Supporting information for:

Diverse Intermolecular Interactions in Metal-Organic Frameworks Constructed with New Supramolecular Synthon Ag_n-L-Ag_n (n = 4 or 5) (H_2L = 2,2'-bis-prop-2-ynyloxy-biphenyl)

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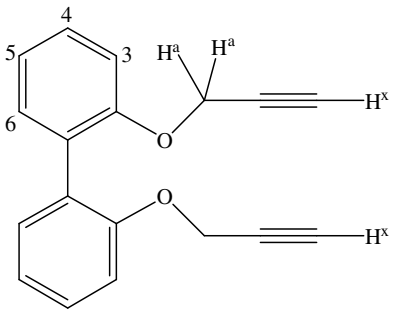
H_2L: Propargyl bromide (2.975g, 25mmol) and K_2CO_3 (3.455g, 25mmol) were added to a solution of biphenyl-2,2'-diol (1.862g, 10mmol) in acetone (60 mL). The solution was heated under reflux for 36h under nitrogen atmosphere, during which a yellow precipitate formed. The precipitate was filtered off and the filtrate was evaporated to dryness yielding the crude product as a yellow solid. It was purified by chromatography on silica gel to afford a pale yellow solid. Yield: 2.26g, 86%. H NMR (300 MHz, $CDCl_3$): δ = 7.06-7.34 (8H, benzene); 4.66 (4H, OCH_2); 2.45 (2H, C≡CH); IR (Nujol): $\nu_{C\equiv C,}$ 2051cm^{-1}; Anal. Calc. For $C_{18}H_{14}O_2$: C 82.42; H 5.38. Found: C 82.39; H 5.43%.



Supporting Figures

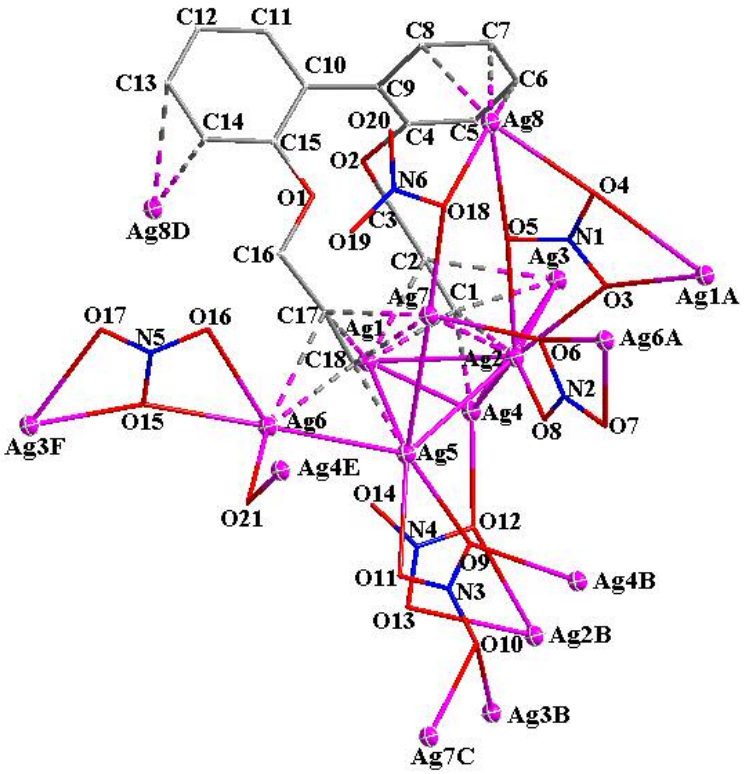


Figure S1. Atom labeling and coordination modes of the **L** ligandand nitrate ions in **1**. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å]: C1-C2, 1.226; C17-C18, 1.223; Ag1-C1, 2.293; Ag1-C2, 2.722; Ag2-C1, 2.322; Ag3-C1, 2.235; Ag3-C2, 2.702; Ag4-C1, 2.172; Ag5-C18, 2.082; Ag6-C18, 2.401; Ag6-C17, 2.686; Ag7-C18, 2.345; Ag7-C17, 2.427; Ag1···Ag2, 3.004; Ag1···Ag4, 2.999; Ag1···Ag5, 2.890; Ag2···Ag3, 2.972; Ag2···Ag4, 2.924; Ag2···Ag5, 3.240; Ag2···Ag7, 3.689; Ag3···Ag4, 3.127; Ag5···Ag6, 3.121; Ag5···Ag7, 3.281; Ag8-C6, 2.996; Ag8-C7, 2.393; Ag8-C8, 2.570; Ag8D-C13, 3.049; Ag8D-C14, 2.668. Symmetry code: A –1 + *x*, *y*, *z*; B - *x*, 2 - *y*, 1 - *z*; C -x, 1 - y, 1 - z; D 1 + x, y, z; E x, -1 + y, z; F 1 + x, -1 + y, z. Color scheme for atoms: Ag purple, C black, O red, N blue.

