Submitted to

Manuscript type: Full paper

Morphology analysis of the near IR sensitized polymer / fullerene organic solar cells by implementing low bandgap polymer analogous of C-/Si-PCPDTBT

By

Tayebeh Ameri[1,*], Parisa Khoram[1], Thomas Heumüller[1], Derya Baran[1], Florian Machui[1], Anna Troeger[3], Vito Sgobba[3], Dirk M. Guldi[3], Marcus Halik[4], Silke Rathgeber[5], Ullrich Scherf[6], and Christoph J. Brabec[1,2]

[1] Institute of Materials for Electronics and Energy Technology (I-MEET), Department of Materials Science and Engineering, Friedrich-Alexander University Erlangen-Nuremberg, Martensstrasse 7, 91058 Erlangen, Germany

[2] Bavarian Center for Applied Energy Research (ZAE Bayern), Haberstr. 2a, 91058 Erlangen, Germany

[3] Department of Chemistry and Pharmacy & Interdisciplinary, Center for Molecular Materials, Friedrich-Alexander University Erlangen-Nuremberg, Egerlandstrasse 3, 91058 Erlangen, Germany

[4] Organic Materials and Devices (OMD), Institute of Polymer Materials, Friedrich-Alexander-University of Erlangen-Nuremberg, Martensstraße 7, 91058 Erlangen, Germany

[5] Institute for Natural Sciences, Physics Department, University of Koblenz-Landau, Universitätsstraße 1, 56070 Koblenz, Germany

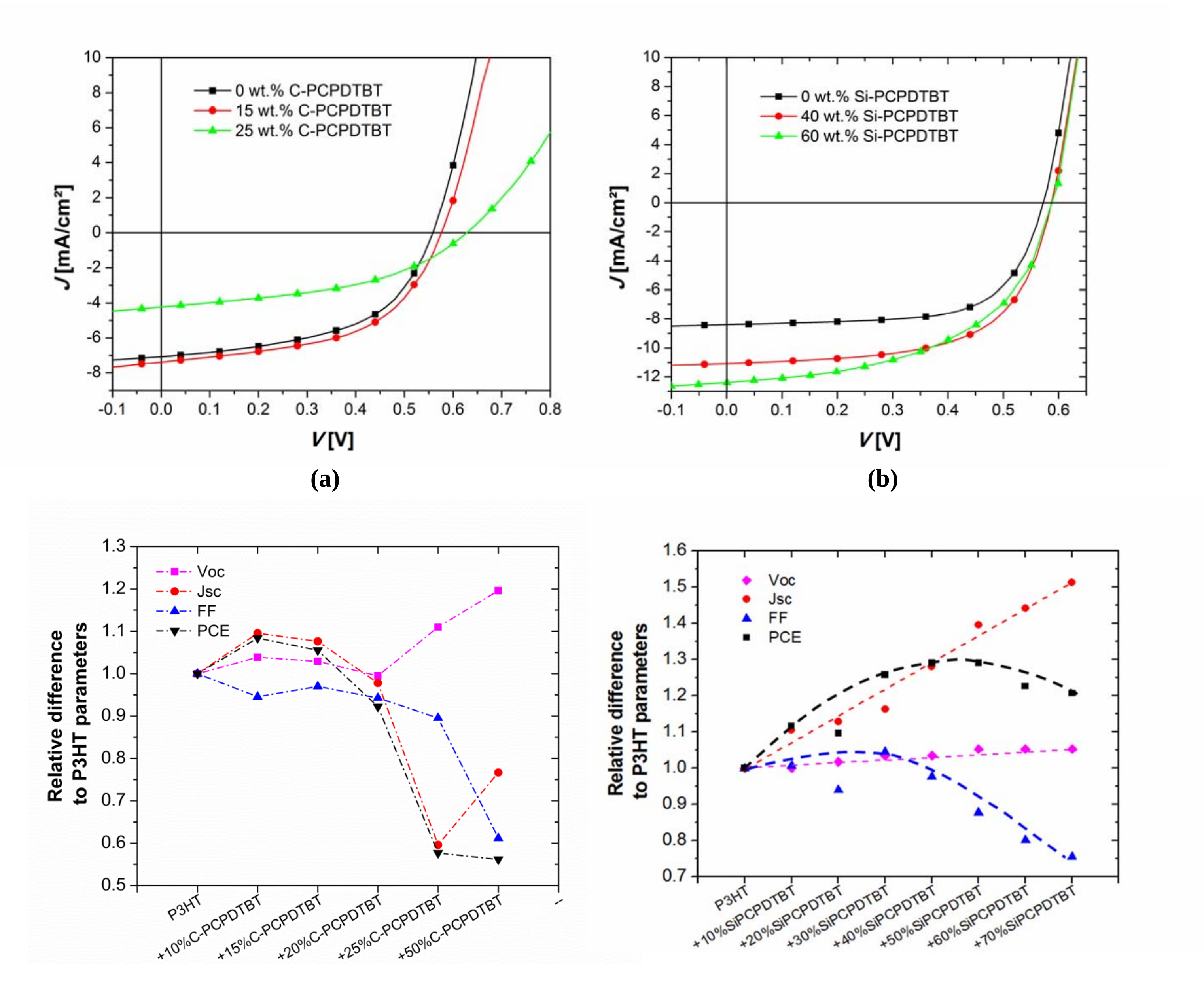
[6] FB C - Mathematik & Naturwissenschaften Fachgebiet Makromolekulare Chemie & Institut für Polymertechnologie, Bergische Universität Wuppertal, Gaußstraße 20, 42097 Wuppertal, Germany

[*] E-mail: tayebeh.ameri@fau.de

Keywords: IR sensitization; Organic solar cells; Small bandgap polymers; Ternary blends; Morphology.

Supplementary Information

1. Device performance of P3HT:C- / Si-PCPDTBT:PCBM ternary solar cells



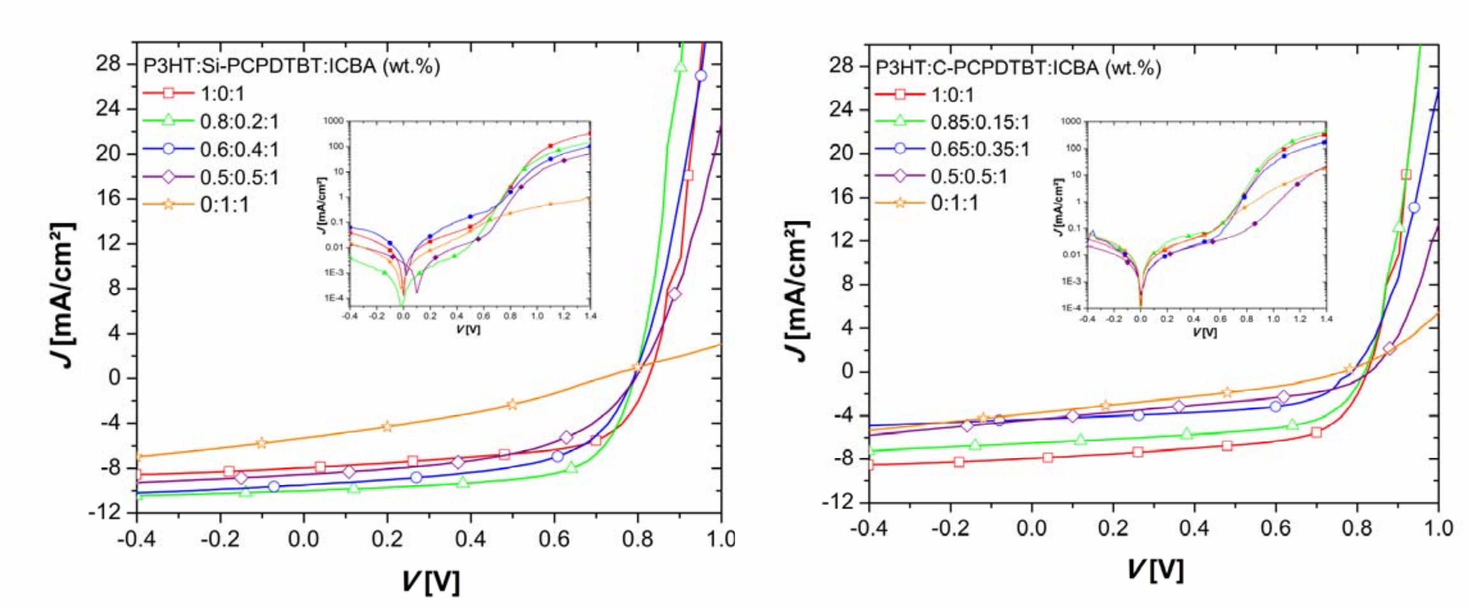
(a) (b)

