Supporting Information

Silver(I) Cage and Infinite Chain Stabilized by Bowl-Shaped Resorcin[4]arene Tetraethynide Ligands

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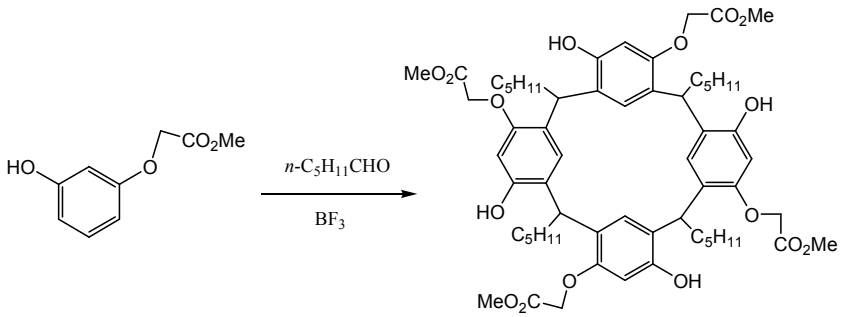
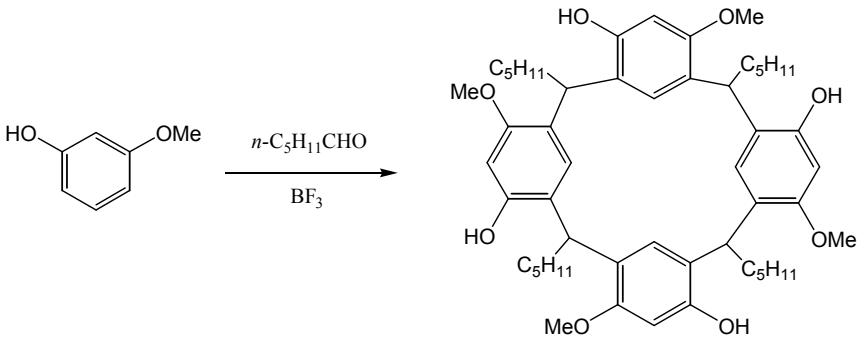
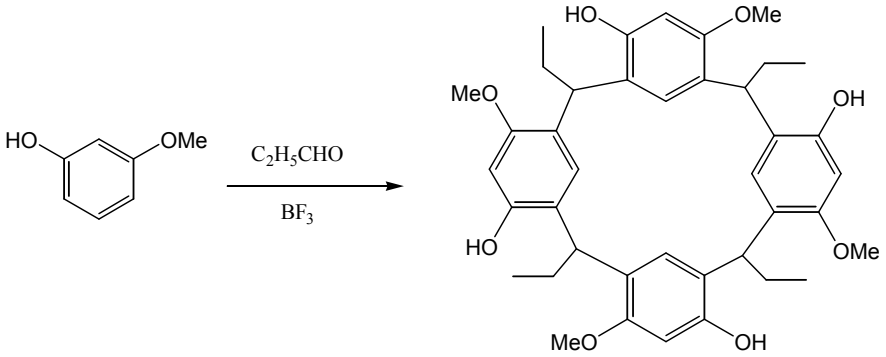


L1'

