

Supplemental

NEXAFS measurements were performed to confirm complete penetration of the fullerenes through the polymer layer during swelling. Unless otherwise noted, the films for NEXAFS were fabricated in a scheme wherein a fullerene film was mechanically laminated to the top of the polymer, the film was heated, and then the bilayer film was delaminated to expose the polymer bottom interface. Because NEXAFS data were collected on films with slightly different preparation conditions than those used in the main manuscript, we present them here only for reference and qualitative comparison. The agreement of NEXAFS with the VASE data, however, is fairly striking, with VASE trends in temperature and solubility being reproduced in the surface compositions measured by NEXAFS.

Figure S1 shows carbon K-edge NEXAFS spectra of reference P3HT and PCBM films. The greatest differences in the spectra are in the π^* manifold. The polymer typically exhibits a single peak (~ 285 eV), whereas the fullerene exhibits a split π^* with a lower-energy (~ 284 eV) and higher-energy (286 eV) peak. Differences in the π^* region are sufficient to follow trends with temperature qualitatively for the the bilayers we present here.

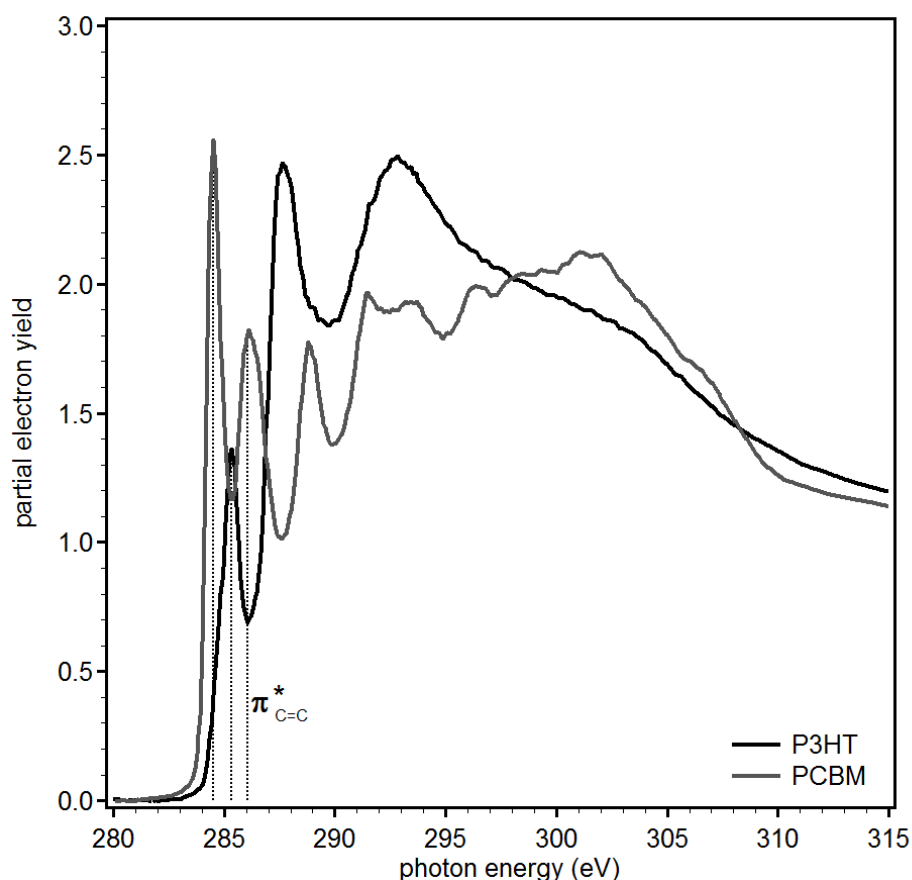


Figure S1. NEXAFS spectra of reference polymer (P3HT) and fullerene (PCBM) films.

Figure S2 shows NEXAFS spectra of delaminated P3HT / PC-61BM bilayers. At lower temperatures, the spectra resemble the polymer, whereas at higher temperatures, the spectra more closely resemble the

fullerene. The data support the conclusion that mixing begins at sub-90C, and that the fullerene can be observed at the top surface of the polymer at relatively mild temperatures.

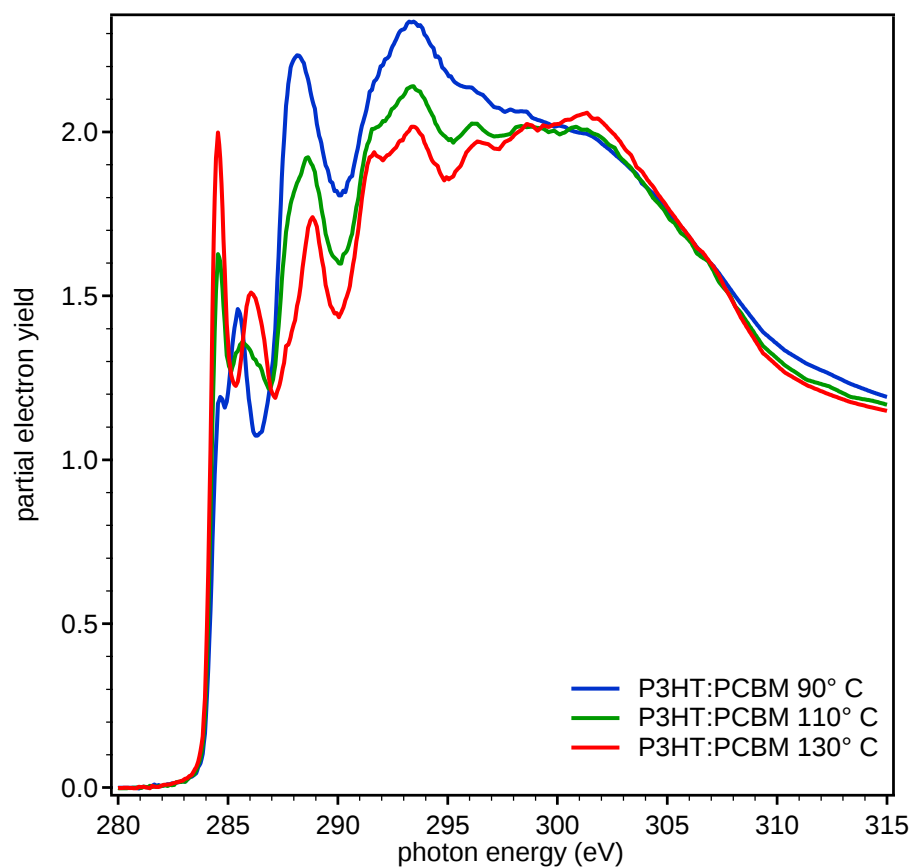


Figure S2. NEXAFS spectra showing increased presence of fullerene with increasing temperature of mixing.

Figure S3 shows the NEXAFS data of the P3HT film swelled with bis-PCBM. Note the lower overall presence of the fullerene on the polymer top surface, consistent with the findings from VASE that this fullerene exhibits less mixing in the bulk of the film.