(c) (d)

Figure S1. J-V characteristics of P3HT:C-PCPDTBT:PCBM (a), and P3HT:Si-PCPDTBT:PCBM (b) ternary solar cells with different concentrations of sensitizers under AM1.5G, 100 mW/cm² illumination; relative changes of the device parameters with increasing C-PCPDTBT (c) or Si-PCPDTBT (d) content. The performance of binary P3HT:PCBM is chosen as reference and set to 100 %. All other device data are normalized to that reference. These results are explained in details in Ref. [1-3].

2. Device performance of P3HT: C- / Si-PCPDTBT:ICBA ternary solar cells

Parallel resistances (R_p) under dark conditions do not show any trend for different devices but all have enough high R_p to prevent losses in the fill factor (FF). Series resistances (R_s) present a clear trend versus the Si-PCPDTBT concentration. Increasing the sensitizer content, results in an increase of the Rs. It can be attributed to the different recombination mechanism of ternary devices. The TPV measurement revealed a recombination order of higher than two for the ternary blends including high concentration of Si-PCPDTBT, which indicates that the recombination mechanism is not ideally bimolecular. Such higher orders, as they are observed in our experiments, are attributed to the effect of trapping and release in energetic traps, as well as trapping due to morphological traps.[2] According to simulations of Deibel et al.,[3] increased energetic disorder in a system with recombination between free and trapped charge carriers can decrease FF and also result in a significantly reduced injection (or seemingly increased R_s).



(a) (b)

Figure S2. J-V characteristics of P3HT:Si- / C-PCPDTBT:ICBA devices with different (a) Si-PCPDTBT and (b) C-PCPDTBT sensitizer content under AM1.5G, 100 mW/cm² illumination; inset presents the corresponding dark curves.

For the ternary device with optimized composition, 0:20:100 wt.% P3HT:Si-PCPDTBT:ICBA, under AM1.5G spectra with an intensity of 100 mW/cm², V_{oc} is slightly reduced and J_{sc} is enhanced by app. 20 % over the P3HT:ICBA reference cell. The binary Si-PCPDTBT:ICBA cell suffers a very low FF and injection current.

The FF drop, Jsc losses (Figure S2b) and very small EQE contribution of sensitizer in near IR region (Figure 2d) at low C-PCPDTBT concentrations suggest that P3HT:C-PCPDTBT:ICBA ternary systems suffer from the more critical transport issues and recombination losses even compared to the P3HT:C-PCPDTBT:PCBM ternary systems. This can be related to the less ordered host system of P3HT:ICBA compared to the P3HT:PCBM.

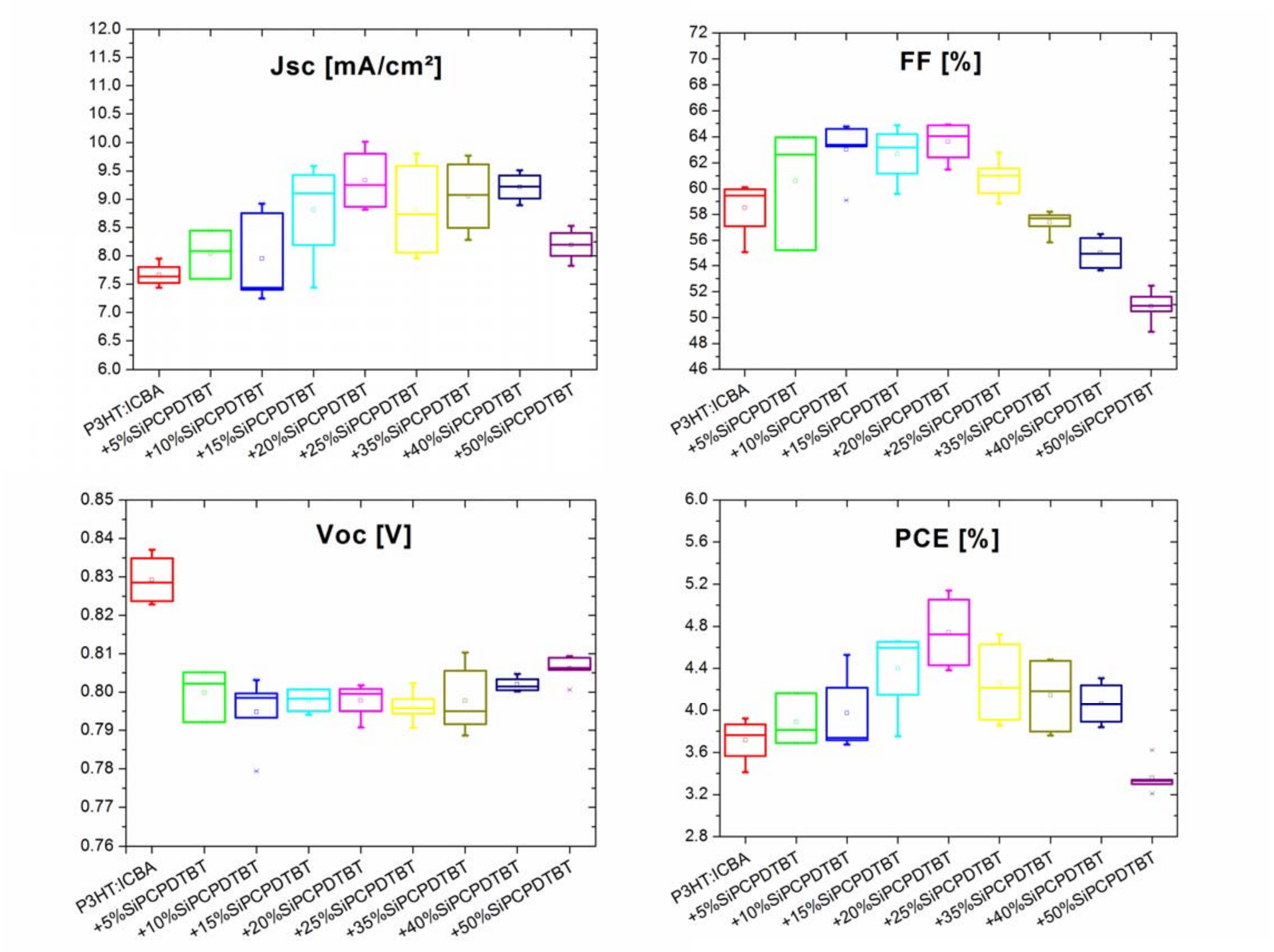


Figure S3. Box chart of the performance key-parameters for the binary and ternary P3HT:Si-PCPDTBT:ICBA devices. Presented data are collected from 18 samples for each concentration, which are fabricated in three different runs.

