Electric Supplemental Information for:

A 3d-4f Heterometallic 3D POMOF Based on Lacunary Dawson Polyoxometalates†

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Electronic Supplementary Material (ESI) for Dalton Transactions
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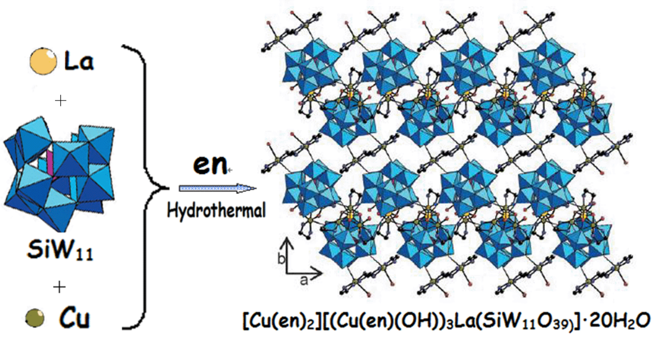
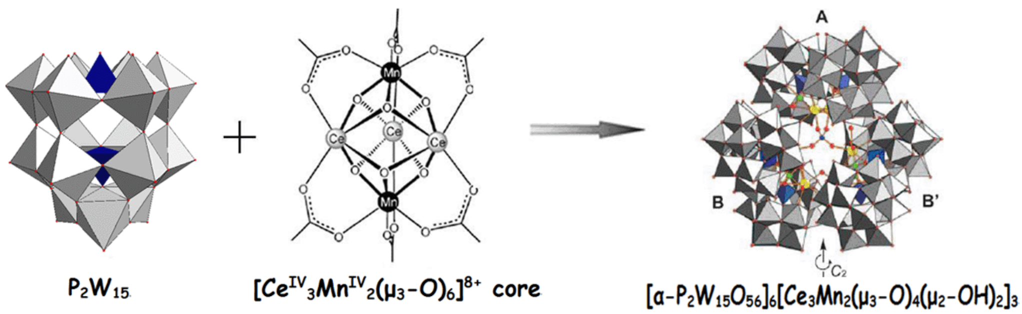


Scheme S1 Scheme show the typical example of one pot methed[1]

1 B. Nohra, P. Mialane, A. Dolbecq, E. Rivière, J. Marrota and F. Sécheressea, *Chem. Commun.*, 2009, 2703.



Scheme S2 Scheme show the typical example of stepwise methed[2]

2 X. K. Fang and P. Kögerler, *Angew. Chem. Int. Ed.,* 2008, **47**, 8123.

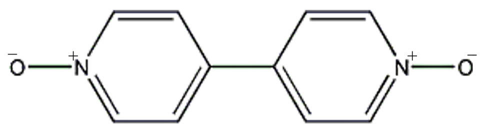


Chart S1 Structure of 4,4'-dipyridine-N,N'-dioxide Ligand

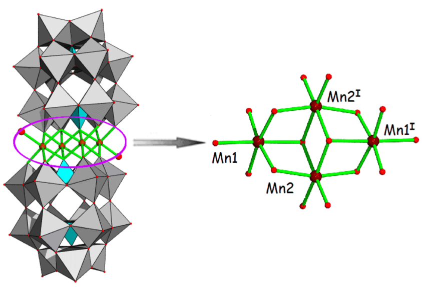


Fig. S1 The structure of $[Mn_4(HP_2W_{15}O_{56})_2]^{14-}$ unit. Symmetry code: (I) 1 + x, 2 + y, z

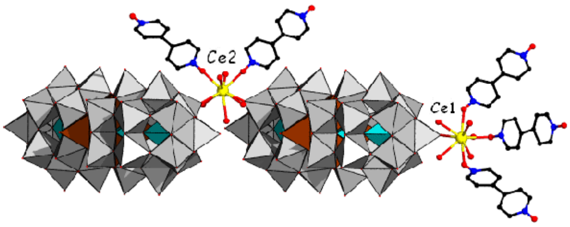


Fig. S2 Coordination environment of the Ce1 and Ce2 cations (H atoms are omitted for clarity)

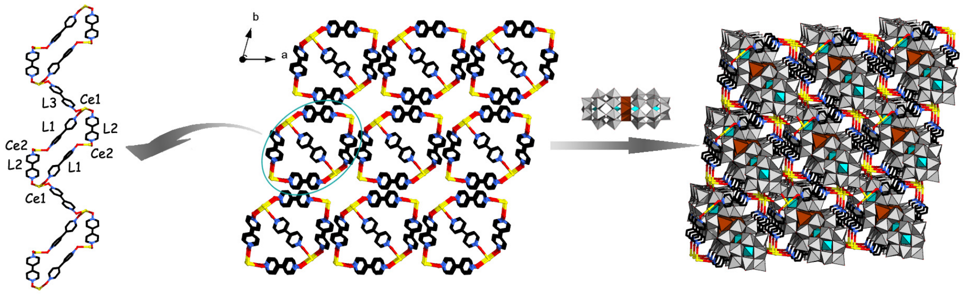


Fig. S3 Schematic view of the formation of the 3D POMOFs.

