

Electronic Supplementary Information

Anion-induced Ag^I self-assemblies with electron deficient aromatic ligands: Anion- π -system interaction as a driving force for the templated coordination networks

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Physical measurements. Infrared spectra were recorded with a Varian 640 FTIR spectrometer equipped with an ATR in the 500–4000 cm⁻¹ range. Scanning electron microscopy (SEM) images were taken of single crystals using a JSM-7500F FESEM (JEOL).

Synthesis of 3,6-bis(2'-pyrimidyl)-1,2,4,5-tetrazine (BPymTz) and 2,4,6-tris(2-pyrimidyl)-1,3,5-triazine (TPymT). The ligands BPymTz¹ and TPymT² were synthesized as described in the literature.

Synthesis of {[Ag₂(BPymTz)₂](PF₆)₂·2CH₃CN}_n (1). A solution of AgPF₆ (0.125 mmol, 0.031 g) in acetonitrile (5 mL) was added to a solution of BPymTz (0.125 mmol, 0.030 g) in the same solvent (5 mL). The mixture was stirred until all of the reactants dissolved. The resulting solution was stored at -18 °C during the next day to produce purple block-like crystals. The same complexes, but with a lower quality of crystals, can be isolated using two, three or four equivalents of AgPF₆. Yield: 0.101 g (76%).

Synthesis of {[Ag₄(BPymTz)₃]c(OTf)₂(CH₃CN)₂·2(OTf)·CH₃CN}_n (2). A solution of AgOTf (0.125 mmol, 0.032 g) in acetonitrile (5 mL) was added to a solution of BPymTz (0.125 mmol, 0.030 g) in the same solvent (5 mL). The mixture was stirred until all of the reactants dissolved. Dark grey block-like crystals were formed during the next day by slow diffusion of diethylether into the mother liquor. The same complexes, but with a lower quality of crystals, can be isolated using two, three or four equivalents of AgOTf. Yield: 0.057 g (73%).

Synthesis of {[AgTPymT]c(ClO₄)_n (3). A hot aqueous (3 mL) solution of AgClO₄ (0.5 mmol, 0.104 g) was added to a suspension of TPymT (0.15 mmol, 0.047 g) in the same solvent (5 mL). The mixture was refluxed until all of the reactants dissolved. The resulting pale yellow solution was cooled yielding orange prism-like crystals during the next two days. The same complex, but with a lower yield, was isolated using one or two equivalents of

AgClO₄. Yield: 0.074 g (94%). *Anal. Calc.* for C₁₅H₉AgClN₉O₄ (522.62): C 34.47, H 1.74, N 24.12. Found: C 34.32, H 1.79, N 24.26%. Yield: 0.043 g (82%).

Powder X-ray diffraction. Powder X-ray diffraction for the bulk sample of **3** was carried out using a Rigaku Ultima IV X-ray powder diffractometer. The Parallel Beam mode was used to collect the data ($\lambda = 1.541836 \text{ \AA}$).

Single crystal X-ray diffraction of 1 and 2. The X-ray data for **1** and **2** were collected at 200(2) K on a Bruker AXS SMART single crystal diffractometer with a sealed Mo tube APEX II CCD detector. The Mo radiation wavelength, 0.71073 \AA , was used. Data collection and processing were performed with APEX software from Bruker AXS.³ The crystal structures were solved by direct methods and refined using the SHELX program.⁴ All non-hydrogen atoms were refined anisotropically and the positions of all hydrogen atoms were obtained from the Fourier map analysis.

1. C₂₄H₁₈Ag₂F₁₂N₁₈P₂, $M_r = 1064.24 \text{ g mol}^{-1}$, orthorhombic, space group *Pnma*, $a = 10.6565(7)$, $b = 16.8754(11)$, $c = 19.1418(13) \text{ \AA}$, $V = 3442.3(4) \text{ \AA}^3$, $Z = 4$, $\rho = 2.054 \text{ g cm}^{-3}$, $\mu(\text{Mo-K}\alpha) = 1.348 \text{ mm}^{-1}$, reflections: 36160 collected, 3821 unique, $R_{\text{int}} = 0.0433$, $R_1(\text{all}) = 0.0820$, $wR_2(\text{all}) = 0.1766$.

