

Supporting information

Unveiling re-entrant phase behavior and crystalline-amorphous interactions in semi-conducting polymer:small molecule blends

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Experimental methods

Materials

PTB7-Th, EH-IDTBR and di-PDI were purchased from 1-Material. PffBT4T-C9C13 was purchased from Raynergy Tek Inc., PC₆₁BM from Nano-C Inc. and PC₇₁BM from American Dye Source, Inc.

Sample Preparation

For ToF-SIMS measurement, the substrates (glass/silicon wafer) were cleaned by sequential sonication in soap deionized (DI) water, DI water, acetone, and isopropanol for 15 min at each step. After ultraviolet/ozone treatment for 15 min, a PSS (polystyrene sulfonate) layer was prepared by spin coating at 3,000 rpm on the glass substrates and a ZnO layer was prepared by spin coating at 3,000 rpm on the Si substrates from a ZnO nanoparticle solution. The neat SMA layers were spun cast onto the ZnO-coated Si substrate with around 150 nm while the polymer layers were spun cast onto the PSS-coated glass substrate with around 100 nm. The PSS layer is coated to enable immersion in deionized water yielding a film of polymer layer floating on a water support. The polymer layers were floated on DI water and picked up with the Si supported SMA film, forming bilayer films. The formed bilayer films were then dried in vacuum for > 24 hours to remove any residual water trapped in the films. For the pre-annealing experiments, the neat polymer films are annealed at different temperatures and then water-transferred to the Si supported SMA film, forming bilayer films.

For the liquidus measurements, the polymer and small molecule are mixed in a certain D/A ratio and dissolved in chlorobenzene (CB) and then spin cast on pre-cleaned glass substrates with ~100nm thick. The blend thin films are annealed at elevated temperatures in N₂ atmosphere.

The DSC samples were prepared by drop casting of the neat materials dissolved in CB on glass slides with a concentration of 20 mg/mL. After being stored inside the glovebox overnight, the samples were transferred into a vacuum chamber and kept under vacuum for 7 days to remove the

residual solvent trapped in the film. The dried samples then were scratched from the glass slides and moved to Tzero aluminum pans to be used for the DSC measurements.

Measurements

The SIMS measurements were performed on a Time-of-Flight Secondary Ion Mass Spectrometer (TOF-SIMS) (Ion-Tof USA Inc., Chestnut Ridge, NY) at NCSU, equipped with a bismuth liquid metal ion gun, Cs⁺ sputtering gun and an electron flood gun for charge compensation. Dual-beam dynamic SIMS mode was used to provide high depth resolution and chemical resolution simultaneously, where Bi³⁺ was used as the primary ion and Cs⁺ was used as the sputtering source. The analysis chamber pressure is maintained below 5.0×10^{-9} mbar to avoid contamination of the surfaces to be analyzed.

Transmission optical micrographs are acquired using a Nikon Labophot-2 microscope. The UV-vis absorption spectra are recorded using a Cary 50 spectrophotometer with the wavelength from 300 to 800/1000 nm. DSC measurements was performed with a TA Discovery DSC with the heating/cooling rate of 10 °C/min.

