Mutual induced coordination in halogen-bonded anionic assemblies with (6.3) cation-templated topologies

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Electronic Supplementary Information

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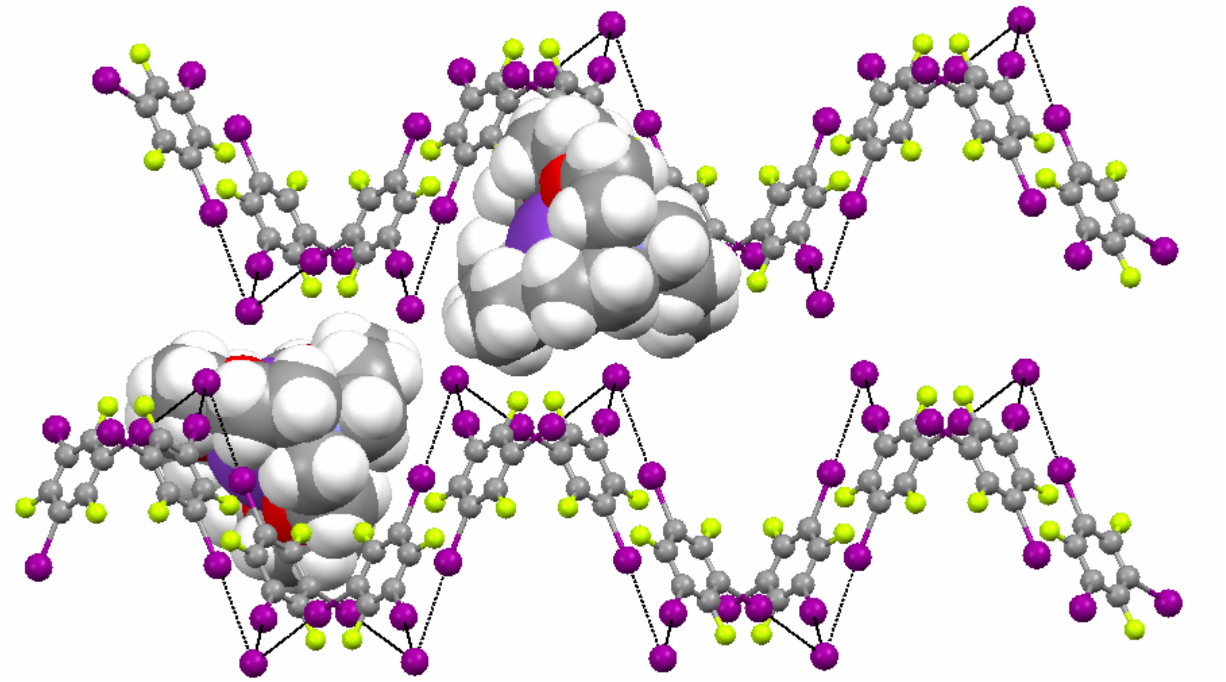
Fig. S1g Overall packing of heteromeric crystal **15**. The adopted view evidences the layers and their corrugation. Anionic networks are in ball-and-stick style while cations are in spacefill style. Colours are as follows: C, grey; I, purple; F, yellow. Halogen bonds as dotted black lines.



SYNTHESIS OF COMPOUND 1 AND COMPLEXES 9-15

General. IR spectra were recorded with a Nicolet Nexus FT-IR spectrophotometer equipped with UATR. Melting points were established with a Reichert instrument. Differential scanning calorimetry (DSC) analysis was performed on a Linkam DSC 600 instrument with a heating rate of 10°C/min. Commercially available chemicals were used without further purification. ^{19}F NMR spectra were recorded on a Bruker ADV 500 spectrometer at 25°C, $CDCl_3$ was used as solvent, $CFCl_3$ were used as internal standards.

1,3,5-triiodo-2,4,6-trifluorobenzene 1[1]

KI (3.57 g, 21.78 mmol) was added slowly to a suspension of periodic acid (1.65 g, 7.25 mmol) in concentrated H_2SO_4 (10 mL) at 0°C. Then, the dark mixture was stirred and cooled with an ice bath, while 1,3,5-trifluorobenzene (0.5 mL, 4.84 mmol) was added over 15 min. The mixture was heated to 70 °C for 4 h. After cooling to room temperature, the solution was poured on ice and extracted with diethyl ether. The organic phase was washed with $Na_2S_2O_3$ sat. and water and dried over Na_2SO_4. After evaporation of the solvent, the compound **1** was recovered as a pure white powder in 80 % yield.

^{19}F NMR ($CDCl_3$, 235MHz) δ 69.9 ppm; m.p. = 158-159°C; IR ν_{max} (cm^{-1}) = 1561, 1401, 1325, 1048, 704, 652.

Typical procedure for the formation of complexes 9-15

Equimolar amounts of organic salt and compound **1** were dissolved in CH_2Cl_2-CH_3CN for **9**, in MeOH for complexes **10**, **11, 14** and in MeOH-CH_2Cl_2 1:1 for **12, 13, 15**. Products **9-15** were recovered as colourless crystals after the slow evaporation of the solvent at room temperature.

Co-crystal 9: trimethylsulfonium iodide 2-1:

m.p. = 200°C; IR ($Me_3S^+I^-$) ν_{max} (cm^{-1}) = 2991, 2977, 1428, 1417, 1060, 1035, 946, 935; IR (**9**) ν_{max} (cm^{-1}) = 2998, 2912, 1563, 1431, 1421, 1398, 1392, 1324, 1317, 1034, 706.

Co-crystal 10: tetraethylammonium iodide 3-1:

m.p. = 258°C; IR ($Et_4N^+I^-$) ν_{max} (cm^{-1}) = 2999, 2978, 1461, 1446, 1411, 1379, 1315, 1183, 1081, 1025, 1003, 795; IR (**10**) ν_{max} (cm^{-1}) = 3003, 2974, 1564, 1456, 1393, 1330, 1309, 1181, 1036, 1001, 790, 708.

Co-crystal 11: tetrapropylammonium iodide 4-1:

m.p. = 229°C; IR ($Pr_4N^+I^-$) ν_{max} (cm^{-1}) = 2966, 2935, 2875, 1472, 1456, 1437, 1394, 1039, 984, 970, 751 cm^{-1}; IR (**11**) ν_{max} (cm^{-1}) = 2966, 2929, 2877, 1560, 1480, 1457, 1391, 1329, 1035, 967, 758, 740, 708.

Co-crystal 12: tetrabutylammonium iodide 5-1:

m.p. = 148°C; IR ($Bu_4N^+I^-$) ν_{max} (cm^{-1}) = 2987, 2956, 2872, 1472, 1396, 1109, 1067, 1031, 922, 896, 880, 736 cm^{-1}; IR (**12**) ν_{max} (cm^{-1}) = 2959, 2927, 2873, 1559, 1465, 1391, 1038, 879, 751.

Co-crystal 13: tetraethyphosphonium iodide 6-1:

m.p. = 249°C; IR ($Et_4P^+I^-$) ν_{max} (cm^{-1}) = 2979, 2929, 2895, 1469, 1417, 1263, 1044, 1002, 785, 775 cm^{-1}; IR (**13**) ν_{max} (cm^{-1}) = 2975, 2937, 2906, 1562, 1451, 1409, 1392, 1330, 1035, 776, 708.

Co-crystal 14: tetraphenylphosphonium iodide 7-1:

m.p. = 176-178°C; IR ($Ph_4P^+I^-$) ν_{max} (cm^{-1}) = 3150, 3134, 1585, 1574, 1378, 1337, 1027, 998 cm^{-1}; IR (**14**) ν_{max} (cm^{-1}) = 3164, 3062, 1579, 1480, 1433, 1235, 1105, 995, 746, 719, 685.

