Supplementary Information for

Flexible "piperazine-pyrazine" building blocks: conformational isomerism of "equatorial-axial" sites toward the constructions of silver(I) coordination chains

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Experimental Section

General Remarks. All reagents were purchased commercially and were used as received without further purification. ^{1}H NMR spectra were recorded on a Bruker AMX-400 FT-NMR spectrometer. FAB-MS data were obtained using a JMS-700 double focusing mass spectrometer. Thermogravimetric analysis (TGA) was performed under nitrogen with a Perkin-Elmer TGA-7 TG analyzer. Elemental analyses were conducted on a Perkin-Elmer 2400 CHN elemental analyzer. X-ray powder diffraction (XRPD) data were recorded on a Siemens D5000 diffractometer at 40 kV, 30 mA for Cu Kα (λ = 1.5406 Å), with a step size of 0.02° in θ and a scan speed of 1 s per step size. Infrared spectra were recorded on a Perkin-Elmer Paragon 1000 FT-IR spectrometer.

Synthesis of *N*,*N*′-Bis(2-pyrazinyl)piperazine (bpzp). To a solution of piperazine (866 mg, 10 mmol) in ethanol (10 mL), triethylamine (NEt_3, 3.5 mL, 25 mmol) and 2-chloropyrazine (2.3 mL, 25 mmol) were added at room temperature, and the reaction mixture was stirred 48 h at 140 °C. After cooling to room temperature, the solution was treated with saturated aqueous of K_2CO_3. After filtered and washed with distilled water for several times, the deep-yellow precipitate was recrystallized from CH_2Cl_2 and *n*-hexane to yield bpzp as yellow crystals. Yield: 77% (1863 mg, 7.7 mmol). ^{1}H NMR (400 MHz, $CHCl_3$-*d*, δ): 8.16 (d , J = 1.3 Hz, 2H), 8.08 (dd, J = 1.5, 1.0 Hz, 2H), 7.88 (d, J = 2.6Hz, 2H), 3.74 (s, 4H) ppm. FAB-MS (*m/z*): 243 $[M+H]^+$. Anal. Calcd for $C_{12}H_{14}N_6$: C, 59.49; H, 5.82; N, 34.69. Found: C, 59.38; H, 5.89; N, 34.69. IR (cm^{-1}, KBr, ν): 3078, 3045, 2995, 2919, 2891, 2853, 1578, 1523, 1485, 1430, 1375, 1315, 1271, 1249, 1200, 1173, 1140, 1078, 1036, 998, 965, 839, 779, 751, 669, 620, 533, 445, 417.

Synthesis of {[Ag(bpzp)](PF$_6$)}$_n$ (1). A solution of $AgPF_6$ (126 mg, 5.0×10^{-1} mmol) in MeOH (5 mL) was carefully layered on top of THF (10 mL, middle), and a solution of bpzp (121 mg, 5.0×10^{-1} mmol) in CH_2Cl_2 (5 mL, bottom) at room temperature. The solution was allowed to stand for approximately three week, resulting in the formation of yellow-colored crystals of **1**. Yield: 36% (89.0 mg, 1.8×10^{-1} mmol). Anal. Calcd for $C_{12}H_{14}AgF_6N_6P$: C, 29.11; H, 2.85; N, 16.97. Found: C, 29.21; H, 2.96; N, 16.78. IR (cm^{-1}, KBr, ν): 3116, 3083, 2919, 2848, 1589, 1523, 1490, 1436, 1392, 1365, 1315, 1271, 1244, 1205, 1173, 1145, 1124, 1085, 1036, 992, 960, 844, 659, 620, 550, 489, 423.

Synthesis of {[Ag(bpzp)](SbF$_6$)}$_n$ (2). A solution of $AgSbF_6$ (68.7 mg, 2.0×10^{-1} mmol) in MeOH (5 mL) was carefully layered on top of THF (10 mL, middle), and a solution of bpzp (48.5 mg, 2.0×10^{-1} mmol) in CH_2Cl_2 (5 mL, bottom) at room temperature. The solution was allowed to stand for approximately one week, resulting in the formation of yellow-colored crystals of **2**. Yield: 55% (62.2 mg, 1.1×10^{-1} mmol). Anal. Calcd for $C_{12}H_{14}AgF_6N_6Sb$: C, 24.60; H, 2.41; N, 14.34. Found: C, 24.81;

H, 2.57; N, 13.89. IR (cm^{-1}, KBr, ν): 3116, 3083, 2919, 2853, 1584, 1518, 1490, 1387, 1359, 1315, 1271, 1244, 1200, 1173, 1140, 1085, 1036, 998, 954, 828, 773, 746, 664, 642, 615, 549, 483, 423.

