Electronic Supplementary Information

Bicapped Keggin polyoxomolybdates: discrete species and experimental and theoretical investigations on the electronic delocalization in a chain compound

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Figure S1. Infrared spectra of **Co-$PMo_{12}Zn_2$**, **Ru-$PMo_{12}Zn_2$**, **Fe-$PMo_{12}Zn_2$** and **Ru-PMo_{14}**.

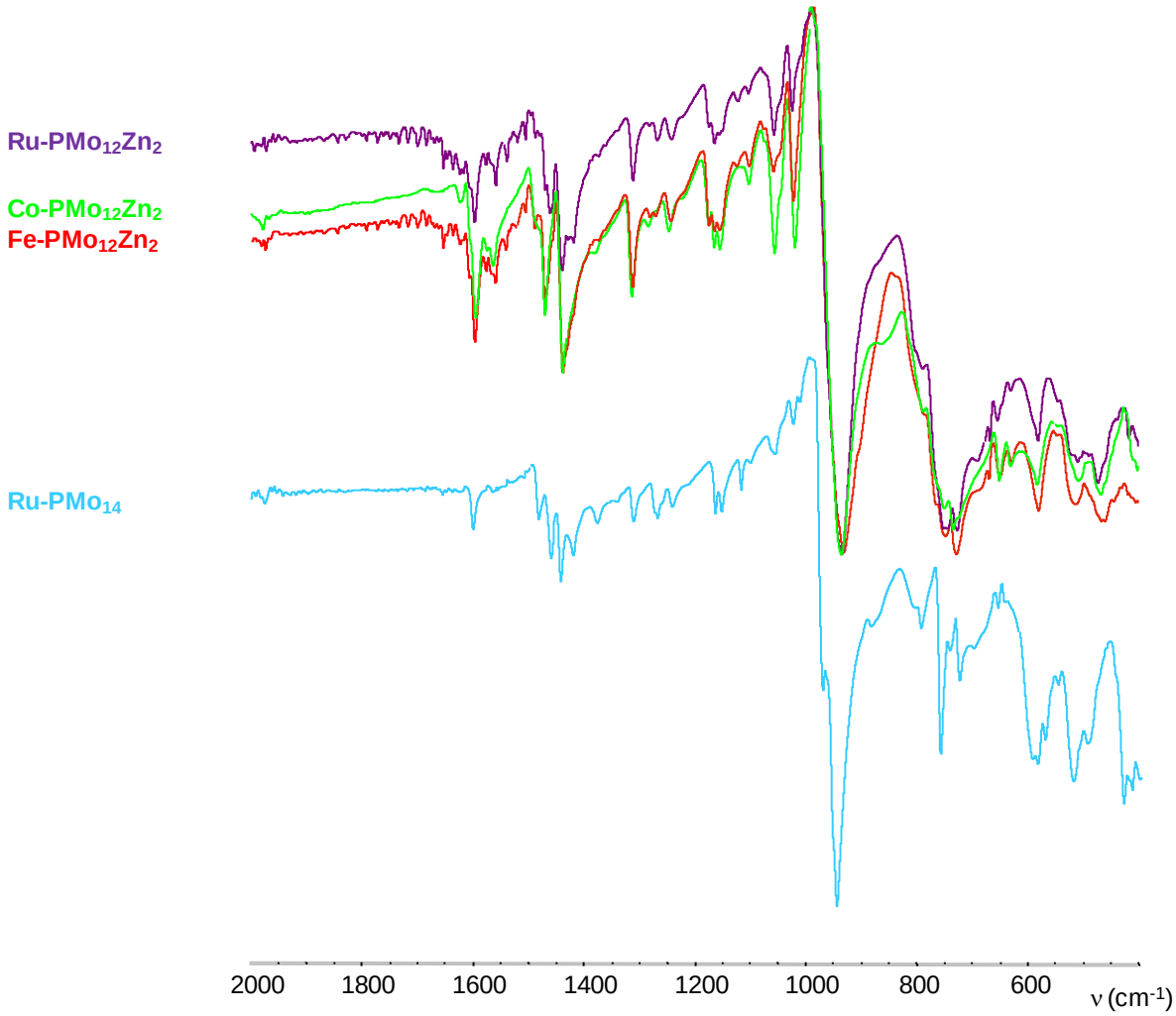
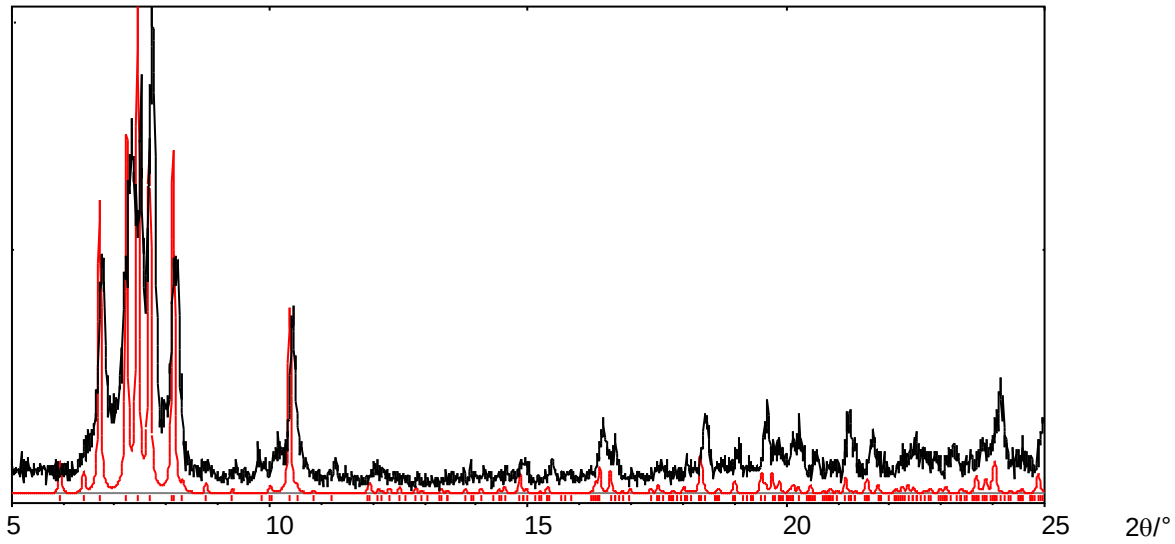
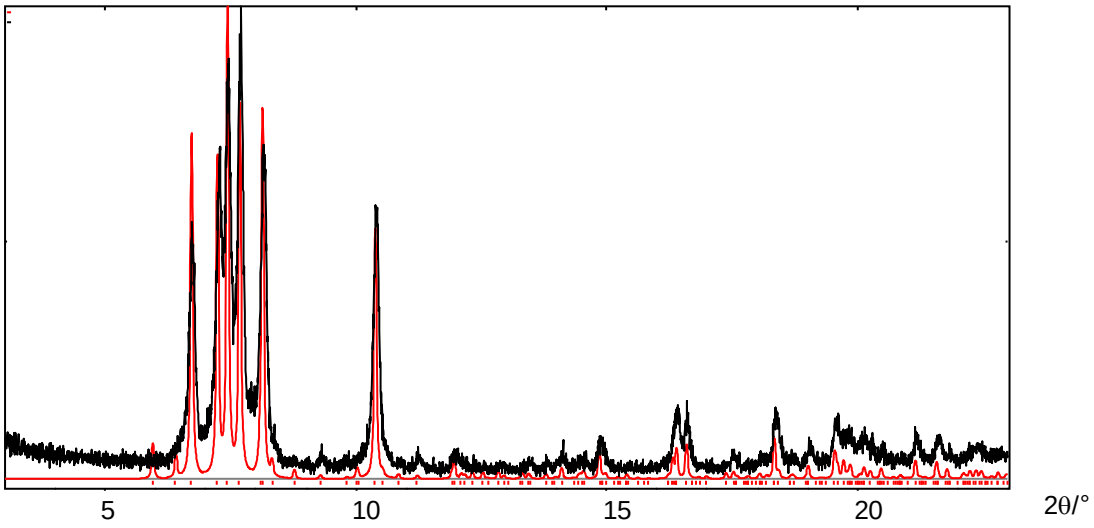


