Supplementary information

Surface modification of polyoxometalate host–guest supramolecular architectures: from metal–organic *pseudo*rotaxane framework to molecular box

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III. Crystallographic studies；

IV. Thermogravimetric analysis；

V. Powder X-Ray diffraction；

VI. SEM image and EDS analysis.

I. Synthesis of compounds.

Reagents were purchased commercially and used without further purification. Infrared (IR) spectra were recorded on a Perkin-Elmer Spectrum using KBr pallets. Elemental analyses of (C, H and N) were carried out with a Vario EL III elemental analyzer.

1. Synthesis of $Ag_{14}(trz)_{10}[SiW_{12}O_{40}]$ 1

$H_4SiW_{12}O_{40}$ (0.49g, 0.17mmol), CH_3COOAg (0.141g, 0.84mmol), and 1,2,4-triazole (0.076g, 1.1mmol) were dissolved in 10ml distilled water at room temperature. The pH value of the solution was adjusted to *ca*. 7.0 by 2M NaOH, and then the suspension was placed in a Teflon-lined autoclave and keep autogenous pressure at 160 ºC for 4 days. After slowly cooling to room temperature for another 4 days, highly pure and slight green sheet crystals were filtered and washed with distilled water. (Yield: 27% based on tungsten).

Elemental analysis: $C_{20}N_{30}H_{20}O_{40}Ag_{14}SiW_{12} = Ag_{14}(C_2N_3H_2)_{10}SiW_{12}O_{40}$
Calcd: N, 8.30; C, 4.74; H, 0.40. Found: N, 8.27; C, 4.84; H, 0.34.

2. Synthesis of $Ag_{10}(Htrz)_2(trz)_6[SiW_{12}O_{40}]$ 2

$H_4SiW_{12}O_{40}$ (0.515g, 0.179mmol), CH_3COOAg (0.095g, 0.57mmol), and 1,2,4-triazole (0.135g, 1.95mmol) were dissolved in 10ml distilled water at room temperature. The pH value of the solution was adjusted to *ca*. 4.5 by 2M NaOH, and then the suspension was placed in a Teflon-lined autoclave and keep autogenous pressure at 160 ºC for 4 days. After slowly cooling to room temperature for another 4 days, highly pure and slight green block crystals were filtered and washed with distilled water. (Yield: 33% based on tungsten).

Elemental analysis: $C_{16}N_{24}H_{18}O_{40}Ag_{10}SiW_{12} = Ag_{10}(C_2N_3H_3)_2(C_2N_3H_2)_6SiW_{12}O_{40}$
Calcd: N, 7.47; C, 4.27; H, 0.40. Found: N, 7.35; C, 4.46; H, 0.33.

II: Infra-Red spectroscopy.

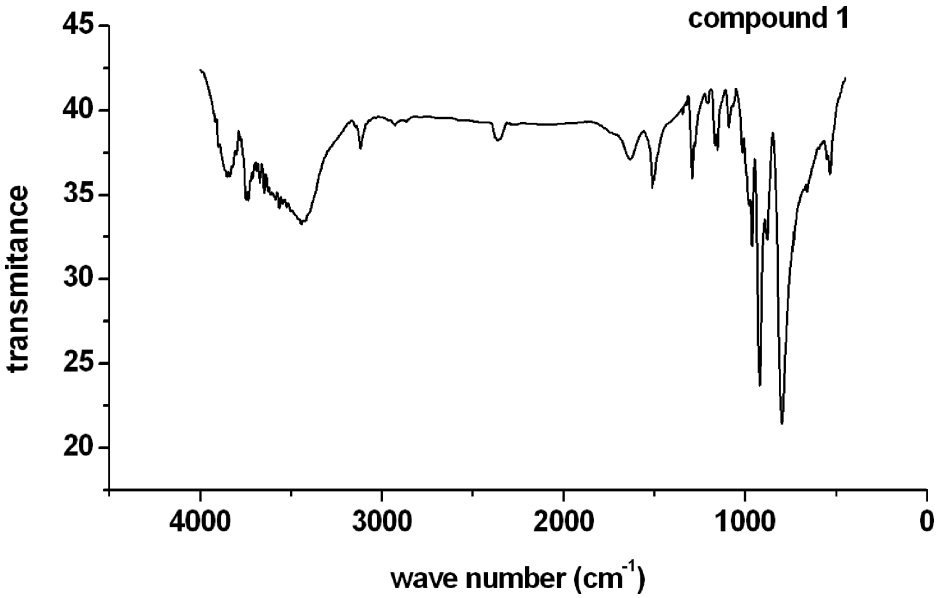


Figure S1. FT-IR spectrum of compound **1.** Intensities denoted as s = strong, m = medium, w = weak. 3444 (s), 3115(w),1632(w), 1508(s), 1288(s), 1149(s), 1087(s), 1012(w), 958(s), 916(s), 874(w), 794(s).