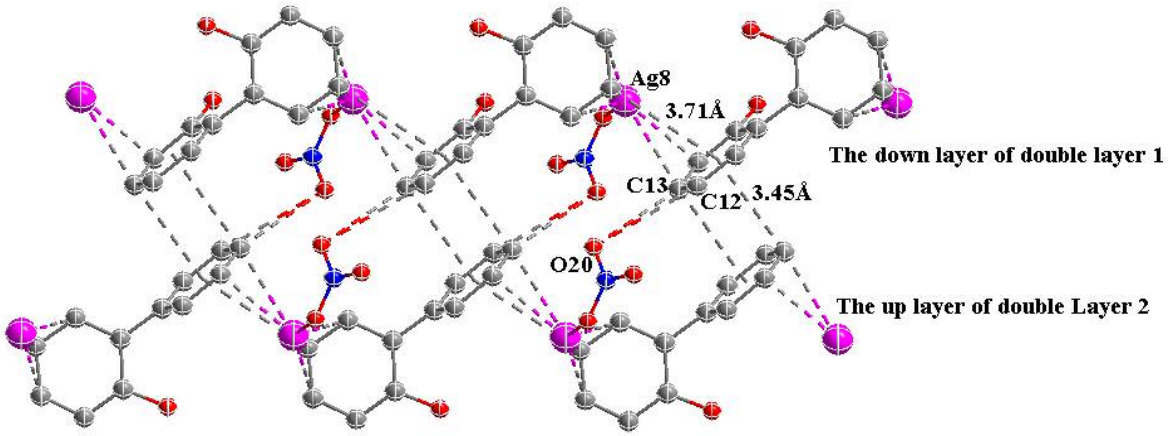


Figure S2. Details of the interactions (Ag-aromatic, edge-to-face π-π, face-to-face π-π interactions and hydrogen bonds) between two adjacent double layers in **1**. O20···C12, 3.40 Å; O20···C13, 3.36 Å. Color scheme for atoms: Ag purple, C black, O red, N blue.

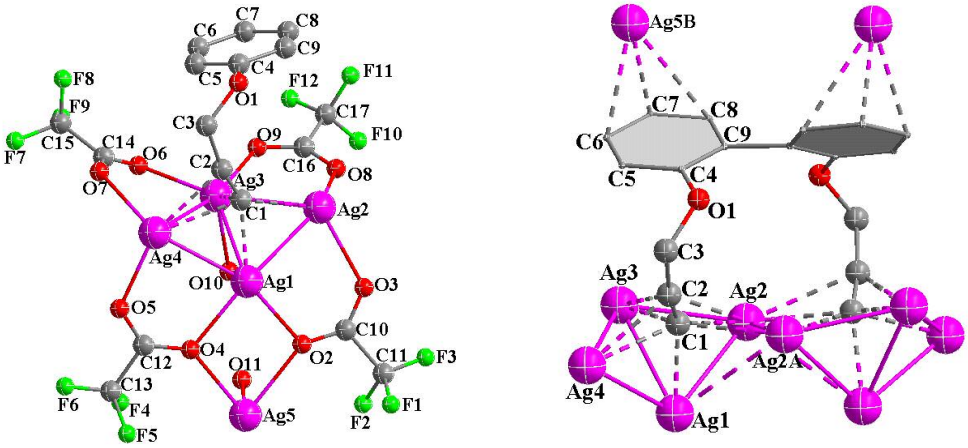


Figure S3. Left: coordination bonding and atom labeling scheme of complex **2**. Right: Coordination modes of L in **2**. Selected bond lengths [Å]: C1-C2, 1.227; Ag1-C1, 2.190; Ag2-C1, 2.380; Ag2A-C1, 2.601; Ag2A-C2, 2.770; Ag3-C1, 2.240; Ag4-C1, 2.443; Ag4-C2, 2.460; Ag1-Ag2, 2.821; Ag1-Ag3, 2.933; Ag1-Ag4, 2.838; Ag1···Ag2A, 3.508; Ag2-Ag2A, 2.878; Ag2-Ag3, 2.890; Ag3-Ag4, 3.104; Ag3···Ag4, 2.841; Ag5B-C6, 2.674; Ag5B-C7, 2.327; Ag5B-C8, 2.880. Symmetry code: A – *x*, *y*, 3/2 – z; B *x*, 1 + *y*, *z*.

