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Supplementary Material

Assembly of Layer-type Organosilver(I) Complexes Incorporating Isomeric Halophenylethynide Ligands and Silver Nitrate

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*1. Description of Crystal Structure of **2** and **5***

(p–BrC$_6$H$_4$C≡CAg)$_2$·AgNO$_3$ (**2**)

Being isomorphous to **1**, the two ethynide moieties are acting in two different coordination modes: μ_4–η^1,η^1,η^1,η^2 mode for C1≡C2 and μ_3–η^1,η^1,η^2 mode for C9≡C10 (Figure S1a). The two Ag_3 and Ag_4 segments are fused to form a Ag_6 aggregate through vertex sharing of silver atom Ag2. Such Ag_6 aggregates are further linked together to generate a similar argentophilic silver(I) layer (Figure S1b). The *p*–BrC$_6$H$_4$C≡C$^-$ groups are arranged on both sides of the layer structure and held tightly by continuous off-set face-to-face π–π stacking interaction (inter-centroid distances ring I···ring II′, 3.790(3) Å; ring II′···ring I′′, 3.948(3) Å) (Figure S1c).

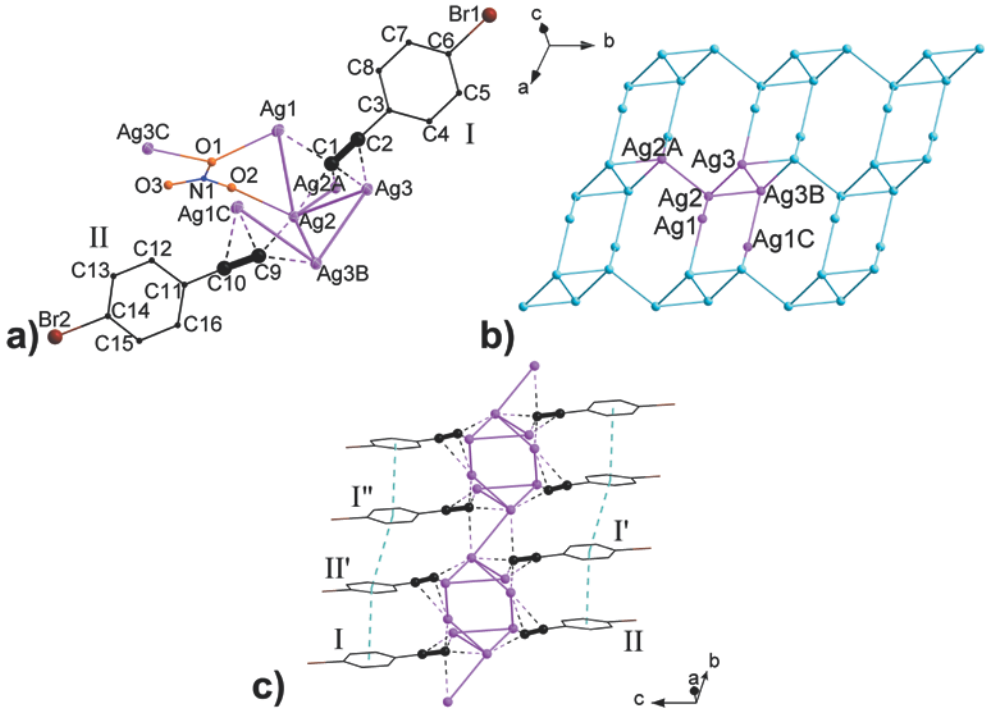

Figure S1. a) Perspective view of coordination geometry in double salt (*p*–BrC$_6$H$_4$C≡CAg)$_2$·AgNO$_3$ (**2**). The argentophilic Ag···Ag distances shown as thick rods lie in the range 2.70–3.40Å. Silver atoms are drawn as thermal ellipsoids (50% probability level) with

atom labeling. b) Perspective view of silver(I) layer in **2**. c) Perspective view of crystal packing in 2, showing all notable π–π stacking interactions. Symmetry code: A: 1–*x*, 1–*y*, 1–*z*, B: 1–*x*, 2–*y*, 1–*z*, C: 2–*x*, 2–*y*, 1–*z*.

(m–BrC$_6$H$_4$C≡CAg)$_2$·AgNO$_3$ (**5**)

Complex **5** is also found to be isomorphous to **4**, the two independent ethynide moieties exhibit different coordination modes: μ_4–η^1,η^1,η^1,η^2 for C1≡C2 and μ_3–η^1,η^1,η^2 for C9≡C10 (Figure S2a). A similar infinite zigzag silver(I) chain is also formed along the *b*-axis through argentophilic interaction and such chains are interconnected by weak Ag···Ag interaction (Ag3···Ag2E, 3.444(5) Å) along the *a*-axis to generate a argentophilic layer structure (Figure S2b).

