Supporting Information

Unexpected 1D self-assembly of carbonate-templated sandwich-like macrocycle-based $Ag_{20}S_{10}$ luminescent nanoclusters

Kun Zhou, Chao Qin, Xin-Long Wang,* Kui-Zhan Shao, Li-Kai Yan and Zhong-Min Su*

Institute of Functional Material Chemistry, Key Lab of Polyoxometalate Science of Ministry of Education, Faculty of Chemistry, Northeast Normal University; Changchun, 130024, Jilin, China. Fax: (+86) 431-85684009; Tel: (+86) 431-85099108; E-mail: zmsu@nenu.edu.cn.

Table of contents

1. Synthetic procedures S2

2. Crystallographic studies.....S2

3. Selected bond lengths (Å) for compound 1.....S2-S3

4. Physical Measurements S3-S8

1. Synthetic procedures

General comments: AgS^{t}Bu was prepared by using Et_3N as organic solvent and reacted with equivalent amounts of $AgNO_3$ with HS^{t}Bu according to the literature.[1] In addition, $(NH_4)_3[CrMo_6O_{24}H_6]\cdot 7H_2O$ were synthesized according to the literature.[2] Other reagents and solvents for synthesis were obtained from commercial sources and used without further purification.

$\{[(CO_3^{2-})@Ag_{20}(S^tBu)_{10}(CH_3COO)_8(DMF)_2]\cdot 2H_2O\}_n$ (1):

Compound **1** was obtianed by one-pot synthesis, namely, AgS^{t}Bu (0.0644 g, 0.3268 mmol) with $(NH_4)_3[CrMo_6O_{24}H_6]\cdot 7H_2O$ (0.0126 g, 0.0105 mmol), $Ni(CH_3COO)_2\cdot 4H_2O$ (0.0306 g, 0.1230 mmol), $AgCF_3COO$ (0.0180 g, 0.0815 mmol) and $AgBF_4$ (0.0123 g, 0.0632 mmol) were dissolved in ethanol–acetonitrile–dimethylformamide(DMF) (v : v : v=1 : 1 : 1) (15 mL) under stir at room temperature to gain a gray-violet suspension (pH ≈ 7.5). Then the gray-violet suspension was uninterruptedly stirred at room temperature for 2d and then was filtered. The filtrate was evaporated slowly in air at room temperature. Compound **1** was deposited as lightyellow polyhedron crystals. Compound **1** can also be obtained by using the same method just without $[CrMo_6O_{24}H_6]^{3-}$ polyoxoanion. Yield: ca. 63% (based on Ag). Elemental analysis (%) calcd for $C_{63}H_{132}O_{23}N_2S_{10}Ag_{20}$: C, 20.10; H, 3.54; N, 0.74; S, 8.52; Ag, 57.32. Found: C, 20.04; H, 3.51; N, 0.75; S, 8.48; Ag, 57.24.

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 = 0.71069 Å) at 298(2) K. Absorption corrections were applied using multi-scan technique and performed by using the SADABS program. The structure of compound **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**: $C_{63}H_{132}O_{23}N_2S_{10}Ag_{20}$; *P*-1; a = 12.947(5) Å, b = 15.169(5) Å, c = 15.922(5) Å; α = 67.605(5) °; β = 82.355(5) °; γ = 65.089(5) °; V = 2620.7(16) Å^3; Z = 1; 15130 reflns measured, 9186 unique (R_{int} = 0.0506); final R_1 = 0.0614, wR_2 = 0.1519 for 5443 observed reflections [$I > 2\sigma(I)$]. CCDC-998570 (**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. Selected bond lengths (Å) for compound 1

Table S1. Selected bond lengths (Å) for compound **1**

Ag(1)-O(10)$^{\#1}$	2.38(2)	Ag(1)-S(5)	2.619(4)
Ag(1)-O(7)	2.452(11)	Ag(1)-Ag(6)	2.9614(18)
Ag(1)-S(1)	2.489(4)	Ag(1)-Ag(5)	3.0343(19)
Ag(1)-O(9)	2.52(2)	Ag(2)-S(1)	2.458(3)

