NH_4]_2$ $[H]\{[H_3CC(CH_2O)_3]\ CrMo_6O_{18}(OH)_3\}$. Then it was precipitated from the aqueous by adding equivalent amount of 2.898g [TBA]Br to substitute the $NH4^+$ cation. The title compounds could be obtained as pink crystalline products (90% yields based on Mo) $C_{37}H_{85}N_2CrMo_6O_{24}$ M_r =1569.72, H 5.42 C 27.35 N 1.74 while calcd H 5.46 C 28.31 N 1.78. IR (KBr pellet, major absorbances, cm^{-1}): 3391, 2958, 2935, 2874, 1478, 1384, 1127, 1026, 938, 921, 901, 747, 663, 563, 511.UV-Vis (MeCN, nm): λ_{LMCT} = 229 (ε_{LMCT}=4.58×10^5 L·mol^{-1}·cm^{-1}), $\lambda_{d\text{-}d}$ =531 ($\varepsilon_{d\text{-}d}$=5.56×10^2 L·mol^{-1}·cm^{-1}). ESI mass spectrometry (MeCN): calcd m/z=1568.70 $\{(TBA)_2[H_3CC(CH_2O)_3]CrMo_6O_{18}(OH)_3\}^-$, 1327.23 $\{(TBA)[H_3CC(CH_2O)_3]\ CrMo_6O_{17}(OH)_4\}^-$, 663.11 $\{(TBA)[H_3CC(CH_2O)_3]CrMo_6O_{18}(OH)_3\}^{2-}$, 1085.76 $\{[H^+][H_3CC(CH_2O)_3]\ CrMo_6O_{17}(OH)_4\}^-$, 542.38 $\{H_3CC(CH_2O)_3]\ CrMo_6O_{17}(OH)_4\}^{2-}$, 361.25 $\{[H_3CC(CH_2O)_3]CrMo_6O_{18}(OH)_3\}^{3-}$; found 1568.61,1327.41,1085.97,542.25,361.51 respectively. ^{13}C NMR (400

MHz, [D_6]DMSO, ppm): δ = 13.8 ($C_α$), 19.0 ($C_β$), 23.5 ($C_γ$), 57.8 ($C_ε$), 14.9 (C_a), 44.8 (C_b), 67.1 (C_c), 76.3 (C_d).

The crystallization of compound **2**: $[TBA]_2[H]\{[H_3CC(CH_2O)_3]\ CrMo_6O_{18}(OH)_3\}$.DMF. [TBA]Br.MeCN.2EtOH

$C_{56}H_{142}N_4CrMo_6O_{32}Br$, M_r =2091.27

1.56 g $[TBA]_2[H]\{[H_3CC(CH_2O)_3]\ CrMo_6O_{18}(OH)_3\}$ were redissolved in mix solvent of 3 mL DMF,1m MeCN and 2ml EtOH and further filtrated to remove some insoluble precipitate. 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 ether vapor diffusion into the solution containing the product.. After crystallization, compound 4 was obtained as pink crystalline products.

The synthesis of $[TBA]_2[H]\{[H_5C_2C(CH_2O)_3]\ CrMo_6O_{18}(OH)_3\}$, compound **3**:

The synthesis process is similar to synthesis of compound **2** while used $(HOCH_2)_3CC_2H_5$ instead of $(HOCH_2)_3CCH_3$. The title compounds could be obtained as orange crystalline products (88% yields based on Mo) $C_{38}H_{87}N_2CrMo_6O_{24}$ M_r =1583.74, H 5.54 C 28.77 N 1.81 while calcd H 5.54 C 28.82 N 1.77. IR (KBr pellet, major absorbances, cm^{-1}): 3390, 2960, 2935, 2874, 1665, 1478, 1384, 1115, 1043, 937, 920, 901, 740, 662, 563.UV-Vis (MeCN, nm): $λ_{LMCT}$ = 229 ($ε_{LMCT}$=4.71×10^5 L·mol^{-1}·cm^{-1}), $λ_{d-d}$ =531 ($ε_{d-d}$=5.68×10^2 L·mol^{-1}·cm^{-1}). ESI mass spectrometry (MeCN): calcd m/z=1582.53 $\{(TBA)_2[H_5C_2C\ (CH_2O)_3]CrMo_6O_{18}(OH)_3\}^-$, 1341.06 $\{(TBA)[H_5C_2C(CH_2O)_3]\ CrMo_6O_{17}(OH)_4\}^-$, 670.03 $\{(TBA)[H_5C_2C(CH_2O)_3]CrMo_6O_{18}\ (OH)_3\}^{2-}$, 365.86 $\{[H_5C_2C(CH_2O)_3]CrMo_6O_{18}(OH)_3\}^{3-}$; found 1582.76,1340.93,670.36,365.95 respectively. ^{13}C NMR (400 MHz, [D_6]DMSO, ppm): δ = 13.8 ($C_α$), 19.0 ($C_β$), 23.5 ($C_γ$), 7.9 (C_a), 22.3 (C_b) , 43.8 (C_c), 64.8 (C_d), 74.1 (C_e).

The crystallization of compound **3**: $[TBA]_2[H]\{[H_5C_2C(CH_2O)_3]\ CrMo_6O_{18}(OH)_3\}$.5DMF. [TBA]Br

$C_{69}H_{158}N_8CrMo_6O_{29}Br$, M_r = 2271.59,

1.58 g $[TBA]_2[H]\{[H_5C_2C(CH_2O)_3]\ CrMo_6O_{18}(OH)_3\}$ were redissolved in 5 mL DMF and further filtrated to remove some insoluble precipitate. 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 ether vapor diffusion into the solution containing the product. After crystallization, compound **3** was obtained as pink crystalline products.

The synthesis of $[TBA]_2[H]\{[HOH_2CC(CH_2O)_3]\ CrMo_6O_{18}(OH)_3\}$, compound **4**:

The synthesis process is similar to synthesis of compound **2** while used $(HOCH_2)_3CCH_2OH$ instead of $(HOCH_2)_3CCH_3$. The title compounds could be obtained as orange crystalline products (91% yields based on Mo) $C_{37}H_{85}N_2CrMo_6O_{25}$ M_r =1583.74, H 5.52 C 28.07 N 1.74 while calcd H 5.40 C 28.03 N 1.77. IR (KBr pellet, major absorbances, cm^{-1}): 3315, 2960, 2935, 2874, 1466, 1381, 1108, 1051, 1029, 938, 915, 895, 800, 739, 664.UV-Vis (MeCN, nm): $λ_{LMCT}$ = 229 ($ε_{LMCT}$=4.67×10^5 L·mol^{-1}·cm^{-1}), $λ_{d-d}$ =531 ($ε_{d-d}$=5.70×10^2 L·mol^{-1}·cm^{-1}). ESI mass spectrometry (MeCN): calcd m/z=1584.70 $\{(TBA)_2[HOH_2CC\ (CH_2O)_3]CrMo_6O_{18}(OH)_3\}^-$, 1343.23 $\{(TBA)[HOH_2CC(CH_2O)_3]\ CrMo_6O_{17}(OH)_4\}^-$, 671.11 $\{(TBA)[HOH_2CC(CH_2O)_3]CrMo_6O_{18}\ (OH)_3\}^{2-}$, 550.38 $\{HOH_2CC(CH_2O)_3]\ CrMo_6O_{17}(OH)_4\}^{2-}$, 366.59 $\{[HOH_2CC(CH_2O)_3]CrMo_6O_{18}(OH)_3\}^{3-}$; found 1584.85,1343.55,671.36,550.62,366.74 respectively. ^{13}C NMR (400 MHz, [D_6]DMSO, ppm): δ = 13.8 ($C_α$), 19.0 ($C_β$), 23.5 ($C_γ$), 51.3 (C_a), 64.1 (C_b) , 65.4 (C_c), 76.7 (C_d).

The crystallization of compound **4**: $[TBA]_2[H]\{[HOH_2CC(CH_2O)_3]\ CrMo_6O_{18}(OH)_3\}$.3DMF.$H_2O$

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

1.58 g $[TBA]_2[H]\{[HOH_2CC(CH_2O)_3]\ CrMo_6O_{18}(OH)_3\}$ were redissolved in 5 mL DMF and further filtrated to remove some insoluble precipitate. 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 ether vapor diffusion into the solution containing the product. After crystallization, compound **4** was obtained as pink crystalline products.

The synthesis of $[TBA]_2[H]\{[H_2NC(CH_2O)_3]MnMo_6O_{18}(OH)_3\}$, compound **5**:

The synthesis process is similar to synthesis of compound **1** while used $[NH_4]_3[MnMo_6O_{18}(OH)_6]$ instead of $[NH_4]_3[CrMo_6O_{18}(OH)_6]$. The title compounds could be obtained as orange crystalline products (80% yields based on Mo) $C_{36}H_{84}N_3MnMo_6O_{24}$ M_r =1573.65, H 5.42 C 27.52 N 2.64 while calcd H 5.38 C 27.48 N 2.67. IR (KBr pellet, major absorbances, cm^{-1}): 3435, 2962, 2935, 2874, 1631, 1469, 1384, 1111, 1040, 944, 936, 905, 754, 692, 591, 559, 568.UV-Vis (MeCN, nm): $λ_{LMCT}$ = 211, $λ_{d-d}$ =464. ESI mass spectrometry (MeCN): calcd m/z=1331.23 $\{(TBA)[NH_2C(CH_2O)_3]\ MnMo_6O_{17}(OH)_4\}^-$, 665.11 $\{(TBA)[NH_2C(CH_2O)_3]\ MnMo_6O_{18}\ (OH)_3\}^{2-}$, 544.38 $\{NH_2C(CH_2O)_3]\ MnMo_6O_{17}(OH)_4\}^{2-}$, 362.59 $\{[NH_2C(CH_2O)_3]\ MnMo_6O_{18}(OH)_3\}^{3-}$; found 1331.49,664.88,544.53,362.68 respectively. ^{13}C NMR (400 MHz, [D_6]DMSO, ppm): δ = 13.8 ($C_α$), 19.0 ($C_β$), 23.5 ($C_γ$), 57.8 ($C_ε$), 60.9 (C_a), 65.2 (C_b), 74.8 (C_c).

The crystallization of compound **5**: $[TBA]_2[H]\{[H_2NC(CH_2O)_3]MnMo_6O_{18}(OH)_3\}$.5DMF. [TBA]Br

$C_{67}H_{155}N_9MnMo_6O_{29}Br$, M_r = 2261.47

1.57 g $[TBA]_2[H]\{[H_2NC(CH_2O)_3]MnMo_6O_{18}(OH)_3\}$ were redissolved in 5 mL DMF and further filtrated to

remove some insoluble precipitate. 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 ether vapor diffusion into the solution containing the product. After crystallization, compound 5 was obtained as orange crystalline products.

The synthesis of $[TMA]_2[CrMo_6O_{17}(\mu_3\text{-}OH)_6(\mu_2\text{-}OH)]$, compound **6**:

3.213g $[NH_4]_3[CrMo_6O_{18}(OH)_6]$ and 3ml 1M HCl were synchronously dissolved in 50ml H_2O then the solution was refluxing for at 100 °C for 0.5 h forming $[NH_4]_2[CrMo_6O_{17}(\mu_3\text{-}OH)_6(\mu_2\text{-}OH)]$. Then it was precipitated from the aqueous by adding equivalent amount of 1.386g [TMA]Br to substitute the $NH4^+$ cation. The title compounds could be obtained as pink crystalline products (90% yields based on Mo) $C_8H_{31}CrMo_6N_2O_{24}$ M_r =1166.97, H 2.64 C 8.27 N 2.37 while calcd H 2.68 C 8.23 N 2.40.

The crystallization of compound **6**: $[TMA]_2[CrMo_6O_{17}(\mu_3\text{-}OH)_6(\mu_2\text{-}OH)].6H_2O$

$C_8H_{43}CrMo_6N_2O_{30}$, M_r = 1275.08

1.27 g $[TMA]_2[CrMo_6O_{17}(\mu_3\text{-}OH)_6(\mu_2\text{-}OH)]$ were redissolved in 10 mL MeCN and 2ml H_2O mix solvent. and further filtrated to remove some insoluble precipitate. Suitable single crystals for X-ray diffraction were grown by ether vapor diffusion into the solution containing the product. After crystallization, compound **6** was obtained as pink crystalline products.

X-ray Crystallographic Structural Determinations

Suitable single crystals were selected. Data collections were performed at 293,100,100,293,109 and 100 K for compound 1-6 respectively, by using graphite-monochromated Mo-Kα radiation (λ = 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^2 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[2] and Olex2 ver 1.2.6[3].

Crystal data and structure refinement for compound **1-6**

§ Crystal data for **1:** $[TBA]_2[H]\{[H_2NC(CH_2O)_3]CrMo_6O_{18}(OH)_3\}.3DMF.2H_2O$ $C_{45}H_{109}N_6CrMo_6O_{29}$, M_r = 1826.00, triclinic, space group $P\bar{1}$, a=13.5540(14), b= 13.7899(10), c= 21.0955(18) Å, α= 86.768(7)°, β= 88.944(8)°, γ= 63.016(9)°,V= 3508.0(5) Å^3, Z=2, T= 293 K, 13739 reflections measured, R_1(final)= 0.0339, wR_2= 0.0737.

Crystal data for **2**: $[TBA]_2[H]\{[H_3CC(CH_2O)_3]$ $CrMo_6O_{18}(OH)_3\}$.DMF. [TBA]Br.MeCN.2EtOH $C_{56}H_{142}N_4CrMo_6O_{32}Br$, M_r =2098.36, monoclinic, space group $P2_1/c$, a= 24.0245(12), b= 13.9963(6), c= 26.7955(14) Å,α=γ=90.00 °, β= 94.540(4)°, V= 8981.8(7) Å^3, Z= 4, T= 100 K, 17618 reflections measured, R_1(final)= 0.0487, wR_2= 0.1051.

Crystal data **3**: $[TBA]_2[H]\{[H_5C_2C(CH_2O)_3]$ $CrMo_6O_{18}(OH)_3\}$.5DMF. [TBA]Br $C_{69}H_{158}N_8CrMo_6O_{29}Br$, M_r = 2271.59,triclinic, space group $P\bar{1}$, a= 13.2494(4), b= 14.7378(6), c= 14.8892(6) Å, α= 119.221(4)°, β= 103.752(3)°, γ= 96.589(3)°, V= 2371.54(16) Å^3, Z= 1, T= 100 K, 18431 reflections measured, R_1(final)= 0.0306, wR_2= 0.0702.

