



Supporting Information

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Anion-directed self-assembly of flexible ligands into anion-specific and highly symmetrical organic solid

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General methods

Chemicals were obtained from Sigma-Aldrich and used without further purification. Solvents and concentrated acids (p.a. grade) were purchased from Kemika, Zagreb.

Preparation of products for data collection

Where needed, the samples were dried in desiccators over CaCl_2 to exclude solvent. The samples for elemental analysis were dried until constant mass. The samples for solvent ratio exploration (TG) were placed in a vessel on a filter paper, in stream of solvent vapor to remove the surface solvent.

Elemental analysis was performed by Central Analytical Service, IRB, Zagreb.

IR spectra were recorded on PerkinElmer *Spectrum RXI* FT-IR spectrometer from dried samples dispersed in KBr pellets (4000-400 cm^{-1} range, 2 cm^{-1}).

DCM stands for dichloromethane and **ACN** for acetonitrile.

Experimental section

Synthesis of **L**, *N,N'*-3-Azapentane-1,5-diylbis(3-(1-iminoethyl)-6-methyl-2H-pyran-2,4(3*H*)-dione, C₂₀H₂₅N₃O₆

Dehydroacetic acid, 3-acetyl-4-hydroxy-6-methyl-2*H*-pyran-2-one, (2.0 g, 12 mmol) was dissolved in ethanol (15 mL) in a round-bottom flask. *Bis*-(2-aminoethyl)-amine (0.61 g, 6 mmol) was added drop-wise and the reaction mixture was heated, with reflux and magnetic stirrer, for two hours. Stirring was continued while cooling, and a pale yellow product, **L**, was obtained, filtered, washed with a small amount of methanol and diethyl ether and dried in air. Yield = 85 % (calculated on dehydroacetic acid). Melting point is at 145.0 °C. ¹H NMR, elemental analysis and IR data are in good agreement with earlier published results.^[1] Product was pure without need for recrystallization.

Infrared spectrum (resolution 2 cm⁻¹, KBr disk): 3432 (broad) (ν_{N-H}, RAHB); 3366(sharp) (ν_{N-H}, central) 1688, 1656, 1636, 1574, 1472 (all νs, mixed C-O, C=C).

Synthesis of **1**, (HL)₃ · (NO₃)₃ · x MeOH

0.050 g (0.124 mmol) of **L** was dissolved in methanol (5 mL), cooled to RT and then HNO₃, diluted in solvent, in a molar ratio (1:1), was added. Other molar ratios gave poorer yield. The reaction mixture was sealed in a vessel and left at RT for two days. Colorless crystals of **1**, suitable for the X-ray structure determination, were obtained (98%, calculated on **L**). The crystals are unstable upon exposure to air and decomposition of the product takes place in seconds. In mother liquor or in solvent vapor, however, they are stable for months.

Elemental analysis (Calcd (found) for (C₂₀H₂₆N₃O₃)NO₃): C 57.42 (57.13) H 6.22 (6.04) N 13.40 (13.61)

Infrared spectrum (resolution 2 cm⁻¹, KBr disk): 3436 (br) (ν_{N-H}, hydrogen bonded); 1695, 1658, 1583, 1473 (all νs, mixed C-O, C=C), 1359, 1348 (s) (ν_{N-O}).

Synthesis of **1-DCM** and **1-ACN**

1-ACN was prepared in a manner described above. For **1-DCM**, 0.050 g (0.124 mmol) of **L** was dissolved in dichloromethane (20 mL). HNO₃ was diluted in solvent and added until precipitation was observed (1:1). The reaction mixture was sealed in a vessel with glass stopper and left at RT for four days. Colorless crystals of **1-DCM** were obtained (100%, calculated on **L**). The crystals are unstable upon air exposure; they decompose momentarily, so the thermogravimetric measurements of the solvated product **1-DCM** were impossible to make.

1-DCM: Elemental analysis (Calcd (found) for (C₂₀H₂₆N₃O₃)NO₃): C 57.42 (57.71) H 6.22 (6.41) N 13.40 (13.27)

Infrared spectrum (resolution 2 cm⁻¹, KBr disk): 3446 (br) (ν_{N-H}, hydrogen bonded); 1694, 1661, 1583, 1472 (all νs, mixed C-O, C=C), 1360, 1342 (s) (ν_{N-O}).

1-ACN: Elemental analysis (Calcd (found) for (C₂₀H₂₆N₃O₃)NO₃): C 57.42 (57.66) H 6.22 (6.40) N 13.40 (13.58)

Infrared spectrum (resolution 2 cm⁻¹, KBr disk): 3440 (br) (ν_{N-H}, hydrogen bonded); 1695, 1661, 1584, 1472 (s) (all νs, mixed C-O, C=C), 1360, 1347 (s) (ν_{N-O}).

Synthesis of **2**, (HL)₃ · (SO₄)_{1.5} · x MeOH

0.050 g (0.124 mmol) of **L** was dissolved in methanol (5 mL), cooled to RT and then conc. H₂SO₄, diluted in the solvent was added in the molar ratio 2:1 for **L**:H₂SO₄. The reaction mixture was sealed in a vessel and left at RT for three days. Colorless crystals of **2**, suitable for the X-ray structure determination, were obtained (95%, calculated on **L**). The crystals are unstable upon air exposure. In mother liquor or in solvent vapor, however, they are stable for months.

Elemental analysis (Calcd (found) for (C₂₀H₂₆N₃O₃)₂SO₄): C 59.40 (59.52) H 6.43 (6.63) N 10.40 (10.22) S 3.96 (3.82)

Infrared spectrum (resolution 2 cm⁻¹, KBr disk): 3428 (br) (ν_{N-H}, hydrogen bonded); 1694, 1640, 1583, 1473 (all νs, mixed C-O, C=C), 1120 (s) (ν_{S=O}).

Competitive crystallization experiments

L was placed in a beaker and dissolved in methanol (0.025 g in 2.5 mL). For an experiment with nitrate 30 systems were prepared. $(\text{NMe}_4^+)_a\text{X}$ or KX ($\text{X} = \text{F}^-$, Cl^- , Br^- , AcO^- , $\text{C}_2\text{O}_4^{2-}$, BO_3^{3-} , CO_3^{2-} , BF_4^- , TsSO_3^- , PO_4^{3-} , NO_3^- or SO_4^{2-} ; a = number of cations to balance the negative charge; Ts = tosil) was added to the reaction mixture in the molar ratio of (1:1, 3:1, 6:1 (competitive anion:L)). HNO_3 was added to the reaction mixtures in the molar ratio HNO_3 :L of 1:1, the beakers were sealed and left for two days. The obtained crystalline material (morphologically identical to **1**) was filtered off and dried. The products were characterized by infrared spectroscopy (nitrate and sulfate showed characteristic peaks in IR spectra) and X-ray powder diffraction. The experiment with sulfate was conducted in a similar way, with the only difference being the solvent volume (4 mL; weaker solubility of sulfate complexes lead to polycrystalline material formation).