Co-crystal 15: K.2.2.2. KI 8-1:

m.p. = 242°C; IR (K.2.2.2. KI) ν_{max} (cm^{-1}) = 3432, 2964, 2862, 2816, 1360, 1099, 935 cm^{-1}; IR (**15**) ν_{max} (cm^{-1}) = 2963, 2886, 2811, 1560, 1390, 1354, 1296, 1258, 1098, 1081, 1036, 946, 932.

Typical procedure for the formation of complexes 16-18

Organic salts and compound **1** were dissolved in MeOH in the following ratios **1**/$Et_4N^+I^-$/$Et_4P^+I^-$: (1:1:1) for **16**, (1:0.7:1.4) for **17** and (1:1.4:0.7) for **18**. The X-ray analysis of one single crystal was realised on the first obtained crystalline materials.

Co-crystal 16: 1/$Et_4N^+I^-$/$Et_4P^+I^-$:

m.p. = 252°C; ratio of compounds: **1**/$Et_4N^+I^-$/$Et_4P^+I^-$ (1:0.42:0.58)

Co-crystal 17: 1/$Et_4N^+I^-$/$Et_4P^+I^-$ (1:1.4:0.7):

m.p. = 252°C; ratio of compounds: **1**/$Et_4N^+I^-$/$Et_4P^+I^-$ (1:0.64:0.36)

Co-crystal 18: 1/$Et_4N^+I^-$/$Et_4P^+I^-$ (1:0.7:1.4):

m.p. = 250°C; ratio of compounds: **1**/$Et_4N^+I^-$/$Et_4P^+I^-$ (1:0.27:0.73)

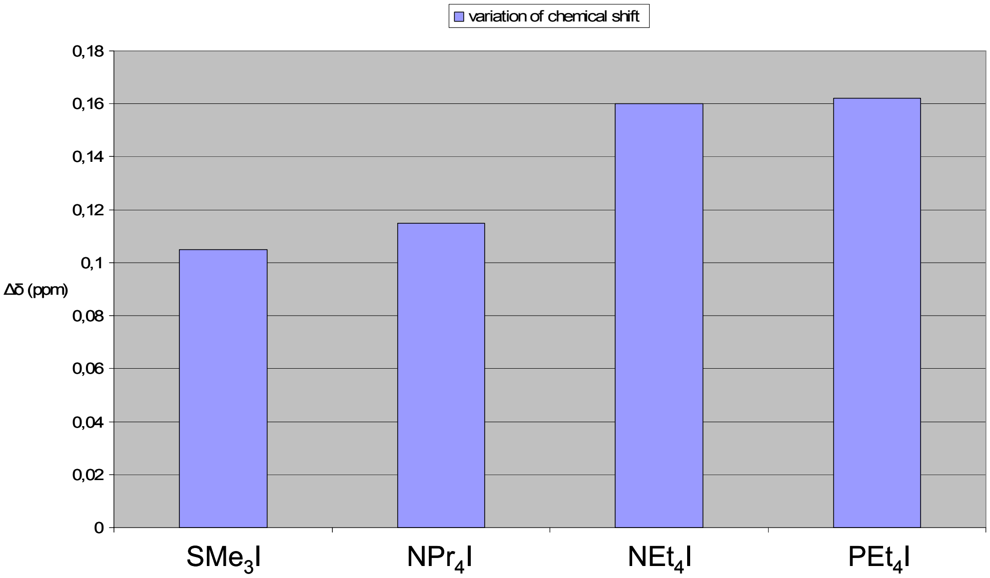
Determination of the ratio of triiodotrifluorobenzene 1 and onium salts 2-4, 6 in complexes 9-11, 13:

The ratio of species was determined by ^{1}H and ^{19}F NMR in the presence of 2,2,2-trifluoroethyl ether (($CF_3CH_2)_2O$) as internal standard. The ratio between the standard and the onium iodide is monitored in ^{1}H NMR spectra through relative integrations of the quartet at 4.00 ppm of the methylene of the standard and the CH_3 end groups of the onium salt. Then, in the ^{19}F NMR spectra, the peak of perfluoroarene **1** has been integrated with respect to the CF_3 group of the standard at -81.3 ppm. This gives the calibrated ratio between the hydrogenated and fluorinated partners, which has been revealed to be 1:1 in all the examined co-crystals.

Determination of the variation of chemical shift in the ^{19}F NMR spectrum of triiodotrifluorobenzene 1 upon complexation by onium salts 2-4, 6, with respect to the pure 1:

The variation of the chemical shift of perfluoroarene **1** upon addition of onium salts **2-4, 6** was determined with respect to the pure form. Experiments were monitored in CD_3OD at a concentration of 5 mM with a ratio triiodotrifluorobenzene **1**/ onium salt (1:10). The variation of chemical shift was calculated as follows, $CFCl_3$ was used as calibration standard:

$$\Delta\delta = \delta_{\text{pure C6F3I3}} - \delta_{\text{complex}}$$



Single crystal X Ray analyses: Data were collected with a Bruker *APEX* CCD area detector diffractometer, equipped with a Bruker *KRIOFLEX* low temperature device, using Mo*K*α radiation (λ = 0.71069 Å), graphite monochromator, ω and φ scans; data collection and data reduction were performed by *SMART* and *SAINT*, absorption correction, based on multi-scan procedure, by *SADABS*.[2] The data of **15** and of tetraethylposhonium and tetraethylammonium solid solutions **16**, **17**, **18** were collected at room temperature; **9**, **11-13** data were collected at 123 K, those of **10** and **14** were measured at 173 and 153 K, respectively, because of crystal breakage or phase transition at lower temperature;. The structures were solved by *SIR*2002,[3] and refined on all independent reflections by full-matrix least-squares based on F_o^2 by using by *SHELX*-97.[4] For all the structures, H atoms were riding in calculated positions; only one restraint needed for the disordered dichloromethane in **12**. P and N disordered atoms of **16**, **17**, **18** solid solutions were refined constraining their coordinates and ADPs to the same value; in spite quite large difference between P-C and N-C bond lengths, no attempts was made to split carbon atoms of tetraethylposhonium/ammonium cations; unusual bond distances and ADPs anomalies of the cations are justified by this bias. Further crystallographic details of the structures reported in this paper, not reported in Table 1, have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication CCDC-665593 (**9**), CCDC-665594 (**10**), CCDC-665596 (**11**), CCDC-665597 (**12**), CCDC-665595 (**13**), CCDC-665598 (**14**), CCDC-665599 (**15**), CCDC-665600 (**16**), CCDC-665601 (**17**), CCDC-665602 (**18**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 2EZ, UK [fax: (++44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk].