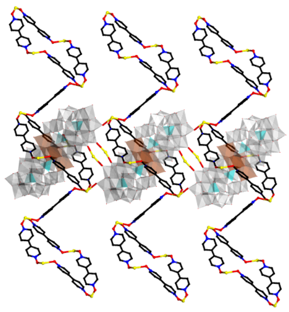


Fig. S4 The coordination relation between the $[Mn_4(HP_2W_{15}O_{56})_2]^{14-}$ clusters and 1D zigzag chains.

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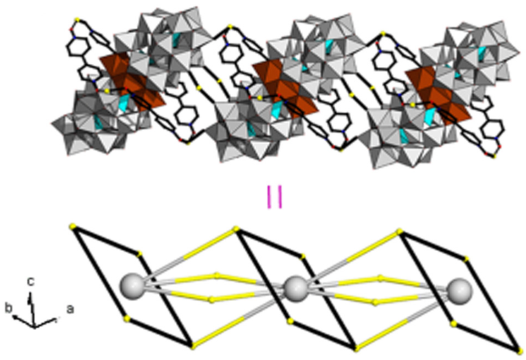

Fig. S5 The detailed view of the self-penetrating structure in **1.**

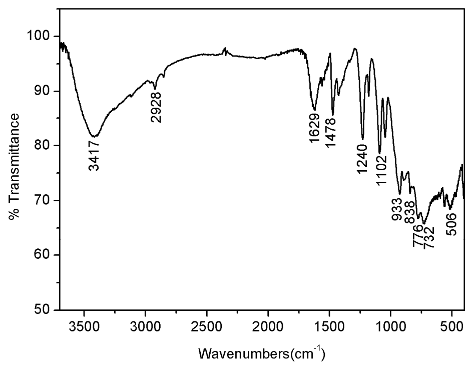

Fig. S6 The IR spectrum of compound **1**

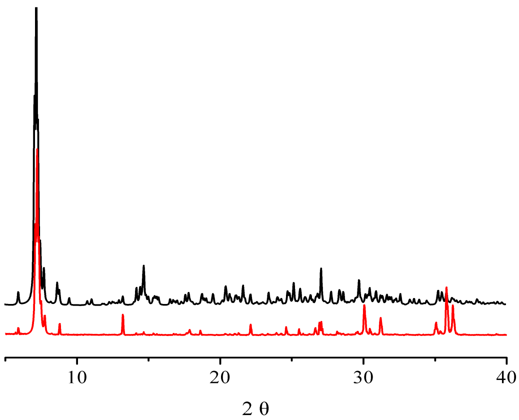

Fig. S7. The simulative (black) and experimental (red) powder X-ray diffraction patterns for **1**

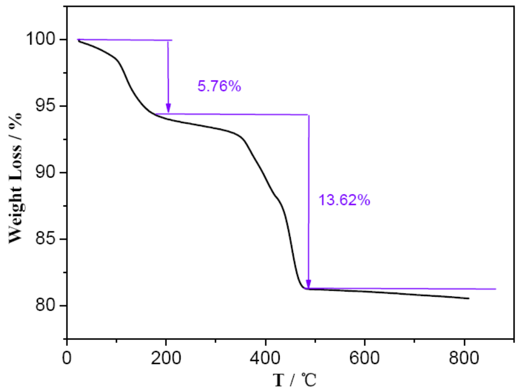

Fig. S8 The TG curve for compound **1**.

atom	R_0	BVS	atom	R_0	BVS
W1	1.921	6.428	W12	1.921	6.095
W2	1.921	6.014	W13	1.921	6.181
W3	1.921	6.247	W14	1.921	6.111
W4	1.921	6.338	W15	1.921	6.135
W5	1.921	6.128	P1	1.604	4.645
W6	1.921	6.476	P2	1.604	4.907
W7	1.921	6.260	Mn1	1.79	2.214
W8	1.921	6.149	Mn2	1.79	2.171
W9	1.921	6.416	Ce1	2.151	3.220
W10	1.921	6.498	Ce2	2.151	3.288
W11	1.921	6.160			