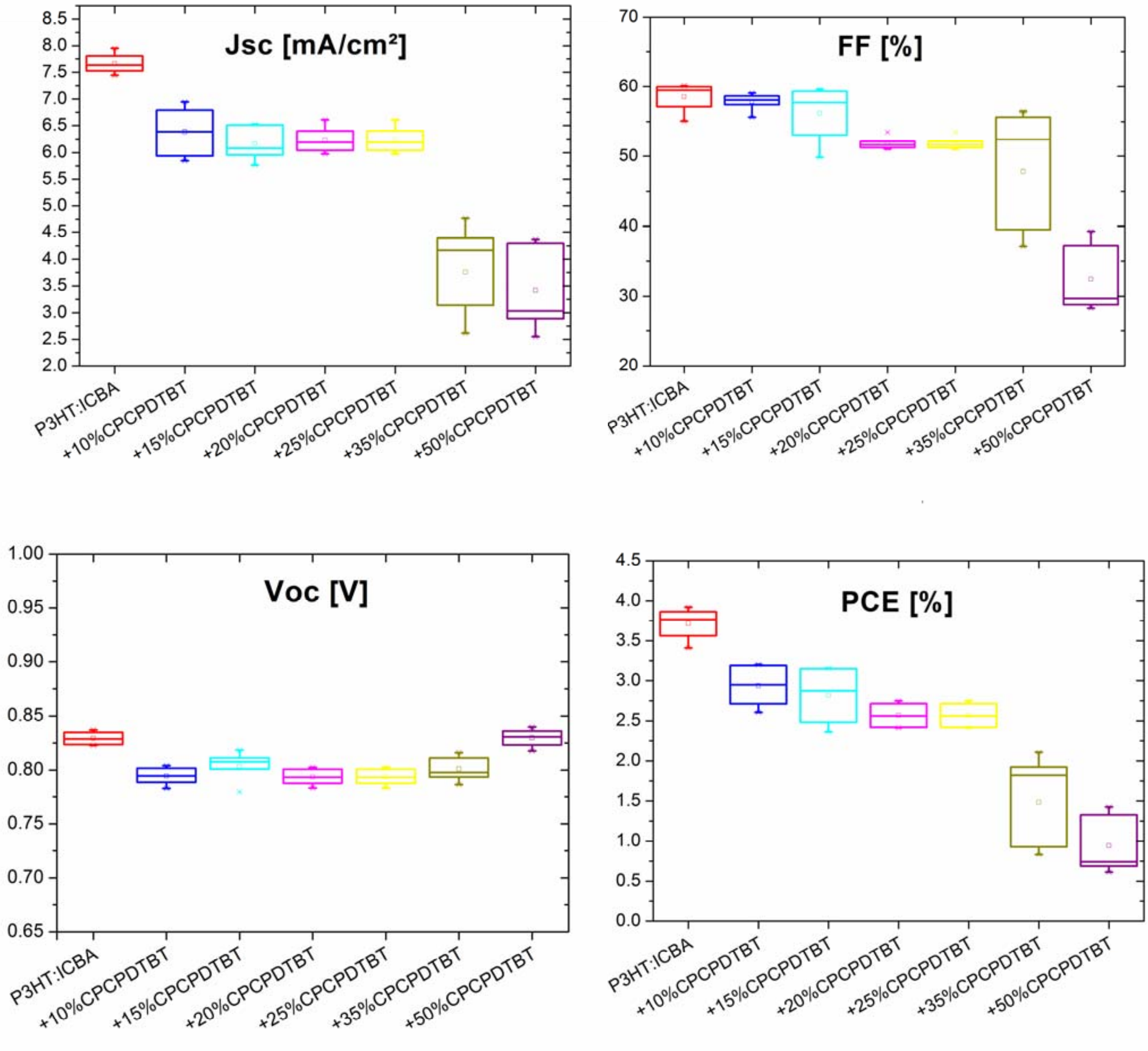


Figure S4. Box chart of the performance key-parameters for the binary and ternary P3HT:C-PCPDTBT:ICBA devices. Presented data are collected from 12 samples for each concentration, which are fabricated in two different runs.

3. UV-Vis spectroscopy of P3HT:C-PCPDTBT:ICBA ternary systems

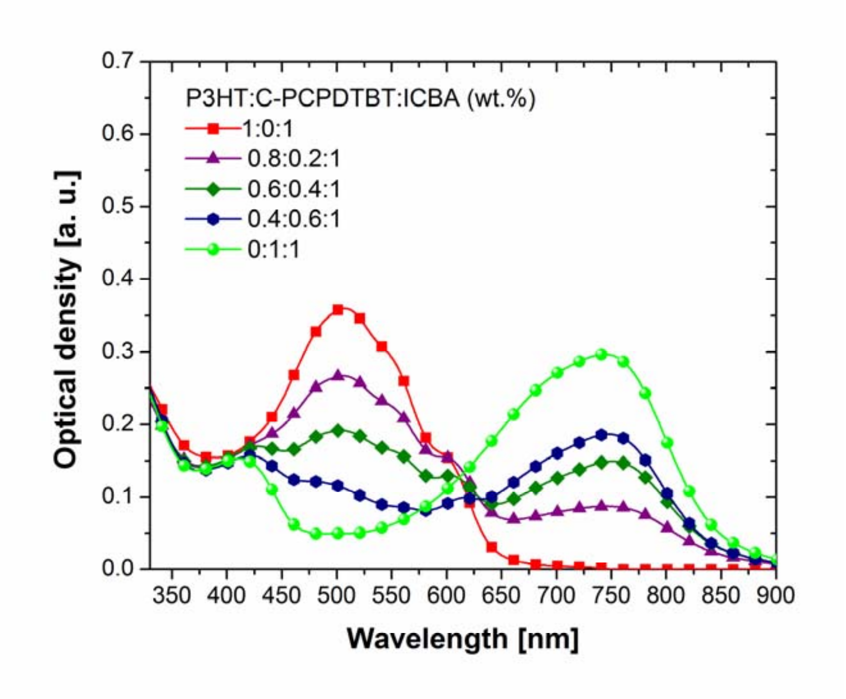
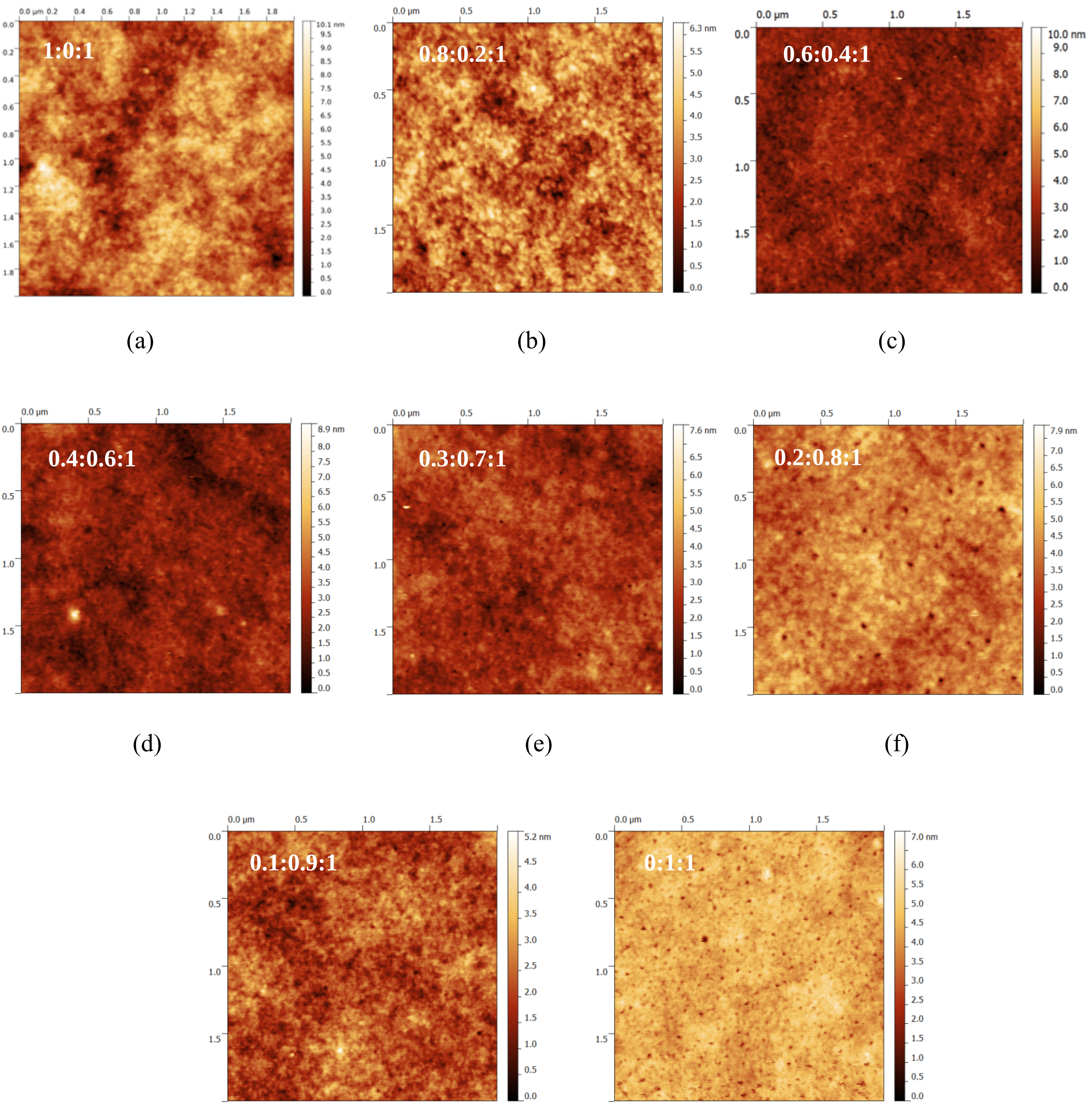


