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Thermal expansion properties of three isostructural co-crystals composed of isosteric components: interplay between halogen and hydrogen bonds

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Supplementary Information:

1) Experimental information
2) Single-crystal X-ray diffraction measurements
3) Unit cell parameters for crystals at 20 K intervals
4) Thermal expansion coefficients
5) X-ray crystal structures and bond lengths
6) Differential Scanning Calorimetry

1) Experimental information

All reagents were obtained from Sigma Aldrich and used without further purification. The resorcinol templates were synthesized using literature procedures.[1]

Preparation of crystals: Single crystals of **4,4'-AP** were grown from a saturated solution of 5:1:1 hexanes:ethanol:toluene (*v*/*v*/*v*). Slow evaporation over 3 days yielded single crystals suitable for X-ray diffraction. Co-crystals of composition (**4,4'-AP**)·(**4,6-diCl res**) (**1a**), (**4,4'-AP**)·(**4,6-diBr res**) (**1b**), and (**4,4'-AP**)·(**4,6-diI res**) (**1c**) were obtained by dissolving **4,4'-AP** (40 mg, 0.22 mmol) and the appropriate resorcinol (0.22 mmol) in EtOH. Slow evaporation over 3 days yielded single crystals suitable for X-ray diffraction.

2) Single-crystal X-ray diffraction measurements

Single crystal XRD for the co-crystals was measured on a Nonius Kappa CCD single-crystal X-ray diffractometer using MoK_α radiation (λ=0.71073 Å). Structure solution and refinement were accomplished using SHELXS and SHELXL, respectively[2] within the Olex2[3] graphical user interface. All non-hydrogen atoms were refined anisotropically.

Table S1. Crystallographic parameters for **4,4'-AP** at variable temperatures.

compound name	**4,4'-AP**	**4,4'-AP**
chemical formula	$C_{10}H_8N_4$	$C_{10}H_8N_4$
formula mass	184.20	184.20
crystal system	Triclinic	Triclinic
space group	*P-1*	*P-1*
a/Å	3.8373(6)	3.7762(4)
b/Å	5.9282(7)	5.8688(7)
c/Å	10.3247(14)	10.3157(12)
α/°	90.671(7)	90.165(5)
β/°	95.227(8)	95.411(5)
γ/°	100.693(8)	99.256(5)
V/Å^3	229.73(6)	224.59(4)
ρ_{calc}/g cm^{-3}	1.331	1.362
T/K	290(2)	190(2)
Z	1	1
radiation type	Mo K_α	Mo K_α
absorption coefficient, μ/mm^{-1}	0.086	0.088
no. of reflections measured	1410	3229
no. of independent reflections	827	827
no of reflection (I > 2σ(I))	523	668
R_{int}	0.0386	0.0251
R_1 (I > 2σ(I))	0.0582	0.0366
$wR(F^2)$ (I > 2σ(I))	0.1378	0.0897
R_1 (all data)	0.0953	0.0477
$wR(F^2)$ (all data)	0.1709	0.1012
Goodness-of-fit	1.073	1.059
CCDC deposition number	1059611	1059610

Table S2. Crystallographic parameters for **1a** at variable temperatures.

compound name	**4,4'-AP·4,6-diCl res**	**4,4'-AP·4,6-diCl res**
chemical formula	$C_{16}H_{12}Cl_2N_4O_2$	$C_{16}H_{12}Cl_2N_4O_2$
formula mass	363.20	363.20
crystal system	Triclinic	Triclinic
space group	*P-1*	*P-1*
a/Å	9.0188(9)	8.9957(11)
b/Å	10.1722(10)	10.0831(13)
c/Å	10.4719(10)	10.4133(14)
α/°	88.254(5)	89.154(5)
β/°	71.579(5)	71.747(5)
γ/°	64.025(5)	64.264(5)
V/Å^3	812.82(14)	799.87(18)
ρ_{calc} /g cm^{-3}	1.484	1.508
T/K	290(2)	190(2)
Z	2	2
radiation type	Mo K_α	Mo K_α
absorption coefficient, μ/mm^{-1}	0.416	0.423
no. of reflections measured	4931	10633
no. of independent reflections	2949	3664
no of reflection (I > 2σ(I))	1809	3060
R_{int}	0.0320	0.0220
R_1 (I > 2σ(I))	0.0460	0.0312
$wR(F^2)$ (I > 2σ(I))	0.1178	0.0784
R_1 (all data)	0.0961	0.0410
$wR(F^2)$ (all data)	0.1420	0.0843
Goodness-of-fit	1.063	1.054
CCDC deposition number	1059605	1059604

Table S3. Crystallographic parameters for **1b** at variable temperatures.