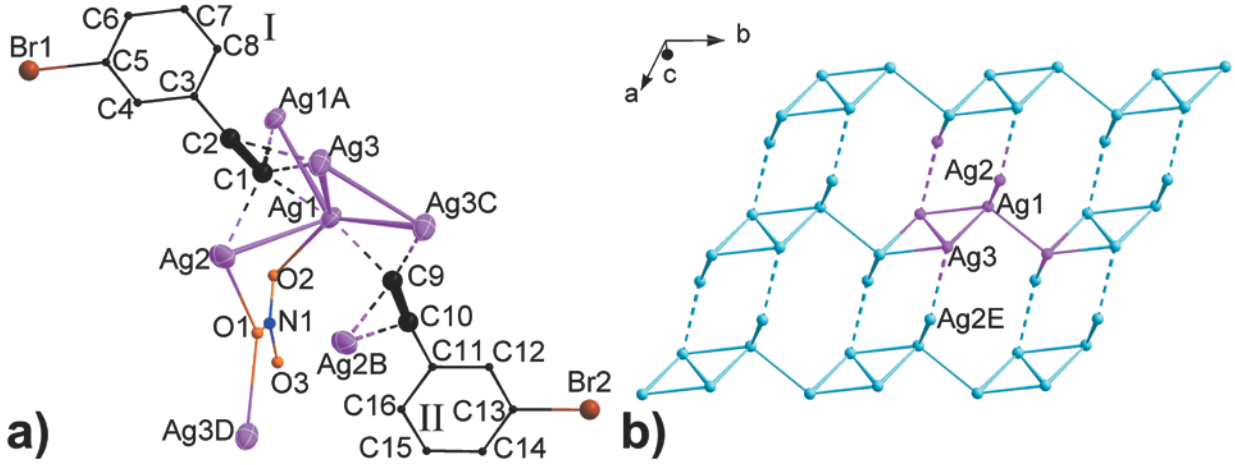

Figure S2. a) Perspective view of coordination geometry in double salt (*m*–BrC$_6$H$_4$C≡CAg)$_2$·AgNO$_3$ (**5**). The argentophilic Ag···Ag distances shown as thick rods lie in the range 2.70–3.40Å. Silver atoms are drawn as thermal ellipsoids (50% probability level) with atom labeling. b) Perspective view of the argentophilic silver(I) layer in **5**. Symmetry code: A: 1–*x*, 2–*y*, 1–*z*, B: –*x*, 1–*y*, 1–*z*, C: 1–*x*, 1–*y*, 1–*z*, D: –*x*, 1–*y*, 1–*z*, E: 1+*x*, *y*, *z*.

And such layer structure is consolidated by μ_3–coordinated nitrate anions (Figure S3a) and is further stabilized by continuous off-set face-to-face π–π stacking interaction between

phenyl rings (inter-centroid distance ring I···ring II′, 3.808(2) Å; ring I′···ring II′′, 4.138(1) Å) (Figure S3b).

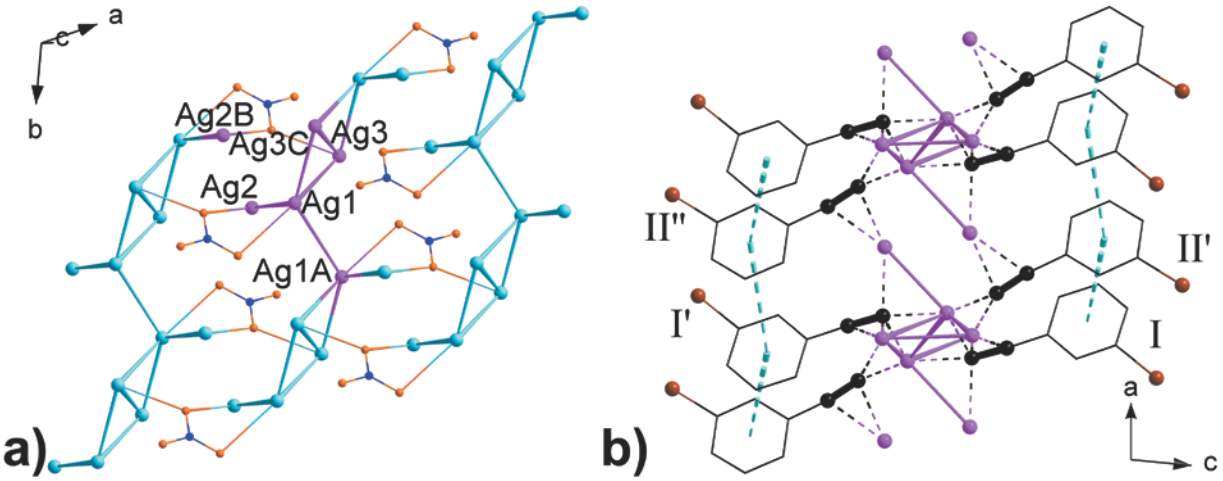

Figure S3. a) Perspective view of coordination geometry of the nitrate anions in **5**. b) Perspective view of the argentophilic layer in **5** along the *b*-axis, showing all notable π–π stacking interactions.