Crystal data for **4**: $[TBA]_2[H]\{[HOH_2CC(CH_2O)_3]$ $CrMo_6O_{18}(OH)_3\}$.3DMF.H_2O $C_{46}H_{108}N_5CrMo_6O_{28}$, M_r = 1807.00, triclinic, space group $P\bar{1}$,, a= 13.6865(8), b= 13.7366(8), c= 21.5248(9) Å, α= 86.727(4)°, β= 83.692(4)°, γ= 62.304(6)°, V= 3561.3(3) Å^3, Z= 2, T= 293 K, 13961 reflections measured, R_1(final)= 0.0374, wR_2= 0.0807.

Crystal data for **5**: $[TBA]_2[H]\{[H_2NC(CH_2O)_3]MnMo_6O_{18}(OH)_3\}$.5DMF. [TBA]Br $C_{67}H_{155}N_9MnMo_6O_{29}Br$, M_r = 2261.47, triclinic, space group $P\bar{1}$, a=13.2671(5), b=14.7560(6), c= 14.8870(4) Å, α= 119.330(4)°, β= 103.729(3)°, γ=96.883(3)°, V=2370.38(14) Å^3, Z=1, T= 109 K, 13556 reflections measured, R_1(final)= 0.0296, wR_2= 0.0601.

Crystal data for **6**: $[TMA]_2[CrMo_6O_{17}(\mu_3\text{-}OH)_6(\mu_2\text{-}OH)].6H_2O$ $C_8H_{43}CrMo_6N_2O_{30}$, M_r = 1275.08, monoclinic, space group $P2_1/n$, a=15.0834(3), b=11.5341(4), c=23.0245(6) Å, α=γ=90°, β=98.122(2)°, V= 3965.45(19) Å^3, Z=4, T= 100 K, 7784 reflections measured, R_1(final)=0.0327, wR_2=0.0763.

CCDC-1049394-1049399, contain the supplementary crystallographic data for for compound **1-6** respectively in this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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.

Details and results of the DFT calculations

Anderson-Evans-δ-$\{[H_2NC(CH_2O)_3]CrMo_6O_{18}(OH)_3\}^{3-}$

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) = -2511.33121703 a.u.

RMS Gradient Norm = 0.00006422 a.u.

Imaginary Freq = 0

Dipole Moment = 2.5893 Debye

Optimization completed Atomic coordinates

Mo	-2.40140000	2.76580000	21.06590000
Mo	-2.15890000	2.19110000	17.79470000
O	-1.99240000	4.20490000	21.90750000
O	-0.75140000	1.28390000	18.12440000
O	-1.76510000	3.25830000	16.51760000
O	-2.12000000	3.44730000	19.26020000
O	-1.05650000	1.73370000	21.21670000
O	-3.34810000	1.27180000	19.57640000
O	-4.53870000	3.44720000	20.56570000
O	-3.59200000	1.90110000	22.28030000
C	-3.30080000	-0.15630000	19.87940000
Mo	-5.33340000	2.67040000	22.54500000
H	-4.68780000	4.38900000	20.33970000
O	-4.33120000	2.82790000	17.64380000
H	-4.52090000	3.76640000	17.43480000
O	-3.12490000	0.79180000	16.85410000
C	-4.68210000	-0.81720000	19.92970000
H	-2.76430000	-0.60220000	19.20550000
H	-2.86230000	-0.28080000	20.73560000
O	-5.87040000	1.16770000	20.85790000
O	-4.94390000	4.10670000	23.37950000
O	-7.02440000	3.21940000	21.76200000
O	-5.86960000	1.56570000	23.73150000
Cr	-5.12100000	2.06910000	19.28180000
Mo	-4.83010000	1.24240000	16.04370000
C	-5.39450000	-0.76870000	18.57460000
N	-4.45990000	-2.30960000	20.23040000
C	-5.55260000	-0.24180000	21.04260000
Mo	-8.08860000	1.93110000	20.78610000
H	-7.04400000	3.72270000	18.75350000

O	-6.56180000	1.99290000	16.27910000
O	-5.19150000	-0.30930000	15.40590000
O	-5.64970000	0.58420000	18.11080000
O	-4.29610000	2.16930000	14.70430000
H	-6.23840000	-1.24180000	18.64540000
H	-4.85120000	-1.22990000	17.91660000
H	-5.24730000	-2.71750000	20.30560000
H	-3.99610000	-2.67990000	19.56720000
H	-5.09280000	-0.35180000	21.88970000
H	-6.37940000	-0.74690000	21.08760000
O	-6.94040000	2.77340000	18.97360000
O	-9.46580000	2.89730000	20.50590000
O	-8.18180000	0.65810000	19.32200000
O	-8.51480000	0.85520000	22.03030000
Mo	-7.80610000	1.20460000	17.52200000
O	-8.06920000	-0.30160000	16.74020000
O	-9.15910000	2.15350000	17.11520000

Mulliken charges with hydrogens summed into heavy atoms:

1	Mo	2.458869
2	Mo	2.457530
3	O	-0.754594
4	O	-0.773038
5	O	-0.755182
6	O	-1.126022
7	O	-0.768319
8	O	-0.193561
9	O	-0.263322
10	O	-1.221416
11	C	0.157797
12	Mo	2.453535
14	O	-0.264806
16	O	-1.222687
17	C	-0.736468
20	O	-0.190025
21	O	-0.754918
22	O	-1.126381
23	O	-0.767827
24	Cr	-0.272520
25	Mo	2.457538
26	C	0.502636
27	N	-0.025474
28	C	0.171409
29	Mo	2.462996
31	O	-1.125222

32	O	-0.773311
33	O	-0.162514
34	O	-0.754922
41	O	-0.263150
42	O	-0.754913
43	O	-1.222670
44	O	-0.773877
45	Mo	2.452933
46	O	-0.772802
47	O	-0.755300

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

Anderson-Evans-χ-{$[H_2NC(CH_2O)_3]CrMo_6O_{18}(OH)_3\}^{3-}$
b3lyp/gen opt freq pop=full int=grid=ultrafine
C N O H 0
6-31+G(d)
****
Mo Cr 0
LANL2DZ
****
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Calculation Method = UB3LYP
Basis Set = Gen
Charge = -3
Spin = Quartet
E(UB3LYP) = -2511.30086463 a.u.
RMS Gradient Norm = 0.00004297 a.u.
Imaginary Freq = 0
Dipole Moment = 3.7182 Debye
Optimization completed Atomic coordinates

Mo	-0.91501400	-3.24511200	-0.13586200
Mo	2.23726600	-2.28076200	-0.52042600
Mo	-2.60055000	2.26361100	0.02488100
Mo	0.56937700	3.33149400	-0.15628800
Cr	-0.11767000	0.02762800	-0.22241300
Mo	-3.30362500	-0.97155300	-0.01791600
Mo	3.01907700	1.11198200	-0.54136300
O	-2.26387100	-2.36260900	0.87001400
O	2.69432900	-3.34311400	0.73853400
O	-3.01385600	3.48411800	-1.09268400
O	2.00075900	2.49139100	-1.25330100
O	-0.35148900	-4.34613400	1.04293800
O	1.48605700	-0.33576500	-1.34299400
H	1.34221500	-0.31054400	-2.31152900
O	0.48955900	-1.55559700	0.76525200
O	-1.67653200	0.37830600	0.92702700
O	0.16208800	4.55710200	-1.25632000
O	-4.12735200	-1.88680100	-1.19626700
O	-4.42678000	-0.70997400	1.23936600
O	0.73177600	-3.10224300	-1.24223900
O	-1.02953500	3.08996400	0.83647900
O	3.93080300	1.86828700	0.68594200
O	3.10001000	-0.67996800	0.51986100
O	-1.30973100	-1.22232200	-1.14881700
H	-1.33098100	-1.19550600	-2.12765400
O	-3.69267600	2.44345000	1.31988800
O	1.53874100	4.07767100	1.03319400
O	-1.81675000	-4.16507600	-1.24219000
O	-3.32974200	0.74112900	-0.90941800
O	4.11389700	0.73211600	-1.78400600
O	1.11166800	1.21692000	0.75058100
O	-0.65044200	1.66720800	-1.18921300
H	-0.68971300	1.64754100	-2.16781600
O	3.40814500	-2.45427200	-1.73831200
C	3.09762100	-0.65595100	1.96992700
H	3.72567900	0.01882700	2.27547000
H	3.40319800	-1.51496400	2.30046400
C	0.71044300	-1.44941100	2.18411300
H	1.02968400	-2.30366400	2.51703300

H	-0.13507200	-1.26062600	2.61987600
C	1.72099900	-0.35706000	2.56311100
N	1.84181400	-0.37412200	4.09903500
H	2.21360000	-1.37985900	4.44217500
H	2.59654100	0.37838800	4.51361100
C	1.24075200	1.04427200	2.17828400
H	0.38104900	1.21024700	2.59555700
H	1.86943000	1.69882900	2.52123900

Mulliken charges with hydrogens summed into heavy atoms:

1	Mo	9.229511
2	Mo	10.140739
3	Mo	10.179190
4	Mo	9.675233
5	Cr	3.767344
6	Mo	9.951467
7	Mo	10.059528
8	O	-6.739819
9	O	-3.991844
10	O	-4.441049
11	O	-5.311376
12	O	-4.864917
13	O	4.905962
15	O	3.365466
16	O	1.877979
17	O	-4.321822
18	O	-4.866717
19	O	-4.734865
20	O	-5.287436
21	O	-6.983303
22	O	-3.938882
23	O	-5.070156
24	O	5.774089
26	O	-5.128104
27	O	-5.017648
28	O	-4.329845
29	O	-6.124490
30	O	-4.506545
31	O	3.812207
32	O	6.048103
34	O	-4.505075
35	C	-3.524930
38	C	-1.535322
41	C	4.529612
42	N	0.281512
45	C	-1.373797

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

Anderson-Evans-$\{[H_2NC(CH_2O)_3]CrMo_6O_{17}(OH)_4\}^{2-}$

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 = -2

Spin = Doublet

E(UB3LYP) = -2511.32006240 a.u.

RMS Gradient Norm = 0.00005072 a.u.

Imaginary Freq = 0

Dipole Moment = 3.2830 Debye

Optimization completed Atomic coordinates

Mo	14.77290000	9.03430000	4.27340000
Mo	16.13230000	12.06130000	4.33690000
Mo	19.70400000	6.75860000	6.20170000
Mo	21.22230000	9.74310000	6.10600000
Cr	17.97090000	9.46170000	5.24510000
Mo	16.52110000	6.44860000	5.34410000

Mo	19.45930000	12.44490000	5.28890000
O	15.65150000	7.39670000	3.87800000
O	15.57460000	12.32280000	2.74220000
O	20.45890000	6.48840000	7.70720000
O	20.37220000	11.47720000	6.58380000
O	14.17480000	9.42180000	2.72050000
O	17.59350000	11.31490000	5.86390000
H	17.31400000	11.40210000	6.79860000
O	16.87190000	9.99000000	3.70760000
O	18.35260000	7.64640000	4.58690000
H	18.61980000	7.54070000	3.64990000
O	21.98810000	9.47400000	7.59570000
O	15.17500000	6.03330000	6.30340000
O	16.92750000	5.03830000	4.47430000
O	14.88380000	10.86960000	5.03220000
O	20.99450000	7.99180000	5.41210000
O	20.68550000	12.95120000	4.21670000
O	18.09110000	12.47090000	3.71690000
O	16.31630000	8.66840000	5.93400000
H	16.05720000	8.87620000	6.85540000
O	20.04980000	5.37840000	5.26490000
O	22.43840000	10.31510000	5.05470000
O	13.42910000	8.52720000	5.17920000
O	17.87310000	6.44420000	6.72280000
O	18.94070000	13.83750000	6.11280000
O	19.58840000	10.28670000	4.48650000
O	19.14220000	8.99410000	6.76700000
H	18.83620000	9.18960000	7.67680000
O	15.82860000	13.49860000	5.18910000
C	18.52890000	12.12330000	2.37870000
H	19.36360000	12.58260000	2.19040000
H	17.86950000	12.43540000	1.73970000
C	17.41790000	9.85620000	2.38200000
H	16.76610000	10.18040000	1.73970000
H	17.56980000	8.91610000	2.19880000
C	18.73490000	10.62110000	2.18570000
N	19.18060000	10.37670000	0.73120000
H	18.39850000	10.76600000	0.02110000
H	20.14230000	10.92390000	0.44230000
C	19.85810000	10.09310000	3.08130000
H	19.98070000	9.14620000	2.91070000
H	20.68460000	10.54640000	2.85170000

Mulliken charges with hydrogens summed into heavy atoms:

1	Mo	9.977707
2	Mo	10.392021
3	Mo	9.305608
4	Mo	10.064064
5	Cr	-0.709565
6	Mo	9.336097
7	Mo	10.229440
8	O	-6.760259
9	O	-3.966736
10	O	-4.433819
11	O	-5.575923
12	O	-5.037444
13	O	4.776049
15	O	2.869812
16	O	6.219647
18	O	-4.252991
19	O	-4.649942
20	O	-4.581948
21	O	-5.234676

22	O	-7.171187
23	O	-3.962524
24	O	-5.243858
25	O	6.240912
27	O	-4.658811
28	O	-5.106612
29	O	-4.446683
30	O	-5.715628
31	O	-4.605532
32	O	4.173554
33	O	6.469147
35	O	-4.543015
36	C	-3.534400
39	C	-1.908101
42	C	4.896338
43	N	0.450589
46	C	-1.301330

Sum of Mulliken charges with hydrogens summed into heavy atoms = -2.00000

Details and results of the BVS calculations

Subroutine Calc_BVS (JRC-LLB, version: March-2005)

Title: Summary of Bond-Valence calculations for file: compound6_cfl.cfl

Atom	Coord	D_aver Sigm	Distort(x10-4)	Valence	BVSum(Sigma)
Mo1	6.00	1.9953(47)	165.501	6.000	5.843(87)
Mo2	6.00	1.9934(48)	178.808	6.000	5.956(94)
Mo3	6.00	2.0208(48)	157.785	6.000	5.546(89)
Mo4	6.00	2.0236(48)	158.461	6.000	5.506(85)
Mo5	6.00	1.9879(48)	157.407	6.000	5.903(88)
Mo6	6.00	1.9916(49)	157.059	6.000	5.830(90)
Cr1	6.00	1.9727(47)	0.447	3.000	3.065(39)
O1	3.00	2.2174(65)	68.576	-2.000	1.140(21)
O2	3.00	2.2276(64)	57.906	-2.000	1.099(20)
O3	3.00	2.2186(65)	53.198	-2.000	1.120(20)
O4	3.00	2.1833(69)	48.217	-2.000	1.226(23)
O5	3.00	2.2034(65)	55.495	-2.000	1.169(21)
O6	3.00	2.1810(65)	52.922	-2.000	1.238(22)
O7	2.00	1.9378(82)	0.004	-2.000	1.840(41)
O8	2.00	1.9306(81)	0.193	-2.000	1.877(41)
O9	2.00	2.1624(86)	0.739	-2.000	1.104(24)
O10	2.00	1.9414(82)	0.408	-2.000	1.823(40)
O11	2.00	1.9467(81)	0.054	-2.000	1.797(39)
O12	2.00	1.9285(88)	0.301	-2.000	1.888(45)
O13	1.00	1.7014(117)	0.000	-2.000	1.743(55)
O14	1.00	1.7266(115)	0.000	-2.000	1.628(50)
O15	1.00	1.7025(122)	0.000	-2.000	1.738(57)
O16	1.00	1.7043(129)	0.000	-2.000	1.730(60)
O17	1.00	1.7018(126)	0.000	-2.000	1.741(59)
O18	1.00	1.7077(123)	0.000	-2.000	1.714(57)
O19	1.00	1.7072(114)	0.000	-2.000	1.716(53)
O20	1.00	1.7069(119)	0.000	-2.000	1.717(55)

