Electronic Supplementary Material (ESI) for Nanoscale.

Electronic Supplementary Information (ESI)

Platonic solid templating Archimedean solid: An unprecedented nanometre-sized Ag_{37} cluster

Xiao-Yu Li,[a] Hai-Feng Su,[b] Kai Yu,[c] Yuan-Zhi Tan,*,[b] Xing-Po Wang, [a] Ya-Qin Zhao,[a] Di Sun*,[a] and Lan-Sun Zheng[b]

[a]*Key Lab of Colloid and Interface Chemistry, Ministry of Education, School of Chemistry and Chemical Engineering, Shandong University, Jinan, 250100, People's Republic of China.*

E-mail: xpw6@sdu.edu.cn; dsun@sdu.edu.cn. Fax: +86-531-88364218.

[b]*State Key Laboratory for Physical Chemistry of Solid Surfaces and Department of Chemistry, College of Chemistry and Chemical Engineering, Xiamen University, Xiamen 361005, People's Republic of China. Email: yuanzhi_tan@xmu.edu.cn*

(1) Experiment details

The precursor $\{(HNEt_3)_2[Ag_{10}(SC_6H_4{}^tBu)_{12}]\}_n$ was synthesized by mixing equivalent amounts of $AgNO_3$ in acetonitrile and $HSC_6H_4Bu^t$ in ethanol in the presence of Et_3N. Other reagents and solvents employed were commercially available and used as received without further purification. Photoluminescence spectra were measured on a Hitachi F-7000 Fluorescence Spectrophotometer. TG curve was measured from 30 to 600 °C on a SDT Q600 instrument at a heating rate 10 °C/min under the N_2 atmosphere (100 mL/min). X-ray powder diffractions were measured on a Panalytical X-Pert pro diffractometer with Cu-Kα radiation. C, N, and H analyses were performed on an EA1110 CHNS-0 CE 65 elemental analyzer. IR (KBr pellet) spectra were recorded on a Nicolet Magna750FT-IR spectrometer. UV-Vis spectra of 1 in solution and solid state were recorded on a Varian Carry 5000 spectrophotometer. Mass spectra were recorded on a ESI spectrometer Agilent 6224 (USA). The morphology of the samples was studied by transmission electron microscopy using a JEM2010 transmission electron microscope (JEOL Ltd.) at an accelerating voltage of 200 kV. Electrochemical measurements were performed with a CHI660 electrochemical workstation. A conventional three electrode system was used. The working electrode was a modified carbon paste electrode. Ag/AgCl (3 M KCl) electrode was used as a reference electrode and a Pt wire as a counter electrode.

Preparation of cluster 1 bulk-modified CPEs: A conventional three-electrode cell was used at room temperature. The compound bulk-modified carbon-paste electrodes (CPEs) were used as the working electrode. A SCE and a platinum wire were used as reference and auxiliary electrodes, respectively. 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 a uniform mixture; then a drop of paraffin oil was added and stirred with a glass rod. 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.

(2) X-ray Crystallography

Single crystal of the complex **1** with appropriate dimensions were removed from the mother liquor, coated with high vacuum grease (Dow Corning Corporation), and transferred to a stream of cold N_2 on the diffractometer as quickly as possible to prevent decomposition due to solvent loss. Data were collected on an Agilent Technologies SuperNova A diffractometer using Cu radiation with an Oxford Cryosystems Cryostream low-temperature device operating at 100 K. Data were processed using the CrysAlisPro software package (Agilent Technologies 2013, CrysAlisPro Software system, version 1.171.35.19, Agilent Technologies UK Ltd, Oxford, UK),[1] solved with SUPERFLIP, and refined using SHELX[2] and the OLEX2[3] refinement programs. Furthermore, it was necessary to use constraints to control the geometry of the aromatic rings and restraints to enforce chemically sensible bond lengths and angles in the ^{t}Bu- groups. Vibrational restraints were also used to control atomic displacement parameters of various atoms, in particular those in the ^{t}Bu-groups, which have considerably greater freedom of movement than the main cluster.

