Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information.

The Transformation of Polyoxometalate in the Formation of Intercluster Compound [Ag_{41}(α-$SiW_{10}O_{37}$)(^{t}BuC≡C)$_{27}$(CH_3CN)$_3$][β-$SiW_{12}O_{40}$]

Kuan-Guan Liu, Xi-Yan Liu, Zong-Jie Guan, Kang Shi*, Yu-Mei Lin* and Quan-Ming Wang

State Key Lab of Physical Chemistry of Solid Surfaces,
Department of Chemistry,College of Chemistry and Chemical Engineering,
Xiamen University, Xiamen, Fujian 361005, P. R. China
kshi@xmu.edu.cn;linyum@xmu.edu.cn

Materials and Methods.

All reagents and solvents employed were commercially available and used as received. Energy-dispersive X-ray spectroscopy (EDS) was performed on a Hitachi S-4800 scanning electron microscope operating at 20 kV for (Ag and W) and a CE instruments EA 1110 elemental analyzer for (C, H, and N). IR spectra were recorded from KBr pellets in the range 4000-400 cm^{-1} with a Nicolet AVATAR FT-IR360 spectrometer.

X-ray Crystallography. Intensity data of **1** were collected on Agilent SuperNova diffractometer with a molybdenum microfocus X-ray source at 173(2) K. Absorption corrections were applied by using the program CrysAlis (multi-scan). The structures were solved by direct methods. All non-hydrogen atoms were refined anisotropically by least-squares on *F*2 using the SHELXTL program. The hydrogen atoms of organic ligands were generated geometrically, while no attempt was made to locate hydrogen atoms of water.

Characterization

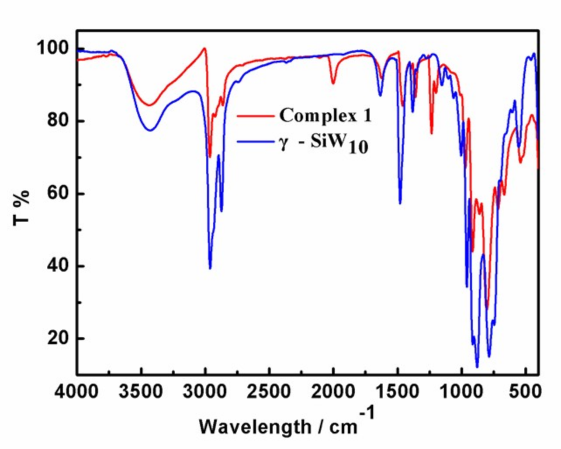

Fig. S1. IR spectra of complex **1** and $(n\text{-}Bu_4N)_4[\gamma\text{-}SiW_{10}(H_2O)_2O_{34}]$.

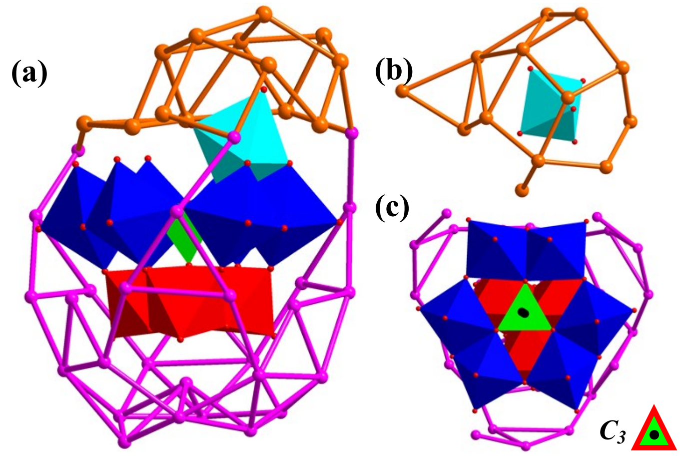

Fig. S2. (a) The core structure of [(α-$SiW_{10}O_{37}$)@Ag_{41}] (The ligands are not shown for clarity); (b) A cap-like (WO_6)@Ag_{13} cluster; (c) A cup-like (SiW_9O_{34})@Ag_{28} cluster with pseudo-***C*₃**-symmetric axis (View along the symmetric axis). Polyhedral Representation Code: Tetrahedron (green), SiO_4; Octahedron (blue, red or cyan), WO_4.