compound name	**4,4'-AP·4,6-diBr res**	**4,4'-AP·4,6-diBr res**
chemical formula	$C_{16}H_{12}Br_2N_4O_2$	$C_{16}H_{12}Br_2N_4O_2$
formula mass	452.10	452.10
crystal system	Triclinic	Triclinic
space group	*P-1*	*P-1*
a/Å	9.0497(9)	9.0278(9)
b/Å	10.3906(10)	10.2948(10)
c/Å	10.6690(11)	10.6009(11)
α/°	87.266(7)	88.180(7)(5)
β/°	70.779(5)	70.936(5)
γ/°	63.659(7)	63.786(7)
V/Å^3	843.19(15)	828.04(15)
ρ_{calc} /g cm^{-3}	1.781	1.813
T/K	290(2)	190(2)
Z	2	2
radiation type	Mo K_α	Mo K_α
absorption coefficient, μ/mm^{-1}	4.823	4.912
no. of reflections measured	9881	13150
no. of independent reflections	3870	4419
no of reflection (I > 2σ(I))	3157	3774
R_{int}	0.0190	0.0206
R_1 (I > 2σ(I))	0.0247	0.0223
wR(F^2) (I > 2σ(I))	0.0681	0.0624
R_1 (all data)	0.0369	0.0311
wR(F^2) (all data)	0.0831	0.0868
Goodness-of-fit	1.137	1.195
CCDC deposition number	1059607	1059606

Table S4. Crystallographic parameters for **1c** at variable temperatures.

compound name	**4,4'-AP·4,6-diI res**	**4,4'-AP·4,6-diI res**
chemical formula	$C_{16}H_{12}I_2N_4O_2$	$C_{16}H_{12}I_2N_4O_2$
formula mass	546.10	546.10
crystal system	Triclinic	Triclinic
space group	*P-1*	*P-1*
a/Å	9.2547(9)	9.2387(9)
b/Å	10.6160(11)	10.4970(10)
c/Å	10.8929(11)	10.8284(11)
α/°	87.326(7)	88.215(5)
β/°	69.459(5)	69.551(5)
γ/°	64.161(7)	64.302(5)
V/Å^3	894.77(17)	877.58(16)
ρ_{calc} /g cm^{-3}	2.027	2.067
T/K	290(2)	190(2)
Z	2	2
radiation type	Mo K_α	Mo K_α
absorption coefficient, μ/mm^{-1}	3.530	3.600
no. of reflections measured	14126	12709
no. of independent reflections	4777	4676
no of reflection ($I > 2\sigma(I)$)	4180	4311
R_{int}	0.0194	0.0182
R_1 ($I > 2\sigma(I)$)	0.0253	0.0179
$wR(F^2)$ ($I > 2\sigma(I)$)	0.1032	0.0562
R_1 (all data)	0.0320	0.0214
$wR(F^2)$ (all data)	0.1231	0.0749
Goodness-of-fit	1.014	1.020
CCDC deposition number	1059609	1059608

3) Unit cell parameters for crystals at 20 K intervals

Table S5. Unit cell parameters from 290-190 K for **4,4'-AP**. Unit cell determinations were performed on a single crystal at 20 K intervals.

Cell Dimensions	290 K	270 K	250 K	230 K	210 K	190 K
a/Å	3.829	3.8201	3.8126	3.7976	3.7883	3.780
b/Å	5.929	5.917	5.913	5.894	5.885	5.8764
c/Å	10.333	10.336	10.342	10.325	10.322	10.325
α/°	90.45	90.371	90.315	90.264	90.214	90.164
β/°	95.056	95.161	95.254	95.31	95.366	95.432
γ/°	100.53	100.197	99.94	99.706	99.479	99.257
V/Å^3	229.7	229	228.6	226.8	226	225.3

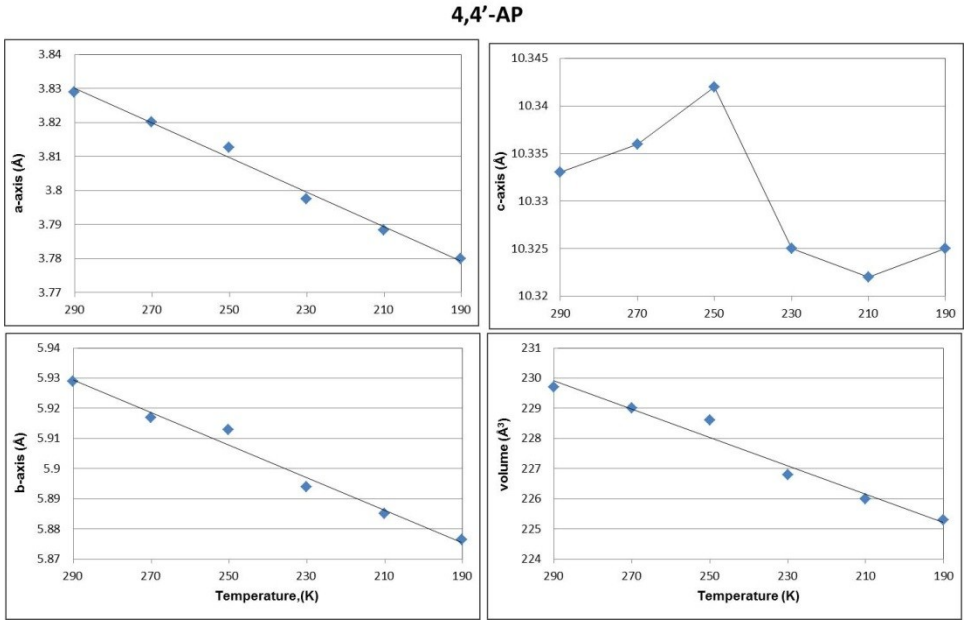

Fig. S1. Unit-cell parameters as a function of temperature for **4,4'-AP**. Linear fits of the data are provided. Non-linear behavior along *c*-axis highlighted with black line as an eye guide.