As usual for cluster complexes of this nature, crystals of the metal complexes scattered weakly due to the extensive disorder of anions and solvent molecules. After integration of the raw data and before merging, an empirical absorption correction was applied (SADABS), based on comparison of multiple symmetry-equivalent measurements. In every case (i) the weakness of the data required extensive use of restraints and/or constraints, to keep the geometries of anions, or aromatic rings reasonable; and (ii) there was disordered associated with cations and solvent molecules. In addition, in all cases there were extensive areas of residual electron density that could not sensibly be modeled as solvent or anions, which were removed via application of the Squeeze function in PLATON.[4]

1. CrysAlisPro Version 1.171.35.19. (2011). Agilent Technologies Inc. Santa Clara, CA, USA.

2. Sheldrick, G. M. (2008). A short history of SHELX. *Acta Cryst*. *A* **64**, 112-122.

3. Dolomanov et al. (2009). OLEX2: a complete structure solution, refinement and analysis program. *J. Appl. Cryst*. **42**, 339-341.

4. Spek, A. L. (2009) *Acta Cryst. D* **65**, 148 – 155.

(3) Synthesis of cluster 1

The $\{(HNEt_3)_2[Ag_{10}(SC_6H_4{}^tBu)_{12}]\}_n$ (0.1 mmol) and CF_3COOAg (0.1 mmol) were dissolved in the mixed solvent of dichloromethane-methanol-N, N'-dimethylformamide (4 mL, v: v: v = 3:3:1). The reaction mixture was sealed and kept at 65 ^{o}C for 30 hours. After cooled to room temperature, the yellow solution was filtered and the filtrate was evaporated slowly in darkness at room temperature. Complex **1** crystallized as yellow crystals for two weeks in a yield of 55%. Anal. Calc. (found) for $\{(HNEt_3)[Ag_{37}S_4(SC_6H_4{}^tBu)_{24}(CF_3COO)_6(H_2O)_{12}]\}$ ($C_{258}H_{352}NAg_{37}F_{18}O_{24}S_{28}$): C, 34.12 (34.59); H, 3.91 (3.66); N, 0.15 (0.18) %. IR (KBr): $\nu(cm^{-1})$ = 3443 (m), 2965 (m), 1647 (s), 1485 (m), 1390 (m), 1264 (w), 1198 (s), 1147 (m), 1007 (w), 823 (m), 720 (w), 550 (w).