Figure S2. Comparison of the experimental X-ray powder patterns (in black) of a) **Co-PMo$_{12}$Zn$_2$**, b) **Ru-PMo$_{12}$Zn$_2$**, c) **Fe-PMo$_{12}$Zn$_2$** and of the powder pattern calculated from the structure solved from single-crystal X-ray diffraction data (in red) of **Ru-PMo$_{12}$Zn$_2$**.

a)



b)



c)

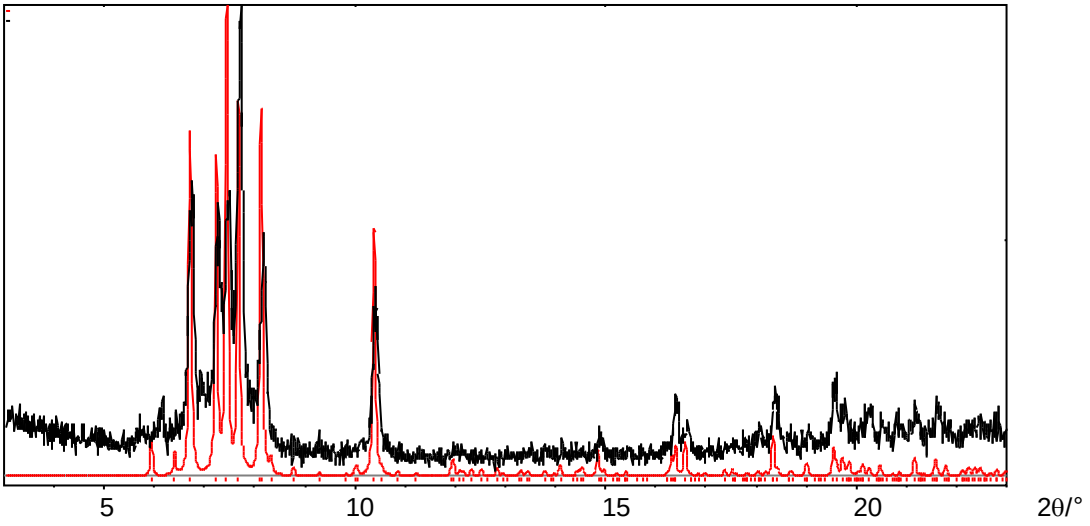


Figure S3. Comparison of the experimental X-ray powder patterns (in black) and of the powder pattern calculated from the structure solved from single-crystal X-ray diffraction data (in red) for **Ru-PMo$_{14}$**.

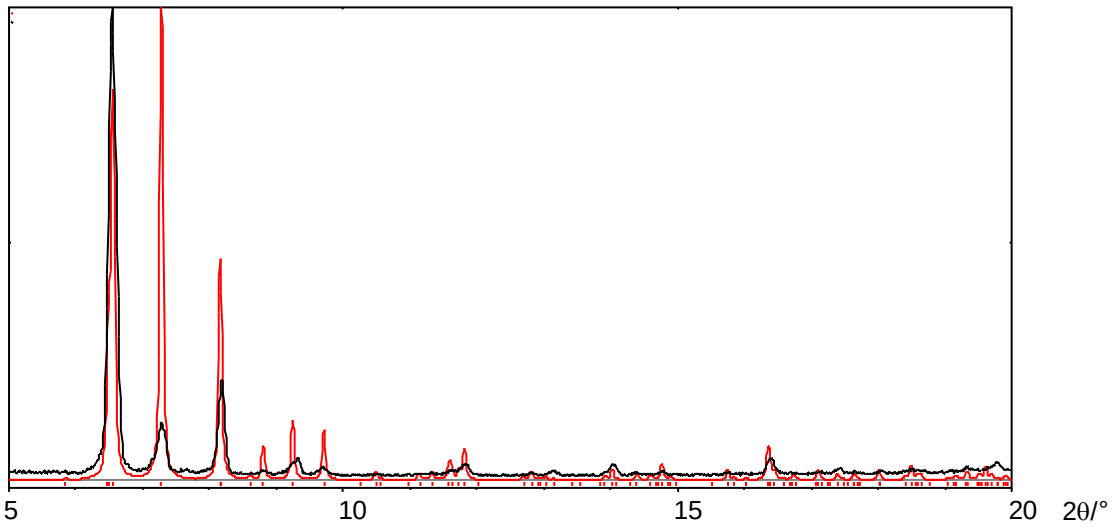
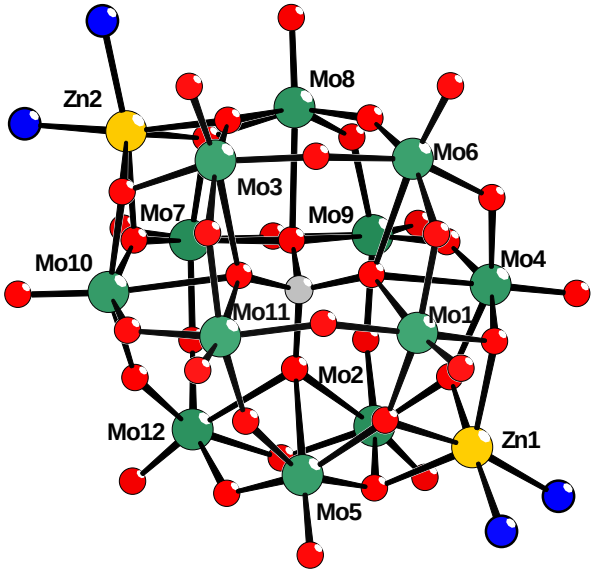


Figure S4. Ball and stick representation with partial atomic labeling scheme, selected bond distances (Å) and bond valence summations (BVS) of the POM unit in **Ru-PMo$_{12}$Zn$_2$**.



