

Supporting Information

Synthesis and Solvent Vapor Induced Transformations of Crystals of 1D Coordination Polymer Assembled with Continuous Void Space

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1. Synthesis and Characteristic Data of Ligands and Complexes

Synthesis and Characteristic Data of Ligands

9-Chloroacridine and **L**₁ were synthesized according to the literatures,^{S1} and the procedures were modified when needed in our laboratory.

Synthesis of 9-chloroacridine ^{S2}

A mixture of *N*-phenylanthranilic acid (2.3 g, 11 mmol) and POCl₃ (5 mL, 50 mmol) was carefully heated at 120 °C for 1.5 hr. After cooling to room temperature, the mixture was poured onto ice and neutralized to pH = 7 with 2 mol/L NaOH. The solution was transferred to 1 L Erlenmeyer flask, then added *n*-hexane (300 mL) and stirred for 12 hr until 9-chloroacridine passed into the organic phase. The yellow organic layer was separated and evaporated to give a 9-chloroacridine as a yellow powder (2.2 g, 95% yield). ¹H NMR (400 MHz, 298K, CDCl₃), δppm): 8.47 (ddd, *J* = 8.7, 1.4, 0.7 Hz, 2H), 8.26 (d, *J* = 8.8 Hz, 2H), 7.84 (ddd, *J* = 7.7, 7.7, 1.4 Hz, 2H), 7.67 (ddd, *J* = 7.7, 7.7, 1.1 Hz, 2H).

Synthesis of 9,9'-biacridine (L**₁)** ^{S1}

9-Chloroacridine (2.0 g, 9.4 mmol) was dissolved in anhydrous methanol (10 mL). The solution was added Zn powder (86 mg, 1.3 mmol) and refluxed at 80 °C for 5 hr under stirring. After cooling to room temperature the yellow solid was collected by vacuum filtration. The solid was washed with methanol, dissolved in hot chloroform, and filtered to remove the Zn powder. The crude product can be purified by recrystallization from chloroform. 9,9'-Biacridine was obtained as a yellow crystal (1.1 g, 66% yield). ¹H NMR (400 MHz, 298K, CDCl₃), δppm): 8.42 (ddd, *J* = 8.8, 1.1, 0.8 Hz, 4H), 7.81 (ddd, *J* = 8.8, 6.5, 1.4 Hz, 4H), 7.29 (ddd, *J* = 8.8, 6.5, 1.3 Hz, 4H), 7.09 (ddd, *J* = 8.8, 1.4, 0.8 Hz, 4H).

Synthesis and Characteristic Data of Complexes

Characteristic Data for 1a·THF

Full details of the synthesis and characteristic data are described in Experimental Section. Anal. Calcd. for C_{26.8}H_{22.6}AgBF₄N₂O_{2.7} : [Ag(**L**₁)]BF₄(THF)_{0.2}(H₂O)_{2.5}: C, 52.72; H, 3.73; N, 4.59. Found: C, 52.71; H, 3.43; N, 4.68. Fourier transform infrared spectroscopy (FT-IR) (KBr tablet,

cm⁻¹): 3748(w), 3734(w), 3061(w), 2971(s), 2866(s), 2360(s), 2342(s), 1610(m), 1559(s), 1541(s), 1456(s), 1282(m), 1264(m), 1053(s), 890(m), 757(s), 538(m), 517(m), 420(m).

Synthesis of **1b**·THF

L₁ (15.0 mg, 4.2×10⁻⁵ mol) was dissolved in THF-methanol (5:1, v/v; 60 mL), and AgClO₄ (20.0 mg, 9.6×10⁻⁵ mol) was dissolved in THF (10 mL). The solution of AgClO₄ was dropped slowly into the solution of **L**₁. After 2 days, **1b**·THF was obtained in 85% yield (25.2 mg) as a yellow crystal. The PXRD data indicated that the crystalline product consists of **1b**·THF. Anal. Calcd. for C_{26.8}H_{23.6}AgClN₂O_{7.2}: [Ag(**L**₁)]ClO₄(THF)_{0.2}(H₂O)₃: C, 50.92; H, 3.76; N, 4.43. Found: C, 51.16; H, 3.43; N, 4.33. FT-IR (KBr tablet, cm⁻¹): 3051(w), 2970(w), 2865(w), 1562(m), 1517(m), 1459(m), 1090(s), 750(s), 622(s). TG analysis data indicated that the guest solvent molecules (THF) released in the range of 26–219 °C (see SI Fig. S7, Table S1).

