Electronic Supplementary Material (ESI) for CrystEngComm.

Supporting Information

for

Thermal expansion along one-dimensional chains and two-dimensional sheets within co-crystals based on halogen or hydrogen bonds

Kristin M. Hutchins,*[a] Daniel K. Unruh,[a] Dontrell D. Carpenter,[b] and Ryan H. Groeneman*[b]

[a]Department of Chemistry & Biochemistry, Texas Tech University, 1204 Boston Avenue, Lubbock, TX 79409, USA.

[b]Department of Biological Sciences, Webster University, 470 E. Lockwood Ave., St. Louis, MO, 63119, USA.

1. Materials and Synthesis of the Co-crystals

Materials

1,4-diiodoperfluorobenzene (**$C_6I_2F_4$**), 1,4-dibromoperfluorobenzene (**$C_6Br_2F_4$**), and 1,2,4,5-tetrabromobenzene (**$C_6Br_4H_2$**) as well as the solvent toluene were all purchased from Sigma-Aldrich Chemical (St. Louis, MO, USA) and used as received. 1,2-bis(4-pyridyl)acetylene (**4,4'-BPA**) was purchased from Synquest Laboratories (Alachua, FL, USA) and used as received. All crystallization studies were performed in 20 mL scintillation vials.

Synthesis of the co-crystal (**$C_6I_2F_4$**)•(**4,4'-BPA**)

The co-crystal (**$C_6I_2F_4$**)•(**4,4'-BPA**) was synthesized by dissolving 25 mg of **4,4'-BPA** in 2 mL of toluene, which was then combined with a separate 2 mL toluene solution containing 56 mg of **$C_6I_2F_4$** (1:1 molar equivalent). The solution was allowed to evaporate slowly. Following a period of two days, single crystals suitable for X-ray diffraction were formed.

Synthesis of the co-crystal (**$C_6Br_2F_4$**)•(**4,4'-BPA**)

The co-crystal (**$C_6Br_2F_4$**)•(**4,4'-BPA**) was synthesized by dissolving 25 mg of **4,4'-BPA** in 2 mL of toluene, which was then combined with a separate 2 mL toluene solution containing 43 mg of **$C_6Br_2F_4$** (1:1 molar equivalent). The solution was allowed to evaporate slowly. Following a period of two days, single crystals suitable for X-ray diffraction were formed.

Synthesis of the co-crystal (**$C_6Br_4H_2$**)•(**4,4'-BPA**)

The co-crystal (**$C_6Br_4H_2$**)•(**4,4'-BPA**) was synthesized by dissolving 25 mg of **4,4'-BPA** in 2 mL of toluene, which was then combined with a separate 2 mL toluene solution containing 55 mg of **$C_6Br_4H_2$** (1:1 molar equivalent). The solution was allowed to evaporate slowly. Following a period of two days, single crystals suitable for X-ray diffraction were formed.

2. X-ray Diffraction Information and Data Tables

Single crystal X-ray diffraction data for the co-crystals were collected on a Bruker PLATFORM three circle diffractometer equipped with an APEX II CCD detector and operated at 1500 W (50kV, 30 mA) to generate (graphite monochromated) Mo Kα radiation (λ = 0.71073 Å). Intensity data were corrected for Lorentz, polarization, and background effects using the Bruker program APEX II. A semi-empirical correction for adsorption was applied using the program *SADABS*[1]. The *SHELXL-2014*[2], series of programs were used for the solution and refinement of the crystal structure. All non-hydrogen atoms were refined anisotropically and hydrogen atoms bound to carbon atoms were located in the difference Fourier map and were geometrically constrained using the appropriate AFIX commands.

