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Supplementary Information

for

Controlling thermal expansion within mixed cocrystals by tuning molecular motion capability

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1. Materials and Synthesis of Mixed Cocrystals

Materials

Resorcinol (**res**), 4,4-azopyridine (**AP**), and *trans*-1,2-bis(4-pyridyl)ethylene (**BPE**) as well as the solvents ethanol and toluene were all purchased from Sigma-Aldrich Chemical (St. Louis, MO, USA) and used as received. 1,2-bis(4-pyridyl)acetylene (**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 res•(AP)$_x$•(BPA)$_y$ Cocrystals

The cocrystal **res**•(**AP**)$_{0.25}$•(**BPA**)$_{0.75}$ was synthesized by dissolving 6.3 mg of **AP**, and 15 mg of **res** in 2 mL of ethanol in different vials then later combined with 18.4 mg of **BPA** dissolved in 2 mL of toluene. The resulting solution was allowed to evaporate slowly, and single crystals suitable for X-ray diffraction were obtained over a period of 3 days.

The cocrystal **res**•(**AP**)$_{0.50}$•(**BPA**)$_{0.50}$ was synthesized by dissolving 12.6 mg of **AP**, and 15 mg of **res** in 2 mL of ethanol in different vials then later combined with 12.3 mg of **BPA** dissolved in 2 mL of toluene. The resulting solution was allowed to evaporate slowly, and single crystals suitable for X-ray diffraction were obtained over a period of 3 days.

The cocrystal **res**•(**AP**)$_{0.75}$•(**BPA**)$_{0.25}$ was synthesized by dissolving 18.6 mg of **AP**, and 15 mg of **res** in 2 mL of ethanol in different vials then later combined with 6.1 mg of **BPA** dissolved in 2 mL of toluene. The resulting solution was allowed to evaporate slowly, and single crystals suitable for X-ray diffraction were obtained over a period of 3 days.

Synthesis of the res•(BPE)$_x$•(BPA)$_y$ Cocrystals

The cocrystal **res**•(**BPE**)$_{0.25}$•(**BPA**)$_{0.75}$ was synthesized by dissolving 6.2 mg of **BPE**, and 15 mg of **res** in 2 mL of ethanol in different vials then later combined with 18.4 mg of **BPA** dissolved in 2 mL of toluene. The resulting solution was allowed to evaporate slowly, and single crystals suitable for X-ray diffraction were obtained over a period of 3 days.

The cocrystal **res**•(**BPE**)$_{0.50}$•(**BPA**)$_{0.50}$ was synthesized by dissolving 12.4 mg of **BPE**, and 15 mg of **res** in 2 mL of ethanol in different vials then later combined with 12.3 mg of **BPA**

dissolved in 2 mL of toluene. The resulting solution was allowed to evaporate slowly, and single crystals suitable for X-ray diffraction were obtained over a period of 3 days.

The cocrystal **res**•(**BPE**)$_{0.75}$•(**BPA**)$_{0.25}$ was synthesized by dissolving 18.6 mg of **BPE**, and 15 mg of **res** in 2 mL of ethanol in different vials then later combined with 6.1 mg of **BPA** dissolved in 2 mL of toluene. The resulting solution was allowed to evaporate slowly, and single crystals suitable for X-ray diffraction were obtained over a period of 3 days.

Synthesis of the res•(AP)$_x$•(BPE)$_y$ Cocrystals

The cocrystal **res**•(**AP**)$_{0.25}$•(**BPE**)$_{0.75}$ was synthesized by dissolving 6.3 mg of **AP**, 18.6 mg of **BPE** and 15 mg of **res** where each were dissolved in 2 mL of ethanol. The solutions were combined and allowed to evaporate slowly, and single crystals suitable for X-ray diffraction were obtained over a period of 3 days.

The cocrystal **res**•(**AP**)$_{0.50}$•(**BPE**)$_{0.50}$ was synthesized by dissolving 12.6 mg of **AP**, 12.4 mg of **BPE** and 15 mg of **res** where each were dissolved in 2 mL of ethanol. The solutions were combined and allowed to evaporate slowly, and single crystals suitable for X-ray diffraction were obtained over a period of 3 days.

The cocrystal **res**•(**AP**)$_{0.75}$•(**BPE**)$_{0.25}$ was synthesized by dissolving 18.2 mg of **AP**, 6.2 mg of **BPE** and 15 mg of **res** where each were dissolved in 2 mL of ethanol. The solutions were combined and allowed to evaporate slowly, and single crystals suitable for X-ray diffraction were obtained over a period of 3 days.

2. X-ray Diffraction Information and Data Tables

Data were collected on a Rigaku XtaLAB Synergy-*i*Kappa diffractometer equipped with a PhotonJet-*i* X-ray source operated at 50 W (50kV, 1 mA) to generate Cu Kα radiation (λ = 1.54178 Å) and a HyPix-6000HE HPC (hybrid photon counting) detector. Crystals were transferred from the vial and placed on a glass slide in polyisobutylene. A Zeiss Stemi 305 microscope was used to identify a suitable specimen for X-ray diffraction from a representative sample of the material. The crystal and a small amount of the oil were collected on a Hampton Research20 micron cryoloop and transferred to the instrument where it was placed under a cold nitrogen stream (Oxford). Data were collected at temperatures of 290 K, 270 K, 250 K, 230 K, 210 K, and 190 K with a transition rate of 2 K/minute between the temperatures. The sample was optically centered with the aid of a video camera to ensure that no translations were observed as the crystal was rotated through all positions. The crystal was measured for size, morphology, and color.

After data collection, the unit cell was re-determined using a subset of the full data collection for each temperature. Intensity data were corrected for Lorentz, polarization, and background effects using *CrysAlis*^{Pro}.[1] A numerical absorption correction was applied based on a Gaussian integration over a multifaceted crystal and followed by a semi-empirical correction for adsorption applied using the program *SCALE3 ABSPACK*.[2] The *SHELX-2014*,[3] series of programs was used for the solution and refinement of the crystal structures. 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 **res**•(**AP**)$_{0.75}$•(**BPA**)$_{0.25}$ at 290, 270, and 250 K.

compound formula	$C_{16.47}H_{14}N_{3.52}O_2$	$C_{16.49}H_{14}N_{3.51}O_2$	$C_{16.48}H_{14}N_{3.52}O_2$
formula mass	293.21	293.28	293.34
crystal system	Triclinic	Triclinic	Triclinic
space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a/Å	8.0903(3)	8.0696(2)	8.0515(2)
b/Å	9.7624(3)	9.7563(3)	9.7483(3)
c/Å	10.8911(3)	10.8866(3)	10.8766(3)
α/°	93.754(3)	93.656(2)	93.548(2)
β/°	106.789(3)	106.798(3)	106.805(2)
γ/°	113.675(4)	113.712(3)	113.770(3)
V/Å^3	737.88(5)	735.23(4)	732.24(4)
ρ_{calc}/g cm^{-3}	1.320	1.325	1.330
T/K	290(2)	270(2)	250(2)
Z	2	2	2
radiation type	CuKα	CuKα	CuKα
absorption coefficient, μ/mm^{-1}	0.734	0.736	0.740
no. of reflections measured	12567	12366	12763
no. of independent reflections	2993	2962	2954
no. of reflection ($I > 2\sigma(I)$)	2273	2337	2388
R_{int}	0.0425	0.0414	0.0450
R_1 ($I > 2\sigma(I)$)	0.0542	0.0462	0.0458
$wR(F^2)$ ($I > 2\sigma(I)$)	0.1510	0.1272	0.1320
R_1 (all data)	0.0676	0.0583	0.0562
$wR(F^2)$ (all data)	0.1790	0.1378	0.1416
Goodness-of-fit	1.081	1.055	1.094
CCDC deposition number	1995717	1995716	1995715

Table S2. X-ray data for **res**•(**AP**)$_{0.75}$•(**BPA**)$_{0.25}$ at 230, 210, and 190 K.

compound formula	$C_{16.51}H_{14}N_{3.49}O_2$	$C_{16.51}H_{14}N_{3.49}O_2$	$C_{16.53}H_{14}N_{3.47}O_2$
formula mass	293.36	293.29	293.15
crystal system	Triclinic	Triclinic	Triclinic
space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a/Å	8.03328(18)	8.01758(17)	7.9981(2)
b/Å	9.7401(2)	9.7320(2)	9.7278(3)
c/Å	10.8685(2)	10.86038(18)	10.8484(3)
α/°	93.4267(17)	93.3010(15)	93.160(2)
β/°	106.8463(19)	106.8700(17)	106.919(3)
γ/°	113.829(2)	113.897(2)	113.993(3)
V/Å^3	729.19(3)	726.41(3)	723.07(4)
ρ_{calc}/g cm^{-3}	1.336	1.341	1.346
T/K	230(2)	210(2)	190(2)
Z	2	2	2
radiation type	CuKα	CuKα	CuKα
absorption coefficient, μ/mm^{-1}	0.742	0.745	0.748
no. of reflections measured	12806	12586	12658
no. of independent reflections	2949	2942	2940
no. of reflection ($I > 2\sigma(I)$)	2433	2484	2582
R_{int}	0.0422	0.0372	0.0350
R_1 ($I > 2\sigma(I)$)	0.0453	0.0442	0.0419
$wR(F^2)$ ($I > 2\sigma(I)$)	0.1279	0.1256	0.1159
R_1 (all data)	0.0542	0.0523	0.0468
$wR(F^2)$ (all data)	0.1357	0.1318	0.1204
Goodness-of-fit	1.041	1.090	1.071
CCDC deposition number	1995714	1995713	1995712

Table S3. X-ray data for **res•(AP)**$_{0.50}$**•(BPA)**$_{0.50}$ at 290, 270, and 250 K.

compound formula	$C_{16.90}H_{14}N_{3.08}O_2$	$C_{16.92}H_{14}N_{3.07}O_2$	$C_{16.96}H_{14}N_{3.04}O_2$
formula mass	292.27	292.33	292.31
crystal system	Triclinic	Triclinic	Triclinic
space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a/Å	8.1338(2)	8.1172(2)	8.10148(18)
b/Å	9.7910(3)	9.7795(3)	9.7713(2)
c/Å	10.9340(3)	10.9256(2)	10.9201(2)
α/°	93.322(2)	93.2084(19)	93.1101(18)
β/°	107.125(2)	107.177(2)	107.2305(19)
γ/°	113.929(3)	113.972(3)	114.004(2)
V/Å^3	744.78(4)	741.59(3)	738.97(3)
ρ_{calc}/g cm^{-3}	1.303	1.309	1.314
T/K	290(2)	270(2)	250(2)
Z	2	2	2
radiation type	CuKα	CuKα	CuKα
absorption coefficient, μ/mm^{-1}	0.717	0.720	0.722
no. of reflections measured	15615	15831	15632
no. of independent reflections	3043	3029	3021
no. of reflection ($I > 2\sigma(I)$)	2418	2488	2525
R_{int}	0.0386	0.0383	0.0399
R_1 ($I > 2\sigma(I)$)	0.0448	0.0455	0.0451
$wR(F^2)$ ($I > 2\sigma(I)$)	0.1175	0.1264	0.1223
R_1 (all data)	0.0565	0.0557	0.0536
$wR(F^2)$ (all data)	0.1251	0.1336	0.1288
Goodness-of-fit	1.052	1.072	1.057
CCDC deposition number	1995711	1995710	1995709

Table S4. X-ray data for **res•(AP)**$_{0.50}$**•(BPA)**$_{0.50}$ at 230, 210, and 190 K.

compound formula	$C_{16.94}H_{14}N_{3.06}O_2$	$C_{16.95}H_{14}N_{3.05}O_2$	$C_{16.97}H_{14}N_{3.01}O_2$
formula mass	292.33	292.34	292.19
crystal system	Triclinic	Triclinic	Triclinic
space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a/Å	8.08726(15)	8.07384(14)	8.0587(2)
b/Å	9.7628(2)	9.7536(2)	9.7436(3)
c/Å	10.91257(18)	10.90755(17)	10.9027(2)
α/°	93.0131(15)	92.9033(15)	92.797(2)
β/°	107.2723(16)	107.3262(15)	107.379(2)
γ/°	114.0439(19)	114.0871(19)	114.108(3)
V/Å^3	736.33(3)	733.82(3)	731.27(4)
ρ_{calc}/g cm^{-3}	1.318	1.323	1.327
T/K	230(2)	210(2)	190(2)
Z	2	2	2
radiation type	CuKα	CuKα	CuKα
absorption coefficient, μ/mm^{-1}	0.725	0.727	0.729
no. of reflections measured	15670	15628	15546
no. of independent reflections	3013	2992	2987
no. of reflection ($I > 2\sigma(I)$)	2579	2595	2614
R_{int}	0.0402	0.0392	0.0388
R_1 ($I > 2\sigma(I)$)	0.0433	0.0442	0.0430
$wR(F^2)$ ($I > 2\sigma(I)$)	0.1199	0.1163	0.1164
R_1 (all data)	0.0503	0.0509	0.0496
$wR(F^2)$ (all data)	0.1240	0.1206	0.1205
Goodness-of-fit	1.099	1.089	1.078
CCDC deposition number	1995708	1995707	1995706

Table S5. X-ray data for **res**•(**AP**)$_{0.25}$•(**BPA**)$_{0.75}$ at 290, 270, and 250 K.

compound formula	$C_{17.31}H_{14}N_{2.69}O_2$	$C_{17.31}H_{14}N_{2.69}O_2$	$C_{17.34}H_{14}N_{2.66}O_2$
formula mass	291.69	291.69	291.64
crystal system	Triclinic	Triclinic	Triclinic
space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a/Å	8.20177(17)	8.18740(15)	8.17264(14)
b/Å	9.80593(19)	9.79793(17)	9.78791(16)
c/Å	10.9558(2)	10.95147(18)	10.94559(17)
α/°	92.6345(16)	92.5603(14)	92.4657(13)
β/°	107.7151(18)	107.7674(16)	107.8278(15)
γ/°	114.3297(19)	114.3678(17)	114.4086(16)
V/Å^3	749.76(3)	747.21(3)	744.37(2)
ρ_{calc}/g cm^{-3}	1.291	1.296	1.300
T/K	290(2)	270(2)	250(2)
Z	2	2	2
radiation type	CuKα	CuKα	CuKα
absorption coefficient, μ/mm^{-1}	0.704	0.706	0.708
no. of reflections measured	23104	23782	23815
no. of independent reflections	2997	3010	2977
no. of reflection ($I > 2\sigma(I)$)	2385	2464	2485
R_{int}	0.0544	0.0568	0.0532
R_1 ($I > 2\sigma(I)$)	0.0405	0.0413	0.0401
$wR(F^2)$ ($I > 2\sigma(I)$)	0.1143	0.1148	0.1117
R_1 (all data)	0.0502	0.0494	0.0470
$wR(F^2)$ (all data)	0.1232	0.1225	0.1185
Goodness-of-fit	1.050	1.047	1.051
CCDC deposition number	1995555	1995554	1995553

