Supplementary information for:

Benzenepolycarboxylate-templated assembly of silver coordination polymers exhibiting argentophilic honeycomb layer and tubular motifs

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This PDF file includes:

Experimental Section.

Single-crystal data of complexes were collected on a Bruker SMART APEX CCD diffractometer[1] with MoKα radiation (λ =0.71073 Å) using the ω scan mode at room temperature. Empirical absorption corrections were applied to the intensities using the SADABS program.[2] The structures were solved using the program SHELXS-97[3] and refined with the program SHELXL-97.[4] All nonhydrogen atoms were subjected to anisotropic refinement. The hydrogen atoms of the organic ligands were included in the structure factor calculation at idealized positions using a riding model and refined isotropically. Possible hydrogen atoms of the coordinated and solvent water molecules were located from difference Fourier maps, and then initially refined making use of SHELXL DFIX restraints. In the final rounds of refinements these H atoms were then placed in fixed positions with assigned isotropic parameters and allowed for as riding atoms.

Synthesis of complex 1

Excess aqueous NH_3 solution was slowly added dropwise to a suspension of Ag_2O (0.023 g, 0.1 mmol) in MeOH/H_2O (6 mL, 5:1 v/v), and the mixture was stirred for 15 min. H_4btca (0.013 g, 0.05 mmol) was then slowly added, and stirring was continued for another 30 min. The resultant colorless solution was allowed to stand in the dark at room temperature for a week to give colorless prism of **1** (yield, 55% based on silver). Anal. Calcd for $C_{11}H_{16}Ag_4N_2O_{11}$ (783.74): C, 16.86; H, 2.06; N, 3.57 %. Found: C, 17.02; H, 2.11; N, 3.69 %. IR /cm^{-1} (KBr): 3463 (s), 3240 (s), 1584 (s), 1365 (m), 909 (w), 814(w), 764 (w), 696 (w), 506 (w).

Synthesis of complex 2

The procedure is similar to the synthesis of **1** except that H_5bpca (0.015 g, 0.05 mmol) was used instead of H_4btca. The resultant colorless solution was allowed to stand in the dark at room temperature for a week to give colorless prism of **2** (yield, 65% based on silver). Anal. Calcd for $C_{11}H_5Ag_5O_{12}$ (868.50): C, 15.21; H, 0.58 %. Found:

C, 15.22; H, 0.66 %. IR /cm^{-1} (KBr): 3440 (s), 1590 (s), 1358 (m), 1326 (m), 1129 (w), 808 (w), 711 (w), 569 (w), 522 (w).

Table S1 Selected bond distances and angles for complexes **1** and **2**.

		1			
Ag1–O3	2.161(1)	Ag1–O6#6	2.159(9)	Ag2–O9	2.056(2)
Ag2–O1W	2.430(5)	Ag3–N1	2.109(2)	Ag3–N2	2.127(2)
Ag4–O8#8	2.146(1)				
O6#6–Ag1–O3	173.5(4)	O9–Ag2–O1W	152.9(1)	N1–Ag3–N2	176.5(6)
O8#7–Ag4–O1	172.3(4)				
		2			
Ag1–O5#9	2.213(7)	Ag1–O3	2.216(8)	Ag1–O2#3	2.558(7)
Ag2–O2	2.399(7)	Ag2–O4#2	2.312(7)	Ag1···Ag2	2.926(1)
Ag1···Ag2#10	3.184(1)	Ag1···Ag3	3.122(3)	Ag3···Ag3#11	2.904(5)
O5#9–Ag1–O3	172.6(3)	O5#9–Ag1–O2#3	95.8(3)	O3–Ag1–O2#3	88.5(3)
O4#2–Ag2–O2	114.9(2)				

Symmetry codes: #6 – *x* + 1.5, *y* – 0.5, *z*; #8 *x*, *y* – 1, *z* for **1**; #2 – *x* + 0.5, – *y* + 1.5, *z* + 0.5; #3 – *x* + 0.5, – *y* +1.5, *z* – 0.5; #9 – *x* + 0.5, *y* – 0.5, *z*; #10 *x*, – *y* + 1, *z* – 1/2; #11 – *x*, *y*, – *z* + 0.5 for **2**.

