

Supplementary Information

Reversible uptake of halogens ($X_2=Cl_2$, Br_2 and I_2) by Cr_8 metallocrown

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S1. Synthesis

Synthetic details

Unless stated otherwise, all reagents and solvents were purchased from Sigma Aldrich Chemicals and used without further purification.

Synthesis of $[\text{Cr}_8(\mu\text{-F})_8(\text{O}_2\text{C}^t\text{Bu})_{16}]$ (**Cr₈**) with empty cavity was reported in a previous study.¹ All the **Cr₈** crystals used in these experiments are from the same batch. ESI-MS (m/z): + 2207 $[\text{M} + \text{Na}]^+$ (100%); Elem. Anal. (calc./exp.): C (43.96/44.07), H (6.64/6.68) and Cr (19.03/19.05).

Synthesis of $[\text{Cr}_8(\mu\text{-F})_8(\text{O}_2\text{C}^t\text{Bu})_{16}] \cdot 0.743(5) \text{Cl}_2 - \text{Cl}_2@ \text{Cr}_8$.

Dry Cl_2 gas was introduced in a conical flask that contained single crystals of **1** at 290K. Chlorine gas was produced by adding acidic water drop-wise in a round-bottom flask with trichloroisocyanuric acid. The produced gas flows through a silicon tube in a drying column and then in the conical flask containing **Cr₈**. Elem. Anal. $\text{Cr}_8\text{F}_8\text{O}_{32}\text{C}_{80}\text{H}_{144}\text{Cl}_{1.486}$ (calc./exp.): C (42.94/43.35), H (6.49/6.59), Cl (2.36/2.24) and Cr (18.59/18.24). TGA – loses 3.5760% between 45.18 and 284.20°C which corresponds to 1.141 Cl_2 molecules.

Synthesis of $[\text{Cr}_8(\mu\text{-F})_8(\text{O}_2\text{C}^t\text{Bu})_{16}] \cdot 0.8017(18) \text{Br}_2 - \text{Br}_2@ \text{Cr}_8$

Liquid Br_2 was put in a large vial, and then in the same vial a smaller vial that contained single crystals of **Cr₈** was introduced at room temperature. The vial was left sealed overnight and the next the crystals were measured. Elem. Anal. $\text{Cr}_8\text{F}_8\text{O}_{32}\text{C}_{80}\text{H}_{144}\text{Br}_{1.603}$ (calc./exp.): C (41.54/38.83), H (6.27/5.96), Br (5.55/9.16) and Cr (17.98/16.57). TGA – loses 7.1165% between 36.73 and 103.73°C corresponding to 1.097 Br_2 molecules and 4.2985 % between 109.36 and 166.02°C which corresponds to 0.663 Br_2 molecules a total of 1.766 Br_2 molecules.

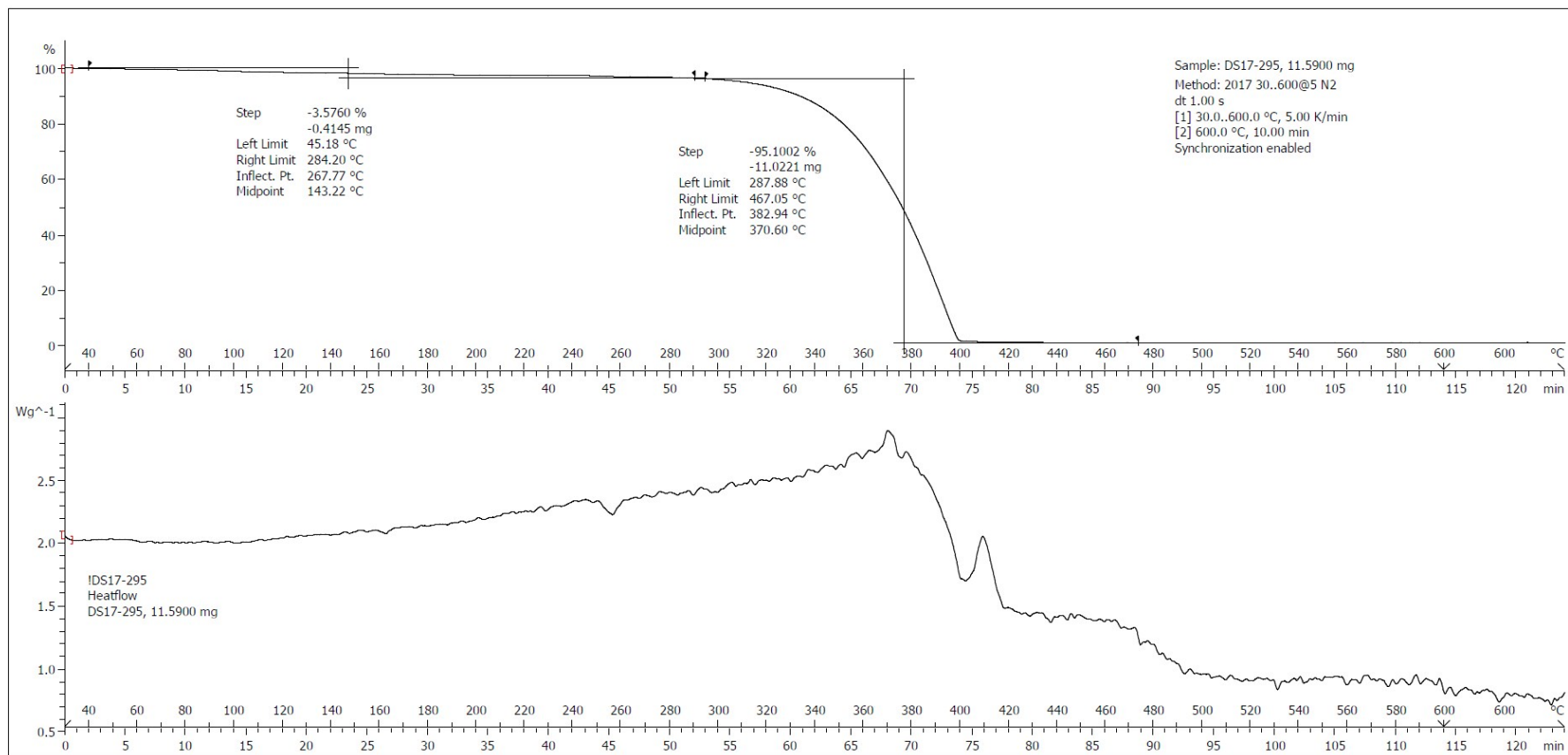
The difference in the elemental analysis comes from the fact the calculations are done for the chemical formula obtained from the crystal data. If we were to re-calculate the percentages based upon the quantity of bromine extracted from TGA the percentages would be: Elem. Anal. $\text{Cr}_8\text{F}_8\text{O}_{32}\text{C}_{80}\text{H}_{144}\text{Br}_{3.532}$ (calc./exp.): C (38.94/38.83), H (5.88/5.96), Br (11.45/9.16) and Cr (16.86/16.57).

