

Supporting Information

Synthesis of Tetrahalide Dianions Directed by Crystal Engineering

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Synthesis and crystallization

Sodium sulfadiazine is commercially available. It was used without purification. For the synthesis of **1a**, 1.0 mL of concentrated hydrochloric acid (38 %) was added to a solution of 0.1 mmol of sodium sulfadiazine (0.0272 g) in 15 mL of methanol in the presence of 0.1 mmol I₂ (0.0253 g). The resulting solution was left undisturbed at room temperature; after two days light brown needle-shaped crystals of **1a** were obtained. Elemental analysis, Calc. for C₁₀H₁₁O₂N₄SCl (1a): C% 29.04; H% 2.68; N% 13.54. Found C% 28.93; H% 2.42; N% 13.34.

The synthesis and crystallization of **2a**, **2b** and **2c** are analogous to that of **1a**, **1b** and **1c** respectively: 1.0 mL of concentrated hydrobromic acid (47 %) was added to a solution of 0.1 mmol of sodium sulfadiazine (0.0272 g) in 15 mL of methanol in the presence of 0.1 mmol I₂ (0.0253 g). The resulting solution was left undisturbed at room temperature; after two days light brown needle-shaped crystals of **2a** were obtained. For the synthesis of **2b**, ethylene glycol (0.5 ml) instead of I₂ was added to the solution, large light yellow block crystals of **2b** were generated after two days. For the synthesis and crystallization of **2c**, 15 ml of ethanol was used as the solvent without I₂ and glycol. The process needed three days by slow evaporation to get the large light yellow block-shaped crystals **2c**. Elemental analysis, Calc. for C₁₀H₁₁O₂N₄SBr (2a): C% 26.22; H% 2.42; N% 12.23. Found C% 26.47; H% 2.44; N% 12.33.

Synthesis and crystallization of **3a**, 1.0 mL of concentrated hydriodic acid (64%) was added to a solution of 0.1 mmol of sodium sulfadiazine (0.0272 g) in 15 mL of methanol in the presence of 0.1 mmol I₂ (0.0253 g). The resulting solution was left undisturbed at room temperature; after two days light brown needle-shaped crystals of **3a** were obtained. For the synthesis of **3b**, ethylene glycol (0.5 ml) instead of I₂ was added to the solution, light yellow plate crystals of **3b** were generated after two days. For the synthesis and crystallization of **3c**, 15 ml of ethanol was used as the solvent without additional I₂ or glycol. The process needed three days by slow evaporation to get the brown plate-shaped crystals **3c**. Elemental analysis, Calc. for C₁₀H₁₁O₂N₄SI₂ (3a): C% 23.78; H% 2.20; N% 11.09. Found C% 23.57; H% 2.04; N% 10.98.

X-Ray Diffraction

Single Crystal Diffraction

All the single crystal data were collected on a Bruker D8 goniometer equipped with an APEX CCD detector using Mo- $K\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$); the radiation source was an INCOATEC $I\text{-}\mu\text{S}$ microsource equipped with multilayer optics. An Oxford Cryosystems 700 controller was used to ensure temperature stability during data collection. For the high resolution data collection, two settings of the detector angle θ for low and high-order reflections with sufficient overlap were used, with several runs of different crystal rotation ϕ for each detector setting and exposure times of 5 s per frame for low-order and 20 s for high-order data. High resolution intensity data extend to $\sin \theta_{\max}/\lambda > 1.105 \text{ \AA}^{-1}$, corresponding to $\theta_{\max} > 51^\circ$ for Mo $K\alpha$ radiation. All frames were collected in ω -scan mode, and the intensities were integrated with the help of the program SAINT (Bruker, 2003). Multi-scan absorption corrections improved both merging (R_{int}) and refinement residuals ($R1$, $wR2$).

All the structures were solved with direct methods and refined using full-matrix least squares on F^2 with SHELXL-2013 (Sheldrick, 2008). Anisotropic displacement parameters were assigned to non-H atoms. In **1a**, **2a** and **3a**, all the hydrogen atoms were located from difference Fourier maps and their positions were freely refined. In **2b**, **2c**, **3b** and **3c**, the hydrogen atoms bonded with N (and O in **3b**) were located from difference Fourier maps, and their positions were refined with distance restraints. All the other H atoms were treated with riding model. Crystal data, data collection and refinement results have been compiled in Table S1.