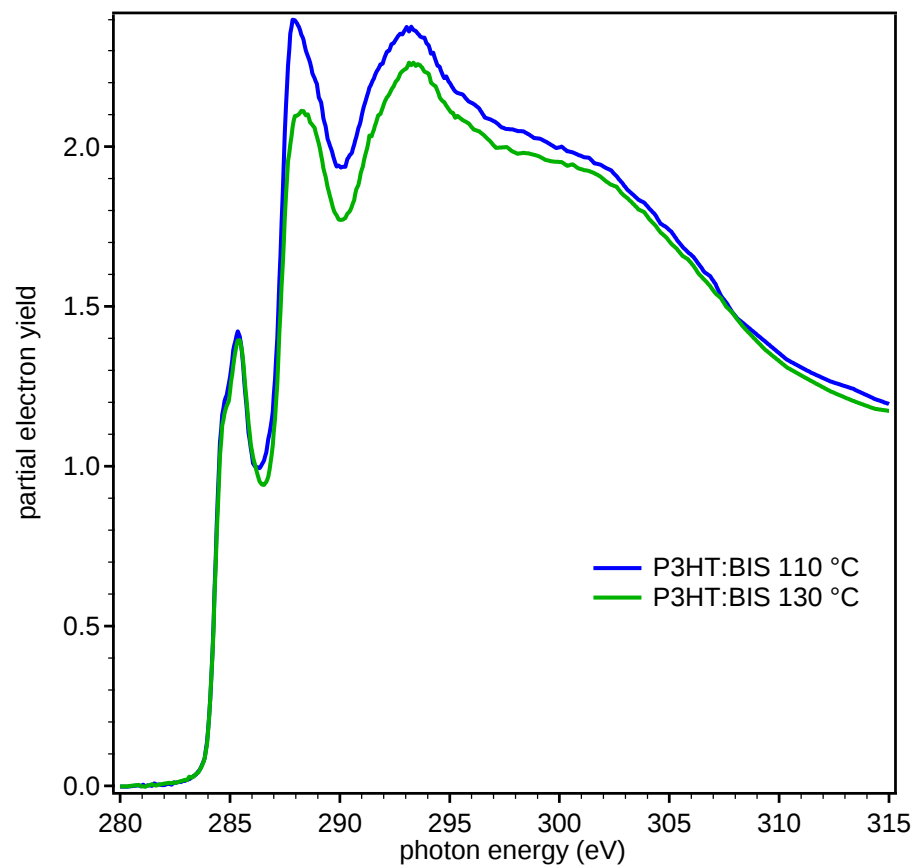


Figure S3. NEXAFS spectra showing limited mixing with bis-PC-61BM upon heating.

Figure S4 shows the mixing of PCDTBT with bis-PCBM. A marked increase in fullerene appearance is noted in the transition from 130°C to 140°C. A monotonic trend with temperature is observed. The amount of fullerene presence saturates at ~150°C. These data are also consistent with the trends provided by VASE.

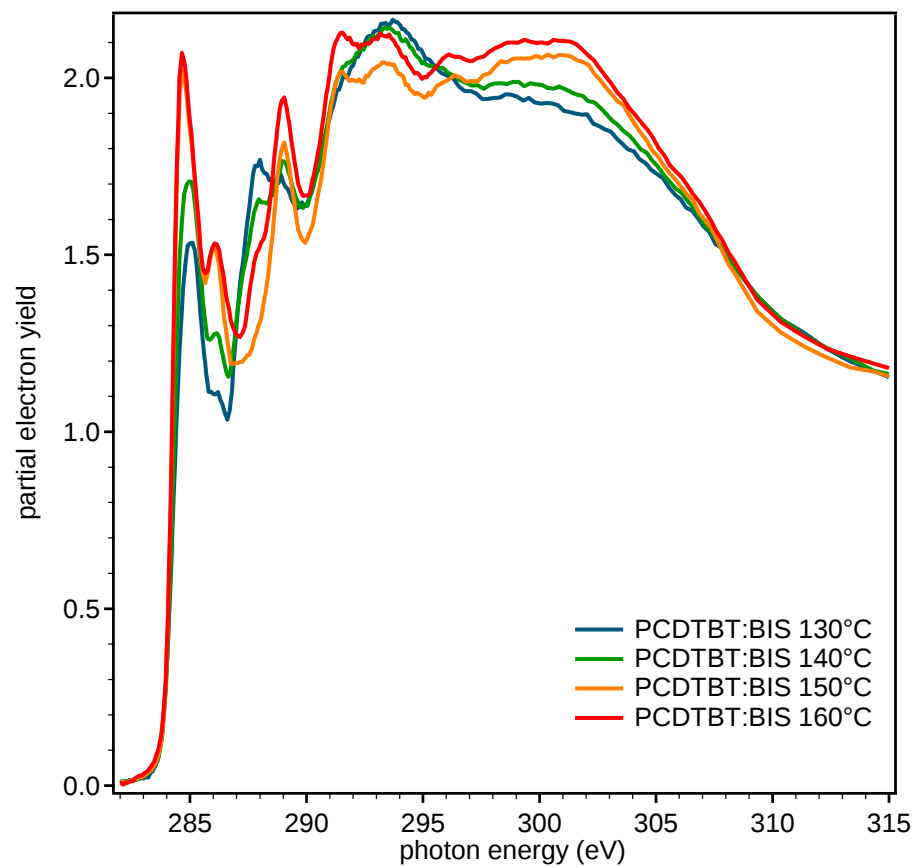
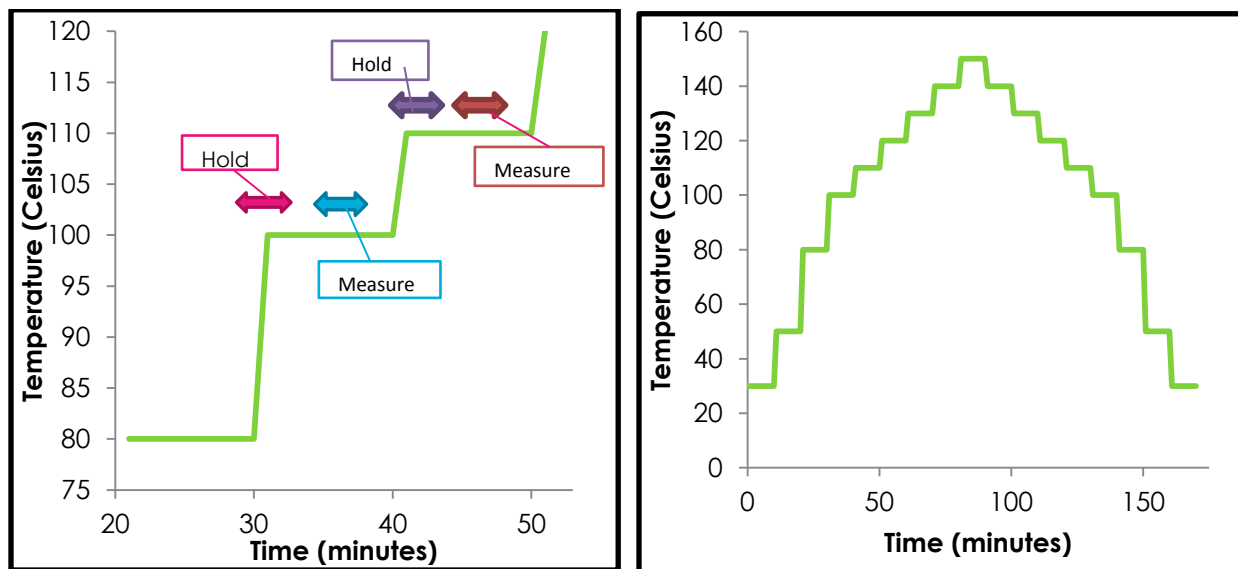


Figure S4. NEXAFS spectra showing substantial mixing of PCDTBT with bis-PC-61BM upon heating.

All spectroscopic ellipsometry was performed with a JA Woollam M2000-XI instrument installed in a N₂ purged glove box. The ellipsometer was equipped with a multi-sample hot plate enabling operation between room temperature and ≈ 200 °C. The system was fully automated, allowing ramp and soak operation of the hot plate and independent alignment (tip, tilt, height) and multi-angle data acquisition on multiple substrates. The ellipsometer has a ≈ 150 μm focused spot and covers the wavelength range of (210 to 1670) nm. All data analysis was performed on multi-angle sets acquired at (50, 60, and 70)° angle-of-incidence.

The temperature dependence of the dielectric functions of all pure materials were acquired following identical thermal schedules to that used in the bilayer stability studies. For the fullerenes, in general, only one film was measured, deposited on a Si wafer with a native oxide. A simple 4 phase (air, fullerene, oxide, Silicon) model was used. The optical properties of the Si and native oxide were taken from the vendor supplied database. The thickness of the native oxide was determined from clean reference substrates. Both the thickness and dielectric properties of the fullerene were fit. The optical properties of the fullerene were modeled with a flexible, Kramers-Kronig consistent “B-spline” with 0.1 eV node spacing. The film absorption was assumed to be 0 below 1.2 eV. For the polymers, a multi-sample analysis was performed on two duplicate layers deposited on a native oxide and a nominally 200 nm thick thermal oxide. This allowed robust determination of both the in-plane and out-of-plane dielectric functions of a uniaxial model for the polymer layer.