Synthesis of **1a**·Furan

L₁ (4.7 mg, 1.3×10⁻⁵ mol) was dissolved in furan-methanol (10:3, v/v; 13 mL) and AgBF₄ (5.2 mg, 2.7×10⁻⁵ mol) was dissolved in furan (3 mL). Then the solution of AgBF₄ was dropped slowly into the solution of **L**₁. After 3 days, **1a**·Furan was obtained in 7.8% yield (1.4 mg) as a yellow crystal. The PXRD data supported that the whole product consists of **1a**·Furan. FT-IR (KBr tablet, cm⁻¹): 3051(w), 1555(m), 1515(m), 1437(m), 1035(s), 750(s), 600(m), 416(m). TG analysis data indicated that the guest solvent molecules (furan) released in the range of 38–286 °C (see SI Fig. S7, Table S1).

Synthesis of **1a**·DCM

L₁ (9.4 mg, 2.6×10⁻⁵ mol) was dissolved in DCM-methanol (15:1, v/v; 16 mL) and AgBF₄ (17.3 mg, 8.9×10⁻⁵ mol) was dissolved in THF (5 mL). The solution of AgBF₄ was dropped slowly into the solution of **L**₁. After a day, **1a**·DCM was obtained in 75% yield (12.8 mg) as a yellow crystal. Anal. Calcd. for C_{26.6}H₁₈AgBCl_{1.2}F₄N₂O_{0.4}: [Ag(**L**₁)]BF₄(DCM)_{0.6}(H₂O)_{0.4}: C, 52.44; H, 2.98; N, 4.60. Found: C, 52.18; H, 3.31; N, 4.64. FT-IR (KBr tablet, cm⁻¹): 3051(w), 1541(m), 1516(s), 1457(m), 1436(m), 1265(w), 1035(s), 751(s), 599(m), 465(m), 449(m), 434(s), 412(s). TG analysis data indicated that the guest solvent molecules (DCM) released in the range of 41–266 °C (see SI Fig. S7, Table S1).

Synthesis of 1b·DCM

L₁ (3.8 mg, 1.1×10^{-5} mol) was dissolved in DCM-methanol (10:4, v/v; 14 mL) and AgClO₄ (17.3 mg, 8.8×10^{-5} mol) was dissolved in THF (11 mL). Then the solution of AgBF₄ was dropped slowly into the solution of **L**₁. After a day, **1b·DCM** was obtained in 1.5% yield (0.1 mg) as a yellow crystal. Anal. Calcd. for C_{26.9}H_{19.2}AgCl_{2.8}N₂O_{4.7}: [Ag(**L**₁)](ClO₄)(DCM)_{0.9}(H₂O)_{0.7}: C, 49.49; H, 2.96; N, 4.29. Found: C, 49.15; H, 3.18; N, 4.28. FT-IR (KBr tablet, cm⁻¹): 3791(w), 3041(w), 1090(s), 749(s), 620(s), 537(w).

Synthesis of 1c

L₁ (4.7 mg, 1.3×10^{-5} mol) was dissolved in DCM (50 mL), and CF₃COOAg (20.5 mg, 9.0×10^{-5} mol) was dissolved in THF (20 mL). Then the solution of CF₃COOAg was aliquoted into five glass vessels (4 mL per one vessel). To each vessel, the solution of **L**₁ (10 mL) was layered onto the solution of CF₃COOAg. Storage of the solution mixture at 20 °C for 2 weeks give yellow crystals in 36% yield (3.8 mg). Anal. Calcd. for C₃₀H₁₈Ag₂F₆N₂O₅: [Ag₂(**L**₁)](CF₃COO)₂·H₂O: C, 44.15; H, 2.22; N, 3.43. Found: C, 43.81; H, 2.35; N, 3.29. FT-IR (KBr tablet, cm⁻¹): 3433(s), 1682(s), 1645(m), 1210(s), 750(s), 600(m), 419(m).

Synthesis of 2a

L₂ (57.7 mg, 3.2×10^{-4} mol) was dissolved in THF (10 mL), and AgBF₄ (270.9 mg, 1.4×10^{-3} mol) was dissolved in THF (10 mL). Then the solution of AgBF₄ was aliquoted into a glass vessel. To the vessel, methanol (5 mL) and the solution of **L**₂ were layered sequentially onto the solution of AgBF₄. Storage of the solution mixture at 20 °C for 1 day, give yellow crystals in 48% yield (58.1 mg). Anal. Calcd. for C₁₂H₈AgBF₄N₂: [Ag(**L**₂)]BF₄: C, 38.45; H, 2.15; N, 7.47. Found: C, 38.43; H, 2.53; N, 7.46. FT-IR (KBr tablet, cm⁻¹): 3060(w), 1524(s), 1474(s), 1436(s), 1353(s), 1033(s), 835(s), 753(s), 665(s), 599(s), 521(s), 408(m).

