

## **AIE ligand-based silver cluster using for ethion detection**

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## 1. Materials and reagents

Unless otherwise noted, all materials used in this work were commercially available and used as received. 2-Bromo-1,1,2-triphenylethylene, trimethylsilylacetylene, tetrabutylammonium fluoride ( $\text{Bu}_4\text{N}^+\text{F}^-$ ), bis(triphenylphosphine)palladium(II) chloride ( $\text{PdCl}_2(\text{PPh}_3)_2$ ) and copper iodide ( $\text{CuI}$ ) were purchased from J&K Chemical, Beijing, China. All the other materials were purchased from Sinopharm Chemical Reagent Beijing Co., Beijing, China. Analytical grade solvents include triethylamine ( $\text{Et}_3\text{N}$ ), dichloromethane (DCM), dimethyl formamide (DMF), tetrahydrofuran (THF), diethyl ether ( $\text{Et}_2\text{O}$ ), methanol (MeOH), acetonitrile ( $\text{CH}_3\text{CN}$ ) and n-hexane were used throughout the experiment.

## 2. Instrumentations

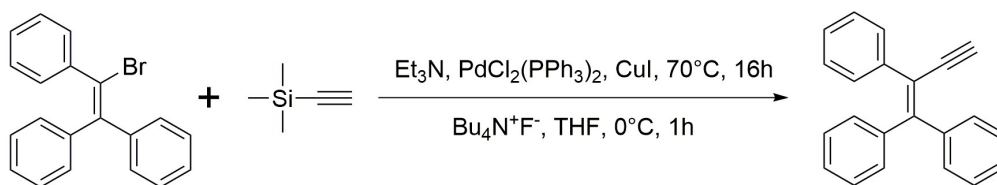
$^1\text{H}$  NMR spectra and  $^{13}\text{C}$  NMR spectra were recorded on a Bruker DRX spectrometer operating at 400 MHz and 100MHz, respectively. Single-crystal X-ray diffraction (SCXRD) of the sample was performed at 200 K on a Rigaku XtaLAB Pro diffractometer with Cu-K $\alpha$  radiation ( $\lambda = 1.54184 \text{ \AA}$ ). Powder X-ray diffraction (PXRD) of the sample was recorded on a PANalytical-X' Pert PRO diffractometer. High-resolution mass spectrometry (HRMS) were recorded on an X500R QTOF spectrometer. Elemental analyses were carried out with a Perkin-Elmer 240 elemental analyzer. Thermogravimetric analysis (TGA) was performed on a TA Q50 system from room temperature to 650 °C at a heating rate of 10 °C/min under nitrogen atmosphere. UV-vis absorption spectra were recorded using a Hitachi UH4150 UV-visible spectrophotometer in the range of 200-800 nm. Luminescence spectra were recorded with a HORIBA FluoroLog-3 fluorescence spectrometer. Microscopy image was recorded on an Olympus BX53 microscope.

## 3. General experimental procedures

### 3.1 Synthesis of the compounds

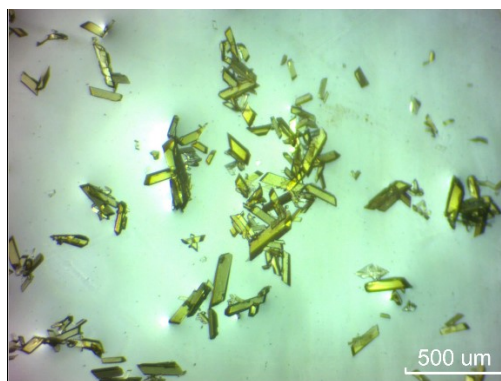
**Synthesis of 1, 1, 2-triphenyl-1-butene-3-acetylene (TPBA).** TPBA was synthesized according to the literature (Scheme S1).<sup>1</sup> 2-Bromo-1,1,2-triphenylethylene (3.35 g, 10.0 mmol), trimethylsilylacetylene (2.14 mL, 15.0 mmol),  $\text{PdCl}_2(\text{PPh}_3)_2$  (140 mg, 0.199 mmol) and  $\text{CuI}$  (19 mg, 0.10 mmol) were added to a stirring triethylamine solution (50 mL). The reaction mixture was heated at 70°C for 16 hours. The saturated organic layer was washed with distilled water (300 mL) and brine (300 mL), dried with anhydrous  $\text{MgSO}_4$ , and evaporated under reduced pressure. The crude residue was purified by flash chromatography (100% hexanes to 1%  $\text{Et}_2\text{O}$ /hexanes) to produce

