

Supporting Information

A Redox Active Triad Nanorod Constructed from Covalently Interlinked Organo-hexametalates

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Supporting Information

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General Remarks

All the chemicals except acetonitrile and pyridine were purchased and used without any further treatment. The acetonitrile and pyridine were dried by refluxing in the presence of calcium hydride and were distilled prior to use. IR spectra were obtained using KBr pellets with a PerkinElmer FT-IR spectrometer. ¹H-NMR spectra were recorded using CD₃CN as solvent with a JEOL JNM-EXC 400 spectrometer. ESI-MS spectra were recorded with a Thermo Q Exactive spectrometer in an acetonitrile solution (negative mode was used for the experiment). UV-Vis spectra were recorded on a UNICO UV-2102PC spectrophotometer in an acetonitrile solution. Elemental analysis was measured with Elementar Vario EL IIIelement analyzer. Cyclic voltammogram were recorded on Corrtest CS350 electrochemical workstation.

Experimental details

Salts of hexamolybdate $[(n\text{-C}_4\text{H}_9)_4\text{N}]_2[\text{Mo}_6\text{O}_{19}]$ and triester of Lindqvist-type hexavanadate $[(n\text{-C}_4\text{H}_9)_4\text{N}]_2[\text{V}_6\text{O}_{13}\{(\text{OCH}_2)_3\text{CNH}_2\}_2]$ were synthesized according to previously reported procedure. A mixture of 1.0 mmol $(\text{Bu}_4\text{N})_2[\text{Mo}_6\text{O}_{19}]$ (1.36 g), 0.5 mmol $(\text{Bu}_4\text{N})_2[\text{V}_6\text{O}_{13}\{(\text{OCH}_2)_3\text{CNH}_2\}_2]$ (0.62 g) and 1.0 mmol *N,N'*-dicyclohexylcarbodiimide (DCC; 0.21g) were refluxed at 105-110 °C in a solution of 10 mL anhydrous acetonitrile and 1 mL anhydrous pyridine. The reaction flask was covered with tin-foil to avoid direct illumination of light. After 22 h refluxing, the resulting solution was cooled down to room temperature naturally and then filtrated to remove the white precipitates. The filtrate was poured into 50 mL cold water to generate precipitation. The resulting precipitates was collected by suction filtration and washed with water and diethyl ether, respectively. The remaining water in crude was removed completed by lyophilisation. The crude product was dissolved in 20 mL anhydrous acetonitrile and after 24 h standing a little amount of precipitates formed in the solution. The precipitates were removed by centrifugation and diffusion of ether into the clear solution over several days resulted in the formation of plated-like orange crystals.

$(\text{Bu}_4\text{N})_6[\text{V}_6\text{O}_{13}\{(\text{OCH}_2)_3\text{CNMo}_6\text{O}_{18}\}_2]$ (**TBA₆·1**): Yield (1.01g, 51%); Elemental analysis calcd (%) for $\text{C}_{106}\text{H}_{231}\text{O}_{55}\text{N}_9\text{V}_6\text{Mo}_{12}$: C 32.08, H 5.87, N 3.18; found: C 32.17, H 5.78, N 3.37; IR (KBr): $\nu = 2961$ (m), 2933 (m), 2874 (m), 1482 (m), 1380 (w), 1079 (m), 974 (w), 953 (vs), 797 (s), 772(s), 723 (m) cm^{-1} . ^1H NMR (400MHz, CD_3CN , standardized by solvent peak): $\delta = 0.99$ (72 H, t, TBA-H), 1.38-1.40 (48H, sextet, TBA-H), 1.64 (48H, quintet, TBA-H), 3.15 (48H, t, TBA-H), 5.16 (12H, s, OCH_2); ESI-MS: m/z (%): 1721.75 (6.6%) [$\mathbf{1}^{6+}+4\text{TBA}^+$], 1601.11 (3.8) [$\mathbf{1}^{6+}+3\text{TBA}^++\text{H}^+$], 1480.47 (2.3) [$\mathbf{1}^{6+}+2\text{TBA}^++2\text{H}^+$], 1066.74 (53.3) [$\mathbf{1}^{6+}+3\text{TBA}^+$], 986.31 (35.5) [$\mathbf{1}^{6+}+2\text{TBA}^++\text{H}^+$], 905.89 (9.5) [$\mathbf{1}^{6+}+\text{TBA}^++2\text{H}^+$], 739.48 (75.4) [$\mathbf{1}^{6+}+2\text{TBA}^+$], 679.16 (100) [$\mathbf{1}^{6+}+\text{TBA}^++\text{H}^+$], 618.59 (38.7) [$\mathbf{1}^{6+}+2\text{H}^+$], 495.07 (26.0) [$\mathbf{1}^{6+}+\text{H}^+$].

