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*Poly(3-hexylthiophene)-block-poly(pyridinium phenylene)s:
Block Polymers of p- and n-Type Semiconductors*

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Poly(3-Hexylthiophene)-block-Poly(Pyridinium Phenylene)s: Block Polymers of P- and N-Type Semiconductors

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Poly(3-Hexylthiophene)-*block*-Poly(Pyridinium Phenylene)s: Block Polymers of P- and N-Type Semiconductors

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ABSTRACT: Conjugated crystalline–crystalline donor–acceptor–donor block copolymer semiconductors, with regioregular poly(3-hexylthiophene) as a donor (p-type) block and poly(pyridinium phenylene) as an acceptor (n-type) block within the backbone, were produced by sequential Grignard metathesis synthesis of poly(3-hexylthiophene), a Yamamoto-type cross-coupling polymerization–cyclization sequence. These conjugated block copolymers are soluble in organic solvents and display broad optical absorption bands extending close to the near-infrared region. They show reversible ambipolar redox properties with high electron affinities of 3.8–4.0 eV as well as useful ionization potentials of 5.1 eV that are characteristic of the respective blocks. Block copolymers from p- and n-type organic semiconductors are of interest for the formation of nanostructured bulk heterojunctions in photovoltaic devices.

Introduction

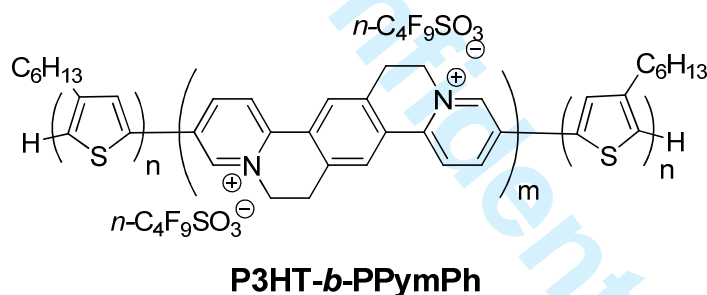
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Conjugated polymer semiconductors are of continuing interest as a result of their applications in optoelectronic and electrochemical devices, such as photovoltaic cells,¹ light emitting diodes,² sensors,³ electrochromics,⁴ and field-effect transistors.⁵ A major element of this interest derives from the fact that polymeric materials offer considerable advantages for the formation of flexible and light-weight devices that can be fabricated over large areas by low-cost solution processing techniques. For integrated material systems, the relative electron affinities of the different elements are of crucial importance. In a conjugated polymer blend, both components can show a high optical absorption coefficient and also cover complementary parts of the solar spectrum. Methodology to tune individual polymer optical band gaps and HOMO/LUMO levels has been broadly developed over the last two decades. However, few studies have been reported concerning heterojunctions between donor and acceptor polymers with improved light absorption for photovoltaic cells,⁶ in part because of the limited n-type polymers with high electron affinity (EA).⁷ Therefore, present polymer photovoltaic devices have focused heavily on acceptor molecules, such as methanofullerene phenyl-C₆₁-butyric-acid-methyl-ester (PCBM, EA = 4.2 eV),^{1b} although a weak absorption in the visible and near-infrared regions is a major drawback of fullerene derivatives.

Emerging applications of conjugated polymers require the patterning of materials on the 5-100 nanometer length scale, and block copolymers made of covalently linked polymers represent an ideal route to control the self-assembly of these nanosized morphologies. As a result, block copolymers have been studied as active materials to construct bulk-heterojunction solar cells and have been compared to the corresponding polymer blends.⁸ A controlled self-assembly of a nanostructure in a conjugated donor-acceptor block copolymer is an attractive approach to create architectures that are commensurate with the short exciton diffusion lengths of polymer semiconductors (ca. 10-100 nm). One challenge for realizing all-polymer bulk-heterojunctions is to produce solution processable n-type polymers with useful electron affinities, high electron mobilities, and good stability. Recently, we have reported on a promising class of soluble electron-accepting conjugated polymers that meet these criteria based upon

pyridinium-phenylene units.⁹ In these materials, the electron-deficient pyridinium rings with low LUMO energies and relatively planar structures for extended π -electron delocalization are produced by post polymerization intramolecular cyclization reactions.

