Donor-Acceptor Diblock Copolymers Based on Polythiophene and Poly(fluorene-*alt*-dithienylbenzothiadiazole) Blocks

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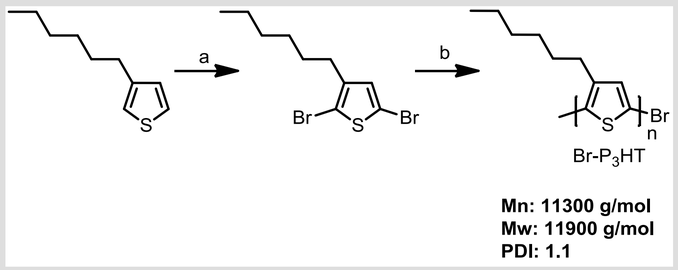
Introduction: Film morphology in organic photovoltaic cells (OPVCs) plays an important role for the efficiency of the cell. The longtime stability of the generated morphologies has a direct effect on the lifetime of OPVCs. The use of covalently bound diblock copolymers can lead to novel and more stable blend systems. Rigid, all-conjugated diblock copolymers are a new, emerging class of functional polymer materials for OPVCs.[1]



Scheme 1: a) NBS, DMF; b) *t*-BuMgCl, Ni(dppp), THF.

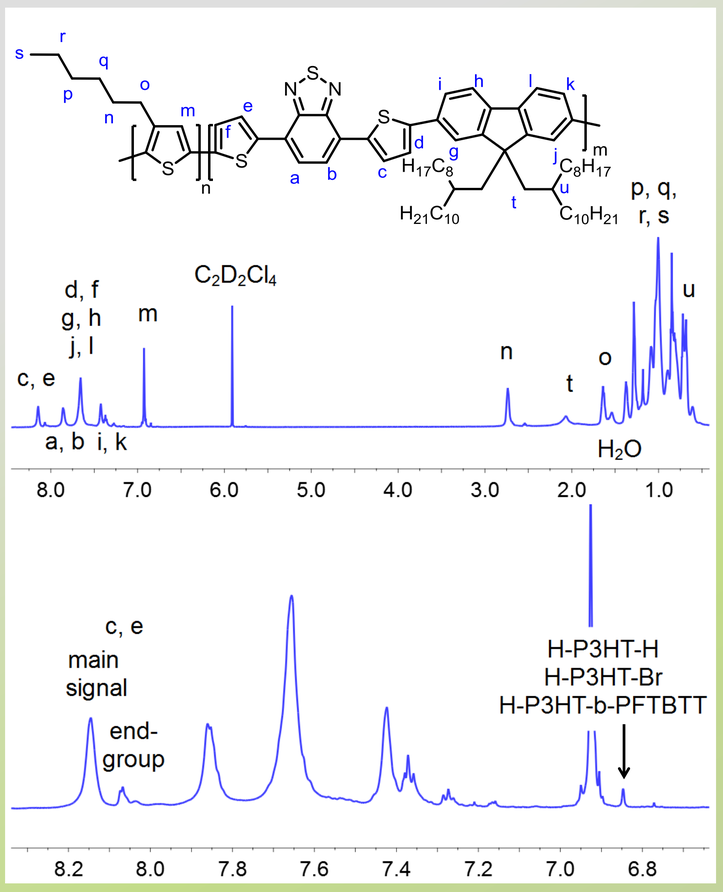
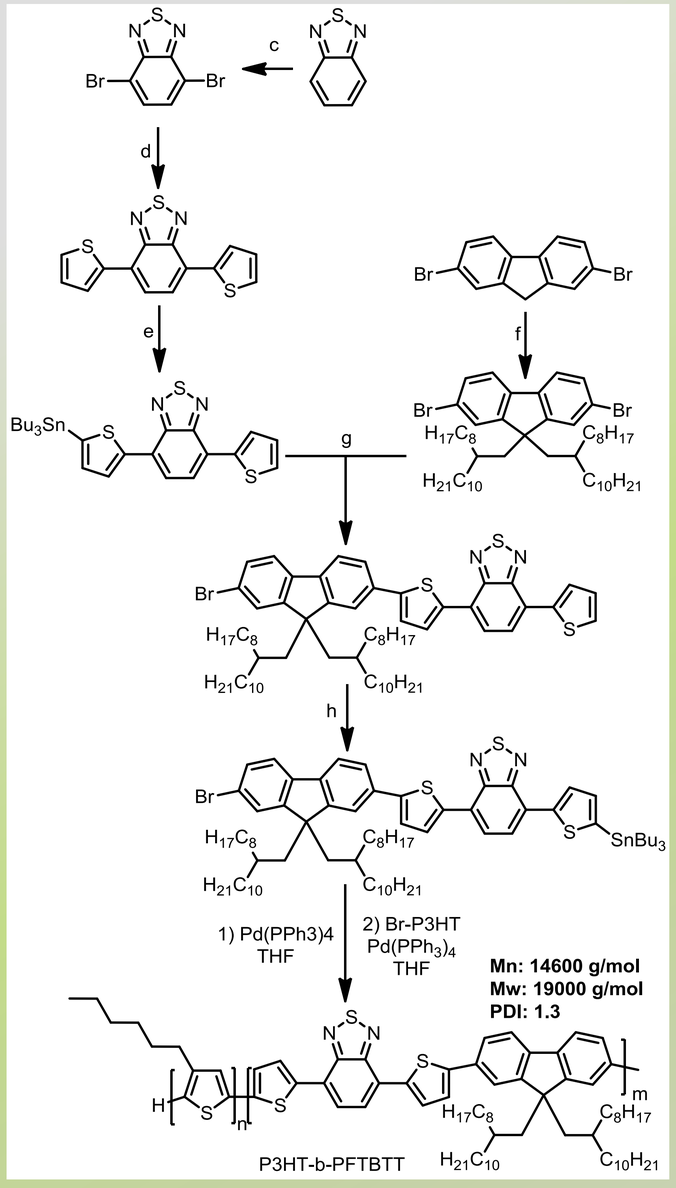