Synthesis of {[Ag(bpzp)](ClO$_4$)}$_n$ (3). A solution of $AgClO_4 \cdot xH_2O$ (42.2 mg, 2.0×10^{-1} mmol) in MeOH (5 mL) was carefully layered on top of THF (10 mL, middle), and a solution of bpzp (48.5 mg, 2.0×10^{-1} mmol) in CH_2Cl_2 (5 mL, bottom) at room temperature. The solution was allowed to stand for approximately one week, resulting in the formation of yellow-colored crystals of **3**. Yield: 75% (66.1 mg, 1.5×10^{-1} mmol). Anal. Calcd for $C_{12}H_{14}AgClN_6O_4$: C, 32.06; H, 3.14; N, 18.69. Found: C, 32.21; H, 3.36; N, 18.35. IR (cm^{-1}, KBr, ν): 3105, 3083, 2925, 2886, 2853, 1584, 1518, 1485, 1447, 1430, 1370, 1315, 1271, 1249, 1217, 1145, 1107, 1085, 1069, 998, 834, 620, 549, 429.

Synthesis of {[Ag(bpzp)](NO$_3$)}$_n$ (4). A solution of $AgNO_3$ (17.9 mg, 1.0×10^{-1} mmol) in MeOH (5 mL) was carefully layered on top of THF (10 mL, middle), and a solution of bpzp (24.6 mg, 1.0×10^{-1} mmol) in CH_2Cl_2 (5 mL, bottom) at room temperature. The solution was allowed to stand for approximately one week, resulting in the formation of yellow-colored plate-shaped crystals of **4**. Yield: 86% (35.6 mg, 8.6×10^{-2} mmol). Anal. Calcd for $C_{12}H_{14}AgN_7O_3$: C, 34.97; H, 3.42; N, 23.79. Found: C, 34.59; H, 3.53; N, 23.97. IR (cm^{-1}, KBr, ν): 3098, 3078, 2976, 2893, 2856, 1584, 1520, 1485, 1452, 1428, 1384, 1314, 1269, 1246, 1196, 1142, 1084, 1043, 1004, 980, 946, 847, 777, 750, 669, 640, 547.

Crystal Structure Determination. Single-crystal X-ray diffraction was performed by using a Nonius Kappa CCD diffractometer for **1**–**3** and a Bruker Smart CCD diffractometer for **4**, equipped with graphite monochromatized Mo Kα radiation (λ = 0.71073 Å). Intensity data were collected at 200(2) K within the limits of $2.66° \leq \theta \leq 25.34°$ for **1**, $2.60° \leq \theta \leq 25.37°$ for **2**, and $2.22° \leq \theta \leq 25.36°$ for **3**, and at 293(2) K within the limits of $2.55° \leq \theta \leq 27.48°$ for **4**. Starting models for structure refinement were found using direct methods (SIR92[S1] for **1**, SHELXS-86[S2] for **2** and **3**, and SHELXS-97[S3] for **4**), and the structural data were refined by full-matrix least-squares methods on F^2 using the WINGX[S4] and SHELX-97[S3] program packages. Anisotropical thermal factors were assigned to non-hydrogen atoms.

The positions of the C–H hydrogen atoms were generated geometrically and were assigned isotropic thermal parameters.

References

(S1) A. Altomare, G. Cascarano, C. Giacovazzo and A. Guagliardi, *SIR92*: A program for crystal structure solution. *J. Appl. Crystallogr.*, 1993, **26**, 343.
(S2) G. M. Sheldrick, *SHELXS-86*, Program for Crystal Structure Determination, University of Göttingen: Göttingen, Germany, 1986.
(S3) G. M. Sheldrick, *SHELX-97* (including *SHELXS* and *SHELXL*); University of Göttingen: Göttingen, Germany, 1997.
(S4) *WINGX*: L. J. Farrugia, *J. Appl. Crystallogr.*, 1999, **32**, 837.

Table S1 Crystallographic data for **1**–**4**

	1	**2**	**3**	**4**
Empirical formula	$C_{12}H_{14}AgF_6N_6P$	$C_{12}H_{14}AgF_6N_6Sb$	$C_{12}H_{14}AgClN_6O_4$	$C_{12}H_{14}AgN_7O_3$
M_w	495.13	585.91	449.61	412.17
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic
Space group	*C*2/*c*	*C*2/*c*	*C*2/*c*	*C2*/c
a (Å)	15.8618(4)	15.7412(6)	28.6770(5)	12.595(3)
b (Å)	6.4886(2)	6.6018(2)	13.7370(4)	10.732(2)
c (Å)	16.1829(5)	16.5704(7)	18.4240(4)	10.892(2)
β (deg)	109.0290(10)	109.108(2)	123.9100(10)	108.52(3)
V (Å^3)	1574.54(8)	1627.12(10)	6023.4(2)	1396.0(5)
Z	4	4	16	4
T (K)	200(2)	200(2)	200(2)	293(2)
λ (Å)	0.71073	0.71073	0.71073	0.71073
D_{calc} (g cm^{-3})	2.089	2.392	1.983	1.961
μ (mm^{-1})	1.459	2.939	1.549	1.473
F_{000}	976	1120	3584	824
GOF	1.026	1.046	1.037	1.093
R_1[a], wR_2[b] ($I > 2\sigma(I)$)	0.0286, 0.0691	0.0315, 0.0756	0.0495, 0.1153	0.0180, 0.0462
R_1[a], wR_2[b] (all data)	0.0340, 0.0721	0.0370, 0.0792	0.1008, 0.1541	0.0195, 0.0465
$\Delta\rho_{max}/\Delta\rho_{min}$ (e Å^{-3})	0.497/–0.507	0.615/–1.777	0.910/–1.033	0.490/0.386

