Supplementary Information

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Crystallographic data

Table S1. Crystallographic parameters of the crystals

	APR:2-ClBA	APR:3-ClBA	APR:4-ClBA	APR:3-BrBA	APR:4-BrBA
CSD no	2477189	2477191	2477193	2477190	2477192
Molecular formula	$C_{22}H_{24}N_2O_7S$, ½($C_7H_5ClO_2$)	$C_{22}H_{24}N_2O_7S$, ½($C_7H_5ClO_2$)	$C_{22}H_{24}N_2O_7S$, ½($C_7H_5ClO_2$)	$C_{22}H_{24}N_2O_7S$, ½($C_7H_5BrO_2$)	$C_{22}H_{24}N_2O_7S$, ½($C_7H_5BrO_2$)
Mr, g/mol	538.79	538.79	538.79	561.02	561.02
Crystal system	Tetragonal	Tetragonal	Orthorhombic	Tetragonal	Orthorhombic
Space group	$P4_12_12$	$P4_12_12$	$P2_12_12_1$	$P4_12_12$	$P2_12_12_1$
a, Å	13.0114(3)	13.01710(10)	13.1247(5)	13.0239(3)	13.2266(3)
b, Å	13.0114(3)	13.01710(10)	13.4043(5)	13.0239(3)	13.4694(3)
c, Å	29.2398(9)	29.3731(5)	28.9113(11)	29.5351(7)	13.4694(3)
V, Å^3	4950.2(3)	4977.12(11)	5086.3(3)	5009.8(3)	5144.58(19)
Z	8	8	8	8	8
ρ_{calc}, g/cm^3	1.446	1.438	1.407	1.488	1.449
F_{000}	2256	2256	2256	2328	2328
μ_{CuKa}, mm^{-1}	2.130	2.118	2.073	2.548	2.481
T, K	180	180	180	180	180
Crystal size, mm	0.19×0.22×0.22	0.06×0.07×0.14	0.26×0.27×0.46	0.09×0.11×0.18	0.16×0.16×0.20
ϑ range, °	3.718 – 72.167	3.714 – 67.941	3.057 – 72.347	3.71 – 72.323	3.61 – 72.380
Data collected	67519	49951	75724	84045	70611
Data obs,. $I > 2\ \sigma(I)$	4882	4494	10005	4846	9881
Data/Restrains/N_{par}	4882/150/388	4494/139/388	10035/10/680	4949/152/388	10186/10/680
R_1 ($I > 2\ \sigma(I)$)	0.0456	0.0394	0.0305	0.0832	0.0418
wR_1 ($I > 2\ \sigma(I)$)	0.1300	0.0833	0.0835	0.1976	0.1230
R	0.0460	0.0450	0.0306	0.0842	0.0427
wR	0.1304	0.0918	0.0837	0.1976	0.1234
GOF	0.9999	0.9999	1.0114	1.0000	1.0000
$\Delta\rho_{min}$, $\Delta\rho_{max}$, e Å^{-3}	-0.43, 0.84	-0.23, 0.25	-0.41, 0.19	-0.50, 0.50	-0.87, 0.63
Flack's *x*[1]	0.002(4)	0.006(4)	0.009(19)	0.052(6)	0.001(2)

1. Parsons, S.; Flack, HD.; Wagner, T. Use of intensity quotients and differences in absolute structure refinement. *Acta Crystallogr B Struct Sci Cryst Eng Mater*. **2013,** *69*,249-59. DOI: 10.1107/S2052519213010014.

List of hydrogen bond distances

Table S2. Important hydrogen bonds data in APR cocrystal structures with 2-ClBA, 3-ClBA, 4-ClBA, 3-BrBA, 4-BrBA