Table S6. X-ray data for **res**•(**AP**)$_{0.25}$•(**BPA**)$_{0.75}$ at 230, 210, and 190 K.

compound formula	$C_{17.35}H_{14}N_{2.65}O_2$	$C_{17.35}H_{14}N_{2.65}O_2$	$C_{17.35}H_{14}N_{2.65}O_2$
formula mass	291.62	291.61	291.60
crystal system	Triclinic	Triclinic	Triclinic
space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a/Å	8.15991(18)	8.14555(15)	8.13293(19)
b/Å	9.7782(2)	9.77001(17)	9.7619(2)
c/Å	10.9363(3)	10.93515(20)	10.9275(3)
α/°	92.3422(18)	92.2730(14)	92.167(2)
β/°	107.888(2)	107.9416(16)	107.990(2)
γ/°	114.448(2)	114.4897(17)	114.537(2)
V/Å^3	741.61(3)	739.23(3)	736.68(3)
ρ_{calc}/g cm^{-3}	1.306	1.310	1.315
T/K	230(2)	210(2)	190(2)
Z	2	2	2
radiation type	CuKα	CuKα	CuKα
absorption coefficient, μ/mm^{-1}	0.711	0.713	0.715
no. of reflections measured	24585	23128	23395
no. of independent reflections	3016	2982	2980
no. of reflection ($I > 2\sigma(I)$)	2570	2577	2626
R_{int}	0.0549	0.0483	0.0478
R_1 ($I > 2\sigma(I)$)	0.0402	0.0386	0.0382
$wR(F^2)$ ($I > 2\sigma(I)$)	0.1123	0.1064	0.1056
R_1 (all data)	0.0457	0.0434	0.0426
$wR(F^2)$ (all data)	0.1172	0.1107	0.1091
Goodness-of-fit	1.061	1.047	1.066
CCDC deposition number	1995552	1995551	1995550

Table S7. X-ray data for **res•(BPE)**$_{0.75}$**•(BPA)**$_{0.25}$ at 290, 270, and 250 K.

compound formula	$C_{18.02}H_{15.52}N_2O_2$	$C_{18.01}H_{15.51}N_2O_2$	$C_{18.01}H_{15.51}N_2O_2$
formula mass	292.05	291.94	292.02
crystal system	Triclinic	Triclinic	Triclinic
space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a/Å	8.18898(10)	8.16783(10)	8.14797(10)
b/Å	9.90985(17)	9.90151(16)	9.89332(16)
c/Å	10.91962(12)	10.91446(11)	10.90921(11)
α/°	92.9620(16)	92.8705(14)	92.7875(14)
β/°	107.4781(11)	107.4858(10)	107.4969(10)
γ/°	114.2775(13)	114.3213(12)	114.3638(12)
V/Å^3	754.69(2)	751.686(19)	748.778(19)
ρ_{calc}/g cm^{-3}	1.285	1.290	1.295
T/K	290(2)	270(2)	250(2)
Z	2	2	2
radiation type	CuKα	CuKα	CuKα
absorption coefficient, μ/mm^{-1}	0.685	0.687	0.690
no. of reflections measured	27967	28189	28413
no. of independent reflections	3101	3100	3097
no. of reflection (I > 2σ(I))	2708	2761	2797
R_{int}	0.0320	0.0293	0.0299
R_1 (I > 2σ(I))	0.0362	0.0348	0.0341
$wR(F^2)$ (I > 2σ(I))	0.1033	0.0985	0.0959
R_1 (all data)	0.0402	0.0381	0.0371
$wR(F^2)$ (all data)	0.1068	0.1015	0.0990
Goodness-of-fit	1.088	1.069	1.071
CCDC deposition number	1995704	1995703	1995702

Table S8. X-ray data for **res•(BPE)**$_{0.75}$**•(BPA)**$_{0.25}$ at 230, 210, and 190 K.

compound formula	$C_{18.01}H_{15.51}N_2O_2$	$C_{18}H_{15.50}N_2O_2$	$C_{18.01}H_{15.51}N_2O_2$
formula mass	291.96	291.88	291.92
crystal system	Triclinic	Triclinic	Triclinic
space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a/Å	8.13025(10)	8.11309(11)	8.09764(12)
b/Å	9.88487(15)	9.87420(17)	9.86690(19)
c/Å	10.90533(11)	10.89995(12)	10.89543(13)
α/°	92.7008(14)	92.6153(16)	92.5280(17)
β/°	107.5192(10)	107.5529(11)	107.5880(12)
γ/°	114.4022(12)	114.4384(13)	114.4693(14)
V/Å^3	746.122(18)	743.20(2)	740.79(2)
ρ_{calc}/g cm^{-3}	1.300	1.304	1.309
T/K	230(2)	210(2)	190(2)
Z	2	2	2
radiation type	CuKα	CuKα	CuKα
absorption coefficient, μ/mm^{-1}	0.692	0.695	0.697
no. of reflections measured	28182	27914	27916
no. of independent reflections	3084	3070	3058
no. of reflection ($I > 2\sigma(I)$)	2814	2835	2829
R_{int}	0.0284	0.0293	0.0280
R_1 ($I > 2\sigma(I)$)	0.0335	0.0330	0.0321
$wR(F^2)$ ($I > 2\sigma(I)$)	0.0937	0.0922	0.0903
R_1 (all data)	0.0362	0.0354	0.0339
$wR(F^2)$ (all data)	0.0961	0.0944	0.0919
Goodness-of-fit	1.057	1.072	1.069
CCDC deposition number	1995701	1995700	1995699

Table S9. X-ray data for **res•(BPE)**$_{0.50}$**•(BPA)**$_{0.50}$ at 290, 270, and 250 K.

compound formula	$C_{18}H_{15.02}N_2O_2$	$C_{18}H_{15.02}N_2O_2$	$C_{18}H_{15.02}N_2O_2$
formula mass	291.34	291.34	291.34
crystal system	Triclinic	Triclinic	Triclinic
space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a/Å	8.20840(10)	8.18944(9)	8.17154(10)
b/Å	9.88002(10)	9.87060(10)	9.86186(11)
c/Å	10.94248(10)	10.93717(11)	10.93238(11)
α/°	92.8140(8)	92.7279(8)	92.6441(8)
β/°	107.7114(9)	107.7404(9)	107.7657(10)
γ/°	114.3110(11)	114.3479(10)	114.3850(11)
V/Å^3	754.704(16)	751.727(15)	748.950(16)
ρ_{calc}/g cm^{-3}	1.282	1.287	1.292
T/K	290(2)	270(2)	250(2)
Z	2	2	2
radiation type	CuKα	CuKα	CuKα
absorption coefficient, μ/mm^{-1}	0.684	0.687	0.690
no. of reflections measured	28018	28258	28234
no. of independent reflections	3093	3094	3093
no. of reflection ($I > 2\sigma(I)$)	2700	2770	2793
R_{int}	0.0339	0.0333	0.0332
R_1 ($I > 2\sigma(I)$)	0.0353	0.0344	0.0340
$wR(F^2)$ ($I > 2\sigma(I)$)	0.0999	0.0974	0.0954
R_1 (all data)	0.0395	0.0377	0.0369
$wR(F^2)$ (all data)	0.1040	0.1005	0.0981
Goodness-of-fit	1.088	1.087	1.081
CCDC deposition number	1995698	1995697	1995696

Table S10. X-ray data for at **res•(BPE)**$_{0.50}$**•(BPA)**$_{0.50}$ at 230, 210, and 190 K.

compound formula	$C_{18}H_{15.02}N_2O_2$	$C_{18}H_{15.01}N_2O_2$	$C_{18}H_{15.03}N_2O_2$
formula mass	291.34	291.33	291.34
crystal system	Triclinic	Triclinic	Triclinic
space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a/Å	8.15433(11)	8.13837(14)	8.12328(14)
b/Å	9.85391(12)	9.8450(2)	9.8351(2)
c/Å	10.92795(12)	10.92312(12)	10.91847(14)
α/°	92.5643(9)	92.4784(16)	92.3839(18)
β/°	107.7884(11)	107.8241(12)	107.8562(13)
γ/°	114.4264(12)	114.4657(15)	114.4977(15)
V/Å^3	746.298(17)	743.63(2)	741.07(2)
ρ_{calc}/g cm^{-3}	1.296	1.301	1.306
T/K	230(2)	210(2)	190(2)
Z	2	2	2
radiation type	CuKα	CuKα	CuKα
absorption coefficient, μ/mm^{-1}	0.692	0.694	0.697
no. of reflections measured	28336	28285	28099
no. of independent reflections	3095	3085	3073
no. of reflection ($I > 2\sigma(I)$)	2836	2850	2863
R_{int}	0.0314	0.0358	0.0311
R_1 ($I > 2\sigma(I)$)	0.0336	0.0332	0.0320
$wR(F^2)$ ($I > 2\sigma(I)$)	0.0919	0.0893	0.0860
R_1 (all data)	0.0360	0.0354	0.0340
$wR(F^2)$ (all data)	0.0939	0.0912	0.0876
Goodness-of-fit	1.061	1.053	1.066
CCDC deposition number	1995695	1995694	1995693

Table S11. X-ray data for **res•(BPE)**$_{0.25}$•**(BPA)**$_{0.75}$ at 290, 270, and 250 K.

compound formula	$C_{18}H_{14.60}N_2O_2$	$C_{18}H_{14.61}N_2O_2$	$C_{18}H_{14.58}N_2O_2$
formula mass	290.92	290.93	290.90
crystal system	Triclinic	Triclinic	Triclinic
space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a/Å	8.23553(13)	8.21931(13)	8.20354(16)
b/Å	9.85058(13)	9.84133(13)	9.82973(15)
c/Å	10.96006(14)	10.95472(14)	10.95062(15)
α/°	92.5489(11)	92.4662(11)	92.3825(12)
β/°	107.9571(13)	108.0057(13)	108.0580(14)
γ/°	114.4335(14)	114.4642(14)	114.4899(17)
V/Å^3	754.73(2)	751.94(2)	749.11(2)
ρ_{calc}/g cm^{-3}	1.280	1.285	1.290
T/K	290(2)	270(2)	250(2)
Z	2	2	2
radiation type	CuKα	CuKα	CuKα
absorption coefficient, μ/mm^{-1}	0.684	0.687	0.689
no. of reflections measured	14795	14792	14771
no. of independent reflections	3117	3110	3099
no. of reflection ($I > 2\sigma(I)$)	2722	2735	2750
R_{int}	0.0293	0.0290	0.0282
R_1 ($I > 2\sigma(I)$)	0.0356	0.0347	0.0343
$wR(F^2)$ ($I > 2\sigma(I)$)	0.0992	0.0982	0.0964
R_1 (all data)	0.0401	0.0387	0.0377
$wR(F^2)$ (all data)	0.1034	0.1016	0.0992
Goodness-of-fit	1.055	1.081	1.108
CCDC deposition number	1995692	1995691	1995690

Table S12. X-ray data for **res•(BPE)**$_{0.25}$**•(BPA)**$_{0.75}$ at 230, 210, and 190 K.

compound formula	$C_{18}H_{14.60}N_2O_2$	$C_{18}H_{14.59}N_2O_2$	$C_{18}H_{14.61}N_2O_2$
formula mass	290.92	290.90	290.92
crystal system	Triclinic	Triclinic	Triclinic
space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a/Å	8.18873(15)	8.17391(17)	8.1603(2)
b/Å	9.82362(13)	9.81420(15)	9.8060(3)
c/Å	10.94583(15)	10.94231(17)	10.9374(2)
α/°	92.3016(11)	92.2144(13)	92.130(3)
β/°	108.0971(14)	108.1472(16)	108.187(2)
γ/°	114.5370(15)	114.5712(17)	114.618(2)
V/Å^3	746.66(2)	744.10(2)	741.61(4)
ρ_{calc}/g cm^{-3}	1.294	1.298	1.303
T/K	230(2)	210(2)	190(2)
Z	2	2	2
radiation type	CuKα	CuKα	CuKα
absorption coefficient, μ/mm^{-1}	0.692	0.694	0.696
no. of reflections measured	14756	14719	14653
no. of independent reflections	3088	3080	3073
no. of reflection ($I > 2\sigma(I)$)	2778	2809	2817
R_{int}	0.0264	0.0262	0.0266
R_1 ($I > 2\sigma(I)$)	0.0336	0.0335	0.0322
$wR(F^2)$ ($I > 2\sigma(I)$)	0.0937	0.0922	0.0896
R_1 (all data)	0.0366	0.0359	0.0345
$wR(F^2)$ (all data)	0.0959	0.0941	0.0912
Goodness-of-fit	1.096	1.109	1.085
CCDC deposition number	1995689	1995688	1995687

Table S13. X-ray data for **res**•(**AP**)$_{0.75}$•(**BPE**)$_{0.25}$ at 290, 270, and 250 K.

compound formula	$C_{16.46}H_{14.46}N_{3.54}O_2$	$C_{16.46}H_{14.46}N_{3.54}O_2$	$C_{16.45}H_{14.45}N_{3.55}O_2$
formula mass	293.86	293.85	293.87
crystal system	Triclinic	Triclinic	Triclinic
space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a/Å	8.04776(11)	8.02672(12)	8.00509(19)
b/Å	9.80445(15)	9.79494(16)	9.78356(18)
c/Å	10.87711(16)	10.86753(18)	10.8603(2)
α/°	94.0306(12)	93.9195(13)	93.8151(16)
β/°	106.4496(13)	106.4603(14)	106.4802(19)
γ/°	113.6558(14)	113.7186(15)	113.764(2)
V/Å^3	737.25(2)	733.83(2)	730.44(3)
ρ_{calc}/g cm^{-3}	1.324	1.330	1.336
T/K	290(2)	270(2)	250(2)
Z	2	2	2
radiation type	CuKα	CuKα	CuKα
absorption coefficient, μ/mm^{-1}	0.735	0.738	0.742
no. of reflections measured	27841	27725	27550
no. of independent reflections	3036	3022	3003
no. of reflection ($I > 2\sigma(I)$)	2556	2606	2641
R_{int}	0.0380	0.0369	0.0358
R_1 ($I > 2\sigma(I)$)	0.0433	0.0422	0.0412
$wR(F^2)$ ($I > 2\sigma(I)$)	0.1247	0.1206	0.1160
R_1 (all data)	0.0494	0.0472	0.0455
$wR(F^2)$ (all data)	0.1308	0.1254	0.1205
Goodness-of-fit	1.079	1.063	1.070
CCDC deposition number	1995493	1995492	1995491