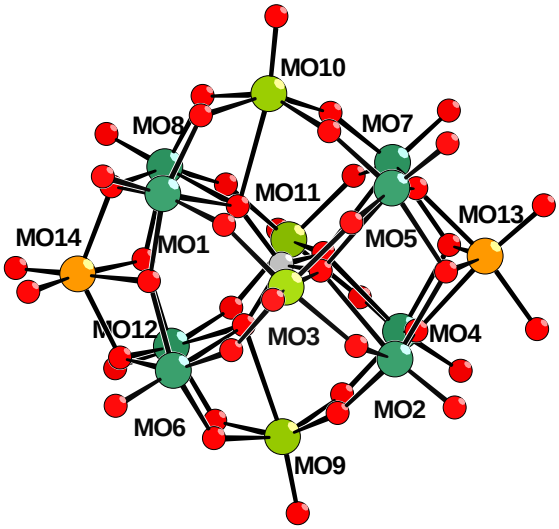
Mo1	O22	1.6890	BVS = 5.48 / 5.93	Mo7	O38	1.6903	BVS = 5.43 / 5.88
	O33	1.8503			O39	1.8541	
	O4	1.8742			O26	1.8832	
	O7	1.9658			O35	1.9723	
	O8	2.0030			O25	1.9959	
	O29	2.4605			O5	2.4394	
Mo2	O18	1.6760	BVS = 5.47 / 5.92	Mo8	O19	1.6777	BVS = 5.43 / 5.88
	O31	1.8490			O1	1.8619	
	O36	1.8696			O23	1.8894	
	O2	1.9870			O14	1.9798	
	O12	2.0184			O25	1.9945	
	O3	2.4556			O5	2.4521	
Mo3	O28	1.6792	BVS = 5.42 / 5.86	Mo9	O24	1.6759	BVS = 5.41 / 5.85
	O13	1.8678			O20	1.8949	
	O37	1.8694			O23	1.9251	
	O14	1.9933			O31	1.9435	
	O10	2.0038			O26	1.9533	
	O9	2.4529			O5	2.4841	
Mo4	O6	1.6681	BVS = 5.48 / 5.92	Mo10	O30	1.6831	BVS = 5.38 / 5.82
	O15	1.8703			O11	1.8523	
	O20	1.8862			O27	1.8885	
	O2	1.9652			O35	1.9813	
	O8	2.0044			O10	2.0154	
	O29	2.4509			O9	2.4691	
Mo5	O34	1.6791	BVS = 5.51 / 5.96	Mo11	O21	1.6729	BVS = 5.35 / 5.78
	O16	1.8602			O16	1.9202	
	O32	1.8679			O33	1.9339	
	O12	1.9805			O11	1.9467	
	O7	1.9831			O13	1.9504	
	O3	2.4545			O9	2.4683	
Mo6	O17	1.6731	BVS = 5.35 / 5.79	Mo12	O40	1.6748	BVS = 5.34 / 5.78
	O37	1.9292			O27	1.9069	
	O1	1.9350			O32	1.9377	
	O15	1.9360			O39	1.9434	
	O4	1.9502			O36	1.9629	
	O29	2.4569			O3	2.4701	

The bond valence for each Mo-O bond was calculated using the formula: $s_{ij}= \exp[(r_{ij}-d_{ij})/b]$ proposed by Brown. From the parameters published by Brown on the Web, we have chosen r_{ij} = 1.878 for Mo^{V}, 1.907 for Mo^{VI} and b = 0.37. The first value is calculated with the parameters of Mo^{V} and the second of Mo^{VI}.

Mean BVS value: 5.42 / 5.86

Calculated BVS value considering the formulae $[Ru(C_{10}H_8N_2)_3][PMo^{VI}_9Mo^{V}_3O_{40}Zn_2(C_{10}H_8N_2)_2]$: 5.75

Figure S5. Ball and stick representation with partial atomic labeling scheme, selected bond distances (Å) and bond valence summations (BVS) of the POM unit in **Ru-PMo$_{14}$**.



