Electronic Supplementary Information for

A Dodecanuclear Zn Cluster Sandwiched by Polyoxometalate Ligands

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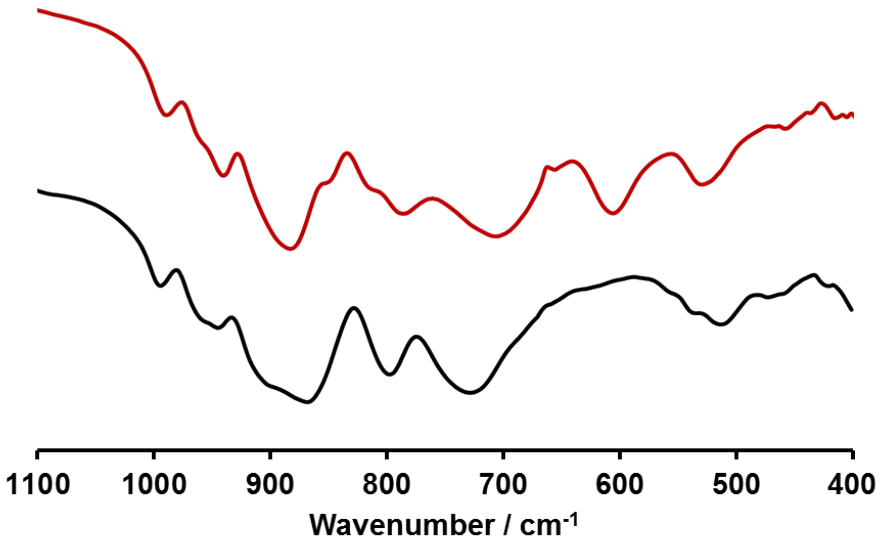


Figure S1. IR spectra of $K_{16}\alpha$-$[Si_2W_{18}O_{66}]\cdot 25H_2O$ (black) and **1** (red)

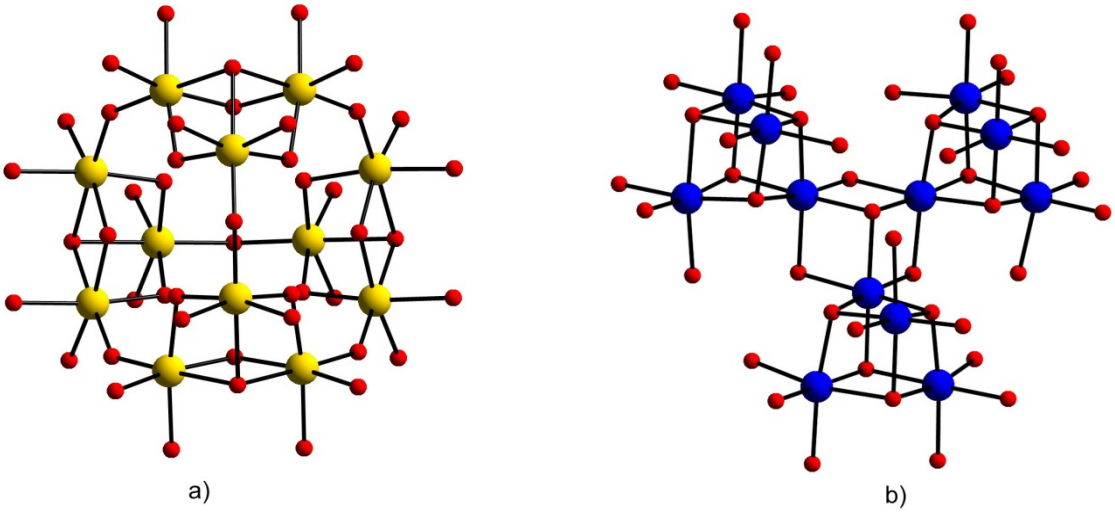


Figure S2. Polyhedral views of the dodecanuclear-transition metal clusters in the reported sandwich-type POMs: Fe_{12}/Ti_{12} cluster (a) and Ni_{12} cluster (b) The color code is as follows: Fe/Ti (yellow), Ni (blue) and oxygen (red).

