Electronic Supplementary Material (ESI) for CrystEngComm.

Supplementary Information

Solid-state behaviors of imines: Colossal biaxial positive thermal expansion, motion capability, and phase transitions

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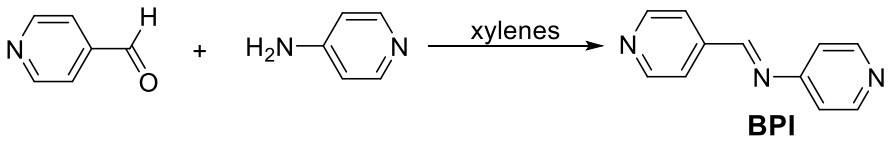
Contents:

1. Synthesis of Imines and Growth of Single Crystals

Benzene-1,4-diamine and 4-pyridine carboxaldehyde were purchased from Oakwood Chemical (730 Columbia Hwy, SC, USA). 4-Aminopyridine was purchased from Acros Organics (New Jersey, USA). Xylenes were purchased from Macron Fine Chemicals. Methanol, petroleum ether, hexanes and acetonitrile were purchased from Fisher Chemical (Fair Lawn, NJ, USA). All the chemicals were used as received.

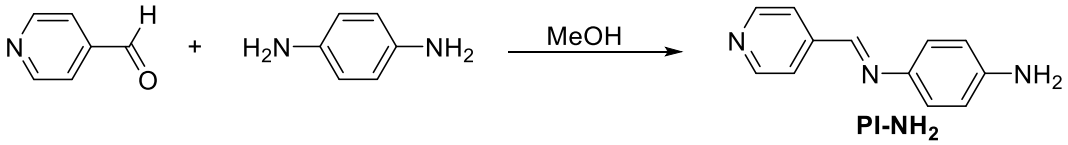
N-(pyridin-4-yl-methylene)pyridin-4-amine (BPI)



BPI

4-aminopyridine (4.235 g, 0.045 mol) and 4-pyridine carboxaldehyde (5 g, 0.046 mol) were heated under reflux in 75 mL of xylenes for 20 h with a Dean-Stark apparatus. The solvent was evaporated under reduced pressure, and the crude product was recrystallized to obtain pure product using petroleum ether or hexanes (2.004 g, 26% yield). Thin, white, needle-shaped crystals suitable for X-ray diffraction were obtained by dissolving **BPI** in a minimum amount of petroleum ether or hexanes over a couple of minutes.[1]

4-((pyridin-4-ylmethylene)amino)aniline (PI-NH_2)



PI-NH_2

PI-NH_2 was prepared by grinding benzene-1,4-diamine (0.86 g, 8 mmol) and 4-pyridine carboxaldehyde (0.86 g, 8 mmol) in 1:1 ratio in the presence of 100 µL of methanol using a mortar and pestle for ca. 15 min. The dark yellow solid obtained after grinding was recrystallized in methanol to obtain the pure product (1.39 g, 90% yield). Single crystals suitable for X-ray diffraction were grown by dissolving 10 mg of the pure product in a minimal amount of acetonitrile over a period of two 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 either Cu Kα radiation (λ = 1.54178 Å) or Mo Kα radiation (λ = 0.71073 Å) and a HyPix-6000HE HPC 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 Research 20 micron cryoloop and transferred to the instrument where it was placed under a cold nitrogen stream (Oxford 700 series). 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 samples were optically centered with the aid of a video camera to ensure that no translations were observed as the crystal was rotated through all positions. For variable temperature experiments, a new set of images of the crystal and its location were recorded before each data collection. A unit cell collection was then carried out, and a data collection strategy was calculated by *CrysAlisPro.*[3] The crystal was measured for size, morphology, and color.

Refinement Details

After data collection, the unit cell was re-determined using a subset of the full data collection. Intensity data were corrected for Lorentz, polarization, and background effects using *CrysAlisPro.*[3] 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*.[4] The *SHELXL-2014*,[5] series of programs was used for the solution and refinement of the crystal structure. Hydrogen atoms bound to carbon atoms were located in the difference Fourier map and were geometrically constrained using the appropriate AFIX commands.

For the **BPI** structure, atom sites C2 < C9, N2, and N3 were positionally disordered and modeled as split sites A and B. The site occupancies of the two sites were constrained to a total value of 1. At 190 K, the A and B sites refined to 0.49 and 0.51, respectively. From 210 K to 270 K, the A and B sites refined to 0.51 and 0.49, respectively. At 290 K, the A and B sites refined to 0.50 and

0.50, respectively. To help maintain reasonable ADP and bond length values for the disordered sites, the rigid bond restraint RIGU and free variable DFIX restraints were applied. The data/parameter ratio is borderline due to the number of modeled disorder atom sites in the structure.

For the **PI-NH$_2$** structure, the hydrogen atoms bound to N1 was allowed to refine their positions while their isotropic displacement parameter was set to ride on N1. For temperatures 290 K, 270 K, 250 K, and 230 K the imine group was undergoing pedal motion. The atoms N2, N3, and C7 < C12 were split into A and B sites and were restrained with an anisotropic displacement parameter similarity (SIMU), rigid bond restraint (RIGU), and free variable DFIX restraints to help maintain reasonable ADP values and bond lengths for the minor components. For temperatures 290 K, 270 K, 250 K, and 230 K the ratio of A to B sites was 0.84:0.16, 0.95 0.05, 0.97:0.03, and 0.98:0.02.

Cooling cycle details for PI-NH$_2$

For the slow cooling cycle, SCXRD data was first collected at 290 K, and the crystal was slowly cooled to 100 K while collecting full data sets every 20 K (Tables S3-S5). For the flash cooling cycle, the crystal was mounted on the instrument at 190 K and a full data set was collected. Then the crystal was warmed to 290 K while collecting full data sets every 20 K, followed by cooling back to 190 K while collecting full data sets every 20 K (Tables S6-S9).

Table S1. X-ray data for **BPI** at 290, 270, and 250 K.