Synthesis of 2b^{S3}

L₂ (78.7 mg, 4.4×10^{-4} mol) was dissolved in THF (10 ml), and AgClO₄ (404.6 mg, 2.0×10^{-3} mol) was dissolved in THF (10 mL). Then the solution of AgClO₄ was aliquoted into a glass vessel. To the vessel, methanol (5 mL) and the solution of **L**₂ were layered sequentially onto the solution of AgClO₄. Storage of the solution mixture at 20 °C for 1 day, give yellow crystals in 80% yield (136.3 mg). Anal. Calcd. for C₁₂H₈AgClN₂O₄: [Ag(**L**₂)]ClO₄: C, 37.19; H, 2.08; N, 7.23. Found: C,

37.11; H, 2.23; N, 7.24. FT-IR (KBr tablet, cm^{-1}): 3440(s), 1726(w), 1665(w), 1563(m), 1074(s), 748(s), 620(s), 596(m), 415(s), 402(s).

Synthesis of 2c

A solution of CF_3COOAg (167.7 mg, 7.6×10^{-4} mol) in THF (10 mL) was placed into a glass vessel. To the vessel, methanol (5 mL) and the solution of L_2 (41.8 mg, 2.3×10^{-4} mol) in DCM (10 mL) were layered sequentially onto the solution of L_2 . Storage of the solution mixture at 20 °C for 1 day, give yellow crystals in 85% yield. Anal. Calcd. for $\text{C}_{16}\text{H}_8\text{Ag}_2\text{F}_6\text{N}_2\text{O}_4$: $[\text{Ag}(\text{L}_2)](\text{CF}_3\text{COO})_2$: C, 30.90; H, 1.30; N, 4.50. Found: C, 30.84; H, 1.46; N, 4.53. FT-IR (KBr tablet, cm^{-1}): 3670(w), 3440(b), 1681(s), 1515(m), 1434(m), 1210(s), 1132(s), 838(m), 804(m), 748(m), 724(m), 594(w).

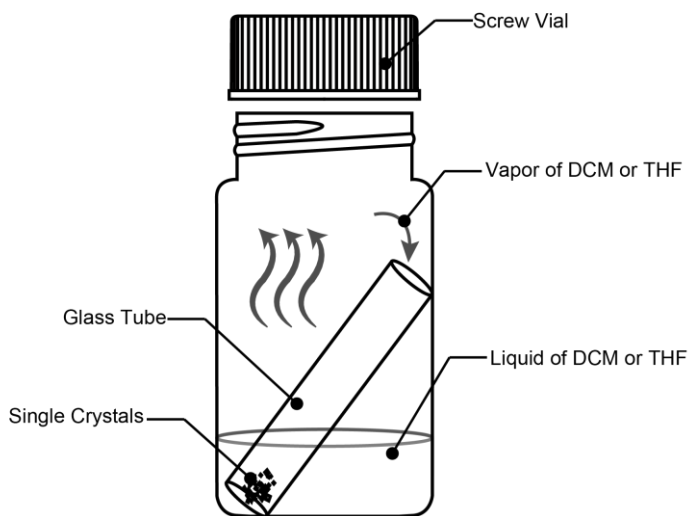


Figure S1. The illustration of the experimental method of solvent exchange.

