Supplementary Information

for

Effects of dynamic pedal motion and static disorder on thermal expansion within halogen-bonded co-crystals

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1. Materials and synthesis of the co-crystals

Materials

The halogen bond acceptors *trans*-1,2-bis(4-pyridyl)ethylene (**4,4'-BPE**) and 4,4'-azopyridine (**4,4'-Azo**) were both purchased from Sigma-Aldrich Chemical (St. Louis, MO, USA) and used as received. The solvents ethanol and toluene were also purchased from Sigma-Aldrich Chemical and were not purified. 1,2-Bis(4-pyridyl)acetylene (**4,4'-BPA**) was purchased from Synquest Laboratories (Alachua, FL, USA) and used as received. The halogen bond donor 1,4-diiodoperchlorobenzene (**C$_6$I$_2$Cl$_4$**) was synthesized using a previously reported method.[1] All crystallization studies were performed in 20 mL scintillation vials.

Synthesis of (C$_6$I$_2$Cl$_4$)•(4,4'-BPE)

The formation of each co-crystal has been previously reported[2] and a similar approach was utilized in this paper. Co-crystals of (**C$_6$I$_2$Cl$_4$**)•(**4,4'-BPE**) were synthesized by dissolving 25.0 mg of **C$_6$I$_2$Cl$_4$** in 3.0 mL of toluene, which was then combined with a separate 3.0 mL ethanol solution containing 9.7 mg of **4,4'-BPE** (1:1 molar equivalent). The solution was allowed to slowly evaporate, and within one day, crystals suitable for X-ray diffraction formed.

Synthesis of (C$_6$I$_2$Cl$_4$)•(4,4'-Azo)

Co-crystals of (**C$_6$I$_2$Cl$_4$**)•(**4,4'-Azo**) were synthesized by dissolving 25.0 mg of **C$_6$I$_2$Cl$_4$** in 3.0 mL of toluene, which was then combined with a separate 3.0 mL ethanol solution containing 9.8 mg of **4,4'-Azo** (1:1 molar equivalent). The solution was allowed to evaporate, and within a day, crystals suitable for X-ray diffraction were realized.

Synthesis of (C$_6$I$_2$Cl$_4$)•(4,4'-BPA)

Co-crystals of (**C$_6$I$_2$Cl$_4$**)•(**4,4'-BPA**) were synthesized by dissolving 25.0 mg of **C$_6$I$_2$Cl$_4$** in 3.0 mL of toluene, which was then combined with a separate 3.0 mL toluene solution containing 9.6 mg of **4,4'-BPA** (1:1 molar equivalent). The solution was allowed to evaporate, and within a day, crystals suitable for X-ray diffraction formed.

2. X-ray diffraction information and data tables

Data for $(C_6I_2Cl_4) \cdot (4,4'\text{-BPE})$ and $(C_6I_2Cl_4) \cdot (4,4'\text{-Azo})$ 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) with a HyPix-6000 HEHPC 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). X-ray data were collected at temperatures of 290, 270, 250, 230, 210, 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 insure 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].[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 structures. Hydrogen atoms bound to carbon atoms were located in the difference Fourier map and were geometrically constrained using the appropriate AFIX commands.

Data for $(C_6I_2Cl_4) \cdot (4,4'\text{-BPA})$ were collected on a Bruker APEX 2 diffractometer generating Mo Kα radiation (λ = 0.71073 Å) with a SMART CCD area detector. A group of crystals too large for data collection were immersed in a drop of viscous oil on a glass slide and several crystals cut and a suitably sized fragment selected. The crystal was mounted on a MiTeGen MicroMount along with small amount of the oil, attached to the goniometer head, and optically centered with the aid of a video camera. The sample was cooled with a cold nitrogen stream (Kryoflex) and X-ray data were collected at temperatures of 290, 270, 250, 230, 210, and 190 K. After data collection, the unit cell was re-determined using a subset of the full data collection for each temperature. Absorption was corrected for by multi-scan methods (SADABS 2014, Bruker AXS) and the *SHELXL-2018* 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 (**C₆I₂Cl₄**)·(**4,4′-BPE**) at 290, 270, and 250 K.