Crystal data for $(\text{Bu}_4\text{N})_6[\text{V}_6\text{O}_{13}\{(\text{OCH}_2)_3\text{CNMo}_6\text{O}_{18}\}_2]\cdot\text{CH}_3\text{CN}$: $\text{C}_{106}\text{H}_{231}\text{O}_{55}\text{N}_9\text{V}_6\text{Mo}_{12}$, $M_r = 3968.92$, crystal size $0.20 \times 0.18 \times 0.10 \text{ mm}^3$, triclinic, space group *P*-1, $a = 16.5395(5)$, $b = 17.4417(6)$, $c = 27.5376(9) \text{ \AA}$, $\alpha = 78.182(3)$, $\beta = 76.559(3)$, $\gamma = 88.334(2)^\circ$, $V = 7561.2(4) \text{ \AA}^3$, $Z = 2$, $\rho_{\text{calcd}} = 1.743 \text{ g/cm}^3$, $\mu = 1.389 \text{ mm}^{-1}$, $F(000) = 4024$. A total of 85369 reflections were collected, of which 29667 were unique ($R_{\text{int}} = 0.0557$, theta and index (hkl)range measured: $2.9328 < \theta < 29.2913$, $[-22, -24, -35] < [h, k, l] < [20, 23, 37]$). $R_1 = 0.0629$ for 21281 independent reflections with $[I > 2\sigma(I)]$, $wR_2 = 0.1503$ for all data. The data were collected at 99.5K on a Agilent Gemini E diffractometer with MoK_α monochromated radiation ($\lambda = 0.71073 \text{ \AA}$). The structure was solved by direct methods using SHELXS-97 and refined using SHELXL-97.¹

Irradiation experiment: 0.02g **TBA₆·1** was completely dissolved in 2ml DMF and then the solution was divided into two test tubes. One tube was irradiated under the sunlight for 10min, another tube was put in the dark for contrast. With the irradiation,

the solution color changed from orange to greyish-green, when the solution color of another tube was unchanged in the dark.

Chemical reduction

A mixture of $(\text{Bu}_4\text{N})_6\cdot\mathbf{1}\cdot\text{CH}_3\text{CN}$ and excess of 1,2-diphenylhydrazine were dissolved with stirring in the anhydrous acetonitrile under nitrogen protection, which immediately resulted in dark green solution. The IR spectrum of the dark green solution shows obvious peak shift of C-O single bond to 1086 cm^{-1} and peak shift of $\text{V}=\text{O}_t$ bond to 945 cm^{-1} , which is consistent with previously reported works (Figure S7).² The ESI-MS result of green solution further confirms the successful reduction of **1**, e.g. the peak centred at m/z 1723.75 corresponded to $\text{TBA}_4[\text{H}_4\text{V}_6\text{O}_{13}\{(\text{OCH}_2)_3\text{CNMo}_6\text{O}_{18}\}_2]^{2-}$ (Figure S8). As it is shown in table S1, the detailed information on the assignment of the major peaks is given. However, as confirmed by single crystal X-ray diffraction, the slow diffusion of diethyl ether into the green solution still resulted in the crystallization of $(\text{Bu}_4\text{N})_6\cdot\mathbf{1}\cdot\text{CH}_3\text{CN}$ yet, indicating that the reduced compound is unstable and easily oxidized back to the oxidation species under crystallization condition. The UV-Vis spectroscopic study of green solution exhibits the absorption band of IVCT transition in the range of 500-1000 nm, while the solution of compound **1** shows no absorption in this range.³ As expected, the intensity of IVCT transition band decreases with time, which should be ascribed to the oxidation of reduced **1** with time (Figure S9).