The near quantitative or quantitative formation of complex **1** was observed in all cases except in the cases of fluoride and bromide anions. In the case of bromide anion, a polycrystalline product was obtained, identical to product from reaction of **L** with HBr. In the case of fluoride, no product was obtained in higher fluoride ratios. The ligand expresses slightly weaker affinity for sulfate in the presence of halogens. In the sulfate/nitrate systems a mixture of **1** and **2** was obtained (Table S1).

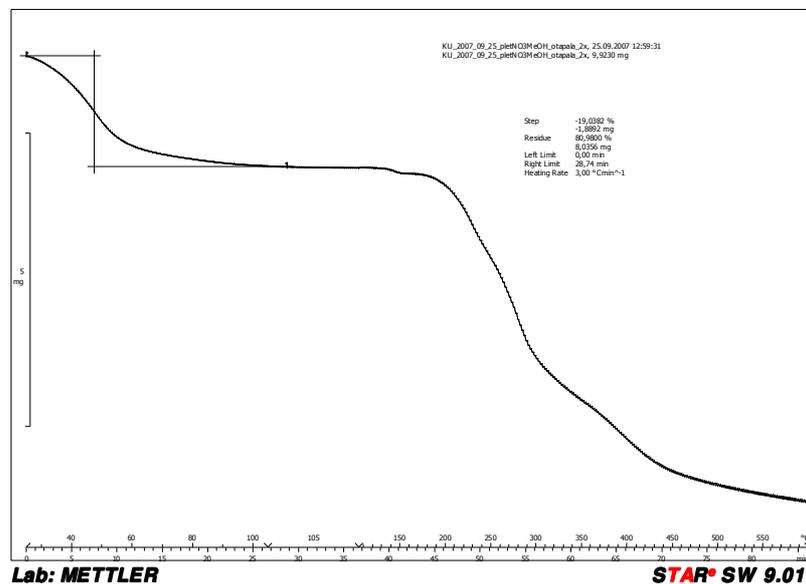
For all systems, blind probe experiments were conducted. In these experiments **L** and competitive anions were dissolved in methanol and were acidified with p-toluensulfonic acid. No positive results were obtained with the probe experiments.

Table S1. Yield of complexes **1** and **2** in the presence of various anions.

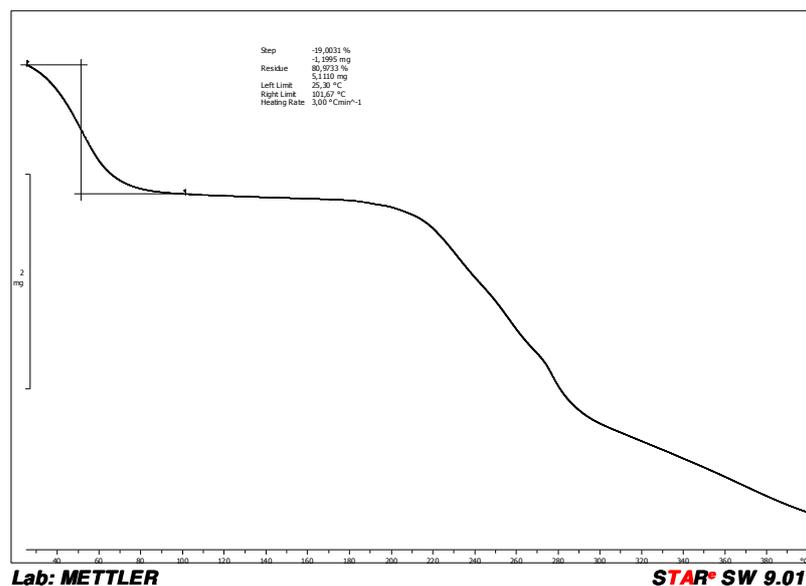
Anion	HNO_3 : L (1:1)			H_2SO_4 : L (1:2)		
	Yield of 1 (%)			Yield of 2 (%)		
F^-	20	-	-	-	-	-
Cl^-	98	100	95	70	66	45
Br^-	10	15	10	24	-	-
AcO^-	100	100	94	100	100	100
$\text{C}_2\text{O}_4^{2-}$	100	100	100	100	100	100
BO_3^{3-}	100	100	100	100	100	100
CO_3^{2-}	100	100	100	100	100	100
BF_4^-	100	100	100	64	40	55
p-TsSO ₃ ⁻	100	100	100	100	100	100
PO_4^{3-}	100	92	100	-	-	-
	1:1	3:1	6:1	1:1	3:1	6:1
	Competitive anion : NO_3^- ratio			Competitive anion : SO_4^{2-} ratio		

Thermogravimetric and DSC measurements

The samples for thermogravimetric measurements were prepared (solvent ratio exploration) in a fashion earlier described. The data were collected on the Mettler–Toledo TGA/SDTA 851^c with STAR^c SW 9.01 in the range of 25–400 °C (heating rate 3 °C/min) under nitrogen stream. The room for the measurements was tempered to 5 °C to prevent solvent loss during sample preparation. In the first step the weight loss was 19 % (Figure S1), corresponding to methanol in the complexes (ca. 320 molecules per unit cell of the complex). The position and number of solvent molecules was impossible to determine from X-ray diffraction electron density map, so this method was used to solve this solvent content. DSC measurements showed that melting point of **2** (178 °C) was for 32 °C higher than the melting point of **1**, proving stronger interactions in **2**.



a)



b)

Figure S1. Thermogravimetric data for **1** (a) and **2** (b).