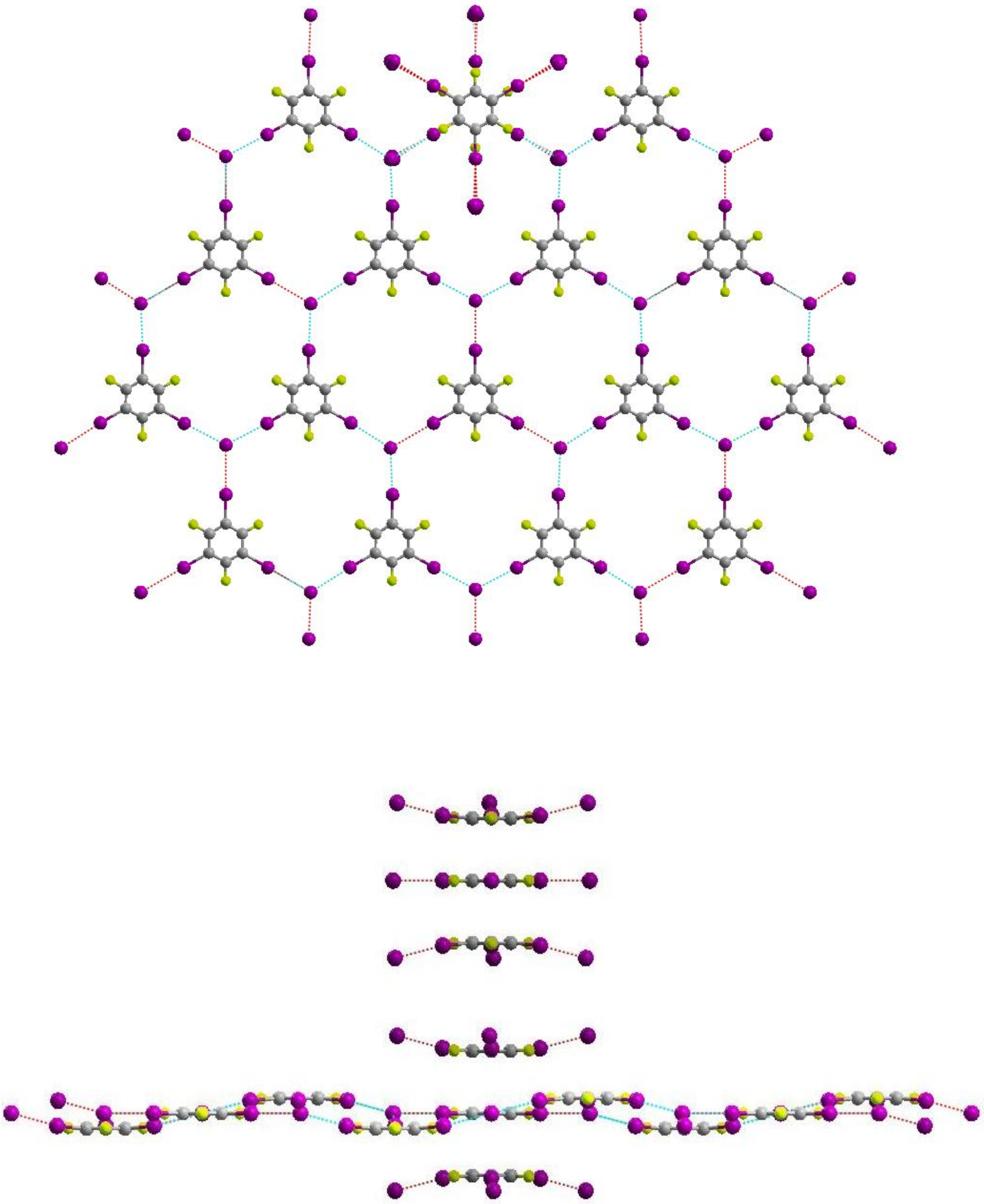


Figure S1. Ball-and-stick views of a mono-layer and of a column of the supramolecular anion $(C_6F_3I_3\cdot I^-)_n$, in tetraethylphosphonium iodide/$C_6F_3I_3$ adduct **13**; projection along 001 (top); projection along 110 (bottom); colour codes: C, grey, F, yellow-green, I, purple; blue or purple dashed lines represent the short I···I$^-$ interactions. The column is made by triplets (sandwich like) of 1,3,5-trifluoro-2,4,6-triiodobenzene rotated of 60° from each other. The barycentres' distance in this molecule is 3.749 Å; if the barycentres are calculated only on the π-π interacting carbon atoms, the distance is reduced to 3.699 Å. Quite remarkably, two contiguous sandwiches are separated by 6.407 Å, so that an unfilled cavity 124 Å^3 is formed: The structure of the complex tetraethylammonium iodide/$C_6F_3I_3$ **10** is very similar and, as expected, the unfilled cavity is 119 Å^3. The π-π interactions between benzene rings are responsible for the mono-layer corrugation, clearly visible in the 110 projection.

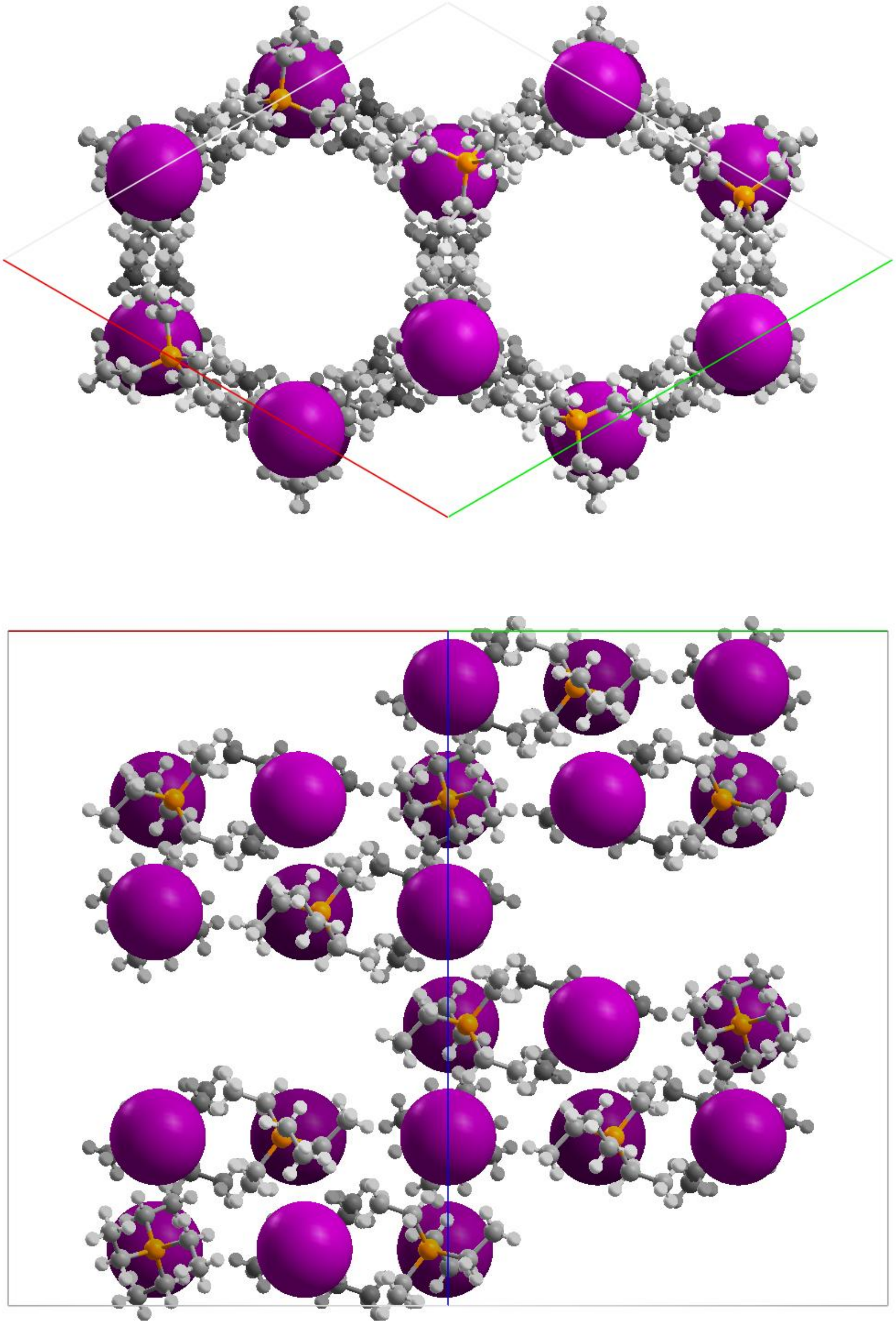


Figure S2. Ball-and-stick representation of tetraethylphosphonium iodide packing in structure **13** (iodide anions are in space-filling representation). Projection along 001 (top) showing the channels for the benzene derivative; projection along 110 (bottom). Colour codes: C, grey, H, white, P, orange, I, purple.