Ag(2)-S(2)	2.472(3)		Ag(7)-O(3)	2.335(12)
Ag(2)-O(11)	2.547(16)		Ag(7)-O(2)	2.442(11)
Ag(2)-Ag(9)	2.9767(19)		Ag(7)-S(1)	2.584(3)
Ag(2)-Ag(8)	3.0748(17)		Ag(7)-S(3)	2.594(4)
Ag(2)-Ag(3)	3.3213(17)		Ag(7)-Ag(8)	3.0041(18)
Ag(3)-S(3)$^{\#1}$	2.437(4)		Ag(8)-O(4)	2.285(11)
Ag(3)-S(2)	2.439(4)		Ag(8)-S(1)	2.536(4)
Ag(3)-O(9)$^{\#1}$	2.526(19)		Ag(8)-O(12)	2.543(10)
Ag(3)-Ag(6)$^{\#1}$	3.1581(18)		Ag(8)-S(4)	2.613(3)
Ag(3)-Ag(4)$^{\#1}$	3.243(2)		Ag(8)-Ag(9)	3.2172(16)
Ag(4)-O(11)	2.26(2)		Ag(9)-O(5)	2.266(11)
Ag(4)-S(3)	2.423(4)		Ag(9)-S(2)	2.565(4)
Ag(4)-S(4)	2.434(4)		Ag(9)-S(4)	2.586(3)
Ag(4)-O(10)$^{\#1}$	2.54(2)		Ag(9)-Ag(10)	2.9251(14)
Ag(4)-Ag(8)	2.9782(19)		Ag(9)-Ag(5)$^{\#1}$	3.0100(18)
Ag(4)-Ag(3)$^{\#1}$	3.243(2)		Ag(10)-O(6)	2.297(9)
Ag(4)-Ag(7)	3.2675(18)		Ag(10)-O(6)$^{\#2}$	2.450(8)
Ag(5)-S(4)$^{\#1}$	2.447(3)		Ag(10)-S(5)$^{\#1}$	2.596(4)
Ag(5)-S(5)	2.464(3)		Ag(10)-S(2)	2.640(3)
Ag(5)-O(11)$^{\#1}$	2.476(17)		Ag(10)-Ag(5)$^{\#1}$	3.2776(19)
Ag(5)-O(9)	2.56(2)		O(6)-Ag(10)$^{\#2}$	2.450(8)
Ag(5)-Ag(9)$^{\#1}$	3.0100(17)		O(9)-Ag(3)$^{\#1}$	2.526(19)
Ag(5)-Ag(10)$^{\#1}$	3.2776(19)		O(10)-Ag(1)$^{\#1}$	2.38(2)
Ag(6)-O(1)	2.253(10)		O(10)-Ag(4)$^{\#1}$	2.54(2)
Ag(6)-S(5)	2.473(4)		O(11)-Ag(5)$^{\#1}$	2.476(17)
Ag(6)-S(3)	2.504(4)		S(3)-Ag(3)$^{\#1}$	2.437(4)
Ag(6)-Ag(7)	3.0108(19)		S(4)-Ag(5)$^{\#1}$	2.447(3)
Ag(6)-Ag(3)$^{\#1}$	3.1581(18)		S(5)-Ag(10)$^{\#1}$	2.596(4)

Symmetry transformations used to generate equivalent atoms: #1 -x,-y+1,-z+2; #2 -x+1,-y,-z+2.

4. Physical Measurements

Elemental analyses (C, H, N and S) were performed on an Elementar Vario EL III elemental analyzer. Ag was analyzed on a PLASMA-SPEC(I) ICP atomic emission spectrometer. The FT-IR spectrum was recorded from KBr pellets in the range of 4000–400 cm^{-1} on a Mattson Alpha-Centauri spectrometer. XPS analysis was performed on a thermo ECSALAB 250 spectrometer with an Al *Kα* (1486.6 eV) achromatic X-ray source running at 15 kV. The XPS binding energy (BE) was internally referenced to the aliphatic C(1s) peak (BE, 284.6 eV). PXRD patterns were recorded on a Siemens D 5005 diffractometer with Cu-Kα (λ= 1.5418 Å) radiation in the range of 3-50 ºC. TGA was performed on a Perkin-Elmer TGA analyzer heated from room temperature to 1000 ºC under nitrogen gas with a heating rate of 10 ºC/min. NMR data were recorded on a Bruker AV spectrometer (500 MHz). Mass spectra were carried out on a Bruker Daltonics flex Analysis instrument. TEM was performed on a JEOL-2100F transmission electron microscope under 200 kV accelerating voltage. Diffuse reflectivity was measured from 200 to 800 nm using barium sulfate ($BaSO_4$) as a standard with 100% reflectance on a Varian Cary 500 UV-Vis spectrophotometer. Luminescence was measured on an F-4500 FL Spectrophotometer. 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.