Single crystal X-ray measurements and structure determinations*

Single crystals suitable for X-ray crystallography were obtained from the mother liquid at RT. The crystals were unstable upon exposure to air so the single crystal diffraction data were collected from the crystal mounted in a loop in a mixture of methanol and glycerol, and cooled in nitrogen vapor stream at 100 K. Diffracted intensities were collected on the Oxford Diffraction Xcalibur 3 and Oxford Diffraction Gemini diffractometers using graphite-monochromated MoK α and CuK α radiation, respectively (Table S2). The CrysAlis^[2] program package was used for data collection, cell refinement and data reduction. The structures were solved by direct methods (SHELXS^[3]). The refinement procedure (SHELXL-97^[4]) by full-matrix least squares methods based on F^2 values against all reflections included anisotropic displacement parameters for all non-H atoms. The SHELX programs operated under the WinGX^[5] program package. A summary of crystal data is presented in Table S2. Programs PLATON^[6], MERCURY^[7] and ORTEP^[8] were used for analysis of the structure and drawings preparation.

It was not possible to build the full structure model due to disorder and high symmetry. Lower symmetry space groups were tested but no ordering could be found. Voids and channels in the crystal structures contain heavily disordered counter-ions and solvent molecules. In the beginning, regarding to the high symmetry of the space group, we tried to find counter-ions in special positions, with a multiplicity corresponding to the missing number of counter-ions and a site symmetry corresponding to the point group symmetry of the anion but with no success. On the other hand, if the very large percentage of unit cell volume is accessible to the great number of counter-ions and solvent molecules which are extremely disordered, there is no reason why the counter-ions should reside in special positions.

There are more than 300 disordered solvent molecules per unit cell (confirmed with TGA and elemental analysis). Approximately 40% of the cell volume is available for solvent absorption. All our extensive attempts to model the electron density with the SQUEEZE procedure in PLATON^[6] and with various restraints proved unsuccessful. After our extensive efforts we contacted the author of the SQUEEZE algorithm (A. Spek). In his experience, this cubic space group is often related with disorder problems and SQUEEZE can not be of much help in such case. With this kind of systems where the data quality is reduced because of the presence of heavily disordered regions in crystals it is very hard to expect high resolution data.

Since it was not possible to describe the disordered molecules meaningfully some peaks were left in the Fourier difference map unassigned. All alerts in CHECKcif test arise from these problems (crystal density, large R-factor, high residual density...). It is very important to stress out that all hydrogen atoms on the positively charged moieties were located in the difference Fourier map but were refined using the riding model.

The sulfate ion in **2** is statistically disordered and so appears to have the symmetry of a trigonal bipyramid (one oxygen and the sulfur atom lie on the three-fold axis and are assigned half of the occupancy of this site, the other oxygen atom lies on the two-fold axis that is perpendicular to the three-fold axis thus generating three oxygen atoms which complete the sulfate tetrahedron).

Two out of four structures (**1-DCM** and **1-ACN**) were not of satisfactory quality since the data were collected on a molybdenum source. These structures were given only as additional data in determining the solvent role in the crystal structure stabilization.

Supplementary crystallographic data sets for the structures are available through the Cambridge Structural Data base with deposition numbers 677195-677198. Copy of this information may be obtained free of charge from the director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44 1223 336 033; e-mail: deposit@ccdc.cam.ac.uk or <http://www.ccdc.cam.ac.uk>).

*It should be noticed that crystallography in these systems is by no means simple. With huge unit cell and heavily disordered molecules habiting voids and channels in the crystal structures it was hard to evaluate the quality of our models in terms of small molecule crystallography. We had to overcome many problems and we employed all our knowledge and experience in crystallography of small molecules and proteins to model our systems in the best way. These complexes are comparable to protein structures which can have high symmetry, even cubic, but the ions and solvent molecules in the voids are disordered and can not be detected by X-ray crystallography.

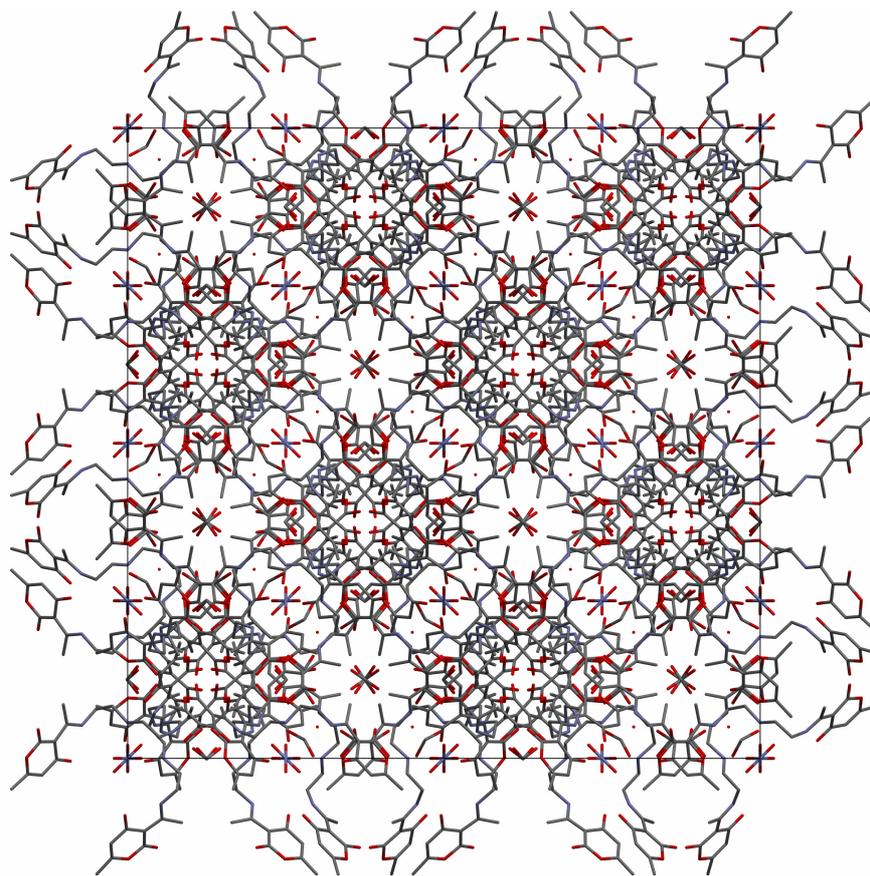
Table S2. Crystal data, collection and refinement.