Compound formula	$C_{11}H_9N_3$	$C_{11}H_9N_3$	$C_{11}H_9N_3$
Formula Mass	183.21	183.21	183.21
Crystal System	Monoclinic	Monoclinic	Monoclinic
Space Group	C2/m	C2/m	C2/m
a/Å	15.7226(13)	15.6931(11)	15.6639(12)
b/Å	7.1311(6)	7.1110(5)	7.0936(6)
c/Å	9.0875(10)	9.0908(8)	9.0904(9)
α/°	90	90	90
β/°	106.081(10)	105.856(18)	105.663(9)
γ/°	90	90	90
V/Å^3	979.02(16)	975.88(13)	972.56(15)
ρ_{calc} / g cm^{-3}	1.243	1.247	1.251
T/K	290.06 (11)	270.06 (10)	250.05 (10)
Z	4	4	4
Radiation Type	MoKα	MoKα	MoKα
Wavelength, Å	0.71073	0.71073	0.71073
Absorption coefficient, μ/mm^{-1}	0.078	0.078	0.079
F(000)	384	384	384
Crystal Size (mm)	0.282 x 0.163 x 0.035	0.282 x 0.163 x 0.035	0.282 x 0.163 x 0.035
Reflections collected	8659	8190	8449
No. of independent reflections	1093	1091	1086
No. of reflection ($I > 2\sigma(I)$)	767	786	808
Data/restraints/parameter	1093 / 164/ 145	1091 / 164 / 145	1086 / 164 / 145
R_{int}	0.0262	0.0287	0.0263
R1 ($I > 2\sigma(I)$)	0.0375	0.0375	0.0369
wR(F2) ($I > 2\sigma(I)$	0.1061	0.1057	0.1034
R1 (all data)	0.0565	0.0528	0.0506
wR(F2) (all data)	0.1174	0.1151	0.1118
Goodness-of-fit on F^2	1.026	1.038	1.037
CCDC deposition number	2072416	2072415	2072414

Table S2. X-ray data for **BPI** at 230, 210, and 190 K.

Compound formula	$C_{11}H_9N_3$	$C_{11}H_9N_3$	$C_{11}H_9N_3$
Formula Mass	183.21	183.21	183.21
Crystal System	Monoclinic	Monoclinic	Monoclinic
Space Group	C2/m	Cm	Cm
a/Å	15.6264(11)	15.5861(9)	15.498(2)
b/Å	7.0823(5)	7.0608(4)	7.0467(10)
c/Å	9.0843(7)	9.0691(6)	9.0692(15)
α/°	90	90	90
β/°	105.399(8)	105.198(7)	104.821(16)
γ/°	90	90	90
V/Å^3	969.27(13)	963.15(11)	957.5(3)
ρ_{calc} / g cm^{-3}	1.255	1.263	1.271
T/K	230.06 (10)	210.05 (10)	190.00 (10)
Z	4	4	4
Radiation Type	MoKα	MoKα	MoKα
Wavelength, Å	0.71073	0.71073	0.710731
Absorption coefficient, μ/mm^{-1}	0.079	0.079	0.080
F(000)	384	384	384
Crystal size (mm)	0.282 x 0.163 x 0.035	0.282 x 0.163 x 0.035	0.282 x 0.163 x 0.035
Reflections collected	8389	8450	5921
No. of independent reflections	1082	1076	1064
No. of reflection (I > 2σ(I))	838	859	766
Data/restraints/parameter	1082 / 164 / 145	1076 / 164 / 145	1064 / 164 / 145
R_{int}	0.0308	0.0253	0.0579
R1 (I > 2σ(I))	0.0370	0.385	0.0784
wR(F2) (I > 2σ(I)	0.1056	0.1083	0.1941
R1 (all data)	0.0482	0.0484	0.0974
wR(F2) (all data)	0.1129	0.1145	0.2021
Goodness-of-fit on F^2	1.033	1.080	1.143
CCDC deposition number	2072413	2072412	2072411

Table S3. X-ray data for **PI-NH$_2$** at 290, 270, and 250 K (slow cooling cycle).

Compound formula	$C_{12}H_{11}N_3$	$C_{12}H_{11}N_3$	$C_{12}H_{11}N_3$
Formula Mass	197.24	197.24	197.24
Crystal System	Orthorhombic	Orthorhombic	Orthorhombic
Space Group	$P2_12_12_1$	$P2_12_12_1$	$P2_12_12_1$
a/Å	5.72610(10)	5.8556(5)	5.85593(8)
b/Å	7.54720(10)	7.4394(6)	7.39741(11)
c/Å	23.5464(4)	23.4466(18)	23.4532(3)
α/°	90	90	90
β/°	90	90	90
γ/°	90	90	90
V/Å^3	1017.58(3)	1021.39(14)	1015.96(3)
ρ_{calc} / g cm^{-3}	1.287	1.283	1.289
T/K	290 (2)	270 (2)	250 (2)
Z	4	4	4
Radiation Type	CuKα	CuKα	CuKα
Wavelength, Å	1.54178	1.54178	1.54178
Absorption coefficient, μ/mm^{-1}	0.631	0.629	0.632
F(000)	416	416	416
Crystal size (mm)	0.174 x 0.112 x 0.035	0.174 x 0.112 x 0.035	0.174 x 0.112 x 0.035
Reflections collected	9716	7420	9716
No. of independent reflections	2062	2045	2053
No. of reflection ($I > 2\sigma(I)$)	1859	1875	1937
Data/restraints/parameter	2062 / 226 / 207	2045 / 403 / 206	2053 / 403 / 206
R_{int}	0.0304	0.0292	0.0289
R1 ($I > 2\sigma(I)$)	0.0311	0.0319	0.0274
wR(F2) ($I > 2\sigma(I)$)	0.0859	0.0870	0.0728
R1 (all data)	0.0346	0.0356	0.0292
wR(F2) (all data)	0.0887	0.0890	0.0733
Goodness-of-fit on F^2	1.056	1.051	1.078
CCDC deposition number	2072254	2072255	2072256

Table S4. X-ray data for **PI-NH$_2$** at 230, 210, and 190 K (slow cooling cycle).

