Electronic Supplementary Information

A general synthesis approach in action: Preparation and characterization of polyoxomolybdenum(VI) organophosphonates through oxidative Mo-Mo bond cleavage in $\{Mo^{V}_{2}O_{4}\}$

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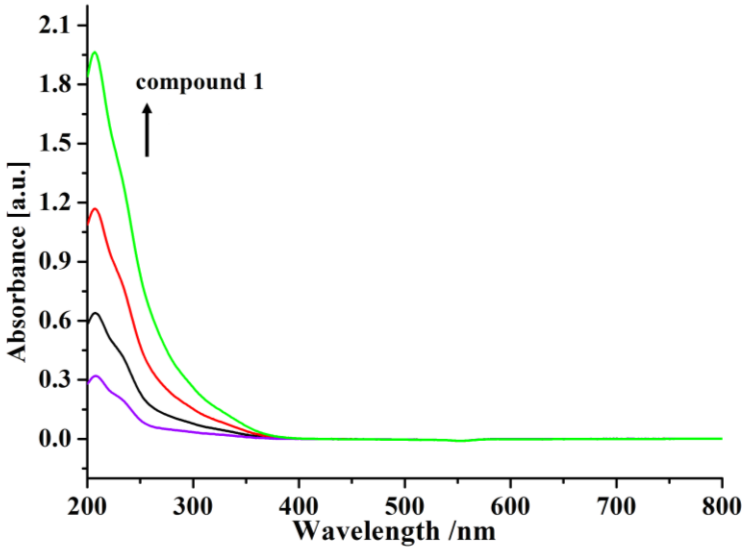

Figure S1 The UV-Vis spectra for compounds **1** in aqueous solution at different arbitrary concentration. The arrow marks the increase of concentration.

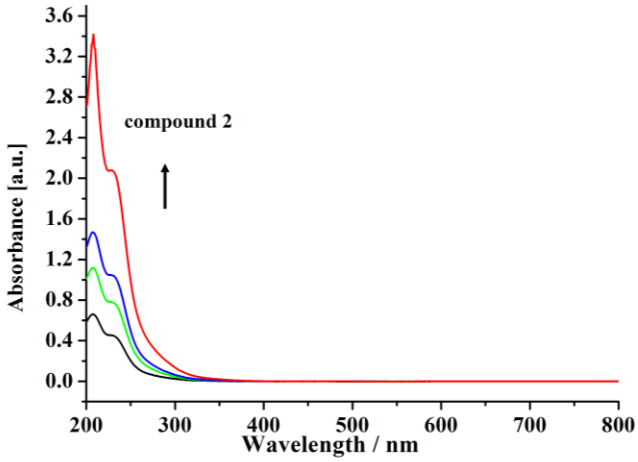

Figure S2 The UV-Vis spectra for compounds **2** in aqueous solution at different arbitrary concentration. The arrow marks the increase of concentration.

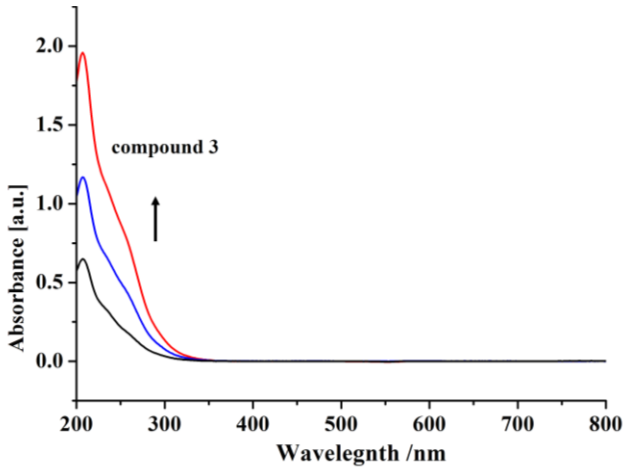

Figure S3 The UV-Vis spectra for compounds **3** in aqueous solution at different arbitrary concentration. The arrow marks the increase of concentration.

