Electronic Supplementary Material

Nucleophilic Substitution Reaction for Rational

Post-Functionalization of Polyoxometalates

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1. Materials and Methods

General. All syntheses and manipulations were performed in air, using ordinary organic synthetic apparatus and techniques. Acetonitrile was dried by refluxing in the presence of CaH₂ and distilled prior to use. $(Bu_4N)_4[\alpha-Mo_8O_{26}]$ was conveniently prepared by the addition of Bu_4NBr to an aqueous solution of $(NH_4)_6Mo_7O_{24}$ •4H₂O, from which the product immediately precipitates. The product was collected by filtration, washed successively with water for several times, and was dried by evaporating the water in 80 °C for about 24 h. The structure of $(Bu_4N)_4[\alpha-Mo_8O_{26}]$ was confirmed by elemental analysis and X-ray single-crystal structure determination.¹ The 3-chloropropylamine hydrochloride, KI,

AgNO₃ and cyclohexene were obtained from commercial sources and were used as received. Elemental analyses were performed by Analysis and Test Center of Peking University. The other characterizations were performed in Analysis Center of Tsinghua University. The ¹H-NMR spectra were recorded on a JOEL JNM ECA-300 spectrometer operating at 300.17 MHz and 75.41 MHz with D₂O inside using the standard pulse sequence at the room temperature. The infrared (IR) spectrum was recorded within the 450-4000cm⁻¹ regions on a spectrum one FT-IR spectrometer (PERKINELMER) using KBr pellets. UV-vis spectra were carried out on an UV-2100s UV-VISIBLE RECORDING Spectrophotometer (Shimadzu). ESI-MS spectra were obtained by using a Finnigan LCQ Deca XP Plus ion trap mass spectrometer (San Jose, CA), and all experiments were carried out in the negative-ion mode.

Synthesis of (Bu₄N)₂[Mo₆O₁₈NCH₂CH₂CH₂Cl], 1

A typical procedure is as follow: A mixture of $(Bu_4N)_4[\alpha-Mo_8O_{26}]$ (2.14g, 1.0 mmol), DCC (0.43g, 2.1 mmol), 3-chloropropylamine hydrochloride (0.17g, 1.33 mmol) and cyclohexene(0.22g, 2.68 mmol) was stirred and heated in anhydrous acetonitrile (10 mL). Such a reaction was maintained under reflux for about 1.5h. The color of the solution turned into green, then to black. After being cooled down to room temperature, the white precipitates were removed by filtration. While most of acetonitrile evaporated out, the resulting black mixture was obtained. The product was washed successively with ethanol and ethyl ether solution, and then was dissolved with acetone and ethanol (1+1). While most of solution evaporated out, the product precipitated from the filtrate as red crystals. The product was collected by filtration, washed successively with ethanol and ethyl ether for several times, and then recrystallized twice from a solution of acetone and ethanol (1+1), the product deposited as red crystals usually in about 70 % yield. Compound 1: (Bu₄N)₂[Mo₆O₁₈NCH₂CH₂CH₂Cl] (1) (70%) : Elemental analysis (%) calcd for C₃₅ H₇₈ Cl Mo₆ N₃ O₁₈ (1440.11): C 29.19, H 5.46, N 2.92; found: C 28.92, H 5.31, N 2.84. ¹H-NMR (300 MHz, d_6 -DSMO, 300K, ppm): $\delta = 0.94$ (t, 24 H, CH₃-, [Bu₄N]⁺), 1.32 (m, 16 H, -CH₂-, [Bu₄N]⁺), 1.56 $(m, 16 \text{ H}, -\text{CH}_2, [Bu_4N]^+), 2.13(m, 2 \text{ H}, -\text{CH}_2, [MoNCH_2CH_2CH_2CI]^{2-}), 3.17 (t, 16 \text{ H}, NCH_2, -1000 \text{ H})$ $[Bu_4N]^+)$, 3.88(t, 2 H, -CH₂Cl, $[MoNCH_2CH_2CH_2Cl]^{2-})$, 4.61 (t, 2 H, NCH₂-, [MoNCH₂CH₂CH₂Cl]²⁻). IR (KBr pellet, major absorbances, cm⁻¹): 2962, 2933, 2873, 1483, 1464, 1380, 1266, 1249, 950 with shoulder at 974, 874, 792, 592. UV/Vis (MeCN): λ_{max}/nm

