

All-Conjugated Block Copolymers for Self-assembled Photovoltaics

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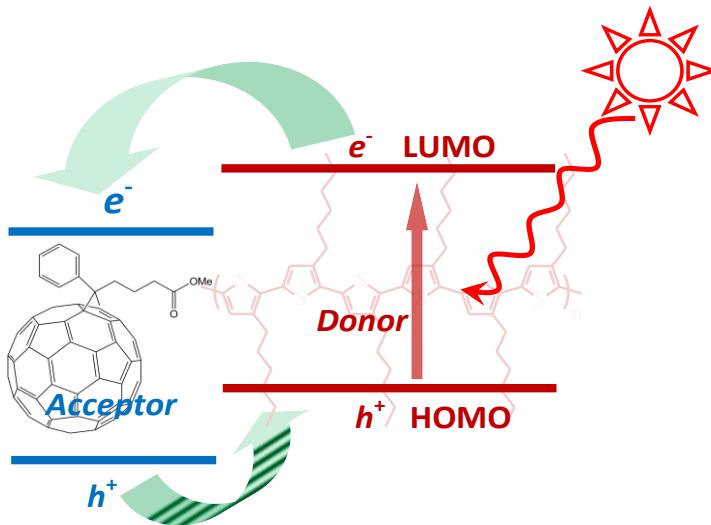
²Center for Nanoscale Materials, Argonne National Laboratory

³Center for Nanophase Materials Sciences Oak Ridge National Laboratory

⁴Department of Chemistry, University of Tennessee, Knoxville

⁵ National Synchrotron Light Source, Brookhaven National Laboratory

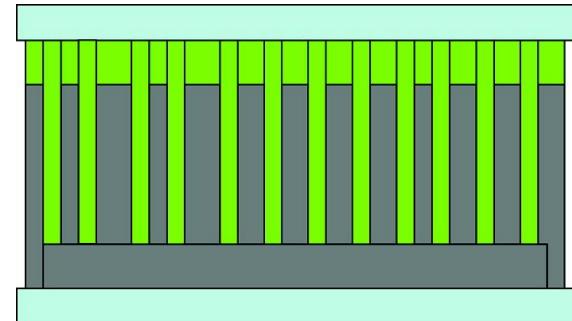
Photovoltaic energy conversion is a multi-step process dependent on structure at several length scales



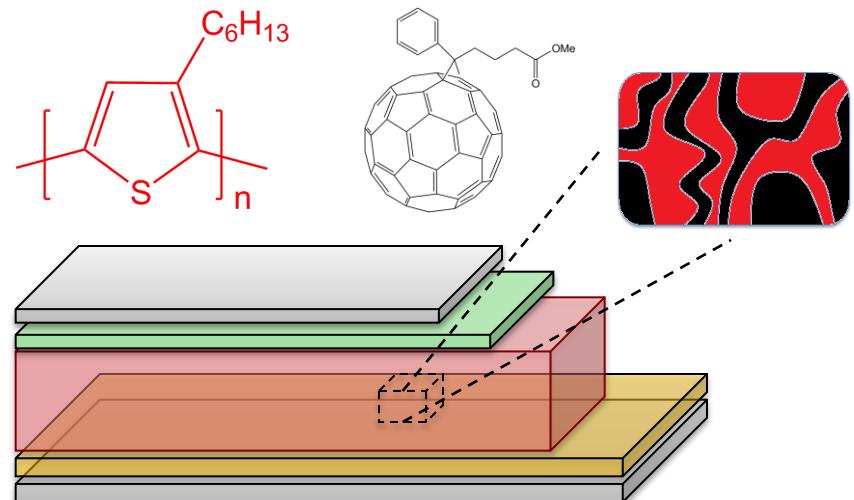
- Photon Absorption
- Exciton Diffusion
- Charge Separation
- Charge Migration

Hoppe, Het al. *J. Mater. Res.* 2004, 19, 1924.

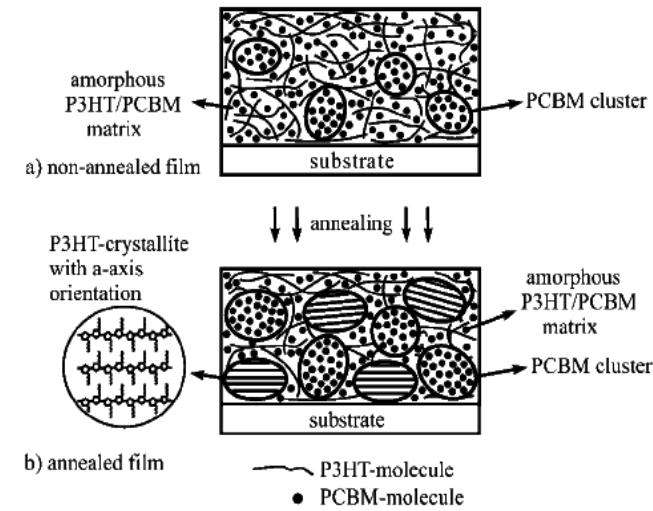
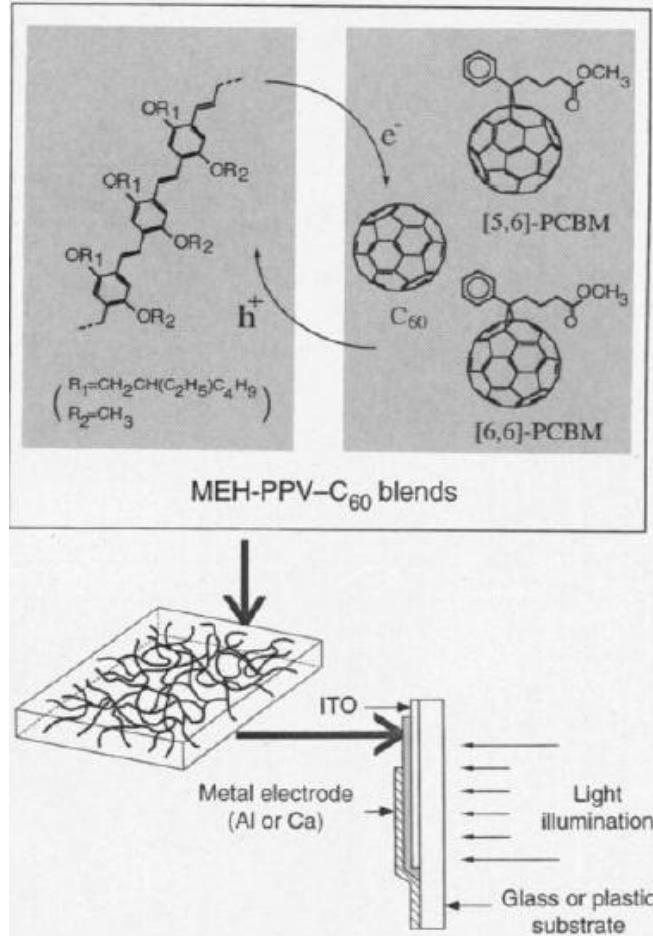
Ideal Morphology?



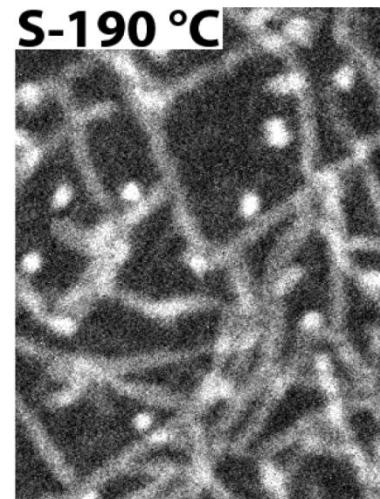
Günes et al. *Chem. Rev.* 2007, 107, 1324.



Spontaneous phase separation leads to hierarchical structure in BHJ OPVs



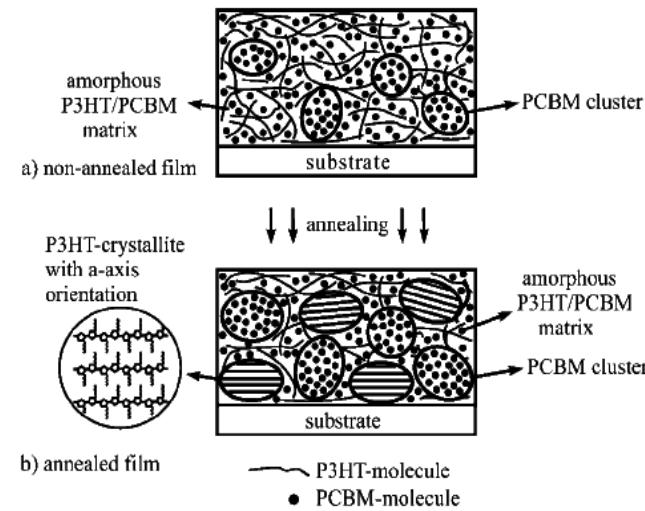
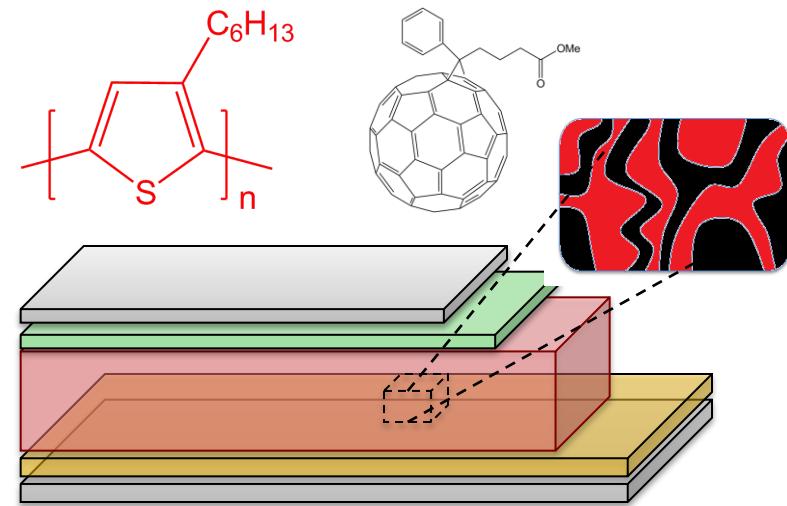
Brabec, et al. *Adv. Funct. Mater.* 2005, 15, 1193.



Gomez, et al. *Macromolecules* 2011, 44, 5722.

Heeger et al., *Science* 1995, 270, 1789.

Spontaneous phase separation leads to hierarchical structure in BHJ OPVs



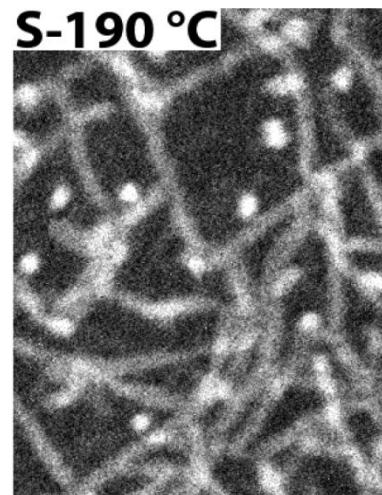
Brabec, et al. *Adv. Funct. Mater.* **2005**, *15*, 1193.

Thompson, B. C.; Fréchet, J. M. J. *Angew. Chem. Int. Ed.* **2008**, *47*, 58.

Polymer Photovoltaics: A Practical Approach; Krebs, F. C., Ed.; SPIE: Bellingham, 2008

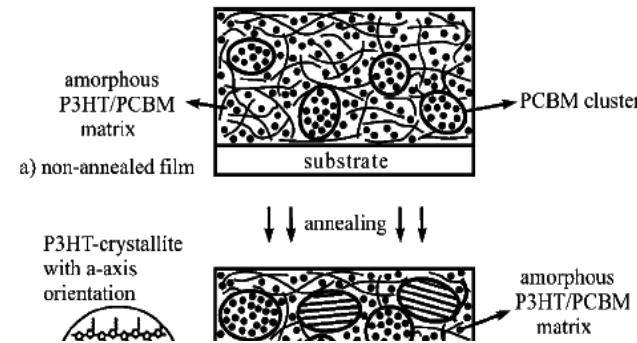
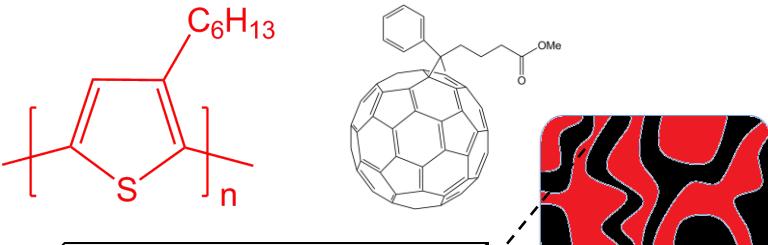
Peet, J.; Heeger, A. J.; Bazan, G. C. *Acc. Chem. Res.* **2009**, *42*, 1700.

Bredas, J.-L.; Durrant, J. R. *Acc. Chem. Res.* **2009**, *42*, 1689.



Gomez, et al. *Macromolecules* **2011**, *44*, 5722.

Spontaneous phase separation leads to hierarchical structure in BHJ OPVs



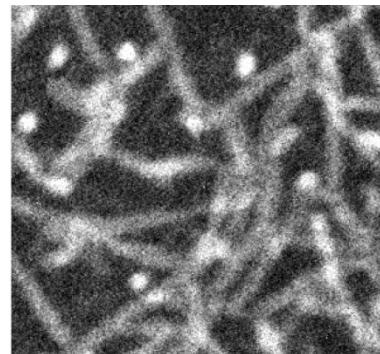
Despite significant advances in the performance of bulk heterojunction OPVs, it remains a challenge to identify the critical parameters governing structure, optoelectronic properties, and consequently performance

T
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C
P

Approach; Krebs, F. C., Ed.; SPIE:
Bellingham, 2008

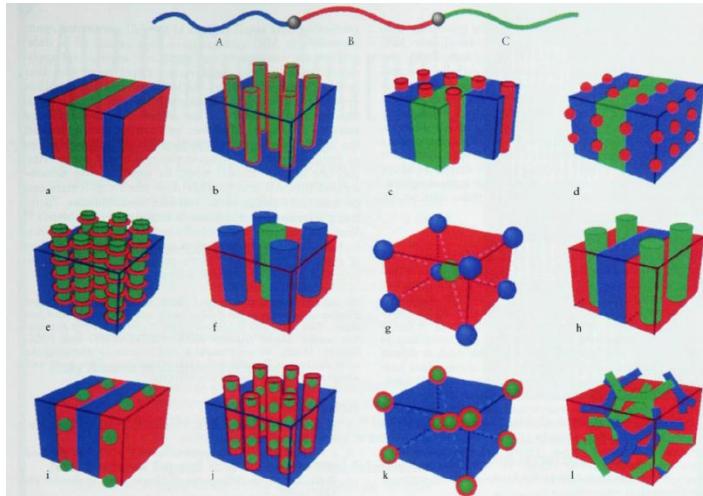
Peet, J.; Heeger, A. J.; Bazan, G. C. *Acc. Chem. Res.* **2009**, *42*, 1700.

Bredas, J.-L.; Durrant, J. R. *Acc. Chem. Res.* **2009**, *42*, 1689.

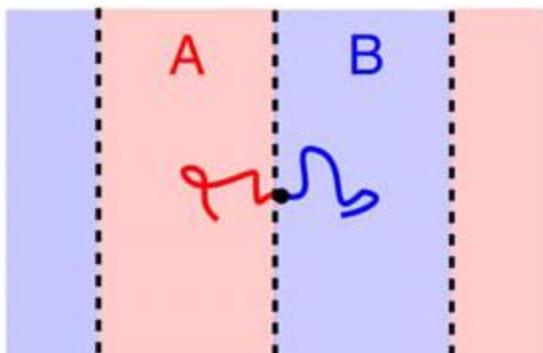


Gomez, et al. *Macromolecules* **2011**, *44*, 5722.

Block Copolymers Form Nanostructured Materials Spontaneously



Bates et al., *Phys. Today*, 1999, **52**, 32.
Wang et al., *Macromolecules* 1995, **28**, 7215.



Matsen et al., *J. Phys.: Condens. Matter* 2002, **14**, R21.