Experimental details for the treatment with 1, 2-diphenylhydrazine: A mixture of 0.0981g $\text{TBA}_6\cdot\mathbf{1}\cdot\text{CH}_3\text{CN}$ (0.025mmol) and 0.0166g 1, 2-diphenylhydrazine (0.090mmol) was dissolved in 5ml anhydrous acetonitrile and stirred for 1h under nitrogen protection.

IR: $\nu = 2961$ (m), 2874 (m), 1481 (m), 1379 (w), 1086 (m), 973 (w), 945 (vs), 786 (s), 769(s) cm^{-1} .

Characterization and Pictures

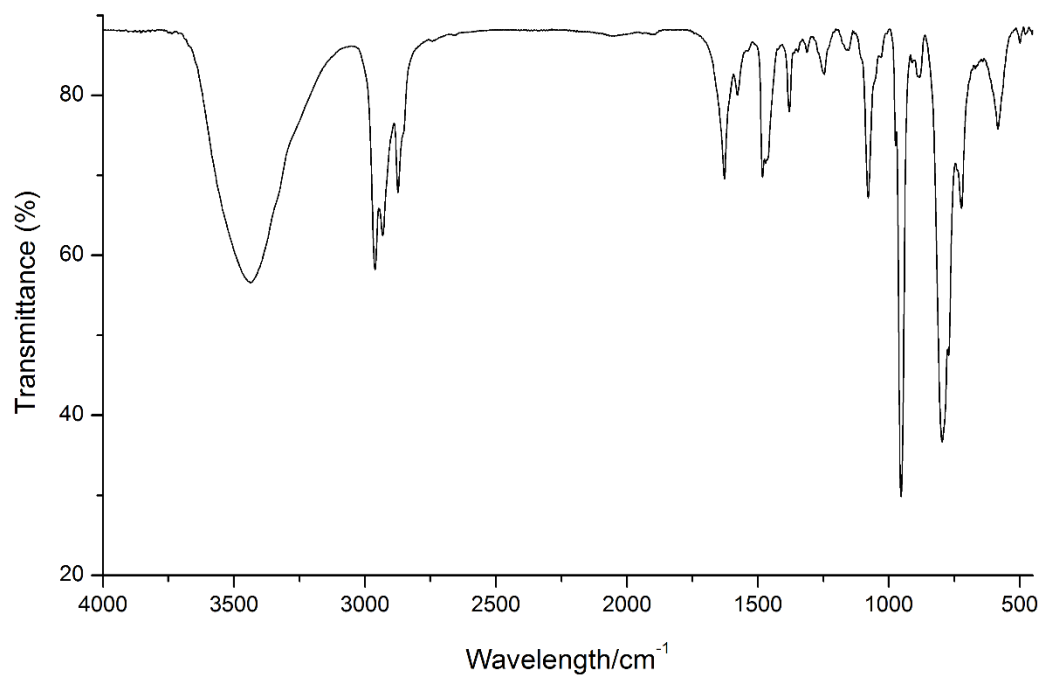


Figure S1. FT-IR spectrum measured for the solid sample of $(\text{Bu}_4\text{N})_6\cdot\mathbf{1}$.

