

Silver(I) Complexes of *Bis*- and *Tris*-(pyrazolyl)azine Derivatives – Dimers, Coordination Polymers and a Pentametallic Assembly

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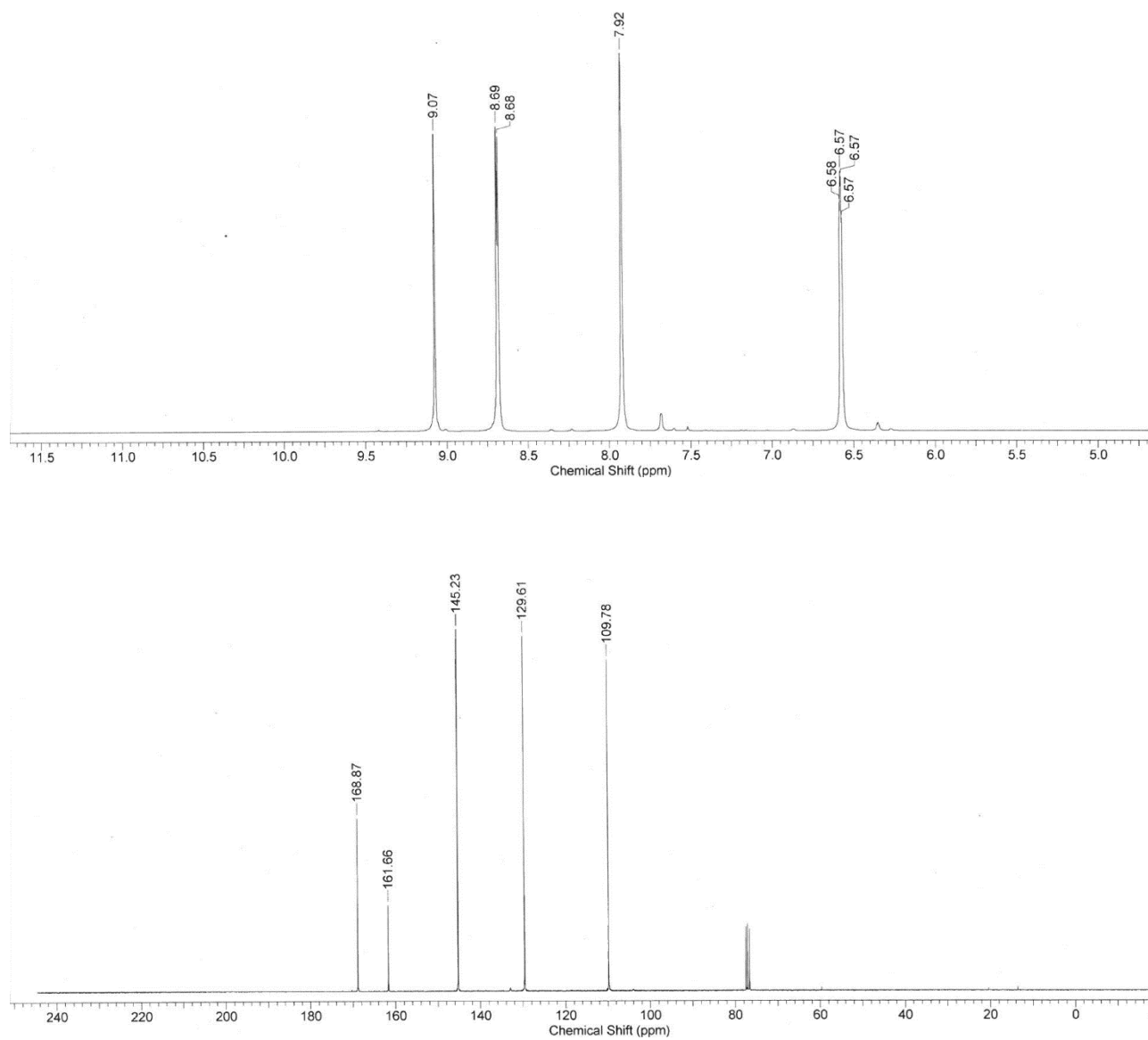


Figure S1. ¹H (top) and ¹³C (bottom) NMR spectra of the new ligand bpt in CDCl₃.

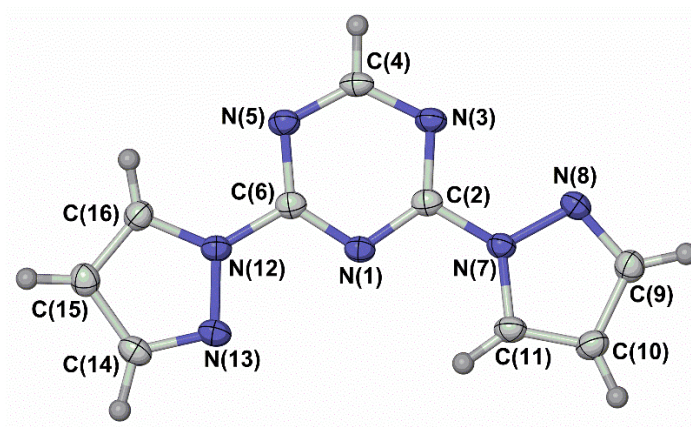


Figure S2. View of the molecule in the crystal structure of bpt, showing the atom numbering scheme. Atomic displacement ellipsoids are at the 50 % probability level, except for H atoms which have arbitrary radii.

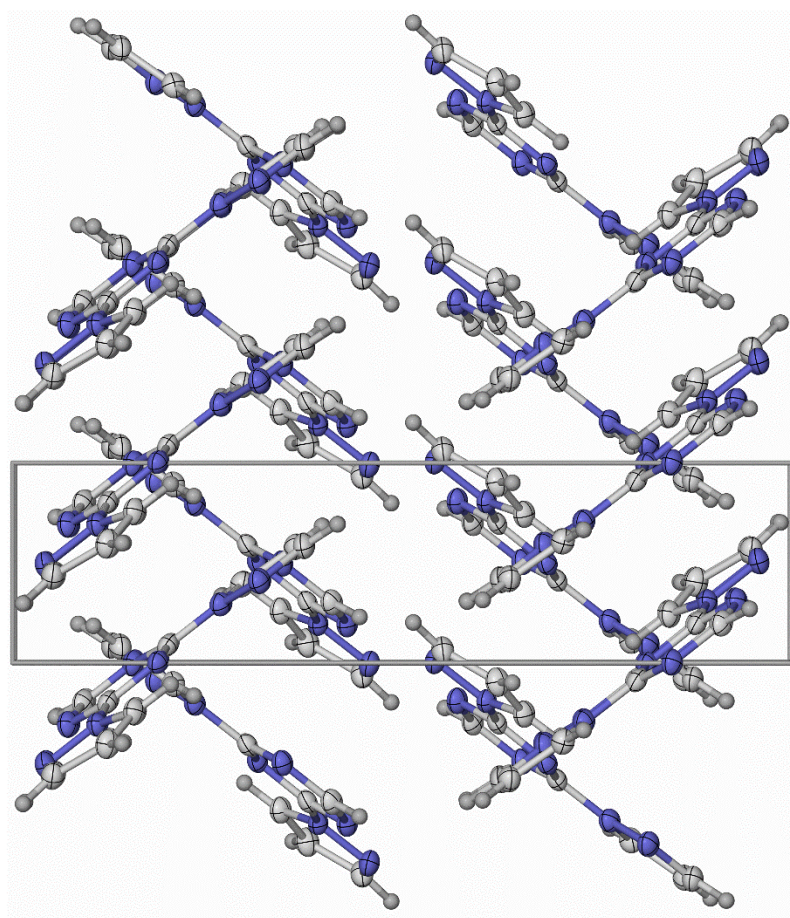


Figure S3. Packing diagram of bpt, showing the organisation of the molecules into canted stacks by translation along the unit cell *b* direction. The view is parallel to the [100] crystal vector, with *b* vertical. The interplanar distance between the stacked molecules is 3.267(2) Å.

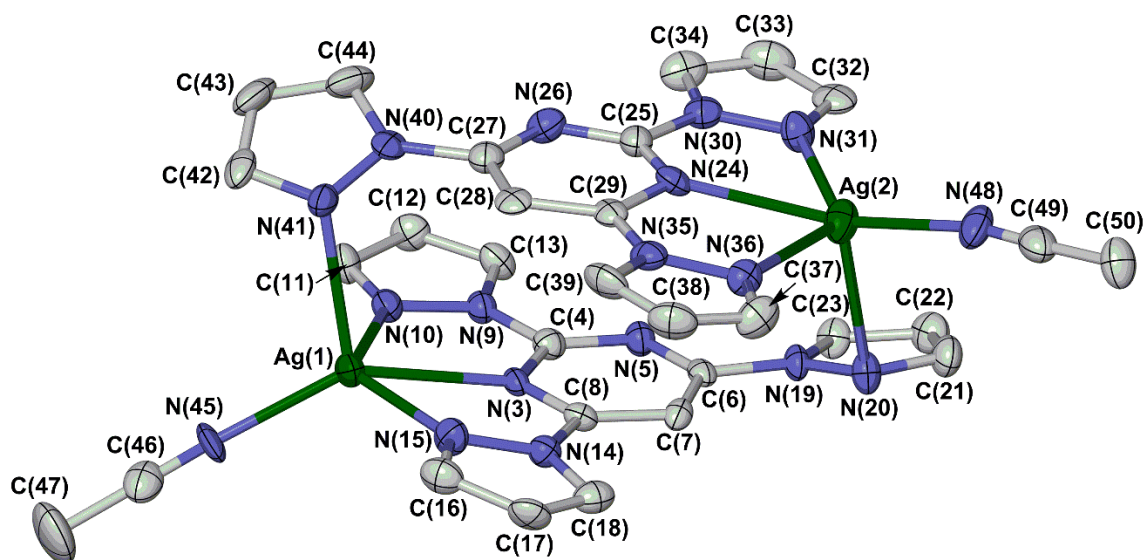
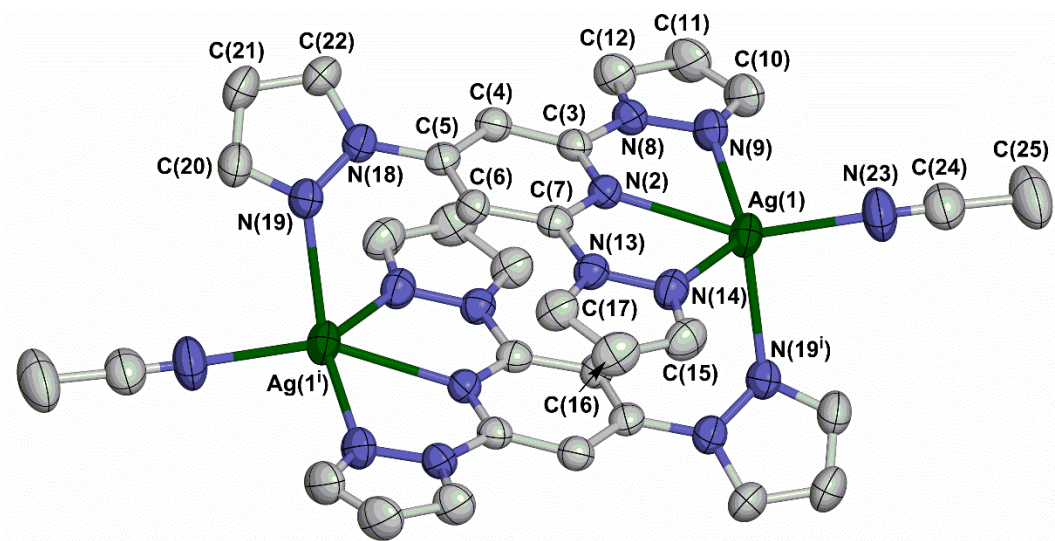


Figure S4. View of the $[\text{Ag}_2(\text{tpp})_2(\text{NCMe})_2]^{2+}$ cation in **1**·2MeCN (top) and of $[\text{Ag}_2(\text{tpym})_2(\text{NCMe})_2]^{2+}$ in **3** (bottom), showing the full atom numbering schemes. Atomic displacement ellipsoids are at the 50 % probability level, and H atoms are omitted for clarity. Symmetry code: (i) $1-x, 1-y, 1-z$.

Colour code: C, white; Ag, green; N, blue.

Table S1. Selected bond lengths (Å) and angles (°) for the crystal structures of the dimeric acetonitrile solvates [Ag₂(tpp)₂(NCMe)₂][BF₄]₂·2MeCN (**1**·2MeCN) and [Ag₂(tpym)₂(NCMe)₂][BF₄]₂ (**3**), including intramolecular Ag...Ag distances. See Fig. S4 for the atom numbering schemes employed. Symmetry code: (i) 1–x, 1–y, 1–z.

1·2MeCN		3	
Ag(1)–N(2)	2.445(3)	Ag(1)–N(3)	2.449(7)
Ag(1)–N(9)	2.461(5)	Ag(1)–N(10)	2.557(8)
Ag(1)–N(14)	2.414(4)	Ag(1)–N(15)	2.384(8)
Ag(1)–N(19 ⁱ)	2.566(4)	Ag(1)–N(41)	2.497(8)
Ag(1)–N(23)	2.250(5)	Ag(1)–N(45)	2.207(8)
		Ag(2)–N(20)	2.621(9)
		Ag(2)–N(24)	2.428(8)
		Ag(2)–N(31)	2.400(7)
		Ag(2)–N(36)	2.531(7)
		Ag(2)–N(48)	2.194(9)
N(2)–Ag(1)–N(9)	65.74(12)	N(3)–Ag(1)–N(10)	64.6(2)
N(2)–Ag(1)–N(14)	65.92(12)	N(3)–Ag(1)–N(15)	66.1(2)
N(2)–Ag(1)–N(19 ⁱ)	113.38(12)	N(3)–Ag(1)–N(41)	106.3(2)
N(2)–Ag(1)–N(23)	153.60(18)	N(3)–Ag(1)–N(45)	143.5(3)
N(9)–Ag(1)–N(14)	131.02(13)	N(10)–Ag(1)–N(15)	130.7(2)
N(9)–Ag(1)–N(19 ⁱ)	117.25(14)	N(10)–Ag(1)–N(41)	85.6(3)
N(9)–Ag(1)–N(23)	99.44(19)	N(10)–Ag(1)–N(45)	107.9(3)
N(14)–Ag(1)–N(19 ⁱ)	88.88(13)	N(15)–Ag(1)–N(41)	106.9(3)
N(14)–Ag(1)–N(23)	121.21(19)	N(15)–Ag(1)–N(45)	112.2(3)
N(19 ⁱ)–Ag(1)–N(23)	92.70(18)	N(41)–Ag(1)–N(45)	108.7(3)
		N(20)–Ag(2)–N(24)	108.2(2)
		N(20)–Ag(2)–N(31)	90.3(3)
		N(20)–Ag(2)–N(36)	105.1(3)
		N(20)–Ag(2)–N(48)	97.8(3)
		N(24)–Ag(2)–N(31)	67.3(3)
		N(24)–Ag(2)–N(36)	64.2(2)
		N(24)–Ag(2)–N(48)	149.1(3)
		N(31)–Ag(2)–N(36)	131.5(3)
		N(31)–Ag(2)–N(48)	130.3(3)
		N(36)–Ag(2)–N(48)	93.5(3)
Ag(1)...Ag(1 ⁱ)	7.2461(7)	Ag(1)...Ag(2)	7.2706(10)
τ[Ag(1)] ^a	0.38	τ[Ag(1)] ^a	0.21
		τ[Ag(2)] ^a	0.29

^aSee ref. [1] for the definition of τ . An ideal square pyramidal geometry gives $\tau = 0$, while an ideal trigonal bipyramidal geometry yields $\tau = 1$.