Table S6. Unit cell parameters from 290-190 K for a second crystal of **4,4'-AP**. Unit cell determinations were performed on a single crystal at 20 K intervals with three different mountings. Note differences in overall behavior of *c*-axis.

Cell Dimensions	**290 K**	**270 K**	**250 K**	**230 K**	**210 K**	**190 K**
a/Å	3.8295	3.8182	3.8074	3.7972	3.7869	3.7777
b/Å	5.9372	5.9278	5.9129	5.9025	5.8918	5.8822
c/Å	10.3348	10.3314	10.3268	10.3213	10.3173	10.3136
α/°	90.526	90.520	90.412	90.348	90.295	90.253
β/°	95.035	95.124	95.172	95.233	95.297	95.359
γ/°	100.582	100.331	100.053	99.817	99.578	99.344
V/Å^3	230.01	229.05	227.92	226.94	225.97	225.11
a/Å	3.8303	3.8169	3.8062	3.7964	3.7860	3.7761
b/Å	5.9351	5.9251	5.9137	5.9020	5.8919	5.8826
c/Å	10.3302	10.3296	10.3263	10.3222	10.3210	10.3209
α/°	90.49	90.473	90.398	90.345	90.300	90.262
β/°	95.027	95.107	95.177	95.242	95.305	95.352
γ/°	100.555	100.301	100.054	99.800	99.567	99.317
V/Å^3	229.90	228.86	227.87	226.90	226.00	225.21
a/Å	3.8283	3.8178	3.8067	3.7964	3.7863	3.7763
b/Å	5.9357	5.9234	5.9120	5.8992	5.8900	5.8790
c/Å	10.3384	10.3325	10.3261	10.3172	10.3110	10.3162
α/°	90.524	90.461	90.397	90.329	90.295	90.242
β/°	95.012	95.083	95.153	95.212	95.262	95.340
γ/°	100.545	100.289	100.031	99.778	99.535	99.310
V/Å^3	230.00	228.93	227.85	226.71	225.77	224.99

Table S7. Unit cell parameters from 290-190 K for co-crystal **1a**. Unit cell determinations were performed on a single crystal at 20 K intervals.

Cell Dimensions	290 K	270 K	250 K	230 K	210 K	190 K
a/Å	9.0208	9.0153	9.0091	9.0048	8.9986	8.9939
b/Å	10.1712	10.1503	10.1309	10.1122	10.0929	10.0761
c/Å	10.4681	10.4526	10.4381	10.425	10.4108	10.3996
α/°	88.316	88.501	88.680	88.842	89.007	89.160
β/°	71.583	71.625	71.665	71.703	71.737	71.773
γ/°	64.05	64.086	64.127	64.161	64.198	64.234
V/Å^3	812.7	809.4	806.4	803.6	800.5	798.0

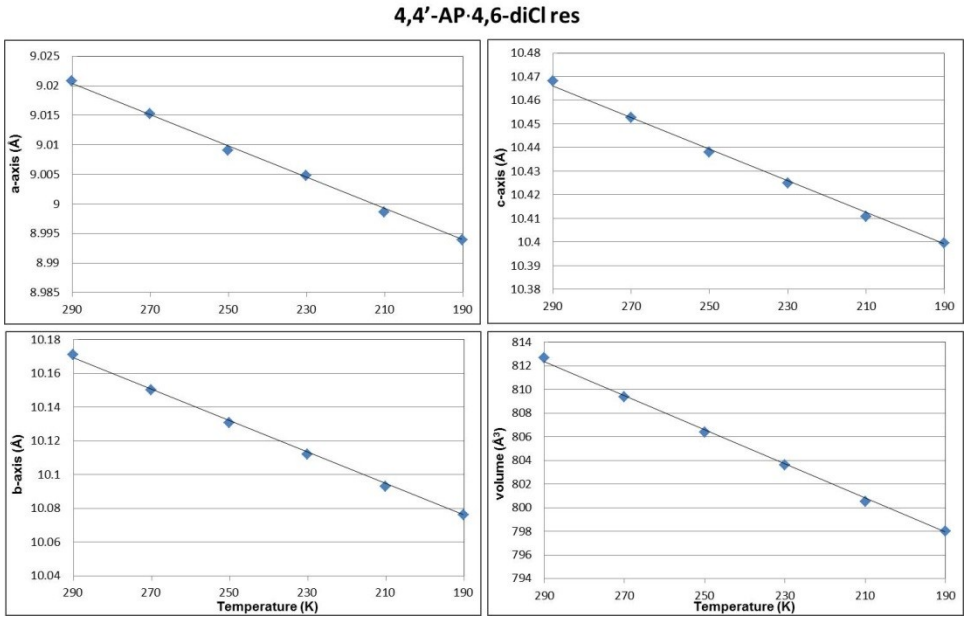

Fig. S2. Unit-cell parameters as a function of temperature for **1a**. Linear fits of the data are provided.