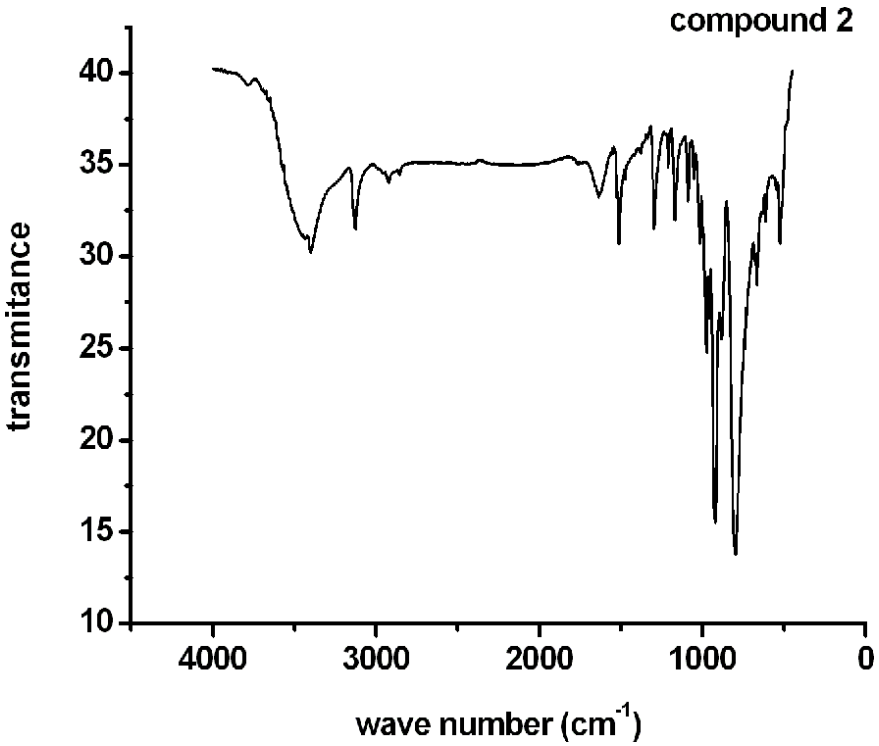


Figure S2. FT-IR spectrum of compound **2**. 3400(s), 3126(s), 1632(m), 1507(s), 1296(s), 1206(w), 1163(s), 1084(s), 1046(w), 1011(w), 971(s), 954(m), 917(s), 880(w), 794(s).

III. **Crystallographic studies of compounds 1 and 2.**

Compound 1: Diffraction data for compound **1** were collected on a Saturn 70 charge-coupled device diffractometer equipped with confocal-monochromated Mo Kα radiation (λ = 0.71073 Å) at room temperature. The CrystalClear program was used for the absorption correction. The structure was solved by direct methods and refined on F^2 by full-matrix, least-squares methods using the SHELXL-97 program package. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms for the trz ligands were placed in calculated positions and treated as riding on their parents. The Ag13, Ag14 atoms in compound **1** are disordered into two positions respectively. Ag13 is separated into Ag13(84%) and Ag15(16%); Ag14 is separated into Ag14(63%) and Ag16(37%). In the article, we only use the Ag13 and Ag14 positions to discuss the structure for clarity. Crystal data collection and refinement parameters are given in Table S1. Complete details can be found in the accompanying cif file. The CCDC reference No. 789149.

Compound 2: Diffraction data for compound **2** were collected on a SCX mini charge-coupled device diffractometer equipped with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) at room temperature. The CrystalClear program was used for the absorption correction. The structure was solved by direct methods and refined on F^2 by full-matrix, least-squares methods using the SHELXL-97 program package. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms for the trz ligands were placed in calculated positions and treated as riding on their parents. Crystal data collection and refinement parameters are given in Table S2. Complete details can be found in the accompanying cif file. The CCDC reference No. 789151.

Table S1. Crystal data and structure refinement for **compound 1**

Empirical formula	$C_{20}H_{20}Ag_{14}N_{30}O_{40}SiW_{12}$	
Formula weight	5065.13	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 13.0124(2) Å	α= 95.155(8) º
	b = 14.2918(2) Å	β = 101.758(6) º
	c = 23.7647(3) Å	γ = 115.984(5) º
Volume	3808.0(3) $Å^3$	
Z	2	
Density (calculated)	4.417 Mg/m^3	
Absorption coefficient	21.653 mm^{-1}	
F(000)	4460	
Crystal size	0.20 × 0.20 × 0.10 mm	
Theta range for data collection	2.15 to 25.00 º	
Index ranges	-14<=h<=15, -16<=k<=16, -28<=l<=28	
Reflections collected	24226	
Independent reflections	12798 [R(int) = 0.0502]	
Completeness to theta = 25.10 º	95.4 %	
Absorption correction	Semi-empirical from equivalents	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	12798 / 258 / 1113	
Goodness-of-fit on F^2	1.015	
Final R indices [I>2sigma(I)]	R_1 = 0.0874, wR_2 = 0.2825	
R indices (all data)	R_1 = 0.0925, wR_2 = 0.2878	
Largest diff. peak and hole	2.979 and -3.591 e. $Å^{-3}$	

Table S2. Crystal data and structure refinement for **compound 2**

Empirical formula	$C_{16}H_{18}Ag_{10}N_{24}O_{40}SiW_{12}$	
Formula weight	4499.53	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/c	
Unit cell dimensions	a = 10.5031(4) Å	α= 90 º
	b = 24.5448(8) Å	β = 103.374(2) º
	c = 12.4659(5) Å	γ = 90 º
Volume	3126.5(2) $Å^3$	
Z	2	
Density (calculated)	4.780 Mg/m^3	
Absorption coefficient	25.145 mm^{-1}	
F(000)	3948	
Crystal size	0.15 × 0.12 × 0.10 mm	
Theta range for data collection	2.16 to 27.52 º	
Index ranges	-13<=h<=13, -31<=k<=29, -12<=l<=16	
Reflections collected	24336	
Independent reflections	7173 [R(int) = 0.0415]	
Completeness to theta = 27.52 º	99.6 %	
Absorption correction	Semi-empirical from equivalents	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	7173 / 229 / 439	
Goodness-of-fit on F^2	1.076	
Final R indices [I>2sigma(I)]	R_1 = 0.0951, wR_2 = 0.2979	
R indices (all data)	R_1 = 0.0976, wR_2 = 0.2998	
Largest diff. peak and hole	4.308 and -2.499 e. $Å^{-3}$	

