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Supporting Information

for

Cooling-rate-dependent single-crystal-to-single-crystal phase transition in an organic co-crystal

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1. Materials and synthesis of the co-crystal	Page S2
2. X-ray diffraction information, data tables, and plots	Pages S3-S6
3. Thermal expansion results	Page S7
4. Differential scanning calorimetry (DSC) experiments	Pages S8-S9

1. Materials and synthesis of the co-crystal

Materials

1,2-Di(4-pyridyl)ethylene (**4,4'-BPE**) was purchased from Sigma-Aldrich, and recrystallized from a hexanes/ethanol mixture. 1,2,4,5-Tetrabromobenzene (**TBrB**) was purchased from Alfa Aesar and used as received. Toluene was purchased from Fisher Scientific and used as received.

Co-crystallization of (4,4'-BPE) (TBrB)

Co-crystals were synthesized as previously reported.¹ Briefly, 40 mg of the recrystallized **4,4'-BPE** was dissolved in 2 mL of toluene. This solution was combined with a separate 2 mL toluene solution containing 86 mg of **TBrB** (1:1 molar equivalent). The solution was allowed to slowly evaporate for 2 days, which yielded large enough crystals for single-crystal X-ray diffraction analysis.

2. X-ray diffraction information, data tables, and plots

Single crystal X-ray diffraction data for the co-crystals were collected on a Bruker PLATFORM three circle diffractometer equipped with an APEX II CCD detector and operated at 1500 W (50kV, 30 mA) to generate (graphite monochromated) Mo K α radiation ($\lambda = 0.71073$ Å). Intensity data were corrected for Lorentz, polarization, and background effects using the Bruker program APEX II. A semi-empirical correction for adsorption was applied using the program *SADABS*². The *SHELXL-2014*³, series of programs were used for the solution and refinement of the crystal structure. For the structures at temperatures of 300 K, 270 K, 250K, 230 K, and flash cooled 100 K the **4,4'-BPE** molecule was disordered about two positions, A and B. The site occupancies of the two sites were allowed to free refine to a constrained total of 1. To help restrain the disordered sites, SIMU, DLEU, and free variable DFIX commands for C-C and C-N bond distances were applied. All non-hydrogen atoms were refined anisotropically and hydrogen atoms bound to carbon atoms were located in the difference Fourier map and were geometrically constrained using the appropriate AFIX commands.

chemical formula	$C_{18}H_{12}Br_4N_2$	$C_{18}H_{12}Br_4N_2$	$C_{18}H_{12}Br_4N_2$	$C_{18}H_{12}Br_4N_2$
formula mass	575.94	575.94	575.94	575.94
crystal system	Triclinic Triclinie		Triclinic	Triclinic
space group	PĪ	$P\overline{1}$	$P\overline{1}$	$P\overline{1}$
a/Å	4.0143(2)	4.0022(2)	3.9924(2)	3.9826(2)
b/Å	13.5219(9)	13.5102(6)	13.5015(6)	13.4966(7)
c/Å	17.3448(11)	17.3261(8)	17.3091(8)	17.2973(8)
α/°	102.786(3)	102.783(2)	102.795(2)	102.810(2)
β/°	93.568(3	93.452(2)	93.323(2)	93.204(2)
γ/°	94.296(3)	94.301(2)	94.316(2)	94.321(2)
V/Å ³	912.56(10)	908.19(7)	904.59(7)	901.51(8)
$ ho_{calc}/g\ cm^{-3}$	2.096	2.106	2.114	2.122
T/K	300	270	250	230
Z	2	2	2	2
radiation type	ΜοΚα	ΜοΚα	ΜοΚα	ΜοΚα
absorption coefficient,				
μ/mm ⁻¹	8.822	8.865	8.900	8.930
no. of reflections measured	14436	14247	14191	14174
no. of independent reflections	4243	4168	4155	4140
no of reflection $(I > 2\sigma(I))$	2837	2900	3022	2762
R _{int}	0.0340	0.0337	0.0335	0.0837
$R_1 (I > 2\sigma(I))$	0.0315	0.0279	0.0278	0.0411
$wR(F^2) (I > 2\sigma(I))$	0.0580	0.0536	0.0535	0.0940
R ₁ (all data)	0.0612	0.0533	0.0494	0.0625
wR(F ²) (all data)	0.0652	0.0603	0.0594	0.0996
major/minor (A:B)				
occupancies	0.88 : 0.12	0.91 : 0.09	0.93 : 0.07	0.95 : 0.05
Goodness-of-fit	1.045	1.008	1.033	0.940
CCDC deposition number	1889834	1889835	1889836	1889837

Table S1. X-ray data for (4,4'-BPE)·(TBrB) at 300, 270, 250, and 230 K.

