SUPPORTING INFORMATION

Artificial Synthetic $Mn^{IV}Ca$-oxido Complexes Mimic the Oxygen-Evolving Complex in Photosystem II

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Experimental Section

All manipulations were carried out under aerobic condition. Solvents were dried by using an A4 molecular sieve. Other chemicals were used as received without further purification.

Synthesis of complex A. Complex **A** was synthesized by a reaction of $Bu^{n}_{4}NMnO_4$ (1.445g, 4 mmol), $Mn(ClO_4)_2(H_2O)_6$ (0.362 g, 1 mmol) and $Ca(CH_3CO_2)_2$ (0.158 g, 1 mmol) in boiling acetonitrile at the presence of pivalic acid (3.064 g, 30.0 mmol), The final dark-brown solution was obtained in 25 min after the addition of all chemicals. Precipitate was removed by filtration. The dark-brown crystal of complex **A**•C_6H_{14} (0.351 g) was formed after mixing of 10% hexane (vol/vol) at 0 ℃ in a few days with a yield of 32.73 % (based on Ca^{2+}). Elemental analysis (%) calculated for **A** ($C_{81}H_{162}Ca_2Mn_6O_{43}$): C, 43.55; H, 7.31; and found: C, 43.30; H, 7.35 .

Synthesis of complex B. Complex **A** (30 mg, 14 μmol) was dissolved in ethyl acetate (1.5 ml), then kept at -20 ℃. Dark-brown crystal of complex **B** (12.3 mg) was obtained for a few days with a yield of 41.90% (based on Ca^{2+}). Elemental analysis (%) calculated for **B** ($C_{69}H_{134}Ca_2Mn_6O_{40}$), C, 41.16; H, 6.71; and found: C, 40.97; H, 6.70 .

Synthesis of complex C. Complex **A** (70 mg, 33 μmol) was dissolved in acetonitrile (3 ml) with the presence of 60 μl pyridine. The black triquetrous crystal of complex **C** (9 mg) with a yield of 14.72 % (based on Mn) was formed after the slow evaporation at room temperature in a few days. Elemental analysis (%) calculated for complex **C** ($C_{100}H_{168}Ca_2Mn_9N_3O_{44}$): C, 44.63; H, 6.29; N, 1.56. found: C, 44.60; H, 6.42; N, 1.83.

Electrochemical measurements:

Electrochemical measurements were performed using a three-electrode system connected to an Electrochemical Workstation (PGSTAT302N, from Metrohm). The working electrode was a glass carbon disc (diameter of 3 mm, freshly polished). The counter electrode was a platinum disc (diameter of 3 mm, freshly polished). The reference electrode was an $Ag/AgNO_3$ electrode (0.01 M $AgNO_3$, 0.1 M $Bu^n_4NPF_6$ in acetonitrile). The electrolyte solution was 0.1 M $Bu^n_4NPF_6$ in 1,2-dichiloroethane. Before the measurements, oxygen was removed from the solution by purging for ~30 min with solvent-saturated argon. During the measurement, the solution was kept under argon. A background voltammogram of the electrolyte was recorded before dissolving the complex **A**. Reported potentials were referenced internally to normal hydrogen electrode (NHE) calibrated by the potential of ferrocene/ferrocenium measured under the same condition. Scan rate: 100 mV/s. Arrows show the scan direction.

Density functional theoretical (DFT) calculation

The calculated model for complex **A** was shown in following **Figure S1**, in which all methyl groups of pivalate groups in complex **A** were simplified by H atom. High spin states of all Mn ions were applied for calculation. DFT calculations were carried out by using the hybrid functional B3LYP at the Lanl2dz basis in the Gaussian 03 program.

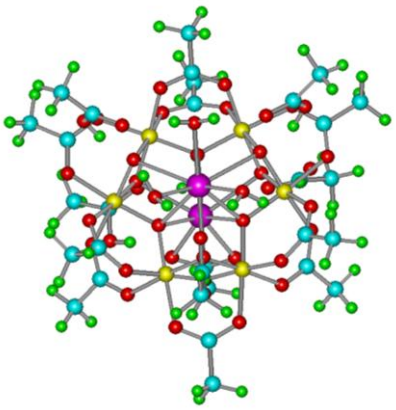

Figure S1. Calculated model for complex **A.** Mn, Ca, O, C, and H were shown in yellow, violet, red, cyan and green, respectively.

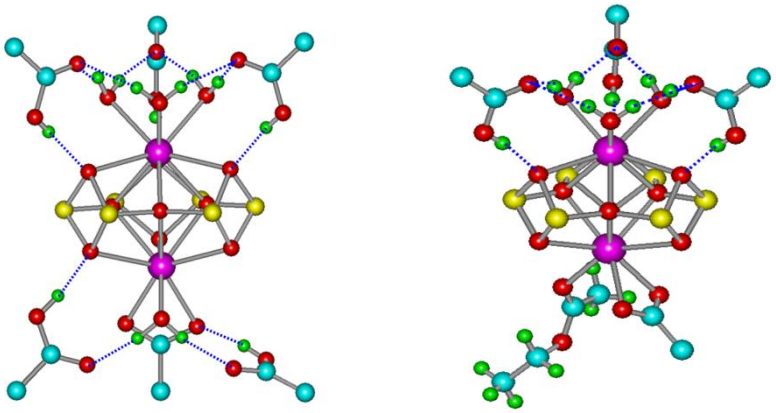

Figure S2. The H-bond networks in complex **A** (left) and complex **B** (right). For clarity, only the core and the peripheral ligands of two Ca^{2+} ions were shown, and all pivalic CH_3 groups were omitted. Mn, Ca, O, C, and H were shown in yellow, violet, red, cyan and green, respectively. The dashed-lines display the H-bond interactions.