Synthesis of $[\text{Cr}_8(\mu\text{-F})_8(\text{O}_2\text{C}^t\text{Bu})_{16}] \cdot 0.38\text{I}_2 - \text{I}_2@ \text{Cr}_8$

I_2 was put in a screw-cap Teflon flask 125 mL volume, and then in the flask a vial that contained single crystals of **Cr₈** was introduced. The vial was left sealed for 1 week at 50 °C and then the crystals were measured. Elem. Anal. $\text{Cr}_8\text{F}_8\text{O}_{32}\text{C}_{80}\text{H}_{144}\text{I}_{1.603}$ (calc./exp.): C (42.11/42.74), H (6.36/6.49), I (4.23/3.41) and Cr (18.23/17.83). TGA – loses 3.7754% between 73.50 and 273.21°C which corresponds to 0.34 I_2 molecules.

S2. Thermogravimetric analysis

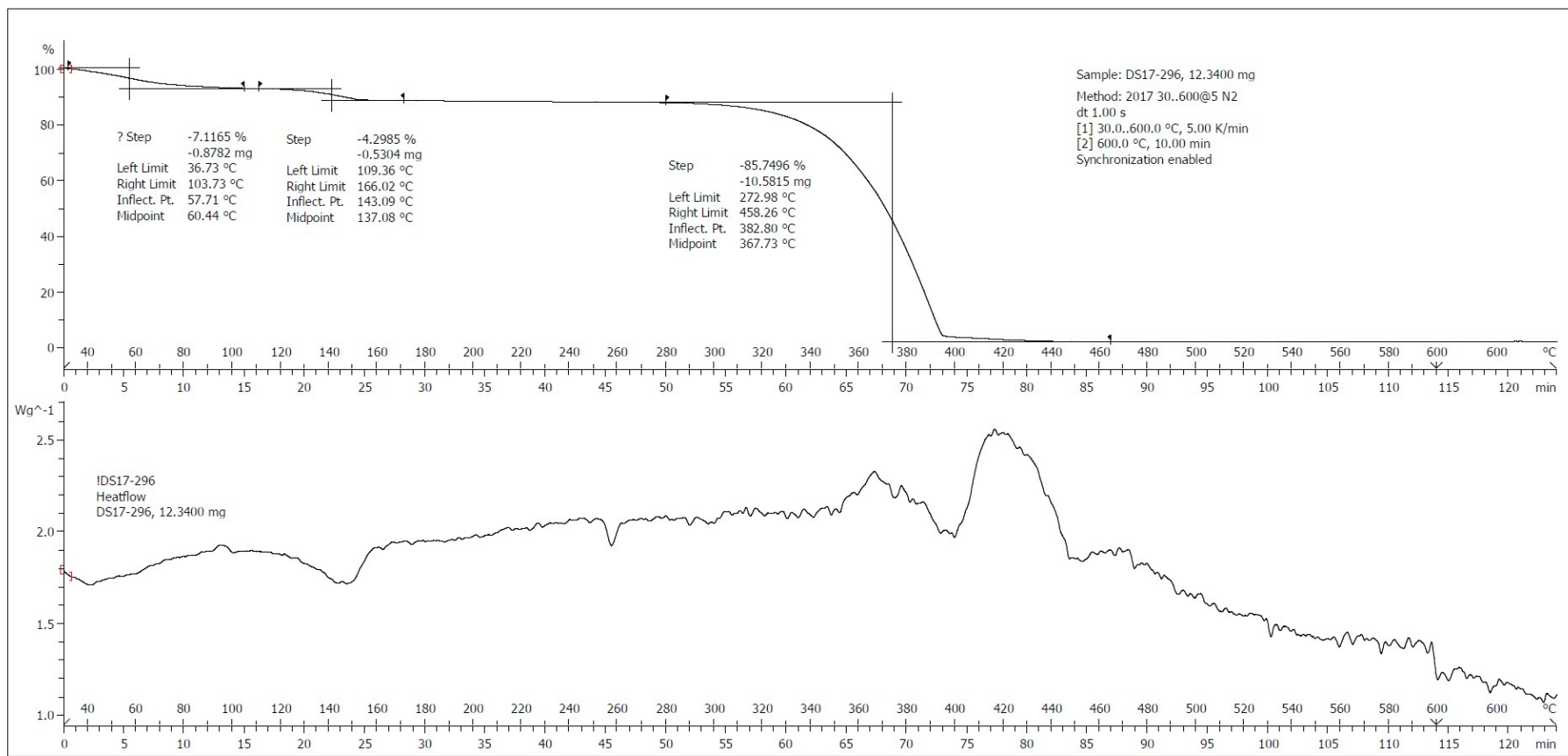
TGA analysis for compound $\text{Cl}_2@\text{Cr}_8$, $\text{Br}_2@\text{Cr}_8$ and $\text{I}_2@\text{Cr}_8$ were done in a Perkin-Elmer instrument. The samples were heated at $5^\circ\text{C}/\text{minute}$ from room temperature to 600°C under a flow of dry nitrogen gas.



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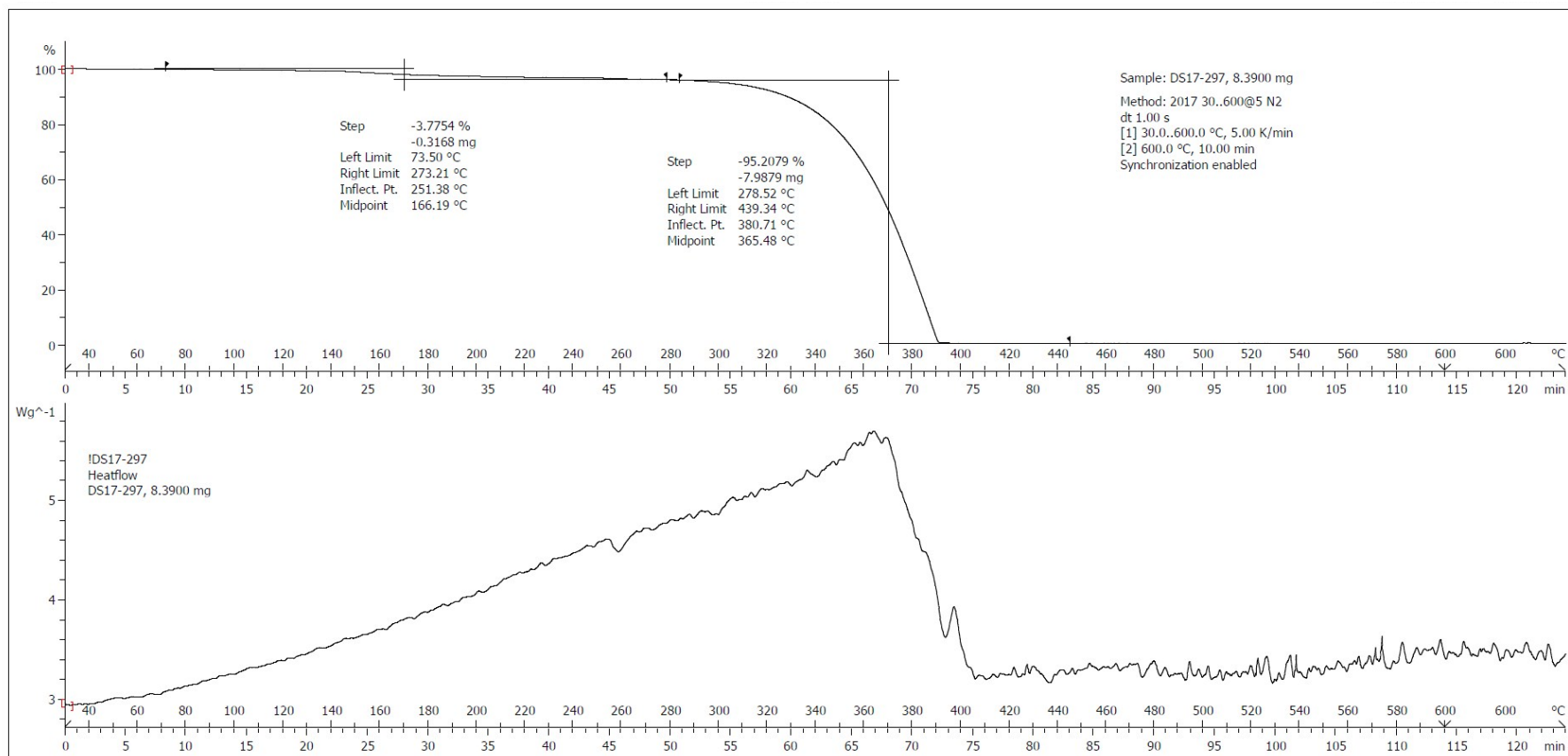
Figure S1 – TGA of $\text{Cl}_2@\text{Cr}_8$