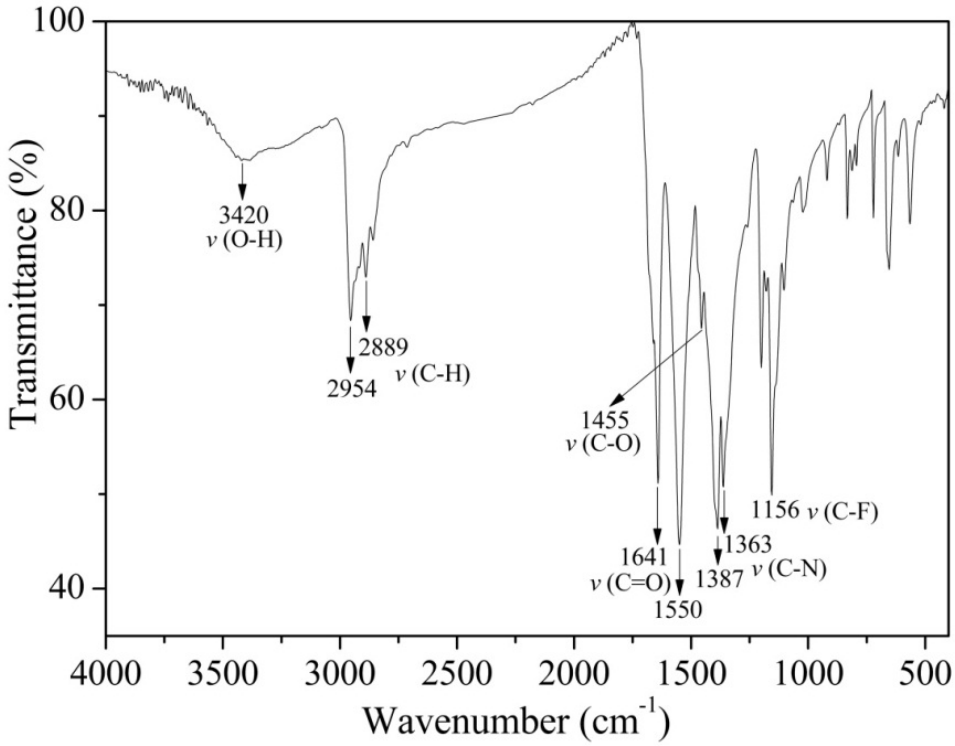

Fig. S1 IR spectrum of **1**.

5

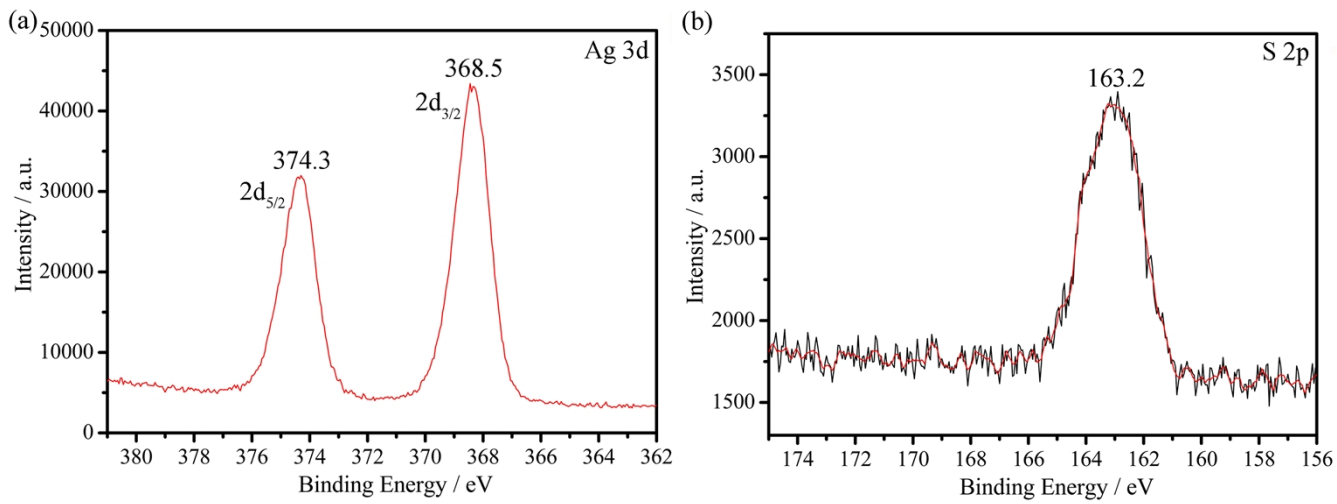

Fig. S2 XPS analysis of Ag (a) and S (b) for **1**.

