Supplementary Material (ESI) for *CrystEngComm*

Site-selective supramolecular synthesis of halogen-bonded cocrystals incorporating the photoactive azo group†

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ELECTRONIC SUPPLEMENTARY INFORMATION

Experimental

General methods: Commercial HPLC-grade solvents were used without further purification. Starting materials were purchased from Sigma-Aldrich and Apollo Scientific. ^{1}H NMR spectra were recorded at ambient temperature using $CDCl_3$ as solvent on a Bruker AV500 spectrometer. ^{19}F NMR spectra were recorded on Bruker AC250 spectrometer, $CDCl_3$ was used as solvent and $CFCl_3$ or bis(2,2,2-trifluoroethyl) were used as internal standard. All chemical shift values are given in ppm. IR spectra were obtained using a Perkin–Elmer 2000 FTIR spectrometer equipment with U-ATR device. Absorptions are specified in wavenumbers, which have been rounded to the nearest 1 cm^{-1} by automatic assignment. Selected IR data of the starting modules are reported to show the changes that occur upon the formation of cocrystals **3a-b**. Melting points were determined with DSC analyses using Mettler Toledo DSC 823e.

General procedure: formation of cocrystal 3a and **3b:** Cocrystals **3a** and **3b** were obtained by dissolving one, five or ten, equivalents of diiodoperfluoroalkane **1a,b** and one equivalent of *trans*-4,4'-azobis(pyridine) **2** in methanol at room temperature in a clear borosilicate glass vial. The methanol was allowed to diffuse slowly (two day) in a closed cylindrical wide-mouth bottle containing paraffine oil at room temperature.

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† Electronic Supplementary Information (ESI) available: General procedures, ^{1}H and ^{19}F NMR, IR spectra, and crystal data for **3a,b**.
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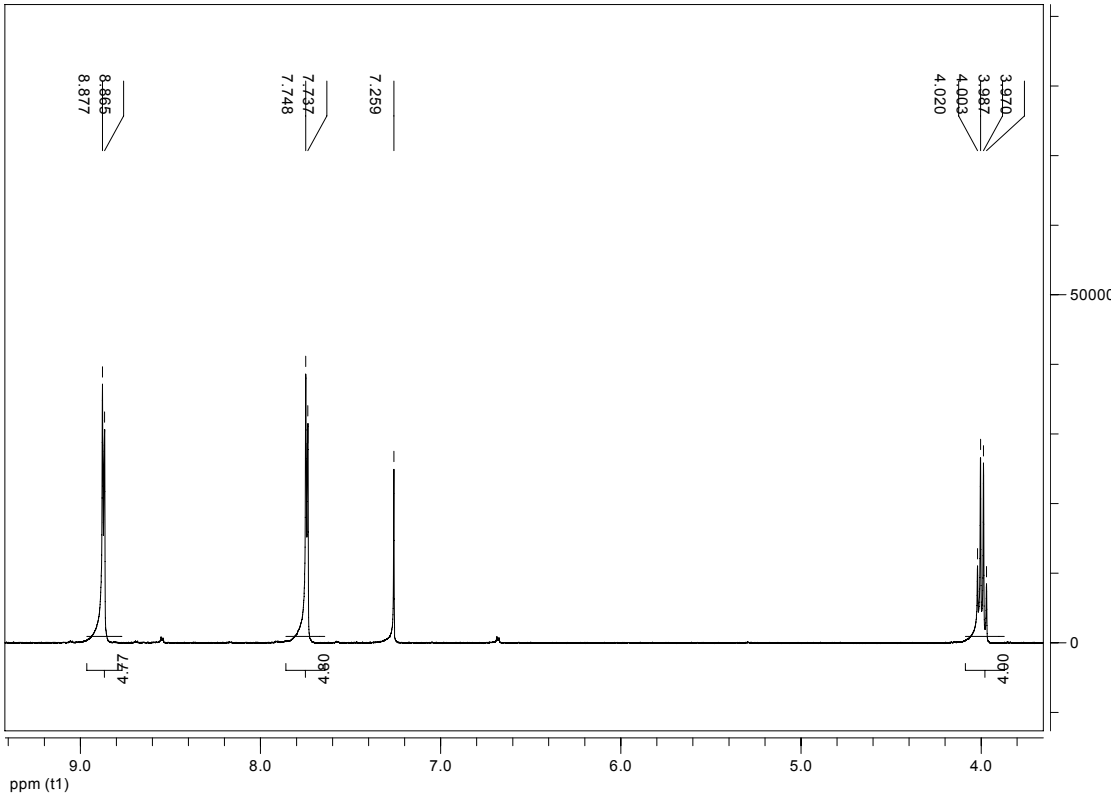
Cocrystal 3a: Perfluoro-1,6-diiodohexane (**1a**) and 4,4'-azobis(pyridine) (**2**): Red-brown solid; m.p.= 125 °C (DSC analysis); IR (ν̃ selected bands): pure perfluoro-1,6-diiodohexane **1a**: 1121, 1087 cm^{-1}; pure 4,4'-azobis(pyridine) **2**: 3091, 3039, 1586, 1412, 989 cm^{-1}; co-crystal **3a**: 3107, 3043, 1588, 1412, 1117, 1077, 998 cm^{-1}; ^{19}F-NMR pure perfluoro-1,6-diiodohexane **1a**: $\delta_{(ICF2CF2CF2)2}$= -60.24, $\delta_{(ICF2CF2CF2)2}$= -114.27, $\delta_{(ICF2CF2CF2)2}$= -122.13; cocrystal **3a**: $\Delta\delta_F=\delta_{pure\mathbf{1a}} - \delta_{\mathbf{3a}}$ (0.05 M), $\Delta\delta_{(ICF2CF2CF2)2}$= 0.18, $\Delta\delta_{(ICF2CF2CF2)2}$= 0.01, $\Delta\delta_{(ICF2CF2CF2)2}$= 0.01; $\Delta\delta_F=\delta_{pure\mathbf{1a}} - \delta_{\mathbf{3a}}$ (0.03 M), $\Delta\delta_{(ICF2CF2CF2)2}$= 0.11, $\Delta\delta_{(ICF2CF2CF2)2}$= 0.01, $\Delta\delta_{(ICF2CF2CF2)2}$= 0.00.