Reduced Entropy of mixing:

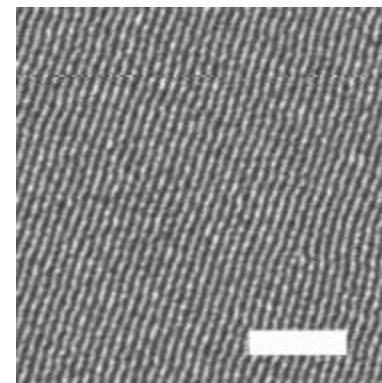
$$S_{mixing} \sim \frac{\phi}{N} \ln \phi$$

Long-range repulsion:

$$F_{repulsion} \sim \chi \phi_A \phi_B$$

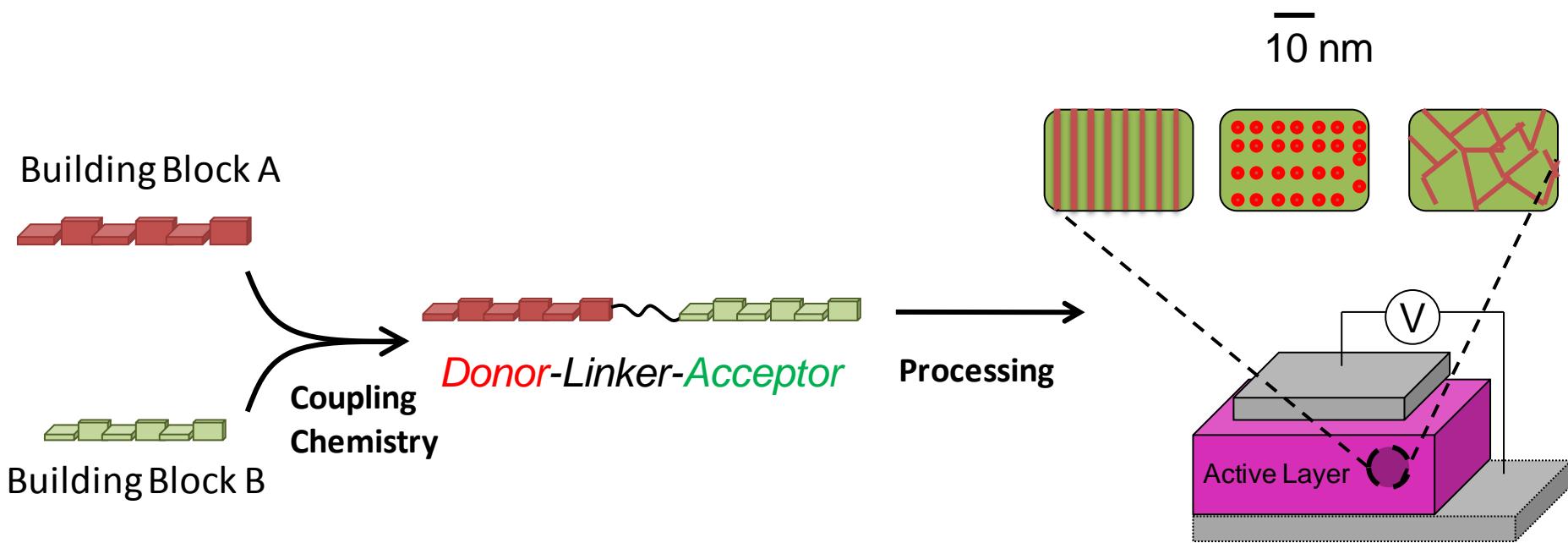
Chain stretching:

$$F_{stretching} \sim \frac{r^2}{Nl^2}$$



Register et al., *Macromolecules* 2002, **35**, 6645.

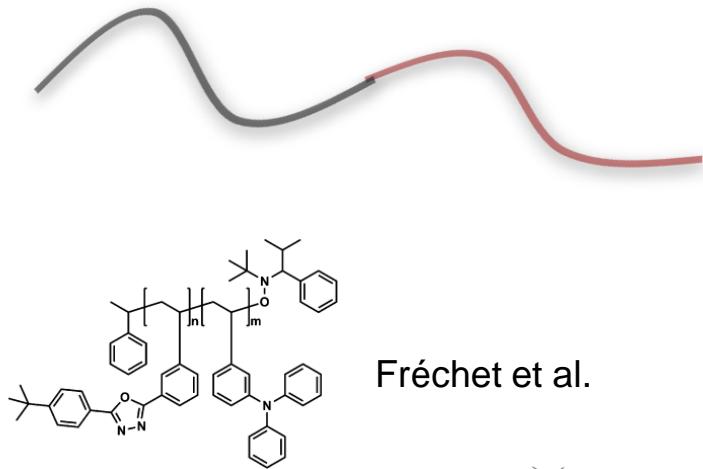
Self-Assembled Polymer Photovoltaics



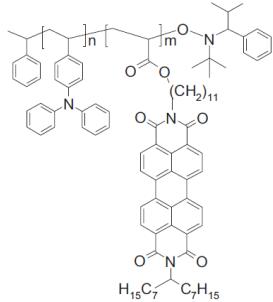
- Elucidate self-assembly of all-conjugated block copolymers
- **Investigate optoelectronic properties of nanostructured OPVs**
- Prepare high-performance polymer OPVs

Rod-Coil and Coil-Coil block copolymers can self-assemble into donor-acceptor nanostructures

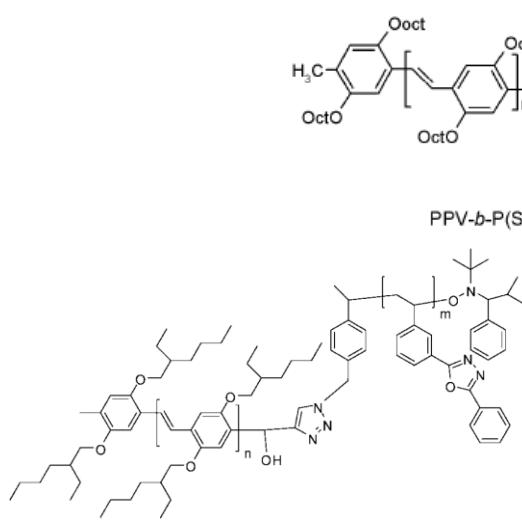
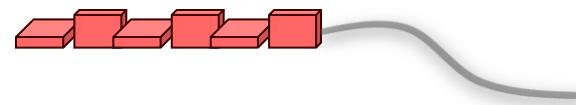
Coil-Coil Copolymers



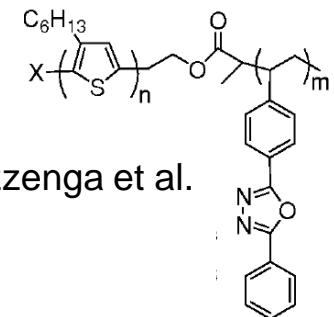
Thekkat et al.



Rod-Coil Copolymers

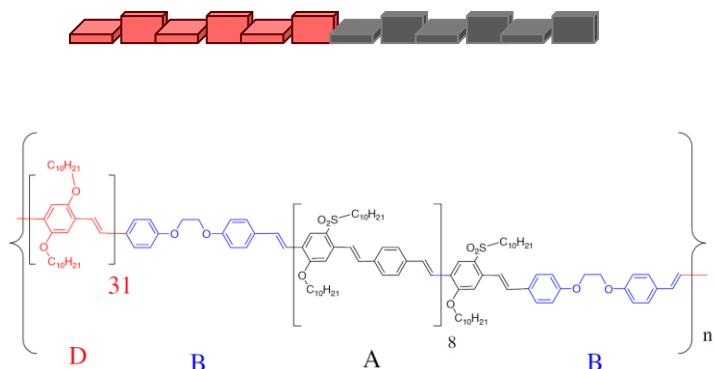


Mezzenga et al.

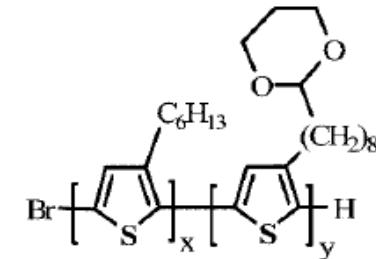


Block copolymers with two conjugated polymers represent excellent model materials and have significant potential for high-performance OPVs

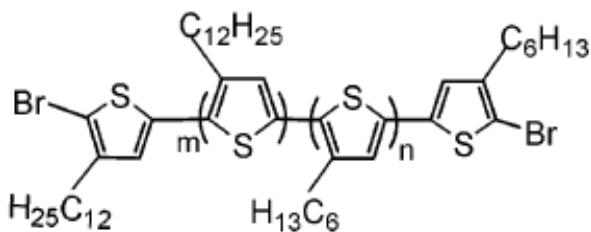
Rod-rod all-conjugated block copolymers



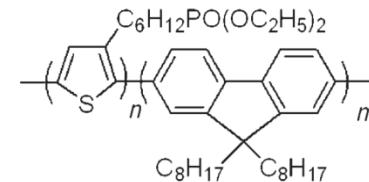
Sun et al.



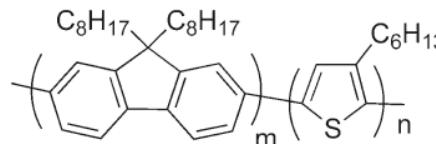
Dagron-Lartigau



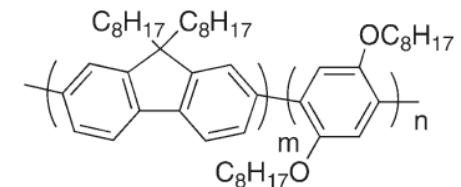
McCullough, Jenhekhe,
Hashimoto, Yokoyama



Scherf et al.



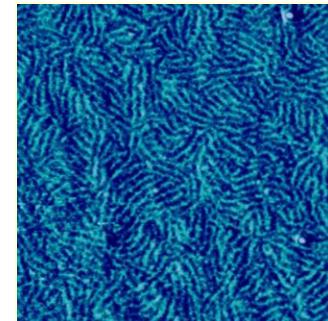
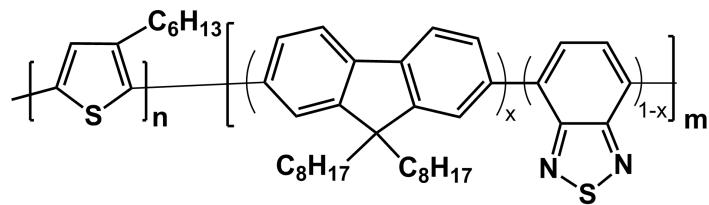
McCullough et al.



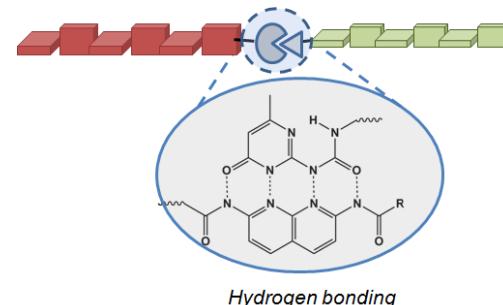
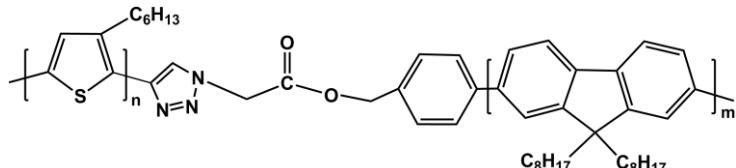
Power conversion efficiencies of 2% have been achieved using blends of conjugated polymers

Outline

- Synthesis and self-assembly of all-conjugated P3HT-PFO block copolymers

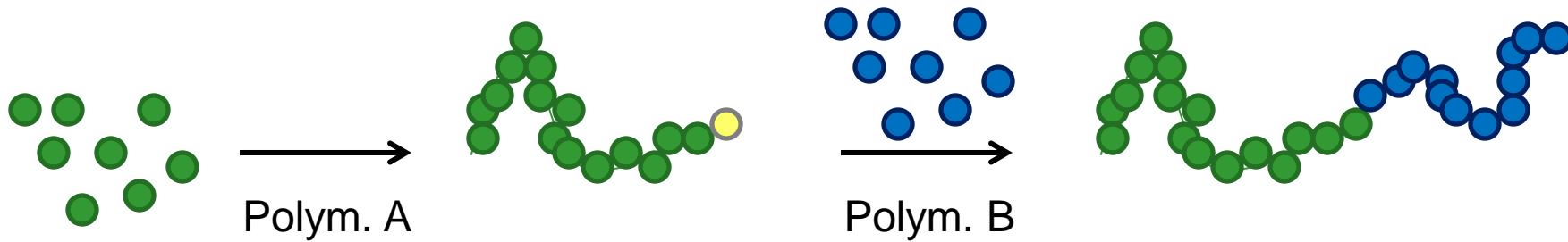


- Optical characterization studies of all-conjugated block copolymers
- “Click” coupling strategy and “Pseudo” block copolymers

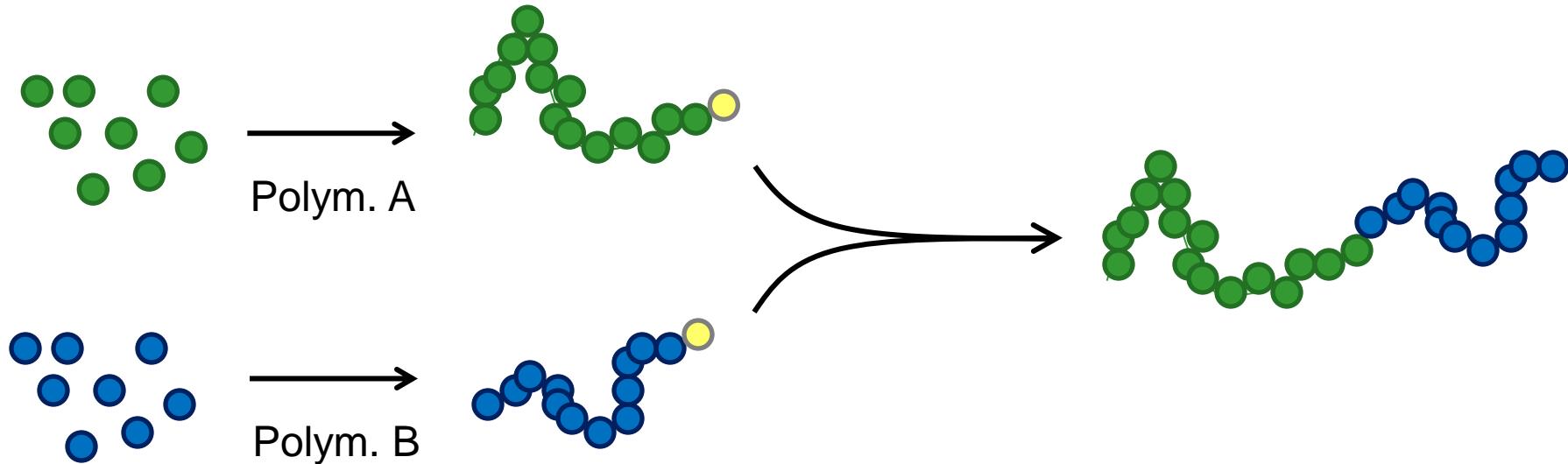


General approaches to block copolymer synthesis

Sequential Monomer Addition

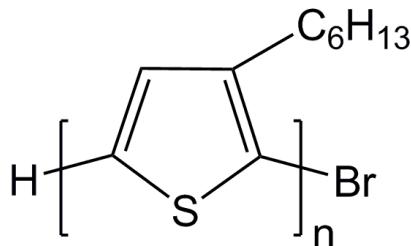


Macroreagent Approach



Polymer blocks for all-conjugated block copolymers

A-block:



HOMO/LUMO: -4.8/-2.6 eV



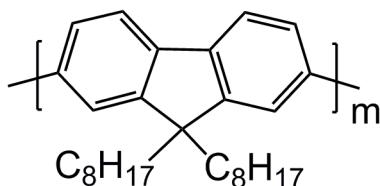
p-type polymer

Chain-growth synthesis with low PDI and endgroup control

Synthesized via Ni-catalyzed Grignard Metathesis

Poly(3-hexylthiophene) (**P3HT**)

B-blocks:



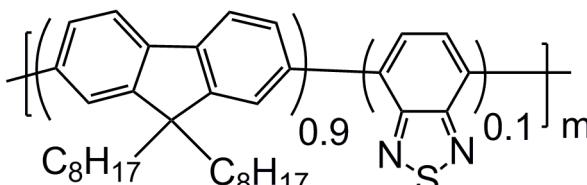
HOMO/LUMO: -5.7/-2.7 eV



p-type polymer

Synthesized via Suzuki polycondensation

Poly(9,9-dioctyl-fluorene) (**PFO**)



HOMO/LUMO: -5.7/-3.7 eV (90 % fluorene groups)