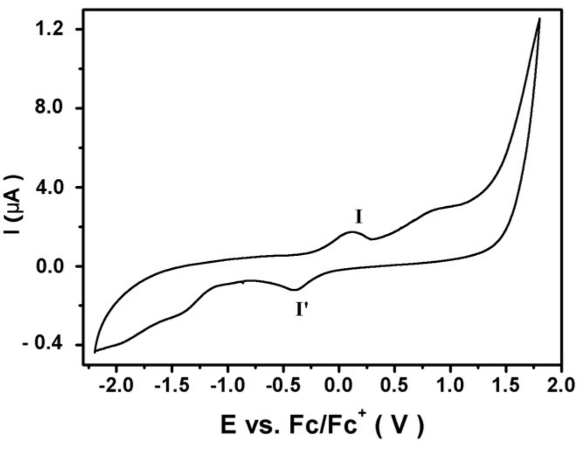

Fig. S3. Cyclic voltammogram of $AgBF_4$ in O_2 free [BMIm]BF_4 electrolyte under N_2 environment at a scan rate of 0.05 Vs^{-1}.

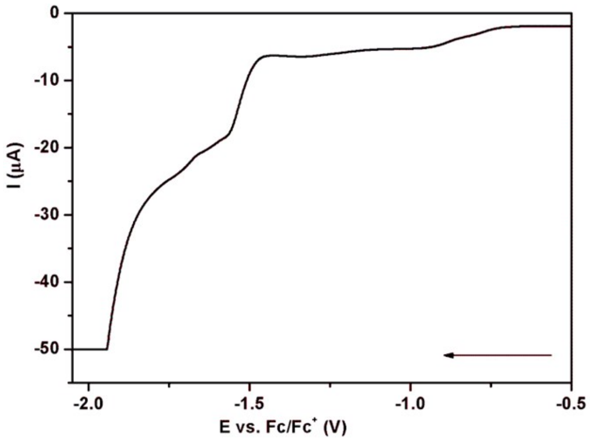

Fig. S4 Linear sweep voltammograme of compound **1** in the degassed CH_3CN solution containing 0.1 M Bu_4NClO_4 at a scan rate of 0.05 V/s. Compound **1** was grinded on glassy carbon electrode.

Table S1. Crystal data for Cluster **1**.

Compound	**1**
Chemical formula	$C_{176}H_{264}O_{78}N_7Si_2W_{22}Ag_{41}$
fw	12251.24
Crystal system	Triclinic
Space group	*P*-1
a, Å	20.0748(4)
b, Å	26.1979(6)
c, Å	28.8126(6)
α, deg	104.876(2)
β, deg	90.485(2)
γ, deg	92.908(2)
V, $Å^3$	14622.7(5)
Z	2
ρ_{calc}, g/cm^3	2.782
μ, mm^{-1}	11.350
Reflections collected	94267
Independent reflections	51270
R_{int}	0.0670
Reflections I > 2σ(I)	51270
Parameters	2942
GOF on F^2	1.030
R_1^a / wR_2^b (I > 2σ(I))	0.0689 / 0.1698
R_1^a / wR_2^b (*all*)	0.0989 / 0.1907

[a] $R_1 = [\Sigma \text{abs}(\text{abs}(Fo) - \text{abs}(Fc))] / [\Sigma \text{abs}(Fo)]$. [b] $wR2 = [\Sigma(w(Fo^2 - Fc^2)^2) / \Sigma[w(Fo^2)^2]^{0.5}$.

Table S2. Selected bonds lengths [Ǻ] for **1**.