Table S1. X-ray data for (**$C_6I_2F_4$**)•(**4,4'-BPA**) at 270, 250, and 230 K.

compound formula	$C_{18}H_8F_4I_2N_2$	$C_{18}H_8F_4I_2N_2$	$C_{18}H_8F_4I_2N_2$
formula mass	582.06	582.06	582.06
crystal system	orthorhombic	orthorhombic	orthorhombic
space group	*Pnnm*	*Pnnm*	*Pnnm*
a/Å	15.7147(10)	15.6860(7)	15.6785(6)
b/Å	5.2415(3)	5.2395(2)	5.2396(2)
c/Å	11.1607(7)	11.1083(5)	11.0860(4)
α/°	90	90	90
β/°	90	90	90
γ/°	90	90	90
V/Å^3	919.29(10)	912.96(7)	910.70(6)
ρ_{calc}/g cm^{-3}	2.103	2.117	2.123
T/K	270	250	230
Z	2	2	2
radiation type	MoKα	MoKα	MoKα
absorption coefficient, μ/mm^{-1}	3.477	3.487	3.496
no. of reflections measured	9793	9763	9756
no. of independent reflections	1598	1591	1589
no of reflection (I > 2σ(I))	1468	1471	1483
R_{int}	0.0305	0.0316	0.0300
R_1 (I > 2σ(I))	0.0200	0.0178	0.0174
wR(F^2) (I > 2σ(I))	0.0486	0.0422	0.0428
R_1 (all data)	0.0231	0.0200	0.0191
wR(F^2) (all data)	0.0500	0.0431	0.0435
Goodness-of-fit	1.127	1.120	1.125
CCDC deposition number	1850148	1850147	1850146

Table S2. X-ray data for (**$C_6I_2F_4$**)•(**4,4'-BPA**) at 210 and 190 K.

compound formula	$C_{18}H_8F_4I_2N_2$	$C_{18}H_8F_4I_2N_2$
formula mass	582.06	582.06
crystal system	orthorhombic	orthorhombic
space group	*Pnnm*	*Pnnm*
a/Å	15.6537(5)	15.6409(8)
b/Å	5.2381(2)	5.2384(3)
c/Å	11.0524(3)	11.0229(5)
α/°	90	90
β/°	90	90
γ/°	90	90
V/Å^3	906.25(5)	903.14(8)
ρ_{calc}/g cm^{-3}	2.133	2.140
T/K	210	190
Z	2	2
radiation type	MoKα	MoKα
absorption coefficient, μ/mm^{-1}	3.513	3.525
no. of reflections measured	9715	9683
no. of independent reflections	1584	1574
no of reflection (I > 2σ(I))	1478	1460
R_{int}	0.0324	0.0724
R_1 (I > 2σ(I))	0.0166	0.0309
wR(F^2) (I > 2σ(I))	0.0406	0.0748
R_1 (all data)	0.0185	0.0328
wR(F^2) (all data)	0.0415	0.0758
Goodness-of-fit	1.131	1.085
CCDC deposition number	1850145	1850144

Table S3. X-ray data for (**$C_6Br_2F_4$**)•(**4,4'-BPA**) at 270, 250, and 230 K.

compound formula	$C_{18}H_8F_4Br_2N_2$	$C_{18}H_8F_4Br_2N_2$	$C_{18}H_8F_4Br_2N_2$
formula mass	488.08	488.08	488.08
crystal system	monoclinic	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1/c$	$P2_1/c$
a/Å	15.1283(5)	15.1069(5)	15.0878(5)
b/Å	5.27450(10)	5.2772(2)	5.2804(2)
c/Å	11.2948(4)	11.2674(4)	11.2408(4)
α/°	90	90	90
β/°	111.348(2)	111.344(2)	111.346(2)
γ/°	90	90	90
V/Å^3	839.42(4)	836.65(5)	834.11(5)
ρ_{calc} /g cm^{-3}	1.931	1.937	1.943
T/K	270	250	230
Z	2	2	2
radiation type	MoKα	MoKα	MoKα
absorption coefficient, μ/mm^{-1}	4.874	4.890	4.905
no. of reflections measured	11249	11205	11175
no. of independent reflections	2808	2797	2791
no of reflection (I > 2σ(I))	2098	2121	1967
R_{int}	0.0407	0.0410	0.0657
R_1 (I > 2σ(I))	0.0303	0.0294	0.0295
wR(F^2) (I > 2σ(I))	0.0596	0.0584	0.0499
R_1 (all data)	0.0534	0.0498	0.0504
wR(F^2) (all data)	0.0664	0.0641	0.0530
Goodness-of-fit	1.020	1.024	0.869
CCDC deposition number	1850143	1850142	1850141

Table S4. X-ray data for (**$C_6Br_2F_4$**)•(**4,4'-BPA**) at 210 and 190 K.