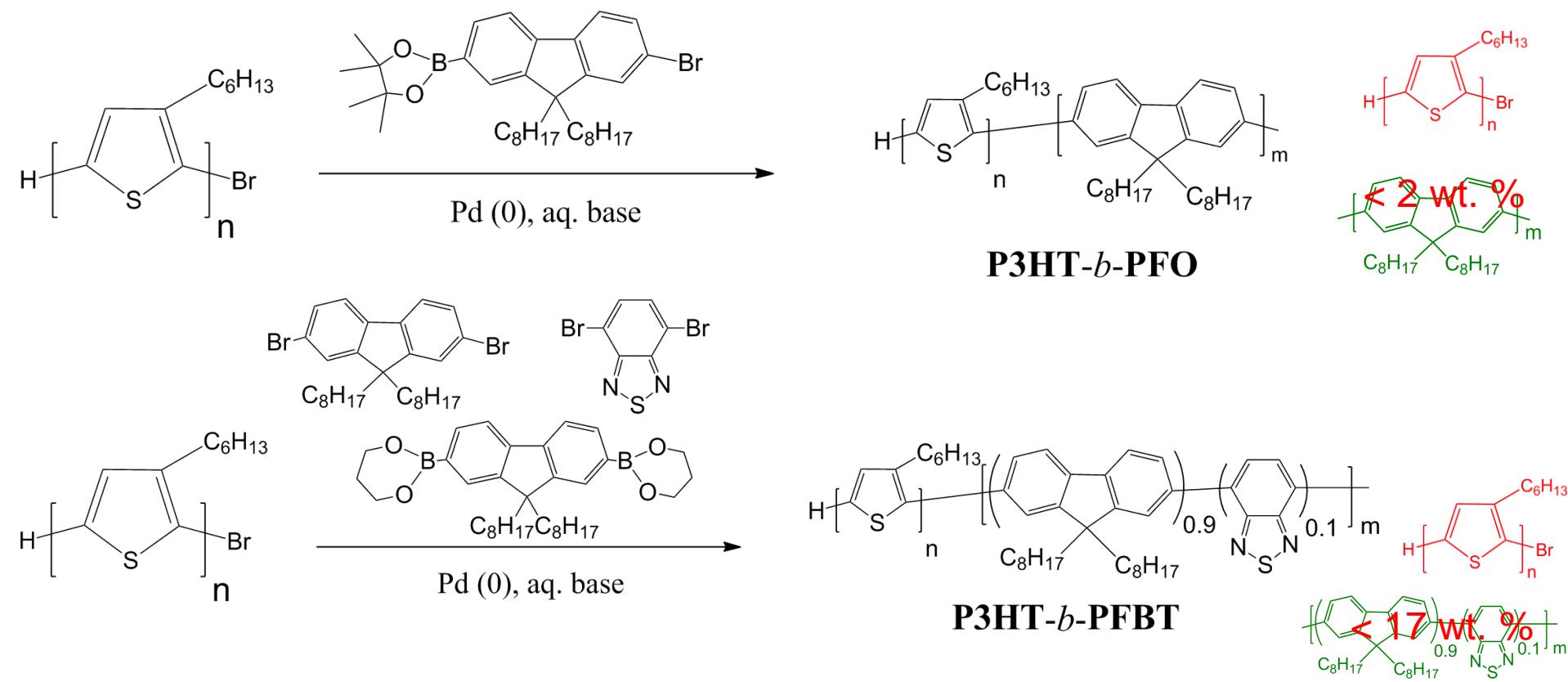
Ambipolar transport (n-type and p-type)

Synthesized via Suzuki polycondensation

Herguth et al., *Macromolecules*, **35**, 6094 (2002).

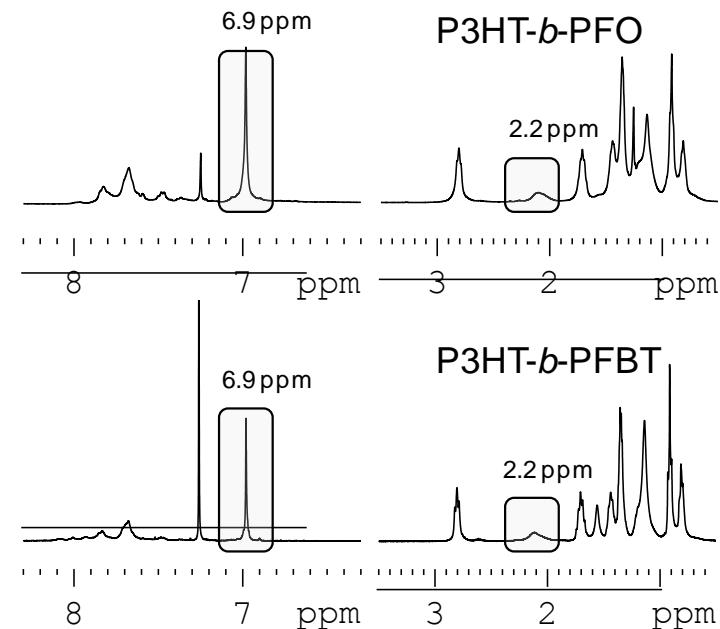
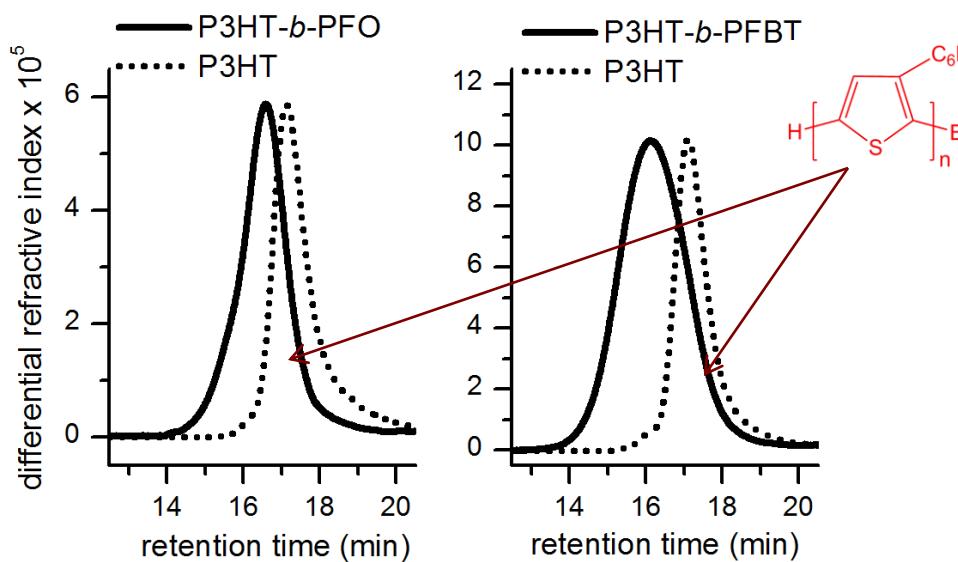
Poly(benzothiadiazole-co-9,9-dioctyl-fluorene) (**PFBT**)

Synthetic Strategy 1: Stepwise synthesis using GRIM polymerization followed by Suzuki polycondensation yields BCPs



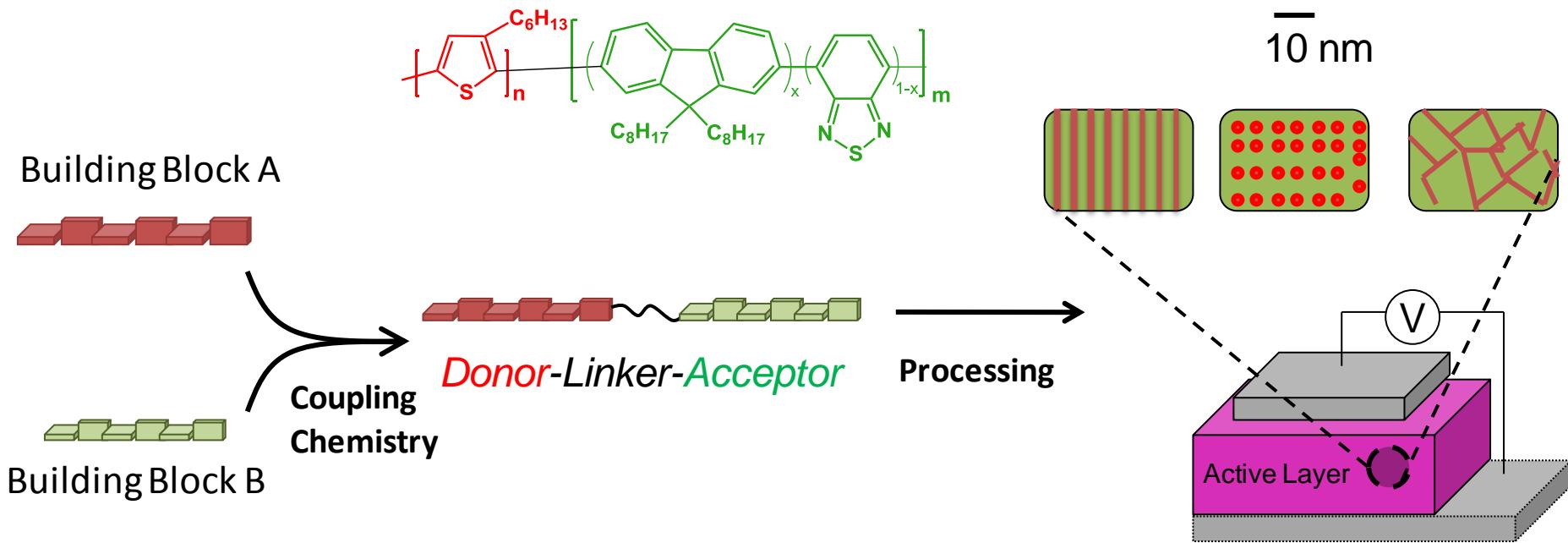
- Prepare P3HT macroreagent via Grignard Metathesis Polymerization
- Attach second polymer block by Suzuki polycondensation
- Remove homopolymer impurities by Soxhlet extraction and Silica Gel Column

Size-exclusion chromatography shows that BCP is the majority product



Polymer	Total MW	PDI	Mole Ratio NMR	Mass Ratio MALLS	Mole Ratio MALLS
P3HT	9900	1.1			
PFO	4900	1.6			
PFBT	3400	2.9			
P3HT- <i>b</i> -PFO	16700	1.3	4.1	1.5	3.4
P3HT- <i>b</i> -PFBT	18900	1.4	1.5	1.1	2.4

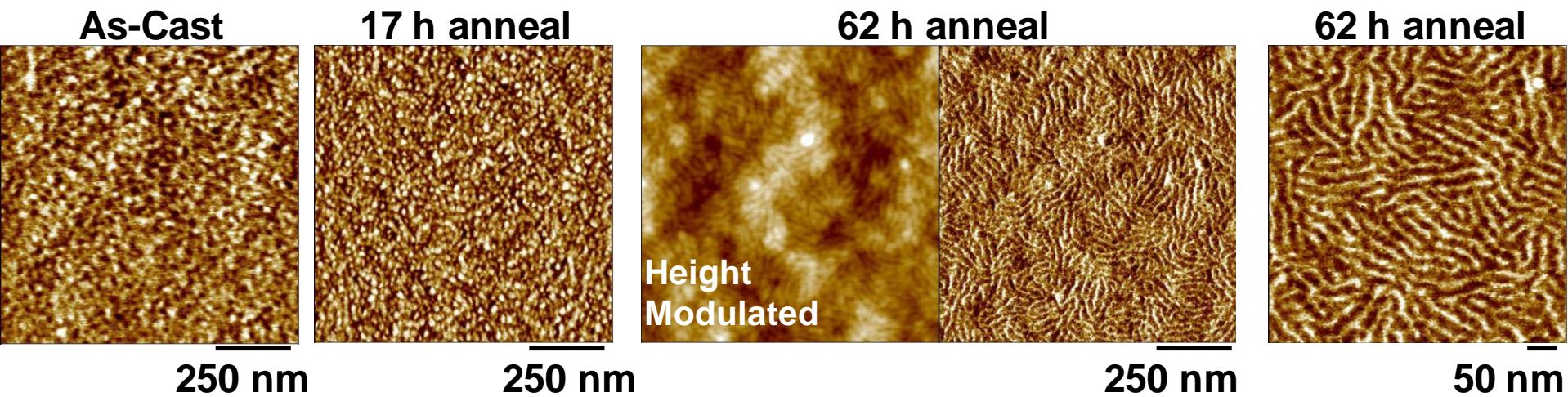
Self-Assembled Polymer Photovoltaics



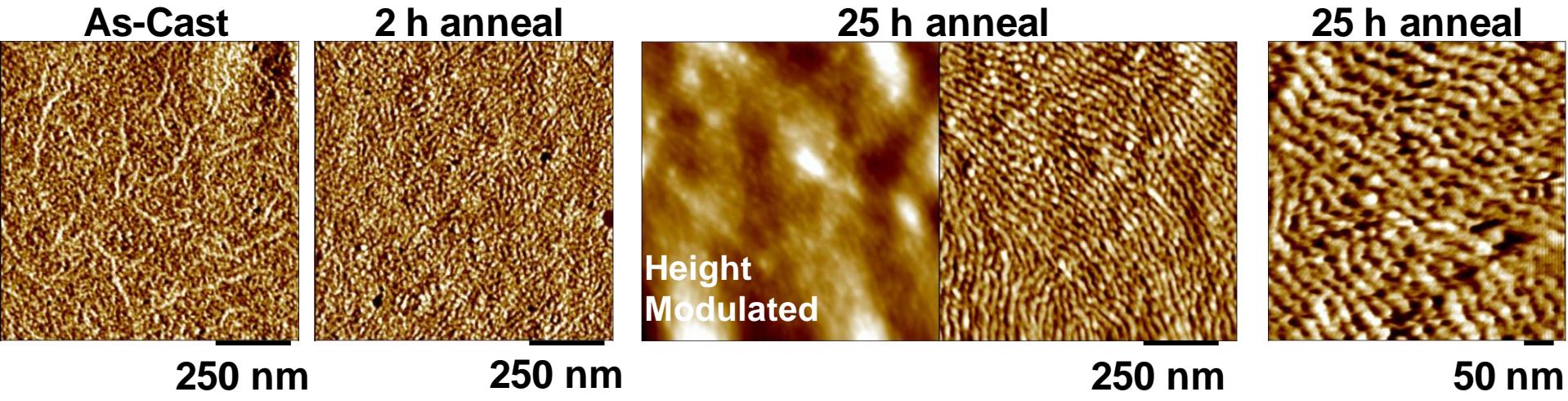
- Elucidate self-assembly of all-conjugated block copolymers
- **Investigate optoelectronic properties of nanostructured OPVs**
- Prepare high-performance polymer OPVs

AFM reveals the formation of a periodic nanostructure after extended annealing in the presence of solvent

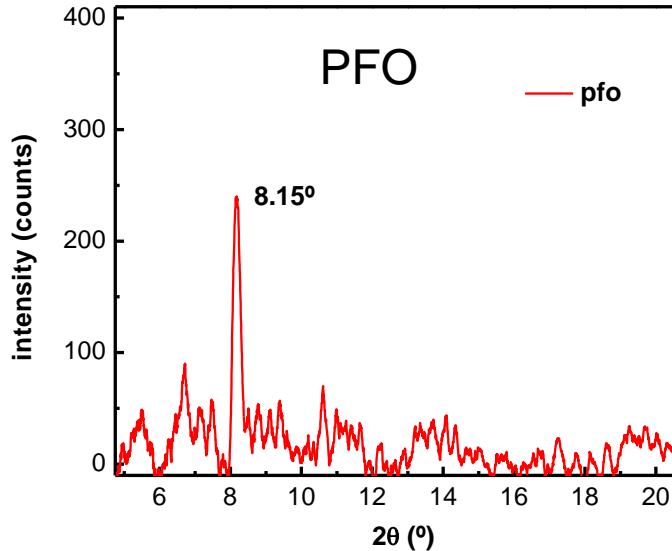
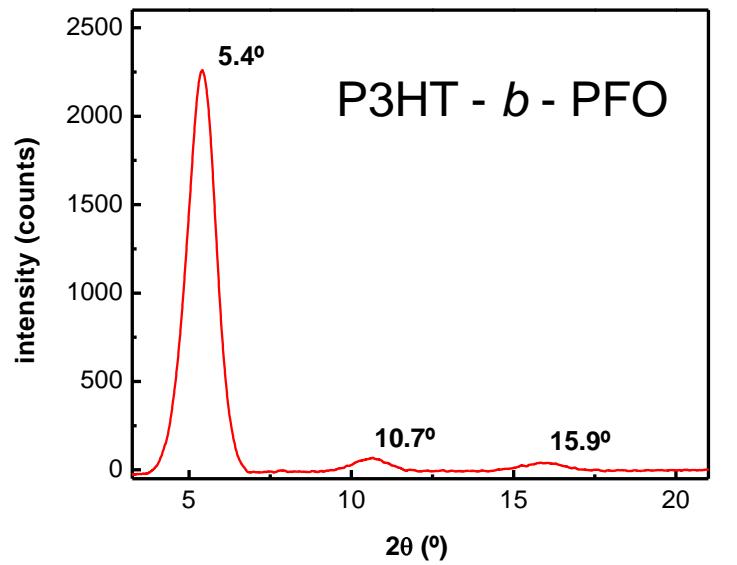
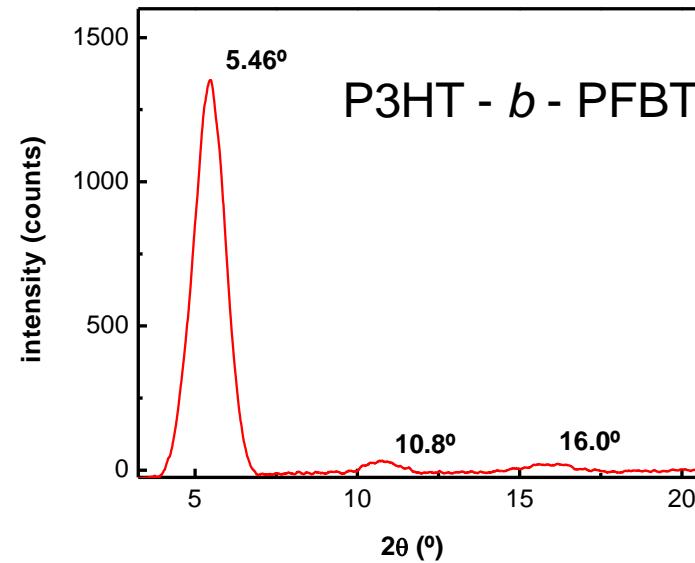
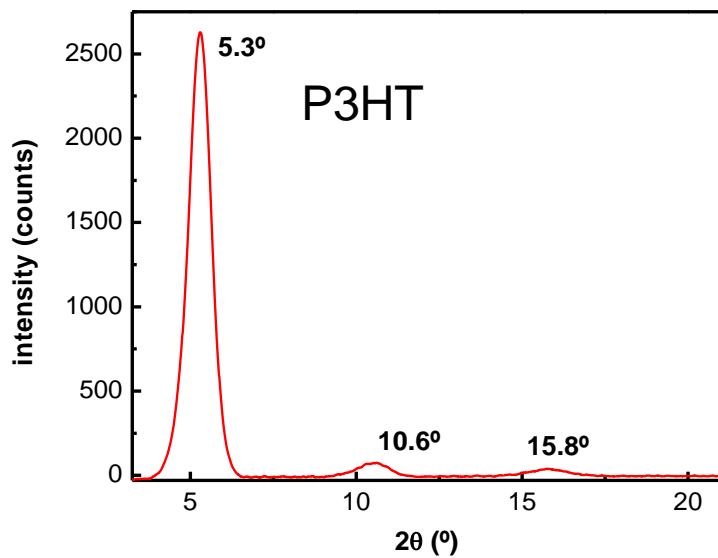
a) P3HT-*b*-PFO:



b) P3HT-*b*-PFBT:

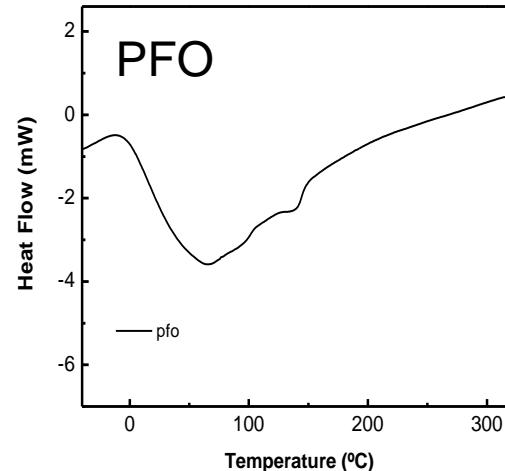
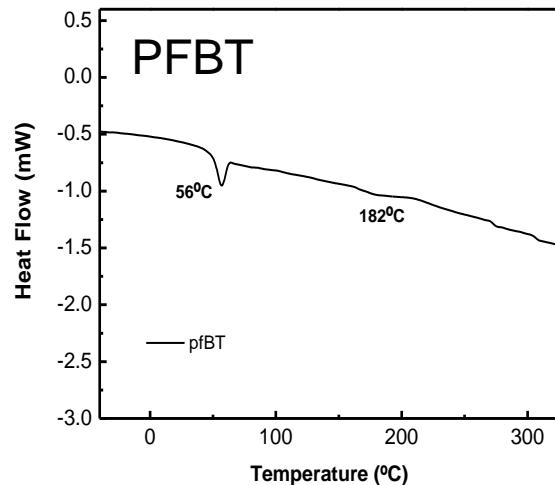
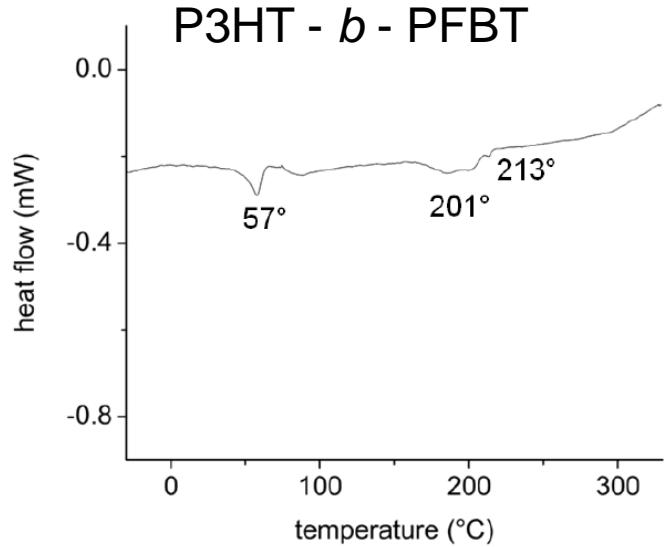
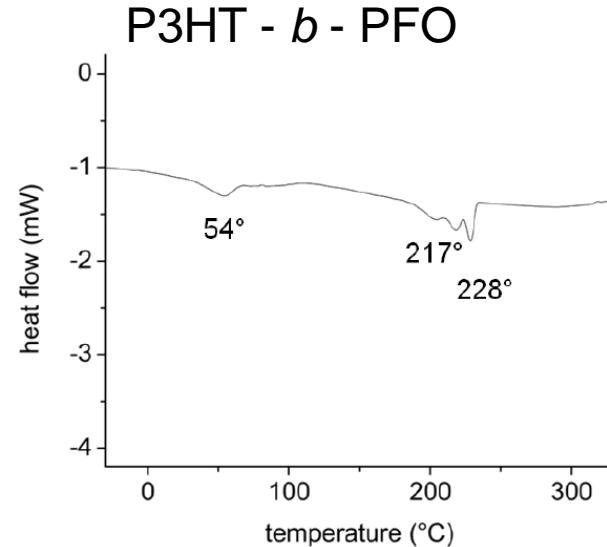
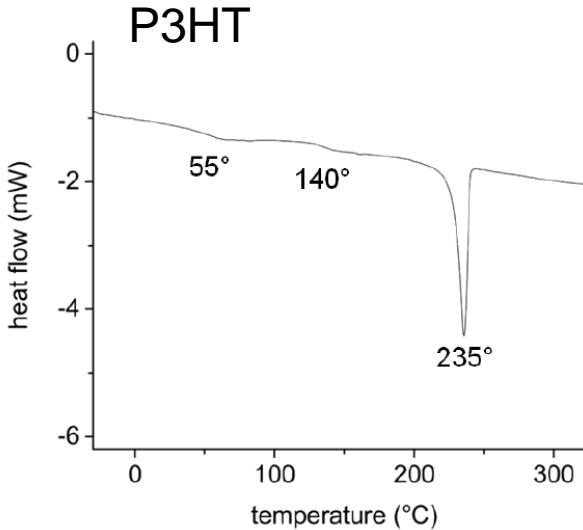


XRD indicates that only P3HT block crystallizes



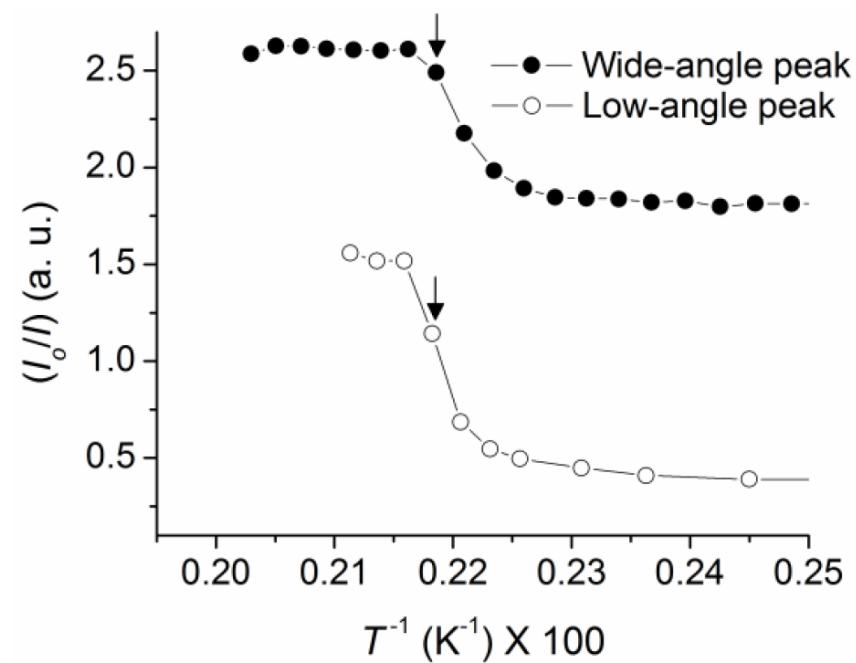
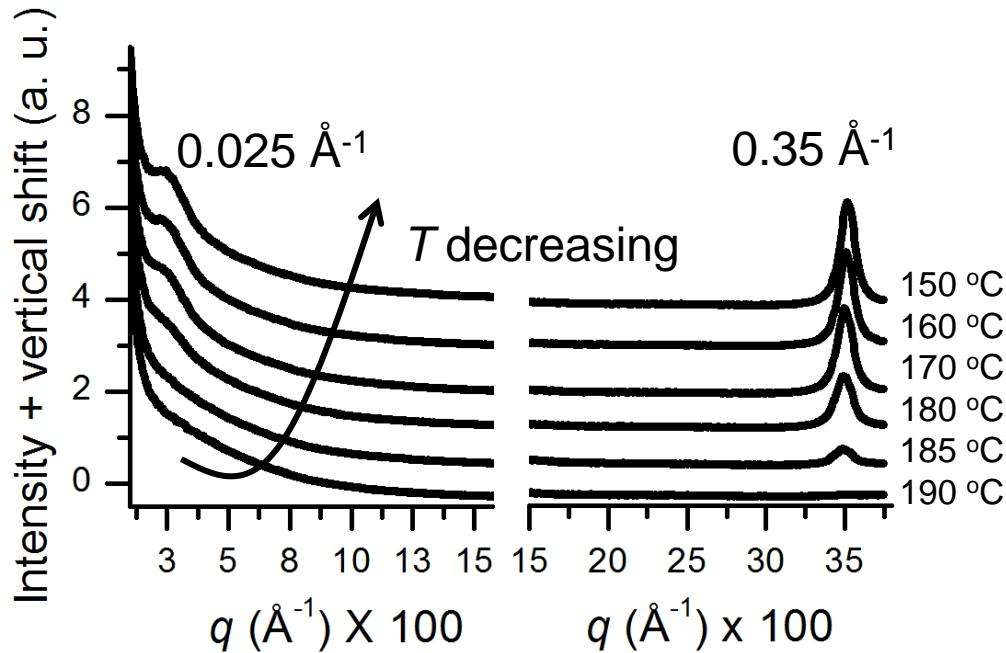
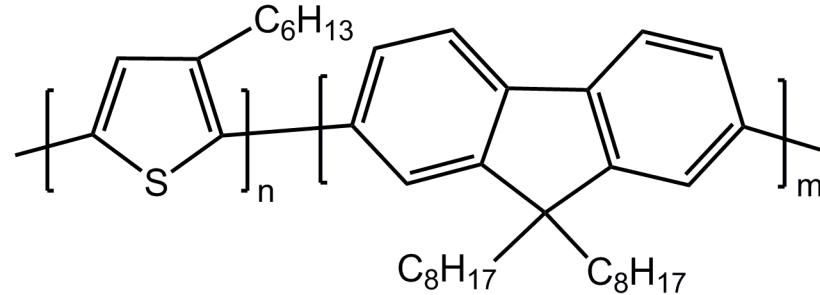
**No peaks
for PFBT
homopolymer
observed**

Thermal transition near 200 °C indicatie of P3HT crystallization



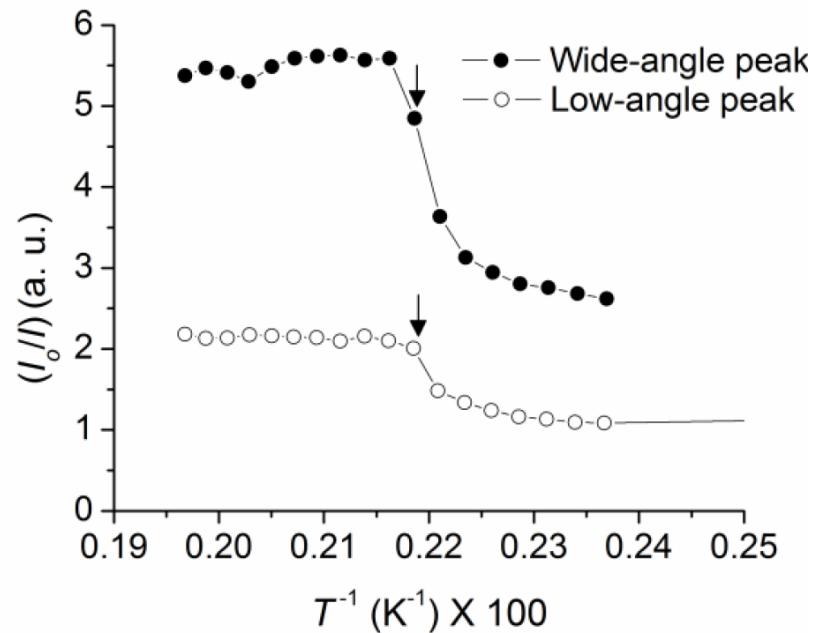
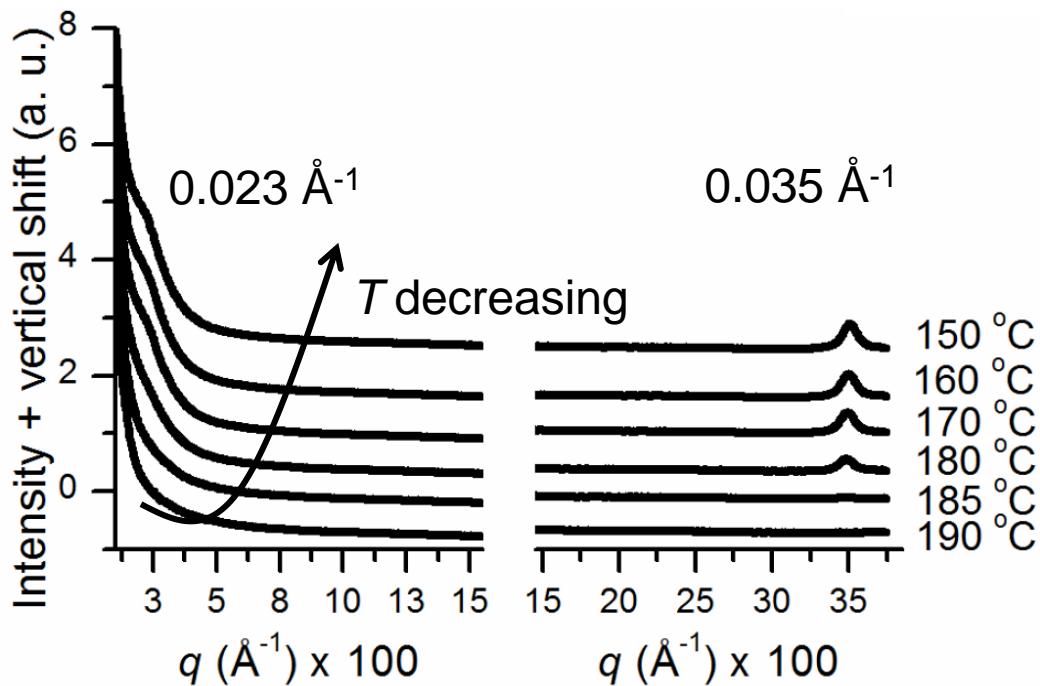
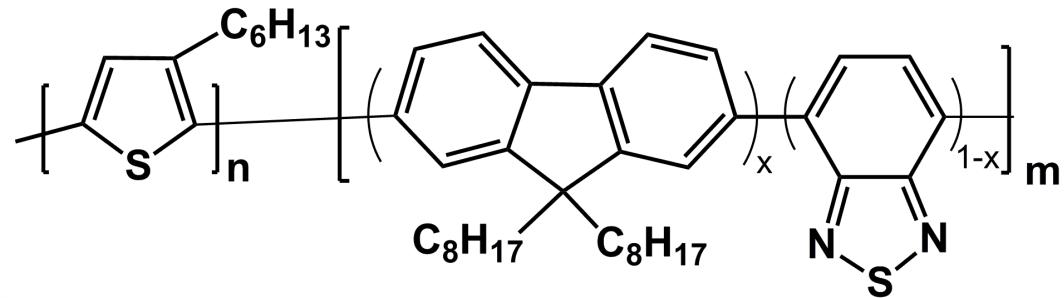
SAXS measurements show simultaneous nanostructure formation and crystallization

