Contents

Ⅰ. Physical measurements

Shimadzu UV-2550 Spectrophotometer was used for the measurements. Spectra were typically measured in the range of 250-900 nm. NMR spectra were recorded on a Bruker Advance II spectrometer that operates at 500 MHz while recording ^{1}H, 76.8 MHz for ^{2}H, and 202 MHz for ^{31}P NMR. ^{1}H NMR spectra was referenced to TMS as an external standard, and ^{31}P chemical shifts were referenced to external 85% H_3PO_4. Mass spectra were recorded on an Agilent Technologies ESI- TOF- MS. X-ray photoelectron spectroscopy (XPS) was recorded on PHI Quantum-2000. The sample was put under UHV to reach the 10^{-8} Pa range. The nonmonochromatized Al Kα source was used at 10 kV and 10 mA. All binding energies were calibrated using the C (1s) carbon peak (284.6 eV), which was applied as an internal standard. High resolution narrow-scan spectra were recorded with the electron pass energy of 50 eV and takeoff angle of 55 ° to achieve the maximum spectral resolution.

X-ray Crystallography. Intensity data of **1** and **2** were collected on an Agilent SuperNova Dual system (Cu Kα) at 100K. Absorption corrections were applied by using the program CrysAlis (multi-scan). The structure of **1** was solved by direct methods, and non-hydrogen atoms except CH_2Cl_2 and toluene solvent molecules were refined anisotropically by least-squares on F^2 using the SHELXTL program. Three phenyl groups (C13—C18; C143—C148; C221—C226) and the toluene solvent (C2S—C7S) were refined using a rigid model (AFIX 66). The largest residual density is near the position of Sb2 (0.92Å). The structure of **2** was solved by direct methods, only all of Ag, P and Sb atoms were refined anisotropically by least-squares on F^2 using the SHELXTL program. All initial refinements were severely restrained and constrained to idealized values (DFIX, AFIX and SADI). There is a level A alert “Large Reported Min. (Negative) Residual Density -14.77” in the crystal structure of **2**. The density minimum is near to atom Sb3 with a distance of 0.86 Å.

II. Synthesis

Materials and reagents.

Ethynylbenzene (PhC≡CH, 98%) bis(diphenylphosphino)methane (dppm, 98%), 1,5-bis(diphenylphosphino) pentane (dpppe, 98%) and Silver hexafluoroantimonate ($AgSbF_6$, 98.0%) were purchased from J&K; sodium borohydride ($NaBH_4$, 98%) and other reagents employed were purchased from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China). PhC≡CAg was prepared by reacting of Ag_2O and PhC≡CH in the presence of ammonium hydroxide. All reagents were used as received.

$[Ag_{19}(PhC\equiv C)_{14}(dppm)_3](SbF_6)_3$

1 mL 0.1 M $AgSbF_6$ (0.1 mmol) in ethanol was added to the mixture of PhC≡CAg (42 mg, 0.2 mmol) and Bis(diphenylphosphino)methane (38.4 mg, 0.1 mmol) in 3 mL ethanol. After ultrasonication, the pale yellow suspension was stirred for 30 min. 1 ml 0.040 M freshly prepared ethanol solution of $NaBH_4$ (0.04 mmol) was added dropwise under vigorous stirring, the color changed to brown in 5 min. The reaction mixture was stirred at room temperature in the absence of light for 9 h in air. The resulted mixture was centrifuged for 3 min at 10000 r/min and washed twice with ethanol. This crude brown solid was dissolved in a mixture of 3 mL CH_2Cl_2 and 0.2 mL toluene. After filtration, the filtrate was subject to the diffusion of a mixture of ether and n-hexane (v : v = 1 : 1) at 4℃ to afford purple blue crystals after 5 days (37.5 mg, yield 46% based on Ag).

Anal. UV-Vis (λ, nm): 441; 590; *E*g = 1.97 eV. ESI-TOF-MS (CH_2Cl_2): 1539.38 ($[Ag_{19}(dppm)_3(PhC\equiv C)_{14}]^{3+}$) and 2427.50 ($[Ag_{19}(dppm)_3(PhC\equiv C)_{14}(SbF_6)]^{2+}$). ^{1}H NMR (500MHz, CD_2Cl_2, δ, ppm): 3.49 (t, $^2J_{PH}$= 10.0 Hz, 6H, CH_2), 6.22-7.65 (m, 130H, Ph). ^{31}P NMR (202 MHz, CD_2Cl_2, δ, ppm): 5.41 [J(^{109}Ag-P) = 760, J(^{107}Ag-P) = 657, ^{3}J(^{109}Ag-P) = -3.6, ^{3}J(^{107}Ag-P) = -1.2, ^{2}J(P-P) = 178 Hz]. XPS (binding energy, eV): Ag $3d_{5/2}$, 368.0; Ag $3d_{3/2}$, 374.0 eV.

$Ag_{25}(MeO\text{-}PhC\equiv C)_{20}(dpppe)_3(SbF_6)_3$

1 mL 0.1 M $AgSbF_6$ (0.1 mmol) in ethanol was added to the mixture of MeO-PhC≡CAg (44 mg, 0.2 mmol) and 1,5-bis(diphenylphosphino) pentane (44 mg, 0.1 mmol) in 3 mL ethanol. After ultrasonication, the pale yellow suspension was stirred for 30 min. 1 ml 0.040 M freshly prepared ethanol solution of $NaBH_4$ (0.04

mmol) was added dropwise under vigorous stirring, the color changed to brown in 10 min. The reaction mixture was stirred at room temperature in the absence of light for 9 h in air. The resulted mixture was centrifuged for 3 min at 10000 r/min and washed twice with ethanol. This crude brown solid was dissolved in a mixture of 3 mL CH_2Cl_2 and 0.2 mL toluene. After filtration, the filtrate was subject to the diffusion of a mixture of ether and n-hexane (v : v = 1 : 1) at 4℃ to afford purple blue crystals after 5 days (31 mg, yield 35% based on Ag).

Anal. UV-vis (λ, nm): 410; 450; 590 nm. Eg = 1.97 eV. ESI-MS (CH_2Cl_2/MeOH = 5 : 1 (V : V): 2213.68 ($[Ag_{25}dpppe_3(MeO\text{-}PhC{\equiv}C)_{20}]^{3+}$) and 3438.48 ($[Ag_{25}dpppe_3(MeO\text{-}PhC{\equiv}C)_{20}(SbF_6)]^{2+}$). ^{31}P NMR (202 MHz, CD_2Cl_2, δ, ppm): 4.0 ppm (external reference 85% H_3PO_4). XPS (binding energy, eV): Ag $3d_{5/2}$, 368.3; Ag $3d_{3/2}$, 374.4 eV.