[1] A. W. Addison, T. N. Rao, J. Reedijk, J. van Rijn and G. C. Verschoor, *J. Chem. Soc., Dalton Trans.*, 1984, 1349.

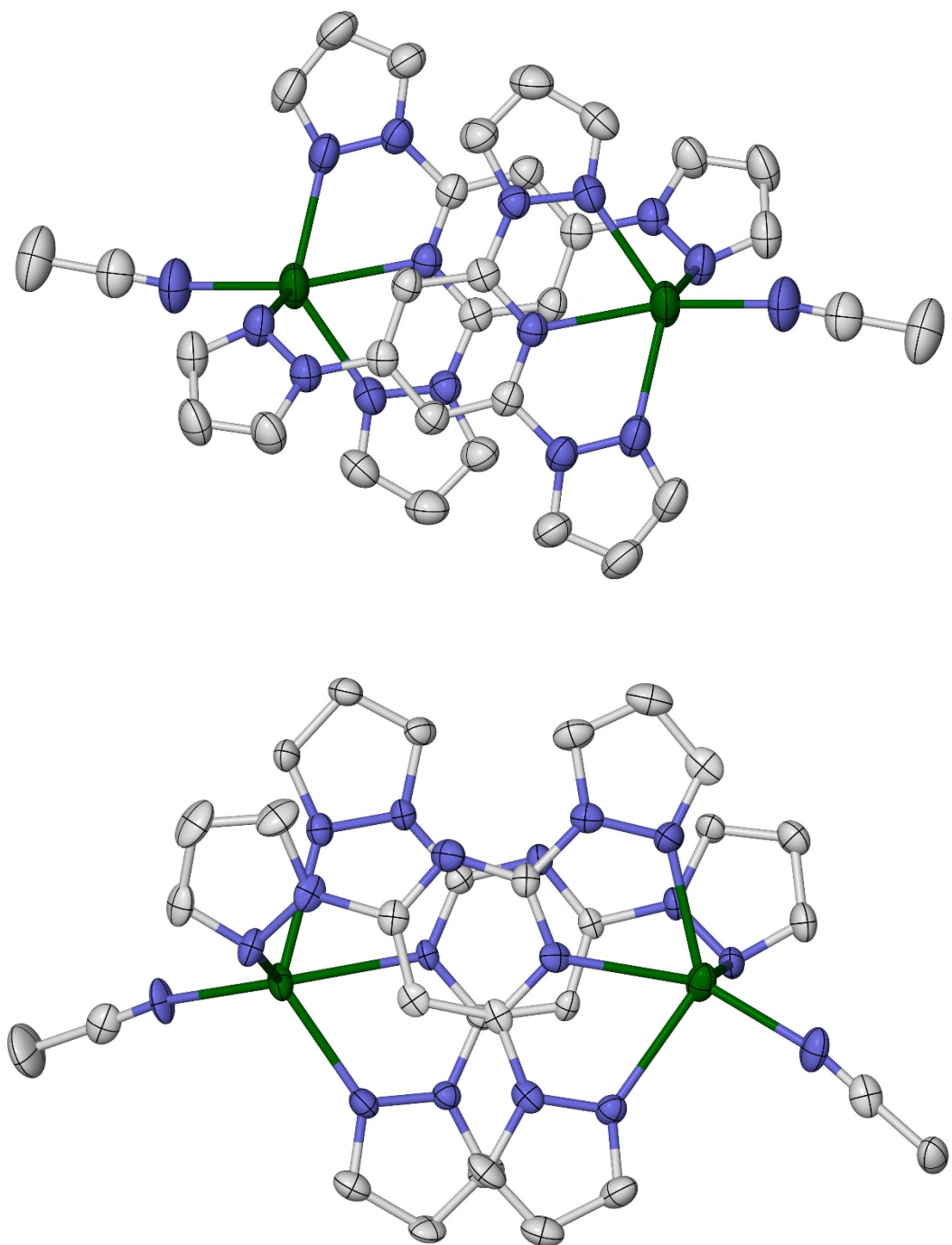


Figure S5. Comparison of centrosymmetric $[\text{Ag}_2(\text{tpp})_2(\text{NCMe})_2]^{2+}$ in **1**·2MeCN (top) and C_1 -symmetric $[\text{Ag}_2(\text{tpym})_2(\text{NCMe})_2]^{2+}$ in **3** (bottom). The views are perpendicular to the least squares planes of the tridentate ligand domains. Other details as for Figure S4. Colour code: C, white; Ag, green; N, blue.

The compounds differ in the relative dispositions of the monodentate pyrazolyl groups on each ligand, which are *transoid* to each other in **1**·2MeCN and *cisoid* in **3**.

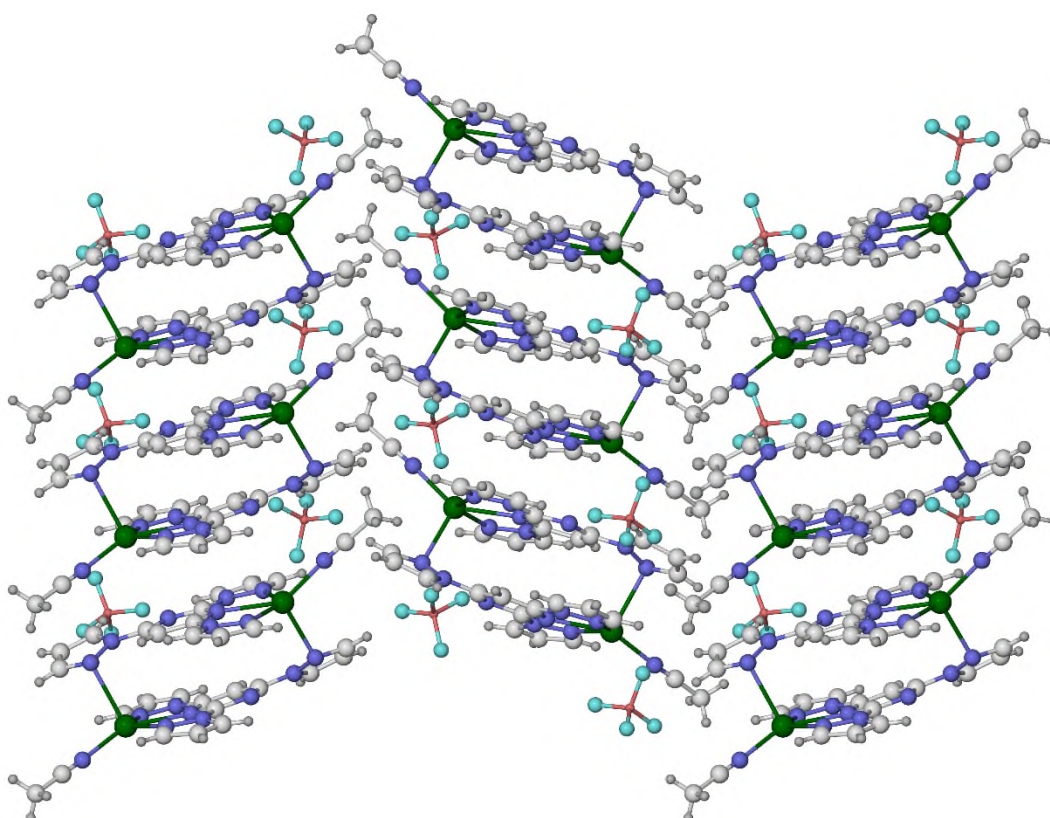
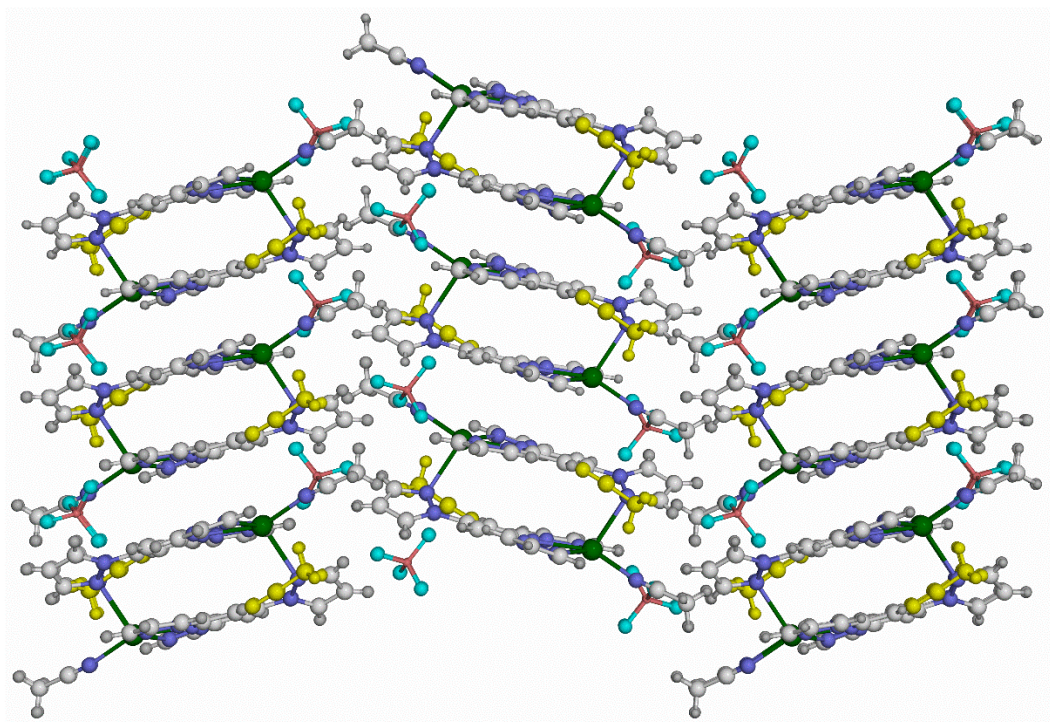


Figure S6. Packing diagrams of 1·2MeCN (top) and 3 (bottom), showing the canted stacks of dimeric cations parallel to the unit cell *b* direction. The views are both along the [100] crystal vector, with *b* vertical. Only one orientation of the disordered residues is shown, and all atoms have arbitrary radii. Colour code: C, white; H, pale grey; Ag, green; B, pink; F, cyan; N, blue; lattice MeCN, yellow.

Table S2. Metric parameters for $\pi\cdots\pi$ interactions in **1**·2MeCN and **3** (Å, °). See Fig. S4 for the atom numbering scheme employed. Symmetry codes: (i) 1–*x*, 1–*y*, 1–*z*; (ii) 1–*x*, –*y*, 1–*z*; (iii) *x*, 1+*y*, *z*.

	Dihedral angle	Interplanar distance	Horizontal offset
1 ·2MeCN			
Intramolecular [N(2)–C(7)]...[N(2 ⁱ)...C(7 ⁱ)]	0	3.338(3)	1.92
Intermolecular [N(2)–C(7)]...[N(13 ⁱⁱ)...C(17 ⁱⁱ)]	4.35(14)	3.395(17)	1.89
3			
Intramolecular [N(3)–C(8)]...[N(24)...C(29)]	1.7(3)	3.28(3)	0.59
Intermolecular [N(3)–C(8)]...[N(24 ⁱⁱⁱ)...C(24 ⁱⁱⁱ)]	1.7(3)	3.19(3)	2.92

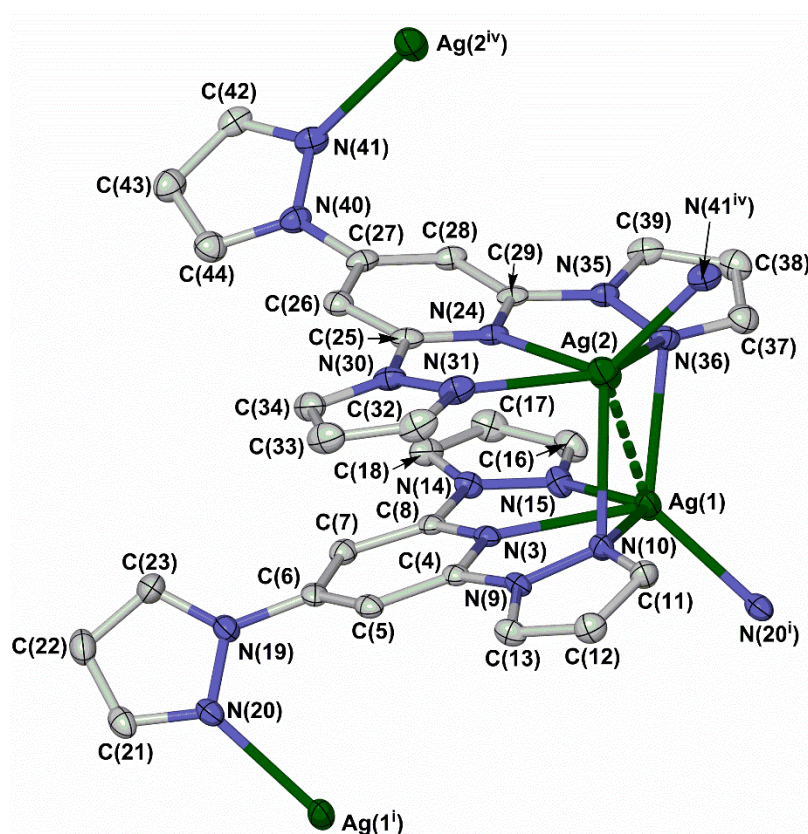


Figure S7. View of the $[\text{Ag}_2(\text{tpp})_2]^{2+}$ moiety in the asymmetric unit of α -2-MeNO₂, showing the full atom numbering scheme. Details as for Figure S4. Symmetry codes: (i) 1–*x*, 1–*y*, 1–*z*; (iv) 1–*x*, 1–*y*, –*z*.

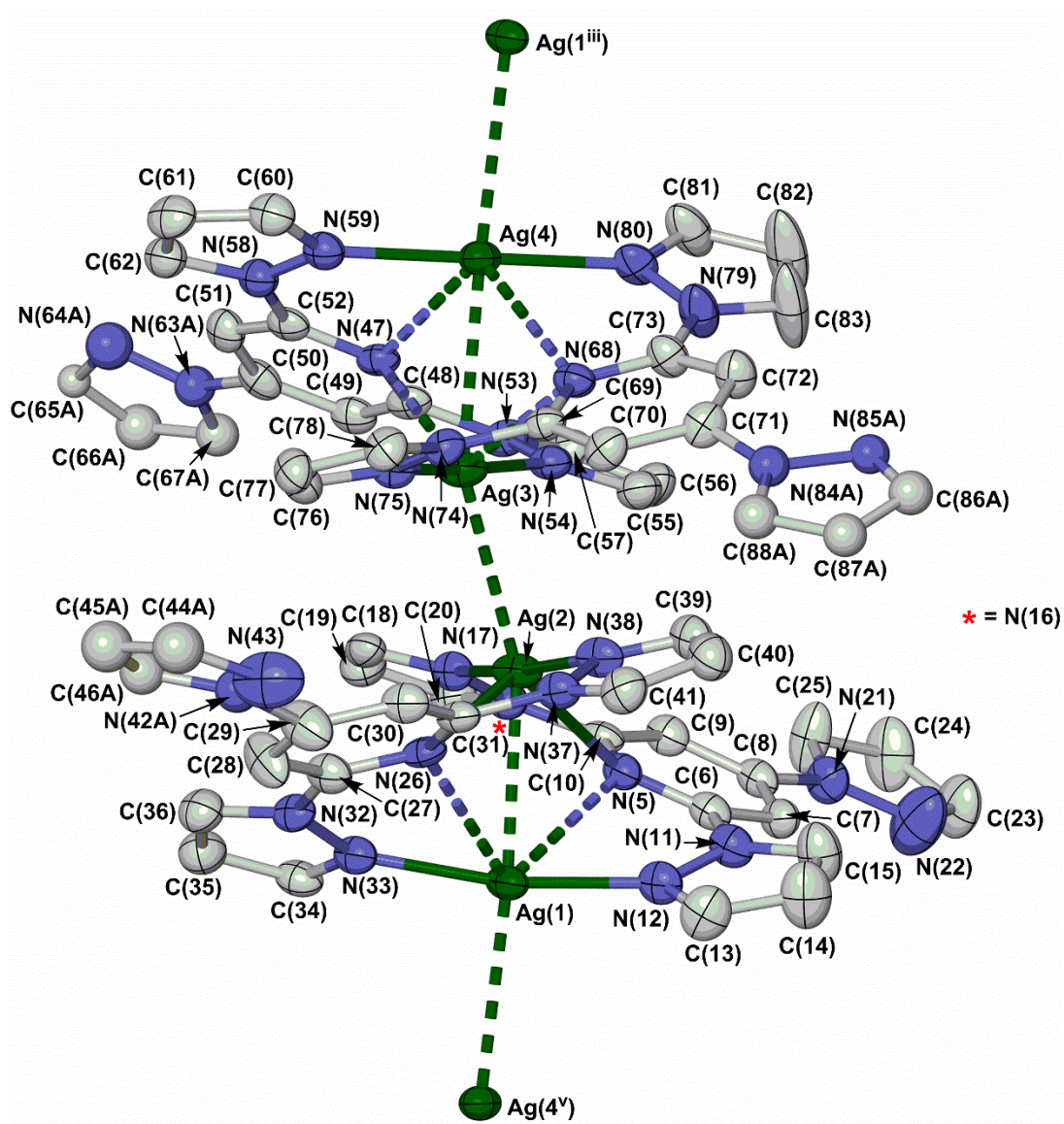


Figure S8. View of the unique $\{[\text{Ag}_2(\text{tp})_2]\}^{4+}$ moiety in the asymmetric unit of β -2-*y*MeNO₂, showing the full atom numbering scheme. Details as for Figure S4. Symmetry codes: (iii) $x, 1+y, z$; (v) $x, -1+y, z$.