Compound formula	C$_{18}$H$_{10}$Cl$_4$I$_2$N$_2$	C$_{18}$H$_{10}$Cl$_4$I$_2$N$_2$	C$_{18}$H$_{10}$Cl$_4$I$_2$N$_2$
Formula Mass	649.88	649.88	649.88
Crystal System	Triclinic	Triclinic	Triclinic
Space Group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a/Å	4.08394(6)	4.07136(7)	4.06096(6)
b/Å	10.93443(15)	10.92294(16)	10.91085(13)
c/Å	12.37987(14)	12.36101(14)	12.34281(12)
α/°	110.9256(12)	110.7818(12)	110.6602(10)
β/°	92.4643(12)	92.5300(13)	92.5824(10)
γ/°	95.0316(12)	94.8692(13)	94.7301(11)
V/Å^3	512.734(13)	510.460(14)	508.363(11)
ρ$_{calc}$ / g cm^{-3}	2.105	2.114	2.123
T/K	290(2)	270(2)	250(2)
Z	1	1	1
Radiation Type	Cu Kα	Cu Kα	Cu Kα
Wavelength, Å	1.54178	1.54178	1.54178
Absorption coefficient, μ/mm^{-1}	28.929	29.058	29.178
F(000)	306	306	306
Reflections collected	11096	19057	18807
No. of independent reflections	1600	2081	2068
No. of reflection (I > 2σ(I))	1507	1979	2001
Data/restraints/parameter	1600 / 343 / 172	2081 / 343 / 172	2068 / 351 / 173
R$_{int}$	0.0597	0.0655	0.0626
R1 (I > 2σ(I))	0.0287	0.0253	0.0252
wR(F2) (I > 2σ(I)	0.0749	0.0646	0.0639
R1 (all data)	0.0303	0.0276	0.0267
wR(F2) (all data)	0.0770	0.0672	0.0657
Goodness-of-fit on F^2	1.061	1.040	1.040
CCDC deposition number	1954983	1954982	1954981

Table S2. X-ray data for (**C₆I₂Cl₄**)·(**4,4′-BPE**) at 230, 210, and 190 K.

Compound formula	$C_{18}H_{10}Cl_4I_2N_2$	$C_{18}H_{10}Cl_4I_2N_2$	$C_{18}H_{10}Cl_4I_2N_2$
Formula Mass	649.88	649.88	649.88
Crystal System	Triclinic	Triclinic	Triclinic
Space Group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a/Å	4.05144(5)	4.04426(6)	4.03440(10)
b/Å	10.90047(11)	10.88792(18)	10.8835(2)
c/Å	12.32575(11)	12.30931(18)	12.2968(2)
α/°	110.5582(9)	110.4771(15)	110.424(2)
β/°	92.6207(9)	92.6533(12)	92.656(2)
γ/°	94.6300(9)	94.5880(13)	94.579(2)
V/Å³	506.406(10)	504.543(15)	502.782(19)
ρ_{calc} / g cm⁻³	2.131	2.139	2.146
T/K	230(2)	210(2)	190(2)
Z	1	1	1
Radiation Type	Cu Kα	Cu Kα	Cu Kα
Wavelength, Å	1.54178	1.54178	1.54178
Absorption coefficient, μ/mm⁻¹	29.291	29.399	29.502
F(000)	306	306	306
Reflections collected	18963	18918	18940
No. of independent reflections	2064	2062	2051
No. of reflection (I > 2σ(I))	1995	2014	1999
Data/restraints/parameter	2064 / 351 / 173	2062 / 0 / 119	2051 / 0 / 118
R_{int}	0.0623	0.0625	0.0552
R1 (I > 2σ(I))	0.0248	0.0242	0.0228
wR(F2) (I > 2σ(I)	0.0638	0.0648	0.0565
R1 (all data)	0.0266	0.0253	0.0239
wR(F2) (all data)	0.0663	0.0659	0.0578
Goodness-of-fit on F^2	1.072	1.027	1.059
CCDC deposition number	1954980	1954979	1954978

Table S3. X-ray data for (**C₆I₂Cl₄**)·(**4,4′-Azo**) at 290, 270, and 250 K.