Bond lengths					
Ag(1)-Ag(2)	2.880(3)	Ag(6)-Ag(13)	2.910(2)	Ag(25)-Ag(33)	3.070(2)
Ag(1)-Ag(4)	2.957(2)	Ag(6)-Ag(40)	2.981(3)	Ag(26)-Ag(39)	3.0178(19)
Ag(1)-Ag(9)	3.052(2)	Ag(7)-Ag(14)	3.010(2)	Ag(26)-Ag(27)	3.019(2)
Ag(1)-Ag(11)	3.329(3)	Ag(7)-Ag(16)	3.144(2)	Ag(27)-Ag(38)	3.005(2)
Ag(2)-Ag(3)	3.073(2)	Ag(7)-Ag(40)	3.365(2)	Ag(27)-Ag(37)	3.0663(19)
Ag(2)-Ag(9)	3.137(2)	Ag(8)-Ag(14)	2.968(2)	Ag(28)-Ag(30)	3.022(2)
Ag(2)-Ag(10)	3.160(2)	Ag(8)-Ag(15)	3.234(2)	Ag(29)-Ag(31)	3.0894(19)
Ag(2)-Ag(12)	3.228(2)	Ag(10)-Ag(13)	3.0088(19)	Ag(29)-Ag(37)	3.364(2)
Ag(3)-Ag(40)	2.932(2)	Ag(10)-Ag(19)	3.3572(19)	Ag(30)-Ag(31)	3.079(2)
Ag(3)-Ag(9)	2.950(3)	Ag(11)-Ag(20)	3.051(2)	Ag(31)-Ag(36)	2.7628(18)
Ag(3)-Ag(10)	3.028(2)	Ag(11)-Ag(18)	3.213(2)	Ag(32)-Ag(34)	2.9598(18)
Ag(3)-Ag(6)	3.075(2)	Ag(12)-Ag(20)	2.851(2)	Ag(33)-Ag(34)	3.010(3)
Ag(4)-Ag(5)	2.952(2)	Ag(12)-Ag(21)	3.159(2)	Ag(34)-Ag(36)	2.957(2)
Ag(4)-Ag(11)	3.1843(19)	Ag(15)-Ag(24)	3.3284(18)	Ag(34)-Ag(35)	3.013(2)
Ag(4)-Ag(9)	3.195(3)	Ag(21)-Ag(22)	3.3015(19)	Ag(35)-Ag(37)	3.016(2)
Ag(4)-Ag(8)	3.2005(19)	Ag(22)-Ag(23)	3.2870(18)	Ag(35)-Ag(39)	3.103(2)
Ag(5)-Ag(40)	2.971(3)	Ag(23)-Ag(33)	2.8420(19)	Ag(36)-Ag(37)	3.292(2)
Ag(5)-Ag(7)	2.9980(18)	Ag(23)-Ag(32)	2.983(2)	Ag(37)-Ag(38)	2.886(3)
Ag(5)-Ag(9)	3.030(2)	Ag(24)-Ag(28)	3.1020(18)	Ag(38)-Ag(39)	2.940(3)
Ag(5)-Ag(8)	3.050(2)	Ag(25)-Ag(39)	3.039(2)	Ag(9)-O(45)	2.297(9)
Ag(9)-O(52)	2.487(12)	Ag(21)-O(64)	2.467(11)	Ag(31)-O(77)	2.380(13)
Ag(9)-O(75)	2.552(9)	Ag(27)-O(53)	2.402(10)	Ag(31)-O(65)	2.534(11)
Ag(14)-O(76)	2.521(9)	Ag(27)-O(66)	2.488(13)	Ag(32)-O(57)	2.459(9)
Ag(15)-O(71)	2.493(10)	Ag(29)-O(53)	2.285(12)	Ag(32)-O(65)	2.552(12)
Ag(16)-O(67)	2.409(10)	Ag(29)-O(70)	2.409(11)	Ag(35)-O(74)	2.598(10)
Ag(18)-O(72)	2.528(11)	Ag(29)-O(66)	2.459(10)	Ag(28)-N(3)	2.147(16)
Ag(20)-O(58)	2.508(9)	Ag(31)-O(57)	2.372(12)	Ag(38)-N(5)	2.24(2)
Si(1)-O(4)	1.598(13)	W(8)-O(30)	1.702(15)	W(15)-O(67)	1.726(9)
Si(1)-O(1)	1.621(11)	W(8)-O(27)	1.870(14)	W(15)-O(66)	1.762(9)
Si(1)-O(2)	1.640(10)	W(8)-O(5)	1.899(12)	W(15)-O(49)	1.929(12)
Si(1)-O(3)	1.645(13)	W(8)-O(31)	1.903(11)	W(15)-O(76)	1.952(12)
W(1)-O(9)	1.677(15)	W(8)-O(32)	1.950(12)	W(15)-O(48)	2.188(10)
W(1)-O(5)	1.910(13)	W(8)-O(3)	2.343(13)	W(15)-O(42)	2.244(8)
W(1)-O(8)	1.926(12)	W(9)-O(33)	1.722(10)	W(16)-O(71)	1.744(13)
W(1)-O(7)	1.929(16)	W(9)-O(24)	1.901(12)	W(16)-O(70)	1.759(9)
W(1)-O(6)	1.929(12)	W(9)-O(34)	1.906(13)	W(16)-O(68)	1.903(9)
W(1)-O(1)	2.354(13)	W(9)-O(35)	1.923(12)	W(16)-O(76)	1.935(10)
W(2)-O(13)	1.706(14)	W(9)-O(31)	1.943(15)	W(16)-O(55)	2.156(9)
W(2)-O(10)	1.920(14)	W(9)-O(3)	2.333(11)	W(16)-O(42)	2.214(11)
W(2)-O(7)	1.921(15)	W(10)-O(36)	1.688(14)	W(17)-O(72)	1.691(12)
W(2)-O(12)	1.934(11)	W(10)-O(14)	1.907(12)	W(17)-O(77)	1.736(10)