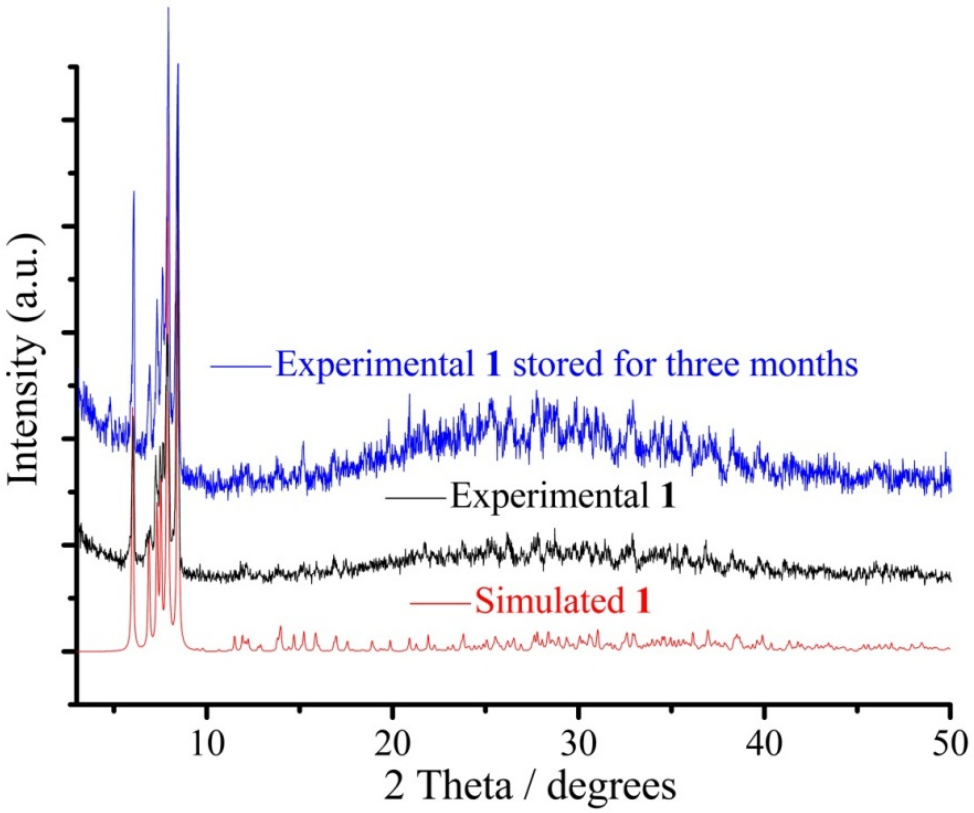

Fig. S3 Experimental and simulated X-ray powder diffraction patterns of **1**.