2. C₄₀H₂₇Ag₄F₁₂N₂₇O₁₂S₄, $M_r = 1865.60 \text{ g mol}^{-1}$, monoclinic, space group *P2₁/n*, $a = 10.6023(8)$, $b = 18.0069(15)$, $c = 33.316(3) \text{ \AA}$, $\beta = 90.1374(16)^\circ$, $V = 6360.5(9) \text{ \AA}^3$, $Z = 4$, $\rho = 1.948 \text{ g cm}^{-3}$, $\mu(\text{Mo-K}\alpha) = 1.458 \text{ mm}^{-1}$, reflections: 72137 collected, 15741 unique, $R_{\text{int}} = 0.0483$, $R_1(\text{all}) = 0.1141$, $wR_2(\text{all}) = 0.2810$.

Single crystal X-ray diffraction of 3. The structure of **3** was solved from single-crystal synchrotron X-ray diffraction data, which were collected at the Swiss-Norwegian Beam Lines BM01A at the European Synchrotron Radiation Facility (ESRF, Grenoble, France), using a PILATUS 2M hybrid pixel detector at a wavelength of 0.71442 \AA , and a sample-to-detector distance of 144 mm; the collection mode was ϕ -scans at 293(2) K. The data were converted and integrated using the SNBL toolbox software⁵ and CrysAlisPro⁶ software. The crystals were well-shaped dodecahedron, but diffracted poorly. Few crystals were tested and best available dataset were chosen for the refinement. Data was cut off up to 1.37 \AA . The multi-scan absorption correction procedure implemented in CrysAlisPro software was applied. The structures were solved by direct methods using program SHELXS-97⁴ and refined by full-matrix least squares on $|F|^2$ using SHELXL-2014⁴ and the shelXLe shell.⁷ Ag and Cl atoms were localized from the solution, positions of the rest of non-hydrogen atoms were consecutively found from Fourier difference map. Ag cation is disordered and was refined with 0.66(6) occupancy. This disorder might be the reason of poor diffraction of the crystal. Geometrical restrains were applied to the model during the refinement. Relative restrains on the C–N and C–C distances were used to make triazine ring close to the hexagon but bond length was variable. Chiral volume restrains were also applied to make flat fragment included triazine ring and corresponding carbon atom from the pyrimidine ring. The C(1)–C(2) bond length was restrained to be close to 1.475 \AA . Pyrimidine ring was modeled as an ideal hexagon with the bond length of 1.39 \AA . Relative restrains were used to make C–C–N angles close to 120°. Relative restrains on Cl–O and O–O distances were used to make perchlorate

anion close to the ideal tetrahedron with variable size. Non-hydrogen atoms were refined anisotropically, but restraints were applied on thermal parameters. Hydrogen atoms were placed on calculated positions in riding mode with temperature factors fixed at 1.2 times U_{eq} of the parent atoms. Two-component inversion twinning was introduced at the late stage of the refinement. Weighting scheme was refined manually.

3. $C_{15}H_9AgN_9$, ClO_4 ; $M_r = 522.63 \text{ g mol}^{-1}$, cubic, space group $I-43d$, $a = 20.2313(6) \text{ \AA}$, $V = 8280.8(7) \text{ \AA}^3$, $Z = 16$, $\rho = 1.677 \text{ g cm}^{-3}$, $\mu(\text{Mo-K}\alpha) = 1.144 \text{ mm}^{-1}$, reflections: 4675 collected, 291 unique, $R_{int} = 0.128$, $R_1(\text{all}) = 0.1682$, $wR_2(\text{all}) = 0.4441$.

All figures were generated using the Mercury program.⁸

CCDC 1028561 (**1**), 1028560 (**2**) and 1027767 (**3**), contain the supplementary crystallographic data. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

References

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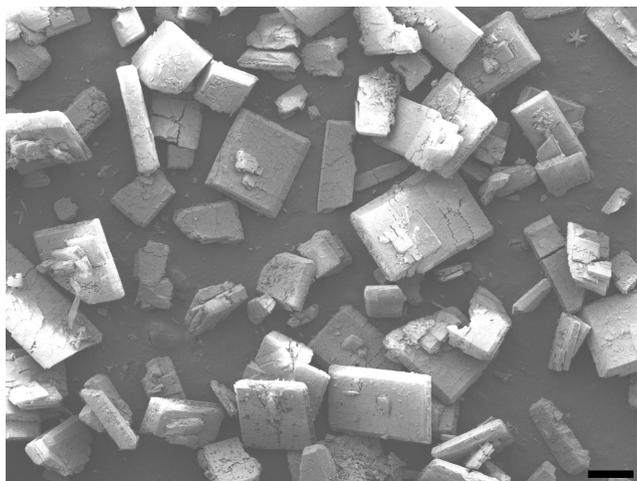


Fig. S1 Crystals of **1** observed under a scanning electron microscope (scale bar = 200 μ m).

