Electric Supplemental Information for:

Structure and Bifunctional Electrocatalytic Activity of A Novel 3D Framework Based on Dimeric Monocopper-Substituted Polyoxoanions as Ten-connected linkages †

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Table S1 Summarization of known hybrids based type II dimers

Compounds	Connection number of the dimers	Dimension of structures	References
$[\{\gamma\text{-}SiTi_2W_{10}O_{36}(OH)_2\}_2(\mu\text{-}O)_2]^{8-}$	0	0D	24d
$[\{\gamma\text{-}SiTi_2W_{10}O_{36}(OMe)_2\}_2(\mu\text{-}O)_2]^{8-}$	0	0D	24d
$A\text{-}\alpha\text{-}[(SiNb_3W_9O_{38})_2(\mu\text{-}O)_2]^{10-}$	0	0D	24e
$[Cu(dap)_2]_2\{[Cu(dap)_2]_2[Cu(dap)_2][PCuW_{11}O_{39}]_2\}$	4	1 D	24f

Table S2. The selected bond lengths (Å) and angles (deg) for **1**.

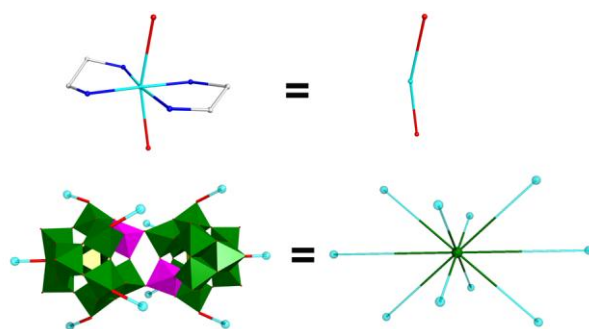|			
W(1)-O(21)	1.707(16)	W(4)-O(14)	1.721(18)
W(1)-O(23)	1.837(16)	W(4)-O(13)	1.78(2)
W(1)-O(20)	1.908(16)	W(4)-O(11)	1.857(15)
W(1)-O(22)	1.960(14)	W(4)-O(16)	1.929(18)
W(1)-O(18)	2.013(16)	W(5)-O(17)	1.70(2)
W(2)-O(9)	1.706(14)	W(5)-O(18)	1.894(19)
W(2)-O(2)	1.828(15)	W(6)-O(10)	1.68(3)
W(2)-O(20)	1.906(16)	W(6)-O(8)	1.828(13)
W(2)-O(7)	1.914(18)	W(6)-O(13)	1.95(2)
W(2)-O(11)	2.006(16)	W(6)-O(12)	2.43(2)
W(2)-O(26)	2.300(14)	W(7)-O(1)	1.844(5)
W(3)-O(5)	1.709(17)	W(7)-O(4)	1.929(8)
W(3)-O(4)	1.851(17)	W(7)-O(23)	1.942(16)
W(3)-O(6)	1.891(5)	W(7)-O(3)	1.948(17)
O(21)-W(1)-O(23)	101.8(8)	O(20)-W(1)-O(19)	85.1(6)
O(21)-W(1)-O(20)	103.1(8)	O(22)-W(1)-O(19)	73.4(8)
O(23)-W(1)-O(20)	91.5(7)	O(9)-W(2)-O(2)	101.8(8)
O(21)-W(1)-O(22)	97.4(9)	O(9)-W(2)-O(20)	101.7(8)
O(23)-W(1)-O(22)	91.3(8)	O(2)-W(2)-O(20)	90.0(7)
O(20)-W(1)-O(22)	158.3(8)	O(9)-W(2)-O(7)	101.0(8)
O(21)-W(1)-O(18)	96.9(9)	O(2)-W(2)-O(7)	89.1(7)
O(23)-W(1)-O(18)	161.1(8)	O(20)-W(2)-O(7)	157.0(7)
O(20)-W(1)-O(18)	86.2(7)	O(9)-W(2)-O(11)	96.6(7)
O(22)-W(1)-O(18)	84.1(8)	O(2)-W(2)-O(11)	161.6(6)
O(21)-W(1)-O(19)	165.6(8)	O(20)-W(2)-O(11)	85.2(6)
O(23)-W(1)-O(19)	89.5(7)	O(7)-W(2)-O(11)	88.4(7)

Fig. S1. Schematic view of $[Cu(en)_2]^{2+}$ complex as a 2-connected node and $(PW_{11}Cu)_2$ dimer as a 10-connected node.