III. Computational details

Density functional theory (DFT) calculations of the Ag_{19} cluster were performed with the quantum chemistry program Turbomole V6.5.[1] Since the phenyl rings did not contribute to the frontier molecular orbitals of the cluster, we replaced Ph- rings in PhCC- and $(Ph_2P)_2CH_2$ ligands with $–CH_3$ groups for computational efficiency. The def2-SV(P) basis sets were used for C, P, S and H, while effective core potentials which have 19 valence electrons and include scalar relativistic corrections were used for Ag.[2] Geometry optimization was done with the TPSS (Tao, Perdew, Staroverov, and Scuseria) functional.[3] Time-dependent DFTs were done at the hybrid B3-LYP level with def2-SV(P) basis sets. All transitions together with their oscillator strengths were then convoluted with a Lorentzian line shape of 0.15 eV broadening to make the optical-absorption spectrum.

[1] R. Ahlrichs, M. Bar, M. Haser, H. Horn, C. Kolmel, *Chem. Phys. Lett.* **1989**, *162*, 165-169.

[2] D. Andrae, U. Häußermann, M. Dolg, H. Stoll, H. Preuß, *Theor. Chim. Acta* **1990**, 77,123-141.

[3] J. Tao, J. P. Perdew, V. N. Staroverov, G. E. Scuseria, *Phys. Rev. Lett.* **2003**, *91*, 146401.