O21	1.00	1.7120(119)	0.000	-2.000	1.694(54)
O22	1.00	1.7087(118)	0.000	-2.000	1.709(55)
O23	1.00	1.7274(123)	0.000	-2.000	1.625(54)
O24	1.00	1.7163(124)	0.000	-2.000	1.674(56)

UV spectra of compound 1-5

It should be noted that the LMCT and d-d bands of compounds **1-4** are very similar to each other. Herein we take compound **1** as example; these bands of compound **1** are shown in Figures S2 and S3. 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 μ_3-OH π t_{2g} to metal-center Mo^{6+} t_{2g}* charge transfer transition (LMCT) ,this LMCT band of compound **1** shows slight hypsochromic shift to 229 nm (Figure S2), 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^{3+} which resulting in the forming of pink colour. Similar hypsochromic shift phenomenon is observed at 531 nm (Figure S3).The UV spectra between δ and χ isomers of single-side triol functionalized $\{[RC(CH_2O)_3]CrMo_6O_{18}(OH)_3\}^{3-}$ derivatives were very similar[].The hypsochromic shift is observed in compound **5** where LMCT band locates at 211 nm and *d-d* transition absorption is at 464 nm (see Figure S4 and S5).

bond lengths (Å)			
Mo_3-(μ_2-O_9) 2.182	Mo_4-(μ_2-O_{10}) 1.954	Mo_1-(μ_3-O_1) 2.352	Mo_5-(μ_3-O_4) 2.276
Mo_4-(μ_2-O_9) 2.143	Mo_5-(μ_2-O_{10}) 1.929	Mo_6-(μ_3-O_1) 2.343	Mo_6-(μ_3-O_4) 2.304
Mo_1-(μ_2-O_7) 1.937	Mo_5-(μ_2-O_{11}) 1.951	Mo_2-(μ_3-O_2) 2.369	Mo_1-(μ_3-O_5) 2.315
Mo_2-(μ_2-O_7) 1.939	Mo_6-(μ_2-O_{11}) 1.943	Mo_3-(μ_3-O_2) 2.324	Mo_2-(μ_3-O_5) 2.323
Mo_2-(μ_2-O_8) 1.921	Mo_1-(μ_2-O_{12}) 1.917	Mo_4-(μ_3-O_3) 2.316	Mo_3-(μ_3-O_6) 2.271
Mo_3-(μ_2-O_8) 1.939	Mo_6-(μ_2-O_{12}) 1.939	Mo_5-(μ_3-O_3) 2.350	Mo_4-(μ_3-O_6) 2.314

Table S1. Selected bond lengths (Å) of the cluster anion for compound **6**

FigS1.The IR spectra of compounds **1-5** and the single side triol functionalized δ isomers of $\{[RC(CH_2O)_3]CrMo_6O_{18}(OH)_3\}^{3-}$(R=$NH_2$, CH_3, C_2H_5, CH_2OH)

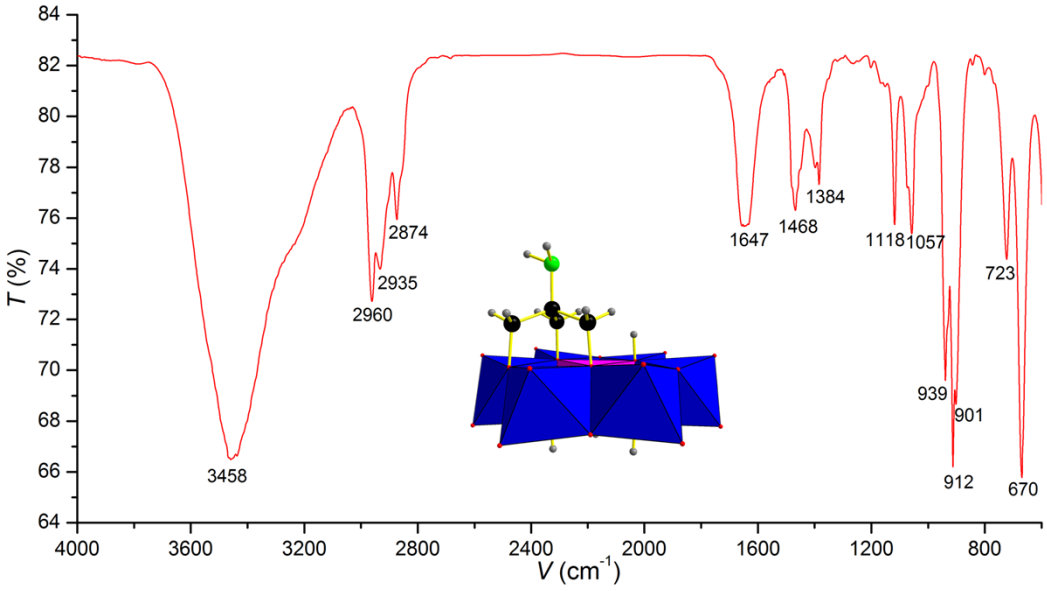

Fig S1a. IR spectrum of compound **1:** χ isomers of $\{[H_2NC(CH_2O)_3]CrMo_6O_{18}(OH)_3\}^{3-}$

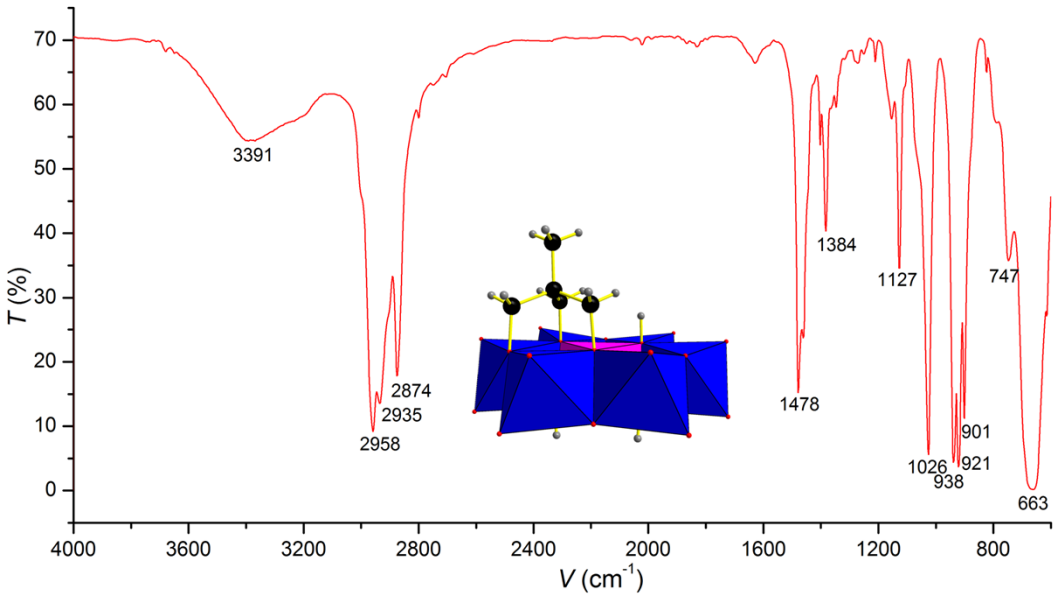

Fig S1b. IR spectrum of compound **2:** χ isomers of $\{[H_3CC(CH_2O)_3]\ CrMo_6O_{18}(OH)_3\}^{3-}$

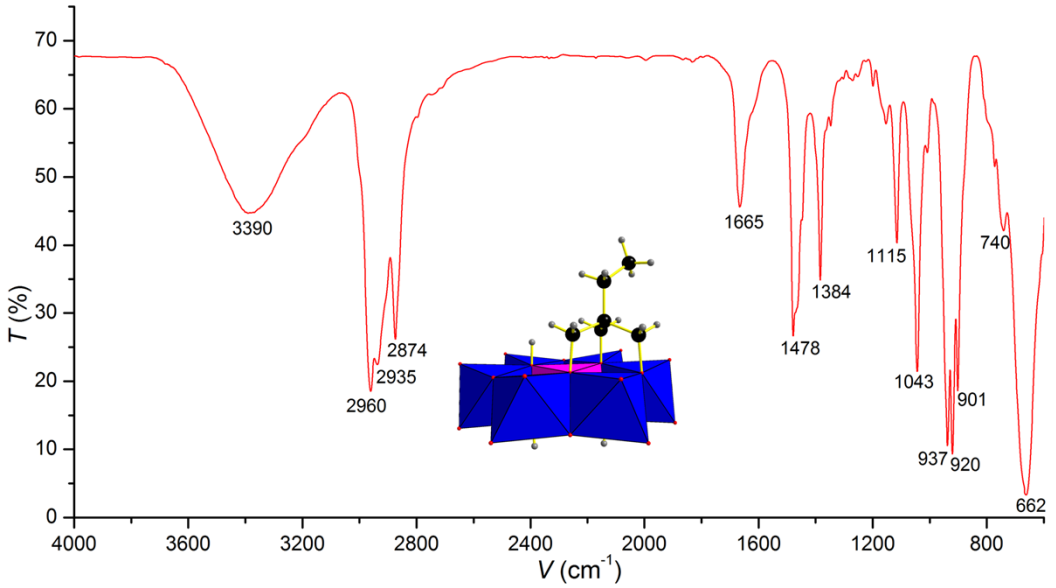

Fig S1c. IR spectrum of compound **3:** χ isomers of $\{[H_5C_2C(CH_2O)_3]\ CrMo_6O_{18}(OH)_3\}^{3-}$

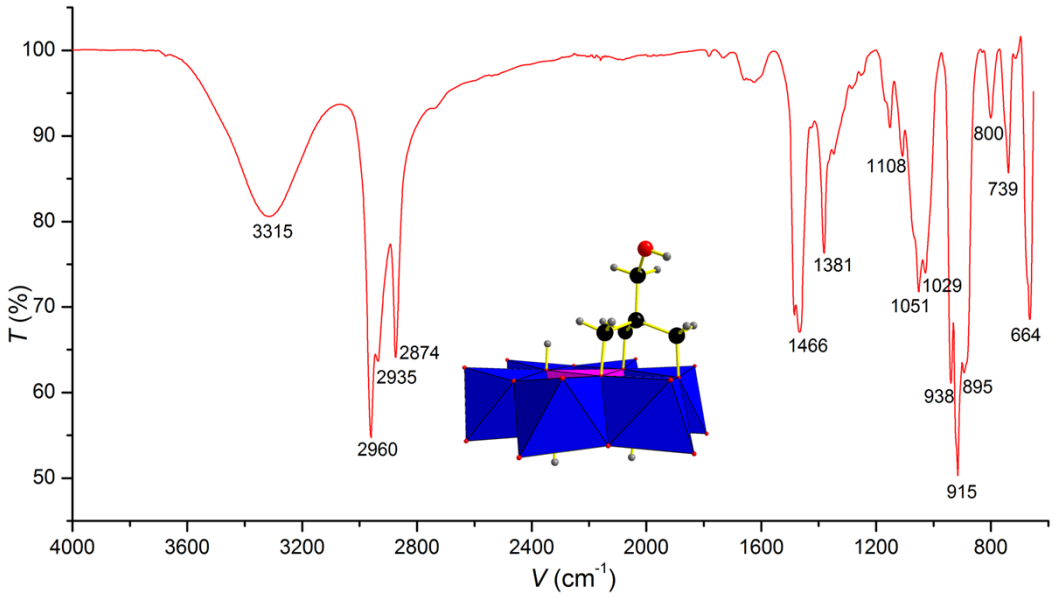

Fig S1d. IR spectrum of compound **4:** χ isomers of $\{[HOH_2CC(CH_2O)_3]\ CrMo_6O_{18}(OH)_3\}^{3-}$

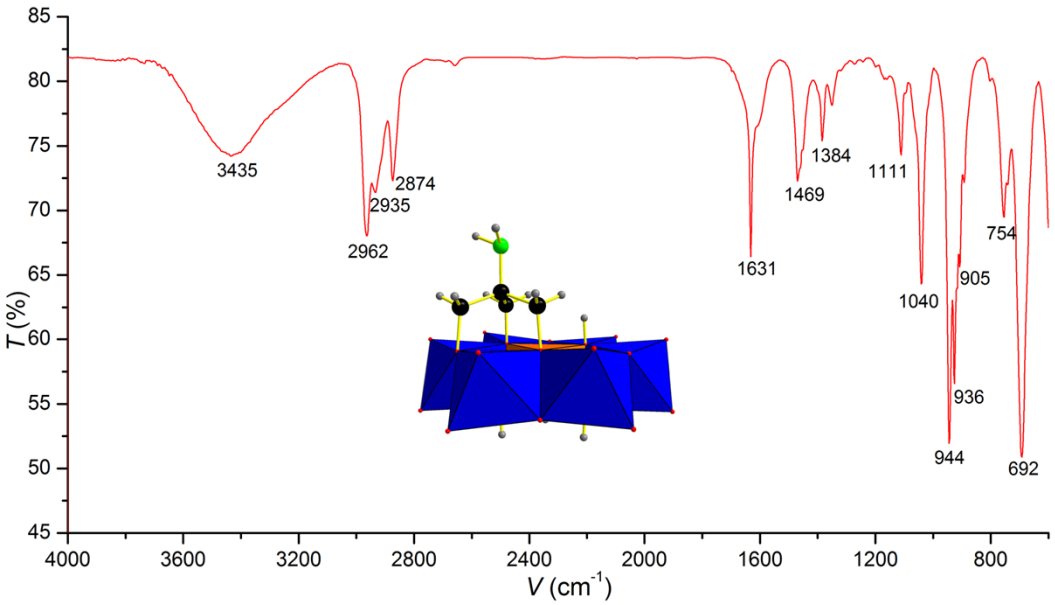

Fig S1e. IR spectrum of compound **5:** χ isomers of $\{[H_2NC(CH_2O)_3]MnMo_6O_{18}(OH)_3\}^{3-}$