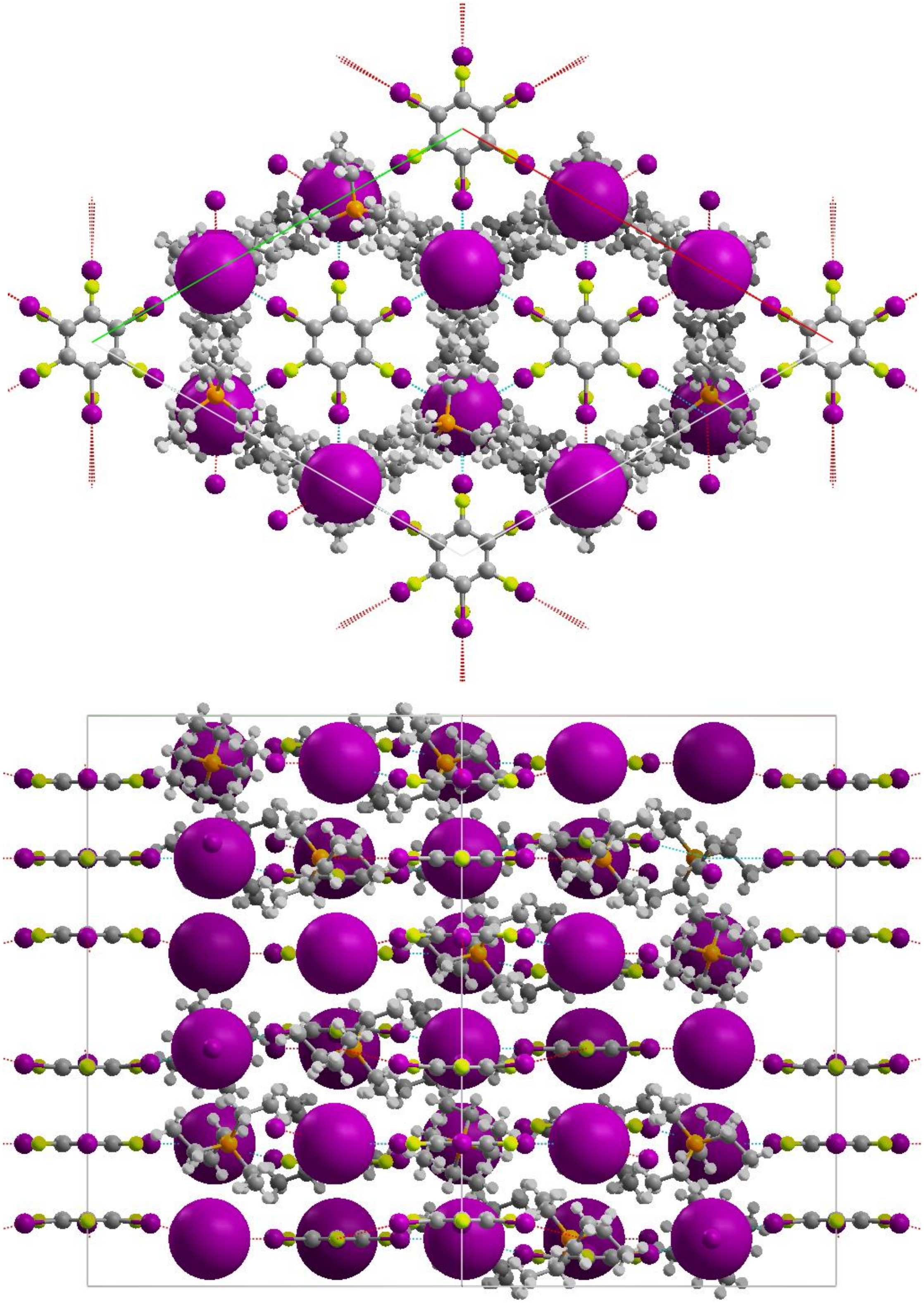


Figure S3. Ball-and-stick representation of the total structure **13** (iodide anions are in space-filling representation). Projection along 001 (top); projection along 110 (bottom). Colour codes: C, grey, H, white, F, yellow-green, P, orange, I, purple; blue or purple dashed lines represent the short $I\cdots I^-$ interactions.

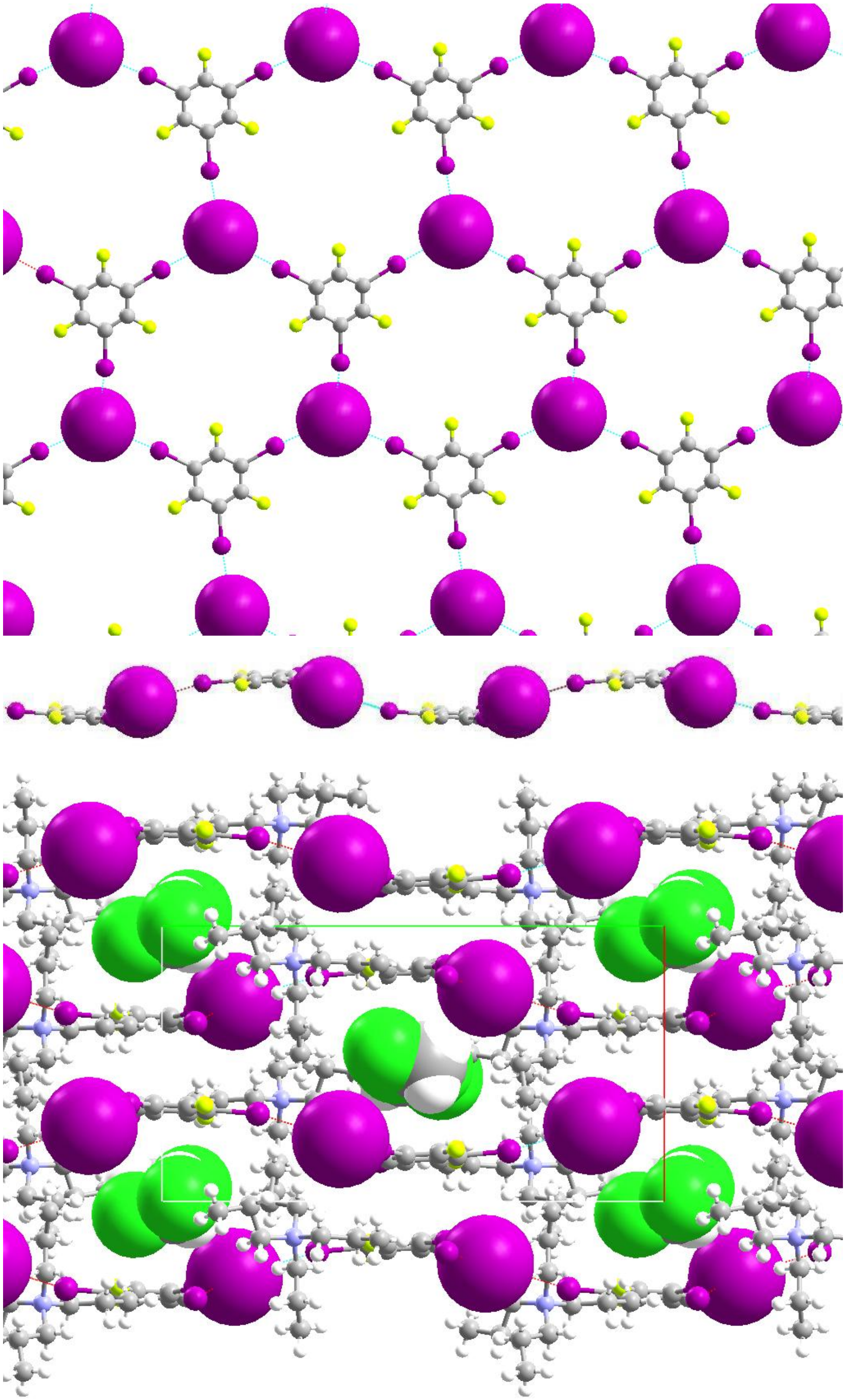


Figure S4. Compound **12**. A mono-layer of the super-anion $(C_6F_3I_3{\cdot}I^-)_n$ viewed along *a* and *c* axes (top and middle, respectively); at the bottom the whole packing. Iodide and dichloromethane in space-fill representation; colour codes: C, grey, H, white, N, blue, F, yellow-green, chlorine, green, I, purple; blue or purple dashed lines represent the short I···I$^-$ interactions.