IV. Supporting figures

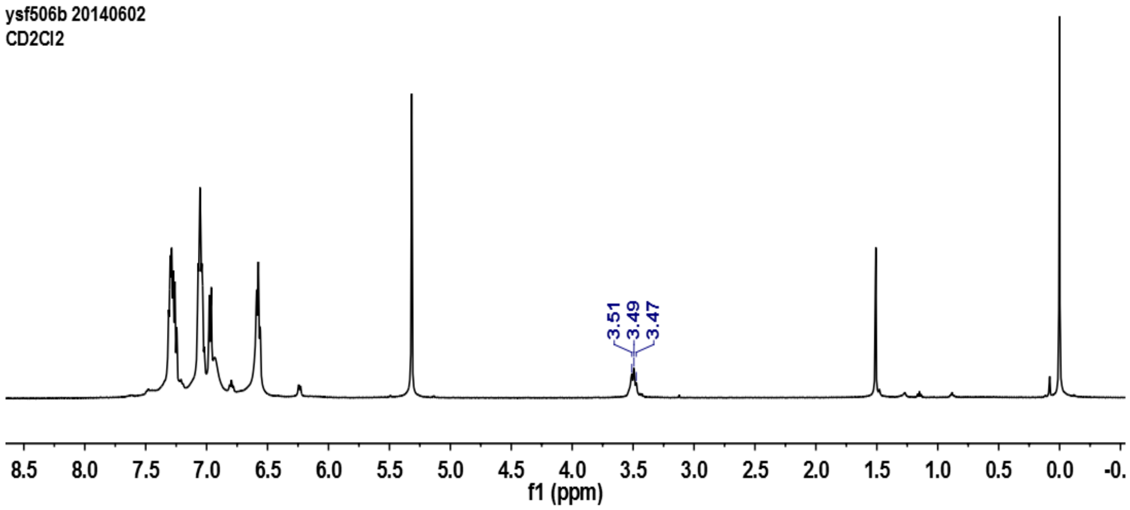


Figure S1. ^{1}H NMR spectrum of **1** in CD_2Cl_2

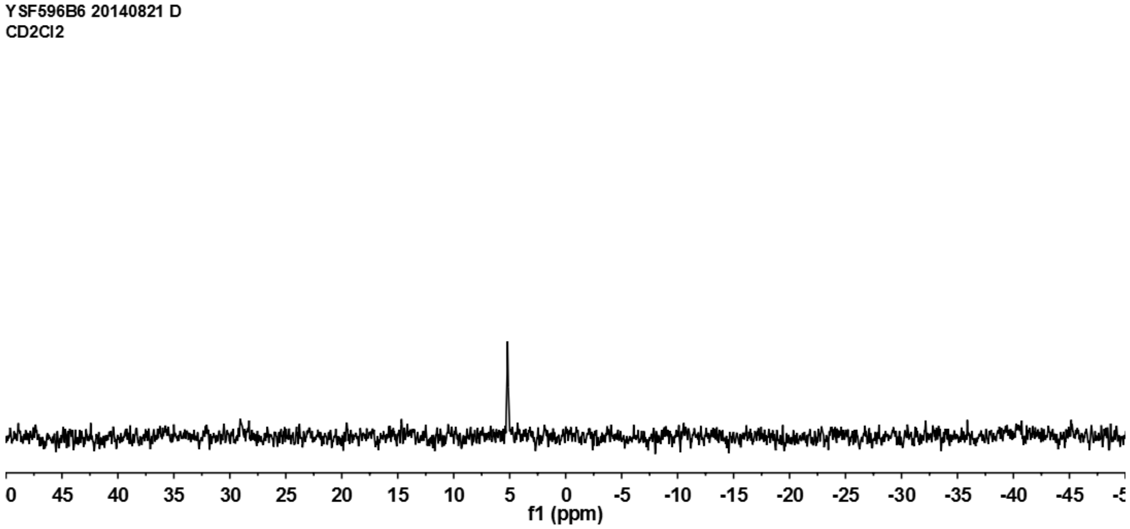
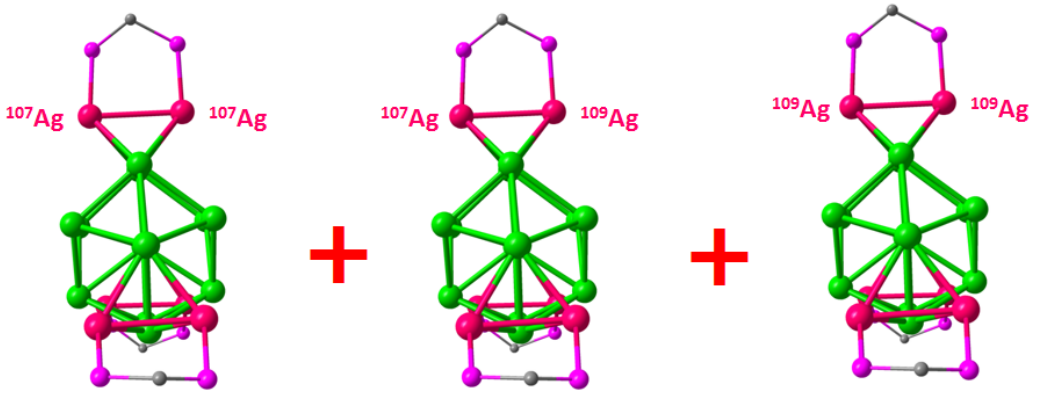
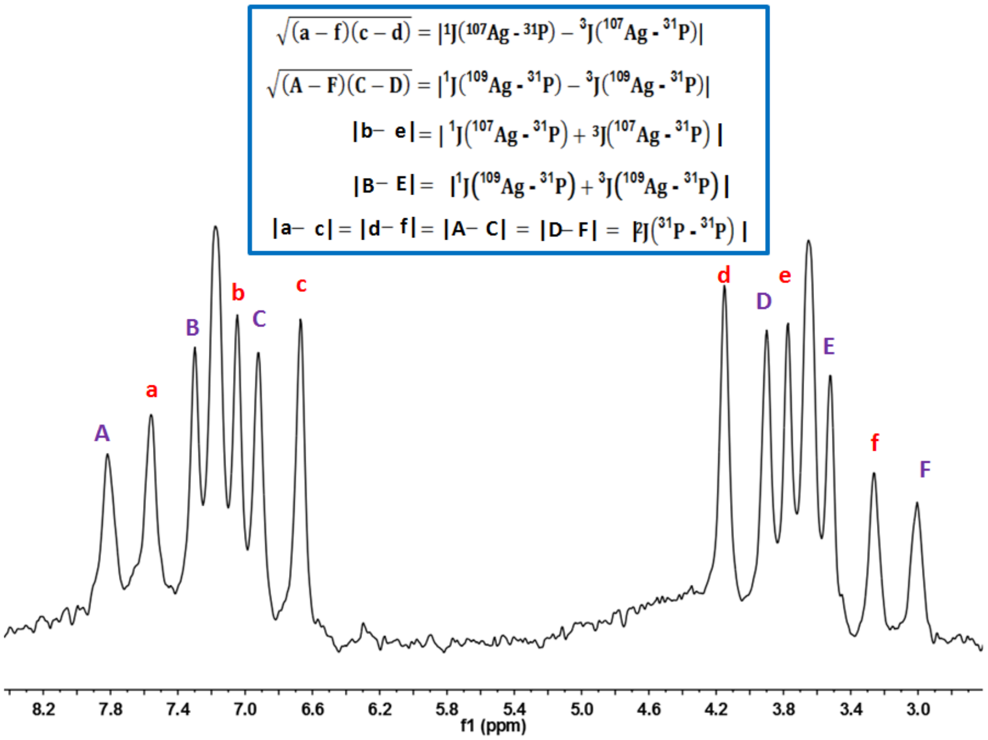


Figure S2. ^{2}H NMR (CH_2Cl_2/CD_2Cl_2, v : v = 500 : 1) spectrum of **1** synthesized by using $NaBD_4$ in place of $NaBH_4$. The peak at 5.32 ppm is from CD_2Cl_2.

AA’XX’ patterns:





$$\sqrt{(a-f)(c-d)} = |{}^1J({}^{107}Ag-{}^{31}P) - {}^3J({}^{107}Ag-{}^{31}P)|$$

$$\sqrt{(A-F)(C-D)} = |{}^1J({}^{109}Ag-{}^{31}P) - {}^3J({}^{109}Ag-{}^{31}P)|$$

$$|b-e| = |{}^1J({}^{107}Ag-{}^{31}P) + {}^3J({}^{107}Ag-{}^{31}P)|$$

$$|B-E| = |{}^1J({}^{109}Ag-{}^{31}P) + {}^3J({}^{109}Ag-{}^{31}P)|$$

$$|a-c| = |d-f| = |A-C| = |D-F| = |{}^2J({}^{31}P-{}^{31}P)|$$

δ	$^1J(^{107}Ag-^{31}P)$	$^3J(^{107}Ag-^{31}P)$	$^1J(^{109}Ag-^{31}P)$	$^3J(^{109}Ag-^{31}P)$	$^2J(^{31}P-^{31}P)$
5.41ppm	657Hz	-1.2Hz	760Hz	-3.6Hz	178Hz

Figure S3. ^{31}P NMR spectrum of **1** in CD_2Cl_2 and the analysis of coupling constants.

