Supporting information for

Crystal structure of a luminescent thiolated Ag nanocluster with an octahedral Ag_6^{4+} core

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Experimental Details

Reagents: Silver tetrafluoroborate ($AgBF_4$, A.R.), 3,4-difluoro-benzenethiol ($C_6H_4F_2S$, 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_2Cl_2, A.R.), triethylamine ($(C_2H_5)_3N$, A.R.), and methanol (CH_3OH, 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 $Ag_{14}(SC_6H_3F_2)_{12}(PPh_3)_8$ 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_2Cl_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 $Ag6@Ag8(SC_6H_3F_2)_{12}(PPh_3)_8(CH_2Cl_2)_6(H_2O)_3$ (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).

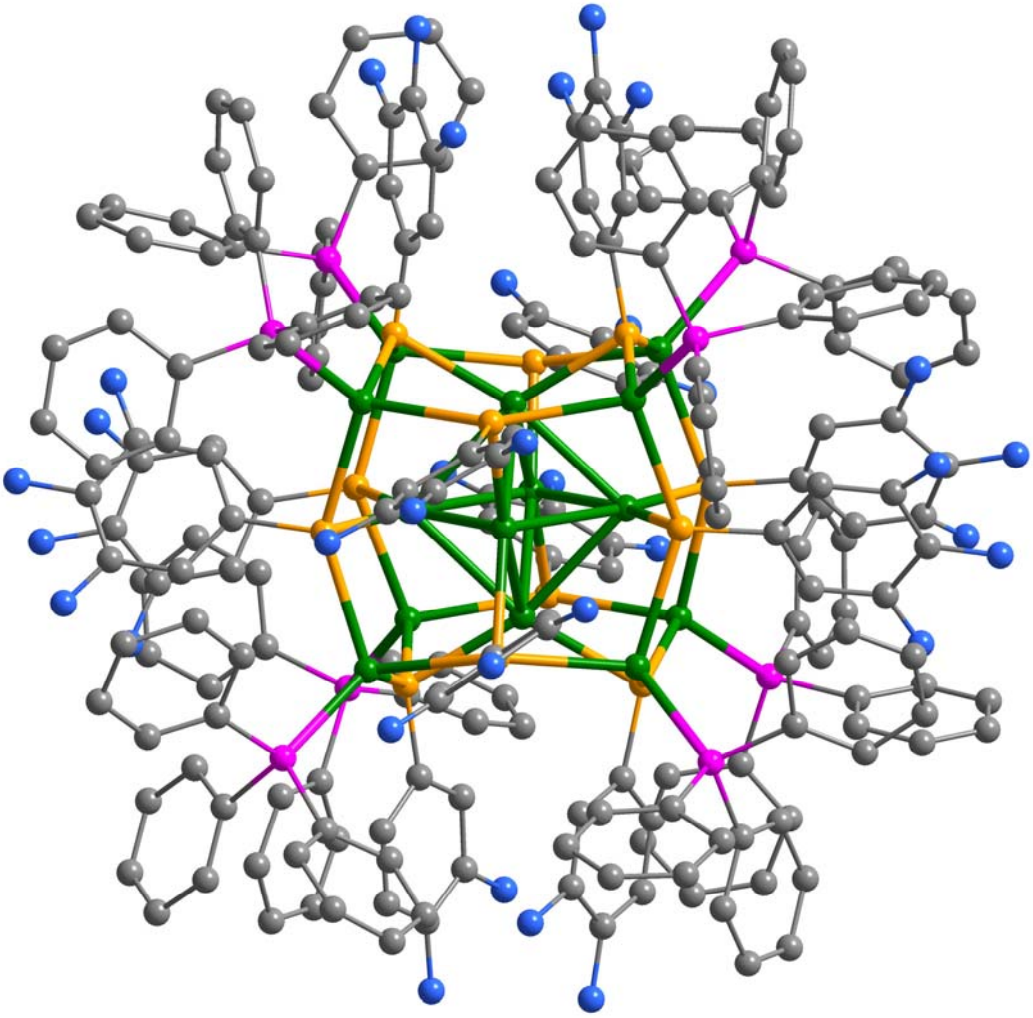


Figure S1 The structure of $Ag_{14}(SC_6H_3F_2)_{12}(PPh_3)_8$. Some 3-F atoms were disordered over both in 3- and 5- position of benzene ring **(**CH_2Cl_2 missing**),**Color legend: green, Ag; yellow, S; pink, P; gray, C; blue, F.