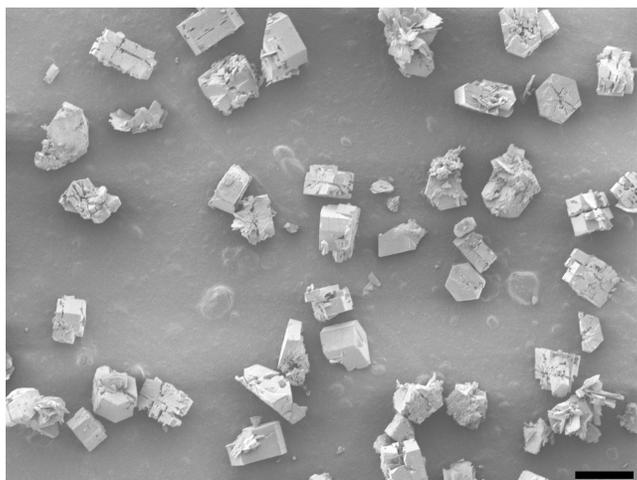


Fig. S2 Crystals of **2** observed under a scanning electron microscope (scale bar = 200 μ m).

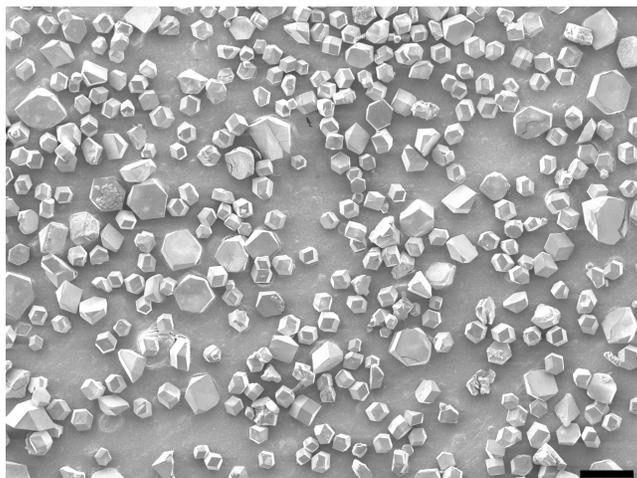


Fig. S3 Crystals of **3** observed under a scanning electron microscope (scale bar = 200 μ m).

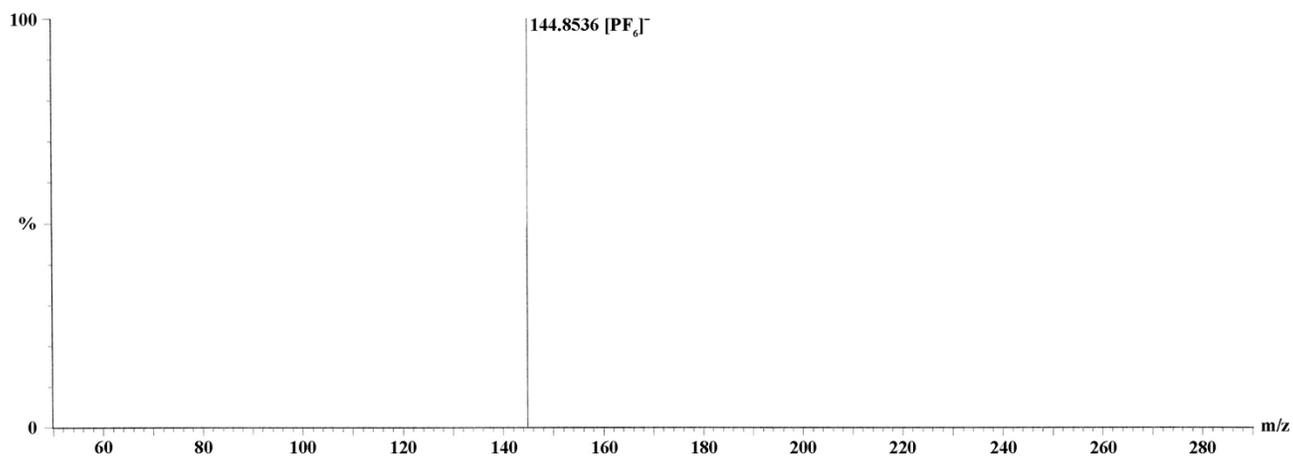
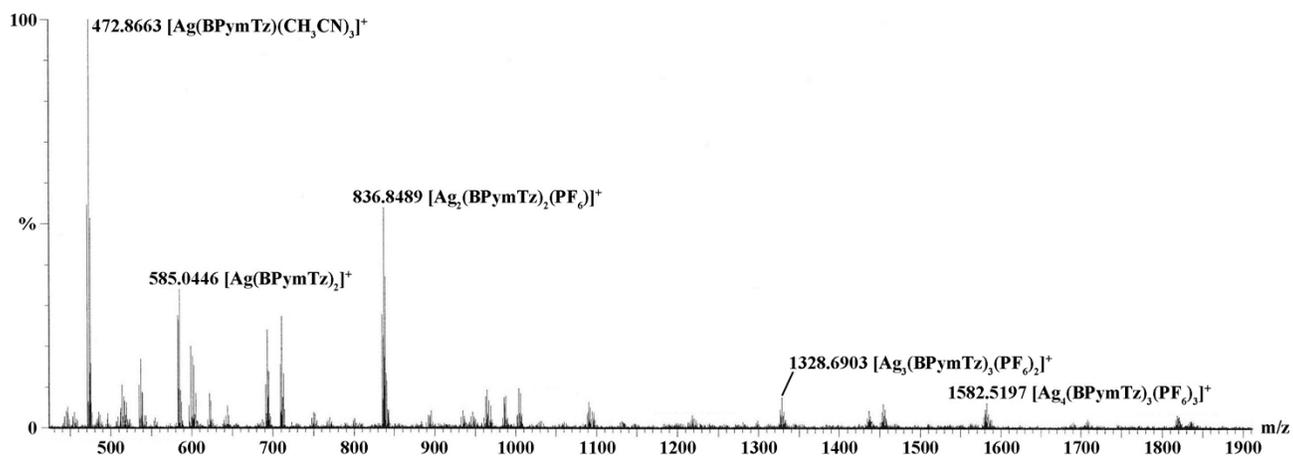