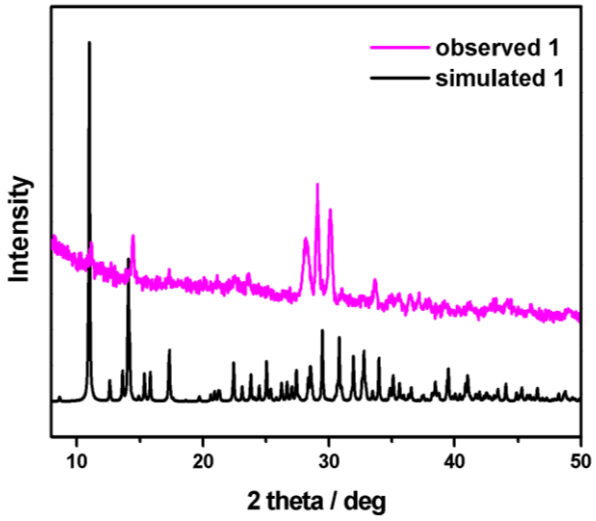

Fig. S1 Simulated and observed PXRD patterns of **1**.

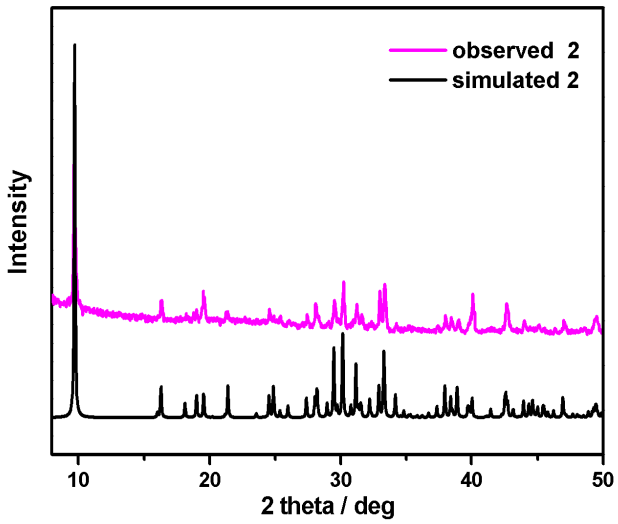

Fig. S2 Simulated and observed PXRD patterns of **2**.

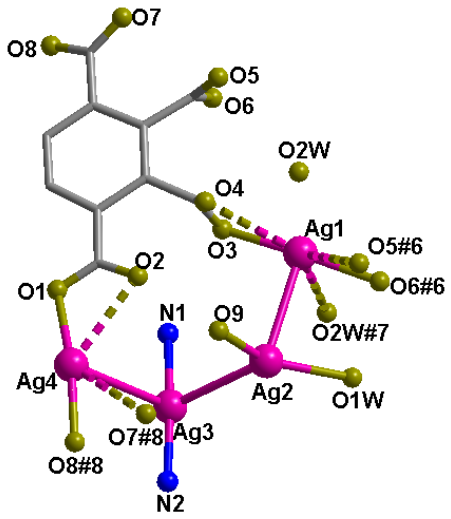

Fig. S3 Perspective view of the asymmetric unit of **1**. Symmetry codes: #6 – *x* + 1.5, *y* – 0.5, *z*; #7 *x*, – *y* +1, *z*– 0.5; #8 *x*, *y* – 1, *z*.

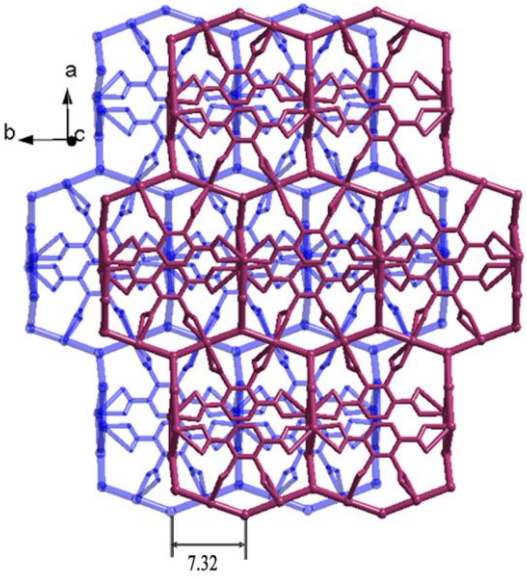

Fig. S4 The silver atoms in two adjacent layers in the complex are arranged staggered and offset by 7.32 Å along the *b* axis.