Compound formula	$C_{12}H_{11}N_3$	$C_{12}H_{11}N_3$	$C_{12}H_{11}N_3$
Formula Mass	197.24	197.24	197.24
Crystal System	Orthorhombic	Orthorhombic	Orthorhombic
Space Group	$P2_12_12_1$	$P2_12_12_1$	$P2_12_12_1$
a/Å	5.85038(8)	5.84449(8)	5.83819(7)
b/Å	7.37100(11)	7.34651(10)	7.32399(9)
c/Å	23.4704(3)	23.4842(3)	23.4915(3)
α/°	90	90	90
β/°	90	90	90
γ/°	90	90	90
V/Å^3	1012.12(3)	1008.33(2)	1004.47(2)
ρ_{calc} / g cm^{-3}	1.294	1.299	1.304
T/K	230 (2)	210 (2)	190 (2)
Z	4	4	4
Radiation Type	CuKα	CuKα	CuKα
Wavelength, Å	1.54178	1.54178	1.54178
Absorption coefficient, μ/mm^{-1}	0.634	0.637	0.639
F(000)	416	416	416
Crystal size (mm)	0.174 x 0.112 x 0.035	0.174 x 0.112 x 0.035	0.174 x 0.112 x 0.035
Reflections collected	9643	9654	9593
No. of independent reflections	2043	2033	2025
No. of reflection (I > 2σ(I))	1952	1956	1949
Data/restraints/parameter	2043 / 403 / 206	2033 / 0 / 143	2025 / 0 / 143
R_{int}	0.0288	0.0268	0.0261
R1 (I > 2σ(I))	0.0273	0.0269	0.0258
wR(F2) (I > 2σ(I)	0.0720	0.0692	0.0674
R1 (all data)	0.0284	0.0281	0.0267
wR(F2) (all data)	0.0728	0.0700	0.0679
Goodness-of-fit on F^2	1.113	1.055	1.048
CCDC deposition number	2072257	2072258	2072259

Table S5. X-ray data for **PI-NH$_2$** at 170, 150, 130 and 100 K (slow cooling cycle).

Compound formula	$C_{12}H_{11}N_3$	$C_{12}H_{11}N_3$	$C_{12}H_{11}N_3$	$C_{12}H_{11}N_3$
Formula Mass	197.24	197.24	197.24	197.24
Crystal System	Orthorhombic	Orthorhombic	Orthorhombic	Orthorhombic
Space Group	$P2_12_12_1$	$P2_12_12_1$	$P2_12_12_1$	$P2_12_12_1$
a/Å	5.83221(8)	5.82676(8)	5.82153(8)	5.81332(8)
b/Å	7.30484(11)	7.28832(12)	7.27320(13)	7.24959(14)
c/Å	23.5004(3)	23.5058(3)	23.5087(3)	23.5153(4)
α/°	90	90	90	90
β/°	90	90	90	90
γ/°	90	90	90	90
V/Å^3	1001.20(2)	998.23(2)	995.39(3)	991.03(3)
ρ_{calc} / g cm^{-3}	1.309	1.312	1.316	1.322
T/K	170 (2)	150 (2)	130 (2)	100 (2)
Z	4	4	4	4
Radiation Type	CuKα	CuKα	CuKα	CuKα
Wavelength, Å	1.54178	1.54178	1.54178	1.54178
Absorption coefficient, μ/mm^{-1}	0.641	0.643	0.645	0.648
F(000)	416	416	416	416
Crystal size (mm)	0.174 x 0.112 x 0.035	0.174 x 0.112 x 0.035	0.174 x 0.112 x 0.035	0.174 x 0.112 x 0.035
Reflections collected	9526	9524	9477	9303
No. of independent reflections	2014	2008	2005	1998
No. of reflection (I > 2σ(I))	1943	1944	1933	1927
Data/restraints/parameter	2014 / 0 / 143	2008 / 0 / 143	2005 / 0 / 143	1998 / 0 / 143
R_{int}	0.0255	0.0255	0.0283	0.0329
R1 (I > 2σ(I))	0.0270	0.0270	0.0279	0.0314
wR(F2) (I > 2σ(I)	0.0686	0.0702	0.0752	0.0859
R1 (all data)	0.0280	0.0279	0.0289	0.0325
wR(F2) (all data)	0.0693	0.0708	0.0760	0.0869
Goodness-of-fit on F^2	1.083	1.066	1.072	1.076
CCDC deposition number	2072260	2072261	2072262	2072263

Table S6. X-ray data for **PI-NH$_2$** at 190, 210 and 230 K (flash cooling cycle).

Compound formula	$C_{12}H_{11}N_3$	$C_{12}H_{11}N_3$	$C_{12}H_{11}N_3$
Formula Mass	197.24	197.24	197.24
Crystal System	Orthorhombic	Orthorhombic	Orthorhombic
Space Group	$P2_12_12_1$	$P2_12_12_1$	$P2_12_12_1$
a/Å	5.66850(5)	5.67404(5)	5.8323(8)
b/Å	7.45207(6)	7.47072(6)	7.3764(7)
c/Å	23.56855(19)	23.5754(2)	23.496(3)
α/°	90	90	90
β/°	90	90	90
γ/°	90	90	90
V/Å^3	995.585(14)	999.343(15)	1010.8(2)
ρ_{calc} / g cm^{-3}	1.316	1.311	1.296
T/K	190 (2)	210 (2)	230 (2)
Z	4	4	4
Radiation Type	CuKα	CuKα	CuKα
Wavelength, Å	1.54178	1.54178	1.54178
Absorption coefficient, μ/mm^{-1}	0.645	0.642	0.635
F(000)	416	416	416
Crystal size (mm)	0.150 x 0.103 x 0.052	0.150 x 0.103 x 0.052	0.150 x 0.103 x 0.052
Reflections collected	18669	18712	8670
No. of independent reflections	2085	2092	1998
No. of reflection (I > 2σ(I))	2021	2018	1626
Data/restraints/parameter	2085 / 0 / 145	2092 / 0 / 145	1998 / 2 / 142
R_{int}	0.0384	0.0400	0.1761
R1 (I > 2σ(I))	0.0289	0.0306	0.0825
wR(F2) (I > 2σ(I)	0.0792	0.0827	0.2013
R1 (all data)	0.0296	0.0317	0.1002
wR(F2) (all data)	0.0798	0.0838	0.2314
Goodness-of-fit on F^2	1.082	1.072	1.046
CCDC deposition number	2072417	2072418	2072420

Table S7. X-ray data for **PI-NH$_2$** at 250, 270, and 290 K (flash cooling cycle).