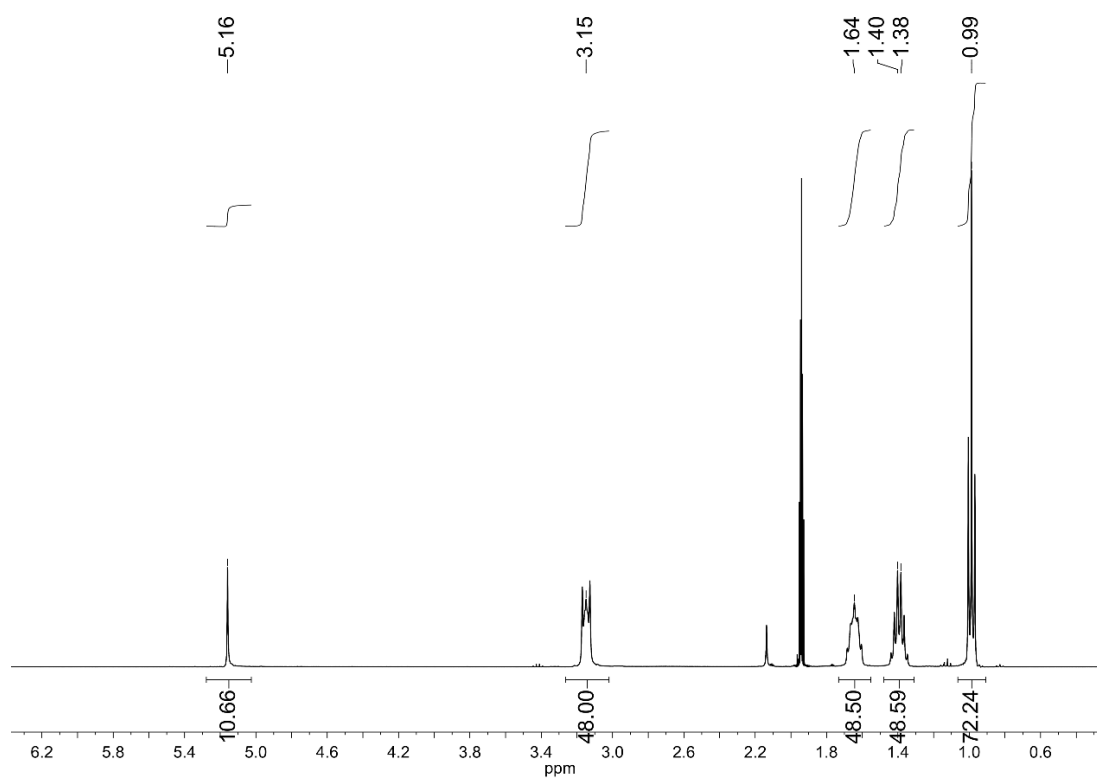


Figure S2. $^1\text{H-NMR}$ result of $(\text{Bu}_4\text{N})_6\cdot\mathbf{1}$.

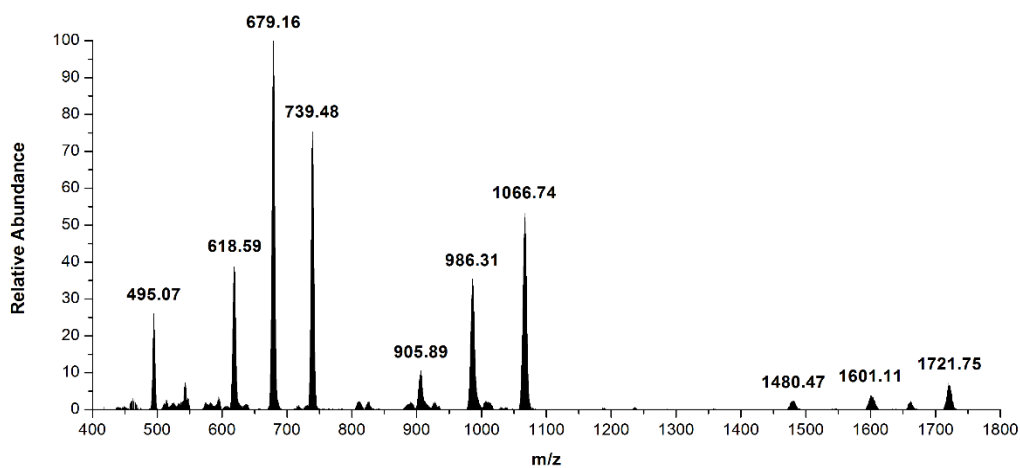


Figure S3. ESI-MS result of $(\text{Bu}_4\text{N})_6\cdot\mathbf{1}$.