Schematic S-1

Shown in Figure S-5 are the thicknesses of the fullerene films as a function of temperature. All films exhibit a significant drop in thickness at ≈ 75 C upon heating, attributed to densification following evaporation of residual chloroform solvent. Upon cooling, simple monotonic thermal expansion is observed. A significant change in the thermal expansion at T_g is not observed for either ICBA or bisPCBM-61.

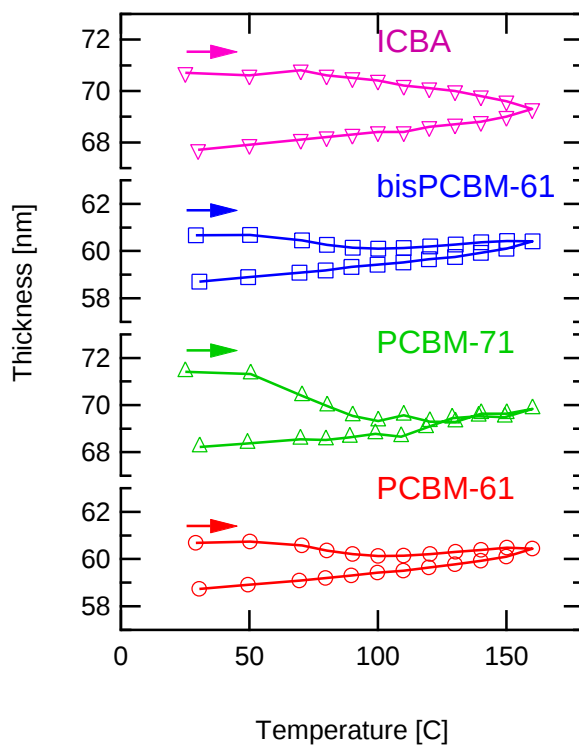


Figure S-5.

Shown in Figure S-6 are the real and imaginary parts of the fullerene dielectric constant, $\epsilon = \epsilon_0\epsilon_r = \epsilon_0(\epsilon_1 + i\epsilon_2)$, for the as cast film at RT, the film at 160 °C, and the annealed film upon cooling back to room temperature. In general, the fullerene films exhibit very little thermochromism. The annealed films exhibit a slighter higher dielectric constant, consistent with densification following removal of trapped solvent. There is no evidence for film degradation during the temperature series.

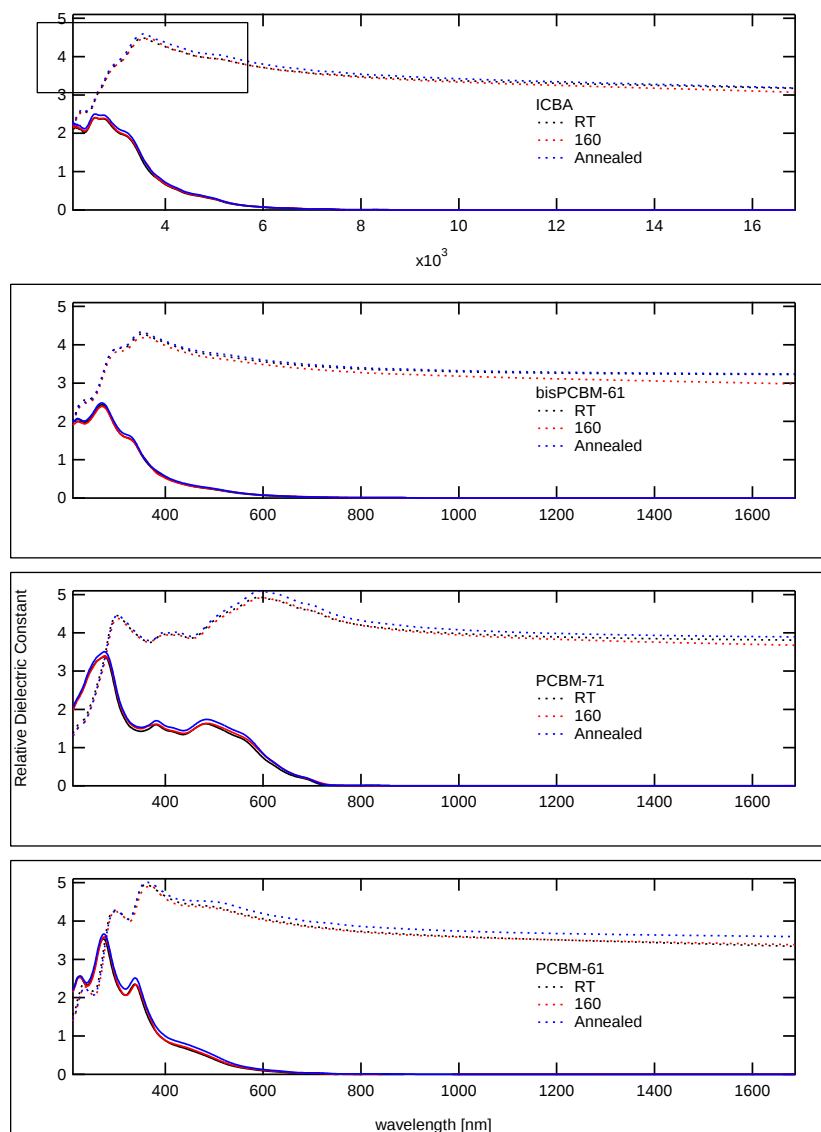


Figure S-6

Shown in Figure S-7 are the film thicknesses for the neat polymer references. Neither polymer exhibits a significant feature associated with solvent release. The P3HT films nominally display simple thermal expansion, consistent with the low ($\approx 9^\circ\text{C}$) T_g and high ($\approx 240^\circ\text{C}$) T_m . The PCDTBT films exhibit a distinct expansion at $\approx 120^\circ\text{C}$, consistent with the $\approx 120^\circ\text{C}$ T_g and diffraction reports of a distinct high temperature crystal structure. There is clear hysteresis upon cooling of the films annealed above the glass transition.

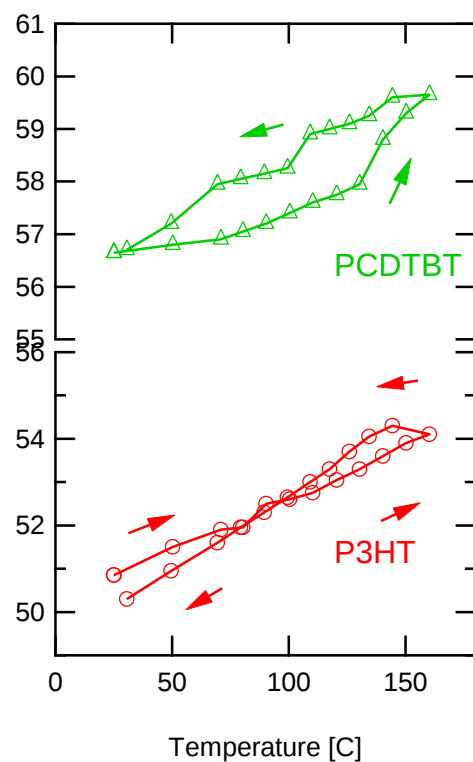


Figure S-7.

Shown in Figure S-8 are the real and imaginary parts of the in-plane and out-of-plane polymer optical constants for the as cast film, the film at 160 °C, and the film upon cooling to room temperature. Consistent with other reports, the P3HT film exhibits considerable thermochromism with a characteristic red shift of the absorption at elevated temperature attributed to increased torsional disorder and loss of conjugation length. The annealed film is slightly more anisotropic (decrease in ϵ_z relative to ϵ_x), consistent with a weak increase in in-plane order. The PCDTBT film exhibits very little thermochromism. The film exhibits a *decrease* in the anisotropy upon exceeding T_g , which persists upon cooling.