Compound	D – H ···A	*d*(D–H) (Å)	*d*(H···A) (Å)	*d*(D···A) (Å)	*d*(D – H··· A) (˚)
APR:2-ClBA	N2 – H22···O2	0.84(2)	2.30(2)	2.972(3)	138(2)
	O69 – H691·· O6$^{\#4}$	0.83(7)	2.05(7)	2.851(7)	165(13)
	C2 – H21·· O3	0.92	2.32	2.891(4)	120
	C11 – H111···O2	0.95	2.43	2.912(3)	111
	C12 – H121·· O1 $^{\#1}$	0.98	2.28	3.149(3)	148
	C12 – H122···O3$^{\#2}$	0.98	2.49	3.446(3)	165
	C13 – H131···O2$^{\#3}$	0.93	2.30	3.081(4)	141
	C13 – H132···O4$^{\#1}$	0.96	2.55	3.368(4)	144
	C15 – H151·· O4$^{\#2}$	0.95	2.54	3.255(3)	132
	C16 – H161···O5$^{\#2}$	0.92	2.47	3.370(3)	168
	C19 – H191···O1$^{\#1}$	0.90	2.49	3.396(3)	179
Symmetry code: #1: 1-y, 1-x, 1/2-z; #2: -1/2 +x, ½-y, ¾-z; #3: ½+x, ½-x, -1/4+z; #4: ½ +x, 3/2-y, ¾-z					
APR:3-ClBA	N2 – H22···O2	0.83(4)	2.31(3)	2.974(3)	137(3)
	O69 – H691···O7	1.05(9)	1.71(9)	2.722(6)	160(7)
	C2 – H21···O3	0.92	2.32	2.880(4)	119
	C11 – H111···O2	0.95	2.42	2.913(3)	112
	C12 – H121···O3$^{\#1}$	0.98	2.46	3.431(3)	172
	C12 – H122···O1	1.00	2.51	3.093(3)	117
	C12 – H122···O1$^{\#2}$	1.00	2.31	3.160(3)	142
	C13 – H131···O2$^{\#3}$	0.99	2.35	3.099(4)	132
	C13 – H133···O4$^{\#2}$	0.98	2.46	3.351(4)	150
	C15 – H151···O1$^{\#2}$	0.94	2.52	3.452(3)	177
	C18 – H181···O5$^{\#1}$	0.92	2.50	3.407(3)	167
	C19 – H191···O4$^{\#1}$	0.95	2.56	3.278(3)	132
	C21 – H211···O69$^{\#2}$	0.97	2.57	3.528(7)	167
	C21 – H213···Cl1$^{\#4}$	0.99	2.58	3.397(5)	141
Symmetry code: #1: 1-y,1-x,1/2-z; #2: 1/2+x,3/2y,3/4-z; #3: -1/2+y,3/2-x,-1/4+z; #4: 3/2-x,1/2+y,1/4-z					
APR:4-ClBA	N2 – H22···O2	0.840(19)	2.273(18)	2.9466(19)	137.4(16)
	N32 – H322···O32	0.846(18)	2.322(18)	2.9773(19)	134.6(16)
	O69 – H691···O6	0.86(2)	2.26(3)	2.955(2)	137(3)
	O69 – H691···O7	0.86(2)	2.08(3)	2.807(2)	141(2)
	C2 – H21···O3	0.93	2.30	2.896(2)	119
	C11 – H111···O2	0.96	2.48	2.9079(19)	107
	C12 – H122···O1	0.94	2.53	3.090(2)	118
	C12 – H122···O31	0.94	2.53	3.182(2)	150
	C12 – H122···O3$^{\#1}$	0.96	2.59	3.535(2)	167
	C13 – H131···O32$^{\#2}$	0.97	2.30	3.058(3)	134
	C13 – H133···O34	1.01	2.43	3.352(3)	151
	C15 – H151···O31	0.92	2.41	3.331(3)	179
	C18 – H181···O5$^{\#1}$	0.95	2.42	3.361(2)	172
	C19 – H191···O4$^{\#1}$	0.95	2.51	3.206(2)	130
	C32 – H321···O33	0.95	2.29	2.882(2)	120
	C34 – H122···O3$^{\#1}$	0.94	2.57	3.502(2)	170
	C41 – H411···O32	0.95	2.46	2.9216(19)	110
	C42 – H421···O33$^{\#3}$	0.96	2.44	3.401(2)	174
	C42– H422···O1	0.96	2.38	3.246(2)	151
	C42– H422···O31	0.96	2.50	3.097(2)	121
	C43– H433···O4	0.96	2.54	3.430(3)	154
	C49– H491···O34$^{\#3}$	0.92	2.59	3.267(2)	130
Symmetry code: #1: 1/2+x,1/2-y,1-z; #2: -x,-1/2+y,3/2-z, #3: -x,1/2+y,3/2-z					

APR:3-BrBA	N2 – H22···O2	0.86(4)	2.31(4)	2.962(6)	132(3)
	O69 – H691···O7	0.82(13)	2.04(13)	2.714(12)	139(1)
	C2 – H21···O3	0.92	2.27	2.875(4)	123
	C11 – H113···O2$^{\#2}$	0.99	2.40	3.312(8)	130
	C11 – H111···O4$^{\#1}$	0.95	2.53	3.362(9)	146
	C12 – H121···O3$^{\#3}$	0.98	2.46	3.431(3)	172
	C12 – H122···O1	0.93	2.53	3.092(8)	119
	C12 – H122···O1$^{\#1}$	0.93	2.35	3.167(8)	145
	C13 – H131···O2	0.99	2.49	2.909(7)	105
	C15 – H151···O1$^{\#1}$	0.91	2.55	3.461(3)	176
	C18 – H181···O5$^{\#3}$	0.94	2.51	3.433(8)	170
	C19 – H191···O4$^{\#3}$	0.94	2.54	3.267(8)	134
	C21 – H211···O69$^{\#5}$	1.02	2.44	3.434(18)	165
	C21 – H213···Br1$^{\#4}$	0.96	2.49	3.319(12)	145
	C21 – H221···O68#1	0.99	2.55	3.071(16)	113
Symmetry code: #1: y,x,1-z; #2: -1/2+y,1/2-x,-1/4+z; #3: 1/2-x,1/2+y,5/4-z; #4: -1/2+y,3/2-x,-1/4+z; #5: 1/2+y,3/2-x,-1/4+z					
APR:4-BrBA	N2 – H22···O2	0.85(3)	2.28(3)	2.949(3)	136(2)
	N32 – H320···O32	0.85(3)	2.31(2)	2.974(3)	135(2)
	O69 – H691···O6	0.83(4)	2.28(7)	2.924(4)	136(5)
	O69 – H691···O7	0.83(7)	2.07(7)	2.794(4)	147(6)
	C2 – H21···O3	0.89	2.32	2.897(4)	122
	C11 – H111···O2	0.95	2.48	2.904(3)	107
	C12 – H121···O3$^{\#1}$	0.94	2.58	3.520(4)	176
	C12 – H122···O31$^{\#2}$	0.95	2.50	3.089(4)	120
	C13 – H131···O32$^{\#3}$	0.96	2.30	3.073(4)	136
	C13 – H133···O34$^{\#2}$	0.98	2.46	3.363(5)	153
	C15 – H151···O31$^{\#2}$	0.90	2.44	3.338(3)	178
	C18 – H181···O5$^{\#1}$	0.90	2.48	3.368(4)	169
	C19 – H191···O4$^{\#1}$	0.93	2.53	3.218(4)	131
	C32 – H321···O33	0.93	2.30	2.888(4)	121
	C34 – H122···O3$^{\#4}$	0.91	2.56	3.458(4)	167
	C41 – H411···O32	0.97	2.51	2.928(3)	106
	C42 – H421···O1	0.97	2.36	3.259(3)	153
	C42– H421···O31	0.97	2.51	3.103(3)	119
	C42– H422···O33$^{\#5}$	0.98	2.42	3.389(4)	171
Symmetry code: #1: -1/2+x,-1/2-y,1-z; #2: 1+x,-1+y,z; #3: 1-x,-3/2+y,1/2-z; #4: -3/2+x,1/2-y,1-z; #5: -x,1/2+y,1/2-z					