Compound formula	$C_{16}H_8Cl_4I_2N_4$	$C_{16}H_8Cl_4I_2N_4$	$C_{16}H_8Cl_4I_2N_4$
Formula Mass	651.86	651.86	651.86
Crystal System	Triclinic	Triclinic	Triclinic
Space Group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a/Å	4.05852(19)	4.05043(19)	4.04169(16)
b/Å	10.8342(4)	10.8317(3)	10.8302(3)
c/Å	12.4194(4)	12.4043(3)	12.3901(3)
α/°	111.498(3)	111.501(3)	111.496(3)
β/°	92.143(3)	92.105(3)	92.077(3)
γ/°	94.631(3)	94.666(3)	94.678(3)
V/Å³	505.12(4)	503.36(3)	501.66(3)
ρ_{calc} / g cm⁻³	2.143	2.150	2.158
T/K	290(2)	270(2)	250(2)
Z	1	1	1
Radiation Type	Cu Kα	Cu Kα	Cu Kα
Wavelength, Å	1.54178	1.54178	1.54178
Absorption coefficient, μ/mm⁻¹	29.398	29.501	29.601
F(000)	306	306	306
Reflections collected	13253	16741	16382
No. of independent reflections	1883	2041	2024
No. of reflection (I > 2σ(I))	1759	1915	1925
Data/restraints/parameter	1883 / 343 / 159	2041 / 343 / 159	2024 / 343 / 159
R_{int}	0.0854	0.0695	0.0799
R1 (I > 2σ(I))	0.0352	0.0338	0.0355
wR(F2) (I > 2σ(I)	0.0896	0.0854	0.0902
R1 (all data)	0.0411	0.0391	0.0408
wR(F2) (all data)	0.0962	0.0911	0.0944
Goodness-of-fit on F²	1.138	1.103	1.089
CCDC deposition number	1954977	1954976	1954975

Table S4. X-ray data for $(\mathbf{C_6I_2Cl_4})\cdot(\mathbf{4,4'\text{-}Azo})$ at 230, 210, and 190 K.

Compound formula	$C_{16}H_8Cl_4I_2N_4$	$C_{16}H_8Cl_4I_2N_4$	$C_{16}H_8Cl_4I_2N_4$
Formula Mass	651.86	651.86	651.86
Crystal System	Triclinic	Triclinic	Triclinic
Space Group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a/Å	4.03260(16)	4.02352(16)	4.01450(14)
b/Å	10.8287(3)	10.8276(3)	10.8241(2)
c/Å	12.3790(3)	12.3666(4)	12.3534(3)
α/°	111.495(3)	111.499(3)	111.476(2)
β/°	92.054(3)	92.051(3)	92.043(3)
γ/°	94.675(3)	94.643(3)	94.580(2)
V/Å^3	500.03(3)	498.38(3)	496.72(3)
ρ_{calc} / g cm^{-3}	2.165	2.172	2.179
T/K	230(2)	210(2)	190(2)
Z	1	1	1
Radiation Type	Cu Kα	Cu Kα	Cu Kα
Wavelength, Å	1.54178	1.54178	1.54178
Absorption coefficient, μ/mm^{-1}	29.697	29.796	29.895
F(000)	306	306	306
Reflections collected	16476	16416	16568
No. of independent reflections	2016	2012	2008
No. of reflection (I > 2σ(I))	1930	1928	1934
Data/restraints/parameter	2016 / 343 / 159	2012 / 343 / 159	2008 / 343 / 159
R$_{int}$	0.0829	0.0536	0.0656
R1 (I > 2σ(I))	0.0347	0.0309	0.0323
wR(F2) (I > 2σ(I)	0.0879	0.0762	0.0816
R1 (all data)	0.0395	0.0363	0.0377
wR(F2) (all data)	0.0913	0.0798	0.0846
Goodness-of-fit on F^2	1.099	1.090	1.095
CCDC deposition number	1954974	1954973	1954972

Table S5. X-ray data for (**C₆I₂Cl₄**)·(**4,4′-BPA**) at 290, 270, and 250 K.