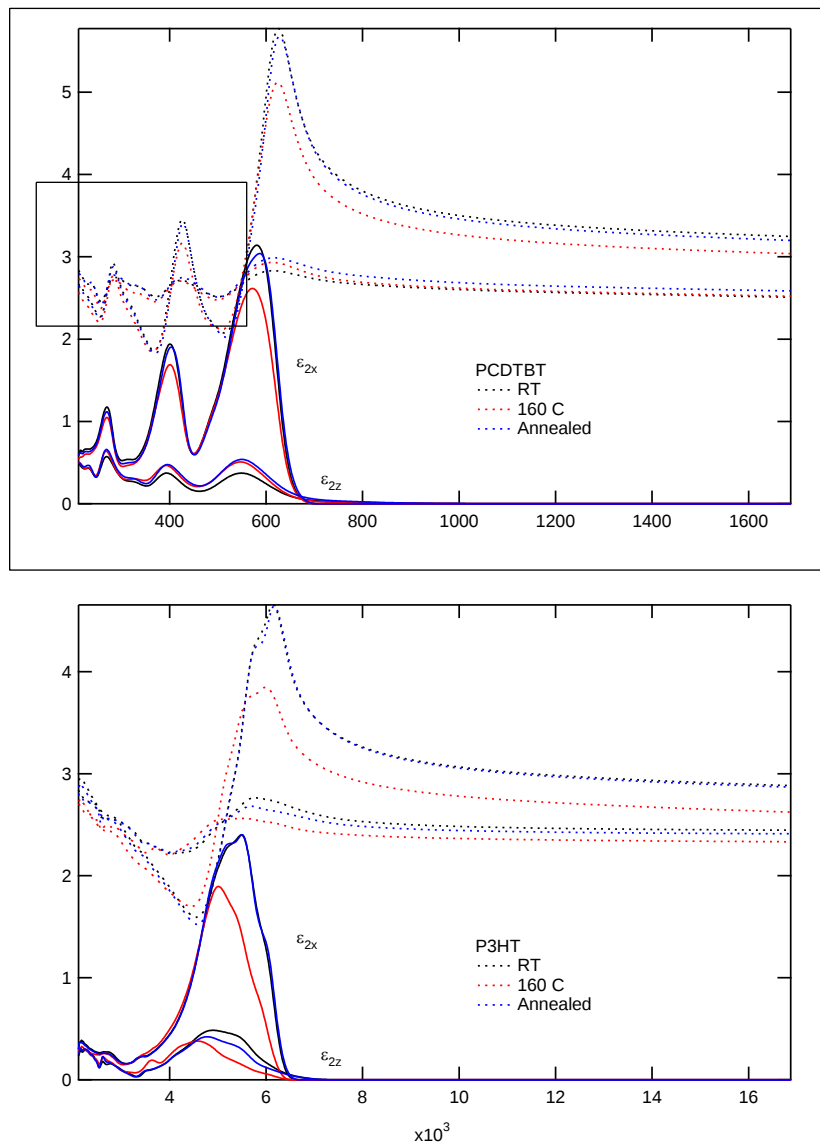


Figure S-8

Shown in Fig. S9 are optical micrographs of bilayers after stepped heating to 160 °C and subsequent stepped cooling. Note the lateral phase segregation due to cold crystallization of the PCBM-61 and the absence of lateral phase segregation for PCBM-71.

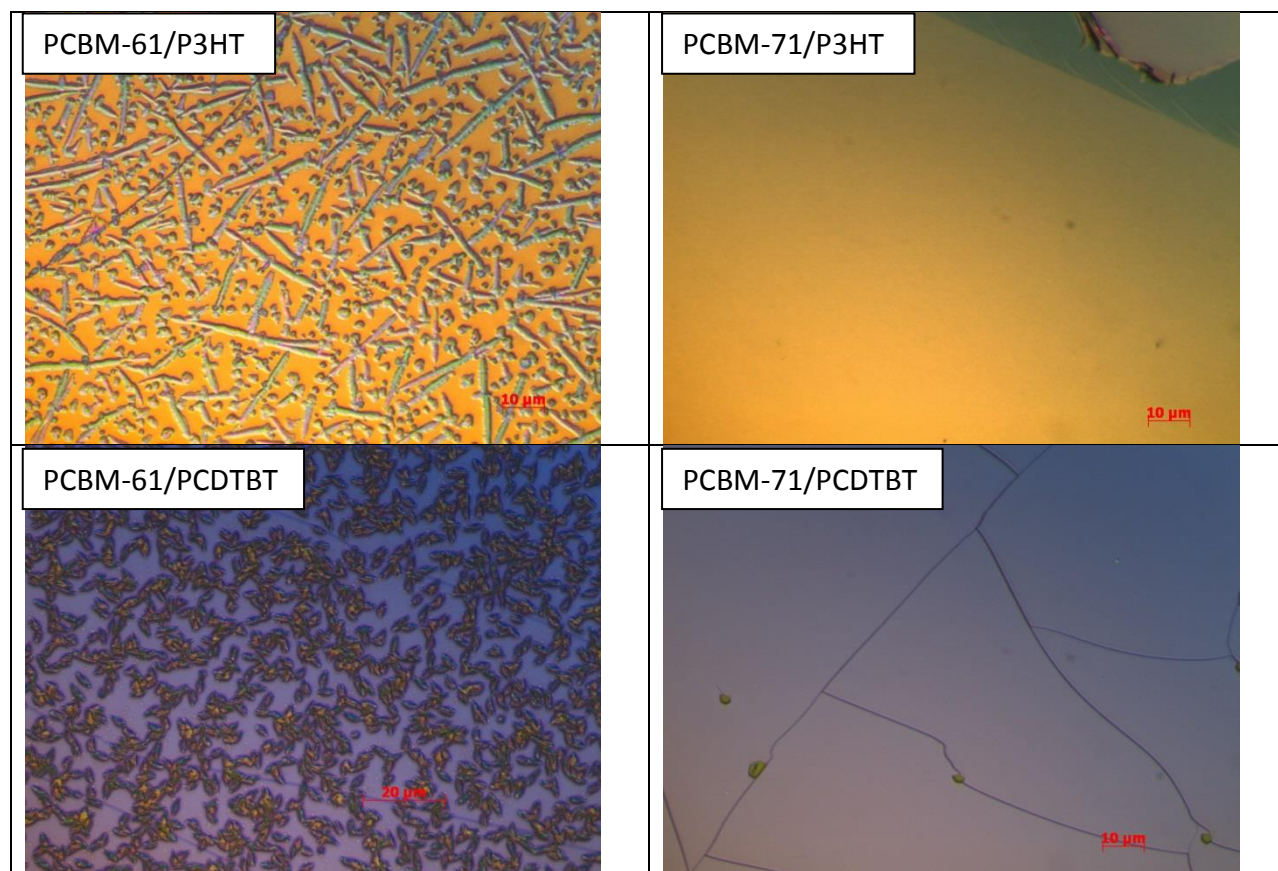


Figure S-9

Shown in Figure S10 are room temperature GIXD measurements for pure fullerene films as-cast and after 10 min anneal at the indicated temperature. Cold crystallization of the PCBM-61 and PCBM-71 is clearly evident, as is the lack of crystallization in the bisPCBM-61 and ICBA.