[a] $R_1 = \sum\left\|F_o\right|-\left|F_c\right\|\Big/\sum\left|F_o\right|$. [b] $wR_2 = \{\sum[w(F_o^2 - F_c^2)^2]\Big/\sum[w(F_o^2)^2]\}^{1/2}$.

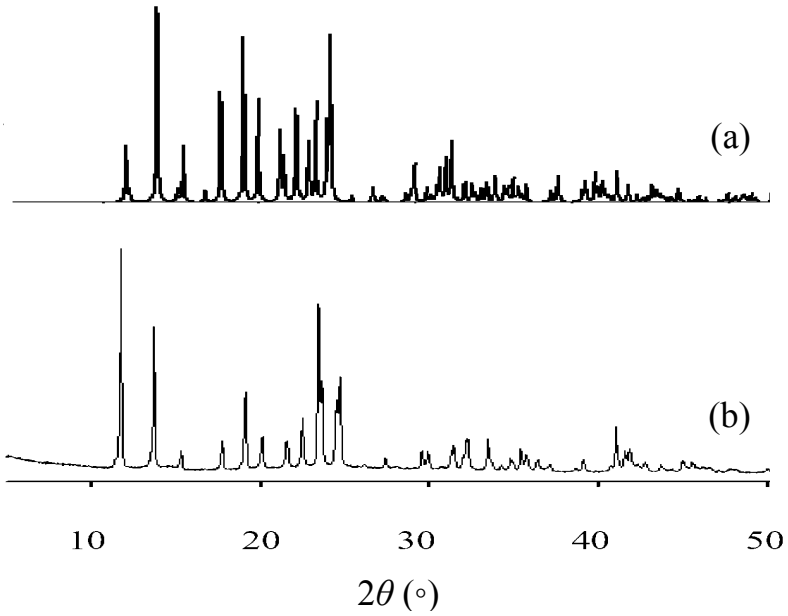


Fig. S1 Powder X-ray diffraction (PXRD) patterns of **1**. (a) Simulated from the single-crystal data. (b) A freshly grounded sample at room temperature.

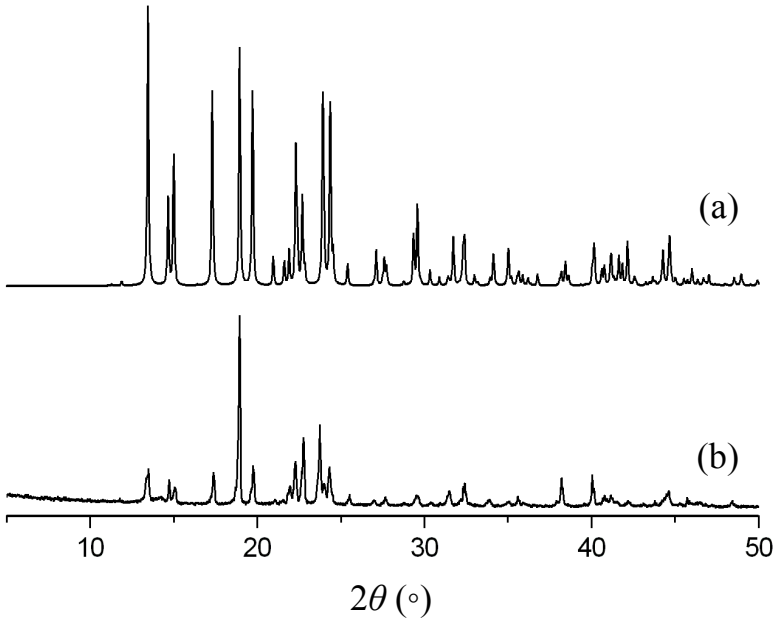


Fig. S2 Powder X-ray diffraction (PXRD) patterns of **2**. (a) Simulated from the single-crystal data. (b) A freshly grounded sample at room temperature.