Compound formula	$C_{18}H_8Cl_4I_2N_2$	$C_{18}H_8Cl_4I_2N_2$	$C_{18}H_8Cl_4I_2N_2$
Formula Mass	647.86	647.86	647.86
Crystal System	Triclinic	Triclinic	Triclinic
Space Group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a/Å	4.0598(6)	4.0502(2)	4.0413(2)
b/Å	11.1929(18)	11.1860(7)	11.1833(6)
c/Å	12.2066(18)	12.1964(7)	12.1828(7)
α/°	111.485(3)	111.4920(10)	111.4890(10)
β/°	90.699(2)	90.6710(10)	90.6370(10)
γ/°	97.282(2)	97.3320(10)	97.4090(10)
V/Å^3	510.94(14)	508.92(5)	507.03(5)
ρ_{calc} / g cm^{-3}	2.106	2.114	2.122
T/K	290(2)	270(2)	250(2)
Z	1	1	1
Radiation Type	Mo Kα	Mo Kα	Mo Kα
Wavelength, Å	0.71073	0.71073	0.71073
Absorption coefficient, μ/mm^{-1}	3.606	3.620	3.634
F(000)	304	304	304
Reflections collected	6470	6363	6351
No. of independent reflections	2292	2278	2267
No. of reflection (I > 2σ(I))	2189	2182	2191
Data/restraints/parameter	2292 / 0 / 118	2278 / 0 / 118	2267 / 0 / 118
R_{int}	0.0141	0.0163	0.0160
R1 (I > 2σ(I))	0.0155	0.0150	0.0146
wR(F2) (I > 2σ(I)	0.0353	0.0356	0.0345
R1 (all data)	0.0166	0.0159	0.0154
wR(F2) (all data)	0.0359	0.0361	0.0349
Goodness-of-fit on F^2	1.061	1.078	1.072
CCDC deposition number	1909926	1955227	1955226

Table S6. X-ray data for (**C₆I₂Cl₄**)·(**4,4′-BPA**) at 230, 210, and 190 K.

Compound formula	$C_{18}H_8Cl_4I_2N_2$	$C_{18}H_8Cl_4I_2N_2$	$C_{18}H_8Cl_4I_2N_2$
Formula Mass	647.86	647.86	647.86
Crystal System	Triclinic	Triclinic	Triclinic
Space Group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a/Å	4.0336(2)	4.0263(3)	4.0179(2)
b/Å	11.1825(7)	11.1831(9)	11.1807(6)
c/Å	12.1732(7)	12.1654(10)	12.1538(7)
α/°	111.4960(10)	111.5010(10)	111.5050(10)
β/°	90.5990(10)	90.5580(10)	90.5190(10)
γ/°	97.4800(10)	97.5490(10)	97.6160(10)
V/Å³	505.53(5)	504.23(7)	502.51(5)
ρ_{calc} / g cm⁻³	2.128	2.134	2.141
T/K	230(2)	210(2)	190(2)
Z	1	1	1
Radiation Type	Mo Kα	Mo Kα	Mo Kα
Wavelength, Å	0.71073	0.71073	0.71073
Absorption coefficient, μ/mm⁻¹	3.644	3.654	3.666
F(000)	304	304	304
Reflections collected	6384	8319	6295
No. of independent reflections	2271	3450	2261
No. of reflection (I > 2σ(I))	2201	3197	2195
Data/restraints/parameter	2271 / 0 / 118	3450 / 0 / 118	2261 / 0 / 118
R_{int}	0.0156	0.0152	0.0153
R1 (I > 2σ(I))	0.0141	0.0205	0.0126
wR(F2) (I > 2σ(I)	0.0335	0.0451	0.0315
R1 (all data)	0.0148	0.0236	0.0133
wR(F2) (all data)	0.0339	0.0482	0.0318
Goodness-of-fit on F²	1.087	1.224	1.088
CCDC deposition number	1955225	1955224	1955223

3. Intermolecular interaction distances

The thermal expansion coefficients were calculated using the PASCal program.[6] The unit cell parameters from the crystallographic data sets at 290, 270, 250, 230, 210 and 190 K were used for the thermal expansion calculations. See main text Table 2 for values.