(4) Table S1 Selected bond distances (Å) and angles (°) for 1

Ag1—Ag1^{i}	3.354 (4)	Ag7—Ag1^{ii}	2.955 (3)
Ag1—Ag2	2.970 (3)	Ag7—S3^{iii}	2.486 (6)
Ag1—Ag7^{ii}	2.955 (3)	Ag7—S5	2.489 (8)
Ag1—S1^{i}	2.518 (7)	Ag7—O3W	2.519 (10)
Ag1—S1	2.820 (7)	Ag8—Ag9^{iii}	2.942 (3)
Ag1—S5^{ii}	2.511 (7)	Ag8—S3^{iii}	2.469 (7)
Ag1—O1	2.37 (2)	Ag8—S6	2.456 (6)
Ag2—Ag3	3.124 (2)	Ag8—O1W	2.47 (2)
Ag2—Ag4	3.149 (3)	Ag9—Ag8^{iii}	2.942 (3)
Ag2—S1	2.468 (6)	Ag9—Ag9^{iii}	3.368 (4)
Ag2—S2	2.485 (6)	Ag9—S3	2.502 (6)
Ag2—S7^{ii}	2.730 (5)	Ag9—S4	2.865 (6)
Ag3—Ag4	3.199 (2)	Ag9—S4^{iii}	2.530 (6)
Ag3—Ag5	3.010 (2)	Ag9—O9	2.38 (3)
Ag3—S2	2.456 (5)	Ag10—S7	2.602 (5)
Ag3—S4	2.486 (5)	Ag10—S7^{i}	2.602 (5)
Ag3—S7	2.703 (4)	Ag10—S7^{iii}	2.602 (5)
Ag4—Ag9	2.955 (3)	Ag10—S7^{ii}	2.602 (5)
Ag4—S1	2.446 (6)	Ag6—Ag7	2.977 (3)
Ag4—S4	2.452 (6)	Ag6—Ag8	2.970 (3)
Ag4—S7^{iii}	2.676 (5)	Ag6—S5	2.463 (6)
Ag5—Ag5^{ii}	3.317 (3)	Ag6—S6	2.487 (6)
Ag5—Ag6	2.946 (3)	Ag6—O2W	2.45 (3)
Ag5—S2^{ii}	2.527 (5)	Ag5—S2	2.820 (5)
Ag5—S6	2.529 (6)	Ag5—O2	2.42 (3)
S1^{iii}—Ag1—S1	87.7 (2)	O2W—Ag6—S5	111.1 (6)
S5^{i}—Ag1—S1^{iii}	136.8 (2)	O2W—Ag6—S6	105.9 (7)
S5^{i}—Ag1—S1	107.3 (2)	S3^{ii}—Ag7—S5	136.98 (19)
O1—Ag1—S1	99.5 (7)	S3^{ii}—Ag7—O3W	102.1 (8)
O1—Ag1—S1^{iii}	103.8 (10)	S5—Ag7—O3W	101.9 (8)
O1—Ag1—S5^{i}	112.8 (7)	S3^{ii}—Ag8—O1W	106.3 (6)
S1—Ag2—S2	147.0 (2)	S6—Ag8—S3^{ii}	139.6 (2)
S1—Ag2—S7^{i}	115.6 (2)	S6—Ag8—O1W	109.9 (6)
S2—Ag2—S7^{i}	93.87 (15)	S3—Ag9—S4	106.0 (2)
S2—Ag3—S4	144.36 (18)	S3—Ag9—S4^{ii}	138.0 (2)
S2—Ag3—S7	117.92 (16)	S4^{ii}—Ag9—S4	89.9 (2)
S4—Ag3—S7	93.20 (17)	O9—Ag9—S3	111.5 (7)
S1—Ag4—S4	143.0 (2)	O9—Ag9—S4^{ii}	106.7 (8)
S1—Ag4—S7^{ii}	92.96 (19)	O9—Ag9—S4	91.1 (9)
S4—Ag4—S7^{ii}	120.63 (17)	S7^{iii}—Ag10—S7	110.71 (18)
S2^{i}—Ag5—S2	88.43 (16)	S7^{iii}—Ag10—S7^{ii}	108.3 (2)
S2^{i}—Ag5—S6	136.35 (18)	S7—Ag10—S7^{ii}	109.5 (2)

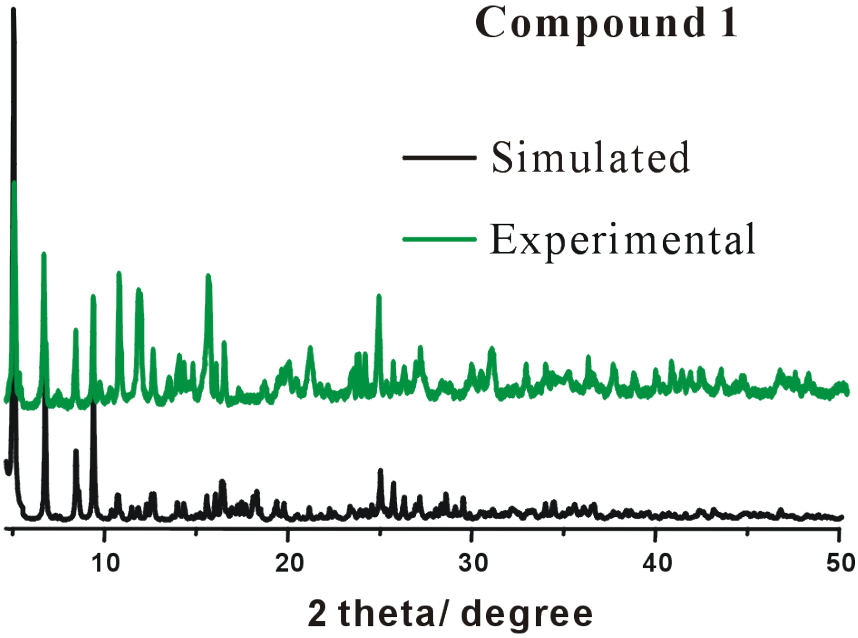
S6—Ag5—S2	104.46 (17)	S7^{iii}—Ag10—S7^{i}	109.5 (2)
O2—Ag5—S2^{i}	104.7 (9)	S7—Ag10—S7^{i}	108.3 (2)
O2—Ag5—S2	96.5 (8)	S7^{ii}—Ag10—S7^{i}	110.71 (18)
O2—Ag5—S6	114.7 (8)		