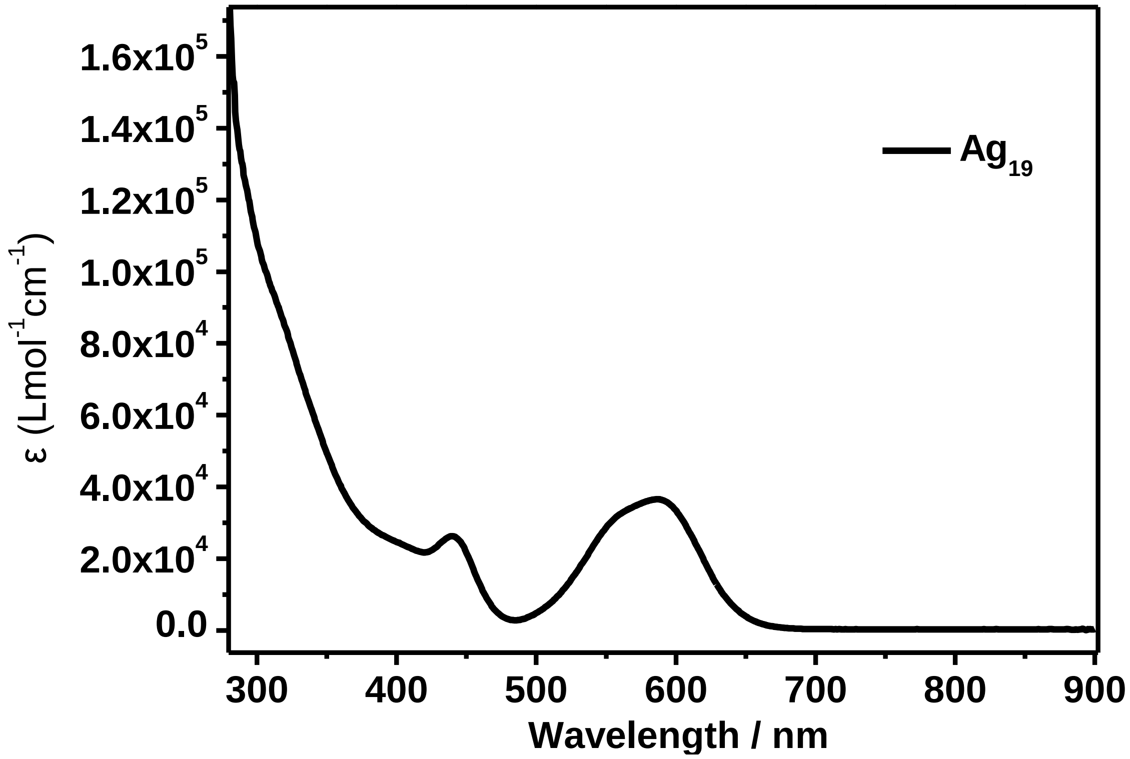


Figure S4. UV-Vis spectrum of $[Ag_{19}(dppm)_3(PhC{\equiv}C)_{14}](SbF_6)_3$ in CH_2Cl_2. For the experimental spectrum shown in Figure 5 of the main text, a Jacobian factor was applied to convert the nm-based to eV-based absorbance.

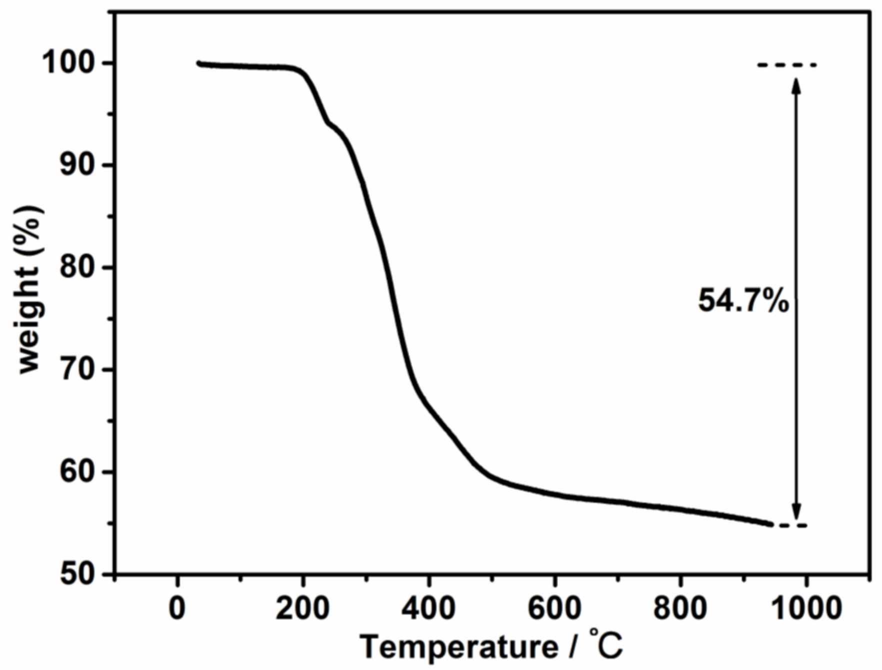
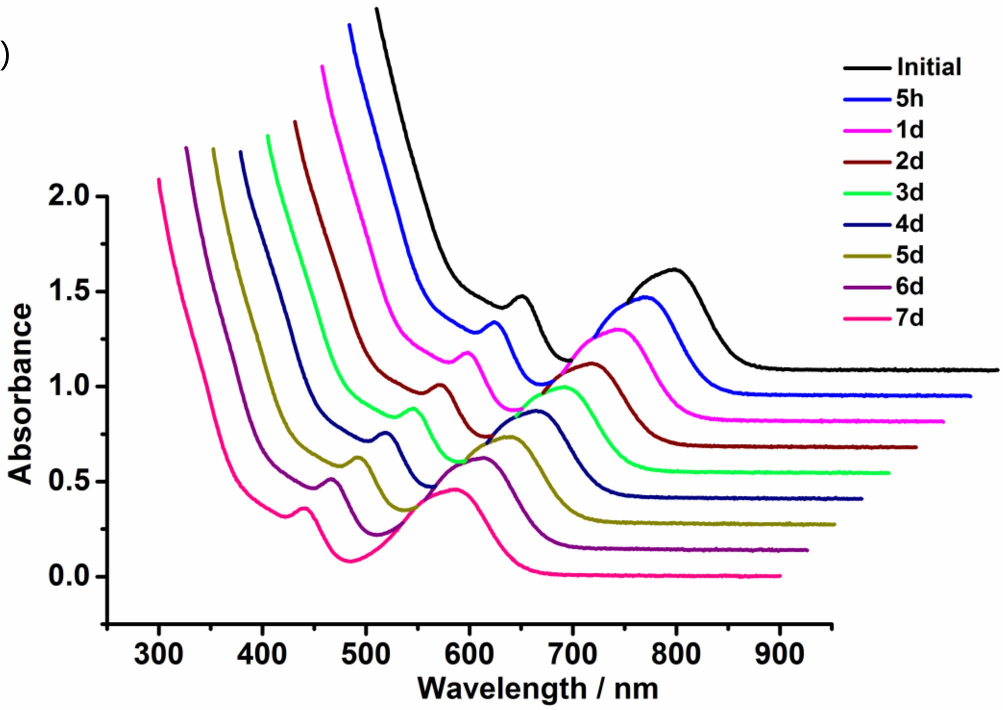
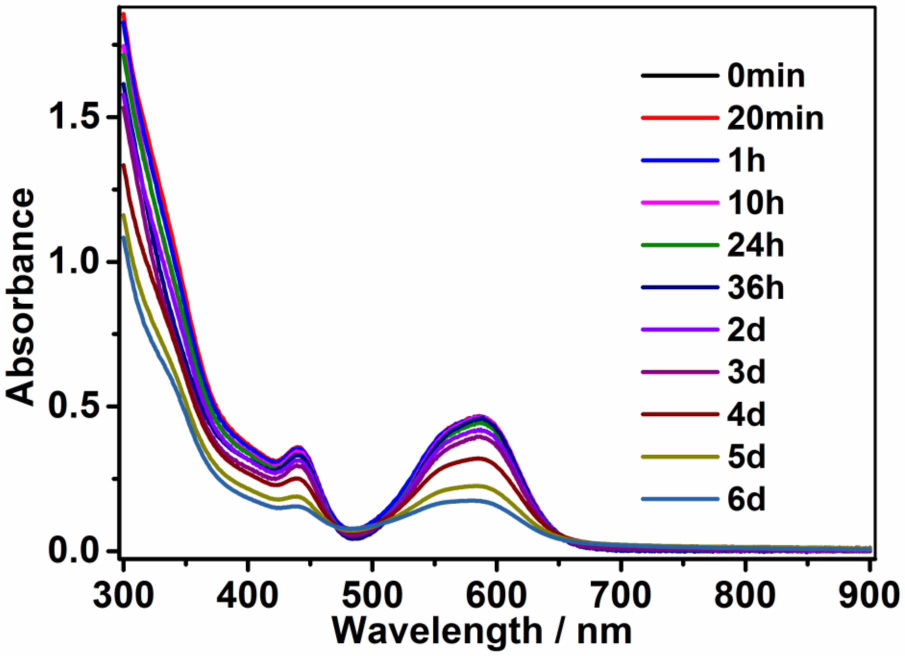


Figure S5. Thermogravimetric analysis (TGA) of **1** in N_2 atmosphere.