Compound	1	2	1-DCM	1-ACN
Crystal system	Cubic	Cubic	Cubic	Cubic
Space group	$Fd\bar{3}c$	$Fd\bar{3}c$	$Fd\bar{3}c$	$Fd\bar{3}c$
a (Å)	41.772(4)	41.775(3)	41.9238(6)	41.7841(9)
b (Å)	41.772(4)	41.775(3)	41.9238(6)	41.7841(9)
c (Å)	41.772(4)	41.775(3)	41.9238(6)	41.7841(9)
α (°)	90.00	90.00	90.00	90.00
β (°)	90.00	90.00	90.00	90.00
γ (°)	90.00	90.00	90.00	90.00
V (Å ³)	72887(11)	72900(10)	73685.5(18)	72951(3)
Z	32	32	32	32
Diffractometer	Oxford Diffraction Gemini S	Oxford Diffraction Gemini S	Oxford Diffraction Xcalibur 3	Oxford Diffraction Xcalibur 3
Radiation, λ (Å)	1.54184	1.54184	0.71073	0.71073
Temperature (K)	103	103	103	103
Crystal size (mm ³)	0.35×0.32×0.30	0.55×0.50×0.45	0.42×0.35×0.23	0.75×0.66×0.54
Crystal colour	Colorless	Colorless	Colorless	Colorless
θ range (°)	7.94 - 65.01	2.99 - 63.73	3.89 - 24.99	3.90 - 25.49
Reflections collected	22152	16681	178337	31618
Independent reflections	2590	2429	2708	2818
Observed reflections	2234	1394	2079	1649
Absorption correction	None	None	None	None
R^a , wR^b [$I \geq 2\sigma(I)$]	0.1229, 0.3750	0.1478, 0.4208	0.2876, 0.6461	0.1707, 0.4818
Goodness-of-fit, S^c	1.680	1.509	2.800	1.757
Maximum/minimum $\Delta\rho$ (e Å ⁻³)	1.454/−0.453	2.182/−0.784	4.002/−1.048	3.261/ −0.668

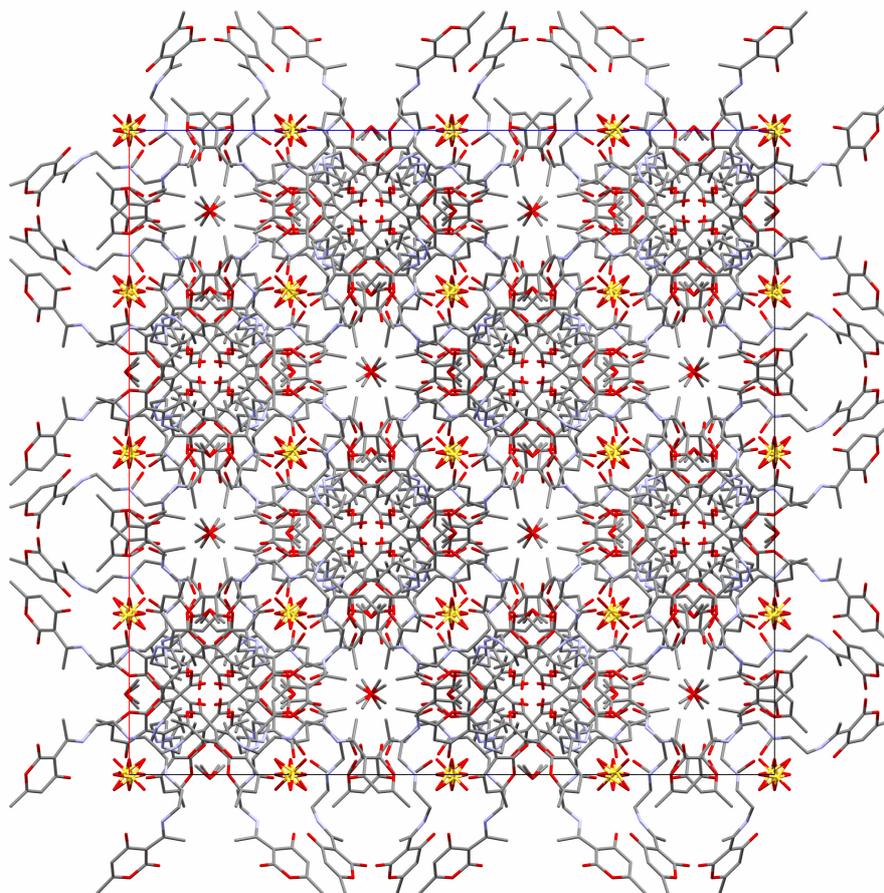
$$^a R = \sum \|F_o\| - \|F_c\| / \sum F_o$$

$$^b w = 1 / [\sigma^2(F_o^2) + (g_1 P)^2 + g_2 P] \text{ where } P = (F_o^2 + 2F_c^2) / 3$$

$$^c S = \sum [w(F_o^2 - F_c^2)^2 / (N_{\text{obs}} - N_{\text{param}})]^{1/2}$$



1



2

Figure S2. Mercury-POV-Ray^[9] rendered view of the crystal packing of **1** and **2** viewed down *a* axis (H atoms have been omitted for clarity). The number of nitrate anions needed to balance the net charge of the **PMH**:anion supramolecular complex (in **1**) is four times greater than of sulfate (in **2**). Methanol molecules are also shown.