a yellow oil. The yellow oil was dissolved in 50 mL THF, cooled to 0°C, Bu<sub>4</sub>N<sup>+</sup>F<sup>-</sup> (1.0 M THF solution, 11 mL, 11 mmol) was added. The reaction mixture was warmed to room temperature and stirred for 1 h, saturated cold NaHCO<sub>3</sub> solution (50 mL) was added slowly. Then dilute the reaction mixture with Et<sub>2</sub>O (50 mL). The organic layer was washed with distilled water (300 mL) and brine (300 mL), dried with anhydrous MgSO<sub>4</sub>, and evaporated under reduced pressure. The crude residue was purified by flash chromatography (100% hexanes to 1% Et<sub>2</sub>O/hexanes) to produce a yellow solid (1.12 g, yield: 40%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm): 7.48 (d, *J* = 4.0 Hz, 2H), 7.34 (m, 3H), 7.28 (d, *J* = 4.0 Hz, 2H), 7.13 (m, 6H), 6.95 (d, *J* = 4.0 Hz, 2H), 3.04 (s, 1H). <sup>13</sup>C NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm): 150.49, 142.37, 141.17, 139.37, 130.99, 130.27, 129.94, 128.07, 127.94, 127.83, 127.82, 127.40, 127.15, 120.43, 85.65, 81.17. ESI-MS spectrometry: *m/z* calculated for C<sub>22</sub>H<sub>16</sub> [*M* - *H*]<sup>+</sup>: 279.1252, found: 279.1161. Elemental analysis calculated for C<sub>22</sub>H<sub>16</sub>: C 94.25%; H 5.75%, found: C 94.29%; H 5.72%.



**Scheme S1** Synthesis of TPBA.

**Synthesis of Ag<sub>24</sub>.** AgNO<sub>3</sub> (8.5 mg, 0.05 mmol) and <sup>1</sup>BuSAg (10 mg, 0.053 mmol) were added to mixed dichloromethane and methanol solution, then it became clear after 1 mL acetonitrile added. After that, a mixed dichloromethane and methanol solution (1:1, 1 mL) of TPBA (10 mg, 0.036 mmol) followed by addition of ammonia water (10 μL) was instilled to the above-mentioned mixture. The solution was stirred in a dark environment for 10 min. Evaporation of the resulting clear solution for 2 days afforded good quality crystals of the desired cluster (Figure S1). Yield: 82% (based on TPBA). Elemental analysis calculated for Ag<sub>24</sub> [(NO<sub>3</sub>)<sub>2</sub>@Ag<sub>24</sub>(<sup>1</sup>BuS)<sub>8</sub>(TPBA)<sub>12</sub>]·2NO<sub>3</sub>: C 51.50%; H 3.68%; N 0.81%, found: C 51.47%; H 3.78%; N 0.80%.