In this paper we report the synthesis and characterization of conjugated donor-acceptor-donor type block copolymer semiconductors, regioregular poly(3-hexylthiophene)-*block*-poly(pyridinium phenylene) (**P3HT-*b*-PPymPh**). In our block copolymers, regioregular poly(3-hexylthiophene) (**P3HT**) segments serve as the electron donors (D) and poly(pyridinium phenylene) segments are used as the electron acceptors (A). The block copolymers were synthesized from a **P3HT** macroinitiator that is extended by a Yamamoto copolymerization to create a siloxyethyl-substituted poly(pyridyl phenylene) block that is then converted by intramolecular cyclization into a polyelectrolyte block copolymer, poly(3-hexylthiophene)-*block*-poly(pyridinium phenylene). We further demonstrate important prerequisites for solar cell applications such as strong optical absorptions, electron-donating/accepting properties, and nanophase separation can be achieved with this block copolymer.



Experimental Section

Instrumentation. NMR spectra were obtained on a Varian Mercury-300 spectrometer, and all chemical shifts are referenced to residual solvent peaks. Polymer molecular weights and polydispersity indexes were estimated by gel permeation chromatography (GPC) using a HP series 1100 GPC system. Polystyrene standards were used for calibration and tetrahydrofuran (THF) was used as the eluent at a flow rate of 1.0 mL/min. Ultraviolet-visible absorption spectra were measured with an Agilent 8453 diode array spectrophotometer and corrected for background signal. X-ray diffraction (XRD) scans of

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polymer thin films were performed on an Inel CPS 120 position sensitive detector using an XRG 3000 generator (Cu K α). Large size ($2 \times 2 \text{ cm}^2$) silicon wafers were used as XRD sample substrates; thin film samples for XRD analysis were prepared by drop-casting polymer solutions in chloroform or DMF onto substrates.

All electrochemical measurements were made with an AUTOLAB PGSTAT 20 potentiostat (Eco Chemie) using an Ag wire reference electrode (BioAnalytical Systems) submersed in 0.01 M AgNO₃/0.1 M tetrabutylammonium hexafluorophosphate (*n*-Bu₄NPF₆) in anhydrous CH₃CN or anhydrous CH₂Cl₂. Typical cyclic voltammograms were recorded using platinum button electrodes as the working electrode and a platinum coil counter electrode. The ferrocene/ferrocenium (Fc/Fc⁺) redox couple was used as an external reference. The potential values obtained versus Fc/Fc⁺ were converted to versus saturated calomel electrode (SCE). Film thickness was determined with a Veeco Dektak 6M Stylus Profiler.

Materials. 6,6'-(2,5-bis(2-(tert-butyldimethylsilyloxy)ethyl)-1,4-phenylene)bis(3-bromopyridine) (**3**) and TBDMS-protected poly(pyridyl phenylene) (**PPyPh**) were synthesized according to the literature procedure.⁹ Anhydrous dichloromethane, acetonitrile, and tetrahydrofuran were obtained using a solvent purification system (Innovative Technologies). Anhydrous DMSO was purchased from Aldrich as Sure-Seal Bottles and used as received. Tetrabutylammonium hexafluorophosphate was recrystallized in ethanol prior to use. All other chemicals were of reagent grade and used as received. Column chromatography was performed using ultra pure silica gel (SILIYCYCLE, 40~63 μm).

