Supporting Information

New Journal of Chemistry

The Effect of Temperature on Interhalogen Interactions in a Series of Isostructural Organic Systems

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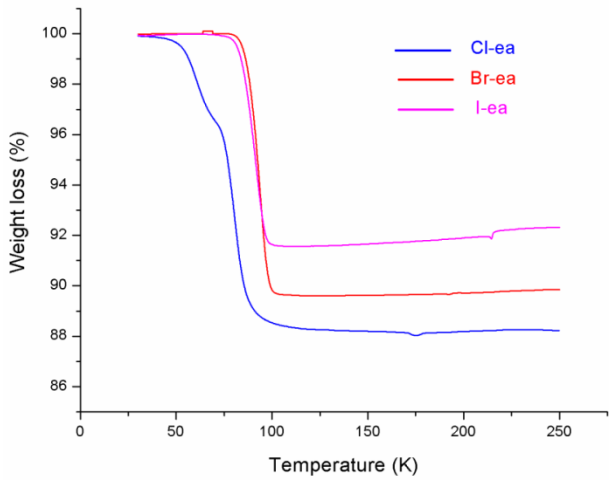
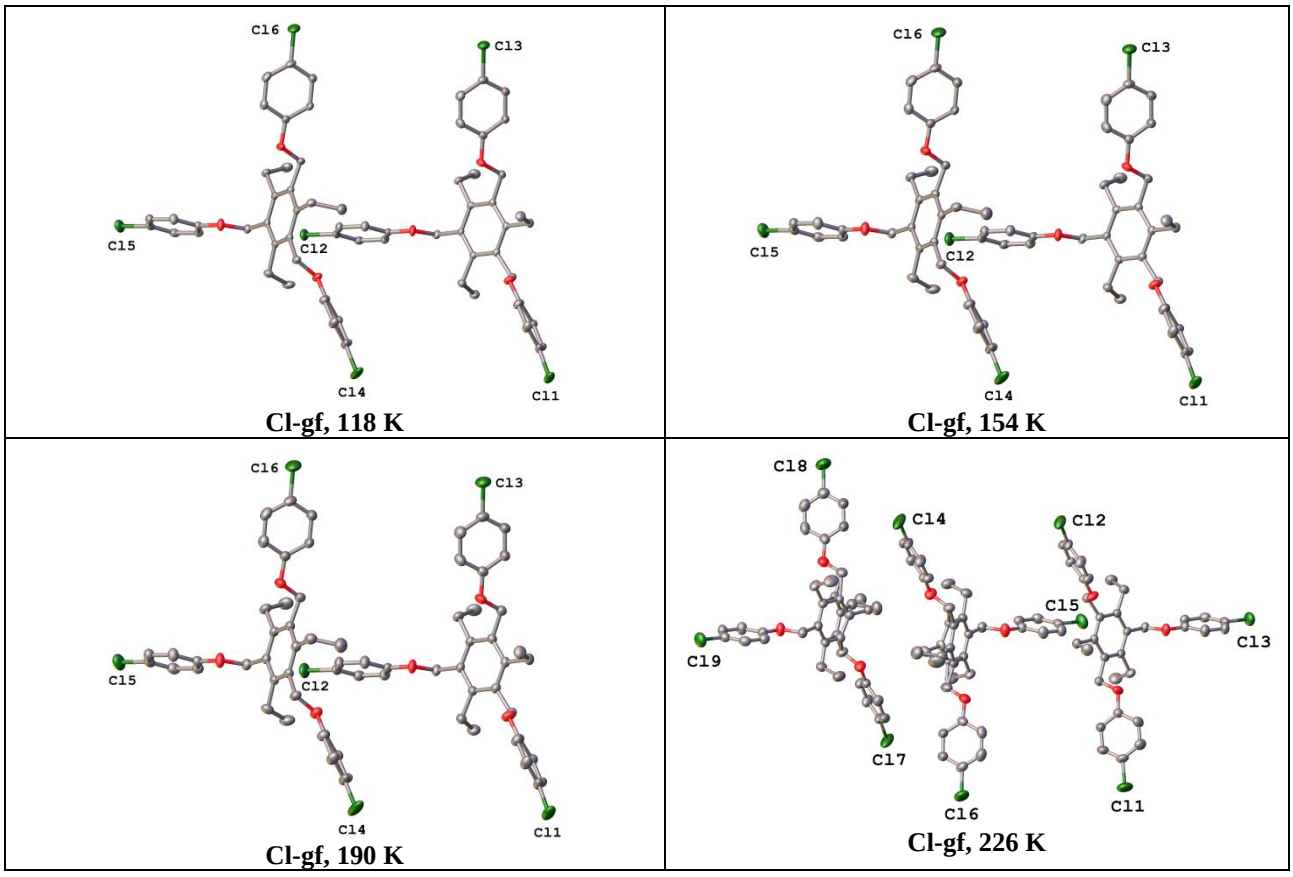
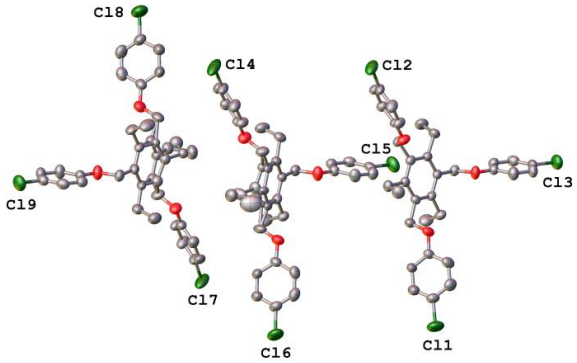
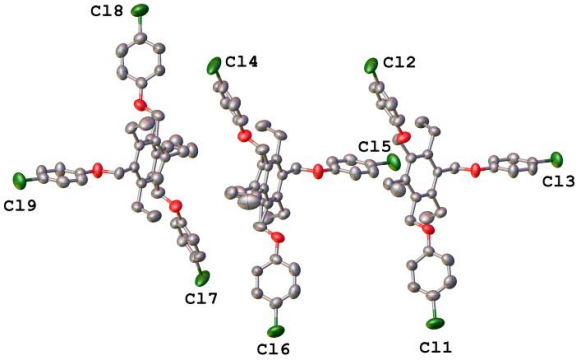


Figure S1. Thermal Gravimetric (TG) plot of the solvates. The experimental weight loss (11.57% for Cl-ea, 10.39% for Br-ea and 8.38% for I-ea) suggest that the host:guest ratios are 1:1 in these cases (calculated weight loss 13.09% for Cl-ea, 10.90% for Br-ea and 9.30% for I-ea).