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Figure S2 – TGA of Br₂@Cr₈



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Figure S3 – TGA of $I_2@Cr_8$

S3. RAMAN Spectra

RAMAN studies were carried out on a Renishaw System 1000 Raman Spectrometer including Modu-Laser 514nm. Each spectrum was obtained as static spectra centred at 520 cm^{-1} , 100% laser power, 10s, Accumulation 5.

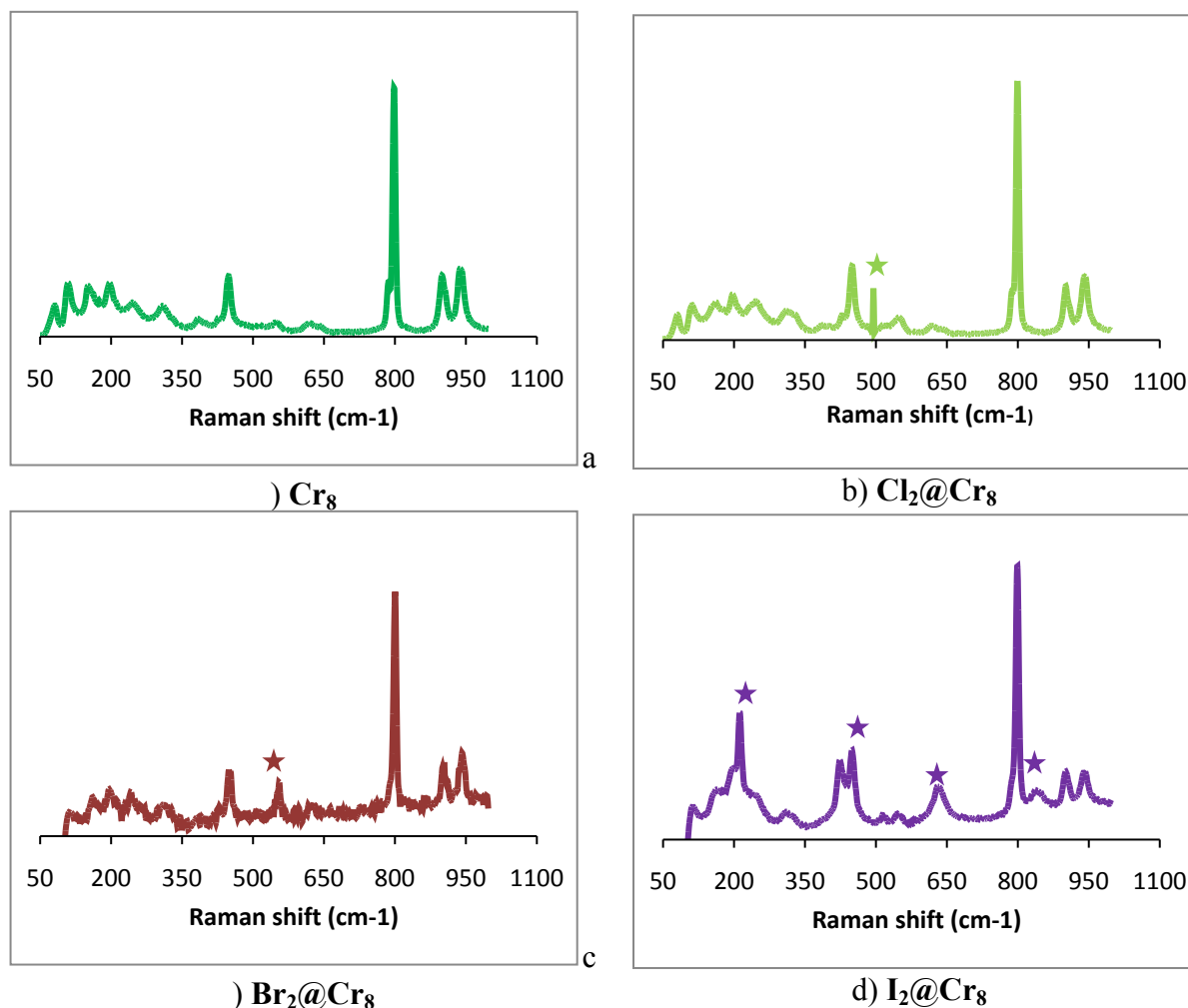


Figure S4 – Raman spectra of a) Cr_8 , b) $\text{Cl}_2@Cr_8$, c) $\text{Br}_2@Cr_8$ and d) $\text{I}_2@Cr_8$

All the peaks in the Raman spectra assigned to the halogen are red shifted compared to the Raman shifts from the gaseous halogens. The ν_1 mode moves to a lower wavenumber when the force constant is lowered. This happens when electron density is donated to an antibonding orbital, which is the exact case of the halogen bonds formed between the F and the gas halogens. The presence of Chlorine is depicted through the peak at 495 cm^{-1} Raman shift which is red shifted from the ν_1 540 cm^{-1} vibration for gaseous Cl_2 .² In the case of the crystal loaded with Bromine, we cannot observe the ν_1 318 cm^{-1} because of its overlap with the Cr_8 vibration peaks. Nonetheless, we observe a peak at 554 cm^{-1} Raman shift, also red-shifted from the $2\nu_1$ 611 cm^{-1} vibration for gaseous Br_2 .³ In the case of Iodine loaded sample we observe a peak at 212 cm^{-1} , very little red shifted from the ν_1 214.5 cm^{-1} vibration of

gaseous I₂. We also observe other different overtones of the iodine stretching vibrations at 422, 628 and 835 cm⁻¹.⁴