P3HT-*b*-PFO



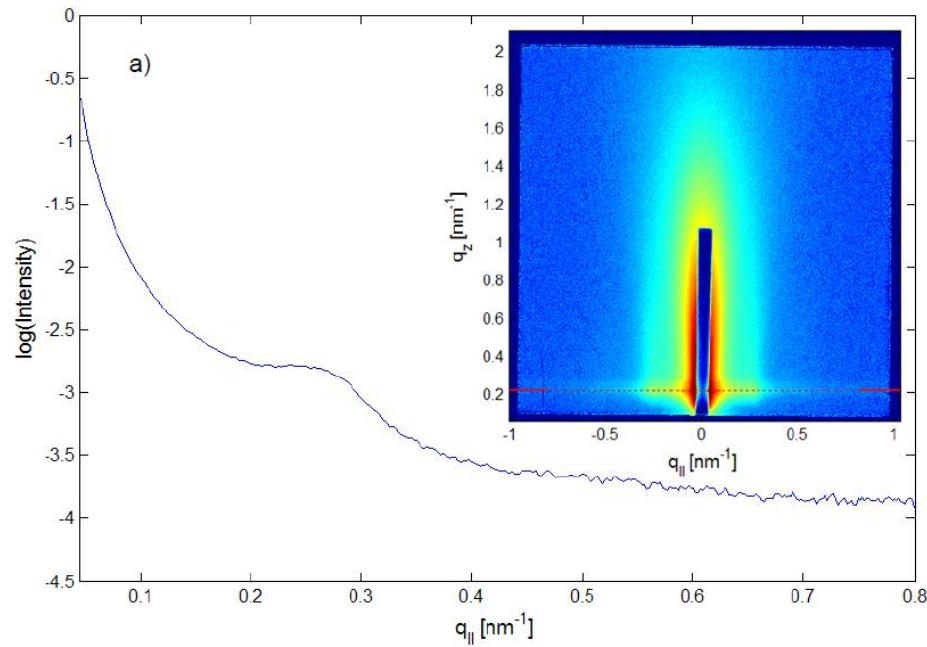
SAXS measurements show simultaneous nanostructure formation and crystallization

P3HT-*b*-PFBT

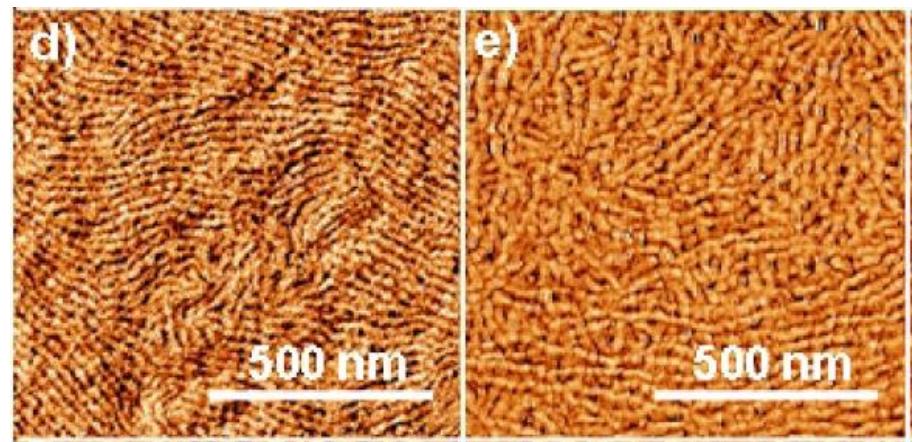


Pure RR-P3HT shows low-angle SAXS peak and nanostructured thin films via AFM

7 kDa RR-P3HT

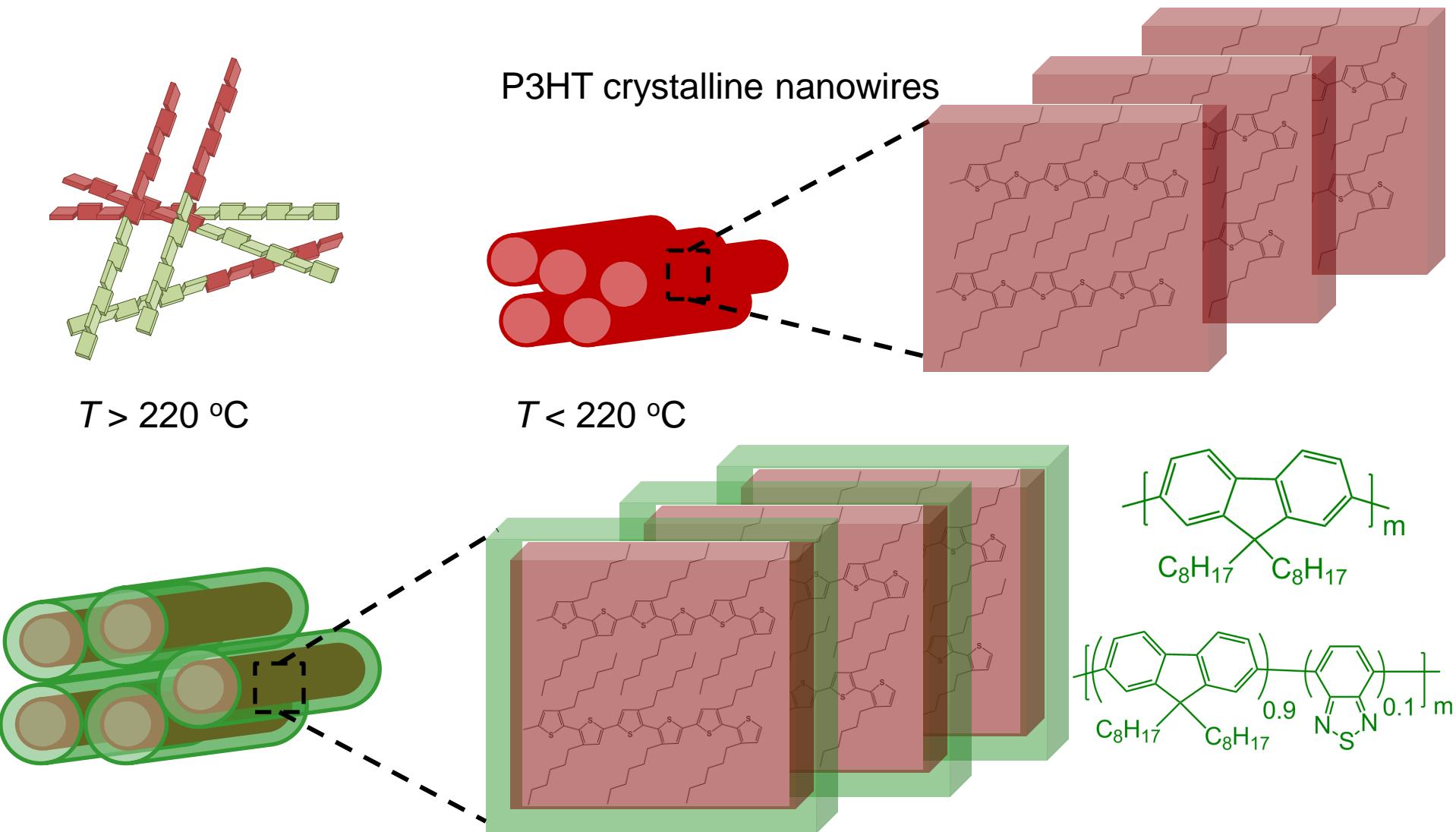


7.0 kDa RR-P3HT 7.5 kDa RR-P3HT



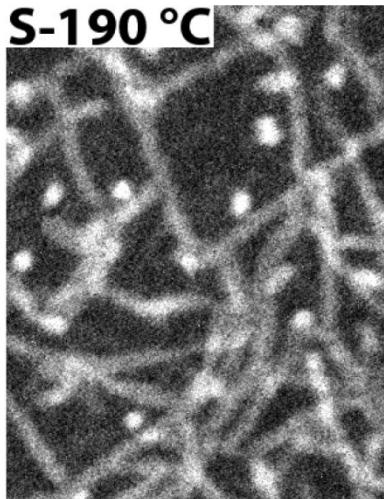
McCullough, R. D.; Kowalewski, T. *Journal of the American Chemical Society* **2006**, *128*, 3480

P3HT crystallization drives self-assembly of all-conjugated block copolymers

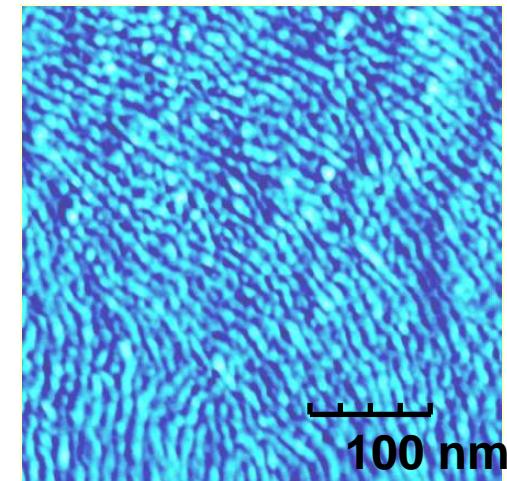
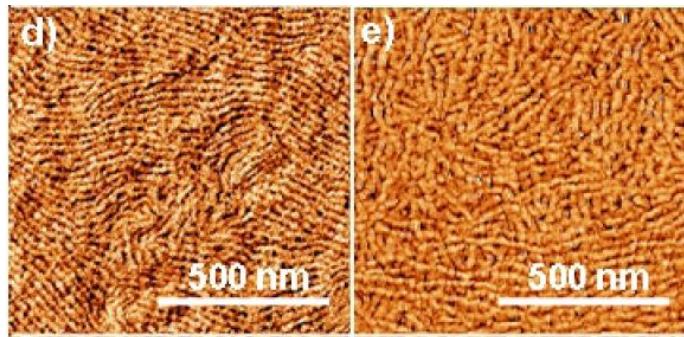


Crystallization in P3HT bulk heterojunctions

S-190 °C



7.0 kDa RR-P3HT 7.5 kDa RR-P3HT



Gomez, et al. *Macromolecules*
2011, 44, 5722.

McCullough, R. D et al., *J. Am. Chem. Soc.* **2006, 128, 3480**

Verduzco, et al. *Macromolecules*
2011, 44, 530.

Long-range repulsion:

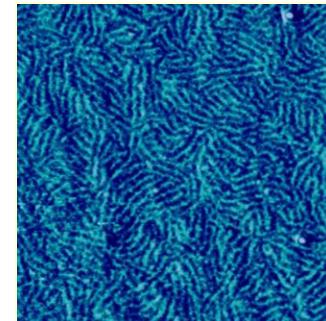
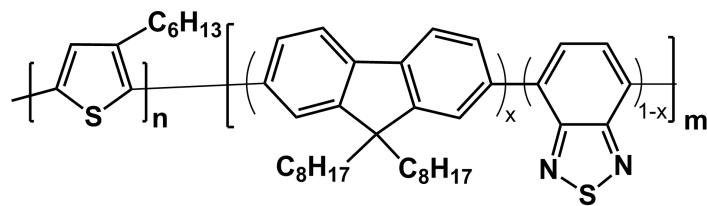
$$F_{repulsion} \sim \chi \phi_A \phi_B$$

χ Decreases with increasing temperature

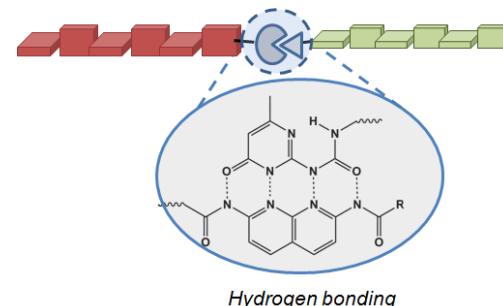
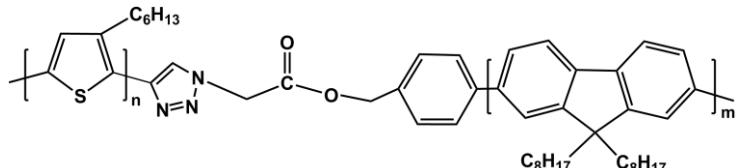
Need lower T_c polymers or higher χ

Outline

- Synthesis and self-assembly of all-conjugated P3HT-PFO block copolymers

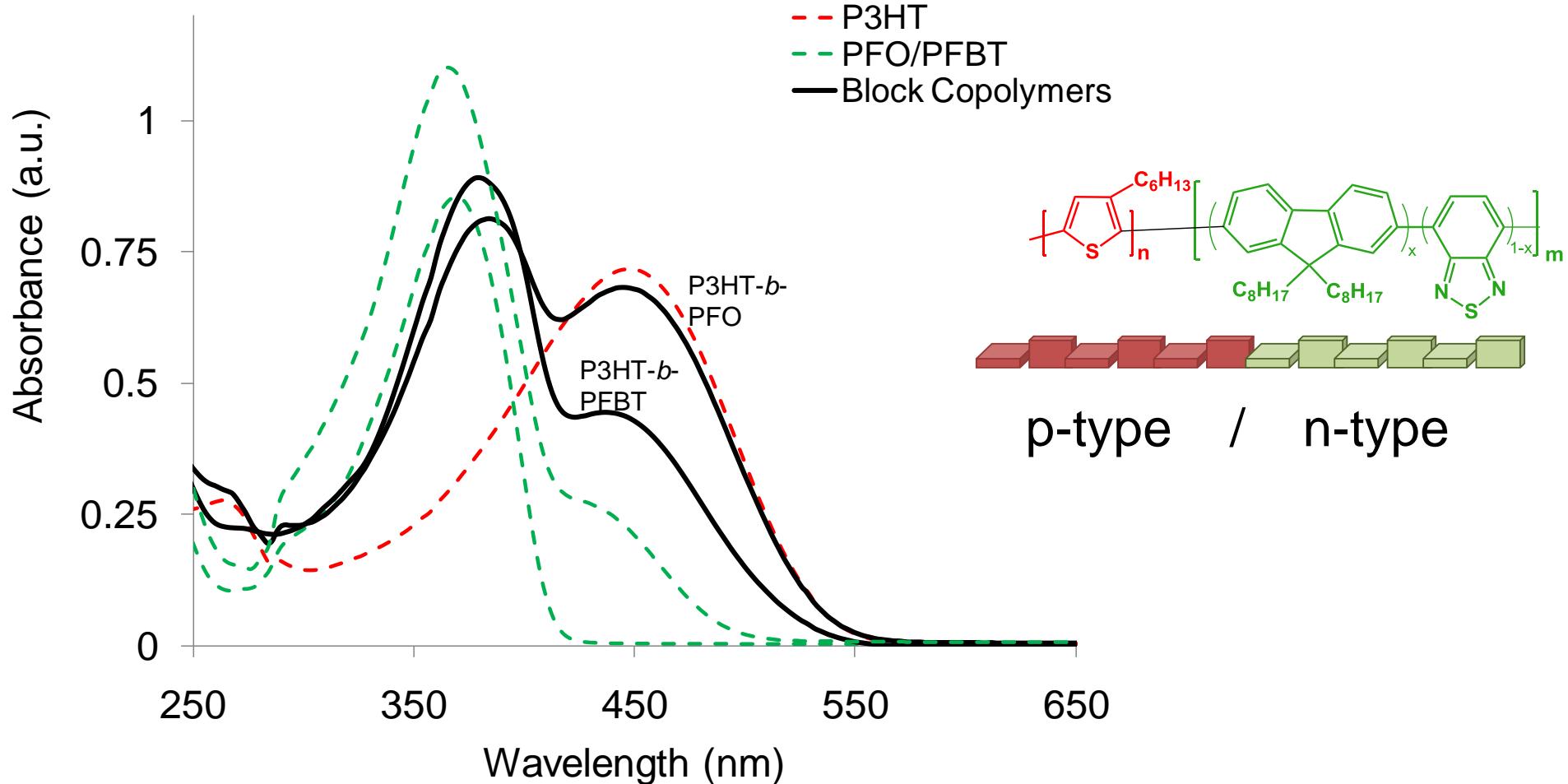


- Optical characterization studies of all-conjugated block copolymers
- “Click” coupling strategy and “Pseudo” block copolymers

