Supporting Information

Assembly of a Luminescent Core-Shell Nanocluster Featuring a $Ag_{34}S_{26}$ Shell and a $W_6O_{21}^{6-}$ Polyoxoanion Core

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1. Synthetic procedures

General comments: AgS^tBu was prepared by using Et_3N as organic solvent and reacted with equivalent amounts of $AgNO_3$ with HS^tBu according to the literature.[1] In addition, $(nBu_4N)_2[W_6O_{19}]$ was synthesized according to the literature.[2] Other reagents and solvents for synthesis were obtained from commercial sources and used without further purification.

$[Ag_{34}(S^tBu)_{26}(W_6O_{21})(CF_3COO)](CF_3COO)\cdot Et_3N\cdot 20CH_3OH$ (1)

AgS^tBu (0.0828 g, 0.420 mmol) was dissolved in methanol (15 mL) under stir. CF_3COOH (0.2 mL) and Et_3N (0.6 mL) were in turn added to the above solution with stir, and then $(nBu_4N)_2[W_6O_{19}]$ (0.0172 g, 0.0090 mmol) was finally added to the mixture after several minutes. The gray-violet suspension was stirred at room temperature for 55h and then was filtered. The filtrate was evaporated slowly in air at room temperature. Complex **1** deposited as bulk light yellow crystals. Yield: ca. 32% (based on W). Elemental analysis (%) calcd for $C_{134}H_{329}F_6S_{26}O_{45}N_1Ag_{34}W_6$: C, 19.18; H, 3.95; N, 0.17; Ag, 43.70; W, 13.14. Found: C, 19.26; H, 3.84; N, 0.20; Ag, 43.62; W, 13.23.

2. Crystallographic studies

Single-crystal X-ray diffraction data for **1** was recorded on a Bruker Apex CCD II area-detector diffractometer with graphite-monochromated Mo-Ka radiation (λ = 0.71073 Å) at 296(2) K. Absorption corrections were applied using multi-scan technique and performed by using the SADABS program. The structure of complex **1** was solved by direct methods and refined on F^2 by full-matrix least squares methods using the SHELXTL package.[3]

Crystal data for **1**: $C_{134}H_{329}F_6S_{26}O_{45}N_1Ag_{34}W_6$; *P-42₁c*; a = 37.905(3) Å, b = 37.905(3) Å, c = 35.309(3) Å; V = 50732(7) Å^3; Z = 8; 255563 reflns measured, 44663 unique (R_{int} = 0.1894); final R_1 = 0.0649, wR_2 = 0.1394 for 19835 observed reflections [$I > 2\sigma(I)$]. CCDC-871786 (**1**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/ data_request/cif for **1**.

3. Physical Measurements

The FT-IR spectra were recorded from KBr pellets in the range of 4000–400 cm^{-1} on a Mattson Alpha-Centauri spectrometer. PXRD patterns were recorded on a Siemens D 5005 diffractometer with Cu-Kα (λ= 1.5418 Å) radiation in the range of 3-50℃. TGA was performed on a Perkin-Elmer TGA analyzer heated from room temperature to 900℃ under nitrogen gas with a heating rate of 10℃/min. The UV-vis-NIR absorption spectroscopy was measured with a U-3010 Spectrophotometer. Luminescence was measured on an F-7000 FL Spectrophotometer. NMR data were recorded on a Bruker AV spectrometer (500 MHz). Elemental analyses (C, H, and N) were performed on a Perkin-Elmer 2400 CHN elemental analyzer. Ag and W were analyzed on a PLASMA-SPEC(I) ICP atomic emission spectrometer. A CHI 440 Electrochemical Quartz Crystal Microbalance was used for the electrochemical experiments. A conventional three-electrode cell was used at room temperature. The compounds bulk-modified carbon-paste electrodes (CPEs) were used as the working electrode. An SCE and a platinum wire were used as reference and auxiliary electrodes, respectively.