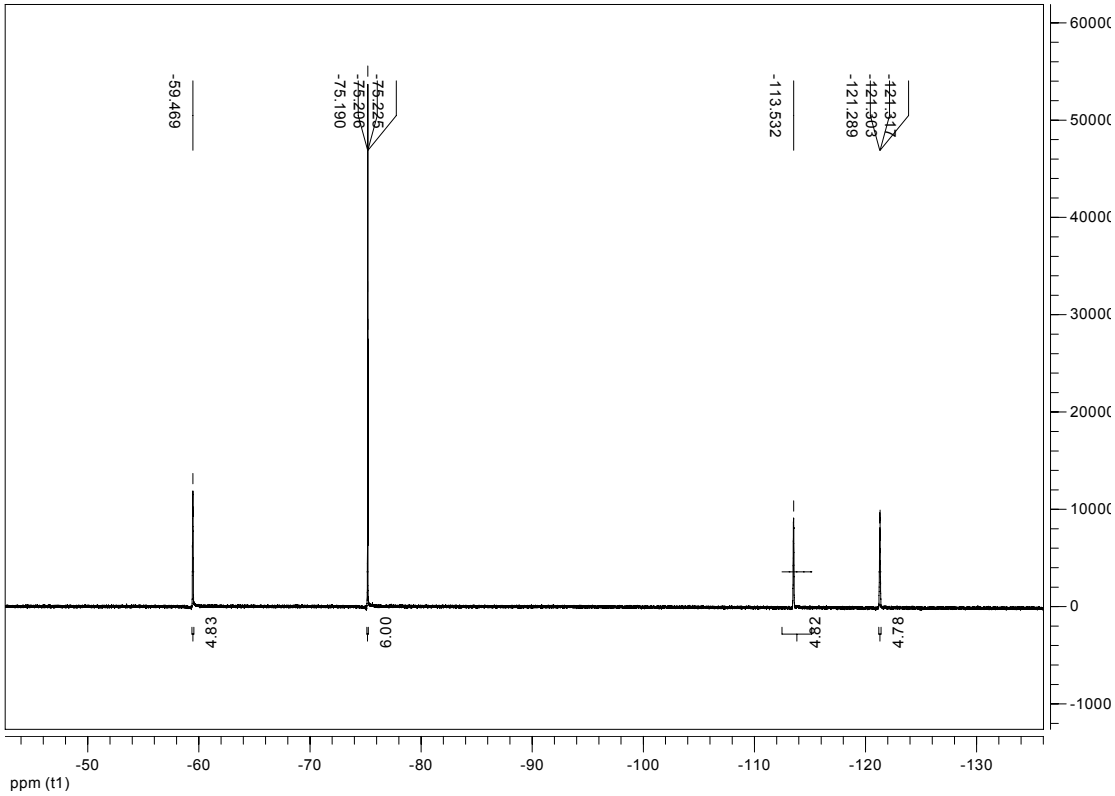
Cocrystal 3b: Perfluoro-1,8-diiodooctane (**1b**) and 4,4'-azobis(pyridine) (**2**): Red-brown solid; m.p.= 130 °C (DSC analysis); IR (ν̃ selected bands): pure perfluoro-1,8-diiodoocatne **1b**: 1147, 1055 cm^{-1}; cocrystal **3b**: 3107, 3042, 1588, 1412, 1138, 1054, 997 cm^{-1}; ^{19}F-NMR pure perfluoro-1,8-diiodoocatane **1b**: $\delta_{(ICF2CF2CF2CF2)2}$= -60.33, $\delta_{(ICF2CF2CF2CF2)2}$= -114.28, $\delta_{(ICF2CF2CF2CF2)2}$= -122.10 $\delta_{(ICF2CF2CF2CF2)2}$= -122.91; cocrystal **3b**: $\Delta\delta_F=\delta_{pure\mathbf{1b}} - \delta_{\mathbf{3b}}$ (0.05 M), $\Delta\delta_{(ICF2CF2CF2CF2)2}$= 0.18, $\Delta\delta_{(ICF2CF2CF2CF2)2}$= 0.04, $\Delta\delta_{(ICF2CF2CF2\ CF2)2}$= 0.02, $\Delta\delta_{(ICF2CF2CF2CF2)2}$= 0.01; $\Delta\delta_F=\delta_{pure\mathbf{1b}} - \delta_{\mathbf{3b}}$ (0.03 M), $\Delta\delta_{(ICF2CF2CF2CF2)2}$= 0.11, $\Delta\delta_{(ICF2CF2CF2CF2)2}$= 0.02, $\Delta\delta_{(ICF2CF2CF2\ CF2)2}$= 0.01, $\Delta\delta_{(ICF2CF2CF2CF2)2}$= 0.00.