Table S7. Intermolecular interaction distances within the co-crystals that contribute to the thermal expansion parameters.

Co-crystal	I•••N(pyr) halogen bonds 290 K (Å)	I•••N(pyr) halogen bonds 190 K (Å)	Δ (Å)
$(C_6I_2Cl_4)\cdot(4,4'-BPE)$	2.918	2.889	0.029
$(C_6I_2Cl_4)\cdot(4,4'-Azo)$	2.971	2.930	0.041
$(C_6I_2Cl_4)\cdot(4,4'-BPA)$	2.929	2.906	0.023

Co-crystal	C-H(pyr)•••Cl interaction in layers at 290 K (Å)	C-H(pyr)•••Cl interaction in layers at 190 K (Å)	Δ (Å)
$(C_6I_2Cl_4)\cdot(4,4'-BPE)$	3.878	3.854	0.024
$(C_6I_2Cl_4)\cdot(4,4'-Azo)$	3.831	3.797	0.034
$(C_6I_2Cl_4)\cdot(4,4'-BPA)$	3.835	3.805	0.030

Co-crystal	Pi-Pi stacking/I•••I interactions 290 K (Å)	Pi-Pi stacking/I•••I interactions 190 K (Å)	Δ (Å)
$(C_6I_2Cl_4)\cdot(4,4'-BPE)$	4.084	4.034	0.050
$(C_6I_2Cl_4)\cdot(4,4'-Azo)$	4.059	4.014	0.045
$(C_6I_2Cl_4)\cdot(4,4'-BPA)$	4.060	4.018	0.042

Co-crystal	Cl•••linker interaction 290 K (Å)	Cl•••linker interaction 190 K (Å)	Δ (Å)
$(C_6I_2Cl_4)\cdot(4,4'-BPE)$	3.291	3.254	0.037
$(C_6I_2Cl_4)\cdot(4,4'-Azo)$	3.164	3.116	0.048
$(C_6I_2Cl_4)\cdot(4,4'-BPA)$	3.431	3.391	0.04

