Supporting information for

Crystal Structures of Two Ag(0)-Containing Nanoclusters Co-Capped by Thiolate and Diphosphine Ligands

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Experimental Details

Reagents: Silver tetrafluoroborate ($AgBF_4$, A.R.), 3,4-difluorothiophenol ($C_6H_4F_2S$, A.R.), 4-(trifluoromethyl)thiophenol ($C_7H_5F_3$, A.R.) 1,2-bis(diphenylphosphino)ethane (DPPE, A.R.), tetraphenylphosphonium bromide (PPh_4Br, A.R.) were purchased from Alfa Aesar Chemical Reagent Co. Ltd. (Tianjin, China), Sodium borohydride ($NaBH_4$, A.R.), dichloromethane (CH_2Cl_2, 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 $Ag_{16}(SC_6H_3F_2)_{14}(DPPE)_4$ clusters: 19.6 mg $AgBF_4$ was dissolved in the mixture solution of dichloromethane and methanol. After the solution was cooled to 0 °C in an ice bath, 10.3 mg 1,2-bis(diphenylphosphino)ethane and 9.7 μL 3,4-difluorothiophenol were added. About 60 minutes later, 1.0 mL aqueous solution containing 30.0 μL triethylamine and 20.0 mg $NaBH_4$ was added quickly to the 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. Then 5.0 mg PPh_4Br were added to the solution. Red sheet

crystals were crystallized from CH_2Cl_2/hexane at 4 °C after 10 days. The yield of XMC-2 was ~ 20%.

Synthesis of $\{Ag_{32}(SC_6H_4CF_3)_{24}(DPPE)_5\}^{2-}$ clusters: 20.0 mg $AgBF_4$ was dissolved in the mixture solution of dichloromethane and methanol. After the solution was cooled to 0 °C, 6.0 mg 1,2-bis(diphenylphosphino)ethane and 20.0 μL 4-(trifluoromethyl)thiophenol were added. About 60 minutes later, 1.0 mL aqueous solution containing 30.0 μL triethylamine and 20.0 mg $NaBH_4$ was added quickly to the above mixture under vigorous stirring. The reaction was aging for 24 hours at 0 °C. The aqueous phase was then removed. The mixture in organic phase was washed several times with water. 5.0 mg PPh_4Br were added to the solution. Black block crystals were crystallized from CH_2Cl_2/hexane at 4 °C after 10 days. The yield of XMC-2 was ~ 25%.

Single Crystal Analysis of XMC-2 and XMC-3:

The diffraction data of XMC-2 were collected on an Agilent Technologies SuperNova system. X-ray single crystal diffractometer with Cu Kα radiation (λ = 1.54184 Å) at 100 K. The data were processed using CrysAlis^{Pro}.[1] The structure was solved and refined using Full-matrix least-squares based on F^2 with program SHELXS-97 and SHELXL-97 [2] within Olex2.[3] In the structure of XMC-2, several F atoms at the 3-position of benzene rings of the ligand of 3,4-difluorothiophenol 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.

Crystallographic data for XMC-2: $I4_1/a$, a = 25.3878(3) Å, b= 25.3878(3) Å, c= 72.3758(11) Å, $\alpha=\beta=\gamma=90°$, V= 46649.2(10) Å^3, Z=8, Cu Kα, T=100 K, 2θ=127.38°. 48569 reflections were measured, of which 19090 were unique with R_{int} = 0.0438. Final R_1=6.94%, wR_2=0.1999 for 1112 parameters and 13710 reflections with $I > 2\sigma(I)$.

The diffraction data of XMC-3 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.

Crystallographic data for XMC-3: *C*2/c, a = 49.221(10) Å, b= 22.630(5) Å, c= 40.889(8) Å, α=90°, β=120.01(3)°, γ=90°, V= 39437(14) Å^3, Z=4, Mo Kα, T=173 K, 2θ=49.42°. 163584 reflections were measured, of which 40266 were unique with R_{int} = 0.1177. Final R_1=6.59%, wR_2=0.1817 for 1973 parameters and 26942 reflections with $I > 2\sigma(I)$.