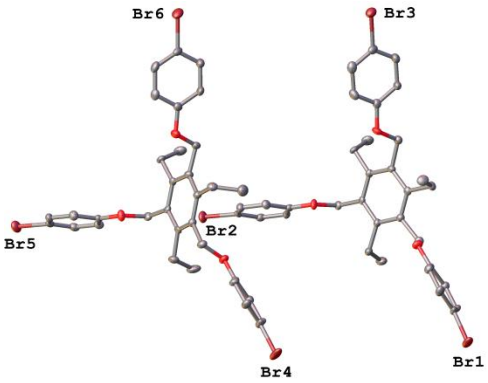


Cl-gf, 262 K

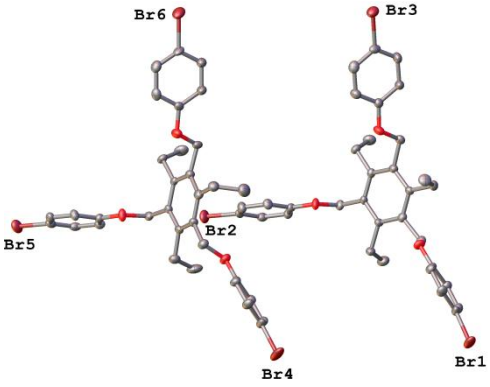


Cl-gf, 298 K

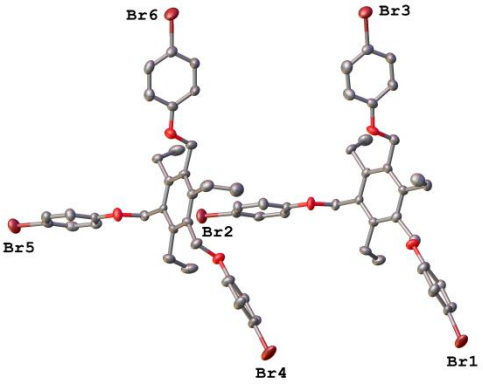
At 226, 262 and 298 K, the C36-C38 (one central ring), C42, C43 (one ethyl group) of one molecule and C69-71 (one central ring), C75, C76 (one ethyl group) atoms of another molecule in the **Cl-gf** structures are disordered over two positions with s.o.f. 0.77/0.23 and 0.21/0.79 at 226K, 0.67/0.33 and 0.23/0.77 at 262K, 0.61/0.39 and 0.28/0.72 at 298 K respectively. C36B, C69A-C71A, C75A and C76A atoms have been refined isotropically in these three structures.



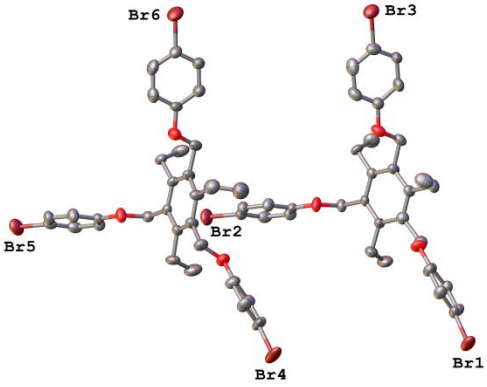
Br-gf, 118 K



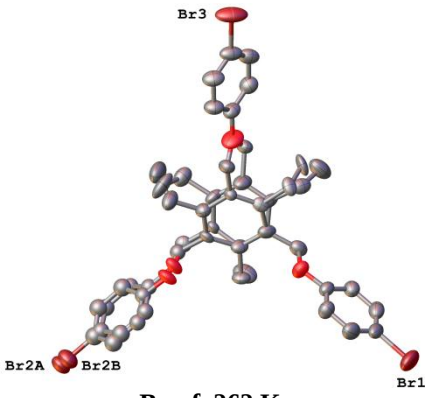
Br-gf, 154 K



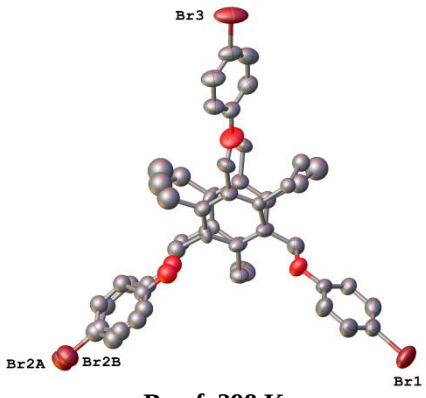
Br-gf, 190 K



Br-gf, 226 K

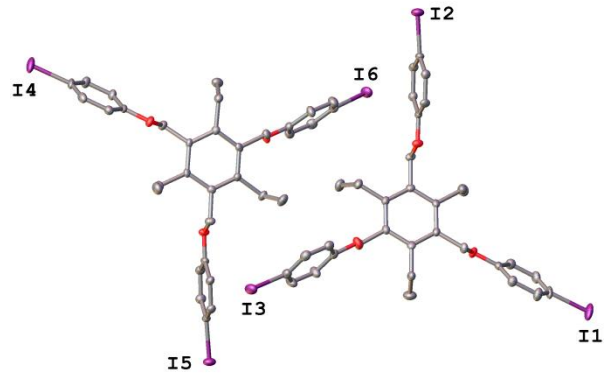


Br-gf, 262 K

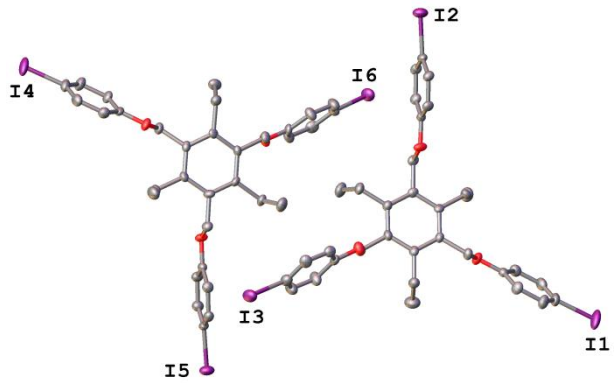


Br-gf, 298 K

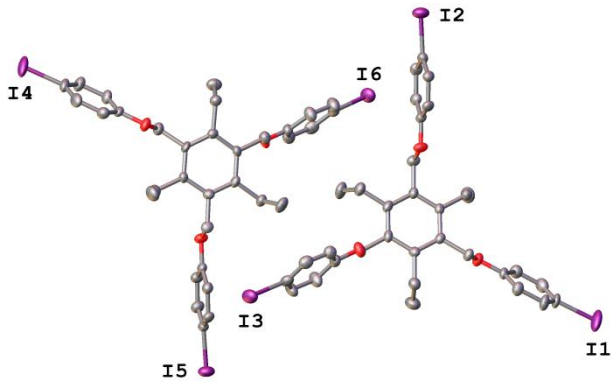
At 262 and 298 K, C3-C6 (central ring), C30-C33 (two ethyl groups), C14, C21 (two CH2 groups), C15-C20 (one side ring), O2 and Br2 atoms in the **Br-gf** structures are disordered over two positions with s.o.f 0.5/0.5. All the C-C bonds of the C15-C20 rings have been refined with SADI command in these two structures. For the 298 data, the O3-C21B and O3-C21A bonds have been refined with SADI command. C21A and C21B atoms for both the temperatures and the C5a and C5B atoms for the 298 K data have been refined with EADP command. C14-C20 atoms have been refined isotropically for these two data sets. For the 298 K data, the C6, C14, C30-33 and O3 disordered atoms also have been refined isotropically at both the sites.