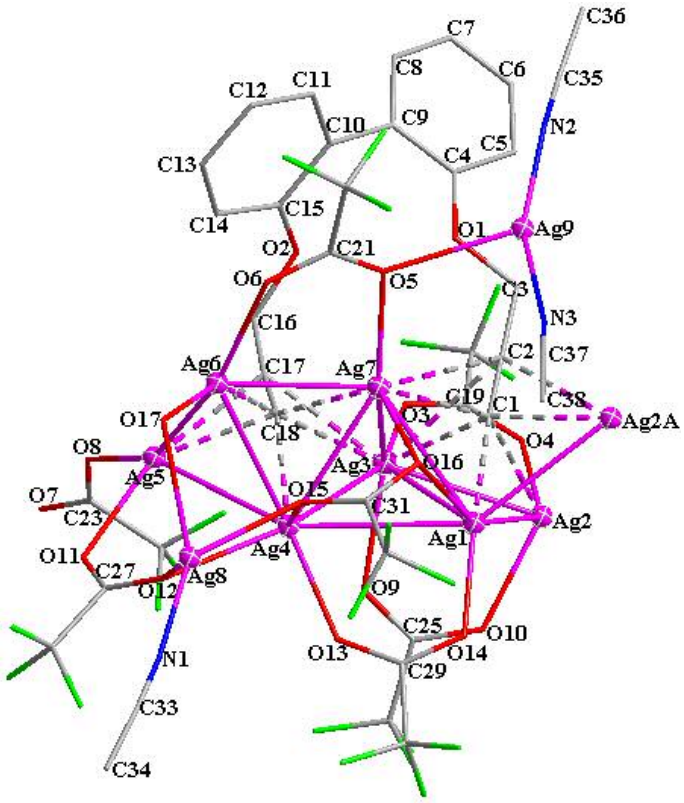


Figure S4. Atom labeling and coordination modes of the L and trifluoroacetate ligands in **3**. Hydrogen atoms are omitted, and the terminal CF_3 groups of trifluoroacetate are not labeled for clarity. Silver atom Ag8 has two disordered positions with an occupancy ratio 0.9:0.1; the minor site Ag8' is omitted for clarity. O17 represents the bridged water molecule. Color scheme for atoms: Ag purple, C black, O red, N blue, F green. Selected bond lengths [Å]: C1-C2, 1.189; C18-C17, 1.213;Ag1-C1, 2.078; Ag2-C1, 2.347; Ag2-C2, 2.659; Ag2A-C1, 2.912; Ag3-C1, 2.538; Ag3-C2, 2.965; Ag7-C1, 2.446; Ag7-C2, 2.942; Ag3-C18, 2.497; Ag3-C17, 2.671; Ag4-C18, 2.210; Ag5-C18, 2.342; Ag5-C17, 2.485; Ag6-C18, 2.377; Ag7-C18, 2.407; Ag1···Ag2, 3.037; Ag1···Ag2A, 3.200; Ag1···Ag3, 3.031; Ag1···Ag7, 2.979; Ag1···Ag4, 3.275; Ag3···Ag4, 3.073; Ag3···Ag7, 3.208; Ag4···Ag5, 3.006; Ag4···Ag6, 3.021; Ag4···Ag7, 2.976; Ag5···Ag6, 3.049; Ag6···Ag7, 2.883. Symmetry code: A 2 - *x*, 1 - *y*, 1 - *z*.

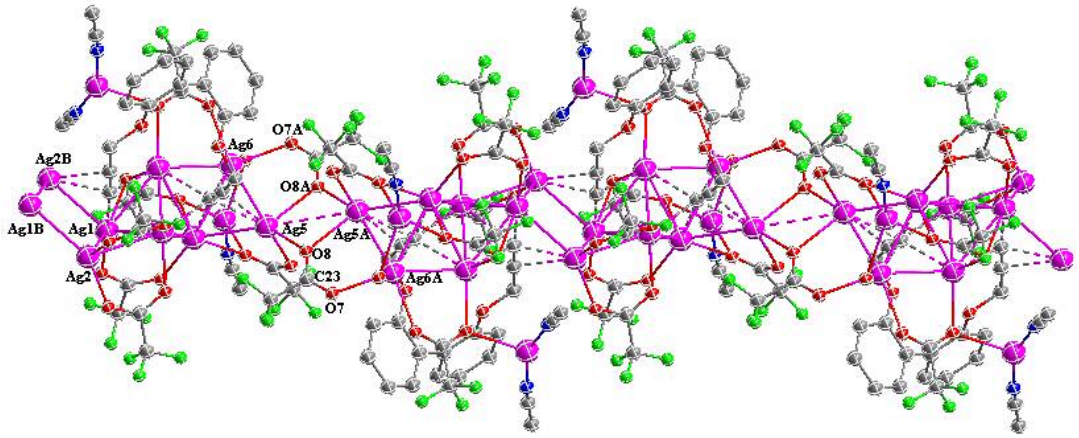


Figure S5. The Ag_{16} cluster in **3** is formed through the Ag1···Ag2B and Ag2-Ag1B (3.037Å) argentophilic interaction between two symmetry-related Ag_8 clusters. These Ag_{16} aggregates are further linked together through trifluoroacetate ligand and weak Ag···Ag interaction between symmetry-related Ag5 ions (3.648Å) to give a polymeric chain. Symmetry code: A 2 - *x*, 1 - *y*, 2 - *z*; B 2 - *x*, 1 - *y*, 1 - *z*. Color scheme for atoms: Ag purple, C black, O red, N blue, F green.