Table S1. Summary of Calculated Values from BVS for **1**

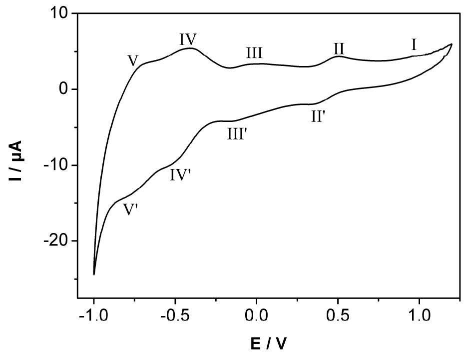

Fig. S9. The CV of **1**-CPE in the Na_2SO_4/H_2SO_4 aqueous solution at the scan rate of 20 $mV{\cdot}s^{-1}$.

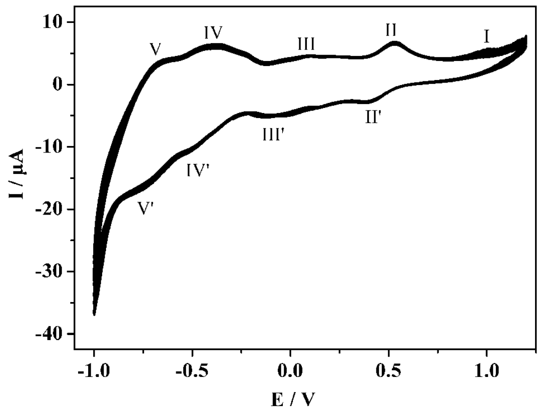

Fig. S10 100 consecutive CV cycles of the **1**-CPE at 20 mV s^{-1}

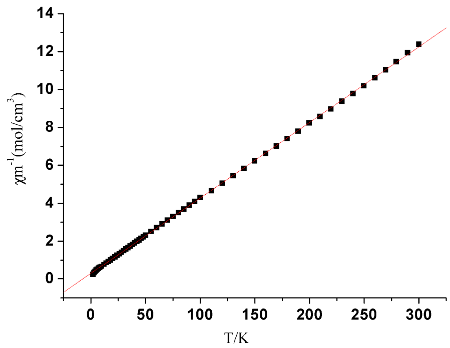

Fig. S11 The χ_m^{-1} versus T plot of **1**

16. Electrocatalytic properties of $Na_{12}[\alpha\text{-}P_2W_{15}O_{56}]\cdot 24H_2O$ and $Na_{16}[Mn_4(H_2O)_2(P_2W_{15}O_{56})_2]\cdot 53H_2O$

The electrocatalytic properties of $Na_{12}[\alpha\text{-}P_2W_{15}O_{56}]\cdot 24H_2O$ (P_2W_{15}) and $Na_{16}[Mn_4(H_2O)_2(P_2W_{15}O_{56})_2]\cdot 53H_2O$ were performed for comparison, and the CAT (catalytic efficiency) of **P_2W_{15}**-CPE towards KIO_3 was calculated and compared to that of **1**-CPE.

Different from the **1**-CPE having bifunctional electrocatalytic activities (please see the Fig. 4 in the MS), the **P_2W_{15}**-CPE only has electrocatalytic reduction activity towards the inorganic molecule iodate (KIO_3), and has no electrocatalytic activity towards ascorbic acid (AA), dopamine (DA) (please see the Fig. S12 below). The CAT of **P_2W_{15}**-CPE (85.30%) towards IO_3^- is lower than the CAT of **1**-CPE (197.50%) towards IO_3^-. And the **$Na_{16}[Mn_4(H_2O)_2(P_2W_{15}O_{56})_2]\cdot 53H_2O$**-CPE has no electrocatalytic activities towards AA, DA, H_2O_2 and KIO_3 (see Fig. S13 and Fig. S14 below). Herein, It can be concluded that both Mn(II) and Ce(III) cations may strongly influence the electrocatalytic activities of P_2W_{15} clusters in **1**, which finally results in the bifunctional electrocatalytic activity of **1**.