Figure S5. Absorbance spectra of P3HT:C-PCPDTBT:ICBA films with different C-PCPDTBT sensitizer contents**.**

4. Atomic Force Microscopy of P3HT:C-PCPDTBT:ICBA ternary systems



(a) (b) (c)

(d) (e) (f)

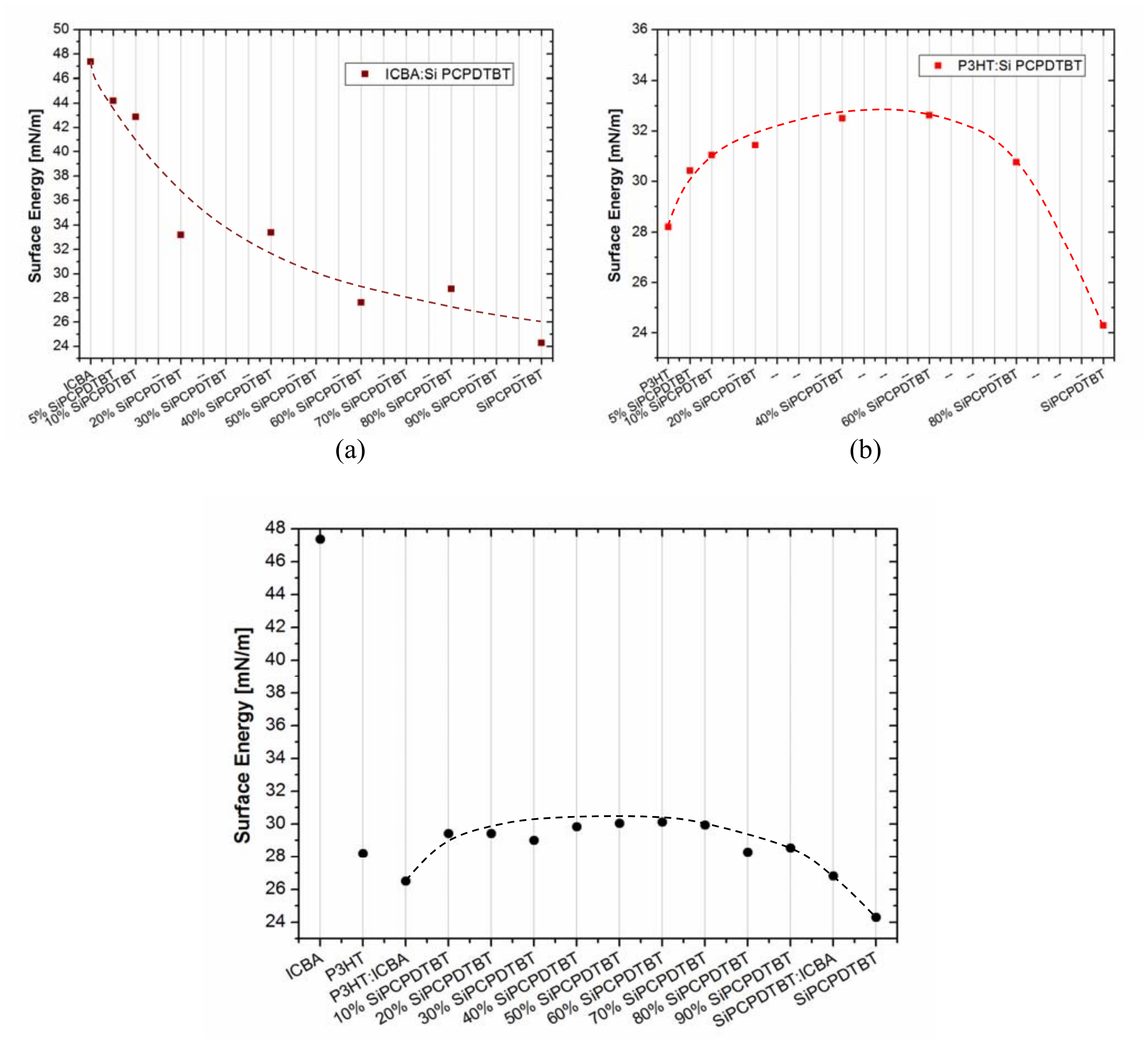
(g) (h)

Figure S6. Non-Contact mode AFM surface scans of 1:1 wt% P3HT:ICBA (a), 0.8:0.2:1 (b), 0.6:0.4:1 (c), 0.4:0.6:1 (d), 0.3:0.7:1 (e), 0.2:0.8:1 (f), 0.1:0.9:1 wt% P3HT:C-PCPDTBT:ICBA (g) and 1:1 wt% C-PCPDTBT:ICBA (h).