Table S3. Selected bond lengths (Å) and angles (°) for the solvatomorphs [Ag₂(tpp)₂][BF₄]₂·MeNO₂ (α -2·MeNO₂) and [Ag₂(tpp)₂][BF₄]₂·yMeNO₂ (β -2·yMeNO₂), including intramolecular Ag...Ag distances. See Figs. S7 and S8 for the atom numbering schemes employed. Symmetry codes: (i) 1-x, 1-y, 1-z; (iv) 1-x, 1-y, -z; (v) x, -1+y, z.

α -2·MeNO ₂		β -2·yMeNO ₂	
Ag(1)–N(3)	2.487(2)	Ag(1)–N(5)	2.845(5)
Ag(1)–N(10)	2.590(2)	Ag(1)–N(12)	2.154(6)
Ag(1)–N(15)	2.389(2)	Ag(1)–N(26)	2.759(5)
Ag(1)–N(20 ⁱ)	2.272(2)	Ag(1)–N(33)	2.153(5)
Ag(1)–N(36)	2.520(2)	Ag(2)–N(5)	2.605(5)
Ag(2)–N(10)	2.610(2)	Ag(2)–N(17)	2.175(5)
Ag(2)–N(24)	2.484(2)	Ag(2)–N(26)	2.547(5)
Ag(2)–N(31)	2.356(2)	Ag(2)–N(38)	2.200(5)
Ag(2)–N(36)	2.636(2)	Ag(3)–N(47)	2.658(5)
Ag(2)–N(41 ^{iv})	2.292(2)	Ag(3)–N(54)	2.176(5)
		Ag(3)–N(68)	2.712(5)
		Ag(3)–N(75)	2.147(5)
		Ag(4)–N(47)	2.755(5)
		Ag(4)–N(59)	2.159(5)
		Ag(4)–N(68)	2.787(5)
		Ag(4)–N(80)	2.162(5)
N(3)–Ag(1)–N(9)	63.39(7)	N(5)–Ag(1)–N(12)	66.16(17)
N(3)–Ag(1)–N(15)	67.08(7)	N(5)–Ag(1)–N(26)	106.82(14)
N(3)–Ag(1)–N(20 ⁱ)	126.47(7)	N(5)–Ag(1)–N(33)	109.47(17)
N(3)–Ag(1)–N(36)	106.23(7)	N(12)–Ag(1)–N(26)	105.42(17)
N(10)–Ag(1)–N(15)	130.36(7)	N(12)–Ag(1)–N(33)	169.90(19)
N(10)–Ag(1)–N(20 ⁱ)	94.94(8)	N(26)–Ag(1)–N(33)	66.48(17)
N(10)–Ag(1)–N(36)	103.95(7)	N(5)–Ag(2)–N(17)	68.89(17)
N(15)–Ag(1)–N(20 ⁱ)	117.44(8)	N(5)–Ag(2)–N(26)	121.70(15)
N(15)–Ag(1)–N(36)	86.31(8)	N(5)–Ag(2)–N(38)	107.88(17)
N(20 ⁱ)–Ag(1)–N(36)	126.92(8)	N(17)–Ag(2)–N(26)	118.45(17)
N(10)–Ag(2)–N(24)	101.71(7)	N(17)–Ag(2)–N(38)	171.60(18)
N(10)–Ag(2)–N(31)	83.61(7)	N(26)–Ag(2)–N(38)	69.93(17)
N(10)–Ag(2)–N(36)	103.95(7)	N(47)–Ag(3)–N(54)	68.55(17)
N(10)–Ag(2)–N(41 ^{iv})	131.09(8)	N(47)–Ag(3)–N(68)	118.29(14)
N(24)–Ag(2)–N(31)	67.32(8)	N(47)–Ag(3)–N(75)	115.86(17)
N(24)–Ag(2)–N(36)	62.93(7)	N(54)–Ag(3)–N(68)	103.77(17)
N(24)–Ag(2)–N(41 ^{iv})	125.51(7)	N(54)–Ag(3)–N(75)	171.97(19)
N(31)–Ag(2)–N(36)	129.86(8)	N(68)–Ag(3)–N(75)	68.31(17)
N(31)–Ag(2)–N(41 ^{iv})	123.23(8)	N(47)–Ag(4)–N(59)	66.11(17)
N(36)–Ag(2)–N(41 ^{iv})	91.57(7)	N(47)–Ag(4)–N(68)	112.59(14)
		N(47)–Ag(4)–N(80)	112.82(17)
		N(59)–Ag(4)–N(68)	114.70(17)
		N(59)–Ag(4)–N(80)	178.51(18)
		N(68)–Ag(4)–N(80)	66.59(16)
Ag(1)...Ag(2)	3.2497(4)	Ag(1)...Ag(2)	2.9089(6)
Ag(1)...Ag(1 ⁱ)	6.8167(7)	Ag(1)...Ag(4 ^v)	3.0660(6)
Ag(2)...Ag(2 ^{iv})	6.8762(7)	Ag(2)...Ag(3)	3.0415(6)
		Ag(3)...Ag(4)	2.9108(6)
τ [Ag(1)] ^a	0.06		
τ [Ag(2)] ^a	0.02		

^aSee ref. [1] for the definition of τ (page 4). An ideal square pyramidal geometry gives $\tau = 0$, while an ideal trigonal bipyramidal geometry yields $\tau = 1$.

Table S4. Metric parameters for intra-dimer $\pi\cdots\pi$ interactions in α -2·MeNO₂ (Å, °). See Fig. S7 for the atom numbering scheme employed. Symmetry codes: (i) 1-*x*, 1-*y*, 1-*z*; (ii) 1-*x*, 1-*y*, -*z*; (v) 1-*x*, -*y*, 1-*z*.

	Dihedral angle	Interplanar distance	Horizontal offset
[N(3)–C(8)]...[N(3 ⁱ)...C(8 ⁱ)]	0	3.255(6)	2.00
[N(24)–C(29)]...[N(24 ⁱⁱ)...C(29 ⁱⁱ)]	0	3.221(9)	2.11

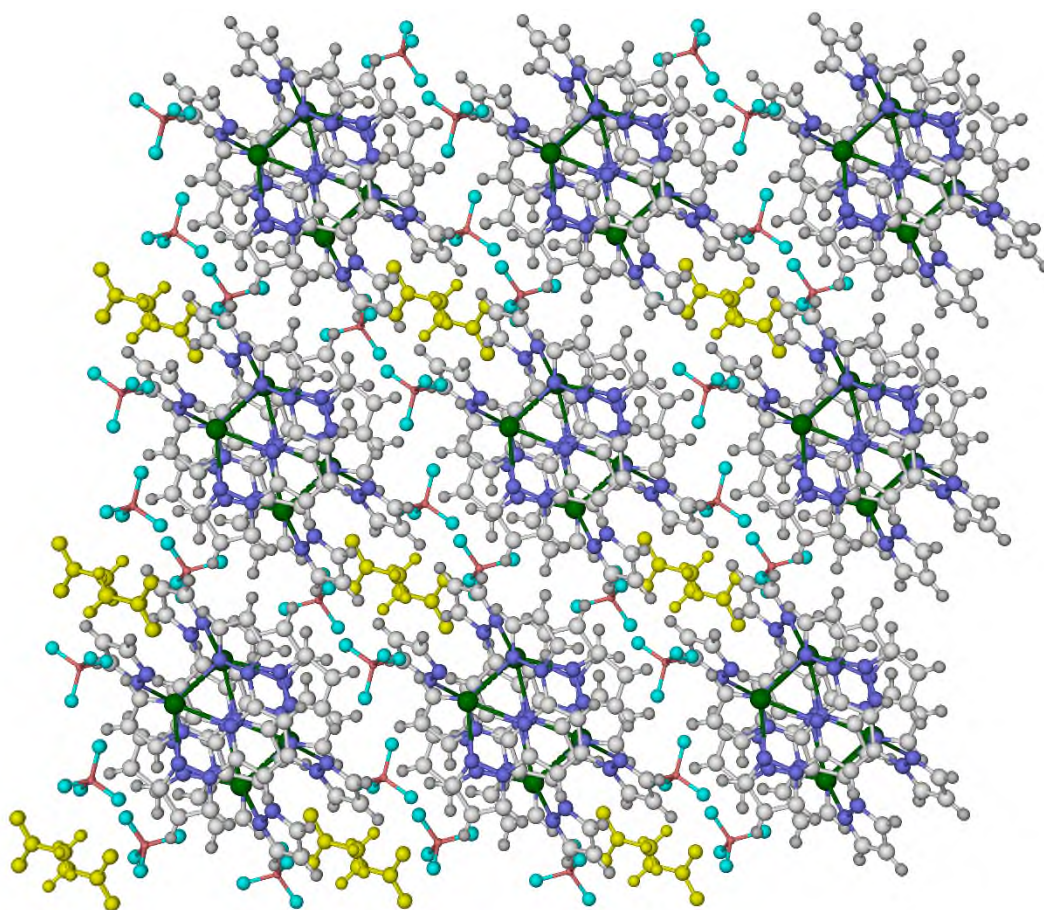


Figure S9. Packing diagram of α -2·MeNO₂, showing the well-separated coordination polymer chains in the lattice. The view is along the [001] crystal vector, with the *b* axis horizontal. Only one orientation of the disordered solvent molecule is shown, and all atoms have arbitrary radii. Colour code: C, white; H, pale grey; Ag, green; B, pink; F, cyan; N, blue; MeNO₂, yellow.

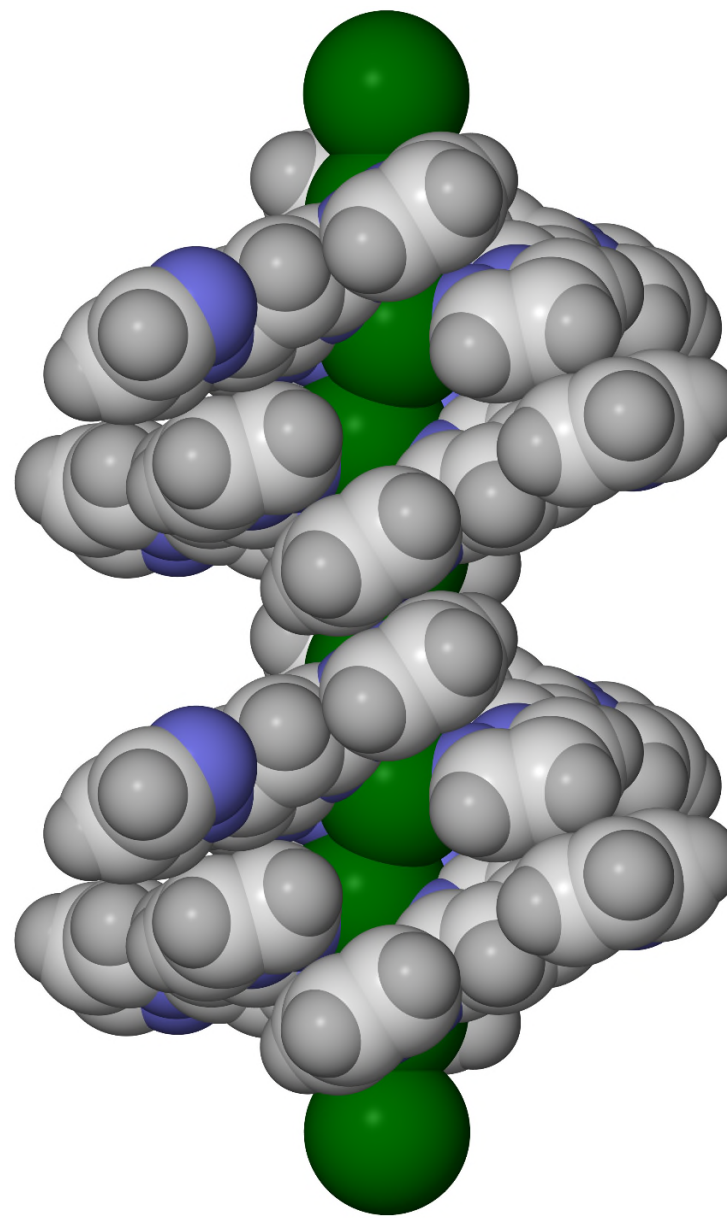
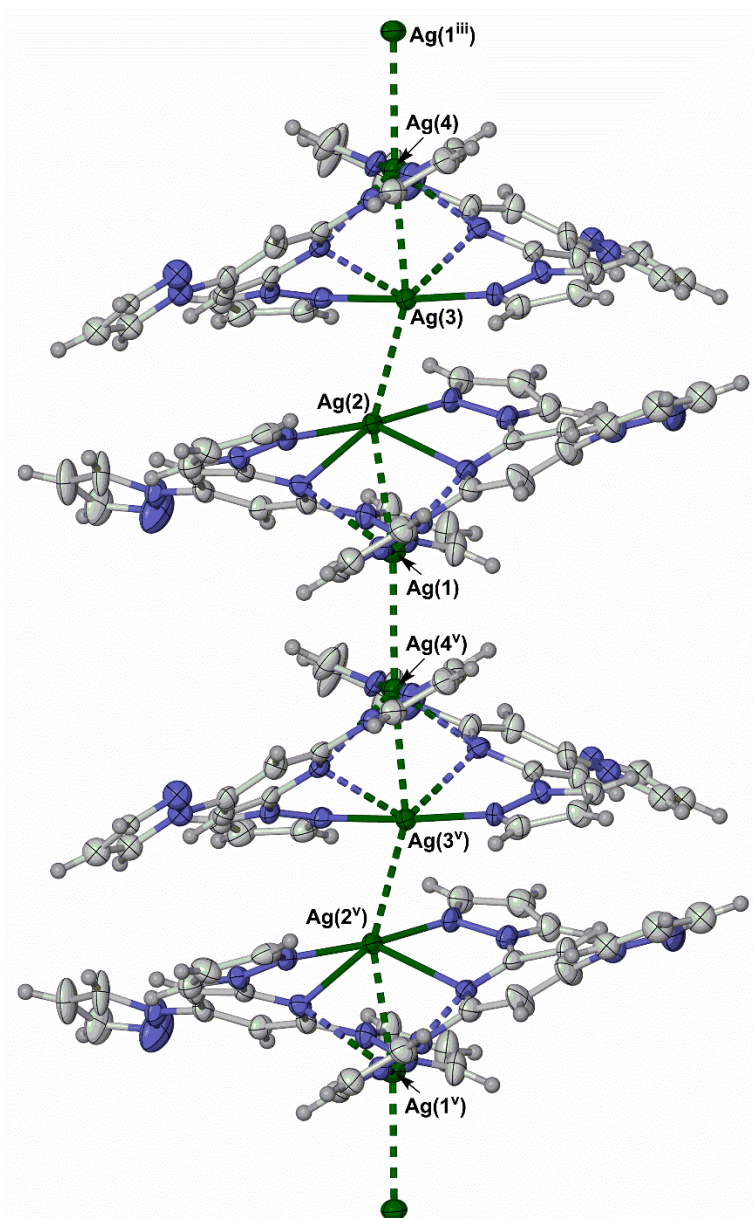


Figure S10. An extended helical chain in β -2-yMeNO₂, plotted with 50 % displacement ellipsoids (left) and space-filling view (right). Only one orientation of the disordered pyrazolyl groups is shown; other details as for Figure S4. Symmetry codes: (iii) $x, 1+y, z$; (v) $x, -1+y, z$.