Symmetry codes: (i) *y*+1/4, *x*−1/4, −*z*+3/4; (ii) −*y*+3/4, −*x*+3/4, −*z*+3/4; (iii) −*x*+1, −*y*+1/2, *z*.

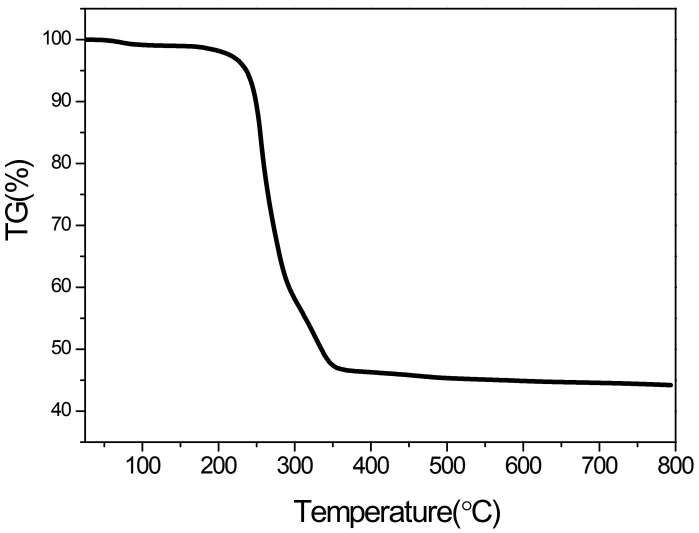
(5) Table S2: Crystal data for 1

Empirical formula	$C_{258}H_{352}NAg_{37}F_{18}O_{24}S_{28}$
Formula weight	9082.49
Temperature/K	100(2)
Crystal system	tetragonal
Space group	$I4_1/acd$
a/Å	32.6712(5)
b/Å	32.6712(5)
c/Å	76.823(2)
α/°	90.00
β/°	90.00
γ/°	90.00
Volume/Å^3	82001(3)
Z	8
ρ_{calc}mg/mm^3	1.451
μ/mm^{-1}	15.528
F(000)	34920.0
2Θ range for data collection	6.96 to 122.32°
Index ranges	$-23 \leqslant h \leqslant 37$, $-27 \leqslant k \leqslant 35$, $-87 \leqslant l \leqslant 62$
Reflections collected	72902
Independent reflections	15755[R(int) = 0.1846]
Data/restraints/parameters	15755/543/826
Goodness-of-fit on F^2	1.043
Final R indexes [I>=2σ (I)]	$R_1 = 0.1380$, $wR_2 = 0.3547$
Final R indexes [all data]	$R_1 = 0.2085$, $wR_2 = 0.4122$
Largest diff. peak/hole / e Å^{-3}	2.79/-1.72