1. CrysAlis^{Pro} 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.

Measurements of Optical Properties:

Pure crystals of XMC-2 and XMC-3 were dissolved in dichloromethane (CH_2Cl_2) for spectrum measurements. UV/Vis absorption spectra ware recorded on a Varian Carry 5000 spectrophotometer. Fluorescence spectra were measured on a Hitachi F-7000 spectrometer.

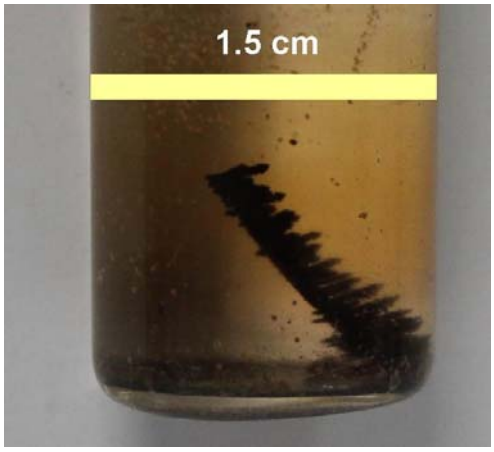

Figure S1 Photograph of XMC-2 crystallized into a single big piece of red crystal.

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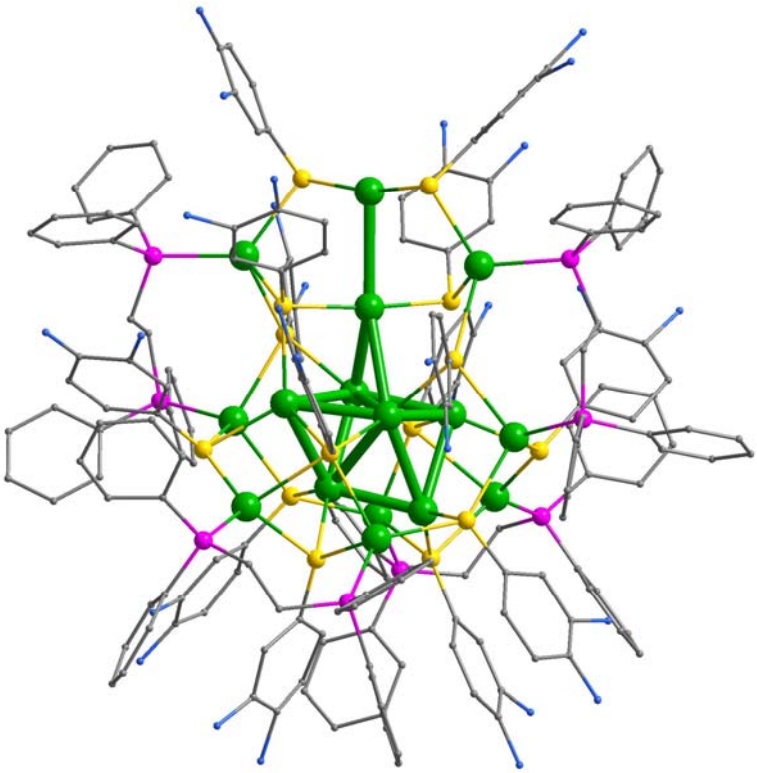

Figure S2 Crystal structure of $Ag_{16}(SC_6H_3F_2)_{14}(DPPE)_4$ (XMC-2) with only hydrogen atoms omitted. Color legend: green, Ag; yellow, S; pink, P; gray, C; blue, F.