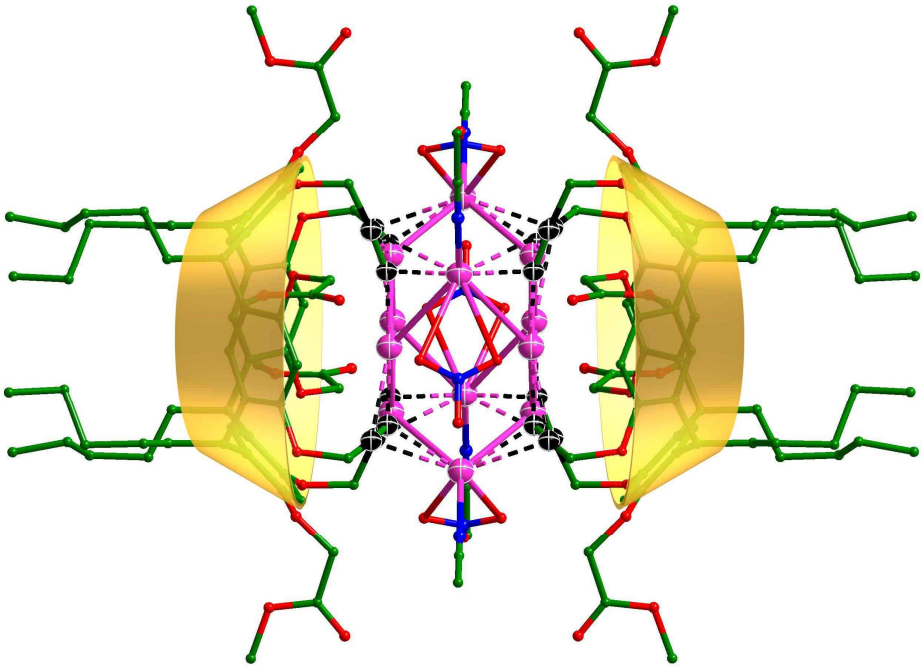


L2'

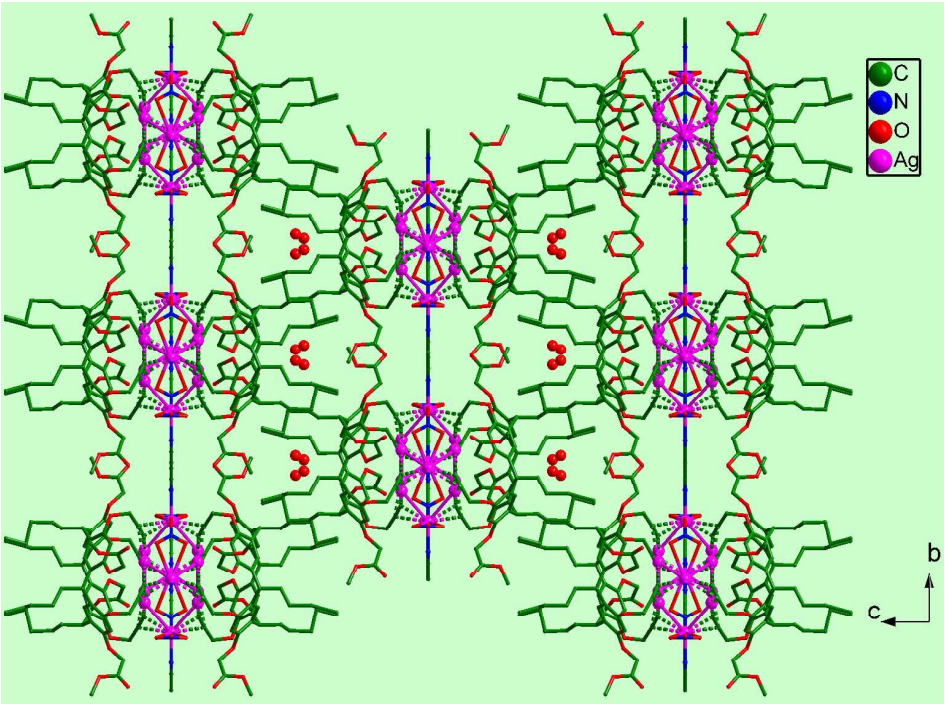


L3'

Scheme S1. Synthetic Procedure of L1', L2' and L3'.



(a)



(b)

Figure S1. (a) Perspective view of the sandwich-type Ag_{12} cage embraced by two bowl-shaped resorcin[4]arene tetraethynide units in **1**. The coordinated nitrate and acetonitrile ligands are shown. The hydrogen atoms and lattice water molecules are omitted. (b) Perspective view of the packing structure of **1**. The disordered lattice

water molecules are shown as red balls.

