

# **Supplementary Material**

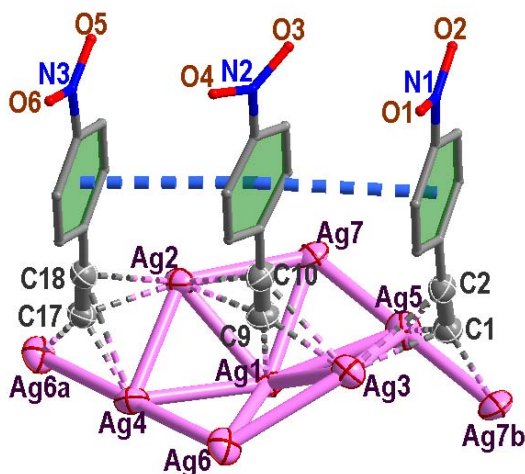
## **Coordination Networks Constructed with the Supramolecular Synthon 4-Nitrophenyl-C≡C $\supset$ Ag<sub>n</sub> (n = 3, 4, 5)**

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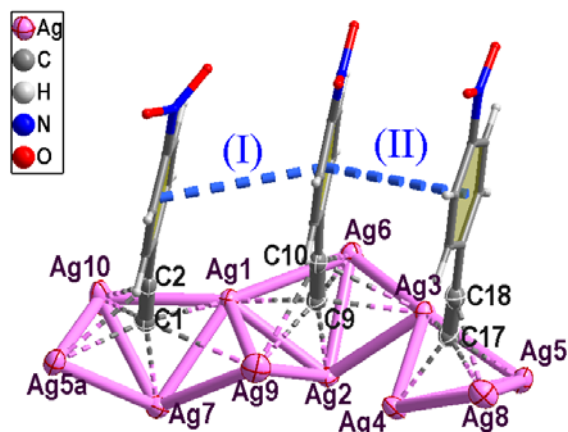
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## Selected bond length information in regard to ethynide-silver coordination geometries in compound 3, 4, 6 and 10.

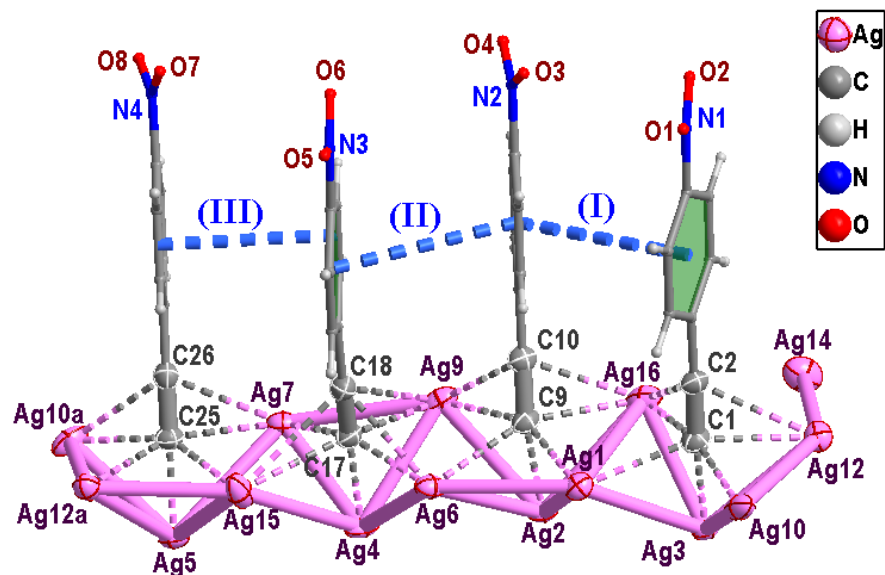
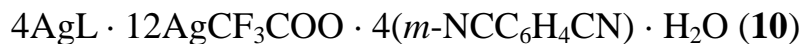


**Fig. S1.** Selected bond lengths information for compound 3 [Å]: C1≡C2 1.216(7), C9≡C10 1.199(7), C17≡C18 1.216(7), C1–Ag7b 2.086(5), C1–Ag3 2.425(5), C1–Ag5 2.172(5), C2–Ag3 2.734(5), C2–Ag5 3.045(5), C9–Ag1 2.114(5), C9–Ag2 2.433(5), C9–Ag3 2.378(5), C10–Ag2 2.906(5), C10–Ag3 2.818(5), C17–Ag6a 2.081(5), C17–Ag2 2.429(5), C17–Ag4 2.165(5), C18–Ag2 2.753(5), C18–Ag4 3.207(5), Ag7b⋯Ag5 2.841(1), Ag6a⋯Ag4 2.839(1), Ag1⋯Ag2 2.910(1), Ag1⋯Ag3 2.937(1), Ag1⋯Ag4 3.160(1), Ag1⋯Ag6 3.269(1), Ag1⋯Ag7 3.257(1), Ag2⋯Ag4 2.973(1), Ag2⋯Ag7 3.256(1), Ag3⋯Ag5 2.944(1), Ag3⋯Ag6 3.183(1), Ag4⋯Ag6 2.839(1), Ag5⋯Ag7 2.841(1), Symmetry code: a 1–x, 2–y, 2–z, b 2–x, 2–y, 2–z.