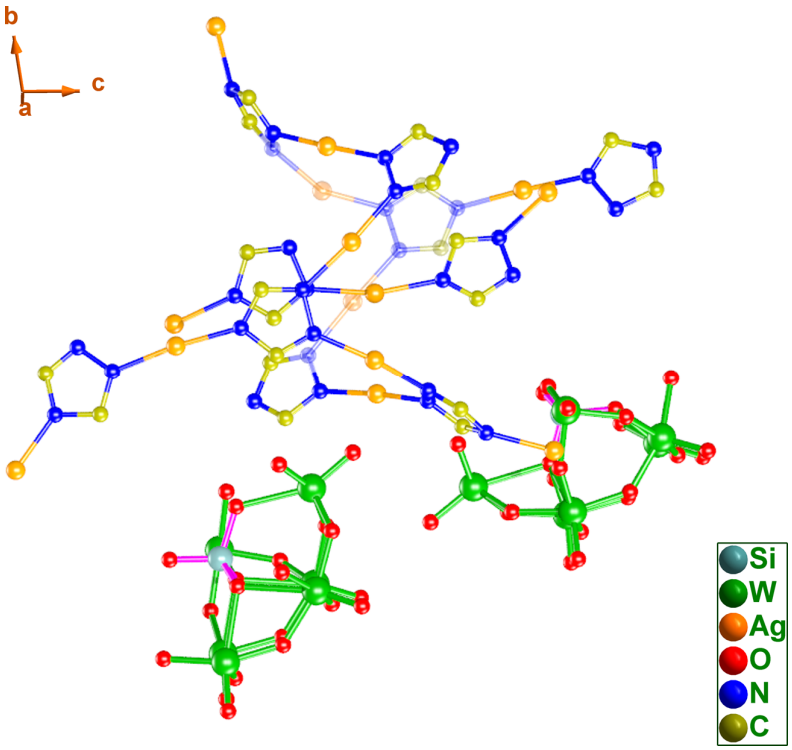


Figure S3. The asymmetric unit of compound **1**.

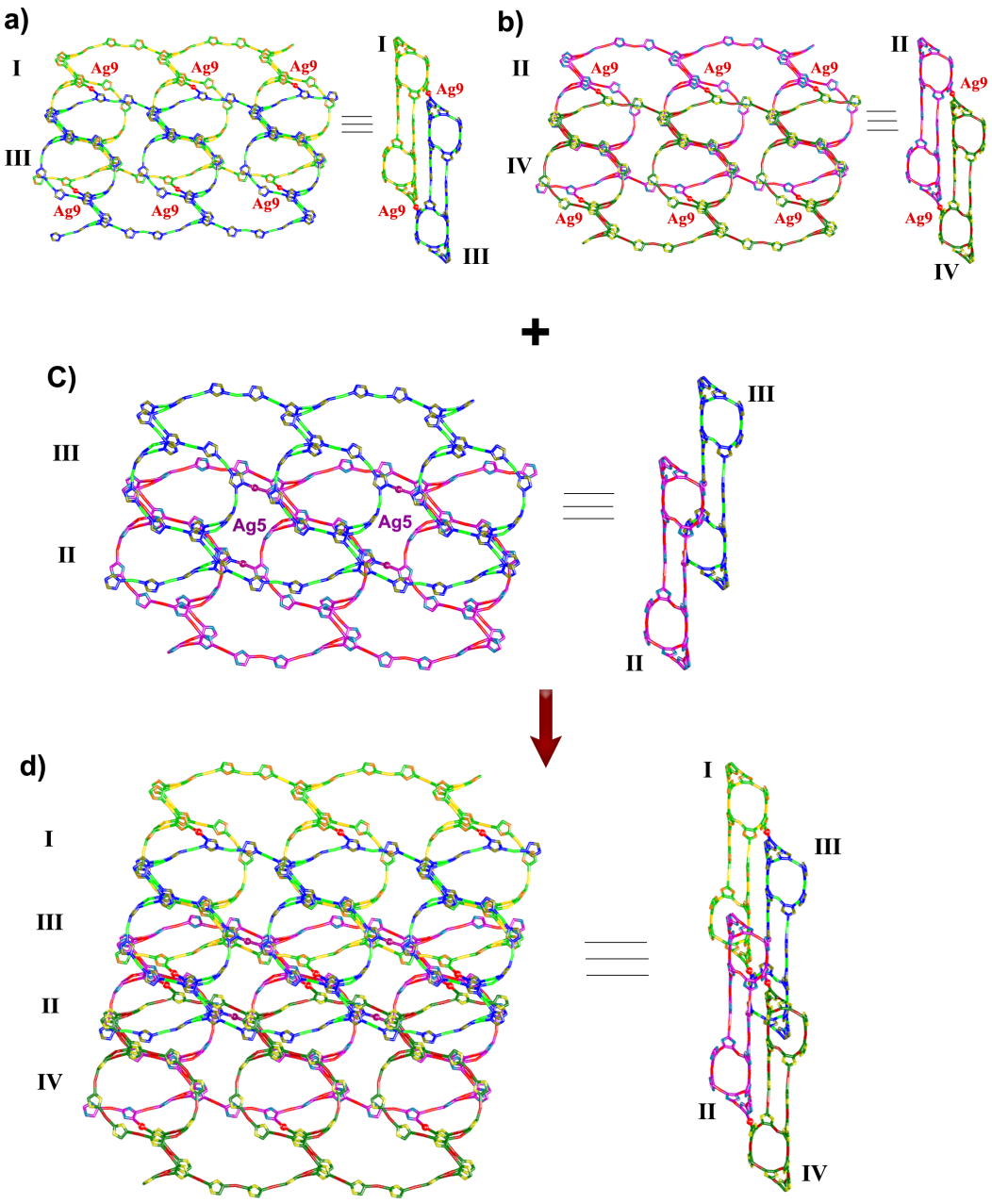


Figure S4. The linkage mode of molecular strand I, II, III, IV connecting by Ag5, Ag9 center. a), I and III link by Ag9, b), II and IV link by Ag9, c), II and III link by Ag 5, d), I, II, III, IV link by Ag5 and Ag9 center.