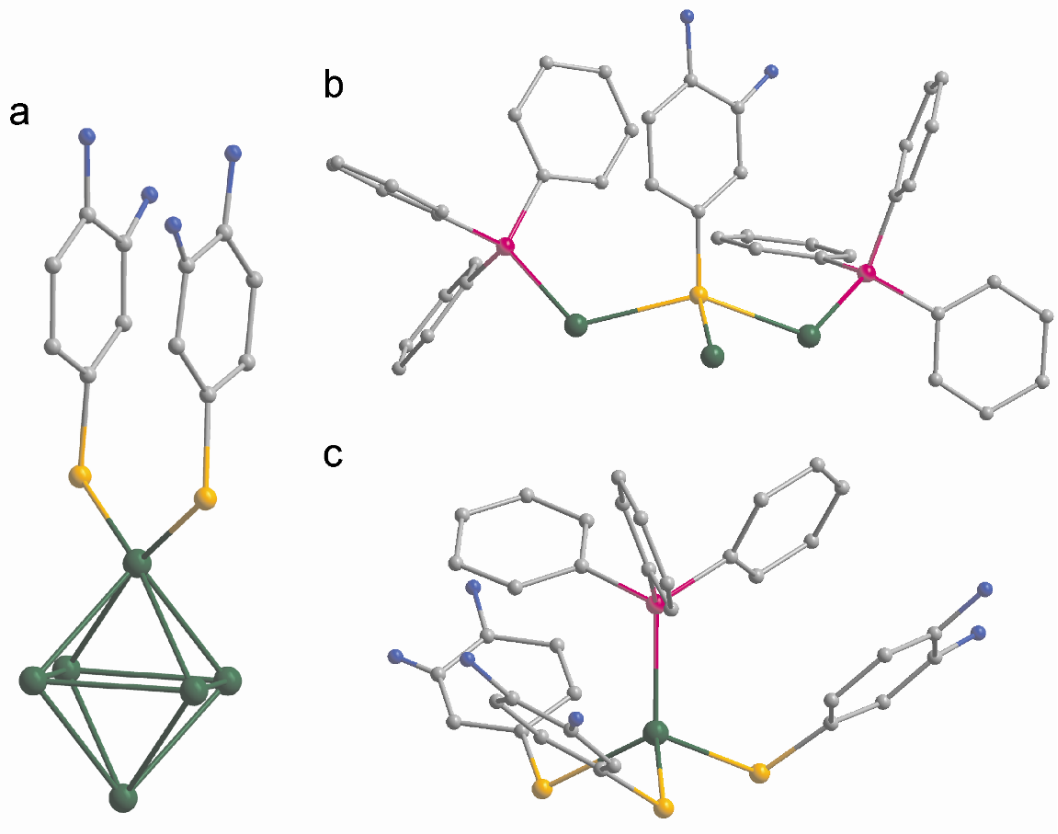


Figure S2. Local coordination structures of (a) the Ag atom at the octahedral Ag6 core, (b) the thiolate ligand, and (c) Ag atom in the third shell of the XMC-1 cluster. Color legend: green, Ag; yellow, S; pink, P; gray, C; blue, F.