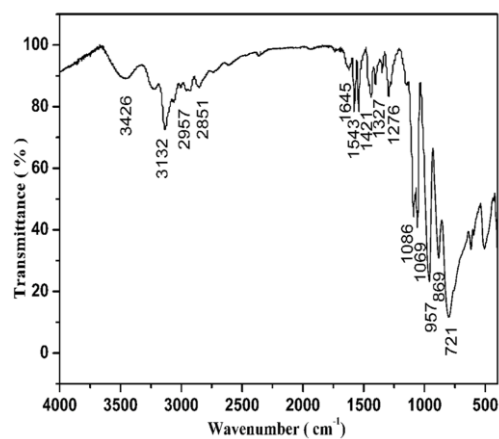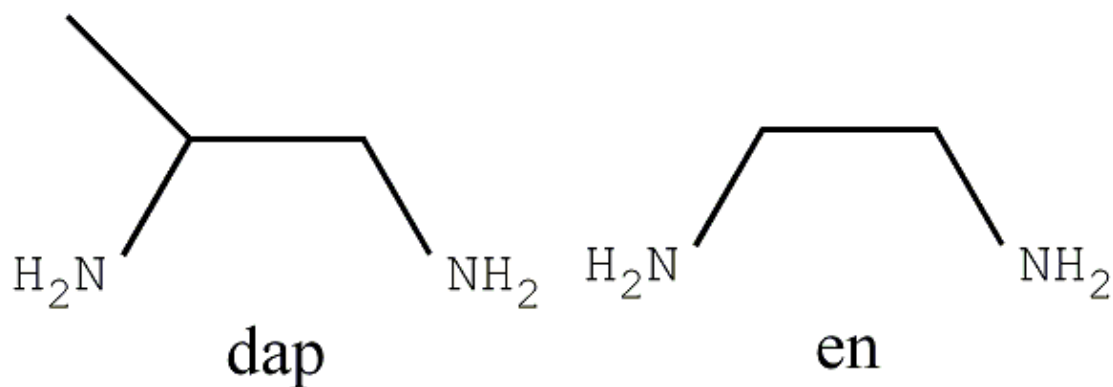**Chart S1.** Structures of dap and en molecules.

Fig. S2. The IR spectrum of **1**.
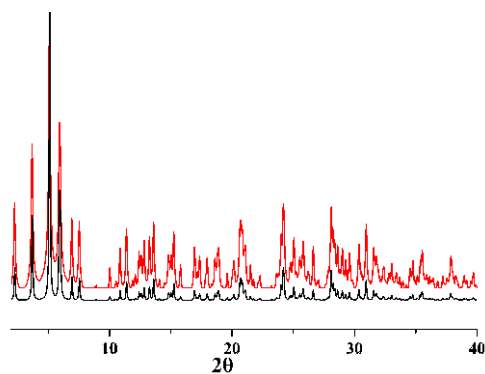
Fig. S3. The simulative (black) and experimental (red) powder X-ray diffraction patterns for **1**.
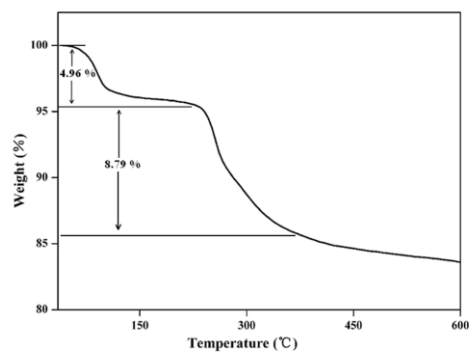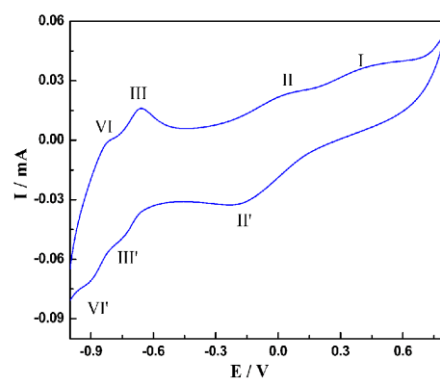

Fig. S4. The TG curve of **1**.

Fig. S5. Cyclic voltammogram for **1**-CPE in 0.2 M HAc-NaAc (pH=4.5) buffer solution at the scan rate of 50 mV·s^{-1}.
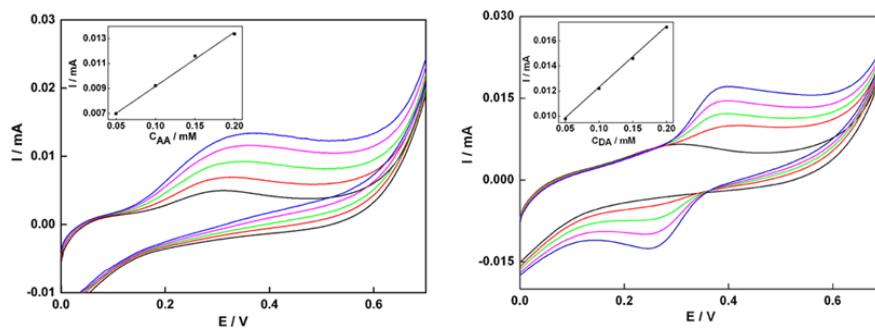
Fig. S6 Oxidation of AA (left) and DA (right) at 1-CPE in HAc-NaAc buffer solution containing AA and DA in various concentrations (from inner to outer): 0.05, 0.10, 0.15, 0.20 mM. Scan rate: 0.05 V·s^{-1}. The inset shows a linear dependence of the anodic catalytic current of wave I with AA and DA concentration.