Supporting information for

The Presence of Mixed-valent Silver in the Uranyl Phenylenediphosphonate Framework

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Table S1. The crystallographic data for compound 1.

Formula	$Ag_{1.51}[Ag_4(UO_2)_3(O_3PC_6H_4PO_3)(O_3PC_6H_4PO_3H)_2]$
*M*r[g mol^{-1}]	2106.01
Crystal system	triclinic
Space group	*P -1*
a(Å)	10.5855(9)
b(Å)	12.1032(10)
c(Å)	15.3446(13)
α(°)	72.036(2)
β(°)	74.699(2)
γ(°)	86.000(2)
V(Å^3)	1803.7(3)
Z	2
ρ_{calcd} (g cm^{-3})	3.878
M (mm^{-1})	16.695
F(000)	1873.0
T(K)	298 K
R_1 [a], wR_2[b] (I>2σ(I))	0.0278, 0.0776
R_1 [a], wR_2[b] (all data)	0.0297, 0.0789

[a]$R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b]$wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$

Table S2. Selected bond distances (Å) of compound 1.

U-based distance (Å)								
U(1)-O(19)	1.759(4)		U(2)-O(21)	1.756(5)		U(3)-O(23)	1.771(5)	
U(1)-O(20)	1.773(4)		U(2)-O(22)	1.789(5)		U(3)-O(24)	1.801(5)	
U(1)-O(16)	2.334(4)		U(2)-O(17A)	2.192(14)*0.37(5)		U(3)-O(14)	2.253(5)	
U(1)-O(15)	2.383(4)	6.08	U(2)-O(3)	2.374(4)	6.08	U(3)-O(8)	2.259(4)	6.01
U(1)-O(2)	2.388(4)		U(2)-O(6)	2.384(4)		U(3)-O(5)	2.259(5)	
U(1)-O(12)	2.407(4)		U(2)-O(17B)	2.378(12)*0.63(5)		U(3)-O(10)	2.270(4)	
U(1)-O(7)	2.416(4)		U(2)-O(11)	2.416(4)				
			U(2)-O(9)	2.418(4)				

Ag-based distance (Å)							
Ag(1)-O(1)	2.349(5)	Ag(2)-O(16)	2.417(4)	Ag(3)-O(4)	2.256(5)	Ag(4)-O(1)	2.427(5)
Ag(1)-O(13)	2.382(6)	Ag(2)-O(15)	2.452(4)	Ag(3)-O(9)	2.287(4)	Ag(4)-O(6)	2.485(4)
Ag(1)-O(12)	2.519(4)	Ag(2)-O(24)	2.505(5)	Ag(3)-O(18B)	2.50(2)	Ag(4)-O(6)	2.582(5)
		Ag(2)-O(3)	2.557(5)	Ag(3)-O(17B)	2.559(17)		

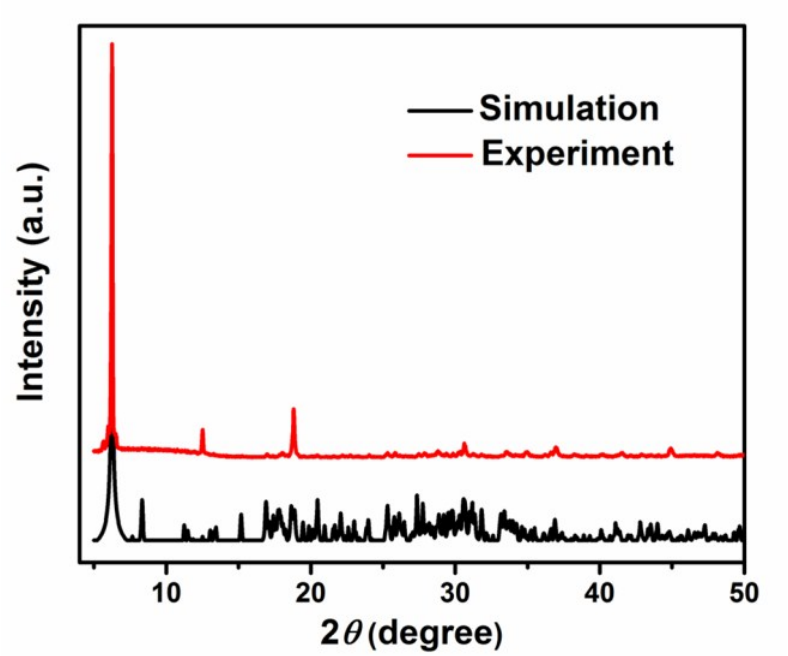

Figure S1. Experimental and simulated PXRD patterns for compound 1.