5

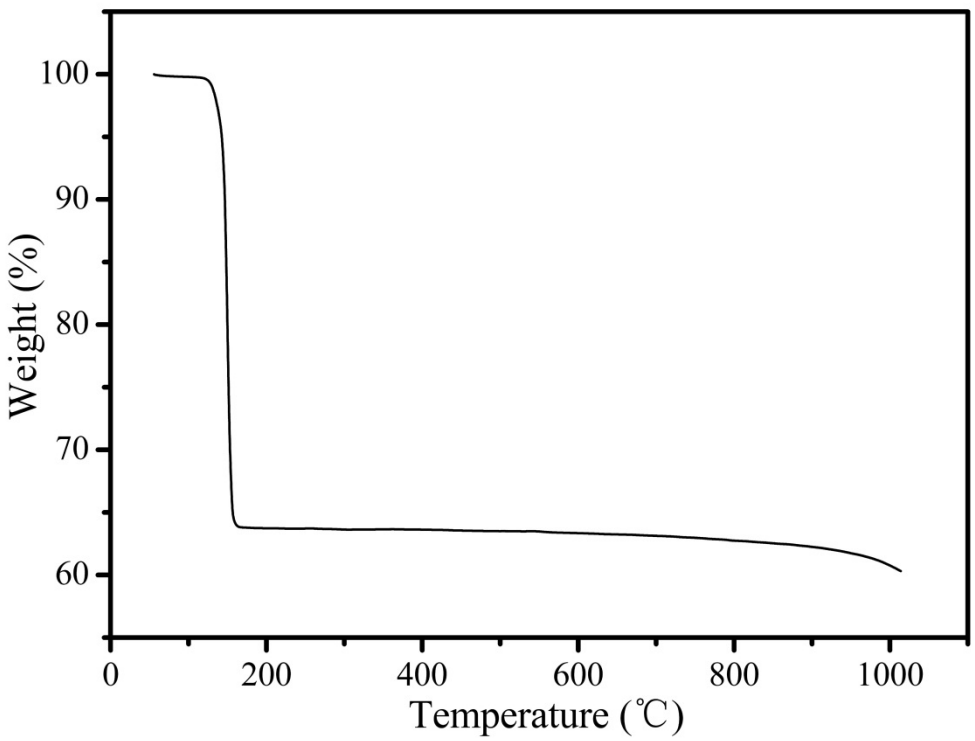

Fig. **S4** TG curve of **1**.

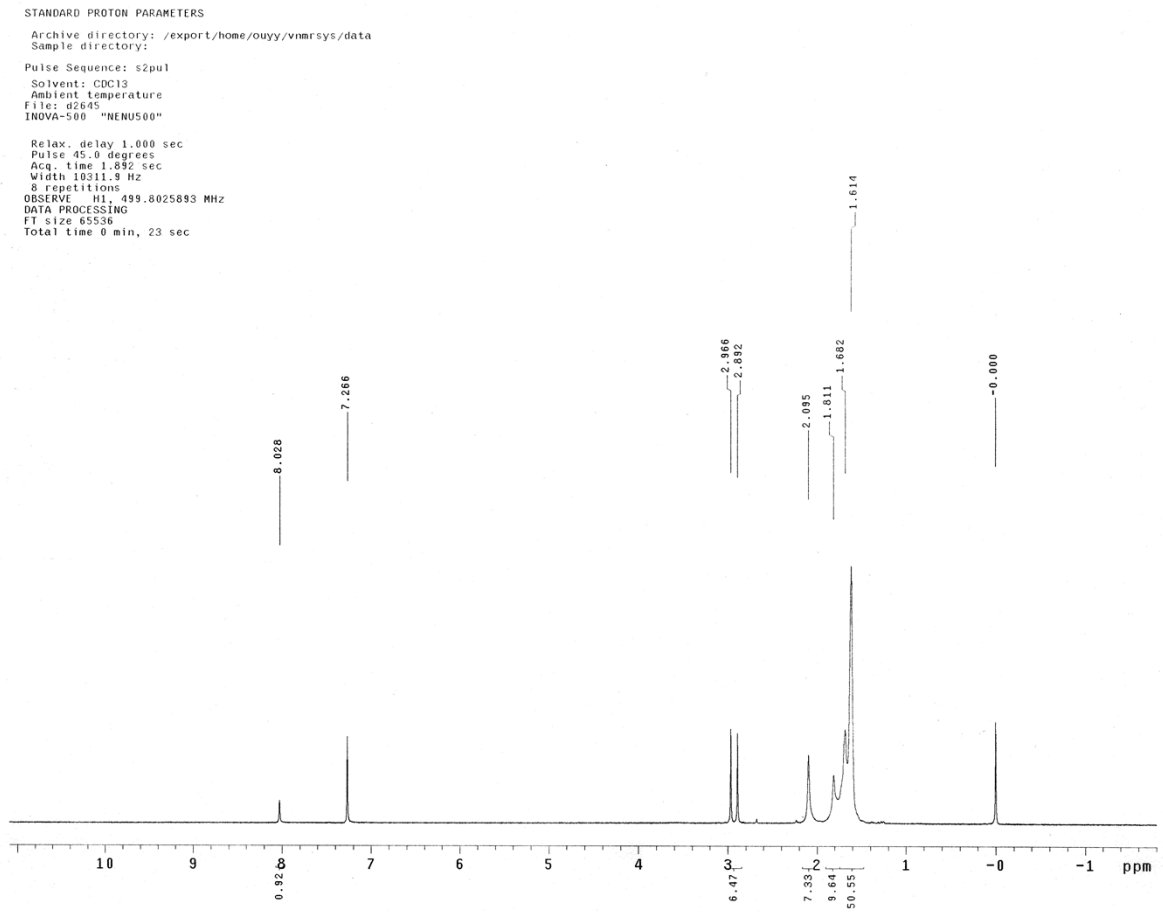

Fig. S5 ^{1}H NMR spectrum of **1** (500MHz, $CDCl_3$, RT).