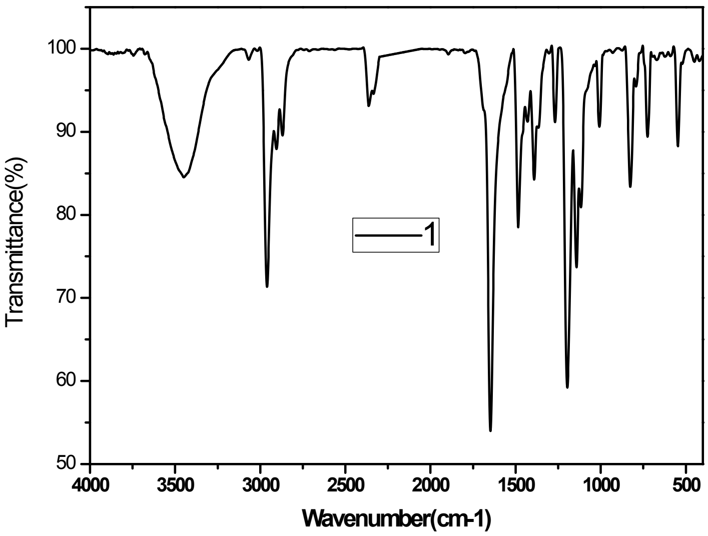
(6) Fig. S1: PXRD patterns



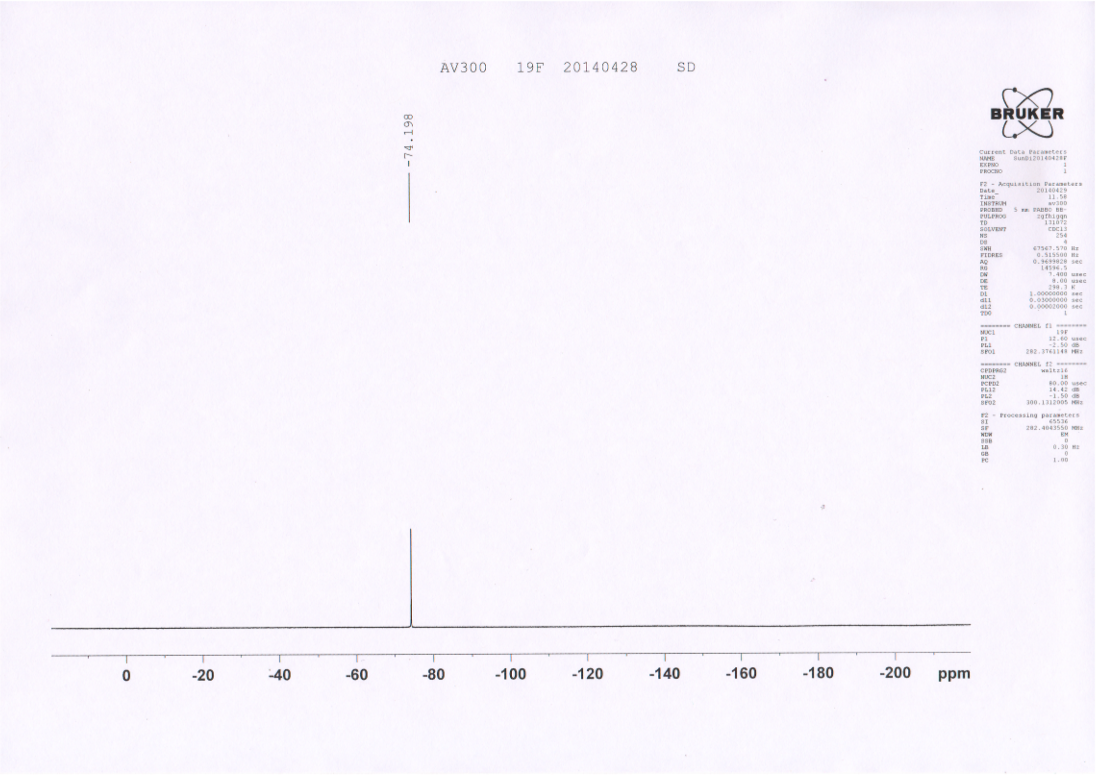
(7) Fig. S2: The TGA curve of 1



(8) Fig. S3: The IR spectrum of 1



(9) Fig. S4: The ^{19}F NMR spectrum of 1 in CD_3Cl.