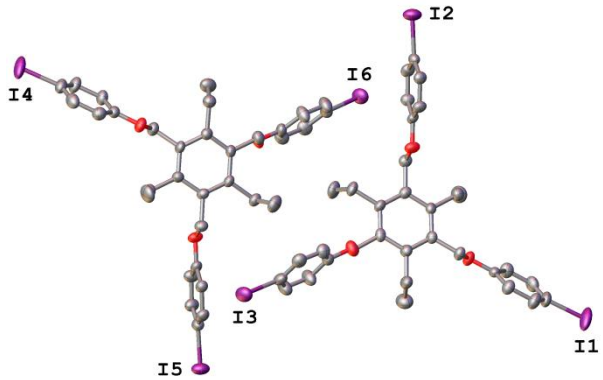
I-gf, 118 K



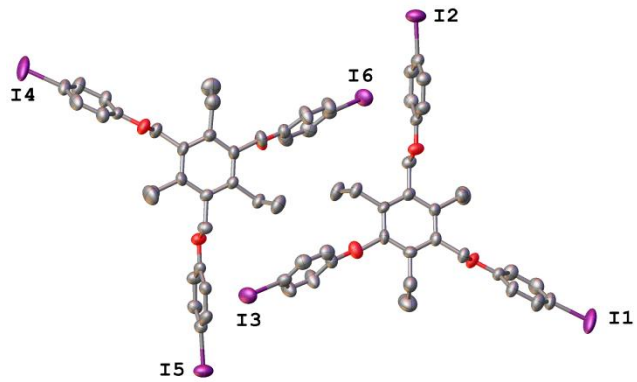
I-gf, 154 K



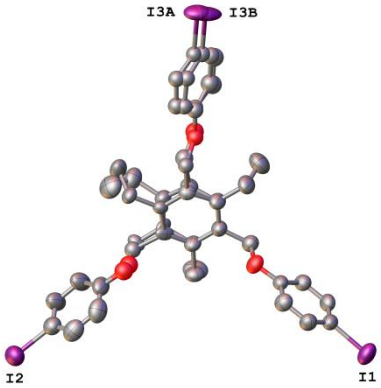
I-gf, 190 K



I-gf, 226 K

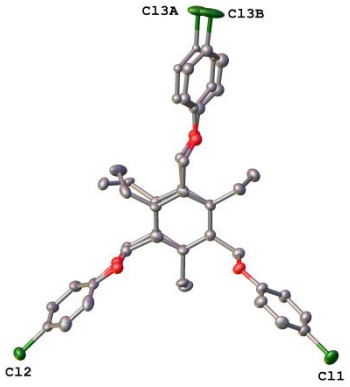


I-gf, 262 K

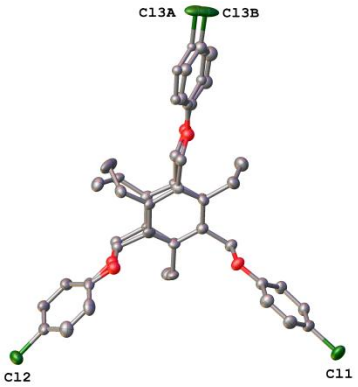


I-gf, 298 K

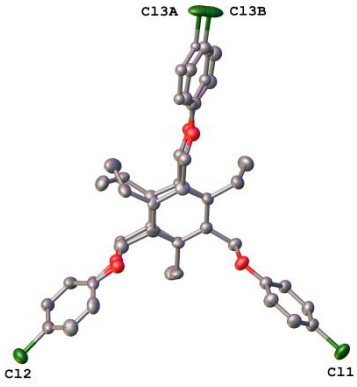
At 298 K in the **I-gf** structure C3-C5 (central ring), C9, C10 (one ethyl group), C20, C27 (two CH_2 groups), C22-C27 (one side ring), O2, O3 and I3 atoms are disordered over two positions with s.o.f 0.5/0.5. All the C-C bonds of the C21(A, B)-C26(A, B) rings have been refined with SADI command in this structure. O2(A, B), O3(A, B) and C20(A, B) and C27B have been refined isotropically.



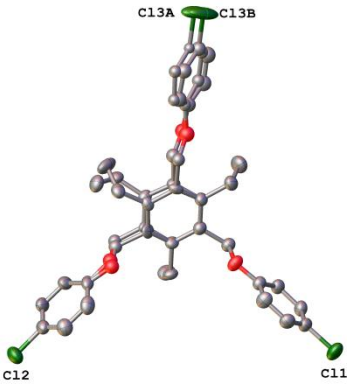
Cl-ea, 118 K



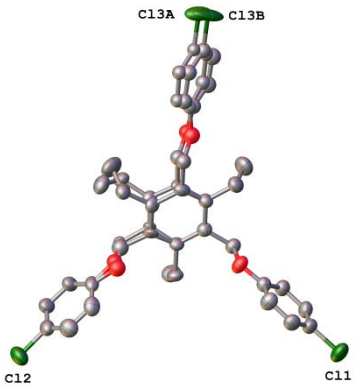
Cl-ea, 154 K



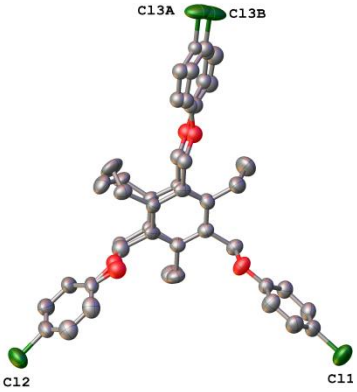
Cl-ea, 190 K



Cl-ea, 226 K

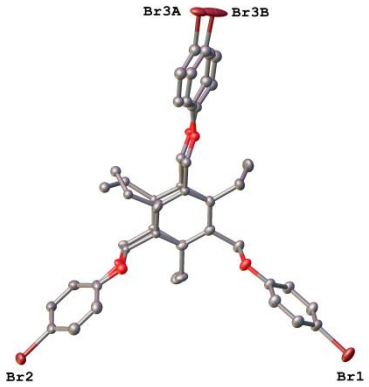


Cl-ea, 262 K

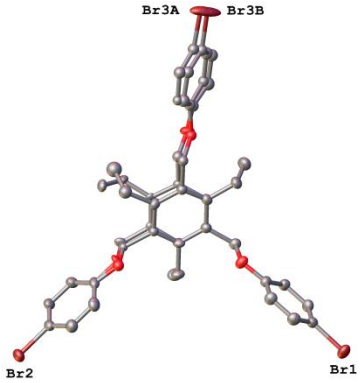


Cl-ea, 298 K

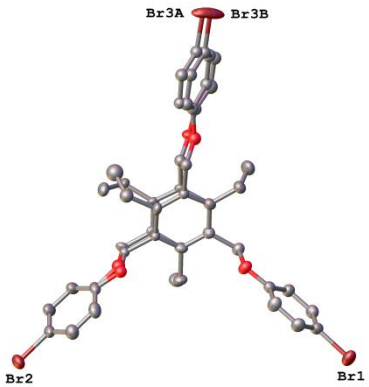
In **Cl-ea**, the C3-5 (central ring), C14, C21 (two CH_2 groups), C22-27 (one side ring), C30, C31 (one ethyl group), O2, O3 and Cl3 atoms are disordered over two positions with s.o.f. 0.61/0.39 at 118 K, 0.63/0.37 at 154 K, 0.62/0.38 at 190 K, 0.61/0.39 at 226 K, 0.58/0.42 at 262 K, 0.57/0.43 at 298 K. In all the structures disordered C2, C14, C21-27, O2 and O3 atoms have been refined isotropically at both the sites. All the C-C bonds of the C22-C27 rings at two sites have been refined with SADI command. C15-O2B and C15-O2A also have been refined with SADI command in all these structures.