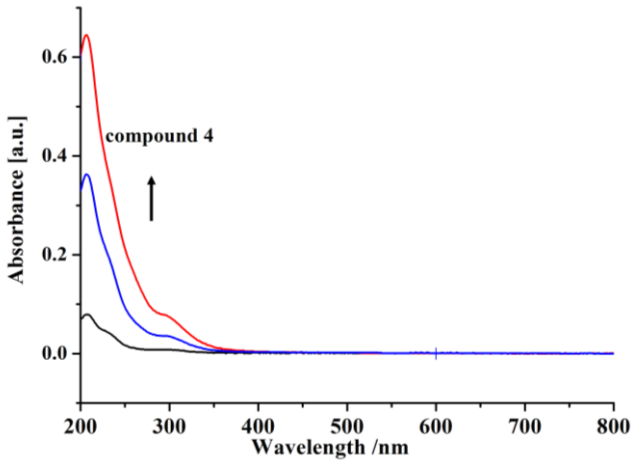

Figure S4 The UV-Vis spectra for compounds **4** in aqueous solution at different arbitrary concentration. The arrow marks the increase of concentration.

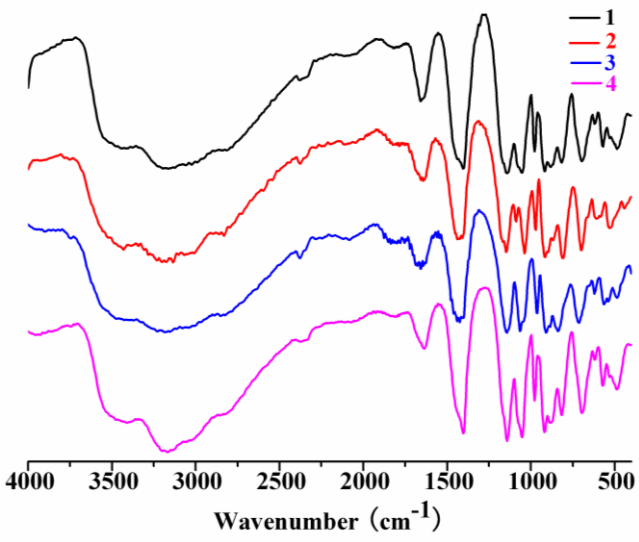

Figure S5. IR spectra of the compounds **1**~ **4**

Table S1. Assignments of IR spectroscopy data (unit: cm^{-1}) of the compounds **1** - **4**

1	**2**	**3**	**4**	Assignment[1,2,3]
3196 (s)	3430 (m)	3178 (s)	3172 (s)	NH_4^+, H_2O
	3136 (s)			
1677 (m)	1641 (m)	1659 (m)	1659 (m)	
1428 (s)	1440 (s)	1425 (s)	1404 (s)	HEDP
1146 (s)	1146 (s)	1143 (s)	1143 (s)	
1088 (w)	1088 (w)	-	1053 (s)	
1038 (s)	1038 (s)	1065 (s)	978 (m)	
970 (m)	955 (m)	969 (m)	918 (s)	Mo=O
915 (s)	915 (s)	908 (s)	879 (m)	Mo-O
801 (s)	810 (s)	840 (s)	815 (m)	
699 (m)	699 (m)	764 (m)	696 (m)	
531 (w)	531 (w)	564 (w)	573 (w)	

[1] H. Tan, W. Chen, D. Liu, E. Wang, *Dalton Trans*. 2010, **39**, 1245.

[2] X. Zhang, J. Xu, J. Yu, J. Lu, Y. Xu, Y. Chen, T. Wang, X. Yu, Q. Yang, Q. Hou, *J. Solid State Chem.*, 2007, **180**, 1949.

[3] C. Wei, J. Chen, Y. Huang, T. Lan, Z. Li, W. Zhang, Z. Zhang, *J. Mol.Struct.*, 2006, **798**, 117.

Table S2. BVS parameters for the Mo and Fe atoms in **1**.