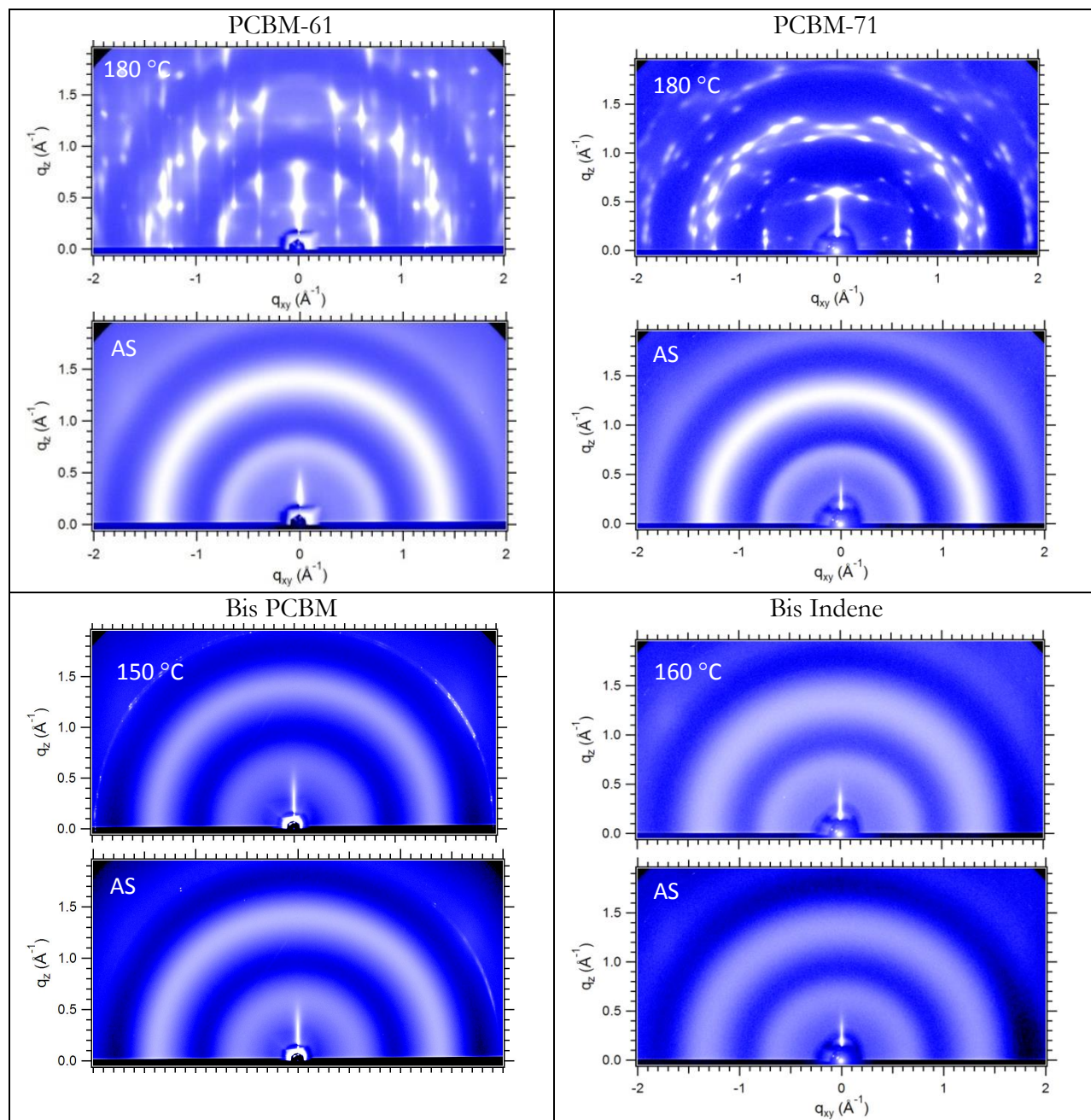


Figure S-10

Shown in Figure S11 are room temperature GIXD measurements for the polymer films as cast and after 10 min anneal at the indicated temperature (150 °C, 200 °C). Also shown are vertical ($q_{xy}=0$) cuts through the diffraction image. The anneal of the P3HT results in slight ripening (increased crystal fraction and grain size) as reported by other²⁸ and a slight increase in the face-on component, indicated by the increase in the (010) intensity at $\approx 1.675 \text{ \AA}^{-1}$. The anneal of the PCDTBT results in a significant increase in the (001) d spacing (decrease in q_z) and the appearance of distinct cross peaks in the diffraction image, as reported earlier.²⁷

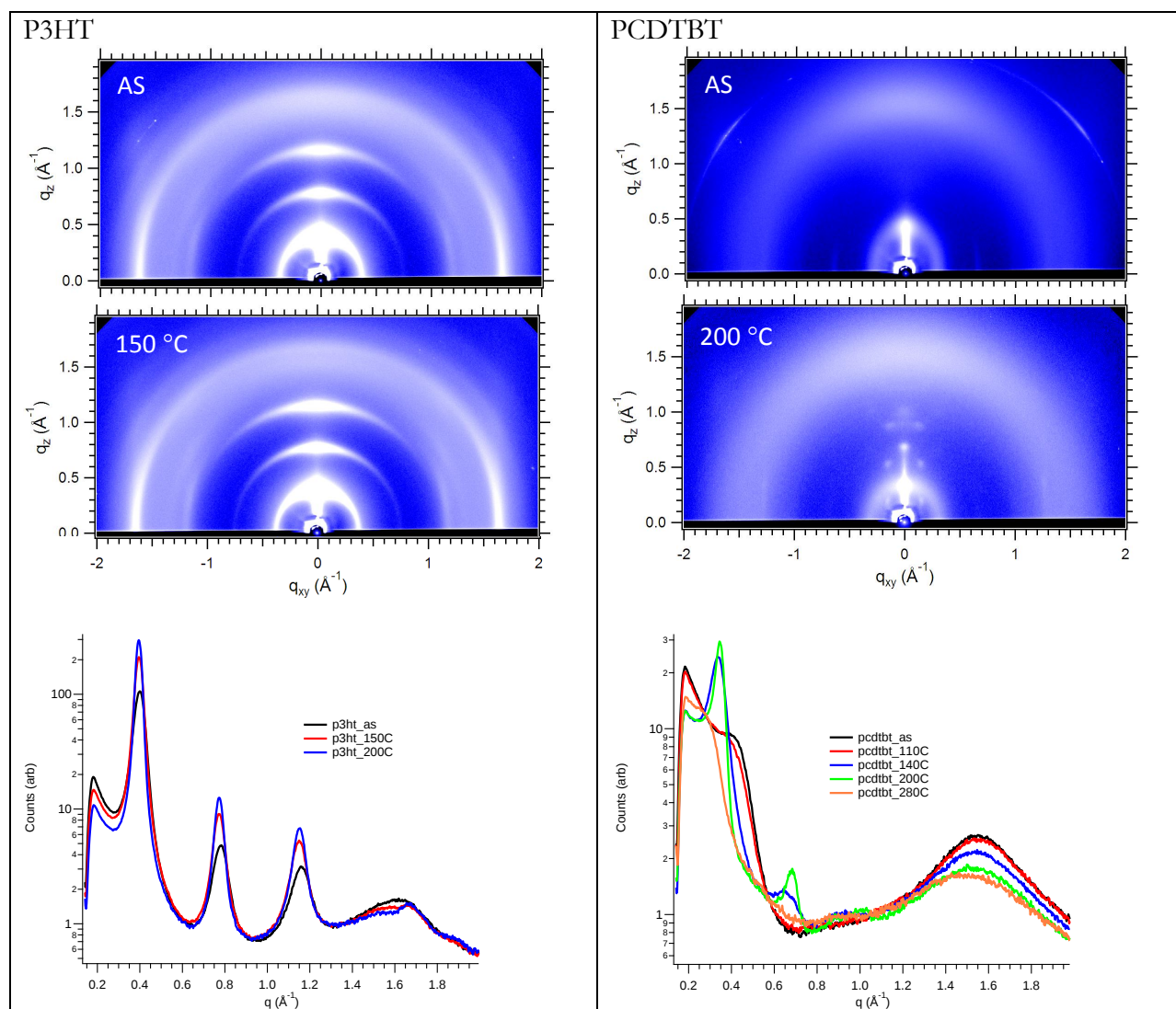


Figure S-11

Shown in Figure S12 are room temperature GIXD measurements for the P3HT bilayer films after 10 min anneal at the indicated temperature. Cold crystallization of the PCBM-61 is clearly apparent. For PCBM-71, ICBA and bis-PCBM there is no evidence for cold crystallization, and no evidence for significant perturbation of the P3HT crystalline region by the fullerene.