Table S5. Metric parameters for intramolecular $\pi\cdots\pi$ contacts in β -2·yMeNO₂ (Å, °). See Fig. S8 for the atom numbering scheme employed.

	Dihedral angle	Interplanar distance	Horizontal offset
[N(11)–C(15)]...[N(37)...C(41)]	12.7(3)	3.60(2)	1.45
[N(16)–C(20)]...[N(32)...C(36)]	16.6(3)	3.54(2)	2.23
[N(16)–C(20)]...[N(53)...C(57)]	14.7(3)	3.20(2)	2.07
[N(26)–C(31)]...[N(74)...C(78)]	9.9(3)	3.54(2)	1.65
[N(37)–C(41)]...[N(68)...C(73)]	12.3(3)	3.62(2)	1.04

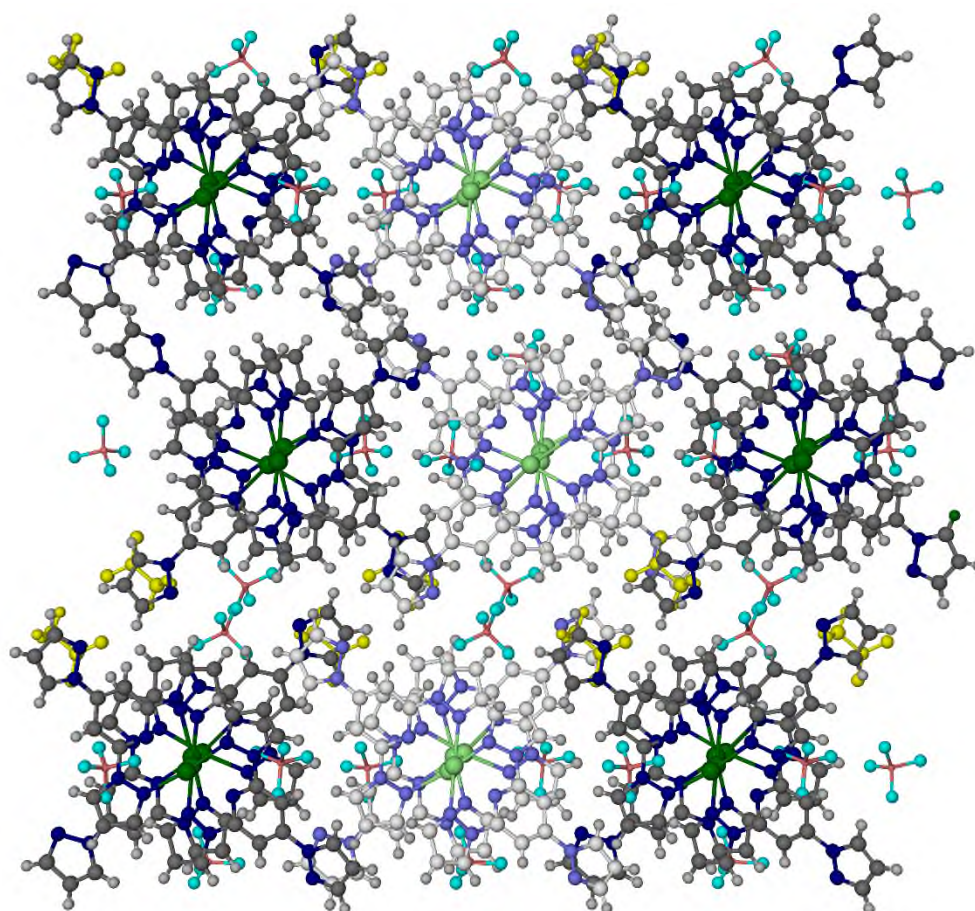


Figure S11. Packing diagram of β -2·yMeNO₂, showing the alternating stripes of Λ (dark colouration) and Δ (pale colouration) helical chains in the lattice. The view shows the (010) crystal plane, with the *c* axis horizontal. Only one orientation of the disordered pyrazolyl groups is shown, and all atoms have arbitrary radii. Colour code: C, dark grey or white; H, pale grey; Ag, dark or pale green; B, pink; F, cyan; N, dark or pale blue; MeNO₂, yellow.

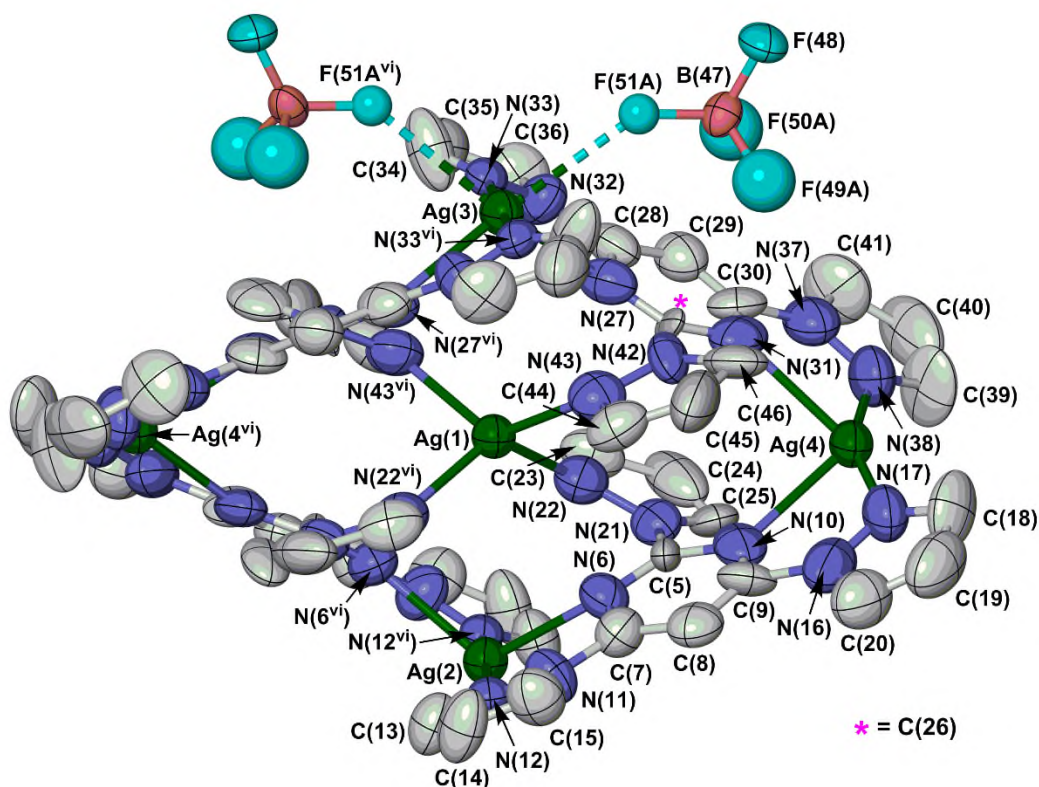


Figure S12. View of the pentanuclear $[\text{Ag}_5(\text{tpym})_4(\text{BF}_4)_2]^{3+}$ assembly in $4 \cdot 2\text{MeNO}_2$, showing the full atom numbering scheme. Only one orientation of the disordered BF_4^- ion is shown. Other details as for Figure S4. Symmetry code: (vi) $1-x, y, 3/2-z$. Colour code: C, white; Ag, green; B, pink; F, cyan; N, blue.

Table S6. Selected bond lengths (Å) and angles ($^\circ$) for $4 \cdot 2\text{MeNO}_2$, including intramolecular Ag...Ag distances. See Fig. S12 for the atom numbering scheme employed. Symmetry code: (vi) $1-x, y, 3/2-z$.

Ag(1)–N(22)	2.374(11)	Ag(3)–N(33)	2.240(10)
Ag(1)–N(43)	2.366(10)	Ag(3)–F(51A/B/C)	2.771(13)/2.902(17)/2.98(2)
Ag(2)–N(6)	2.491(10)	Ag(4)–N(10)	2.578(11)
Ag(2)–N(12)	2.238(10)	Ag(4)–N(17)	2.282(13)
Ag(3)–N(27)	2.498(10)	Ag(4)–N(31)	2.563(11)
		Ag(4)–N(38)	2.216(14)
N(22)–Ag(1)–N(22 ^{xviii})	128.6(5)	N(27)–Ag(3)–F(51A/B/C ^{xviii})	76.7(4)/70.7(4)/79.6(4)
N(22)–Ag(1)–N(43)	97.7(3)	N(33)–Ag(3)–N(33 ^{xviii})	176.1(4)
N(22)–Ag(1)–N(43 ^{xviii})	104.2(4)	N(33)–Ag(3)–F(51A/B/C)	84.4(6)/97.3(5)/73.8(5)
N(43)–Ag(1)–N(43 ^{xviii})	128.1(5)	N(33)–Ag(3)–F(51A/B/C ^{xviii})	93.1(6)/80.4(5)/103.9(5)
N(6)–Ag(2)–N(6 ^{xviii})	114.4(5)	F(51A/B/C)–Ag(3)–F(51A/B/C ^{xviii})	103.2(5)–109.6(7)
N(6)–Ag(2)–N(12)	68.2(4)	N(10)–Ag(4)–N(17)	66.2(4)
N(6)–Ag(2)–N(12 ^{xviii})	113.7(3)	N(10)–Ag(4)–N(31)	89.0(4)
N(12)–Ag(2)–N(12 ^{xviii})	176.8(4)	N(10)–Ag(4)–N(38)	133.6(4)
N(27)–Ag(3)–N(27 ^{xviii})	115.0(5)	N(17)–Ag(4)–N(31)	130.3(4)
N(27)–Ag(3)–N(33)	69.3(4)	N(17)–Ag(4)–N(38)	157.1(4)
N(27)–Ag(3)–N(33 ^{xviii})	113.0(3)	N(31)–Ag(4)–N(38)	68.4(4)
N(27)–Ag(3)–F(51A/B/C)	153.6(6)/166.5(5)/143.1(5)		
Ag(1)...Ag(2)	3.7443(16)	Ag(2)...Ag(3)	7.4758(16)
Ag(1)...Ag(3)	3.7315(16)	Ag(2)...Ag(4)	6.9279(11)
Ag(1)...Ag(4)	5.8354(9)	Ag(3)...Ag(4)	6.9319(11)

Table S7. Metric parameters for intramolecular and intermolecular $\pi\cdots\pi$ interactions in **4**·2MeNO₂ (Å, °). See Fig. S12 for the atom numbering scheme employed. Symmetry code: (vi) $1-x, y, \frac{3}{2}-z$; (vii) $1-x, -1+y, \frac{3}{2}-z$; (viii) $\frac{1}{2}-x, \frac{1}{2}-y, 1-z$.

	Dihedral angle	Interplanar distance	Horizontal offset
Intramolecular			
[N(11)–C(15)]...[N(21 ^{vi})...C(25 ^{vi})]	6.7(7)	3.28(4)	1.82
[N(21)–C(25)]...[C(26)...N(31)]	4.6(6)	3.34(4)	0.84
[N(32)–C(36)]...[N(42 ^{vi})...C(46 ^{vi})]	5.1(7)	3.23(5)	1.80
[N(42)–C(46)]...[C(5)...N(10)]	5.0(6)	3.35(4)	0.80
Intermolecular			
[N(11)–C(15)]...[N(32 ^{viii})–C(36 ^{viii})]	9.2(8)	3.37(4)	1.23
[N(16)–C(21)]...[N(16 ^{viii})–C(21 ^{viii})]	0	3.37(12)	1.13

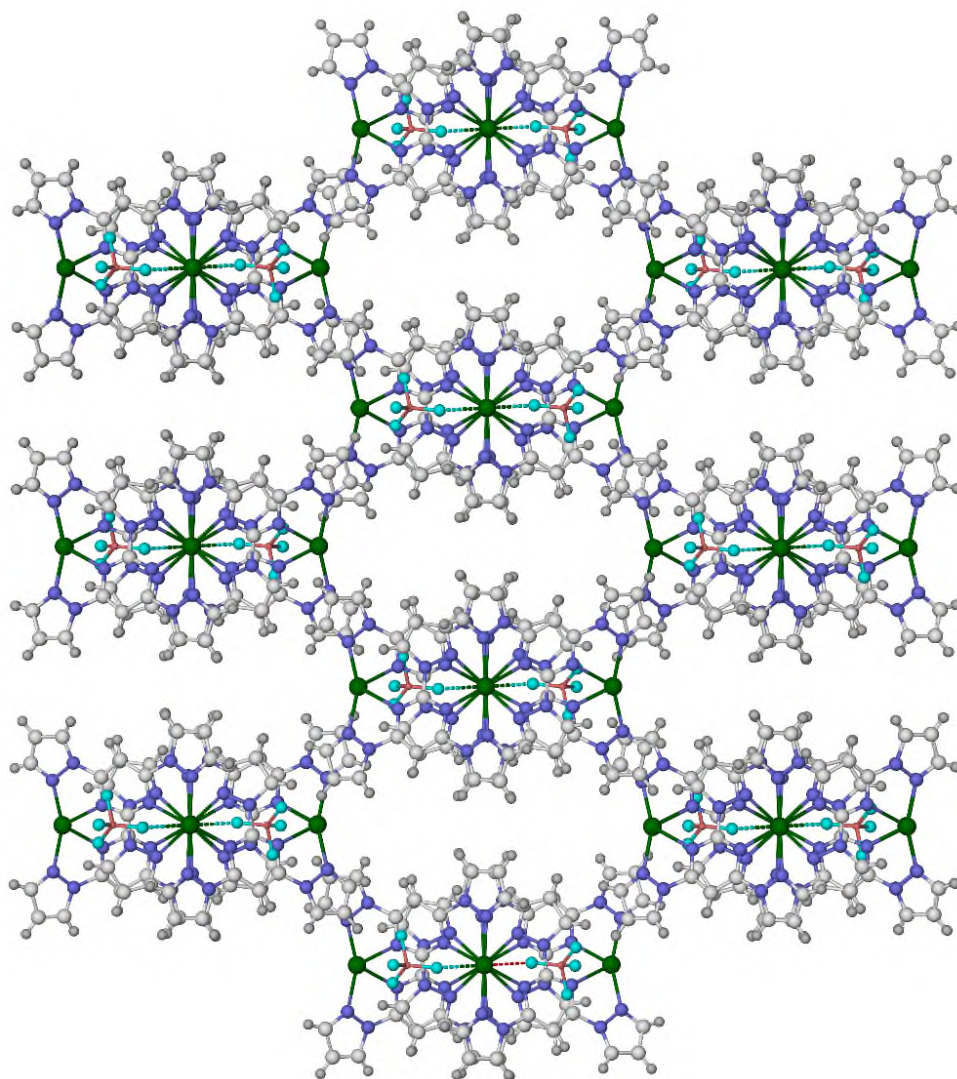


Figure S13. Packing diagram of **4**·2MeNO₂, showing the anion- and solvent-filled voids in the lattice. The view shows the (010) crystal plane, with the *c* axis vertical. All atoms have arbitrary radii.

