

Supporting Information

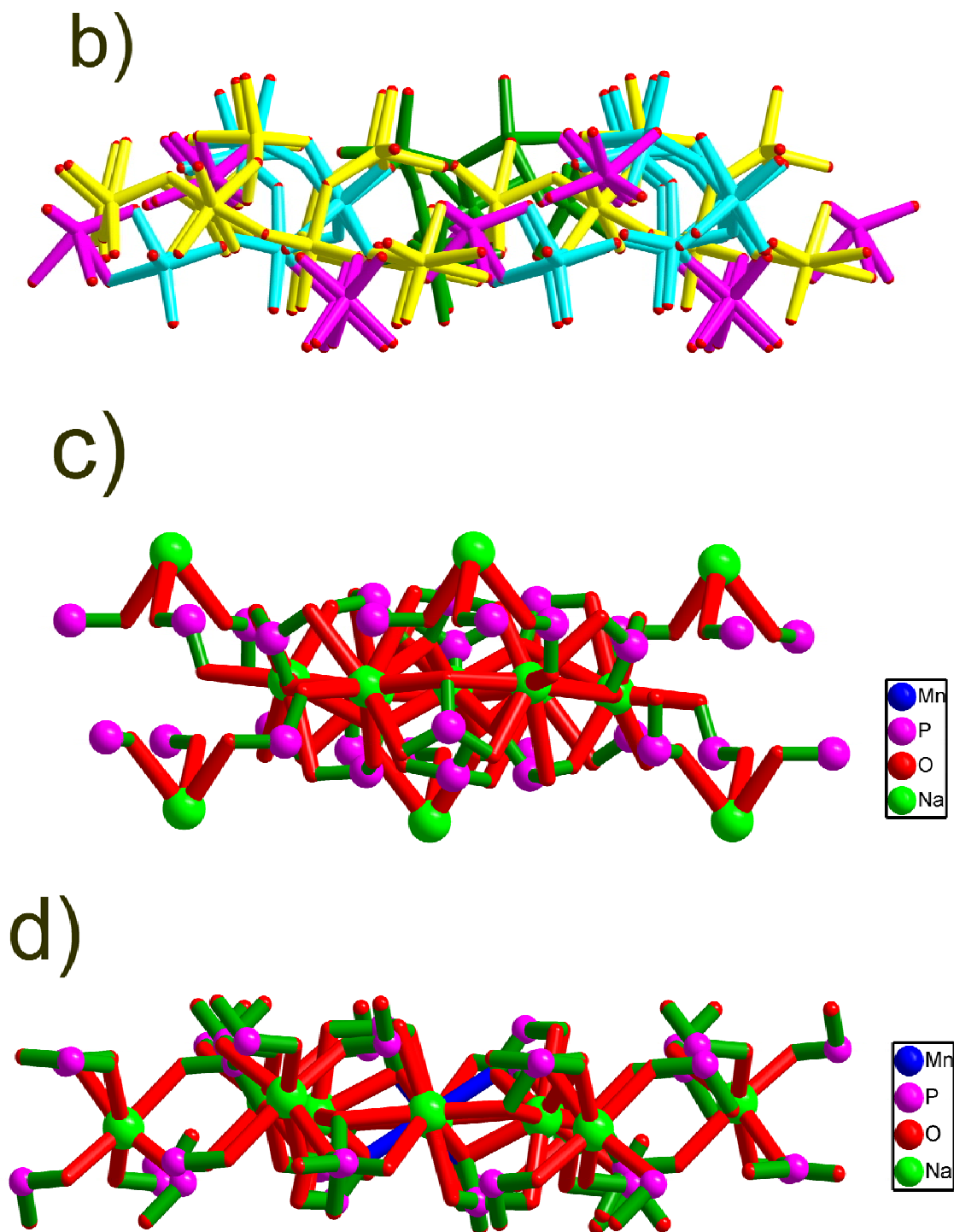


Figure S1. The side view of the building blocks of **1**, and the number of the pictures are in accord with Figure 1 in the article. (b) The aggregation mode of the Mn-chains, showing the same type of connection nodes (pink) are in a nearly linear array, at the same time all of them are in a zigzag array. (c) A side view of the $\{\text{Na}(1)[\text{Na}(4)]_6\text{P}_{18}\}$ unit. (d) A side view of the $\{\text{Mn}(10)[\text{Na}(5)]_6\text{P}_{12}\}$ unit.