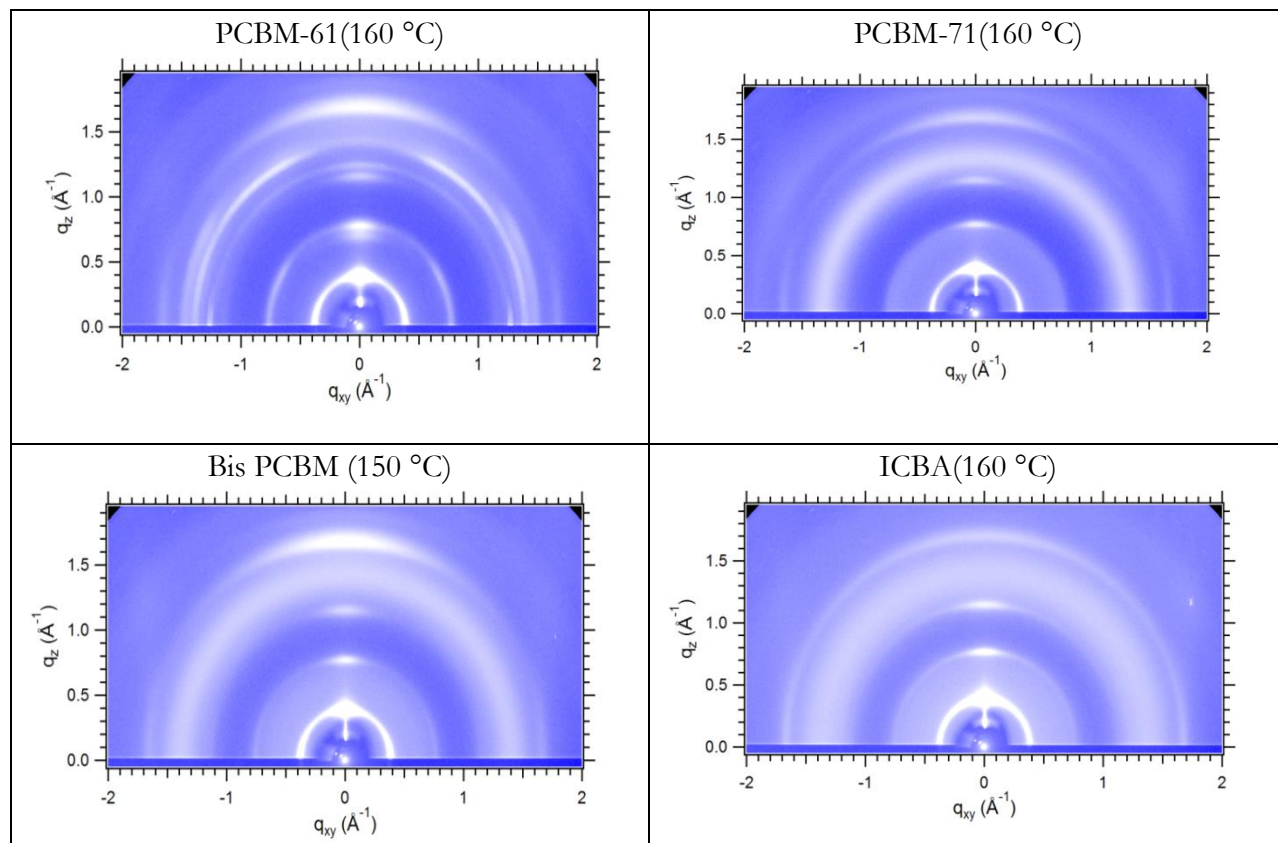


Figure S-12

Shown in Figure S13 are room temperature GIXD measurements for the PCDTBT bilayer films after 10 min at the indicated temperature. Notice the suppression of cold crystallization of the PCBM-61 by the PCDTBT. Also note that the presence of the fullerene inhibits the development of the high temperature phase of the PCDTBT as evidenced by the weak (001) feature and absence of (002) and (003) features.

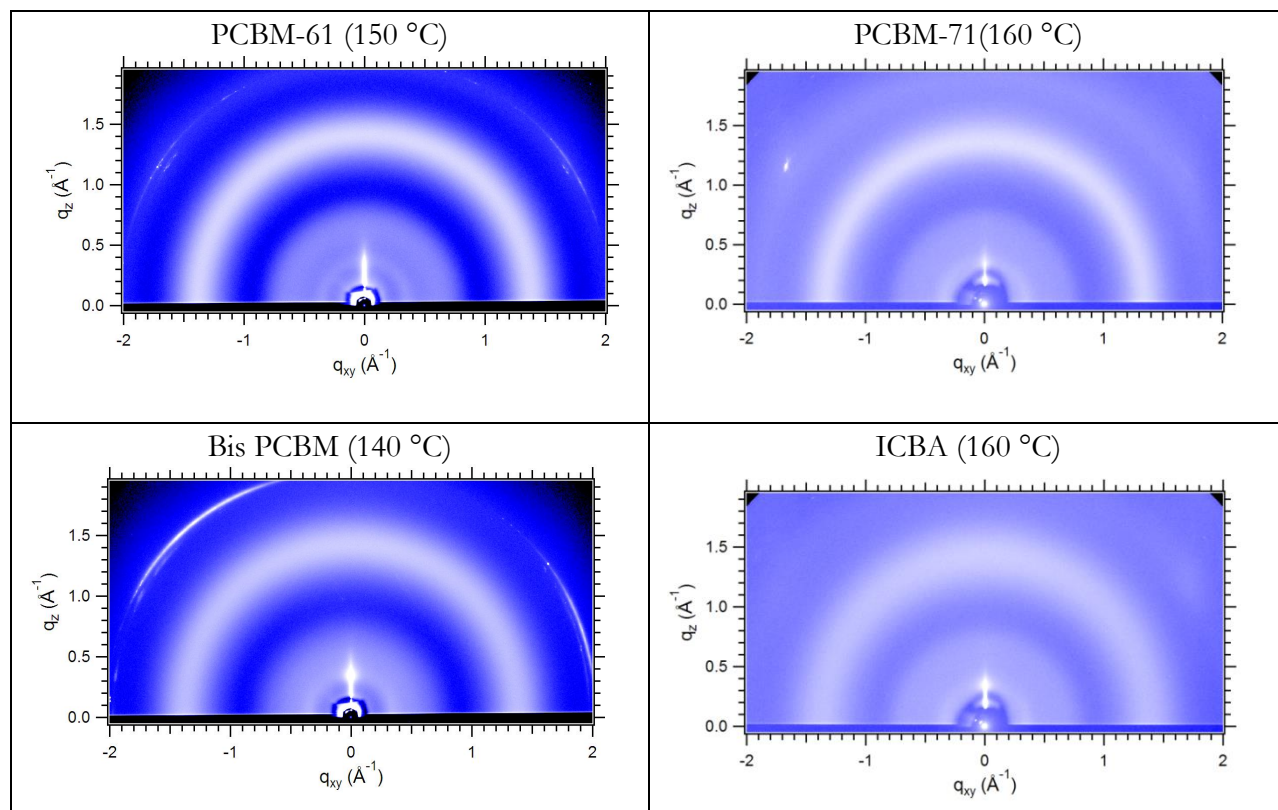


Figure S-13

Table S1 Summary of in-situ ellipsometry swelling studies of EMA volume fraction (in %)

% EMA	PCBM 61			PCBM 71	PCBM 71 (x)	PCBM 61 (x)	bis	Bis indene
P3HT	Amorphous On top	Amorphous On bottom	On PEDOT	Amorphous On top	Annealed On bottom	Annealed On bottom	Amorphous On top	Amorphous On top
110 °C	13.	13.	12.	13.±4.	3.5	2.	4.	9.
120 °C	14.	14.	15.	15.±2.	4.1	3.	5.	10.
130 °C	16.	16.	18.	14.9±0.8	4.7	2.5	6.	11.
Ratio to <61(a)>	--	1.00±0.02	1.01±0.07	1.00±0.12	0.28±0.00	0.17±.02	0.34±0.01	0.68±0.03
PCDTBT								
130 °C	12.	25.	21.	5.±5.	0.	4.	12 ±3	7.
140 °C	27.	39.	32.	19.±5.	5.	8.	27±3	15.
150 °C	42.	52.	42.	28±4.	11.	13.	39.7±0.3	24.
Ratio to 61 top	--	1.57±0.04	1.29±0.10	0.49±0.19	0.14±0.13	0.24±0.05	0.77±0.15	0.45±0.10

Error bars, where shown, are the standard deviation of the mean from multiple runs, or from the average over the 3 temperatures. Estimated precision of the fit parameter (from single runs) is $< \approx 1\%$.