5. Surface Energy of P3HT:Si-PCPDTBT:ICBA ternary systems

Before considering ternary blends, we first examined the location of sensitizer in binary blend films of ICBA:Si-PCPDTBT and P3HT:Si-PCPDTBT. **Figure S7** shows the surface energy of the binary blend films with various Si-PCPDTBT contents. **Figure S7a** shows a super linear decrease of the ICBA surface energy (γ_{ICBA}=47.4 mN/m) for ICBA:Si-PCPDTBT blends, adding higher content of Si-PCPDTBT ($\gamma_{Si\text{-}PCPDTBT}$=24.3 mN/m). This fact can be rationally explained in terms of the surface energy: the component with the lowest surface energy, namely Si-PCPDTBT, is segregated into the air/film interface to decrease the total energy of the system. This phenomenon is also reported by Honda et al.[4] The binary blends of P3HT:Si-PCPDTBT show a puzzling behavior (see **Figure S7b**). The surface energy increases continuously from 28.2 mN/m for pristine P3HT to a value of 32.6 mN/m with increasing the Si-PCPDTBT content up to 60%. For the binary P3HT:Si-PCPDTBT system with 80 wt.% sensitizer, the surface energy starts to drop towards the Si-PCPDTBT surface energy. Changes in surface energy measurements can provide hints about orientational and compositional changes as well as changes in crystallinity at the surface. This observation might be attributed to a polymer surface layer with modified chains/crystallites orientation and crystallinity The GIWAXS measurements are suitable to shed more light on the aforementioned, where the crystallinity of the P3HT and Si-PCPDTBT changes as a function of the Si-PCPDTBT content in the bulk and at the surface (discussed in section 2.1.2 of the article). The surface energy of the binary P3HT:ICBA films is even lower than that of the pristine P3HT film, indicating an P3HT surface layer which is most likely less organized than the pristine P3HT. It can be attributed to this fact that the presence of ICBA substantially perturbs the organization and longer-ranged order of P3HT in the blend.[5]

Interestingly, surface energies of the ternary blends, adding different amounts of Si-PCPDTBT into the P3HT:ICBA host, follow a very similar trend of the P3HT:Si-PCPDTBT binary systems (**Figure S7c**). These findings suggest that ternary films are mainly governed by the interaction mechanisms of P3HT:Si-PCPDTBT rather than ICBA:Si-PCPDTBT. However, it is important to note that the surface information may not be necessarily representative of the bulk properties.



(a) (b)

(c)

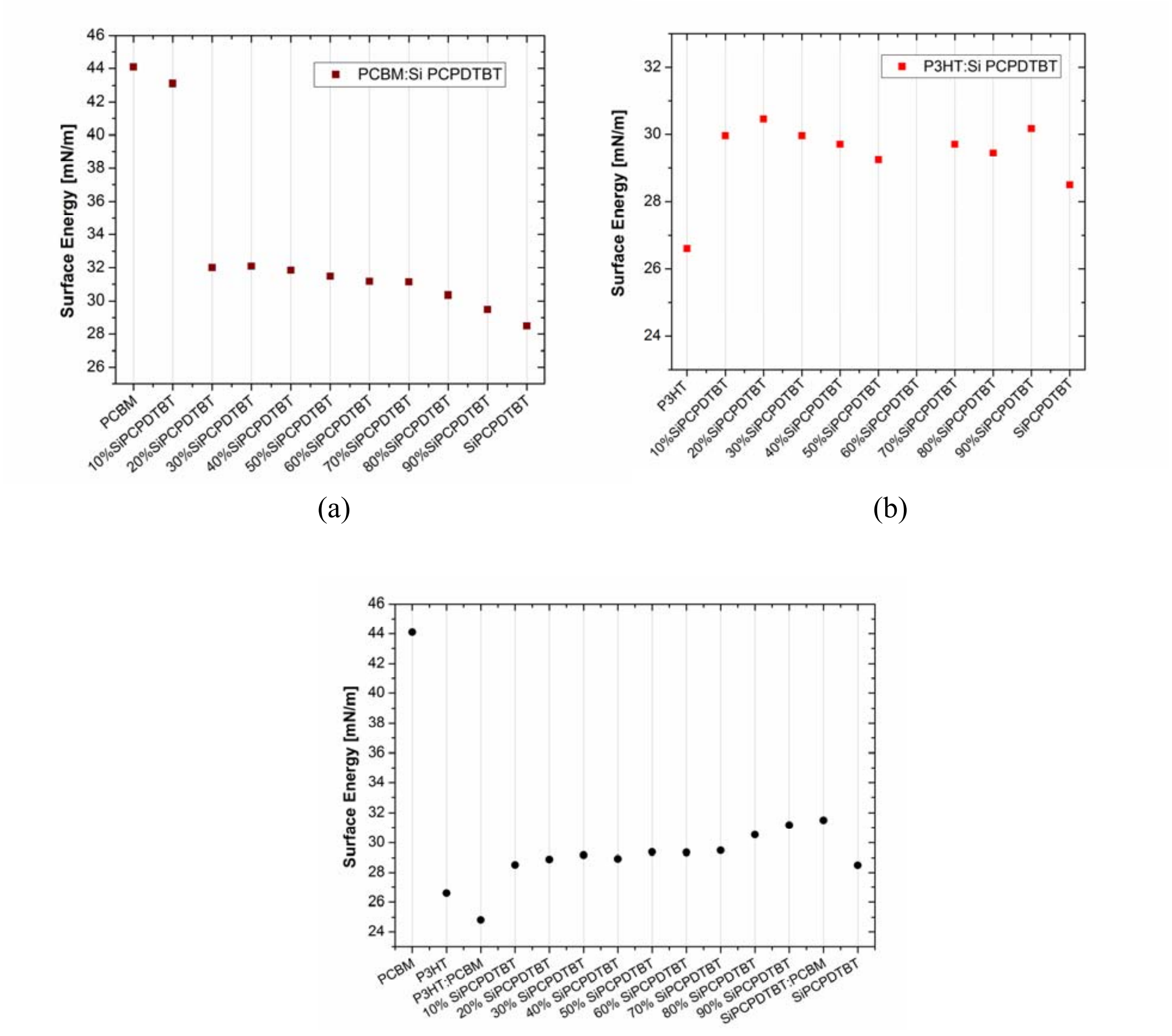
Figure S7. Surface energy of the binary blends ICBA:Si-PCPDTBT vs Si-PCPDTBT content (a); binary P3HT:Si-PCPDTBT vs Si-PCPDTBT content (b); and ternary P3HT:Si-PCPDTBT:ICBA vs Si-PCPDTBT (c). All data are measured in a single run.

Table S1. Contact angle and total surface energy of pristine, binary and ternary systems calculated by Owens-Wendt and Kaelble method. All data are measured in a single run.

