Supplemantary Information

Synthesis, Characterization and Electrochemical Properties of New Water-Soluble Mn₁₂O₁₂(O₂CR)₁₆(H₂O)₄ Clusters

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Figure S1: XPS spectrum of 2. (a) Full range (b) Enlargement of Mn2P region.



Figure S2: UV-Vis spectrum of 2 (red) and the free ligand dabH (blue) in water.



Figure S3: MS spectrum of **2**, showing cluster's full mass with 8 water molecules attached - $[Mn_{12}O_{12}(O_2CC_6H_3(NH_2)_2)_{16}(H_2O)_4]\cdot 8H_2O$ at 3484.2 m/z.



Figure S4: XPS spectrum of **3**. (a) Full range (b) Enlargement of Mn2P region.



Figure S5: UV-Vis spectrum of **3** (red) and the free ligand proH (blue) in water, and of **1** (black) in methanol.



Figure S6: MS spectrum of **3**, showing the mass of the cluster with 5 ethanolamine molecules as solvates - $[Mn_{12}O_{12}(O_2CC_4H_8N)_{16}(H_2O)_4]$ ·5ETA at 3054.7 m/z



Figure S7: Powder X-ray diffraction patterns within the range of 2θ (0–60°) for **3**, compared to **1**.



Figure S8: FTIR spectra of (a) The free ligand ascH, showing characteristic bands assigned to the normal (reduced) form of L-ascorbic acid (red circles): stretching bands of the four O-H groups in the section of \sim 3200-3600cm⁻¹, and the carbonyl peak at \sim 1700cm⁻¹.

(b) Mn cluster **4**, showing characteristic bands assigned to the "dehydro" (oxidized) form of L-ascorbic acid (blue circles): two O-H groups in the section of \sim 3200-3600cm⁻¹, and the two carbonyl peaks at \sim 1300 and \sim 1550cm⁻¹. Orange circle - some missing Mn- μ -O core bands at ν =500-715cm⁻¹, suggesting different oxidation state of one or more Mn atoms.



Figure S9: Enlargement of the750-350cm⁻¹ area in the FTIR spectrum of 4





Figure S11: XPS spectrum of 4. (a) Full range (b) Enlargement of Mn2P region.



Figure S12: UV-Vis spectrum of 4 (red) and the free ligand ascH (blue) in water.



Figure S13: MS spectrum of **4**, showing $[Mn_{12}O_{12}(O_2CCH_3)_{14}(C_6H_6O_6)_2 \cdot (H_2O)_4] \cdot 9H_2O$ mass at 2259 m/z.



Figure S 14: Powder X-ray diffraction patterns within the range of 2θ (0–60°) for 4, compared to 1.



Figure S15: Cyclic Voltammograms at 100 mV/s of 0.1 M acetate buffer at pH 6.0 (black), deoxygenated 0.1 M acetate buffer at pH 6.0 containing 0.5 mM **3** (red), and deoxygenated 0.1 M acetate buffer at pH 6.0 containing 8 mM of the free ligand proH (blue).