2. Crystal structures of complexes

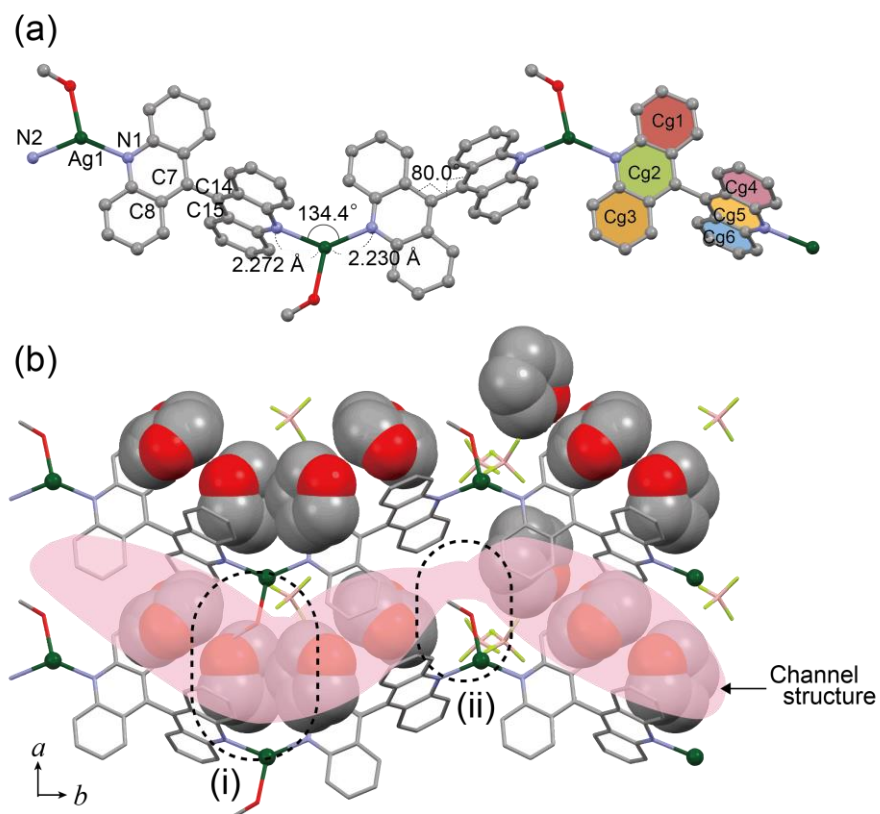


Figure S2. Crystal structure of **1a·Furan**: (a) 1D structure consisting of **L1**, Ag(I) ions and methanol, (b) viewing along the *c*-axis. The 1D structure featured channels were zigzag-shaped and filled with furan. The maximum cross section is 6.6×6.2 Å² (see (i)), and its minimum was 3.8×0.1 Å² (see (ii)). Colors: C, gray spheres; Ag, green spheres; B, pink spheres; Cl, light green spheres; F, yellow spheres; N, violet spheres; O, red spheres. H atoms have been omitted for clarity.