NMR Experiments: To establish the **1** : **2** ratio in co-crystals **3a,b**, their ^{1}H and ^{19}F NMR spectra were registered in the presence of 2,2,2-trifluoroethyl ether as an internal standard. On calibrating integration parameters so that in the ^{1}H NMR spectrum the CH_2O quartet of 2,2,2-trifluoroethyl ether was corresponding to four and in the ^{19}F NMR spectrum the CF_3 triplet of 2,2,2-trifluoroethyl ether was corresponding to six, the ratio of the NCH doublet area (deriving from **2**) and the CF_2I triplet area (deriving from **1**) is one thus revealing that the **1** : **2** ratio in **3a,b** is one. This **1** : **2** ratio was observed for all solids obtained from solutions where the **1** : **2** ratio was varied from 1 : 1 to 10 : 1.

^{1}H NMR (500 MHz, $CDCl_3$ + $(CF_3CH_2)_2O$) cocrystal **3a**

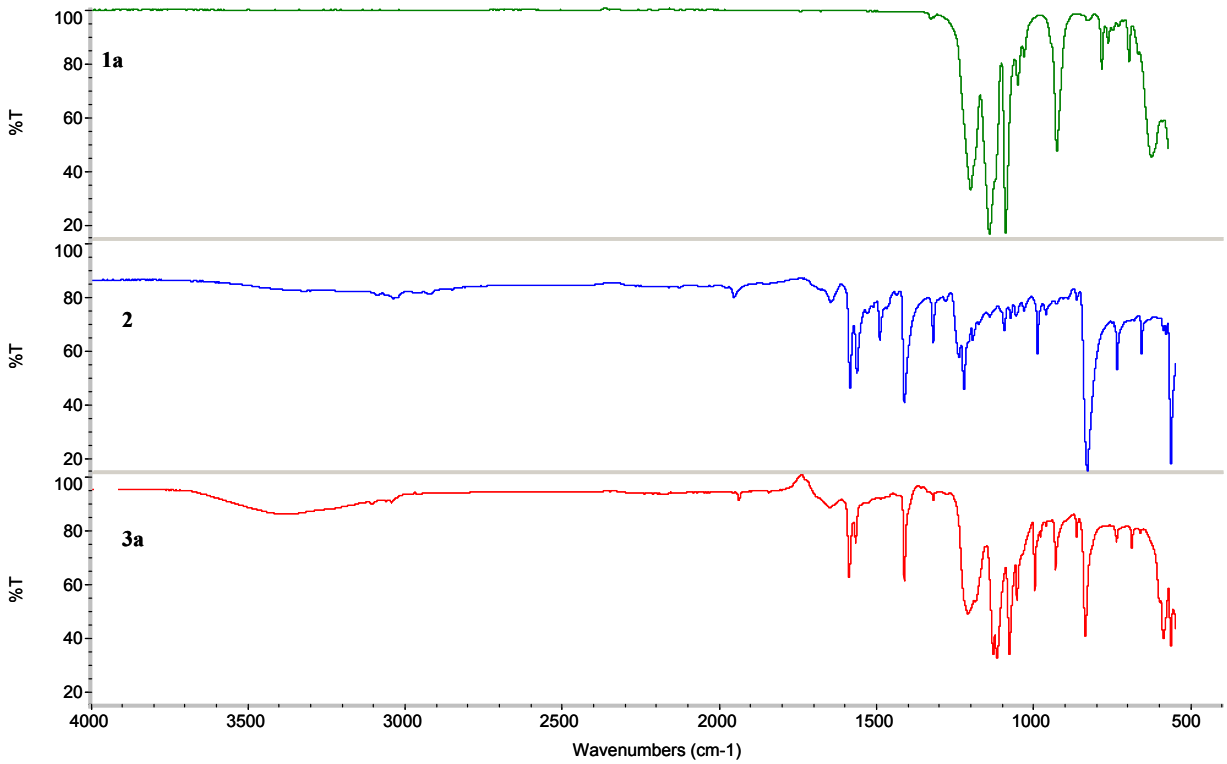


^{19}F NMR (480 MHz, $CDCl_3$ + $(CF_3CH_2)_2O$) cocrystal **3a**

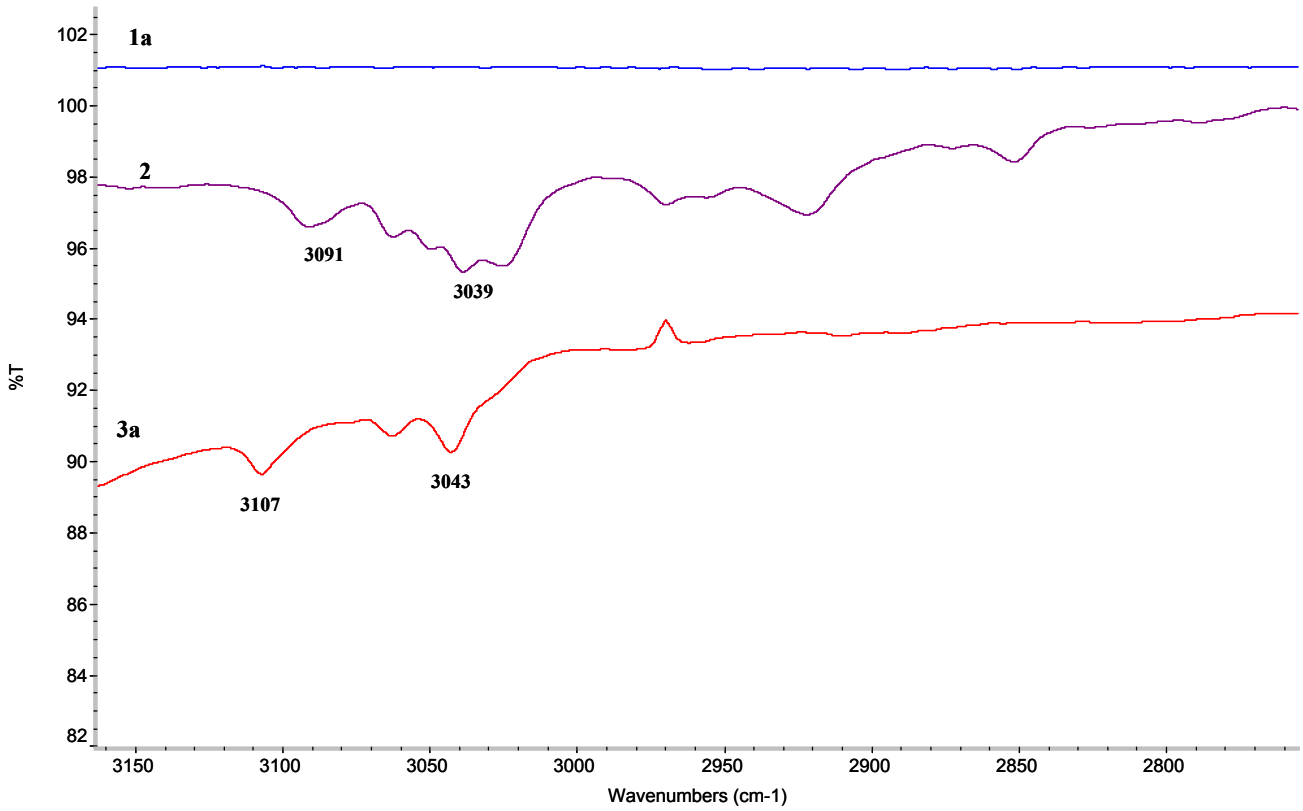


FT-IR spectra.

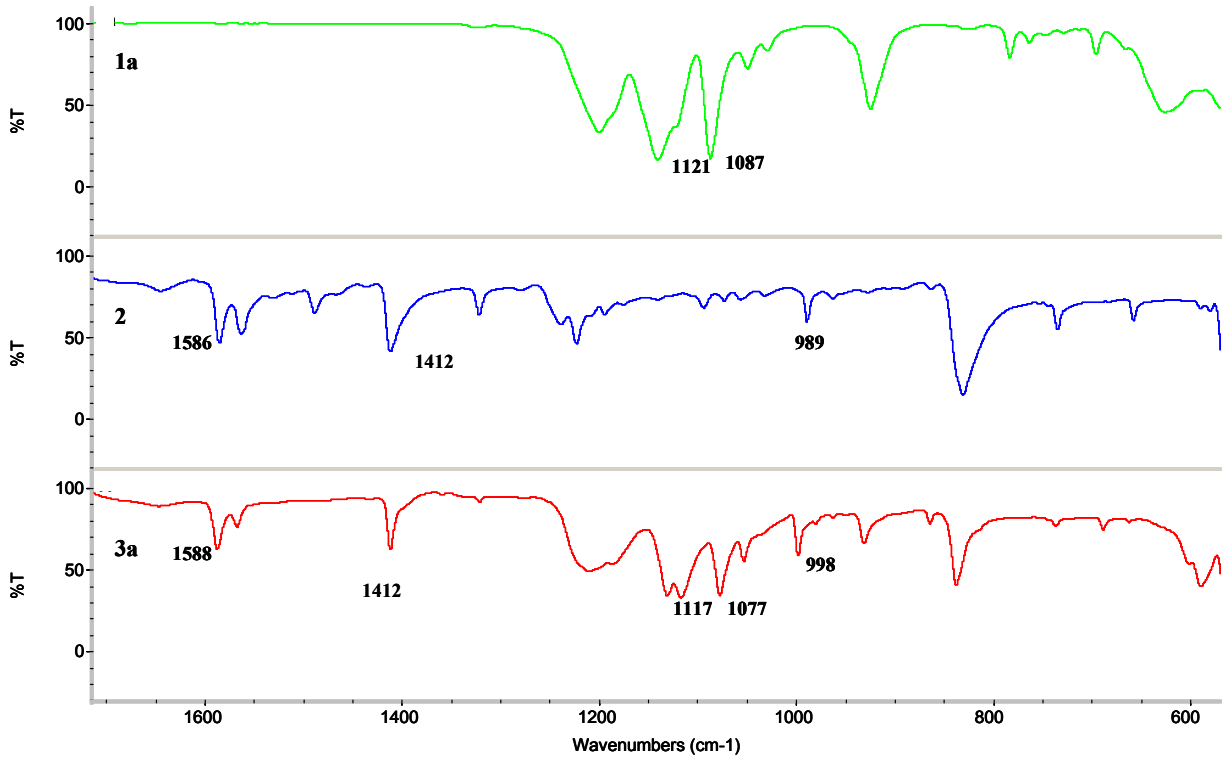
Cocrystal 3a (4000-500 cm^{-1})