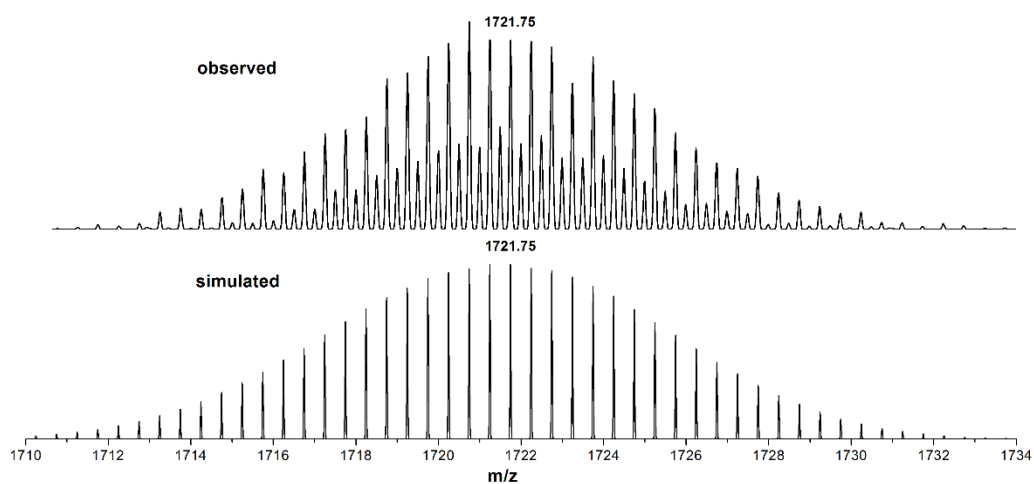


Figure S4. Observed and simulated isotopic distribution of $[\mathbf{1}^{6-} + 4\text{TBA}^+]$.

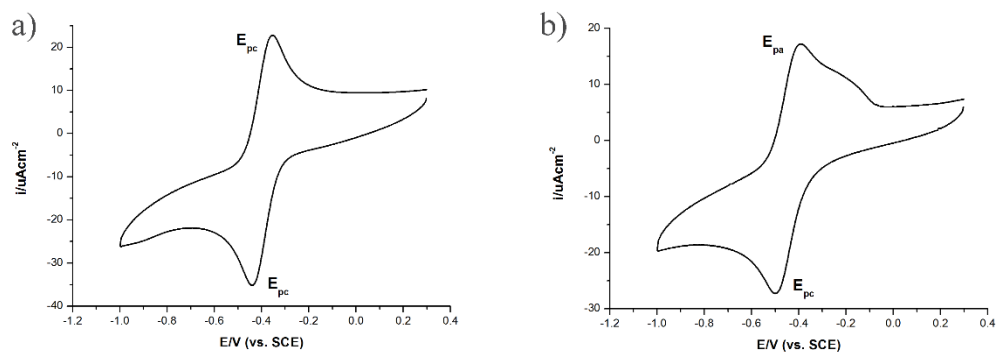


Figure S5. Cyclic voltammogram of a) hexamolybdate and b) hexavanadate derivative.

