Supplementary Information for

Elastic Flexibility of Ferroelectric Supramolecular Co-crystals

Qianqian Luo,[a] Chunli Jiang,[b] Hechun Lin, [a] Chunhua Luo,*[a] Ruijuan Qi*[a] and Hui Peng, [a,c]

[a]Key Laboratory of Polar Materials and Devices (MOE), Department of Optoelectronics, East China Normal University, Shanghai 200241, China.

[b]National Laboratory for Infrared Physics, Shanghai Institute of Technical Physics, Chinese Academy of Sciences, 500 Yu Tian Road, Shanghai 200083, China

[c]Collaborative Innovation Center of Extreme Optics, Shanxi University, Taiyuan, Shanxi 030006, China

Crystallographic Data

Table S1. Crystal data and structure refinement for Phz-H_2ca and Phz-H_2ba

Empirical formula	$C_{18}H_{10}Cl_2N_2O_4$	$C_{18}H_{10}Br_2N_2O_4$
Temperature / K	298	298
Wavelength / Å	1.54178	1.54178
Formula weight /g mol^{-1}	389.18	478.10
Crystal system	monoclinic	monoclinic
Phase	$P2_1/n$	$P2_1/n$
a / Å	12.420(3)	12.3823(10)
b / Å	3.793(3)	3.9230(3)
c / Å	16.904(1)	17.4208(13)
α / °	90	90
β / °	107.88(1)	107.852(2)
γ / °	90	90
Volume/ $Å^3$	757.87(20)	805.48(11)
Z	2	2
Calc. density/ $g·cm^{-3}$	1.70533	1.97113
μ /mm^{-1}	4.135	6.651
F(000)	396.0	478.1
h, k, l_{max}	14,4,20	14,4,20
θ_{max}	68.244	68.285
R (reflections)	0.0310(1245)	0.0193(1410)
wR2(reflections)	0.0765(1383)	0.0559(1461)
Data completeness	0.991	0.988

S	1.125		1.090

Table S2 Selected bond lengths (Å) and bond angles (°) for Phz-H$_2$ca.

$C_{12}H_8N_2$-$C_6H_2O_4Cl_2$ (1)			
Bond lengths (Å)		Bond angles (°)	
Cl1-C8	1.7208(19)	C4-N1-C3	118.46(17)
O1-H1A	0.8400	N1-C4-C3^{i}	121.03(17)
O1-C7	1.310(2)	N1-C4-C5	119.77(18)
O2-C9	1.224(2)	C5-C4-C3^{i}	119.20(18)
N1-C4	1.344(3)	N1-C3-C4^{i}	120.51(18)
N1-C3	1.350(2)	N1-C3-C2	120.05(18)
C4-C3^{i}	1.436(3)	C2-C3-C4^{i}	119.44(17)
C4-C5	1.422(3)	O1-C7-C9^{ii}	117.16(17)
C3-C2	1.424(3)	O1-C7-C8	121.71(18)
C7-C9^{ii}	1.518(3)	C8-C7-C9^{ii}	121.13(17)
C7-C8	1.354(3)	O2-C9-C7^{ii}	118.15(17)
C9-C8	1.446(3)	O2-C9-C8	124.66(18)
C2-H2	0.9500	C8-C9-C7^{ii}	117.19(17)
C2-C1	1.355(3)	C1-C2-C3	119.57(19)
C5-H5	0.9500	C7-C8-Cl1	120.08(15)
C5-C6	1.361(3)	C7-C8-C9	121.67(18)
C1-H1	0.9500	C9-C8-Cl1	118.26(15)
C1-C6^{i}	1.424(3)	C6-C5-C4	119.45(19)
C6-H6	0.9500	C2-C1-C6^{i}	121.05(19)
		C5-C6-C1^{i}	121.27(18)

Symmetry Operators: (i) -x, 2-y, 1-z; (ii) 1-x, 1-y, 1-z.

Table S3 Selected bond lengths (Å) and bond angles (°) for Phz-H$_2$ba.