Regioregular Br-P3HT: Monobromo-terminated, regioregular head-to-tail poly(3-hexylthiophene) (**Br-P3HT**) was synthesized following a literature procedure.¹⁰ 2,5-Dibromo-3-hexylthiophene (3.26 g, 10 mmol) was dissolved in 5 mL of THF (resulting in a 2 M solution) and stirred under argon. *tert*-Butylmagnesium chloride (5.0 mL, 10 mmol, 2.0 M solution in diethyl ether) was added, and the mixture was stirred at room temperature for 2 hours. The reaction mixture was then diluted 95 mL with THF. Ni(dppp)Cl₂ (163 mg, 3.0 mol %) was added in one portion. After 30 min at room temperature, the reaction was poured over methanol and then filtered through a Soxhlet thimble, which was then subjected to Soxhlet extractions with methanol, hexanes, and chloroform. The purple polymer was

1 recovered from the chloroform fraction by rotary evaporation (60% yield). ^1H NMR (300 MHz, CDCl_3):
2 δ 0.91 (br, 3H), 1.25-1.36 (br, 6H), 1.71 (br, 2H), 2.80 (t, 2H), 6.98 (s, 1H). GPC: $M_n = 13400$, $M_w/M_n =$
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7 **Representative Synthesis of Precursor Block Copolymer P3HT-*b*-PPyPh:** A solution of **3** (71 mg,
8 0.10 mmol), **Br-P3HT** (50 mg, 0.3 mmol based upon the repeating unit), bis(1,5-cyclooctadiene)nickel
9 (0) (88 mg, 0.32 mmol), 1,5-cyclooctadiene (40 μL , 0.32 mmol), and 2,2'-bipyridine (50 mg, 0.32
10 mmol) in 6 mL of anhydrous THF was stirred for 48 h at 75 $^\circ\text{C}$ under argon. The reaction mixture was
11 cooled to room temperature and precipitated into methanol. The precipitate was collected by
12 centrifugation, dried, dissolved in chloroform, and then re-precipitated from methanol. The resulting
13 purple precipitate was collected by centrifugation and dried (96% yield). ^1H NMR (300 MHz, CDCl_3): δ
14 -0.04, 0.83, 1.35, 1.70, 2.80, 3.09, 3.79, 6.98, 7.47, 7.66, 8.06, 9.03 GPC: $M_n = 26200$, $M_w/M_n = 1.55$.
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26 **Ethylene-Bridged Poly(Pyridinium Phenylene) PPymPh:** To a solution of **PPyPh** (28 mg, 0.051
27 mmol) in 10 mL of CHCl_3 , $n\text{-C}_4\text{F}_9\text{SO}_2\text{F}$ (2.0 mL) and a 1 M solution of $[n\text{-Bu}_4\text{N}]\text{F}$ (2.0 mL) in THF
28 were added and the mixture was stirred at 67 $^\circ\text{C}$ for 24 hours. The reaction mixture was cooled to room
29 temperature and precipitated into hexane. The precipitate was collected by centrifugation, dried,
30 dissolved in DMF, and then reprecipitated from hexane. The resulting yellow precipitate was collected
31 by centrifugation and dried (92% yield). ^1H NMR (300 MHz, $\text{DMSO-}d_6/\text{D}_2\text{O}$): δ 3.46 (br, 4H), 4.91 (br,
32 4H), 8.32 (br, 2H), 8.74 (br, 2H), 8.95 (br, 2H), 9.41 (br, 2H).
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43 **Representative Synthesis of Block Copolymer P3HT-*b*-PPymPh:** To a solution of precursor
44 **P3HT-*b*-PPyPh** (30 mg) in 10 mL of CHCl_3 , $n\text{-C}_4\text{F}_9\text{SO}_2\text{F}$ (2.0 mL) and a 1 M solution of $[n\text{-Bu}_4\text{N}]\text{F}$
45 (2.0 mL) in THF were added and the mixture was stirred at 67 $^\circ\text{C}$ for 24 hours. The reaction mixture
46 was cooled to room temperature and precipitated into hexane. The precipitate was collected by
47 centrifugation, dried, dissolved in DMF, and then reprecipitated from hexane. The resulting orange
48 precipitate was collected by centrifugation and dried (90% yield).
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56 57 58 59 **Results and Discussion** 60