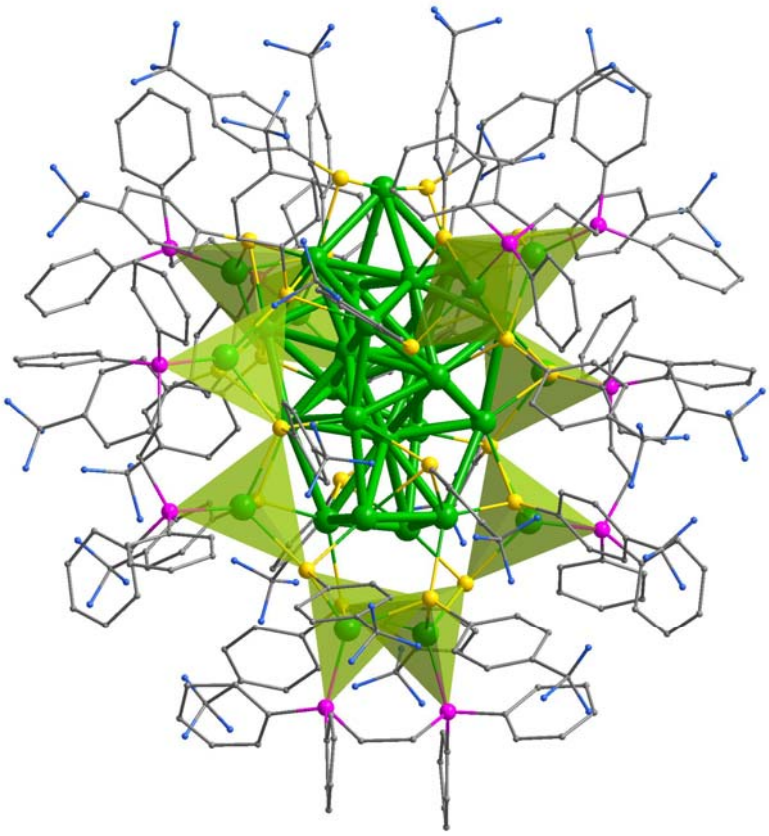

Figure S3 Crystal structure of $\{Ag_{32}(DPPE)_5(SC_6H_4CF_3)_{24}\}^{2-}$ (XMC-3) with only hydrogen atoms omitted. Color legend: green, Ag; yellow, S; pink, P; gray, C; blue, F.

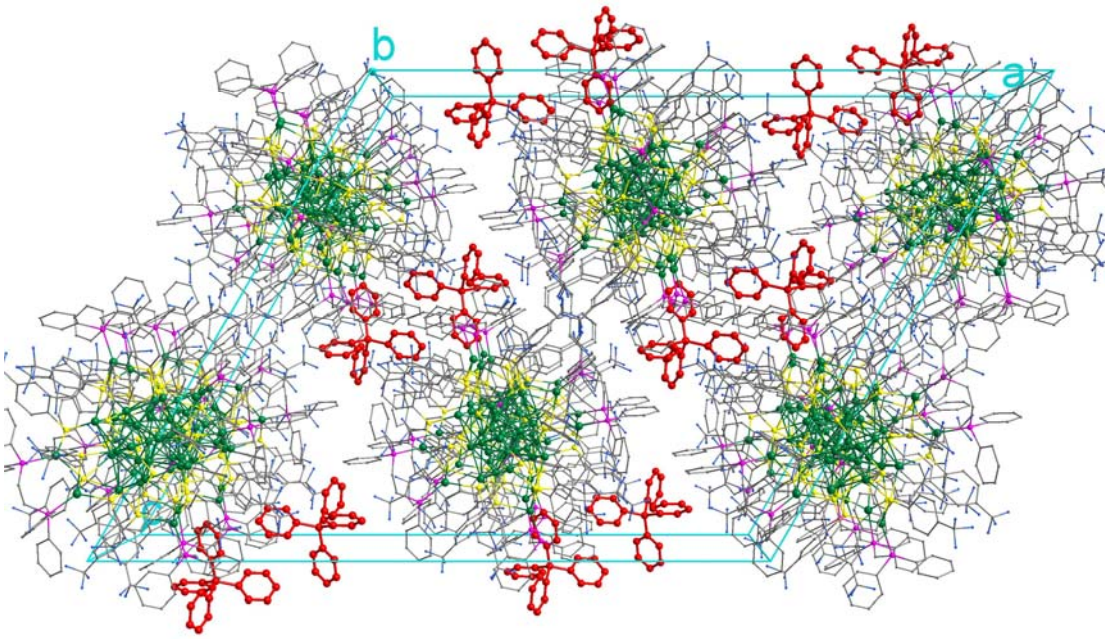

Figure S4 The packing structure of XMC-3 with PPh_4^+. The PPh_4^+ cations are highlighted in red for better visualization. Color legend for the cluster parts: green, Ag; yellow, S; pink, P; gray, C; blue, F.