Table S8. Unit cell parameters from 290-190 K for co-crystal **1b**. Unit cell determinations were performed on a single crystal at 20 K intervals.

Cell Dimensions	290 K	270 K	250 K	230 K	210 K	190 K
a/Å	9.0497(9)	9.0490(8)	9.0451(7)	9.0397(7)	9.0382(7)	9.0332(4)
b/Å	10.3906(10)	10.3680(8)	10.3493(29)	10.3282(6)	10.3119(6)	10.2945(4)
c/Å	10.6690(11)	10.6529(9)	10.6403(9)	10.6226(8)	10.6116(8)	10.5975(5)
α/°	87.266(7)	87.560(3)	87.729(3)	87.877(3)	88.036(3)	88.190(2)
β/°	70.779(5)	70.867(2)	70.891(2)	70.9180(18)	70.942(2)	70.971(1)
γ/°	63.659(7)	63.705(6)	63.729(13)	63.748(5)	63.762(5)	63.773(3)
V/Å^3	843.2(2)	840.3(2)	837.4(2)	833.80(19)	831.39(19)	828.33(13)

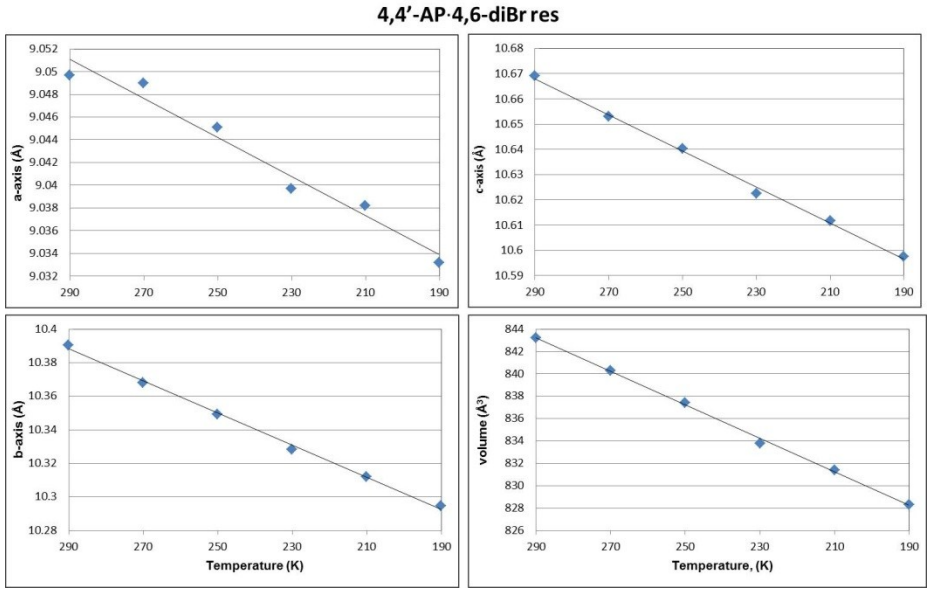

Fig. S3. Unit-cell parameters as a function of temperature for **1b**. Linear fits of the data are provided.

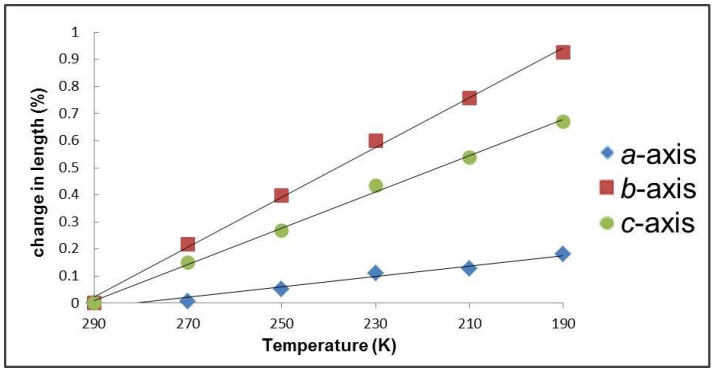

Fig. S4. Percent change in unit-cell parameters as a function of temperature for **1b**. Linear fits of the data provided.

Table S9. Unit cell parameters from 290-190 K for co-crystal **1c**. Unit cell determinations were performed on a single crystal at 20 K intervals.