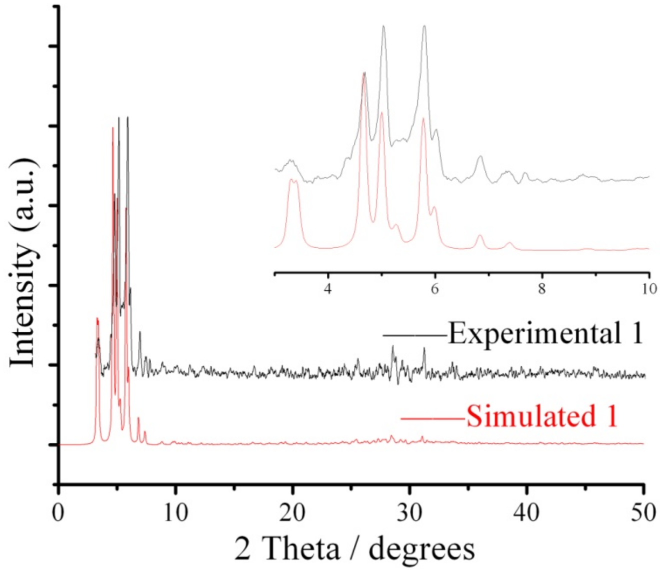

Fig. S1 The experimental and simulated X-ray powder diffraction patterns of **1**.

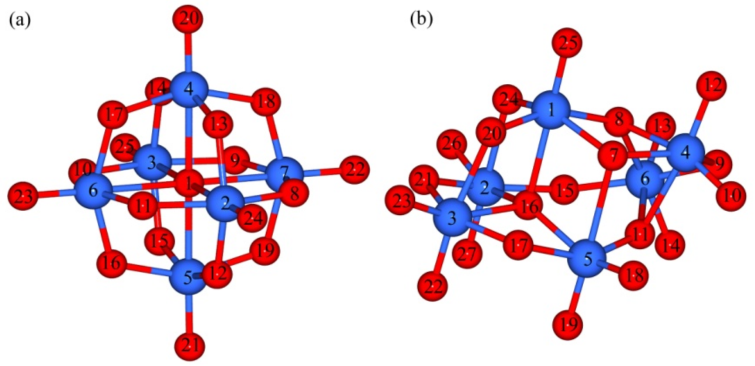

Fig. S2 (a) Theoretical calculation model of $W_6O_{19}^{2-}$. (b) Theoretical calculation model of $W_6O_{21}^{6-}$.

Table S1 The theoretical calculation charge density of $W_6O_{19}^{2-}$ and $W_6O_{21}^{6-}$.

$W_6O_{19}^{2-}$			$W_6O_{21}^{6-}$		
Atom	No	Natural Charge/ e	Atom	No	Natural Charge/ e
W	1	-0.88059	W	1	1.42240
W	2	1.54221	W	2	1.39977
W	3	1.54221	W	3	1.33068
W	4	1.54221	W	4	1.35412
W	5	1.54221	W	5	1.41779
W	6	1.54221	W	6	1.40033
O	7	-0.61840	O	7	-0.70585
O	8	-0.61840	O	8	-0.75469
O	9	-0.61840	O	9	-0.72276
O	10	-0.61840	O	10	-0.65667
O	11	-0.61840	O	11	-0.71290
O	12	-0.61840	O	12	-0.65409
O	13	-0.61840	O	13	-0.68878
O	14	-0.61840	O	14	-0.66378
O	15	-0.61840	O	15	-0.65908
O	16	-0.61840	O	16	-0.79168
O	17	-0.61840	O	17	-0.71260
O	18	-0.61840	O	18	-0.65759
O	19	-0.61840	O	19	-0.61949
O	20	-0.49197	O	20	-0.67699
O	21	-0.49197	O	21	-0.71050
O	22	-0.49197	O	22	-0.63720
O	23	-0.49197	O	23	-0.71362
O	24	-0.49197	O	24	-0.67696
O	25	-0.49197	O	25	-0.63346
			O	26	-0.69814
			O	27	-0.57824