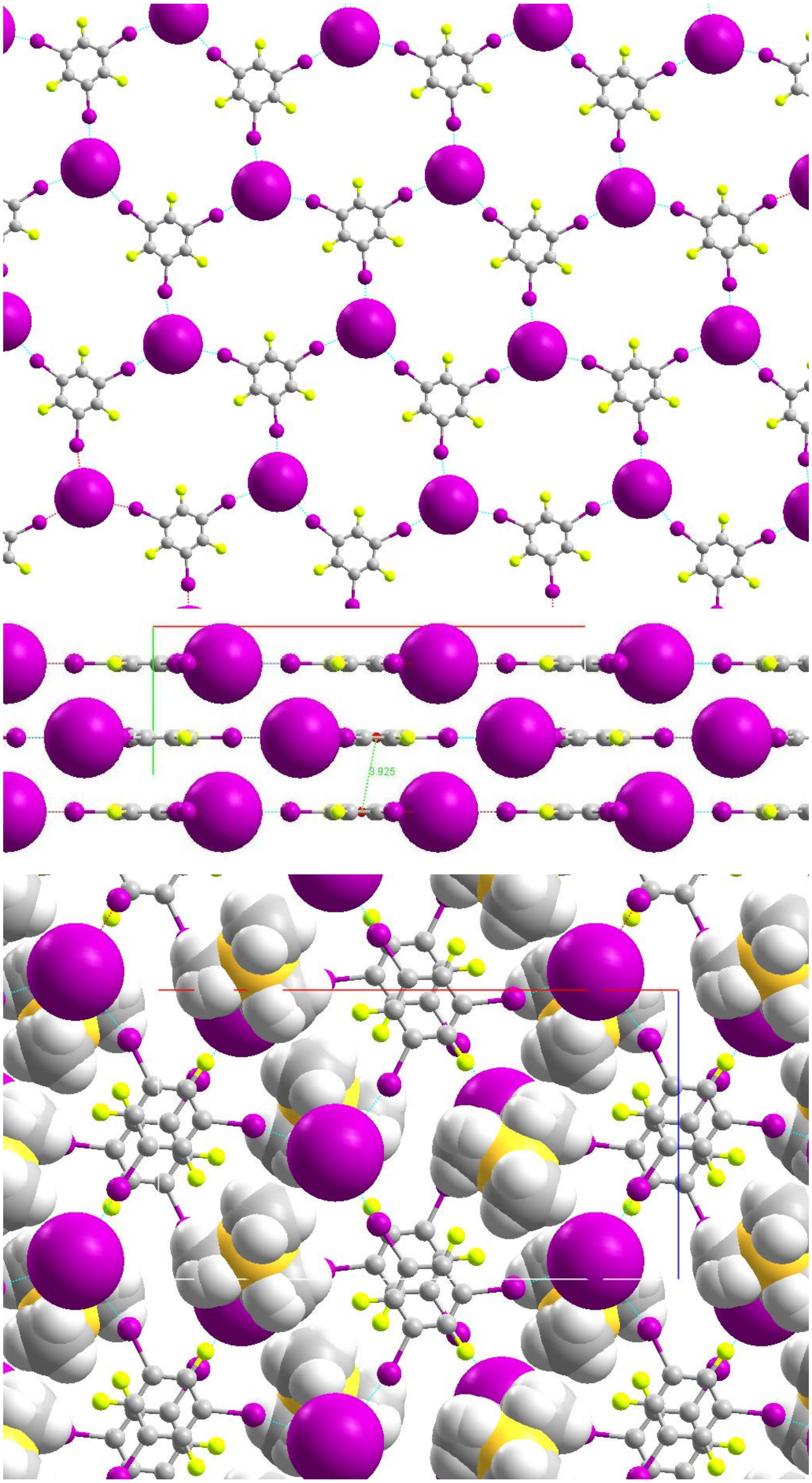


Figure S5. Compound **9**. A mono-layer of the super-anion $(C_6F_3I_3\cdot I^-)_n$ viewed along *b* (top); super-anion couple through the π-π interaction between 1,3,5-trifluoro-2,4,6-triiodobenzene molecules (middle, projection along *c*); the whole packing (bottom). Iodide and disordered trimethylsulphonium cation in space-fill representation; colour codes: C, grey, H, white, blue, F, yellow-green, S, yellow, I, purple; blue or purple dashed lines represent the short $I\cdots I^-$ interactions.