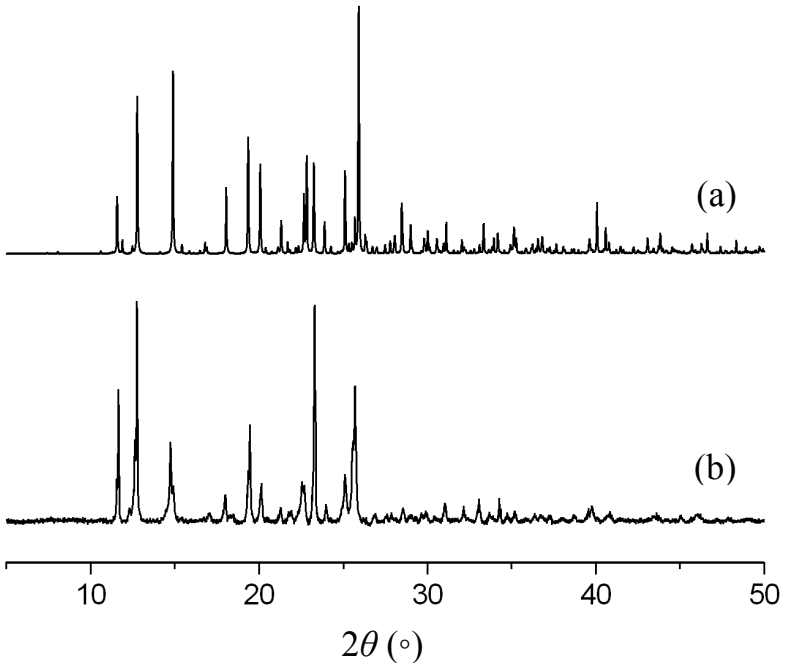


Fig. S3 Powder X-ray diffraction (PXRD) patterns of **3**. (a) Simulated from the single-crystal data. (b) A freshly grounded sample at room temperature.

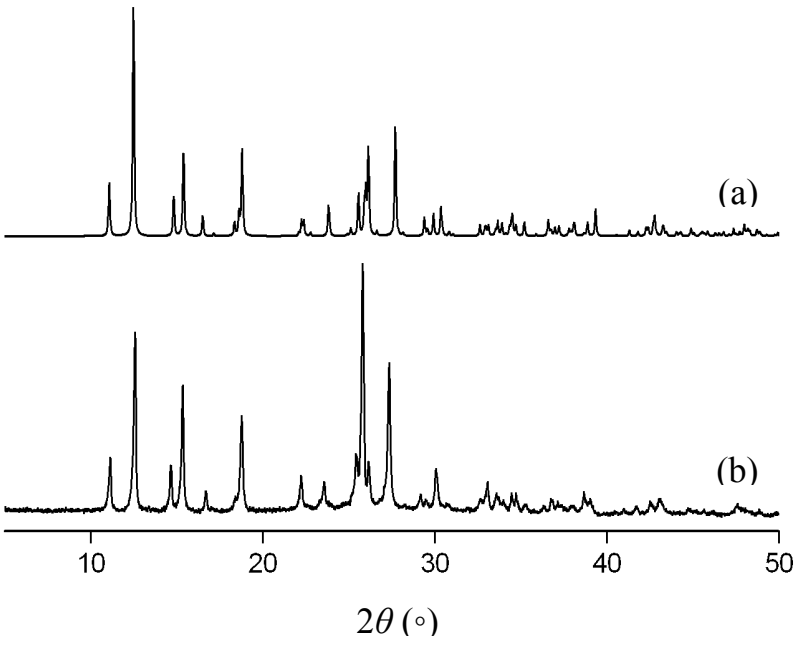


Fig. S4 Powder X-ray diffraction (PXRD) patterns of **4**. (a) Simulated from the single-crystal data. (b) A freshly grounded sample at room temperature.