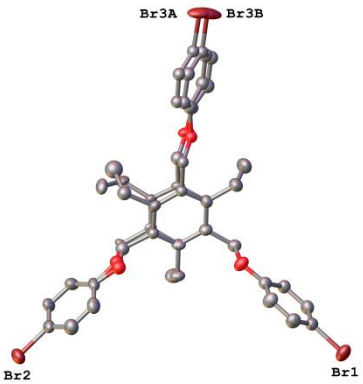
Br-ea, 118 K



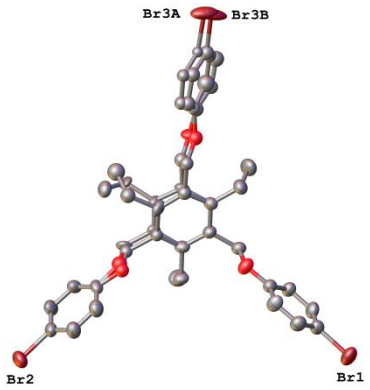
Br-ea, 154 K



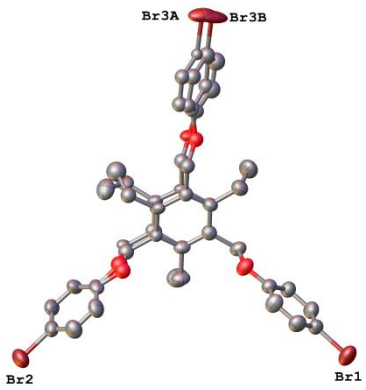
Br-ea, 190 K



Br-ea, 226 K

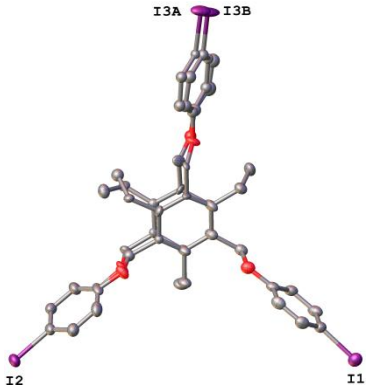


Br-ea, 262 K

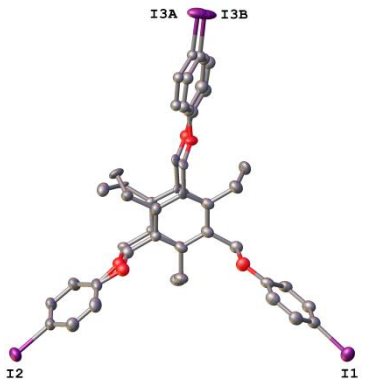


Br-ea, 298 K

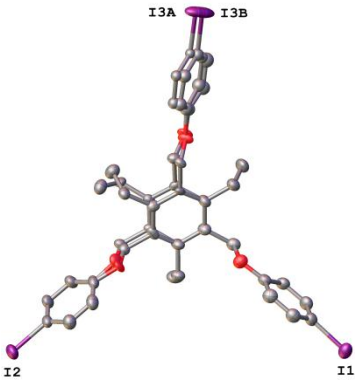
In **Br-ea** structures, the C3-5 (central ring), C14, C21 (two CH_2 groups), C22-27 (one side ring), C30, C31 (one ethyl group), O2, O3 and Br3 are disordered over two positions with s.o.f. 0.69/0.31 at 118 K, 0.64/0.36 at 154 K, 0.62/0.38 at 190 K, 0.60/0.40 at 226 K, 0.58/0.42 at 262 K, 0.59/0.41 at 298 K. All the C-C bonds of the C22-C27 disordered rings at two orientations have been refined with SADI command. C3A, 4B, C5A, C14A, C30A, C31A, C21-27(A, B), O2A and O3A have been refined isotropically in all these structures. C4B, C30B and C31B at 118K and O2B at 190-298 K also have been refined isotropically. Disordered atoms C25, C26, C24, C30, C31, C27, C22, C23 at 118 K, C24, C25 C26 at 154 and 190 K, and C24, C25 at 226 K at two sites (A and B) have been refined with EADP command.



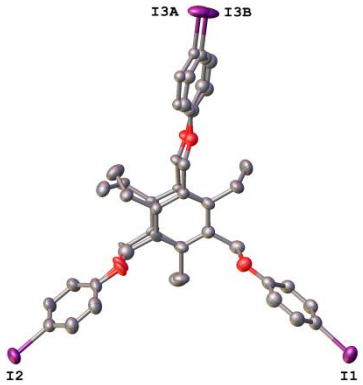
I-ea, 118 K



I-ea, 154 K



I-ea, 190 K



I-ea, 226 K

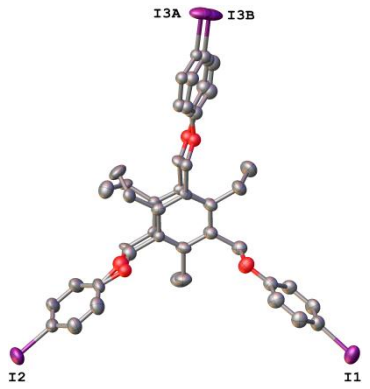
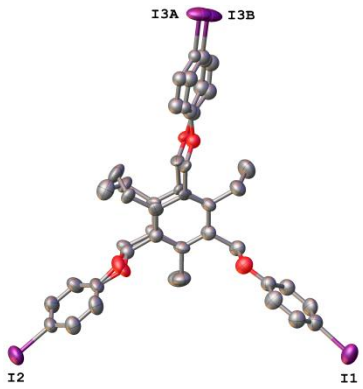
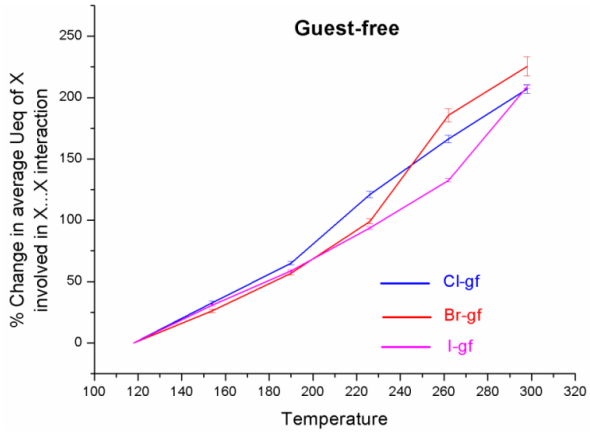
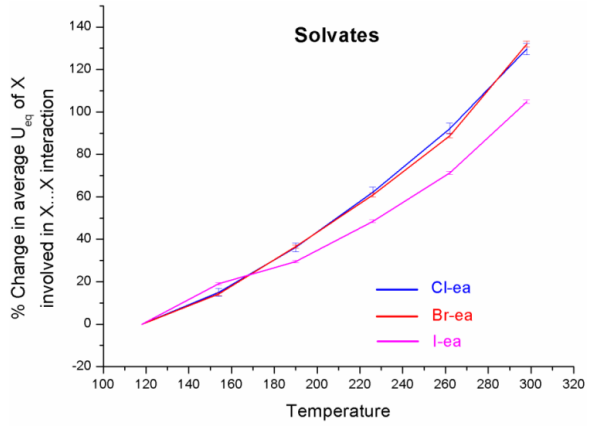
	