Powder Diffraction

Flat samples were prepared for all the compounds by fixing the sample powder on a Mylar X-ray Film (6.0 μm thick) using Vaseline oil. X-ray powder diffractions were performed by Cu $K\alpha_1$ radiation (1.54056 \AA) monochromated by germanium with a linear Position Sensitive Detector (PSD).

Raman Spectroscopy

Raman spectroscopy measurements were done at room temperature with single crystals using Bruker SENTERRA Dispersive Raman Microscope. In a typical experiment, a green laser (532 nm) was focused on the single crystal placed on a glass slide with a 50x objective lens.

Table S1. Details of the crystal data, data collection and refinement results.

Crystal data	1a	2a	2b	2c
Chemical formula	C ₁₀ H ₁₁ ClIN ₄ O ₂ S	C ₁₀ H ₁₁ BrIN ₄ O ₂ S	C ₁₀ H ₁₁ N ₄ O ₂ S·Br·0.5(C ₂ H ₆ O ₂)	2(C ₁₀ H ₁₁ N ₄ O ₂ S)·2Br·C ₂ H ₆ O
<i>M_r</i>	413.64	458.10	362.23	708.46
Crystal system, space group	Triclinic, <i>P</i> $\bar{1}$	Triclinic, <i>P</i> $\bar{1}$	Triclinic, <i>P</i> $\bar{1}$	Triclinic, <i>P</i> $\bar{1}$
<i>a, b, c</i> (Å)	5.6561(6), 11.4126(12), 12.2064(12)	5.7185(3), 11.6440(6), 12.3493(6)	5.7078(5), 11.5383(10), 12.198(1)	5.709(3), 11.532(6), 12.116(6)
α, β, γ (°)	116.6140(10), 91.131(2), 104.114(2)	116.6971(6), 91.7117(6), 104.1699(8)	62.8640(10), 79.4180(10), 76.9800(12)	62.675(8), 79.693(9), 77.507(9)
<i>V</i> (Å ³)	675.58 (12)	702.93(6)	693.50(10)	689.0(6)
<i>Z</i>	2	2	2	1
μ (mm ⁻¹)	2.73	5.27	3.13	3.14
Crystal size (mm)	0.28×0.04×0.02	0.20×0.08×0.03	0.32×0.16×0.14	0.19×0.08×0.02
Data collection				
No. of measured, independent and observed [<i>I</i> > 2σ(<i>I</i>)] reflections	52171, 15116, 11174	32221, 15396, 11601	10816, 4018, 3652	8218, 2849, 2084
<i>R</i> _{int}	0.078	0.042	0.035	0.092
Refinement (based on all <i>F</i>²)				
<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.048, 0.120, 1.04	0.039, 0.097, 0.98	0.036, 0.082, 1.05	0.055, 0.118, 1.00
No. of reflections	15116	15396	4018	2849
No. of parameters	205	205	197	190
No. of restraints	0	0	0	13
$\Delta\rho_{\max}, \Delta\rho_{\min}$ (e Å ⁻³)	2.85, -2.27	3.15, -1.93	1.75, -1.00	0.70, -0.76

Crystal data	3a	3b	3c
Chemical formula	C ₁₀ H ₁₁ I ₂ N ₄ O ₂ S	C ₁₀ H ₁₁ N ₄ O ₂ S, C ₂ H ₆ O ₂ ,I ₃	C ₁₀ H ₁₁ N ₄ O ₂ S·I ₅
<i>M_r</i>	505.65	694.07	885.79
Crystal system, space group	Triclinic, <i>P</i> $\bar{1}$	Triclinic, <i>P</i> $\bar{1}$	Triclinic, <i>P</i> $\bar{1}$
<i>a, b, c</i> (Å)	5.7879(14), 11.983(3), 12.568(3)	8.0577(9), 10.8694(12), 11.7471(13)	8.004(2), 11.247(3), 11.473(3)
α, β, γ (°)	61.725(3), 87.456(2), 76.227(2)	84.291(2), 74.230(2), 85.792(2)	83.925(4), 89.442(4), 72.371(4)
<i>V</i> (Å ³)	743.2(3)	984.05(19)	978.6(5)
<i>Z</i>	2	2	2
μ (mm ⁻¹)	4.38	4.89	8.06
Crystal size (mm)	0.08×0.07×0.03	0.25×0.12×0.02	0.31×0.12×0.04
Data collection			