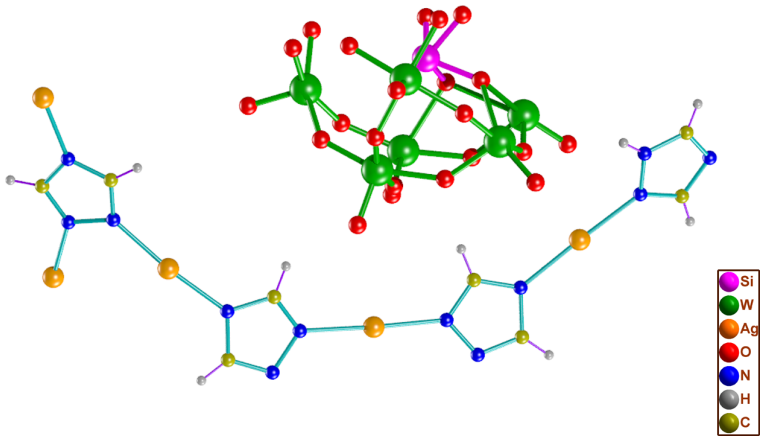


Figure S5. The asymmetric unit of compound **2.**

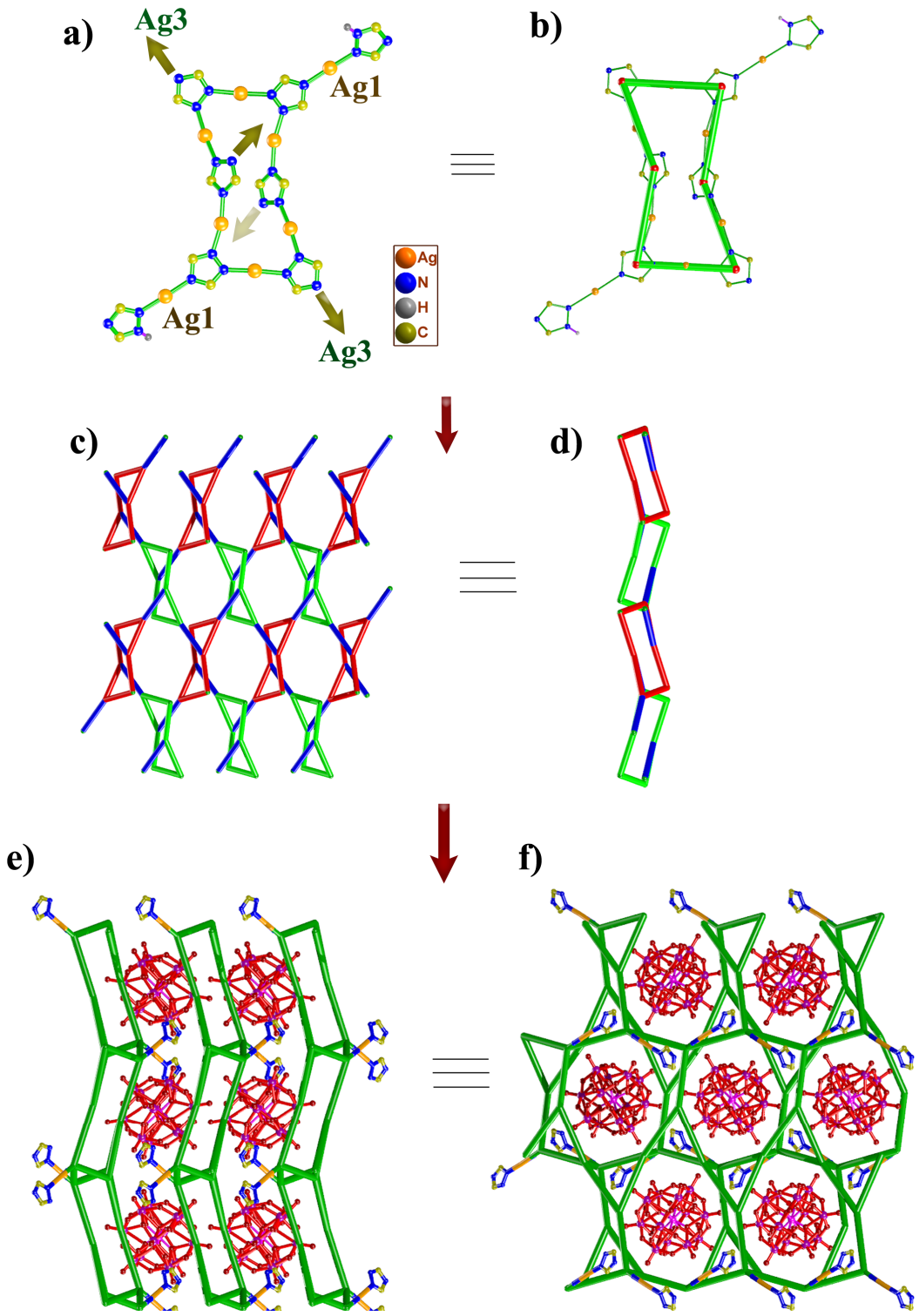


Figure S6. The hierarchical building blocks for assembly of compound **2**. a) the coordination mode of the quadrangular $[Ag_6(trz)_6]$ unit. b) the simplified structure of a). c) the 2D layer using the quadrangular $[Ag_6(trz)_6]$ unit as building blocks. d) a side view of c). e) the POMs units encapsulating into the molecular box, f) the supramolecular architecture of compound **2**.