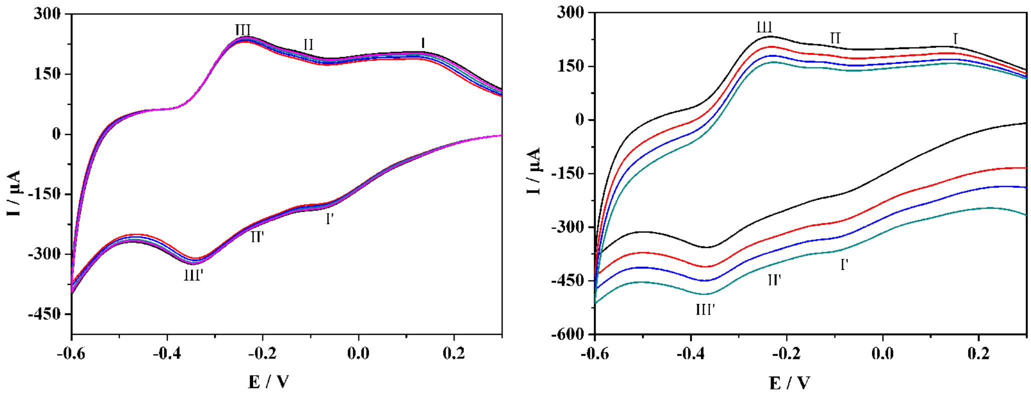

Fig. S12 Reduction of H_2O_2 (left) and IO_3^- (right) at **P_2W_{15}**-CPE in 1 M H_2SO_4 solution. Scan rate: 0.05 $V \cdot s^{-1}$.

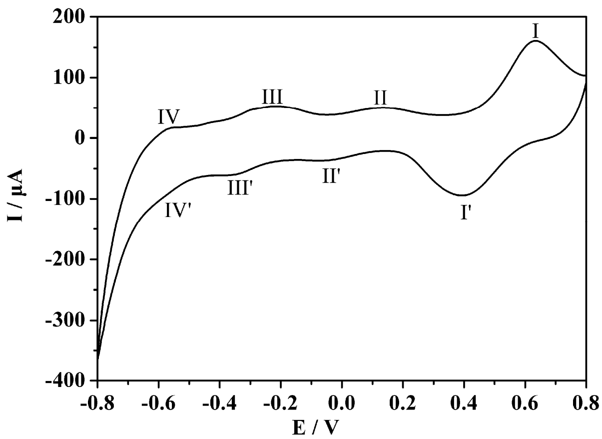

Fig. S13 The CV of **$Na_{16}[Mn_4(H_2O)_2(P_2W_{15}O_{56})_2] \cdot 53H_2O$** -CPE in the 1 M H_2SO_4 solution at the scan rate of 0.02 $V \cdot s^{-1}$.

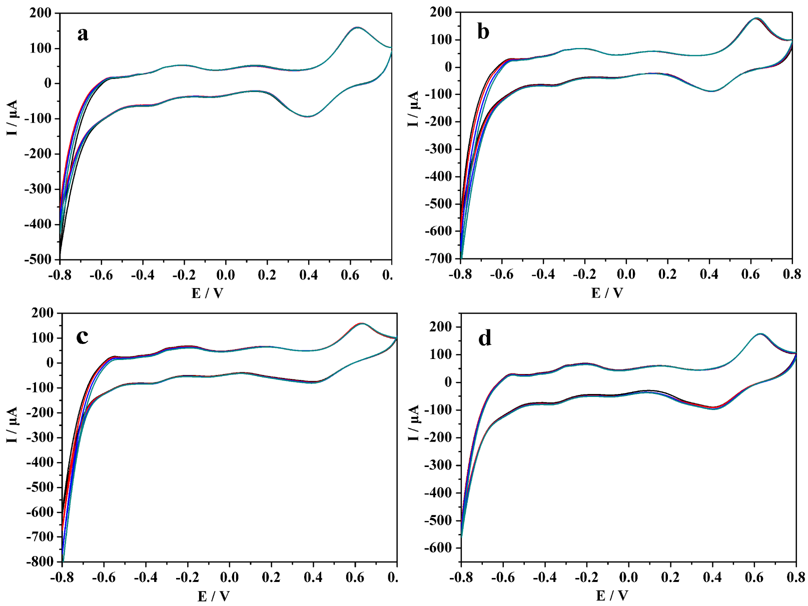

Fig. S14 Electrocatalytic reaction of AA (a), DA (b), H_2O_2 (c) and KIO_3 (d) at **$Na_{16}[Mn_4(H_2O)_2(P_2W_{15}O_{56})_2]\cdot 53H_2O$**-CPE in 1 M H_2SO_4 solution at the scan rate of 0.02 $V\cdot s^{-1}$.