The PXRD pattern of the bulky sample of compound 1 was collected and shown in **Figure S1,** indicating the compound 1 was obtained as the only isolated product since no additional peaks can be observed in the experimental pattern compared with the simulated one.

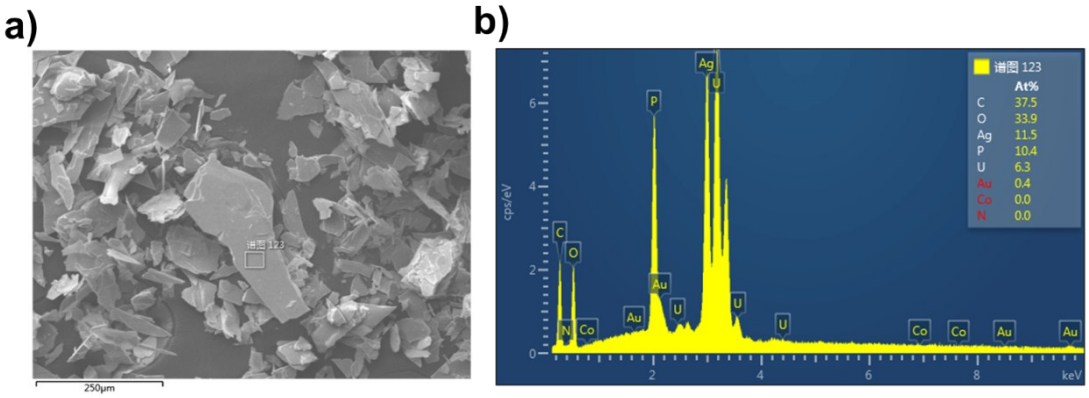

Figure S2. (a) SEM-EDS image and (b) SEM-EDS analysis result of compound 1.