No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	58775, 16488, 12136	14607, 5581, 4921	13904, 5420, 4289
R_{int}	0.057	0.049	0.059
Refinement (based on all F^2)			
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.043, 0.097, 1.03	0.031, 0.079, 1.04	0.048, 0.125, 1.07
No. of reflections	16488	5581	5420
No. of parameters	216	239	215
No. of restraints	0	2	4
$\Delta\rho_{\text{max}}, \Delta\rho_{\text{min}}$ ($e \text{ \AA}^{-3}$)	2.65, -1.03	1.47, -0.97	2.92, -1.41
Crystal size (mm)	0.08×0.07×0.03	0.25×0.12×0.02	0.31×0.12×0.04

Table S2. Secondary interactions in the parent compound **1b** and in the tetrahalide derivatives **1a**, **2a** and **3a**.

D...A (\AA)	Parent compound	1a	2a	3a
Contacts	1b			
N1-H1...N3^d	2.9037(9)	2.8908(17)	2.9010(15)	2.908(2)
N4-H4A...O1^b	3.1452(7)	2.8589(18)	2.8274(16)	2.796(2)
N4-H4B...X^c	3.2125(9)	3.2495(14)	3.3618(12)	3.5302(16)
N4-H4C...X^d	3.1443(7)	3.1635(14)	3.2910(12)	3.4742(16)
N4...X^e	3.2184(7)	3.2543(16)	3.3511(14)	3.517(2)
O3-H3O...X^f	3.2215(9)	—	—	—
$\pi_{\text{pm}} \cdots \pi_{\text{pm}}$	3.693 (2)	3.664 (2)	3.675 (2)	3.693 (2)
$\pi_{\text{aniline}} \cdots \pi_{\text{aniline}}$	3.858 (2)	3.763 (2)	3.786 (2)	3.832 (2)
I-I^g	—	2.7192(6)	2.7368(2)	2.7660(8)
H...X^h	—	3.2416(6)	3.2836(2)	3.3686(9)
R_{XB}	—	0.87	0.86	0.85

Note: for **parent compound**, *a*, 1-*x*, 1-*y*, -*z*; *b*, 1-*x*, 1-*y*, -*z*; *c*, *x*, *y*, *z*; *d*, *x*-1, *y*, *z*; *e*, 1-*x*, 2-*y*, -*z*; for the **1a** and **2a**, *a*, 1-*x*, 2-*y*, -*z*; *b*, 1-*x*, 2-*y*, 1-*z*; *c*, *x*-1, *y*, *z*; *d*, *x*, *y*, *z*; *e*, 1-*x*, 1-*y*, 1-*z*; *f*, 1-*x*, 1-*y*, *z*; for **3a**, *a*, 1-*x*, 2-*y*, 1-*z*; *b*, 1-*x*, 2-*y*, -*z*; *c*, *x*-1, *y*, *z*; *d*, *x*, *y*, *z*; *e*, 2-*x*, 1-*y*, -*z*; *f*, 2-*x*, 1-*y*, 1-*z*.

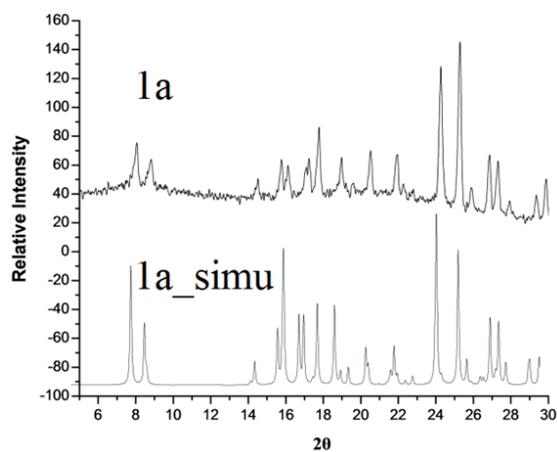


Figure S1. Comparison of the experimental powder diffraction with the simulated one from X-ray structure for **1a**.