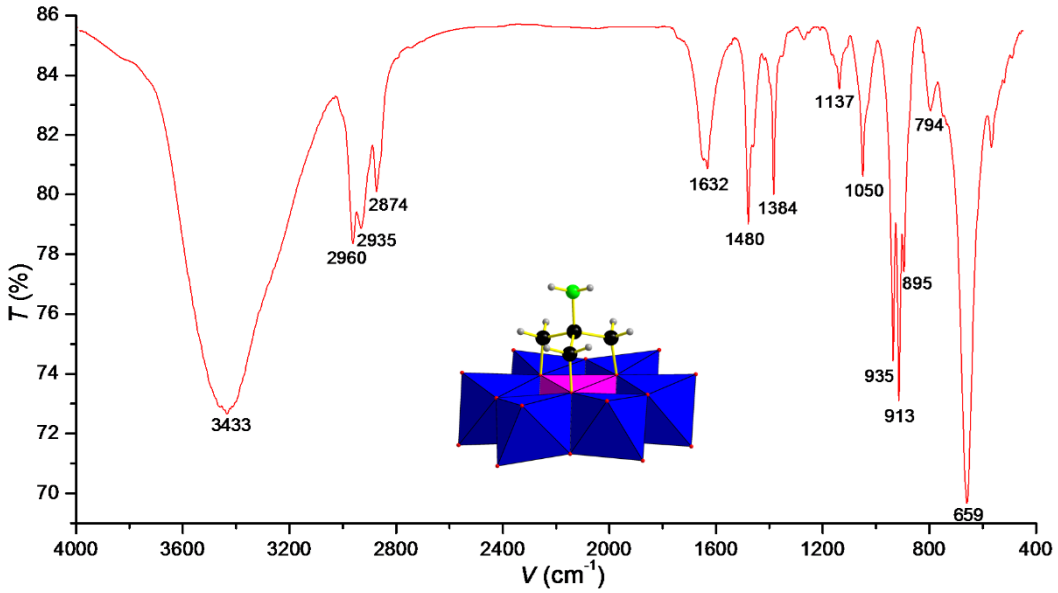

Fig S1f. IR spectrum of δ isomers of $\{[H_2NC(CH_2O)_3]CrMo_6O_{18}(OH)_3\}^{3-}$

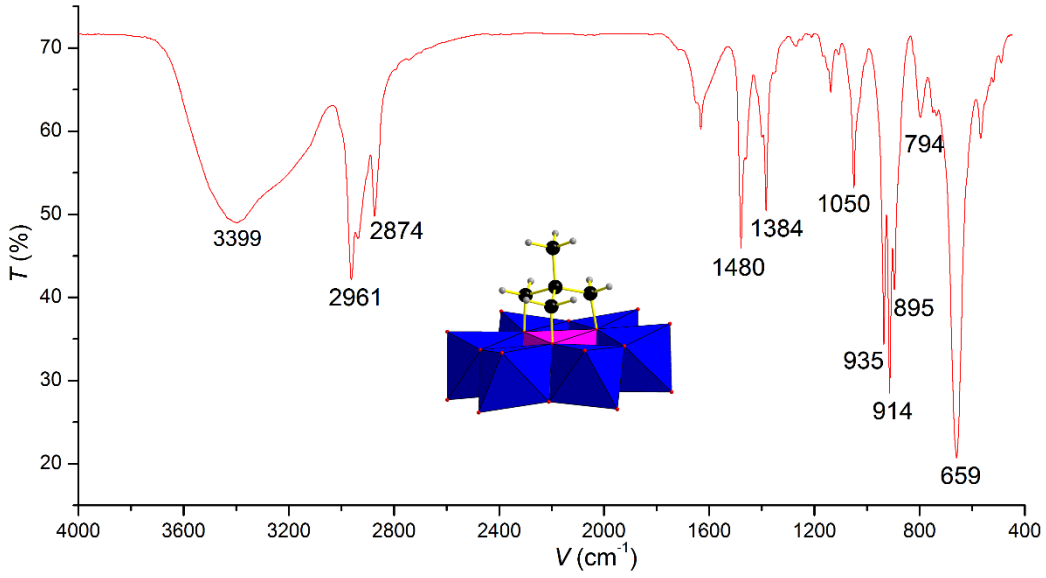

Fig S1g. IR spectrum of δ isomers of $\{[H_3CC(CH_2O)_3]\ CrMo_6O_{18}(OH)_3\}^{3-}$

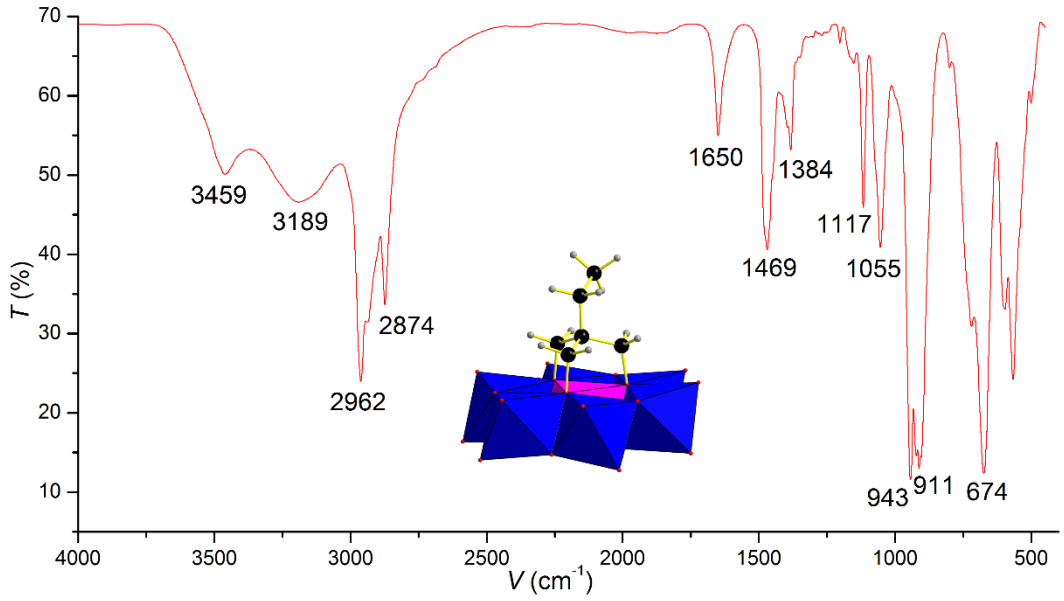

Fig S1h. IR spectrum of δ isomers of $\{[H_5C_2C(CH_2O)_3]\ CrMo_6O_{18}(OH)_3\}^{3-}$

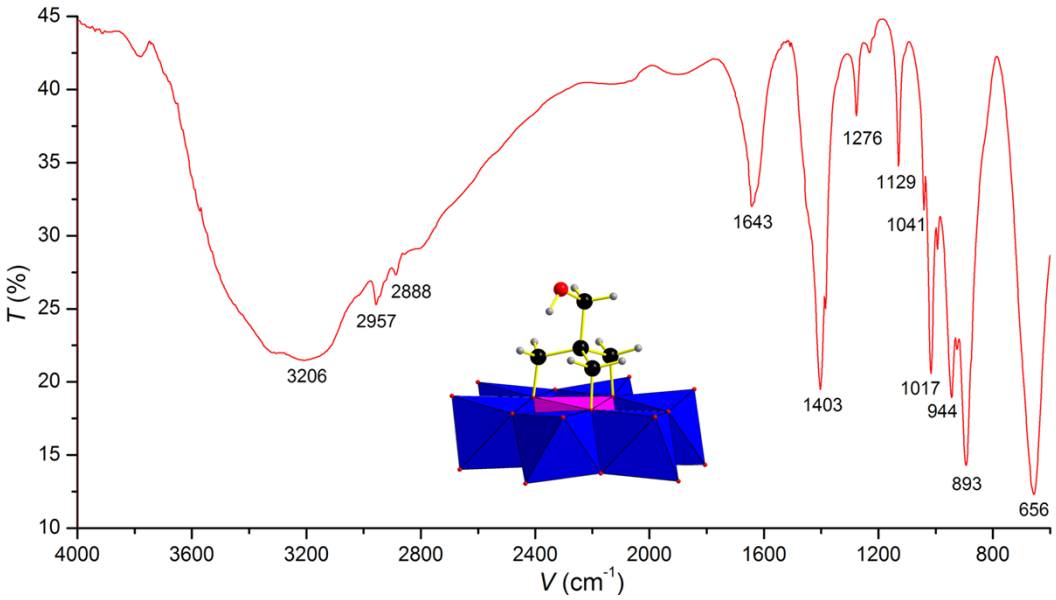

Fig S1i. IR spectrum of δ isomers of $\{[HOH_2CC(CH_2O)_3]\ CrMo_6O_{18}(OH)_3\}^{3-}$

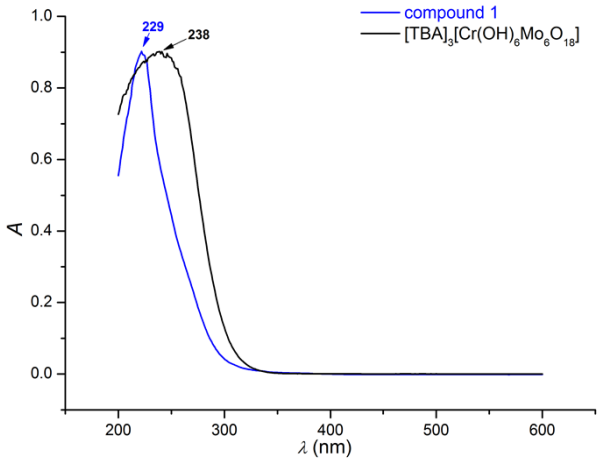

Fig S2. UV/Vis LMCT spectra of $[TBA]_3[CrMo_6O_{18}(OH)_6]$ and compounds **1**

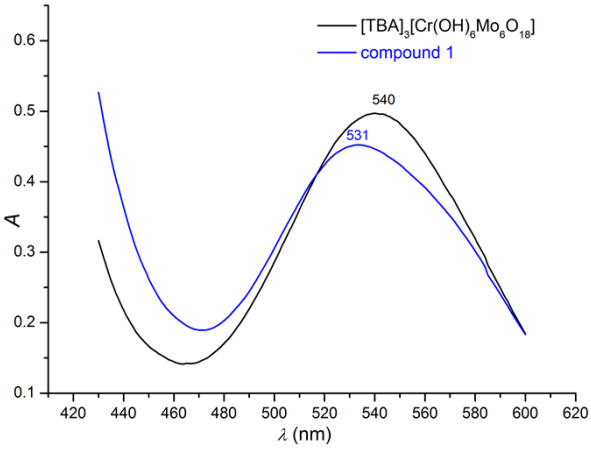

Fig S3. UV/Vis d-d transition spectra of $[TBA]_3[CrMo_6O_{18}(OH)_6]$ and compounds **1**

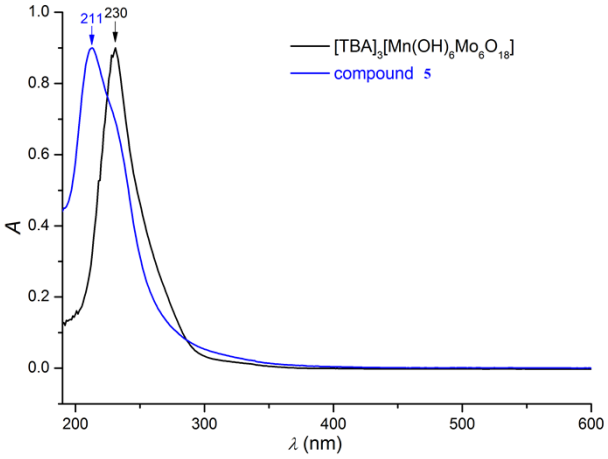

Figure S4. UV/Vis LMCT spectra of $[TBA]_3[MnMo_6O_{18}(OH)_6]$ and compounds **5**

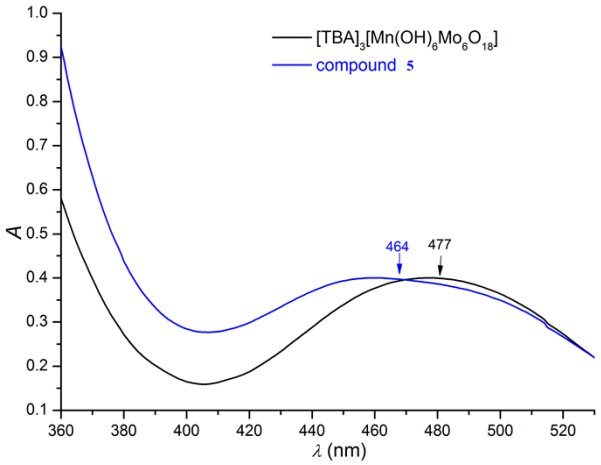

Figure S5. UV/Vis d-d transition spectrum of $[TBA]_3[MnMo_6O_{18}(OH)_6]$ and compounds **5**

Figure S6. The ^{13}C NMR spectra of compounds **1-5** and the single side triol functionalized δ isomers of $\{[RC(CH_2O)_3]CrMo_6O_{18}(OH)_3\}^{3-}$(R=$NH_2$, CH_3, C_2H_5, CH_2OH)