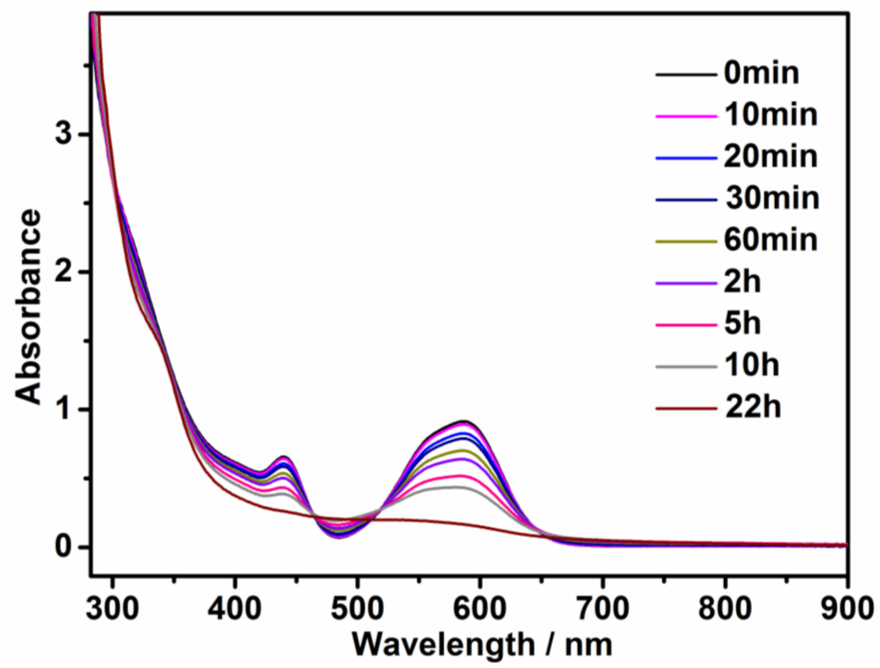
a)


Initial
5h
1d
2d
3d
4d
5d
6d
7d
Absorbance
2.0
1.5
1.0
0.5
0.0
300
400
500
600
700
800
900
Wavelength / nm

b)

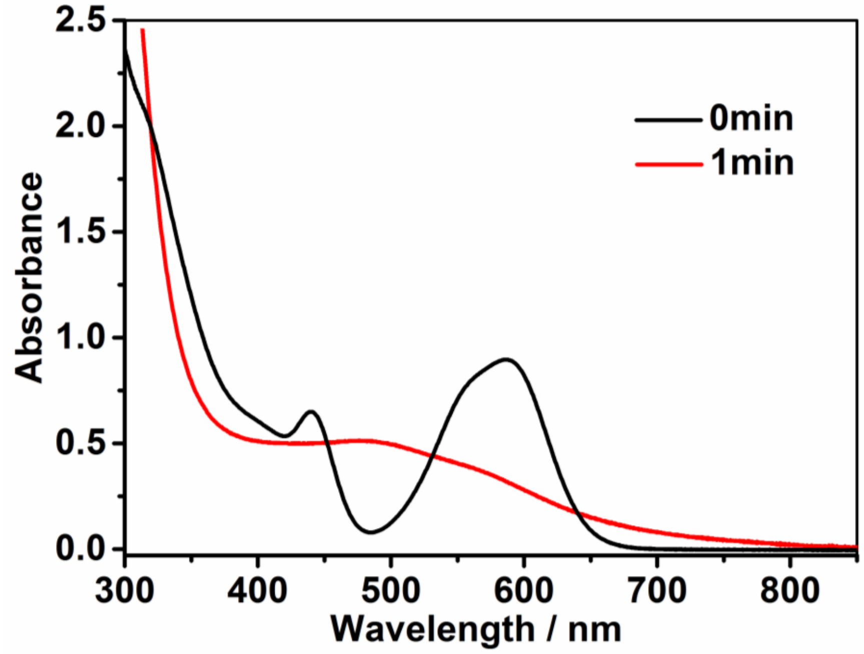

0min
20min
1h
10h
24h
36h
2d
3d
4d
5d
6d
Absorbance
1.5
1.0
0.5
0.0
300
400
500
600
700
800
900
Wavelength / nm

c)



Absorbance
Wavelength / nm
0
1
2
3
300
400
500
600
700
800
900
0min
10min
20min
30min
60min
2h
5h
10h
22h

d)



Absorbance
Wavelength / nm
0.0
0.5
1.0
1.5
2.0
2.5
300
400
500
600
700
800
0min
1min

e)