Three centered hydrogen bond in APR:CA[12] crystal structure

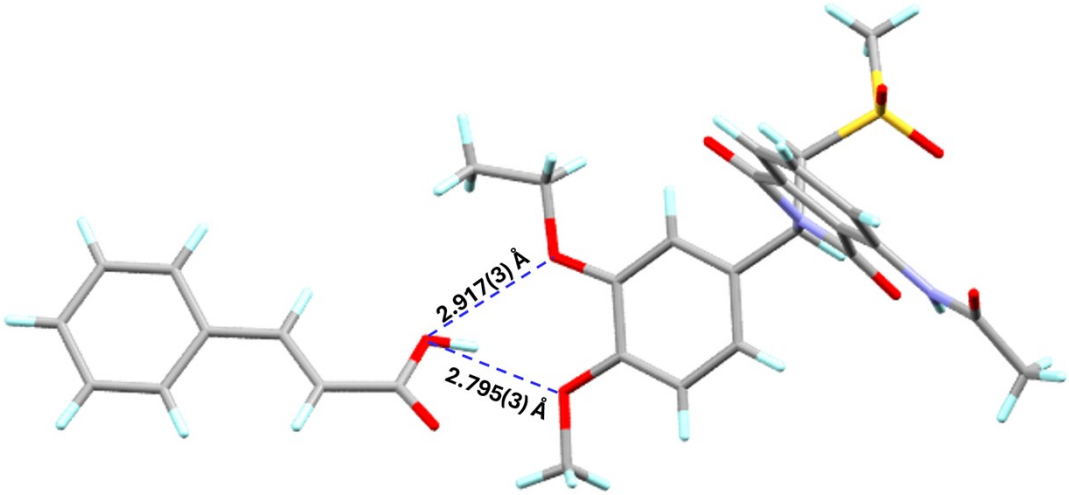

Figure S1. D···A distances in the structure of APR:CA$^-$

π – π interaction in the crystal structures

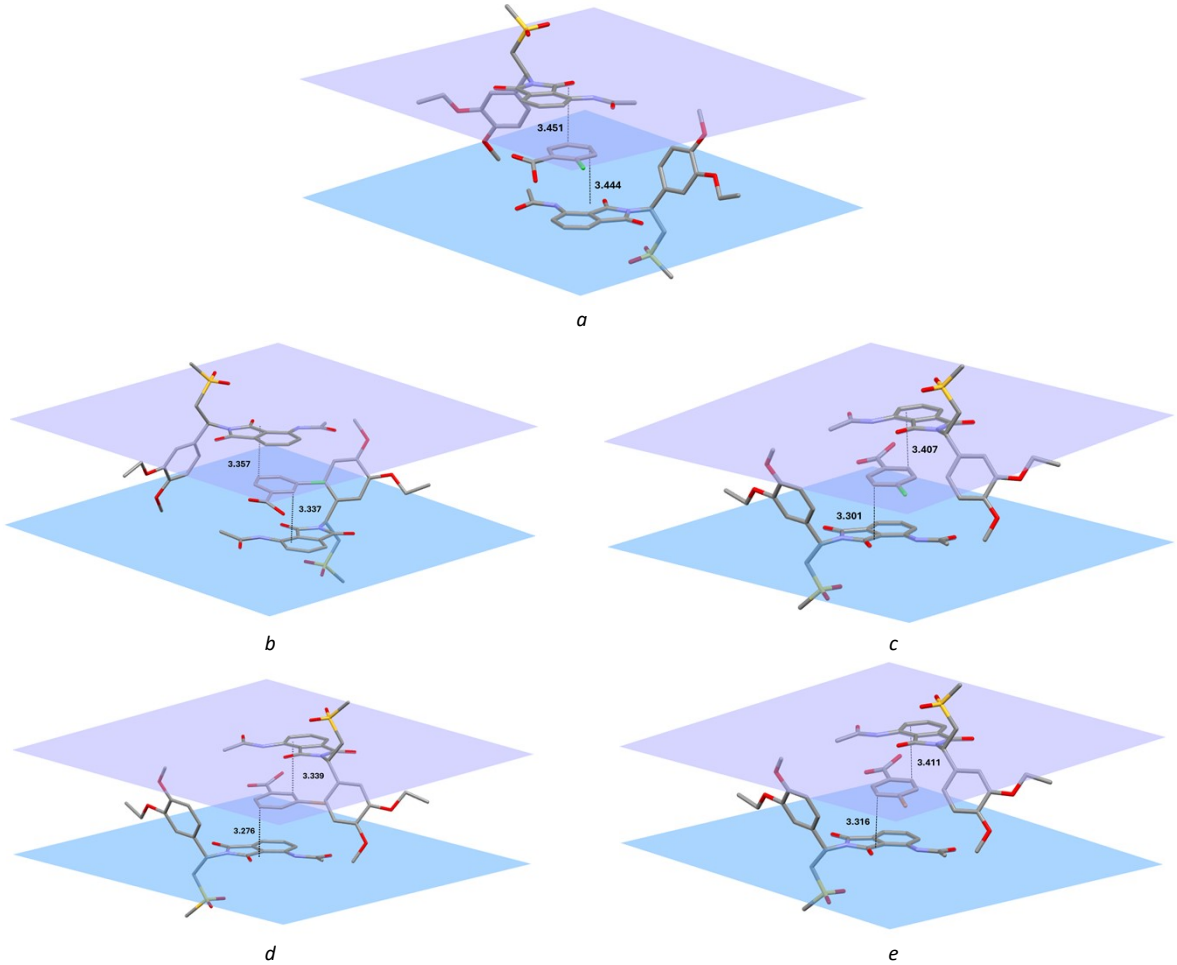

Figure S2. Distance between the coformer and APR benzene rings involved in the π – π interaction in structures *a*: APR:2-ClBA; *b*: APR:3-ClBA; *c*: APR:4-ClBA; *d*: APR:3-BrBA; *e*: APR:4-ClBA