Compound formula	$C_{12}H_{11}N_3$	$C_{12}H_{11}N_3$	$C_{12}H_{11}N_3$
Formula Mass	197.24	197.24	197.24
Crystal System	Orthorhombic	Orthorhombic	Orthorhombic
Space Group	$P2_12_12_1$	$P2_12_12_1$	$P2_12_12_1$
a/Å	5.85572(6)	5.86140(6)	5.86556(7)
b/Å	7.39661(7)	7.42624(8)	7.46244(9)
c/Å	23.4514(2)	23.4280(3)	23.3965(3)
α/°	90	90	90
β/°	90	90	90
γ/°	90	90	90
V/Å^3	1015.738(18)	995.585(14)	1024.09(2)
ρ_{calc} / g cm^{-3}	1.290	1.285	1.279
T/K	250 (2)	270 (2)	290 (2)
Z	4	4	4
Radiation Type	CuKα	CuKα	CuKα
Wavelength, Å	1.54178	1.54178	1.54178
Absorption coefficient, μ/mm^{-1}	0.632	0.630	0.627
F(000)	416	416	416
Crystal size (mm)	0.150 x 0.103 x 0.052	0.150 x 0.103 x 0.052	0.150 x 0.103 x 0.052
Reflections collected	19288	18668	16960
No. of independent reflections	2122	2131	2117
No. of reflection (I > 2σ(I))	2011	1976	1895
Data/restraints/parameter	2122 / 403 / 206	2131 / 403 / 206	2117 / 403 / 206
R_{int}	0.0416	0.0431	0.0448
R1 (I > 2σ(I))	0.0294	0.0306	0.0333
wR(F2) (I > 2σ(I)	0.0786	0.0818	0.0929
R1 (all data)	0.0309	0.0331	0.0371
wR(F2) (all data)	0.0799	0.0844	0.0963
Goodness-of-fit on F^2	1.047	1.053	1.050
CCDC deposition number	2072421	2072422	2072423

Table S8. X-ray data for **PI-NH$_2$** at 270, 250, and 230 K (flash cooling cycle).

Compound formula	$C_{12}H_{11}N_3$	$C_{12}H_{11}N_3$	$C_{12}H_{11}N_3$
Formula Mass	197.24	197.24	197.24
Crystal System	Orthorhombic	Orthorhombic	Orthorhombic
Space Group	$P2_12_12_1$	$P2_12_12_1$	$P2_12_12_1$
a/Å	5.86137(6)	5.85561(6)	5.85010(6)
b/Å	7.42616(8)	7.39670(7)	7.36978(7)
c/Å	23.4265(3)	23.4494(2)	23.4676(2)
α/°	90	90	90
β/°	90	90	90
γ/°	90	90	90
V/Å^3	1019.695(19)	1015.647(17)	1011.783(16)
ρ_{calc} / g cm^{-3}	1.285	1.290	1.295
T/K	270 (2)	250 (2)	230 (2)
Z	4	4	4
Radiation Type	CuKα	CuKα	CuKα
Wavelength, Å	1.54178	1.54178	1.54178
Absorption coefficient, μ/mm^{-1}	0.630	0.632	0.635
F(000)	416	416	416
Crystal size (mm)	0.150 x 0.103 x 0.052	0.150 x 0.103 x 0.052	0.150 x 0.103 x 0.052
Reflections collected	18569	19051	19324
No. of independent reflections	2128	2119	2107
No. of reflection (I > 2σ(I))	1970	2002	2009
Data/restraints/parameter	2128 / 403 / 206	2119 / 403 / 206	2107 / 403 / 206
R_{int}	0.0432	0.0433	0.0426
R1 (I > 2σ(I))	0.0305	0.0299	0.0282
wR(F2) (I > 2σ(I)	0.0837	0.0819	0.0751
R1 (all data)	0.0331	0.0316	0.0297
wR(F2) (all data)	0.0863	0.0835	0.0764
Goodness-of-fit on F^2	1.042	1.059	1.053
CCDC deposition number	2072424	2072425	2072426

Table S9. X-ray data for **PI-NH$_2$** at 210 and 190 K (flash cooling cycle).

Compound formula	$C_{12}H_{11}N_3$	$C_{12}H_{11}N_3$
Formula Mass	197.24	197.24
Crystal System	Orthorhombic	Orthorhombic
Space Group	$P2_12_12_1$	$P2_12_12_1$
a/Å	5.84375(5)	5.83741(5)
b/Å	7.34622(6)	7.32430(6)
c/Å	23.48048(20)	23.48978(19)
α/°	90	90
β/°	90	90
γ/°	90	90
V/Å^3	1008.005(14)	1004.304(14)
ρ_{calc} / g cm^{-3}	1.300	1.304
T/K	210 (2)	190 (2)
Z	4	4
Radiation Type	CuKα	CuKα
Wavelength, Å	1.54178	1.54178
Absorption coefficient, μ/mm^{-1}	0.637	0.639
F(000)	416	416
Crystal size (mm)	0.150 x 0.103 x 0.052	0.150 x 0.103 x 0.052
Reflections collected	19537	19699
No. of independent reflections	2112	2105
No. of reflection (I > 2σ(I))	2032	2031
Data/restraints/parameter	2112 / 0 / 143	2105 / 0 / 143
R_{int}	0.0411	0.0404
R1 (I > 2σ(I))	0.0279	0.0274
wR(F2) (I > 2σ(I)	0.0734	0.0725
R1 (all data)	0.0289	0.0283
wR(F2) (all data)	0.0742	0.0732
Goodness-of-fit on F^2	1.072	1.095
CCDC deposition number	2072427	2072428

3. Thermal Expansion Data and Intermolecular Interaction Distances

The thermal expansion coefficients were calculated using the PASCal program.[6] 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 S10. Thermal expansion coefficients for **BPI** with errors denoted in the parentheses and approximate crystallographic axes denoted in brackets.

Crystal	α_{X_1} **(MK^{-1}) [axis]**	α_{X_2} **(MK^{-1}) [axis]**	α_{X_3}**(MK^{-1}) [axis]**	α_V **(MK^{-1})**
BPI	-73 (5) [-1 0 -2]	118 (3) [0 1 0]	176 (16) [-4 0 3]	228 (14)

Table S11. Intermolecular interaction distances within **BPI** that contribute to the thermal expansion parameters.