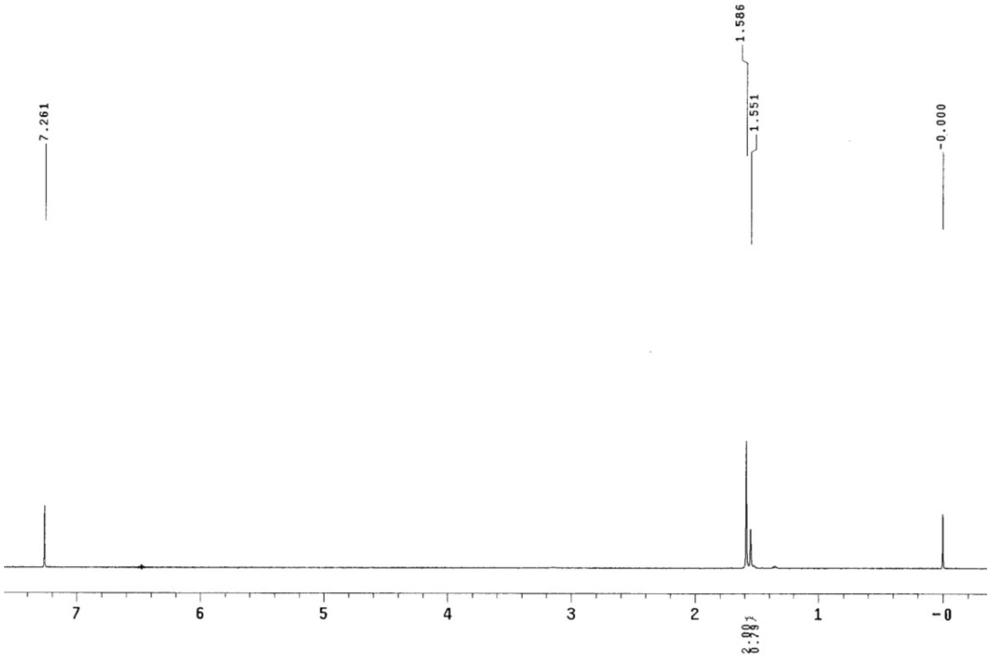

Fig. S3 The ^{1}H NMR spectrum of ligand AgS^{t}Bu (500MHz, CDCl$_3$, RT).

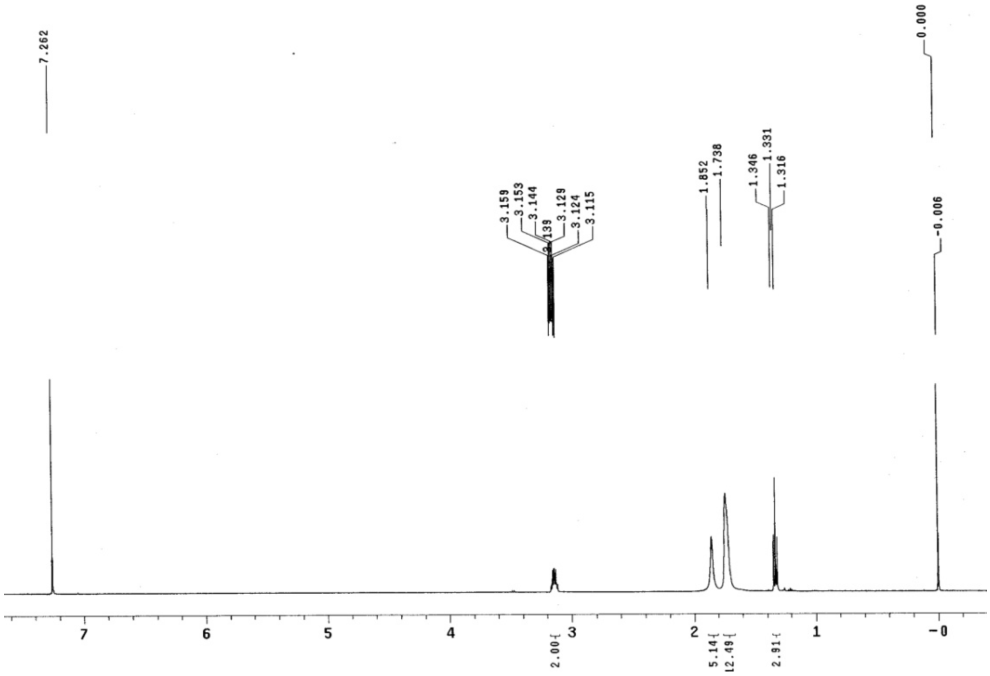

Fig. S4 The ^{1}H NMR spectrum of **1** (500MHz, CDCl$_3$, RT).