Mo1	O28	1.6759	BVS = 5.39 / 5.84	Mo8	O34	1.6669	BVS = 5.41 / 5.85
	O30	1.8410			O3	1.8411	
	O6	1.8644			O22	1.8421	
	O17	1.9566			O7	2.0136	
	O9	2.1241			O9	2.1202	
	O5	2.4674			O5	2.4416	
Mo2	O31	1.6759	BVS = 5.46 / 5.90	Mo9	O37	1.6722	BVS = 5.22 / 5.65
	O12	1.8239			O4	1.9308	
	O11	1.8415			O19	1.9353	
	O8	1.9587			O12	1.9603	
	O21	2.1624			O35	1.9687	
	O23	2.4683			O16	2.5262	
Mo3	O43	1.6788	BVS = 5.16 / 5.58	Mo10	O41	1.6665	BVS = 5.28 / 5.72
	O30	1.9252			O6	1.9252	
	O25	1.9466			O1	1.9331	
	O18	1.9710			O20	1.9546	
	O11	1.9787			O22	1.9723	
	O23	2.4885			O5	2.5039	
Mo4	O40	1.6770	BVS = 5.39 / 5.83	Mo11	O36	1.6745	BVS = 5.23 / 5.65
	O4	1.8489			O26	1.9346	
	O26	1.8496			O2	1.9375	
	O8	1.9542			O3	1.9528	
	O13	2.1351			O27	1.9714	
	O14	2.4811			O14	2.4935	
Mo5	O38	1.6718	BVS = 5.35 / 5.79	Mo12	O10	1.6680	BVS = 5.40 / 5.84
	O1	1.8434			O2	1.8358	
	O25	1.8530			O19	1.8489	
	O24	1.9903			O7	2.0061	
	O21	2.1298			O15	2.1104	
	O23	2.4853			O16	2.4791	
Mo6	O32	1.6779	BVS = 5.46 / 5.90				
	O18	1.8317		Mo13	O39	1.6620	BVS = 5.24 / 5.67
	O35	1.8341			O33	1.9070	
	O17	1.9606			O21	1.9929	
	O15	2.1534			O13	2.0040	
	O16	2.4639			O24	2.0540	
					O8	2.1671	
Mo7	O29	1.6746	BVS = 5.42 / 5.86				
	O27	1.8286		Mo14	O42	1.6813	BVS = 5.08 / 5.49
	O20	1.8393			O33	1.9257	
	O24	2.0121			O15	1.9960	
	O13	2.1213			O9	2.0129	
	O14	2.4347			O7	2.0465	
					O17	2.1794	

The bond valence for each Mo-O bond was calculated using the formula: $s_{ij}= \exp[(r_{ij}-d_{ij})/b]$ proposed by Brown. From the parameters published by Brown on the Web, we have chosen r_{ij} = 1.878 for Mo^{V}, 1.907 for Mo^{VI} and b = 0.37. The first value is calculated with the parameters of Mo^{V} and the second of Mo^{VI}.

Mean BVS value: 5.35 / 5.78

Calculated BVS value considering the formulae $[N(C_4H_9)_4][Ru(C_{10}H_8N_2)_3][PMo^{VI}_8Mo^{V}_6O_{43}]$: 5.57.

Figure S6. Top and side views of the polyhedral representations of the POM in **Ru-PMo$_{12}$Zn$_2$** (left) and {ε-$PMo^{VI}_4Mo^{V}_8O_{40}Zn_4$} POM (right).