IV. Thermogravimetric analysis of compound 1 and 2.

Thermogravimetric analysis (TGA) performed with a STA449C-QMS 403C at a heating rate of 10 ºC min^{-1} under N_2atmosphere on crystalline samples.

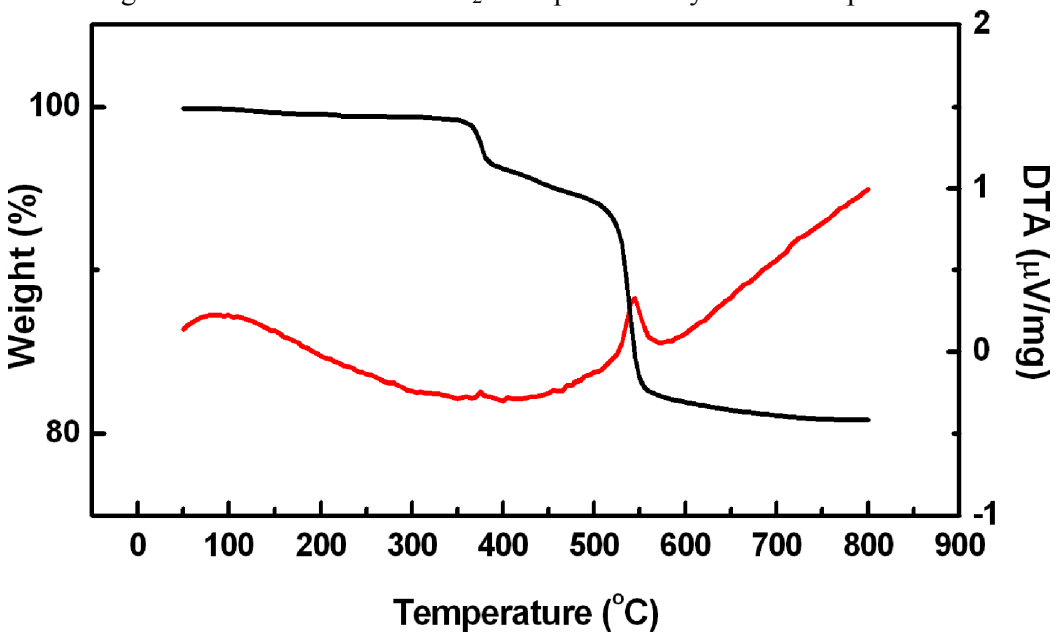


Figure S7. TG analysis of compound **1**. the thermal decomposition residue are Ag(0) microparticles tungsten oxides and slight silicon oxide.

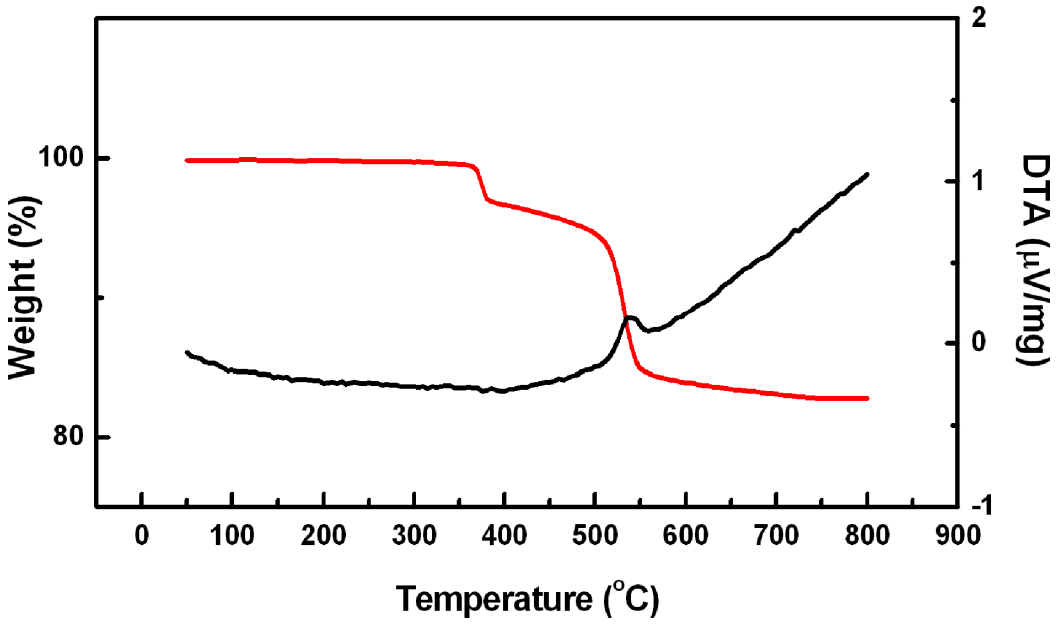


Figure S8. TG analysis of compound **2.** the thermal decomposition residue are Ag(0) microparticles tungsten oxides and slight silicon oxide.

V. Powder X-Ray diffraction.

X-ray powder diffraction (XRPD) was performed with a Rigaku DMAX 2500 diffractometer.