P3HT:Si-PCPDTBT:ICBA [wt.%]	C. A. [°] Water	C. A. [°] Diiodomethane	C. A. [°] Ethylene glycol	Surface energy [mN/m]
1:0:0	98.1	59.0	71.7	28.2
0:1:0	103.6	65.0	81.3	24.3
0:0:1	97.2	22.8	62.2	47.4
1:0:1	99.5	60.3	76.9	26.5
0.9:0.1:1	100.1	56.0	74.8	29.4
0.8:0.2:1	99.5	56.0	74.1	29.4
0.7:0.3:1	102.3	57.1	78.1	29
0.6:0.4:1	98.5	55.5	72.2	29.8
0.5:0.5:1	100.6	57.4	76.1	30
0.4:0.6:1	100.8	58.2	77.4	30.1
0.3:0.7:1	102.8	55.7	77.2	29.9
0.2:0.8:1	100.7	57.6	76.7	28.3
0.1:0.9:1	97.3	54.7	76.6	28.5
0:1:1	100.3	59.9	77.4	26.8
0:0.05:0.95	105.5	32.4	76.4	44.2
0:0.1:0.9	101.6	31.4	73.6	42.9
0:0.2:0.8	103.7	51.8	75.0	33.2
0:0.4:0.6	105.1	52.4	75.8	33.4
0:0.6:0.4	104.4	60.3	79.1	27.6
0:0.8:0.2	105.3	58.8	79.3	28.7
0.95:0.05:0	103.6	56.5	75.5	30.4
0.9:0.1:0	103.8	55.5	75.5	31
0.8:0.2:0	104.9	55.7	75.8	31.4
0.6:0.4:0	106.2	53.6	78.1	32.5
0.4:0.6:0	106.7	53.2	79.2	32.6
0.2:0.8:0	109.4	57.7	81.5	30.7

6. Surface Energy of P3HT:Si-PCPDTBT:PCBM ternary systems

The slight variation of the surface energies measured for pristine P3HT and Si-PCPDTBT in Figure S8 compared to Figure S7 can be due to the different solvents used for the film preparation (see experimental section). The wetting coefficients were calculated based on the average values of γ_{P3HT}=27.4 and $\gamma_{PCBM\ /\ ICBA}$=46 mN/m and the sensitizer interfacial surface energies of $\gamma_{Si\text{-}PCPDTBT}$=26.4±2.1 and $\gamma_{C\text{-}PCPDTBT}$=40.5±1.5 mN/m.



(a) (b)

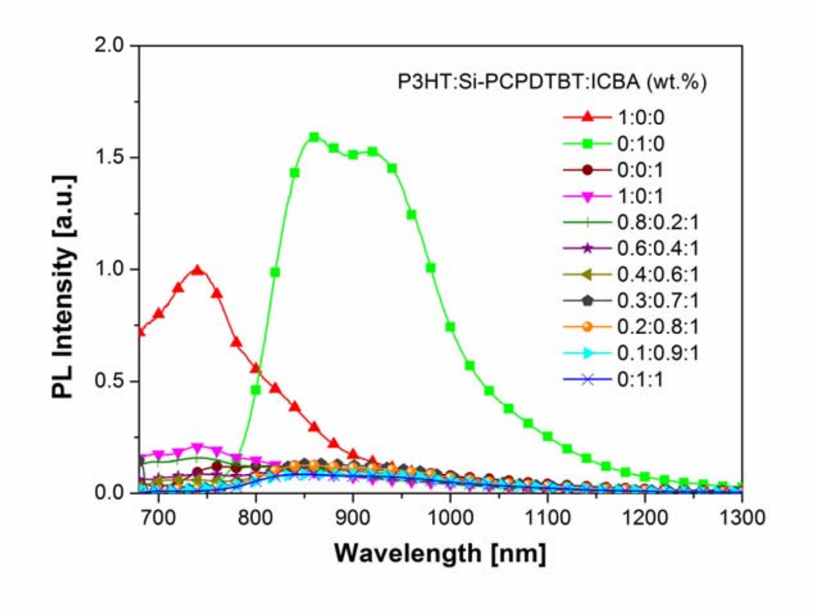
(c)

Figure S8. Surface energy of the binary PCBM:Si-PCPDTBT vs Si-PCPDTBT content (a); binary P3HT:Si-PCPDTBT vs Si-PCPDTBT content (b); and ternary P3HT:Si-PCPDTBT:PCBM vs Si-PCPDTBT content (c). All presented data are measured in a single run.

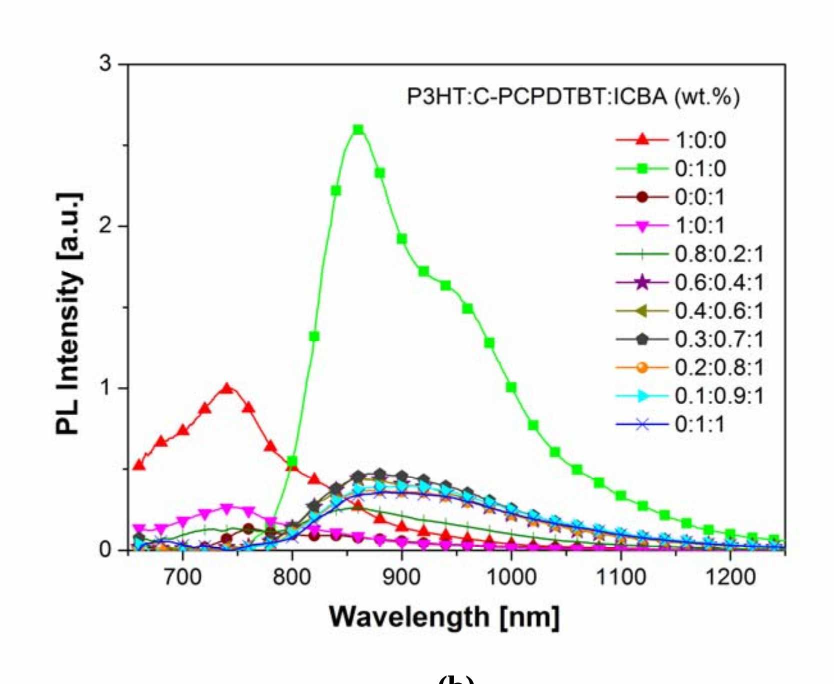
Table S2. Contact angle and total surface energy of pristine, binary and ternary systems calculated by Owens-Wendt and Kaelble method. All data are measured in a single run.

P3HT:Si-PCPDTBT:PCBM [wt.%]	C. A. [°] Water	C. A. [°] Diiodomethane	C. A. [°] Ethylene glycol	Surface energy [mN/m]
1:0:0	102.2	60.4	81.4	26.5
0:1:0	104.3	59.8	77.9	28.16
0:0:1	87.5	13.8	62.1	44.14
1:0:1	103.2	65.5	77.9	24.82
0.9:0.1:1	98.7	58.4	72.2	28.51
0.8:0.2:1	98.6	57.5	72.4	28.88
0.7:0.3:1	97.9	57.0	71.4	29.16
0.6:0.4:1	97.8	57.4	71.5	28.92
0.5:0.5:1	98.4	56.7	71.8	29.37
0.4:0.6:1	99.0	56.6	72.7	29.35
0.3:0.7:1	98.7	56.2	72.5	29.47
0.2:0.8:1	99.6	54.5	72.9	30.54
0.1:0.9:1	99.5	53.8	72.0	31.17
0:1:1	99.2	53.3	71.3	31.50
0:0.1:0.9	98.2	27.9	70.8	43.11
0:0.2:0.8	98.2	51.4	71.4	32.01
0:0.3:0.7	100.3	52.6	72.1	32.09
0:0.4:0.6	99.4	52.5	71.8	31.85
0:0.5:0.5	100.0	52.8	73.3	31.48
0:0.6:0.4	99.8	52.9	73.9	31.17
0:0.7:0.3	102.5	53.6	76.4	31.14
0:0.8:0.2	102.4	54.7	77.0	30.36
0:0.9:0.1	103.1	56.7	77.2	29.50
0.9:0.1:0	100.0	55.0	74.5	29.96
0.8:0.2:0	100.9	54.0	75.8	30.46
0.7:0.3:0	107.1	56.8	81.9	29.96
0.6:0.4:0	106.7	61.1	83.4	29.7
0.5:0.5:0	106.9	61.8	83.8	29.24
0.3:0.7:0	106.9	56.9	82.0	29.70
0.2:0.8:0	104.2	56.6	79.4	29.44
0.1:0.9:0	102.8	55.4	77.0	30.17

7. Photoluminescence (PL) of P3HT:Si- / C-PCPDTBT:ICBA ternary systems



(a)



(b)

Figure S9. Photoluminescence (PL) spectra of pristine P3HT, sensitizer and ICBA and ternary P3HT:Sensitizer:ICBA films containing different amounts of (a) Si-PCPDTBT and (b) C-PCPDTBT sensitizer.