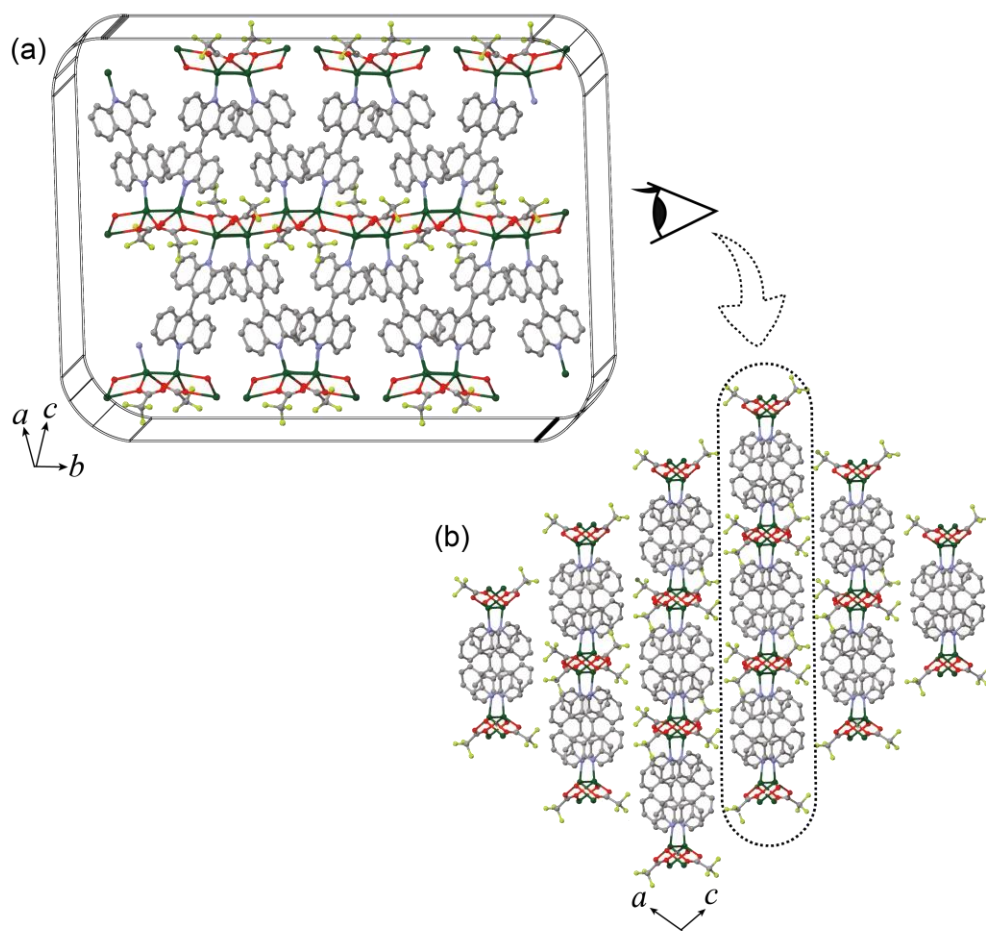


Figure S3. Crystal structure of **1c**: (a) 2D layer, (b) viewing along the *b*-axis. Colors: C, gray spheres; Ag, green spheres; B, pink spheres; F, yellow spheres; N, violet spheres; O, red spheres. H atoms have been omitted for clarity.

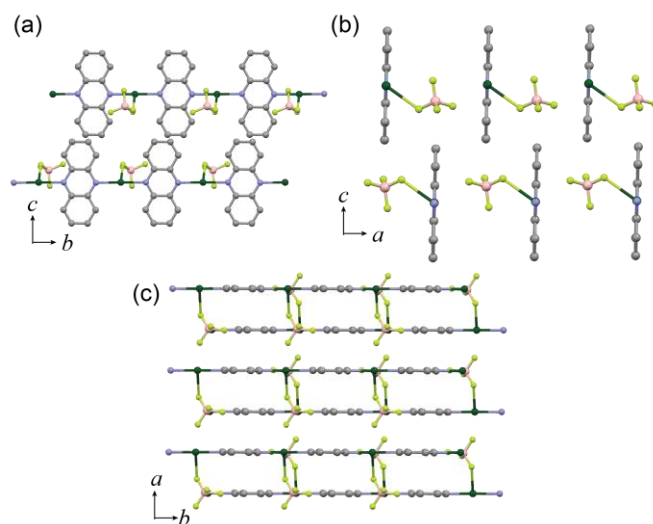


Figure S4. Crystal structure of **2a** is viewed along the *a*-axis (a), *b*-axis (b), *c*-axis (c). Colors: C, gray spheres; Ag, green spheres; B, pink spheres; F, yellow spheres; N, violet spheres. H atoms have been omitted for clarity.

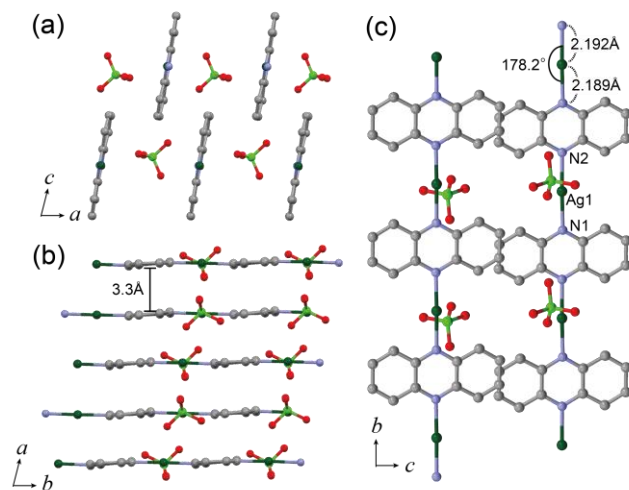


Figure S5. Crystal structure of **2b** is viewed along the (a) *b*-axis, (b) *c*-axis and (c) *a*-axis. Colors: C, gray spheres; Ag, green spheres; B, pink spheres; F, yellow spheres; N, violet spheres. H atoms have been omitted for clarity.