Table S14. X-ray data for **res**•(**AP**)$_{0.75}$•(**BPE**)$_{0.25}$ at 230, 210, and 190 K.

compound formula	$C_{16.46}H_{14.46}N_{3.54}O_2$	$C_{16.59}H_{14.59}N_{3.41}O_2$	$C_{16.50}H_{14.50}N_{3.50}O_2$
formula mass	293.85	293.73	293.82
crystal system	Triclinic	Triclinic	Triclinic
space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a/Å	7.98898(12)	7.9687(2)	7.9561(2)
b/Å	9.77584(13)	9.7664(2)	9.75452(15)
c/Å	10.85419(16)	10.8474(2)	10.8395(2)
α/°	93.7189(12)	93.6260(17)	93.5338(16)
β/°	106.5072(14)	106.527(2)	106.566(2)
γ/°	113.8224(14)	113.856(2)	113.8855(19)
V/Å^3	727.76(2)	724.71(3)	722.05(3)
ρ_{calc}/g cm^{-3}	1.341	1.346	1.351
T/K	230(2)	210(2)	190(2)
Z	2	2	2
radiation type	CuKα	CuKα	CuKα
absorption coefficient, μ/mm^{-1}	0.745	0.745	0.750
no. of reflections measured	27433	27317	27314
no. of independent reflections	2997	2988	2987
no. of reflection ($I > 2\sigma(I)$)	2686	2703	2731
R_{int}	0.0353	0.0354	0.0347
R_1 ($I > 2\sigma(I)$)	0.0394	0.0388	0.0372
$wR(F^2)$ ($I > 2\sigma(I)$)	0.1134	0.1084	0.1058
R_1 (all data)	0.0428	0.0420	0.0398
$wR(F^2)$ (all data)	0.1168	0.1117	0.1083
Goodness-of-fit	1.086	1.064	1.058
CCDC deposition number	1995490	1995489	1995488

Table S15. X-ray data for **res•(AP)**$_{0.50}$**•(BPE)**$_{0.50}$ at 290, 270, and 250 K.

compound formula	$C_{17.05}H_{15.05}N_{2.95}O_2$	$C_{17.03}H_{15.03}N_{2.97}O_2$	$C_{17.04}H_{15.04}N_{2.96}O_2$
formula mass	293.27	293.29	293.28
crystal system	Triclinic	Triclinic	Triclinic
space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a/Å	8.0886(2)	8.06741(16)	8.04836(15)
b/Å	9.8583(2)	9.8484(2)	9.83877(18)
c/Å	10.9012(2)	10.8930(2)	10.88786(18)
α/°	93.7995(18)	93.6858(16)	93.5909(14)
β/°	106.674(2)	106.6746(17)	106.7035(16)
γ/°	113.898(2)	113.951(2)	113.9933(18)
V/Å^3	744.61(3)	741.36(3)	738.39(3)
ρ_{calc}/g cm^{-3}	1.308	1.314	1.319
T/K	290(2)	270(2)	250(2)
Z	2	2	2
radiation type	CuKα	CuKα	CuKα
absorption coefficient, μ/mm^{-1}	0.715	0.718	0.721
no. of reflections measured	25036	20462	21652
no. of independent reflections	3000	2931	2966
no. of reflection ($I > 2\sigma(I)$)	2311	2327	2431
R_{int}	0.0577	0.0485	0.0503
R_1 ($I > 2\sigma(I)$)	0.0415	0.0404	0.0387
$wR(F^2)$ ($I > 2\sigma(I)$)	0.1105	0.1087	0.1032
R_1 (all data)	0.0562	0.0519	0.0479
$wR(F^2)$ (all data)	0.1288	0.1226	0.1148
Goodness-of-fit	1.047	1.036	1.042
CCDC deposition number	1995487	1995486	1995485

Table S16. X-ray data for **res•(AP)**$_{0.50}$**•(BPE)**$_{0.50}$ at 230, 210, and 190 K.

compound formula	$C_{17.09}H_{15.09}N_{2.91}O_2$	$C_{17.07}H_{15.07}N_{2.93}O_2$	$C_{17.08}H_{15.08}N_{2.92}O_2$
formula mass	293.23	293.25	293.24
crystal system	Triclinic	Triclinic	Triclinic
space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a/Å	8.03047(14)	8.01388(15)	7.99695(15)
b/Å	9.82913(17)	9.81882(18)	9.8077(3)
c/Å	10.88163(17)	10.87660(17)	10.8728(2)
α/°	93.5015(14)	93.4063(14)	93.323(3)
β/°	106.7347(15)	106.7767(15)	106.8183(17)
γ/°	114.0289(17)	114.0626(18)	114.090(2)
V/Å^3	735.48(2)	732.70(2)	729.91(3)
ρ_{calc}/g cm^{-3}	1.324	1.329	1.334
T/K	230(2)	210(2)	190(2)
Z	2	2	2
radiation type	CuKα	CuKα	CuKα
absorption coefficient, μ/mm^{-1}	0.723	0.726	0.728
no. of reflections measured	22021	22578	23005
no. of independent reflections	2979	2977	2976
no. of reflection (I > 2σ(I))	2505	2557	2596
R_{int}	0.0480	0.0478	0.0465
R_1 (I > 2σ(I))	0.0390	0.0376	0.0370
$wR(F^2)$ (I > 2σ(I))	0.1026	0.1044	0.1024
R_1 (all data)	0.0465	0.0438	0.0423
$wR(F^2)$ (all data)	0.1114	0.1123	0.1090
Goodness-of-fit	1.043	1.045	1.052
CCDC deposition number	1995484	1995483	1995482

Table S17. X-ray data for **res•(AP)**$_{0.25}$**•(BPE)**$_{0.75}$ at 290, 270, and 250 K.

compound formula	$C_{17.54}H_{15.54}N_{2.46}O_2$	$C_{17.54}H_{15.54}N_{2.46}O_2$	$C_{17.56}H_{15.56}N_{2.44}O_2$
formula mass	292.78	292.78	292.76
crystal system	Triclinic	Triclinic	Triclinic
space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a/Å	8.13099(12)	8.10962(13)	8.09014(10)
b/Å	9.90773(12)	9.89822(18)	9.88806(15)
c/Å	10.90319(14)	10.89834(15)	10.89279(13)
α/°	93.3530(10)	93.2450(18)	93.1584(16)
β/°	107.0207(13)	107.0364(13)	107.0442(11)
γ/°	114.1614(13)	114.2057(13)	114.2427(11)
V/Å^3	750.133(19)	747.06(2)	744.094(19)
ρ_{calc}/g cm^{-3}	1.296	1.302	1.307
T/K	290(2)	270(2)	250(2)
Z	2	2	2
radiation type	CuKα	CuKα	CuKα
absorption coefficient, μ/mm^{-1}	0.699	0.702	0.704
no. of reflections measured	26809	27405	27432
no. of independent reflections	3064	3053	3046
no. of reflection (I > 2σ(I))	2616	2643	2690
R_{int}	0.0386	0.0345	0.0350
R_1 (I > 2σ(I))	0.0398	0.0381	0.0372
$wR(F^2)$ (I > 2σ(I))	0.1081	0.1089	0.1068
R_1 (all data)	0.0452	0.0432	0.0409
$wR(F^2)$ (all data)	0.1131	0.1141	0.1104
Goodness-of-fit	0.991	1.069	1.080
CCDC deposition number	1995480	1995479	1995478

Table S18. X-ray data for **res•(AP)**$_{0.25}$**•(BPE)**$_{0.75}$ at 230, 210, and 190 K.

compound formula	$C_{17.55}H_{15.55}N_{2.45}O_2$	$C_{17.57}H_{15.57}N_{2.43}O_2$	$C_{17.60}H_{15.60}N_{2.40}O_2$
formula mass	292.77	292.75	292.72
crystal system	Triclinic	Triclinic	Triclinic
space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a/Å	8.07233(10)	8.05644(11)	8.0377(3)
b/Å	9.87774(15)	9.86768(17)	9.8551(4)
c/Å	10.88779(14)	10.88249(16)	10.8773(3)
α/°	93.0700(16)	92.9895(18)	92.913(4)
β/°	107.0652(11)	107.0934(13)	107.077(3)
γ/°	114.2729(11)	114.3019(13)	114.297(3)
V/Å^3	741.293(19)	738.62(2)	735.96(5)
ρ_{calc}/g cm^{-3}	1.312	1.316	1.321
T/K	230(2)	210(2)	190(2)
Z	2	2	2
radiation type	CuKα	CuKα	CuKα
absorption coefficient, μ/mm^{-1}	0.707	0.709	0.711
no. of reflections measured	27752	27429	27457
no. of independent reflections	3038	3036	3022
no. of reflection ($I > 2\sigma(I)$)	2721	2761	2782
R_{int}	0.0359	0.0352	0.0361
R_1 ($I > 2\sigma(I)$)	0.0364	0.0364	0.0357
$wR(F^2)$ ($I > 2\sigma(I)$)	0.1047	0.1055	0.1023
R_1 (all data)	0.0397	0.0393	0.0378
$wR(F^2)$ (all data)	0.1080	0.1084	0.1042
Goodness-of-fit	1.071	1.088	1.085
CCDC deposition number	1995477	1995476	1995475

Table S19. Percentages of each bipyridine in the **res**•(**AP**)$_x$•(**BPA**)$_y$ cocrystals based on single-crystal X-ray diffraction. The first component is **AP**, and the second component is **BPA**.

Mixed cocrystal	Temperature (K)	First component major (%)	First component minor (%)	Second component (%)
res•(**AP**)$_{0.75}$•(**BPA**)$_{0.25}$	290	61	15	24
	270	64	12	24
	250	66	10	24
	230	67	8	25
	210	69	6	25
	190	70	4	26
res•(**AP**)$_{0.50}$•(**BPA**)$_{0.50}$	290	45	10	45
	270	45	8	47
	250	45	7	48
	230	48	5	47
	210	48	4	48
	190	48	3	49
res•(**AP**)$_{0.25}$•(**BPA**)$_{0.75}$	290	29	5	66
	270	30	4	66
	250	30	3	67
	230	30	3	67
	210	31	2	67
	190	31	1	68

Table S20. Percentages of each bipyridine in the **res**•(**BPE**)$_x$•(**BPA**)$_y$ cocrystals based on single-crystal X-ray diffraction. The first component is **BPE**, and the second component is **BPA**.

Mixed cocrystal	Temperature (K)	First component major (%)	First component minor (%)	Second component (%)
res•(**BPE**)$_{0.75}$•(**BPA**)$_{0.25}$	290	66	9	25
	270	67	8	25
	250	68	7	25
	230	69	6	25
	210	70	5	25
	190	71	4	25
res•(**BPE**)$_{0.50}$•(**BPA**)$_{0.50}$	290	43	8	49
	270	44	7	49
	250	46	5	49
	230	48	3	49
	210	51	0	49
	190	51	0	49
res•(**BPE**)$_{0.25}$•(**BPA**)$_{0.75}$	290	30	0	70
	270	31	0	69
	250	29	0	71
	230	30	0	70
	210	29	0	71
	190	30	0	70

Table S21. Percentages of each bipyridine in the **res**•(**AP**)$_x$•(**BPE**)$_y$ cocrystals based on single-crystal X-ray diffraction. The first component is **AP**, and the second component is **BPE**.

Mixed cocrystal	Temperature (K)	First component major (%)	First component minor (%)	Second component (%)
res•(**AP**)$_{0.75}$•(**BPE**)$_{0.25}$	290	64	13	23
	270	68	9	23
	250	71	7	22
	230	72	5	23
	210	72	4	24
	190	73	2	25
res•(**AP**)$_{0.50}$•(**BPE**)$_{0.50}$	290	37	11	52
	270	41	8	51
	250	42	6	52
	230	42	4	54
	210	44	3	53
	190	44	2	54
res•(**AP**)$_{0.25}$•(**BPE**)$_{0.75}$	290	14	9	77
	270	17	6	77
	250	18	4	78
	230	20	3	77
	210	20	2	78
	190	20	0	80

3. Thermal Expansion Data and Intermolecular Interaction Distances

The thermal expansion coefficients were calculated using the PASCal program.[4] The unit cell parameters from the crystallographic data sets collected at 290, 270, 250, 230, 210, and 190 K were used for the thermal expansion calculations.

Table S22. Thermal expansion coefficients for the mixed cocrystals. Errors are denoted in parentheses and approximate crystallographic axes are denoted in brackets.

Mixed cocrystal	α_{X_1} (MK^{-1}) [axis]	α_{X_2} (MK^{-1}) [axis]	α_{X_3} (MK^{-1}) [axis]	α_V (MK^{-1})
res•(AP)$_{0.75}$**•(BPA)**$_{0.25}$	-20 (1) [-1 -5 -4]	84 (2) [1 -2 2]	140 (2) [3 1 0]	205 (3)
res•(AP)$_{0.50}$**•(BPA)**$_{0.50}$	-13 (1) [1 4 4]	82 (1) [1 6 -4]	112 (2) [-5 -1 -1]	183 (4)
res•(AP)$_{0.25}$**•(BPA)**$_{0.75}$	-9 (1) [0 1 1]	77 (1) [0 3 -2]	110 (1) [-4 -1 -1]	179 (1)
res•(BPE)$_{0.75}$**•(BPA)**$_{0.25}$	-14 (1) [1 3 3]	70 (1) [0 3 -2]	131 (3) [-6 -2 -1]	188 (3)
res•(BPE)$_{0.50}$**•(BPA)**$_{0.50}$	-11 (1) [1 3 3]	71 (1) [-1 8 -5]	123(2) [-6 -2 -1]	183 (2)
res•(BPE)$_{0.25}$**•(BPA)**$_{0.75}$	-9 (1) [1 4 5]	70 (1) [0 4 -3]	114 (1) [-6 -2 -1]	177 (2)
res•(AP)$_{0.75}$**•(BPE)**$_{0.25}$	-10 (1) [1 3 3]	82 (1) [-1 4 -3]	136 (5) [-3 -1 0]	210 (4)
res•(AP)$_{0.50}$**•(BPE)**$_{0.50}$	-12 (1) [1 3 4]	79 (1) [0 2 -1]	132 (2) [-6 -2 -1]	200 (3)
res•(AP)$_{0.25}$**•(BPE)**$_{0.75}$	-13 (1) [1 2 2]	77 (1) [0 2 -1]	127 (3) [-4 -1 0]	192 (3)

Table S23. Intermolecular interaction distances within the mixed cocrystals that contribute to the thermal expansion along X_1.