compound formula	$C_{18}H_8F_4Br_2N_2$	$C_{18}H_8F_4Br_2N_2$
formula mass	488.08	488.08
crystal system	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1/c$
a/Å	15.0775(9)	15.0550(7)
b/Å	5.2848(3)	5.2838(2)
c/Å	11.2151(7)	11.1874(5)
α/°	90	90
β/°	111.405(4)	111.335(3)
γ/°	90	90
V/Å^3	832.00(9)	828.94(6)
ρ_{calc} /g cm^{-3}	1.948	1.955
T/K	210	190
Z	2	2
radiation type	MoKα	MoKα
absorption coefficient, μ/mm^{-1}	4.918	4.936
no. of reflections measured	11083	11101
no. of independent reflections	2777	2770
no of reflection (I > 2σ(I))	2010	2061
R_{int}	0.0648	0.0605
R_1 (I > 2σ(I))	0.0277	0.0277
wR(F^2) (I > 2σ(I))	0.0493	0.0496
R_1 (all data)	0.0462	0.0451
wR(F^2) (all data)	0.0520	0.0523
Goodness-of-fit	0.870	0.890
CCDC deposition number	1850140	1850139

Table S5. X-ray data for (**$C_6Br_4H_2$**)•(**4,4'-BPA**) at 270, 250, and 230 K.

compound formula	$C_{18}H_{10}Br_4N_2$	$C_{18}H_{10}Br_4N_2$	$C_{18}H_{10}Br_4N_2$
formula mass	573.92	573.92	573.92
crystal system	triclinic	triclinic	triclinic
space group	*P-1*	*P-1*	*P-1*
a/Å	3.9684(4)	3.9578(3)	3.9472(3)
b/Å	13.2770(14)	13.2665(11)	13.2528(10)
c/Å	18.217(2)	18.2186(18)	18.2138(15)
α/°	73.014(3)	72.926(3)	72.838(2)
β/°	85.807(3)	85.798(3)	85.776(2)
γ/°	84.125(3)	84.065(2)	83.982(2)
V/Å^3	912.18(17)	908.60(14)	904.43(12)
ρ_{calc} /g cm^{-3}	2.090	2.098	2.107
T/K	270	250	230
Z	2	2	2
radiation type	MoKα	MoKα	MoKα
absorption coefficient, μ/mm^{-1}	8.826	8.860	8.901
no. of reflections measured	10298	10374	10322
no. of independent reflections	4461	4510	4483
no of reflection (I > 2σ(I))	3332	3452	3203
R_{int}	0.0305	0.0307	0.0890
R_1 (I > 2σ(I))	0.0320	0.0305	0.0530
wR(F^2) (I > 2σ(I))	0.0678	0.0662	0.1277
R_1 (all data)	0.0516	0.0470	0.0701
wR(F^2) (all data)	0.0740	0.0715	0.1329
Goodness-of-fit	1.020	1.006	0.966
CCDC deposition number	1850153	1850152	1850151

Table S6. X-ray data for (**$C_6Br_4H_2$**)•(**4,4'-BPA**) at 210 and 190 K.

compound formula	$C_{18}H_{10}Br_4N_2$	$C_{18}H_{10}Br_4N_2$
formula mass	573.92	573.92
crystal system	triclinic	triclinic
space group	*P-1*	*P-1*
a/Å	3.9366(3)	3.9272(3)
b/Å	13.2445(10)	13.2313(11)
c/Å	18.2177(16)	18.2212(16)
α/°	72.763(2)	72.682(2)
β/°	85.794(2)	85.789(2)
γ/°	83.955(2)	83.900(2)
V/Å^3	901.25(13)	897.90(13)
ρ_{calc} /g cm^{-3}	2.115	2.123
T/K	210	190
Z	2	2
radiation type	MoKα	MoKα
absorption coefficient, μ/mm^{-1}	8.933	8.966
no. of reflections measured	10293	10236
no. of independent reflections	4471	4453
no of reflection (I > 2σ(I))	3312	3418
R_{int}	0.0865	0.0852
R_1 (I > 2σ(I))	0.0527	0.0507
wR(F^2) (I > 2σ(I))	0.1264	0.1258
R_1 (all data)	0.0664	0.0625
wR(F^2) (all data)	0.1303	0.1298
Goodness-of-fit	0.994	0.965
CCDC deposition number	1850150	1850149

3. Thermal Expansion Data and Intermolecular Interaction Distances

The thermal expansion coefficients were calculated using the PASCal program.[3] The crystallographic data sets were collected at 270, 250, 230, 210, and 190 K and used for the thermal expansion calculations.