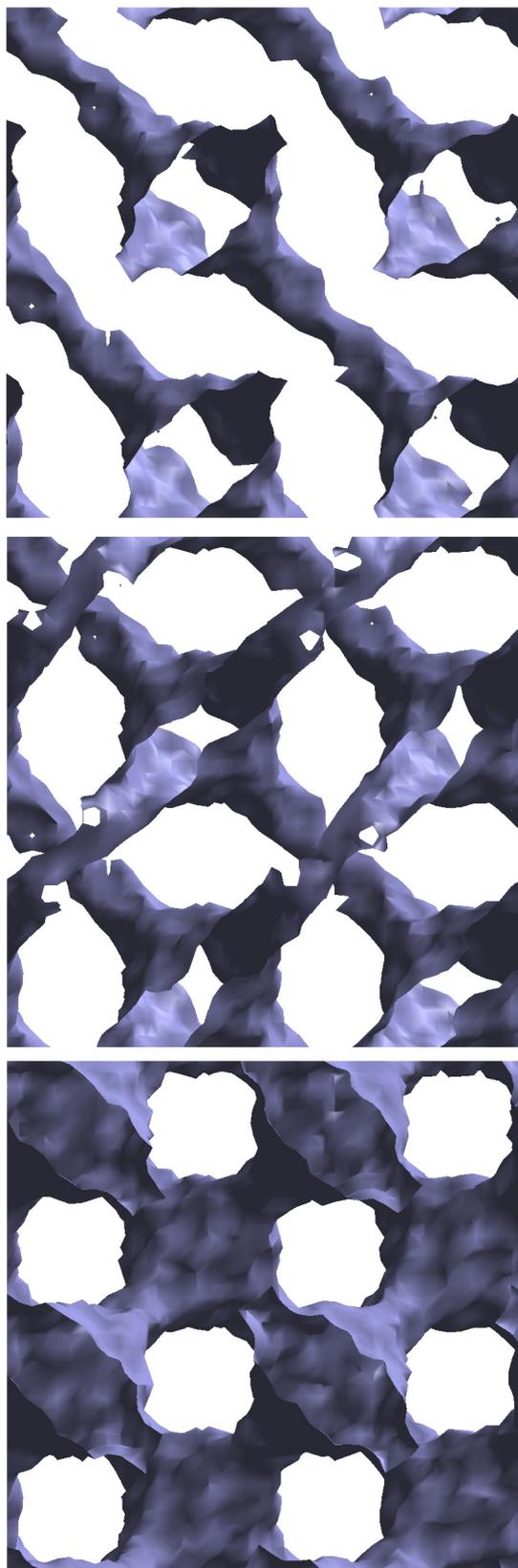


Figure S3. Voids and channels (blue colored) in the crystal structure of **2**. Consecutive figures depict how two independent systems of channels are formed if we take a look from the backside to the front. At channels intersections large voids are formed. Only part of the unit cell is shown. All atoms have been omitted for clarity (white sections).

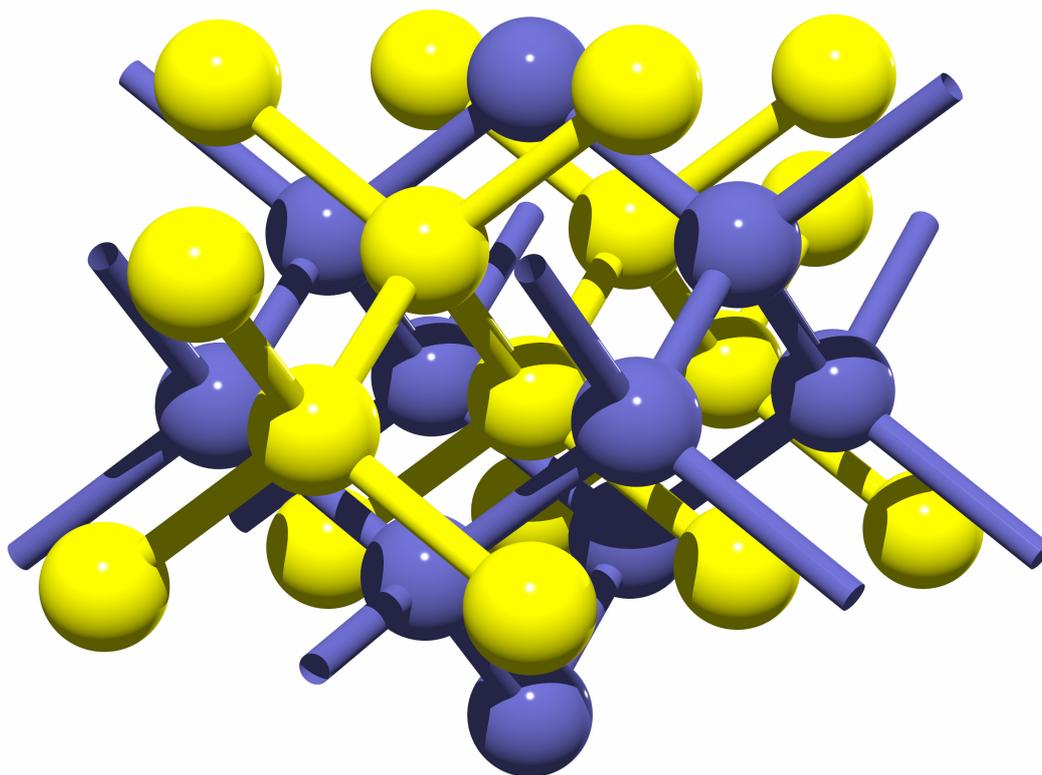


Figure S4. Schematic representation of two interpenetrating networks of voids and channels in the crystal structures of **1** and **2** (different networks are colored in different colors). Spheres and hollow cylinders represent voids and channels, respectively.