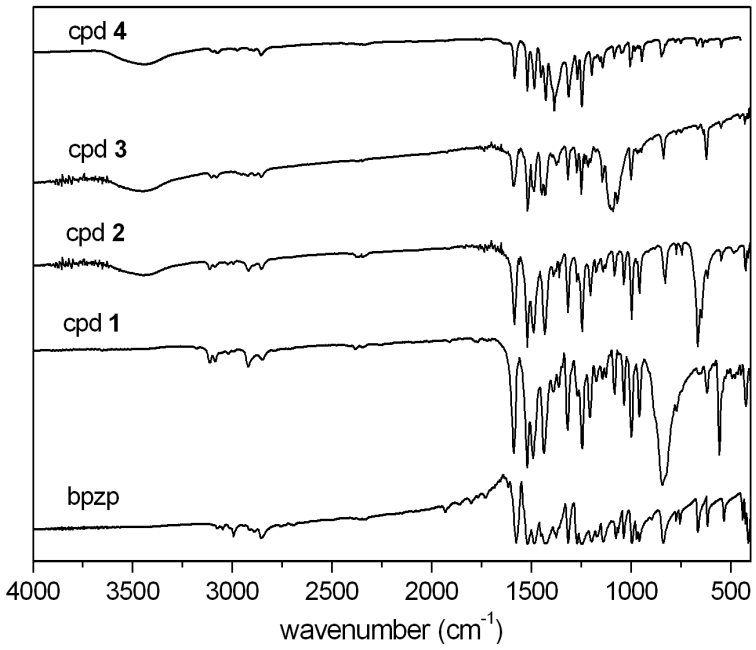


Fig. S5 Infrared spectra of bpzp ligand and snake-like silver(I) coordination polymers **1–4**.

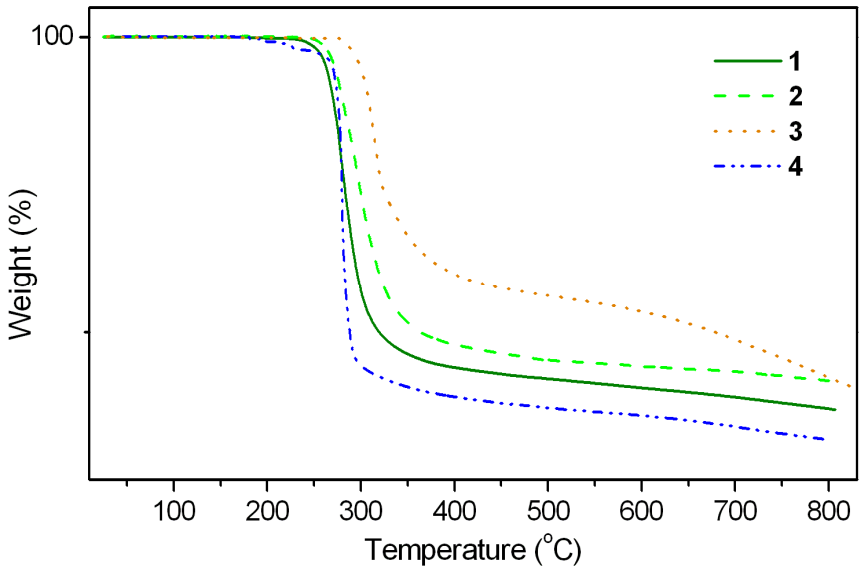


Fig. S6 Thermogravimetric (TG) curves of **1–4**.