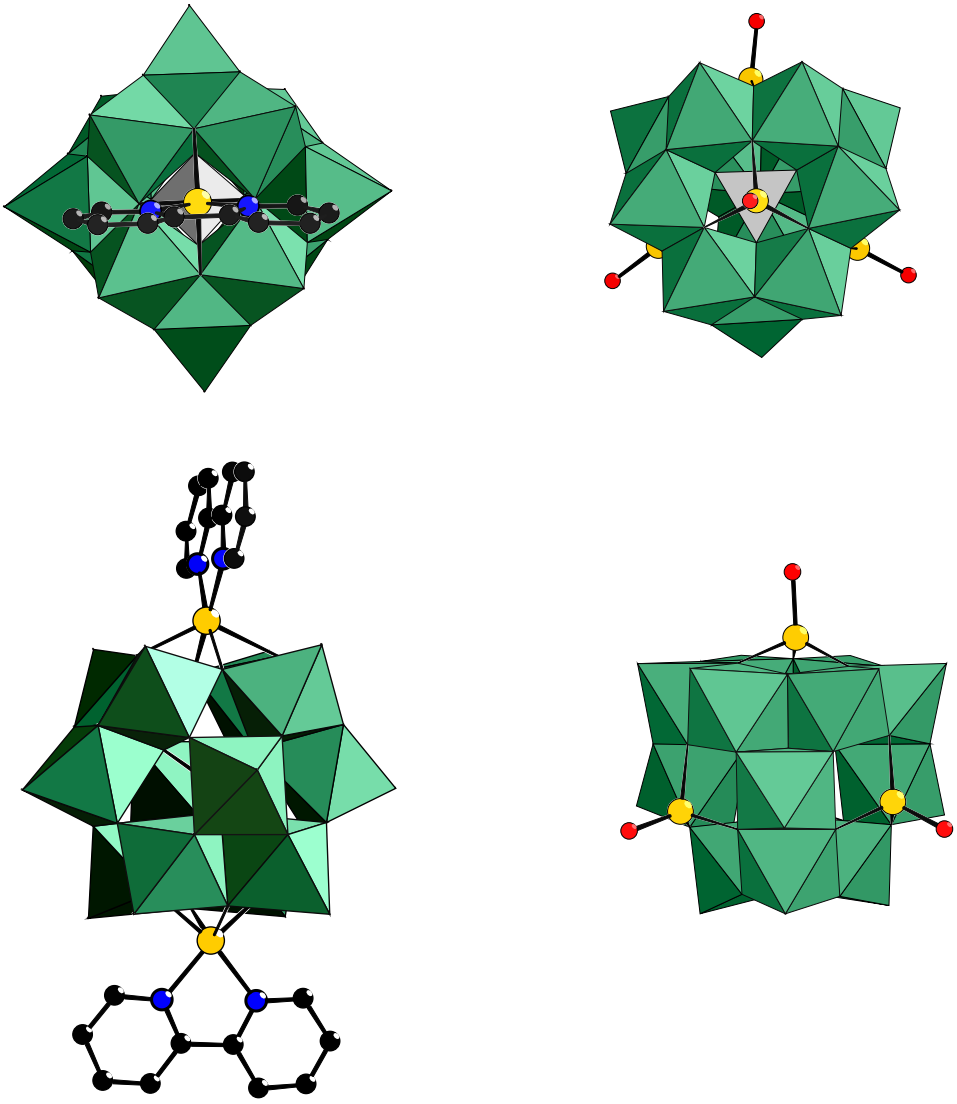
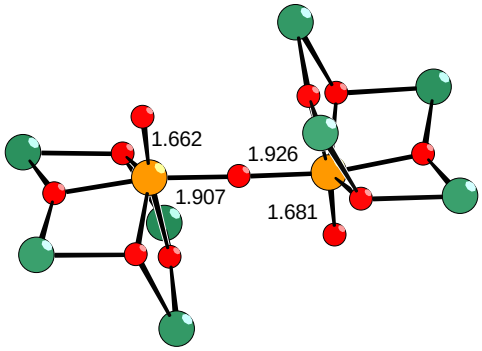
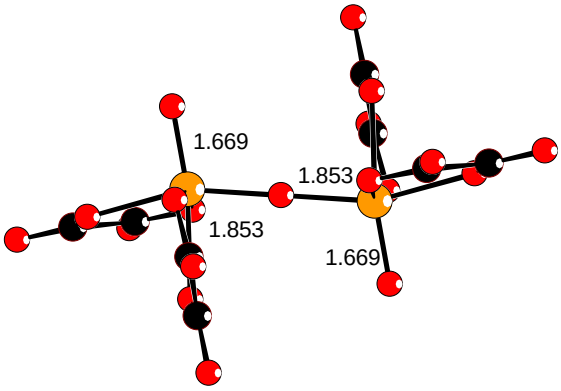


Figure S7. Comparison of the geometrical parameters of the connections between Mo^{V} ions in **Ru-PMo$_{14}$**, $[Mo_2O_3(C_2O_4)_4]^{4-}$, $[Mo_2O_4(C_2O_4)_5]^{6-}$ and ε-Keggin ions. Green spheres: Mo (Mo^{V} or Mo^{VI}), orange spheres : Mo^{V}.

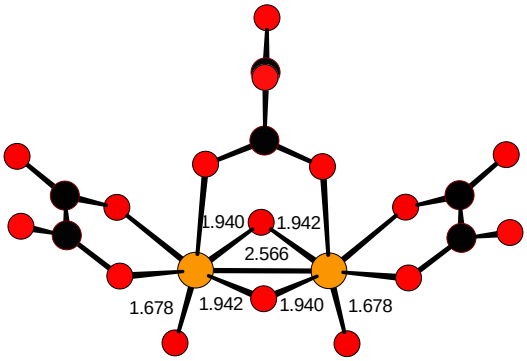
Ru-PMo$_{14}$



$[Mo_2O_3(C_2O_4)_4]^{4-}$ Modec et al. *Eur. J. Inorg. Chem.*, 2004, 1611



$[Mo_2O_4(C_2O_4)_5]^{6-}$ Modec et al. *Eur. J. Inorg. Chem.*, 2004, 1611



{ε-$PMo_{12}O_{40}$} Nohra et al. *J. Am. Chem. Soc.*, 2011, **133**, 13363

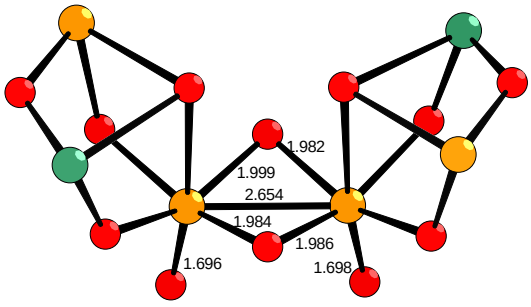


Figure S8. π–π and C-H···O hydrogen bond interactions between $[Ru(bpy)_3]^{2+}$ and adjacent POMs in **Ru-PMo$_{12}$Zn$_2$**.