Figure 1: ^{1}H-NMR spectra of the *diblock* sample.



Scheme 2:, c) Br_2, HBr; d) 2-Bu_3Sn-thiophene, $Pd(PPh_3)_4$, THF; e) TMP, *n*-BuLi, Bu_3SnCl, THF; f) 1-Iodo-2-octyldodecane $(PhCH_2)(C_2H_5)_3NCl$, NaOH, DMSO; g) $Pd(PPh_3)_4$, THF; h) TMP, *n*-BuLi, Bu_3SnCl, THF.

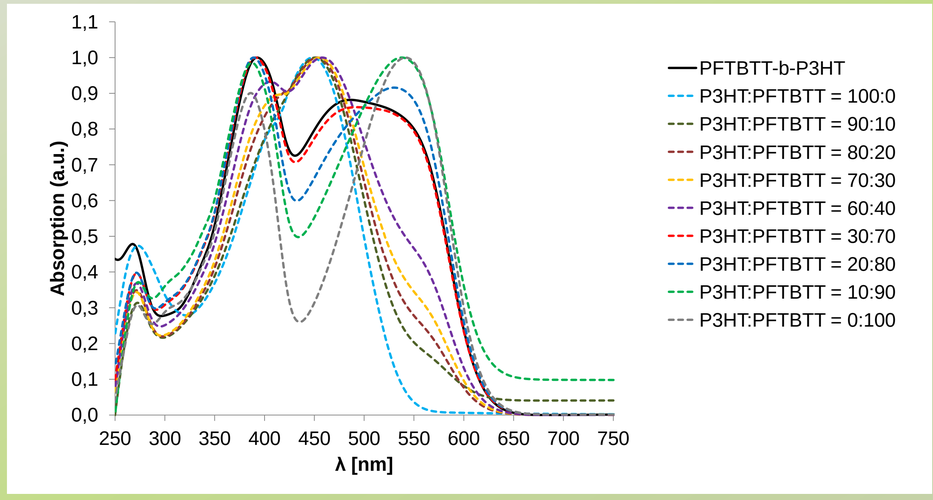


Figure 2: Normalized absorption spectra of mixtures of P3HT and PFTBTT with different weight ratios. The absorption of the final *diblock* sample (black solid line) and spectrum for a 30:70 weight ratio P3HT:PFTBTT blend (red dashed line) match closely.