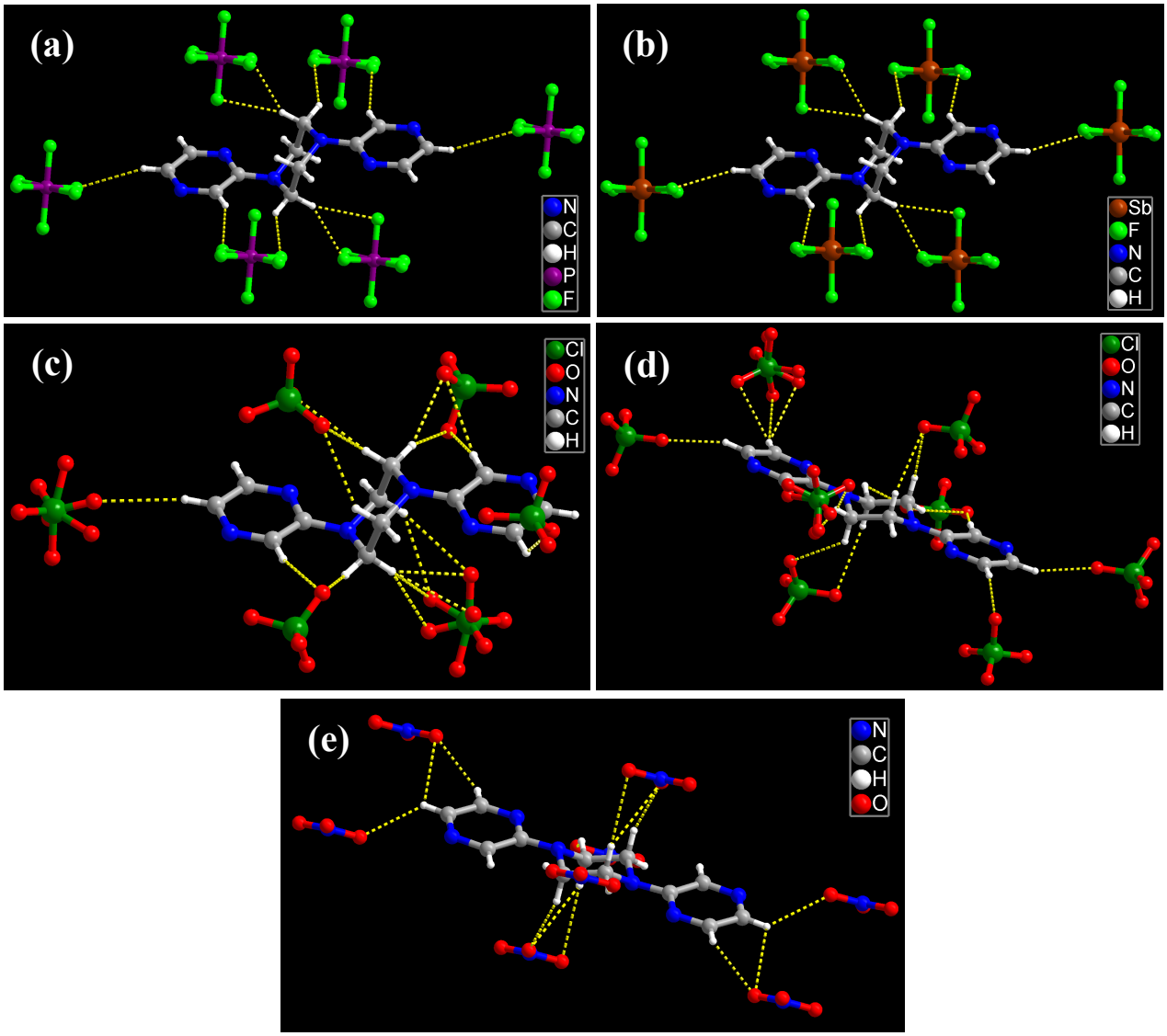
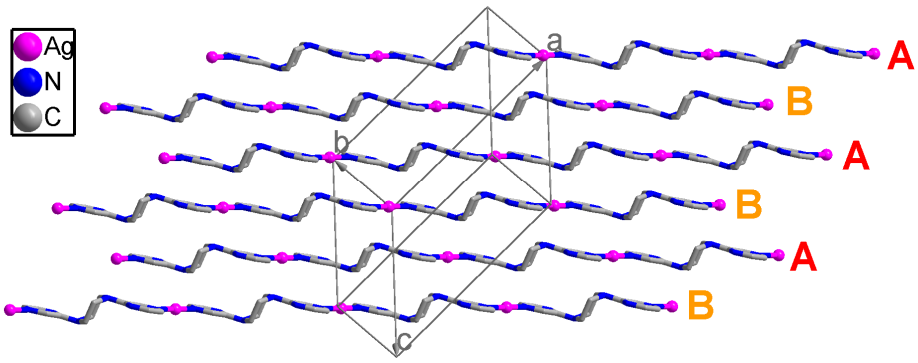
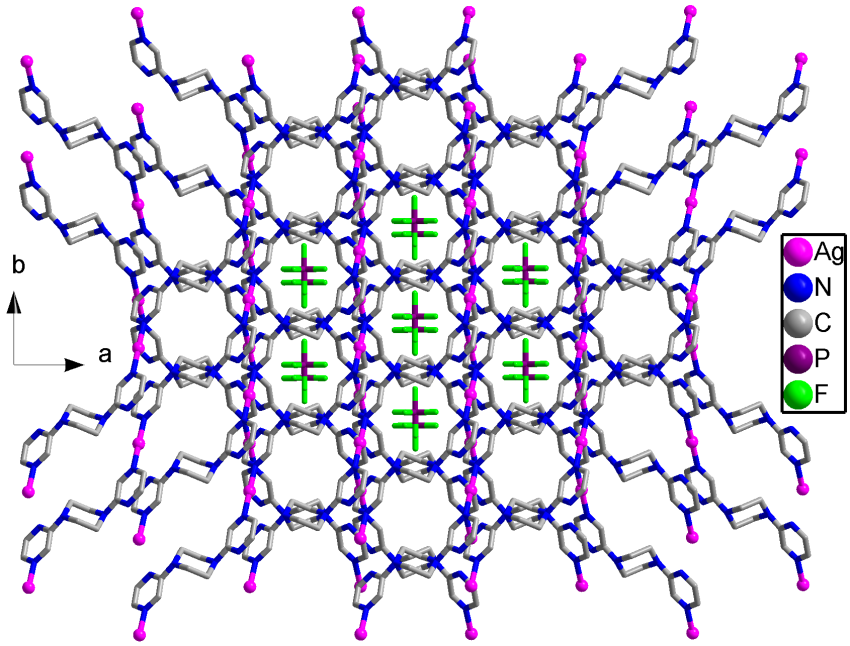


Fig. S7 Perspective views of the nonclassical C–H···F/O hydrogen bonding interactions between the conformation-flexible bpzp ligand and anions in (a) polymer **1**, (b) polymer **2**, (c, d) polymer **3**, and (e) polymer **4**.