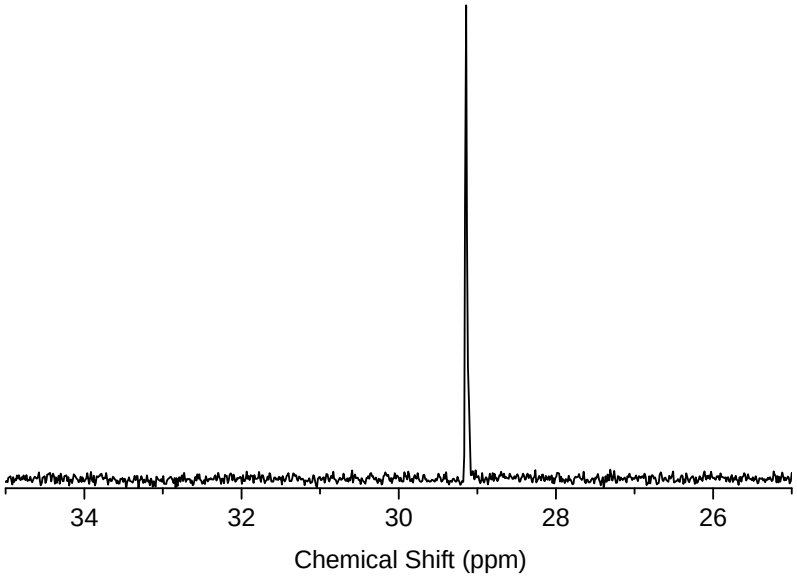


Figure S3. ^{31}P NMR spectrum of XMC-1 in CD_2Cl_2.

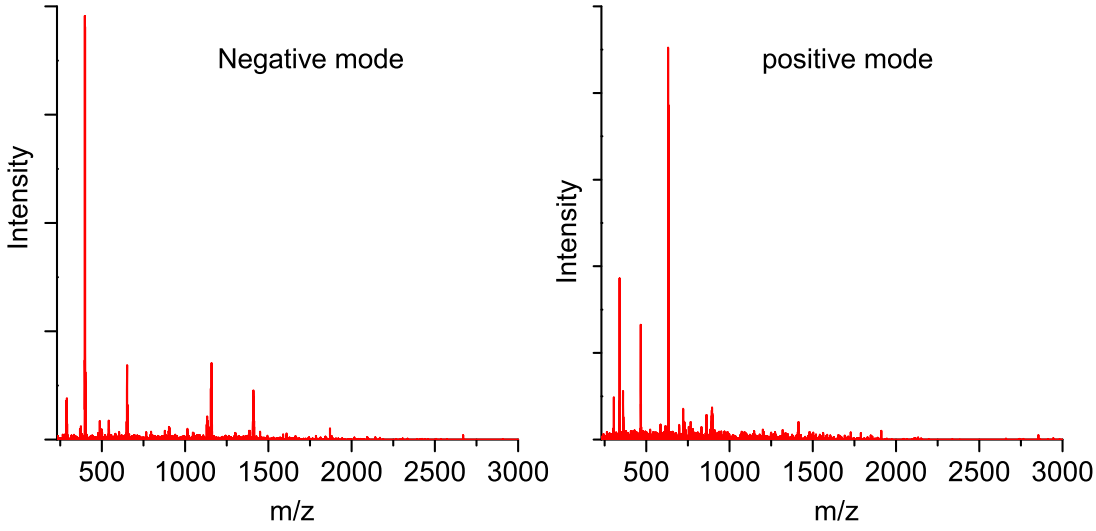


Figure S4. ESI-mass spectrum of XMC-1.