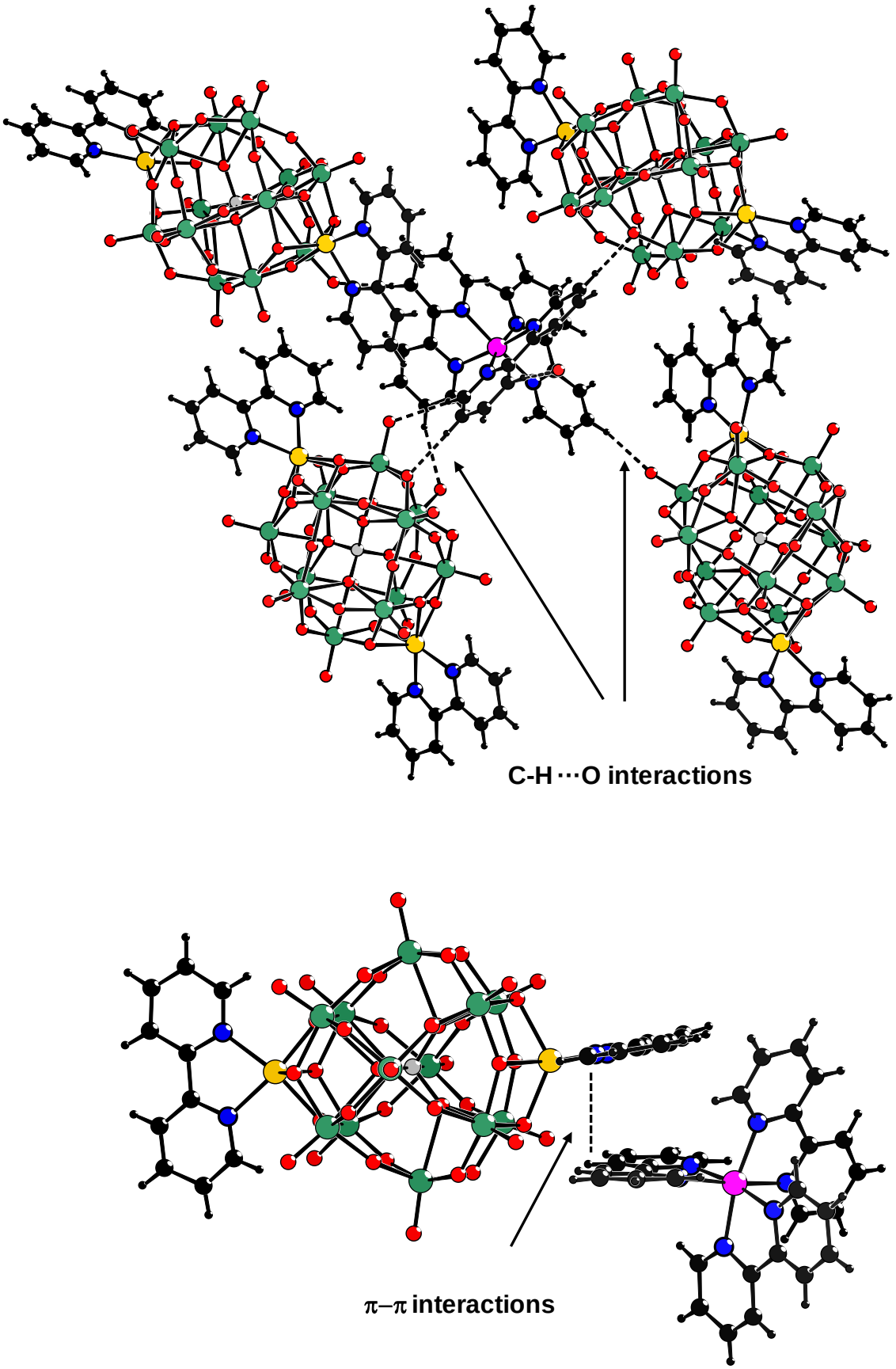


Figure S9. C-H···O hydrogen bond interactions between $[Ru(bpy)_3]^{2+}$ and four adjacent POMs in **Ru-PMo$_{14}$**.