Interaction	**290 K**	**190 K**	**Δ (Å)**
Centroid-centroid distance between molecules in adjacent sheets	6.062 (arrow 1 in Fig. 3b, main text) 5.050 (arrow 2 in Fig. 3b, main text)	6.156 4.899	-0.094 0.151
C-H(imine)···N(pyr) interaction	3.618	3.650	-0.032
C-H(β)···N(pyr) interactions between sheets	3.782	3.863	-0.081
C-H(α)···N(pyr) interactions	3.638	3.586	0.052
C-H(β)···N(pyr) interactions within sheet	3.556	3.516	0.04
C-H(β)···π interactions	3.632	3.489	0.143
π···π interactions	3.969	3.927	0.042

4. TGA and DSC curves

TGA data were collected on a Mettler Toledo TGA2. The samples were heated from 25 to 600 ºC at 10 K/min heating rate in nitrogen gas at 20 mL/min flow rate. DSC data were collected on a Mettler Toledo DSC 823 with intra cooler (freon cooler). The sample was cooled from 25 to -65 ºC at 20 K/min and warmed back to 25 ºC at 10 K/min. The cycle was repeated twice. No discernible transition was observed for the sample.

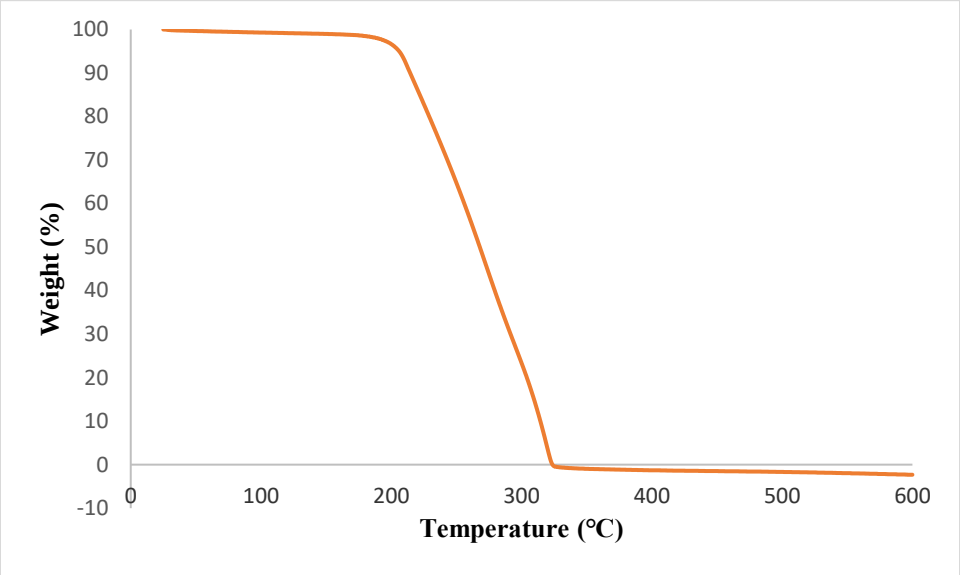


Figure S1. TGA curve for **PI-NH$_2$**.

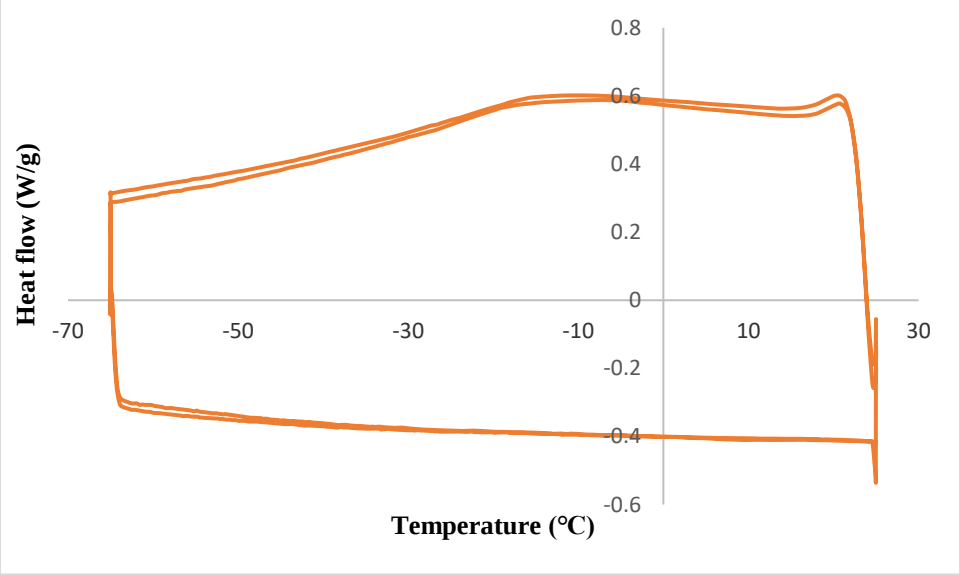


Figure S2. DSC curve for **PI-NH$_2$**.

5. Expansivity Indicatrix Diagram

Axes	α(MK^{-1})	σα (MK^{-1})	Direction a	b	c
X_1	-73.2390	5.3000	-0.3592	0.0000	-0.9333
X_2	118.3735	2.6017	0.0000	1.0000	-0.0000
X_3	175.8093	16.0165	-0.7713	0.0000	0.6365
V	227.7485	13.9108			

