Electronic Supplementary Material (ESI) for CrystEngComm

Electronic Supplementary Information for the paper

Low-melting molecular complexes. Halogen bonds in molecular complexes of bromoform.

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Table S1. The pair-wise energy and parameters of intermolecular interactions in LmMC **1**. All pairs are classified as belonging to basic heterotetramer, column of tetramers and layer of columns.

Dimer	Molecule 1	Molecule 2	Symmetry operation	E_{int}, kcal/mol	Tetramer	Column	Layer
1	CON	BF	x,y,z	-5,25	+	+	+
2	CON	BF	x,y,-1+z	-2,45		+	+
3	CON	BF	-x,1/2+y,1/2-z	-2,12			
4	CON	BF	1-x,1/2+y,1/2-z	-2,28			
5	CON	BF	-x,1-y,-z	-2,61		+	+
6	CON	BF	-x,1-y,1-z	-3,46		+	+
7	CON	BF	1-x,1-y,-z	-2,53			+
8	CON	BF	1-x,1-y,1-z	-3,13			+
9	CON	CON	-x,1-y,-z	-6,15	+	+	+
10	CON	CON	1-x,1-y,-z	-2,21			+
11	CON	CON	x,3/2-y,-1/2+z	-1,86			
12	CON	CON	x,3/2-y,1/2+z	-1,86			
13	BF	CON	x,y,z	-5,25	+	+	+
14	BF	BF	-x,1-y,1-z	-0,59	+	+	+
15	BF	BF	1-x,1-y,1-z	-3,27			+
16	BF	BF	x,1/2-y,-1/2+z	-2,19			
17	BF	BF	x,1/2-y,1/2+z	-2,19			
18	BF	CON	x,y,1+z	-2,45		+	+
19	BF	CON	-x,-1/2+y,1/2-z	-2,12			
20	BF	CON	1-x,-1/2+y,1/2-z	-2,28			
21	BF	CON	-x,1-y,-z	-2,61		+	+
22	BF	CON	-x,1-y,1-z	-3,46		+	+
23	BF	CON	1-x,1-y,-z	-2,53			+
24	BF	CON	1-x,1-y,1-z	-3,13			+

Table S2. The pair-wise energy of intermolecular interactions in LmMC **2**. All pairs are classified as belonging to a pair and a chain.

Dimer	Molecule 1	Molecule 2	Symmetry operation	E_{int}, kcal/mol	Dimer	Chain
1	DMSO	BF	x,y,z	-7,92	+	+
2	DMSO	DMSO	-1/2+x,-1/2+y,z	-0,23		
3	DMSO	DMSO	-1/2+x,1/2+y,z	-2,71		
4	DMSO	DMSO	1/2+x,-1/2+y,z	-2,71		
5	DMSO	DMSO	1/2+x,1/2+y,z	-0,23		
6	DMSO	BF	1+x,y,z	-2,52		
7	DMSO	BF	x,1-y,1/2+z	-4,77		+
8	DMSO	BF	1+x,1-y,1/2+z	-3,35		
9	DMSO	BF	1/2+x,-1/2+y,z	-1,38		
10	DMSO	BF	1/2+x,1/2+y,z	-3,52		
11	DMSO	BF	1/2+x,1/2-y,1/2+z	-1,57		
12	DMSO	BF	1/2+x,3/2-y,1/2+z	-1,92		
13	BF	DMSO	x,y,z	-7,92	+	+
14	BF	DMSO	-1+x,y,z	-2,52		
15	BF	DMSO	-1+x,1-y,-1/2+z	-3,35		
16	BF	DMSO	x,1-y,-1/2+z	-4,77		+
17	BF	DMSO	-1/2+x,-1/2+y,z	-3,52		
18	BF	DMSO	-1/2+x,1/2+y,z	-1,38		
19	BF	DMSO	-1/2+x,1/2-y,-1/2+z	-1,57		
20	BF	DMSO	-1/2+x,3/2-y,-1/2+z	-1,92		
21	BF	BF	x,1-y,-1/2+z	-1,11		+
22	BF	BF	x,1-y,1/2+z	-1,11		+
23	BF	BF	-1/2+x,-1/2+y,z	-0,87		
24	BF	BF	-1/2+x,1/2+y,z	-1,71		
25	BF	BF	1/2+x,-1/2+y,z	-1,71		
26	BF	BF	1/2+x,1/2+y,z	-0,87		

Table S3. The pair-wise energy of intermolecular interactions in LmMC **3**. Pairs belonging to basic columns are highlighted in bold.

Dimer	Molecule 1	Molecule 2	Symmetry operation	E_{int}, kcal/mol
1	**DO**	**BF**	**x,y,z**	**-3,60**
2	DO	DO	-1+x,y,-1+z	-1,38
3	**DO**	**DO**	**-1+x,y,z**	**-3,82**
4	DO	DO	x,y,-1+z	-3,25
5	DO	DO	x,y,1+z	-3,25
6	**DO**	**DO**	**1+x,y,z**	**-3,82**
7	DO	DO	1+x,y,1+z	-1,38
8	DO	BF	-1+x,y,-1+z	-2,14
9	DO	BF	x,y,-1+z	-2,13
10	**DO**	**BF**	**-x,1/2+y,-z**	**-3,60**
11	DO	BF	-x,1/2+y,1-z	-2,13
12	DO	BF	1-x,1/2+y,1-z	-2,14
13	**BF**	**DO**	**x,y,z**	**-3,60**
14	BF	DO	x,y,1+z	-2,13
15	BF	DO	1+x,y,1+z	-2,14
16	**BF**	**DO**	**-x,-1/2+y,-z**	**-3,60**
17	BF	DO	-x,-1/2+y,1-z	-2,13
18	BF	DO	1-x,-1/2+y,1-z	-2,14
19	BF	BF	-1+x,y,-1+z	-1,40
20	**BF**	**BF**	**-1+x,y,z**	**-4,91**
21	BF	BF	x,y,-1+z	-1,53
22	BF	BF	x,y,1+z	-1,53
23	**BF**	**BF**	**1+x,y,z**	**-4,91**
24	BF	BF	1+x,y,1+z	-1,40

Table S4. Bond Lengths for **1**.

