

Electronic Supplementary Information

Revisiting Ag- π interactions with bis((pyrrol-2-yl)methylene)hydrazine: CC versus CN bond complexation

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Synthesis

Compound **1** has been synthesized as described.¹ Elemental analyses were performed by the *Service commun d'analyse* (University of Strasbourg).

Network **3**: In a vial (hx \varnothing = 65x22 mm), a CH₂Cl₂ (5 mL) solution of **1** (10 mg, 0.053 mmol) was first layered with a CH₂Cl₂/AcOEt 1/1 mixture (2 mL) and then with a concentrated AcOEt solution (2 mL) of AgOTf. Upon diffusing over a week, yellow crystals of **3** formed and were recovered by filtration (24.9 mg, 63 %). Anal. Calcd. for C₁₂H₁₄Ag₂F₆N₄O₈S₂: C, 19.58%; H, 1.92%; N, 7.61%; Found: C, 19.61%; H, 1.95%; N, 7.57%.

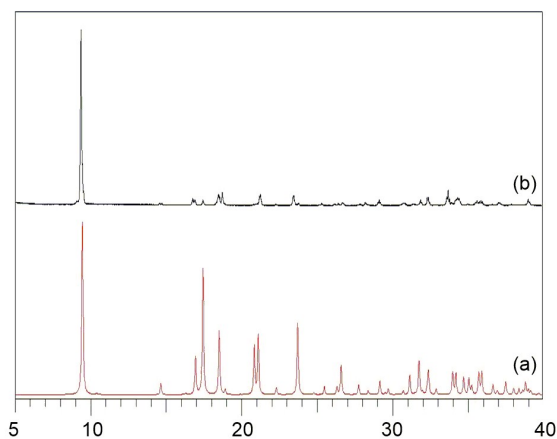


Fig. ESI1 Simulated (a) and experimental (b) PRXD pattern for network **3**.

Network 4: In a vial (hx \varnothing = 65x22 mm), a CHCl₃ (5 mL) solution of **1** (10 mg, 0.053 mmol) was first layered with a CHCl₃/MeOH 1/1 mixture (2 mL) and then with a concentrated MeOH solution (2 mL) of AgOTs. Upon diffusing over a week, the clear yellow solution was filtered. Upon Et₂O vapor diffusion over the mixture, yellow crystals of **4** formed. They were recovered by filtration (8 mg, 20 %).

Alternative synthesis: 10 mg of **1** and 30 mg of AgTsO were loaded into a 10 mL agate container equipped with an agate ball. Milling using a Retsch MM 400 for 30 min at 300 Hz afforded quantitatively **4** as a yellow powder in pure form. Anal. Calcd. for C₂₄H₂₄Ag₂N₄O₆S₂: C, 38.73%; H, 3.25%; N, 7.53%; Found: C, 37.96%; H, 3.24%; N, 6.92%.

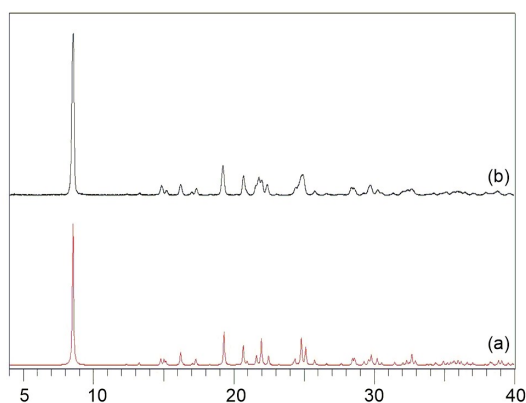


Fig. ESI2 Simulated (a) and experimental (b) PRXD pattern for network **4**.

Network 5: In a vial (hx \varnothing = 65x22 mm), a CHCl₃ (5 mL) solution of **1** (10 mg, 0.053 mmol) was first layered with a CHCl₃/MeOH 1/1 mixture (2 mL) and then with a concentrated MeOH solution (2 mL) of AgBF₄. Upon diffusing over four weeks, few yellow crystals of **5** incorporating the SiF₆²⁻ anion and a yellow precipitate formed.