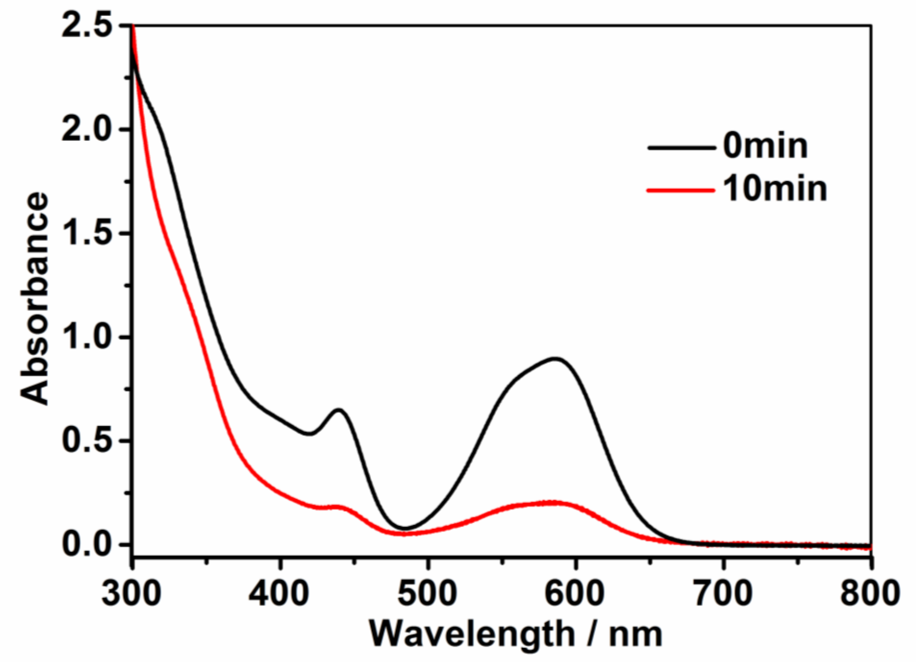


Figure S6. Time-dependent UV-Vis spectra of **1** for monitoring stability under various conditions. a) in N_2 atmosphere at room temperature in CH_2Cl_2; b) under ambient conditions in CH_2Cl_2; c) alkaline environment: Ag_{19} (2 mg) was dissolved in 2 mL CH_2Cl_2 and mixed with 20 μL 0.2 M MeONa in MeOH; d) acidic environment: Ag_{19} (2 mg) was dissolved in 2 mL CH_2Cl_2 and mixed with 2μL CH_3COOH; e) high temperature environment: Ag_{19} (2 mg) was dissolved in 1 mL CH_2Cl_2 and 3mL toluene at 80 ℃.

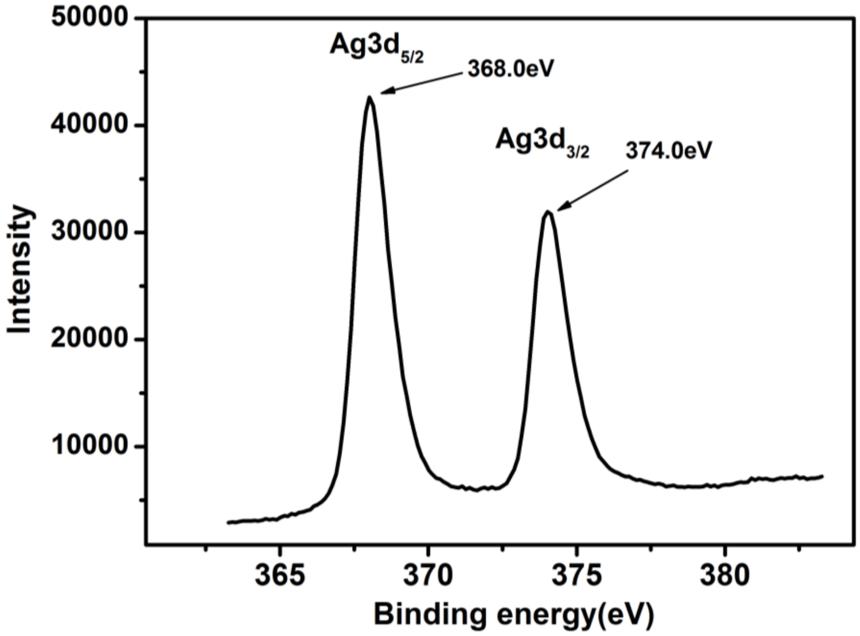


Figure S7. XPS spectrum of **1**.

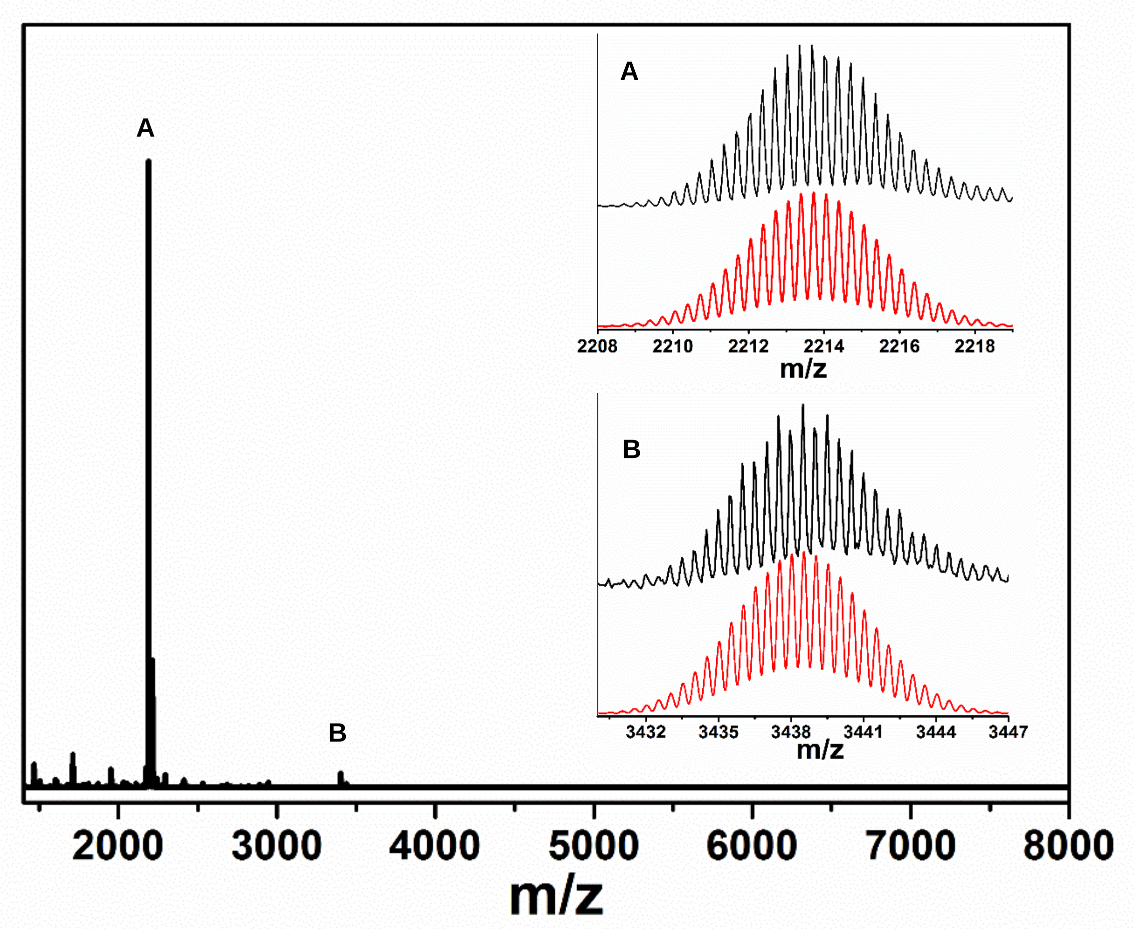


Figure S8. Mass spectra of $[Ag_{25}(dpppe)_3(PhC{\equiv}C)_{20}](SbF_6)_3$ (**2**). Inset: the experimental (black trace) and simulated (red trace) isotopic patterns of molecular ion.