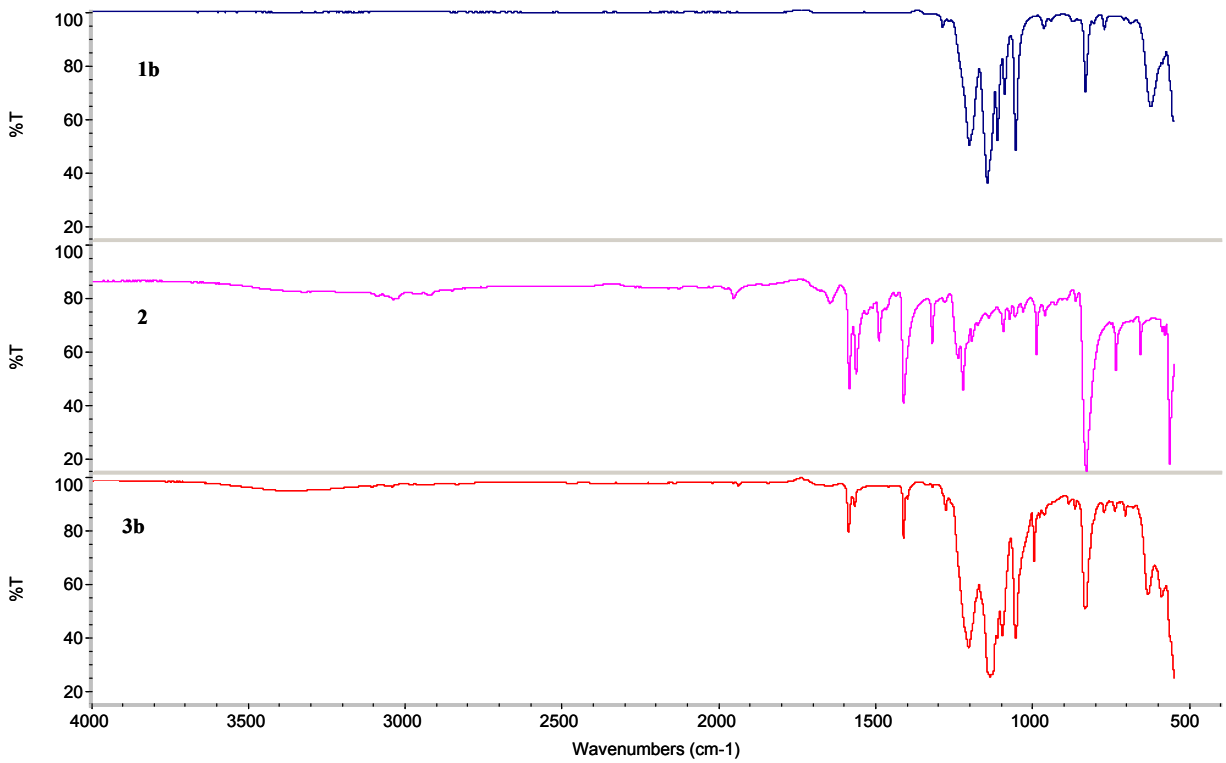
Cocrystal 3a (3200-2700 cm^{-1})