8. GIWAXS measurements

8.1 Pristine polymer and binary film spectra plotted on optimized scales

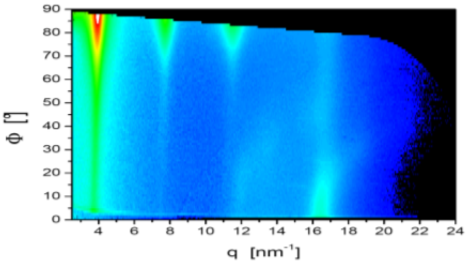
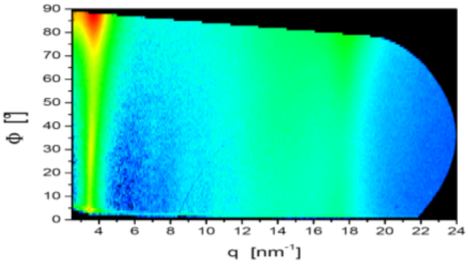
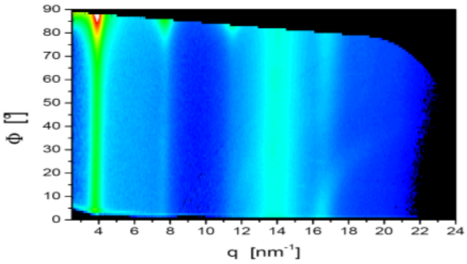
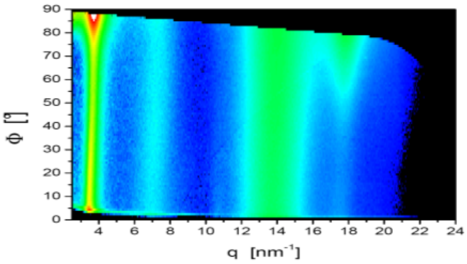
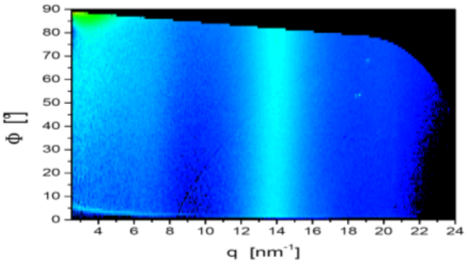
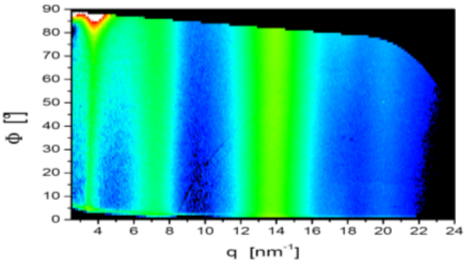
	P3HT:PCBM		Si-PCPDTBT:PCBM	
(a)		(d)		(1:0)
(b)		(e)		(1:1)
(c)		(f)		(0.2:0.8)

Figure S10. Two-dimensional GIWAXS detector patterns obtained for the pristine films, P3HT (a) [ΔI=10000] and Si-PCPDTBT (d) [ΔI=1000], and binary blends: P3HT:PCBM 1:1 wt.% (b) and 0.2:0.8 wt.% (c) as well as Si-PCPDTBT:PCBM 1:1 wt.% (e) and 0.2:0.8 wt.% (f). Intensity scales ΔI are given in brackets. For the binary films ΔI is adjusted to the polymer volume fraction.

8.2 Film spectra normalized to the PCBM volume fraction

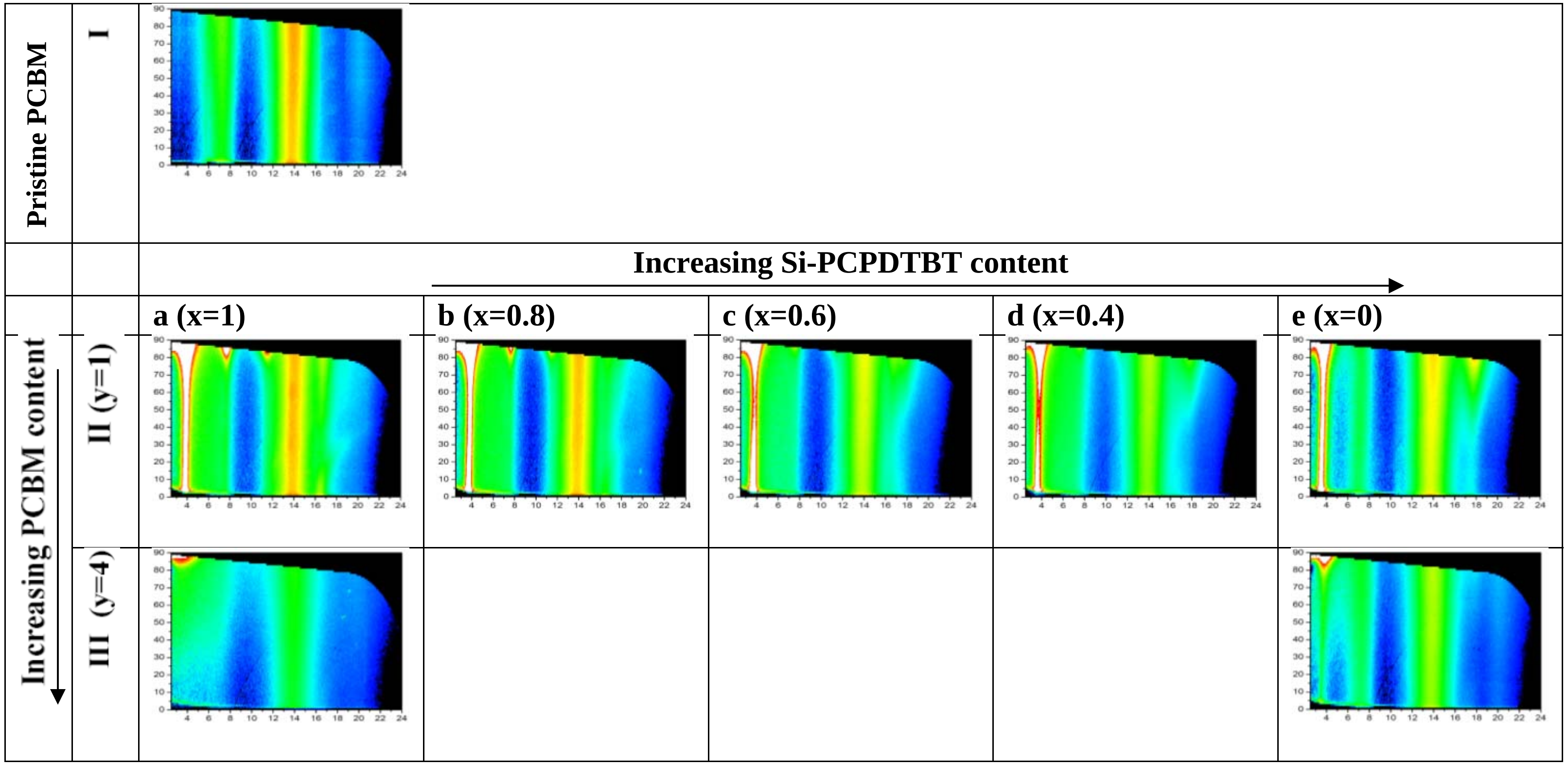
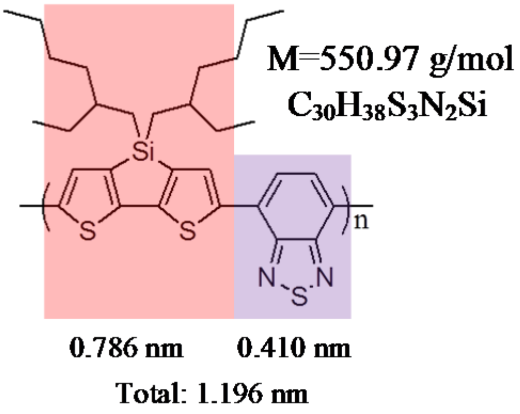


