

Supporting Information For

Postfunctionalization of Polyoxometalates: An Efficient Strategy to Construct Organic-inorganic Zwitterions

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1. Experiment and Characterization

General methods and materials

(Bu₄N)₂[Mo₆O₁₉] was synthesized according to the modified literature method^{s1} and dried before use. Acetonitrile was dried by refluxing in the presence of CaH₂ and was distilled prior to use. *N,N'*-dicyclohexylcarbodiimide (DCC), acetone and ethyl ether were directly used without further purification. IR spectra were measured using the method of KBr pellets and recorded on PerkinElmer FT-IR spectrometer. UV-Vis spectra were measured in acetonitrile with a UV2100s spectrophotometer. ¹H NMR spectra were obtained on a JOEL JNM-ECA400 spectrometer and are reported in ppm. The mass spectra were obtained using an ion trap mass spectrometer (Thermofisher LTQ). Negative mode was chosen for the experiment (capillary voltage 33 V). Sample solution (in acetonitrile) was infused into the ESI source at a flow rate of 300 μL/min.

Crystallographic structural determinations

Suitable single crystals were mounted on a glass fiber and transferred directly to a Rigaku RAXIS-RAPID diffractometer, an Agilent Xcalibur Eos Gemini diffractometer or a Rigaku Saturn724+ diffractometer, respectively. Data collections were performed by using graphite-monochromated Mo-Kα radiation (λ=0.71073 Å). Data reduction, cell refinement and experimental absorption correction were respectively performed with the corresponding software package of Rigaku RAPID AUTO (Rigaku, 1998, Ver2.30), CrysAlisPro (Agilent Technologies, Version 1.171.35.11) or CrystalClear (Rigaku Inc., 2008). Structures were solved by direct methods and refined against *F*² by full matrix least squares. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were generated geometrically. All calculations were carried out by the program package of SHELXTL-Ver 5.1.^{s2}

Imidoylization

Synthesis of [Bu₄N]₂[Mo₆O₁₈(NC₅NH₃CH₃)] (Mo₆-Me-2Py)

A mixture of (Bu₄N)₂[Mo₆O₁₉] (1.36 g, 1.0 mmol), 3-methyl-2-aminopyridine (0.11 g, 1.0 mmol) and DCC (0.23 g, 1.1 mmol) dissolved in 15 mL anhydrous acetonitrile and then heated to reflux at 110 °C for about 12 hs. After 3 hours cooling, the reaction solution was filtrated to remove the white precipitates of 1,3-dicyclohexylurea (DCU) and then the filtrate poured into ether, resulted in precipitation. After the solution changed to clear, the supernatant liquid was poured off. Then the precipitated solid deposit in the bottom of the beaker was redissolved in acetone

and filtrated to remove some octamolybdate. After the solvent evaporated, the resulting cruded products were redissolved in anhydrous acetonitrile and red block crystal obtained by diffusion of ether into the solution. Yield, 82%. IR(KBr pellet, major absorbances, cm^{-1}): 3055, 2962, 2873, 1481, 1382, 1320, 966, 941, 781.

Synthesis of $[\text{Bu}_4\text{N}]_2[\text{Mo}_6\text{O}_{18}(\text{NC}_5\text{H}_4\text{N})]$ ($\text{Mo}_6\text{-3Py}$)

It was synthesized similar to $\text{Mo}_6\text{-Me-2Py}$ just by replacing the 3-methyl-2-aminopyridine with 3-aminopyridine. Red block crystals obtained by slow diffusion of Et_2O into the solution in acetonitrile with approximately 76% yield. IR(KBr pellet, major absorbances, cm^{-1}): 2961, 2874, 1556, 1470, 1409, 1338, 975, 952, 787. UV-vis (DMF, nm): $\lambda_{\text{max}}=340$.

Synthesis of $[\text{Bu}_4\text{N}]_2[\text{Mo}_6\text{O}_{18}(\text{NC}_5\text{H}_4\text{N})]$ ($\text{Mo}_6\text{-4Py}$)

It was synthesized similar to $\text{Mo}_6\text{-Me-2Py}$ just by replacing the 3-methyl-2-aminopyridine with 4-aminopyridine. Red rod crystals obtained by slow diffusion of Et_2O into the solution in acetonitrile with approximately 6% yield.