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Synthesis and Characterization. Scheme 1 shows the synthetic routes to the homopolymer **PPymPh** and the block copolymer **P3HT-*b*-PPymPh**.⁹ Our synthetic approach to the conjugated donor-acceptor-type block copolymers **P3HT-*b*-PPymPh** involves three steps. We begin with the synthesis of monobromo-terminated poly(3-hexylthiophene) (**Br-P3HT**) macromonomer building blocks as adapted from McCullough's Grignard metathesis (GRIM) regioregular living polymerization of 2,5-dibromo-3-hexylthiophene.¹⁰ The degree of polymerization was found to be 20, which was estimated from ¹H NMR analysis (Figure 2, top) by integrating the two small triplets at 2.6 ppm (4H) vs. the methylene protons of the repeating units at 2.8 ppm (2H). This value seems reasonable since 3 mol % of Ni catalyst was used and the yield was 60% in this polymerization. The GPC analysis of the resulting donor macromonomer displayed number-average molecular weights M_n of 13,400 and a polydispersity index of 1.18.

In the second step, we synthesize a pyridyl precursor triblock copolymer **P3HT-*b*-PPyPh** that is subsequently subjected to intramolecular nucleophilic substitution reactions to produce cyclic pyridiniums. The triblock precursor copolymers **P3HT-*b*-PPyPh** were synthesized under Yamamoto conditions with the dibromo building blocks **3** as central acceptor segments and the monobromo **Br-P3HT**s as donor segments. High-molecular-weight siloxyethyl-substituted block copolymers **P3HT-*b*-PPyPh** with different compositions were obtained that were soluble in common organic solvents (e.g. CHCl₃, THF). The symmetrical monomer **3** provides a head-to-head skeleton that displays reversible viologen-like redox behavior.¹¹ This material is prepared from boronation of 2,5-bis(2-(tert-butyl)dimethylsilyloxy)ethyl)-1,4-benzenedibromide (**1**) to give the diboronic acid bis(pinacol) ester (**2**). The head-to-head pyridine monomer **3**, 1,4-bis[2-(5-bromopyridyl)]-2,5-bis(2-(tert-butyl)dimethylsilyloxy)ethyl) benzene, is prepared by regioselective Suzuki coupling of **2** with 2,5-dibromopyridine.⁹ The block copolymers were characterized by size exclusion chromatography (GPC), as summarized in Table 1 and shown in Figure 1. The chromatograms clearly shifted to a higher molecular weight region from the first stage to the second one. It is likely that there is a certain amount of coupled-P3HT, PPyPh homopolymer, and P3HT-*b*-PPyPh diblock copolymer as evidenced by the

1 low molecular weight shoulder and increased polydispersity indices of the block copolymers relative to
2 the homopolymers. However, the molecular weight distributions are dominantly monomodal for the
3 block copolymers in consideration with the respective area of chromatograms, indicating that the main
4 product is the block copolymer. Additionally, the structure and the molar ratios of block copolymers
5 were characterized by ^1H NMR spectroscopy, as summarized in Table 1 and shown in Figure 2. Two
6 small triplets at $\delta \sim 2.6$ ppm of the same intensity for H/Br terminated **rr-P3HT** can be assigned to the
7 methylene protons directly attached to the terminal thiophene units.^{10b} When the H/Br terminated
8 polymer is subjected to a block copolymerization with comonomer **3**, one of the triplets are absent
9 indicating that the **Br-P3HT** macromonomers has been consumed in the reaction.

10 In the final step, quaternizative cyclization induced by tetra-*n*-butylammonium fluoride and
11 nonafluorobutanesulfonyl fluoride gave block copolymers **P3HT-*b*-PPymPh**.¹² In our previous paper,
12 we used thionyl chloride as a cyclization reagent.⁹ However, P3HT blocks are easily doped by thionyl
13 chloride, and as a result we have developed new cyclization reaction conditions for block copolymers
14 that do not result in doping of **P3HT** segments. Additionally, these efforts are complicated by the fact
15 that **P3HT** is only soluble in nonpolar solvents (CHCl_3 , THF, etc), whereas the polyelectrolyte **PPymPh**
16 and the copolymers **P3HT-*b*-PPymPh** are only soluble in aprotic polar solvents, such as DMF and
17 DMSO.