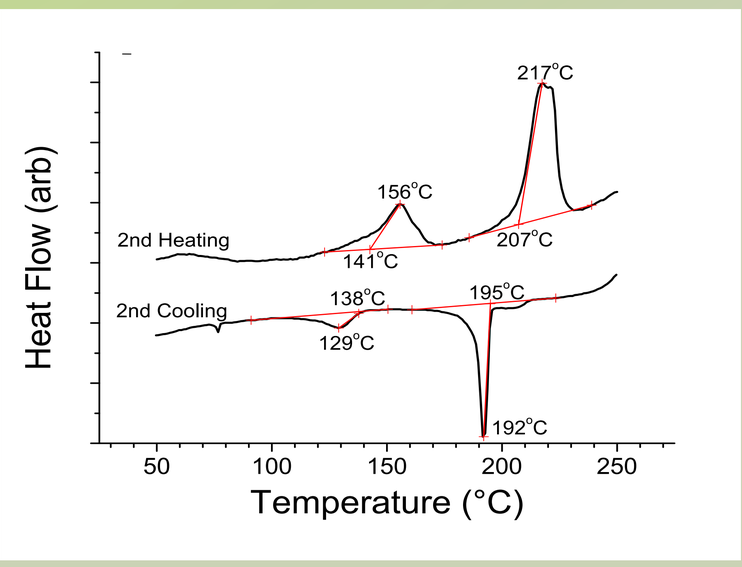


Figure 3: Differential scanning calorimetry (DSC) curves of the *diblock*:PFTBTT sample. Second cooling and heating curves are shown. Curves are offset for clarity.

	P3HT	PFTBTT	*diblock*	*diblock*:P3HT
In P3HT-*b*-PFTBTT	**27%**	**26%**	52%	39%
Free	**5%**	**42%**	48%	61%
diblock	32%	68%		
diblock:P3HT	50%	50%		

Table 1: The estimated components break down of the *diblock* sample and *diblock*:P3HT blend.

Annealed at 130°C	Voc [V]	Jsc [mAcm^{-2}]	FF [%]	PCE [%]
PFTBTT:P3HT	0.95	3.72	42.4	1.50
Diblock(17%): PFTBTT:P3HT	0.92	3.27	37.6	1.13
Diblock(40%): PFTBTT:P3HT	0.89	2.69	31.6	0.76
Annealed at 200°C				
PFTBTT:P3HT	0.95	2.26	28.7	0.61
Diblock(17%): PFTBTT:P3HT	0.95	3.32	37.1	1.17
Diblock(40%): PFTBTT:P3HT	0.90	3.40	31.9	0.98

Table 2: Device statistics for homopolymer blend and *diblock*:PFTBTT:P3HT blends under AM 1.5G illumination (see *Figure 5*).