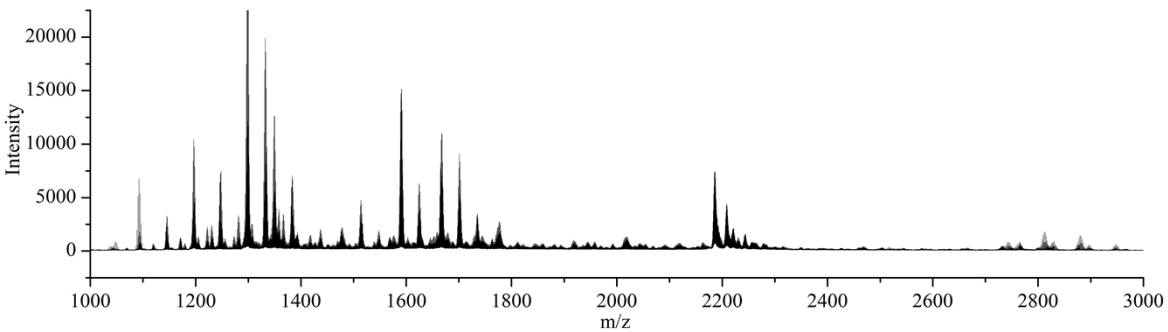

Fig. S6 (a) ESI mass spectrum of nanoparticles in **1**.

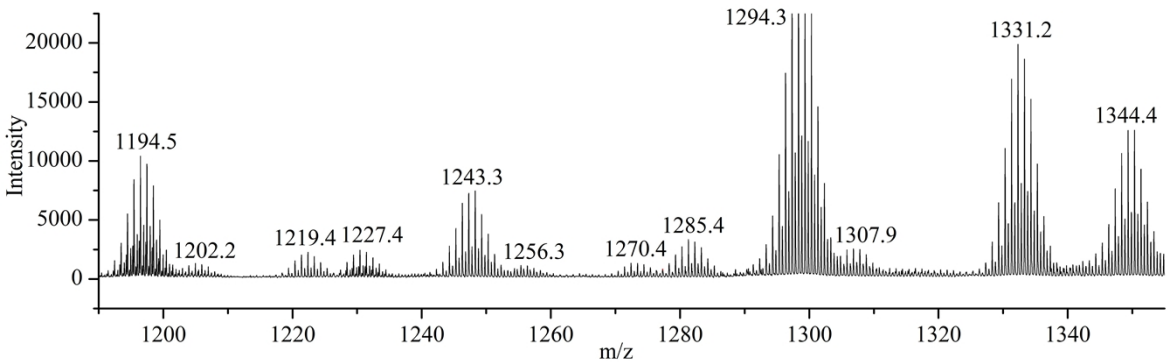

Fig. S6 (b) Zoomed-in spectrum of the 3+ ion sets.

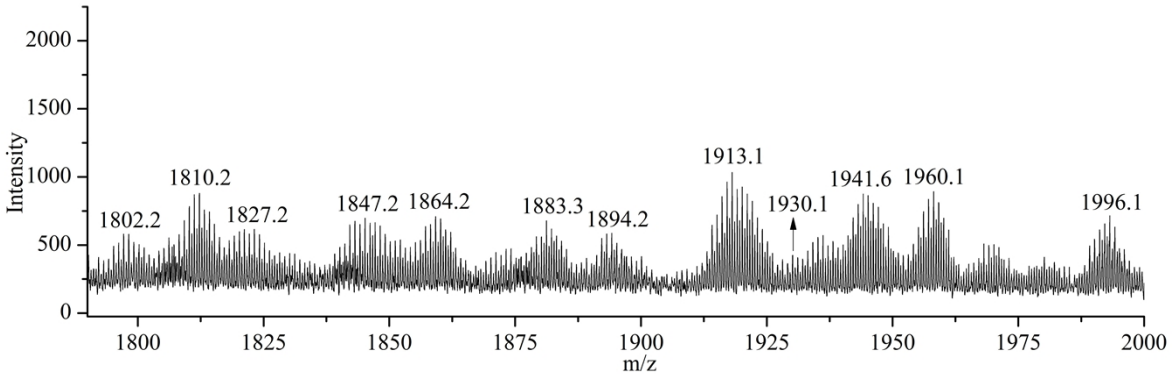

Fig. S6 (c) Zoomed-in spectrum of the 2+ ion sets.