I-ea, 262 K	**I-ea, 298 K**
In **I-ea** structures, the C3-5 (central ring), C14, C21 (two CH_2 groups), C22-27 (one side ring), C30, C31 (one ethyl group), O2, O3 and I3 are disordered over two positions with s.o.f. 0.52/0.48 at 118 K, 0.52/0.48 at 154 K, 0.54/0.46 at 190 K, 0.51/0.49 at 226 K, 0.52/0.48 at 262 K, 0.53/0.47 at 298 K. All the C-C bonds of the C22-C27 disordered rings at two orientations have been refined with SADI command. C14A and C22-27 (A, B) have been refined isotropically in all these structures. C3A at 118, 154, 262 and 298 K, C5A at 226 K, C21A at 226 and 262 K, C31 A at 118 K, O3A 226, 262 and 298 K, O3B at 118, 154 and 262 K also have been refined isotropically.	

Figure S2. ORTEP diagrams of the systems drawn at 50 % probability level.

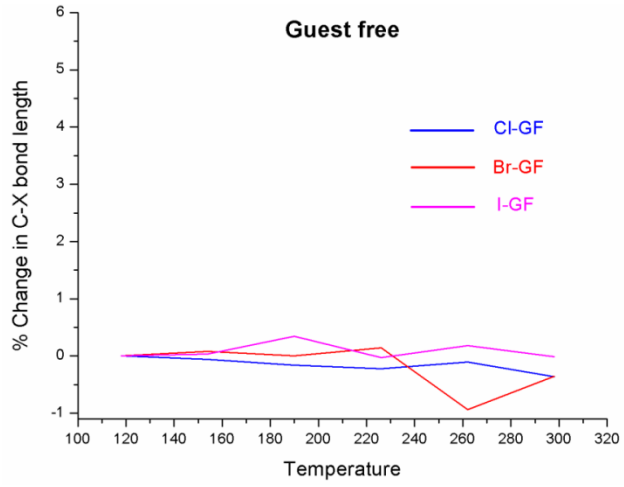


(a)

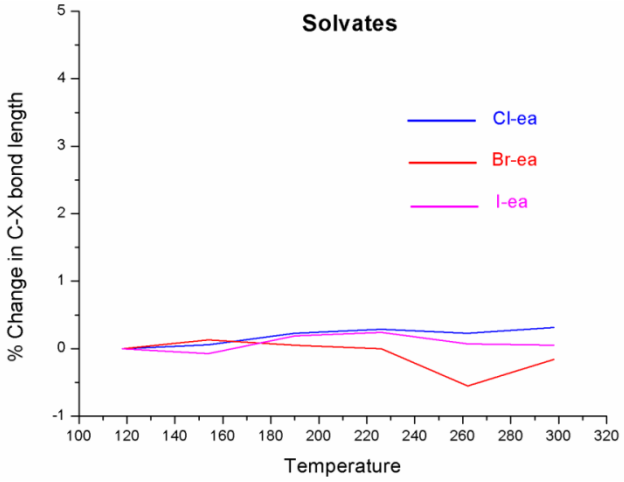


(b)

Figure S3. % Change in the average Ueq values of the halogens involved in interhalogen interactions with temperature in (a) guest-free forms and (a) solvates.



(a)



(b)

Figure S4. % Change in the average C–X bond lengths of those involved in interhalogen interactions with temperature in (a) guest-free forms and (a) solvates. Change in C–X bond lengths are much smaller compared to the change in X···X distances shown in Figure 2.

Table S1. Crystallographic details of the structures.

	Cl-gf, 118K	Cl-gf, 154K	Cl-gf, 190K	Cl-gf, 226K	Cl-gf, 262K	Cl-gf, 298K
Formula	$C_{33}H_{33}Cl_3O_3$	$C_{33}H_{33}Cl_3O_3$	$C_{33}H_{33}Cl_3O_3$	$C_{33}H_{33}Cl_3O_3$	$C_{33}H_{33}Cl_3O_3$	$C_{33}H_{33}Cl_3O_3$
*M*r	583.94	583.94	583.94	583.94	583.94	583.94
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_1/a$	$P2_1/a$	$P2_1/a$
a (Å)	19.0393(3)	19.0690(7)	19.0913(8)	24.8803(10)	24.9516(10)	25.0300(11)
b (Å)	13.3551(2)	13.3847(4)	13.3962(5)	13.4318(4)	13.4628(4)	13.4909(5)
c (Å)	24.7011(5)	24.7369(9)	24.8034(11)	28.8166(11)	28.8673(11)	28.9380(11)
α(°)	90.00	90.00	90.00	90.00	90.00	90.00
β (°)	110.139(2)	110.263(4)	110.348(5)	110.512(5)	110.600(4)	110.676(5)
γ(°)	90.00	90.00	90.00	90.00	90.00	90.00
V (Å^3)	5896.77(17)	5922.9(4)	5947.6(4)	9019.5(6)	9077.0(6)	9142.3(6)
Crystal size (mm)	0.6*0.6*0.5	0.6*0.6*0.5	0.6*0.6*0.5	0.6*0.6*0.5	0.6*0.6*0.5	0.6*0.6*0.5
T (K)	118(2)	154(2)	190(2)	226(2)	262(2)	298(2)
Z	8	8	8	12	12	12
F(000)	2448	2448	2448	3672	3672	3672
μ(mm^{-1})	0.343	0.342	0.341	0.337	0.335	0.332
Ref. collected/unique	14417	13589	13686	21164	21259	21821
Parameters	709	709	709	1123	1123	1123
Final R indices [I>2σ(I)]	0.0452	0.0506	0.0554	0.0717	0.0753	0.0710
R indices (all data)	0.1093	0.1310	0.1508	0.1786	0.2145	0.2235
Goodness of fit on F^2	1.028	0.994	1.035	1.030	1.010	1.017