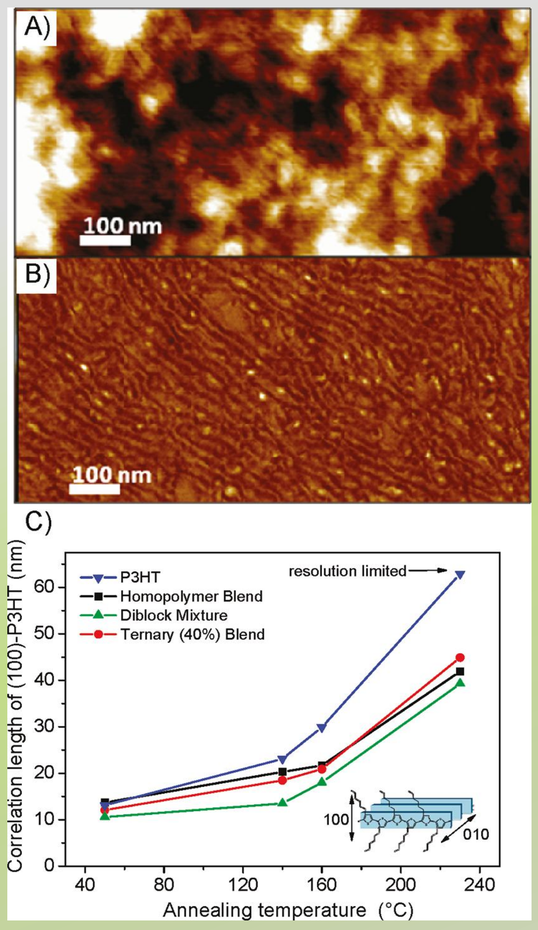


Figure 4:
A: Height (image height 4nm).
B: phase image of the *diblock*:PFTBTT sample after annealing (2 hours at 220°C). With over 80% of the P3HT bound in P3HT-*b*-PFTBTT this appears to be the block copolymer structure. The phase image shows good contrast between P3HT and PFTBTT domains with features repeating on a 25 nm scale.
C: The correlation length of the 100 crystallization peak of P3HT orientated perpendicular to the substrate. PFTBTT:P3HT (squares), *diblock*:PFTBTT:P3HT (circles), *diblock*:PFTBTT (up triangles) and P3HT (down triangles). Inset: physical interpretation of lattice indices.

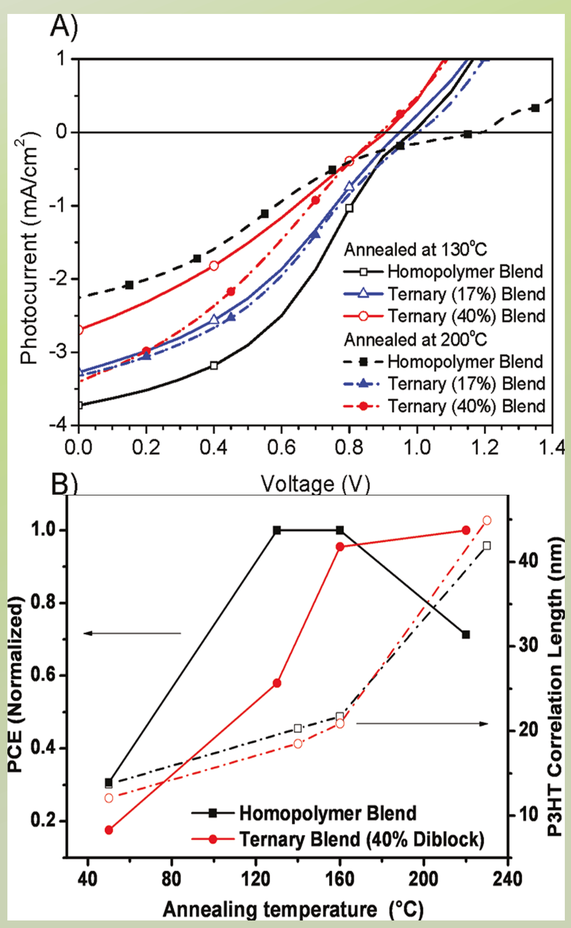


Figure 5:
A: Photocurrent vs applied bias for homopolymer blend (squares), ternary (17%) blend (triangles), and ternary (40%) blend (circles), annealed at 130°C (open symbols) and 200°C (closed symbols), measured under AM1.5G illumination at 1 sun.
B: PCE (normalized to the peak value for each device) vs annealing temperature (solid line). Increase relative to pristine device PCE with annealing vs *diblock* content. Ten minutes at 130°C (squares) and 200°C (circles) (dash-dotted line).

Conclusion: A diblock copolymer consisting of poly(3-hexylthiophene) as donor and poly{[9,9-*bis*-(2-octyldodecyl)fluorene-2,7-diyl]-*alt*-[4,7-di(thiophene-2-yl)-2,1,3-benzothiadiazole]-5′,5″-diyl} as acceptor block was synthesized and its use as a compatibilizer in ternary polymer blends for OPVC applications was studied.[1]

[1] R. C. Mulherin, S. Jung, S. Huettner, K. Johnson, P. Kohn, M. Sommer, S. Allard, U. Scherf, N. C. Greenham, *Nano Lett* **2011**; *11*, 4846.