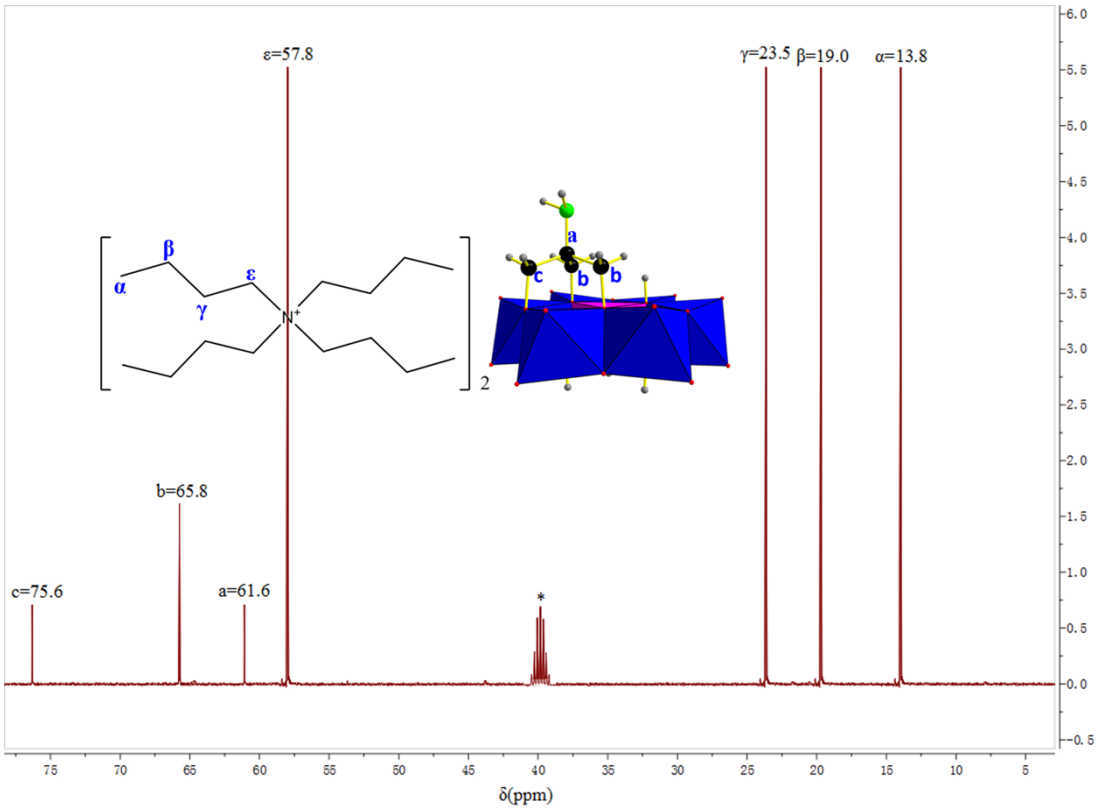

Figure S6a. The ^{13}C NMR spectra of compounds **1:** χ isomers of $\{[H_2NC(CH_2O)_3]CrMo_6O_{18}(OH)_3\}^{3-}$

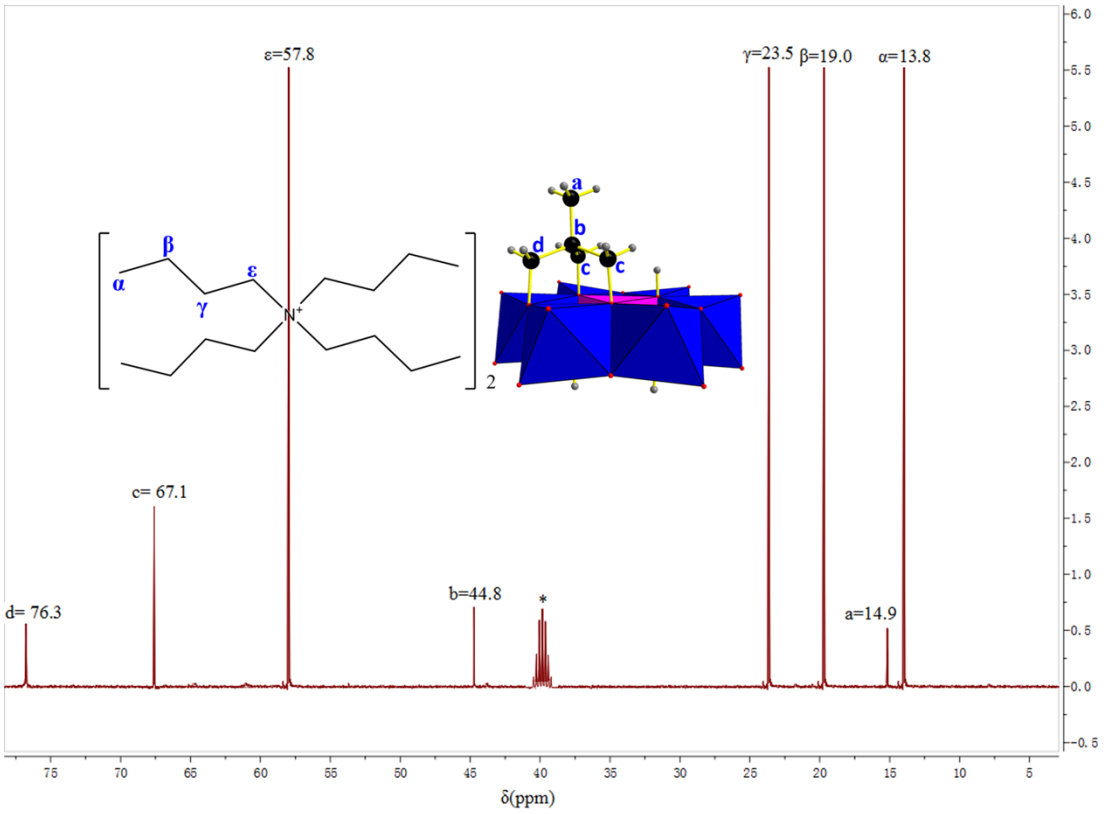

Figure S6b. The ^{13}C NMR spectra of compounds **2:** χ isomers of $\{[H_3CC(CH_2O)_3]CrMo_6O_{18}(OH)_3\}^{3-}$

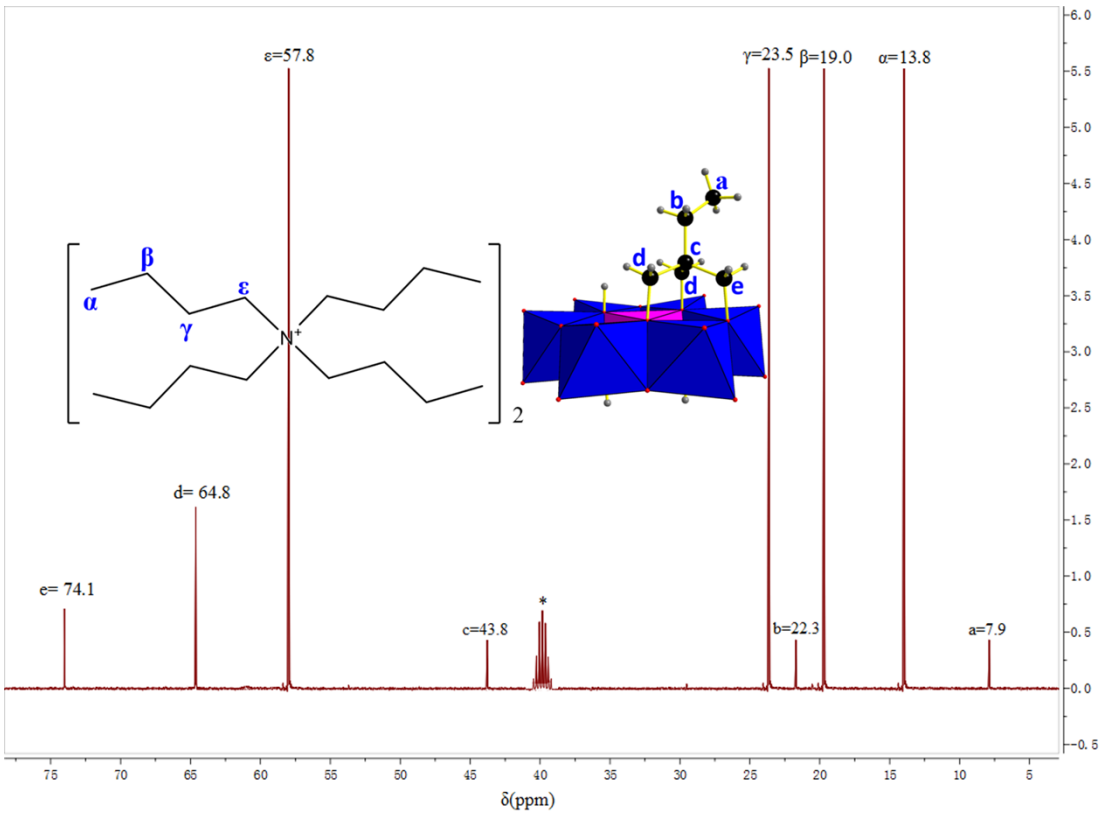

Figure S6c. The ^{13}C NMR spectra of compounds **3:** χ isomers of $\{[H_5C_2C(CH_2O)_3]CrMo_6O_{18}(OH)_3\}^{3-}$

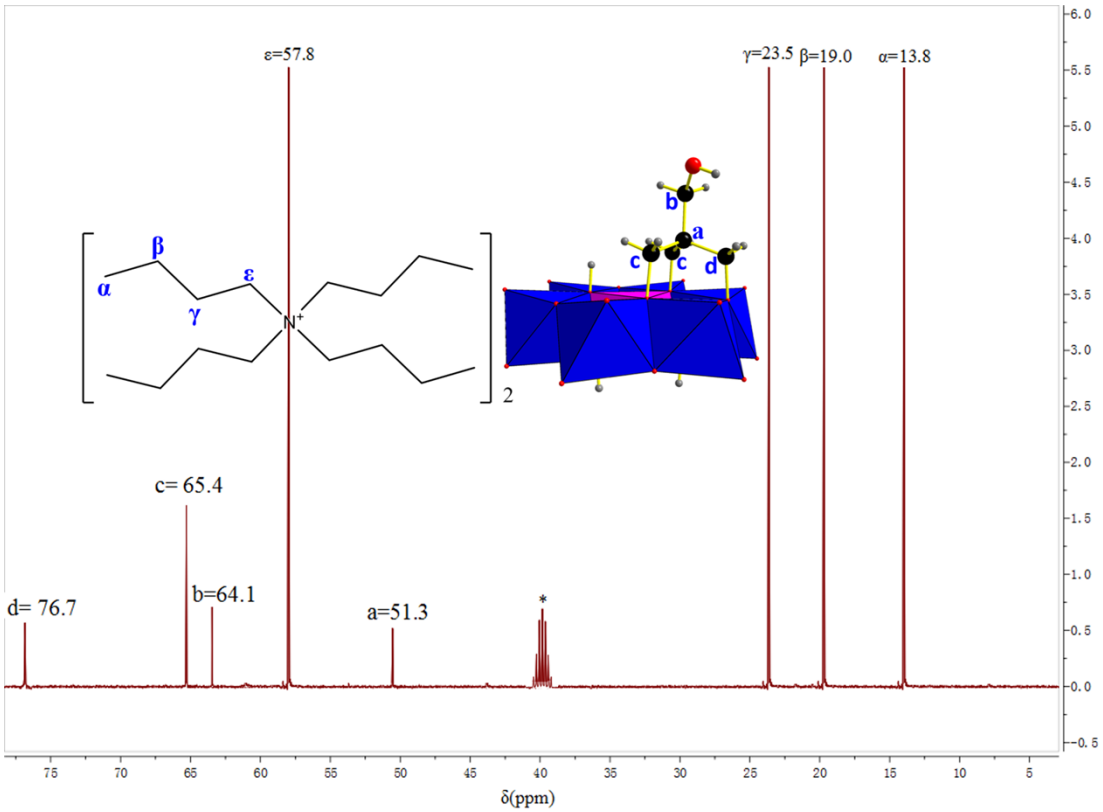

Figure S6d. The ^{13}C NMR spectra of compounds **4:** χ isomers of $\{[HOH_2CC(CH_2O)_3]CrMo_6O_{18}(OH)_3\}^{3-}$

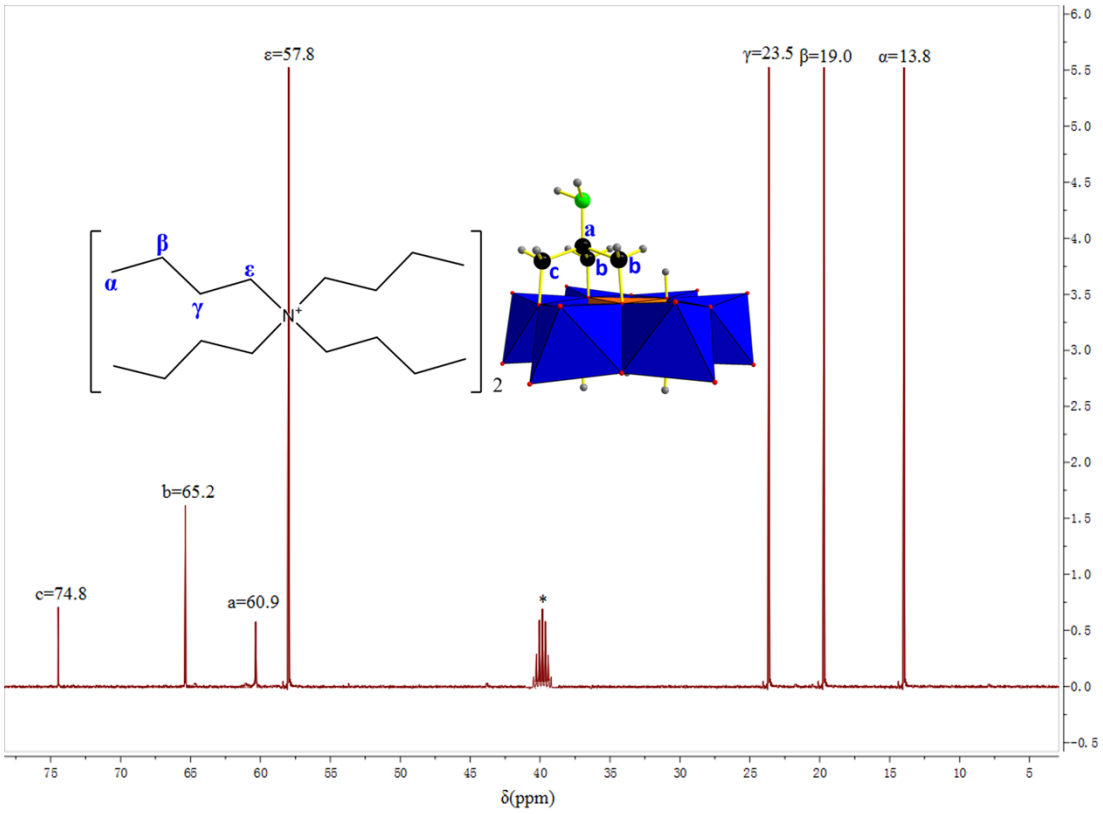

Figure S6e. The ^{13}C NMR spectra of compounds **5:** χ isomers of $\{[H_2NC(CH_2O)_3]MnMo_6O_{18}(OH)_3\}^{3-}$