Table S2. X-ray data for (**4,4'-BPE**)·(**TBrB**) at 210, 190, and 100 K. The 100 K sample was flash cooled to 100 K and held for 20 hr before data collection.

chemical formula	$C_{18}H_{12}Br_4N_2$	$C_{18}H_{12}Br_4N_2$	$C_{18}H_{12}Br_4N_2$
formula mass	575.94	575.94	575.94
crystal system	Triclinic	Triclinic	Triclinic
space group	$P\overline{1}$	$P\overline{1}$	PĪ
a/Å	3.9561(17)	3.9240(8)	3.9431(6)
b/Å	9.702(4)	9.667(2)	13.4500(19)
c/Å	12.444(5)	12.375(3)	17.231(2)
α/°	75.878(7)	75.801(10)	102.747(2)
β/°	84.947(5)	84.980(11)	92.460(2)
γ/°	78.556(5)	78.541(11)	94.329(2)
V/Å ³	453.6(3)	445.65(17)	887.1(2)
$\rho_{calc}/g \text{ cm}^{-3}$	2.108	2.146	2.156
			100 K (flash cooled
T/K	210	190	and held 20 hr)
Z	1	1	2
radiation type	ΜοΚα	ΜοΚα	ΜοΚα
absorption coefficient,			
μ/mm ⁻¹	8.874	9.033	9.075
no. of reflections measured	7547	6392	12565
no. of independent reflections	2017	1972	3590
no of reflection $(I > 2\sigma(I))$	1633	1587	2714
R _{int}	0.0575	0.0879	0.0496
$R_1 (I > 2\sigma(I))$	0.0534	0.0346	0.0360
$wR(F^2) (I > 2\sigma(I))$	0.1384	0.0861	0.0796
R ₁ (all data)	0.1004	0.0490	0.0539
wR(F ²) (all data)	0.1645	0.0922	0.0869
major/minor (A:B)	1.0	1.0	$0.93 \cdot 0.07$
Goodness_of_fit	1.051	1.02	1 032
CCDC deposition purchas	1,001	1.002	1.032
CCDC deposition number	1009030	1889839	1889840



Figure S1. Changes in length as a function of temperature for the *a*-, *b*-, and *c*-crystallographic axes of (**4**,**4'-BPE**)·(**TBrB**). Phase change occurs between 230-210 K.



Figure S2. Change in volume as a function of temperature for (**4,4'-BPE**)·(**TBrB**). Phase change occurs between 230-210 K.



Figure S3. Plot of major site occupancy for disordered olefin in 4,4'-BPE-1 as a function of temperature.



Figure S4. (4,4'-BPE)·(TBrB): *left*: co-crystal following flash cooling to 100 K and holding for 2 hrs (for comparison), *right*: co-crystal following flash cooling, re-warming, and cooling cycle demonstrating crystal fracture.

3. Thermal expansion results

PASCal⁴ was used to calculate the TE coefficients and the principal axes for $(4,4'-BPE) \cdot (TBrB)$ using the unit cell parameters from 300-230 K (Table S1).



Figure S5. Expansivity indicatrix representing the 3D plot of the calculated thermal expansion coefficients along the crystallographic axes for (4,4'-BPE)·(TBrB).



Figure S6. X-ray structure of $(4,4'-BPE) \cdot (TBrB)$ highlighting layered packing and X₃ axis, which experiences the most thermal expansion upon cooling.

4. Differential scanning calorimetry (DSC) experiments

Experiment 1: cooling rate of 10 K/min. Result: weak endothermic peak (transition peak like melting) at 258 K, no peak near 230 K on heating.

Experiment 2: cooling rate dependence study from 30 K/min to 0.3 K/min. Result, same as Experiment 1 (see Figure S6 below).

Experiment 3: isothermal hold at 235 K for 3 hr, cool to 195 K at 0.3 K/min, heat to room temperature at 10 K/min. Result: small peak at 258 K, no evidence of phase transition peak.

Experiment 4: isothermal hold at 225 K for 3 hr, cool to 195 K at 0.3 K/min, heat to room temperature at 10 K/min. Result: small peak at 258 K, no evidence of phase transition peak.

Experiment 5: isothermal hold at 220 K for 3 hr, cool to 195 K at 0.3 K/min, heat to room temperature at 10 K/min. Result: small peak at 258 K, no evidence of phase transition peak (see Figure S7 below).



Figure S7. DSC heating scans at 10 K/min following different cooling rates (q) ranging from 0.3 to 30 K/min.



Figure S8. DSC heating scans at 10 K/min after isothermal hold at 220 K for 3 hrs.

References

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