Table S2 Literature Device Performance for P3HT/fullerene solar cells

	Jsc/A cm ⁻²	FF	Voc/V	Efficiency/%
PCBM	10.4	.67	.58	3.8
Bis-PCBM	9.6	.68	.73	4.5
Ratio ^a	.92	1.01	1.25	1.18
PCBM-61	8.46	.66	.64	3.6
PCBM-71	9.31	.63	.65	3.8
Ratio ^b	1.10	0.95	1.01	1.06
PCBM-61	9.91	.644	.59	3.73
ICBA	10.61	.727	.84	6.48
Ratio ^c	1.07	1.13	1.42	1.73

^aLenes, M., Wetzelaer, G., J. A.H., Kooistra, F.B., Veenstra, S.C., Hummelen, K.J., Blom, P.W.M, *Adv. Mater.***2008**, ## 1-4.

^bYamanari, T., Taima, T., Sakai, J., Saito, K., *Jap. J. Appl. Phys.***2008**, 47, 1230-1233 .

^cZhao, G., He, Y., Li, Y., *Adv. Mater.***2010**, 22, 4355-4358.

Table S3 Device Performance for PCDTBT/fullerene solar cells

	Isc/A	FF	Voc/V	Efficiency/%
PCBM-61 (1:4)	2.4±0.4	0.64±0.04	0.895±0.009	3.4±0.4
Bis-PCBM (1:2)	1.1±0.1	0.37±0.02	1.04±0.06	1.1±0.22
Ratio	0.45	0.58	1.16	0.32
PCBM-71(1:3)	3.0±0.1	0.55±0.05	.91±0.02	3.7±0.4
Ratio	1.25	0.86	1.02	1.09
ICBA (1:4)	0.9±0.2	0.33±0.02	1.03±0.09	0.5±0.4
Ratio	0.38	0.52	1.16	0.15

Figure S14 shows electroluminescence spectra of 1:3 polymer fullerene solar cells made with PCDTBT. The driving current was in the range from (10 to 200) mA/cm² and the cell area 4 mm². Raw spectra were recorded using a custom build setup, which included a Princeton Instruments Acton SP2150 Monochromator and PIXIS CCD Detector as well collecting optics. To reduce noise in the recorded wavelength range (500 to 1000) nm the detector temperature was controlled to be −70 °C. Recorded raw spectra were corrected for relative intensity using a black body reference ($T = 3000$ K) and each normalized to their respective maximum. The high performing devices exhibit a CT state emission at ≈ 1.25 eV. For the poor performing BHJs with the bis-adducts, the EL peaks at a significantly higher energy: ≈ 1.4 eV, where the overlapping EL of both PCDTBT and the fullerenes appears, consistent with recombination in the neat materials regions and failure to form a CT state.

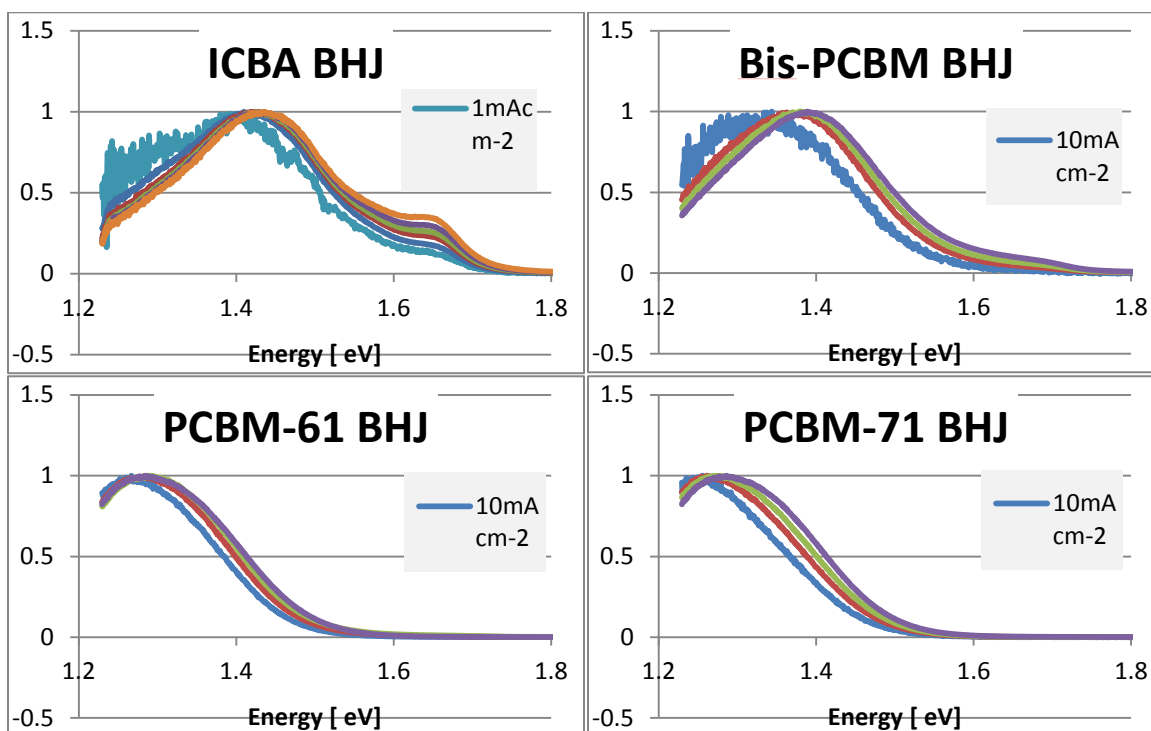


Fig S-14

Estimation of Glass Transition Temperatures of Fullerene Derivatives Studied

Characterization of the glass transition temperature of fullerene derivatives has been difficult because of the extremely weak step in heat capacity ΔC_p at the glass transition of these materials. Additionally, the fact that at least PCBM-61 has been shown to photo-oligomerize[Ref. Li, Z.; Wong, H. C.; Huang, Z.; Zhong, H.; Tan, C. H.; Tsoi, W. C.; Kim, J. S.; Durrant, J. R.; Cabral, J. T. Nat Commun **2013**, 4.] combined with measurements in our laboratory (not shown) that have indicated that repeated cycling into the melt results in a continuously increasing glass transition temperature, and hence a likely thermally induced oligomerization, makes it difficult to cool from sufficiently above T_g to produce a properly defined glass without chemically changing the material. The occurrence of dimerization also indicates that measurements of the glass transition on samples that have been previously melted are suspect.[Ref. (1) Zhao, J.; Swinnen, A.; Van Assche, G.; Manca, J.; Vanderzande, D.; Mele, B. V. J. *Phys. Chem. B* **2009**, 113, 1587–1591.] Thus, it seems that where possible, 1st heats are the best choice for characterizing these materials, unless it can be shown that T_g does not change on thermal cycling.