Colour code: C, white; H, pale grey; Ag, green; B, pink; F, cyan; N, blue.

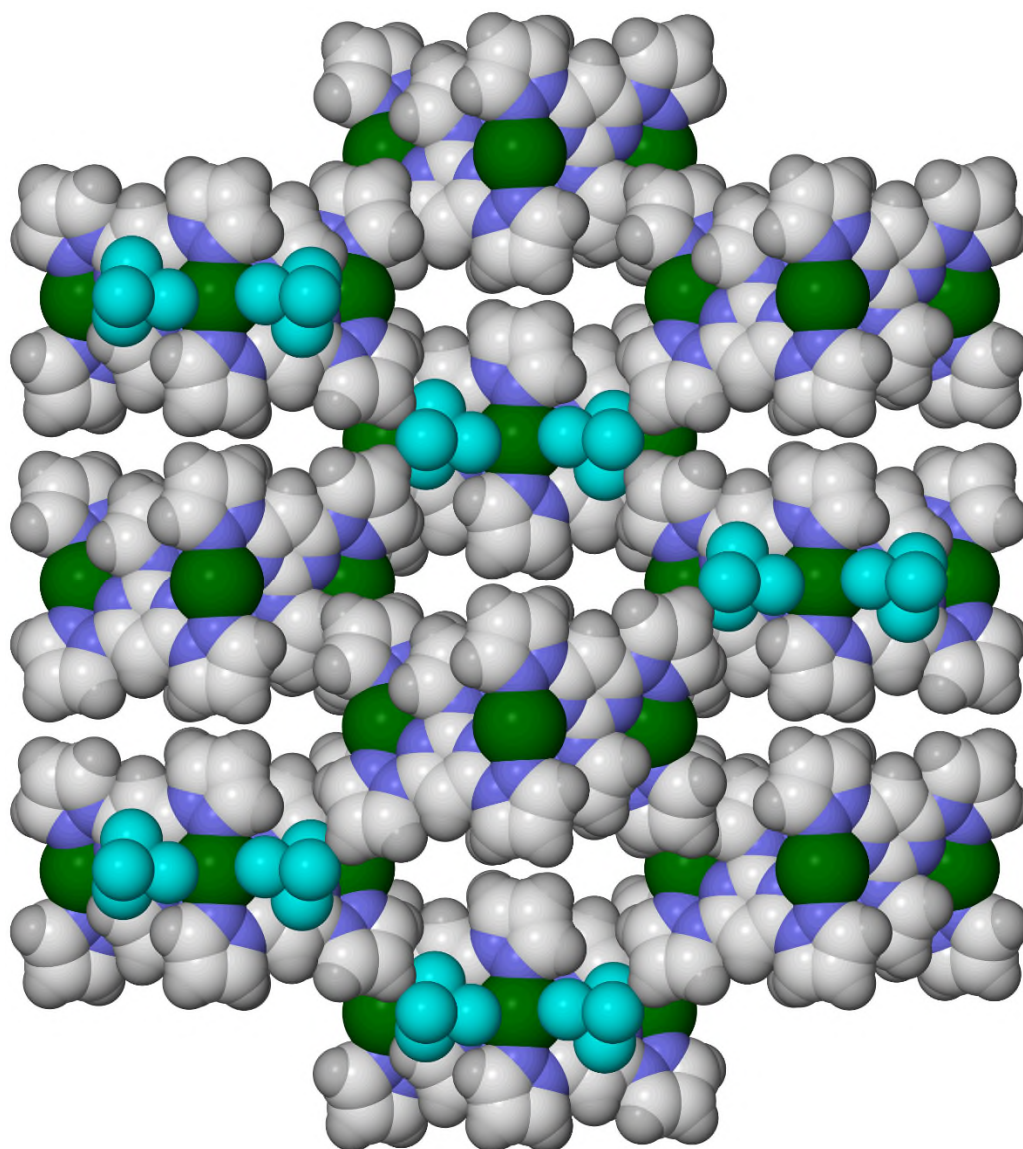


Figure S14. Space-filling packing diagram of $4 \cdot 2\text{MeNO}_2$, showing the anion- and solvent-filled voids in the lattice. The view is the same as in Figure S13.

Colour code: C, white; H, pale grey; Ag, green; B, pink; F, cyan; N, blue.

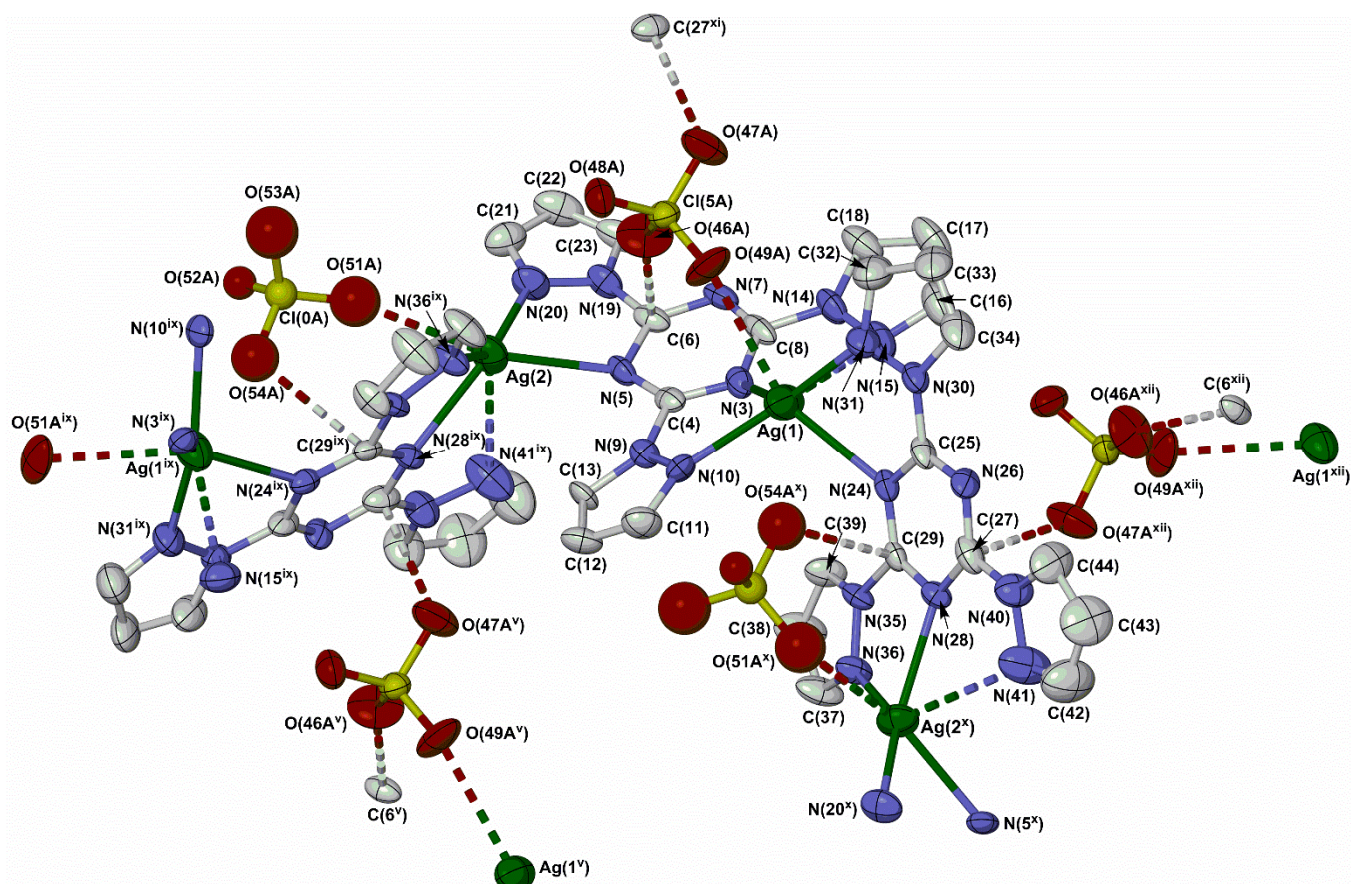
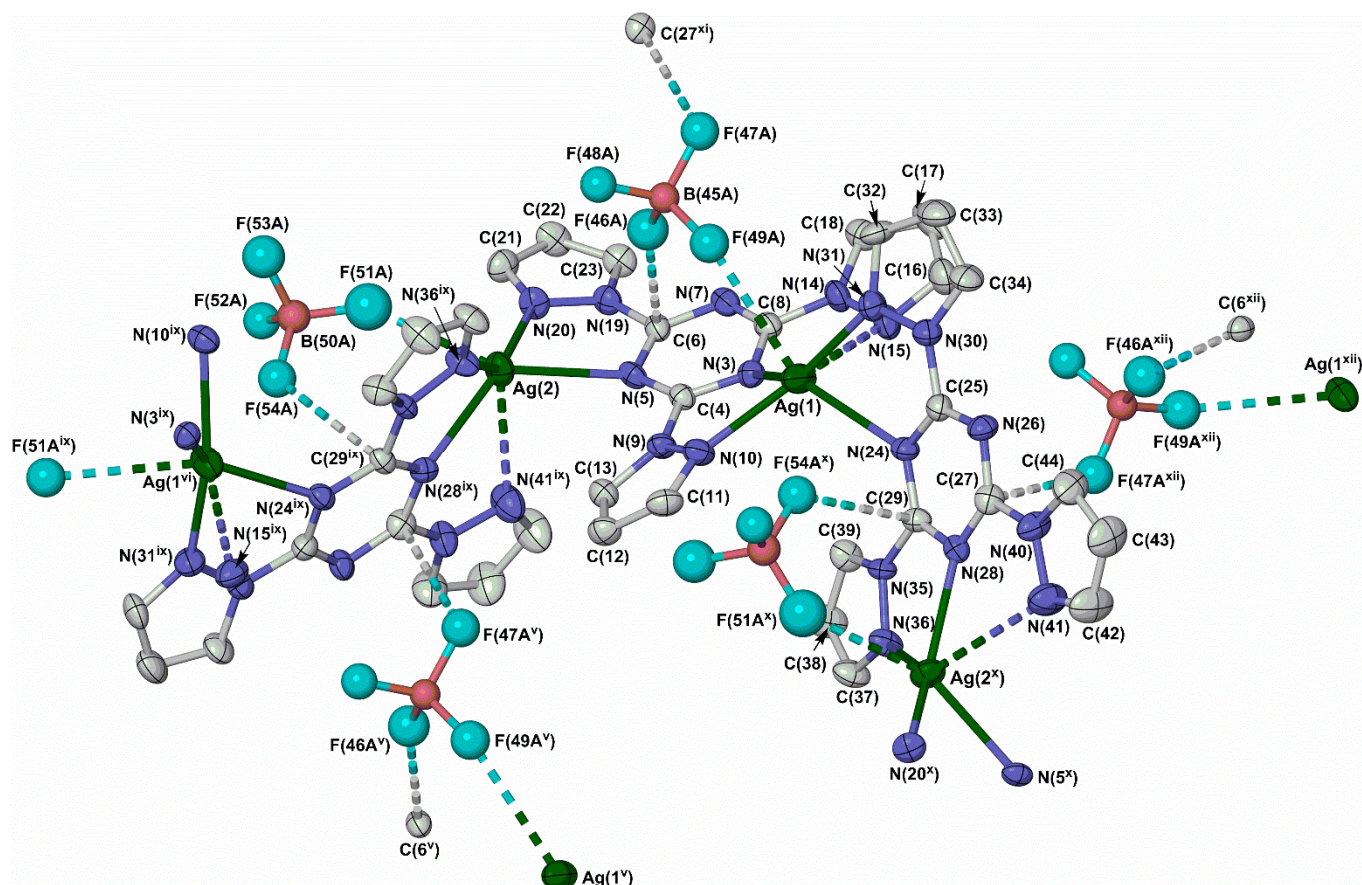


Figure S15. Views of the full asymmetric unit of isostructural [Ag(tpt)]BF₄ (**5a**, top) and [Ag(tpt)]ClO₄ (**5b**, bottom), showing the full atom numbering scheme. Only one orientation of the disordered anions is shown; other details as for Figure S4. Symmetry codes: (v) $x, -1+y, z$; (ix) $1-x, -y, 1/2+z$; (x) $1-x, -y, -1/2+z$; (xi) $1-x, 1-y, 1/2+z$; (xii) $1-x, 1-y, -1/2+z$. Colour code: C, white; Ag, green; B, pink; Cl, yellow; F, cyan; N, blue; O, red.

Table S8. Selected bond lengths (Å) and angles (°) for the isostructural complexes **5a** and **5b**, including intramolecular Ag...Ag distances and anion... π contacts. See Fig. S15 for the atom numbering schemes employed. Symmetry codes: (ix) 1–x, –y, $1/2+z$; (x) 1–x, –y, $-1/2+z$; (xii) 1–x, 1–y, $-1/2+z$.