	Br-gf, 118K	Br-gf, 154K	Br-gf, 190K	Br-gf, 226K	Br-gf, 262K	Br-gf, 298K
Formula	$C_{33}H_{33}Br_3O_3$	$C_{33}H_{33}Br_3O_3$	$C_{33}H_{33}Br_3O_3$	$C_{33}H_{33}Br_3O_3$	$C_{33}H_{33}Br_3O_3$	$C_{33}H_{33}Br_3O_3$
*M*r	717.32	717.32	717.32	717.32	717.32	717.32
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_1/c$
a (Å)	19.1589(7)	19.1937(7)	19.2260(7)	19.2670(8)	9.6682(4)	9.6977(5)
b (Å)	13.3863(4)	13.4082(4)	13.4255(5)	13.4479(5)	13.4772(7)	13.4907(7)
c (Å)	25.1489(10)	25.1997(11)	25.2443(13)	25.3027(16)	23.8893(14)	23.9687(19)
α(°)	90.00	90.00	90.00	90.00	90.00	90.00
β (°)	109.755(4)	109.775(4)	109.776(5)	109.815(6)	92.463(5)	92.416(6)
γ(°)	90.00	90.00	90.00	90.00	90.00	90.00
V (Å^3)	6070.3(4)	6102.8(4)	6131.7(4)	6167.8(5)	3109.9(3)	3133.0(3)
Crystal size (mm)	0.4*0.4*0.4	0.4*0.4*0.4	0.4*0.4*0.4	0.4*0.4*0.4	0.4*0.4*0.4	0.4*0.4*0.4
T (K)	118(2)	154(2)	190(2)	226(2)	262(2)	298(2)
Z	8	8	8	8	4	4
F(000)	2880	2880	2880	2880	1440	1440
μ(mm^{-1})	4.019	3.998	3.979	3.956	3.923	3.894
Ref. collected/unique	14148	14202	14340	14411	7074	7244
Parameters	709	709	709	709	448	377
Final R indices [I>2σ(I)]	0.0587	0.0638	0.0680	0.0824	0.0644	0.0701
R indices (all data)	0.1471	0.1569	0.1754	0.2408	0.1538	0.1989
Goodness of fit on F^2	1.025	1.014	1.008	1.011	1.005	0.999

	I-gf, 118K	I-gf, 154K	I-gf, 190K	I-gf, 226K	I-gf, 262K	I-gf, 298K
Formula	$C_{33}H_{33}I_3O_3$	$C_{33}H_{33}I_3O_3$	$C_{33}H_{33}I_3O_3$	$C_{33}H_{33}I_3O_3$	$C_{33}H_{33}I_3O_3$	$C_{33}H_{33}I_3O_3$
*M*r	858.29	858.29	858.29	858.29	858.29	858.29
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1/n$	$P2_1/n$	$P2_1/n$	$P2_1/n$	$P2_1/n$
a (Å)	19.4397(4)	19.4896(6)	19.5482(7)	19.6173(7)	19.7104(9)	9.9304(5)
b (Å)	13.3256(3)	13.3369(3)	13.3514(5)	13.3722(4)	13.3901(5)	13.4111(6)
c (Å)	26.3234(6)	26.3205(7)	26.3226(8)	26.3254(9)	26.3231(10)	24.9283(15)
α(°)	90.00	90.00	90.00	90.00	90.00	90.00
β (°)	108.968(3)	108.892(3)	108.848(4)	108.829(4)	108.829(5)	93.303(5)
γ(°)	90.00	90.00	90.00	90.00	90.00	90.00
V (Å^3)	6448.7(2)	6473.0(3)	6501.7(4)	6536.3(4)	6575.5(5)	3314.4(3)
Crystal size (mm)	0.4*0.4*0.07	0.4*0.4*0.07	0.4*0.4*0.07	0.4*0.4*0.07	0.4*0.4*0.07	0.4*0.4*0.07
T (K)	118(2)	154(2)	190(2)	226(2)	262(2)	298(2)
Z	8	8	8	8	8	4
F(000)	3312	3312	3312	3312	3312	1656
μ(mm^{-1})	2.939	2.928	2.915	2.899	2.882	2.859
Ref. collected/unique	15017	14787	14718	14919	14981	7532
Parameters	709	709	709	709	709	405
Final R indices [I>2σ(I)]	0.0388	0.0504	0.0542	0.0576	0.0625	0.0471
R indices (all data)	0.0873	0.1090	0.1150	0.1373	0.1596	0.1198
Goodness of fit on F^2	1.026	1.022	1.017	1.009	1.007	1.005

	Cl-ea, 118K	Cl-ea, 154K	Cl-ea, 190K	Cl-ea, 226K	Cl-ea, 262K	Cl-ea, 298K
Formula	$C_{37}H_{41}Cl_3O_5$	$C_{37}H_{41}Cl_3O_5$	$C_{37}H_{41}Cl_3O_5$	$C_{37}H_{41}Cl_3O_5$	$C_{37}H_{41}Cl_3O_5$	$C_{37}H_{41}Cl_3O_5$
*M*r	672.05	672.05	672.05	672.05	672.05	672.05
Crystal system	triclinic	triclinic	triclinic	triclinic	triclinic	triclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a (Å)	9.6153(3)	9.6338(4)	9.6558(4)	9.6879(5)	9.7104(4)	9.7599(7)
b (Å)	13.3561(6)	13.3820(8)	13.4048(7)	13.4280(8)	13.4378(9)	13.4660(12)
c (Å)	14.5104(8)	14.5496(11)	14.5814(11)	14.6215(11)	14.6582(12)	14.7073(15)
α(°)	111.810(5)	111.658(6)	111.503(6)	111.346(6)	111.156(7)	110.972(9)
β (°)	92.311(4)	92.203(5)	92.122(5)	92.071(5)	92.048(5)	92.061(7)
γ(°)	90.228(3)	90.170(4)	90.099(4)	90.031(5)	89.974(4)	89.844(7)
V (Å^3)	1728.31(13)	1741.71(18)	1754.51(18)	1770.3(2)	1782.5(2)	1803.6(3)
Crystal size (mm)	0.6*0.4*0.4	0.6*0.4*0.4	0.6*0.4*0.4	0.6*0.4*0.4	0.6*0.4*0.4	0.6*0.4*0.4
T (K)	118(2)	154(2)	190(2)	226(2)	262(2)	298(2)
Z	2	2	2	2	2	2
F(000)	708	708	708	708	708	708
μ(mm^{-1})	0.306	0.304	0.302	0.299	0.297	0.294
Ref. collected/unique	7900	7875	7972	8040	8157	8212
Parameters	401	401	401	401	401	401
Final R indices [I>2σ(I)]	0.1196	0.1068	0.1086	0.1069	0.1114	0.0899
R indices (all data)	0.3444	0.3252	0.3354	0.3326	0.3675	0.3056
Goodness of fit on F^2	1.112	1.049	1.049	1.042	1.075	1.026