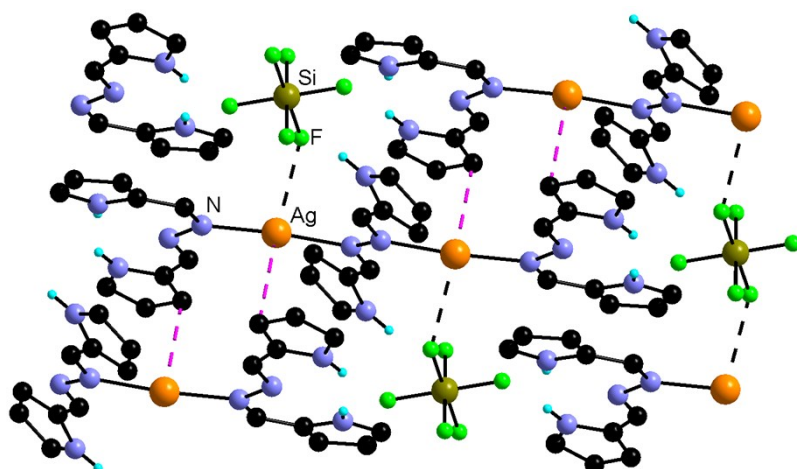


Fig. ESI1 Crystal structure of network **5**. Ag- π interactions are highlighted in purple dash lines. CH₂Cl₂ molecules have been omitted for clarity.

Networks **2'** and **6**: In a vial (hx \varnothing = 65x22 mm), a CHCl₃ (5 mL) solution of **1** (10 mg, 0.053 mmol) was first layered with a CHCl₃/MeOH 1/1 mixture (2 mL) and then with a concentrated MeOH solution (2 mL) of AgNO₃ (18.2 mg, 0.107 mmol). Upon diffusing over a week, yellow crystals of **2'** and **6** formed and were recovered by filtration (22 mg). Both compounds could not be separated from each other. Furthermore, crystals of **6** were shown to desolvate upon exposure to air, preventing further analysis.

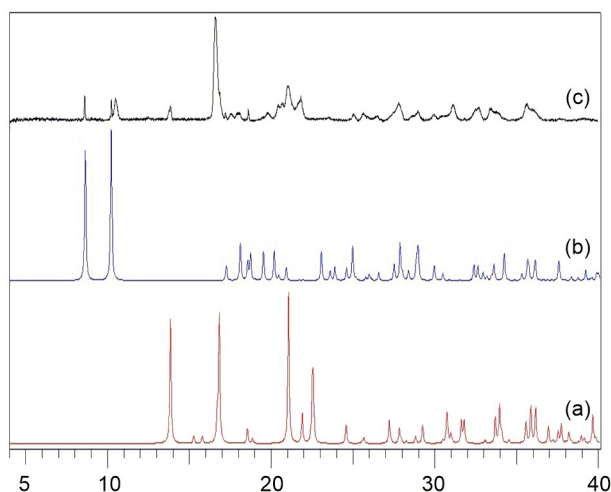


Fig. ESI4 Simulated PRXD pattern for network **2'** (a) and **6** (b) and experimental pattern showing the mixture of the two phases obtained (c).

X-Ray diffraction

Single-crystal data (Table ESI1) were collected on a Bruker SMART CCD diffractometer with Mo–K α radiation at 173 K. The structures were solved using SHELXS-97 and refined by full matrix least-squares on F^2 using SHELXL-2014 with anisotropic thermal parameters for all non-hydrogen atoms.² The hydrogen atoms were introduced at calculated positions and not refined (riding model).

In the structure of **6**, one nitrate anion is disordered over two positions that have been modeled accordingly.

CCDC 1893848-1893853 contain the supplementary crystallographic data for compounds **1**(H₂O), **2'**-**6**. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif.

Table ESI1 Crystallographic data for compounds **1**(H₂O), **2'** and **3**.

