

ESI

Exploring the Solvent Mediated Assembly and Redox Activity of a POM-Organic Hybrid $[\text{Na}(\text{SO}_3)_2(\text{PhPO}_3)_4\text{Mo}^{\text{V}}_4\text{Mo}^{\text{VI}}_{14}\text{O}_{49}]^{5-}$

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= Contents =

1. Electrochemical study
2. BVS
3. NMR

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1. Electrochemical study

Table S1-1. Summary of electrochemical data

E^{ox} / V	$E^{\text{red}} / \text{V}$	$\Delta E = E^{\text{ox}} - E^{\text{red}} / \text{mV}$	$E_{\text{mid}} / \text{V}$	reaction
-0.580	-0.683	103	-0.63	I
0.266	0.204	62	0.24	II
0.713	0.636	77	0.67	III

2. BVS

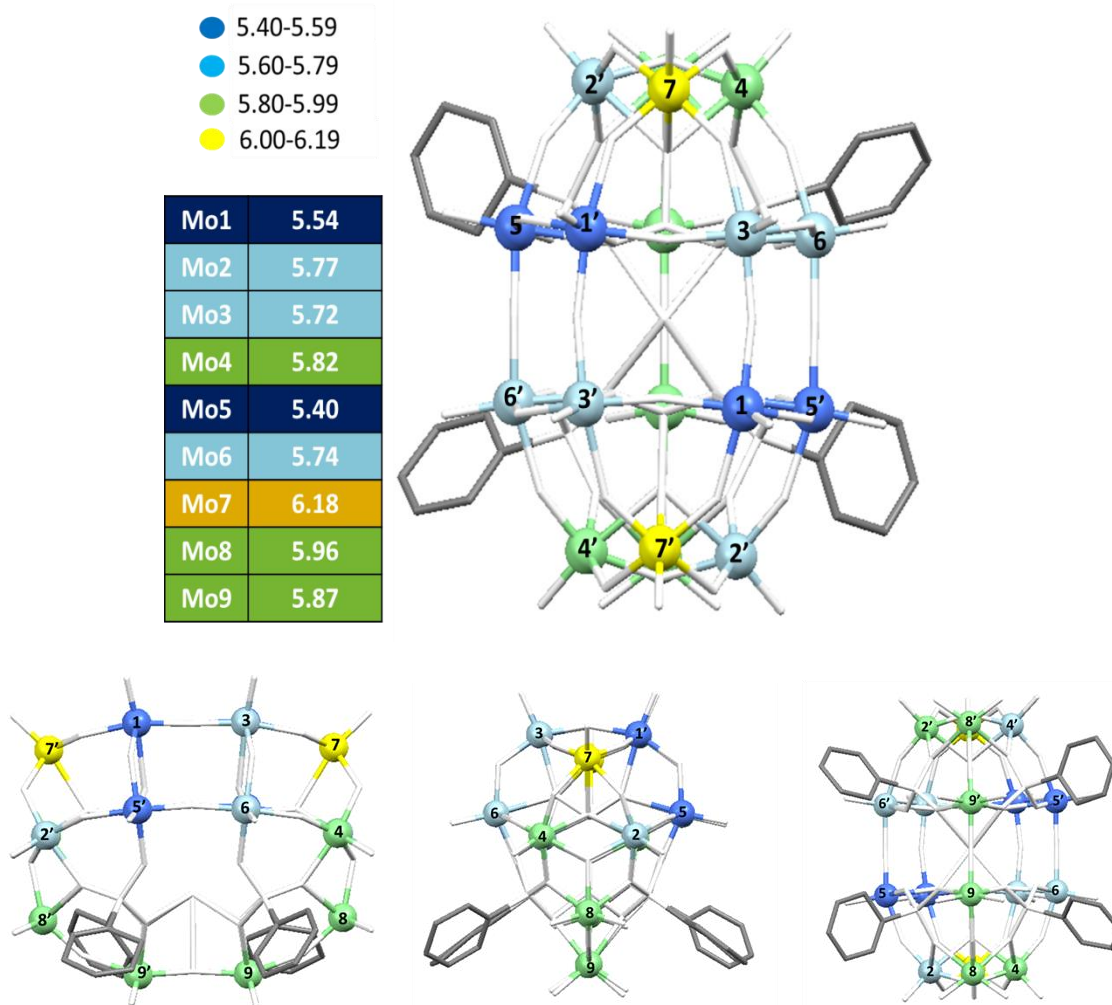


Figure S1-1. BVS values and cluster structure coloured by BVS values. Bond valence values were estimated by to $s = \exp[-(l_{ij} - l_o)/B]$ where $l_{ij} = 1.89$ and $B = 0.314$.