 $(\epsilon/M^{-1}cm^{-1}) = 231 \ (2.5 \times 10^{4}),\ 250 \ (2.1 \times 10^{4}),\ 326 \ (8.8 \times 10^{3}).$ ESI-Ms (m/z): $[M]^{-}$ calcd for $[Bu_4N] \ [Mo_6O_{18}NCH_2CH_2CH_2CH_2CI]^{-},\ 1197.64;\ found,\ 1198.60(52\%);\ [M]^{-}$ calcd for $[HMo_6O_{18}NCH_2CH_2CH_2CI]^{-},\ 956.15;\ found,\ 975.59(12\%);\ [M]^{2-}$ calcd for $[Mo_6O_{18}NCH_2CH_2CH_2CI]^{2-},\ 477.58;\ found,\ 478.67(100\%).$ Single crystals used for X-ray diffraction studies were obtained by diffusion of ether into a solution of compound **1** in acetone.

Synthesis of (Bu₄N)₂[Mo₆O₁₈NCH₂CH₂CH₂I], 2

A mixture of 1 (Bu₄N)₂[Mo₆O₁₈NCH₂CH₂CH₂Cl] (0.72g, 0.5 mmol), NaI (0.75g, 5.0 mmol) was kept at ca. 50 °C under nitrogen gas in acetone (20 mL) for about 5 days. After being cooled down to room temperature, some white precipitates were removed by filtration, which can be confirmed to be NaCl. The resulting red solution was allowed to evaporate in the open air. While most of acetone evaporated out, the product precipitated from the filtrate as red crystals. The product was washed successively with ethanol and ethyl ether solution, and then was dissolved with acetone and ethanol (1+1). The product was collected by filtration, washed successively with ethanol and ethyl ether for several times, and then recrystallized twice from a solution of acetone and ethanol (1+1), the product deposited as red crystals usually in about 85 % yield. Compound 2: $(Bu_4N)_2[Mo_6O_{18}NCH_2CH_2CH_2I]$ (2) (85%) : Elemental analysis (%) calcd for $C_{35}H_{78}IMo_6N_3$ O₁₈ (1531.56): C 27.45, H 5.13, N 2.74; found: C 27.25, H 4.94, N 2.78. ¹H-NMR (300 MHz, d_6 -DSMO, 300K, ppm): $\delta = 0.94$ (t, 24 H, CH₃-, [Bu₄N]⁺), 1.33 (m, 16 H, -CH₂-, [Bu₄N]⁺), 1.57 (m, 16 H, -CH₂-, [Bu₄N]⁺), 2.16(m, 2 H, -CH₂-, [MoNCH₂CH₂CH₂CH₂I]²⁻), 3.17 (t, 16 H, NCH₂-, $[Bu_4N]^+$, 3.49(t, 2 H, -CH₂I, $[MoNCH_2CH_2CH_2I]^{2-}$), 4.56 (t, 2 H, NCH₂-, [MoNCH₂CH₂CH₂[]²⁻). IR (KBr pellet, major absorbances, cm⁻¹): 2962, 2934, 2873, 1483, 1464, 1380, 1266, 1249, 950 with shoulder at 974, 874, 791, 591. UV/Vis (MeCN): $\lambda_{max}/nm (\epsilon/M^{-1}cm^{-1})$ $= 228 (1.8 \times 10^4), 249 (1.3 \times 10^4), 328 (4.8 \times 10^3)$. ESI-Ms (m/z): [M]⁻ calcd for [Bu₄N] $[Mo_6O_{18}NCH_2CH_2CH_2I]^{-}$, 1289.09; 1288.53(100%); found, $[M]^{-}$ calcd for $[M]^{2-}$ [HMo₆O₁₈NCH₂CH₂CH₂I]⁻, found, 1047.38(6%); 1047.63; calcd for [Mo₆O₁₈NCH₂CH₂CH₂CH₂I]²⁻, 523.31; found, 524.29(68%). Single crystals used for X-ray diffraction studies were obtained by diffusion of ether into a solution of compound 2 in acetone.