	1 (H ₂ O)	2'	3
Formula	C ₁₀ H ₁₂ N ₄ O	C ₁₀ H ₁₀ Ag ₂ N ₆ O ₆	C ₁₂ H ₁₄ Ag ₂ F ₆ N ₄ O ₈ S ₂
FW	204.24	525.98	607.41
Crystal system	Monoclinic	Monoclinic	Triclinic
Space group	<i>P2/c</i>	<i>P2₁/n</i>	<i>P</i> -1
<i>a</i> / Å	11.9283(6)	9.8391(4)	6.1112(3)
<i>b</i> / Å	6.5439(3)	6.9334(3)	9.5660(5)
<i>c</i> / Å	6.8123(3)	10.9235(5)	10.6221(6)
α / °			63.173(2)
β / °	105.114(2)	103.517(2)	82.885(2)
γ / °			89.971(2)
<i>V</i> / Å ³	513.36(4)	724.54(5)	548.79(5)
<i>Z</i>	2	2	1
<i>T</i> / K	173(2)	173(2)	173(2)
μ / mm ⁻¹	0.091	2.748	2.073
Refls. coll.	32009	50156	50377
Ind. refls. (Rint)	1501 (0.0415)	2152 (0.0401)	2985 (0.0649)
R_1 ($I > 2\sigma(I)$) ^a	0.0437	0.0194	0.0204
wR_2 ($I > 2\sigma(I)$) ^a	0.1189	0.0446	0.0477
R_1 (all data) ^a	0.0483	0.0205	0.0211
wR_2 (all data) ^a	0.1223	0.0454	0.0480
GOF	1.079	1.049	1.052

^a $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$; $wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum wF_o^4]^{1/2}$

Table ESI2 Crystallographic data for compounds 4-6.

	4	5	6
Formula	C ₂₄ H ₂₄ Ag ₂ N ₄ O ₆ S ₂	C ₃₁ H ₃₂ Ag ₂ Cl ₂ F ₆ N ₁₂ Si	C ₁₁ H ₁₄ Ag ₂ N ₆ O ₇
FW	1334.19	1001.41	558.02
Crystal system	Monoclinic	Monoclinic	Orthorhombic
Space group	<i>P2₁/c</i>	<i>C2/c</i>	<i>Pnma</i>
<i>a</i> / Å	10.6098(4)	13.5975(7)	20.5483(12)
<i>b</i> / Å	7.3320(3)	13.8536(7)	16.1886(10)
<i>c</i> / Å	16.7744(7)	19.2691(9)	4.8655(2)
β / °	101.451(2)	92.402(3)	
<i>V</i> / Å ³	1278.92(9)	3626.6(3)	1618.50(15)
<i>Z</i>	2	4	4
<i>T</i> / K	173(2)	173(2)	173(2)
μ / mm ⁻¹	1.743	1.335	2.290
Refls. coll.	12611	56710	10291
Ind. refls. (Rint)	3744 (0.0440)	5034 (0.0534)	2414 (0.0343)
<i>R</i> ₁ (<i>I</i> >2 σ (<i>I</i>)) ^a	0.0474	0.0468	0.0250
<i>wR</i> ₂ (<i>I</i> >2 σ (<i>I</i>)) ^a	0.1134	0.1132	0.0584
<i>R</i> ₁ (all data) ^a	0.0642	0.0791	0.0318
<i>wR</i> ₂ (all data) ^a	0.1239	0.1259	0.0626
GOF	1.050	1.048	1.027

$$^a R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|; wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum wF_o^4]^{1/2}$$

Computational calculations

All calculations were carried out using planewave based density functional theory (DFT) with Quantum-ESPRESSO.³ All geometry optimizations were carried out using the PBE functional. Core electrons were described using PAW pseudopotentials. The DFT-D2 method of Grimme was used to describe van der Waals interactions.⁴ A planewave cut-off energy of 80 Ry was used to describe the wavefunctions in all calculations, The total energy and force convergence threshold was set up at 5.10⁻⁶ Ry and 5.10⁻⁵ Ry/Bohr³, respectively. The Brillouin zone was sampled using a 4×6×4, 4×6×4, 7×5×4, 5×6×3, 5×5×4 and 2×3×8 k-point Monkhorst-Pack grid for the in-slab dimensions, for compound **2**, **2'**, **3**, **4**, **5** and **6**, respectively.

References

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