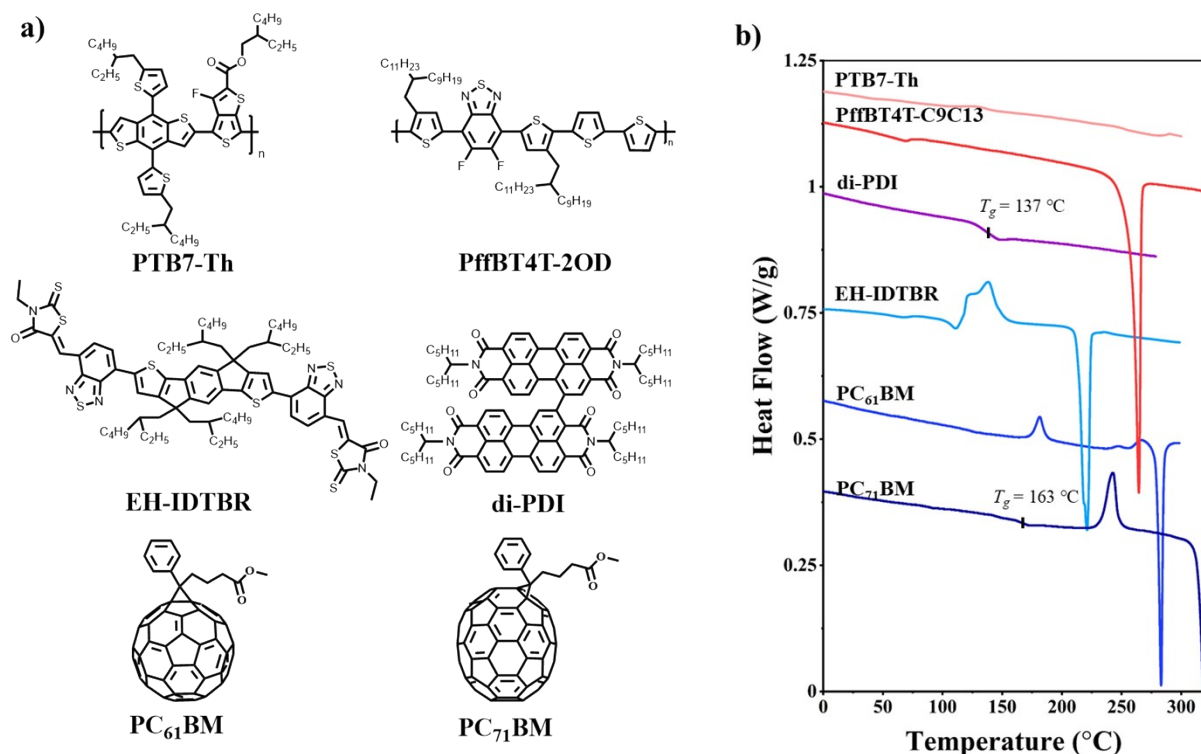


Figure S1: a) Chemical structure of the materials used and b) DSC (1st heating) thermograms with a heating rate of 10 °C/min of materials drop cast from chlorobenzene. The thermograms were vertically shifted for clarity.