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PROCNO                  1

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PULPROG          zgfhigqn
TD                 131072
SOLVENT             CDCl3
NS                    254
DS                      4
SWH             67567.570 Hz
FIDRES           0.515500 Hz
AQ              0.9699828 sec
RG                14596.5
DW                  7.400 usec
DE                   8.00 usec
TE                  298.3 K
D1             1.00000000 sec
d11            0.03000000 sec
d12            0.00002000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                  19F
P1                  12.60 usec
PL1                 -2.50 dB
SFO1          282.3761148 MHz

======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                   1H
PCPD2               80.00 usec
PL12                14.42 dB
PL2                 -1.50 dB
SFO2          300.1312005 MHz

F2 - Processing parameters
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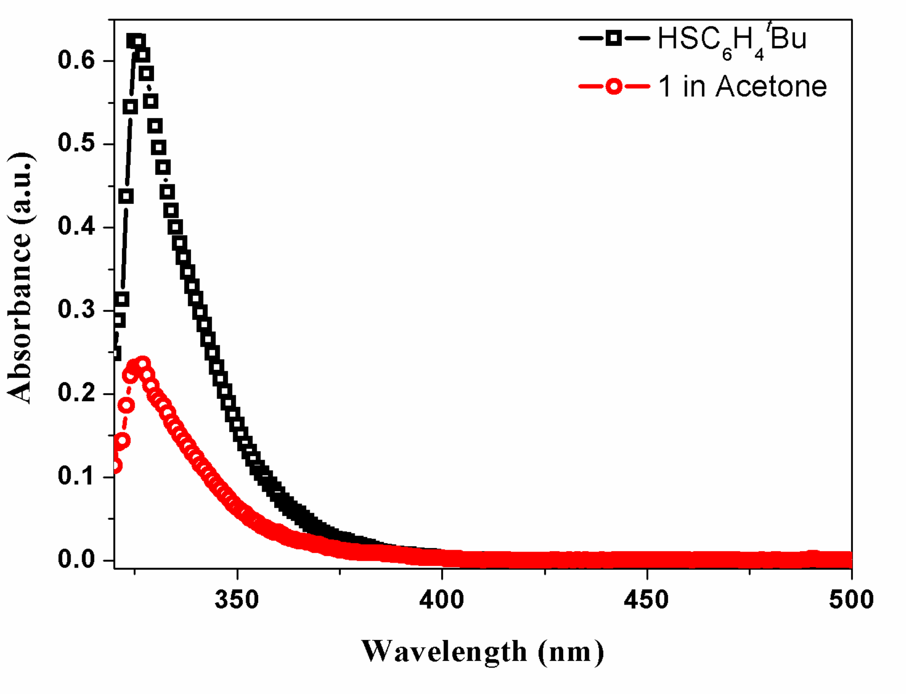
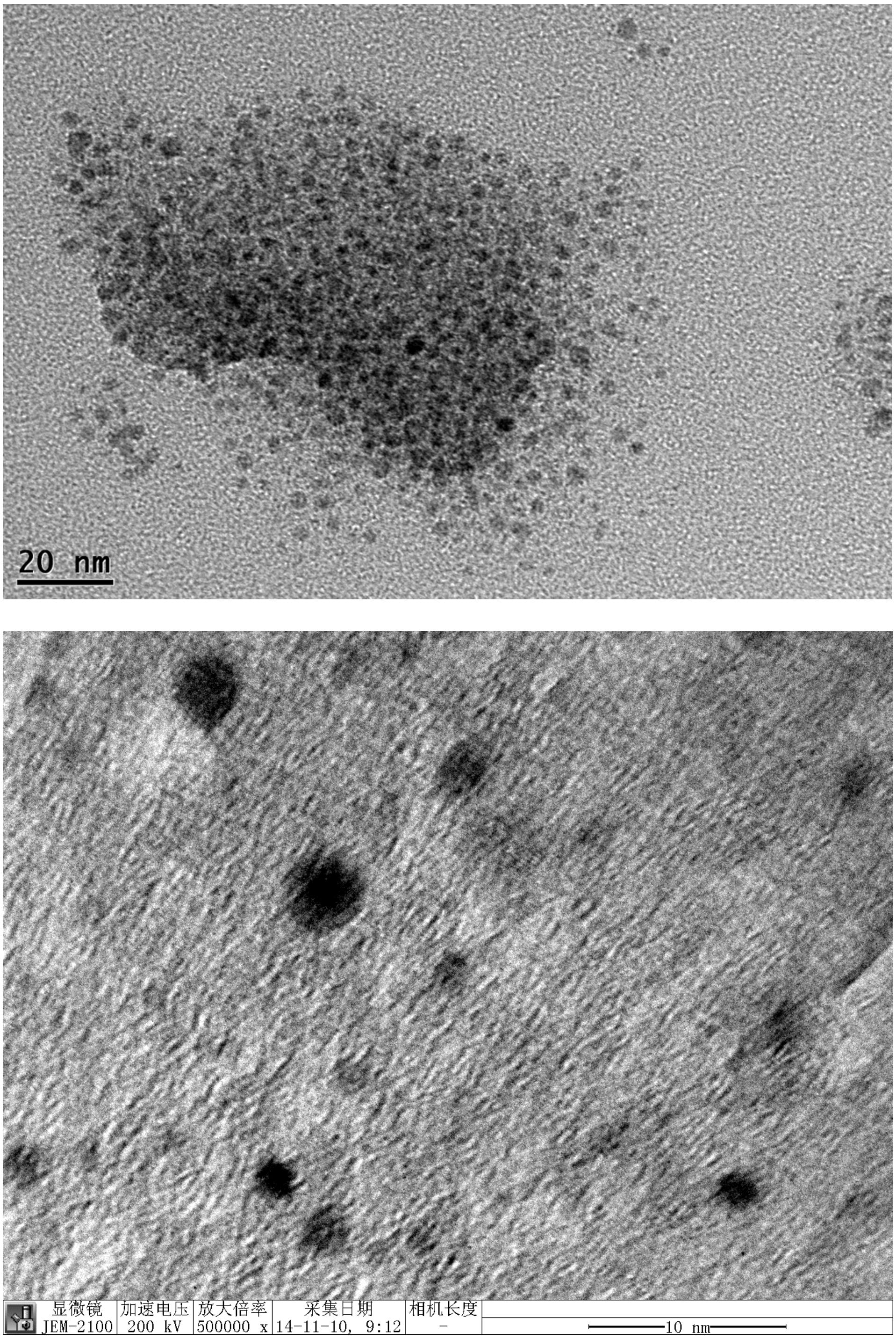
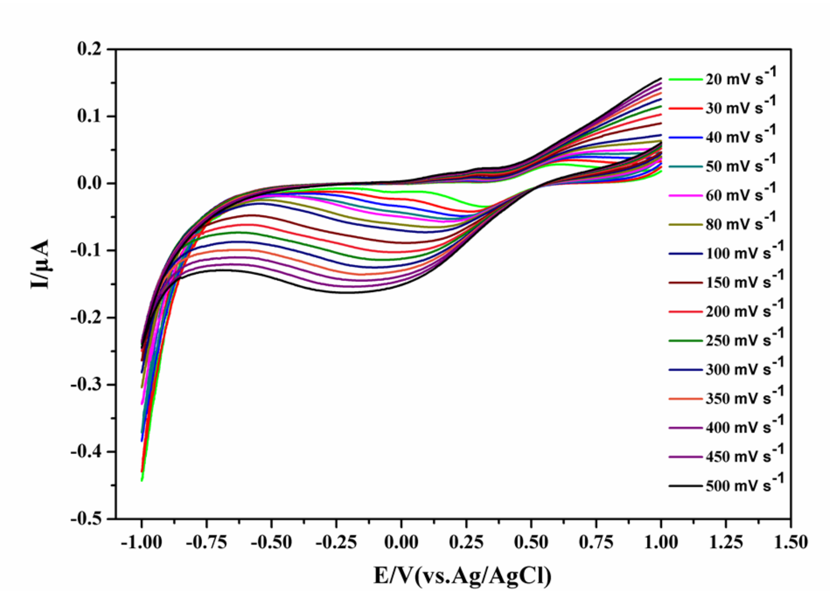
(10) Fig. S5: The UV-Vis spectrum of free ligand and 1 in acetone.