Mixed cocrystal	Donor-Acceptor	O-H···N (Å) 290 K	O-H···N (Å) 190 K	Δ (Å)
res•(**AP**)$_{0.75}$•(**BPA**)$_{0.25}$	**res**-major **AP**	2.771	2.765	0.006
	res-major **AP**	2.827	2.828	-0.001
	res-minor **AP**/**BPA**	2.771	2.765	0.006
	res-minor **AP**/**BPA**	2.727	2.650	0.077
res•(**AP**)$_{0.50}$•(**BPA**)$_{0.50}$	**res**-major **AP**	2.767	2.758	0.009
	res-major **AP**	2.854	2.897	-0.043
	res-minor **AP**/**BPA**	2.767	2.758	0.009
	res-minor **AP**/**BPA**	2.721	2.654	0.067
res•(**AP**)$_{0.25}$•(**BPA**)$_{0.75}$	**res**-major **AP**	2.762	2.749	0.013
	res-major **AP**	2.871	2.881	-0.010
	res-minor **AP**/**BPA**	2.762	2.749	0.013
	res-minor **AP**/**BPA**	2.738	2.717	0.021
res•(**BPE**)$_{0.75}$•(**BPA**)$_{0.25}$	**res**-major **BPE**	2.749	2.740	0.009
	res-major **BPE**	2.786	2.782	0.004
	res-minor **BPE**/**BPA**	2.749	2.740	0.009
	res-minor **BPE**/**BPA**	2.699	2.668	0.031
res•(**BPE**)$_{0.50}$•(**BPA**)$_{0.50}$	**res**-major **BPE**	2.753	2.741	0.012
	res-major **BPE**	2.805	2.792	0.013
	res-minor **BPE**/**BPA**	2.753	2.741	0.012
	res-minor **BPE**/**BPA**	2.724	2.698	0.026
res•(**BPE**)$_{0.25}$•(**BPA**)$_{0.75}$	**res**-**BPE**	2.756	2.745	0.011
	res-**BPE**	2.820	2.822	-0.002
	res-**BPA**	2.756	2.745	0.011
	res-**BPA**	2.740	2.725	0.015
res•(**AP**)$_{0.75}$•(**BPE**)$_{0.25}$	**res**-**AP**/**BPE**	2.771	2.762	0.009
	res-**AP**/**BPE**	2.789	2.779	0.010
res•(**AP**)$_{0.50}$•(**BPE**)$_{0.50}$	**res**-**AP**/**BPE**	2.763	2.754	0.009
	res-**AP**/**BPE**	2.780	2.771	0.009
res•(**AP**)$_{0.25}$•(**BPE**)$_{0.75}$	**res**-**AP**/**BPE**	2.752	2.744	0.008
	res-**AP**/**BPE**	2.769	2.759	0.010

Mixed cocrystal	C-H (β)···O (Å) 290 K	C-H (β)···O (Å) 190 K	Δ (Å)
res•(**AP**)$_{0.75}$•(**BPA**)$_{0.25}$	3.297	3.254	0.043
res•(**AP**)$_{0.50}$•(**BPA**)$_{0.50}$	3.299	3.262	0.037
res•(**AP**)$_{0.25}$•(**BPA**)$_{0.75}$	3.292	3.254	0.038
res•(**BPE**)$_{0.75}$•(**BPA**)$_{0.25}$	3.301	3.263	0.038
res•(**BPE**)$_{0.50}$•(**BPA**)$_{0.50}$	3.298	3.262	0.036
res•(**BPE**)$_{0.25}$•(**BPA**)$_{0.75}$	3.294	3.257	0.037
res•(**AP**)$_{0.75}$•(**BPE**)$_{0.25}$	3.300	3.257	0.043
res•(**AP**)$_{0.50}$•(**BPE**)$_{0.50}$	3.304	3.262	0.042
res•(**AP**)$_{0.25}$•(**BPE**)$_{0.75}$	3.301	3.263	0.038

Table S24. Intermolecular interaction distances within the mixed cocrystals that contribute to the thermal expansion along X_2. The C-H(α) and C-H(β) are on the pyridine ring.

Mixed cocrystal	C-H (α)···O (Å) 290 K	C-H (α)···O (Å) 190 K	Δ (Å)	C-H (β)···O (Å) 290 K	C-H (β)···O (Å) 190 K	Δ (Å)	Avg. Δ for all (Å)
res•(**AP**)$_{0.75}$•(**BPA**)$_{0.25}$	3.614	3.583	0.031	3.402	3.321	0.081	0.056
res•(**AP**)$_{0.50}$•(**BPA**)$_{0.50}$	3.589 3.804 3.380	3.555 3.751 3.349	0.034 0.053 0.031	3.299 3.427	3.262 3.353	0.037 0.074	0.046
res•(**AP**)$_{0.25}$•(**BPA**)$_{0.75}$	3.817 3.561 3.398	3.770 3.528 3.359	0.047 0.033 0.039	3.446 3.292	3.382 3.254	0.064 0.038	0.044
res•(**BPE**)$_{0.75}$•(**BPA**)$_{0.25}$	3.685 3.613	3.656 3.554	0.029 0.059	3.409 3.301	3.349 3.263	0.060 0.038	0.047
res•(**BPE**)$_{0.50}$•(**BPA**)$_{0.50}$	3.635 3.642	3.605 3.589	0.030 0.053	3.423 3.298	3.370 3.262	0.053 0.036	0.043
res•(**BPE**)$_{0.25}$•(**BPA**)$_{0.75}$	3.635 3.587	3.601 3.557	0.034 0.030	3.294 3.400	3.257 3.371	0.037 0.029	0.033
res•(**AP**)$_{0.75}$•(**BPE**)$_{0.25}$	3.382 3.664 3.672	3.351 3.625 3.614	0.031 0.039 0.058	3.338	3.282	0.056	0.046
res•(**AP**)$_{0.50}$•(**BPE**)$_{0.50}$	3.657 3.692	3.600 3.656	0.057 0.036	3.304 3.364	3.262 3.307	0.042 0.057	0.048
res•(**AP**)$_{0.25}$•(**BPE**)$_{0.75}$	3.714 3.634	3.678 3.577	0.036 0.057	3.378 3.301	3.322 3.263	0.056 0.038	0.047

Mixed cocrystal	C-H···π (Å) 290 K	C-H···π (Å) 190 K	Δ (Å)	Avg. Δ (Å)
res•(**AP**)$_{0.75}$•(**BPA**)$_{0.25}$	3.668 3.565	3.618 3.531	0.050 0.034	0.042
res•(**AP**)$_{0.50}$•(**BPA**)$_{0.50}$	3.560 3.728	3.531 3.672	0.029 0.056	0.043
res•(**AP**)$_{0.25}$•(**BPA**)$_{0.75}$	3.827 3.562	3.752 3.528	0.075 0.034	0.055
res•(**BPE**)$_{0.75}$•(**BPA**)$_{0.25}$	3.585 3.649	3.558 3.615	0.027 0.034	0.031
res•(**BPE**)$_{0.50}$•(**BPA**)$_{0.50}$	3.622 3.571	3.589 3.531	0.033 0.040	0.037
res•(**BPE**)$_{0.25}$•(**BPA**)$_{0.75}$	3.595 3.581	3.562 3.548	0.033 0.033	0.033
res•(**AP**)$_{0.75}$•(**BPE**)$_{0.25}$	3.595 3.653	3.555 3.610	0.040 0.043	0.042
res•(**AP**)$_{0.50}$•(**BPE**)$_{0.50}$	3.668 3.621	3.625 3.582	0.043 0.039	0.041
res•(**AP**)$_{0.25}$•(**BPE**)$_{0.75}$	3.677 3.645	3.637 3.610	0.040 0.035	0.038

Mixed cocrystal	layer-layer(res) (Å) 290 K	layer-layer(res) (Å) 190 K	Δ (Å)	centroid(res)-centroid(pyr) (Å) 290 K	centroid(res)-centroid(pyr) (Å) 190 K	Δ (Å)	Avg. Δ (Å)
res•(AP)$_{0.75}$**•(BPA)**$_{0.25}$	9.762	9.728	0.034	5.109 4.952	5.048 4.884	0.061 0.068	0.065
res•(AP)$_{0.50}$**•(BPA)**$_{0.50}$	9.791	9.744	0.047	5.113 4.941	5.067 4.882	0.046 0.059	0.053
res•(AP)$_{0.25}$**•(BPA)**$_{0.75}$	9.806	9.762	0.044	5.086 4.936	5.053 4.884	0.033 0.052	0.043
res•(BPE)$_{0.75}$**•(BPA)**$_{0.25}$	9.910	9.867	0.043	5.091 4.912	5.047 4.864	0.044 0.048	0.046
res•(BPE)$_{0.50}$**•(BPA)**$_{0.50}$	9.880	9.835	0.045	5.100 4.912	5.067 4.874	0.033 0.038	0.036
res•(BPE)$_{0.25}$**•(BPA)**$_{0.75}$	9.851	9.806	0.045	5.101 4.922	5.064 4.875	0.037 0.047	0.042
res•(AP)$_{0.75}$**•(BPE)**$_{0.25}$	9.804	9.755	0.049	5.092 4.956	5.036 4.887	0.056 0.069	0.063
res•(AP)$_{0.50}$**•(BPE)**$_{0.50}$	9.858	9.808	0.050	5.096 4.950	5.048 4.888	0.048 0.062	0.055
res•(AP)$_{0.25}$**•(BPE)**$_{0.75}$	9.908	9.855	0.053	5.081 4.927	5.038 4.877	0.043 0.050	0.047

Table S25. Intermolecular interaction distances within the mixed cocrystals that contribute to the thermal expansion along X_3.

Mixed cocrystal	π-π stacking (within/between assemblies) (Å) 290 K	π-π stacking (within/between assemblies) (Å) 190 K	Δ (Å)
res•(AP)$_{0.75}$**•(BPA)**$_{0.25}$	3.884 4.531	3.833 4.494	0.051 0.037
res•(AP)$_{0.50}$**•(BPA)**$_{0.50}$	3.874 4.600	3.831 4.593	0.043 0.007
res•(AP)$_{0.25}$**•(BPA)**$_{0.75}$	3.887 4.669	3.847 4.654	0.040 0.015
res•(BPE)$_{0.75}$**•(BPA)**$_{0.25}$	3.888 4.633	3.848 4.583	0.040 0.050
res•(BPE)$_{0.50}$**•(BPA)**$_{0.50}$	3.893 4.653	3.856 4.600	0.037 0.053
res•(BPE)$_{0.25}$**•(BPA)**$_{0.75}$	3.928 4.655	3.889 4.617	0.039 0.038
res•(AP)$_{0.75}$**•(BPE)**$_{0.25}$	3.875 4.490	3.831 4.442	0.044 0.048
res•(AP)$_{0.50}$**•(BPE)**$_{0.50}$	3.880 4.530	3.837 4.481	0.043 0.049
res•(AP)$_{0.25}$**•(BPE)**$_{0.75}$	3.885 4.575	3.844 4.523	0.041 0.052

4. Expansivity Indicatrix Images

Axes	α(MK^{-1})	σα (MK^{-1})	Direction a	b	c
X_1	-20.3306	1.0290	-0.1464	-0.7554	-0.6387
X_2	84.2989	2.1936	0.3439	-0.6002	0.7221
X_3	139.6940	1.9713	0.9251	0.3728	0.0720
V	204.9107	3.0257			

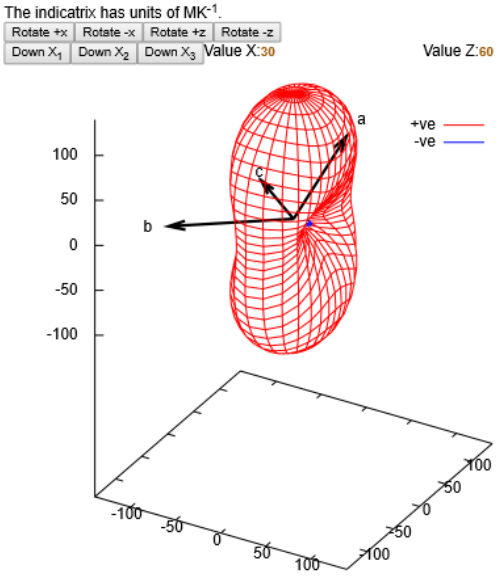

Figure S1. Thermal expansivity indicatrix for the mixed cocrystal **res**•(**AP**)$_{0.75}$•(**BPA**)$_{0.25}$.

Axes	α(MK^{-1})	σα (MK^{-1})	Direction a	b	c
X_1	-12.5367	0.8484	0.1604	0.6744	0.7207
X_2	82.0069	1.2167	0.1261	0.8323	-0.5399
X_3	112.3593	1.5830	-0.9507	-0.2372	-0.1996
V	183.0378	3.6320			

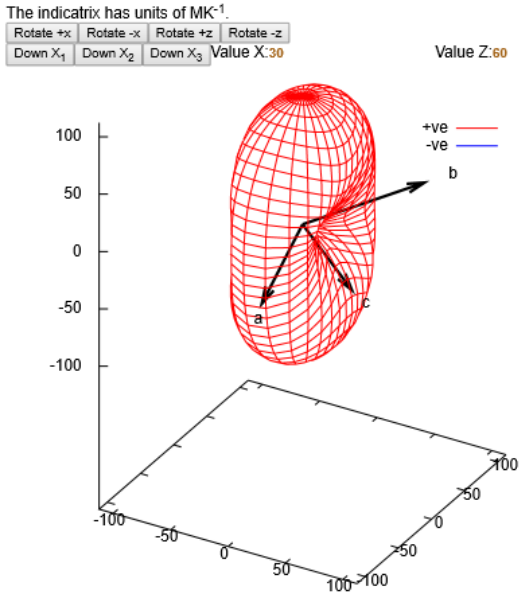

Figure S2. Thermal expansivity indicatrix for the mixed cocrystal **res**•(**AP**)$_{0.50}$•(**BPA**)$_{0.50}$.