Cell Dimensions	290 K	270 K	250 K	230 K	210 K	190 K
a/Å	9.2547	9.2469	9.2444	9.2422	9.2396	9.237
b/Å	10.6077	10.5763	10.5528	10.5306	10.5089	10.489
c/Å	10.8949	10.8761	10.8643	10.8532	10.8423	10.8316
α/°	87.382	87.5767	87.7399	87.8988	88.0518	88.1925
β/°	69.4499	69.4487	69.4556	69.4613	69.4697	69.4737
γ/°	64.1784	64.2404	64.2678	64.2899	64.3071	64.3181
V/Å^3	894.2	889.29	885.98	882.84	879.69	876.66

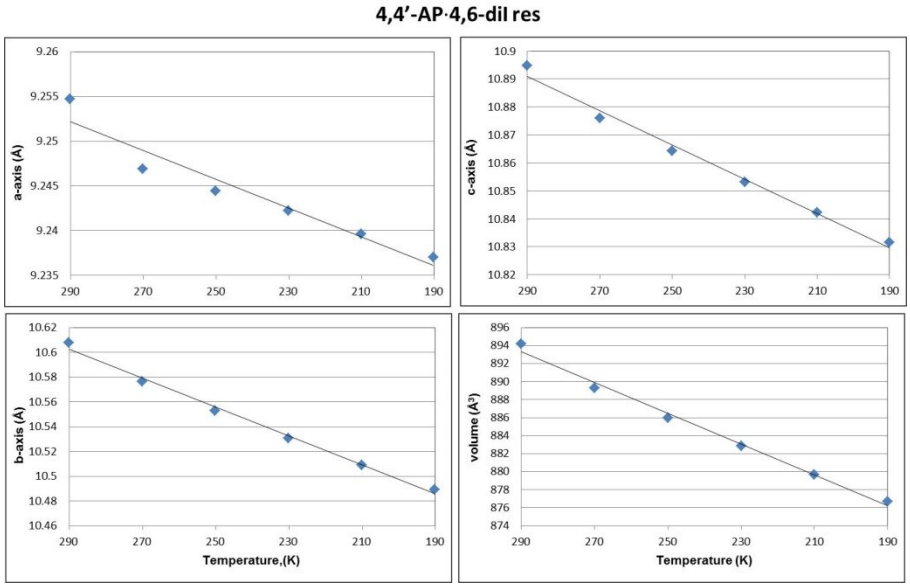

Fig. S5. Unit-cell parameters as a function of temperature for **1c**. Linear fits of the data are provided.

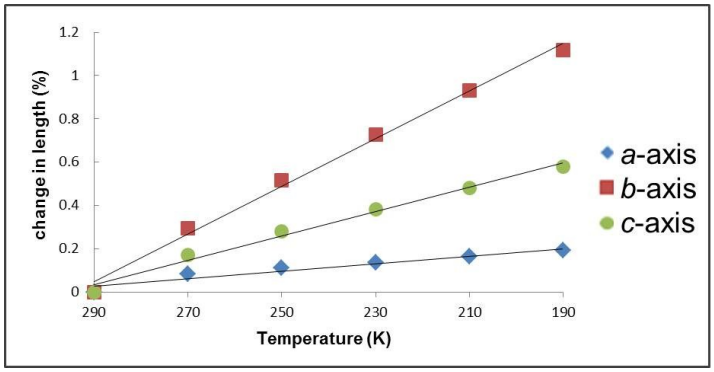

Fig. S6. Percent change in unit-cell parameters as a function of temperature for **1c**. Linear fits of the data provided.

4) Thermal expansion coefficients

The thermal expansion coefficients were calculated using the PASCal program.[4] The coefficients were calculated from unit cell determinations of a single crystal at 20 K increments from 290-190 K unless otherwise noted (Tables S5, S7-S9).

Table S10. Thermal expansion coefficients for **4,4'-AP** and co-crystals **1a-c**. Sigma values denoted in parenthesis. Approximate crystallographic axes denoted in brackets.

Crystal	**α_{X1} (MK^{-1}) [crystallographic axis]**	**α_{X2} (MK^{-1}) [crystallographic axis]**	**α_{X3} (MK^{-1}) [crystallographic axis]**	**α_{v} (MK^{-1})**
4,4'-AP (290-250 K)[a]	-68(0.9) [1 1 0]	-30(2) [-1 1 4]	212(8) [-3 1 0]	119(11)
4,4'-AP (250-210 K)[a]	16(9) [1 1 0]	46(8) [-1 0 2]	235(10) [2 -1 0]	312(28)
4,4'-AP (210-190 K)[a,b]	-26 [1 1 0]	-18 [-2 -1 2]	185 [-2 1 0]	141
1a	2(0.3) [-1 2 -2]	17(0.3) [1 0 0]	164(3) [-1 2 2]	185(3)
1b	-2(4) [0 1 -1]	9(3) [1 0 0]	172(6) [-1 2 2]	181(2)
1c	-4(0.5) [-1 1 -1]	19(3) [2 0 -1]	178(5) [-1 2 1]	196(9)

[a] We performed PASCal calculations for the data set described in Table S5. Due to the non-linear behaviour along the *c*-axis, we provide data over the three linear ranges. Significant twinning and inconsistent non-linear behaviour along the *c*-axis (see Table S6) afforded inconsistent calculation results.