Fig. S4 Positive-ion (top) and negative-ion (bottom) ES mass spectra of **1** measured in CH_3CN .

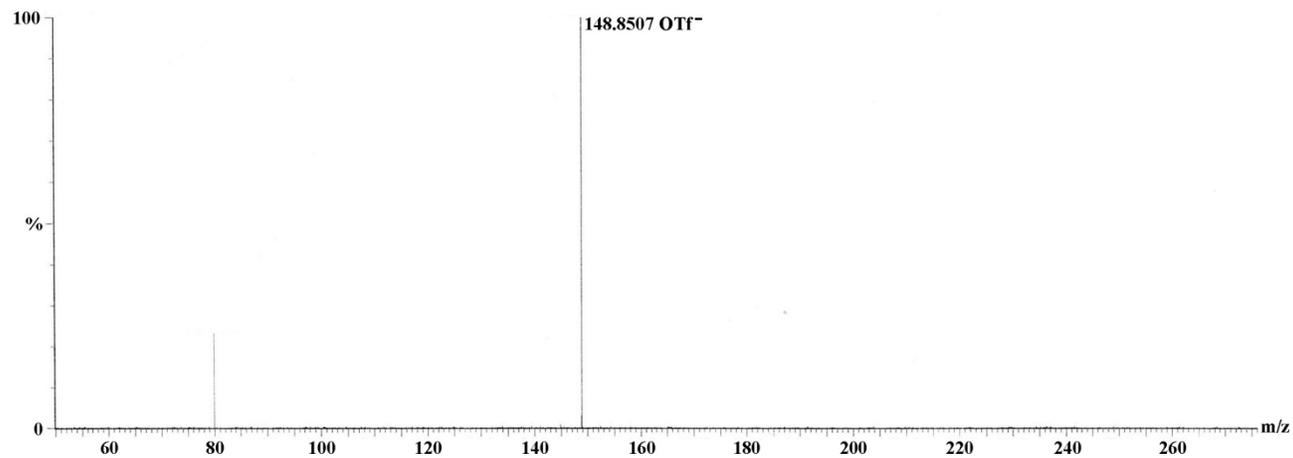
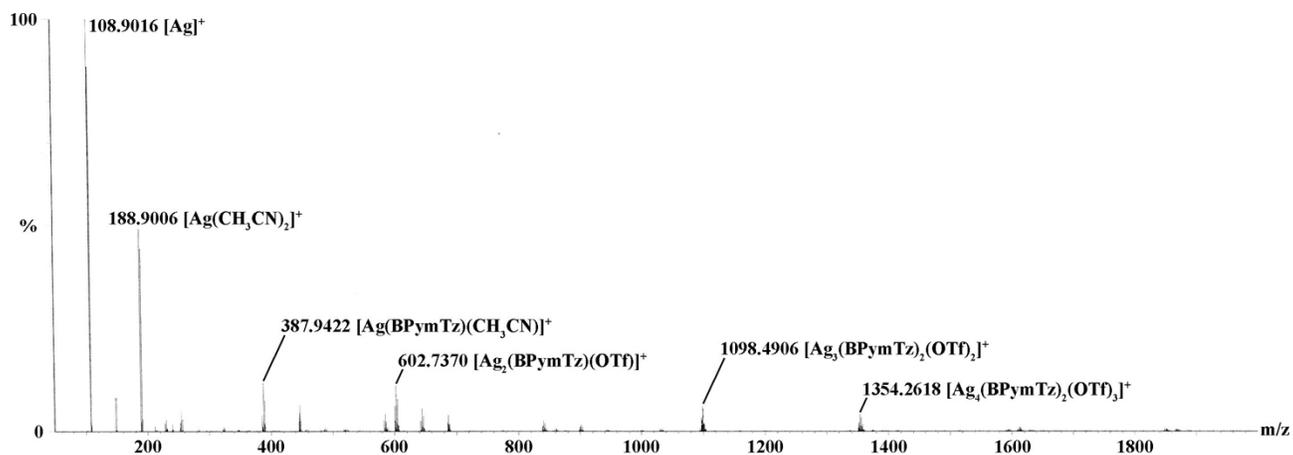