5a		5b	
Ag(1)–N(3)	2.398(6)	Ag(1)–N(3)	2.395(10)
Ag(1)–N(10)	2.286(6)	Ag(1)–N(10)	2.285(10)
Ag(1)–N(15)	2.951(7)	Ag(1)–N(15)	2.964(12)
Ag(1)–N(24)	2.573(6)	Ag(1)–N(24)	2.586(9)
Ag(1)–N(31)	2.193(6)	Ag(1)–N(31)	2.210(10)
Ag(1)–F(49A/B)	2.971(9)/3.133(16)	Ag(1)–O(49A/B)	2.897(15)/2.95(5)
Ag(2)–N(5)	2.466(6)	Ag(2)–N(5)	2.469(9)
Ag(2)–N(20)	2.245(5)	Ag(2)–N(20)	2.218(9)
Ag(2)–N(28 ^{ix})	2.400(6)	Ag(2)–N(28 ^{ix})	2.423(8)
Ag(2)–N(36 ^{ix})	2.286(6)	Ag(2)–N(36 ^{ix})	2.300(9)
Ag(2)–N(41 ^{ix})	2.906(8)	Ag(2)–N(41 ^{ix})	2.950(13)
Ag(2)–F(51A/B)	2.795(15)/2.904(13)	Ag(2)–O(51A/B/C)	2.91(3)/2.892(19)/2.70(2)
N(3)–Ag(1)–N(10)		N(3)–Ag(1)–N(10)	70.2(3)
N(3)–Ag(1)–N(15)		N(3)–Ag(1)–N(15)	58.9(3)
N(3)–Ag(1)–N(24)		N(3)–Ag(1)–N(24)	130.4(3)
N(3)–Ag(1)–N(31)		N(3)–Ag(1)–N(31)	131.9(4)
N(3)–Ag(1)–F(49A/B)		N(3)–Ag(1)–O(49A/B)	81.6(4)/81.5(10)
N(10)–Ag(1)–N(15)		N(10)–Ag(1)–N(15)	126.1(3)
N(10)–Ag(1)–N(24)		N(10)–Ag(1)–N(24)	109.5(3)
N(10)–Ag(1)–N(31)		N(10)–Ag(1)–N(31)	154.0(4)
N(10)–Ag(1)–F(49A/B)		N(10)–Ag(1)–O(49A/B)	94.9(6) 97.6(13)
N(15)–Ag(1)–N(24)		N(15)–Ag(1)–N(24)	91.7(3)
N(15)–Ag(1)–N(31)		N(15)–Ag(1)–N(31)	79.7(4)
N(15)–Ag(1)–F(49A/B)		N(15)–Ag(1)–O(49A/B)	94.4(5)/91.8(12)
N(24)–Ag(1)–N(31)		N(24)–Ag(1)–N(31)	68.5(3)
N(24)–Ag(1)–F(49A/B)		N(24)–Ag(1)–O(49A/B)	144.4(5)/143.2(11)
N(31)–Ag(1)–F(49A/B)		N(31)–Ag(1)–O(49A/B)	78.1(5)/76.2(12)
N(5)–Ag(2)–N(20)		N(5)–Ag(2)–N(20)	70.2(4)
N(5)–Ag(2)–N(28 ^{ix})		N(5)–Ag(2)–N(28 ^{vi})	121.4(3)
N(5)–Ag(2)–N(36 ^{ix})		N(5)–Ag(2)–N(36 ^{vi})	113.0(3)
N(5)–Ag(2)–N(41 ^{ix})		N(5)–Ag(2)–N(41 ^{vi})	80.9(4)
N(5)–Ag(2)–F(51A/B)		N(5)–Ag(2)–O(51A/B/C)	147.3(6)/141.0(4)/145.9(6)
N(20)–Ag(2)–N(28 ^{ix})		N(20)–Ag(2)–N(28 ^{vi})	140.7(3)
N(20)–Ag(2)–N(36 ^{ix})		N(20)–Ag(2)–N(36 ^{vi})	145.7(4)
N(20)–Ag(2)–N(41 ^{ix})		N(20)–Ag(2)–N(41 ^{vi})	90.0(4)
N(20)–Ag(2)–F(51A/B)		N(20)–Ag(2)–O(51A/B/C)	78.5(7)/80.8(4)/76.8(6)
N(28 ^{ix})–Ag(2)–N(36 ^{ix})		N(28 ^{vi})–Ag(2)–N(36 ^{vi})	69.0(3)
N(28 ^{ix})–Ag(2)–N(41 ^{ix})		N(28 ^{vi})–Ag(2)–N(41 ^{vi})	58.9(3)
N(28 ^{ix})–Ag(2)–F(51A/B)		N(28 ^{vi})–Ag(2)–O(51A/B/C)	78.3(7)/68.3(4)/89.6(6)
N(36 ^{ix})–Ag(2)–N(41 ^{ix})		N(36 ^{vi})–Ag(2)–N(41 ^{vi})	124.2(3)
N(36 ^{ix})–Ag(2)–F(51A/B)		N(36 ^{vi})–Ag(2)–O(51A/B/C)	98.0(7)/105.7(4)/89.8(7)
N(41 ^{ix})–Ag(2)–F(51A/B)		N(41 ^{vi})–Ag(2)–O(51A/B/C)	90.3(8)/73.4(4)/107.7(7)
Ag(1)...Ag(2)		Ag(1)...Ag(2)	6.2276(15)
Ag(1)...Ag(2 ^x)		Ag(1)...Ag(2 ^x)	6.5019(14)
C(6)...F(46A/B)		C(6)...O(46A/B)	2.889(14)/3.01(4)
C(27)...F(47A ^{xii})/F(48B ^{xii})		C(27)...O(47A/B ^{xii})	3.01(2)/2.99(5)
C(29)...F(54A/B ^x)		C(29)...O(54A/B/C ^x)	3.10(3)/3.07(3)/2.97(3)

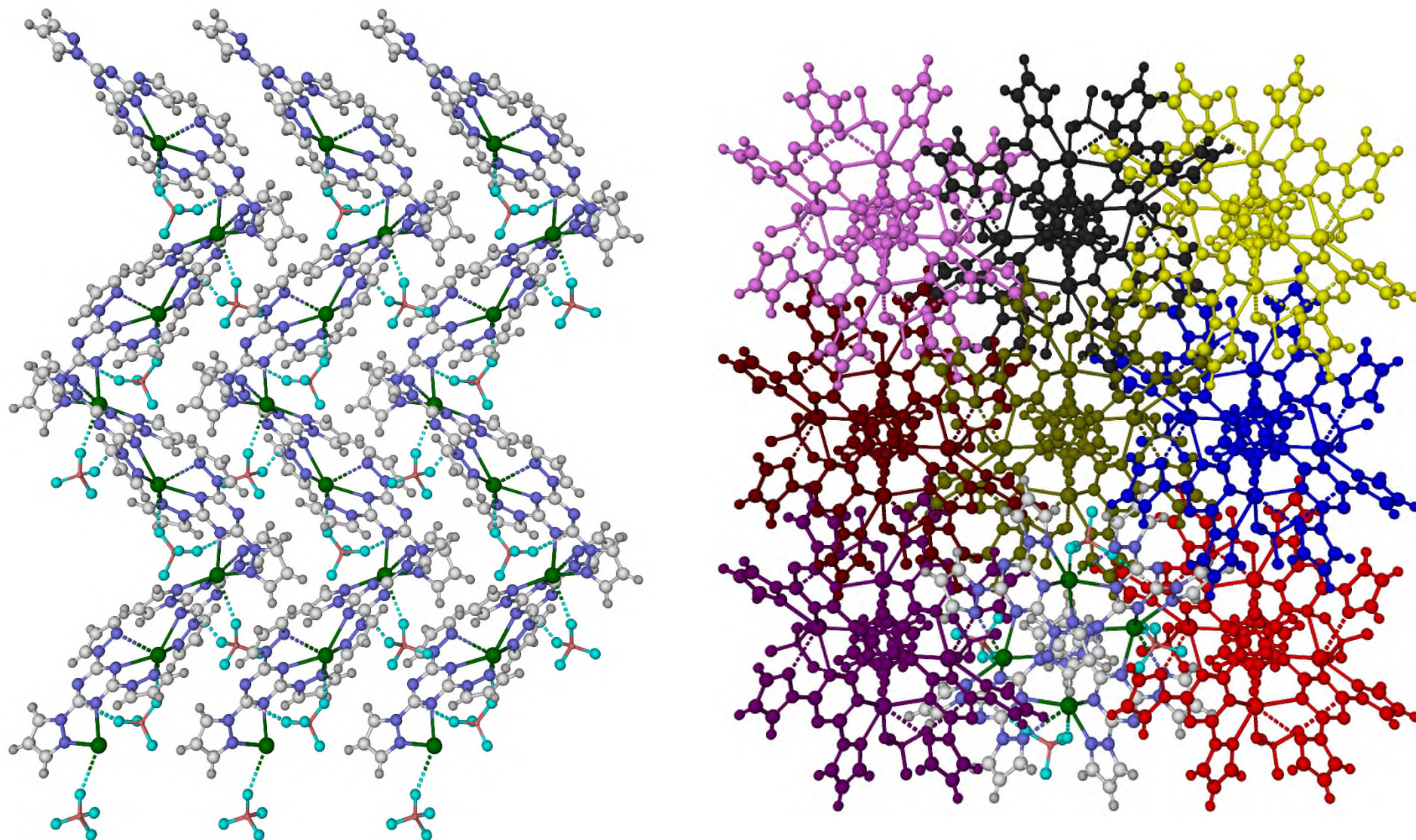


Figure S16. Packing diagrams of **5a**, showing the coparallel helical chains in the lattice. Only one orientation of the disordered anions is shown, and all atoms have arbitrary radii. Left: view shows the (010) crystal plane, with the *c* axis vertical. Colour code: C, white; H, pale grey; Ag, green; B, pink; F, cyan; N, blue. Right: view shows the (001) crystal plane with the *b* axis vertical. Each polymer chain is plotted with a different colour scheme, for clarity.

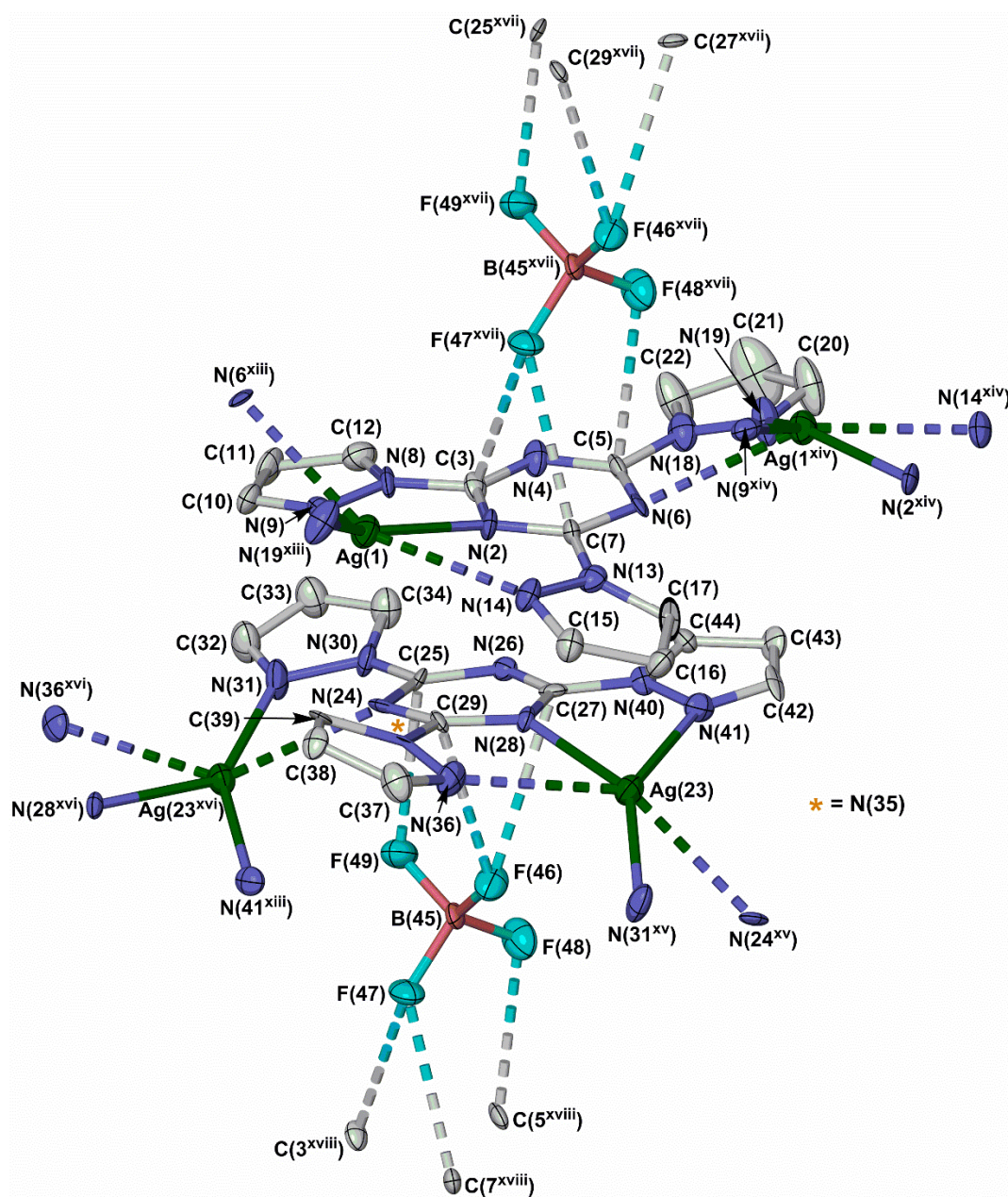


Figure S17. Views of the $[\{\text{Ag}(\text{tpt})\}_2(\text{BF}_4)]^+$ coordination polymer asymmetric unit of **5a**·MeNO₂, showing the full atom numbering schemes. The other BF₄[−] ion and solvent, which do not take part in anion... π interactions, are omitted for clarity. Other details as for Figure S4.

Symmetry codes: (xiii) $2-x, 1/2+y, 1-z$; (xiv) $2-x, -1/2+y, 1-z$; (xv) $1-x, -1/2+y, 1-z$; (xvi) $1-x, 1/2+y, 1-z$; (xvii) $1+x, y, z$; (xviii) $-1+x, y, z$. Colour code: C, white; H, pale grey; Ag, green; B, pink; F, cyan; N, blue; O, red.

Table S9. Selected bond lengths (Å) and angles (°) for **5a**·MeNO₂, including intramolecular Ag...Ag distances and anion... π contacts. See Fig. S17 for the atom numbering scheme employed. Symmetry codes: (xiii) $2-x, \frac{1}{2}+y, 1-z$; (xiv) $2-x, -\frac{1}{2}+y, 1-z$; (xv) $1-x, -\frac{1}{2}+y, 1-z$; (xvi) $1-x, \frac{1}{2}+y, 1-z$; (xvii) $1+x, y, z$.

Ag(1)–N(2)	2.388(11)	Ag(23)–N(24 ^{xv})	2.821(10)
Ag(1)–N(6 ^{xiii})	2.849(10)	Ag(23)–N(28)	2.376(10)
Ag(1)–N(9)	2.372(11)	Ag(23)–N(31 ^{xv})	2.223(12)
Ag(1)–N(14)	2.832(11)	Ag(23)–N(36)	2.877(12)
Ag(1)–N(19 ^{xiii})	2.226(12)	Ag(23)–N(41)	2.416(11)
N(2)–Ag(1)–N(6 ^{xiii})	128.8(3)	N(24 ^{xv})–Ag(23)–N(28)	127.9(3)
N(2)–Ag(1)–N(9)	68.8(4)	N(24 ^{xv})–Ag(23)–N(31 ^{xv})	64.8(4)
N(2)–Ag(1)–N(14)	61.9(4)	N(24 ^{xv})–Ag(23)–N(36)	139.3(3)
N(2)–Ag(1)–N(19 ^{xiii})	144.6(5)	N(24 ^{xv})–Ag(23)–N(41)	83.1(3)
N(6 ^{xiii})–Ag(1)–N(9)	85.1(3)	N(28)–Ag(23)–N(31 ^{xv})	140.4(4)
N(6 ^{xiii})–Ag(1)–N(14)	139.2(3)	N(28)–Ag(23)–N(36)	62.4(3)
N(6 ^{xiii})–Ag(1)–N(19 ^{xiii})	63.3(4)	N(28)–Ag(23)–N(41)	67.9(4)
N(9)–Ag(1)–N(14)	128.1(4)	N(31 ^{xv})–Ag(23)–N(36)	84.7(4)
N(9)–Ag(1)–N(19 ^{xiii})	144.0(4)	N(31 ^{xv})–Ag(23)–N(41)	146.4(4)
N(14)–Ag(1)–N(19 ^{xiii})	87.8(4)	N(36)–Ag(23)–N(41)	128.5(4)
Ag(1)...Ag(1 ^{xiv})	6.9609(9)	Ag(23)...Ag(23 ^{xvi})	6.9518(8)
τ [Ag(1)] ^a	0.09	τ [Ag(23)] ^a	0.02
C(3)...F(47 ^{xvii})	3.016(13)	C(25)...F(49)	2.897(15)
C(5)...F(48 ^{xvii})	2.929(15)	C(27)...F(46)	3.092(14)
C(7)...F(47 ^{xvii})	2.995(15)	C(29)...F(46)	2.980(14)

^aSee ref. [1] for the definition of τ (page 4). An ideal square pyramidal geometry gives $\tau = 0$, while an ideal trigonal bipyramidal geometry yields $\tau = 1$.

Table S10. Metric parameters for intra-chain and inter-chain π ... π interactions in **5a**·MeNO₂ (Å, °). See Fig. S17 for the atom numbering scheme employed. Symmetry code: (xiii) $2-x, \frac{1}{2}+y, 1-z$; (xvi) $1-x, \frac{1}{2}+y, 1-z$.

