Supplementary Material

Title: Silver···X–Aryl (X = I and Br) interaction in network assembly with a flexible polynuclear silver-ethynide supramolecular synthon

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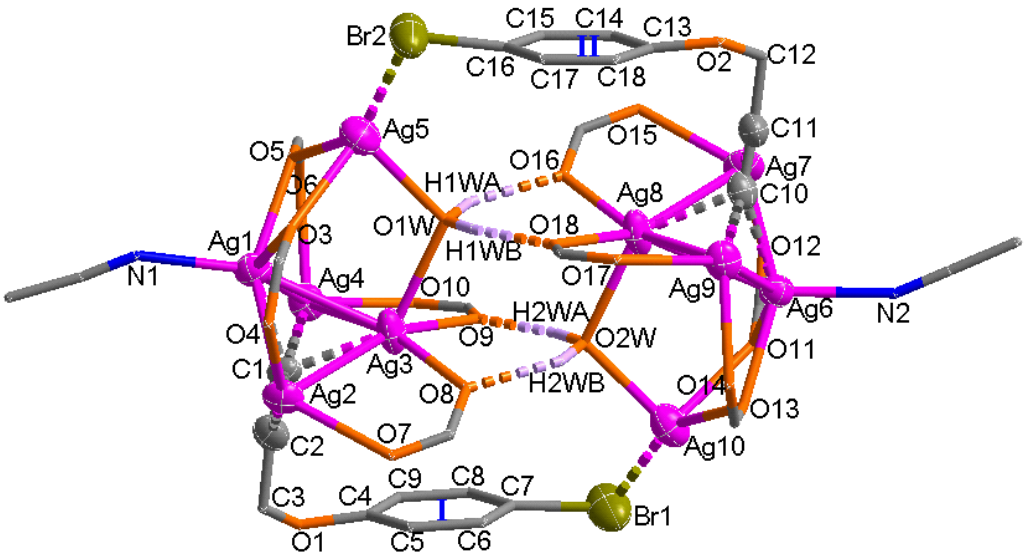

Fig. S1 Atom labeling (50% thermal ellipsoids) and coordination mode of L2 in **4**. All irrespective hydrogen atoms, CH_3 groups of acetonitrile and CF_3 moieties of $CF_3CO_2^-$ are omitted for clarity. Selected bond lengths [Å] can be seen in Table 1.

As shown in Fig. S1, the ethynide groups (C1≡C2) and (C10≡C11) are bound to butterfly-shaped Ag_4 baskets with μ_4-η^1,η^1,η^1,η^2-mode. Such two independent Ag_4 baskets are glued together through strong Ag···Br–aryl interactions (Ag5···Br2 2.584 Å and Ag10···Br1 2.599Å) to give a silver-organic cycle, which is stabilized by O1W···O16 2.820Å, O1W···O17 2.765Å, O2W···O8 2.824Å and O2W···O9 2.746Å hydrogen bonds.

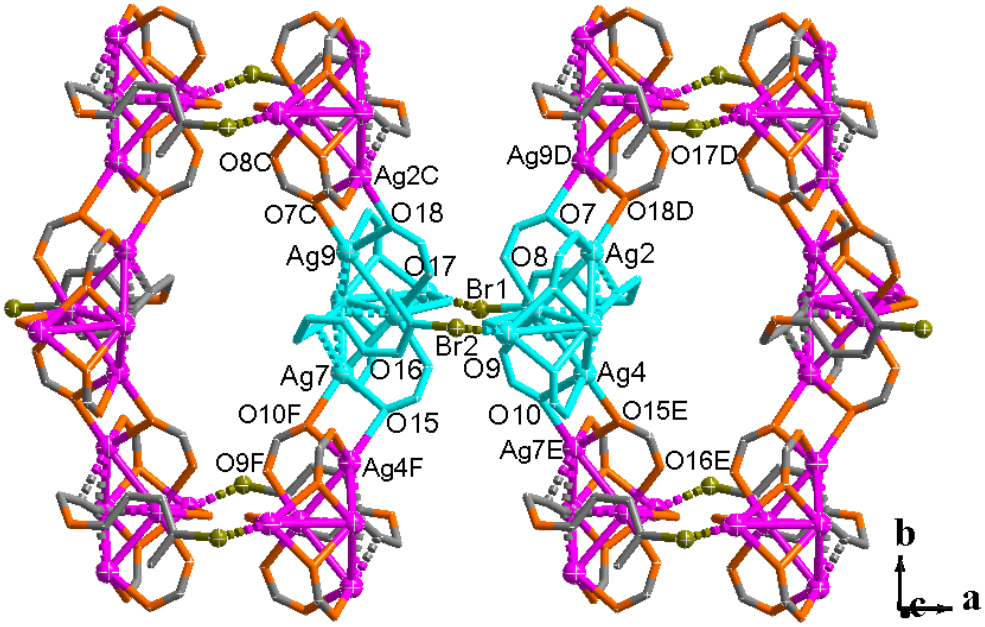

Fig. S2 2D metal-organic network of **4.** One segment is marked as blue. All hydrogen atoms, acetonitrile molecules and CF_3 moieties of $CF_3CO_2^-$ are omitted for clarity. All irrespective atoms are omitted for clarity. Symmetry codes: A –1/2 + *x*, 2 – *y*, *z*; B 1/2 + *x*, 2 – *y*, *z*; C 1/2 + *x*, 1 – *y*, *z*; D –1/2 + *x*, 1 – *y*, *z*.

Such silver-organic cycles are connected together through four types of μ_3-*O,O′,O′* trifluoroacetate groups (O7–O8, O9–O10, O15–O16 and O17–O18) to generate a 2D metal-organic network parallel to the *ab* plane(Fig. S2). In fact, we can also regard that two kinds of Ag_4 baskets are firstly united together through the trifluoroacetate groups to give chain structure along the *b* axis and then two kinds of supramolecular chains as building units are further fused together through Ag···Br–aryl interactions along the *a* axis to give a 2D metal-organic network.