The $Fe_{12}O_{46}/Ti_{12}O_{46}$ core (Figure S2a)[1, 2] is composed of four groups of three edge-shared, corner-linked FeO_6/TiO_6 octahedra, and outside the metal cluster are four $\{P_2W_{15}\}$ units. The Ni_{12} (Figure S2b)[3] is formed by the connection of three distorted $[Ni_4O(OH)_3]$ units, and outside the Ni_{12} cluster are three $\{PW_9\}$ units, a WO_4 tetrahedron and a $[W_7O_{26}(OH)]^{11-}$ unit.

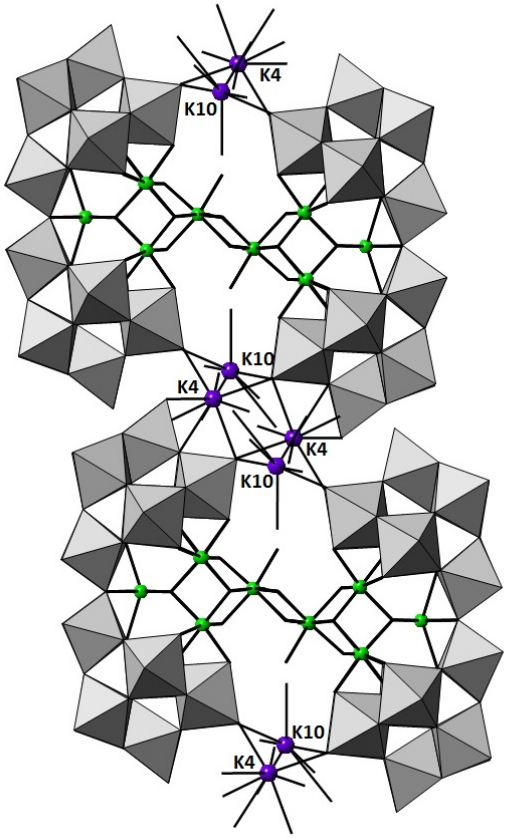


Figure S3. Combined polyhedral/ball-and-stick representation of **1** in the lattice. The color code is as follows: zinc (green), tungsten (grey), silicon (yellow), and K (purple).