4. Expansivity indicatrix images
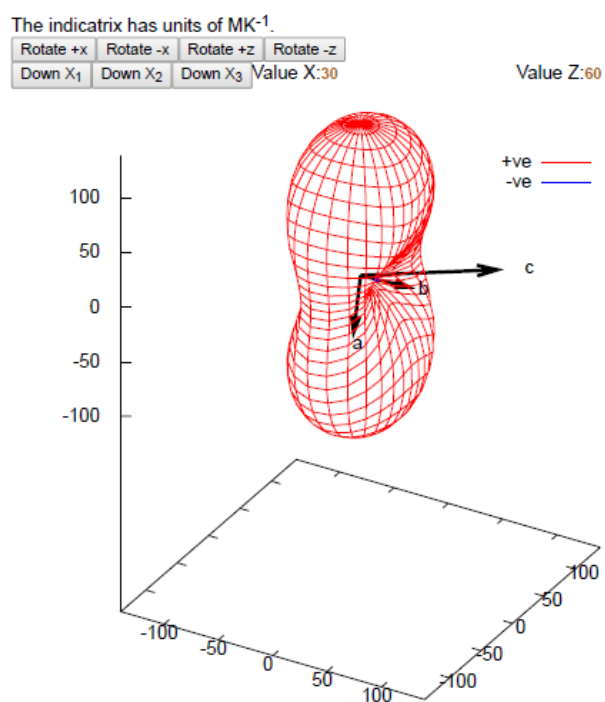
Figure S1. Thermal expansivity indicatrix for (**C₆I₂Cl₄**)·(**4,4′-BPE**).
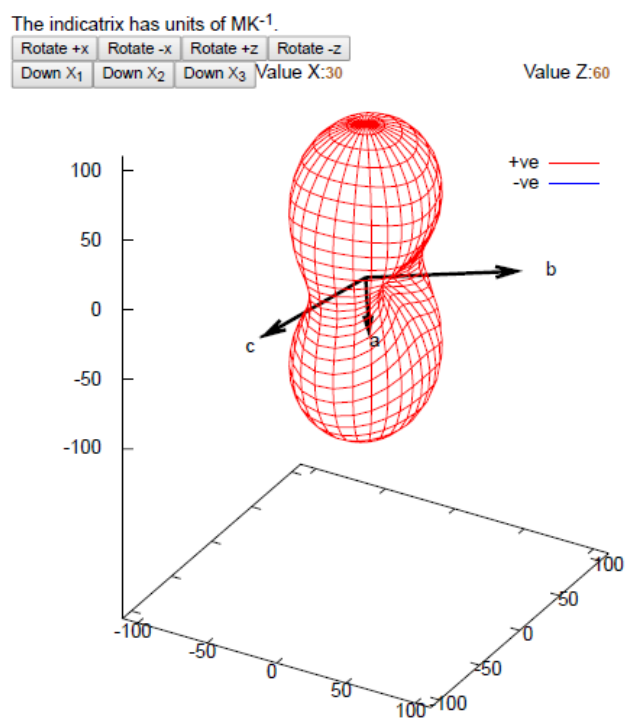
Figure S2. Thermal expansivity indicatrix for (**C₆I₂Cl₄**)·(**4,4′-Azo**).

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