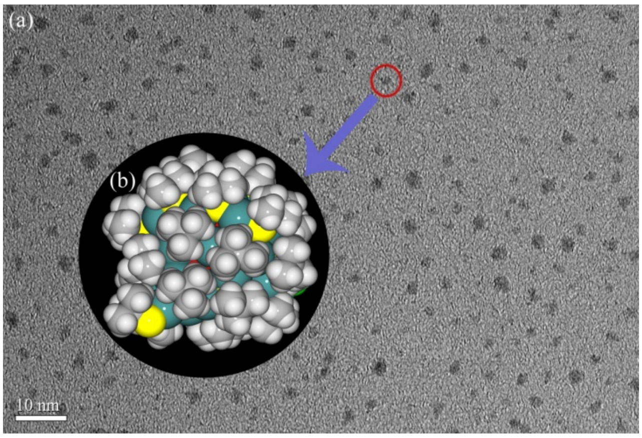

Fig. S5 (a) TEM image of **1**. (b) Single cluster unit of **1**. Color legend: green, Ag; yellow, S; gray, C; white, H; red, O; blue, W.

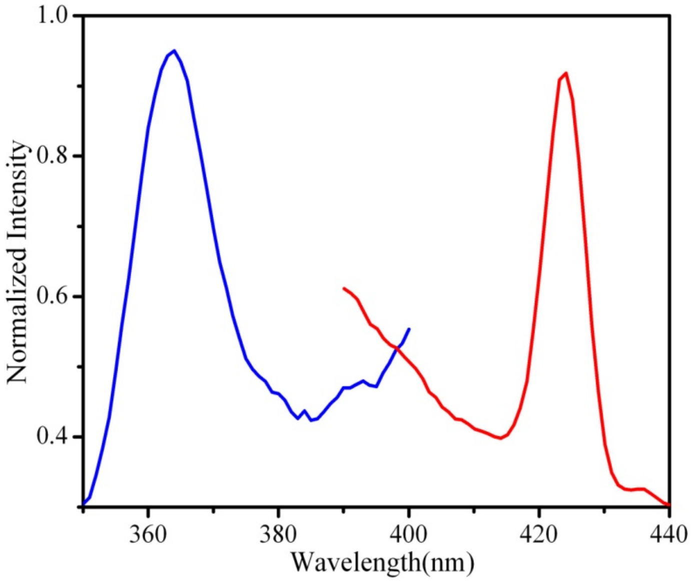

Fig. S6 Excitation and emission spectra of **1** in the solid state.

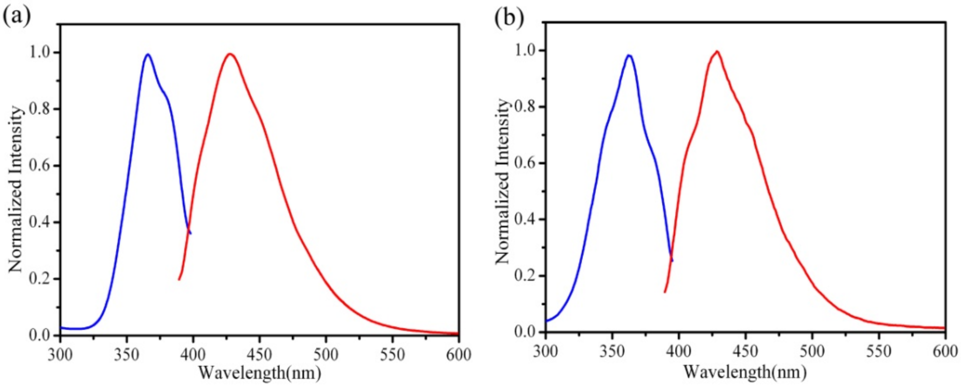

Fig. S7 (a) Excitation (blue trace) and emission (red trace) spectra of **1** in EtOH solution. (b) Excitation (blue trace) and emission (red trace) spectra of **1** in EtOH solution after being stored for about five months.