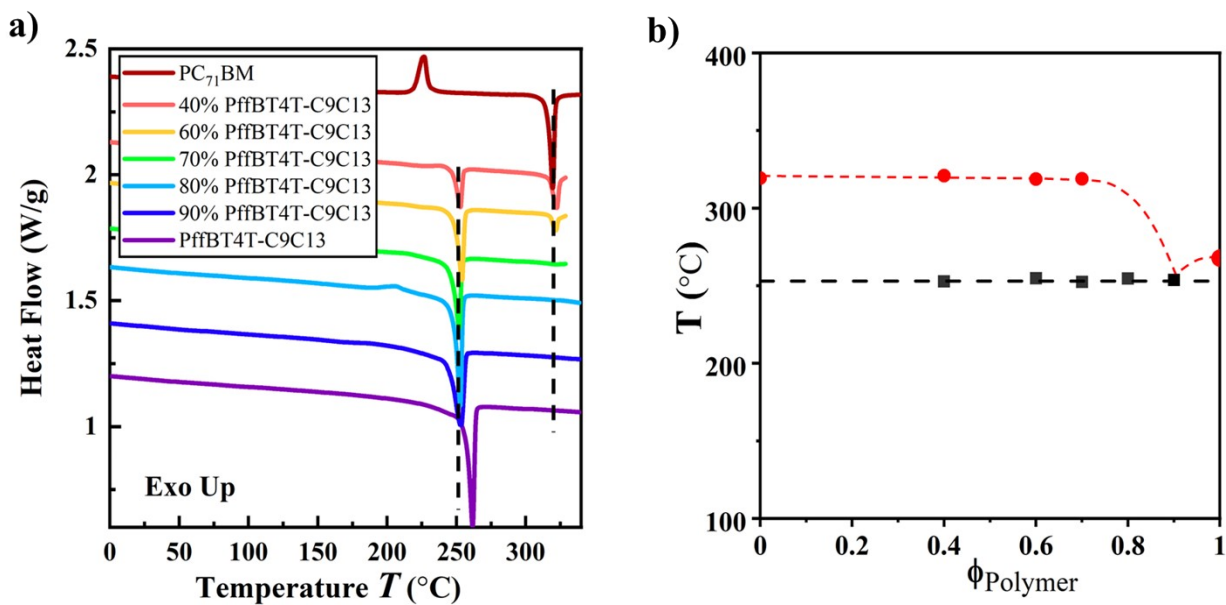


Figure S2: a) The second DSC heating scan (10°C/min) of PffBT4T-C9C13:PC₇₁BM blends drop cast with chlorobenzene. b) The corresponding liquidus (red dashed line) and solidus (eutectic line, black dashed line) constructed with the melting points, suggesting eutectic phase behavior with eutectic temperature at ~253 °C.

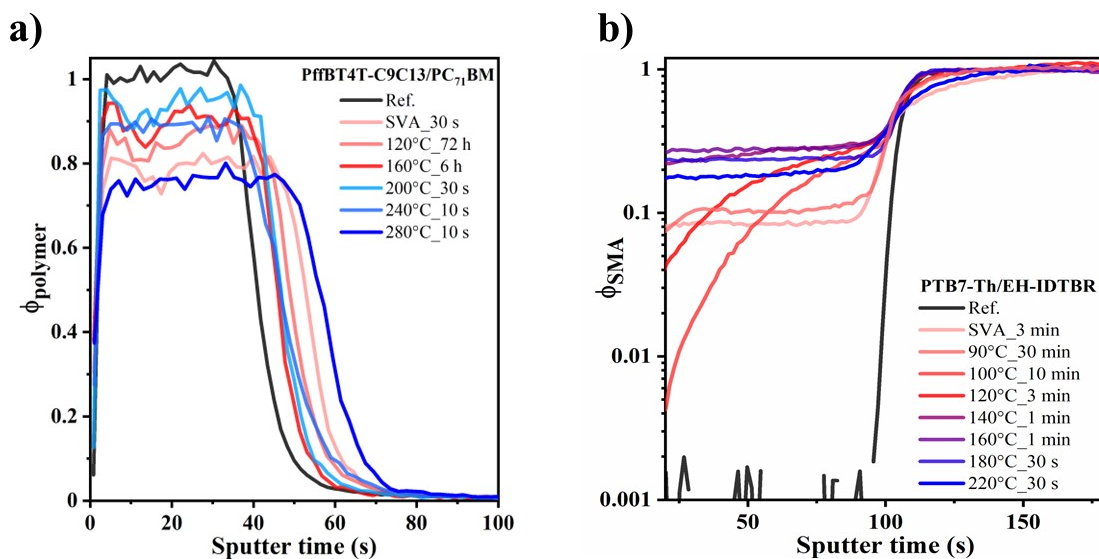


Figure S3: SIMS profiles of a) PffBT4T-C9C13:PC₇₁BM and b) PTB7-Th:EH-IDTBR. SVA is referring to solvent annealing with chlorobenzene.