| Rotate +x | Rotate -x | Rotate +z | Rotate -z |
| Down X$_1$ | Down X$_2$ | Down X$_3$ | Value X:30 |

Value Z:60
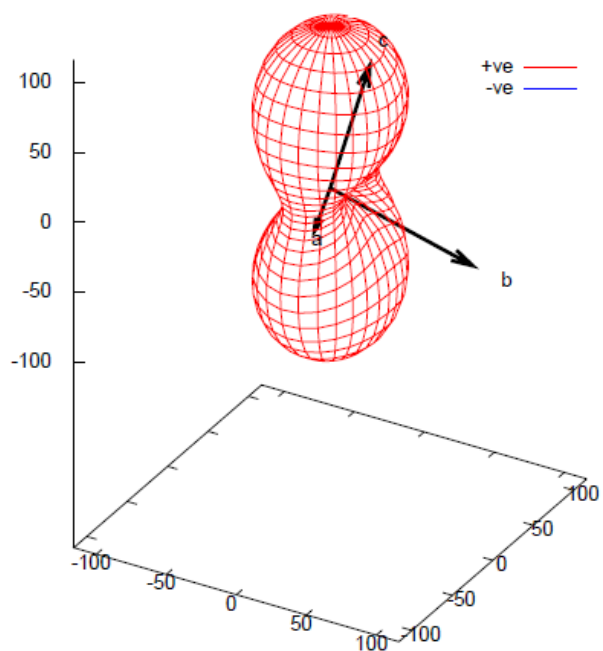
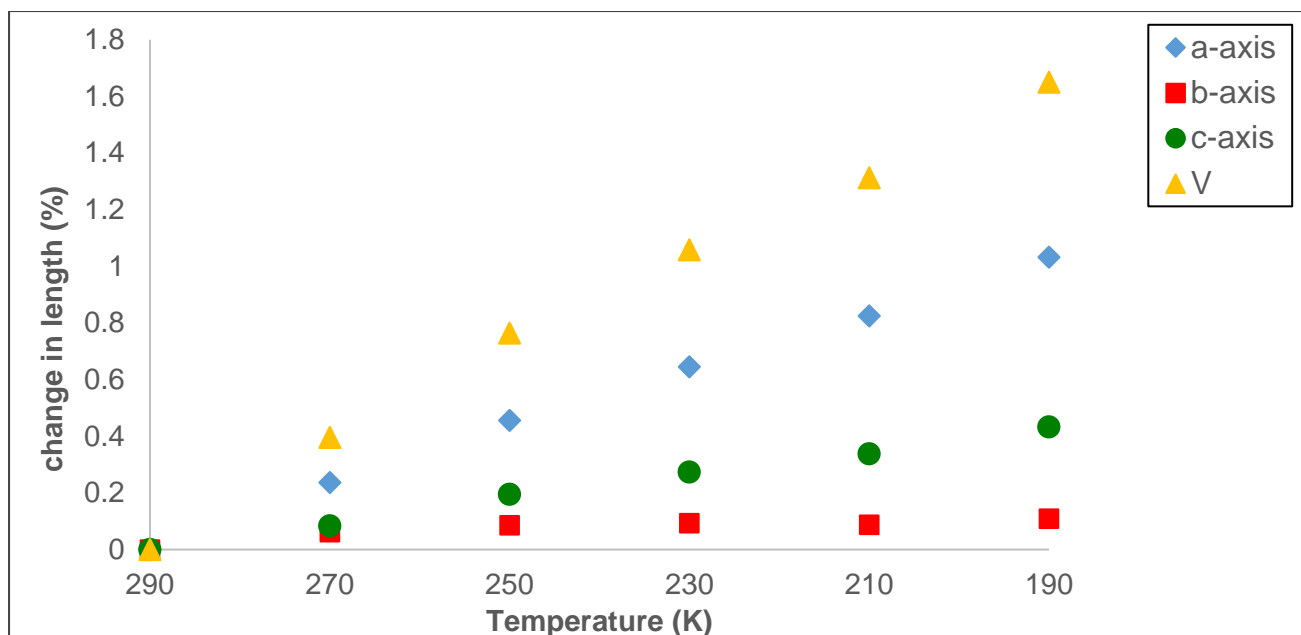**Figure S3.** Thermal expansivity indicatrix for ($C_6I_2Cl_4$)·($4,4'$-BPA).

