Supporting information for

Crystal structure of a luminescent thiolated Ag nanocluster with an octahedral Ag$_6^{4+}$ core

Huayan Yang, Jing Lei, Binghui Wu, Yu Wang, Meng Zhou, Andong Xia, Lansun Zheng, and Nanfeng Zheng

1 State Key Laboratory for Physical Chemistry of Solid Surfaces and Department of Chemistry, College of Chemistry and Chemical Engineering, Xiamen University, Xiamen 361005, China
Email: nfzheng@xmu.edu.cn
2 The State Key Laboratory of Molecular Reaction Dynamics, and Beijing National Laboratory for Molecular Sciences (BNLMS), Institute of Chemistry, Chinese Academy of Sciences, Beijing 100080, China

Experimental Details

Reagents: Silver tetrafluoroborate (AgBF$_4$, A.R.), 3,4-difluoro-benzenethiol (C$_6$H$_4$F$_2$S, AR) were purchased from Alfa Aesar Chemical Reagent Co. Ltd. (Tianjin, China), Sodium borohydride (NaBH$_4$, A.R.), triphenylphosphine (PPh$_3$, A.R.), dichloromethane (CH$_2$Cl$_2$, A.R.), triethylamine (C$_2$H$_5$N, A.R.), and methanol (CH$_3$OH, A.R.) were purchased from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China). The water used in all experiments was ultrapure. All reagents were used as received without further purification.

Synthesis of Ag$_{14}$(C$_6$H$_3$F$_2$)$_{12}$(PPh$_3$)$_8$ clusters: For a typical synthesis of XMC-1, AgBF$_4$ was dissolved in the mixture solution of dichloromethane and methanol. The solution was cooled to 0°C in an ice bath, triphenylphosphine and 3,4-difluoro-benzenethiol were then added. After 20 minutes, triethylamine and NaBH$_4$ aqueous solution was added quickly to above mixture under vigorous stirring. The reaction was aging for 12 hours at 0 °C. The aqueous phase was then removed. The mixture in organic phase was then washed several times with water. Yellow block crystals were crystallized from CH$_2$Cl$_2$/hexane at 4 °C after 10 days in a yield of ~35%. 
**Single Crystal Analysis of Ag_{14}(SC_6H_3F_2)_{12}(PPh_3)_8(CH_2Cl_2)_6(H_2O)_3:** The diffraction data of Ag_{6}@Ag_{8}(SC_6H_3F_2)_{12}(PPh_3)_8(CH_2Cl_2)_6(H_2O)_3 (XMC-1) were collected on a Rigaku RAXIS-RAPID (Mo Kα). Absorption corrections were applied by using the program ABSCOR (Higashi, 1995). The structure was solved by direct methods and refined by the least-squares method using the program SHELXS. Several F atoms at the 3-position of benzene rings of the ligand of 3,4-difluoro-benzenethiol were found to be disordered and modeled over both in 3- and 5- positions of benzene ring. All non-hydrogen atoms in the cluster were anisotropically refined to obtain the final R factor.

**Measurements of Optical Properties:**
Pure crystals of XMC-1 were dissolved in dichloromethane (CH_2Cl_2) for spectra measurements. UV/Vis absorption spectrum was recorded on a Varian Carry 5000 spectrophotometer. Fluorescence spectra were measured on a Hitachi F-7000 spectrometer.

**Fluorescence lifetime measurements:**
Fluorescence lifetimes were measured by a standard time-correlated single-photon counting (TCSPC) from Ortac at room temperature. The excitation source was a Titanium sapphire laser (Coherent Mira 900) with 150 fs pulse duration operated at 76MHz. The fundamental beam was sent through a pulse picker (coherent 9200) and a second harmonic generation (SHG) crystal to obtain the 365nm laser pulse at 4.7MHz for excitations of XMC-1. Fluorescence was detected by using a monochromator (EI-121, Edinburgh Instruments) and fast photomultiplier tube (XP2020). The instrument response function (IRF) measured by scattering the excitation light from a dilute suspension of colloidal silica was about 220 ps to provide ~50 ps time resolution with deconvolution. All the temporal evolution profiles are fitted by the convolution between the IRF with a mono-exponential function according to iterative deconvolution by FluoFit software based on the Levenberg-Marquardt and Simplex algorithms (Version 3.3, PicoQuant, Germany).
**Figure S1** The structure of Ag$_{14}$(SC$_6$H$_3$F$_2$)$_{12}$(PPh$_3$)$_8$. Some 3-F atoms were disordered over both in 3- and 5- position of benzene ring (CH$_2$Cl$_2$ missing). Color legend: green, Ag; yellow, S; pink, P; gray, C; blue, F.
Figure S2. Local coordination structures of (a) the Ag atom at the octahedral Ag6 core, (b) the thiolate ligand, and (c) Ag atom in the third shell of the XMC-1 cluster. Color legend: green, Ag; yellow, S; pink, P; gray, C; blue, F.

Figure S3. $^{31}$P NMR spectrum of XMC-1 in CD$_2$Cl$_2$. 
**Figure S4.** ESI-mass spectrum of XMC-1.

**Figure S5.** Emission spectrum with excitation at 420 nm
**Figure S6.** The emission decay curves for the emissions at 420 nm and 536 nm. Both curves follow single exponential decay.

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<th>420nm</th>
<th>536nm</th>
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<tr>
<td>A1</td>
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<td>208</td>
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<tr>
<td>$\tau$ I</td>
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**Figure S7.** Temperature-dependent magnetic susceptibility of XMC-1 in an applied field of 200Oe.