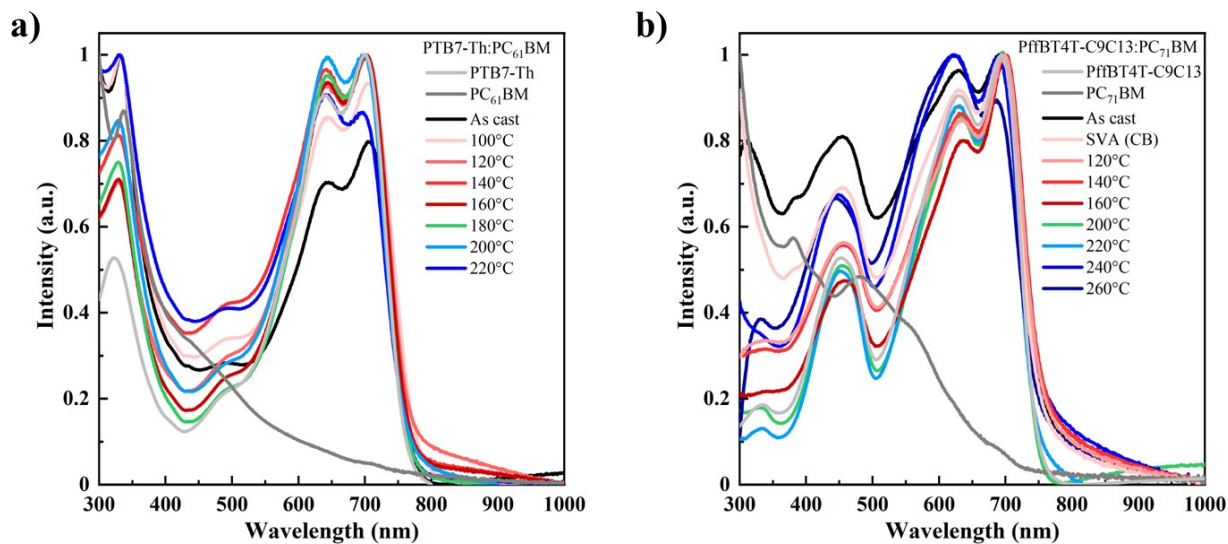


Figure S4. UV-vis absorption spectra of a) 6:4 (w/w) PTB7-Th:PC₆₁BM blends and b) 5:5 (w/w) PffBT4T-C9C13:PC₇₁BM blends annealed at different temperatures and the highest intensity of each spectrum is normalized to be 1. ‘SVA(CB)’ is referring to solvent vapor annealing with chlorobenzene.