Axes	α(MK^{-1})	σα (MK^{-1})	Direction a	b	c
X_1	-8.8931	0.5206	0.0935	0.6843	0.7232
X_2	76.8947	1.2732	0.0467	0.8163	-0.5757
X_3	109.7630	1.0093	-0.9348	-0.2886	-0.2070
V	178.7459	1.4668			

Expansivity Indicatrix

The indicatrix has units of MK^{-1}.

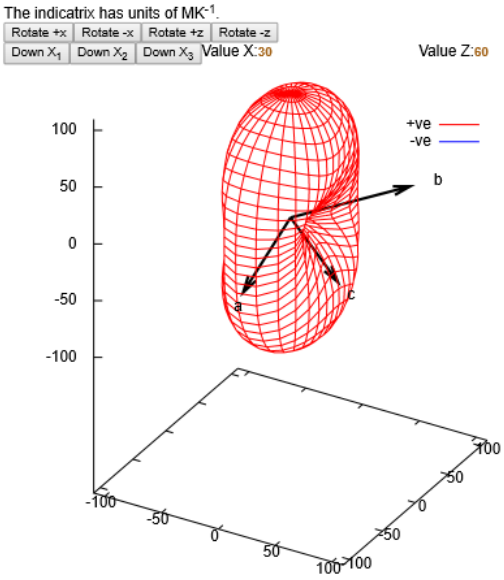

Figure S3. Thermal expansivity indicatrix for the mixed cocrystal **res•(AP)**$_{0.25}$**•(BPA)**$_{0.75}$.

Axes	α(MK^{-1})	σα (MK^{-1})	Direction a	b	c
X_1	-13.6426	0.6891	0.2291	0.6370	0.7360
X_2	70.4750	0.3682	-0.0420	0.8309	-0.5548
X_3	130.5231	3.0978	-0.9514	-0.2789	-0.1306
V	188.3941	2.8301			

Expansivity Indicatrix

The indicatrix has units of MK^{-1}.

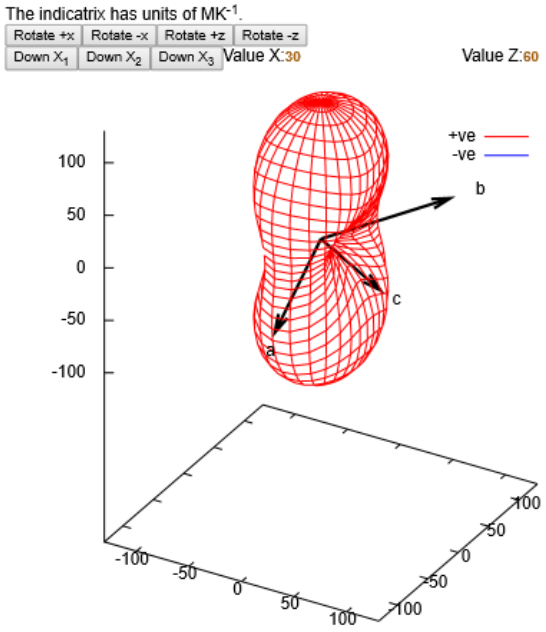

Figure S4. Thermal expansivity indicatrix for the mixed cocrystal **res•(BPE)**$_{0.75}$**•(BPA)**$_{0.25}$.

			Direction		
Axes	α(MK^{-1})	σα (MK^{-1})	a	b	c
X_1	-11.3865	0.2123	0.2208	0.6351	0.7402
X_2	70.5660	0.6820	-0.0914	0.8246	-0.5583
X_3	123.3513	2.2343	-0.9457	-0.3004	-0.1246
V	183.4948	2.2617			

Expansivity Indicatrix

The indicatrix has units of MK^{-1}.

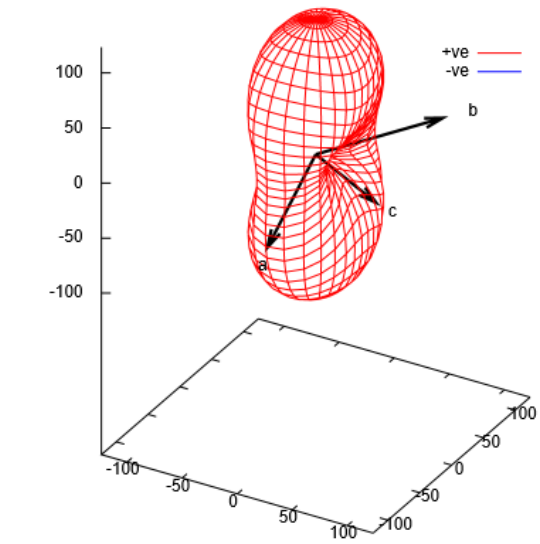

Figure S5. Thermal expansivity indicatrix for the mixed cocrystal **res•(BPE)**$_{0.50}$**•(BPA)**$_{0.50}$.

			Direction		
Axes	α(MK^{-1})	σα (MK^{-1})	a	b	c
X_1	-8.7795	0.4975	0.1348	0.6549	0.7436
X_2	70.0128	0.5449	-0.0493	0.8195	-0.5709
X_3	114.3446	1.0067	-0.9349	-0.3111	-0.1709
V	176.5120	2.0501			

Expansivity Indicatrix

The indicatrix has units of MK^{-1}.

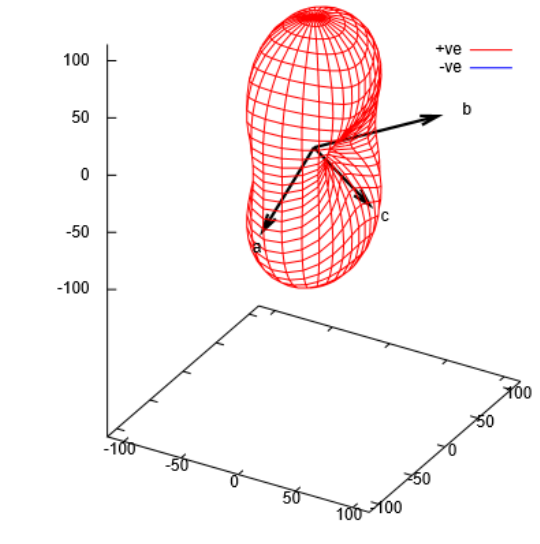

Figure S6. Thermal expansivity indicatrix for the mixed cocrystal **res•(BPE)**$_{0.25}$**•(BPA)**$_{0.75}$.

			Direction		
Axes	α(MK^{-1})	σα (MK^{-1})	a	b	c
X_1	-9.7068	1.1890	0.2099	0.6672	0.7147
X_2	82.1967	0.8590	-0.1738	0.7775	-0.6044
X_3	136.0834	5.0063	-0.9434	-0.3169	-0.0976
V	210.2356	4.4026			

Expansivity Indicatrix

The indicatrix has units of MK^{-1}.

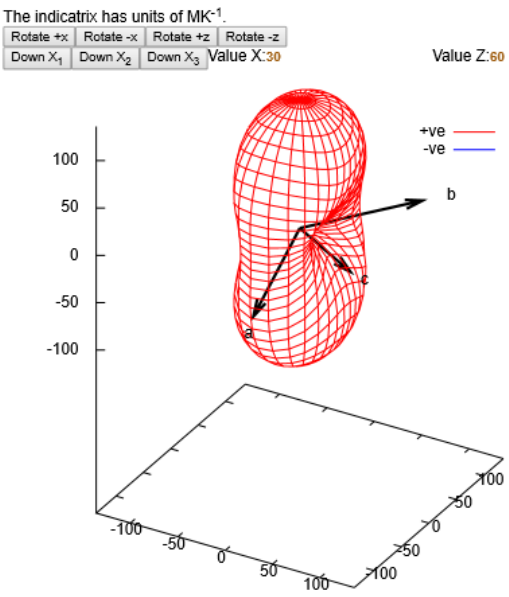

Figure S7. Thermal expansivity indicatrix for the mixed cocrystal **res•(AP)**$_{0.75}$**•(BPE)**$_{0.25}$.

			Direction		
Axes	α(MK^{-1})	σα (MK^{-1})	a	b	c
X_1	-11.7039	0.7821	0.2012	0.6243	0.7548
X_2	79.2121	0.9794	0.0391	0.8589	-0.5107
X_3	131.7113	2.4613	-0.9540	-0.2578	-0.1530
V	200.4207	2.8004			

Expansivity Indicatrix

The indicatrix has units of MK^{-1}.

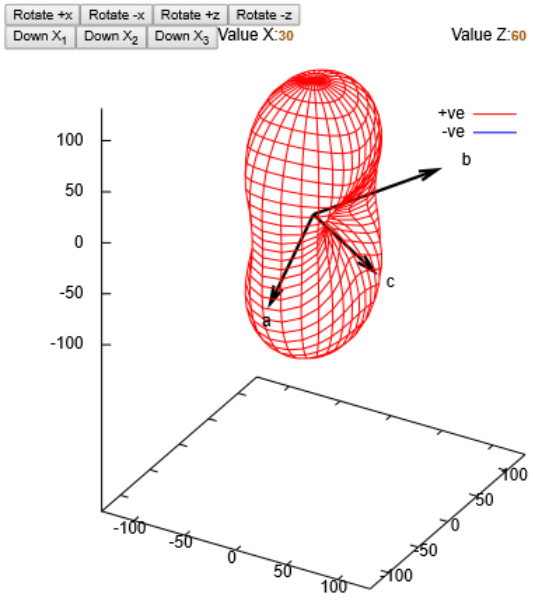

Figure S8. Thermal expansivity indicatrix for the mixed cocrystal **res•(AP)**$_{0.50}$**•(BPE)**$_{0.50}$.

Axes	α(MK^{-1})	σα (MK^{-1})	Direction a	b	c
X_1	-12.5064	1.3288	0.3363	0.5933	0.7314
X_2	77.0971	0.4183	-0.0056	0.8677	-0.4971
X_3	126.5613	3.3220	-0.9690	-0.2340	-0.0790
V	192.3073	2.6394			

Expansivity Indicatrix

The indicatrix has units of MK^{-1}.

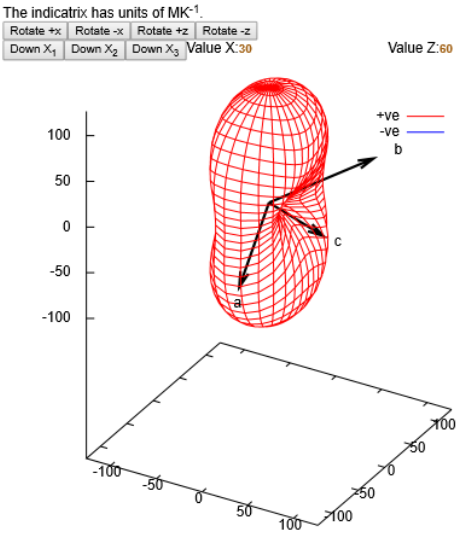

Figure S9. Thermal expansivity indicatrix for the mixed cocrystal **res**•(**AP**)$_{0.25}$•(**BPE**)$_{0.75}$.

5. ^{1}H NMR Spectra of Mixed Cocrystals

Single crystals from the cocrystallization experiments were removed from the vial and dissolved in DMSO-d_6 for ^{1}H NMR experiments. NMR data was collected using a JOEL ECS 400 MHZ Spectrometer with multinuclear, direct and inverse detection probes, automatic sample changer, variable temperature, and Z-gradient capabilities.

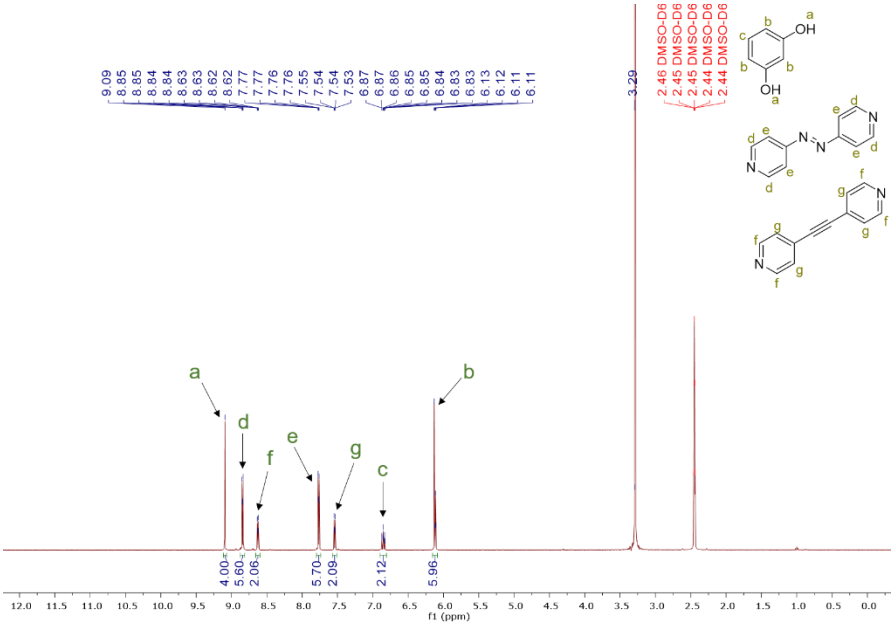

Figure S10. ^{1}H NMR spectrum for the mixed cocrystal **res•(AP)**$_{0.75}$**•(BPA)**$_{0.25}$.