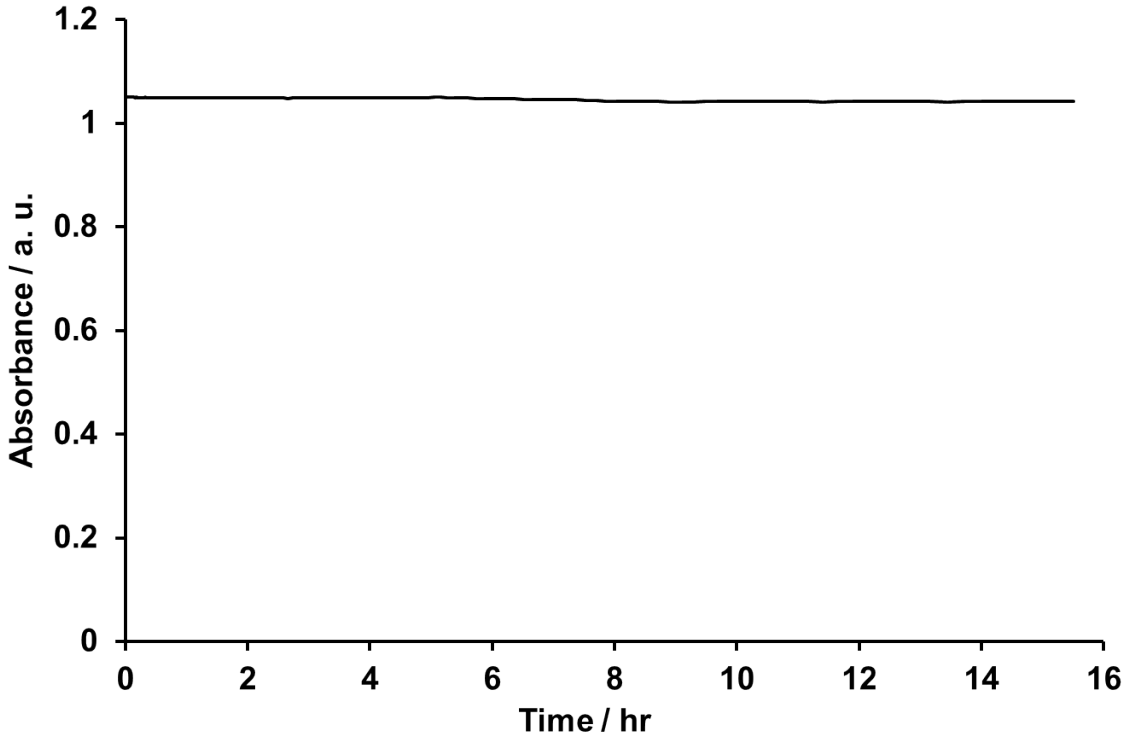
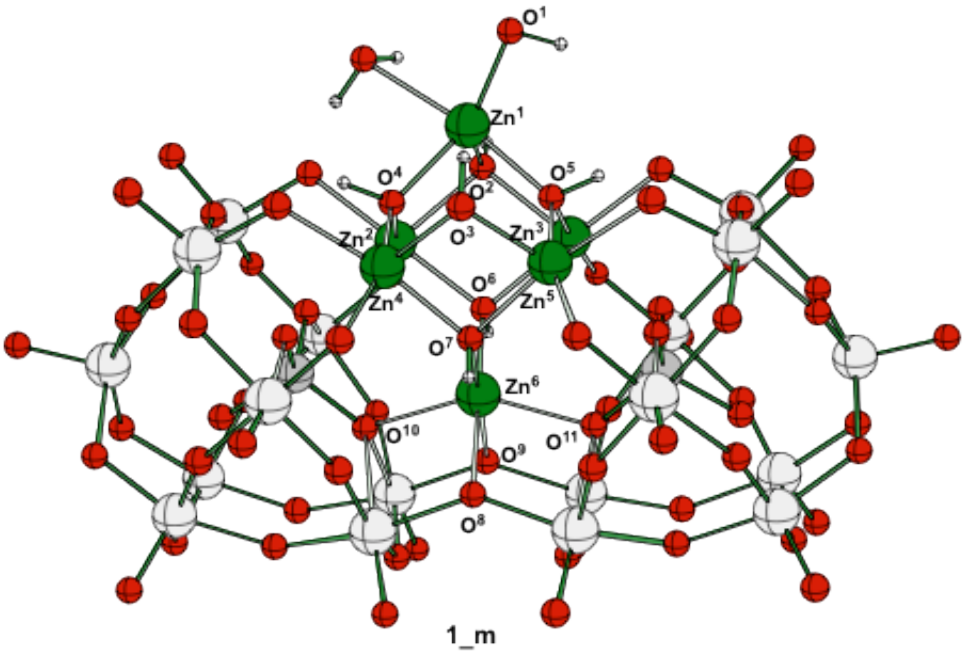


Figure S4. The absorption of **1** (9 μM in water) at 250 nm as a function of time showing no change.