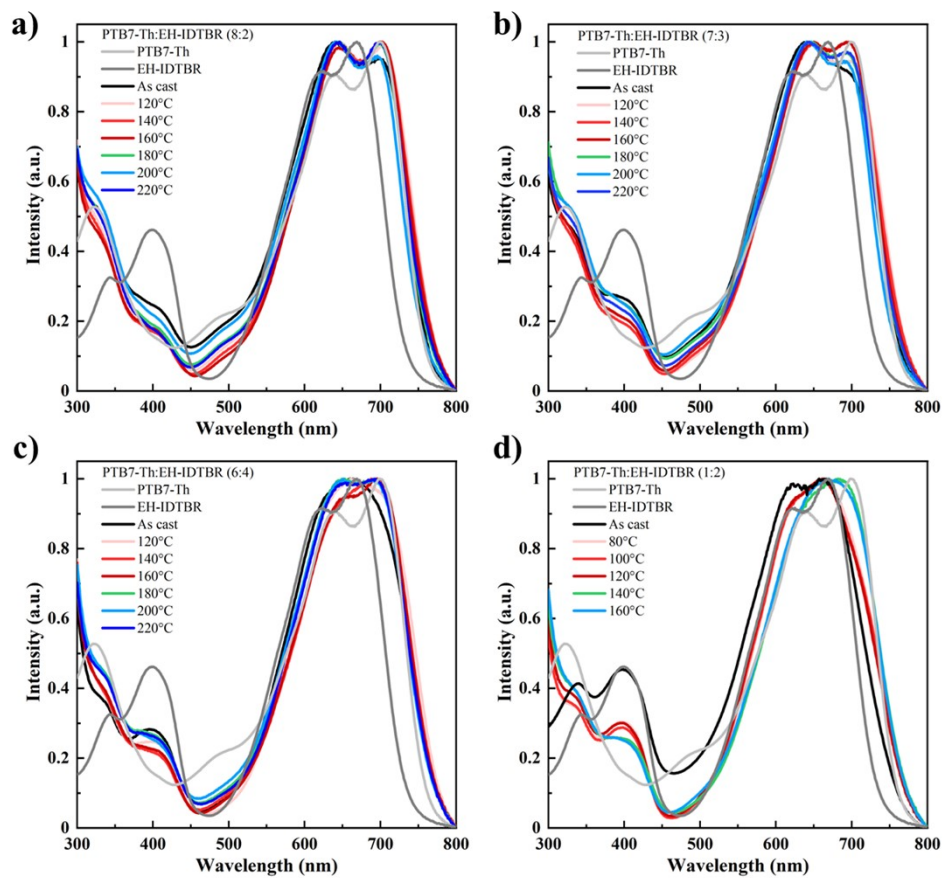


Figure S5. UV–vis absorption spectra of a) 8:2 (w/w), b) 7:3 (w/w), c) 6:4 (w/w) and d) 1:2 (w/w) PTb7-Th:PC₆₁BM blends annealed at different temperatures and the highest intensity of each spectrum is normalized to be 1.

Table S1: Fit-parameters from FH-like models when fitting the low-*T* and high-*T* branches of the binodal or liquidus phase boundaries as shown in Figure 1 and 2 separately for the

branches with
$$\chi = A + \frac{B}{T}$$

		Low- <i>T</i> branch		High- <i>T</i> branch	
		A (or ΔA)	B (or ΔB)	A (or ΔA)	B (or ΔB)
PTB7-Th: PC₆₁BM	binodal	2.9	-615	-1.94	1397
	liquidus	2.9	-555	-1.94	1484
	Difference between liquidus and binodal (ΔA or ΔB)	0	60	0	87
PffBT4T- C9C13: PC₇₁BM	binodal	2.58	-384	-1.48	1517
	liquidus	3.83	-696	-2	1970
	Difference between liquidus and binodal (ΔA or ΔB)	1.25	-312	-0.52	453
PTB7-Th: EH- IDTBR	binodal	-5.46	2549	2.787	-690
	liquidus	-5.46	2700	2.787	-585
	Difference between liquidus and binodal (ΔA or ΔB)	0	151	0	105

We observe from **Table S1**, PTB7-Th:PC₆₁BM and PTB7-Th:EH-IDTBR keep *A* unchanged between binodal and liquidus while PffBT4T-C9C13:PC₇₁BM does not. Since χ_{ca} is assumed to be proportional to $1/T$, we can get the $\chi_{ca} = 60/T$ and $\chi_{ca} = 87/T$ for the low-*T* branch and high-*T* branch respectively for PTB7-Th:PC₆₁BM and $\chi_{ca} = 151/T$ and $\chi_{ca} = 105/T$ respectively for PTB7-Th: EH-IDTBR. We note that there is slightly difference in χ_{ca} for the two branches. Since the low-*T* branch is below T_g of SMA while the high-*T* branch is above T_g , it implies that χ_{ca} is slightly different below and above T_g .