PXRD patterns of APR cocrystals

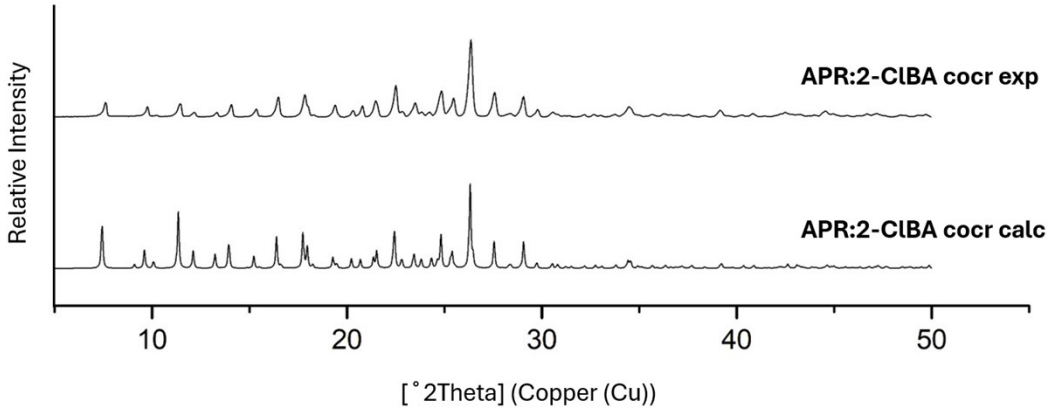

Figure S3-a PXRD of 2-ClBA system

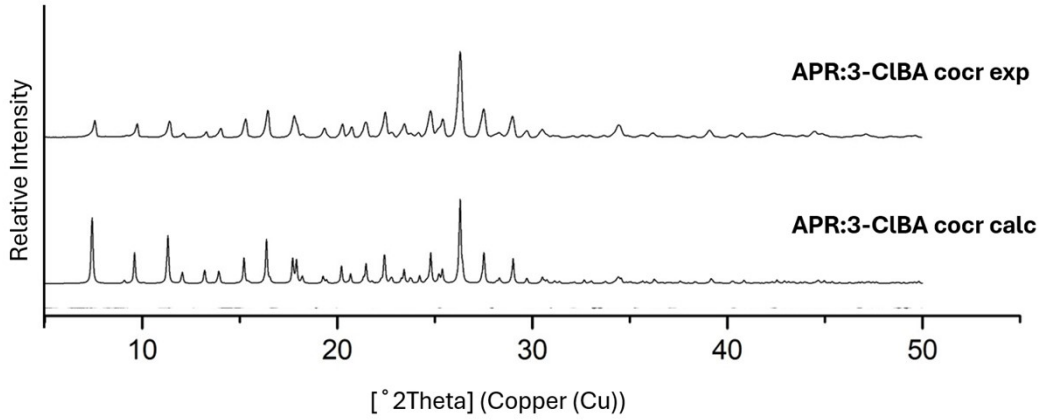

Figure S3-b PXRD of 3-CLBA system

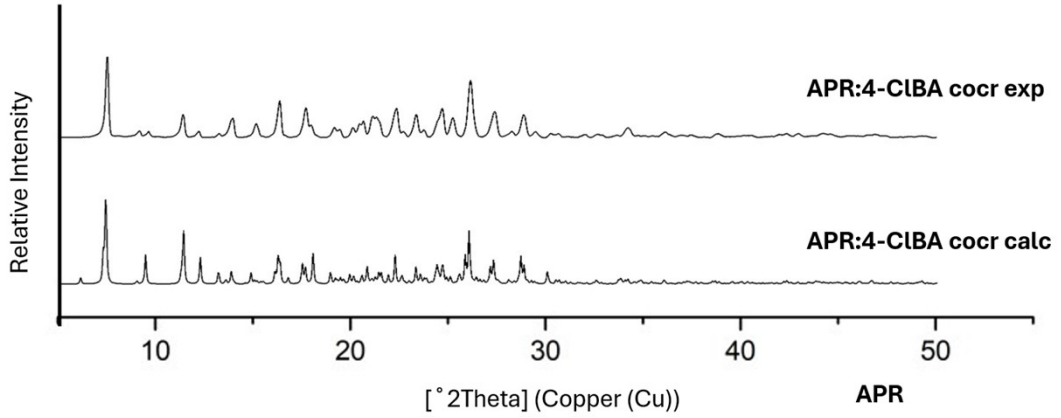