3. NMR

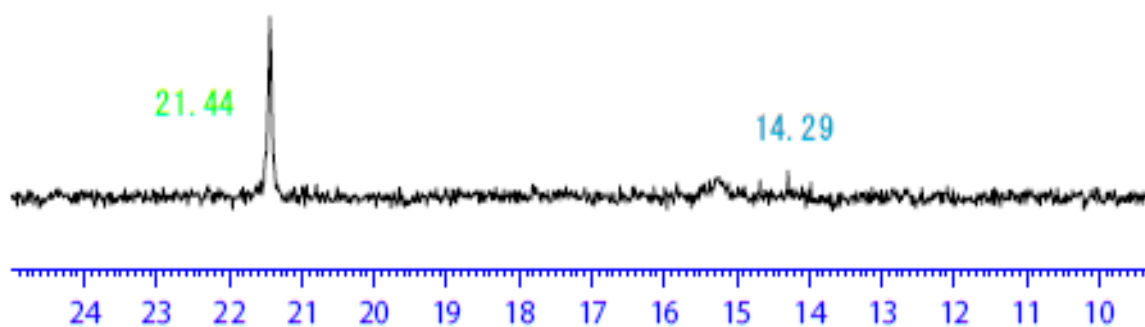


Figure S2-1. ^{31}P -NMR of an aqueous solution of TEAH salt of cluster **1**.

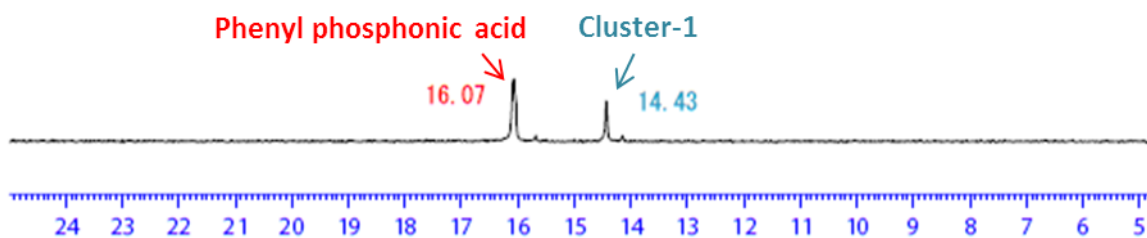


Figure S2-2. ^{31}P -NMR of water-acetonitrile mixed solution (5:2) of mixture of cluster **1** and phenylphosphonic acid.

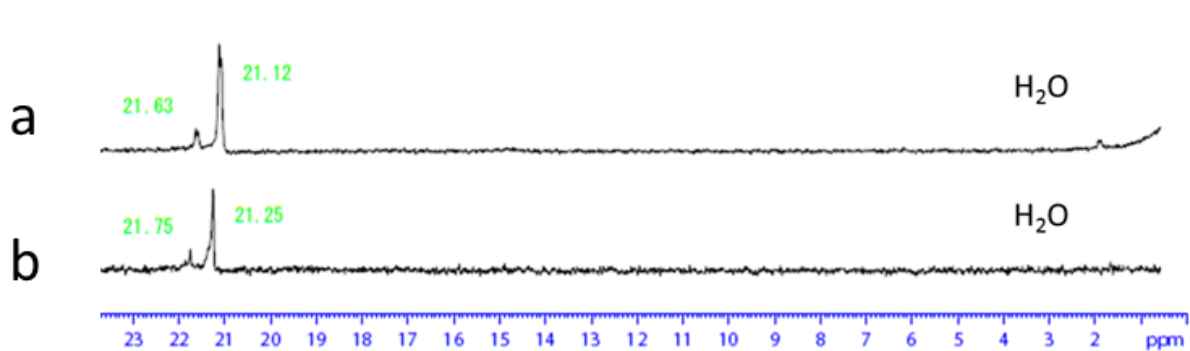


Figure S2-3. ^{31}P -NMR of aqueous solution after reacting (a) 0.5 h and (b) 3 days.