	Br-ea, 118K	Br-ea, 154K	Br-ea, 190K	Br-ea, 226K	Br-ea, 262K	Br-ea, 298K
Formula	$C_{37}H_{41}Br_3O_5$	$C_{37}H_{41}Br_3O_5$	$C_{37}H_{41}Br_3O_5$	$C_{37}H_{41}Br_3O_5$	$C_{37}H_{41}Br_3O_5$	$C_{37}H_{41}Br_3O_5$
*M*r	805.43	805.43	805.43	805.43	805.43	805.43
Crystal system	triclinic	triclinic	triclinic	triclinic	triclinic	triclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a (Å)	9.6357(4)	9.6832(5)	9.7089(4)	9.7426(4)	9.7760(5)	9.8063(6)
b (Å)	13.3206(6)	13.3456(7)	13.3527(7)	13.3708(7)	13.3875(7)	13.4053(12)
c (Å)	14.8618(8)	14.8992(9)	14.9175(9)	14.9451(9)	14.9897(10)	15.0177(10)
α(°)	111.930(5)	111.677(6)	111.537(5)	111.356(5)	111.204(6)	110.995(8)
β (°)	93.132(4)	92.868(5)	92.790(4)	92.755(4)	92.694(5)	92.706(5)
γ(°)	90.688(3)	90.530(4)	90.451(4)	90.399(4)	90.304(4)	90.183(6)
V (Å^3)	1765.81(14)	1786.18(18)	1796.06(16)	1810.44(17)	1826.44(18)	1840.6(2)
Crystal size (mm)	0.6*0.4*0.4	0.6*0.4*0.4	0.6*0.4*0.4	0.6*0.4*0.4	0.6*0.4*0.4	0.6*0.4*0.4
T (K)	118(2)	154(2)	190(2)	226(2)	262(2)	298(2)
Z	2	2	2	2	2	2
F(000)	816	816	816	816	816	816
μ(mm^{-1})	3.467	3.428	3.409	3.382	3.352	3.326
Ref. collected/unique	8345	8389	8439	8504	8539	8657
Parameters	373	393	388	389	391	391
Final R indices [I>2σ(I)]	0.0468	0.0450	0.0489	0.0520	0.0632	0.0623
R indices (all data)	0.1393	0.1215	0.1424	0.1543	0.2057	0.1906
Goodness of fit on F^2	1.057	0.988	1.020	0.968	1.035	0.926

	I-ea, 118K	I-ea, 154K	I-ea, 190K	I-ea, 226K	I-ea, 262K	I-ea, 298K
Formula	$C_{37}H_{41}I_3O_5$	$C_{37}H_{41}I_3O_5$	$C_{37}H_{41}I_3O_5$	$C_{37}H_{41}I_3O_5$	$C_{37}H_{41}I_3O_5$	$C_{37}H_{41}I_3O_5$
*M*r	946.40	946.40	946.40	946.40	946.40	946.40
Crystal system	triclinic	triclinic	triclinic	triclinic	triclinic	triclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a (Å)	9.8275(5)	9.8405(7)	9.8581(4)	9.9060(5)	9.9501(4)	9.9945(5)
b (Å)	13.2269(8)	13.2389(11)	13.2593(6)	13.3034(6)	13.3296(5)	13.3552(7)
c (Å)	15.4915(8)	15.5067(10)	15.5438(6)	15.5724(7)	15.5931(7)	15.6205(8)
α(°)	111.605(5)	111.319(7)	111.200(4)	111.092(4)	110.937(4)	110.795(5)
β (°)	94.919(4)	94.776(5)	94.483(3)	94.353(4)	94.265(4)	94.271(4)
γ(°)	91.912(5)	91.678(6)	91.411(4)	91.198(4)	91.077(4)	90.921(4)
V (Å^3)	1860.74(18)	1871.5(2)	1885.38(14)	1906.61(15)	1923.95(14)	1941.73(17)
Crystal size (mm)	0.45*0.4*0.2	0.45*0.4*0.2	0.45*0.4*0.2	0.45*0.4*0.2	0.45*0.4*0.2	0.45*0.4*0.2
T (K)	118(2)	154(2)	190(2)	226(2)	262(2)	298(2)
Z	2	2	2	2	2	2
F(000)	924	924	924	924	924	924
μ(mm^{-1})	2.559	2.544	2.525	2.497	2.474	2.452
Ref. collected/unique	8591	8576	8725	8720	8923	8949
Parameters	421	416	436	421	406	426
Final R indices [I>2σ(I)]	0.0460	0.0493	0.0425	0.0471	0.0506	0.0618
R indices (all data)	0.1313	0.1368	0.1207	0.1363	0.1523	0.1923
Goodness of fit on F^2	1.056	1.007	1.087	1.085	1.100	1.126

Table S2. Interhalogen interaction geometries.

Cl-gf							
Temp.	**d(Cl2···Cl3)**	**θ1**	**θ2**	**d (Cl5···Cl6)**	**θ1**	**θ2**	**d (average)**
118 K	3.6194(8)	91.44(7)	161.93(7)	3.7561(9)	86.97(7)	171.14(7)	3.688(1)
154 K	3.652(1)	91.75(8)	161.85(8)	3.782(1)	87.26(8)	171.00(8)	3.717(1)
190 K	3.682(1)	92.04(9)	162.01(9)	3.805(1)	87.40(9)	170.97(9)	3.744(1)

Temp.	**d(Cl3···Cl8)**	**θ1**	**θ2**	**d(Cl1···Cl9)**	**θ1**	**θ2**	**d(Cl5···Cl6)**	**θ1**	**θ2**	**d(average)**
226 K	3.744(2)	87.4(1)	167.0(1)	3.837(2)	95.3(1)	164.8(1)	3.845(2)	87.0(1)	171.8(1)	3.809(3)
262 K	3.784(2)	87.9(1)	166.9(1)	3.868(2)	95.8(1)	164.3(1)	3.868(2)	87.8(1)	171.3(1)	3.837(3)
298 K	3.828(2)	88.7(1)	166.9(1)	3.906(2)	95.8(1)	164.0(1)	3.903(2)	87.9(1)	171.2(1)	3.879(3)

Br-gf							
Temp.	**d (Br2···Br3)**	**θ1**	**θ2**	**d (Br5···Br6)**	**θ1**	**θ2**	**d (average)**
118 K	3.6623(9)	89.1(2)	163.5(1)	3.7289(9)	85.9(2)	173.3(2)	3.696(1)
154 K	3.6825(9)	89.6(2)	163.4(2)	3.746(1)	85.9(2)	173.2(2)	3.714(1)
190 K	3.707(1)	89.5(2)	163.8(2)	3.760(1)	86.2(2)	173.4(2)	3.734(1)
226 K	3.737(1)	89.7(2)	164.4(2)	3.777(2)	86.6(2)	173.2(2)	3.757(2)

Temp.	**d (Br1···Br2A)**	**θ1**	**θ2**	**d (Br1···Br2B)**	**θ1**	**θ2**	**d (average)**
262 K	3.803(7)	85.3(5)	172.9(2)	3.792(8)	91.6(5)	166.6(2)	3.798(11)
298 K	3.84(1)	86.2(8)	172.8(3)	3.84(1)	90.8(7)	166.4(3)	3.84(1)