Alkylation

Synthesis of $[\text{Bu}_4\text{N}][\text{Mo}_6\text{O}_{18}(\text{NC}_5\text{H}_4\text{N-CH}_3)]$ ($\text{Mo}_6\text{-3Py-Me}$)

The reaction of $\text{Mo}_6\text{-3Py}$ and iodomethane in acetonitrile without stirring at 50°C for one week, red chunk crystal can be successfully obtained with 57% yield. IR(KBr pellet, major absorbances, cm^{-1}):3086, 2962, 2874, 1513, 1358, 1287, 1171, 981, 958, 789. UV-vis (DMF, nm): $\lambda_{\text{max}}=343$.

Synthesis of $[\text{Bu}_4\text{N}][\text{Mo}_6\text{O}_{18}(\text{NC}_5\text{H}_4\text{N-C}_2\text{H}_5)]$ ($\text{Mo}_6\text{-3Py-Et}$)

The reaction of $\text{Mo}_6\text{-3Py}$ and iodoethane in acetonitrile without stirring at 50°C for one week, block yellow crystal can be successfully obtained with 59% yield. IR(KBr pellet, major absorbances, cm^{-1}): 3062, 2961, 2873, 1619, 1565, 1494, 1351, 1163, 981, 957, 787. UV-vis (DMF, nm): $\lambda_{\text{max}}=347$.

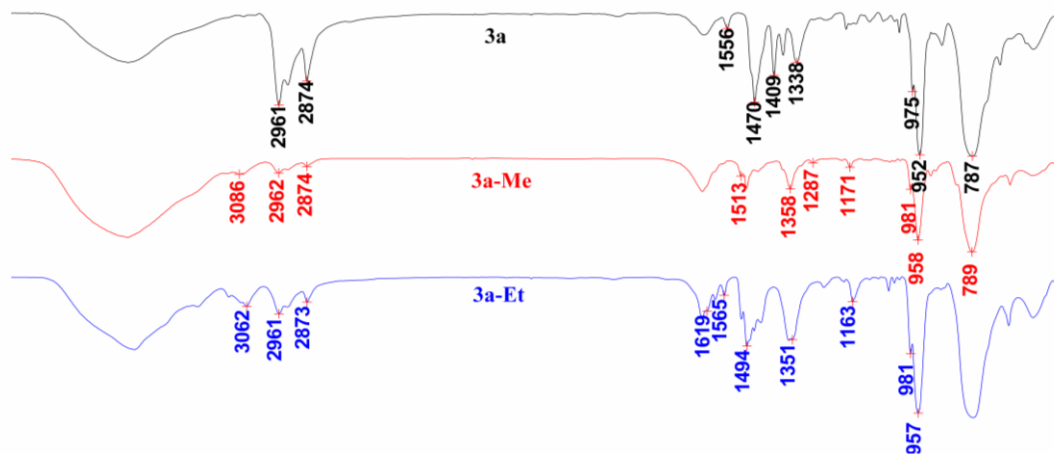


Fig. S1 IR spectra of $\text{Mo}_6\text{-3Py}$ (black line), $\text{Mo}_6\text{-3Py-Me}$ (red line) and $\text{Mo}_6\text{-3Py-Et}$ (blue line)