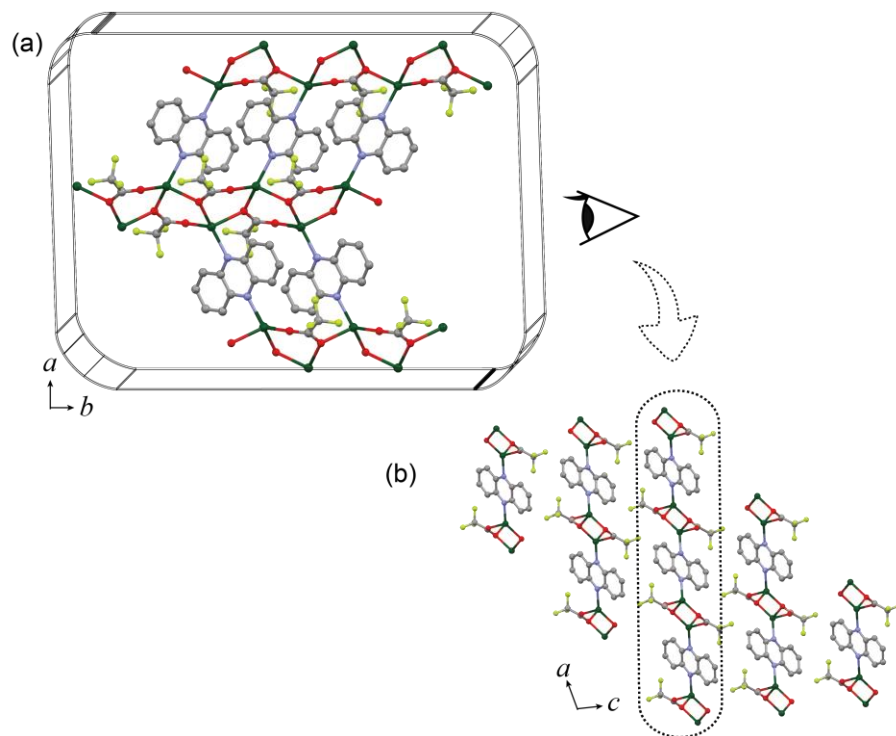


Figure S6. Crystal structure of **2c**: (a) 2D layer, (b) viewing along the *b*-axis. Colors: C, gray spheres; Ag, green spheres; B, pink spheres; F, yellow spheres; N, violet spheres; O, red spheres. H atoms have been omitted for clarity.

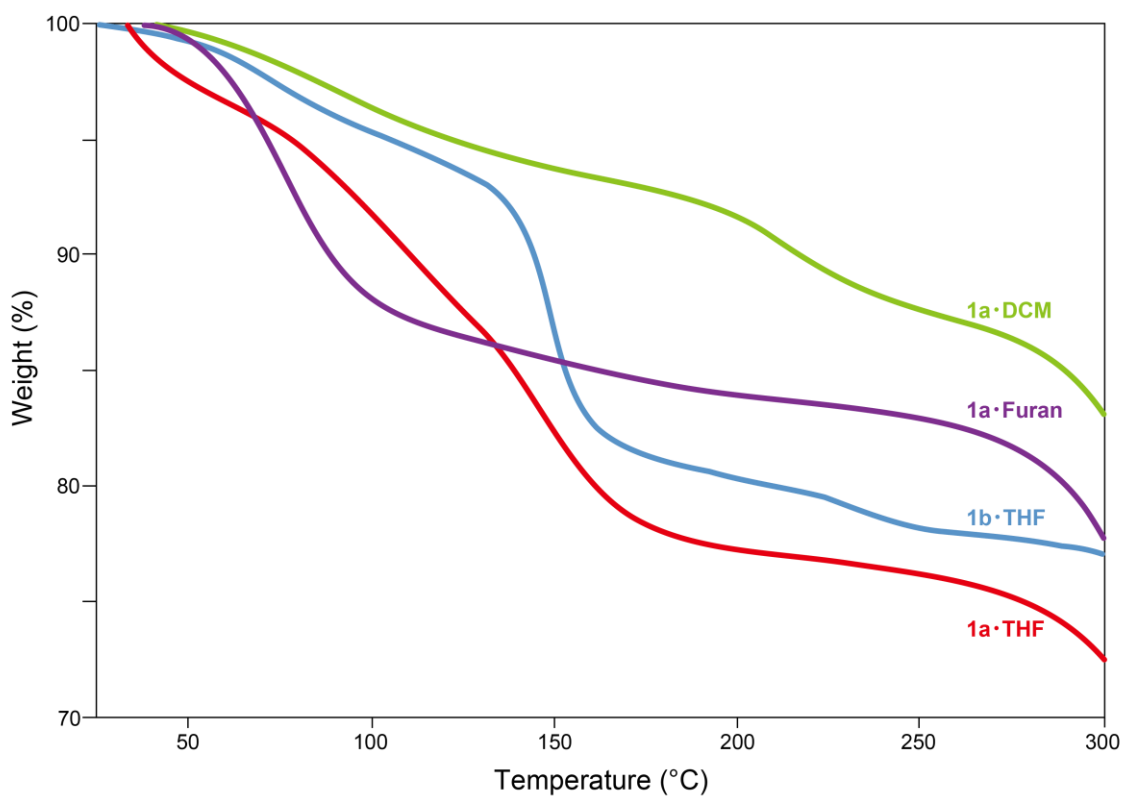


Figure S7. TG curves of **1a·THF**, **1b·THF**, **1a·Furan** and **1a·DCM**.