	Dihedral angle	Interplanar distance	Horizontal offset
Intra-chain			
[N(8)–C(12)]...[N(13 ^{xiii})...C(17 ^{xiii})]	11.2(4)	3.27(4)	1.02
[N(35)–C(39)]...[N(40 ^{xvi})...C(44 ^{xvi})]	11.91(4)	3.38(3)	0.71
Inter-chain			
[N(2)–C(12)]...[N(24)...C(34)]	2.5(2)	3.25(5)	1.32

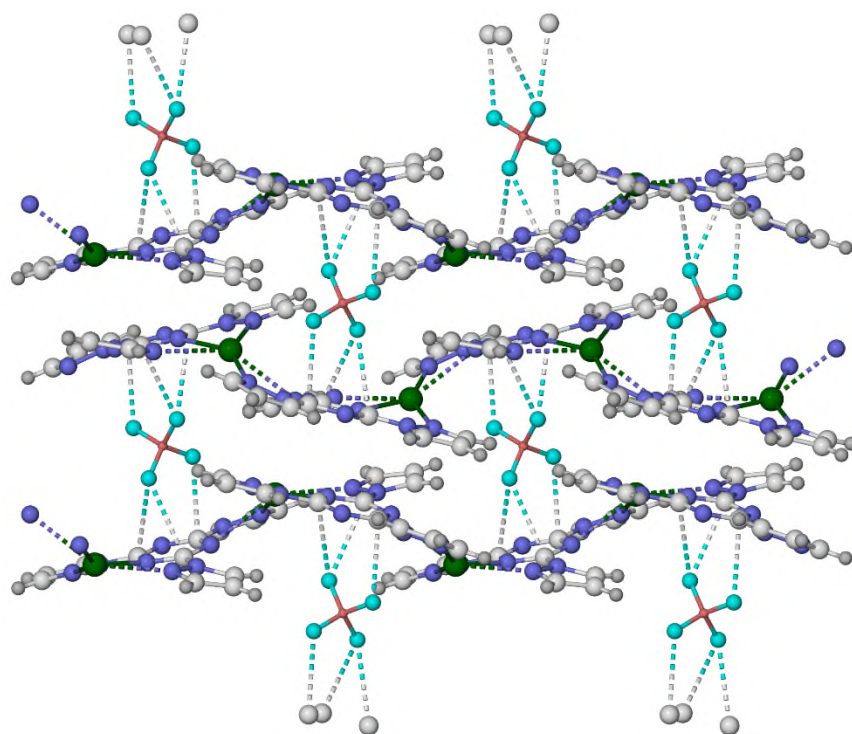


Figure S18. Packing diagram of $5\mathbf{a} \cdot \text{MeNO}_2$, showing the anion... π interactions linking the zig-zag coordination polymer chains. The view is parallel to the [105] crystal vector, with the b axis horizontal. All atoms have arbitrary radii. Colour code: C, white; H, pale grey; Ag, green; B, pink; F, cyan; N, blue.

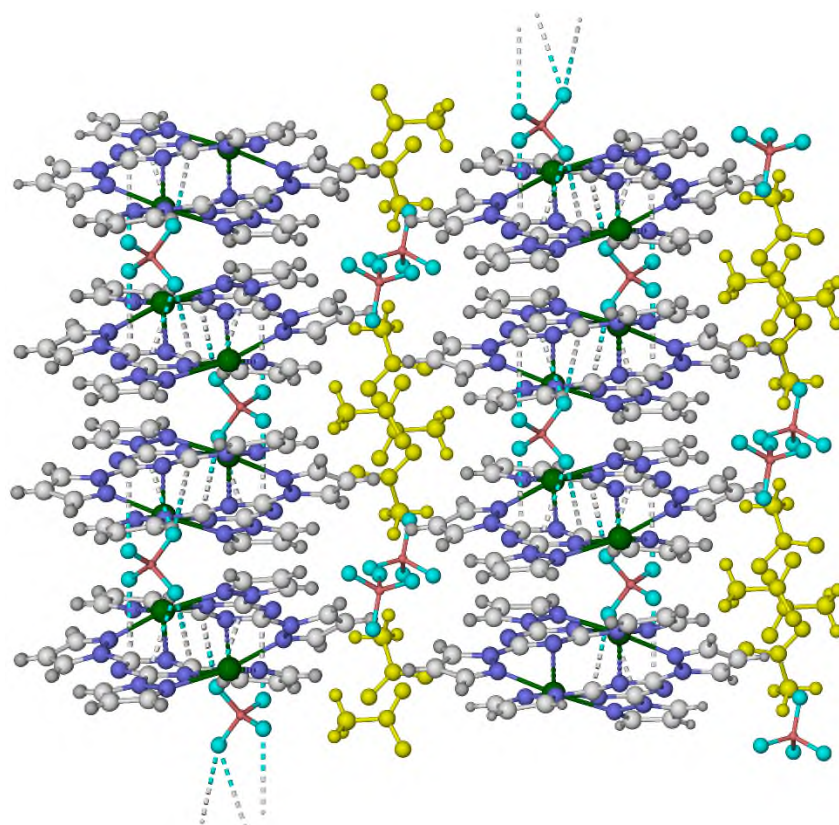


Figure S19. Packing diagram of $5\mathbf{a} \cdot \text{MeNO}_2$, showing the coordination polymer/anion... π layers separated by the remaining anions and solvent. The view shows the (010) crystal plane, with the a axis vertical. All atoms have arbitrary radii. Colour code: C, white; H, pale grey; Ag, green; B, pink; F, cyan; N, blue; MeNO_2 , yellow.

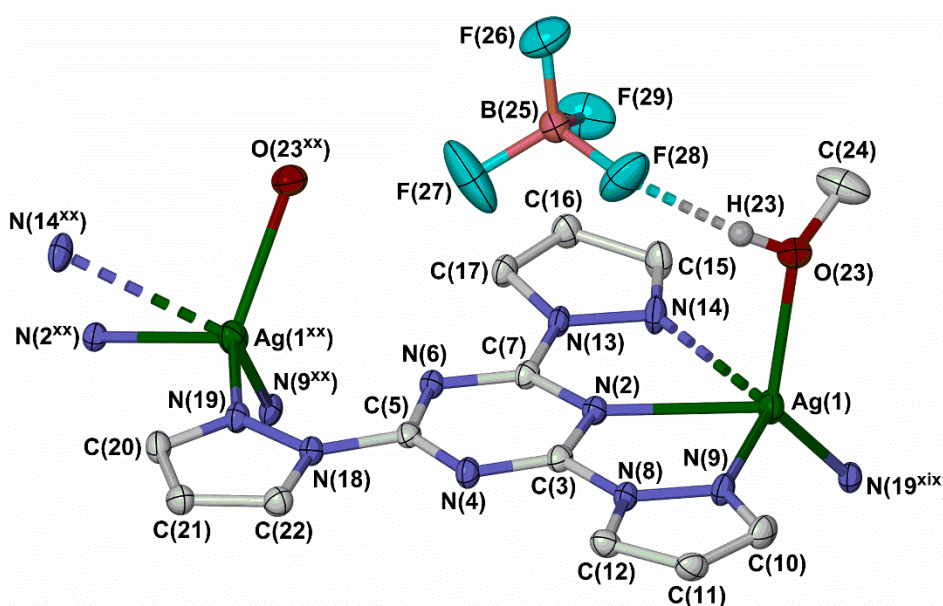


Figure S20. View of the full $[\text{Ag}(\text{tpf})(\text{MeOH})]\text{BF}_4$ asymmetric unit of **5a**·MeOH, showing the full atom numbering schemes. Details as for Figure S4. Symmetry codes: (xix) $1/2+x, y, 3/2-z$; (xx) $-1/2+x, y, 3/2-z$. Colour code: C, white; H, pale grey; Ag, green; B, pink; F, cyan; N, blue; O, red.

Table S11. Selected bond lengths (Å) and angles (°) for **5a**·MeOH, including intramolecular Ag...Ag distances. See Fig. S20 for the atom numbering schemes employed. Symmetry codes: (xix) $1/2+x, y, 3/2-z$; (xx) $-1/2+x, y, 3/2-z$.

Ag(1)–N(2)	2.458(2)	Ag(1)–N(19 ^{xix})	2.217(2)
Ag(1)–N(9)	2.381(2)	Ag(1)–O(23)	2.387(2)
Ag(1)–N(14)	2.797(2)		
N(2)–Ag(1)–N(9)	68.10(7)	N(9)–Ag(1)–N(19 ^{xix})	122.93(8)
N(2)–Ag(1)–N(14)	60.61(7)	N(9)–Ag(1)–O(23)	96.60(7)
N(2)–Ag(1)–N(19 ^{xix})	124.21(7)	N(14)–Ag(1)–N(19 ^{xix})	88.93(7)
N(2)–Ag(1)–O(23)	96.43(7)	N(14)–Ag(1)–O(23)	87.78(7)
N(9)–Ag(1)–N(14)	128.68(7)	N(19 ^{xix})–Ag(1)–O(23)	130.25(7)
Ag(1)...Ag(1 ^{xx})	7.7359(2)	τ^a	0.03

^aSee ref. [1] for the definition of τ (page 4). An ideal square pyramidal geometry gives $\tau = 0$, while an ideal trigonal bipyramidal geometry yields $\tau = 1$.

Table S12. Hydrogen bond parameters ($\text{\AA}$, $^\circ$) for **5a**·MeOH. See Fig. S20 for the atom numbering scheme.

	O–H	H...F	O...F	O–H...F
O(23)–H(23)...F(28)	0.80(4)	1.94(4)	2.727(3)	166(4)

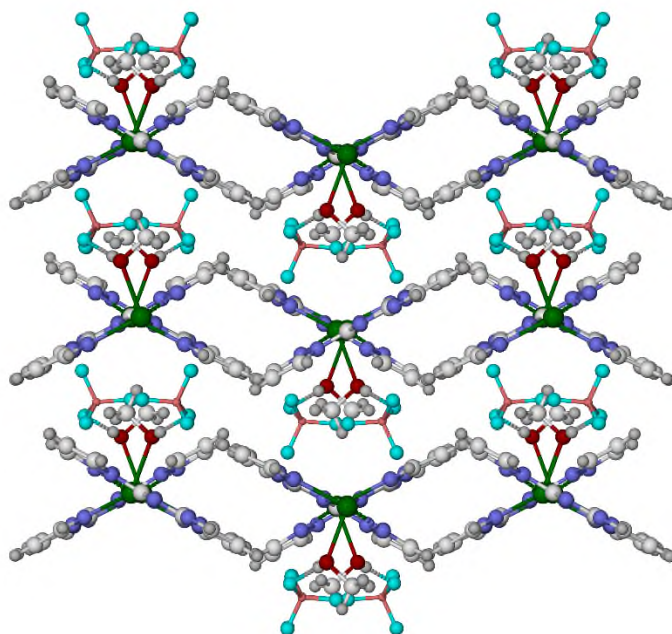


Figure S21. Packing diagram of **5a**·MeOH, showing well-separated polymer chains in the lattice. The view shows the (100) crystal plane, with the unit cell *c* axis horizontal. Colour code: C, white; H, pale grey; Ag, green; B, pink; F, cyan; N, blue; O, red.

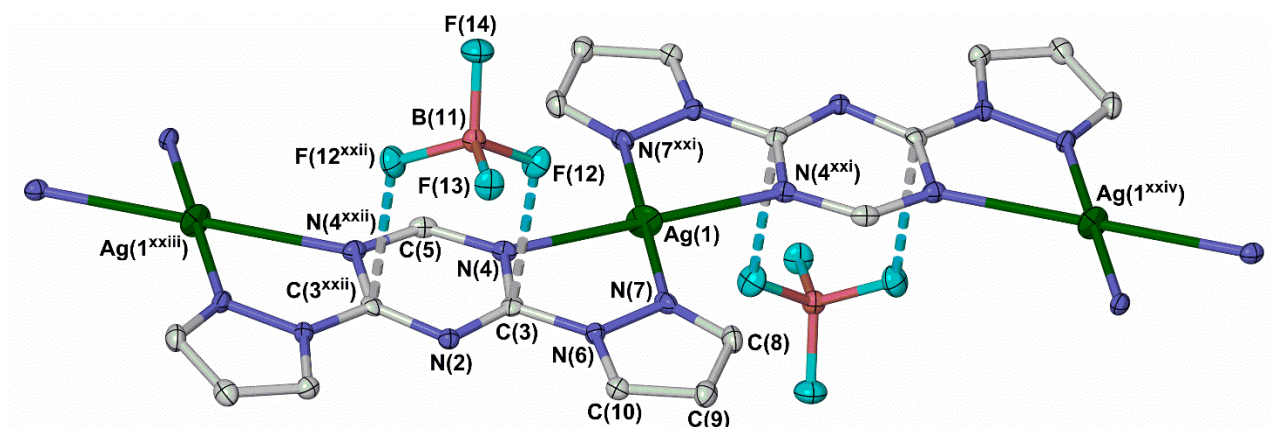


Figure S22. View of the $\{[Ag(bpt)]BF_4\}_n$ coordination polymer chain in **6**, showing the full atom numbering scheme. Details as for Figure S4. Symmetry codes: (xxi) $2-x, 1-y, -z$; (xxii) $x, 3/2-y, z$; (xxiii) $2-x, 1/2+y, -z$; (xxiv) $2-x, -1/2+y, -z$. Colour code: C, white; Ag, green; B, pink; F, cyan; N, blue.

Table S13. Selected bond lengths (Å) and angles (°) for **6**, including intramolecular Ag...Ag distances and anion... π contacts. See Fig. S22 for the atom numbering scheme employed. Symmetry codes: (xxi) $2-x, 1-y, -z$; (xxiii) $2-x, 1/2+y, -z$.