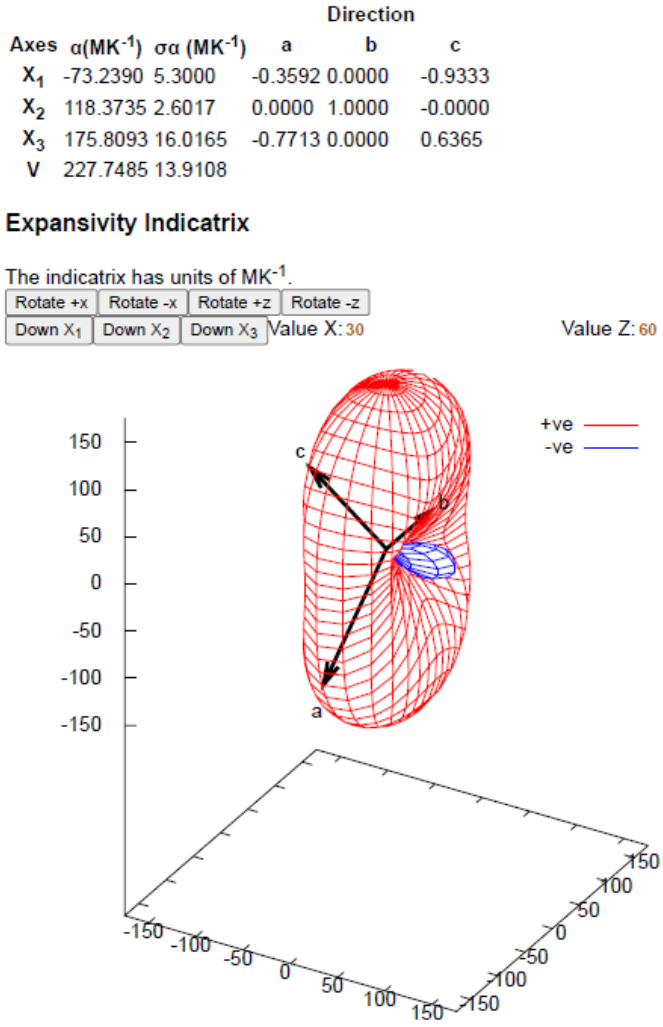


Figure S3. Thermal expansivity indicatrix for **BPI**.

6. Solution NMR Spectra of Materials

Single crystals of **BPI** and recrystallized solid **PI-NH$_2$** were dissolved in $CDCl_3$ for NMR experiments. NMR data was collected using a JOEL ECS 400 MHZ Spectrometer.

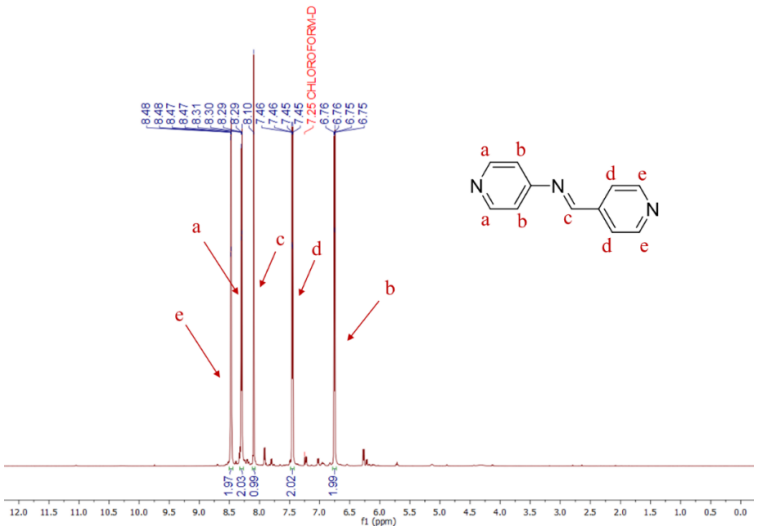


Figure S4. ^{1}H NMR spectrum of **BPI**.

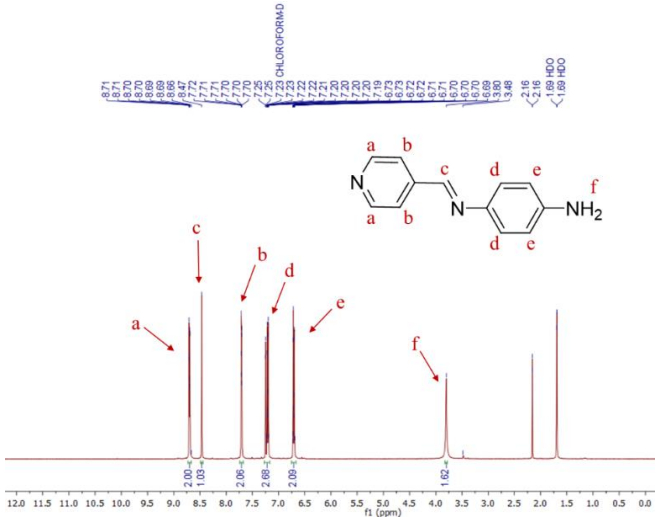


Figure S5. ^{1}H NMR spectrum of **PI-NH$_2$**.

7. Variation of the Unit Cell Parameters

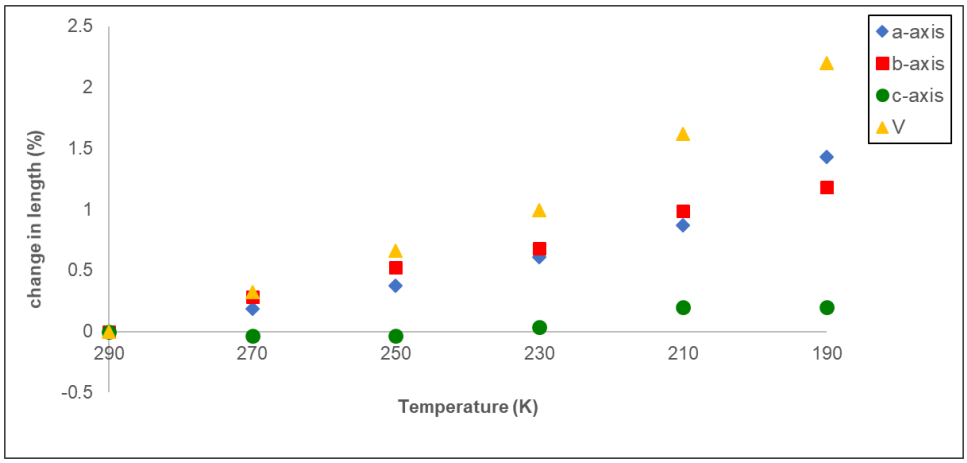


Figure S6. Percent change in length as a function of temperature for **BPI**. 290 K is used as the reference point.