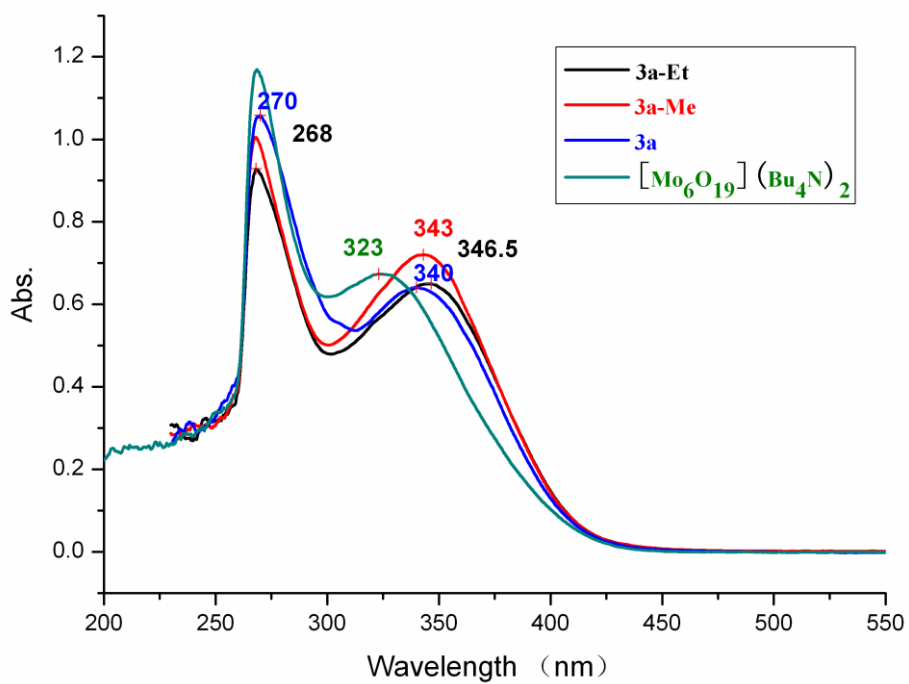


Fig. S2 UV-Vis spectra of $(\text{Bu}_4\text{N})_2(\text{Mo}_6\text{O}_{19})$ (green, 1×10^{-4} mol/L), $\text{Mo}_6\text{-3Py}$ (blue, 3×10^{-5} mol/L), $\text{Mo}_6\text{-3Py-Me}$ (red, 3×10^{-5} mol/L) and $\text{Mo}_6\text{-3Py-Et}$ (black, 3×10^{-5} mol/L)

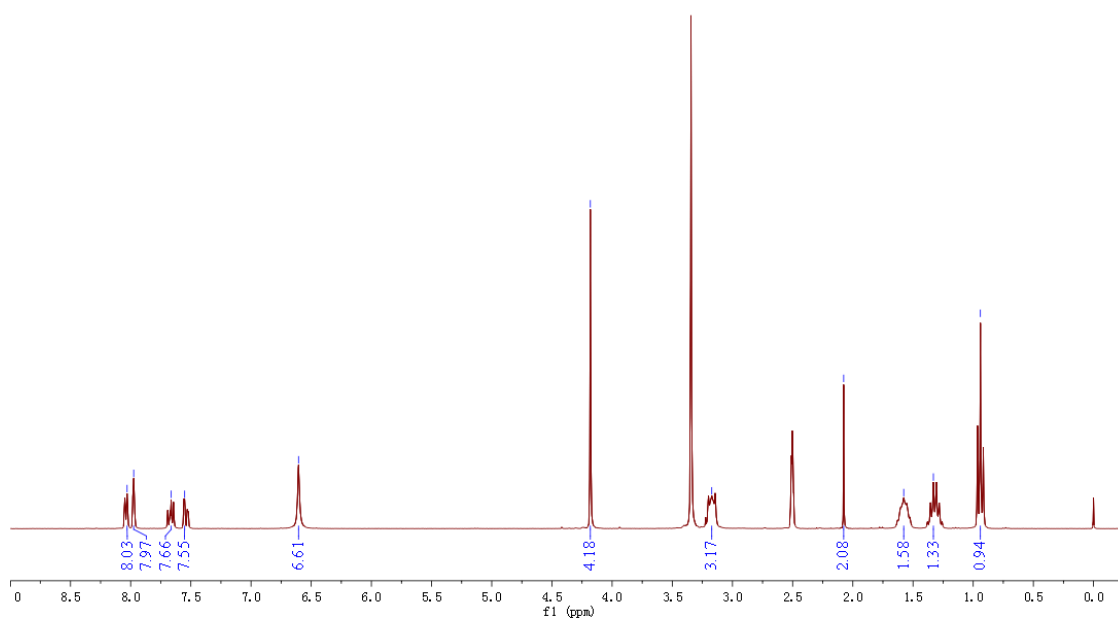


Fig. S3 ^1H NMR spectrum of $\text{Mo}_6\text{-3Py-Me}$ in $d_6\text{-DMSO}$ (0.035 mol/L)