Figure S3-c PXRD of 4-ClBA system

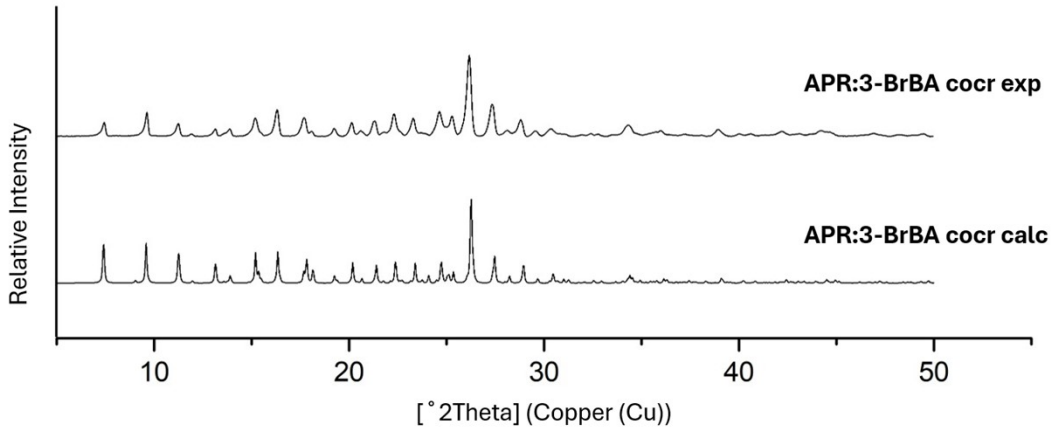

Figure S3-d PXRD of 3-BrBA system

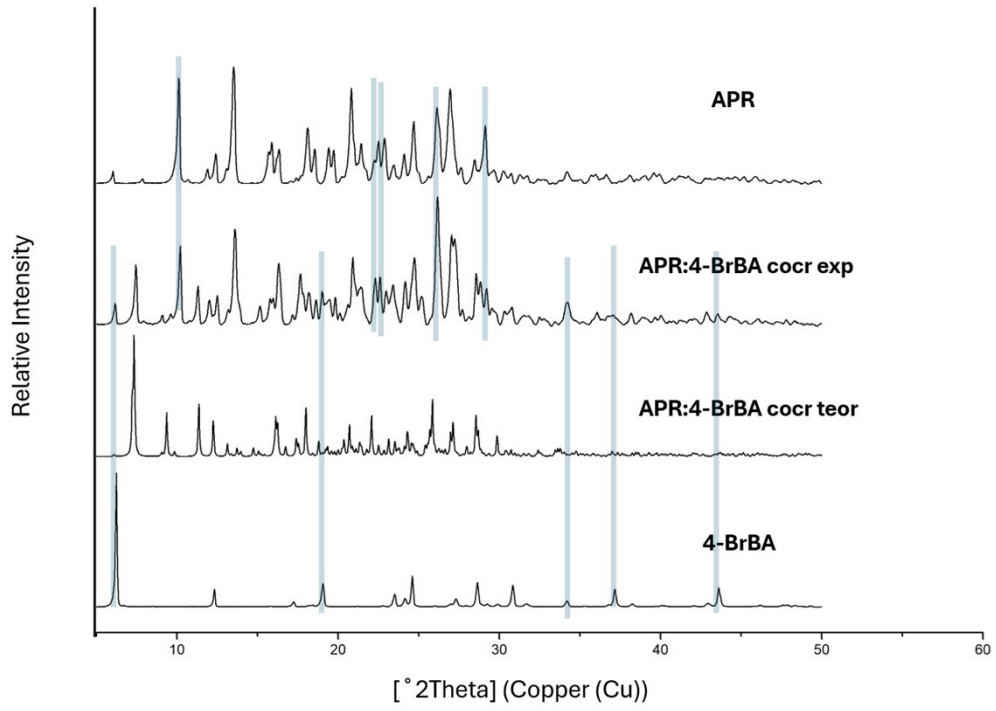

Figure S3-f PXRD of 4-BrBA system

DSC patterns of APR cocrystals