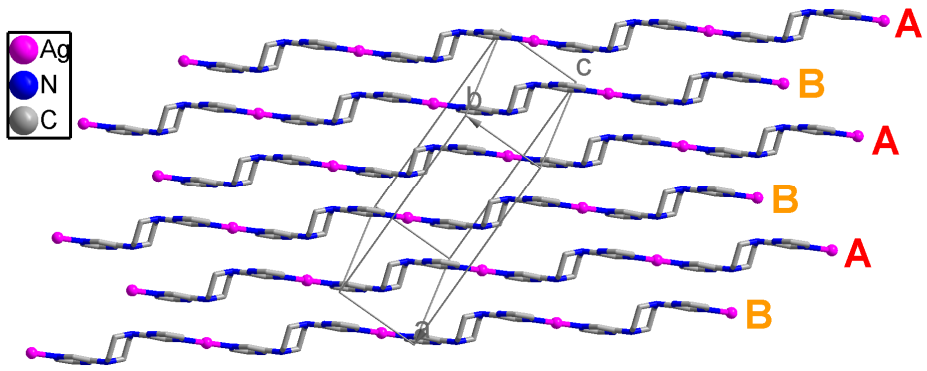


(a)

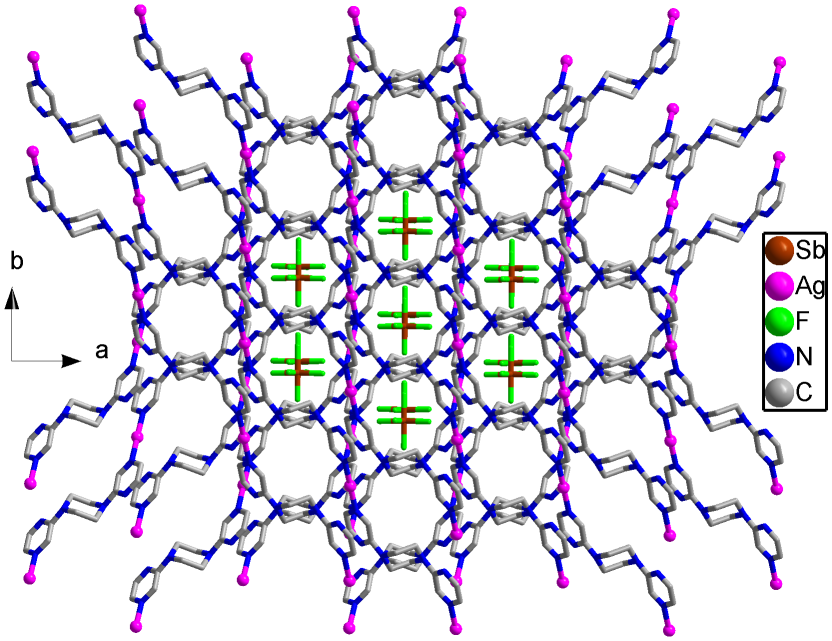


(b)

Fig. S8 (a) Perspective view of the 1D chain structures of **1**, showing the arrangement in an ABAB order. (b) Packing diagrams of **1** viewed along the crystallographic *c*-axis. Hydrogen atoms are omitted for clarity.

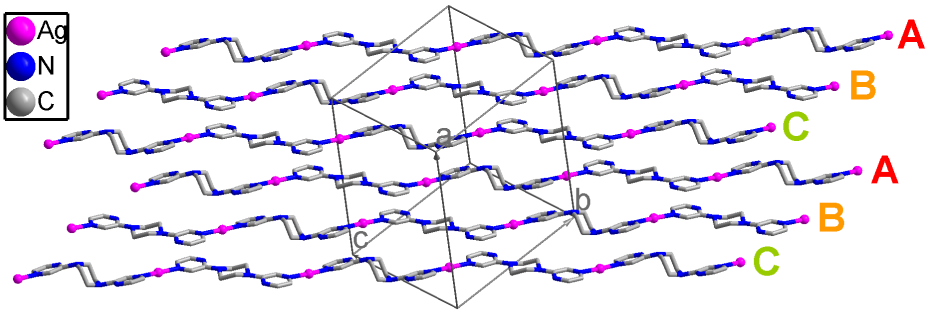


(a)