[b] No sigma values as there are only two data points in the listed range.

5) X-ray crystal structures and bond lengths

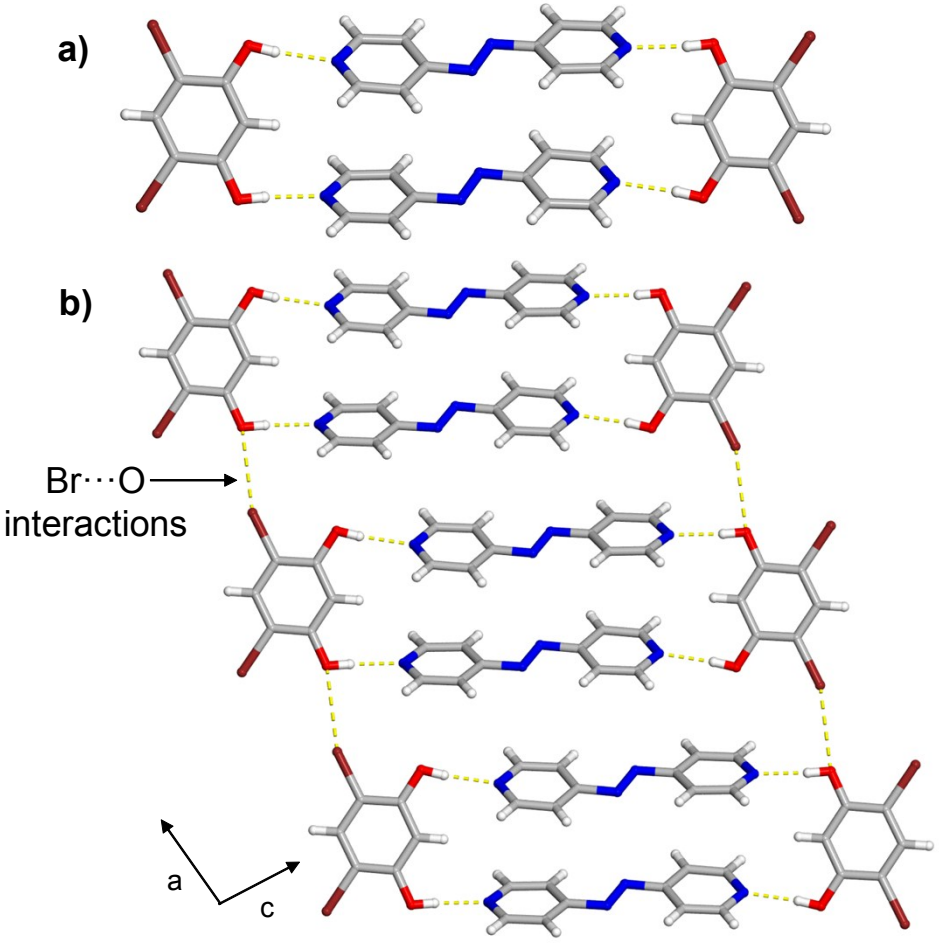

Fig. S7. X-ray structures of **1b** highlighting: (a) four-component assembly and (b) halogen interactions.