TableS1. TG data.

Sample	Estimated formula	Weight loss (%) (calcd)	
1a·THF	$[\text{Ag}(\text{L}_1)]_n(\text{BF}_4)_n \cdot 2n\text{THF}$	20.2	(20.7)
1b·THF	$[\text{Ag}(\text{L}_1)]_n(\text{ClO}_4)_n \cdot 2n\text{THF}$	20.1	(20.4)
1a·Furan	$[\text{Ag}(\text{L}_1)(\text{CH}_3\text{OH})]_n(\text{BF}_4)_n \cdot 1.5n(\text{furan})$	18.4	(19.6)
1a·DCM	$[\text{Ag}(\text{L}_1)]_n(\text{BF}_4)_n \cdot n\text{DCM}$	13.1	(13.4)

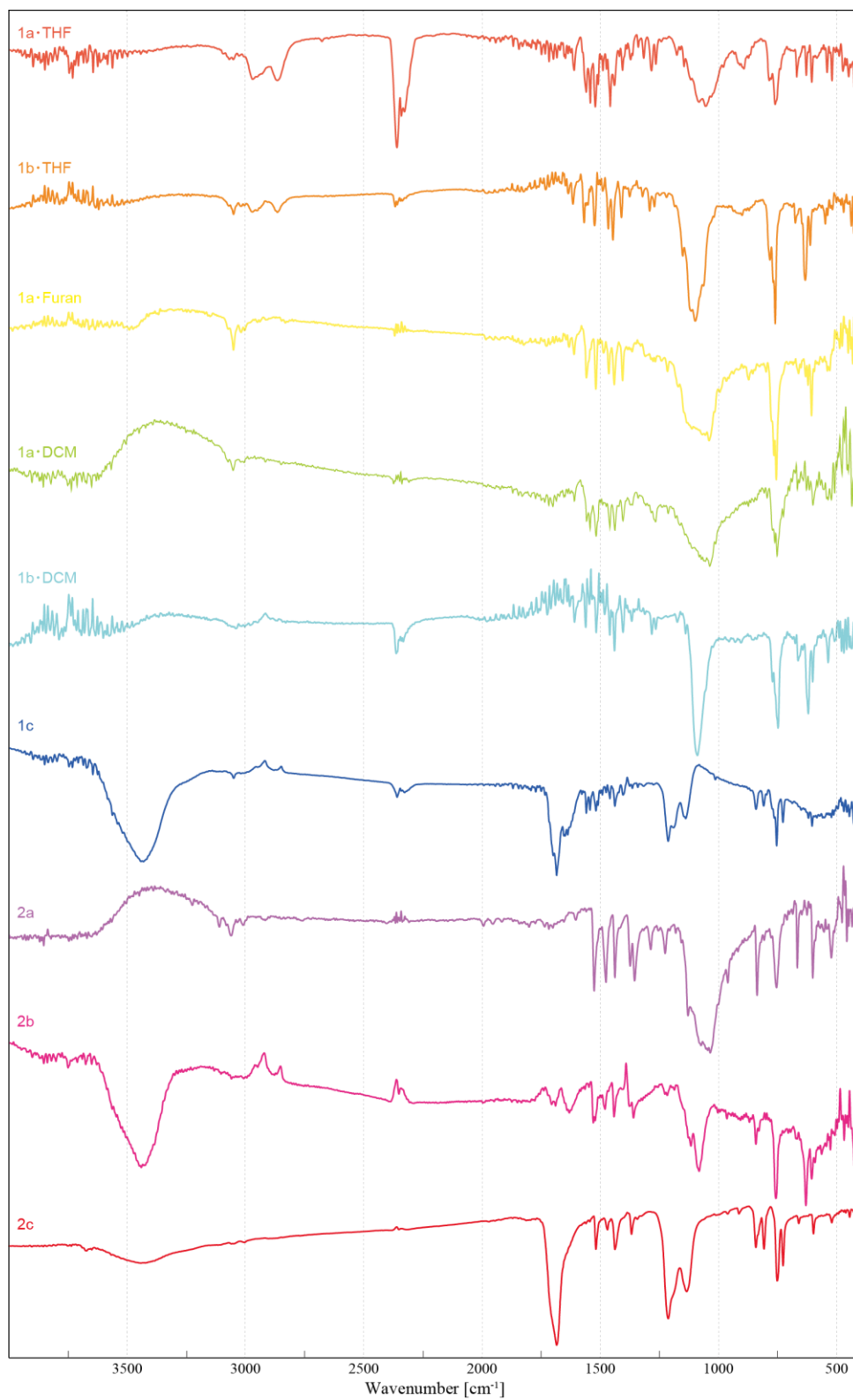


Figure S8. IR spectra of the complexes.