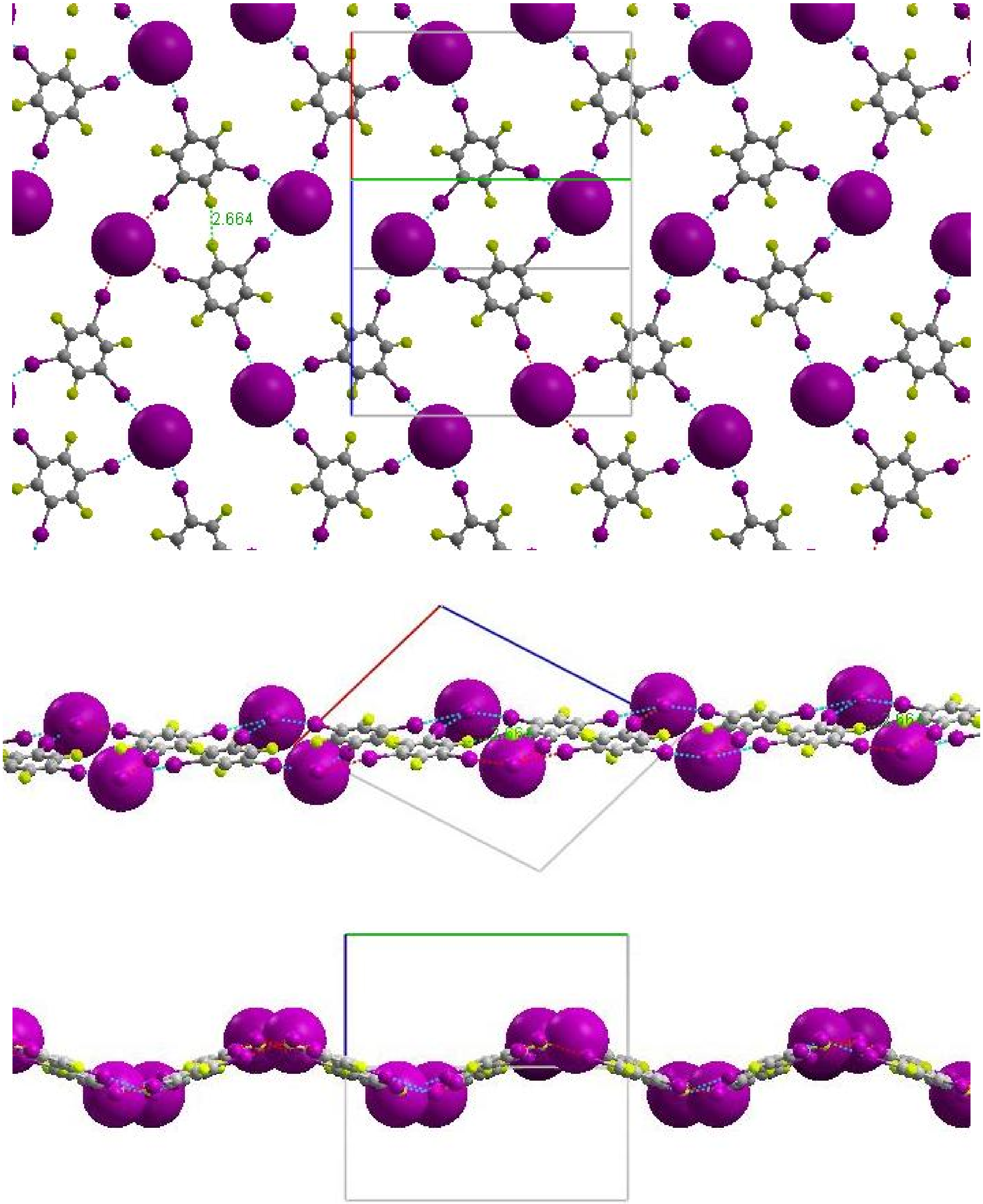


Figure S6. Ball-and-stick views of a mono-layer of the supramolecular anion $(C_6F_3I_3\cdot I^-)_n$, in tetrabutylammonium iodide/$C_6F_3I_3$/CH_2Cl_2) adduct **12** (iodide anions are in space-filling representation). Projection in its mean-square plane showing that the (6,3 network is not present. A remarkable 2.664 F···F interaction of 2.664 Å (top) is also reported; projection along *b* axis (middle); projection perpendicular to the previous ones (bottom), evidencing the waved conformation of the mono-layer. Colour codes: C, grey, H, white, F, yellow-green, I, purple; blue or purple dashed lines represent the short $I\cdots I^-$ interactions.

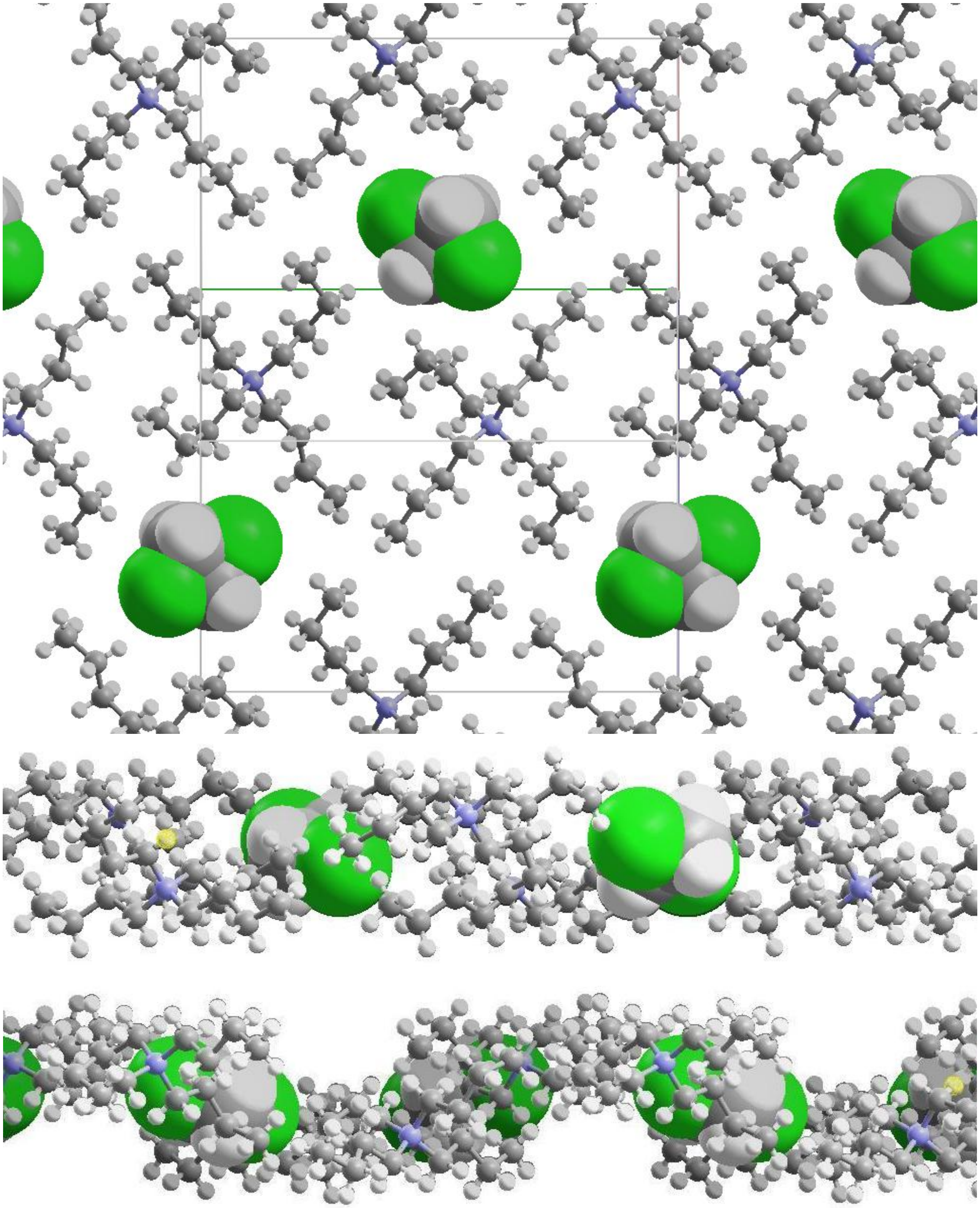


Figure S7. Ball-and-stick views of a mono-layer of cations $N^+(C_4H_9)_4$ and of the disordered dichloromethane, in compound **12** (dichloromethane is in space-filling representation); the three projections follows the same scheme of Figure S4; colour codes: C, grey, H, white, Cl, green, N, blue.