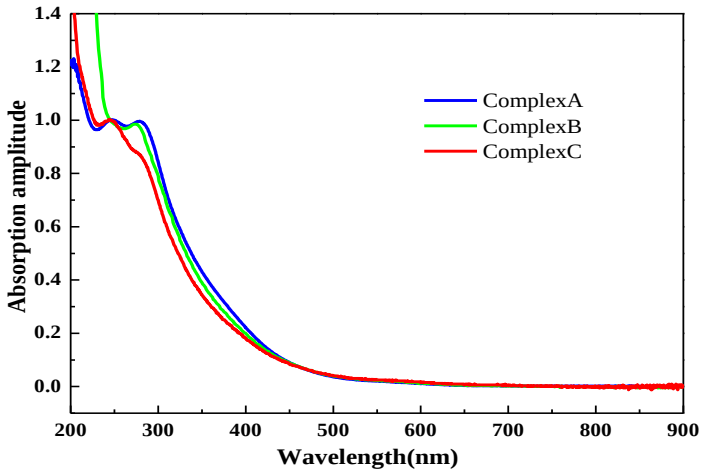

Figure S3. UV-vis absorption spectra for complex **A** (blue, in hexane)**, B** (green, in hexane) and **C** (red, in acetonitrile). For comparison, all spectra were normalized at the peak of the maximum wavelengths.

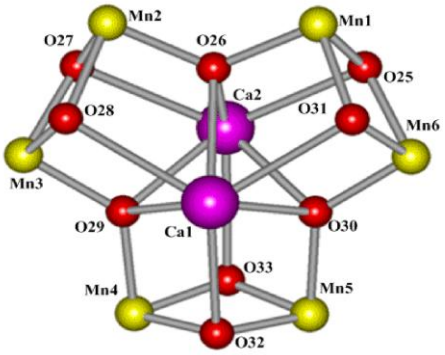

Figure S4. $[Mn_6Ca_2O_9]$ core of complex **A.**

Table S1. The calculated bond valence sum (BVS) for the $[Mn_6Ca_2O_9]$ core of complex **A** as shown in **Figure S4.**

Atom	BVS	Assignment
Mn1	4.080	Mn^{IV}
Mn2	4.161	Mn^{IV}
Mn3	4.145	Mn^{IV}
Mn4	4.124	Mn^{IV}
Mn5	4.114	Mn^{IV}
Mn6	4.121	Mn^{IV}
Ca1	2.129	Ca^{2+}
Ca2	2.241	Ca^{2+}
O26	2.19799	O^{2-}
O29	2.21398	O^{2-}
O30	2.21022	O^{2-}
O25	1.69902	O^{2-}
O27	1.69666	O^{2-}
O28	1.84823	O^{2-}
O31	1.71517	O^{2-}
O32	1.82042	O^{2-}
O33	1.69433	O^{2-}

Table S2. X-ray Crystal and refinement data for Complexes **A, B** and **C.**

	A	**B**	**C**
Empirical formula	$C_{75}H_{148}Ca_2Mn_6O_{43}$	$C_{73}H_{142}Ca_2Mn_6O_{42}$	$C_{106}H_{177}Ca_2Mn_9N_6O_{44}$
Formula weight	2147.73	2101.67	2814.14
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system	Triclinic	Monoclinic	Cubic
Space group	*P*-1	*I*2/a	$P2_13$
a (Å)	14.878(3)	26.486(5)	24.4452(4)
b (Å)	15.831(3)	30.822(6)	24.4452(4)
c (Å)	26.221(5)	26.925(4)	24.4452(4)
α (°)	93.680(2)	90	90
β (°)	97.730(3)	109.39(2)	90
γ (°)	112.599(3)	90	90
V (Å^3)	5604(2)	20734(7)	14607.7(7)
Z	2	8	4
Calculated density (g/cm^3)	1.273	1.347	1.280
Temperature (K)	100.15	173.15	173.15
θ range (°)	1.405 to 27.485	1.321 to 27.480	1.666 to 27.458
Absorption coefficient (mm^{-1})	0.823	0.887	0.894
F(000)	2264	8848	5888
Crystal size(mm^3)	0.20×0.17×0.15	0.263×0.241×0.203	0.09×0.09×0.07
Completeness	99.4%	99.7%	99.6%
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents	Semi-empirical from equivalents
Goodness-of-fit on F^2	1.042	1.262	1.118
Final R indices [$I > 2\theta(I)$]	*R1* = 0.0907, *wR2* = 0.2389	*R1* = 0.1067, *wR2* = 0.1816	*R1* = 0.0892, *wR2* = 0.2094
R indices (all data)	*R1* = 0.1148, *wR2* = 0.2570	*R1* = 0.1297, *wR2* = 0.1914	*R1* = 0.1187, *wR2* = 0.2423