S4. DSC Analysis

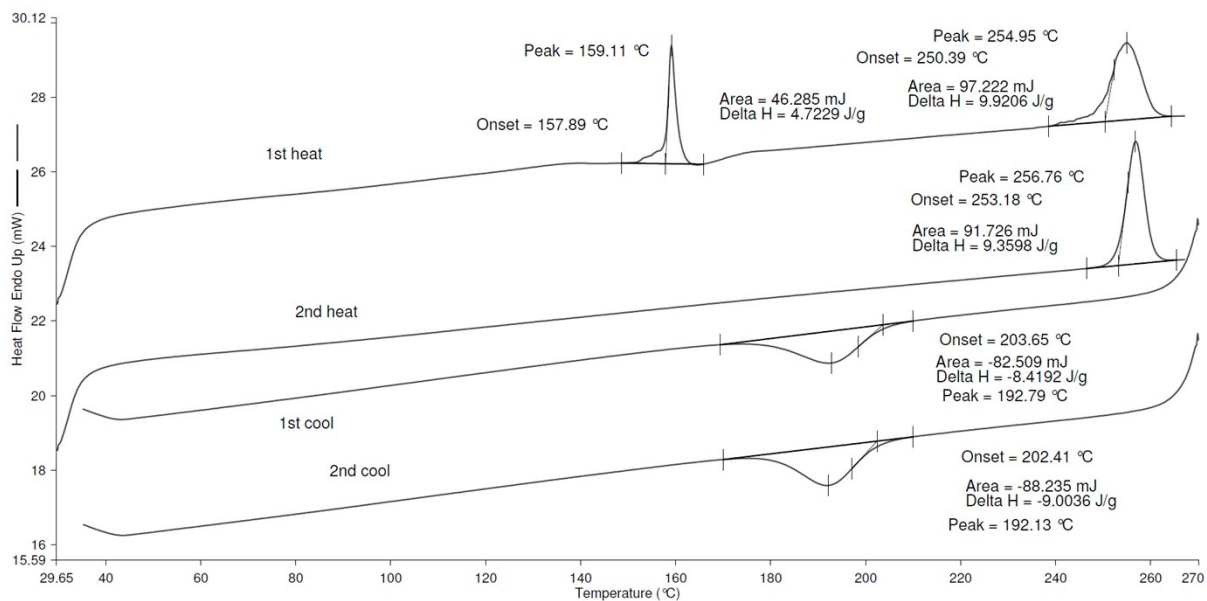


Figure S5 – DSC of Cl₂@Cr₈

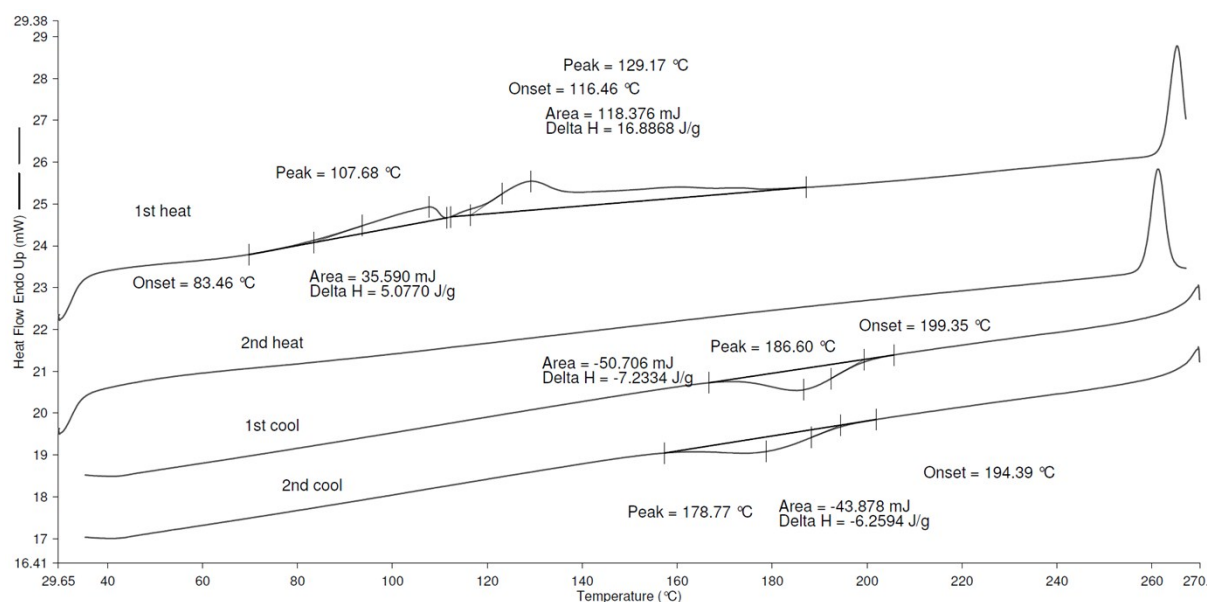


Figure S6 – DSC of Br₂@Cr₈

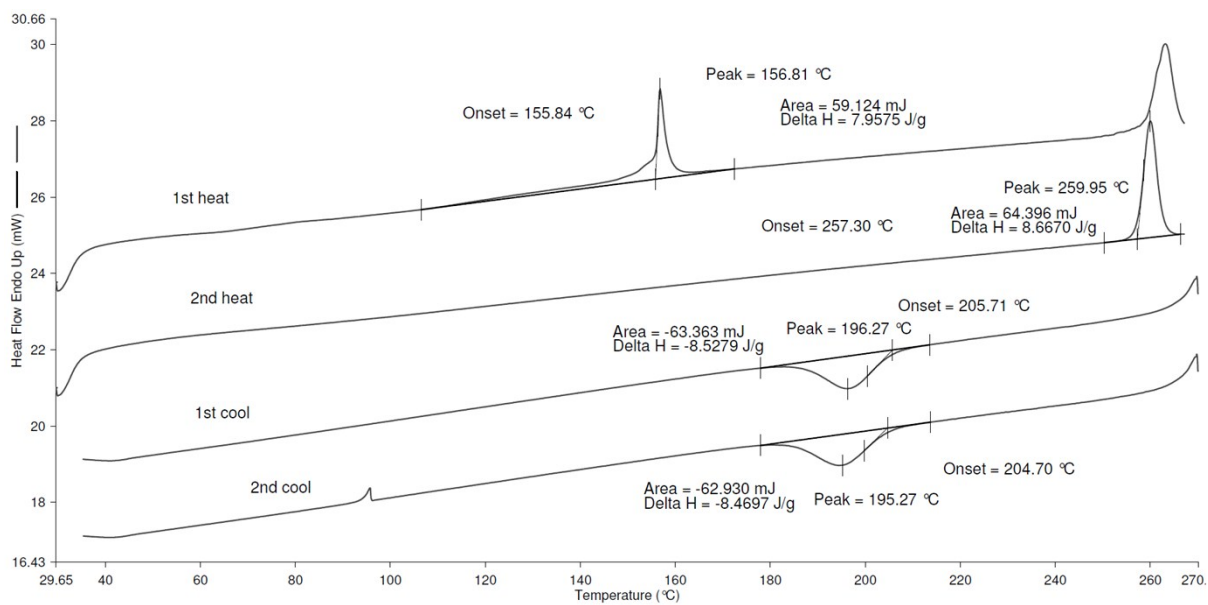


Figure S7 – DSC of $I_2@Cr_8$

S5. Single crystal X-ray diffraction

Data Collection.