Bond	Bond length	Bond Valence	Valence Sum
Mo1-O1	1.700	1.831	Σ(Mo1) = 6.135
Mo1-O1	1.700	1.831	
Mo1-O2	1.796	1.349	
Mo1-O3	2.015	0.672	
Mo1-O4	2.357	0.226	
Mo1-O4	2.357	0.226	
Bond	Bond length	Bond Valence	Valence Sum
Mo2-O3	1.848	1.143	Σ(Mo5) = 5.532
Mo2-O4	2.386	0.206	
Mo2-O4	2.386	0.206	
Mo2-O7	1.955	0.813	
Mo2-O8	1.746	1.582	
Mo2-O8	1.746	1.582	
Bond	Bond length	Bond Valence	Valence Sum
Fe1-O2	1.951	0.595	Σ(Fe1) = 3.161
Fe1-O2	1.951	0. 595	
Fe1-O6	2.021	0.493	
Fe1-O6	2.021	0.493	
Fe1-O6	2.021	0.493	
Fe1-O6	2.021	0.493	

Table S3. BVS parameters for the Mo and Cr atoms in **2**.

Bond	Bond length	Bond Valence	Valence Sum
Mo1-O2	2.327	0.249	Σ(Mo1) = 5.931
Mo1-O2	2.327	0.249	
Mo1-O5	1.792	1.366	
Mo1-O6	2.014	0.674	
Mo1-O7	1.724	1.697	
Mo1-O7	1.724	1.697	
Bond	Bond length	Bond Valence	Valence Sum
Mo2-O2	2.370	0.217	Σ(Mo2) = 5.730
Mo2-O2	2.370	0.217	
Mo2-O4	1.958	0.805	
Mo2-O6	1.867	1.076	
Mo2-O8	1.722	1.708	
Mo2-O8	1.722	1.708	
Bond	Bond length	Bond Valence	Valence Sum
Cr1-O1	1.975	0.507	Σ(Cr1) = 3.173
Cr1-O1	1.975	0.507	
Cr1-O1	1.975	0.507	
Cr1-O1	1.975	0.507	
Cr1-O5	1.931	0.572	

Table S4. BVS parameters for the Mo atoms in **4.**

Bond	Bond length	Bond Valence	Valence Sum
Mo1-O2	2.332	0.245	Σ(Mo1) = 5.866
Mo1-O5	2.338	0.240	
Mo1-O7	1.980	0.751	
Mo1-O8	1.857	1.111	
Mo1-O9	1.696	1.855	
Mo1-O10	1.730	1.665	
Bond	Bond length	Bond Valence	Valence Sum
Mo2-O2	2.332	0.245	Σ(Mo2) = 5.926
Mo2-O5	2.308	0.264	
Mo2-O8	2.010	0.682	
Mo2-O11	1.774	1.447	
Mo2-O12	1.740	1.612	
Mo2-O13	1.728	1.675	
Bond	Bond length	Bond Valence	Valence Sum
Mo3-O1	2.131	0.464	Σ(Mo3) = 4.976
Mo3-O4	2.129	0.467	
Mo3-O11	2.161	0.422	
Mo3-O14	1.680	1.952	
Mo3-O15	1.947	0.834	
Mo3-O16	1.940	0.837	
Bond	Bond length	Bond Valence	Valence Sum
Mo4-O15	1.952	0.821	Σ(Mo4) = 4.973
Mo4-O16	1.950	0.826	
Mo4-O17	1.682	1.939	
Mo4-O18	2.121	0.479	
Mo4-O21	2.140	0.451	
Mo4-O26	2.136	0.457	
Bond	Bond length	Bond Valence	Valence Sum
Mo5-O19	2.305	0.267	Σ(Mo5) = 5.928
Mo5-O22	2.316	0.258	
Mo5-O25	2.034	0.632	
Mo5-O26	1.787	1.388	
Mo5-O27	1.730	1.665	
Mo5-O28	1.720	1.718	
Bond	Bond length	Bond Valence	Valence Sum
Mo6-O2	2.354	0.228	Σ(Mo6) = 5.899
Mo6-O5	2.346	0.234	
Mo6-O7	1.963	0.793	
Mo6-O8	1.872	1.059	
Mo6-O9	1.720	1.718	
Mo6-O10	1.694	1.867	