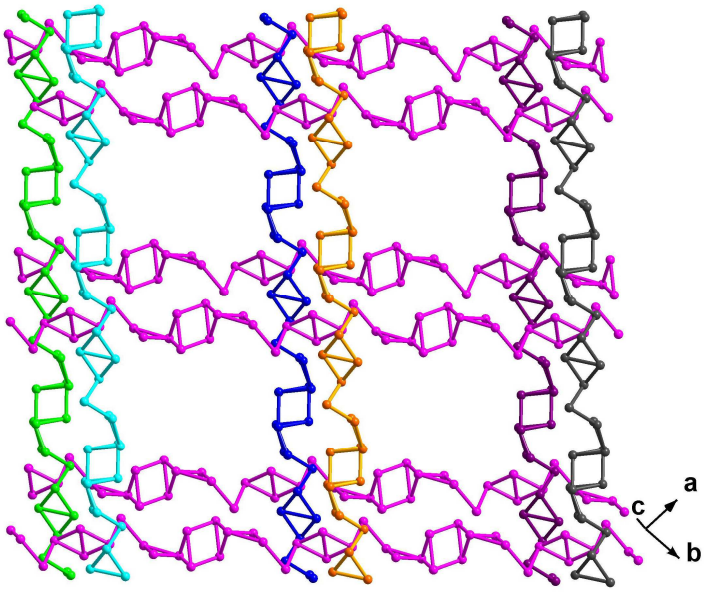
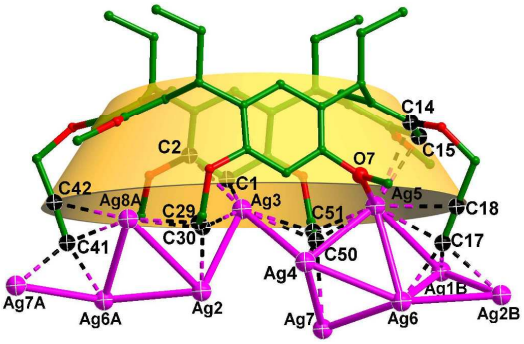
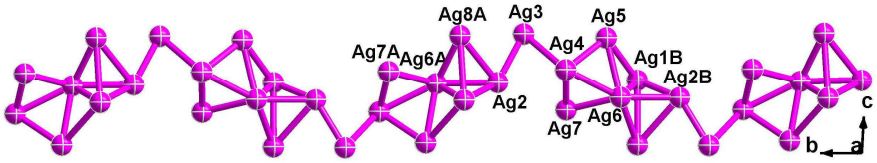


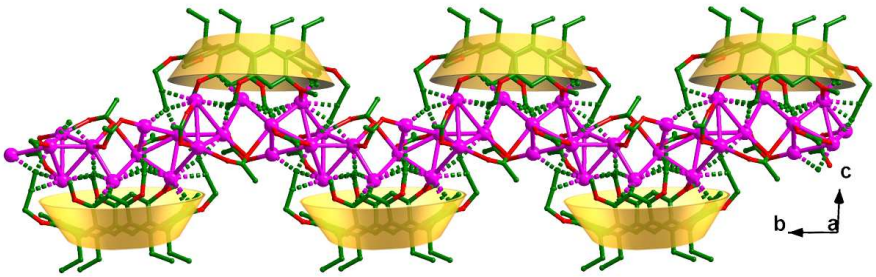
Figure S2. Intersected packing manner of adjacent silver(I) chains in **2**.



(a)



(b)



(c)

Figure S3. (a) Coordination modes of the ethynide groups on the $L3^{4-}$ anion with atom labeling in **4**. (b) Characteristic cationic silver(I) chain formed from the linkage of adjacent Ag_{11} aggregates *via* argentophilic interactions. (c) Infinite zigzag silver(I) chain alternately decorated by the bowl-shaped resorcin[4]arene tetra-ethynide units *via* Ag···C bonds. Hydrogen atoms, fluorine atoms and acetone molecules are omitted for clarity.

Electrochemical properties

The electrochemical properties were also studied for **3**, **4** and $AgCF_3CO_2$. Cyclic voltammograms of **3** and **4** exhibit quasi-reversible redox couples E_c/E_a (E_c and E_a are cathodic and anionic peak potentials, respectively) of 350 mV/1100 mV and 250 mV/1000 mV, respectively. These peaks are very similar to the redox couples of $AgCF_3CO_2$ (E_c/E_a of 200 mV/1200 mV) (Figure S4). Thereby, the redox peaks for **3** and **4** mainly account for the redox process of Ag^+/Ag couples. The different E_c and E_a values also demonstrate that the bulk ethynide functionalized resorcin[4]arene ligands probably play a role in affecting the redox behaviors. Controlled-potential electrolyses of **3** and **4** show a consumption of 8 electrons per molecule, respectively. These multi-electron transfer processes also hold promise for the generation of mixed-valent silver(0,I) materials by electroreduction of multinuclear silver(I)−alkynyl complexes.