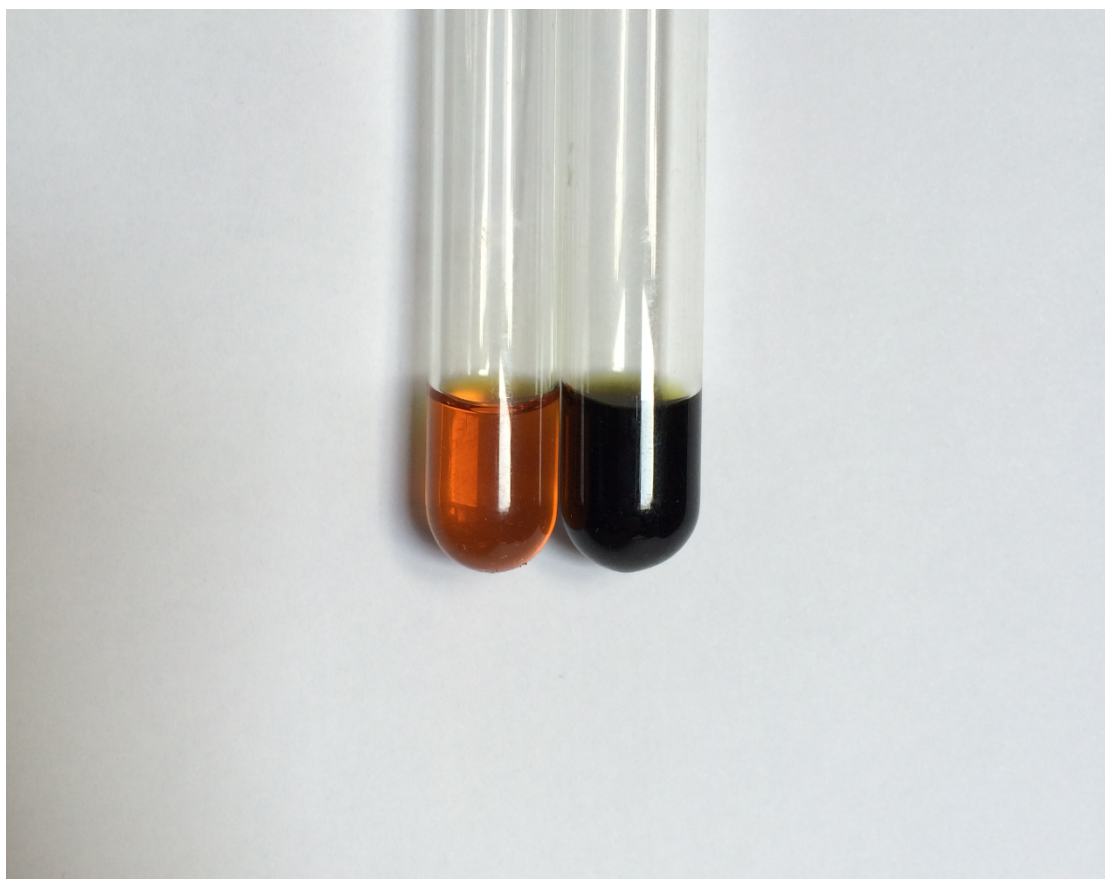


Figure S6. The DMF solution of $(\text{Bu}_4\text{N})_6\cdot\mathbf{1}$: right, after irradiation under the sunlight; left, without irradiation.

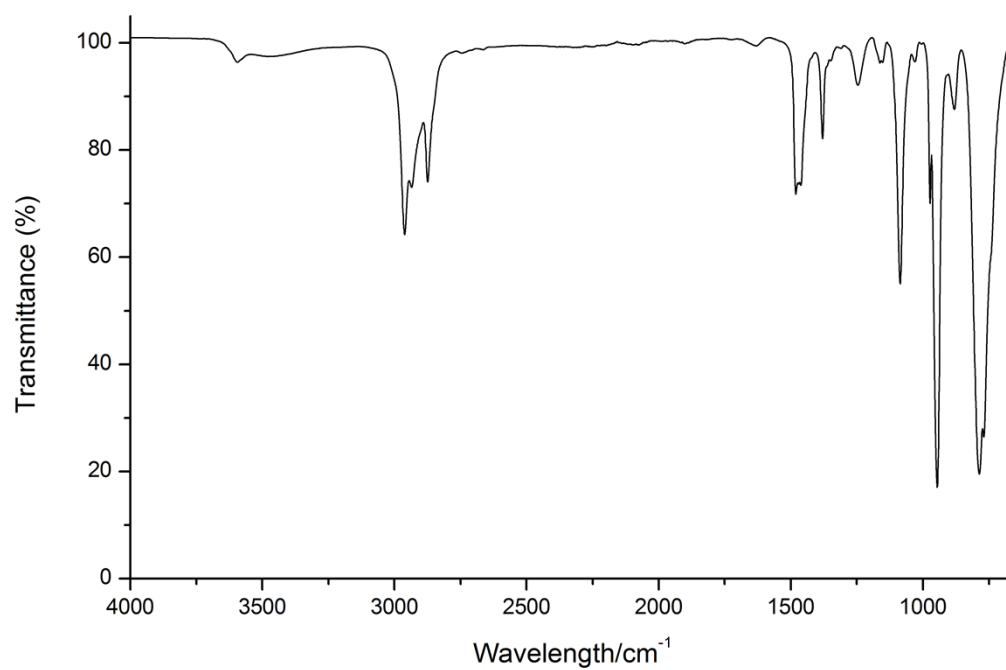


Figure S7. FT-IR spectrum measured for 1, 2-diphenylhydrazine reduced green solution