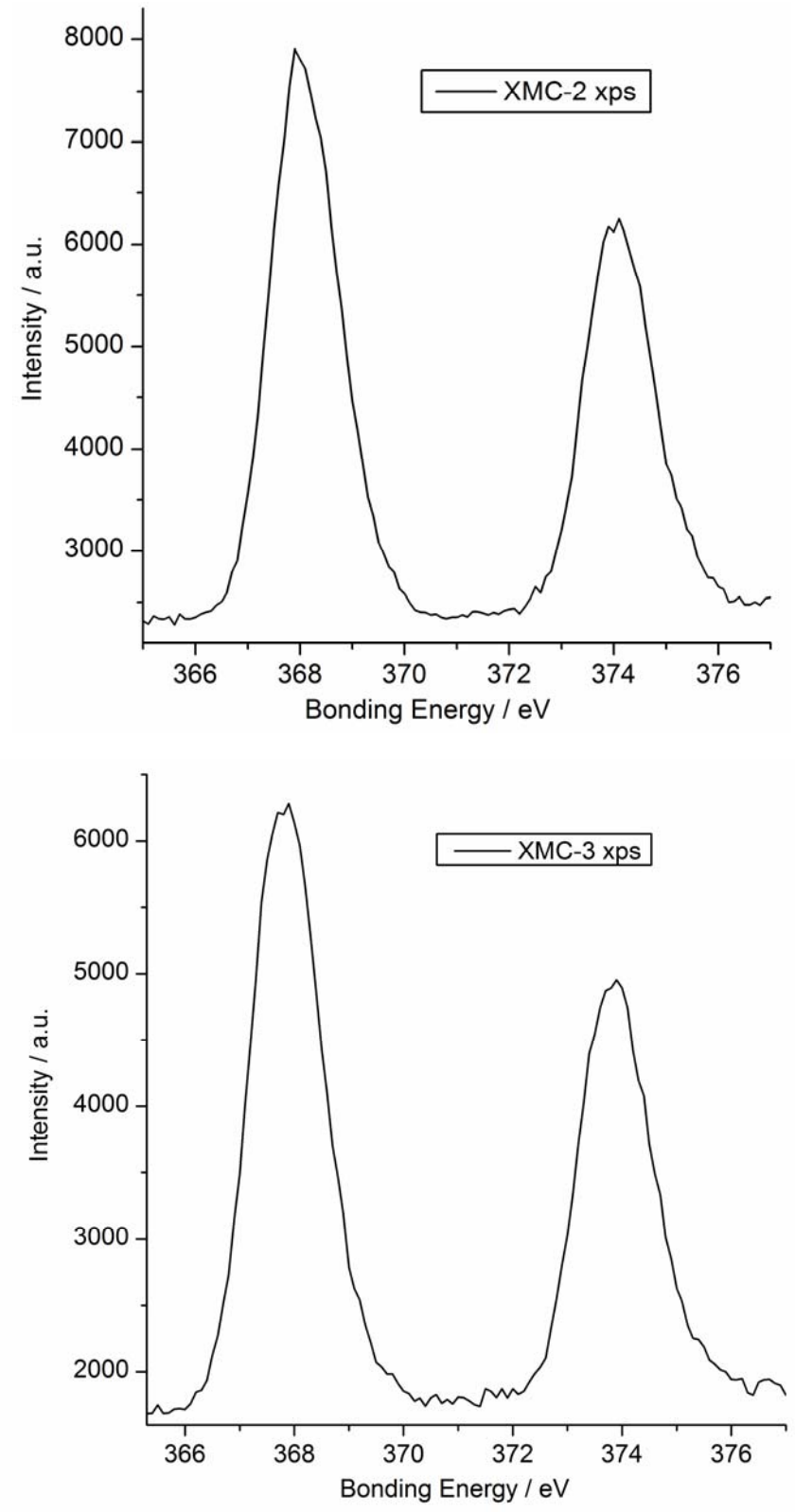

Figure S5 Ag-3d XPS spectra of XMC-2 and XMC-3.