8. Images Showing Structural Changes as a Function of Temperature

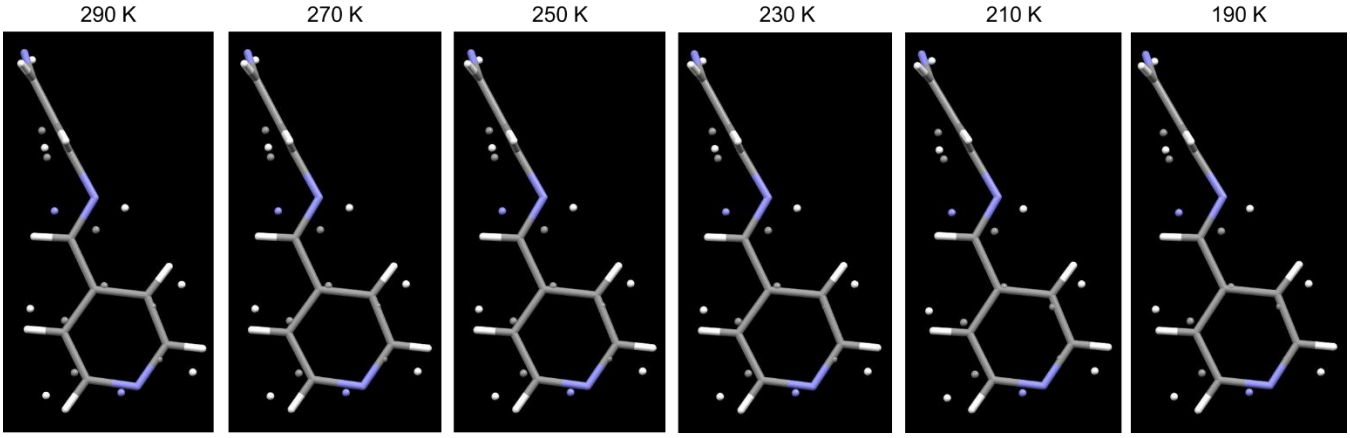


Figure S7. Crystal structure of **BPI** as a function of temperature. Disordered atom sites are shown with dots.

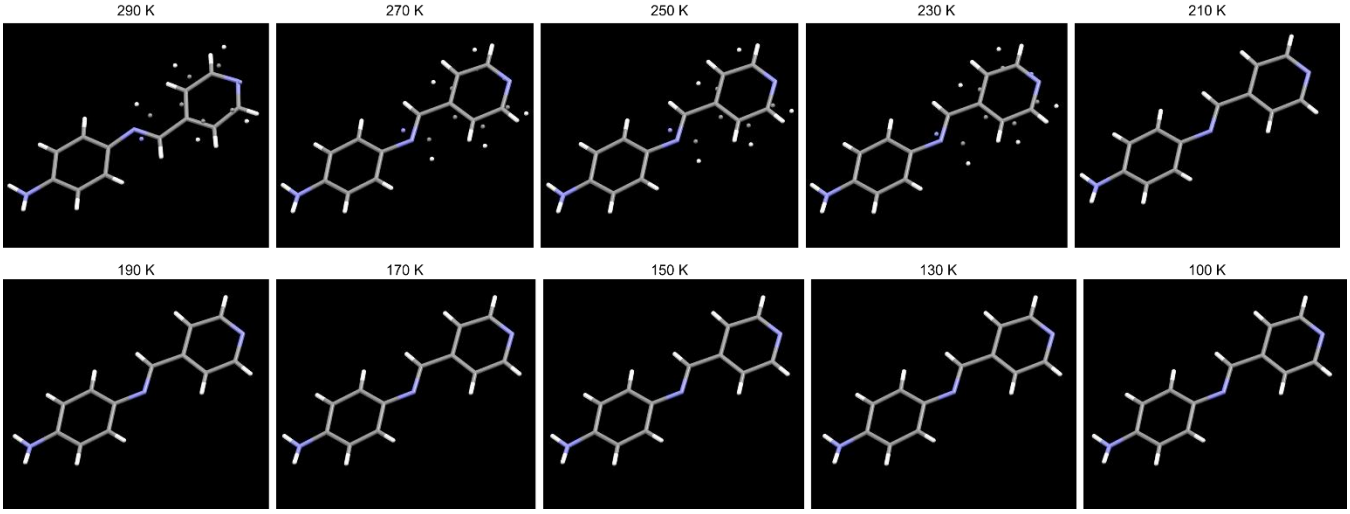


Figure S8. Crystal structure of **PI-NH$_2$** as a function of temperature during the slow cooling cycle from 290-100 K. Disordered atom sites are shown with dots.