Table S2. Detailed assignment of mass spectral data for nanoparticles in compound **1**

m/z observed	ion set	mass calculated	m/z calculated
1194.5	$[(CO_3^{2-})@Ag_{20}(S^tBu)_{10}(CH_3COO)_8H_3]^{3+}$	3584.5	1194.8
1202.4	$[(CO_3^{2-})@Ag_{20}(S^tBu)_{10}(CH_3COO)_8H_2Na_1]^{3+}$	3606.5	1202.2
1219.4	$[(CO_3^{2-})@Ag_{20}(S^tBu)_{10}(CH_3COO)_8(DMF)H_3]^{3+}$	3657.6	1219.2
1227.4	$[(CO_3^{2-})@Ag_{20}(S^tBu)_{10}(CH_3COO)_8(DMF)H_2Na_1]^{3+}$	3679.6	1226.5
1243.3	$[(CO_3^{2-})@Ag_{20}(S^tBu)_{10}(CH_3COO)_8(DMF)_2H_3]^{3+}$	3730.7	1243.6
1256.3	$[(CO_3^{2-})@Ag_{20}(S^tBu)_{10}(CH_3COO)_8(DMF)_2H_2K_1]^{3+}$	3768.8	1256.3
1270.4	$[(CO_3^{2-})@Ag_{20}(S^tBu)_{10}(CH_3COO)_8(DMF)_2Na_2K_1]^{3+}$	3812.8	1270.9
1285.4	$[(CO_3^{2-})@Ag_{20}(S^tBu)_{10}(CH_3COO)_8(DMF)_2H_2Cs_1]^{3+}$	3862.6	1287.5
1294.3	$[(CO_3^{2-})@Ag_{20}(S^tBu)_{10}(CH_3COO)_8(DMF)_2H_1Na_1Cs_1]^{3+}$	3884.6	1294.9
1307.9	$[(CO_3^{2-})@Ag_{20}(S^tBu)_{10}(CH_3COO)_8(DMF)_2Na_1K_1Cs_1]^{3+}$	3922.7	1307.6
1331.2	$[(CO_3^{2-})@Ag_{20}(S^tBu)_{10}(CH_3COO)_8(DMF)_2H_1Cs_2]^{3+}$	3994.5	1331.5
1344.4	$[(CO_3^{2-})@Ag_{20}(S^tBu)_{10}(CH_3COO)_8(DMF)_2K_1Cs_2]^{3+}$	4032.6	1344.2
1802.2	$[(CO_3^{2-})@Ag_{20}(S^tBu)_{10}(CH_3COO)_8H_1Na_1]^{2+}$	3605.5	1802.8
1810.2	$[(CO_3^{2-})@Ag_{20}(S^tBu)_{10}(CH_3COO)_8H_1K_1]^{2+}$	3621.6	1810.8
1827.2	$[(CO_3^{2-})@Ag_{20}(S^tBu)_{10}(CH_3COO)_8(DMF)H_2]^{2+}$	3656.6	1828.3
1847.2	$[(CO_3^{2-})@Ag_{20}(S^tBu)_{10}(CH_3COO)_8(DMF)H_1K_1]^{2+}$	3694.7	1847.4
1864.2	$[(CO_3^{2-})@Ag_{20}(S^tBu)_{10}(CH_3COO)_8(DMF)_2H_2]^{2+}$	3729.7	1864.9
1883.3	$[(CO_3^{2-})@Ag_{20}(S^tBu)_{10}(CH_3COO)_8(DMF)_2H_1K_1]^{2+}$	3767.8	1883.9
1894.2	$[(CO_3^{2-})@Ag_{20}(S^tBu)_{10}(CH_3COO)_8(DMF)_2Na_1K_1]^{2+}$	3789.8	1894.9
1913.1	$[(CO_3^{2-})@Ag_{20}(S^tBu)_{10}(CH_3COO)_8(DMF)K_1Cs_1]^{2+}$	3826.6	1913.3
1930.1	$[(CO_3^{2-})@Ag_{20}(S^tBu)_{10}(CH_3COO)_8(DMF)_2H_1Cs_1]^{2+}$	3861.6	1930.8
1941.6	$[(CO_3^{2-})@Ag_{20}(S^tBu)_{10}(CH_3COO)_8(DMF)_2Na_1Cs_1]^{2+}$	3883.6	1941.8
1960.1	$[(CO_3^{2-})@Ag_{20}(S^tBu)_{10}(CH_3COO)_8(DMF)Cs_2]^{2+}$	3920.4	1960.2
1996.1	$[(CO_3^{2-})@Ag_{20}(S^tBu)_{10}(CH_3COO)_8(DMF)_2Cs_2]^{2+}$	3993.5	1996.8