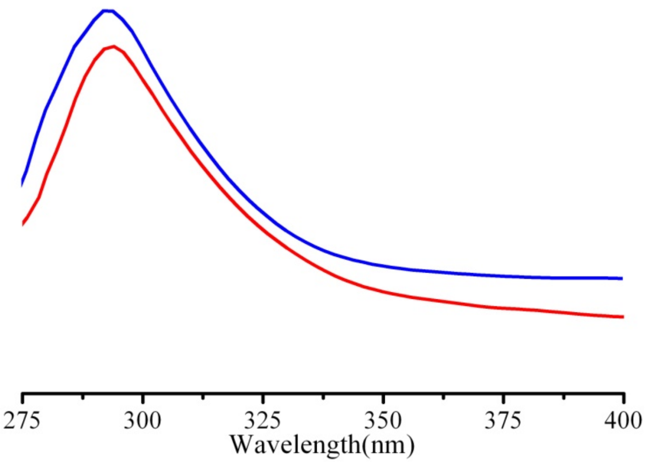

Fig. S8 Electronic absorption spectrum (blue trace) of **1** in EtOH solution and electronic absorption spectrum(red trace) of **1** in EtOH solution after being stored for about five months.

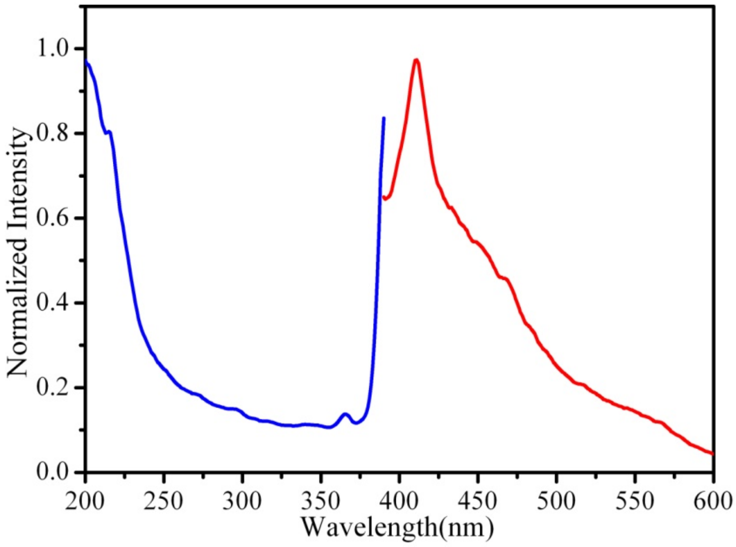

Fig. S9 Excitation and emission spectra of ligand AgS^{t}Bu in EtOH solution.

Electrochemistry

Preparation of compound 1, AgS^{t}Bu and (nBu$_4$N)$_2$[W$_6$O$_{19}$] bulk-modified CPEs: The compound **1** bulk-modified CPE (**1**–CPE) was fabricated by mixing 0.10 g graphite powder and 0.010 g compound **1** in an agate mortar for approximately 30 min to achieve an uniform mixture; then a drop of paraffin oil was added and stirred with a glass rod.[2] The homogenized mixture was packed into a 3 mm inner diameter glass tube and the tube surface was wiped with weighing paper. The electrical contact was established with the copper wire through the back of the electrode. In a similar manner, AgS^{t}Bu and (nBu$_4$N)$_2$[W$_6$O$_{19}$] bulk-modified CPEs were prepared by similar process without compound **1**.