Zn^1-O^1 = 1.976 (2.068)	Zn^2-O^2 = 2.098 (2.061)	Zn^3-O^2 = 2.115 (2.049)
Zn^1-O^2 = 2.155 (2.240)	Zn^2-O^4 = 2.138 (2.064)	Zn^3-O^5 = 2.104 (2.039)
Zn^1-O^4 = 2.068 (2.117)	Zn^2-O^6 = 2.113 (2.052)	Zn^3-O^6 = 2.160 (2.094)
Zn^1-O^5 = 2.158 (2.170)		

Zn^4-O^4 = 2.106 (2.022)	Zn^6-O^6 = 2.057 (1.979)
Zn^4-O^7 = 2.133 (2.087)	Zn^6-O^7 = 2.067 (1.978)
Zn^4-O^3 = 2.099 (2.057)	Zn^6-O^8 = 2.213 (2.131)
	Zn^6-O^9 = 2.226 (2.163)
Zn^5-O^5 = 2.089 (2.020)	Zn^6-O^{10} = 2.261 (2.238)
Zn^5-O^3 = 2.097 (2.056)	Zn^6-O^{11} = 2.283 (2.241)
Zn^5-O^7 = 2.138 (2.069)	

Figure S5. Notation of atoms and comparison of the calculated important bond distances (in Å) of **1_m** with their experimental values (in parenthesis) in **1**. The calculated important geometry parameters of **1_m** are in good agreement with their experimental values reported for the dimer complex **1**. These findings justify the use of model **1_m** to study electronic properties of **1**.

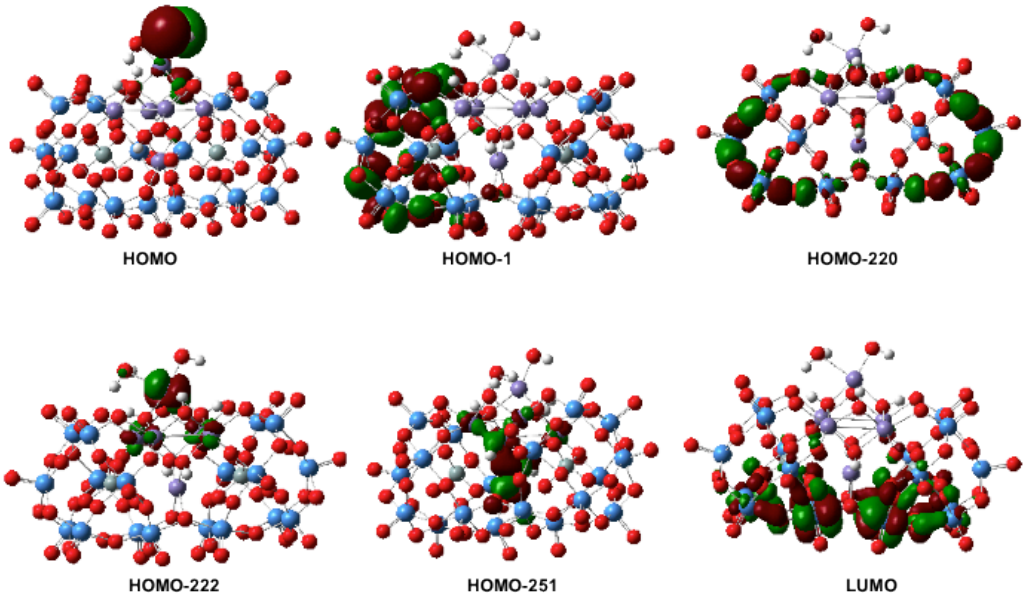


Figure S6. Representative HOMO and LUMO orbitals of **1_m** calculated at the B3LYP/[Lanl2dz + 6-31G(d)] level of theory.

References

1. C. P. Pradeep, D. L. Long, P. Kogerler and L. Cronin, *Chem Commun*, 2007, 4254-4256.
2. Y. Sakai, S. Ohta, Y. Shintoyo, S. Yoshida, Y. Taguchi, Y. Matsuki, S. Matsunaga and K. Nomiya, *Inorg. Chem.*, 2011, **50**, 6575-6583.
3. H. M. Zhang, Y. G. Li, Y. Lu, R. Clerac, Z. M. Zhang, Q. Wu, X. J. Feng and E. B. Wang, *Inorg Chem*, 2009, **48**, 10889-10891.