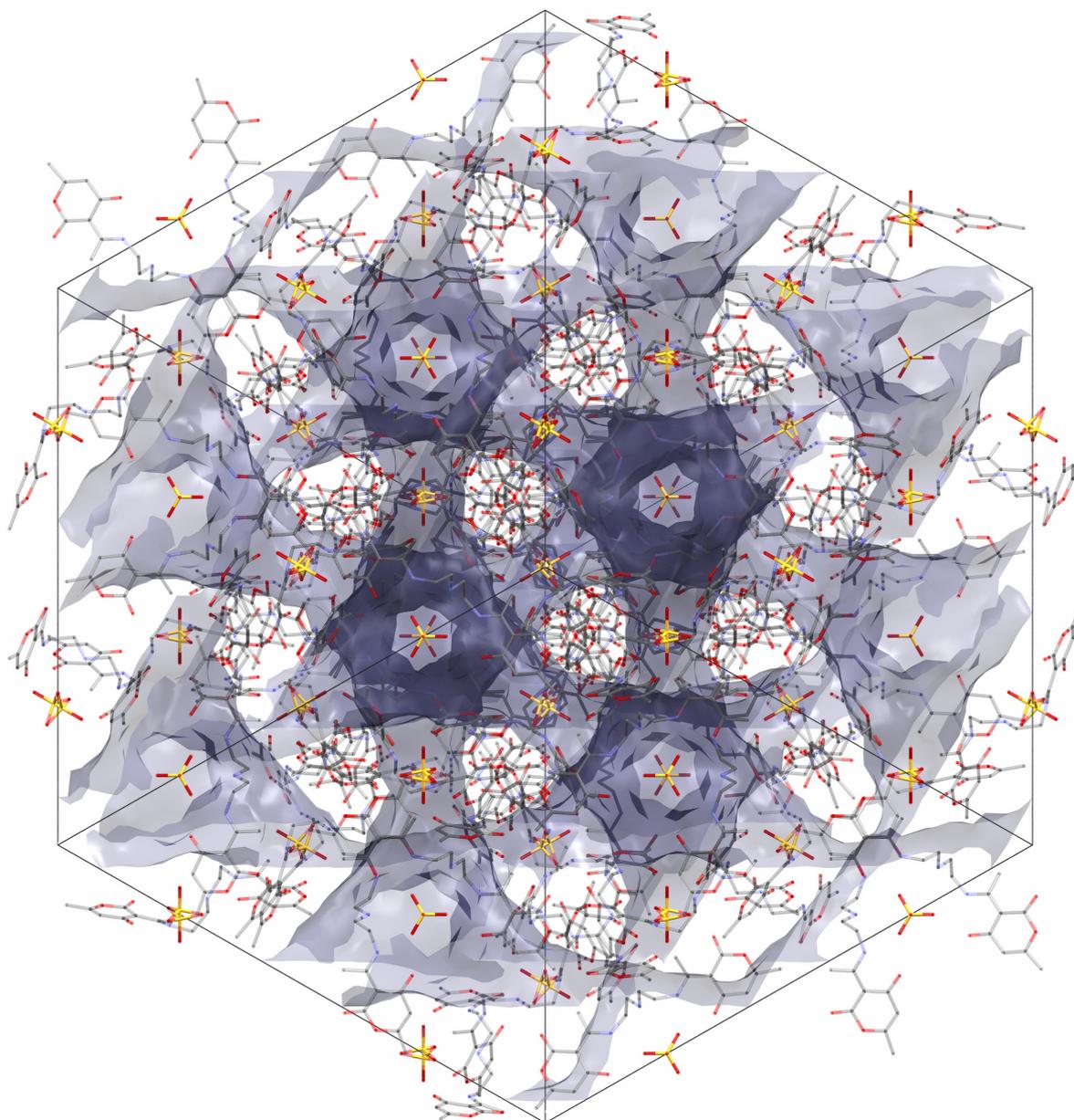


Figure S5. Mercury-POV-Ray rendered view of voids in the crystal packing of **2** viewed down the three-fold axis. H atoms are omitted for the sake of clarity. Voids are blue, S yellow.

Powder X-ray data

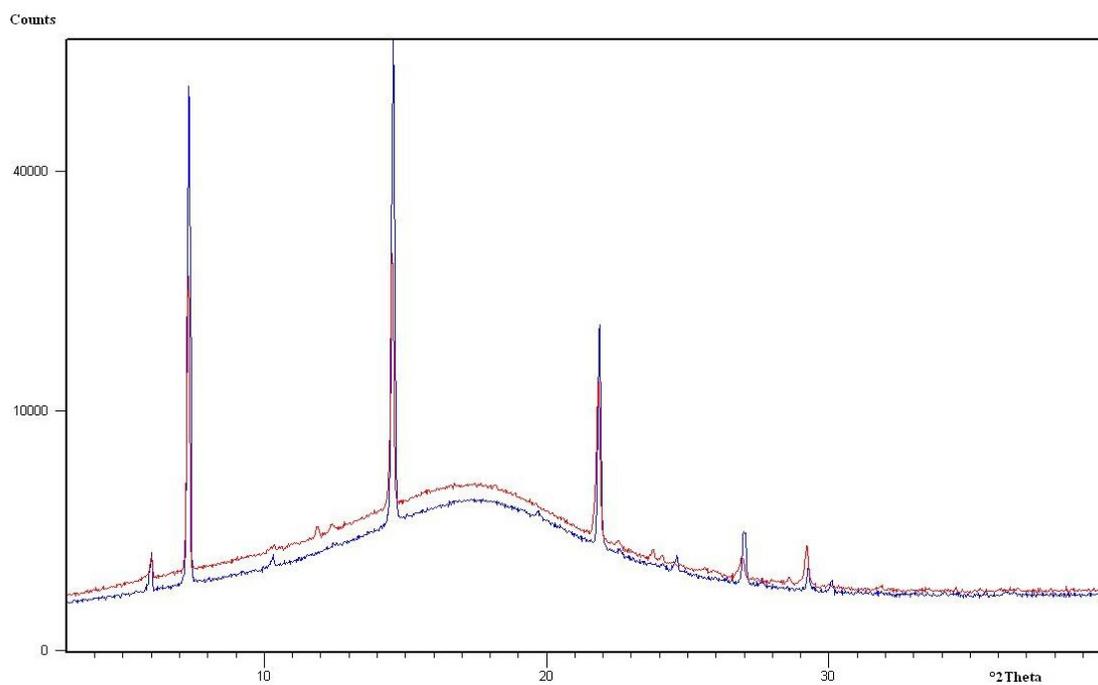
Powder X-ray data were collected on X'PertPro, PANalytical, Cu K α radiation, flat plate sample on a zero background in Bragg-Brentano geometry; soller slits 0.04 radians; antiscatter slit 1/2 degrees; detector Xcelerator (RTMS detector); instrument validated with NIST standards; 40kV, current 45 mA.

Powder X-ray data for Figure S5b were collected on Philips PW 3710 diffractometer, Cu K α 1 radiation, flat plate sample on a zero background in Bragg-Brentano geometry, tension 40kV, current 40 mA.

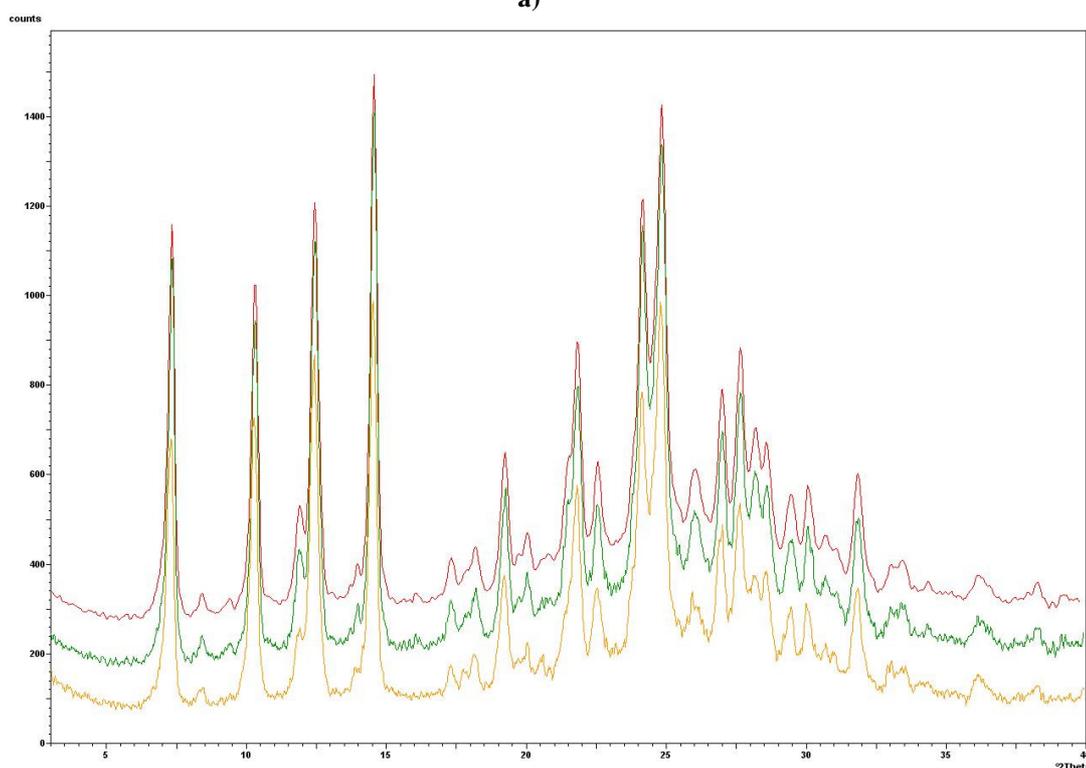
Calculated patterns were generated using X'PertHighScorePlus: Version 2.2.^[10]