**Figure S1** The photograph of Ag<sub>24</sub> in daylight.

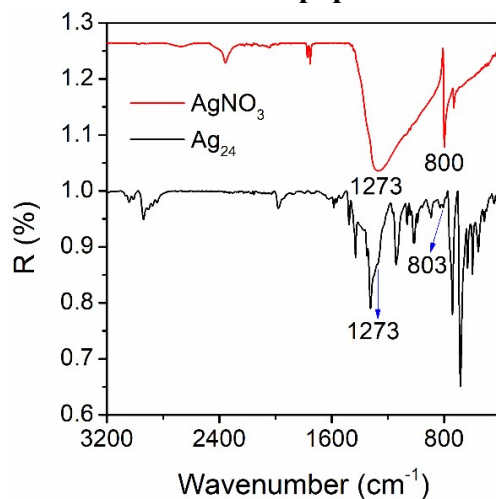
### 3.2 Density functional theory (DFT) calculation

The density functional theory (DFT) was performed with Gaussian 09<sup>6</sup> under Perdew-Burke-Ernzerhof (PBE) functional.<sup>2</sup> All calculations were conducted using 6-31g\* basis set for Ag, S, H, N, C, and O atoms.<sup>3</sup> The single crystal structure was chosen as initial guess for ground state optimization and all reported stationary points were verified as true minima by the absence of negative eigenvalues in the vibrational frequency analysis. Hirshfeld population analysis was conducted by Multiwfn 3.4.<sup>4</sup>

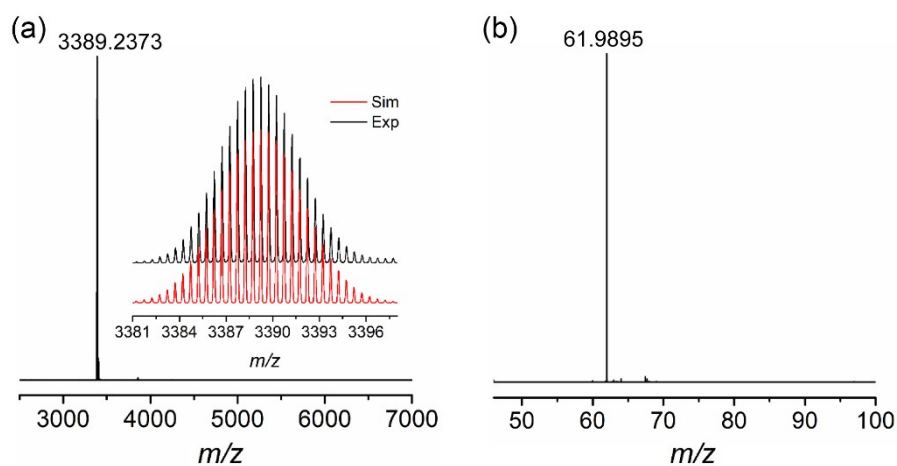
### References

- 1 K. S. Feldman, D. K. Hester, C. S. Lopez, O. N. Faza, Allenyl azide cycloaddition chemistry photochemical initiation and CuI mediation leads to improved regioselectivity, *Org. Lett.*, 2008, **10**, 1665-1668.
- 2 J. P. Perdew, K. Burke, M. Ernzerhof, Generalized gradient approximation made simple, *Phys. Rev. Lett.*, 1996, **77**, 3865-3868.
- 3 a) P. C. Hariharan, J. A. Pople, The influence of polarization functions on molecular orbital hydrogenation energies, *Theor. Chim. Acta*, 1973, **28**, 213-222; b) M. M. Francl, W. J. Pietro, W. J. Hehre, J. S. Binkley, M. S. Gordon, D. J. DeFrees, J. A. Pople, Self-consistent molecular orbital methods. XXIII. A polarization-type basis set for second-row elements, *J. Chem. Phys.*, 1982, **77**, 3654-3665.
- 4 T. Lu, F. W. Chen, Multiwfn: A multifunctional wavefunction analyzer, *J. Comput. Chem.*, 2012, **33**, 580-592.