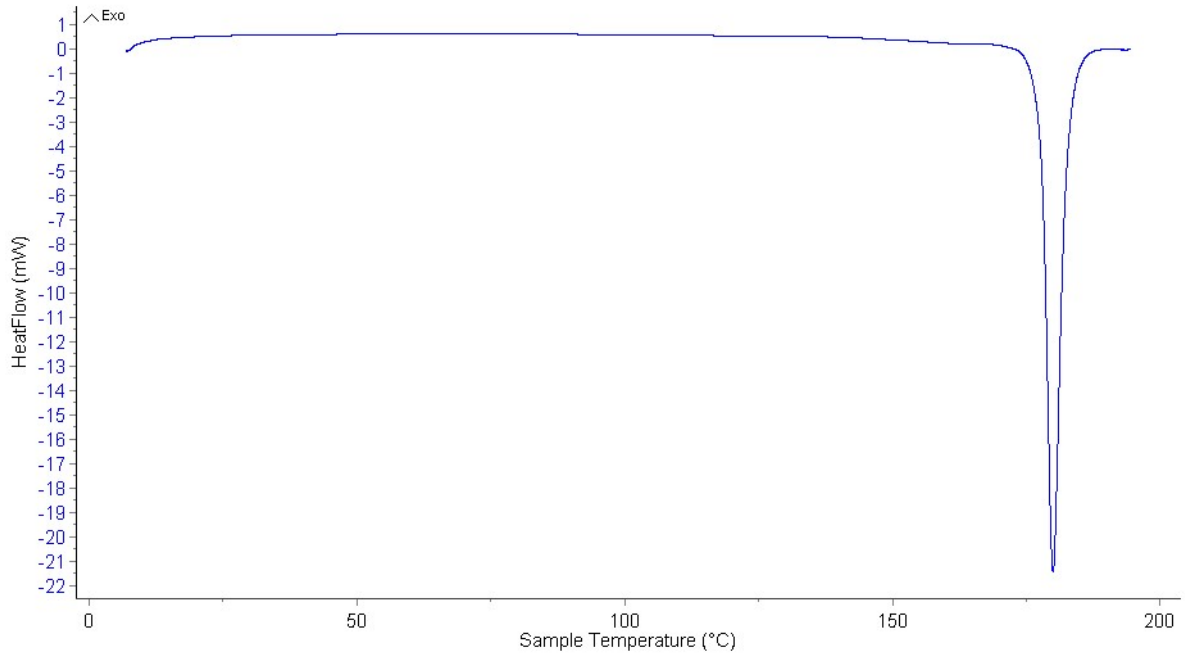

Figure S4-a DSC of APR:2-ClBA

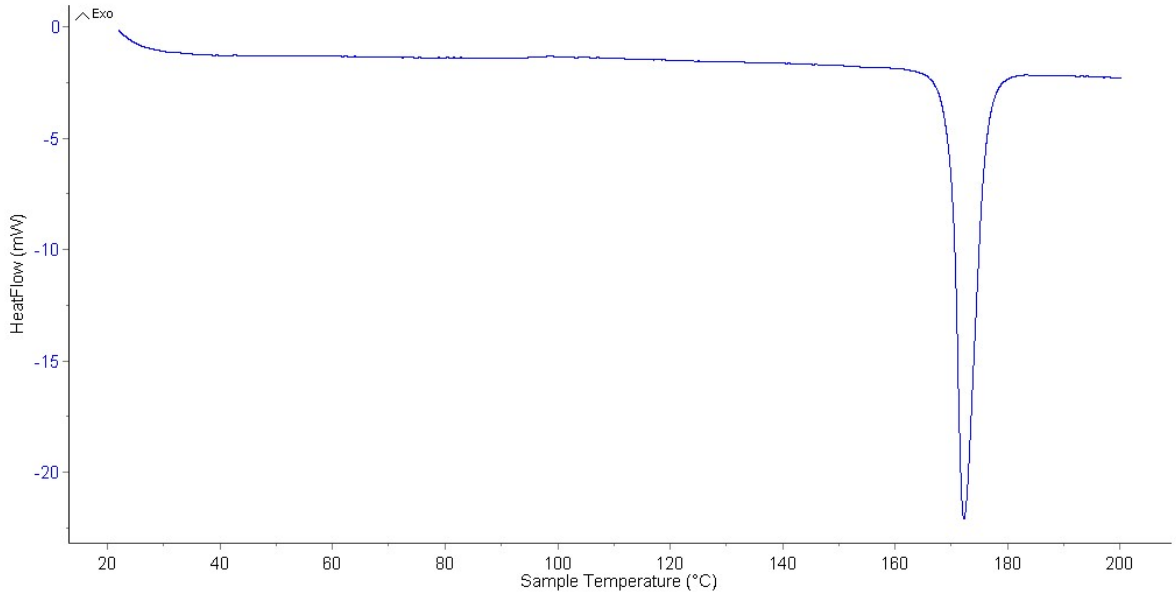

Figure S4-b DSC of APR: 3-ClBA

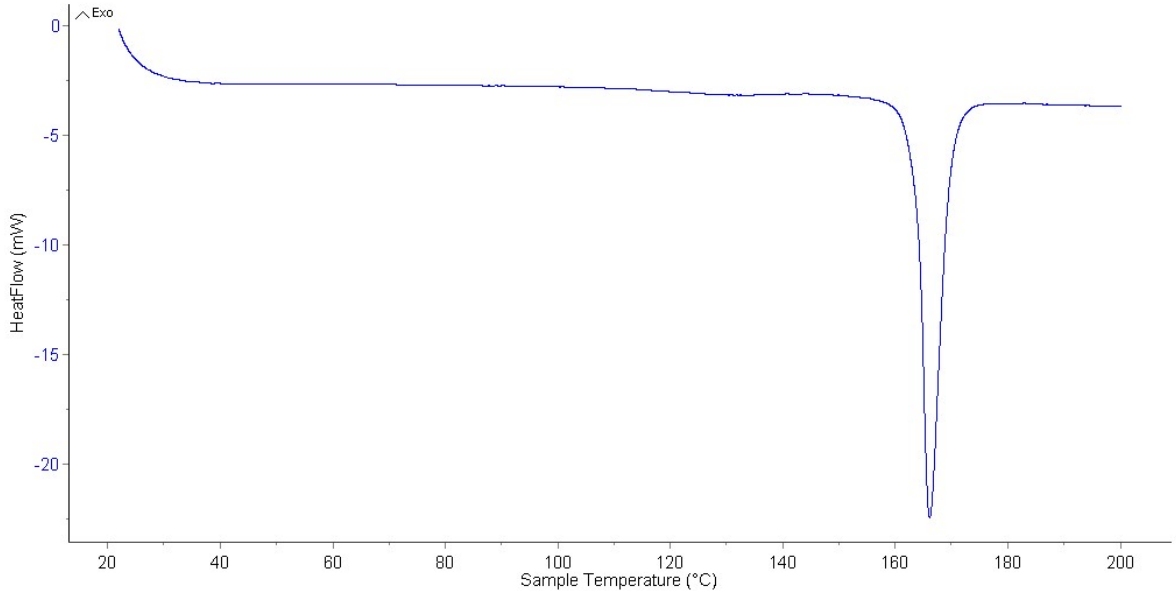

Figure S4-c DSC of APR:3-BrBA

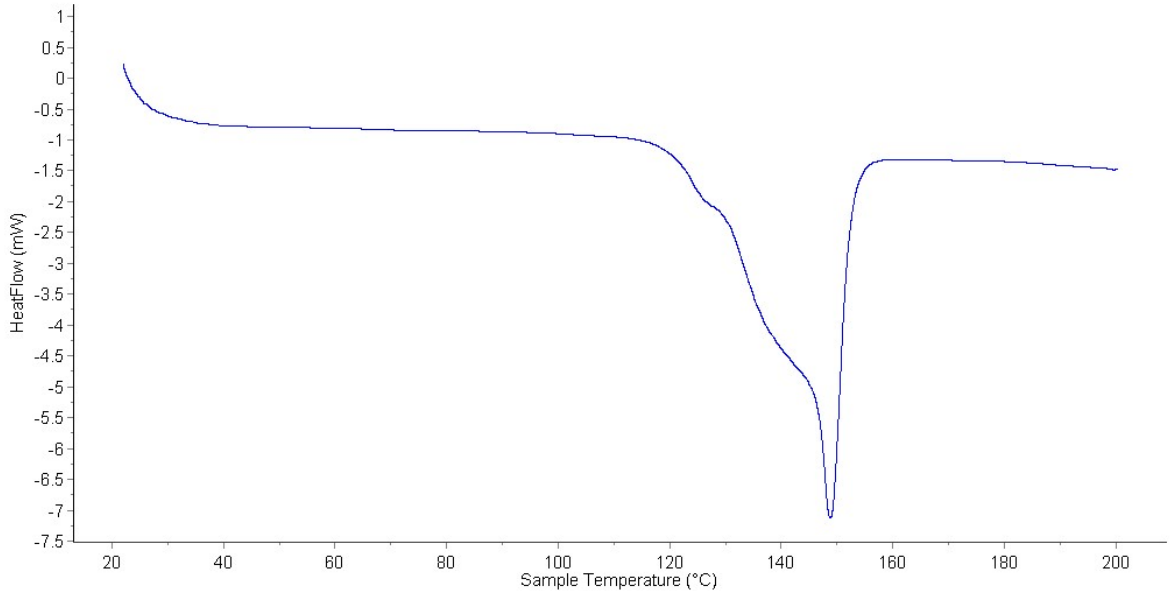