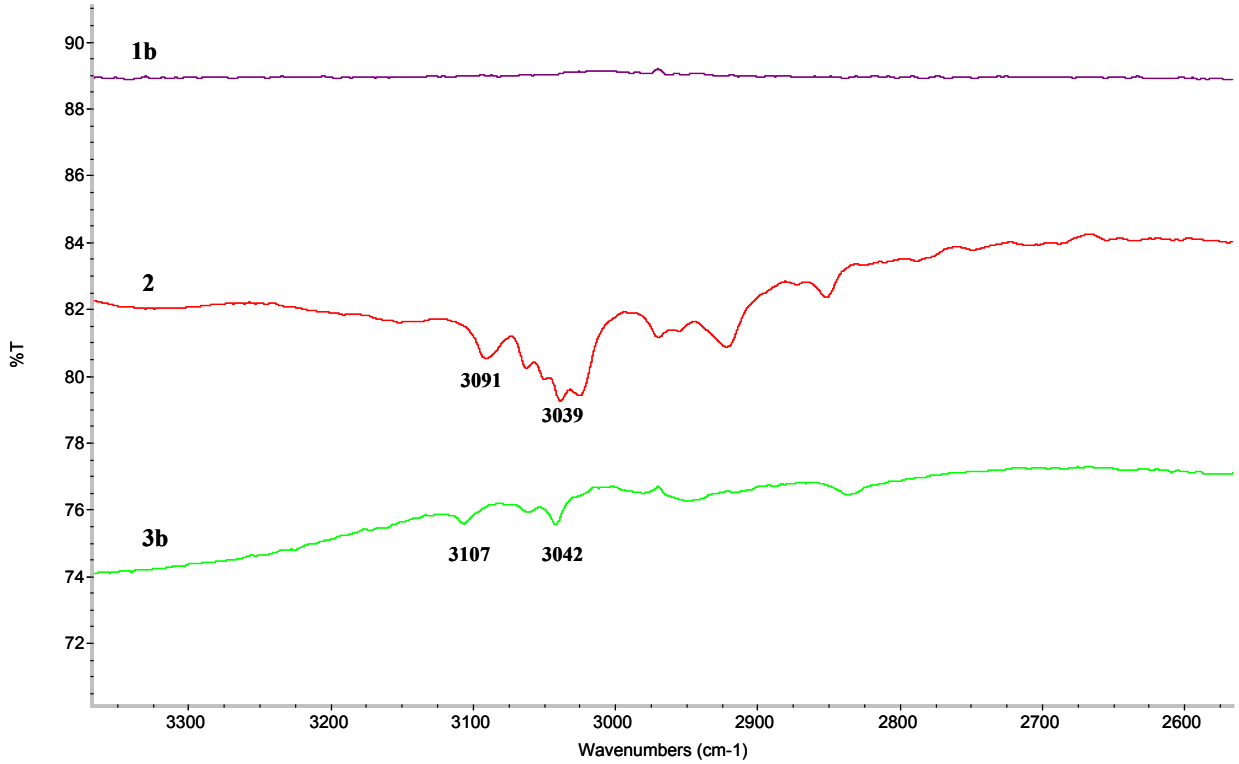
Cocrystal 3a (1700-550 cm^{-1})



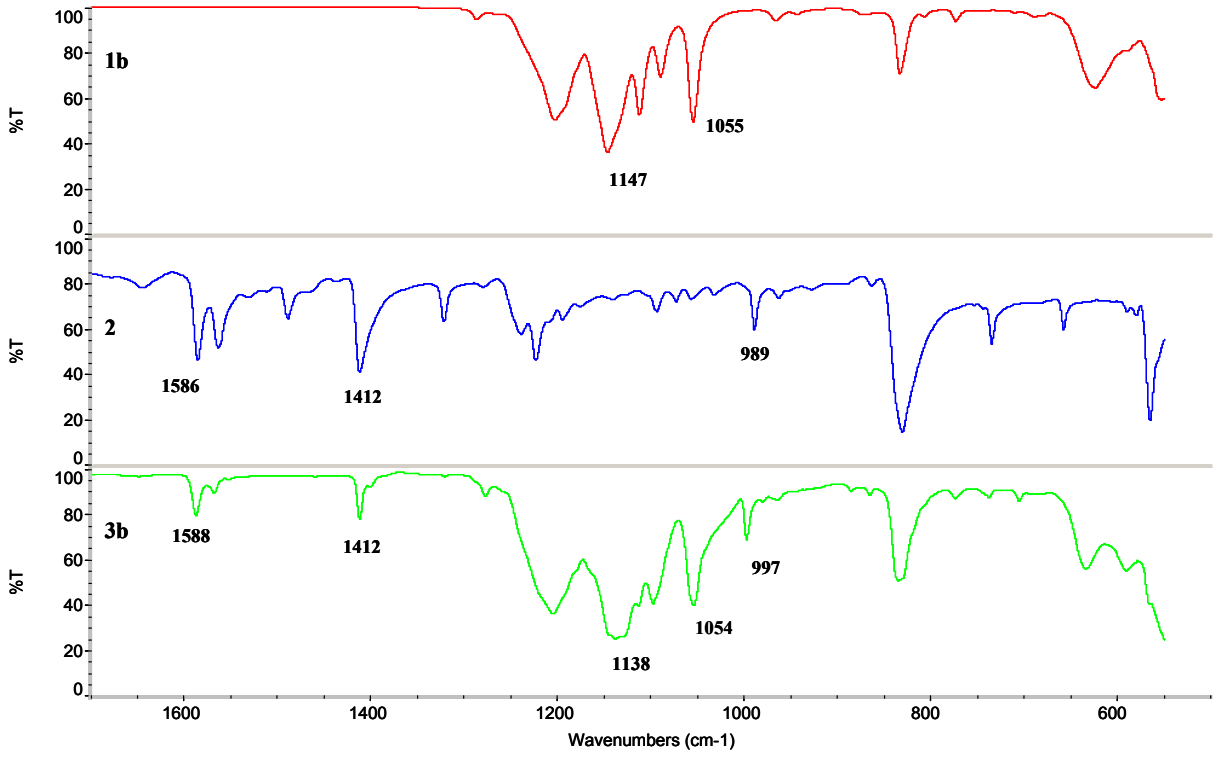
Cocrystal 3b (4000-500 cm^{-1})



Cocrystal 3b (3300-2500 cm^{-1})



Cocrystal 3b (1700-550 cm^{-1})



Crystal data and structure refinement for 3a.