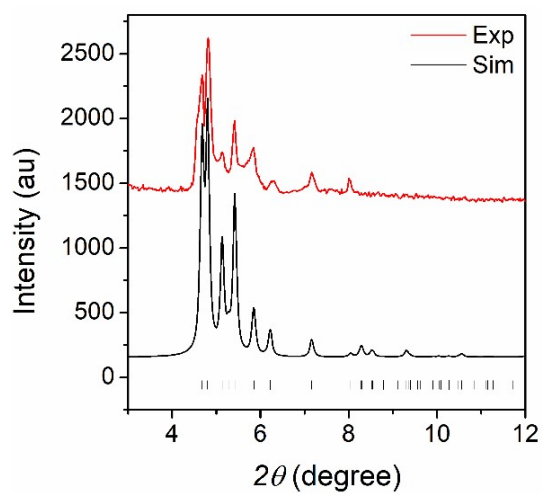
#### 4. Selected spectra and data referred in the paper



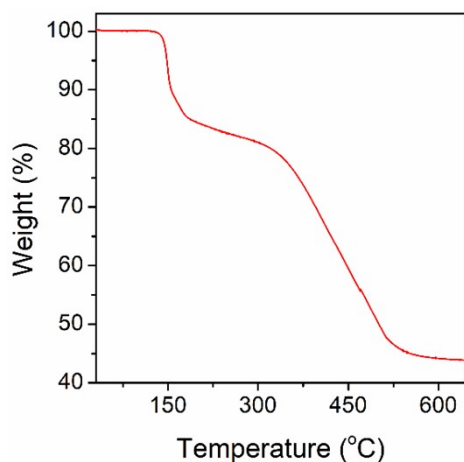
**Figure S2** The comparison of IR spectra between Ag<sub>24</sub> and AgNO<sub>3</sub>.



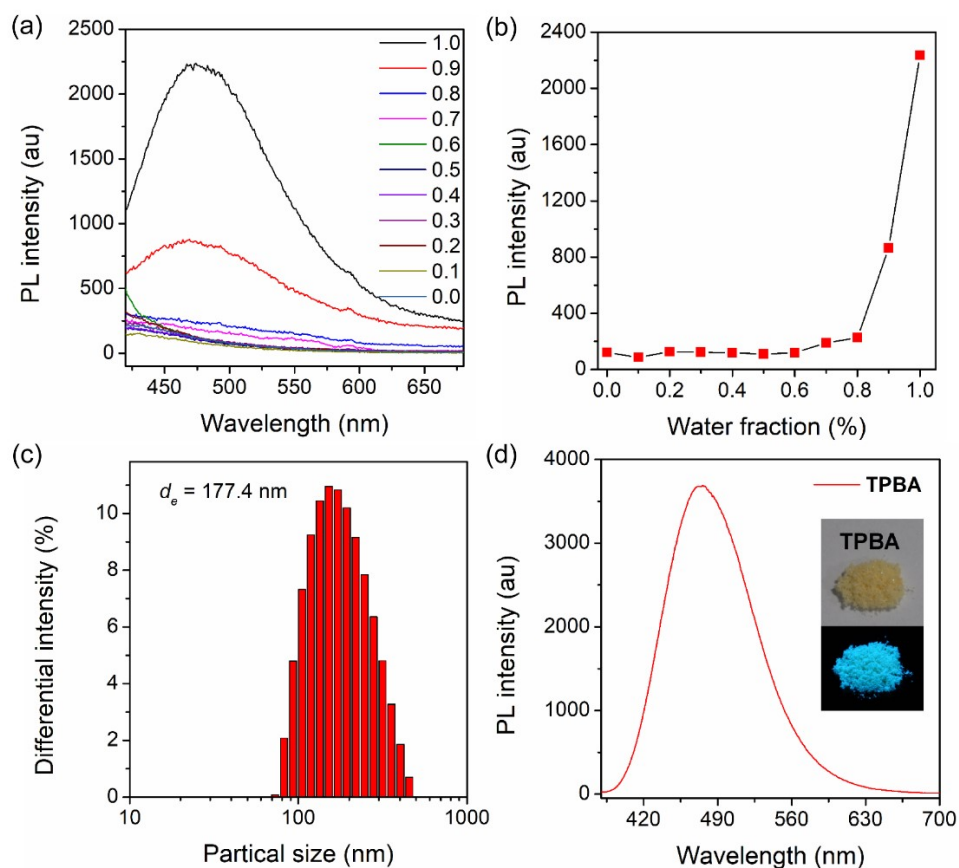
**Figure S3** The HRMS of (a) [(NO<sub>3</sub>)<sub>2</sub>@Ag<sub>24</sub>(<sup>t</sup>BuS)<sub>8</sub>(TPBA)<sub>12</sub>]<sup>2+</sup> and (b) dissociated NO<sub>3</sub><sup>-</sup>.