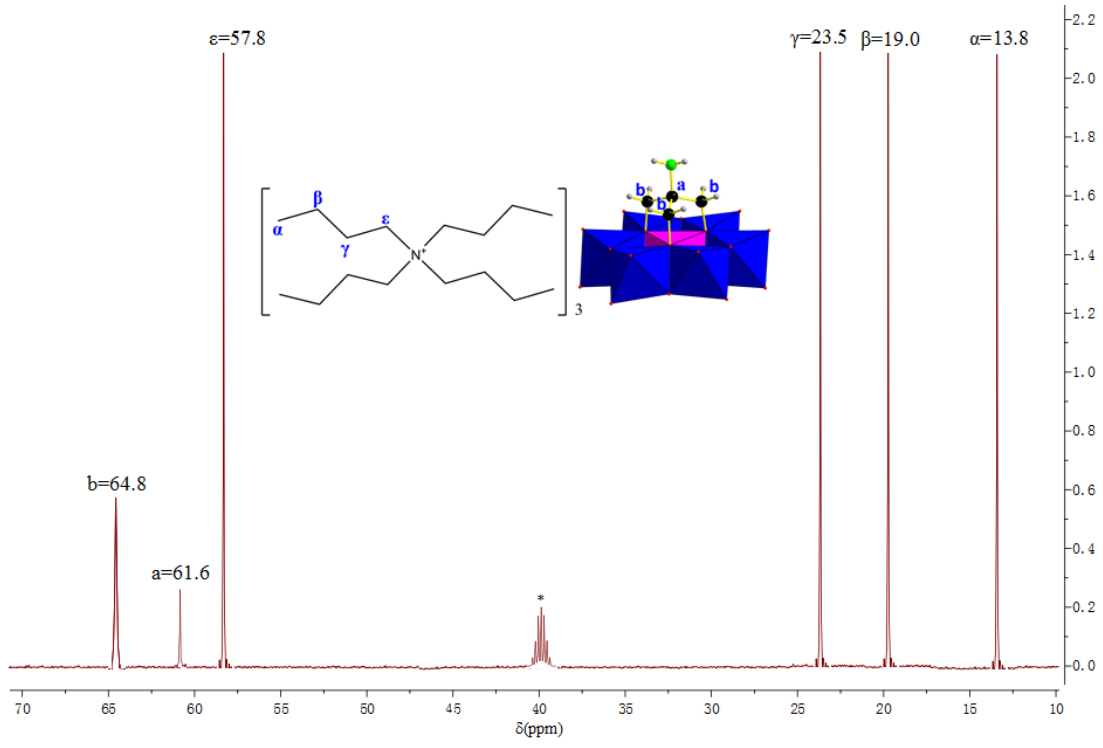

Figure S6f. The ^{13}C NMR spectra of δ isomers of $\{[H_2NC(CH_2O)_3]CrMo_6O_{18}(OH)_3\}^{3-}$

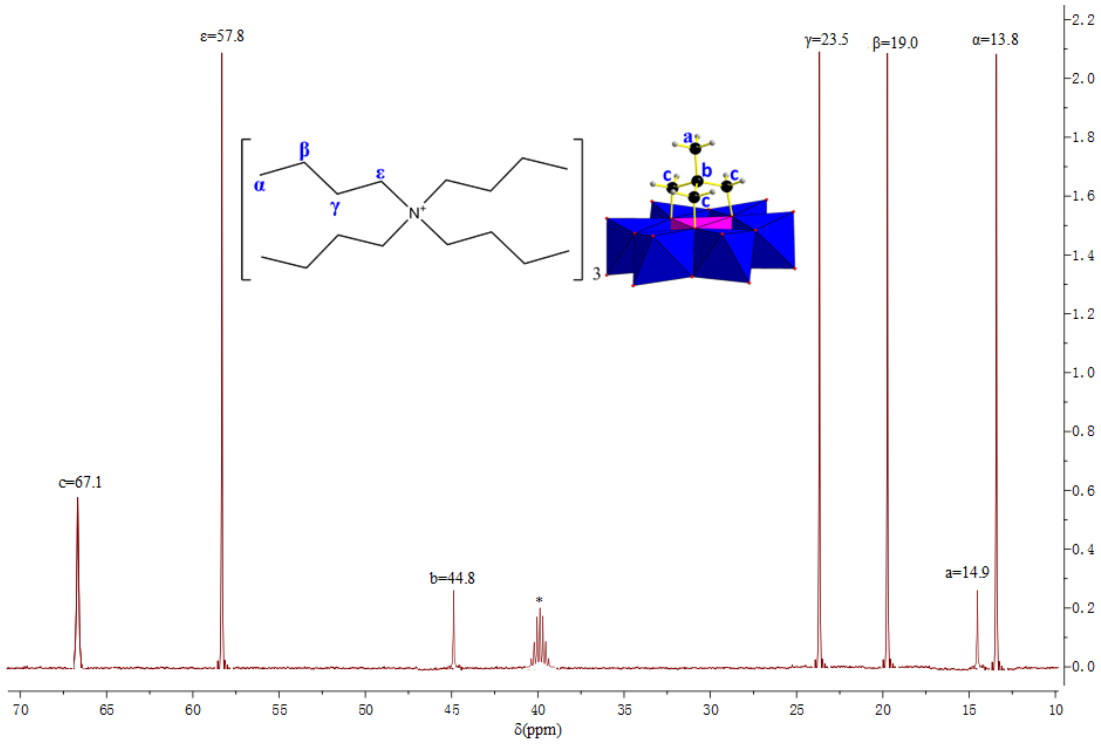

Figure S6g. The ^{13}C NMR spectra of δ isomers of $\{[H_3CC(CH_2O)_3]\ CrMo_6O_{18}(OH)_3\}^{3-}$

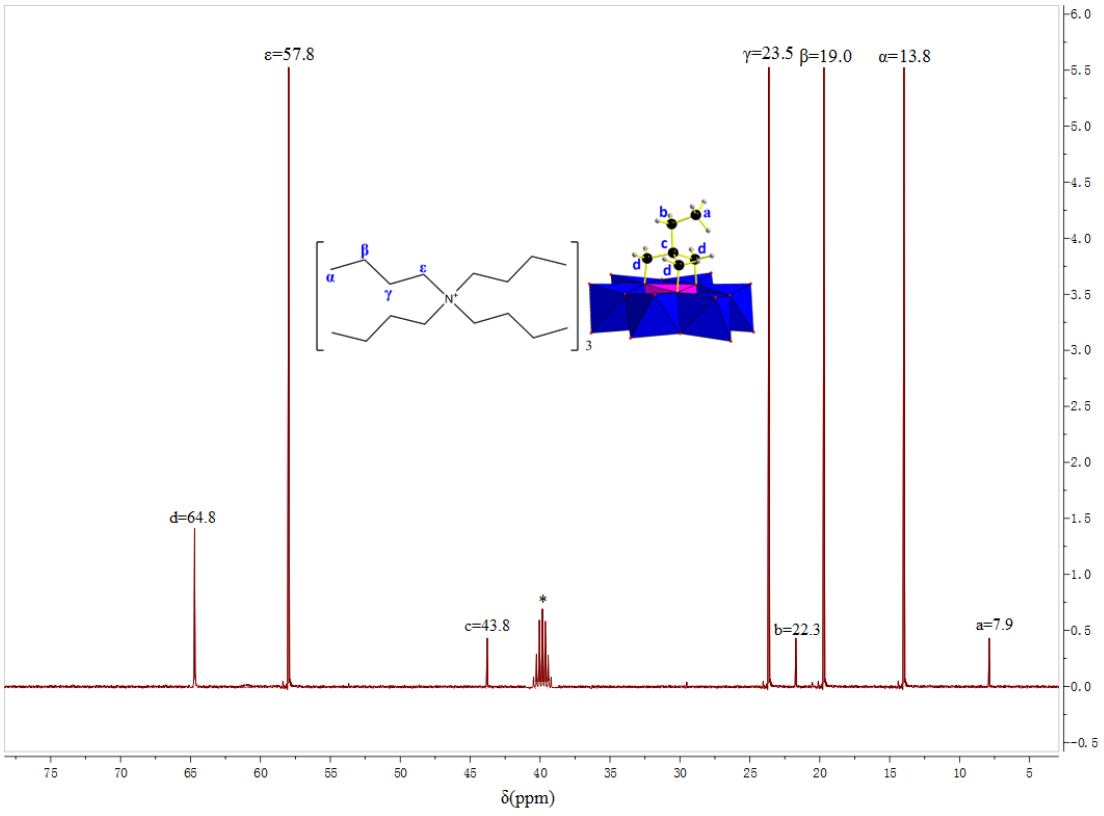

Figure S6h. The ^{13}C NMR spectra of δ isomers of $\{[H_5C_2C(CH_2O)_3]\ CrMo_6O_{18}(OH)_3\}^{3-}$

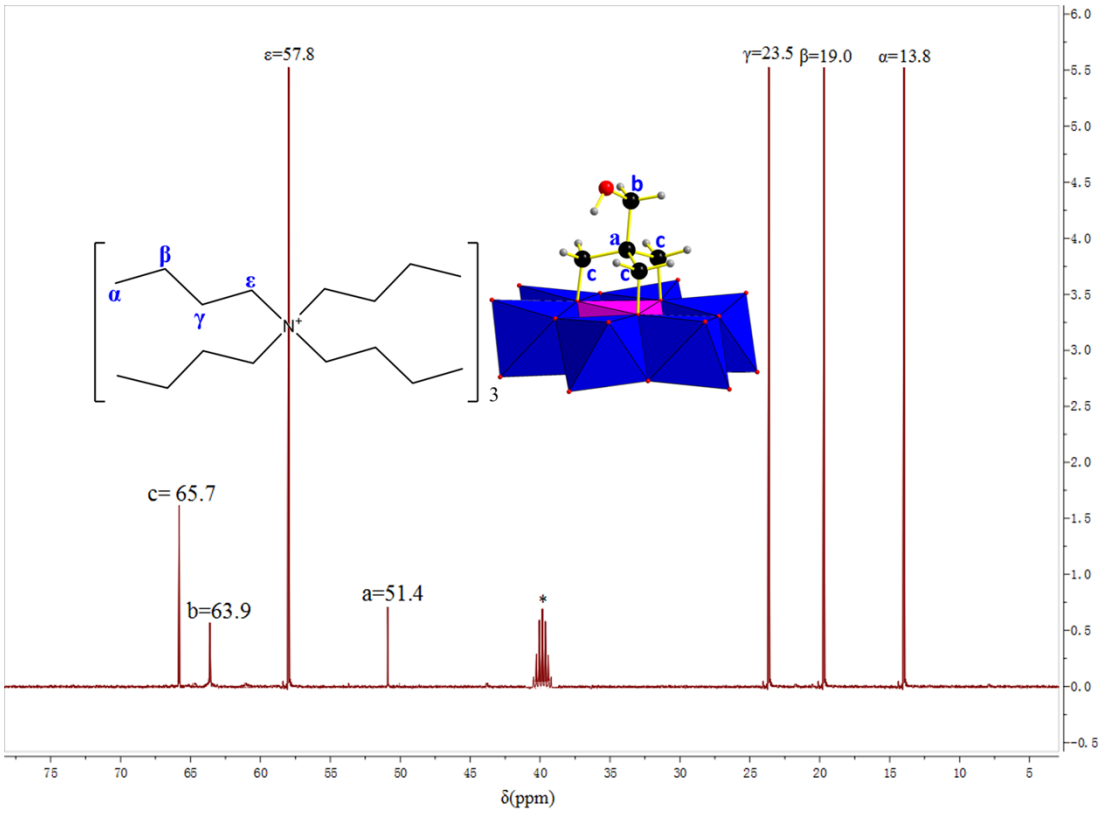

Figure S6i. The ^{13}C NMR spectra of δ isomers of $\{[HOH_2CC(CH_2O)_3]\ CrMo_6O_{18}(OH)_3\}^{3-}$

Fig S7. ESI mass spectrometry of compounds **1-5**

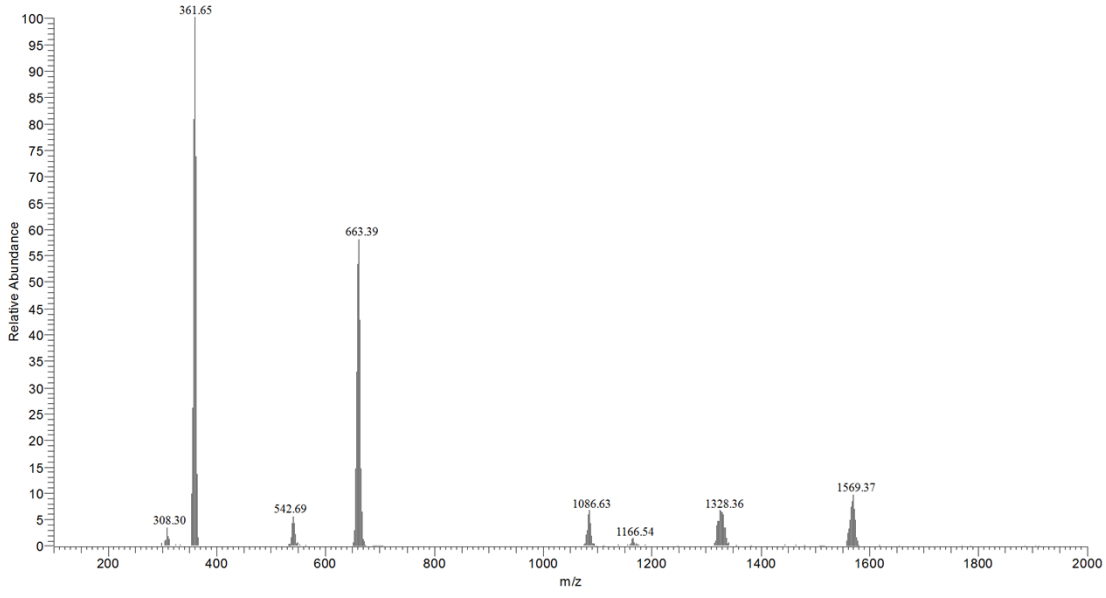

Fig S7a ESI mass spectrometry of compounds **1**

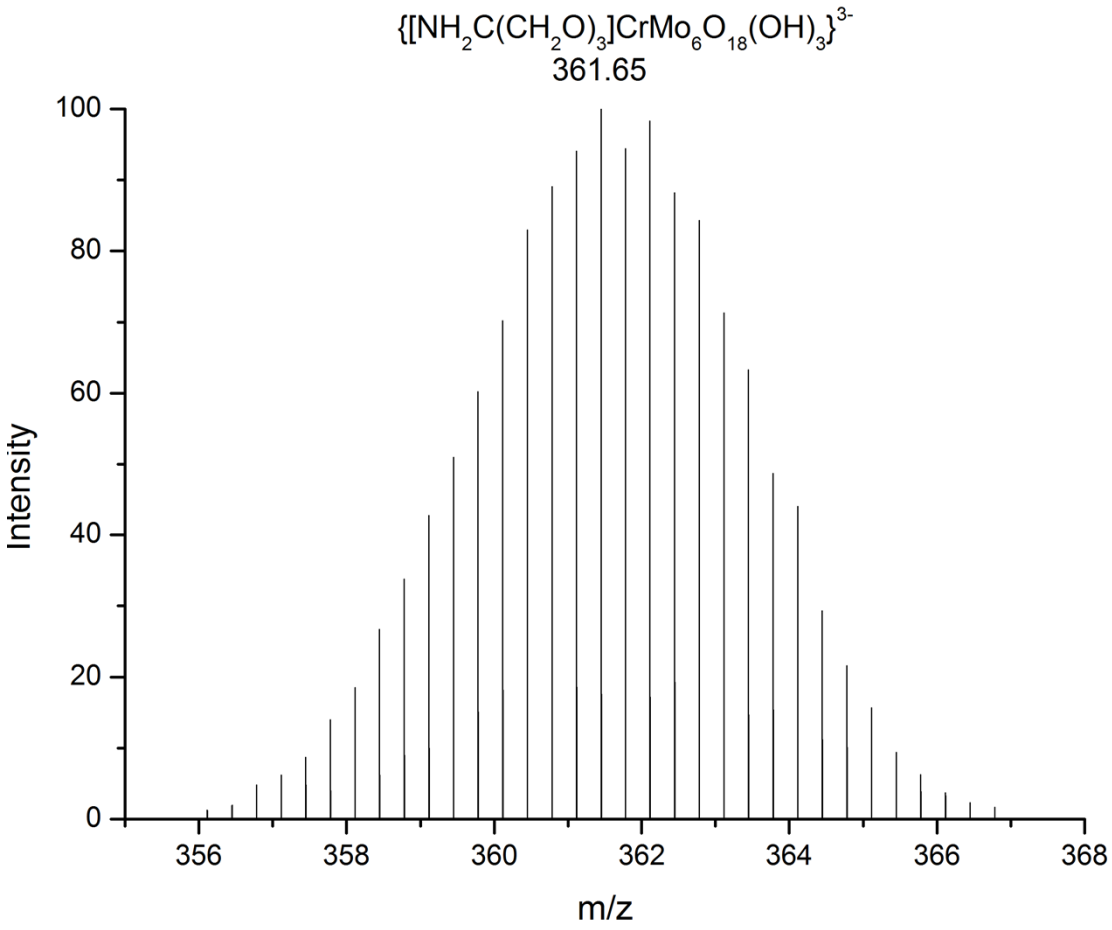

Fig S7b.ESI-MS of compound **1**(100% intensity peak in original size)