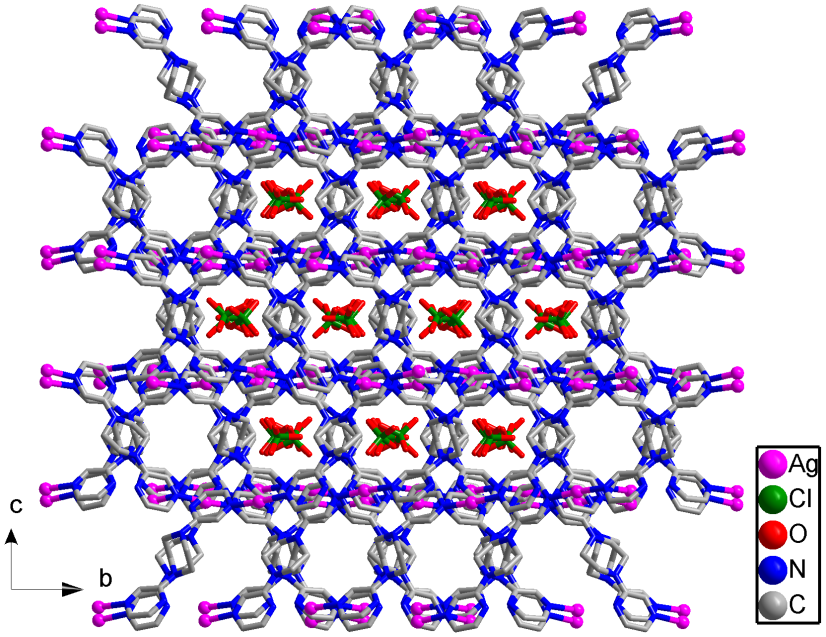


(b)

Fig. S9 (a) Perspective view of the 1D chain structures of **2**, showing the arrangement in an ABAB order. (b) Packing diagrams of **2** viewed along the crystallographic *c*-axis. Hydrogen atoms are omitted for clarity.

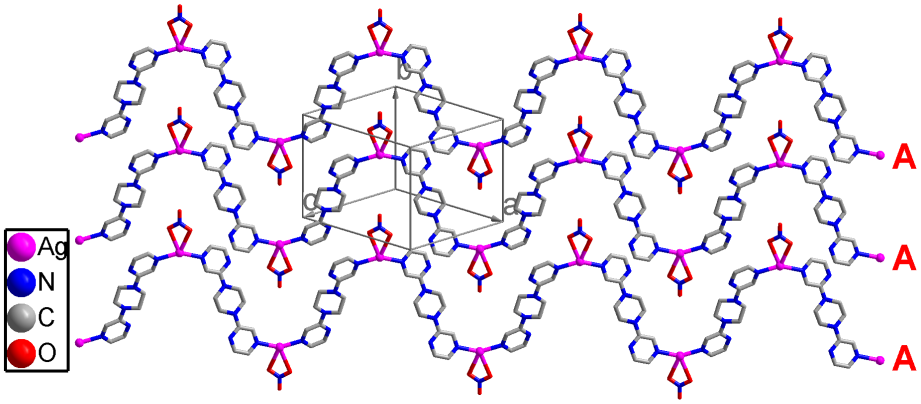


(a)

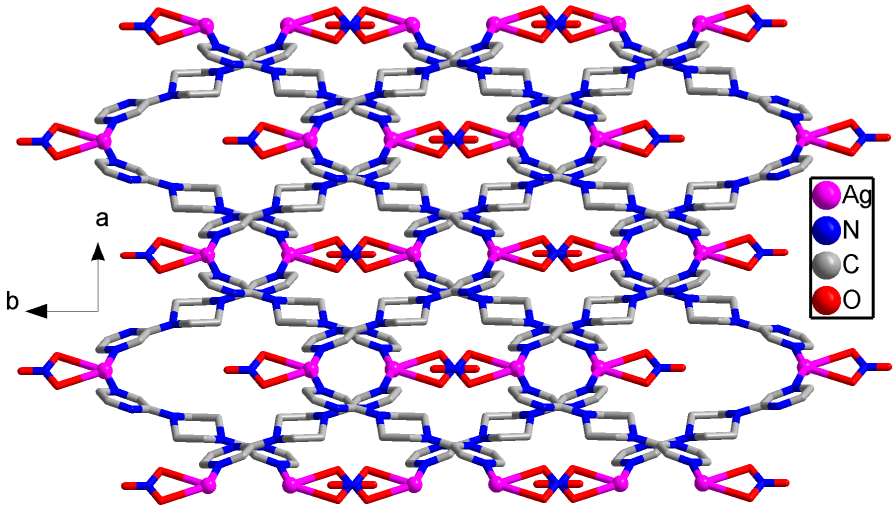


(b)

Fig. S10 (a) Perspective view of the 1D chain structures of **3**, showing the arrangement in an ABCABC order. (b) Packing diagrams of **3** viewed along the crystallographic *a*-axis. Hydrogen atoms are omitted for clarity.



(a)



(b)

Fig. S11 (a) Perspective view of the 1D chain structures of **4**, showing the arrangement in an AAA order. (b) Packing diagrams of **4** viewed along the crystallographic *c*-axis. Hydrogen atoms are omitted for clarity.