Table S7. Thermal expansion coefficients (270-190 K) for co-crystals with error denoted in parentheses and approximate crystallographic axes denoted in brackets.

Co-crystal	α_{X_1} (MK^{-1}) [axis]	α_{X_2} (MK^{-1}) [axis]	α_{X_3} (MK^{-1}) [axis]	α_V (MK^{-1})
($C_6I_2F_4$)•(4,4'-BPA)	4(1) [0 1 0]	46(3) [-1 0 0]	124(4) [0 0 1]	177
($C_6Br_2F_4$)•(4,4'-BPA)	-25(4) [0 1 0]	58(2) [-3 0 -1]	121(1) [1 0 5]	155
($C_6Br_4H_2$)•(4,4'-BPA)	-13(1) [0 1 2]	69(1) [2 2 -1]	143(2) [-5 1 0]	200

Table S8. Intermolecular interaction distances within the various co-crystals that contribute to the thermal expansion parameters.

Co-crystal	N···X halogen bond or C-H···N hydrogen bond (Å) 270 K	N···X halogen bond or C-H···N hydrogen bond (Å) 190 K	Change (Å)
($C_6I_2F_4$)•(4,4'-BPA)	2.5861	2.5714	0.0147
($C_6Br_2F_4$)•(4,4'-BPA)	2.8928	2.8640	0.0288
($C_6Br_4H_2$)•(4,4'-BPA)	3.394 3.345	3.381 3.322	0.013 0.023

Co-crystal	C-H(pyr) ···F/Br (Å) 270 K	C-H(pyr) ···F/Br (Å) 190 K	Change (Å)
($C_6I_2F_4$)•(4,4'-BPA)	3.170 3.265	3.135 3.228	0.035 0.037
($C_6Br_2F_4$)•(4,4'-BPA)	3.401	3.364	0.037
($C_6Br_4H_2$)•(4,4'-BPA)	3.577 3.697 3.952	3.548 3.694 3.921	0.029 0.003 0.031

Co-crystal	C(benz, pyr)···X (Å) 270 K	C(benz, pyr)···X (Å) 190 K	Change (Å)
($C_6I_2F_4$)•(4,4'-BPA)	3.921 3.932 3.891	3.906 3.918 3.878	0.015 0.014 0.013
($C_6Br_2F_4$)•(4,4'-BPA)	3.630 3.489 3.703	3.614 3.470 3.688	0.016 0.019 0.015
($C_6Br_4H_2$)•(4,4'-BPA)	-	-	-

Co-crystal	C(benz)···F/Br (Å) 270 K	C(benz)···F/Br (Å) 190 K	Change (Å)
($C_6I_2F_4$)•(4,4'-BPA)	-	-	-
($C_6Br_2F_4$)•(4,4'-BPA)	3.144	3.110	0.034
($C_6Br_4H_2$)•(4,4'-BPA)	3.694	3.648	0.046

Co-crystal	Br···Br (Å) 270 K	Br···Br (Å) 190 K	Change (Å)
($C_6I_2F_4$)•(4,4'-BPA)	-	-	-
($C_6Br_2F_4$)•(4,4'-BPA)	-	-	-
($C_6Br_4H_2$)•(4,4'-BPA)	3.678	3.633	0.045

Co-crystal	π··· π (Å) 270 K	π··· π (Å) 190 K	Change (Å)
($C_6I_2F_4$)•(4,4'-BPA)	-	-	-
($C_6Br_2F_4$)•(4,4'-BPA)	-	-	-
($C_6Br_4H_2$)•(4,4'-BPA)	3.480 3.507	3.432 3.478	0.048 0.029

References

1. Krause *et al.*, (2015) SADABS v 2016/2.

2. G. M. Sheldrick, *Acta Crystallogr*. 2015, **C71**, 3.

3. M. J. Cliffe, A. L. Goodwin, *J. Appl. Crystallogr*. 2012, **45**, 1321.