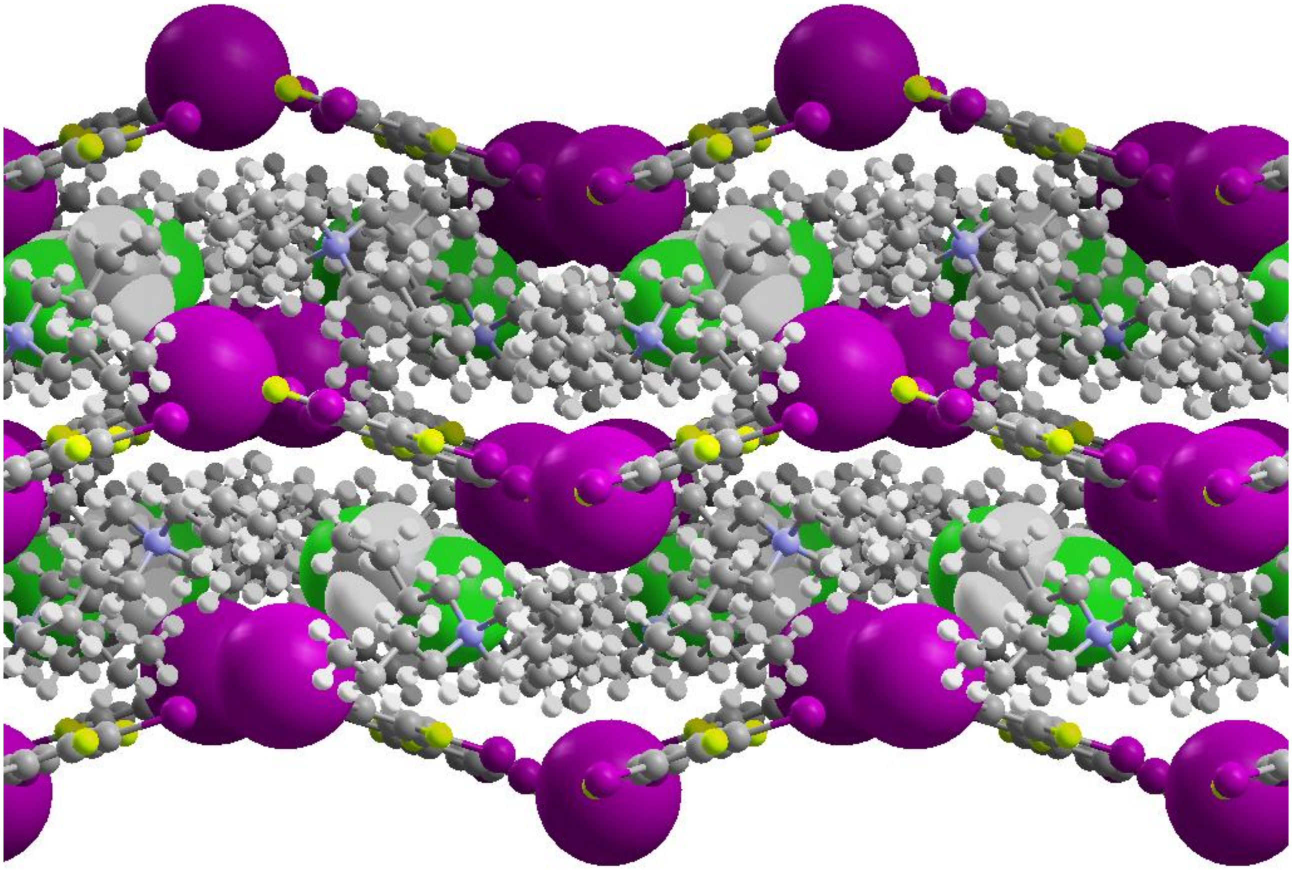


Figure S8. Packing of **12**; colour codes as in Figure 4 and 6.

DSC OF CO-CRYSTALS 10, 13, 16-18:

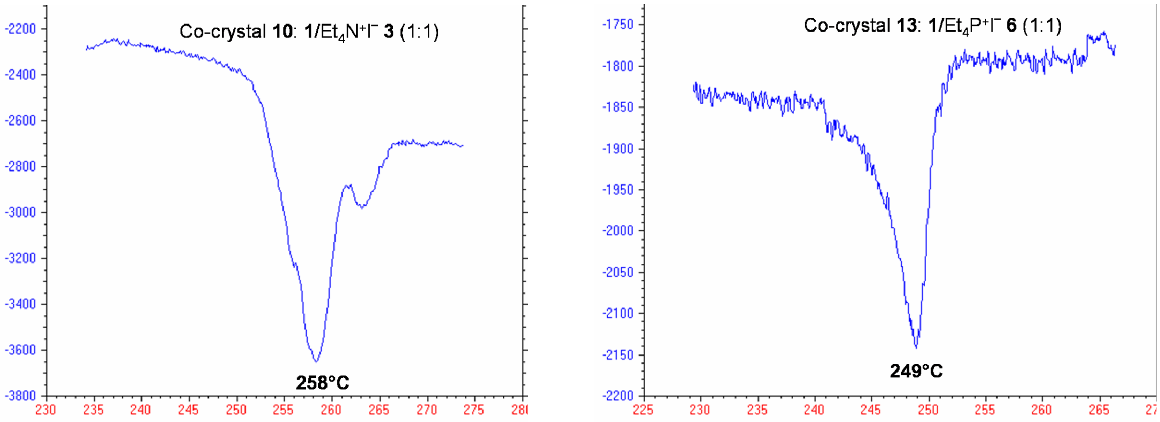


Figure S9. Melting points of co-crystals **10**,**13** obtained by differential scanning calorimetry.

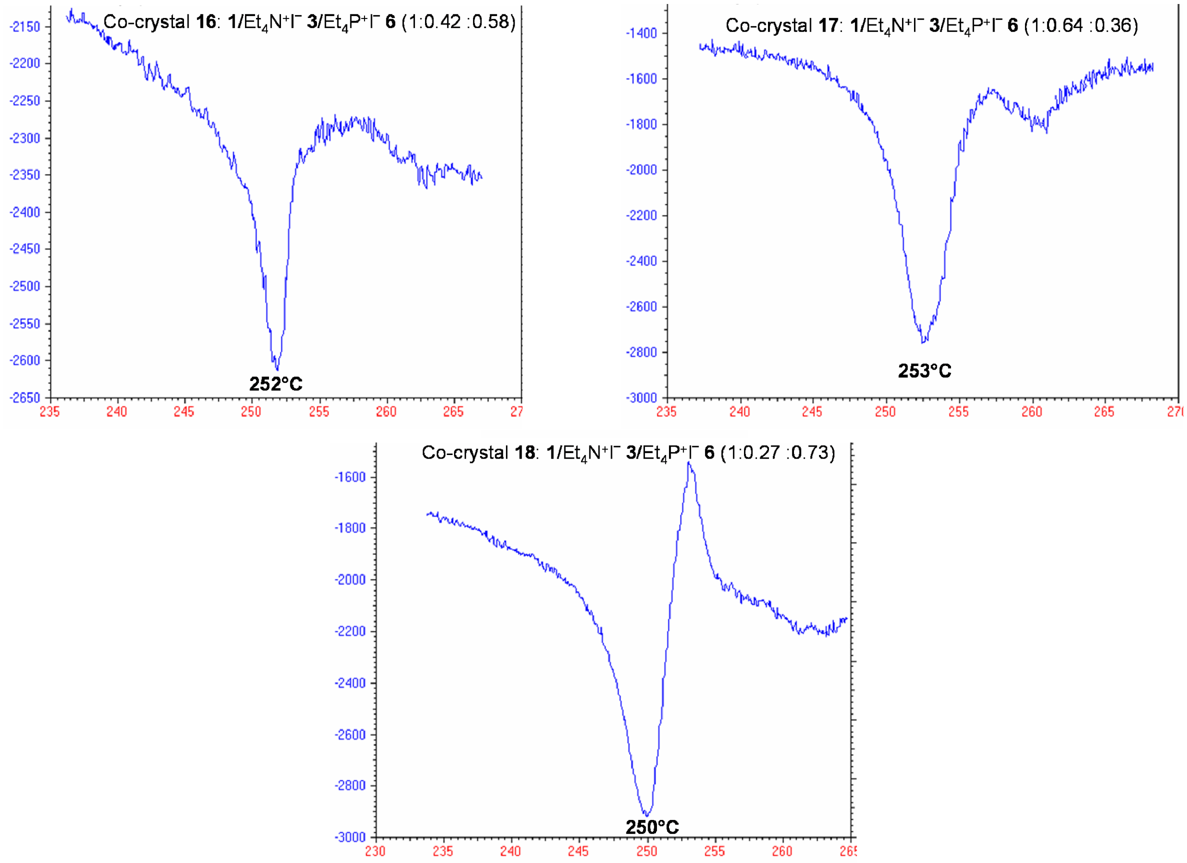


Figure S10. The melting points of co-crystals **16**, **17** and **18** are at intermediate temperatures with respect to compounds **10** and **13**.