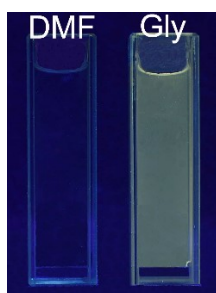
**Figure S4** The PXRD pattern of Ag<sub>24</sub>.



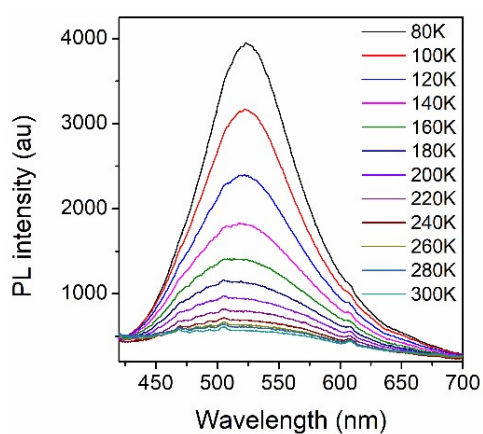
**Figure S5** TGA curve of Ag<sub>24</sub>.



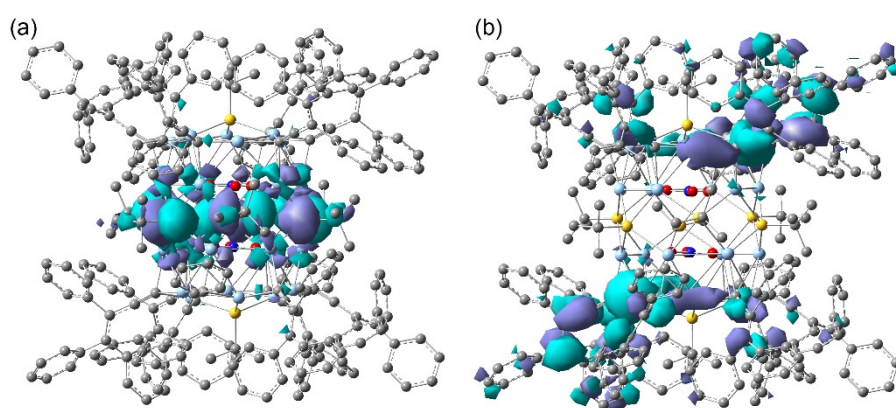
**Figure S6** (a) Luminescence spectra of TPBA in water/DMF mixtures with different  $f_w$ . (b) Luminescence intensity of TPBA at 475 nm as a function of  $f_w$ . (c) Dynamic light scattering measurements of TPBA in aqueous solution of 99% water/DMF (v/v). (d) Fluorescence emission spectra of TPBA in the solid state. Inset: photographs of TPBA in the solid state excited by sunlight (upper) and 365 nm UV light (lower). The concentrations of TPBA was 100  $\mu\text{mol/L}$ .



