Electronic Supplementary Information (ESI)

An Unusual 1D Ladder-like Silver(I) Coordination Polymer Involving Novel 1D → 3D Five-Folded Interpenetrated and [3+2] Catenaned Features Generated by Ag···O Interactions

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Materials and Physical Measurements. All the solvents and reagents for synthesis were commercially available and used without further purification. The synthesis was carried out in 25

mL Teflon-lined vessel under autogenous pressure. Elemental analyses (C, H, and N) were determined with a VarioEL III Elemental analyzer. Fourier transform (FT) IR spectra (KBr pellets) were recorded with a BRUKER EQUINOX-55 spectrometer in the range of 4000 – 400 cm^{-1}. The X-ray powder diffraction patterns were recorded with a Rigaku D/MAX-3C diffractometer with a scan speed of 2 °/min and a step size of 0.02° in 2θ. Thermogravimetric analyses (TGA) was performed on a NETZSCH STA 449C microanalyzer in a nitrogen atmosphere at a heating rate of 10 °C/min between ambient temperature and 1000 °C. Luminescence spectra of the solid samples were recorded with a Hitachi F-4500 fluorescence spectrophotometer at room temperature.

Preparation of $[Ag_3(cis\text{-pda})(bipy)_3]_n \cdot 0.5n(trans\text{-pda}) \cdot 5nH_2O$ (1): The mixture of AgOAc (16.7 mg, 0.1 mmol), H_2pda (9.7 mg, 0.05 mmol), bipy (15.6 mg, 0.1 mmol), and H_2O 15 mL was adjusted to pH = 6 with 0.5M NaOH solution and then placed in a sealed Teflon-lined stainless steel vessel, heating at 130 °C for three days. Then the reaction system was cooled to the room temperature over two days. Colorless needle shaped crystals of **1** were obtained. Yield: 53%. FT-IR (KBr, cm^{-1}): 3420s, 3047m, 1732w, 1593s, 1483w, 1409m, 1384m, 1316w, 1269w, 1219m, 1040w, 848w, 804m, 716w, 622m, 508w; elemental analysis calcd (%) for $C_{45}H_{46}O_{11}N_6Ag_3$: C 46.18, H 3.96, N 7.18; found: C 46.03, H 3.84, N 7.12.

Single-crystal X-ray diffraction: X-ray diffraction data for complex **1** was collected on a Bruker Apex II CCD diffractometer with Mo-Kα radiation (λ = 0.71073 Å) at 296(2) K. The semi-empirical absorption correction was applied using SADABS and the SAINT program was used for integration of the diffraction profiles. The structure was solved by direct methods using the SHELXS program of SHELXTL and refined using SHELXL by full-matrix least-squares methods on F^2 with anisotropic thermal parameters for all non-H atoms. In general, C-bound H atoms were located geometrically and refined as riding, whereas O-bound H atoms were first determined in difference Fourier syntheses and then fixed at the calculated positions. Isotropic displacement parameters of the H atoms were derived from their parent atoms. Further crystallographic details are summarized in **Table S1**. The selected bond parameters and hydrogen-bonding geometries are listed in **Table S2** and **Table S3**, respectively.

Table S1. Crystallographic Data of 1.

Complex	**1**
Empirical formula	$C_{45}H_{46}O_{11}N_6Ag_3$
Formula weight	1170.49
Crystal system	monoclinic
Space group	*C2/c*
a/Å	39.052(6)
b/Å	9.8693(13)
c/Å	26.197(4)
α/°	90
β/°	120.120(5)
γ/°	90
V/Å^3	8733(2)
Z	8
T/K	296(2)
d_{calcd}/g·cm^{-3}	1.780
μ/mm^{-1}	1.402
F(000)	4696
θ Range(°)	1.21 – 25.00
Reflections collected	21186
R_{int}	0.0587
Goodness-of-fit on F^2	1.008
R_1[a], wR_2[b] [$I>2\sigma(I)$]	0.0678, 0.1953
R_1, wR_2 (all data)	0.1255, 0.2236

[a] $R_1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$; [b] $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$

Table S2. Selected bond lengths (Å) and angles (°) of 1.

Ag(1)-N(5)	2.188(7)	Ag(2)-N(3)	2.200(7)
Ag(1)-N(1)	2.212(6)	Ag(2)-N(2)	2.227(7)
Ag(1)-O(3)	2.547(7)	Ag(3)-N(4)#2	2.163(7)
Ag(1)-Ag(1)#1	3.2282(16)	Ag(3)-N(6)	2.172(7)
Ag(2)-Ag(3)#1	3.0903(13)	Ag(3)-Ag(2)#1	3.0903(13)
N(5)-Ag(1)-N(1)	151.1(3)	N(5)-Ag(1)-Ag(1)#1	77.8(2)
N(5)-Ag(1)-O(3)	120.2(3)	N(1)-Ag(1)-Ag(1)#1	103.87(19)
N(1)-Ag(1)-O(3)	87.5(2)	O(3)-Ag(1)-Ag(1)#1	106.29(15)
N(3)-Ag(2)-N(2)	173.0(3)	N(4)#2-Ag(3)-N(6)	165.9(3)
N(3)-Ag(2)-Ag(3)#1	102.03(19)	N(4)#2-Ag(3)-Ag(2)#1	88.2(2)
N(2)-Ag(2)-Ag(3)#1	83.90(19)	N(6)-Ag(3)-Ag(2)#1	105.6(2)

Symmetry codes: #1 -x, -y, -z+1; #2 x-1/2, y-5/2, z-1; #3 x+1/2, y+5/2, z+1; #4 -x, y, -z+3/2.