Figure S4-d DSC of APR:4-ClBA

PXRD of APR:4-ClBA cocrystal after heating

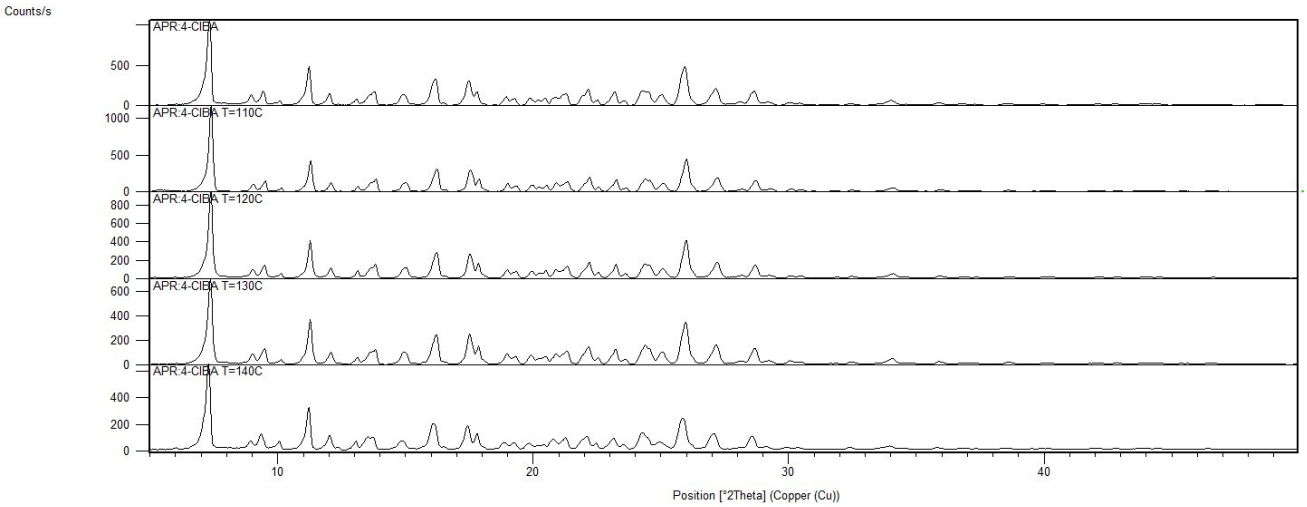

Figure S5. PXRD of APR:4-ClBA cocrystal after heating of materials at 110 ˚C, 120 ˚C, 130 ˚C and 140 ˚C