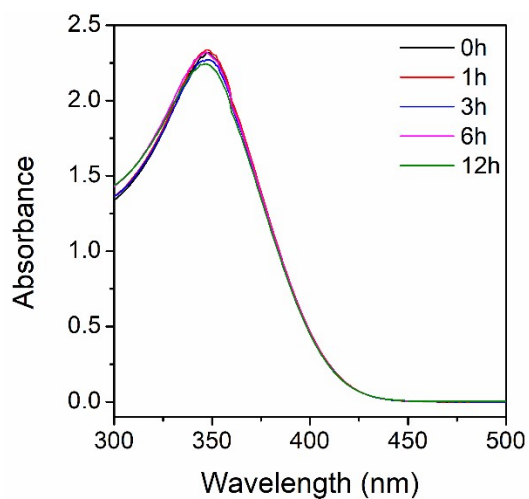
**Figure S7** The fluorescence photograph of  $\text{Ag}_{24}$  in pure DMF and 99% glycerin/DMF (v/v). Conditions: the concentration of  $\text{Ag}_{24}$  was  $5 \mu\text{mol/L}$ . The photograph was taken under irradiation by 365 nm UV light.



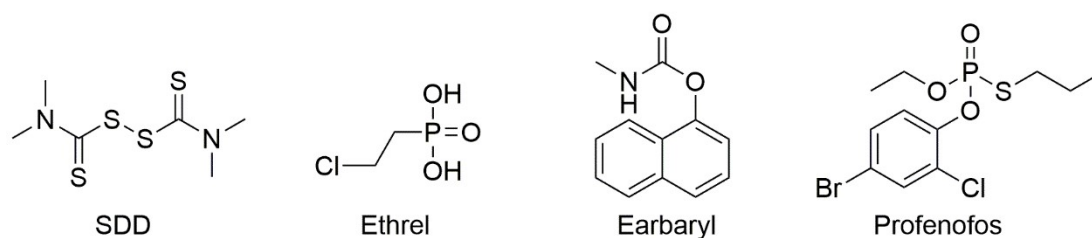
**Figure S8** Temperature dependence of the fluorescence spectra of  $\text{Ag}_{24}$  in solid state.



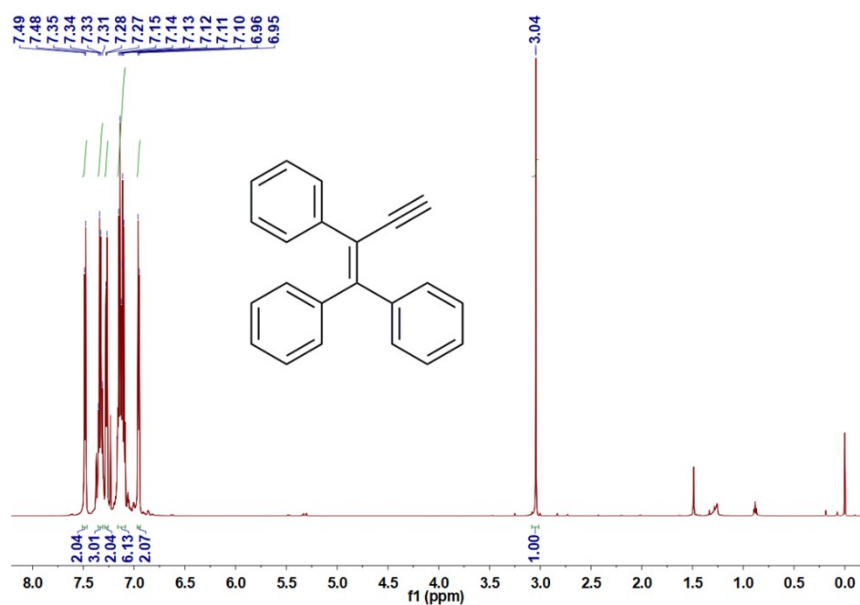
**Figure S9** The frontier molecular orbitals of (a) HOMO (-7.80 eV) and (b) LUMO (-4.57 eV) energy levels of  $\text{Ag}_{24}$  obtained via DFT calculations.