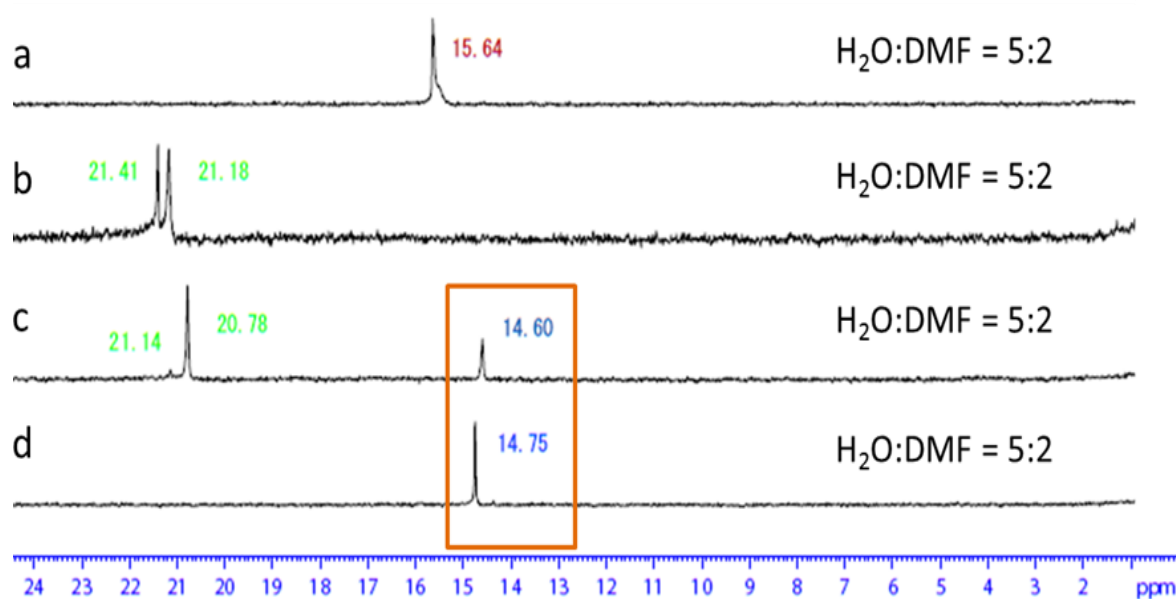


Figure S2-4. ^{31}P -NMR of water-DMF mixed solution (5:2) of (a) PhPO_3H_2 , reaction solution after (b) 0.5 h, (c) 3 days and (d) TBA salt of **1**.

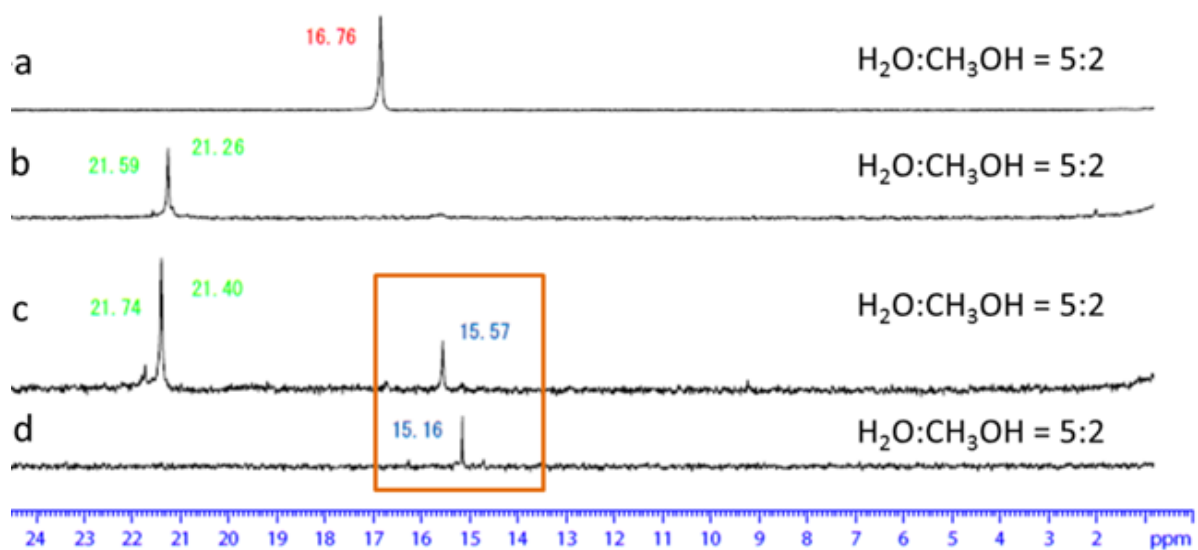


Figure S2-5. ^{31}P -NMR of water-MeOH mixed solution (5:2) of (a) PhPO_3H_2 , reaction solution after (b) 0.5 h, (c) 3 days and (d) TBA salt of **1**.