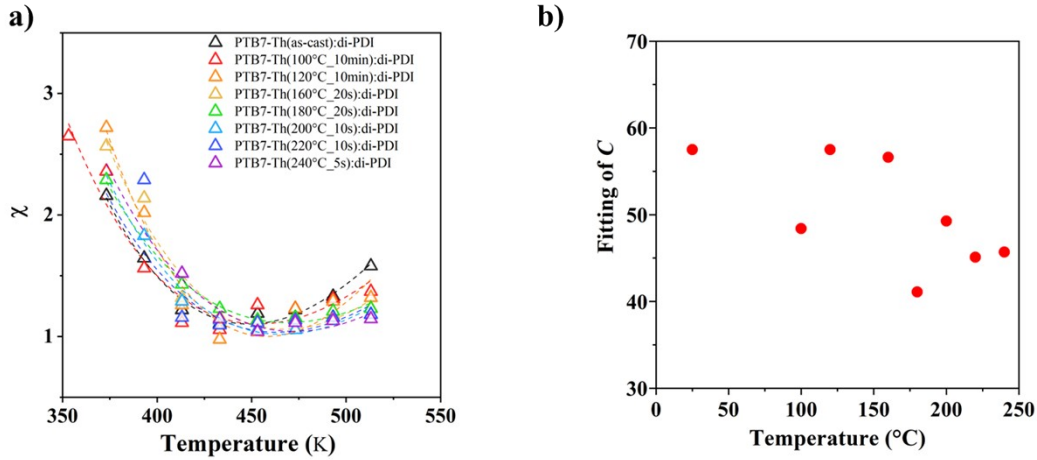


Figure S6. a) χ -T phase diagram for PTB7-Th:di-PDI with PTB7-Th thin film pre-annealed at different temperatures. The dashed lines represent the fitting with $\chi = A + \frac{B}{T} + C \ln T$. b) C from the fitting as a function of pre-annealing temperature.

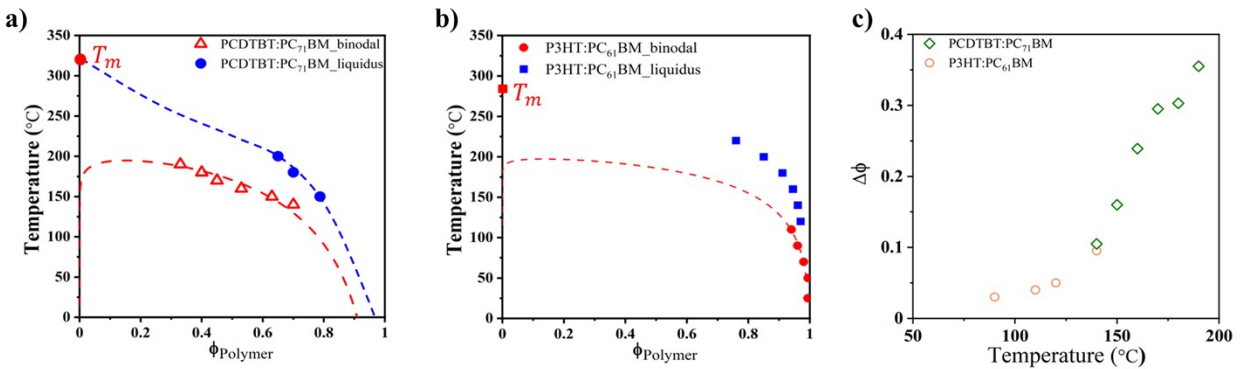


Figure S7. a) $T - \phi$ phase diagram with binodal and liquidus for PCDTBT:PC₇₁BM. The red dot represents the melting temperature T_m of PC₇₁BM from DSC. The binodal is reproduced from ref.¹ Copyright 2018 Springer Nature. The liquidus is reproduced from ref.² Copyright 2018 John Wiley and Sons. b) $T - \phi$ phase diagram with binodal (from ToF-SIMS) and liquidus (from UV-vis method) for P3HT:PC₆₁BM. The red square represents the melting temperature T_m of PC₆₁BM from DSC. The binodal is reproduced from ref.³ Copyright 2013 American Chemical Society. The liquidus is reproduced from ref.² Copyright 2018 John Wiley and Sons. c) $-\Delta\phi$ vs. T plot with some data points extrapolated from the trend denoted with dashed lines.

References

1. L. Ye, H. W. Hu, M. Ghasemi, T. H. Wang, B. A. Collins, J. H. Kim, K. Jiang, J. H. Carpenter, H. Li, Z. K. Li, T. McAfee, J. B. Zhao, X. K. Chen, J. L. Y. Lai, T. X. Ma, J. L. Bredas, H. Yan and H. Ade, *Nat. Mater.*, 2018, **17**, 253-260.

2. L. Ye, B. A. Collins, X. C. Jiao, J. B. Zhao, H. Yan and H. Ade, *Adv. Energy Mater.*, 2018, **8**, 1703058.
3. N. D. Treat, T. E. Mates, C. J. Hawker, E. J. Kramer and M. L. Chabinyc, *Macromolecules*, 2013, **46**, 1002-1007.