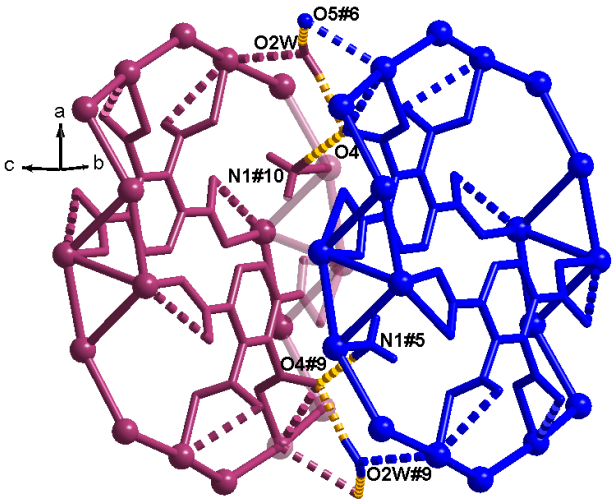

Fig. S5 Presentation view of O2W–H2WA···O4, O2W–H2WB···O5#6 and N1#10–H1A···O4 hydrogen bonding between adjacent layers in complex **1**. Symmetry codes: #5 – *x* + 1, *y*, – *z* + 0.5; #6 – *x* + 1.5, *y* – 0.5, *z*; #9 – *x* + 1, – *y* + 1, – *z* + 1; #10 *x*, – *y* + 1, *z* + 0.5.

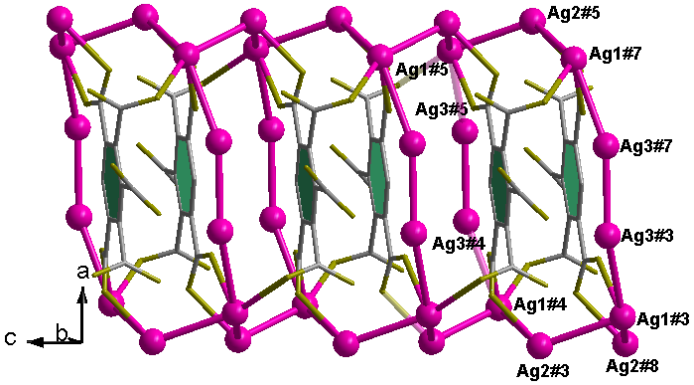

Fig. S6 View of the silver tubular motif in **2**. Symmetry codes: #3 – *x* + 0.5, – *y* + 1.5, *z* – 0.5; #4 – *x* + 0.5, *y* + 0.5, *z*; #5 *x* + 0.5, *y* + 0.5, – *z* + 0.5; #7 *x* + 0.5, – *y* + 1.5, – *z*; #8 – *x* + 0.5, *y* + 0.5, *z* – 1.

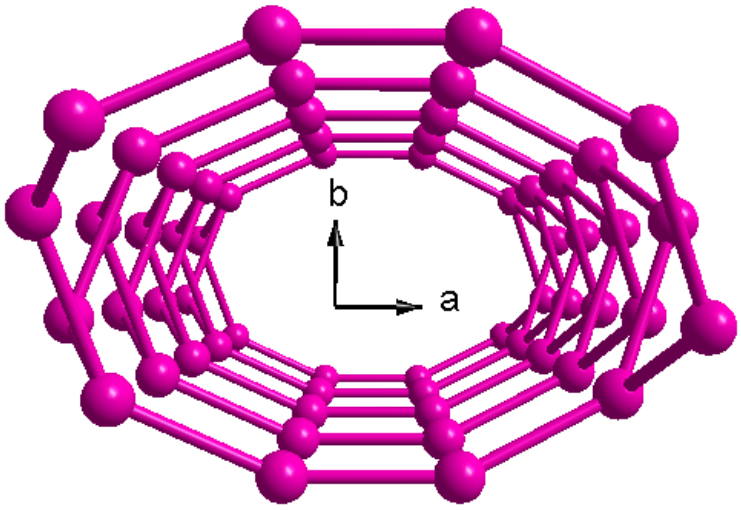

Fig. S7 Top view of the silver tubular motif viewed down the *c* axis.

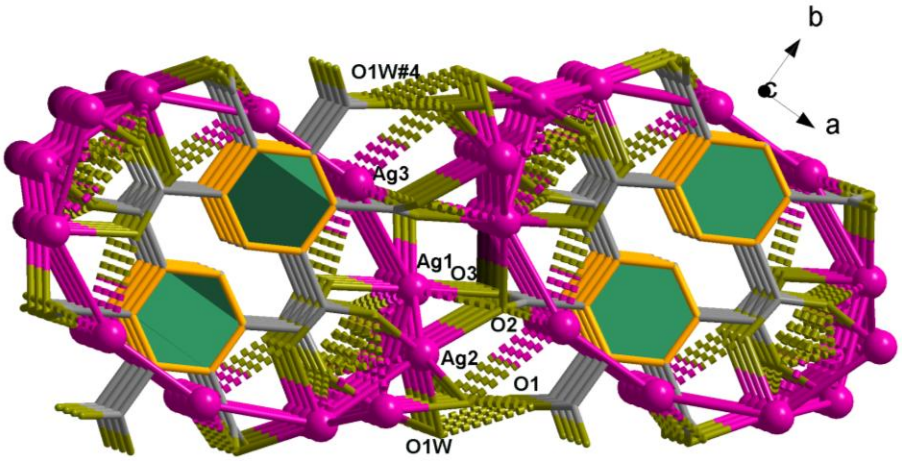

Fig. S8 Adjacent silver tubes linked with each other through Ag–O (Ag1–O3 2.216 Å and Ag2–O2 2.399 Å) and weak Ag–O (Ag1–O2 2.922 Å and Ag3–O1W#4 3.088 Å) bonds to form three-dimensional coordination framework in **2**.