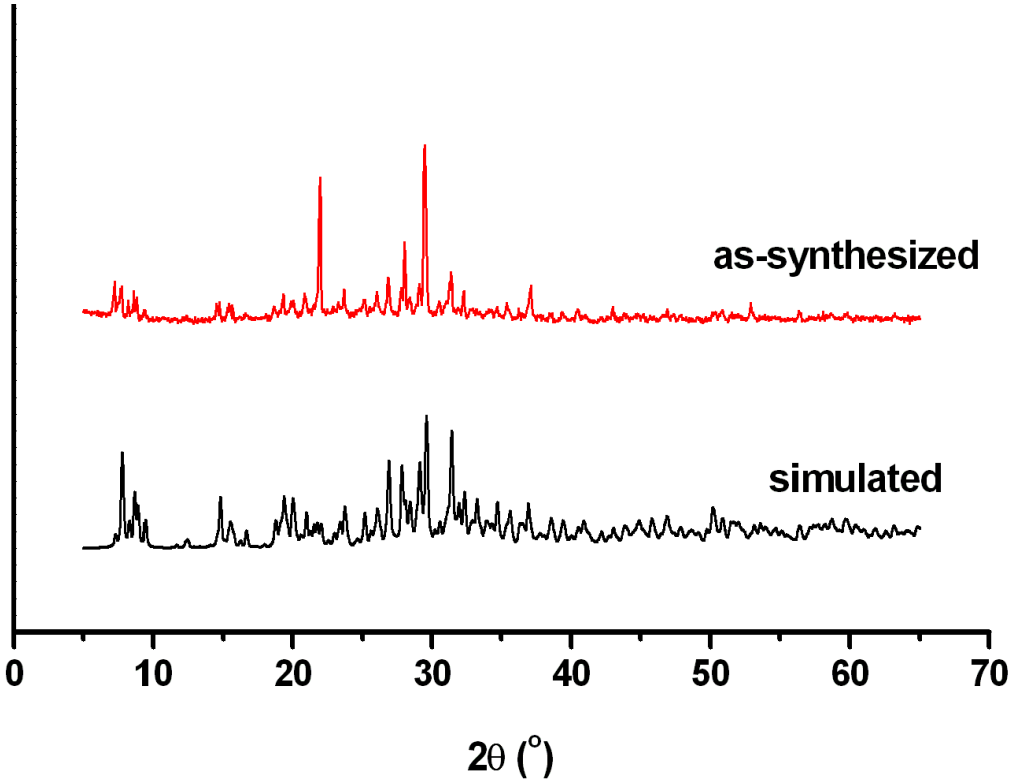


Figure S9. PXRD patterns of as-synthesized and simulated PXRD patterns for compound **1**, indicating the phase purity of the as-synthesized product.

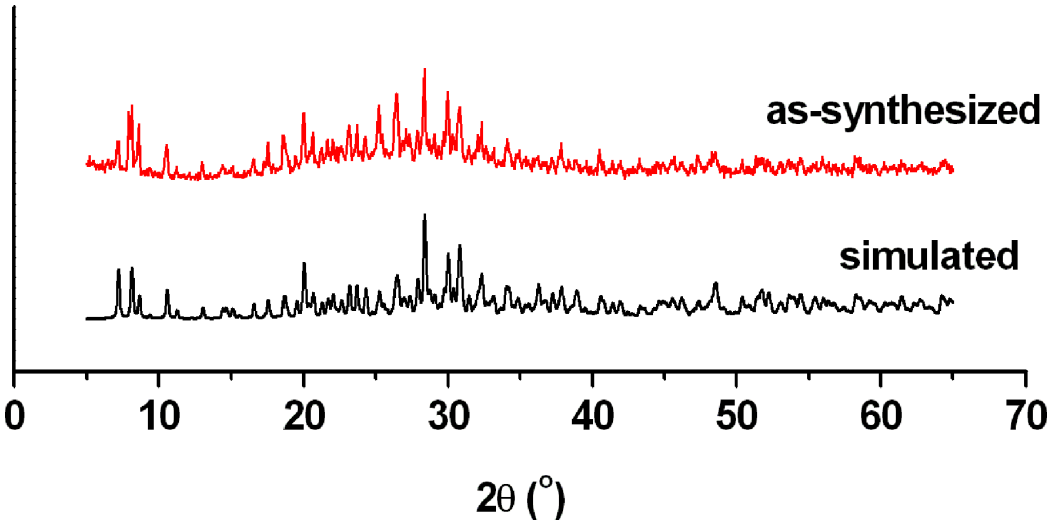
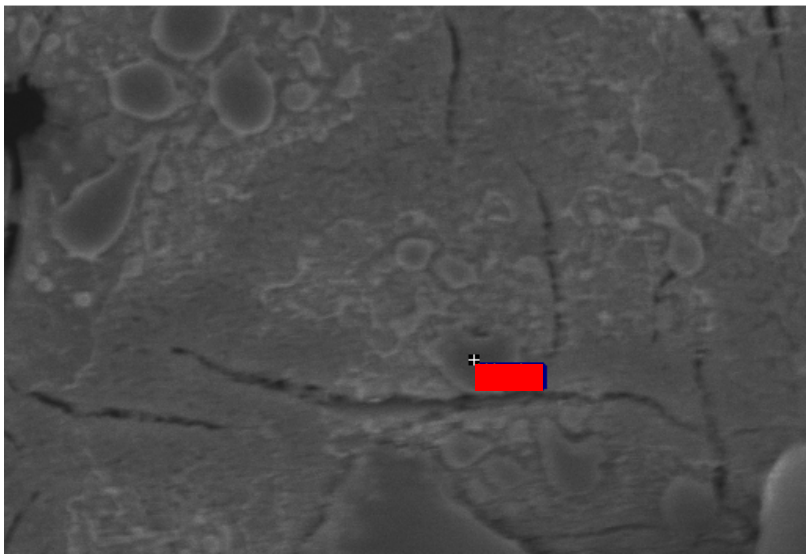


Figure S10. PXRD patterns of as-synthesized and simulated PXRD patterns for compound **2**, indicating the phase purity of the as-synthesized product.