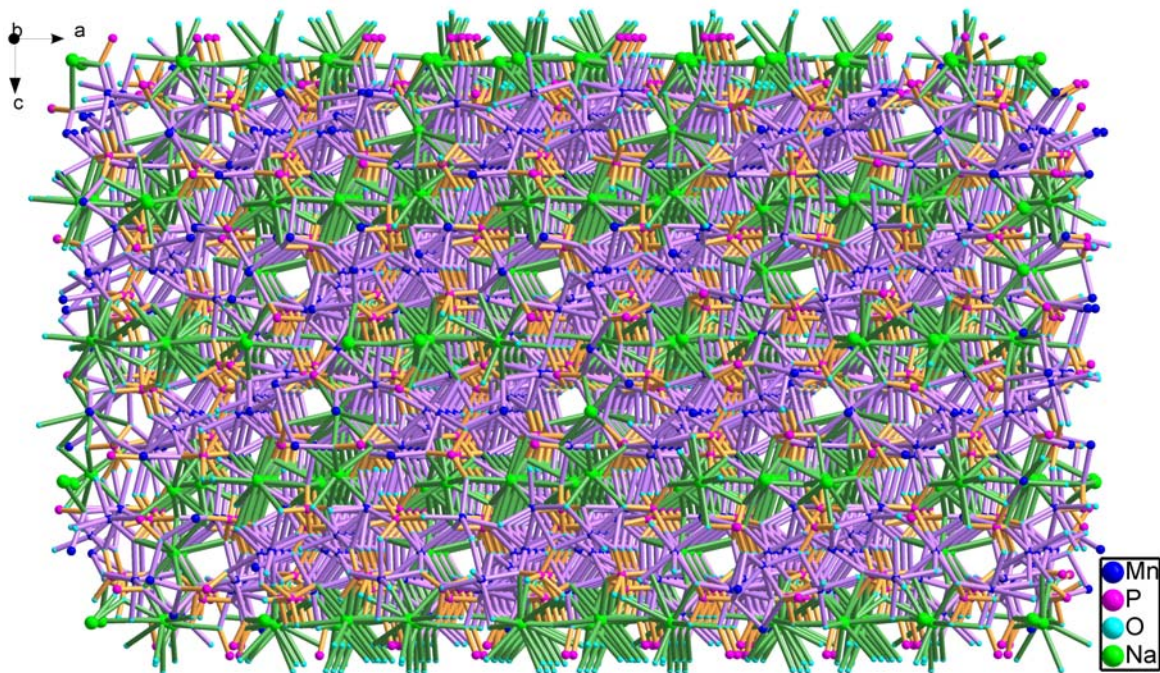


Figure S2. The 3D network of the heterocluster $[\text{Na}_{17}\text{Mn}_{43}(\text{PO}_4)_{36}]^{5-}$. Color code: Na-O: dark green; P-O: orange; M-O: purple.

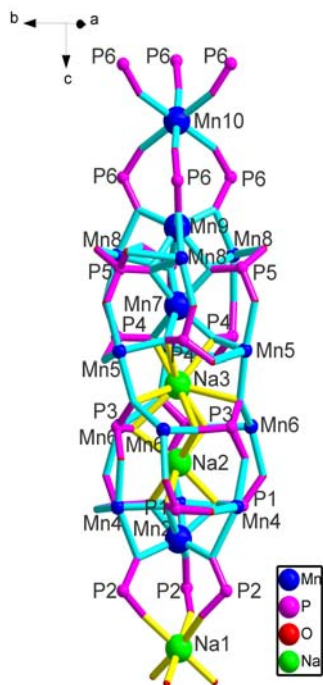


Figure S3. View of the connection mode of the linkers (P₁₋₆, Na(2)-Na(3) group), the wheel centers (Na(1), Mn(10)) and the connection nodes (Mn(2), Mn(7), Mn(9)) of the manganese clusters.