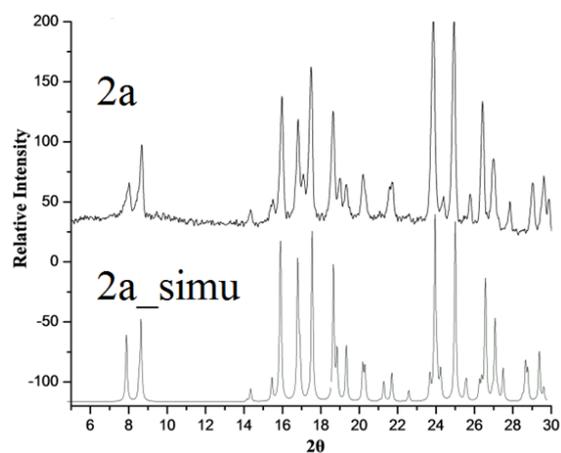


Figure S2. Comparison of the experimental powder diffraction with the simulated one from X-ray structure for **2a**.

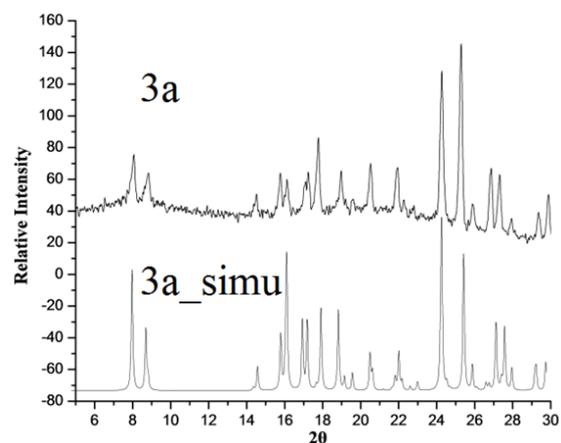


Figure S3. Comparison of the experimental powder diffraction with the simulated one from X-ray structure for **3a**.

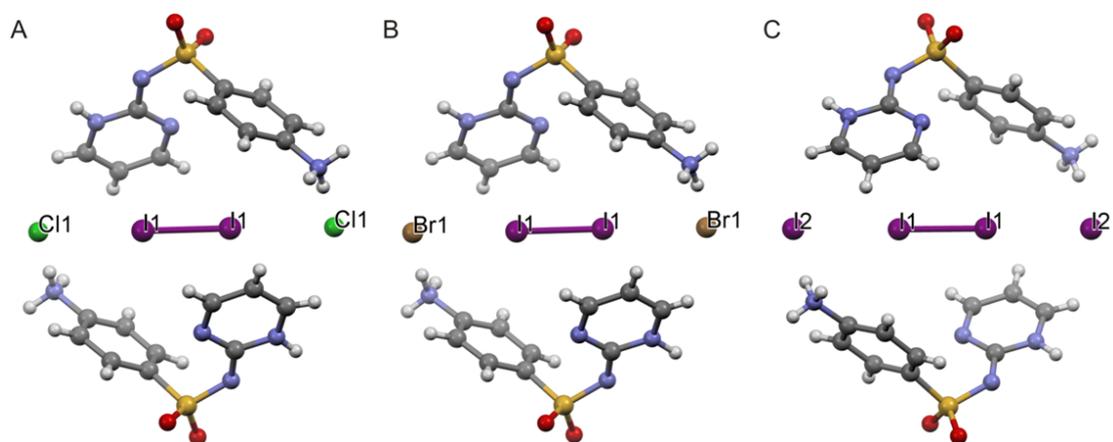


Figure S4. Plots of the macrocyclic structures of **1a** (A), **2a** (B) and **3a** (C) to show the isomorphism.