Single crystal X-ray diffraction data were collected for the crystal structures $\text{Cl}_2@Cr_8$ and $\text{Br}_2@Cr_8$ at a using Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$) on an Agilent Supernova, equipped with an Oxford Cryosystems Cobra nitrogen flow gas system and

Single crystal X-ray diffraction data were collected for the crystal structures $\text{I}_2@Cr_8$, $\text{Cl}_2@Cr_8_VT350K_1-2$, $\text{Br}_2@Cr_8_VT350K_1-3$, $\text{I}_2@Cr_8_VT350K_1-7$ and $\text{I}_2@Cr_8_VT400K_1-4$ on a Rigaku FR-X diffractometer with a HyPix 6000HE detector and microfocus optics with Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$). Data were measured using CrysAlisPro suite of programs.

VT350K – is a variable temperature experiment where Single crystal X-ray diffraction data were collected at 240 K, and then the crystal was heated up to 350K where it was kept for one hour, before the temperature was decreased at 200 K for another collection. (This cycles was repeated up to 6 times)

VT400K – is a variable temperature experiment where Single crystal X-ray diffraction data were collected at 240 K, and then the crystal was heated up to 400K where it was kept for three hours, before the temperature was decreased at 200 K for another collection.

Crystal structure determinations and refinements.

X-ray data were processed and reduced using CrysAlisPro suite of programs for crystals. Absorption correction was performed using empirical methods based upon symmetry-equivalent reflections combined with measurements at different azimuthal angles using SCALE3 ABSPACK. The crystal structures were solved and refined against all F^2 values using the SHELX and Olex2 suite of programs^{5, 6}. All the non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in calculated positions and refined using idealized geometries (riding model) and assigned fixed isotropic displacement parameters. Pivalate ligands in all the crystal structures were disordered and modelled over two positions where possible. SHELX SADI, and DFIX commands were used to restrain the C-C bonds. SIMU, ISOR and RIGU commands were used to restrain the atomic displacement parameters. Halogens were modelled as disordered over 2 to 4 position. SHELX SADI, and DFIX commands were used to restrain the halogen-halogen bonds. SIMU commands were used to restrain the atomic displacement parameters of the halogens.

CCDC 1859929-1859947 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; fax: (+44)1223-336-033; or deposit@ccdc.cam.ac.uk). Diamond and POV-Ray software packages were used for graphical images.

Table S1. Crystallographic information for **Cl₂@Cr₈**, **Br₂@Cr₈** and **I₂@Cr₈**

	Cl₂@Cr₈	Br₂@Cr₈	I₂@Cr₈
Crystal colour	Dark green	Dark green	Dark green
Crystal size (mm)	0.4 × 0.2 × 0.1	0.4 × 0.2 × 0.1	0.4 × 0.05 × 0.05
Crystal system	monoclinic	monoclinic	monoclinic
Space group, <i>Z</i>	I2/a	I2/a	I2/a
<i>a</i> (Å)	34.8424(9)	44.1693(11)	34.7598(3)
<i>b</i> (Å)	16.5213(3)	16.5140(3)	16.47840(10)
<i>c</i> (Å)	44.0605(19)	34.8521(10)	43.8863(4)
β (°)	111.359(4)	111.369(3)	111.2800(10)
<i>V</i> (Å ³)	23621.0(14)	23673.9(11)	23423.5(4)
Density (Mg.m ⁻³)	1.259	1.298	1.294
Wavelength (Å)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	CuKα (λ = 1.54184)
Temperature (K)	149.9(5)	150.02(11)	100.01(10)
μ (mm ⁻¹)	0.817	1.322	8.110
2θ range (°)	6.784 to 52.744	6.562 to 50.7	5.456 to 140.15
Reflns collected	49902	83715	82510
Independent reflns (<i>R</i> _{int})	24024 [Rint = 0.0240, Rsigma = 0.0369]	21611 [Rint = 0.0579, Rsigma = 0.0564]	22150 [Rint = 0.0418, Rsigma = 0.0424]
L.S. parameters, <i>p</i>	1331	1425	1322
No. of restraints, <i>r</i>	397	612	354
<i>R</i> 1 (<i>F</i>) ^a <i>I</i> > 2.0σ(<i>I</i>)	0.0471	0.0472	0.0487
<i>wR</i> 2(<i>F</i> ²), ^b all data	0.1324	0.1194	0.1369
<i>S</i> (<i>F</i> ²), ^c all data	1.022	1.016	1.047

^a $R1(F) = \sum(|F_o| - |F_c|)/\sum|F_o|$; [b] $wR2(F^2) = [\sum w(F_o^2 - F_c^2)^2/\sum wF_o^4]^{1/2}$; [c] $S(F^2) = [\sum w(F_o^2 - F_c^2)^2/(n + r - p)]^{1/2}$

Table S2. Crystallographic information for **Cl₂@Cr₈_VT350K_1-2**, **Br₂@Cr₈_VT350K_1-3**

	Cl ₂ @Cr ₈ _VT350K_1	Cl ₂ @Cr ₈ _VT350K_2	Br ₂ @Cr ₈ _VT350K_1	Br ₂ @Cr ₈ _VT350K_2	Br ₂ @Cr ₈ _VT350K_3
Crystal colour	Dark green	Dark green	Dark green	Dark green	Dark green
Crystal size (mm)	0.45 × 0.1 × 0.1	0.45 × 0.1 × 0.1	0.15 × 0.1 × 0.1	0.15 × 0.1 × 0.1	0.15 × 0.1 × 0.1
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic
Space group, <i>Z</i>	I2/a	I2/a	I2/a	I2/a	I2/a
<i>a</i> (Å)	34.7964(9)	34.7097(10)	34.8657(8)	34.8212(8)	34.7987(8)
<i>b</i> (Å)	16.5728(3)	16.5768(3)	16.5762(3)	16.6141(3)	16.6176(3)
<i>c</i> (Å)	44.4195(13)	44.5614(15)	44.5490(12)	44.6966(12)	44.7185(12)
β (°)	111.368(3)	111.273(4)	111.427(3)	111.247(3)	111.180(3)
<i>V</i> (Å ³)	23854.7(11)	23892.5(13)	23967.2(11)	24100.3(11)	24112.6(11)
Density (Mg.m ⁻³)	1.246	1.215	1.274	1.225	1.204
Wavelength (Å)	MoK α (λ = 0.71073)	MoK α (λ = 0.71073)	MoK α (λ = 0.71073)	MoK α (λ = 0.71073)	MoK α (λ = 0.71073)
Temperature (K)	200.0	199.14(10)	200.0	200.0	200.0
μ (mm ⁻¹)	0.808	0.774	1.241	0.918	0.766
2 θ range (°)	3.938 to 54.204	3.834 to 54.206	6.736 to 51.362	6.782 to 51.364	6.782 to 51.362
Reflns collected	147914	147474	59591	60002	60001
Independent reflns (<i>R</i> _{int})	26196 [Rint = 0.0451, Rsigma = 0.0356]	26283 [Rint = 0.0548, Rsigma = 0.0414]	22679 [Rint = 0.0345, Rsigma = 0.0524]	22815 [Rint = 0.0293, Rsigma = 0.0445]	22824 [Rint = 0.0293, Rsigma = 0.0450]
L.S. parameters, <i>p</i>	1499	1463	1539	1501	1463
No. of restraints, <i>r</i>	1465	1602	1588	1627	1620
<i>R</i> 1 (<i>F</i>) ^a <i>I</i> > 2.0 σ (<i>I</i>)	0.0586	0.0639	0.0609	0.0626	0.0692
<i>wR</i> 2(<i>F</i> ²), ^b all data	0.1495	0.1714	0.1639	0.1706	0.2005
<i>S</i> (<i>F</i> ²), ^c all data	1.024	1.027	1.024	1.018	1.014