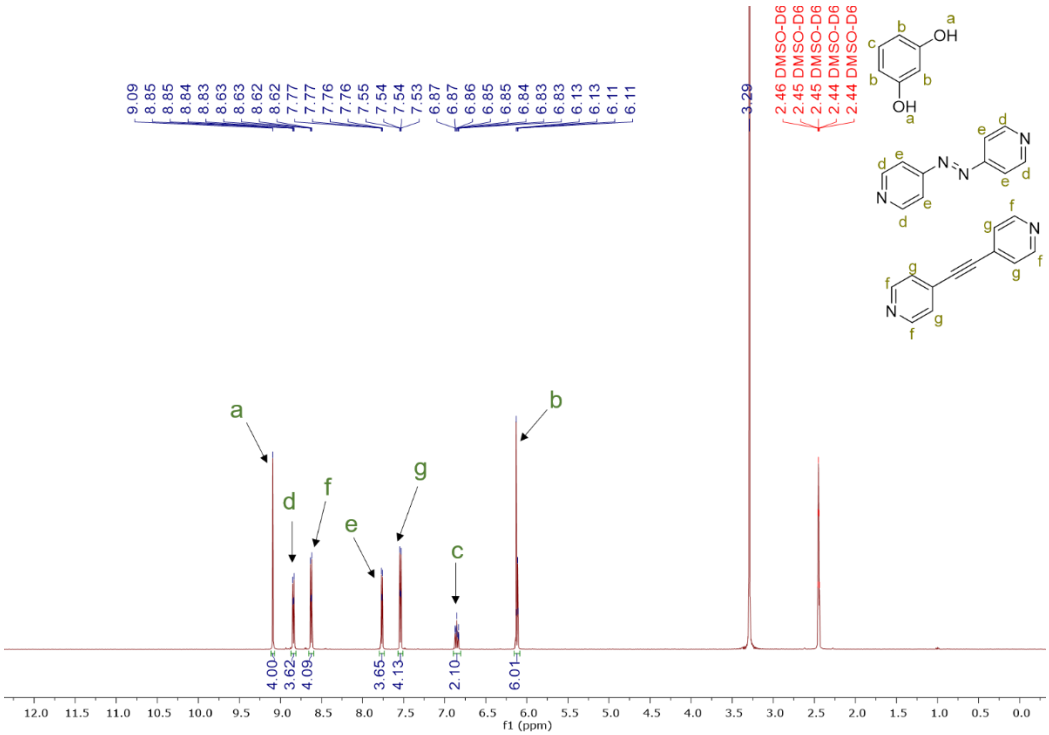

Figure S11. ^{1}H NMR spectrum for the mixed cocrystal **res•(AP)**$_{0.50}$**•(BPA)**$_{0.50}$.

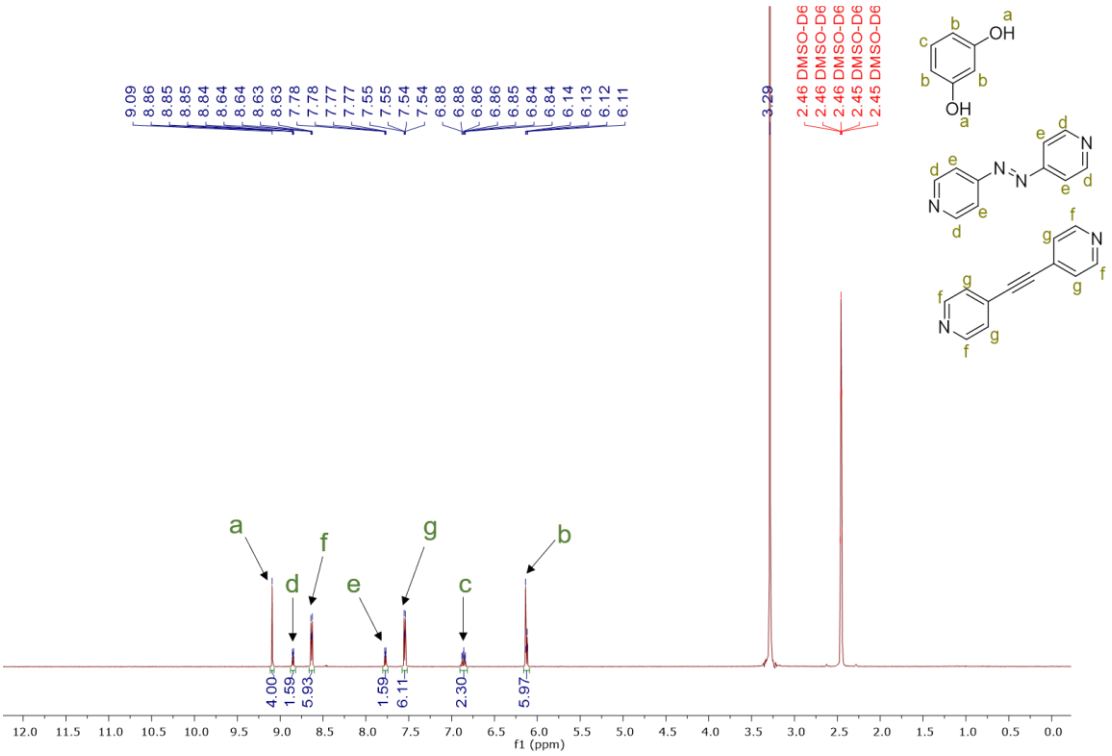

Figure S12. ^{1}H NMR spectrum for the mixed cocrystal **res**•(**AP**)$_{0.25}$•(**BPA**)$_{0.75}$.

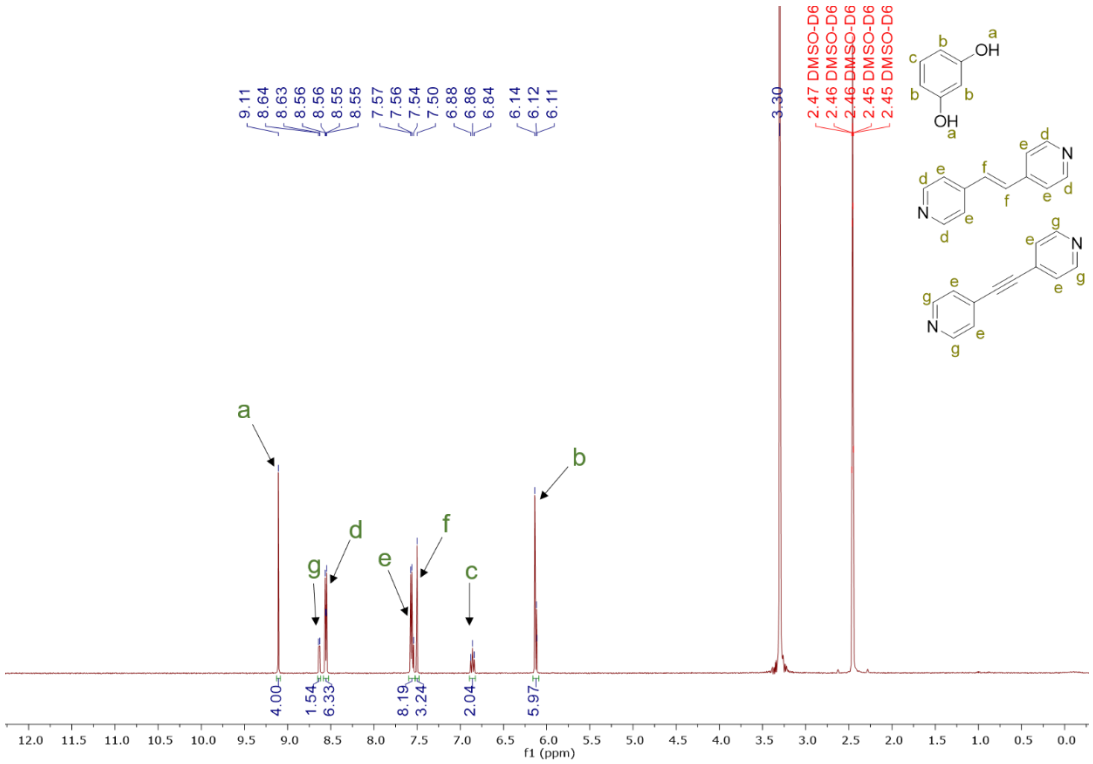

Figure S13. ^{1}H NMR spectrum for the mixed cocrystal **res**•(**BPE**)$_{0.75}$•(**BPA**)$_{0.25}$.

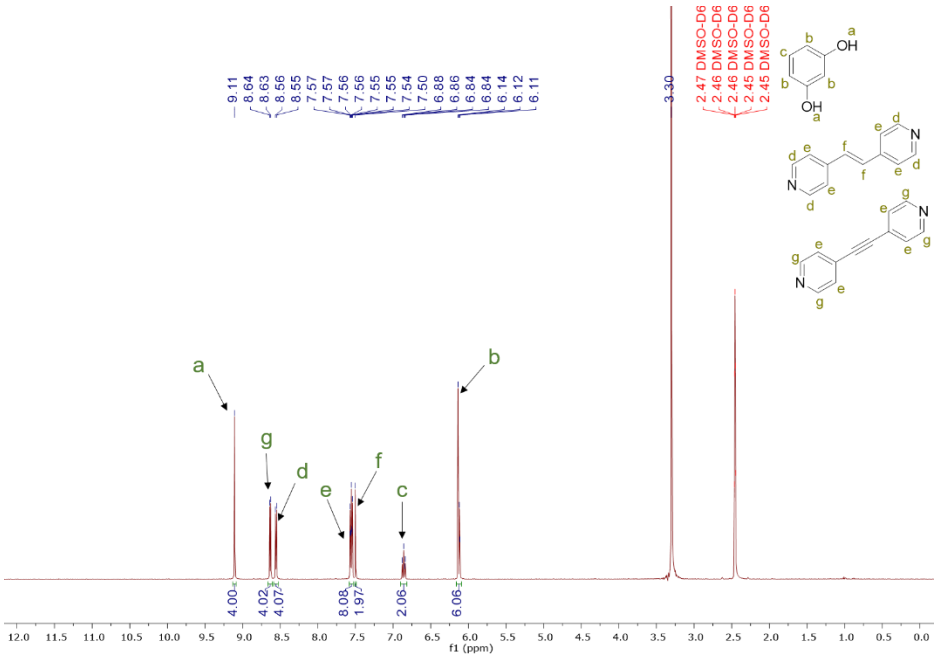

Figure S14. ^{1}H NMR spectrum for the mixed cocrystal **res•(BPE)**$_{0.50}$**•(BPA)**$_{0.50}$**.**

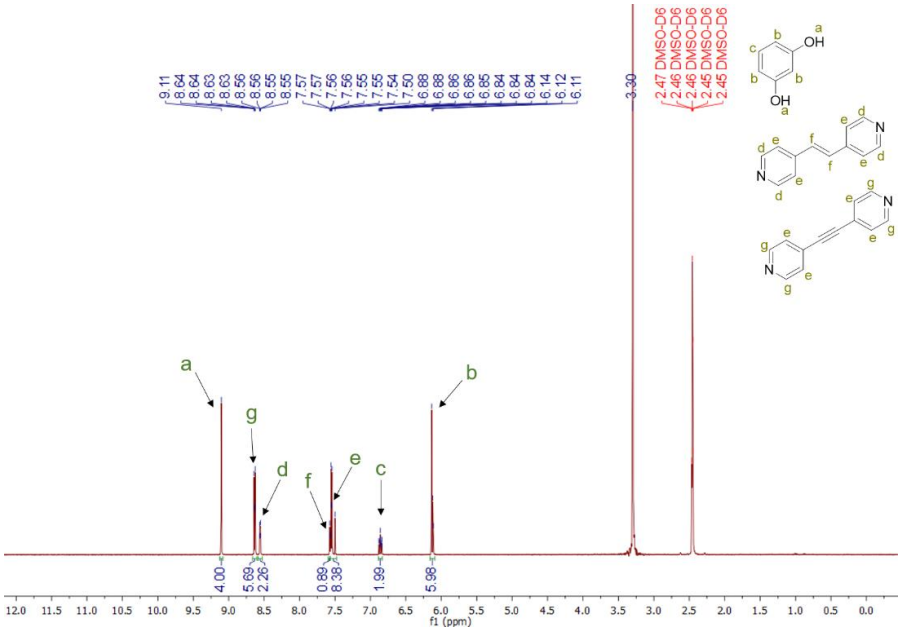

Figure S15. ^{1}H NMR spectrum for the mixed cocrystal **res•(BPE)**$_{0.25}$**•(BPA)**$_{0.75}$**.**

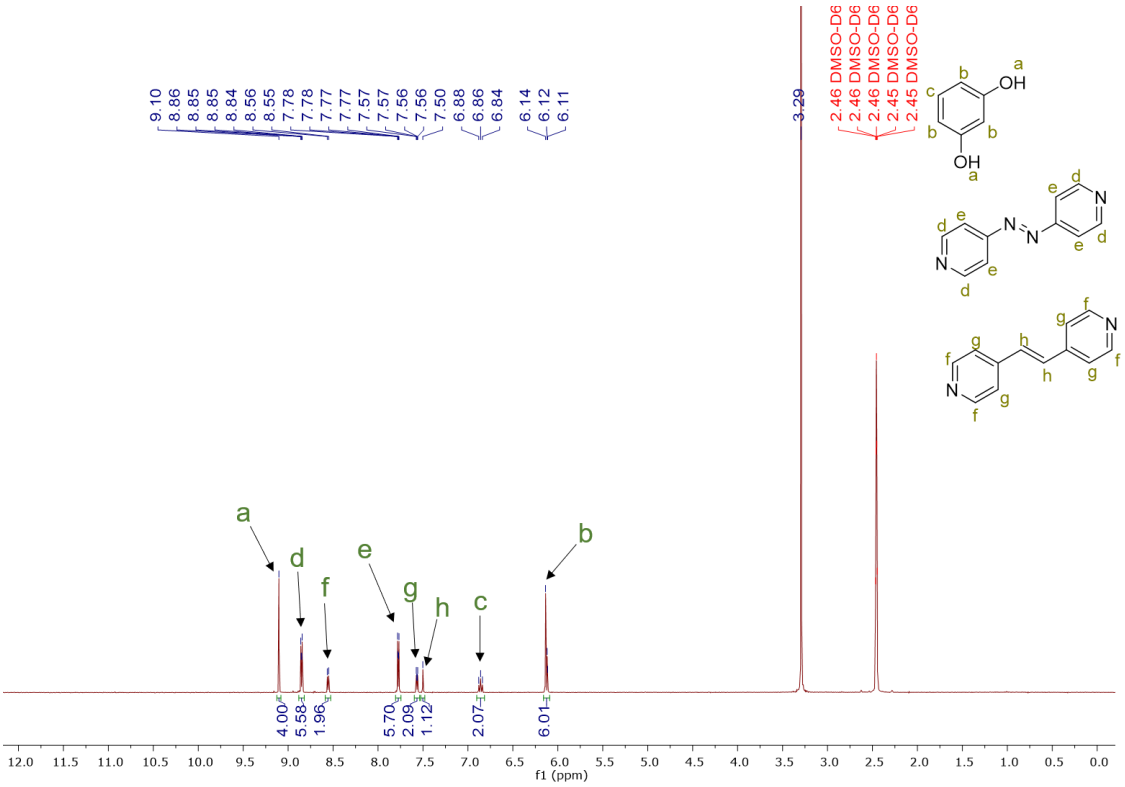

Figure S16. ^{1}H NMR spectrum for the mixed cocrystal **res**•(**AP**)$_{0.75}$•(**BPE**)$_{0.25}$.