Table S1. Selected crystallographic and data collection parameters for co-crystal **9-18**.

	9	**10**	**11**	**12**	**13**
formula	$C_6F_3I_3$, $C_3H_9S^+I^-$	$C_6F_3I_3$, $C_8H_{20}N^+I^-$	$2(C_6F_3I_3)$, $C_{12}H_{28}N^+I^-$ CH_2Cl_2	$C_6F_3I_3$, $C_{16}H_{36}N^+I^-$, $0.5(CH_2Cl_2)$	$C_6F_3I_3$, $C_8H_{20}P^+I^-$
M_r	713.82	766.91	907.94	921.58	783.87
System	orthorhombic	trigonal	monoclinic	monoclinic	trigonal
Space group	*Pnma*	*R*-3*c*	*P*2$_1$/*n*	*P*2$_1$/*n*	*R*-3*c*
a (Å)	21.052(5)	20.758(2)	11.0985(12)	11.983(3)	20.834(3)
b (Å)	7.2160(18)	-	20.323(2)	16.974(2)	-
c (Å)	11.691(2)	27.172(3)	12.4108(15)	16.379(4)	27.606(4)
(°)	-	-	91.49(2)	109.03	-
V (Å^3)	1775.9(7)	10140(2)	2798.4(5)	3149.4(13)	10377(2)
T (K)	123(2)	173(2)	12382)	123(2)	123(2)
Z	4	18	4	4	18
D_c (g cm^{-3})	2.670	2.261	2.155	1.944	2.258
Crystal form	hexagonal prism	amigdala	irregular block	elongated prism	tabular
Dimensions (mm^3)	0.26x0.13 x0.12	0.26x0.22x0.12	0.20x0.14 x0.10	0.22x0.10x0.06	0.24x0.19 x0.05
μ(Mo K) (mm^{-1})	7.144	5.551	4.672	4.071	5.491
Absorption T_{min}/T_{max}	0.498	0.488	0.770	0.541	0.704
$_{max}$ (°)	34.41	31.44	34.47	31.82	32.52
No reflect. collected	26050	30654	55107	29255	50074
R_{ave}	0.0279	0.0507	0.0276	0.298	0.266
No. independent	3858	3525	11375	10518	4192
No. *I*>2 (*I*)	3789	2042	10788	9029	3556
No. refined parameters	143	103	264	288	103
No. restraints	39	0	0	1	0
R_w (F^2, all)	0.0658	0.1223	0.0720	0.0973	0.0605
R_w [F^2, *I*>2 (*I*)]	0.0653	0.1157	0.0707	0.0930	0.0575
R (F, all)	0.0321	0.0790	0.0352	0.0478	0.0377
R [*F*, *I*>2 (*I*)]	0.0311	0.0483	0.0326	0.0397	0.0282
Goodness-of-fit	1.278	0.869	1.164	1.022	1.115
Min. residue (e Å^{-3})	-1.11	-0.84	-1.35	-1.75	-0.99
Max. residue (e Å^{-3})	1.19	2.39	1.27	2.33	1.31

	14	**15**	**16**	**17**	**18**
formula	$C_6F_3I_3$, $C_{24}H_{20}P^+I^-$, $CHCl_3$	$C_6F_3I_3$, $C_{18}H_{36}K\,N_2O_6^{+}I^-$	$C_6F_3I_3$, 0.58 $(C_8H_{20}N^+I^-)$, 0.42 $(C_8H_{20}P^+I^-)$	$C_6F_3I_3$, 0.36 $(C_8H_{20}N^+I^-)$, 0.64 $(C_8H_{20}P^+I^-)$	$C_6F_3I_3$, 0.27 $(C_8H_{20}N^+I^-)$, 0.73 $(C_8H_{20}P^+I^-)$
M_r	1095.40	1052.25	776.79	772.98	779.28
System	orthorhombic	monoclinic	trigonal	trigonal	trigonal
Space group	$Pna2_1$	$P2_1/c$	R-3c	R-3c	R-3c
a (Å)	18.725(2)	12.2152(12)	20.903(3)	20.891(3)	20.908(3)
b (Å)	9.5403(12)	14.222(2)	-	-	-
c (Å)	20.180(2)	20.531(2)	27.778(4)	27.594(4)	27.918(4)
(°)	-	91.89(2)	-	-	-
V (Å^3)	3605.0(7)	3564.8(8)	10511(2)	10430(2)	10569(2)
T (K)	153(2)	295(2)	296(2)	296(2)	296(2)
Z	4	4	18	18	18
D_c (g cm^{-3})	2.018	1.961	2.209	2.215	2.204
Crystal form	prism	prism	hexagonal prism	prism	Prim
Dimensions (mm^3)	0.36x0.19 x0.08	0.29x0.16 x0.13	0.25x0.22 x0.17	0.30x0.28 x0.22	0.28x0.22 x0.17
μ(Mo K) (mm^{-1})	3.760	3.664	5.393	5.420	5.374
Absorption T_{min}/T_{max}	0.571	0.668	0.738	0.735	0.812
$_{max}$ (°)	34.57	28.25	26.00	26.09	29.08
No reflect. collected	86581	73188	29699	59062	34978
R_{ave}	0.0352	0.0294	0.0286	0.0274	0.0346
No. independent	14696	8821	2302	2306	3104
No. I>2 (I)	12594	7454	1616	1725	1767
No. refined parameters	494	362	104	104	104
No. restraints	514	0	0	0	0
R_w (F^2, all)	0.0818	0.0896	0.0994	0.1031	0.1114
R_w [F^2, I>2 (I)]	0.0777	0.0849	0.0786	0.0858	0.0900
R (F, all)	0.0415	0.0398	0.0586	0.0548	0.0822
R [F, I>2 (I)]	0.0324	0.0330	0.0357	0.0369	0.0390
Goodness-of-fit	1.056	1.049	1.104	1.111	1.040
Min. residue (e Å^{-3})	-0.75	-1.54	-1.04	-1.23	-1.10
Max. residue (e Å^{-3})	1.92	2.45	1.13	1.27	1.06

Table S2. Crystallographically symmetry imposed on the various components of supramolecular complexes **9-18**.

structure	**Trifluorotriiodobenzene**	**Cation**	**Iodide Ion**
9	C_s (*m*).	**1** C_s (*m*), disordered	C_s (*m*)
10	(1) D_3; (2) C_3	**2**, C_2	D_3
11	C_1	**4**, C_1	C_1
12	C_1	**5**, C_1	C_1
13	(1) D_3; (2) C_3	**3**, C_2	D_3 (32)
14	C_1	**6**, C_1	C_1
15	C_1	**7**, C_1	C_1
16	(1) D_3; (2) C_3	**2+3** solid solution, C_2	D_3
17	(1) D_3; (2) C_3	**2+3** solid solution, C_2	D_3
18	(1) D_3; (2) C_3	**2+3** solid solution, C_2	D_3

1 = trimethylsulfonium, **2** = triethylammonium, **3** = triethylphosphonium, **4** = tripropylammonium, **5** = tributylammonium, **6** = tetraphenylphosphonium, **7** = $K^+ \subset$K.2.2.2.

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[1] H. H. Wenk, W. Sander *Eur. J. Org. Chem.* **2002**, 3927

[2] Bruker, *SMART, SAINT* and *SADABS.* Bruker AXS Inc., Madison, Wisconsin, USA, **1999**.

[3] M. C. Burla, M. Camalli, B. Carrozzini, G. L. Cascarano, C. Giacovazzo, G. Polidori, R. Spagna, *J. Appl. Crystallogr.* **2003**, *36*, 1103.

[4] G.M. Sheldrick, SHELXL97. *Program for the Refinement of Crystal Structures*. University of Göttingen, Germany, **1997**.