^a $R1(F) = \sum(|F_o| - |F_c|)/\sum|F_o|$; [b] $wR2(F^2) = [\sum w(F_o^2 - F_c^2)^2/\sum wF_o^4]^{1/2}$; [c] $S(F^2) = [\sum w(F_o^2 - F_c^2)^2/(n + r - p)]^{1/2}$

Table S3. Crystallographic information for **I₂@Cr₈_VT350K_1-4**

	I₂@Cr₈_VT350K_1	I₂@Cr₈_VT350K_2	I₂@Cr₈_VT350K_3	I₂@Cr₈_VT350K_4
Crystal colour	Dark green	Dark green	Dark green	Dark green
Crystal size (mm)	0.4 × 0.1 × 0.1	0.4 × 0.1 × 0.1	0.4 × 0.1 × 0.1	0.4 × 0.1 × 0.1
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic
Space group, <i>Z</i>	I2/a	I2/a	I2/a	I2/a
<i>a</i> (Å)	34.7183(8)	44.5160(14)	34.6969(9)	34.6995(9)
<i>b</i> (Å)	16.5480(3)	16.5380(3)	16.5495(3)	16.5534(3)
<i>c</i> (Å)	44.5613(13)	34.6653(9)	44.5379(13)	44.5351(13)
β (°)	111.390(3)	111.347(3)	111.304(3)	111.281(3)
<i>V</i> (Å ³)	23837.9(11)	23769.9(12)	23826.8(11)	23836.4(11)
Density (Mg.m ⁻³)	1.282	1.274	1.261	1.255
Wavelength (Å)	MoK α (λ = 0.71073)	MoK α (λ = 0.71073)	MoK α (λ = 0.71073)	MoK α (λ = 0.71073)
Temperature (K)	200.01(10)	200.0	200.0	198.94(10)
μ (mm ⁻¹)	1.011	0.969	0.930	0.912
2 θ range (°)	3.716 to 53.464	3.72 to 53.464	3.714 to 53.466	3.714 to 53.464
Reflns collected	74413	74339	74644	74695
Independent reflns (<i>R</i> _{int})	25197 [Rint = 0.0287, Rsigma = 0.0382]	25138 [Rint = 0.0296, Rsigma = 0.0393]	25189 [Rint = 0.0285, Rsigma = 0.0365]	25199 [Rint = 0.0285, Rsigma = 0.0367]
L.S. parameters, <i>p</i>	1548	1462	1529	1529
No. of restraints, <i>r</i>	1701	1332	1600	1618
<i>R</i> 1 (<i>F</i>) ^a <i>I</i> > 2.0 σ (<i>I</i>)	0.0586	0.0599	0.0578	0.0588
<i>wR</i> 2(<i>F</i> ²), ^b all data	0.1594	0.1644	0.1655	0.1662
<i>S</i> (<i>F</i> ²), ^c all data	1.025	1.024	1.042	1.034

^a $R1(F) = \sum(|F_o| - |F_c|) / \sum |F_o|$; [b] $wR2(F^2) = [\sum w(F_o^2 - F_c^2)^2 / \sum w F_o^4]^{1/2}$; [c] $S(F^2) = [\sum w(F_o^2 - F_c^2)^2 / (n + r - p)]^{1/2}$

Table S4. Crystallographic information for **I₂@Cr₈_VT350K_5-7**

	I₂@Cr₈_VT350K_5	I₂@Cr₈_VT350K_6	I₂@Cr₈_VT350K_7
Crystal colour	Dark green	Dark green	Dark green
Crystal size (mm)	0.4 × 0.1 × 0.1	0.4 × 0.1 × 0.1	0.4 × 0.1 × 0.1
Crystal system	monoclinic	monoclinic	monoclinic
Space group, <i>Z</i>	I2/a	I2/a	I2/a
<i>a</i> (Å)	34.6926(9)	34.6932(9)	34.6879(9)
<i>b</i> (Å)	16.5516(3)	16.5547(3)	16.5552(3)
<i>c</i> (Å)	44.5170(13)	44.5153(14)	44.5048(13)
β (°)	111.263(3)	111.259(3)	111.249(3)
<i>V</i> (Å ³)	23822.3(11)	23826.9(12)	23820.0(11)
Density (Mg.m ⁻³)	1.252	1.247	1.244
Wavelength (Å)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
Temperature (K)	200.0	200.0	200.0
μ (mm ⁻¹)	0.896	0.880	0.869
2θ range (°)	3.714 to 53.466	3.714 to 53.466	3.714 to 53.466
Reflns collected	74717	74695	74708
Independent reflns (<i>R</i> _{int})	25182 [Rint = 0.0285, Rsigma = 0.0365]	25190 [Rint = 0.0283, Rsigma = 0.0367]	25181 [Rint = 0.0296, Rsigma = 0.0383]
L.S. parameters, <i>p</i>	1529	1529	1529
No. of restraints, <i>r</i>	1600	1630	1612
<i>R</i> 1 (<i>F</i>) ^a <i>I</i> > 2.0σ(<i>I</i>)	0.0582	0.0587	0.0580
<i>wR</i> 2(<i>F</i> ²), ^b all data	0.1656	0.1672	0.1654
<i>S</i> (<i>F</i> ²), ^c all data	1.032	1.038	1.037

^a $R1(F) = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$; [b] $wR2(F^2) = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma wF_o^4]^{1/2}$; [c] $S(F^2) = [\Sigma w(F_o^2 - F_c^2)^2/(n + r - p)]^{1/2}$