W(2)-O(11)	1.973(14)	W(10)-O(37)	1.918(13)	W(17)-O(68)	1.903(9)
W(2)-O(1)	2.329(13)	W(10)-O(34)	1.919(13)	W(17)-O(58)	1.921(10)
W(3)-O(16)	1.717(12)	W(10)-O(32)	1.920(15)	W(17)-O(73)	2.124(10)
W(3)-O(15)	1.894(13)	W(10)-O(3)	2.330(11)	W(17)-O(43)	2.323(11)
W(3)-O(14)	1.898(13)	W(11)-O(39)	1.703(10)	W(18)-O(64)	1.742(9)
W(3)-O(8)	1.909(13)	W(11)-O(37)	1.884(13)	W(18)-O(65)	1.773(10)
W(3)-O(10)	1.918(15)	W(11)-O(38)	1.933(10)	W(18)-O(46)	1.903(11)
W(3)-O(1)	2.371(11)	W(11)-O(19)	1.943(13)	W(18)-O(58)	1.941(13)
W(4)-O(20)	1.702(15)	W(11)-O(15)	1.952(12)	W(18)-O(59)	2.179(9)
W(4)-O(11)	1.843(13)	W(11)-O(4)	2.330(9)	W(18)-O(43)	2.217(8)
W(4)-O(19)	1.903(11)	W(12)-O(40)	1.705(12)	W(19)-O(61)	1.735(11)
W(4)-O(17)	1.933(11)	W(12)-O(35)	1.884(12)	W(19)-O(50)	1.843(9)
W(4)-O(18)	1.943(11)	W(12)-O(18)	1.889(13)	W(19)-O(46)	1.914(11)
W(4)-O(4)	2.373(13)	W(12)-O(29)	1.907(10)	W(19)-O(69)	1.930(9)
W(5)-O(23)	1.708(13)	W(12)-O(38)	1.925(10)	W(19)-O(62)	1.976(9)
W(5)-O(6)	1.892(15)	W(12)-O(4)	2.359(11)	W(19)-O(44)	2.327(11)
W(5)-O(12)	1.902(12)	Si(2)-O(44)	1.611(12)	W(20)-O(60)	1.757(11)
W(5)-O(22)	1.919(16)	Si(2)-O(43)	1.621(9)	W(20)-O(51)	1.817(9)
W(5)-O(21)	1.934(14)	Si(2)-O(42)	1.637(9)	W(20)-O(49)	1.885(11)
W(5)-O(2)	2.345(10)	Si(2)-O(41)	1.652(8)	W(20)-O(69)	1.905(9)
W(6)-O(26)	1.698(13)	W(13)-O(56)	1.742(11)	W(20)-O(54)	1.986(9)
W(6)-O(25)	1.884(17)	W(13)-O(55)	1.827(9)	W(20)-O(44)	2.382(10)
W(6)-O(21)	1.916(12)	W(13)-O(73)	1.835(10)	W(21)-O(74)	1.747(11)
W(6)-O(24)	1.925(11)	W(13)-O(45)	2.026(9)	W(21)-O(57)	1.779(10)
W(6)-O(27)	1.943(16)	W(13)-O(75)	2.035(10)	W(21)-O(53)	1.804(10)
W(6)-O(2)	2.358(12)	W(13)-O(41)	2.382(10)	W(21)-O(51)	2.063(9)
W(7)-O(28)	1.709(16)	W(14)-O(47)	1.782(9)	W(21)-O(50)	2.067(10)
W(7)-O(25)	1.900(15)	W(14)-O(48)	1.796(10)	W(22)-O(63)	1.751(9)
W(7)-O(22)	1.920(12)	W(14)-O(54)	1.882(10)	W(22)-O(59)	1.814(10)
W(7)-O(17)	1.922(12)	W(14)-O(75)	1.941(12)	W(22)-O(62)	1.885(11)
W(7)-O(29)	1.928(11)	W(14)-O(52)	2.002(10)	W(22)-O(45)	1.967(10)
W(7)-O(2)	2.354(14)	W(14)-O(41)	2.330(8)	W(22)-O(52)	1.993(10)
				W(22)-O(41)	2.317(8)