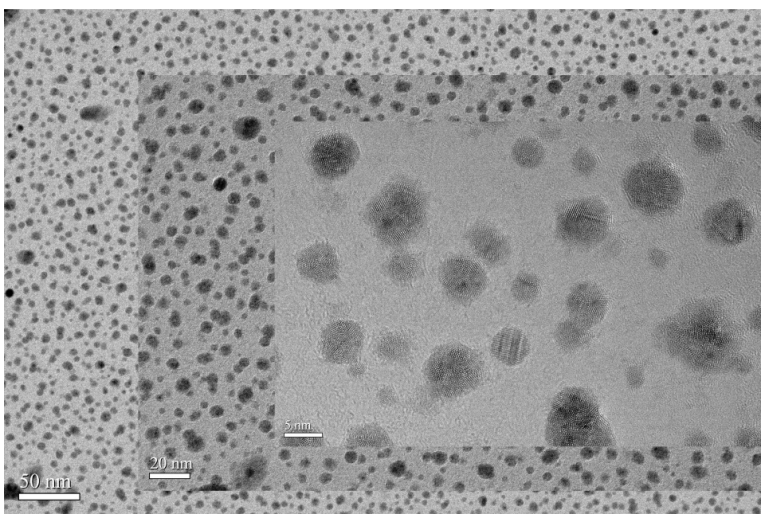

Fig. **S7** TEM images of **1**.

Preparation of compound 1 and AgS^{t}Bu 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.[4] 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 bulk-modified CPE was prepared by similar process without compound **1**.

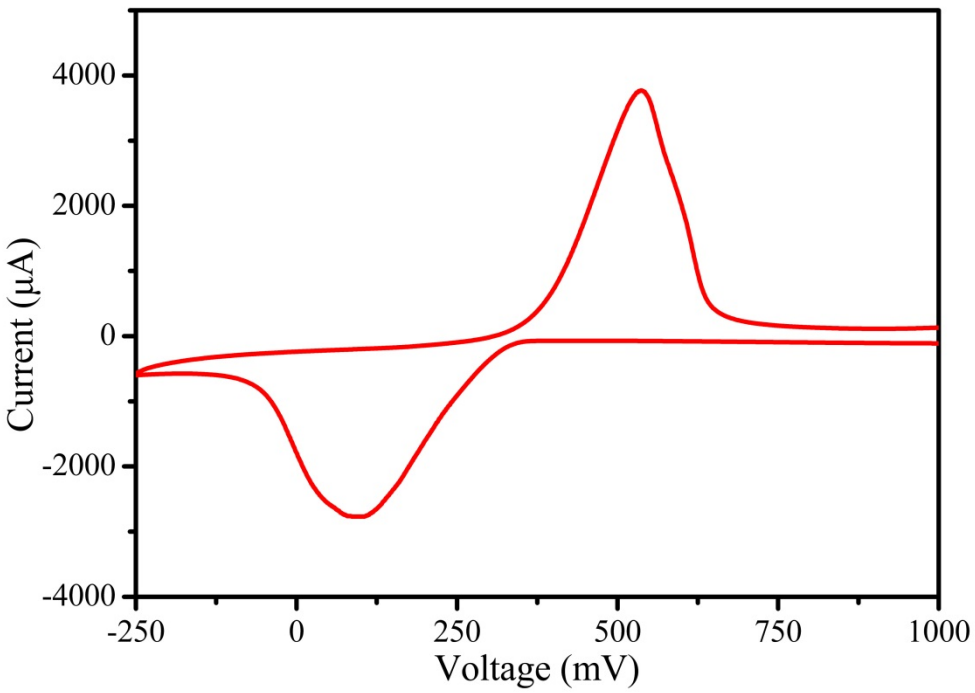

Fig. S8 Cyclic voltammogram of AgS^{t}Bu ligand.

Reference:

1 G. Li, Z. Lei and Q.-M. Wang, *J. Am. Chem. Soc.*, 2010, **132**, 17678.
2 K. Nomiya, T. Takahashi, T. Shirai and M. Miwa, *Polyhedron*, 1987, **6**, 213.
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.