Chemical formula (moiety)	$C_6F_{12}I_2 \cdot C_{10}H_8N_4$	
Chemical formula (total)	$C_{16}H_8F_{12}I_2N_4$	
Formula weight	738.06	
Temperature	153(2) K	
Radiation, wavelength	MoKα, 0.71073 Å	
Crystal system, space group	triclinic, $P\bar{1}$	
Unit cell parameters	a = 5.2392(5)Å	α = 94.526(8)°
	b = 8.8344(9) Å	β = 95.701(7)°
	c = 11.5520(13) Å	γ = 91.302(8)°
Cell volume	530.13(10) Å^3	
Z	1	
Calculated density	2.312 g/cm^3	
Absorption coefficient μ	3.083 mm^{-1}	
F(000)	346	
Crystal colour and size	red, 0.42 × 0.21 × 0.20 mm^3	
Reflections for cell refinement	9860 (θ range 2.3 to 29.9°)	
Data collection method	Bruker APEX 2000 CCD diffractometer	
	ϕ and ω scans	
θ data collection	< 30.0°	
Index ranges	h −7 to 7, k −12 to 12, l −16 to 16	
Completeness to θ = 30.0°	99.5 %	
Reflections collected	12026	
Independent reflections	3089 (R_{int} = 0.0239)	
Reflections with $F^2>2\sigma$	2970	
Absorption correction	multi-scan	
Min. and max. transmission	0.4062 and 0.5488	
Structure solution	direct methods	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3089 / 0 / 170	
Final R indices [$F^2>2\sigma$]	R1 = 0.0315, wR2 = 0.0807	
R indices (all data)	R1 = 0.0325, wR2 = 0.0813	
Goodness-of-fit on F^2	1.121	
Largest and mean shift/s.u.	0.001 and 0.000	
Largest diff. peak and hole	1.76 and −2.78 e Å^{-3}	

Crystal data and structure refinement for 3b.

Chemical formula (moiety)	$C_{10}H_8N_4 \cdot C_8F_{16}I_2$	
Chemical formula (total)	$C_{18}H_8F_{16}I_2N_4$	
Formula weight	838.08	
Temperature	153(2) K	
Radiation, wavelength	MoKα, 0.71073 Å	
Crystal system, space group	triclinic, $P\bar{1}$	
Unit cell parameters	a = 5.2482(7) Å	α = 84.316(7)°
	b = 8.6925(14) Å	β = 86.245(7)°
	c = 13.289(2) Å	γ = 88.241(8)°
Cell volume	601.79(16) Å^3	
Z	1	
Calculated density	2.313 g/cm^3	
Absorption coefficient μ	2.754 mm^{-1}	
F(000)	394	
Crystal colour and size	red, 0.36 × 0.10 × 0.08 mm^3	
Reflections for cell refinement	6523 (θ range 2.4 to 29.4°)	
Data collection method	Bruker APEX 2000 CCD diffractometer	
	ϕ and ω scans	
θ data collection	< 30.0°	
Index ranges	h –7 to 7, k –12 to 12, l –18 to 18	
Completeness to θ = 30.0°	99.2 %	
Reflections collected	12848	
Independent reflections	3491 (R_{int} = 0.0228)	
Reflections with $F^2>2\sigma$	3219	
Absorption correction	semi-empirical from equivalents	
Min. and max. transmission	0.6761 and 0.8187	
Structure solution	direct methods	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3491 / 0 / 197	
Final R indices [$F^2>2\sigma$]	R1 = 0.0249, wR2 = 0.0628	
R indices (all data)	R1 = 0.0278, wR2 = 0.0642	
Goodness-of-fit on F^2	1.067	
Largest and mean shift/s.u.	0.001 and 0.000	
Largest diff. peak and hole	1.20 and –0.92 e Å^{-3}	