Figure S11: Two-dimensional GIWAXS detector patterns in (Φ [°],q [nm^{-1}])-presentation of pristine PCBM (I), binary and ternary P3HT:Si-PCPDTBT:PCBM films with (x:1-x:y) weight ratio. 1. binary films: P3HT:PCBM (y=1, x=1, IIa and y=4,x=1, IIIa) and Si-PCPDTBT:PCBM (y=1, x=0, IIe and y=4, x=0, IIIe). 3. ternary films (y=1): 0.8 (IIb),0.6 (IIc), 0.4 (IId). Intensity scales are adjusted to the PCBM volume fraction (see below: Section 8.3).

8.3 Normalization to polymer and PCBM volume fractions



Si-PCPDTBT

Figure S12. Estimation of the monomer dimensions of Si-PCPDTBT, assuming fully stretched conformation.

From the peak locations in the GIWAXS spectra the interlayer and π-π stacking distance can be calculated to be d_{inter}=1.70 nm and $d_{\pi\text{-}\pi}$=0.35 nm, respectively. Assuming a fully stretched conformation, the length of the monomer unit along the backbone direction (no peaks visible in the GIWAXS spectra) is estimated to be about d_b=1.20 nm. These considerations lead to the volume of the repeating unit V= d_{inter} $d_{\pi\text{-}\pi}$ d_b =0.714 nm^3, from which the density can be calculated:

$$\rho_{\text{Si-PCPDTBT,exp}} = \frac{550.97\ \text{g/mol}}{0.714 \cdot 10^{-21}\text{cm}^3 \times 6.022\ 10^{23}\ \ 1/\text{mol}} \approx 1.28\ \text{g/cm}^3,$$

where M=550.97 g/mol is the molecular weight of the repeating unit of Si-PCPDTBT. Analogous considerations for P3HT (d_{inter}=1.59 nm, $d_{\pi\text{-}\pi}$=0.38 nm, d_b=0.38 nm, M=166.28 g/mol) result in a calculated density of $\rho_{P3HT,calc}$=1.20 g/mol. For the following considerations we use the experimentally determined average density of P3HT $\rho_{P3HT,exp}$=1.13 g/cm^3 as reported in literature (values range between 1.10 g/cm^3 and 1.15 g/cm^3)[6,7] and $\rho_{\text{Si-PCPDTBT,calc}}=\rho_{\text{Si-PCPDTBT,exp}}\times\rho_{P3HT,exp}/\rho_{P3HT,calc}$=1.21 g/mol. For PCBM, density values ranging from ρ_{PCBM}=1.3 g/cm^3 up to 1.5 g/cm^3 are reported.[8,9,10] The resulting polymer and PCBM volume fractions used for GIWAXS spectra normalization were calculated with ρ_{PCBM}=1.4 g/cm^3 and are summarized in the **Table S3**.

Table S3. Polymer and PCBM volume fractions calculated for the binary and ternary films used for GIWAXS spectra normalization.

Binary films	P3HT:PCBM wt.%			Si-PCPDTBT:PCBM wt.%	
	1:1		0.2:0.8	1:1	0.2:0.8
$\Phi_{vol\%,PCBM}$	45		76	46	78
$\Phi_{vol\%,Polymer}$	55		24	54	22
Ternary films	P3HT:Si-PCPDTBT:PCBM wt.%				
	1:0:1	0.8:0.2:1	0.6:0.4:1	0.4:0.6:1	0:1:1
$\Phi_{vol\%,P3HT}$	55	45	34	23	0
$\Phi_{vol\%,SiPCPDTBT}$	0	10	21	32	54
$\Phi_{vol\%,PCBM}$	45	45	45	46	46

For a comparison between the polymer peaks of the pristine and ternary films, artificial spectra were calculated under the assumption that the P3HT and Si-PCPDTBT spectra simply superimpose: $\Phi_{vol\%,P3HT}.I_{P3HT}+\Phi_{vol\%,SiPCPDTBT}.I_{SiPCPDTBT}$. For the blended films the intensity scales of all spectra (artificial and experimental) are rescaled according to $\Phi_{vol\%,polymer}.\Delta I_{polymer}$ and $\Phi_{vol\%,PCBM}.\Delta I_{PCBM}$ to those obtained for the corresponding pristine films, in order to allow a comparison of the polymer and PCBM peak intensities, respectively. Here $\Delta I_{polymer}$ and ΔI_{PCBM} are the intensity scales of the pristine polymer and PCBM films.

References

---

1 F. Machui, S. Rathgeber, Ning Li, T. Ameri1, and C. J. Brabec, *J. Mater. Chem.* **2012**, *22*, 15570.

2 A. Baumann, T. J. Savenije, D. H. K. Murthy, M. Heeney, V. Dyakonov and C. Deibel, *Adv. Funct. Mater.* **2011**, *21*, 1687.

3 C. Deibel, J. Lorrmann, A. Baumann, J. Gorenflot, A. Wagenpfahl, J. Rauh, V. Dyakonov, Influence of trap assisted recombination on polymer–fullerene solar cells, SPIE **2011** in San Diego, http://www.scribd.com/doc/69183438/Influence-of-Trap-Assisted-Recombination-on-Polymer%E2%80%93Fullerene-Solar-Cells-Carsten-Deibel-et-al-SPIE-2011-in-San-Diego.

4 S. Honda, H. Ohkita, H. Benten, S. Ito, *Chem. Commun.* **2010**, *46*, 6596.

5 Y. H. Lin, *Organic Electronics* **2012**, *13*, 2333.

6 J. W Kiel, B. J. Kirby, C. F. Majkrzak, B. B. Maranville, M. E. Mackay, *Soft Matter* **2010**, *6*, 641.

7 T. J. Prosa, M. J. Winokur, J. Moulton, P. Smith, A. J. Heeger, *Macromolecules* **1992**, *25*, 4364.

8 A. C. Arias, *J. Macromol. Sci. Polym. Rev.* **2006**, *46*, 103.

9 J. W Kiel, B. J. Kirby, C. F. Majkrzak, B. B. Maranville, M. E. Mackay, *Soft Matter* **2010**, *6*, 641.

10 C. W. T. Bulle-Lieuwma, W. J. H. van Gennip, J. K. J. van Duren, P. Jonkheijm, R. A. J. Janssen, and J. W. Niemantsverdriet, *Appl. Surf. Sci.* **2003**, *203*, 547.