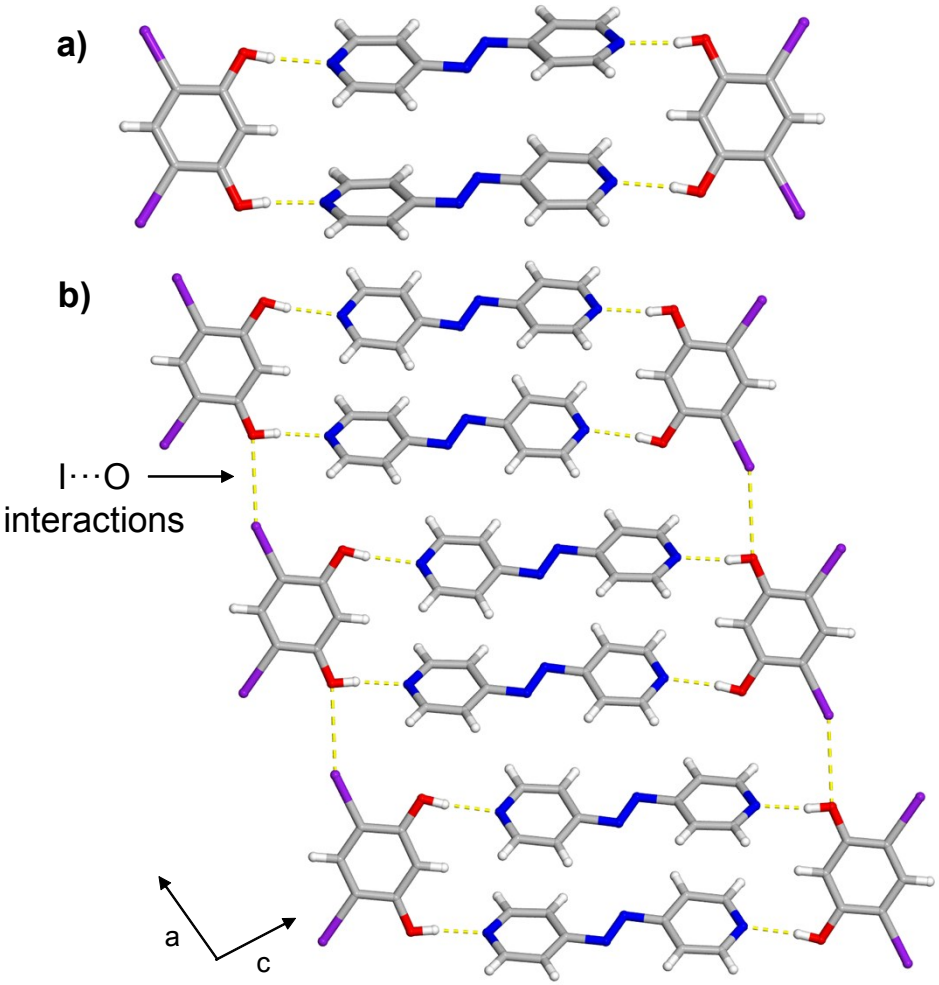

Fig. S8. X-ray structures of **1c** highlighting: (a) four-component assembly and (b) halogen interactions.

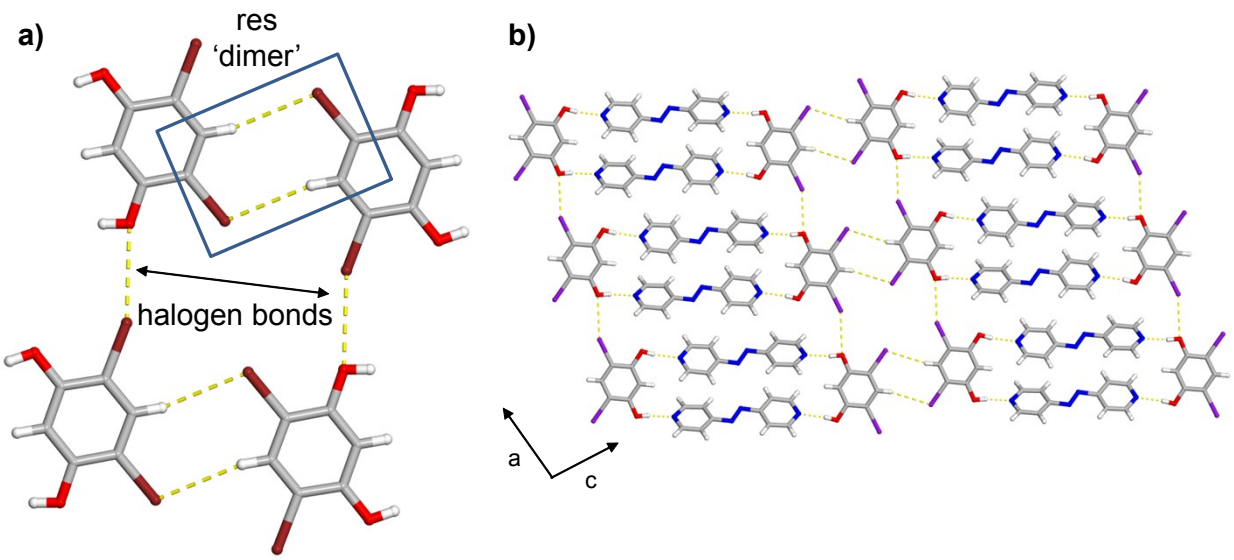

Fig. S9. X-ray structures of highlighting: (a) CCF interactions in **1b** and (b) extended packing in **1c**.

Table S11. Hydrogen-bond distances, angles, and halogen-bond distances for co-crystals **1a-c**.

Co-crystal	O···N separation (Å)	O-H-N angle (°)	O···X separation (Å)	C···X separation (Å)
1a (290 K)	2.745(3) 2.772(3)	165.0(2) 173.3(2)	3.254(2)	3.791(3)
1a (190 K)	2.738(2) 2.764(2)	172.0(2) 178.0(2)	3.217(1)	3.765(2)
1b (290 K)	2.715(2) 2.783(3)	176.5(6) 175.8(6)	3.181(2)	3.904(3)
1b (190 K)	2.709(2) 2.771(3)	174.0(3) 174.7(2)	3.152(2)	3.880(2)
1c (290 K)	2.696(4) 2.792(4)	173.1(2) 174.3(2)	3.249(3)	4.075(3)
1c (190 K)	2.689(3) 2.788(3)	173.0(2) 174.1(2)	3.226(2)	4.045(2)

6) Differential Scanning Calorimetry

Differential scanning calorimetry was performed on powdered samples using a TA DSC Q100. Approximately 5 mg of sample was sealed in a crimped aluminum pan. The experiment was conducted using nitrogen purge. Samples were cooled from RT to 183 K, equilibrated, and warmed to RT. The cycle was repeated a second time.