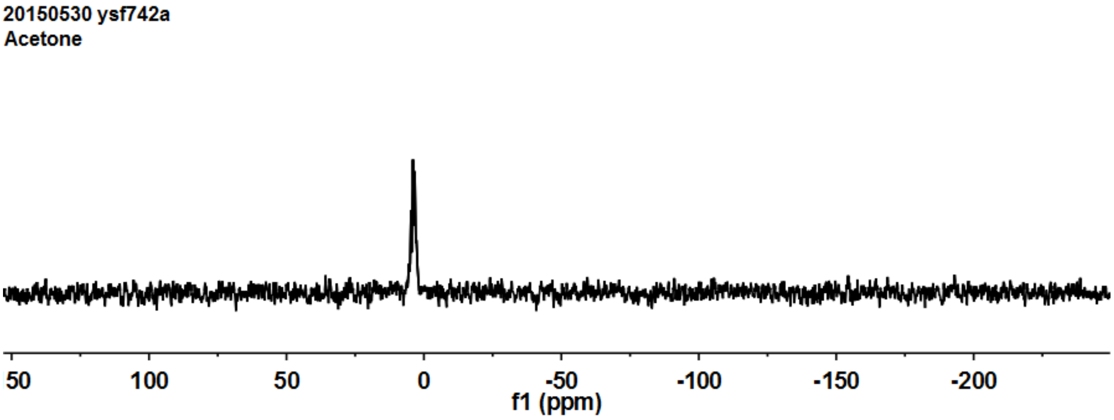


Figure S9. ^{31}P NMR spectrum of **2** in acetone-D_6.

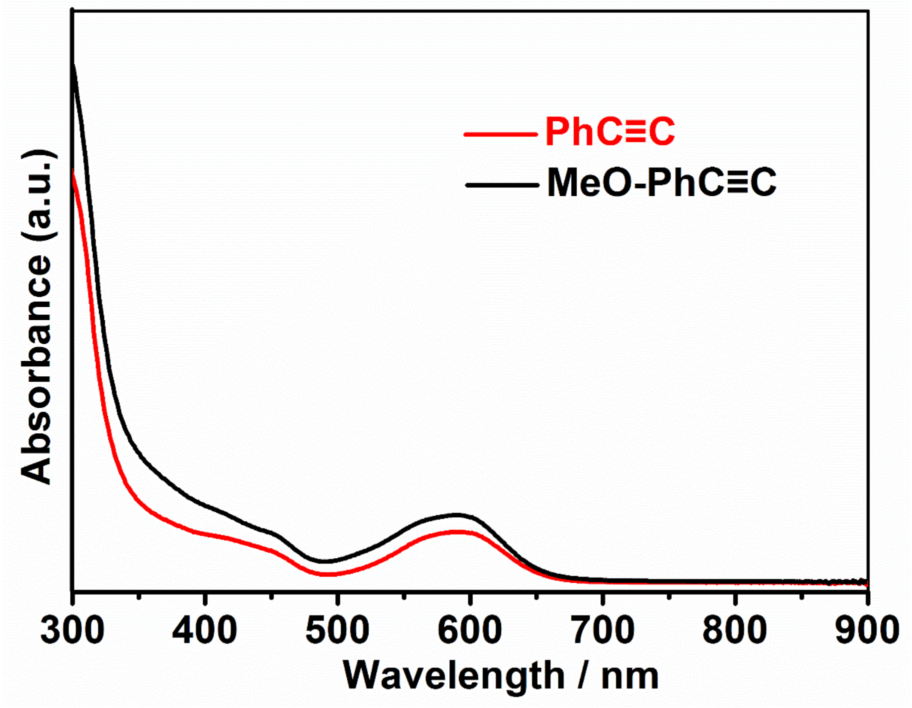


Figure S10. UV-vis spectra of **Ag_{25}** in CH_2Cl_2 protected by different alkynyl groups.

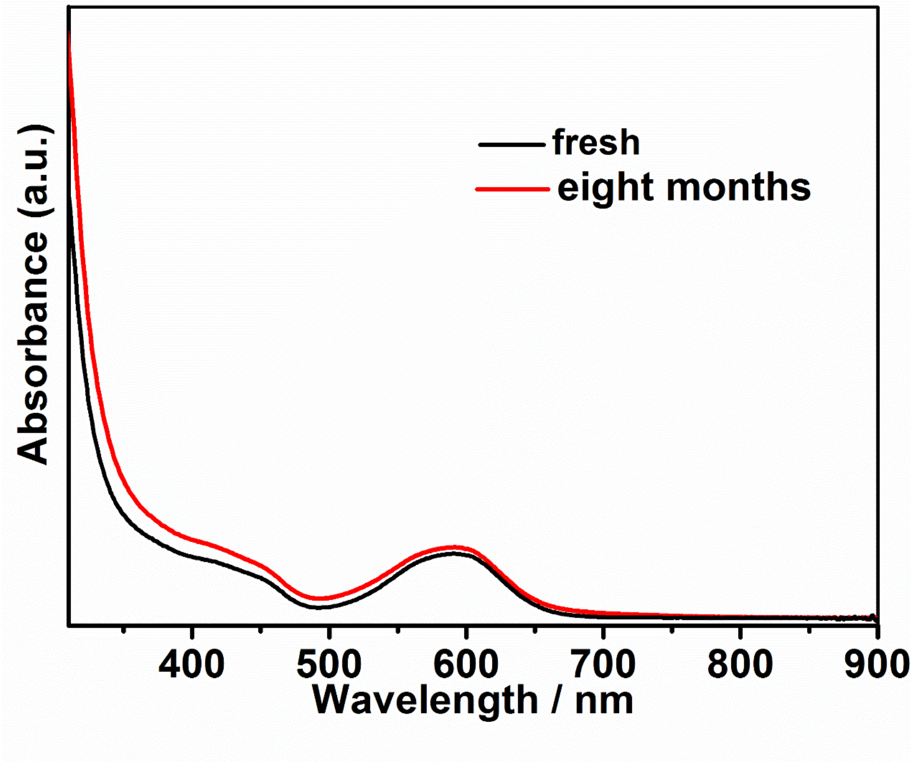


Figure S11. UV-vis spectra of **2** in CH_2Cl_2 measured at different time for stability check (solid stored for eight months).