Table S3. Instrumental parameters for XRPD measurements.

	1 and 2(in glycerol)	1 and 2 (dried sample)
Sample holder	Flat plate, zero background silicon plate, crystals in glycerol, RT	Flat plate, zero background silicon plate, RT, 65, 100°C
Instrument	Philips X'Pert PRO	Philips X'Pert PRO
Goniometer	PW3050/60	PW3050/60
Generator	PW3040; 45 kV, 40 mA	PW3040; 45 kV, 40 mA
X-ray tube	PW3373/00; Cu anode LFF	PW3373/00; Cu anode LFF
Focus	Linear	Linear
Sample stage	Spinner	Spinner
Measurement range (2θ)	3 – 40°	3 – 40°
Type of measurement	Continuous absolute measurement	Continuous absolute measurement
Step size (2θ)	0.017°	0.017°
Time per step	255.5 s	203.75 s
Filter	Nickel	Nickel
Radiation	CuK α	CuK α
Primary soller slit	0.04 rad	0.04 rad
Antiscatter slit	Fixed, (0,5°)	Fixed, (0,5°)
Primary mask	/	/
Sekundary soller slit	0.04 rad	0.04 rad
Detector	X'Celerator ($2.022^\circ 2\theta$)	X'Celerator ($2.022^\circ 2\theta$)
Control program	X'Pert Data Collector ^[10]	X'Pert Data Collector
PreFix module	Mirror Cu W/Si (focusing MPD)	Mirror Cu W/Si (focusing MPD)
Offset	1.220°	1.220°

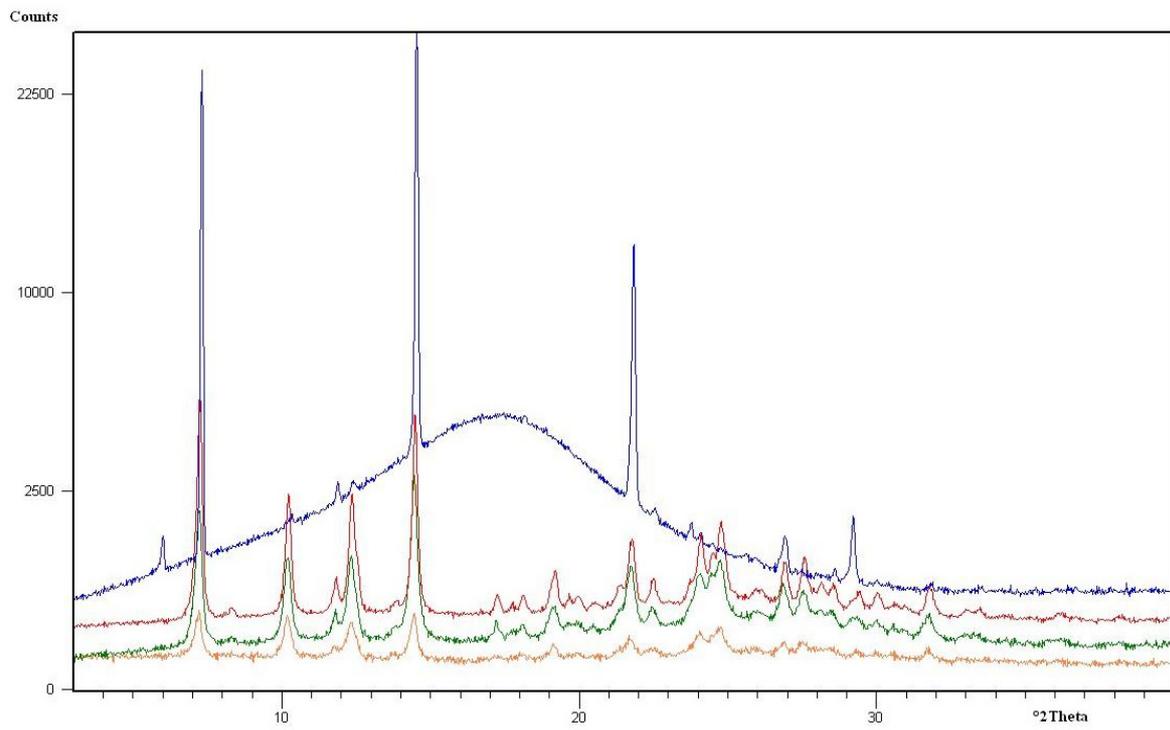


a)

