## **Supporting Information**

## An Extended Architecture built upon the Double-Dawson-Type Polyoxoanion

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Fig. S1. Ball-and-stick representation of the structure of H<sub>2</sub>L.



Fig. S2. Chemical equation shows the formation process of L.



Fig. S3. View of coordination modes of hydrogen bonds between enMe molecules and  $\left[(W_4Mn_4O_{12})(P_2W_{14}O_{54})_2\right]^{20}$  subunit in 1. Hydrogen atoms are omitted for clarity.



Fig. S4. View of coordination modes of hydrogen bonds between  $H_2L$  and  $[(W_4Mn_4O_{12})(P_2W_{14}O_{54})_2]^{20-}$  subunit in **1**. Hydrogen atoms are omitted for clarity.



Fig. S5. Polyhedral and ball-and-stick view of unit cell in compound 2.



Fig. S6.View of the 3D framework of 2 along *a* axis. Hydrogen atoms are omitted for clarity.



**Fig. S7.** View of coordination modes of hydrogen bonds between  $H_2L$  and  $H_2L$  ligand,  $H_2L$  ligand and  $[P_2W_{18}O_{62}]^{6-}$  subunit in **2**. Hydrogen atoms are omitted for clarity.



Fig. S8. The IR spectrum of 1.



Fig. S9. TGA curve of 1.