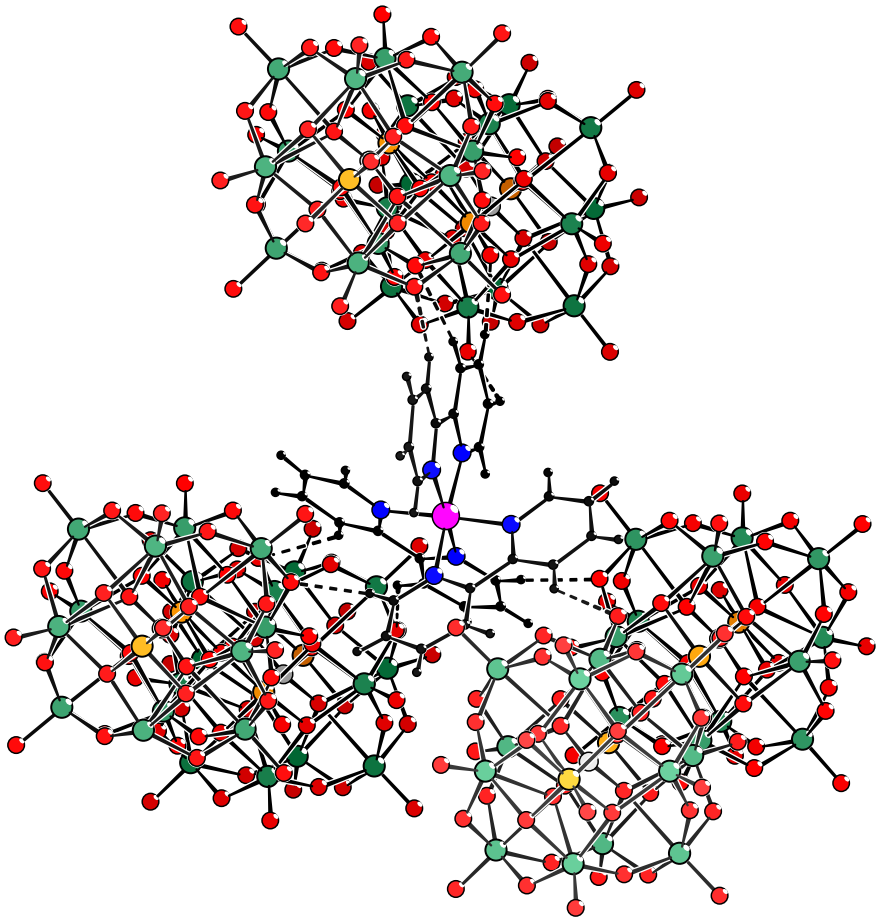


Figure S10. Atomic distances and lengths between bicapped Keggin units in the **Ru-PMo$_{14}$** structure.

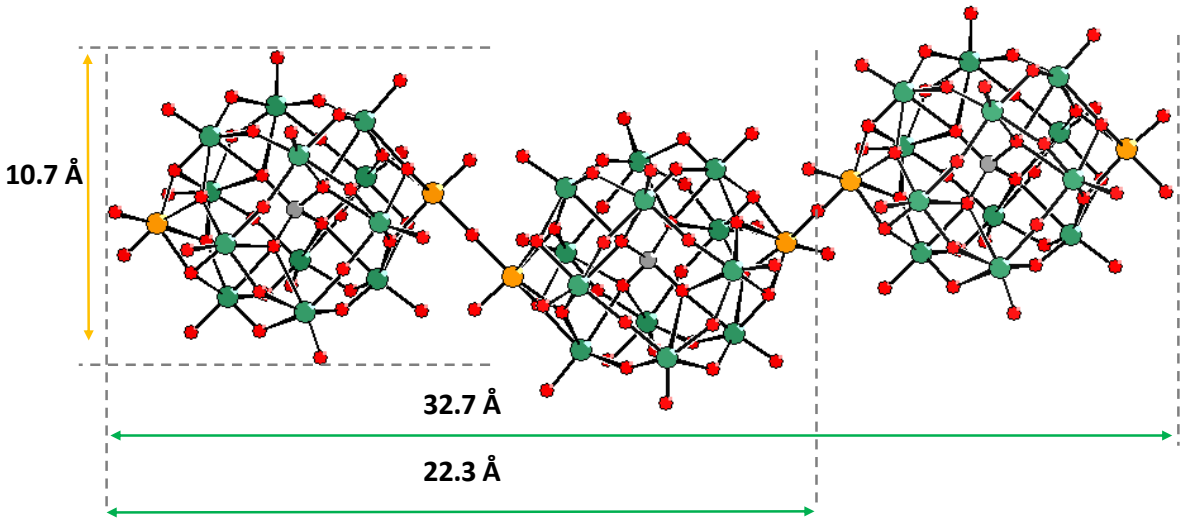
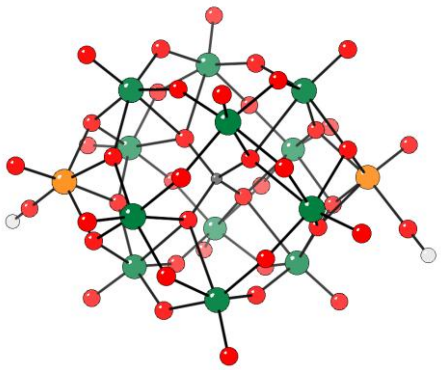


Figure S11. Structural models used for DFT calculations, with H atoms (white spheres) at bridging oxygen positions. (A) Monomer and (B) dimer.

(A)



(B)