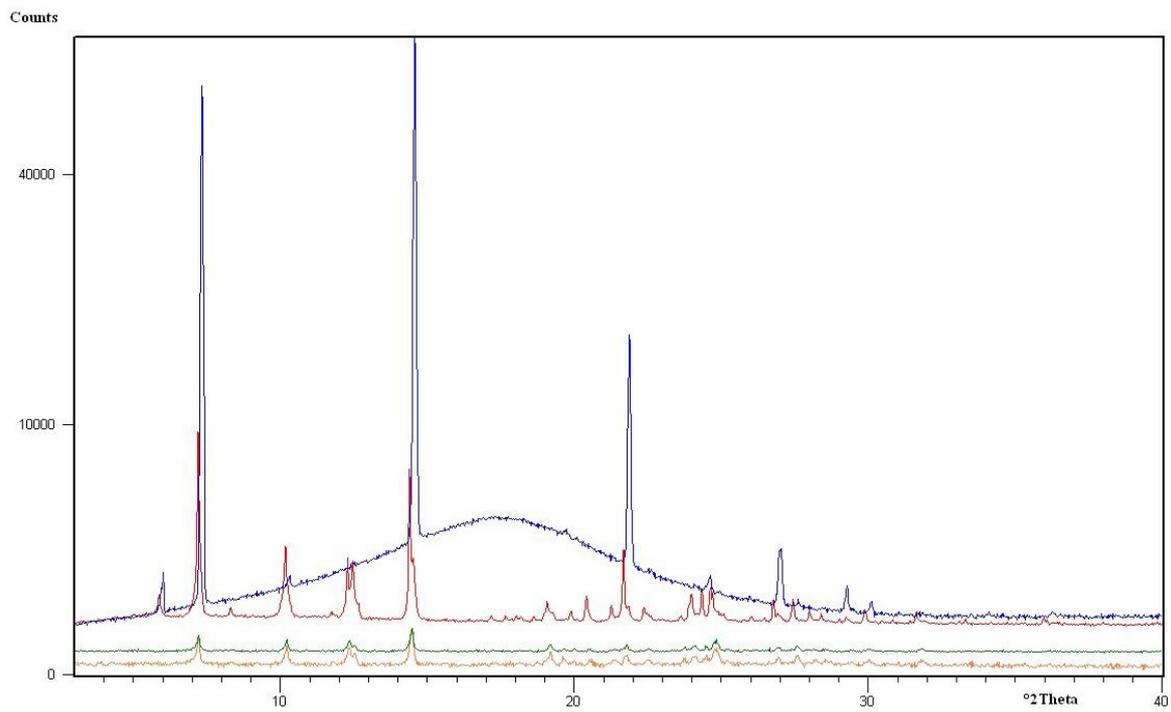


b)

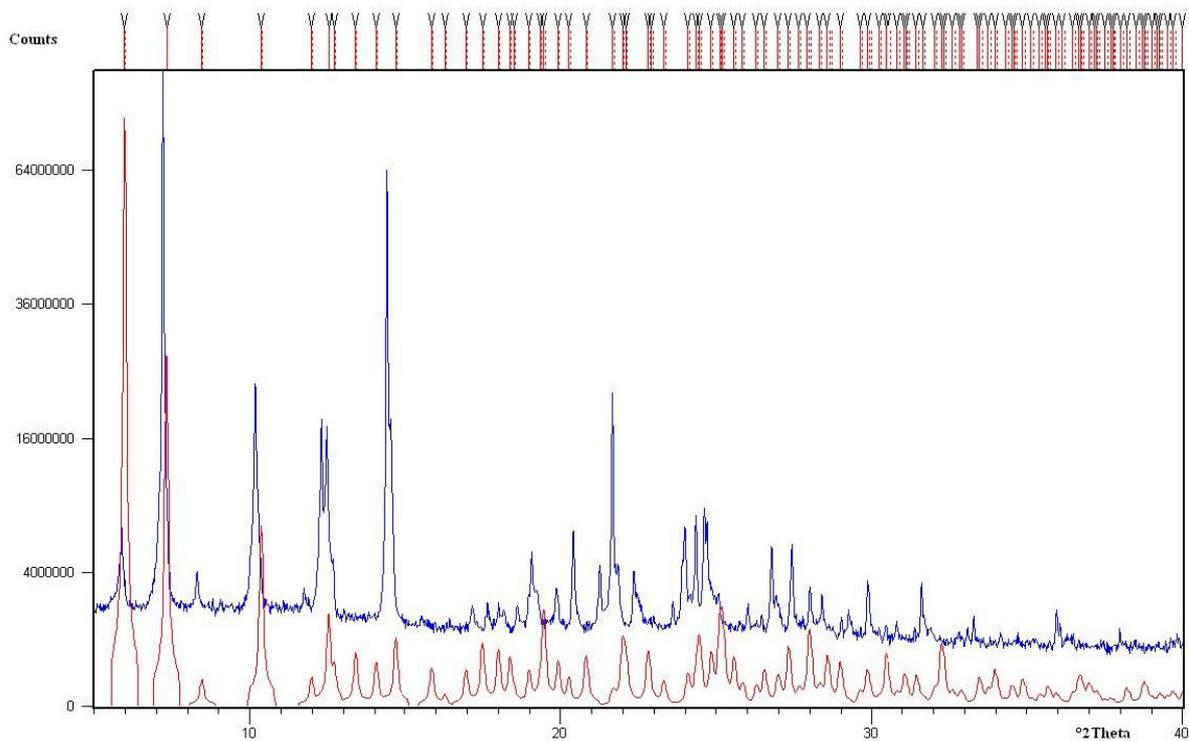
Figure S6. a) Compared powder patterns of **1** (red) and **2** (blue) in glycerol show that they are isostructural. b) Powder patterns of product **1** prepared from methanol, acetonitrile and dichloromethane. **1** from methanol (yellow); **1** from acetonitrile (green); **1** from dichloromethane (red).



a)

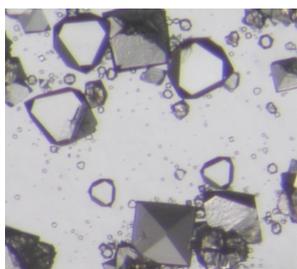


b)

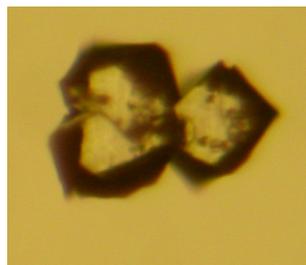


c)

Figure S7. a) Powder patterns of **1** at RT, 65 and 100°C. **1** in glycerol at RT (blue); **1** exposed to air at RT (red); **1** exposed to air at 65°C (green); **1** exposed to air at 100°C (orange); b) Powder patterns of **2** at RT, 65 and 100°C. **2** in glycerol at RT (blue); **2** exposed to air at RT (red); **2** exposed to air at 65°C (green); **2** exposed to air at 100°C (orange); c) Powder pattern of **2** dried at RT (blue) compared to a calculated^[10] powder pattern of 2 at 100 K. The calculated powder pattern is displayed on square root scale.



a)



b)

Figure S8. a) **1** in methanol; b) **1** after one month at 4 °C, without methanol. The picture was taken after 3 hours at RT. The micro-crystals remain lucid at RT for days.

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