$C_{12}H_8N_2$-$C_6H_2O_4Br_2$ (2)			
Bond lengths (Å)		Bond angles (°)	
Br1-C8	1.8761(18)	C1-N1-C6^{i}	118.01(16)
O1-H1	0.8400	C7-C8-Br1	120.23(14)
O1-C7	1.311(2)	C7-C8-C9	121.54(16)
O2-C9	1.221(2)	C9-C8-Br1	118.22(13)
N1-C6^{i}	1.347(3)	O1-C7-C8	121.87(17)
N1-C1	1.344(3)	O1-C7-C9^{ii}	117.25(15)
C8-C7	1.357(3)	C8-C7-C9^{ii}	120.87(16)
C8-C9	1.450(3)	O2-C9-C8	124.22(18)
C7-C9^{ii}	1.510(3)	O2-C9-C7^{ii}	118.20(17)
C6-C1	1.438(3)	C8-C9-C7^{ii}	117.58(16)
C6-C5	1.422(3)	N1^{i}-C6-C1	120.86(18)
C1-C2	1.426(3)	N1^{i}-C6-C5	119.57(18)
C3-H3	0.9500	C5-C6-C1	119.57(18)

C3-C2	1.353(3)	N1-C1-C6	121.13(17)
C3-C4	1.420(3)	N1-C1-C2	120.22(16)
C2-H2	0.9500	C2-C1-C6	118.65(17)
C5-H5	0.9500	C2-C3-C4	121.1(2)
C5-C4	1.364(4)	C3-C2-C1	120.17(18)
C4-H4	0.9500	C4-C5-C6	119.43(19)
		C5-C4-C3	121.1(2)

Symmetry Operators: (i) 1-x, 1-y, 1-z; (ii) 2-x, 2-y, 1-z.

Table S4 Selected hydrogen-bond parameters for Phz-H_2ca and Phz-H_2ba.

D−H···A	d(D−H) (Å)	d(H···A) (Å)	d(D···A) (Å)	∠(DHA) (°)
1				
O(1)-H(1A)···N(1)	0.8401(16)	2.0385(18)	2.7114(24)	136.636(111)
C(5)-H(5)···O(2)	0.9501(22)	2.6094(16)	3.3602(28)	136.201(126)
2				
O(1) -H(1) ···N(1)	0.8394(16)	2.0493(17)	2.7435(24)	139.666(109)
C(5)-H(5)···O(2)	0.9502(22)	2.5807(18)	3.320(30)	134.859(140)

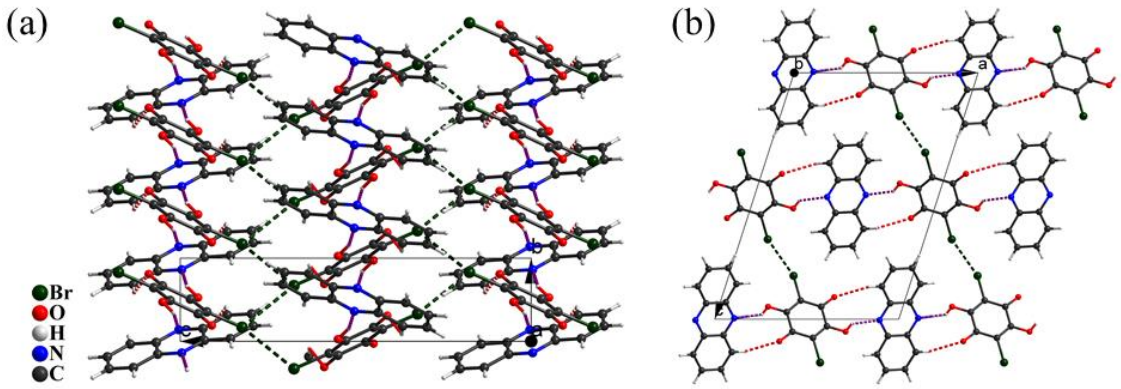

Figure S1. The molecular stacking of Phz-H_2ba viewed along *a* axis (a) and along *b* axis (b) showing O–H···N (purple) and C–H···O (red) hydrogen bonds and C–Br···Br halogen bonds (dark green).