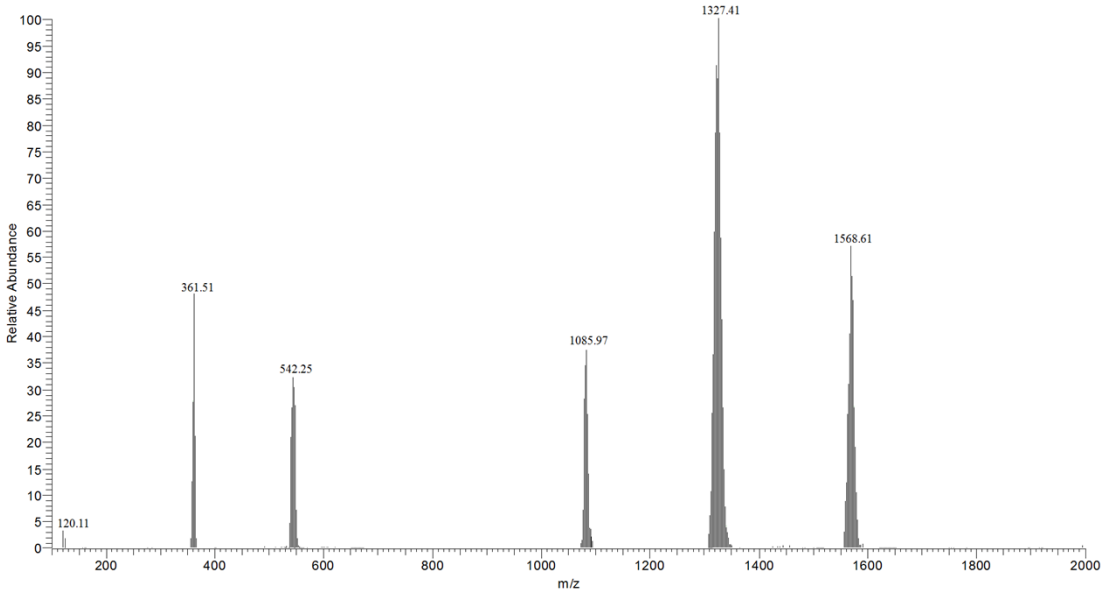

Fig S7c ESI mass spectrometry of compounds **2**

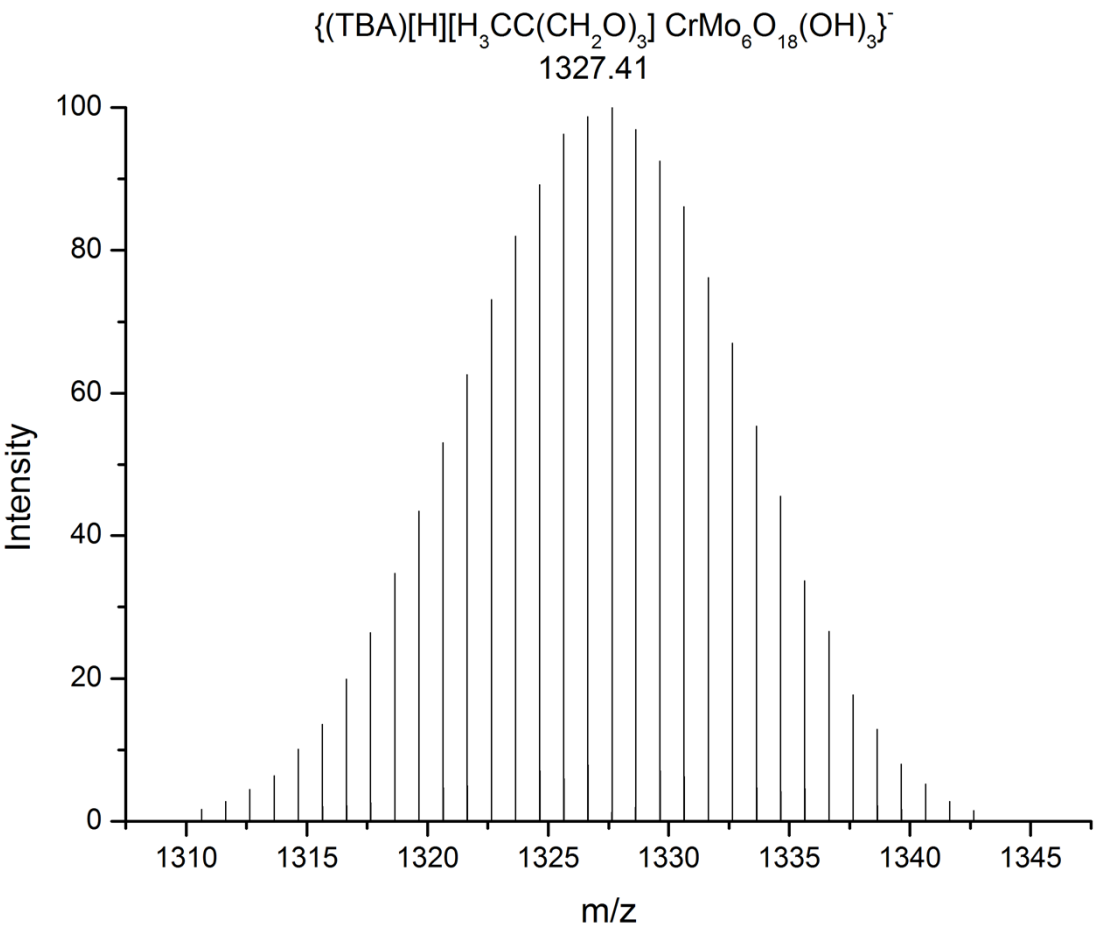

Fig S7d.ESI-MS of compound **2**(100% intensity peak in original size)

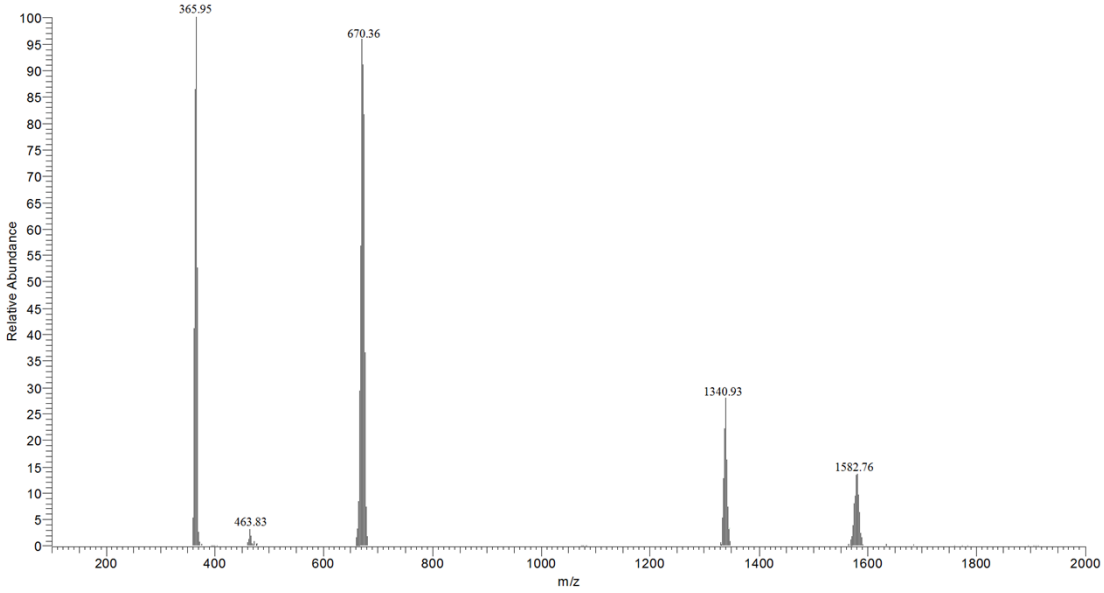

Fig S7e ESI mass spectrometry of compounds **3**

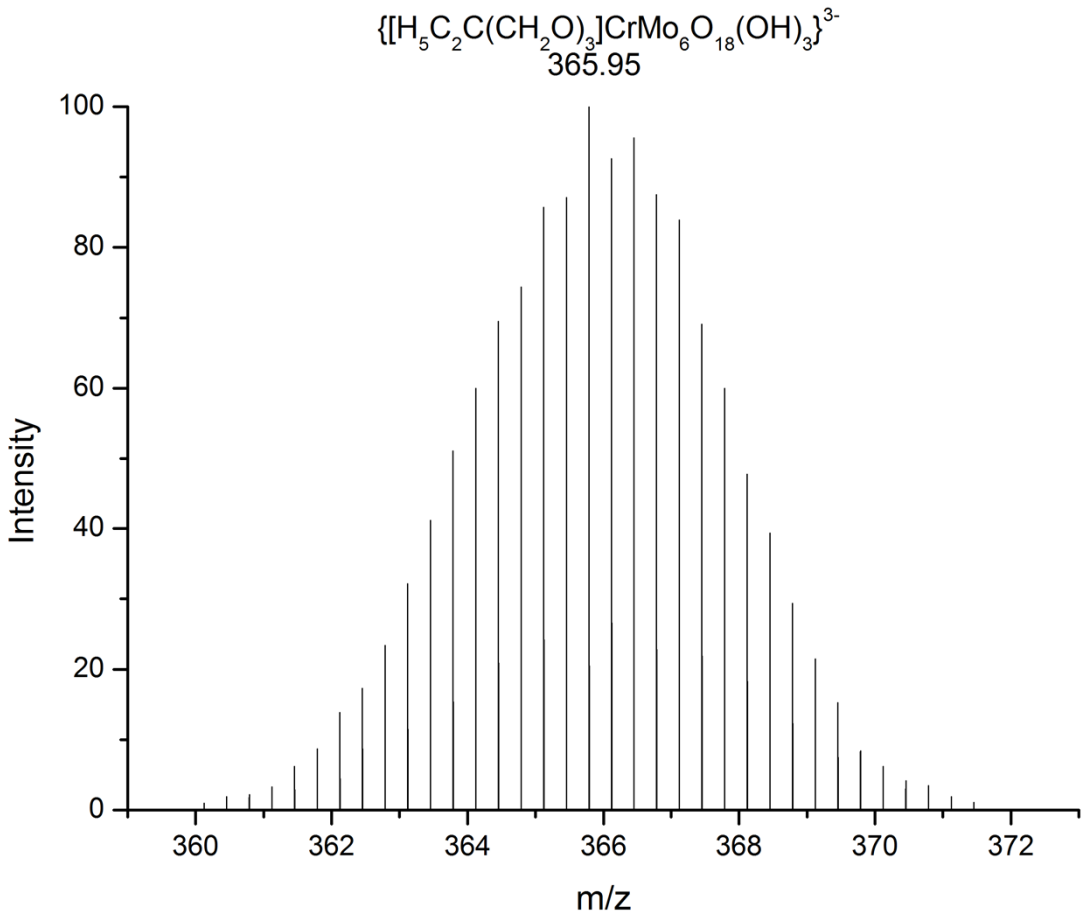

Fig S7f.ESI-MS of compound **3**(100% intensity peak in original size)