**Figure S10** The stability test of  $\text{Ag}_{24}$  in DMF monitored by UV-vis absorption spectra.

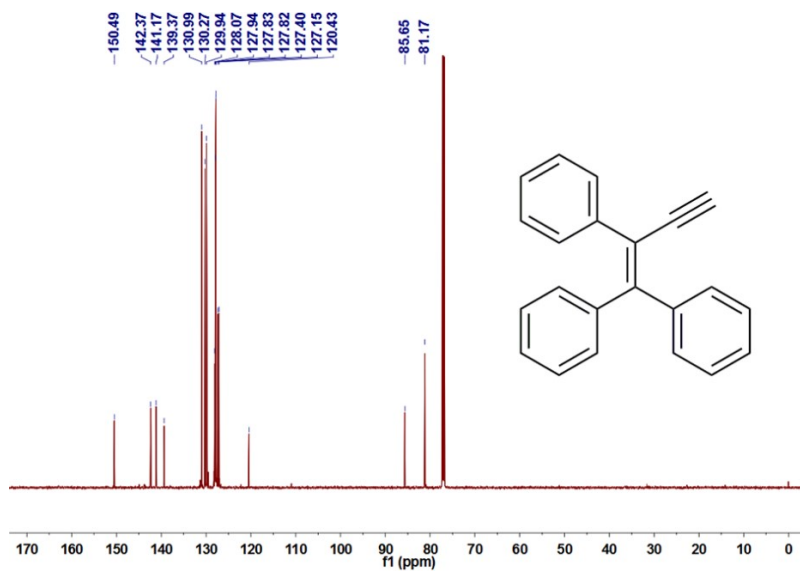


**Figure S11** The structures of organic competitive compounds used in Figure 4(d).

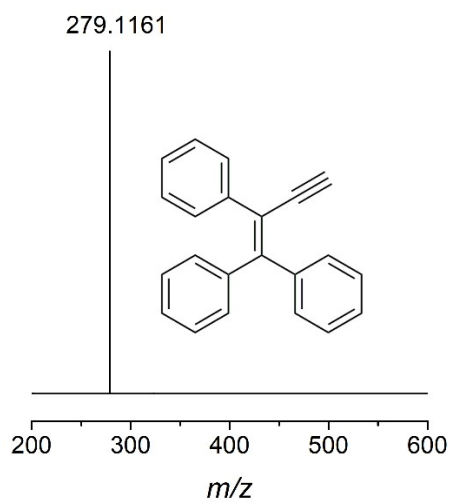


**Figure S12**  $^1\text{H}$ -NMR spectrum of TPBA.





**Figure S13** <sup>13</sup>C-NMR spectrum of TPBA.



**Figure S14** HRMS spectrum of TPBA.

**Table S1** Crystallographic data and structure refinement.

Compound	<b>Ag<sub>24</sub></b>
CCDC number	2102634
Empirical formula	[C <sub>296</sub> H <sub>252</sub> Ag <sub>24</sub> N <sub>2</sub> O <sub>6</sub> S <sub>8</sub> ] <sup>2+</sup>
Formula weigh	6778.34
Temperature/K	200(10)
Wavelength	1.54184
Crystal system	triclinic
Space group	<i>P</i> -1
a/Å	20.3661(2)
b/Å	20.8433(2)
c/Å	21.4825(2)
α/°	62.5110(10)
β/°	85.6090(10)
γ/°	65.7300(10)
Volume/Å <sup>3</sup>	7302.15(14)
Z	1
R <sub>int</sub>	0.0352
Density(calculated)	1.541
Reflections collected	81341
Goodness-of-fit on F <sup>2</sup>	1.064
Final R <sub>1</sub> indexes [I ≥ 2σ(I)]	0.0390
Final wR <sub>2</sub> indexes [all data]	0.1110