Ag(1)–N(4)	2.523(2)
Ag(1)–N(7)	2.289(4)
N(4)–Ag(1)–N(4 ^{xxi})	180
N(4)–Ag(1)–N(7)	68.71(7)
N(4)–Ag(1)–N(7 ^{xxi})	111.29(7)
N(7)–Ag(1)–N(7 ^{xxi})	180
Ag(1)...Ag(1 ^{xxiii})	7.1038(2)
C(3)...F(12)	2.823(3)

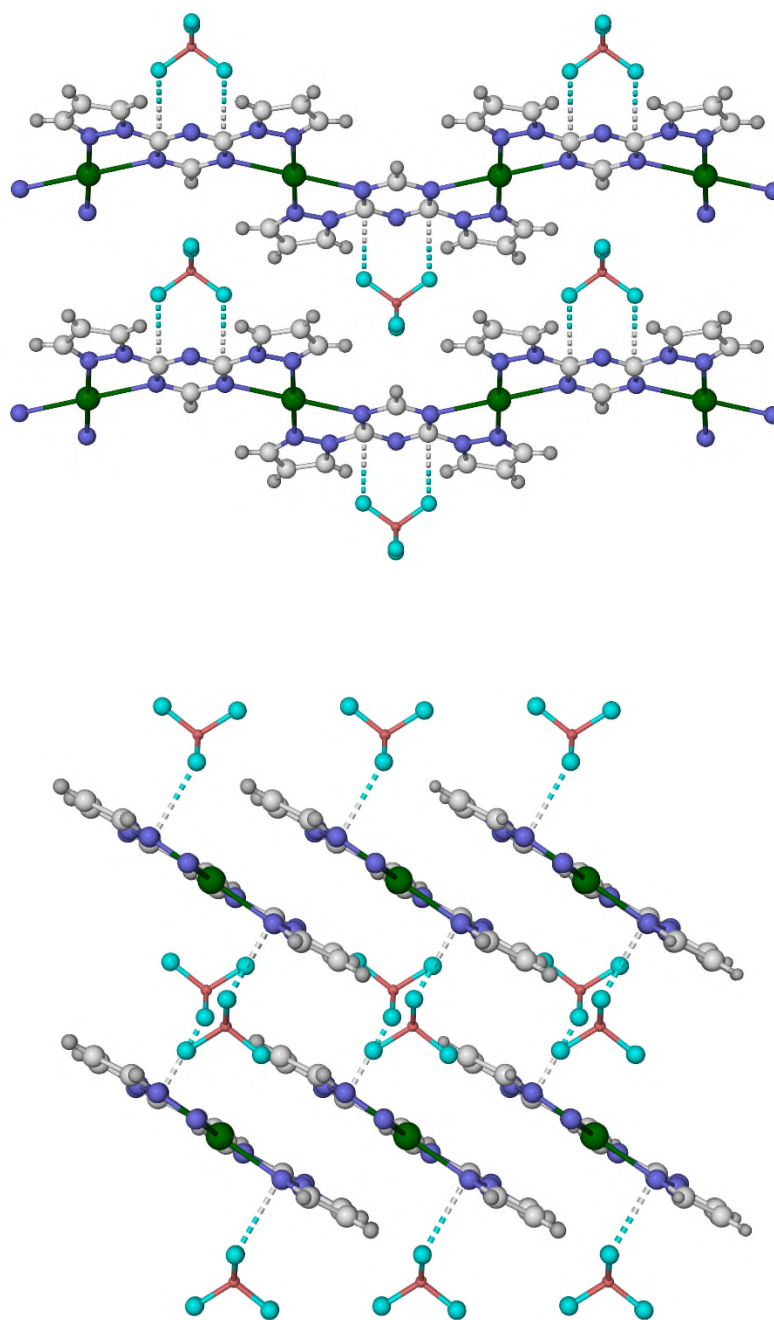


Figure S23. Two packing diagrams of **6**, showing the planar coordination polymer chains and anion... π interactions. Top: view parallel to the [100] crystal vector, with the *b* axis horizontal. Bottom: view shows the (010) crystal plane with the *c* axis horizontal. All atoms have arbitrary radii. Colour code: C, white; H, pale grey; Ag, green; B, pink; F, cyan; N, blue.

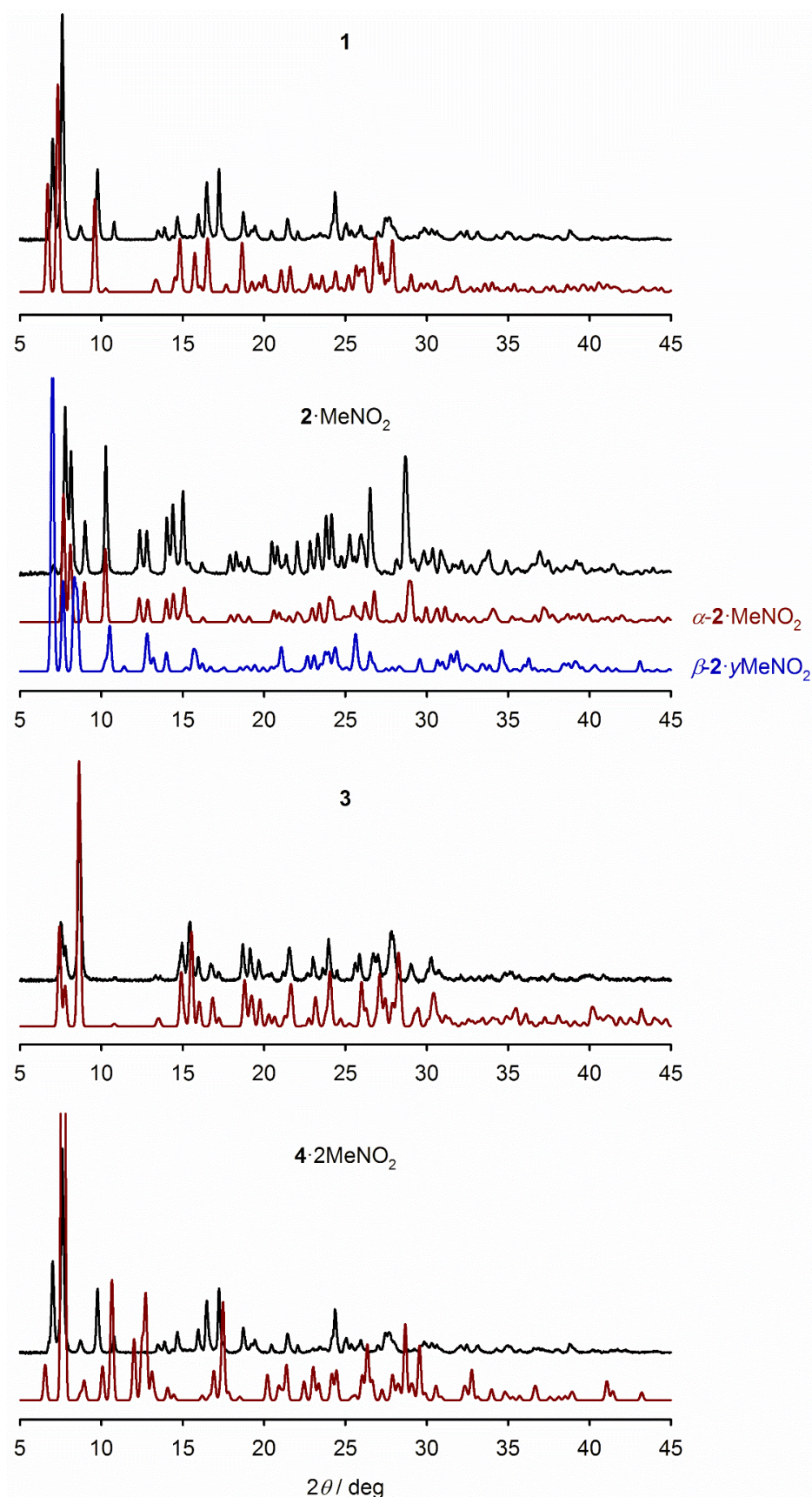


Figure S24. Measured (black) and simulated (red, blue) powder diffraction data from the tpp and tpym complexes.

Bulk samples of $2 \cdot \text{MeNO}_2$, which retains its lattice solvent, predominantly contain the α -form of the compound. Discrepancies between the measured and simulated data for **1** and **4** may reflect desolvation of the samples (their crystals contain lattice solvent, but the dried materials are solvent-free by microanalysis).

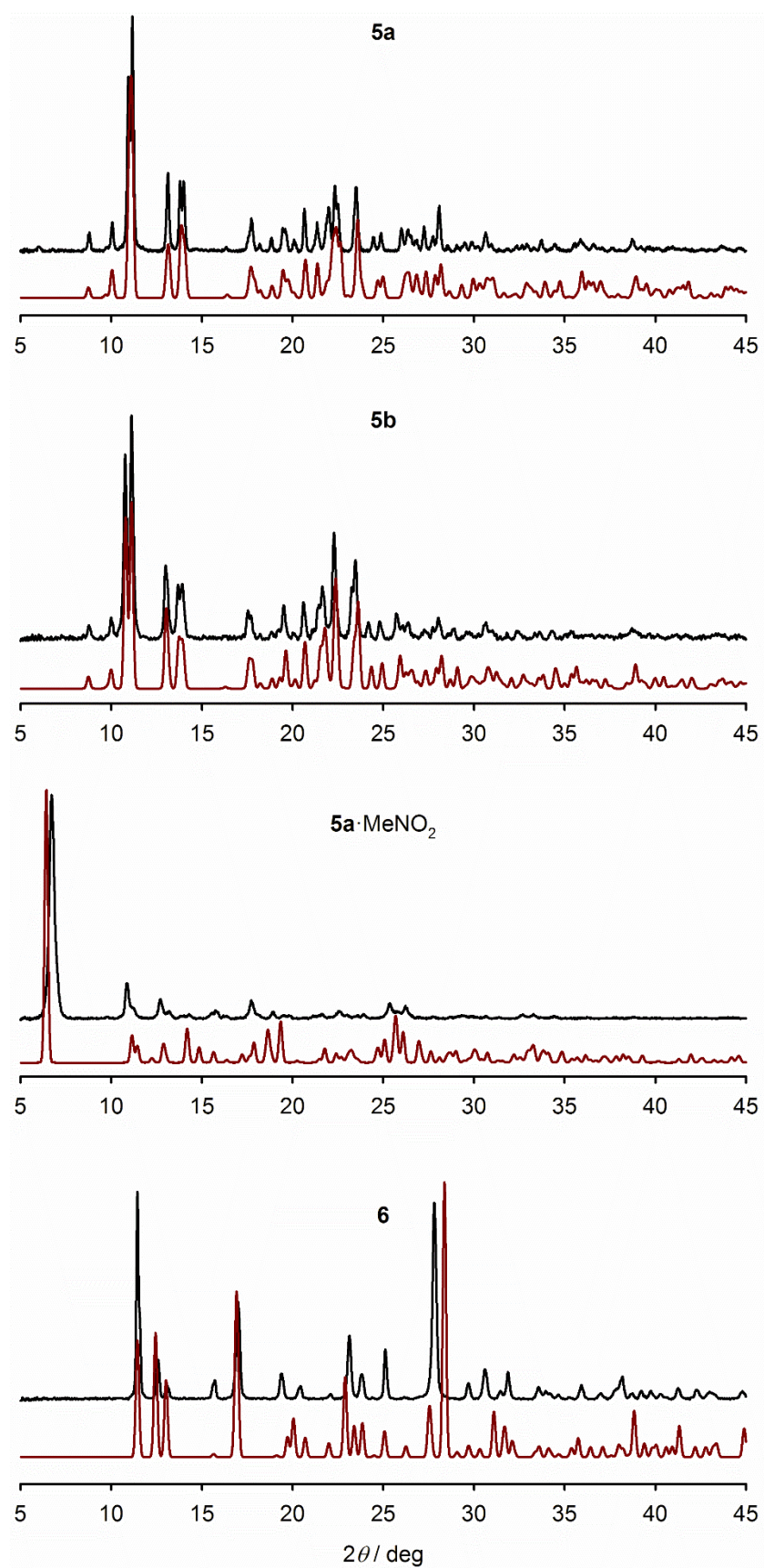
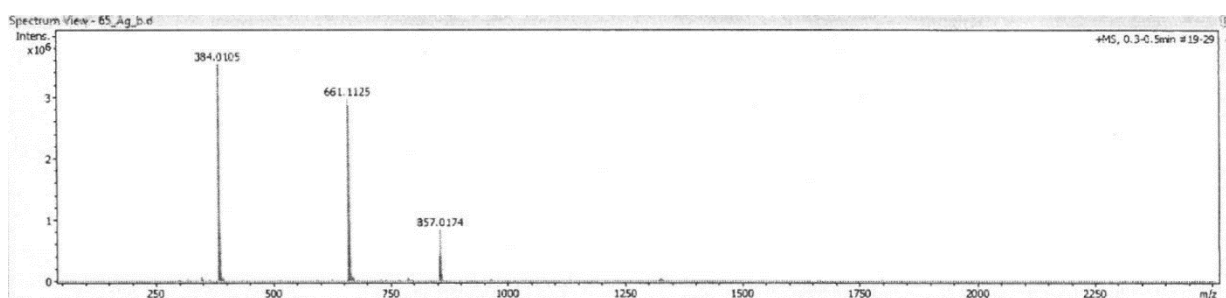
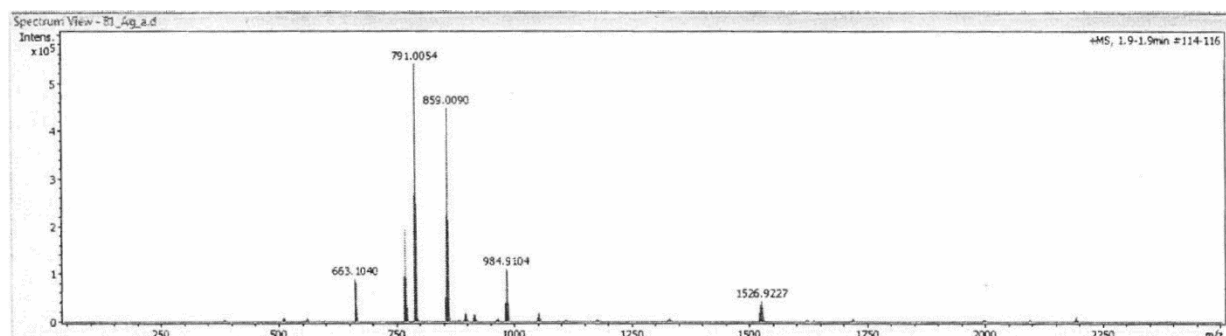


Figure S25. Measured (black) and simulated (red) powder diffraction data from the tpt and bpt complexes.

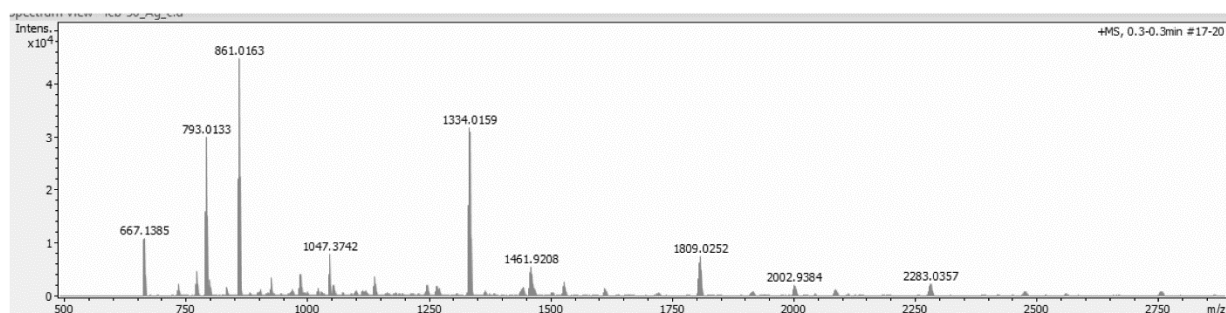
2



4



5



6

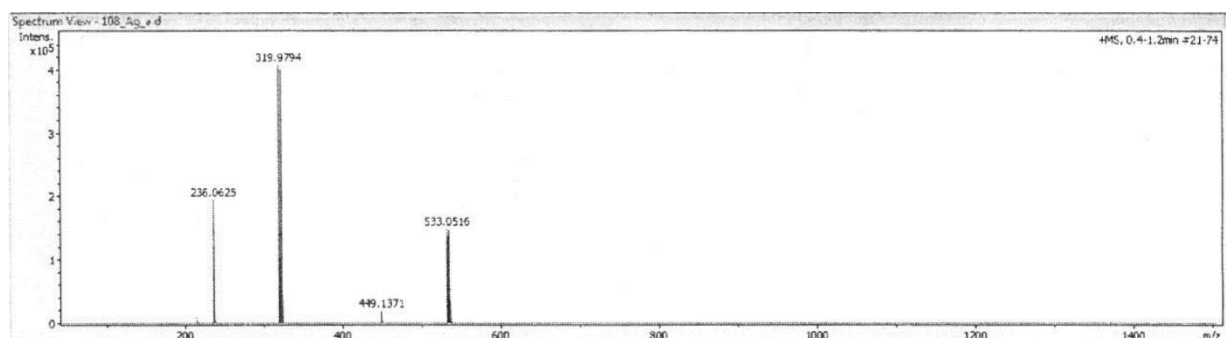


Figure S26. Electrospray mass spectra of the silver complexes of tpp, tpym, tpt and bpt from MeNO₂ solution.

Peak assignments are listed in the Experimental Section of the main article.