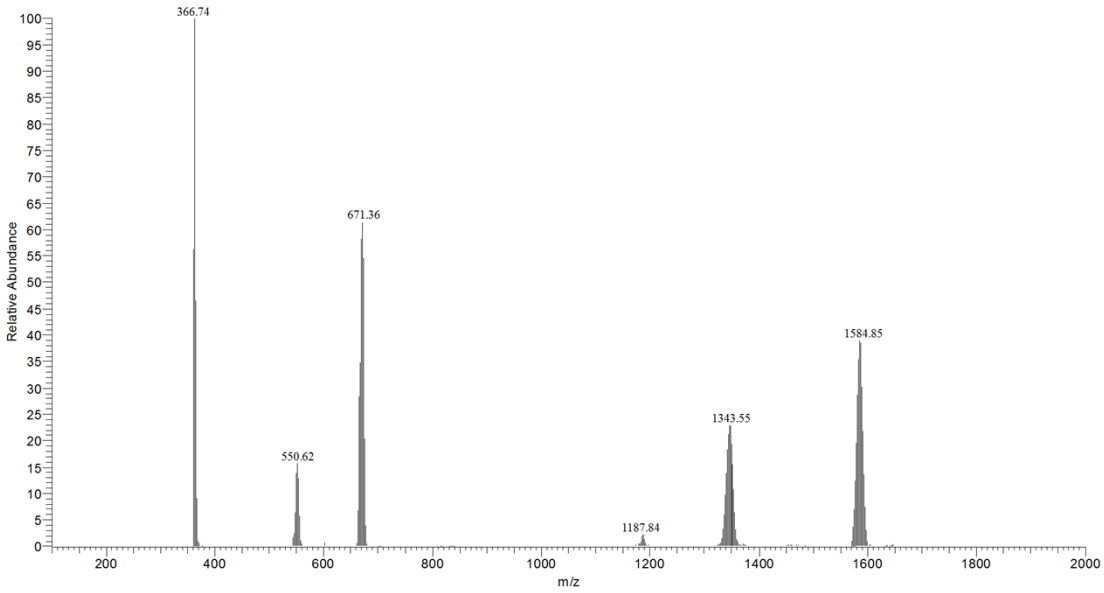

Fig S7g ESI mass spectrometry of compounds **4**

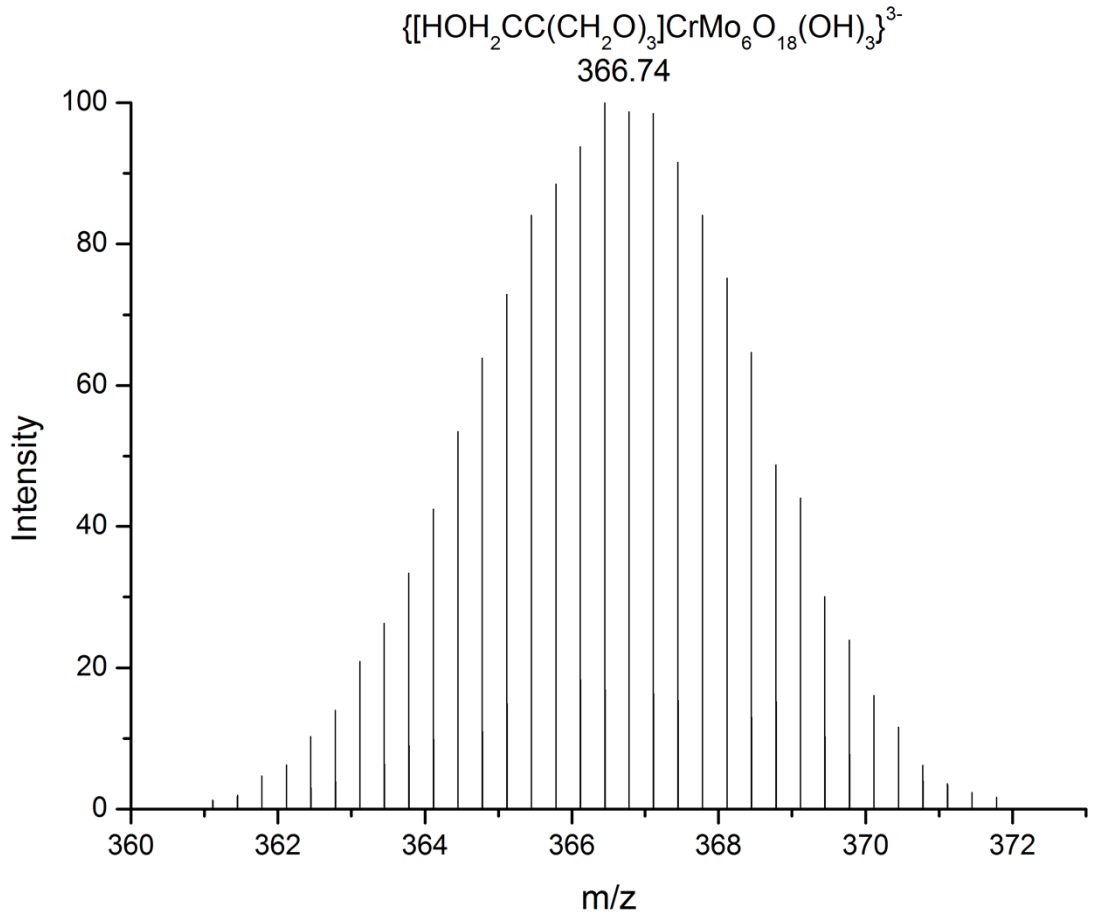

Fig S7h.ESI-MS of compound **4**(100% intensity peak in original size)

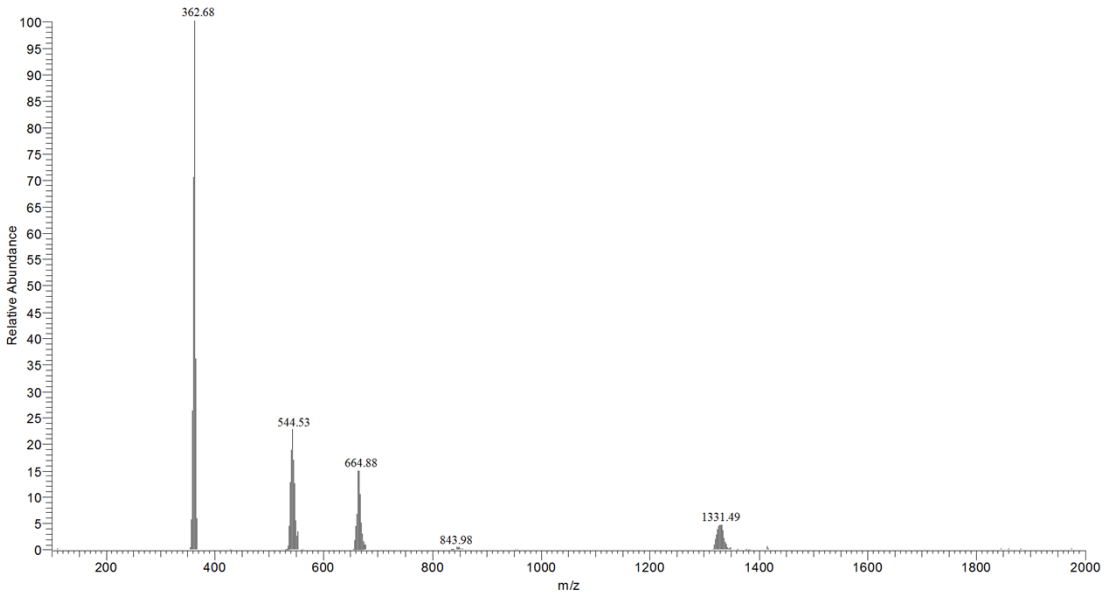

Fig S7i ESI mass spectrometry of compounds **5**

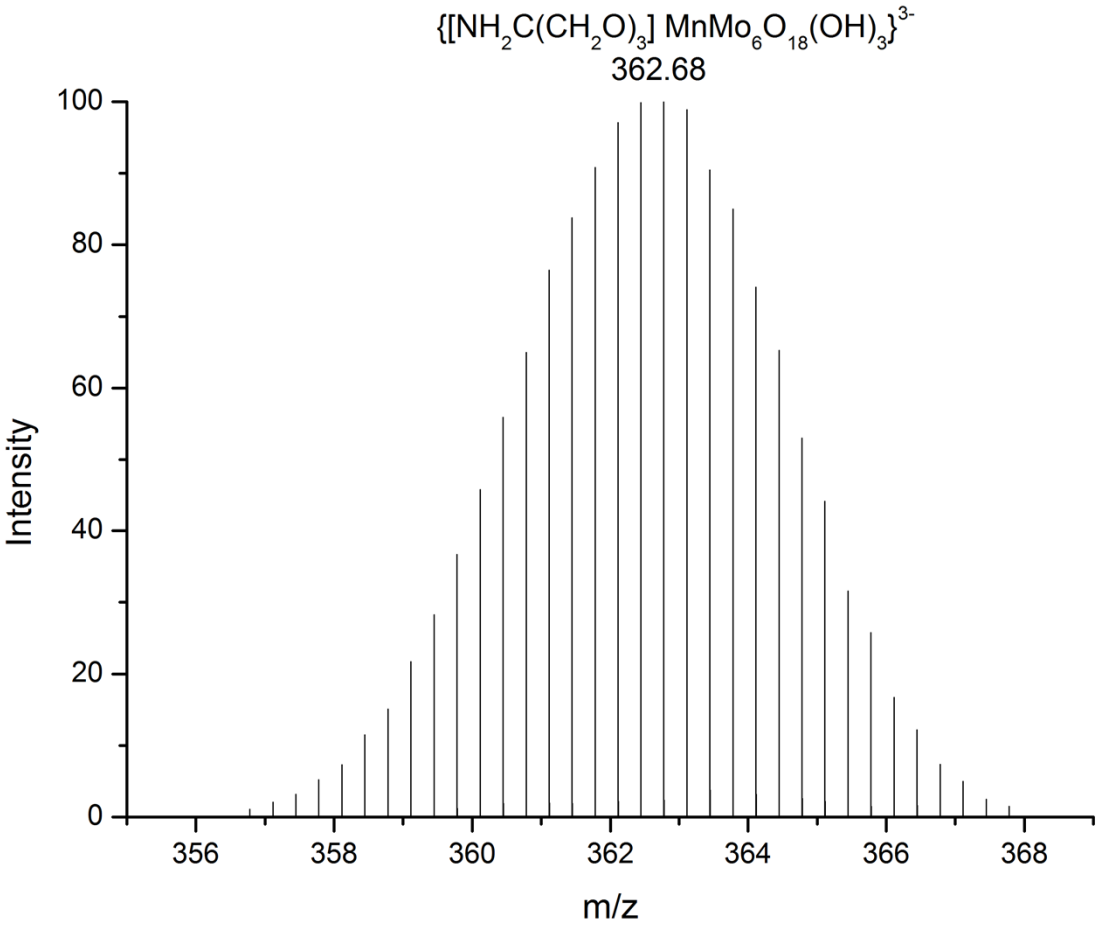

Fig S7j.ESI-MS of compound **5**(100% intensity peak in original size)

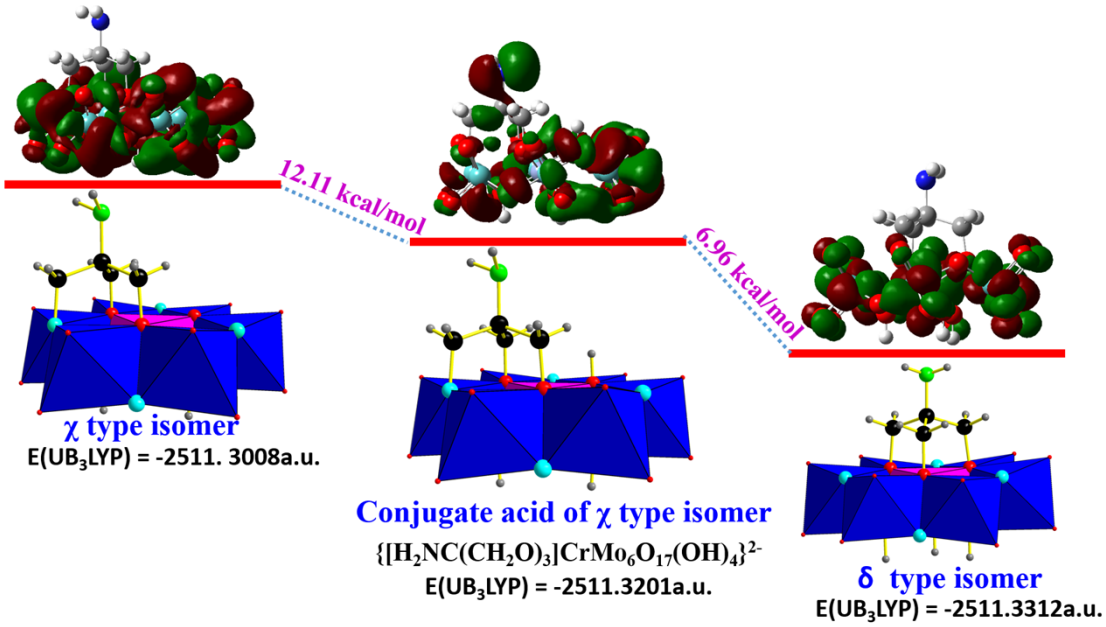

Figure S8. The energy E(UB_3LYB) and HUMO, LUMO Molecular Orbital(MO) of δ and χ isomer and the corresponding conjugate acid of χ isomer.

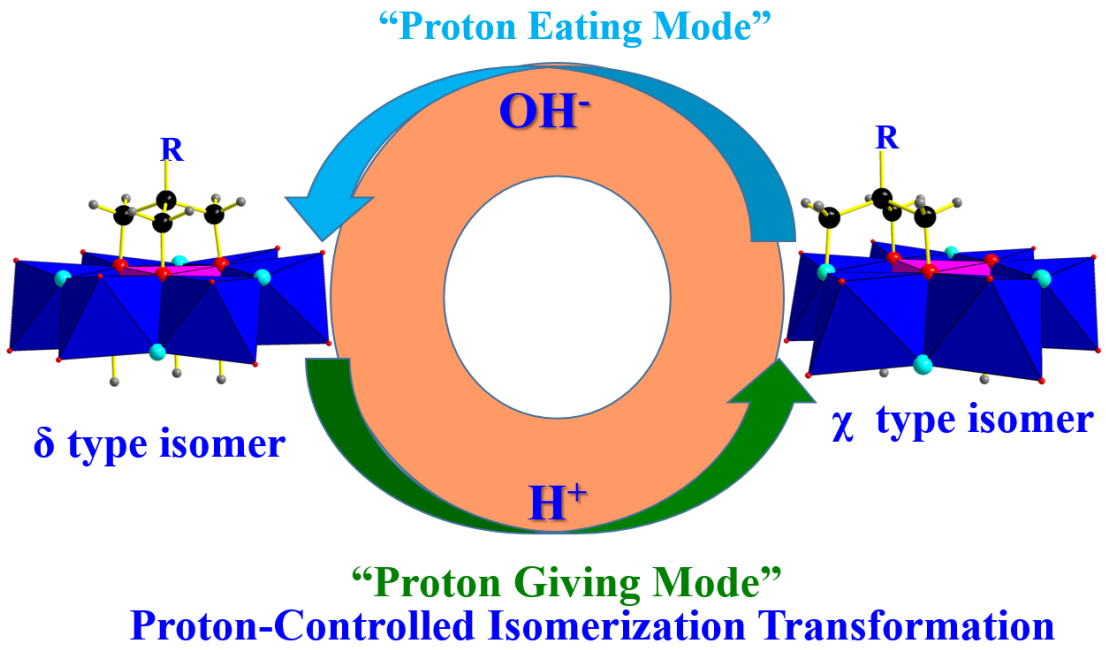

Figure S9. The proton-Controlled isomerization transformation cycling between δ and χ isomer controlled by proton switch

Reference:

1 K. Nomiya, T. Takahashi, T. Shirai and M. Miwa, *Polyhedron*, 1987, **6**, 213.

2 G. M. Sheldrick, *Acta Crystallogr A*, 2008, **64**, 112.

3 O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, *J Appl Crystallogr*, 2009, **42**, 339.