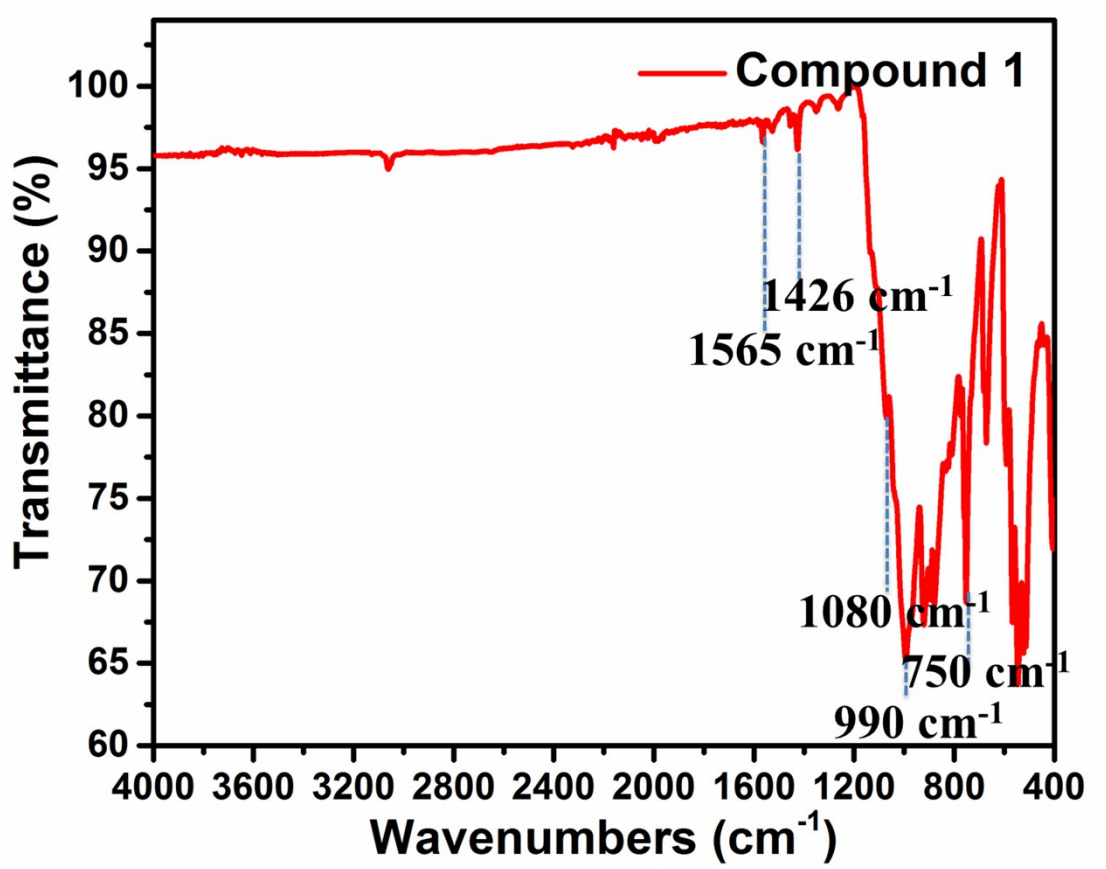

Figure S3. (a) FT-IR spectrum for compound 1.