VI. SEM image and EDS analysis.

SEM images and EDS spectra were carried on JSM-6700F.

a)



b)

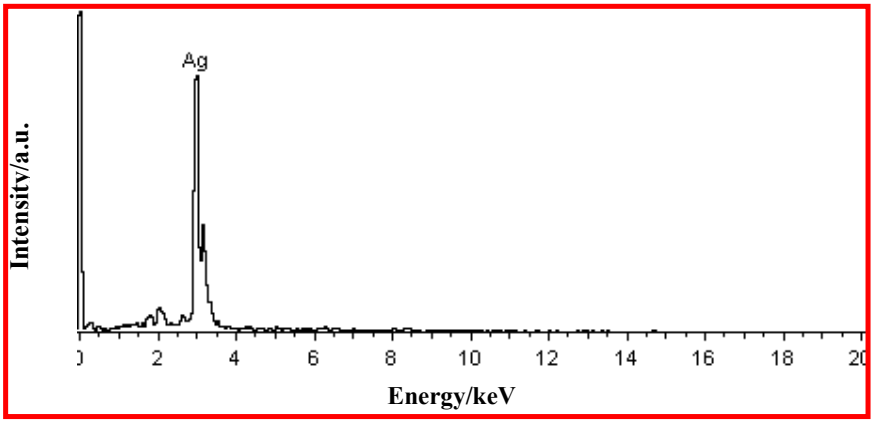


Figure S11. SEM images and EDX spectra for compound **1**. a) SEM micrographs of Ag(0) microparticles embedded in the tungsten oxides. b) EDX spectra of spherical microparticles with resulting Ag singles.

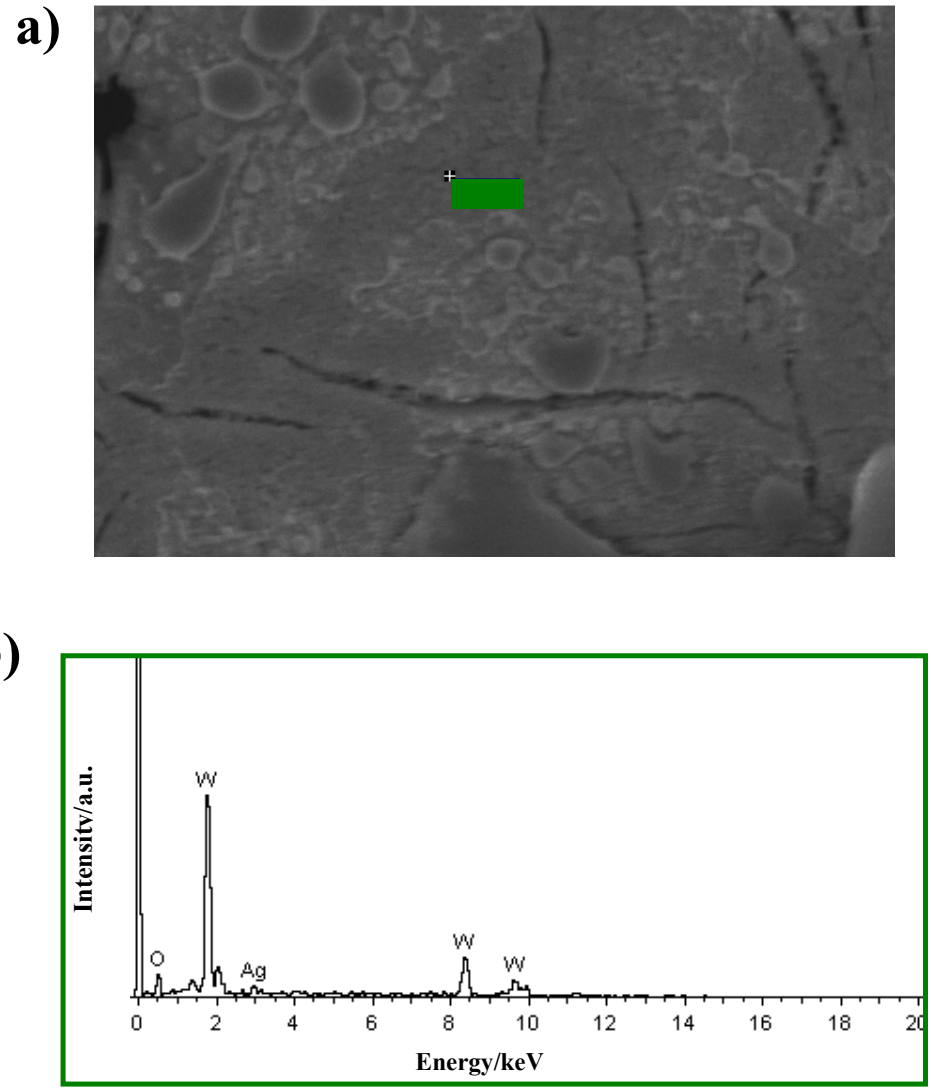


Figure S12. SEM images and EDX spectra for compound **1**. a) SEM micrographs of silver microparticles on tungsten oxide matrix are displayed. b) EDX spectra of tungsten oxide with resulting W singles.