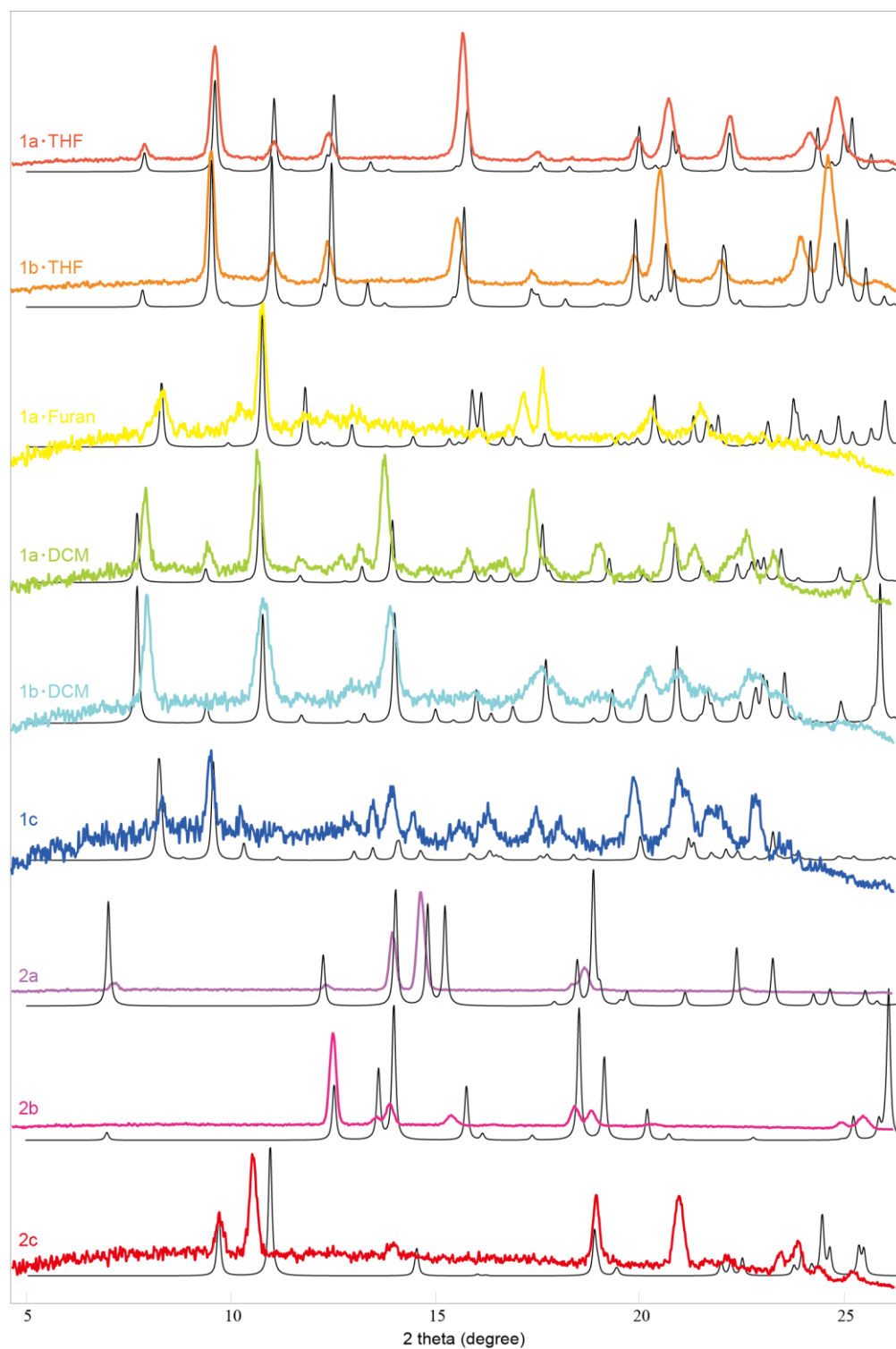


Figure S9. PXRD patterns of all complexes. Colored lines: experimental data, black lines: simulation data.

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