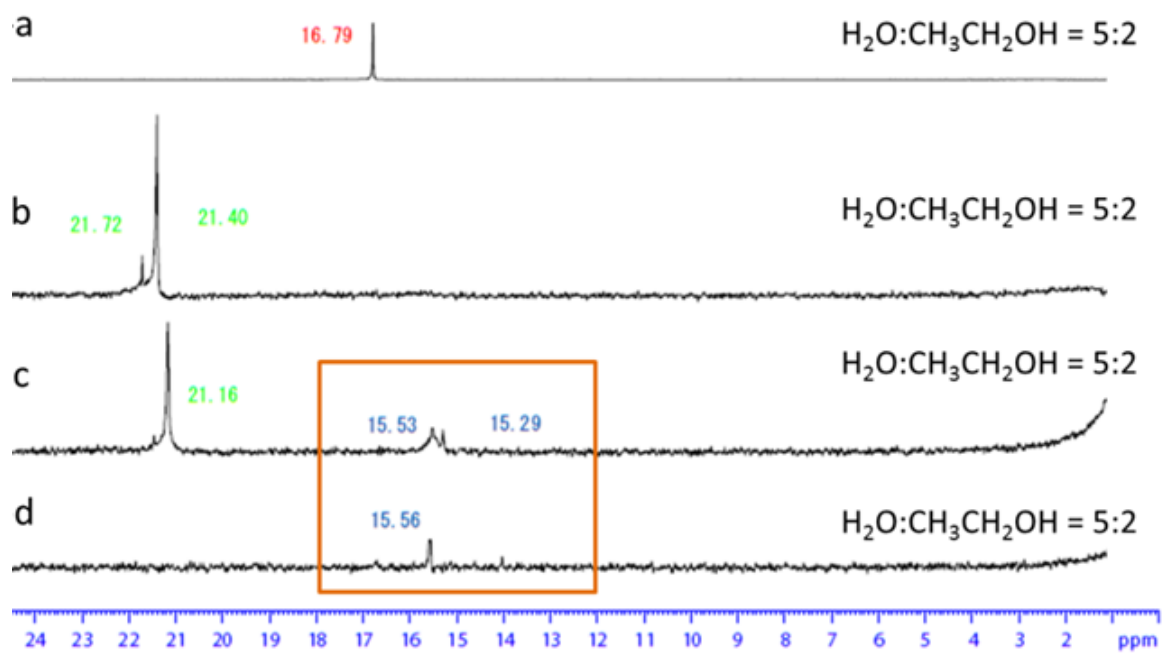


Figure S2-6. ^{31}P -NMR of water-EtOH mixed solution (5:2) of (a) PhPO_3H_2 , reaction solution after (b) 0.5 h, (c) 3 days and (d) TBA salt of **1**.