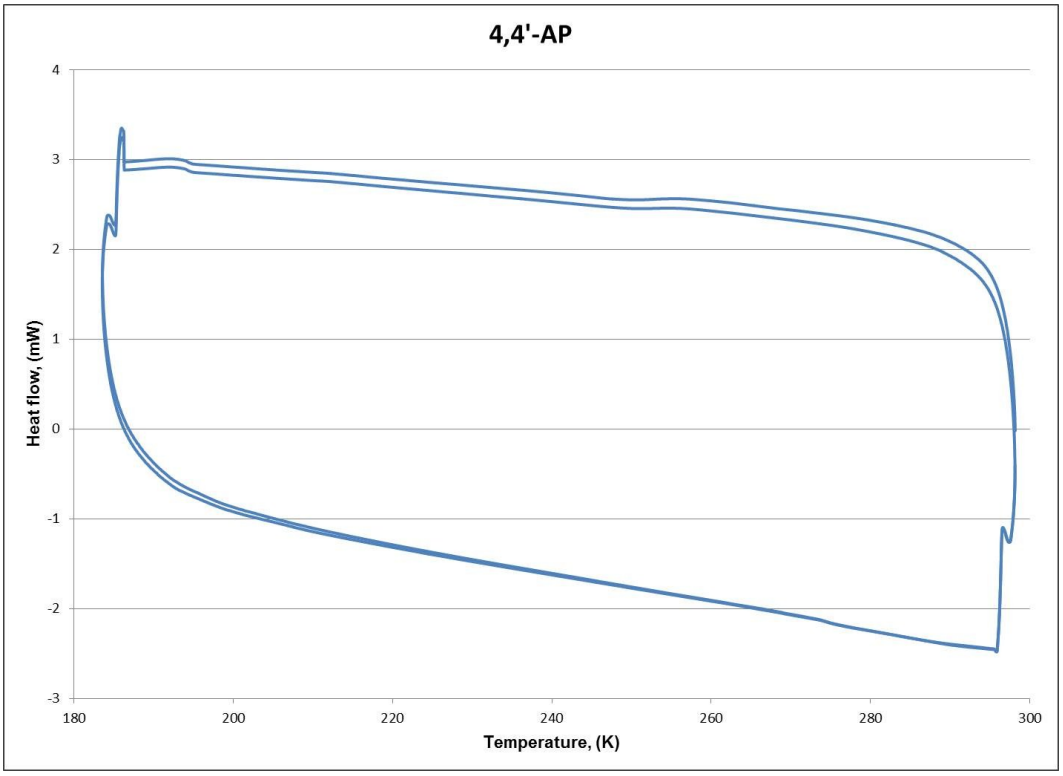

Fig. S10. DSC of **4,4'-AP**.

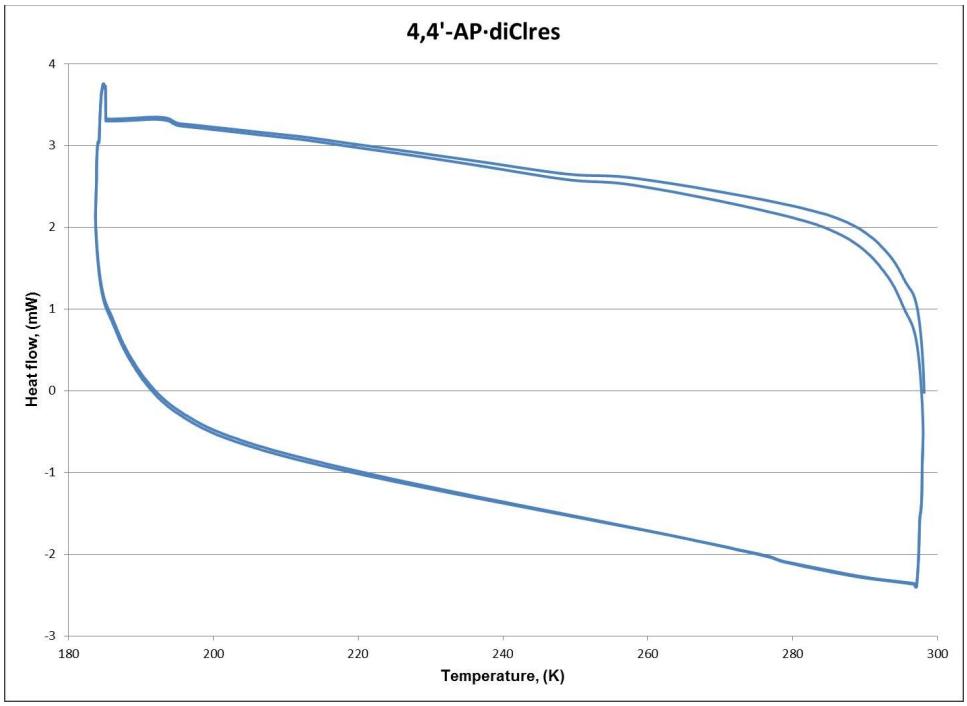

Fig. S11. DSC of co-crystal **1a**.

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