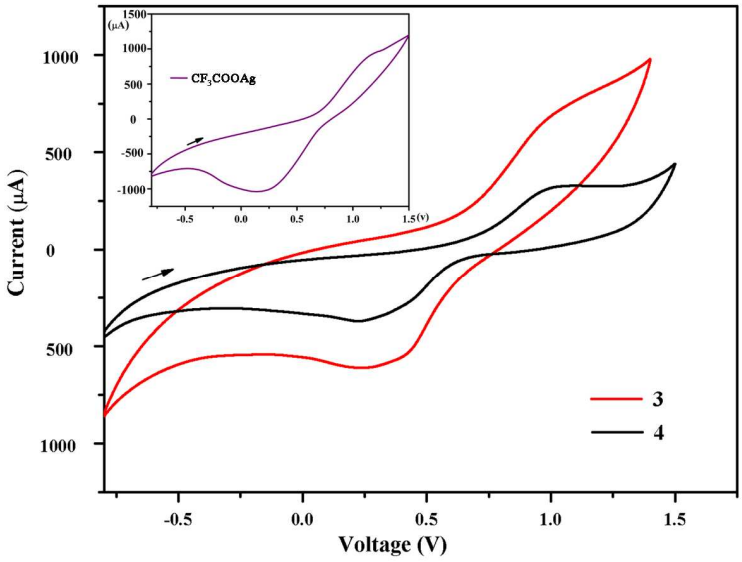


Figure S4. Cyclic voltammograms for **3**, **4** and $AgCF_3CO_2$ in methanol solutions containing 1 mol/L $LiClO_4$ and 0.5 mol/L CF_3COOH.

Luminescence

The luminescent properties of H_4L2 and complex **3** were studied in the solid state at room temperature. As shown in Figure S5, the main emission peak of the free H_4L2 ligand is at 525 nm upon excitation at 370 nm, which is probably from the $\pi^* \rightarrow \pi$ or $\pi^* \rightarrow n$ transition. Complex **3** exhibits an emission peak at 526 nm upon excitation at 363 nm, which is very close to that of the free H_4L2 ligand. Thereby, the emission of complex **3** is probably attributed to ligand-to-ligand charge transition.

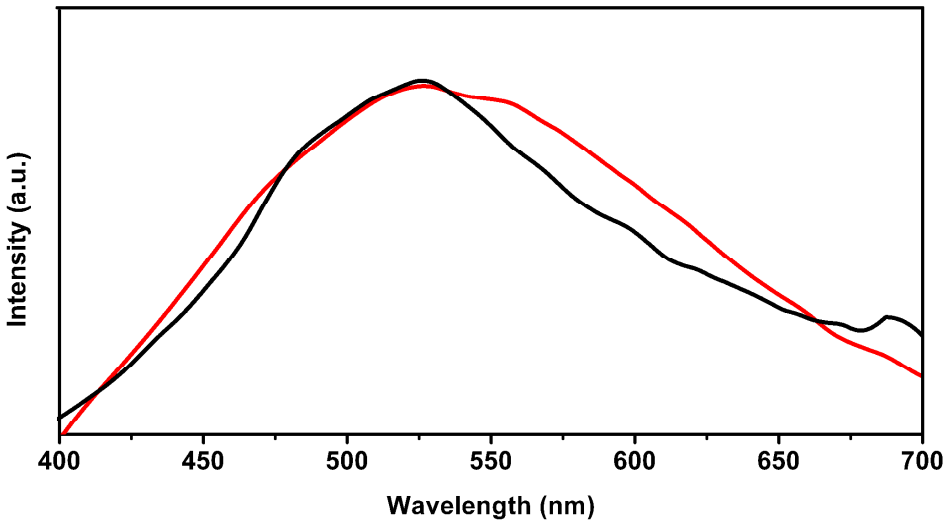


Figure 5. Solid state luminescence spectra of H_4L2 (red) and complex **3** (black) at room temperature.