Table S5. Crystallographic information for **I₂@Cr₈_VT400K_1-4**

	I₂@Cr₈_VT400K_1	I₂@Cr₈_VT400K_2	I₂@Cr₈_VT400K_3	I₂@Cr₈_VT400K_4
Crystal colour	Dark green	Dark green	Dark green	Dark green
Crystal size (mm)	0.4 × 0.1 × 0.1	0.4 × 0.1 × 0.1	0.4 × 0.1 × 0.1	0.4 × 0.1 × 0.1
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic
Space group, <i>Z</i>	I2/a	I2/a	I2/a	I2/a
<i>a</i> (Å)	34.7173(10)	34.7020(10)	34.7258(10)	34.7238(10)
<i>b</i> (Å)	16.5607(5)	16.5610(5)	16.5727(5)	16.5752(5)
<i>c</i> (Å)	44.517(2)	44.493(2)	44.528(2)	44.522(2)
β (°)	111.303(5)	111.207(4)	111.190(4)	111.178(4)
<i>V</i> (Å ³)	23845.8(18)	23838.8(16)	23893.2(16)	23894.1(16)
Density (Mg.m ⁻³)	1.262	1.239	1.233	1.215
Wavelength (Å)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
Temperature (K)	200.03(10)	199.70(10)	199.73(10)	199.78(10)
μ (mm ⁻¹)	0.937	0.851	0.840	0.773
2θ range (°)	3.114 to 52.744	3.114 to 52.744	3.112 to 52.742	3.112 to 52.744
Reflns collected	67798	68594	68754	68754
Independent reflns (<i>R</i> _{int})	24321 [Rint = 0.0645, Rsigma = 0.0859]	24213 [Rint = 0.0401, Rsigma = 0.0617]	24279 [Rint = 0.0418, Rsigma = 0.0631]	24279 [Rint = 0.0419, Rsigma = 0.0632]
L.S. parameters, <i>p</i>	1555	1555	1536	1500
No. of restraints, <i>r</i>	1431	1587	1623	1728
<i>R</i> 1 (<i>F</i>) ^a <i>I</i> > 2.0σ(<i>I</i>)	0.0706	0.0661	0.0671	0.0703
<i>wR</i> 2(<i>F</i> ²), ^b all data	0.1819	0.1641	0.1653	0.1879
<i>S</i> (<i>F</i> ²), ^c all data	1.017	1.011	1.013	1.013

^a $R1(F) = \sum(|F_o| - |F_c|) / \sum |F_o|$; [b] $wR2(F^2) = [\sum w(F_o^2 - F_c^2)^2 / \sum wF_o^4]^{1/2}$; [c] $S(F^2) = [\sum w(F_o^2 - F_c^2)^2 / (n + r - p)]^{1/2}$

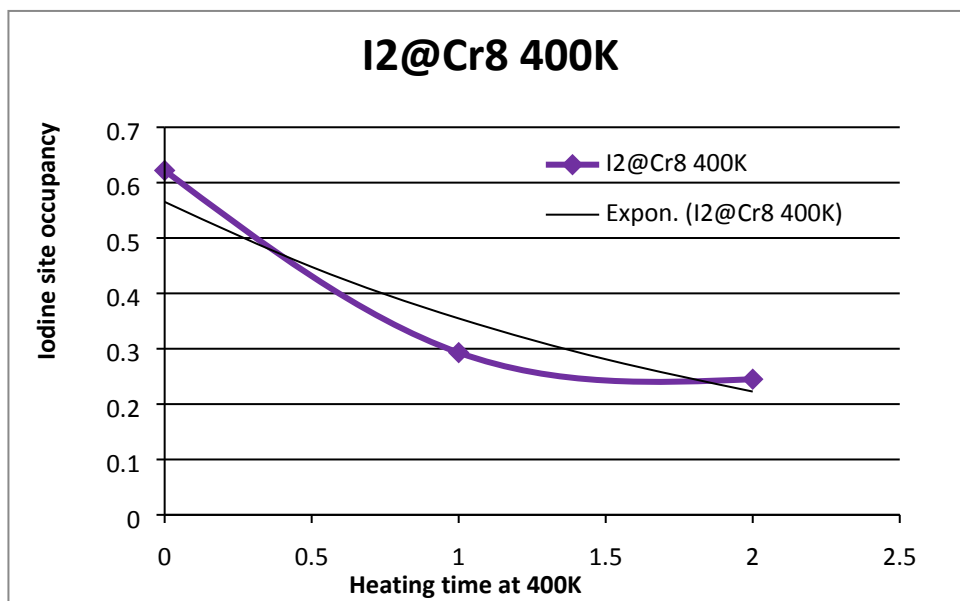


Figure S8 - Site occupancy of iodine molecules inside Cr₈ vs heating time at 400K with exponential regression.

From the exponential regression with extract the reaction rate coefficient is equal to 0.466 h⁻¹. Having two release rate coefficients at two different temperatures (350 and 400K) we can calculate an activation energy with the following equation:

$$\ln(k_1/k_2) = (1/T_2 - 1/T_1) \cdot E_a/R$$

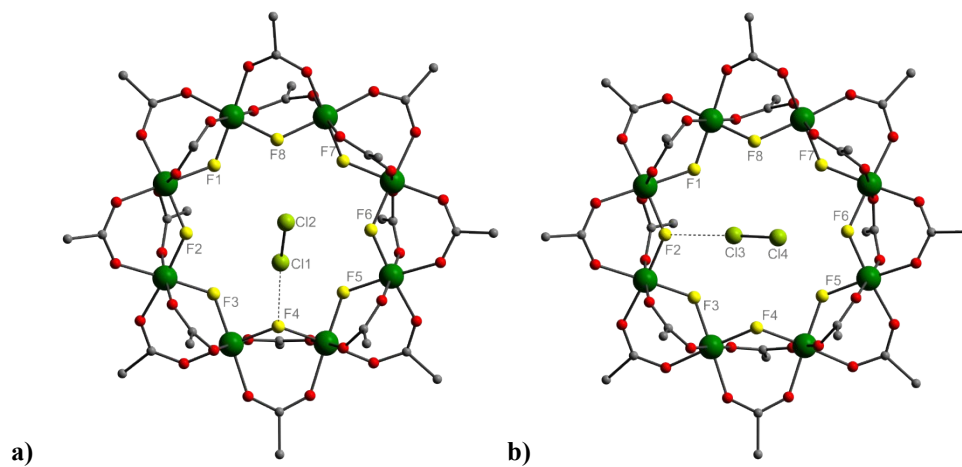


Figure S8. a) First component of the Chlorine disorder inside the cavity of **1**, with 0.419(5) occupancy and b) is the other position of the Chlorine disorder with 0.324(5) occupancy.