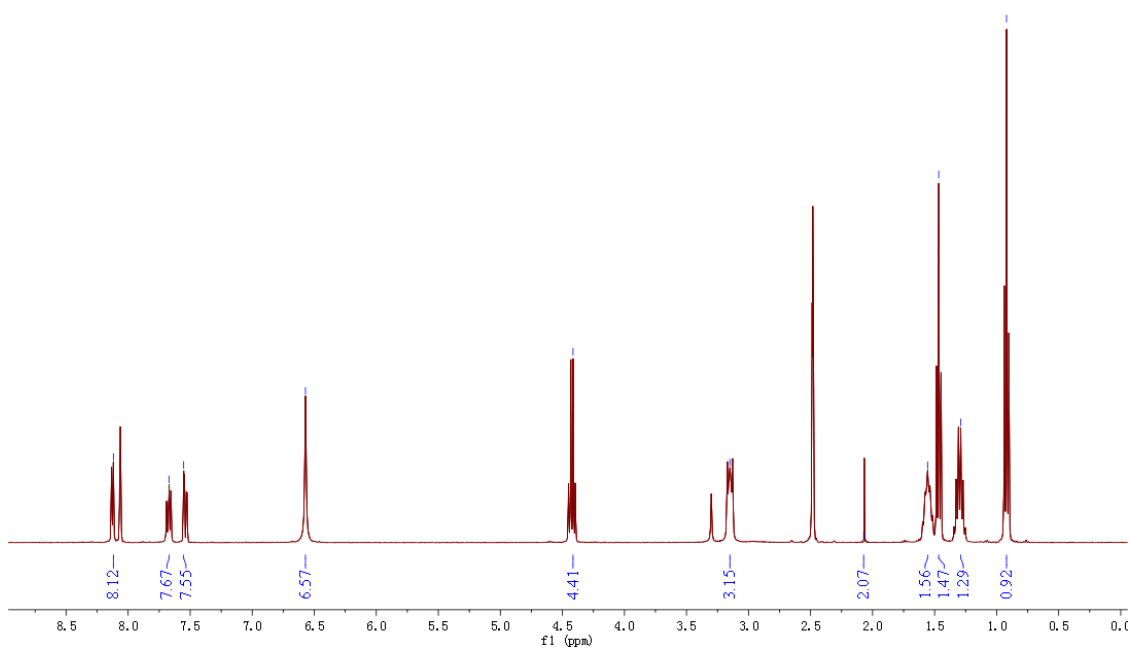


Fig. S4 ^1H NMR spectrum of $\text{Mo}_6\text{-3Py-Et}$ in $d_6\text{-DMSO}$ (0.034 mol/L)