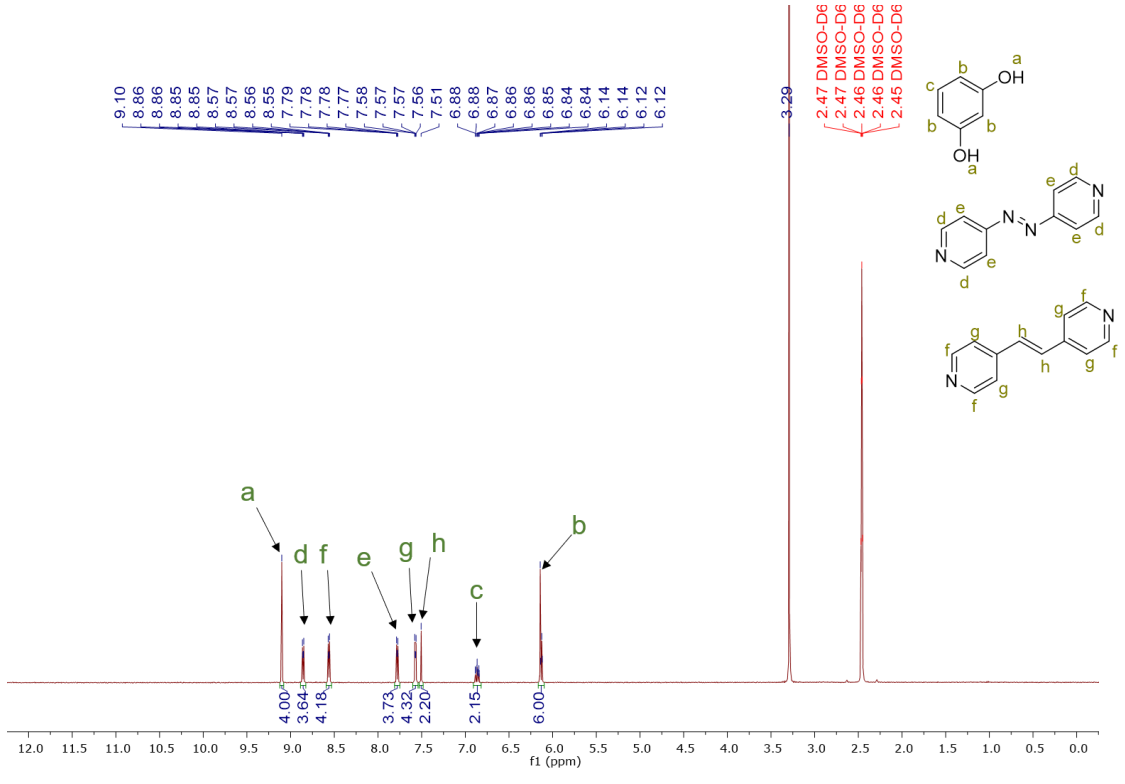

Figure S17. ^{1}H NMR spectrum for the mixed cocrystal **res**•(**AP**)$_{0.50}$•(**BPE**)$_{0.50}$.

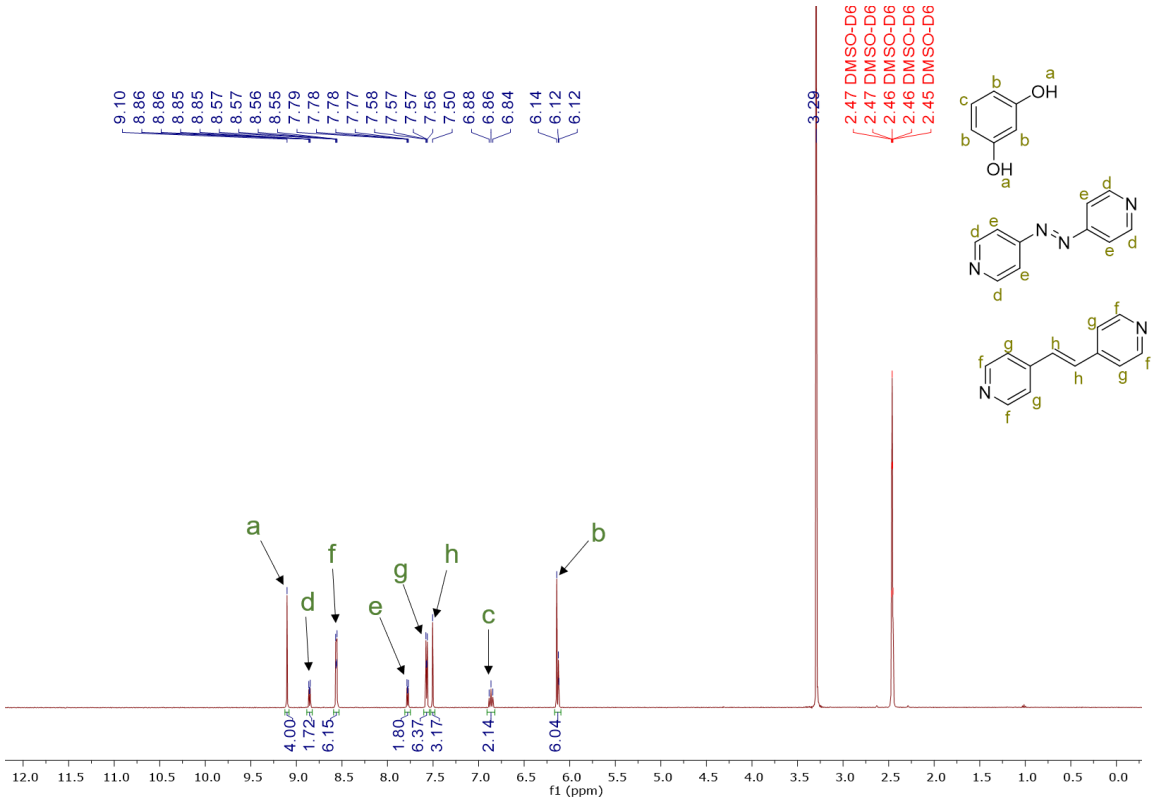

Figure S18. ^{1}H NMR spectrum for the mixed cocrystal **res**•(**AP**)$_{0.25}$•(**BPE**)$_{0.75}$.

6. Variation of the Unit Cell Parameters

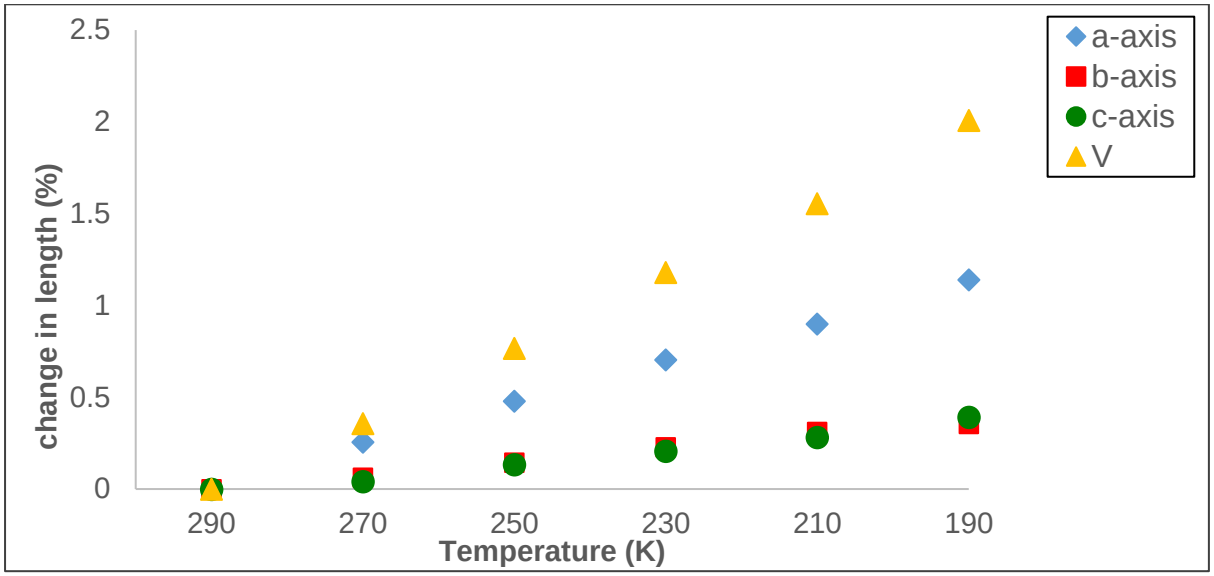

Figure S19. Percent change in length as a function of temperature for the mixed cocrystal **res•(AP)**$_{0.75}$**•(BPA)**$_{0.25}$.

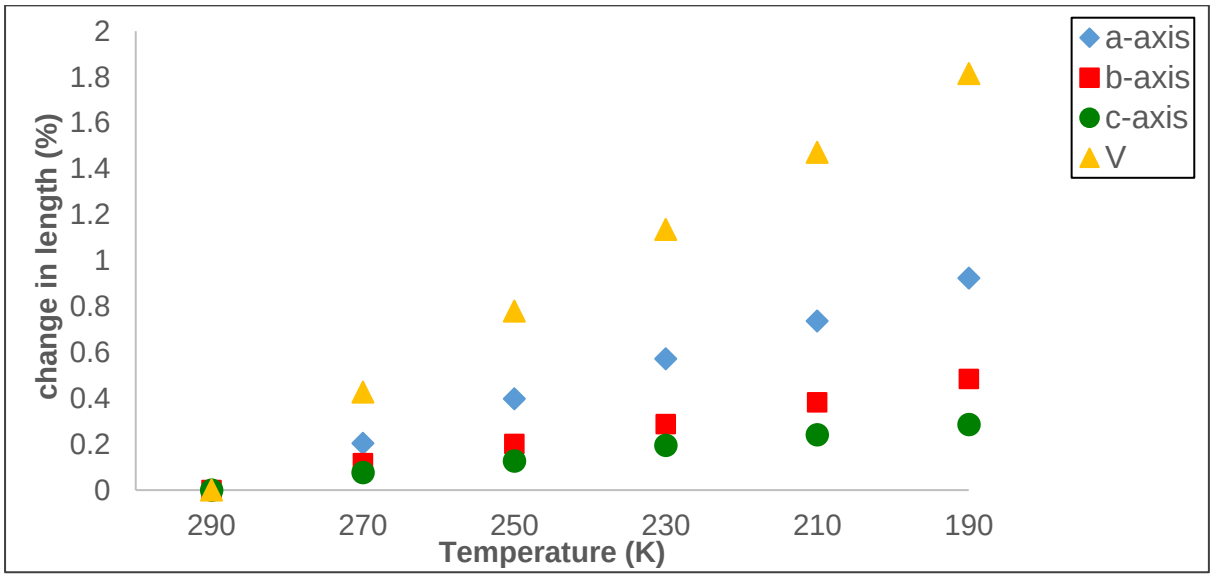

Figure S20. Percent change in length as a function of temperature for the mixed cocrystal **res•(AP)**$_{0.50}$**•(BPA)**$_{0.50}$.

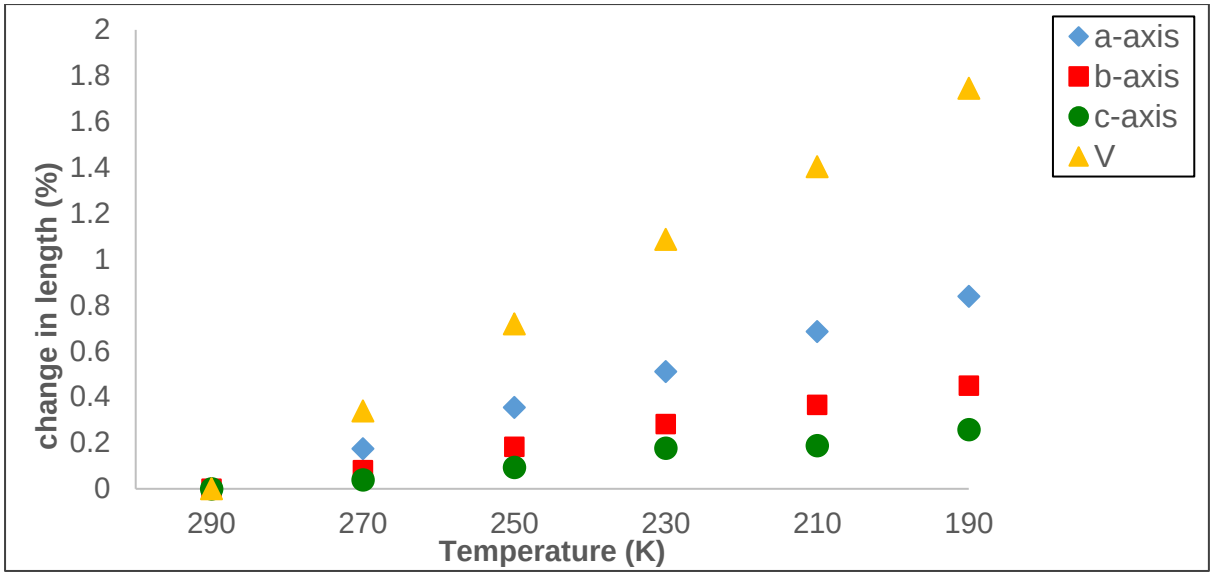

Figure S21. Percent change in length as a function of temperature for the mixed cocrystal **res•(AP)**$_{0.25}$**•(BPA)**$_{0.75}$.