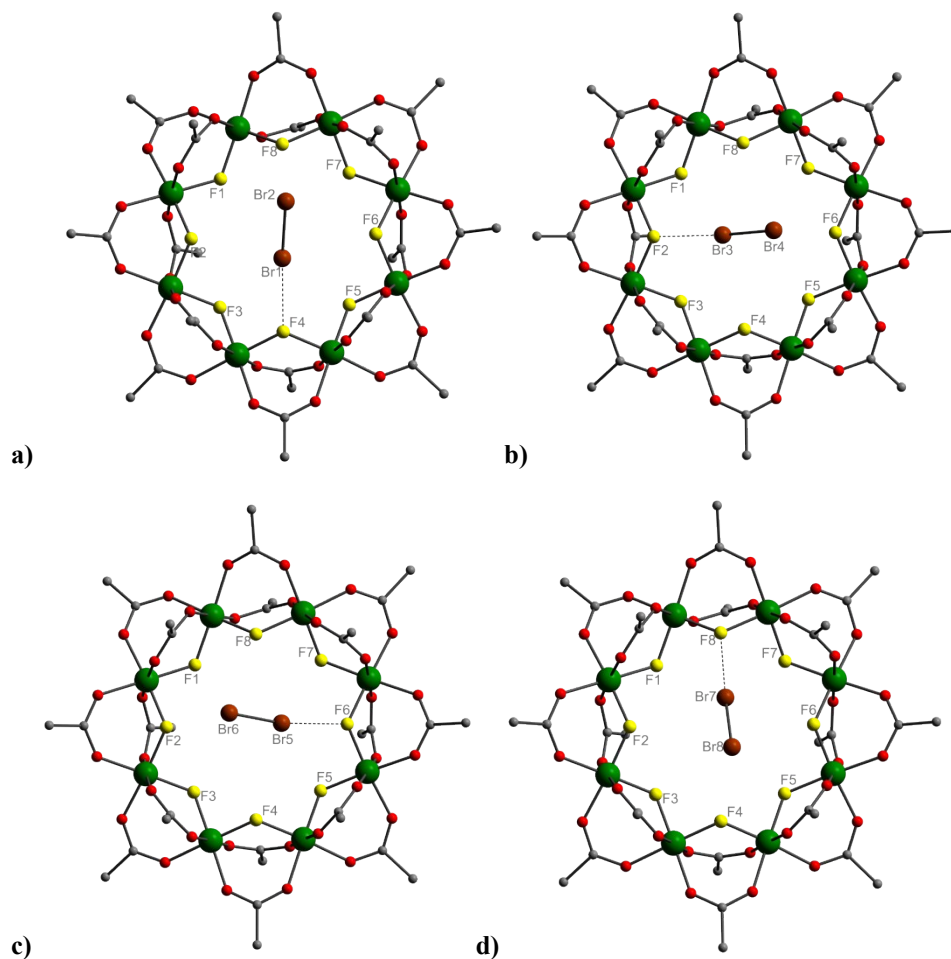


Figure S9. a) First component of the Bromine disorder inside the cavity of **Cr₈**, with 0.3901(18) occupancy, b) is the second component of the Bromine disorder with 0.2829(18) occupancy, c) is the third component of the disorder with 0.0673(18) occupancy and d) is the fourth component of the disorder with 0.0614(18) occupancy.

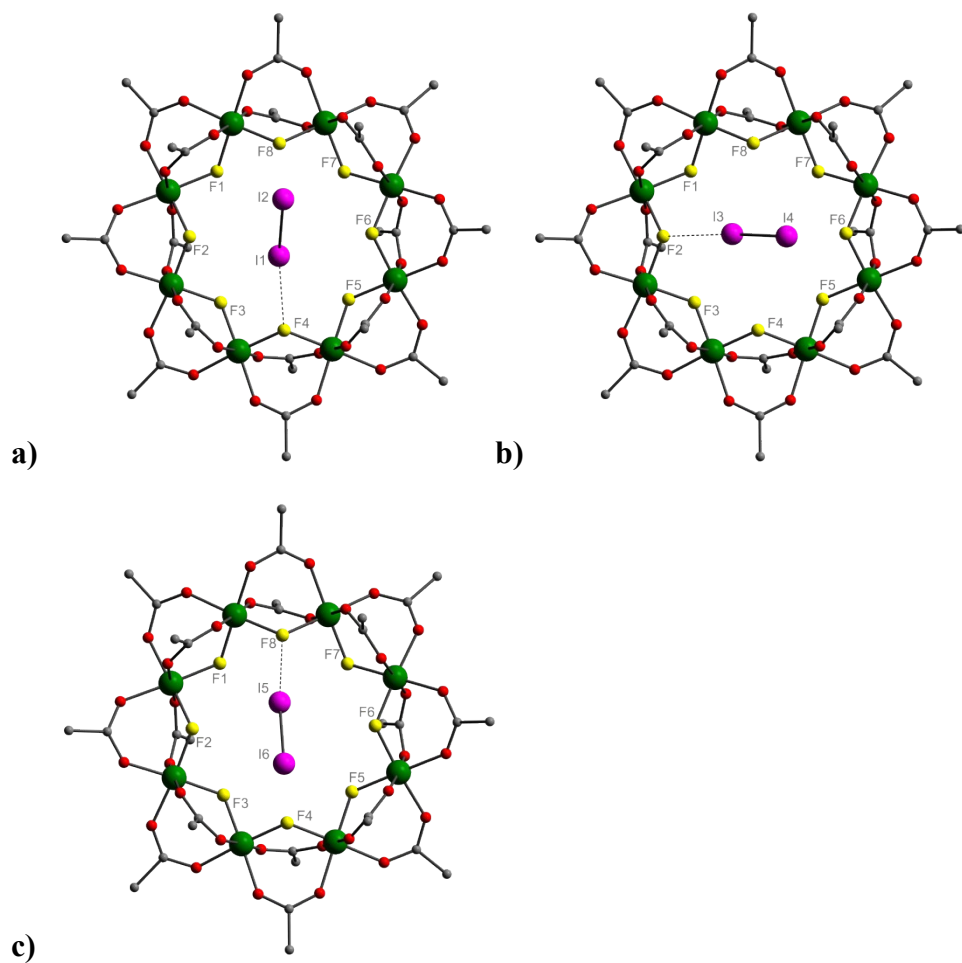


Figure S10. a) First component of the Iodine disorder inside the cavity of Cr_8 , with 0.2143(11) occupancy, b) is the second component of the Iodine disorder with 0.1245(12) occupancy and c) is the third component of the disorder with 0.0404(11) occupancy.

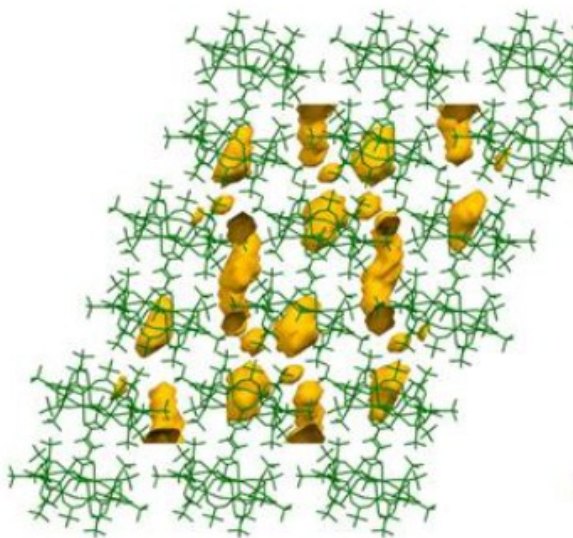


Figure S11. [010] views of crystal packing of Cr_8 . Molecules of Cr_8 are drawn in green and capped sticks. Hydrogens were omitted for clarity.

S6. References

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