I-gf							
Temp.	**d (I2···I3)**	**θ1**	**θ2**	**d (I5···I6)**	**θ1**	**θ2**	**d (average)**
118 K	3.9048(4)	85.2(1)	170.7(1)	3.9174(4)	86.0(1)	168.5(1)	3.911(1)
154 K	3.9185(6)	85.4(2)	170.3(2)	3.9327(6)	86.4(1)	168.4(2)	3.926(1)
190 K	3.9352(7)	85.8(1)	170.1(2)	3.9486(6)	87.0(2)	168.4(2)	3.942(1)
226 K	3.9534(9)	86.2(2)	169.8(2)	3.9700(8)	87.3(2)	167.9(2)	3.962(1)
262 K	3.9764(9)	86.6(2)	169.6(2)	3.9921(9)	88.0(2)	168.1(2)	3.984(1)

Temp.	**d (I1···I2A)**	**θ1**	**θ2**				**d (average)**
298 K	4.0140(7)	87.9(1)	169.0(1)				4.0140(7)

Cl-ea							
Temp.	**d (Cl2···Cl2)**	**θ1**	**θ2**	**d (Cl1···Cl2)**	**θ1**	**θ2**	**d (average)**
118 K	3.471(3)	149.2(2)	149.2(2)	3.505(2)	95.9(2)	171.2(2)	3.488(4)
154 K	3.497(3)	149.6(2)	149.6(2)	3.525(2)	96.2(2)	171.1(2)	3.511(4)
190 K	3.523(3)	150.1(2)	150.1(2)	3.547(2)	96.3(2)	170.6(2)	3.535(4)
226 K	3.547(3)	150.5(2)	150.5(2)	3.581(2)	96.2(2)	170.6(2)	3.564(4)
262 K	3.563(3)	150.9(2)	150.9(2)	3.611(2)	96.3(2)	170.0(2)	3.587(4)
298 K	3.588(2)	151.7(2)	151.7(2)	3.653(2)	96.7(1)	170.3(2)	3.620(3)

Br-ea							
Temp.	**d (Br2···Br2)**	**θ1**	**θ2**	**d (Br1···Br2)**	**θ1**	**θ2**	**d (average)**
118 K	3.6389(6)	144.8(1)	144.8(1)	3.5482(5)	93.9(1)	170.9(1)	3.594(1)
154 K	3.6476(6)	145.3(1)	145.3(1)	3.5749(5)	94.1(1)	170.8(1)	3.611(1)
190 K	3.6551(8)	146.0(1)	146.0(1)	3.5984(6)	94.4(1)	170.6(1)	3.627(1)
226 K	3.6651(8)	146.4(1)	146.4(1)	3.6264(7)	94.5(1)	170.3(1)	3.646(1)
262 K	3.676(1)	146.5(2)	146.5(2)	3.6514(9)	94.4(2)	169.7(2)	3.664(1)
298 K	3.689(1)	147.1(2)	147.1(2)	3.6877(9)	94.8(2)	169.8(1)	3.688(1)

I-ea							
Temp.	**d (l2···l2)**	**θ1**	**θ2**	**d (l1···l2)**	**θ1**	**θ2**	**d (average)**
118 K	4.0607(6)	137.6(1)	137.6(1)	3.8175(5)	90.3(1)	170.7(1)	3.939(1)
154 K	4.0335(7)	138.0(1)	138.0(1)	3.8317(6)	90.4(1)	170.5(1)	3.933(1)
190 K	4.0132(6)	139.4(1)	139.4(1)	3.8441(5)	91.0(1)	170.0(1)	3.929(1)
226 K	3.9994(6)	140.1(1)	140.1(1)	3.8678(6)	91.2(1)	169.6(1)	3.934(1)
262 K	3.9868(7)	141.2(1)	141.2(1)	3.8941(6)	91.7(1)	169.1(1)	3.940(1)
298 K	3.9779(8)	142.1(2)	142.1(2)	3.9261(7)	92.0(2)	168.7(2)	3.952(1)

Table S3. Volume of unit cell (Vuc) / no. of host molecules per unit cell (Z).

	Vuc/Z in Cl-gf	**Vuc/Z in Br-gf**	**Vuc/Z in I-gf**		**Vuc/Z in Cl-ea**	**Vuc/Z in Br-ea**	**Vuc/Z in I-ea**
118 K	737.09625(2)	758.78750(7)	806.08750(3)		864.1550(1)	882.9050(1)	930.3700(1)
154 K	740.36250(7)	762.85000(7)	809.12500(5)		870.8550(1)	893.0900(1)	935.7500(1)
190 K	743.45000(7)	766.46250(7)	812.71250(6)		877.2550(1)	898.0300(1)	942.6900(1)
226 K	751.62500(7)	770.97500(8)	817.03750(6)		885.1500(1)	905.2200(1)	953.3050(1)
262 K	756.41666(7)	777.47500(9)	821.93750(8)		891.2500(1)	913.2200(1)	961.9750(1)
298 K	761.85833(7)	783.25000(9)	828.60000(9)		901.8000(1)	920.3000(1)	970.8650(1)

Table S4. Average Ueq values for the halogen atoms involved in interhalogen interactions.

	Guest-free systems				**Solvates**		
	Cl Ueq	**Br Ueq**	**I Ueq**		**Cl Ueq**	**Br Ueq**	**I Ueq**
118 K	33.5(3)	32.3(3)	31.1(2)		43.2(6)	36.9(2)	41.5(2)
154 K	44.5(4)	40.8(3)	40.7(2)		49.8(6)	42.2(2)	49.5(2)
190 K	55.3(4)	50.7(4)	49.3(3)		58.9(6)	50.5(2)	53.8(2)
226 K	74.1(8)	64.4(6)	60.2(3)		70.2(7)	59.5(2)	61.7(2)
262 K	89.2(9)	92.4(16)	72.3(4)		83.2(8)	69.9(3)	71.1(2)
298 K	102.9(9)	105.2(24)	96.1(3)		99.4(7)	85.8(4)	85.1(3)

Table S5. Average C–X bond lengths for the halogen atoms involved in interhalogen interactions.

	Guest-free systems				**Solvates**		
	C–Cl	**C–Br**	**C–I**		**C–Cl**	**C–Br**	**C–I**
118 K	1.750(4)	1.903(10)	2.100(8)		1.745(8)	1.904(5)	2.100(8)
154 K	1.749(5)	1.904(11)	2.101(11)		1.745(8)	1.907(5)	2.098(8)
190 K	1.747(6)	1.903(11)	2.107(11)		1.749(8)	1.905(6)	2.104(6)
226 K	1.746(7)	1.906(16)	2.099(12)		1.750(8)	1.904(6)	2.105(7)
262 K	1.748(10)	1.885(29)	2.104(16)		1.749(8)	1.894(8)	2.101(8)
298 K	1.743(9)	1.896(43)	2.100(7)		1.750(7)	1.901(8)	2.101(9)

Table S6: Statistical analysis on interhalogen interactions (CSD version 5.34, update November 2012).

Only C, H and Cl/Br/I are present, 3D coordinates available, not disordered, no error, not polymeric, no powder, no ions, only organic, X···X distance within the sum of the van der Waals radii + 0.2 Å.

	Total hits	X···X interaction present	% of occurrence
Cl	596	315	53
Br	554	324	58
I	130	82	63