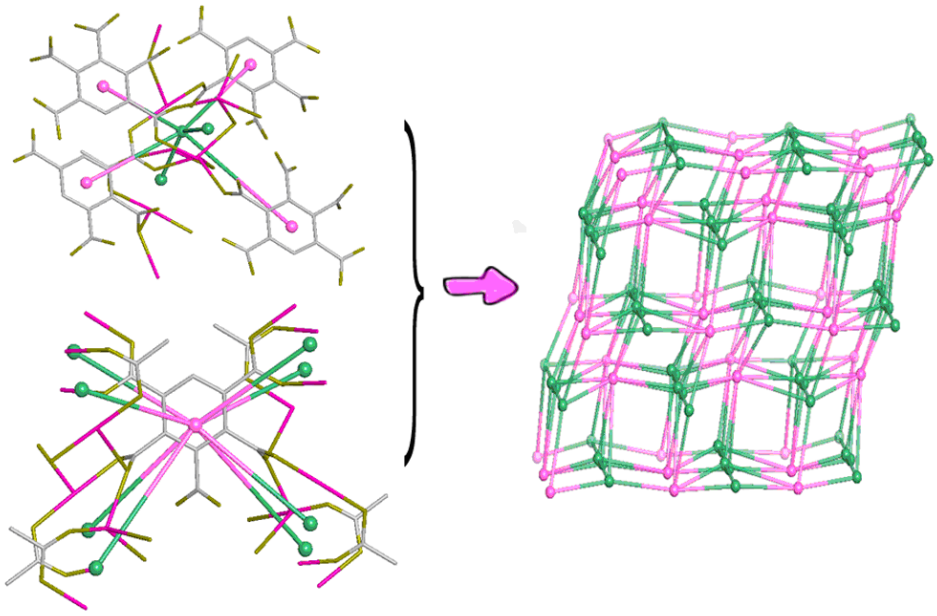

Fig. S9 The two-nodal (6,8) connected topology of **2**.

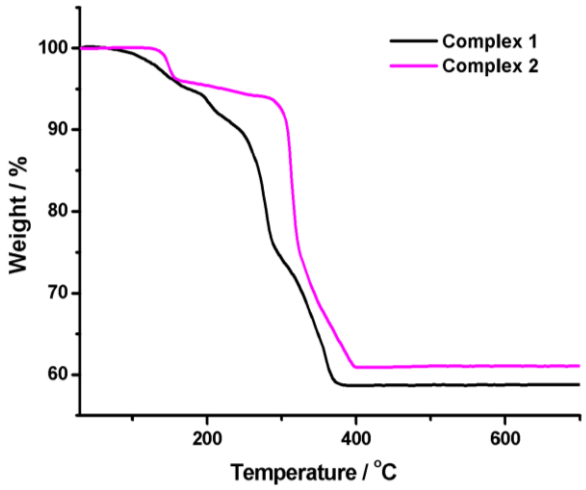

Fig. S10 TG curves for compounds **1** and **2**.

Thermogravimetric analysis (TG) was performed on complexes **1** and **2** to study the thermal stability of these polymers. Complex **1** begins to decompose from room temperature, and end at 220 ^{o}C. The weight loss (found: 13.1 %) corresponds to the loss of all of the water, methanol and ammonia molecules (calculated 11.9%), then the host framework started to decompose and ends above 378 ^{o}C. The TG curve of **2** shows that the first weight loss of 3.9 % in the region of 30–160 ^{o}C corresponds to the expulsion of the water molecules (calculated 4.1 %). The residual framework starts to decompose beyond 288 ^{o}C with a series of complicated weight losses.

References

1. SMART and SAINT. *Area Detector Control and Integration Software; Siemens Analytical X-Ray Systems*, Inc.: Madison, WI, 1996.
2. G. M. Sheldrick, *SADABS 2.05*, University of Göttingen, Germany.
3. G. M. Sheldrick, *Acta Crystallogr., Sect. A: Found. Crystallogr.*, 1990, **46**, 457; G. M. Sheldrick, *SHELXS-97, Program for solution of crystal structures*, University of Göttingen, Germany, 1997.
4. G. M. Sheldrick, *Acta Crystallogr., Sect. A: Found. Crystallogr.*, 2008, **64**, 112.