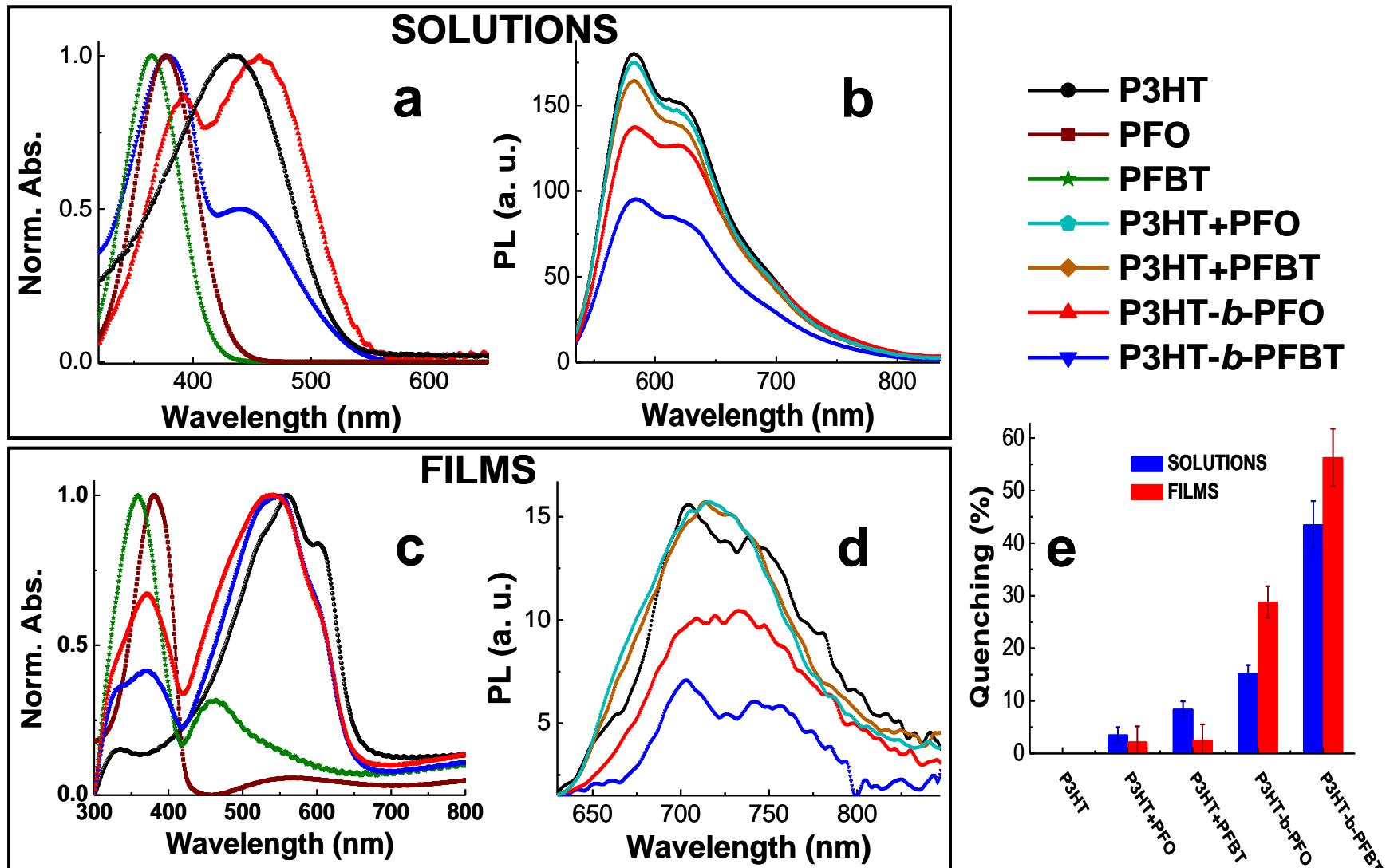


BCP absorbance is a superposition of that of the separate polymer blocks

Solution absorbance measurements in tetrahydrofuran

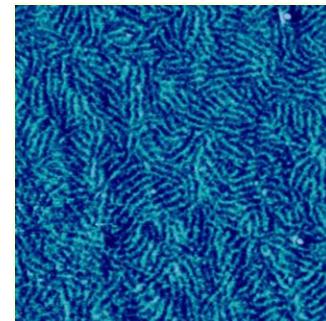
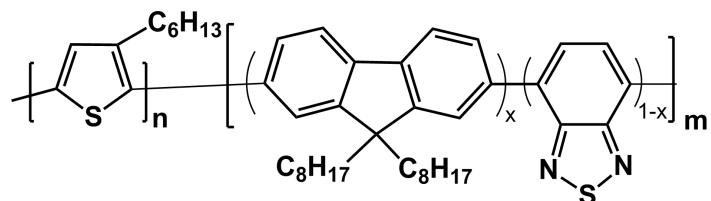


Block copolymer films exhibit enhanced fluorescence quenching compared to homopolymer blends

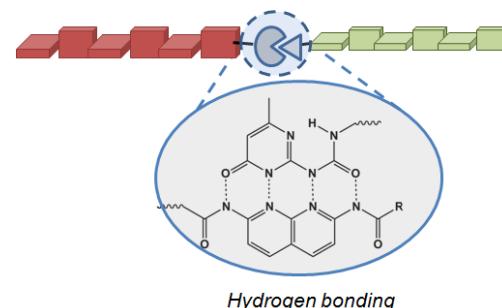
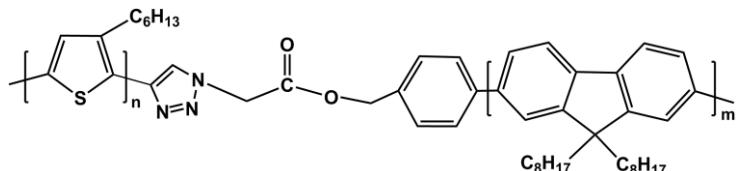


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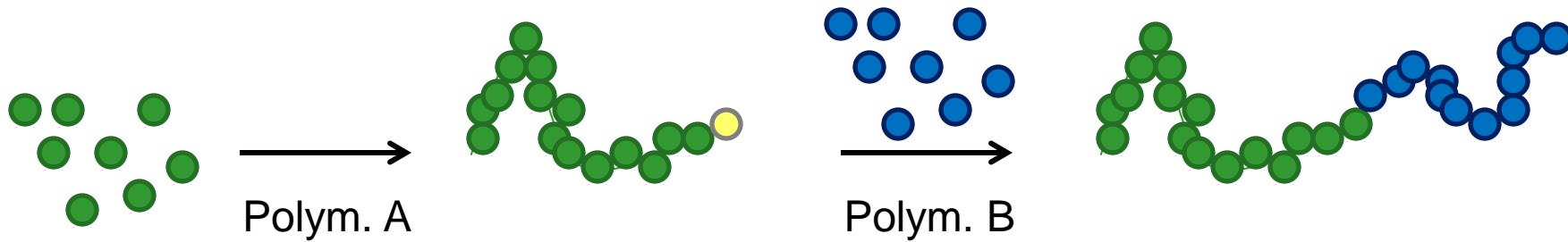


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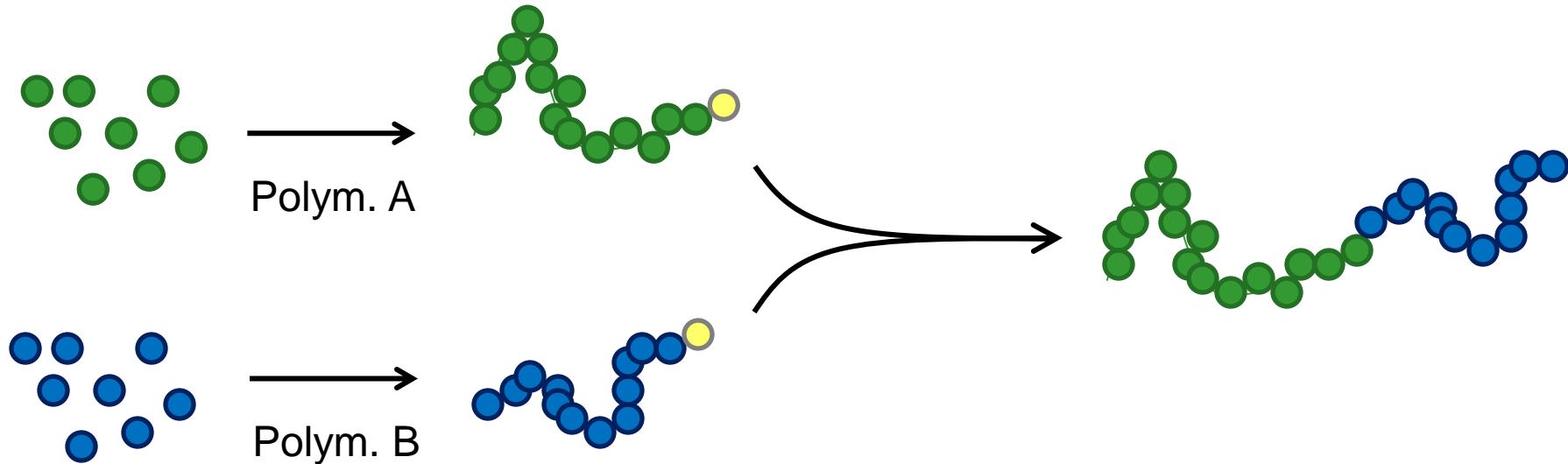


General approaches to block copolymer synthesis

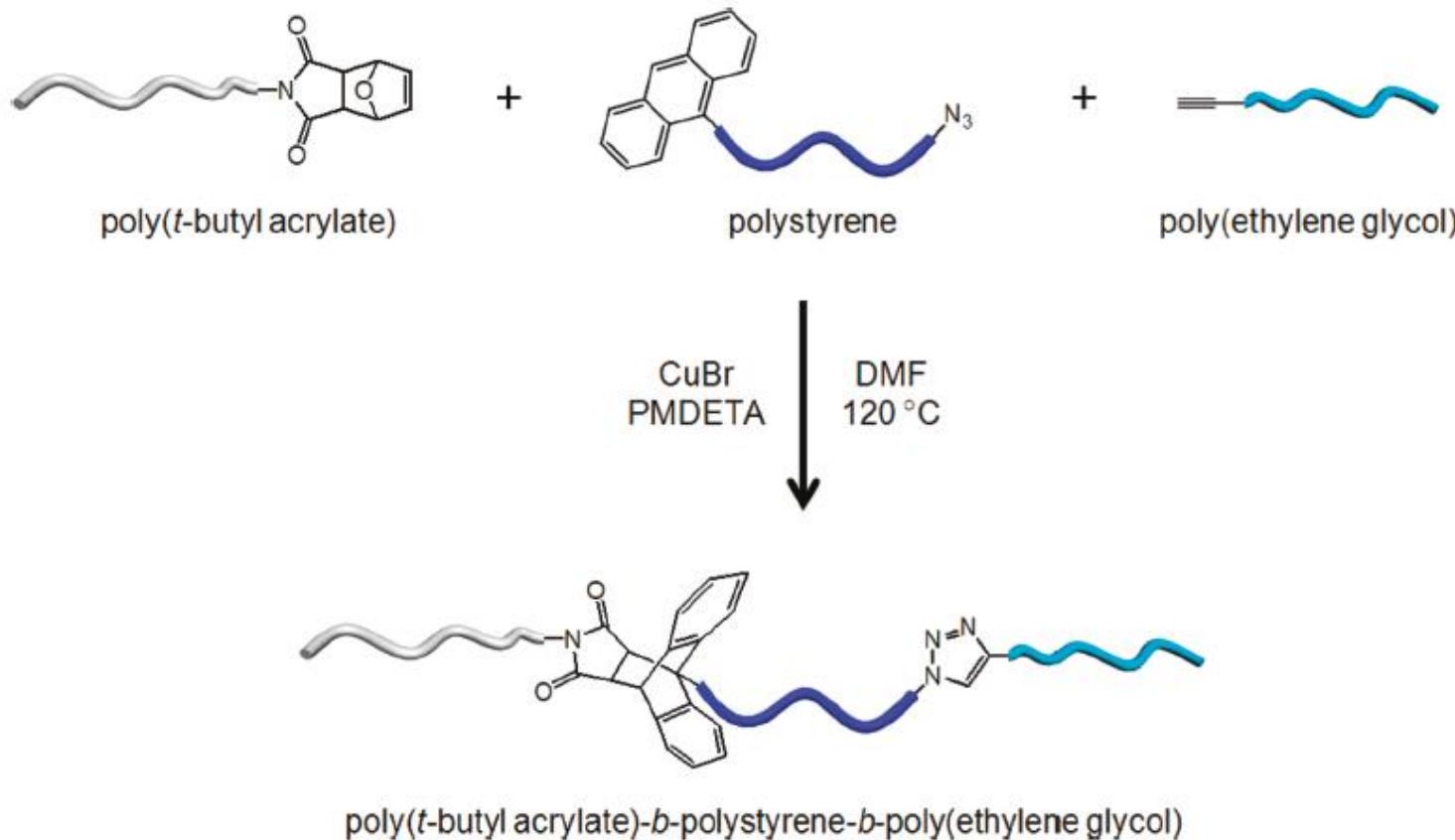
Sequential Monomer Addition



Macroreagent Approach

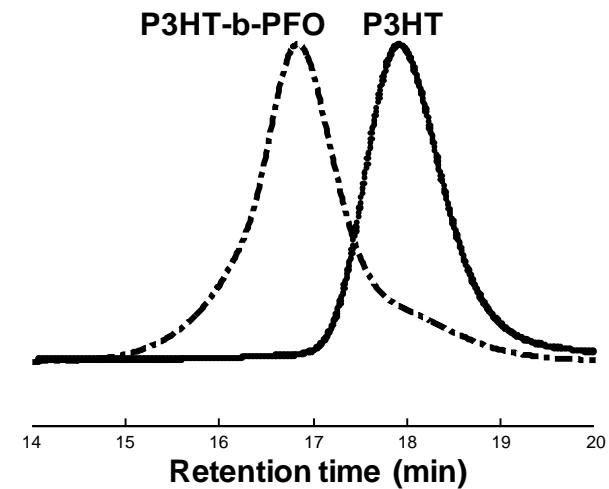
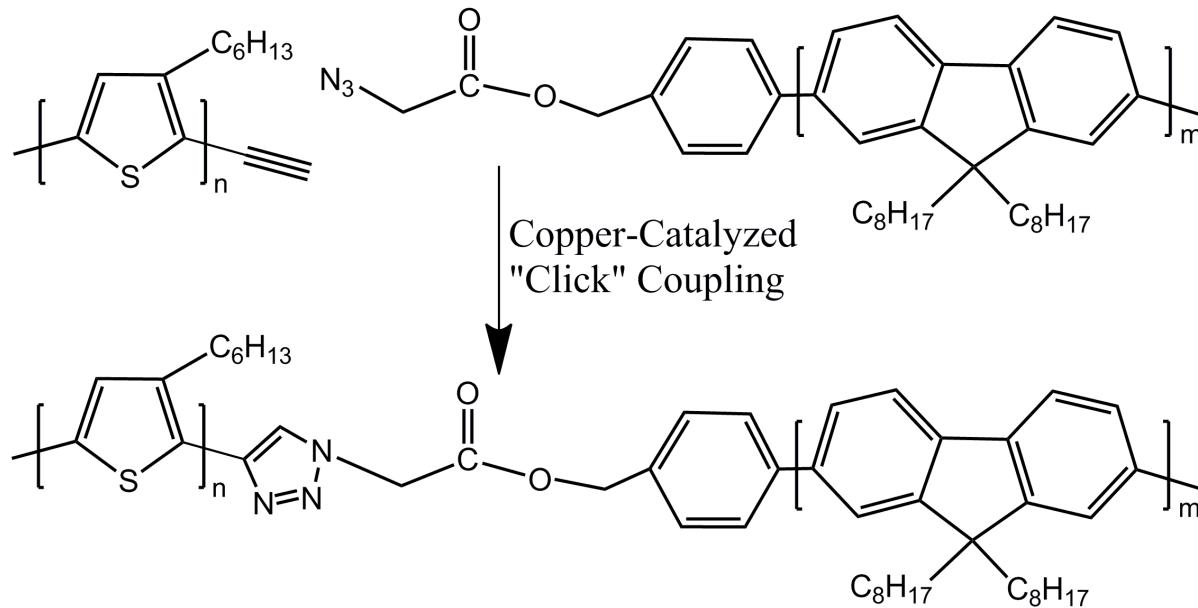


“Click” chemistry enables efficient coupling of polymer chains



Sumerlin et al., *Macromolecules* 2010, **43**, 1.