Several methods can be used to circumvent the problem of weak ΔC_p 's: (1) increasing sample mass, (2) increasing heating rate, (3) precise heat capacity measurements as can be obtained via temperature modulated differential scanning calorimetry (DSC), or (4) mechanical property measurements. Method (1) is limited by the DSC pans used, and the fullerenes are often quite “fluffy”. Herein, samples masses between $\approx$ (4 and 10) mg of the fullerenes were used depending upon how much could be placed in the pans. For method (2) HyperDSC techniques[Ref. V.B.F. Mathot, B. Goderis, R.L. Scherrenberg, E.W. Vegte, *Macromolecules* **2002**, 35, 3601-3613] were employed and most measurements were performed at 200 °C/min. In one case, ICBA, no ΔC_p step at T_g could be detected, so a variation of method (4) was employed. When “fluffy” materials relax at T_g in a DSC pan, a dramatic change occurs in the heat flow as the sample makes more intimate contact with the sample pan and thermal conductivity increases accordingly. This mechanical relaxation was observed in BisPCBM, PCBM-71, and ICBA. Temperature corrections at 200 °C/min were performed using M24 liquid crystal, indium, and lead standards. While this corrects the temperature for heating rate, as the glass transition is a dynamic process, it cannot be considered the same as that measured at typical rates of 10 °C/min corresponding to normal experimental conditions. (A method to approximately correct for this will be employed.) Figure S15 shows the DSC traces for the fullerenes studied in this paper. Curves with arrows up indicate the T_g determined from the typical ΔC_p step, while the curves with arrows down indicate the mechanical relaxation onset temperature T_r .

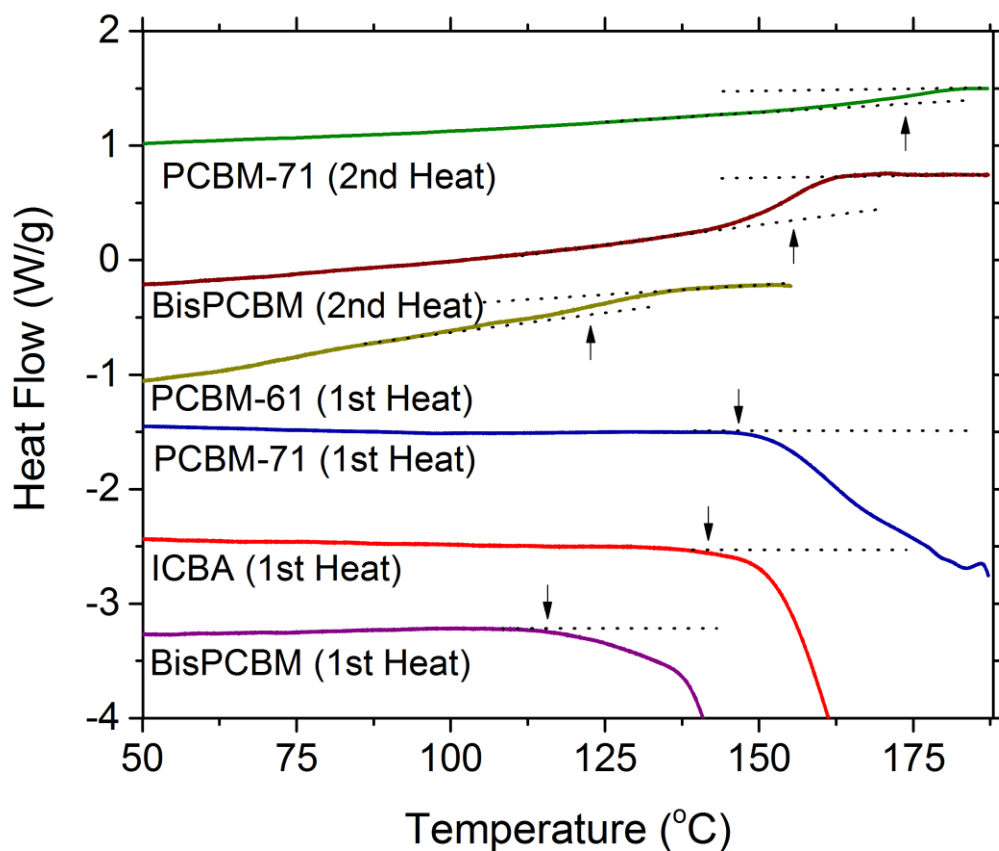


Figure S15. Typical DSC traces indicating glass transition temperatures obtained on heating at 200 °C/min. Endotherm direction is up. Curves have been temperature corrected to take into account thermal lag. Curves have been slope corrected and shifted vertically for improved clarity. Arrows pointing up correspond to approximate locations of the location of T_g as estimated by the midpoint of the extrapolated melt and glasses heat capacities. In all cases the dotted lines show the approximate tangents used for all computations. The arrows pointing down indicate transitions that have been attributed to thermomechanical relaxations occurring near the glass transition that cause a dramatic change in contact with the DSC pan. (Table S-4 summarizes the values obtained from the DSC measurements.)

Before proceeding with the glass transition analysis, it seems appropriate to provide a brief explanation for the weak ΔC_p step at T_g for these materials. Wunderlich demonstrated that [Ref. B. Wunderlich, J. Phys. Chem., 1960, 64 (8), pp 1052–1056] every “mobile bead” typically contributes ≈ 11 J/mol to the step in heat capacity. As it is unlikely that the fullerene cage itself would contribute to T_g , a prediction for the step in heat capacity could be made from the methyl ester alone. For PCBM-61, the phenyl group would contribute approximately 2 mobile beads [ref B. Wunderlich, *Thermal Analysis of Polymeric Materials*, Springer, New York, 2005.], the remainder of the chain, excluding the bridging carbon, would contribute an additional 6 mobile beads. Thus, there are

approximately 8 mobile beads at a contribution of ≈ 11 J/mol, for a total of ≈ 88 J/mol of PCBM-61. As a DSC performs measurements based on mass, using the molar mass of PCBM-61 of 910.88 g/mol, the step in heat capacity is expected to be on the order of ≈ 0.1 J/g, which is extremely low and, as will be shown, reasonably close to the measured value. This also would account for the undetected ΔC_p for ICBA, as its pendant groups are rigid ring structures rather than the flexible esters in the other fullerene derivatives.

Table S4 Experimental and estimated values for T_g and ΔC_p at varying heating rates.

Fullerene	Heating Rate (°C/min)	T_g (°C)	ΔC_p (J/g)	T_r (°C)	Estimated T_g at 10 °C/min
PCBM-61	200	126	0.05	n/a	117
bis-PCBM	10	145	0.13	n/a	145 ^a
bis-PCBM	50	149	0.13	n/a	
bis-PCBM	200	155	0.13	120	
ICBA	200	n/a	n/a	145	164 ^a
PCBM-71	200	174	0.05	150	163

^a The value for bis-PCBM was the measured value.

^b The value for ICBA was determined from T_r as described in the text.

The bis-PCBM had a large enough ΔC_p that it could be used to compute an apparent activation energy Δh^* using the model of Moynihan and coworkers relating the heating rate q , measured glass transition temperature T_g and activation energy by [C.T. Moynihan, A.J. Easteal, J. Wilder and J. Tucker, *J. Phys. Chem.* **78** (26), 2673-2677 (1974).]

$$\frac{d \ln(q)}{d(1/T_g)} \approx \frac{-\Delta h^*}{R}.$$

Bis-PCBM's T_g was reproducible under repeated heating and cooling cycles, so a proper thermal history could be employed, i.e., the samples were cooled from above the glass transition temperature at the same rate as the subsequent measured heating trace; thus, the assumptions of the Moynihan et al. theory were satisfied. The activation energy so determined was ≈ 51 J/mol. In Table S4, estimates were made using this activation energy and the measured T_g s at 200 °C/min for PCBM-61 and PCBM-71 of T_g at a heating rate of 10 °C/min. The T_g for bis-PCBM was measurable at 10 °C/min and so that value is provided. The values of T_r were similarly corrected to 10 °C/min using the above equation and the activation energy for bis-PCBM. The difference between the values of T_r obtained for bis-PCBM and PCBM-71 and the estimated values for T_g was averaged and used as the final correction factor in estimating the T_g of ICBA at 10 °C/min. It should be noted that the corrections to T_g are only ≈ 11 °C and the trend is unchanged from the measurements at 200 °C/min.