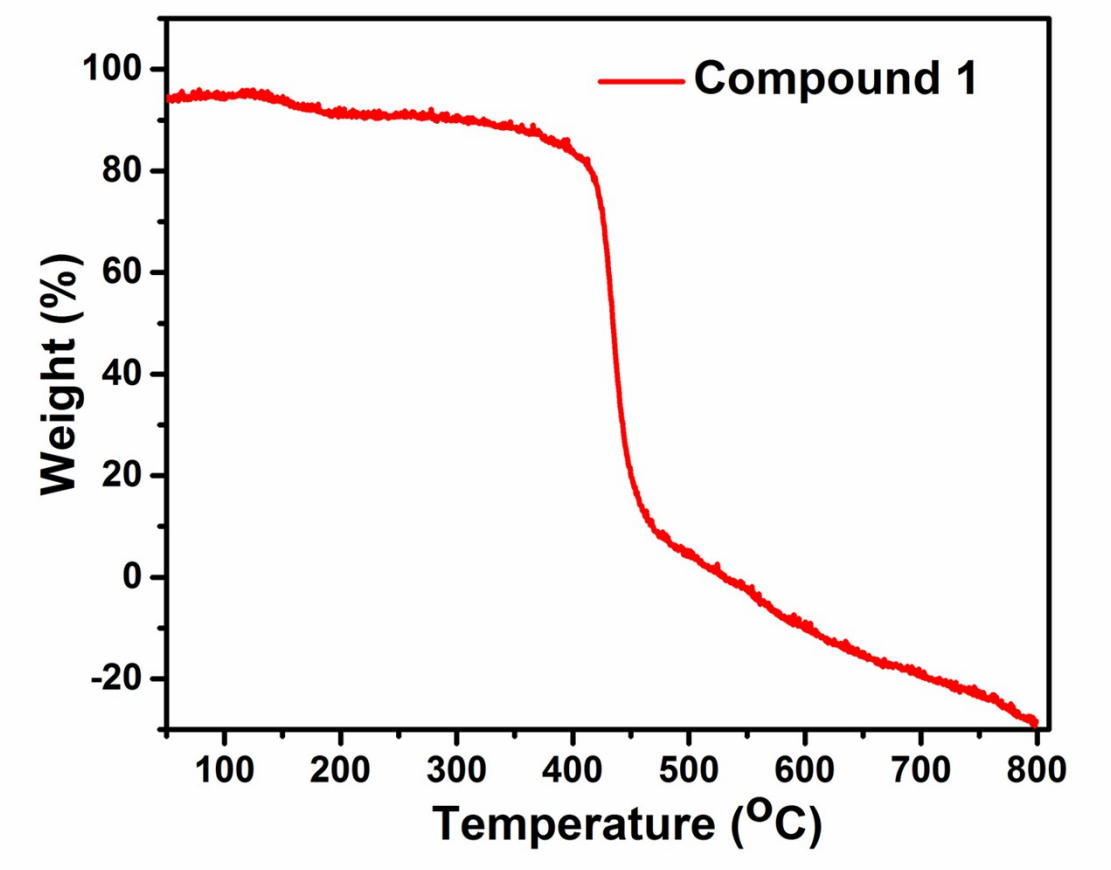

Figure S4. Thermal-gravimetric data for compound 1.

Thermal analysis shows that compound 1 begins to lose weight in the range of 30−187 °C and is thermally stable up to 350 °C. The 9.14% weight-loss is corresponded to the loss of free water molecules adsorbed on the sample. The structure of compound 1 starts to collapse when the temperature is beyond 350 °C

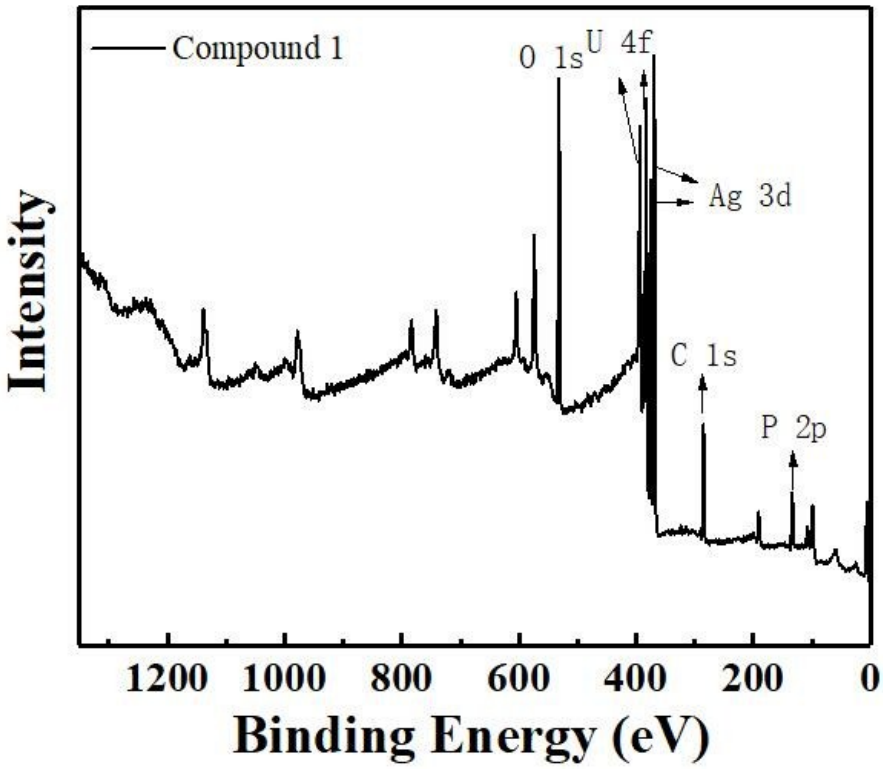

Figure S5. XPS survey spectra of compound 1.

Table S3. The fitting parameters of XPS data for compound 1.

Fitting parameters	Ag^{+}	Ag^{0}
BE of Ag $3d_{5/2}$; [FWHM] (eV)	1.11	0.93
BE of Ag $3d_{3/2}$; [FWHM] (eV)	1.07	0.88
3d peak separation (eV)	6.0	6.0
Area of Ag $3d_{5/2}$	54306.55	19320.51
Area of Ag $3d_{3/2}$	36385.39	12944.74
U4f5/2:U4f7/2 Ratio	Ag^{+} : Ag^{0} = 2.81:1,	