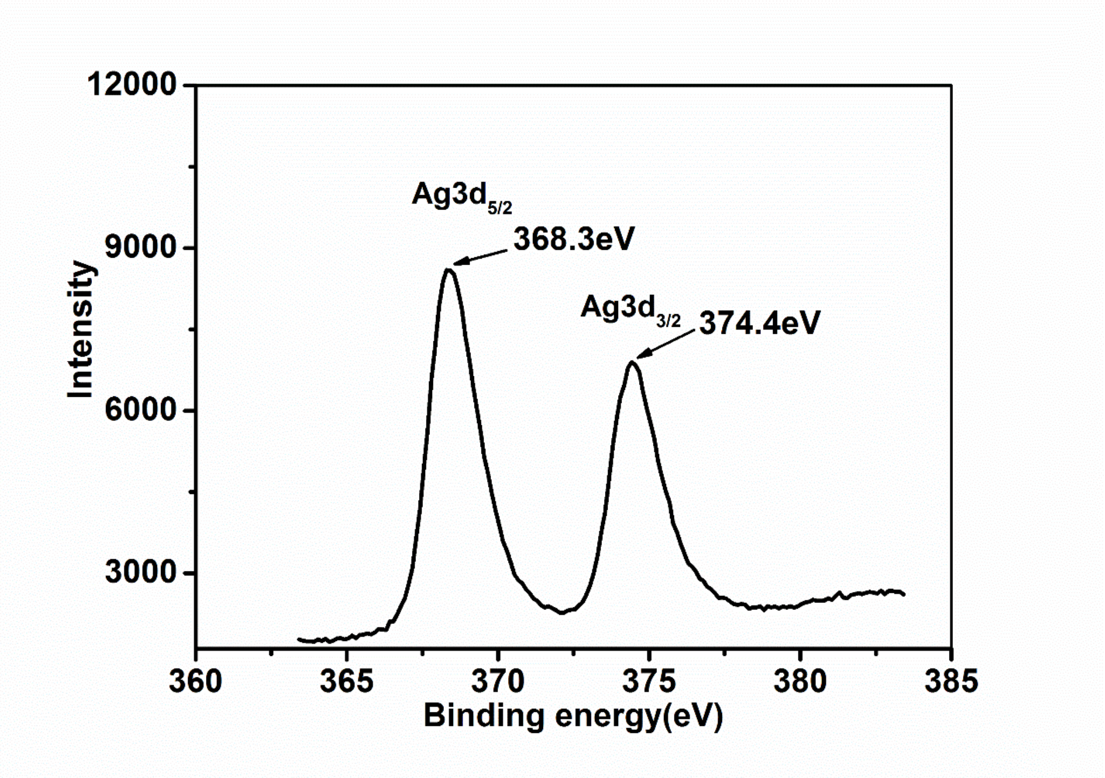


Figure S12. XPS spectrum of **2**.

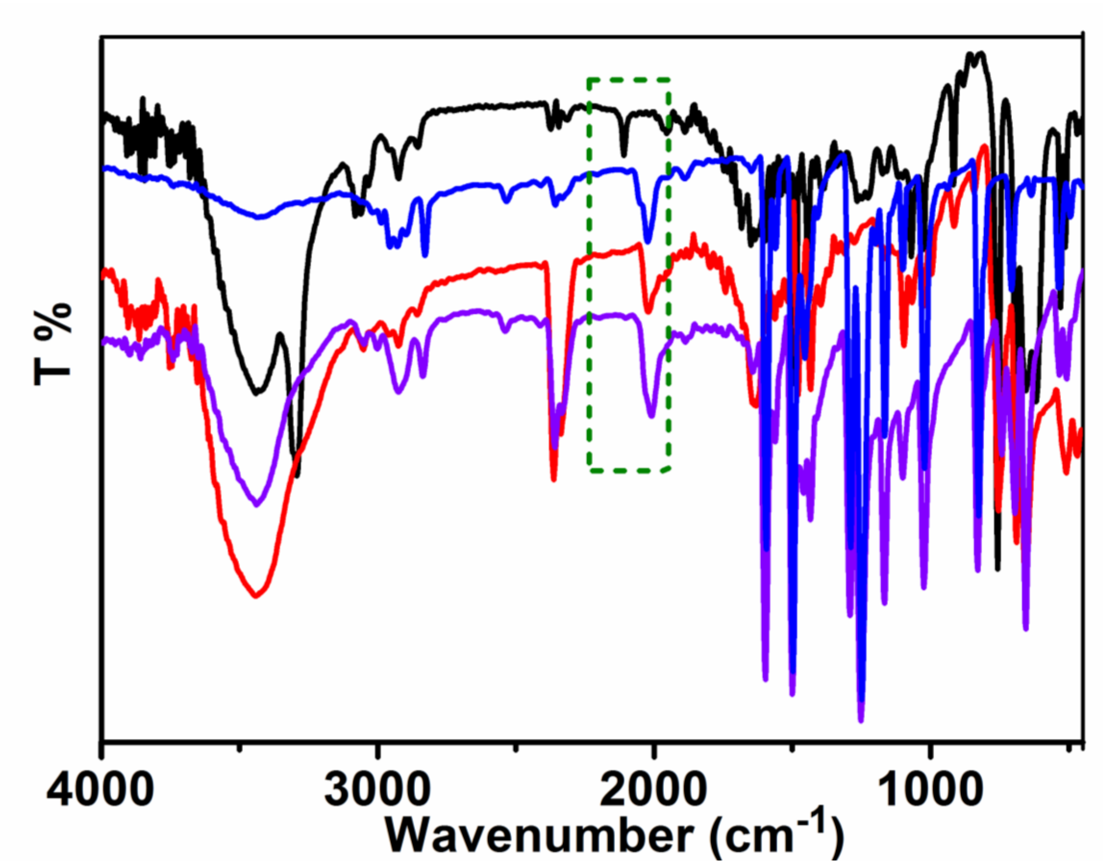


Figure S13. IR spectrum of PhC≡CH (black trace), MeOPhC≡CAg (blue trace), Ag_{19} (red trace) and Ag_{25} (purple trace).