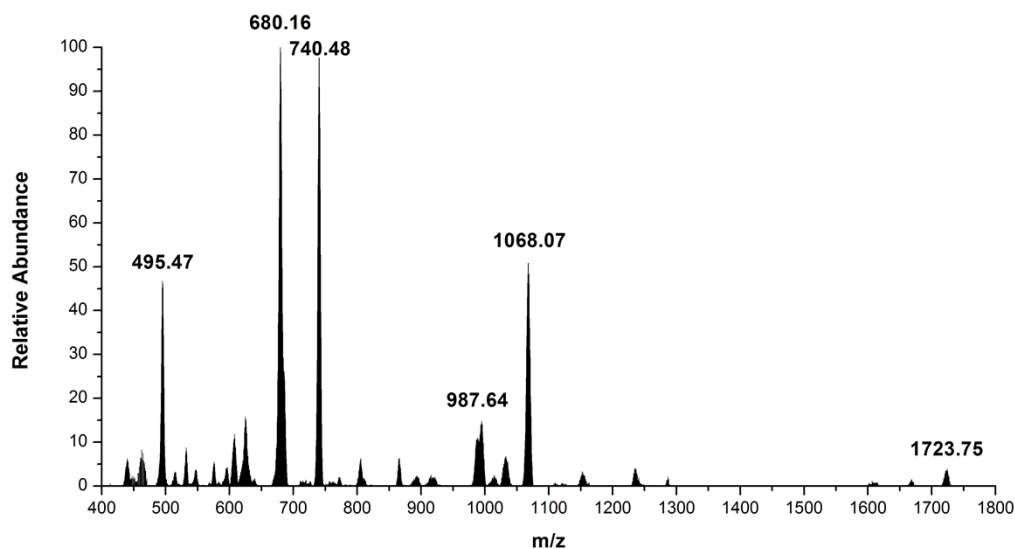


Figure S8. ESI-MS result of 1, 2-diphenylhydrazine reduced green solution

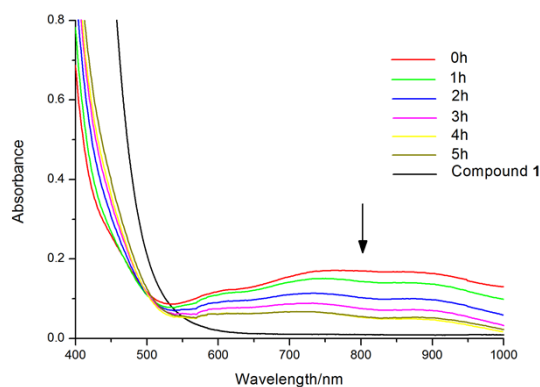


Figure S9. UV-Vis spectrum of chemical reduced **1** as a function of time compared to spectrum of **1** (black line)

Table S1. The detailed information on the assignment of the major peaks in ESI-MS.

Peaks	Ion pairs
1723.75	$\text{TBA}_4[\text{H}_4\text{V}_6\text{O}_{13}\{(\text{OCH}_2)_3\text{CNMo}_6\text{O}_{18}\}_2]^{2-}$
1068.07	$\text{TBA}_3[\text{H}_4\text{V}_6\text{O}_{13}\{(\text{OCH}_2)_3\text{CNMo}_6\text{O}_{18}\}_2]^{3-}$
987.64	$\text{TBA}_2\text{H}[\text{H}_4\text{V}_6\text{O}_{13}\{(\text{OCH}_2)_3\text{CNMo}_6\text{O}_{18}\}_2]^{3-}$
740.48	$\text{TBA}_2[\text{H}_4\text{V}_6\text{O}_{13}\{(\text{OCH}_2)_3\text{CNMo}_6\text{O}_{18}\}_2]^{4-}$
680.16	$\text{TBAH}[\text{H}_4\text{V}_6\text{O}_{13}\{(\text{OCH}_2)_3\text{CNMo}_6\text{O}_{18}\}_2]^{4-}$
495.47	$\text{H}[\text{H}_2\text{V}_6\text{O}_{13}\{(\text{OCH}_2)_3\text{CNMo}_6\text{O}_{18}\}_2]^{5-}$

(1) G. M. Sheldrick, SHELXTL v. 5.10, Structure Determination Software Suite, Bruker AXS,

Madison, Wisconsin (USA), 1998.

(2) C. Daniel and H. Hartl, *J. Am. Chem. Soc.*, 2005, **127**, 13978.

(3) A. Seliverstov and C. Streb, *Chem. Commun.* 2014, **50**, 1827