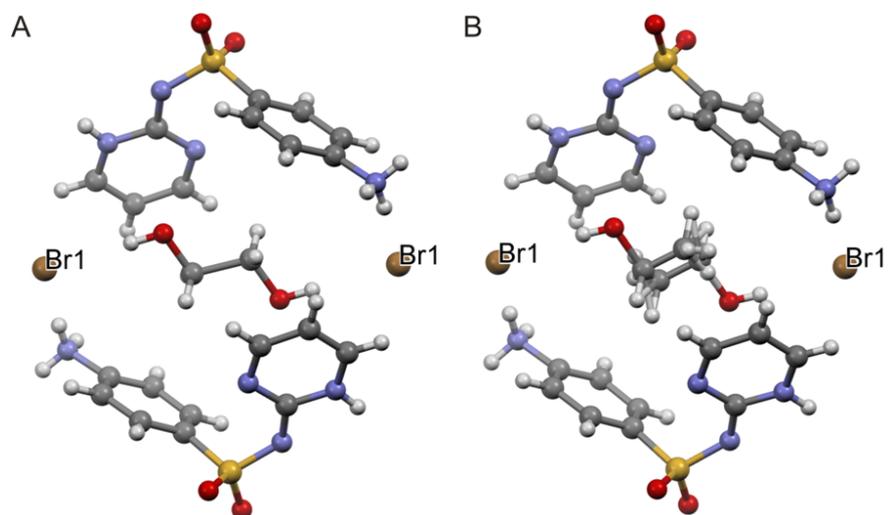


Figure S5. Plots of the macrocyclic structures **2b** (A) and **2c** (B).

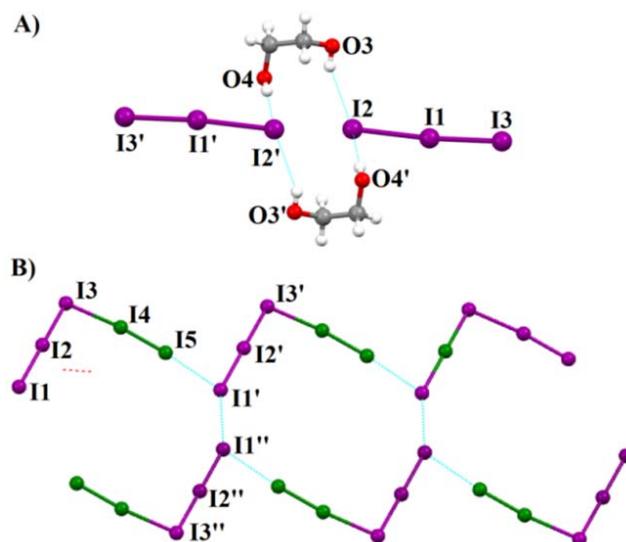


Figure S6. Hydrogen bonds between glycol and triiodide in **3b** (A) and halogen bonds between neighbouring pentaiodides in **3c** (B). The bonding distances in **3b**: $O3 \cdots I2 = 3.543$, $O4 \cdots I2' = 3.551$; the bonding distances and angles in **3c**: $I1-I2 = 2.842$, $I2-I3 = 3.025$, $I3-I4 = 3.219$, $I4-I5 = 2.776$, $I5 \cdots I1' = 3.576$, $I1' \cdots I1'' = 3.676$, $I1-I2-I3 = 173.25$, $I2-I3-I4 = 96.17$, $I3-I4-I5 = 173.99$; $I4-I5 \cdots I1' = 175.38$, $I5 \cdots I1' \cdots I2' = 85.55$, $I2' \cdots I1' \cdots I1'' = 151.58$ Å. Symmetry operators: $1-x, 1-y, -x$ in A and $x, 1+y, z$ for I' , $-x, 2-y, 1-z$ for I'' in B.

Raman spectroscopy in 1a, 2a and 3a

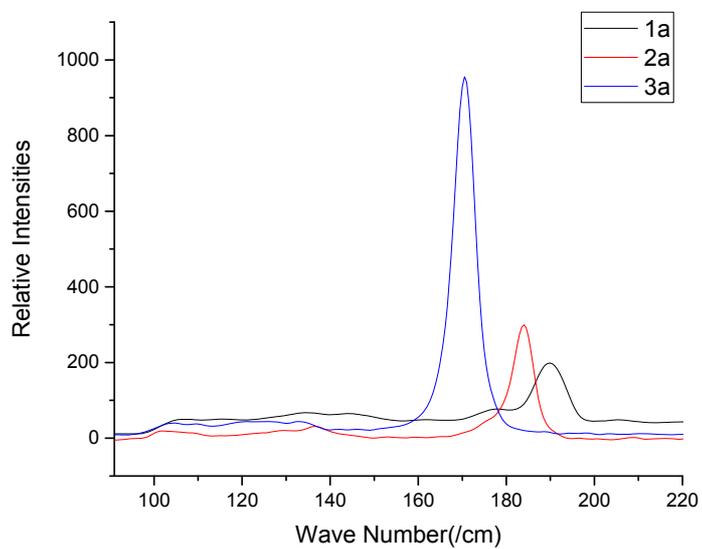


Figure S7. Shift of the Raman band associated with the central I-I bond in the tetrahalide derivatives **1a**, **2a** and **3a**.