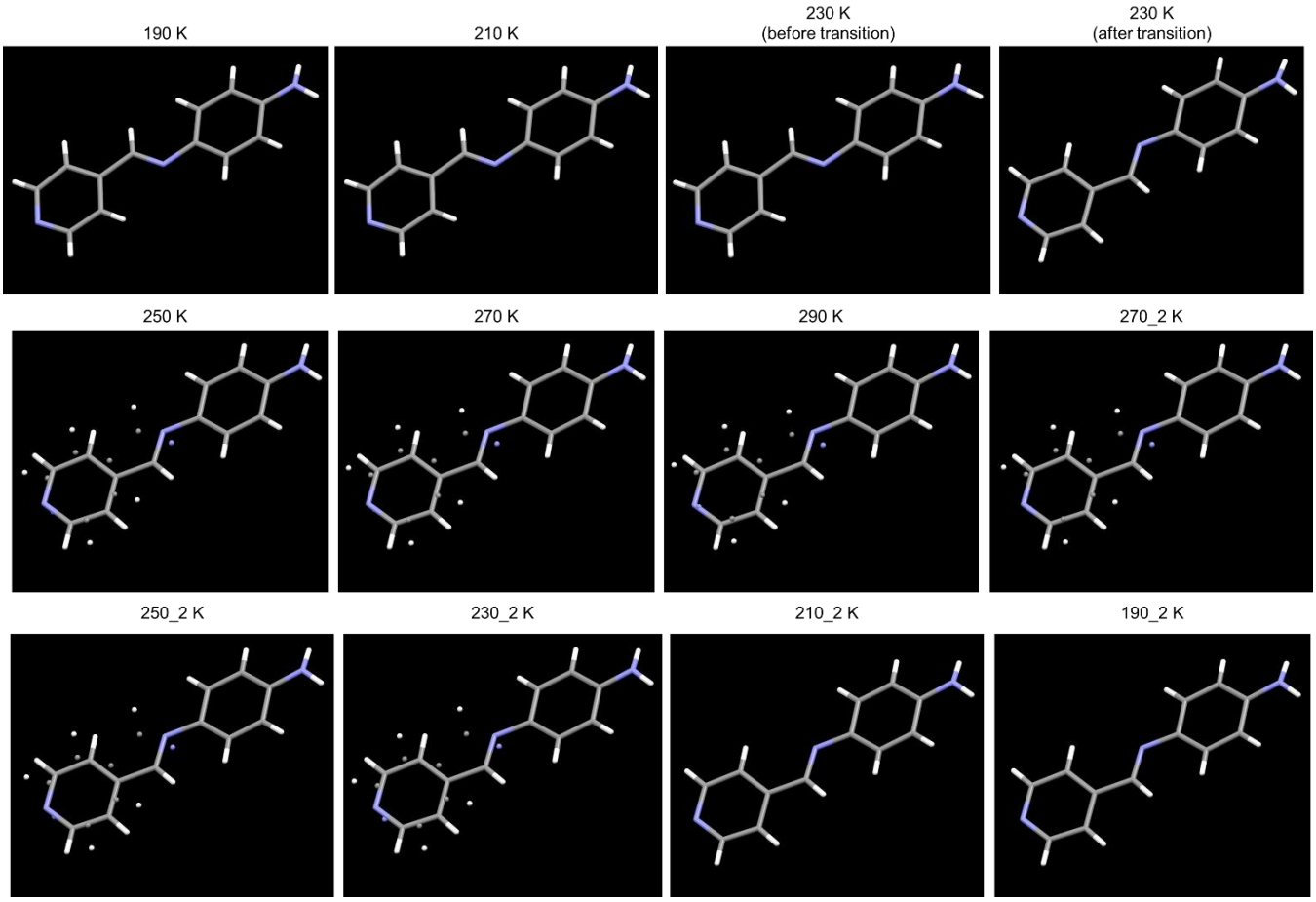


Figure S9. Crystal structure of **PI-NH$_2$** as a function of temperature during the flash cooling-heating-cooling cycle. The cycle starts at 190 K, heats to 290 K, then cools to 190 K. The images are in cycle order from left to right. Disordered atom sites are shown with dots.

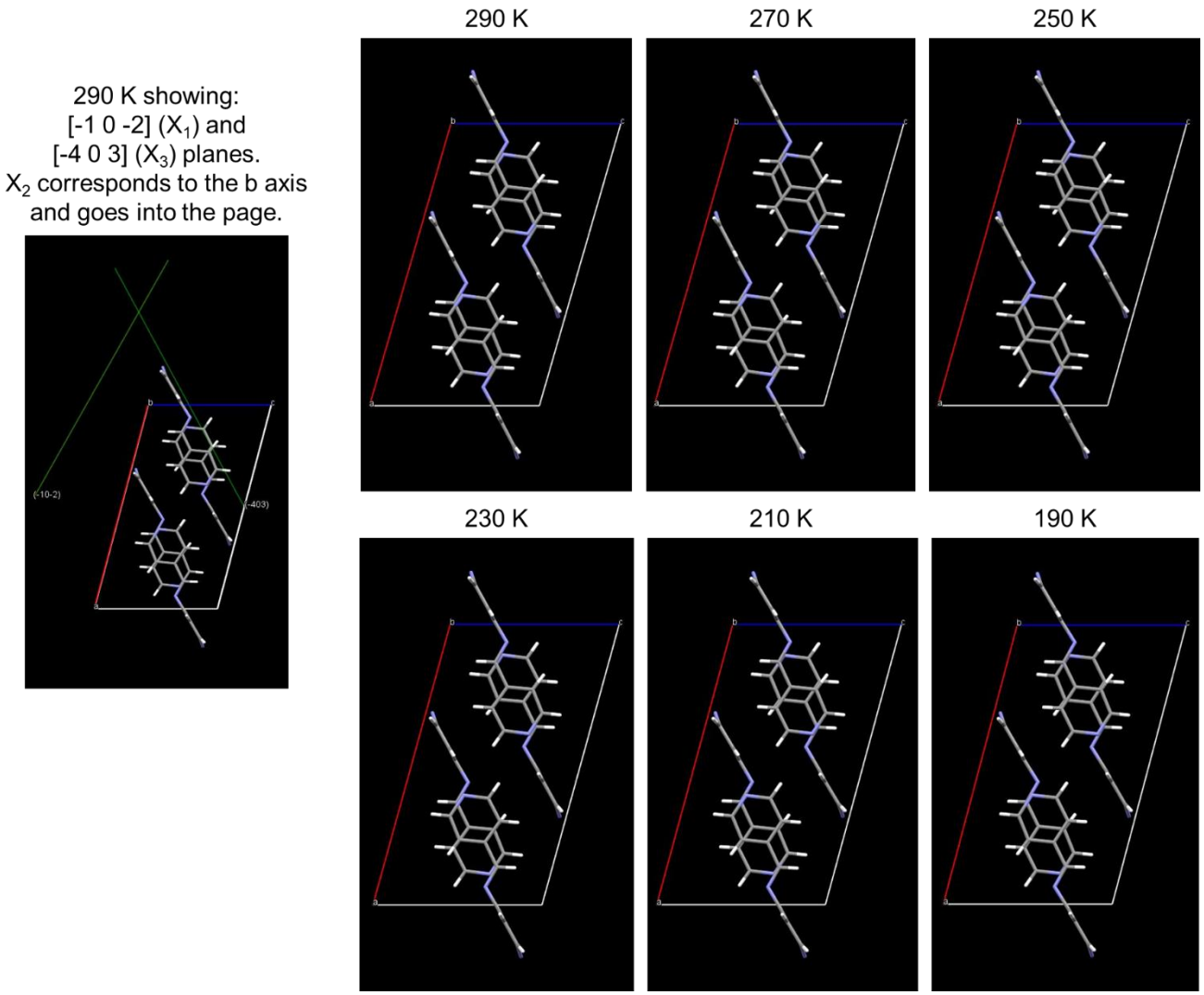


Figure S10. Unit cell packing of **BPI** as a function of temperature. Disordered sites are omitted for clarity. TE axes are highlighted in the left image.

9. References

(1) J. E. Rockley, L. A. Summers, *Aust. J. Chem.* 1980, **33**, 1397-1400.
(2) CrysAlis^{Pro} (2018) Oxford Diffraction Ltd.
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