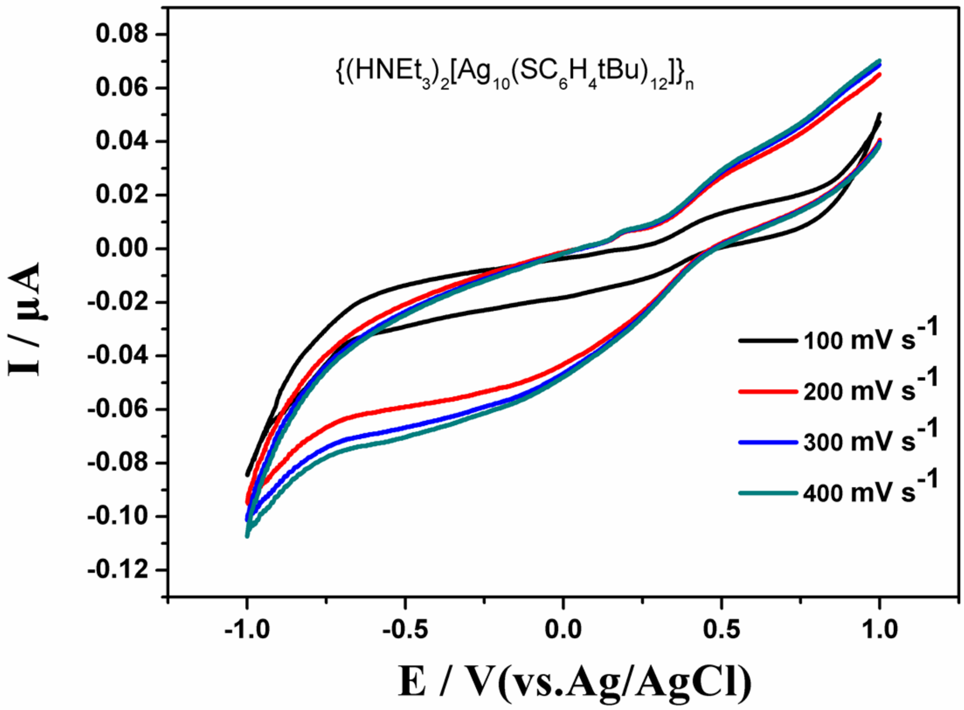
(11) Fig. S6: The TEM images of complex 1.