Synthesis of (Bu₄N)₂[Mo₆O₁₈NCH₂CH₂CH₂ONO₂], 3

A mixture of 1 (Bu₄N)₂[Mo₆O₁₈NCH₂CH₂CH₂Cl] (0.72g, 0.5 mmol), AgNO₃ (0.85g, 5.0 mmol) was kept at ca. 50 °C under nitrogen gas in acetonitrile (10 mL) for about 24h. With the reaction went on, some white precipitates were presented and the solution's red color was disappeared. After being cooled down to room temperature, some white precipitates were removed by filtration, which can be confirmed to be AgCl. The resulting yellow solution was allowed to evaporate in the open air. While most of acetone evaporated out, the product precipitated from the filtrate as yellow crystals. The product was washed successively with ethanol and ethyl ether solution, and then was dissolved with acetone and ethanol (1+1). The product was collected by filtration, washed successively with ethanol and ethyl ether for several times, and then recrystallized twice from a solution of acetone and ethanol (1+1), the product deposited as yellow crystals usually in about 82% yield. Compound 3: $(Bu_4N)_2[Mo_6O_{18}NCH_2CH_2CH_2ONO_2]$ (3) (82%) : Elemental analysis (%) calcd for C₃₅H₇₈Mo₆N₄O₂₁ (1466.66): C 28.66, H 5.36, N 3.82; found: C 28.42, H 5.31, N 3.64. ¹H-NMR (300 MHz, d₆-DSMO, 300K, ppm): $\delta = 0.94$ (t, 24 H, CH₃-, [Bu₄N]⁺), 1.32 $(m, 16 \text{ H}, -\text{CH}_2-, [Bu_4N]^+)$, 1.57 $(m, 16 \text{ H}, -\text{CH}_2-, [Bu_4N]^+)$, 2.10 $(m, 2 \text{ H}, -\text{CH}_2-, -\text{CH}_2$ $[MoNCH_2CH_2CH_2ONO_2]^{2-}$, 3.17 (t, 16 H, NCH₂-, $[Bu_4N]^+$), 4.75 (t, 2 H, -CH₂ONO₂, $[MoNCH_2CH_2CH_2ONO_2]^{2-}$, 4.60 (t, 2 H, NCH₂-, $[MoNCH_2CH_2 CH_2ONO_2]^{2-}$). IR (KBr pellet, major absorbances, cm⁻¹): 2962, 2933, 2874, 1633, 1483, 1464, 1380, 1279, 1265, 951 with shoulder at 974, 867, 791, 596. UV/Vis (MeCN): $\lambda_{max}/nm (\epsilon/M^{-1}cm^{-1}) = 228 (2.7 \times 10^4)$, 250 (1.9) $\times 10^4$), 327 (6.5 $\times 10^3$). ESI-Ms (m/z): [M]⁻ calcd for [Bu₄N] [Mo₆O₁₈NCH₂CH₂CH₂ONO₂]⁻, 1224.19; found, 1225.56(28%); [M]⁻ calcd for [HMo₆O₁₈NCH₂CH₂CH₂ONO₂]⁻, 982.73; found, 982.73(8%); $[M]^{2-}$ calcd for $[Mo_6O_{18}NCH_2CH_2CH_2ONO_2]^{2-}$, 490.86; found, 490.89(100%). Single crystals used for X-ray diffraction studies were obtained by diffusion of ether into a solution of compound **3** in acetone.

X-ray Crystallographic Structural Determinations

Three suitable single crystals having approximate dimensions $0.30 \ge 0.30 \ge 0.20 \mod^3$ (1), $0.30 \ge 0.15 \ge 0.10 \mod^3$ (2) and $0.50 \ge 0.40 \ge 0.30 \mod^3$ (3) were mounted on a glass fiber, respectively. Measurements were made on a Bruker Smart Apex CCD diffractometer. Data collection was performed at 293 K by using graphite-monochromated Mo- K_{α} radiation ($\lambda = 0.71073$ Å). The raw

frame data was processed using SAINT² and SADABS³ to yield the reflection data. Subsequent calculations were carried out using SHELXTL-97⁴ program. Structure was solved by direct methods. Refinement was performed by full-matrix least-squares analysis. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined.