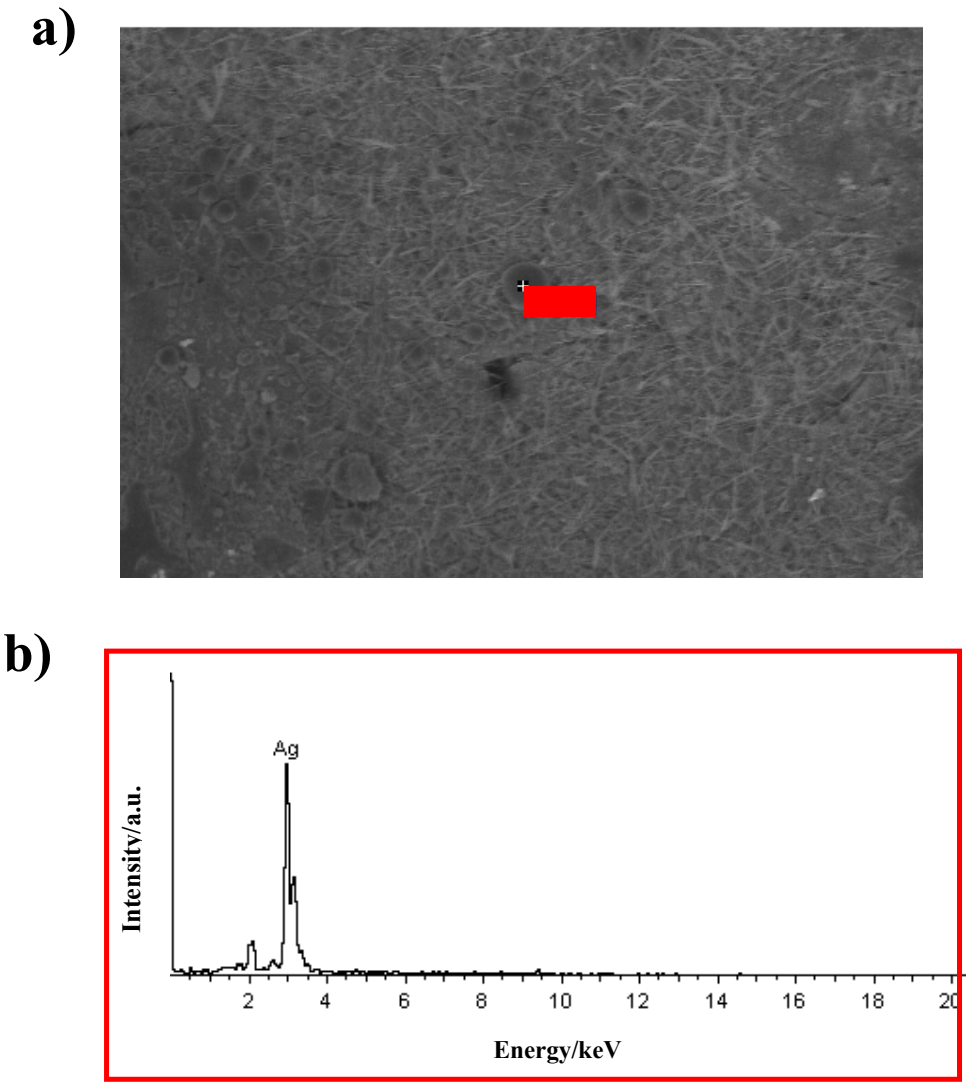
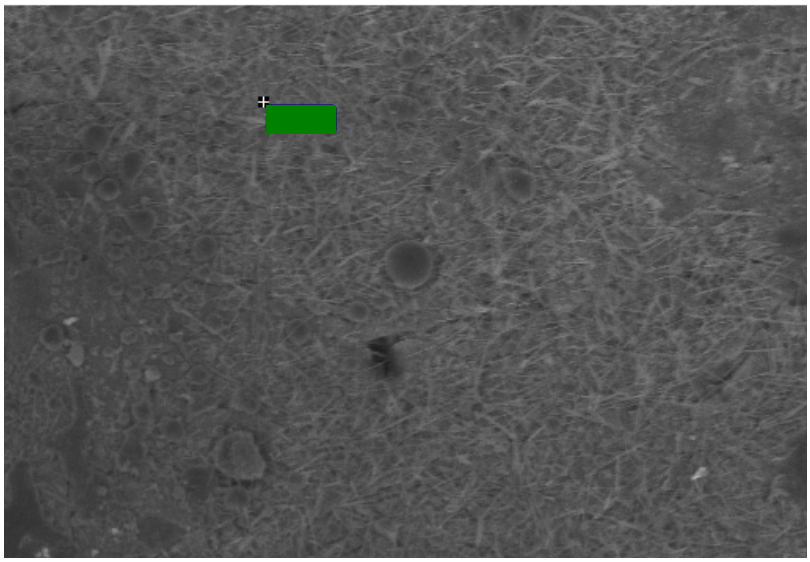


Figure S13. SEM images and EDX spectra for compound **2**. a) SEM micrographs of Ag(0) microparticles embedded in the tungsten oxides. b) EDX spectra of spherical microparticles with resulting Ag singles.

a)



b)

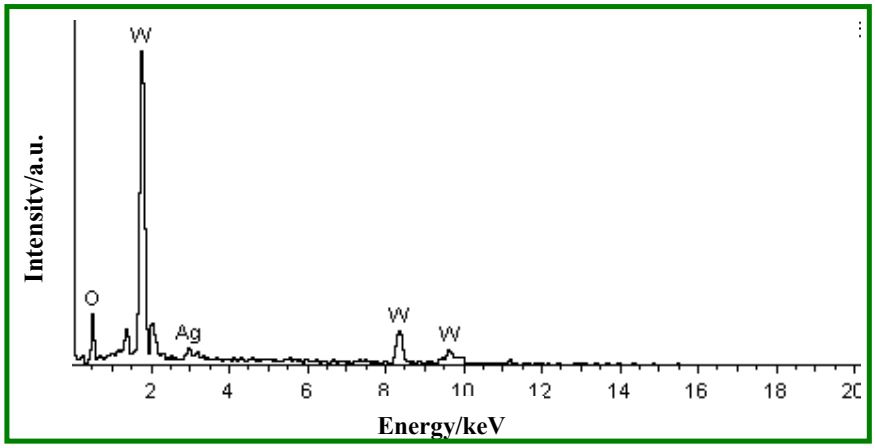


Figure S14. SEM images and EDX spectra for compound **2**. a) SEM micrographs of silver microparticles on tungsten oxide matrix are displayed. b) EDX spectra of tungsten oxide with resulting W singles.