Crystal structure similarities

Table S3. Similarity matrix of APR with halogen derivates of benzoic acids crystal structures

	APR:2-ClBA	APR:3-ClBA	APR:4-ClBA	APR:3-BrBA	APR:4-BrBA
	0	1	2	3	4
0: APR:2-ClBA	0.0000	0.1119	0.4091	0.0962	0.5440
1: APR:3-ClBA	0.1119	0.0000	0.3900	0.0702	0.5041
2: APR:4-ClBA	0.4091	0.3900	0.0000	0.4162	0.1003
3: APR:3-BrBA	0.0962	0.0702	0.4162	0.0000	0.4977
4: APR:4-BrBA	0.5440	0.5041	0.1003	0.4977	0.0000

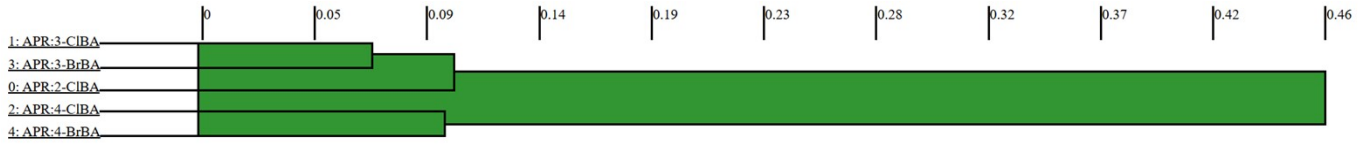

Figure S6. Dendrogram of similarity of APR with halogen substituted benzoic acids crystal structures

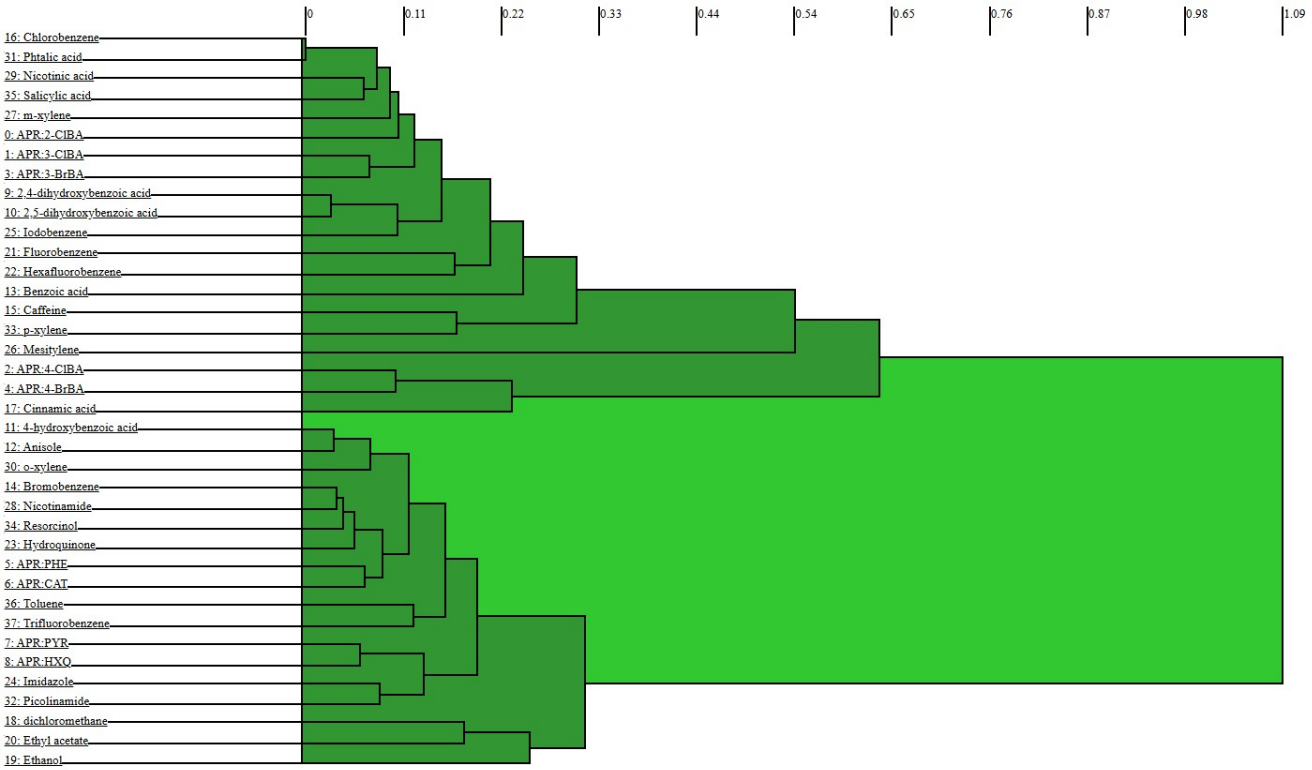

Figure S7. Dendrogram of the packing similarity for known APR crystal structures with various coformers