Details of the crystal data and a summary of the intensity data collection parameters for **1**,**2** and **3** can be obtained from the supplementary CIF files, respectively.

Crystal data for **1**, $C_{35}H_{78}CIMo_6N_3O_{18}$: Mr = 1440.09, orthorhombic, space group *P*bca, *a* = 16.709(3), *b* = 20.059(4), *c* = 31.916(6) Å, *V* = 10697(4) Å³, Z = 8, ρ_{calcd} = 1.788 g·cm⁻³, μ = 1.479 mm⁻¹, *F*(000) = 5776, crystal size = 0.30×0.30×0.20 mm³. A total of 80216 reflections were collected of which 10484 reflections were unique (R(int) = 0.0351). R₁ = 0.0587 for 8423 independent reflections with I>2 σ (I)], wR₂ = 0.1487 for all data

Crystal data for **2**, $C_{35}H_{76}IMo_6N_3O_{18}$: Mr = 1529.53, orthorhombic, space group *P*bca, *a* = 16.882(3), *b* = 20.088(4), *c* = 31.929(6) Å, *V* = 10828(4) Å³, Z = 8, $\rho_{calcd} = 1.876 \text{ g}\cdot\text{cm}^{-3}$, $\mu = 1.982 \text{ mm}^{-1}$, *F*(000) = 6048, crystal size = 0.30×0.15×0.10 mm³. A total of 85490 reflections were collected of which 10624 reflections were unique (R(int) = 0.0560). R₁ = 0.0657 for 7742 independent reflections with I>2 σ (I)], wR₂ = 0.1528 for all data.

Crystal data for a cocrystallized crystal of **3** and **1**, $C_{35}H_{78}Cl_{0.5}Mo_6N_{3.5}O_{19.5}$: Mr = 1456.03, orthorhombic, space group *P*bca, a = 16.779(3), b = 20.069(4), c = 31.884(6) Å, V = 10737(4) Å³, Z = 8, $\rho_{calcd} = 1.801$ g·cm³, $\mu = 1.448$ mm⁻¹, F(000) = 5843, crystal size = $0.50 \times 0.40 \times 0.30$ mm³. A total of 81646 reflections were collected of which 10533 reflections were unique (R(int) = 0.0542). R₁ = 0.0583 for 8540 independent reflections with I>2 σ (I)], wR₂ = 0.1343 for all data.

Comments concerning the synthesis and purity of compound 3

We tried to increase the quantity of $AgNO_3$ and elongating the reactions. However, the tiny amount of compound **1** is observed in the final product. The possible reaction could be due to the chemical nature of nitrate group. It cannot fully substitute Cl group. Meanwhile, compound **1** and compound **3** seem to like to co-crystallize with each other, which hinder us separating them out.

2. Figures.





Figure S1. ¹H-NMR of compound **1**, **2** and **3**





Compound 3

Figure S2.ESI-MS of compound 1, 2 and 3.

Table S1. Bond length and angle of organic fragment of compound 1 (A an

C1-C2	1.5454(334)	C2-C3	1.4208(340)
C3-Cl	1.7823(271)	C1-C2-C3	115.078(2030)
C2-C3-Cl	109.327(1767)		

Table S2. Selected bond length and angle of organic fragment of compound 2

and 3 (Å and °).

C3-I (2)	2.122(15)	C3-O19 (3)	1.435(10)
O19-N2 (3)	1.410(17)	N2-O20 (3)	1.210(12)
N2-O21 (3)	1.209(13)	O19-N2-O20 (3)	109.9(15)



Figure S3 FT-IR spectrum of compound 1.



Figure S4 FT-IR spectrum of compound 2.



Figure S5 FT-IR spectrum of compound 3.

5. Reference

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