Fig. S5 Positive-ion (top) and negative-ion (bottom) ES mass spectra of **2** measured in CH_3CN .

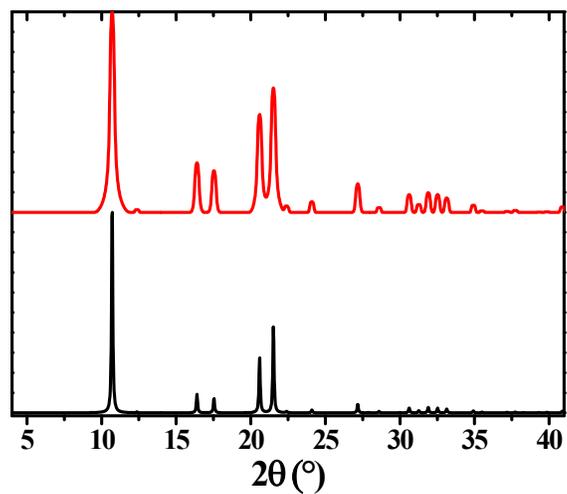


Fig. S6 Normalized calculated (black) and experimental (red) X-ray powder diffraction patterns of **3**.

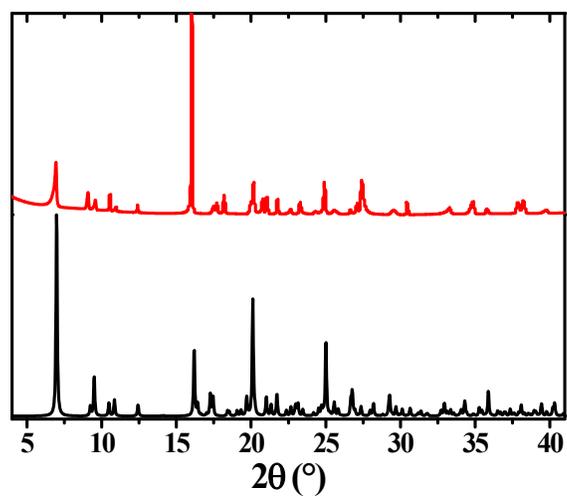


Fig. S7 Normalized calculated (black) and experimental (red) X-ray powder diffraction patterns of **1**.

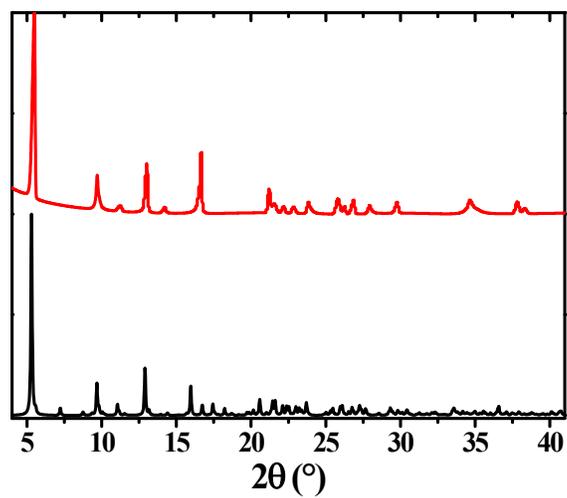


Fig. S8 Normalized calculated (black) and experimental (red) X-ray powder diffraction patterns of **2**.