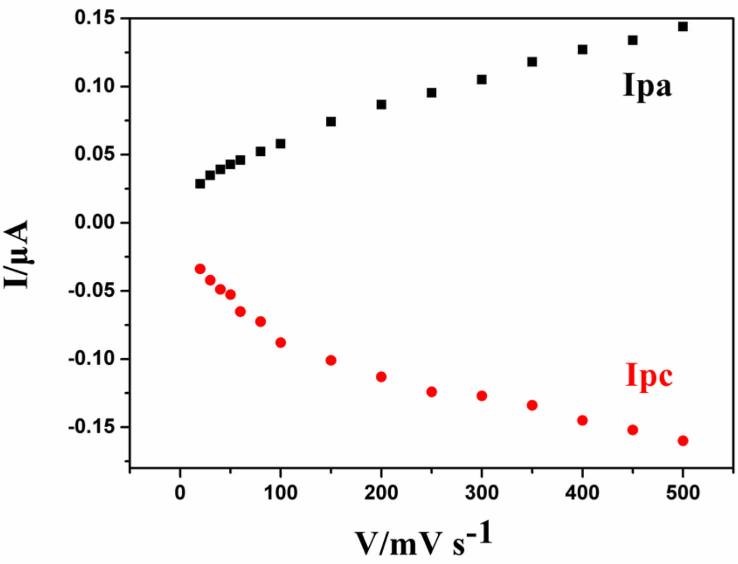
(12) Fig. S7: Cyclic voltammograms of the 1-CPE in 1 M H_2SO_4 aqueous solution at different scan rates.



(13) Fig. S8: Cyclic voltammograms of the precursor in 1 M H_2SO_4 aqueous solution at different scan rates.



(14) **Fig. S9: The plotting of peak current of anode and cathode versus scanning rate.**



(15) **Fig. S10: Cyclic voltammograms of the 1-CPEs in 1 mol/L sulfuric acid aqueous solution containing 0.0, 5.0, 10.0, 15.0 mmol/L H_2O_2 with scanning speed of 50 mV/s.**