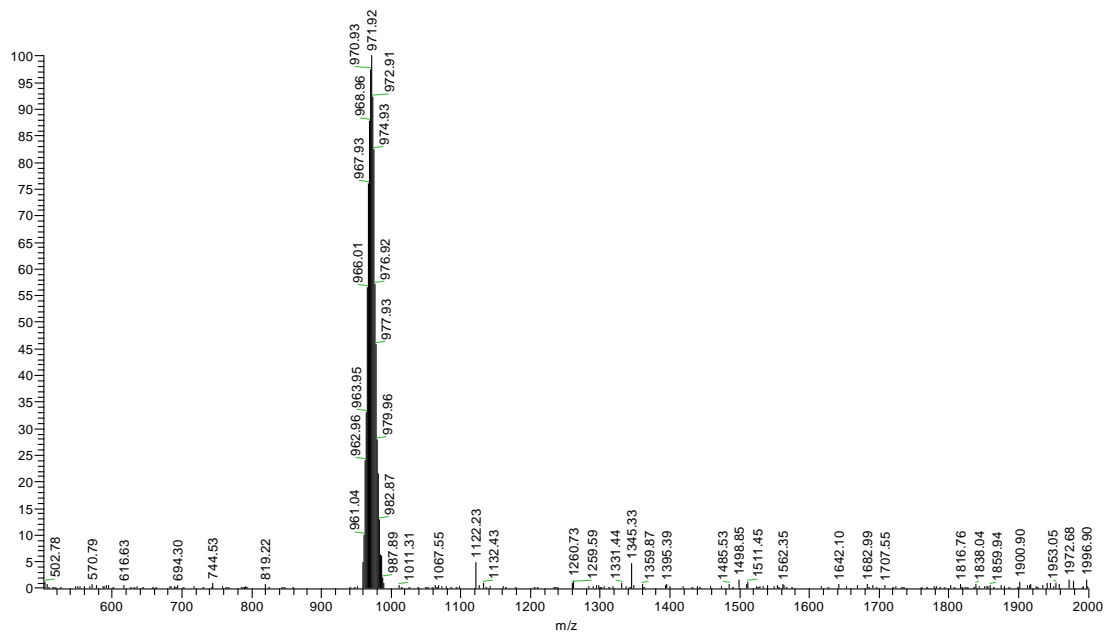


Fig. S5 ESI-MS spectra of $\text{Mo}_6\text{-3Py-Me}$

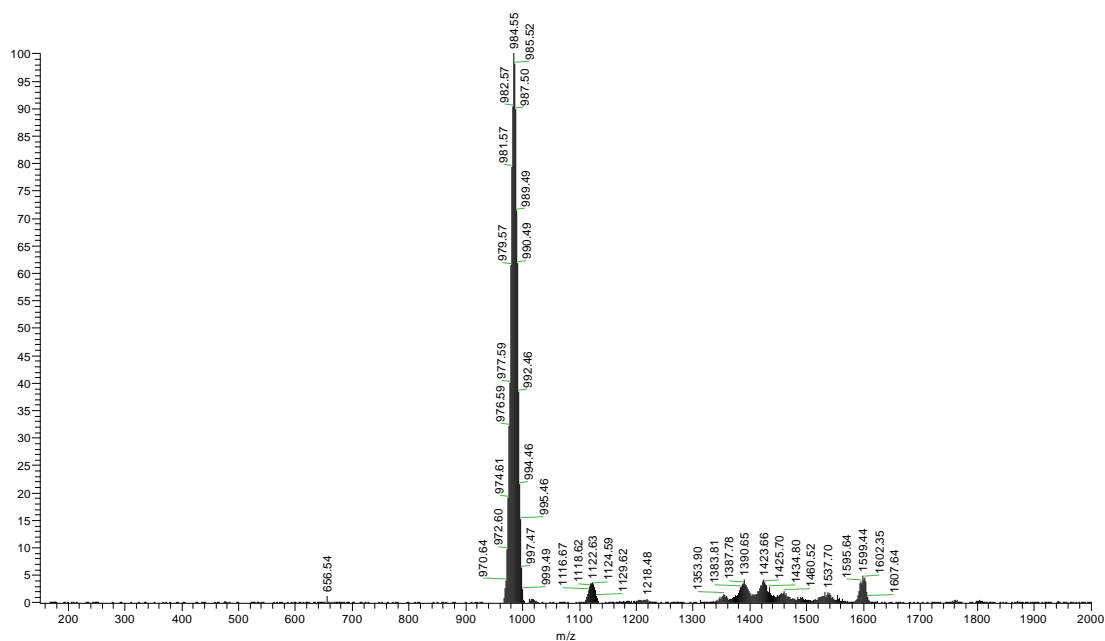


Fig. S6 ESI-MS spectra of $\text{Mo}_6\text{-3Py-Et}$

Table S1 Summary of Hydrogen Bonding in Compound $\text{Mo}_6\text{-3Py-Me}$

D-H...A	d_{DH}	d_{AH}	d_{DA}	< DHA
C1-H1...O15	0.93	2.28	3.11	148.6
C4-H4...O8	0.93	2.33	3.07	136.2
C7-H7...O36	0.93	2.32	3.04	134.4
C11-H11...O27	0.93	2.47	3.28	146.6
C10-H10...O28	0.93	2.48	3.24	139.4
N5-H5A...O10	0.86	2.12	2.95	162.7
N5-H5B...O13	0.86	2.19	3.00	156.2

Table S2 Summary of Hydrogen Bonding in Compound $\text{Mo}_6\text{-3Py-Et}$

D-H...A	d_{DH}	d_{AH}	d_{DA}	< DHA
C1-H1...O17	0.93	2.34	3.11	144.4
C4-H4...O8	0.93	2.36	3.07	132.9
C8-H8...O35	0.93	2.36	3.16	143.3
C11-H11...O23	0.93	2.48	3.20	134.5
C12-H12...O36	0.93	2.35	3.22	154.0

2. Computation details

All the calculations presented in this work were carried out with the GAUSSIAN-09 program package.^{S3} The structures of each stationary point was fully optimized using the B3LYP method, in combination with the LANL2DZ basis set for molybdate atoms and the 6-31G(d) basis set for rest atoms. Vibrational frequencies of each stationary point were calculated at the same level of theory to characterize the nature of the stationary points.

3. References

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S2 (a) G. M. Sheldrick, *Acta Crystallogr. A* 1990, **46**, 467; (b) G. M. Sheldrick, *Acta Crystallogr. A* 2008, **64**, 112.

S3 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2010, Gaussian 09, Revision C.01.