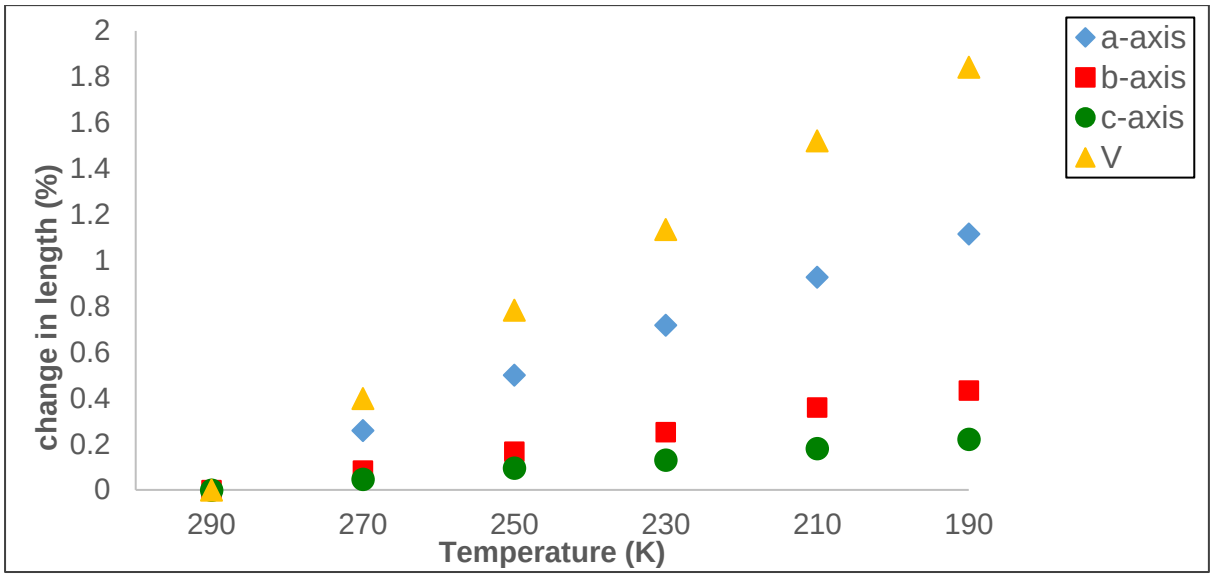

Figure S22. Percent change in length as a function of temperature for the mixed cocrystal **res•(BPE)**$_{0.75}$**•(BPA)**$_{0.25}$.

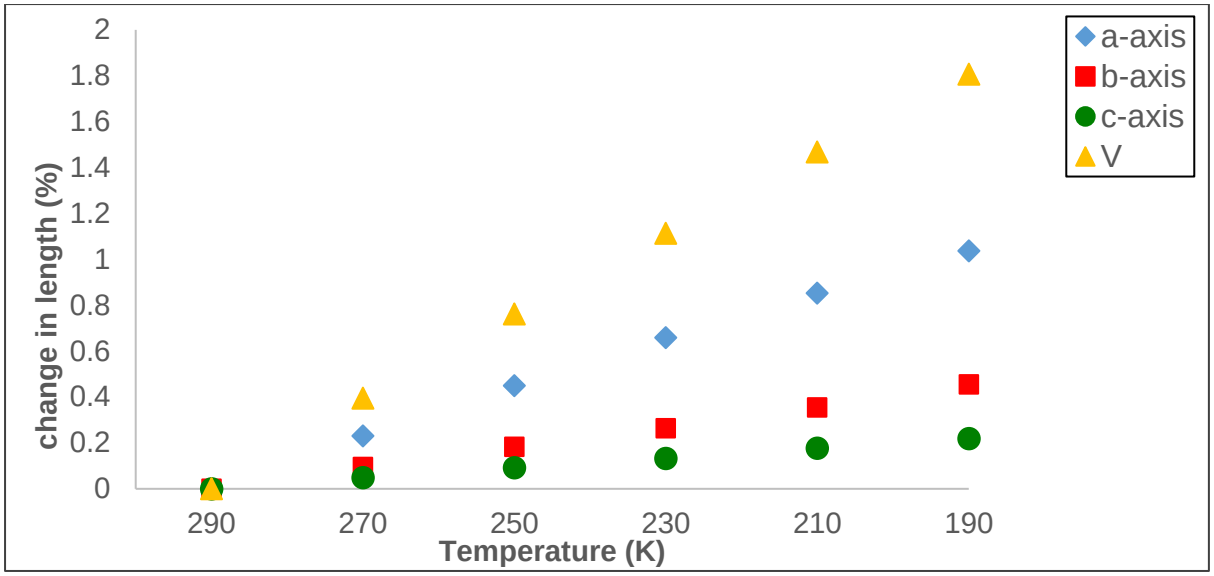

Figure S23. Percent change in length as a function of temperature for the mixed cocrystal **res•(BPE)**$_{0.50}$**•(BPA)**$_{0.50}$.

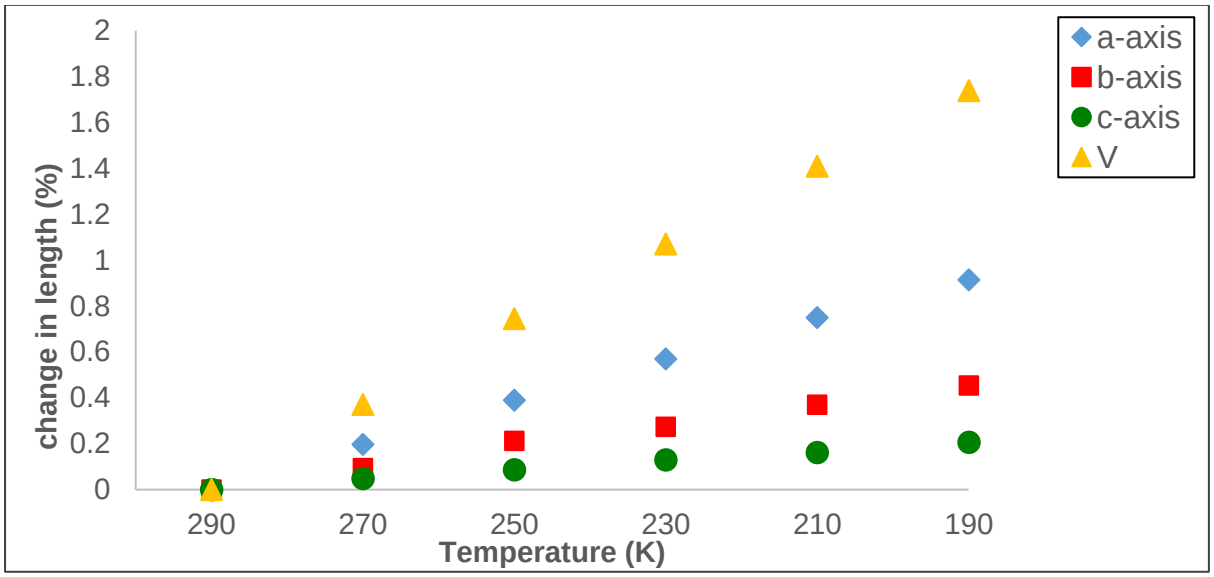

Figure S24. Percent change in length as a function of temperature for the mixed cocrystal **res•(BPE)**$_{0.25}$**•(BPA)**$_{0.75}$.

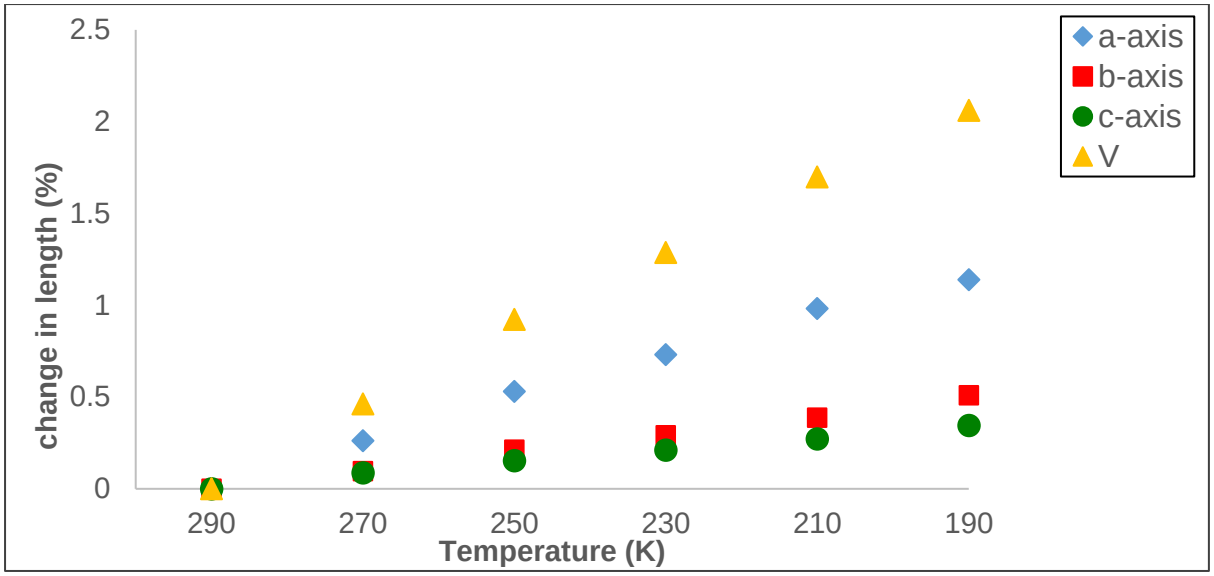

Figure S25. Percent change in length as a function of temperature for the mixed cocrystal **res•(AP)**$_{0.75}$**•(BPE)**$_{0.25}$**.**

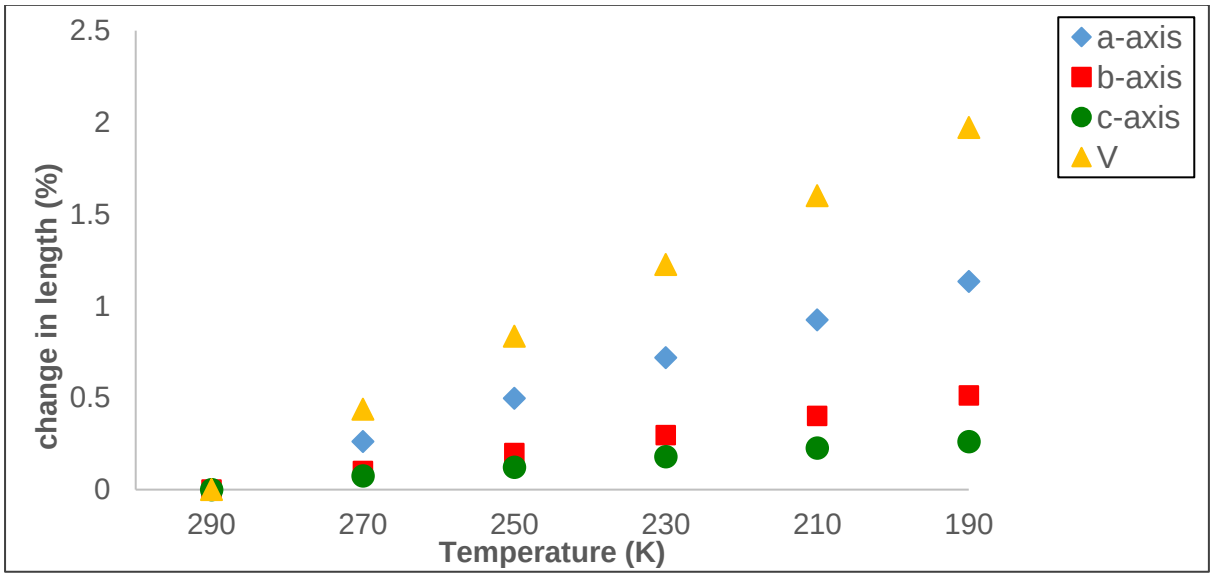

Figure S26. Percent change in length as a function of temperature for the mixed cocrystal **res•(AP)**$_{0.50}$**•(BPE)**$_{0.50}$**.**

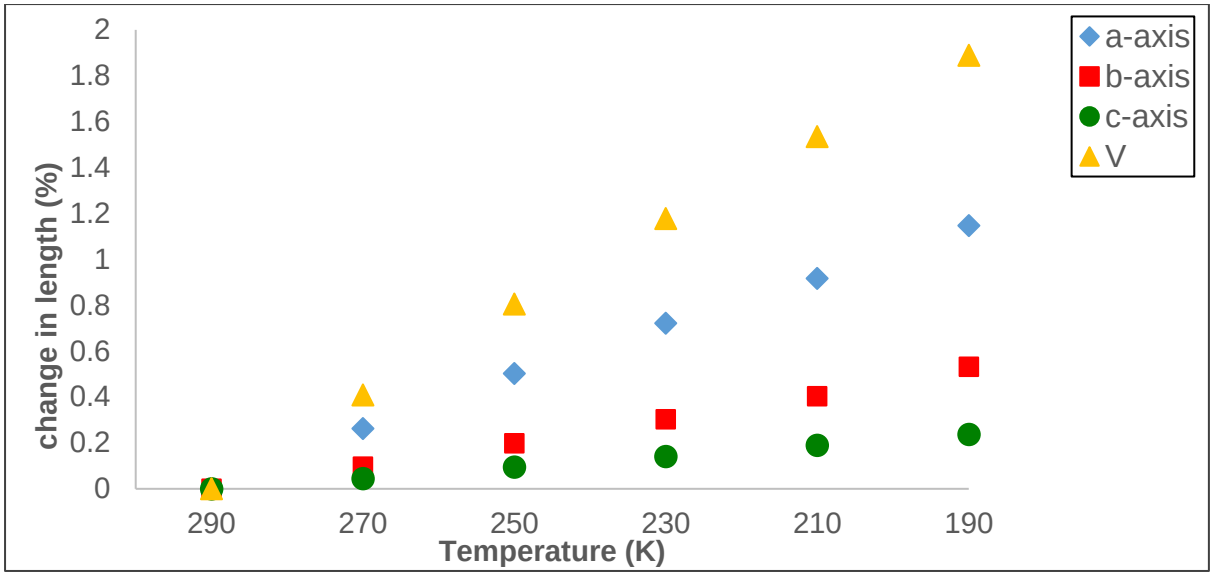

Figure S27. Percent change in length as a function of temperature for the mixed cocrystal **res•(AP)**$_{0.25}$**•(BPE)**$_{0.75}$.

7. References

(1) CrysAlis^{Pro} (2018) Oxford Diffraction Ltd.

(2) SCALE3 ABSPACK (2005) Oxford Diffraction Ltd.

(3) Sheldrick, G. M. Crystal structure refinement with SHELXL. *Acta. Cryst*. **2015**, *71*, 3-8.

(4) Cliffe, M. J.; Goodwin, A. L. PASCal: a principal axis strain calculator for thermal expansion and compressibility determination. *J. Appl. Cryst*. **2012**, *45*, 1321-1329.