Table S3. Hydrogen-bonding lengths (Å) and angles (°) of 1.

D-H···A	d(H···A)	d(D···A)	<(DHA)
O(7)-H(7C)...O(7)#1	2.11	2.925(15)	179.8
O(7)-H(7D)...O(6)#2	1.98	2.785(11)	166.9
O(8)-H(8C)...O(7)	2.05	2.868(10)	179.6
O(8)-H(8D)...O(4)#3	1.98	2.795(11)	179.7
O(9)-H(9C)...O(5)#4	1.97	2.786(11)	179.4
O(9)-H(9D)...O(8)	2.06	2.883(11)	179.8
O(10)-H(10C)...O(9)#4	2.00	2.821(12)	179.5
O(10)-H(10D)...O(3)#4	2.03	2.855(11)	179.1
O(11)-H(11C)...O(10)	1.88	2.703(18)	178.8
O(11)-H(11D)...O(2)#4	1.78	2.60(3)	179.2

Symmetry codes: #1 -x, y, -z+1/2; #2 x, -y+2, z-1/2; #3 x, y+1, z; #4 x, -y+1, z-1/2.

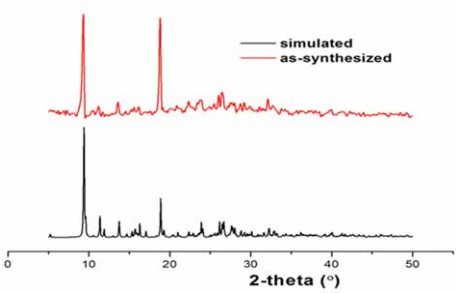

Figure S1. Powder X-ray diffraction (PXRD) patterns of **1**.

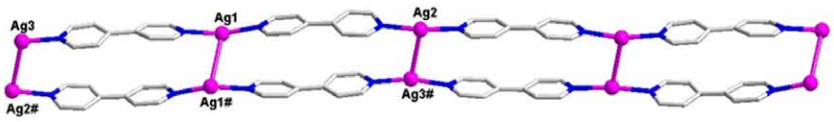

Figure S2. 1D ladder-like sheet based on such Ag–Ag interactions and bridging bipy ligands.

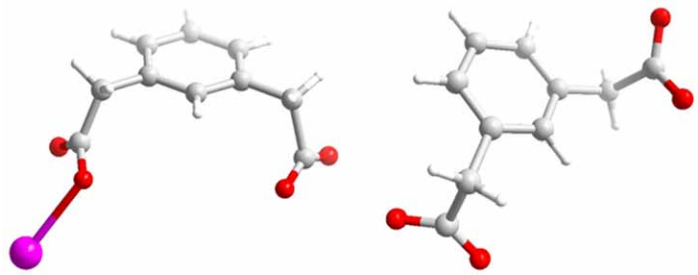

Figure S3. Two distinct steric conformations of pda ligands in **1**: *cis* monodentate mode (left) and free uncoordinated *trans* mode (right).

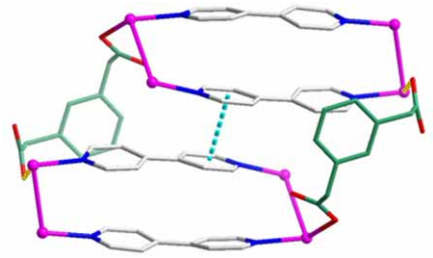

Figure S4. The strong π···π stacking with the nearest separation of 3.445(4) Å in **1**.

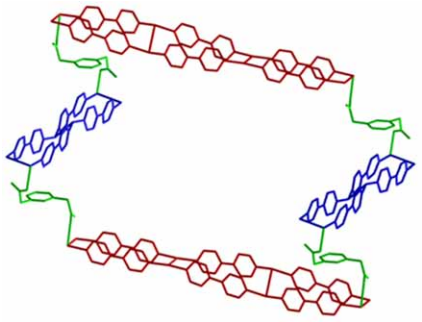

Figure S5. The free *trans* pda ligands linked the 1D host chains into a 3D supramolecular framework.

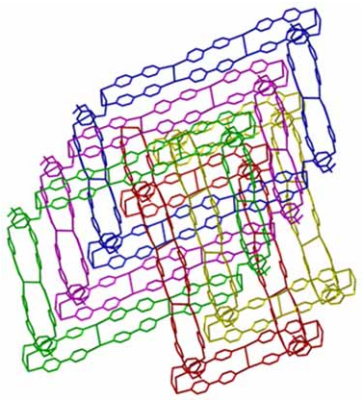

Figure S6. Perspective view of the unique five [3+2] catenations in **1**.

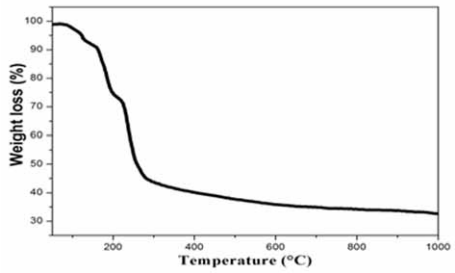

Figure S7. The TGA curve of complex **1**.