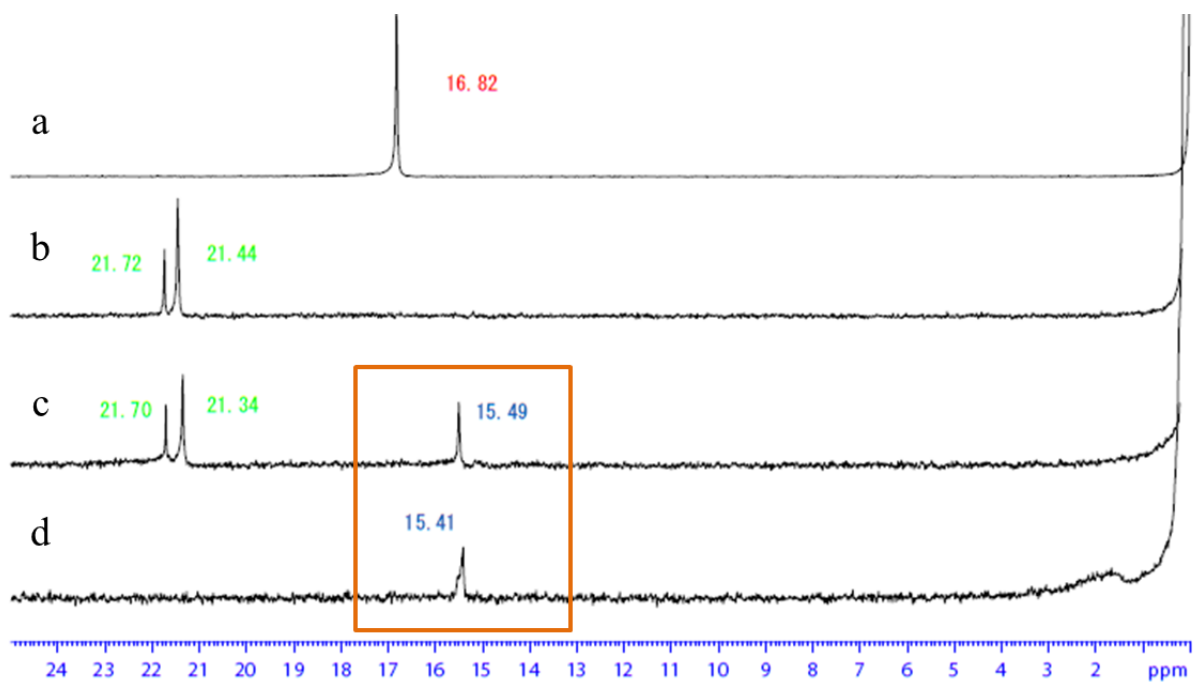


Figure S2-7. ^{31}P -NMR of water-2-propanol mixed solution (5:2) of (a) PhPO_3H_2 , reaction solution after (b) 0.5 h, (c) 3 days and (d) TBA salt of **1**.

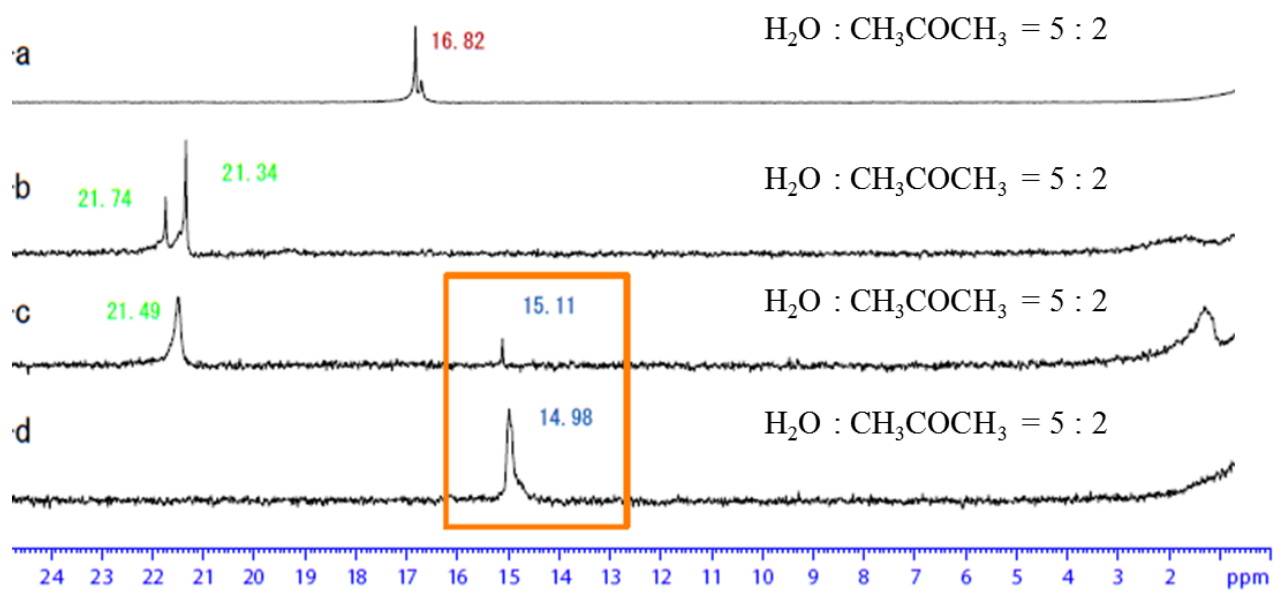


Figure S2-8. ^{31}P -NMR of water-acetone mixed solution (5:2) of (a) PhPO_3H_2 , reaction solution after (b) 0.5 h, (c) 3 days and (d) TBA salt of **1**.