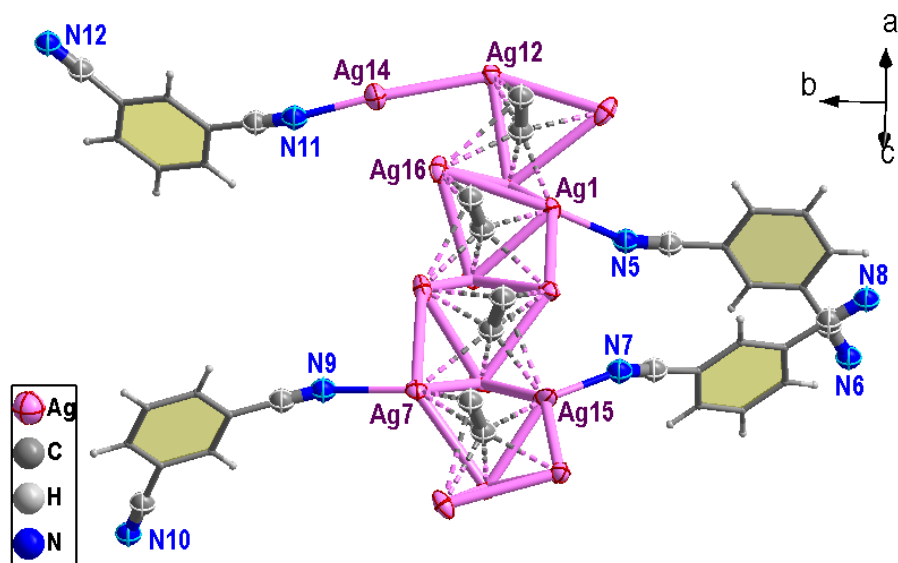


**Fig. S2.** Selected bond lengths information for compound **4** [Å]: C1≡C2 1.219(6), C9≡C10 1.223(6), C17≡C18 1.215(6), C1–Ag1 2.477(4), C1–Ag7 2.132(4), C1–Ag9 2.928(4), C1–Ag10 2.180(4), C1–Ag5a 2.432(4), C2–Ag10 2.973(4), C2–Ag5a 2.761(4), C9–Ag1 2.370(4), C9–Ag2 2.148(4), C9–Ag3 2.487(4), C9–Ag6 2.409(4), C9–Ag9 2.461(4), C10–Ag3 2.798(4), C10–Ag9 3.000(4), C17–Ag3 2.378(4), C17–Ag4 2.150(4), C17–Ag5 2.271(4), C17–Ag8 2.422(4), C18–Ag8 2.539(4), Ag1⋯Ag2 2.839(1), Ag1⋯Ag6 3.075(1), Ag1⋯Ag7 3.026(1), Ag1⋯Ag9 3.037(1), Ag1⋯Ag10 2.947(1), Ag2⋯Ag3 2.977(1), Ag2⋯Ag6 2.952(1), Ag2⋯Ag9 2.981(1), Ag3⋯Ag4 2.859(1), Ag3⋯Ag5 2.932(1), Ag3⋯Ag6 3.067(1), Ag4⋯Ag5 3.143(1), Ag4⋯Ag8 3.043(1), Ag5⋯Ag8 3.123(1), Ag7⋯Ag9 3.010(1), Ag7⋯Ag10 3.022(1), Ag7⋯Ag5a 3.011(1), Ag10⋯Ag5a 3.244(1). Symmetry code:  $a-x-1, y, z$ .





(a)



(b)

**Fig. S4.** (a) Silver-ethynide coordination environment in compound **10**. Selected bond lengths information for compound **10** [Å]: C1≡C2 1.223(9), C9≡C10 1.231(9), C17≡C18 1.211(9), C25≡C26 1.225(9), C1–Ag1 2.494(6), C1–Ag3 2.096(7), C1–Ag10 2.592(7), C1–Ag12 2.453(6), C1–Ag16 2.561(7), C2–Ag12, C2–Ag16, C9–Ag1 2.356(6), C9–Ag2 2.814(6), C9–Ag6 2.823(7), C9–Ag9 2.552(6), C9–Ag16 2.468(6), C10–Ag9 2.743(7),

C10–Ag16 2.683(6), C17–Ag4 2.111(7), C17–Ag6 2.748(6), C17–Ag7 2.659(7),  
C17–Ag9 2.382(7), C17–Ag15 2.529(7), C18–Ag6 2.732(6), C18–Ag9 2.884(6),  
C18–Ag15 2.898(7), C25–Ag5 2.122(7), C25–Ag7 2.679(6), C25–Ag15 2.352(6),  
C25–Ag10a 2.493(6), C25–Ag12a 2.427(7), C26–Ag7 2.941(6), C26–Ag10a 2.843(7),  
Ag1…Ag2 2.853(1), Ag1…Ag3 2.896(1), Ag1…Ag6 2.987(1), Ag1…Ag16 3.162(1),  
Ag2…Ag6 3.108(1), Ag2…Ag9 3.115(1), Ag2…Ag16 3.032(1), Ag3…Ag10 3.228(1),  
Ag3…Ag12 2.971(1), Ag3…Ag16 3.058(1), Ag4…Ag6 3.028(1), Ag4…Ag7 2.880(1),  
Ag4…Ag9 2.972(1), Ag4…Ag15 3.066(1), Ag5…Ag7 3.208(1), Ag5…Ag15 2.818(1),  
Ag5…Ag10a 2.922(1), Ag5…Ag12a 3.009(1), Ag7…Ag9 3.264(1), Ag12…Ag14 3.175(1),  
Ag15…Ag12a 3.003(1), Ag10a…Ag12a 3.204(1). Symmetry code: a  $x$ ,  $1.5-y$ ,  $0.5+z$ , b  $x$ ,  
 $1.5-y$ ,  $-0.5+z$ . **(b)** Geometrical arrangement of the nitrile ligands.