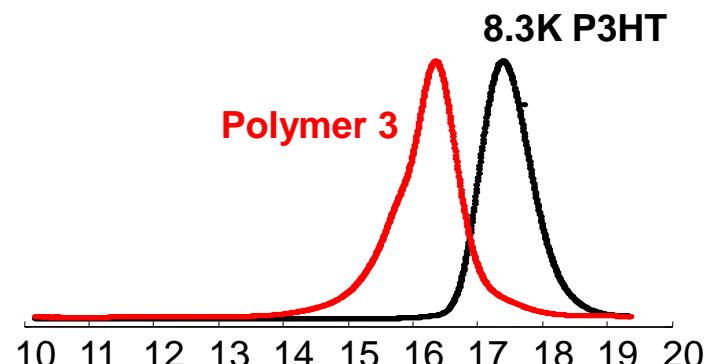
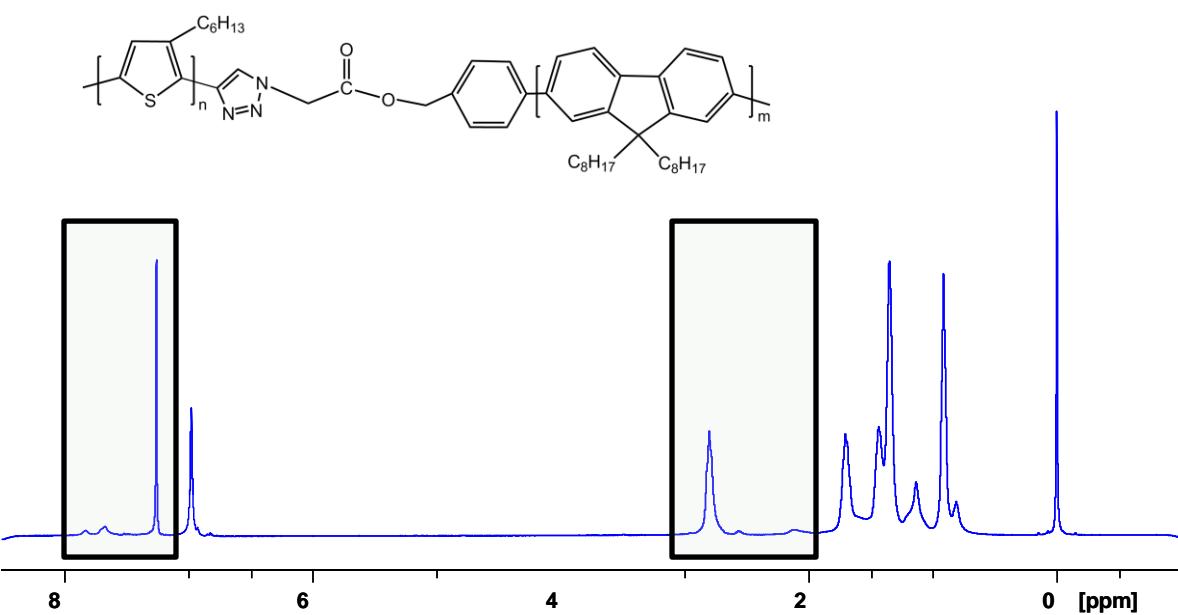
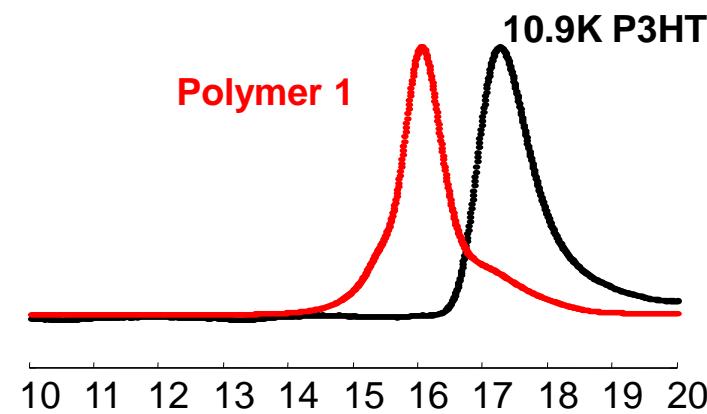
Synthetic Strategy 2: Click Coupling of end-functionalized homopolymers



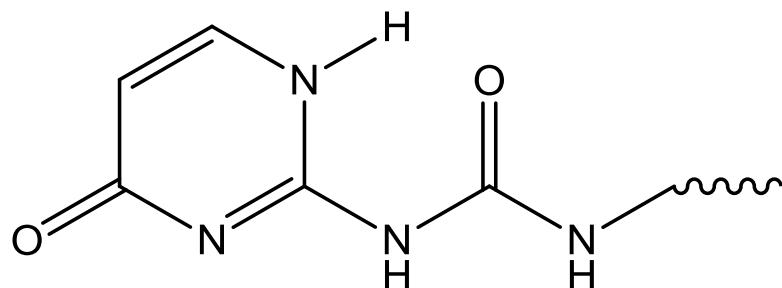
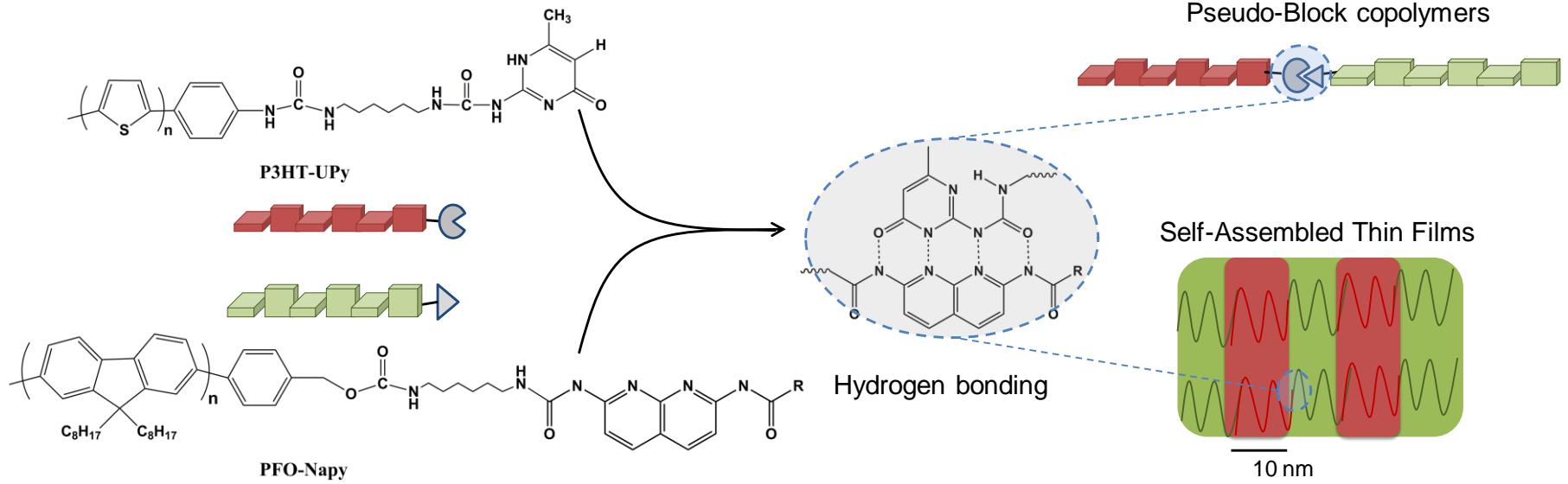
- Control over MW and PDI of each block; can explore larger MW
- Excellent coupling efficiency – avoid homopolymer impurities
- Enables the preparation of model rod-rod block copolymers

Click coupling strategy for systematic series of all-conjugated block copolymers

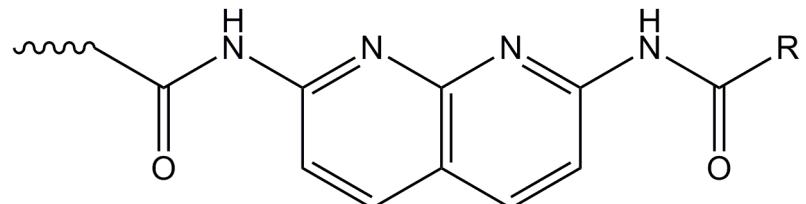
Polymer	P3HT		PFO		P3HT-b-PFO	
	M_w	PDI	M_w	PDI	M_w	PDI
1	8.3	1.1	7.6	1.3	15.7	1.27
2	8.3	1.1	29.2	2.0	23.4	1.25
3	10.9	1.3	7.6	1.3	18.7	1.20
4	10.9	1.3	29.2	2.0	27.2	1.36



Physical associations enable the preparation of pseudo-block copolymers



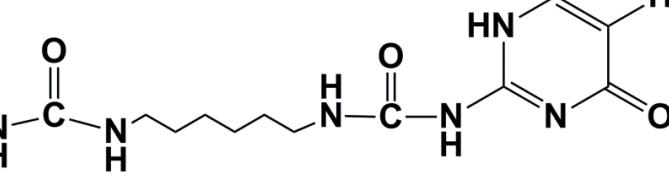
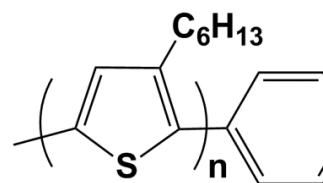
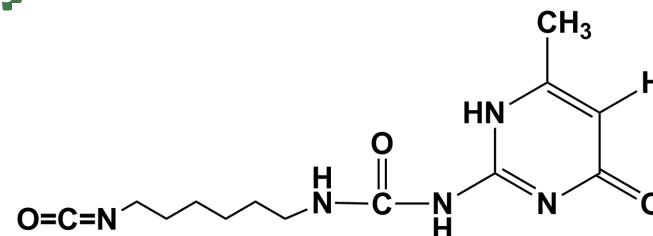
Upy = 2-ureido-4[1H]-pyrimidinone



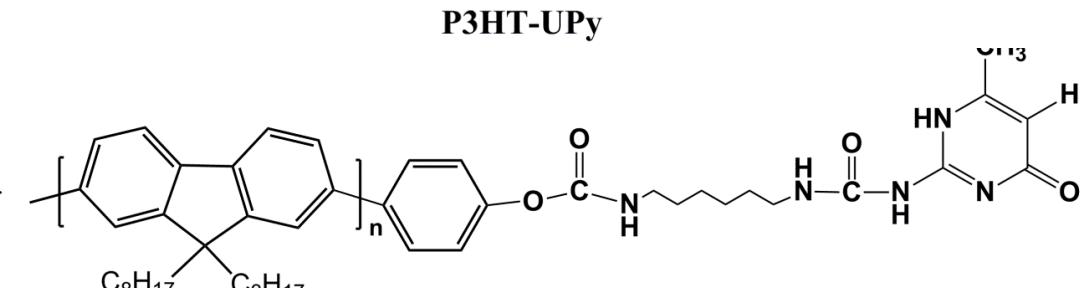
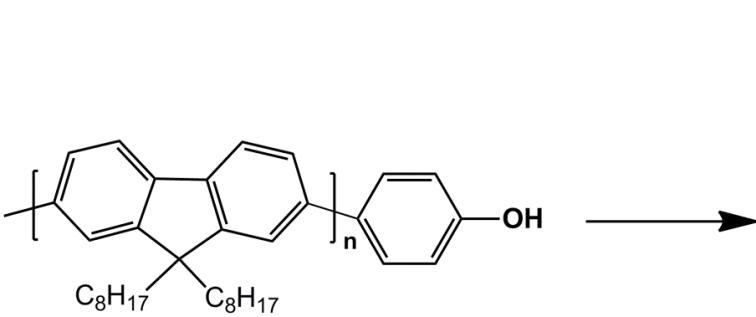
Napy = 2,7-diamido-1,8-naphthyridine

Synthetic Strategy 3: Physical associations for pseudo-block copolymers

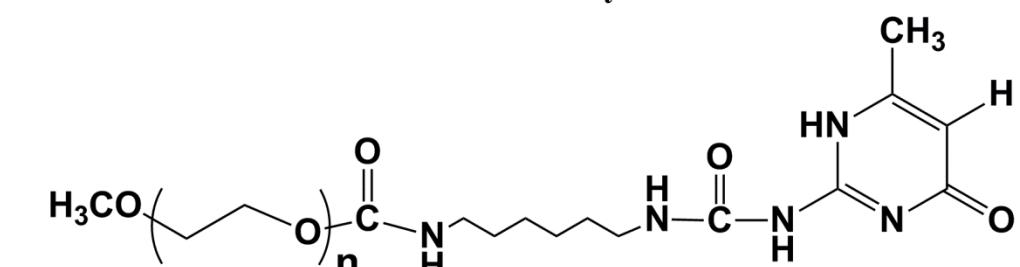
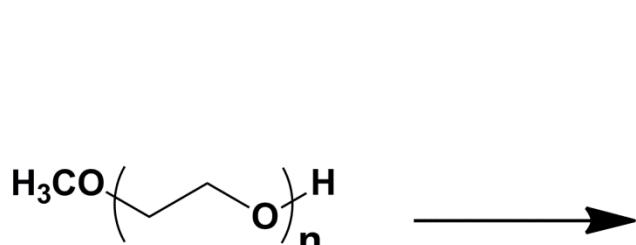
Isocyanate functionalized Upy:



P3HT-UPy

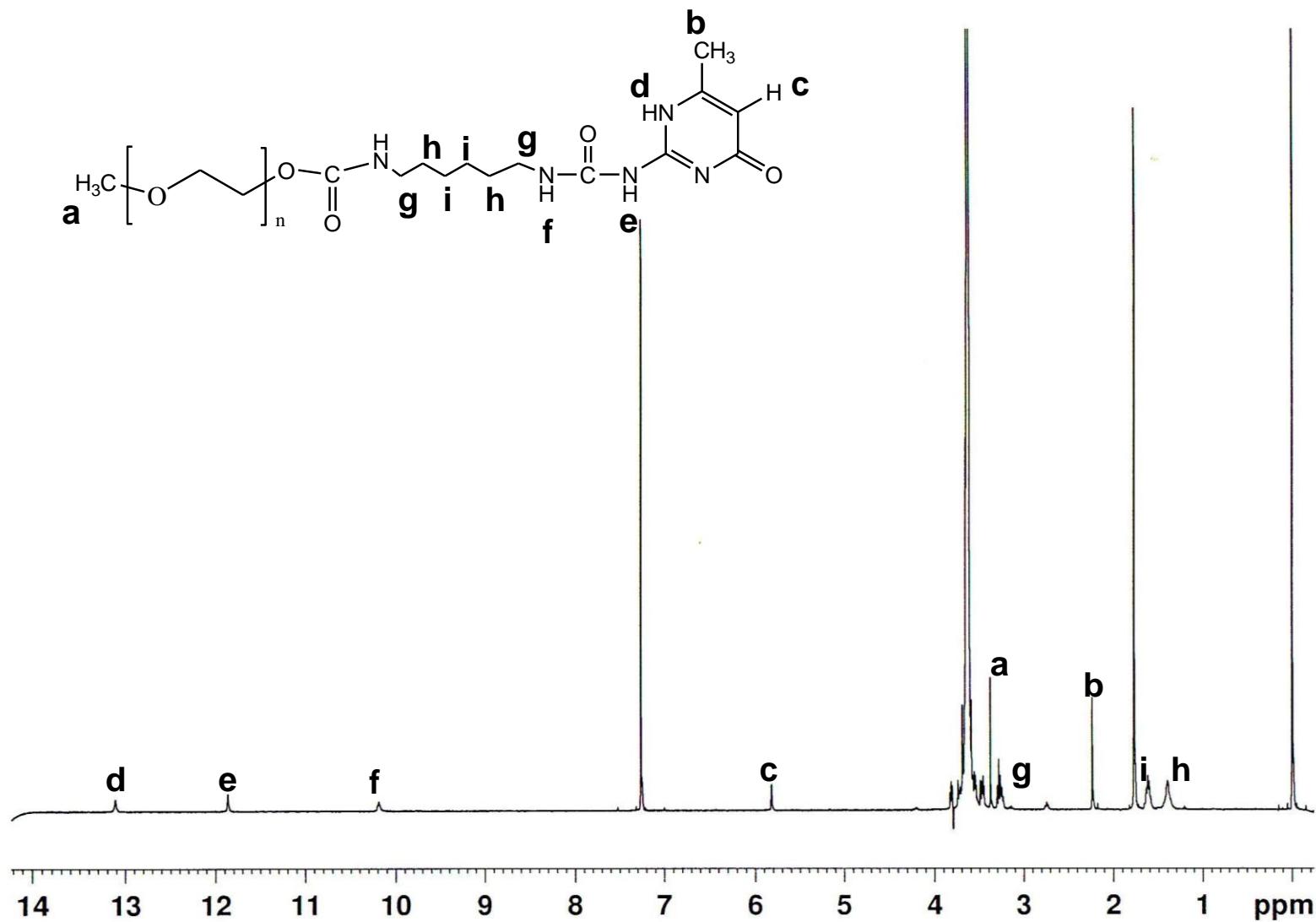


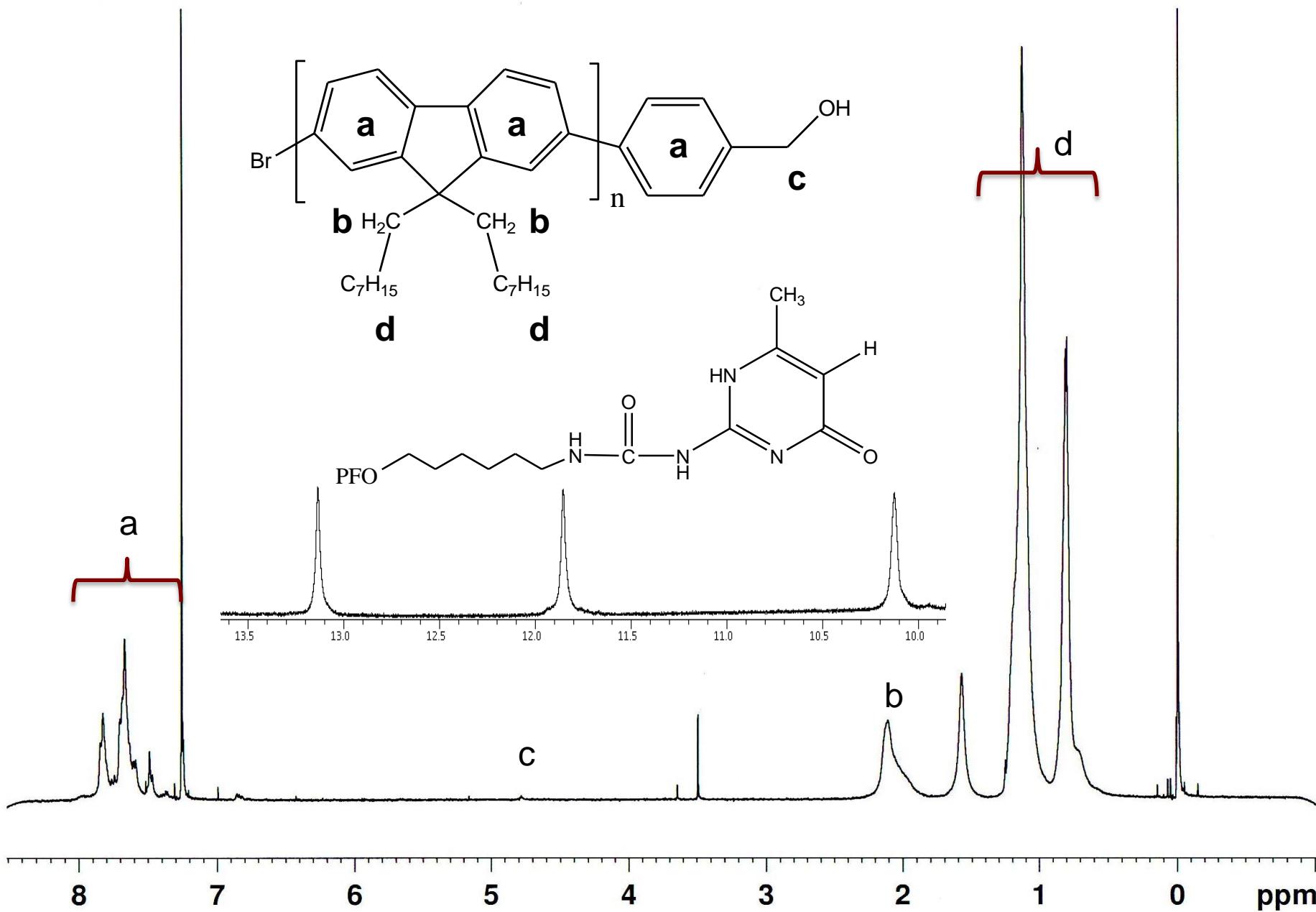
PFO-UPy

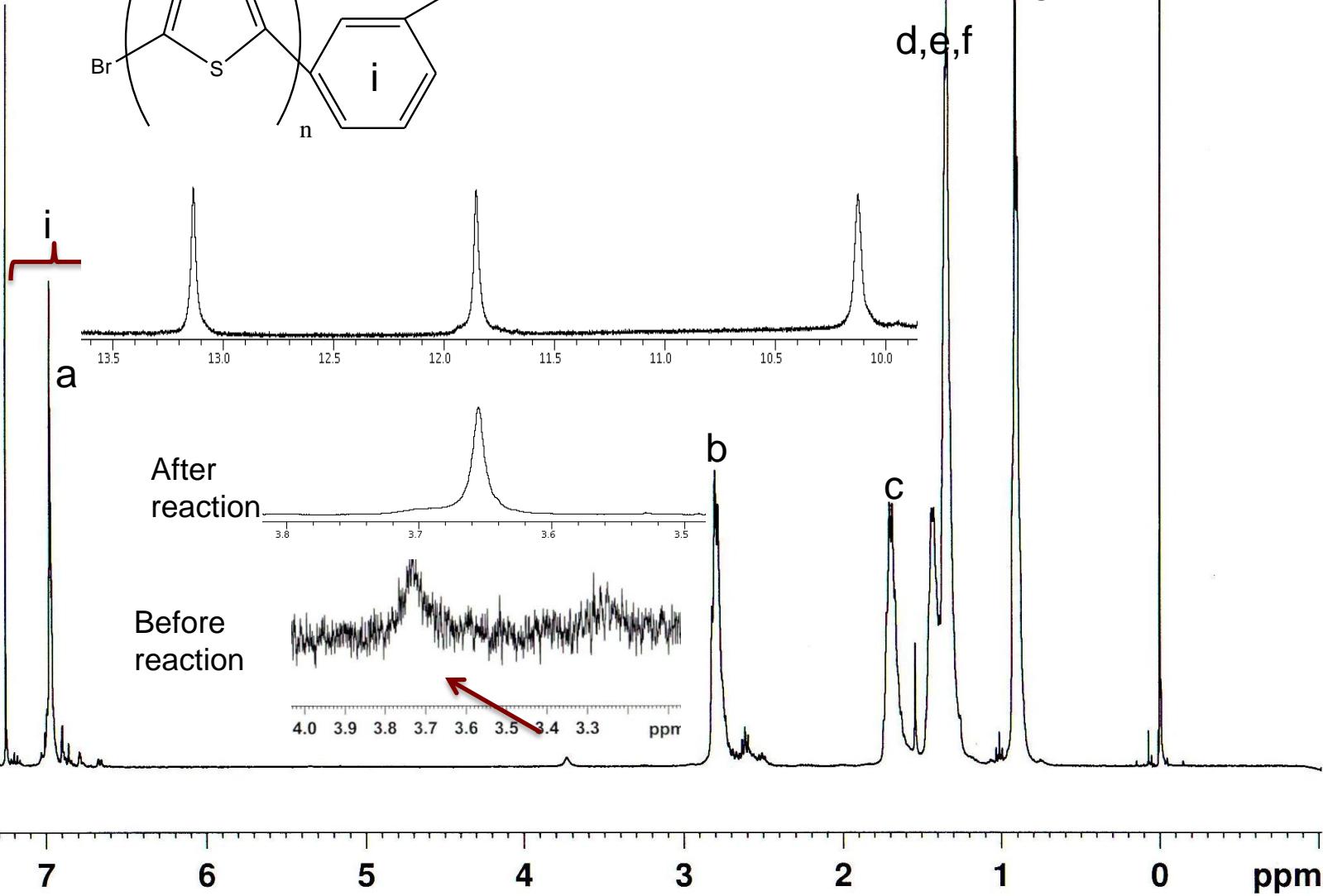
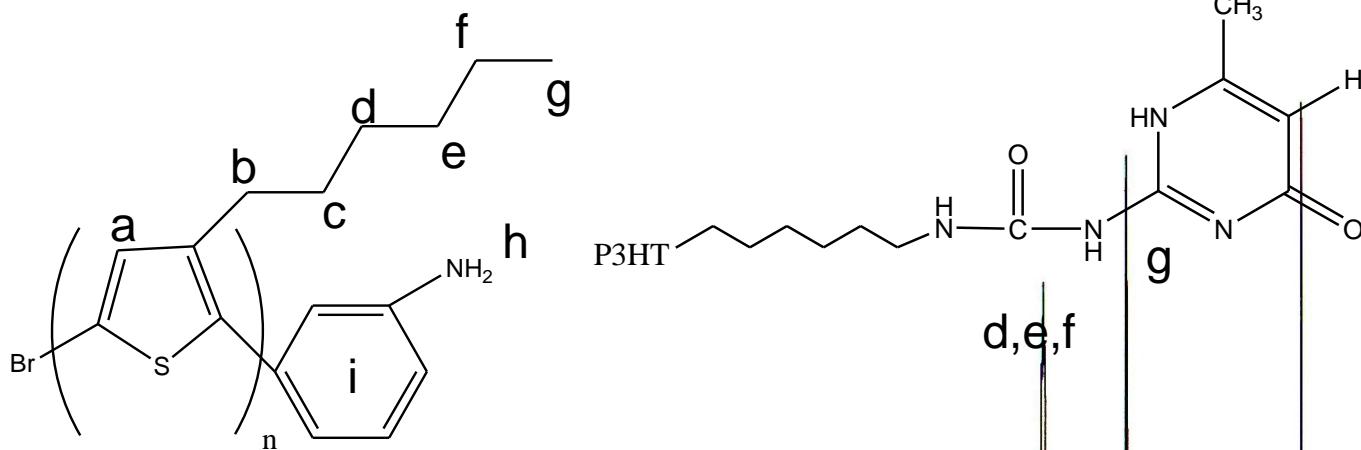


PEG-UPy

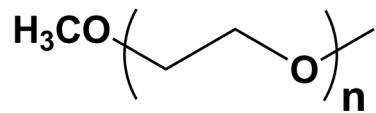
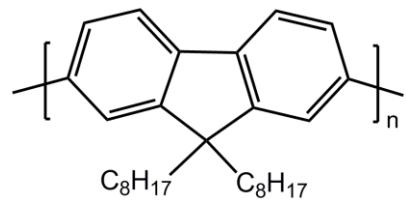
^1H NMR shows successful Upy end-functionalization



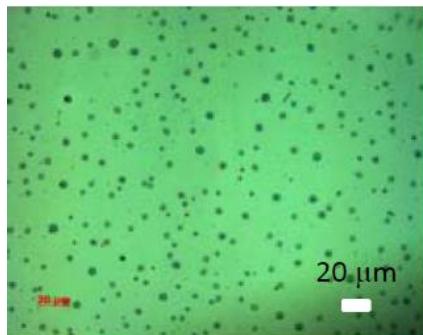




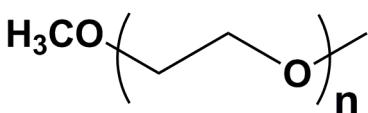
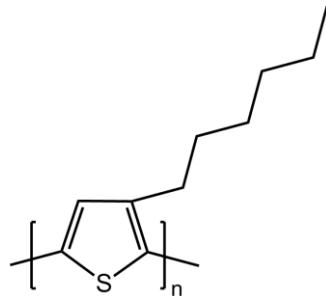
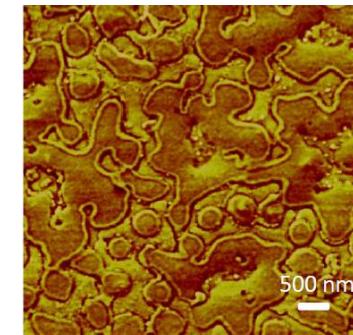
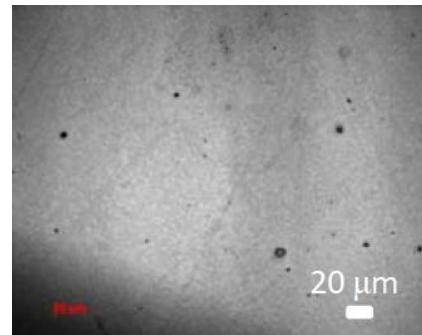
Hydrogen bonding interactions decrease rate of phase separation and reduce large-scale phase separated domains



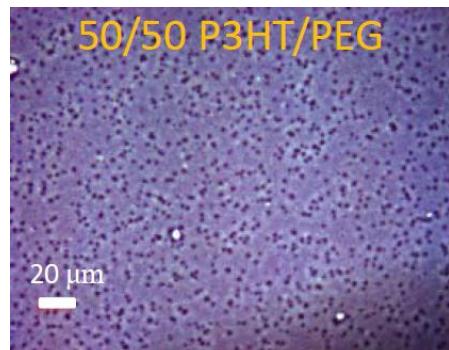
PEG/PFO Blend



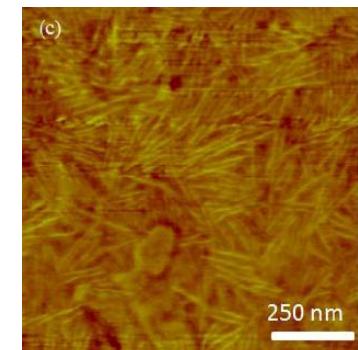
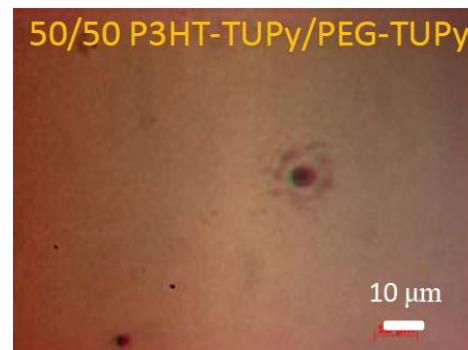
PEG-UPy/PFO-UPy Blend



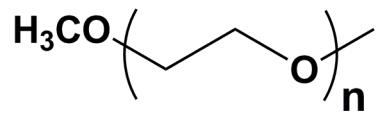
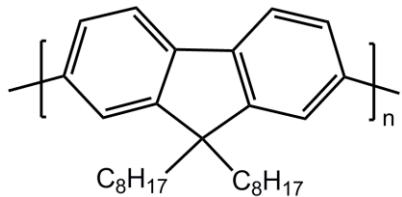
PEG/P3HT Blend



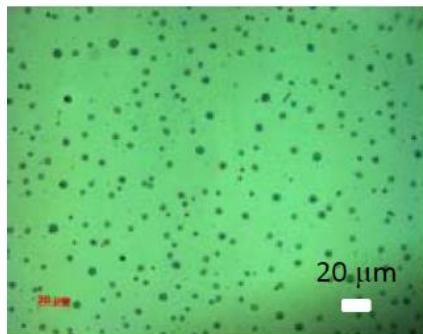
PEG-UPy/P3HT-UPyBlend



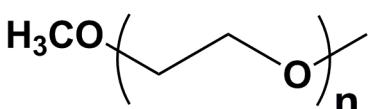
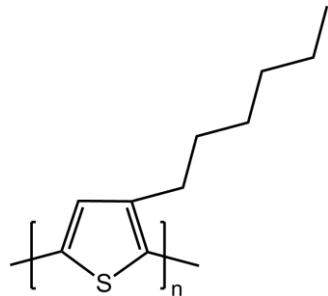
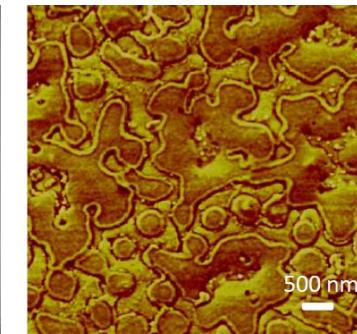
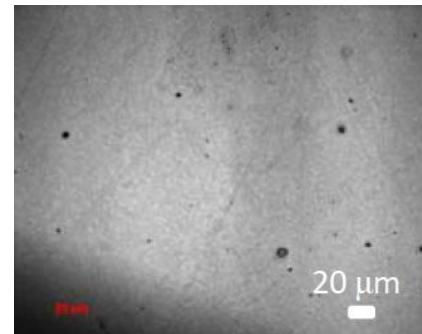
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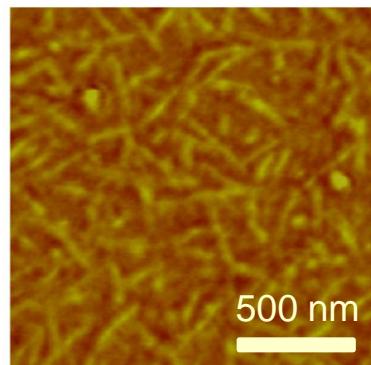
PEG/PFO Blend



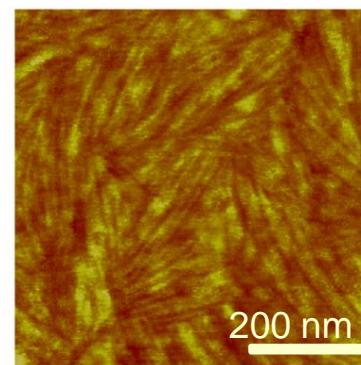
PEG-UPy/PFO-UPy Blend



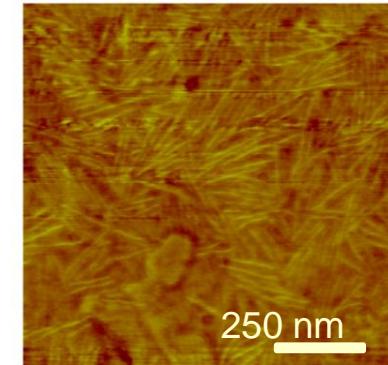
P3HT-NH₂



P3HT-UPy



P3HT-UPy/
PEG-UPy Blend



Acknowledgments

Collaborators:

- Mike Kilbey, CNMS ORNL
- Deanna Pickel, CNMS ORNL
- Kunlun Hong, CNMS ORNL
- Seth Darling, CNM ANL
- Enrique Gomez, Penn State

- Elaine Dimasi (NSLS, BNL)
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- Beamline X6B, BNL, supported by DOE (DE-AC02-98CH10886)

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Verduzco laboratory at Rice: <http://polymers.rice.edu>

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