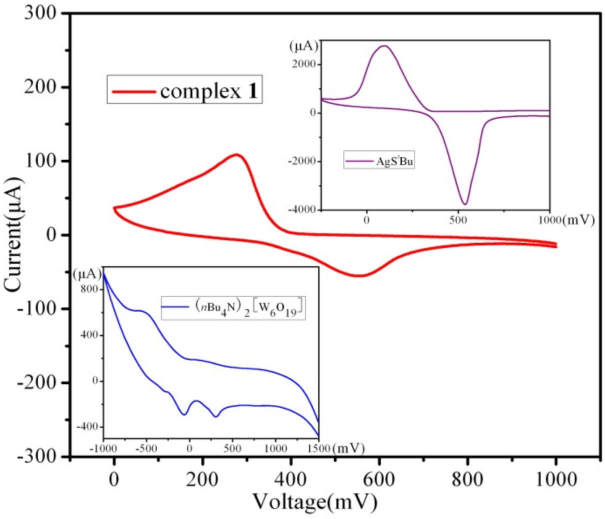

Fig. S10 Cyclic voltammograms of complex **1**, AgS^{t}Bu and (nBu$_4$N)$_2$[W$_6$O$_{19}$].

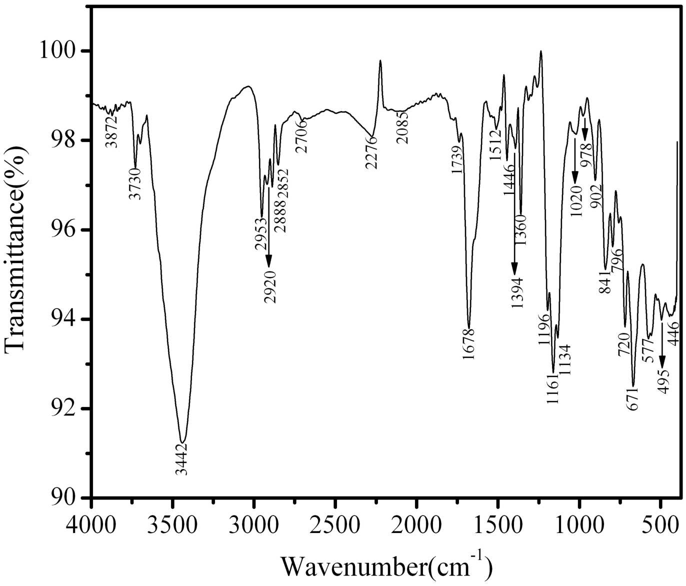

Fig. S11 The IR spectrum of **1**.

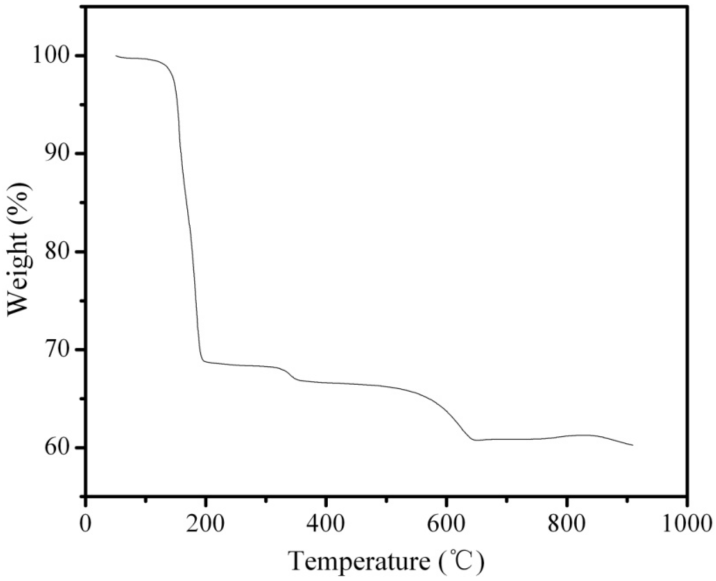

Fig. S12 TG curve of **1**.

Reference:

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2 W. G. Klemperer, *Inorg. Synth.*, 1990, **27**, 80–81.

3 (*a*) G. M. Sheldrick, *SHELX-97, Program for Crystal Structure Refinement*, University of Göttingen, Germany, 1997; (*b*) G. M. Sheldrick, *SHELXL-97, Program for Crystal Structure Solution*, University of Göttingen, Germany, 1997.

4 X. L. Wang, Z. H. Kang, E. B. Wang and C. W. Hu, *Mater. Lett.*, 2002, **56**, 393–396.