5. Unit cell parameters of co-crystals
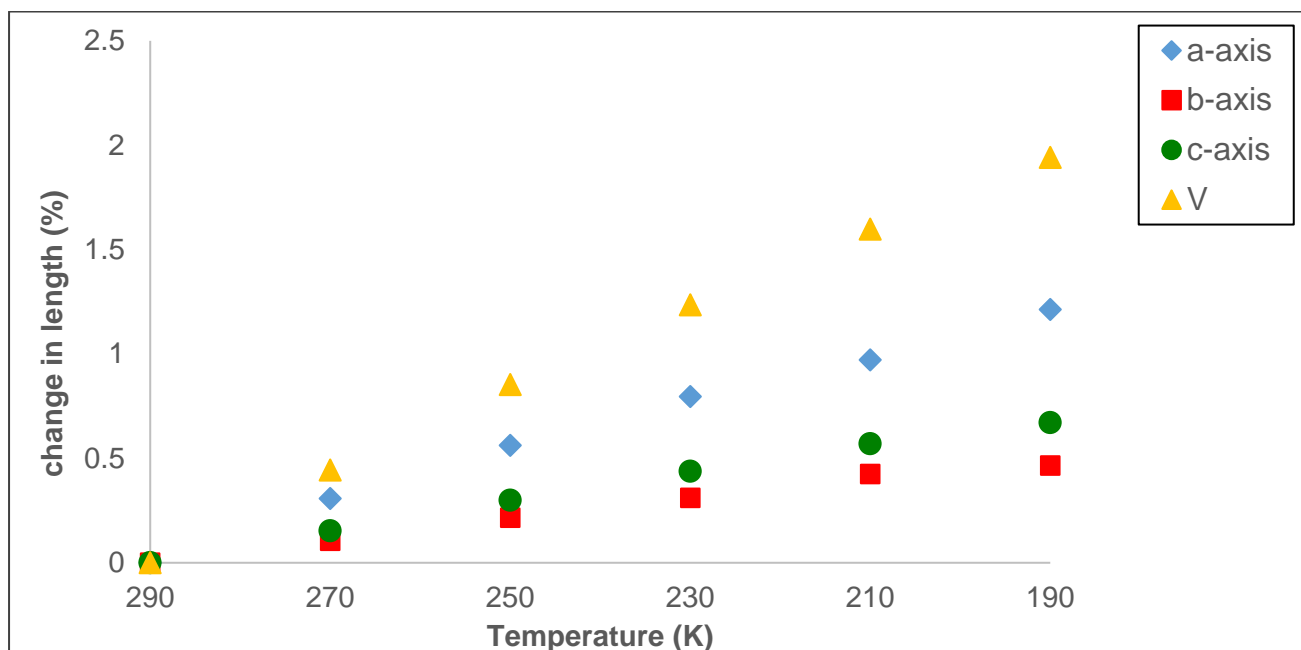
Figure S4. Percent change in length as a function of temperature for ($C_6I_2Cl_4$)·(**4,4′-BPE**).
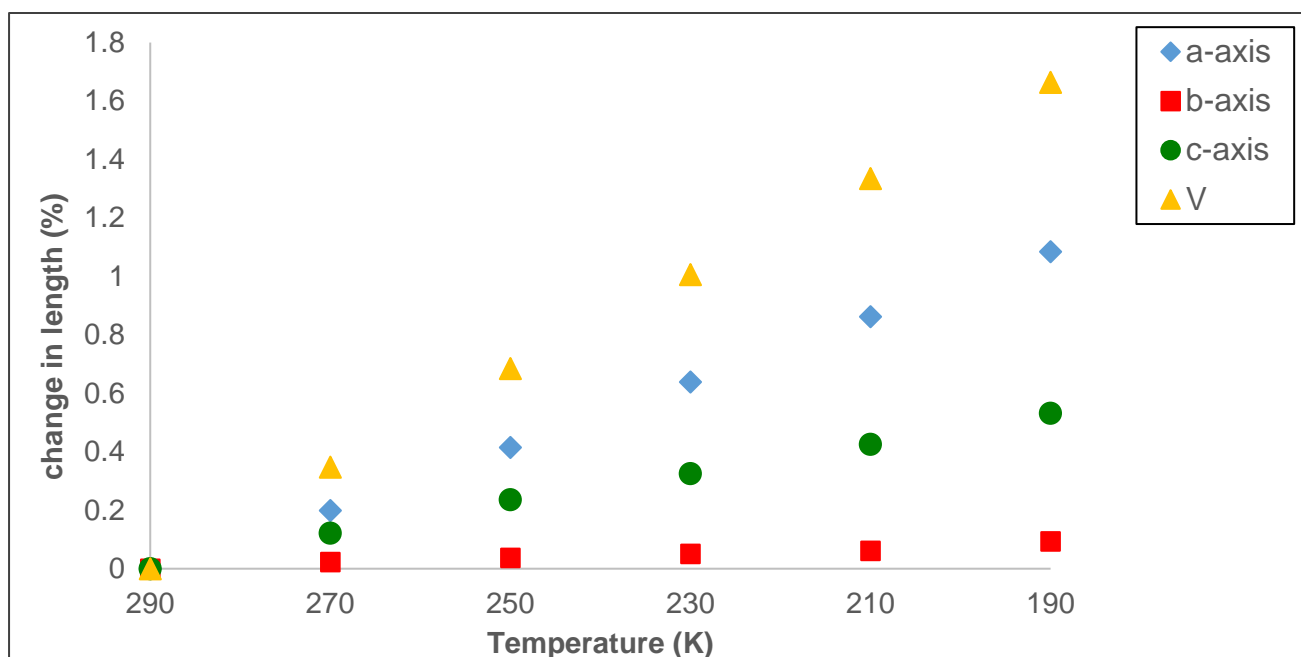
Figure S5. Percent change in length as a function of temperature for ($C_6I_2Cl_4$)·(**4,4′-Azo**).

Figure S6. Percent change in length as a function of temperature for ($C_6I_2Cl_4$)·($4,4'$-BPA).

References

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