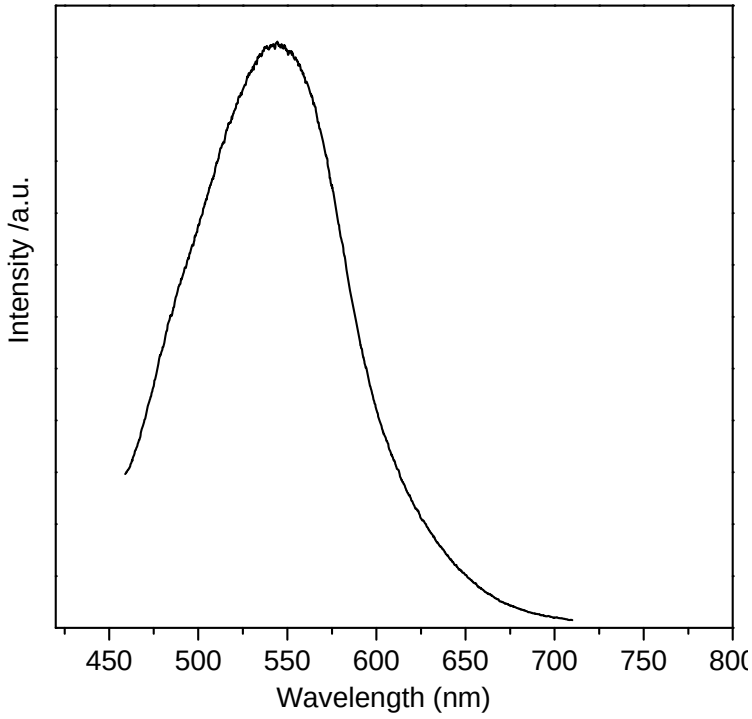
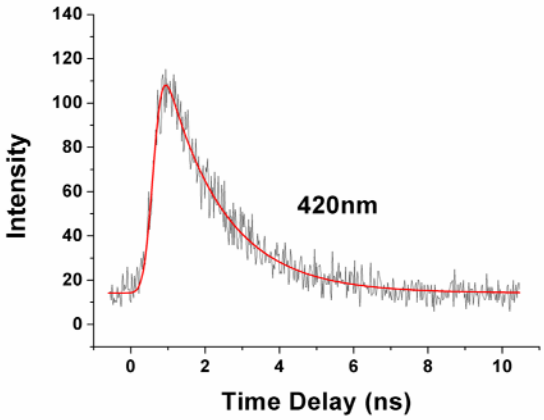
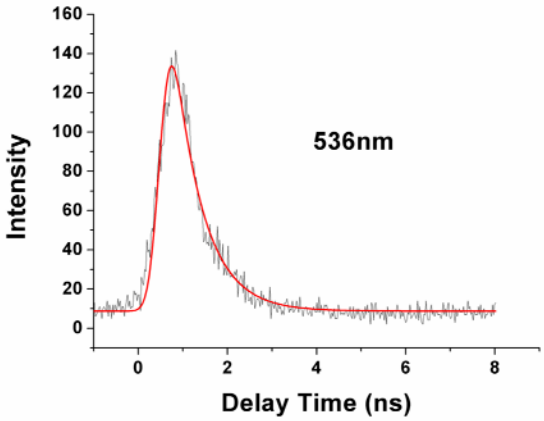


Figure S5. Emission spectrum with excitation at 420 nm





Fitting Parameters

emission	420nm	536nm
A1	112	208
τ 1	1.6ns	643ps

Figure S6. The emission decay curves for the emissions at 420 nm and 536 nm. Both curves follow single exponential decay.

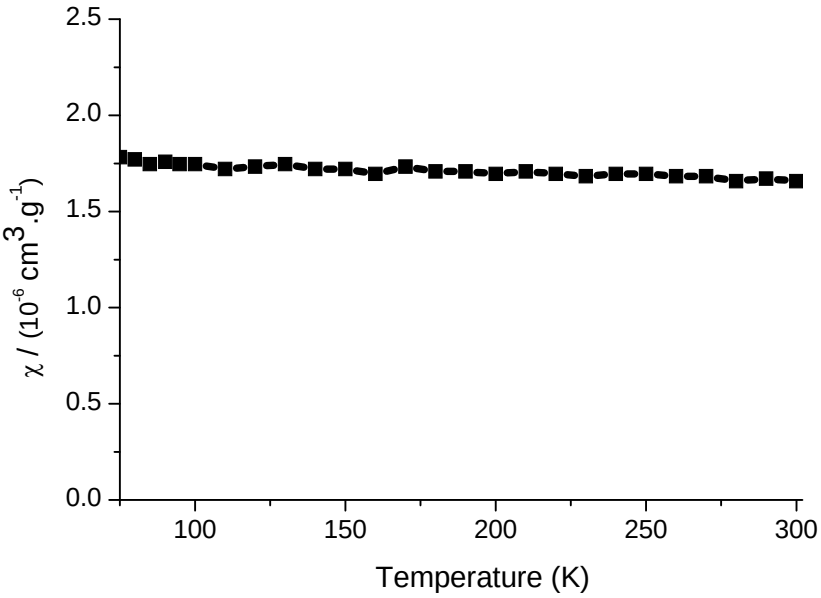


Figure S7. Temperature-dependent magnetic susceptibility of XMC-1 in an applied field of 200Oe