Atom	Atom	Length/Å		Atom	Atom	Length/Å
Br1	C1S	1.922(5)		C1	C6	1.475(8)
Br2	C1S	1.923(5)		C2	C3	1.511(8)
Br3	C1S	1.926(5)		C3	C4	1.501(9)
O1	C1	1.222(6)		C4	C5	1.482(8)
C1	C2	1.473(7)		C5	C6	1.521(8)

Table S5. Bond Angles for **1**.

Atom	Atom	Atom	Angle/˚		Atom	Atom	Atom	Angle/˚
O1	C1	C2	121.6(5)		C1	C2	C3	112.1(5)
O1	C1	C6	122.1(5)		C4	C3	C2	112.5(5)
C2	C1	C6	116.3(5)		C5	C4	C3	110.3(5)
Br1	C1S	Br2	111.6(2)		C4	C5	C6	112.8(5)
Br1	C1S	Br3	110.2(2)		C1	C6	C5	111.1(5)
Br2	C1S	Br3	110.7(2)					

Table S6. Bond Lengths for 2.						
Atom	**Atom**	**Length/Å**		**Atom**	**Atom**	**Length/Å**
S1	O1	1.504(11)		Br1	C1S	1.910(14)
S1	C1	1.770(16)		Br2	C1S	1.918(14)
S1	C2	1.774(17)		Br3	C1S	1.957(12)

Table S7. Bond Angles for 2.								
Atom	**Atom**	**Atom**	**Angle/˚**		**Atom**	**Atom**	**Atom**	**Angle/˚**
O1	S1	C1	107.5(7)		Br1	C1S	Br2	112.5(6)
O1	S1	C2	106.5(8)		Br1	C1S	Br3	110.0(7)
C2	S1	C1	96.8(8)		Br2	C1S	Br3	110.2(7)

Table S8. Bond Lengths for 3.						
Atom	**Atom**	**Length/Å**		**Atom**	**Atom**	**Length/Å**
O1	C1	1.431(3)		C2	C1[1]	1.508(3)
O1	C2	1.431(3)		Br1	C1S	1.925(2)
O1	Br1	2.9697(16)		Br2	C1S	1.928(3)
C1	C2[1]	1.508(3)		C1S	Br1[2]	1.925(2)

[1]-X,1-Y,-Z; [2]+X,1/2-Y,+Z

Table S9. Bond Angles for 3.								
Atom	**Atom**	**Atom**	**Angle/˚**		**Atom**	**Atom**	**Atom**	**Angle/˚**
C1	O1	Br1	96.43(12)		C1S	Br1	O1	175.00(9)
C2	O1	C1	109.10(16)		Br1	C1S	Br1[2]	111.42(18)
C2	O1	Br1	118.83(15)		Br1[2]	C1S	Br2	110.84(10)
O1	C1	C2[1]	110.67(18)		Br1	C1S	Br2	110.84(10)
O1	C2	C1[1]	110.6(2)					

[1]-X,1-Y,-Z; [2]+X,1/2-Y,+Z

Table S10. Crystal data and structure refinement for 3 at 200K	
Empirical formula	$C_4H_8O_2$ x $CHBr_3$
Formula weight	340.85
Temperature/K	200
Crystal system	monoclinic
Space group	$P2_1/m$
a/Å	4.2028(4)
b/Å	19.3569(18)
c/Å	6.0247(5)
α/°	90.00
β/°	106.761(10)
γ/°	90.00
Volume/$Å^3$	469.31(7)
Z	2
ρ_{calc} mg/mm^3	2.412
μ/mm^{-1}	12.839
Reflections collected	4033
Independent reflections	1055[R(int) = 0.0179]
Data/restraints/parameters	1055/0/66
Goodness-of-fit on F^2	1.069
Final R indexes [I>=2σ (I)]	R_1 = 0.0212, wR_2 = 0.0506
Final R indexes [all data]	R_1 = 0.0234, wR_2 = 0.0516

Table S11. Crystal data and structure refinement for 3 at 240K	
Empirical formula	$C_4H_8O_2$ x $CHBr_3$
Formula weight	340.85
Temperature/K	240
Crystal system	monoclinic
Space group	$P2_1/m$
a/Å	4.2311(5)
b/Å	19.421(2)
c/Å	6.0413(6)
α/°	90.00
β/°	106.76(1)
γ/°	90.00
Volume/Å^3	475.33(9)
Z	2
ρ_{calc} mg/mm^3	2.381
μ /mm^{-1}	12.677
F(000)	320
Reflections collected	3946
Independent reflections	1075[R(int) = 0.0222]
Data/restraints/parameters	1075/0/66
Goodness-of-fit on F^2	1.064
Final R indexes [I>=2σ (I)]	R_1 = 0.0244, wR_2 = 0.0595
Final R indexes [all data]	R_1 = 0.0283, wR_2 = 0.0614