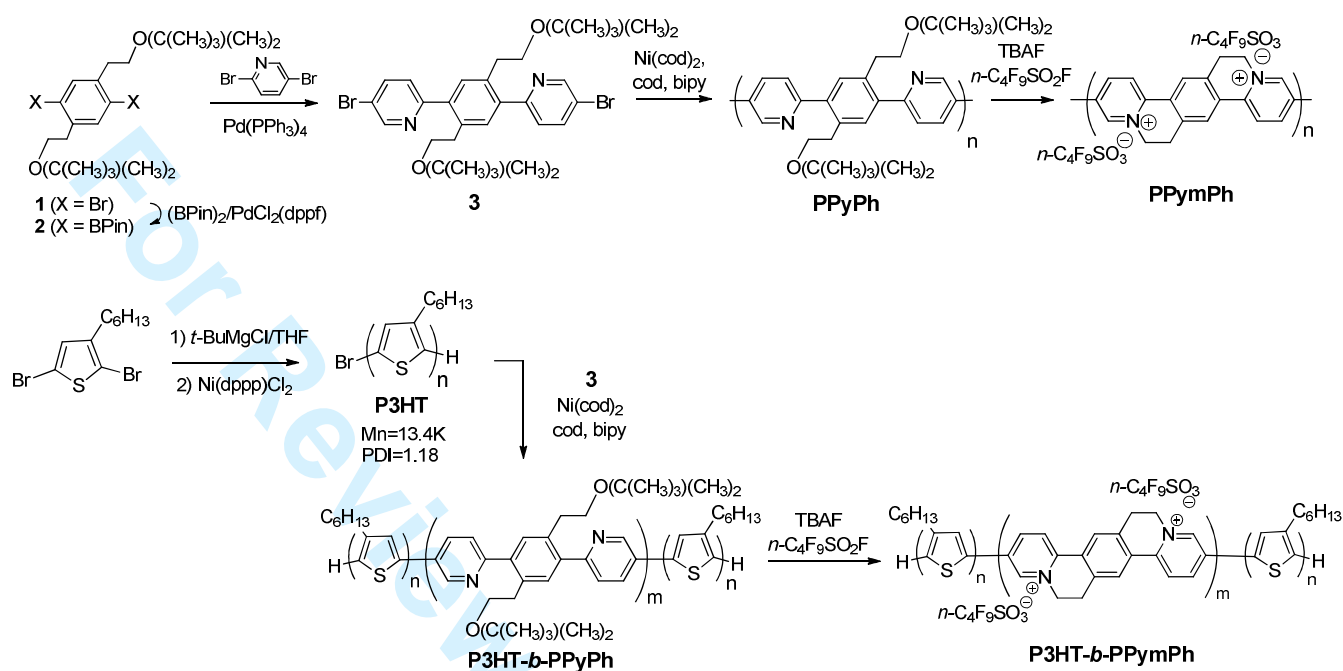
Scheme 1. Synthetic Routes to P3HT-*b*-PPyPh.

Table 1. Molar ratios of repeat units, molecular weights, and polydispersity indices of P3HT-*b*-PPyPh.

Polymer	Molar ratio of repeat unit	Molar ratio of repeat unit	M_n	M_w/M_n
	in the feed (P3HT/PPyPh)	as determined ¹ H NMR (P3HT/PPyPh)		
P3HT	100/0	100/0	13400	1.18
P3HT90- <i>b</i> -PPyPh10	86/14	90/10	29700	2.11
P3HT80- <i>b</i> -PPyPh20	75/25	80/20	26200	1.55
PPyPh	0/100	0/100	17000	1.44

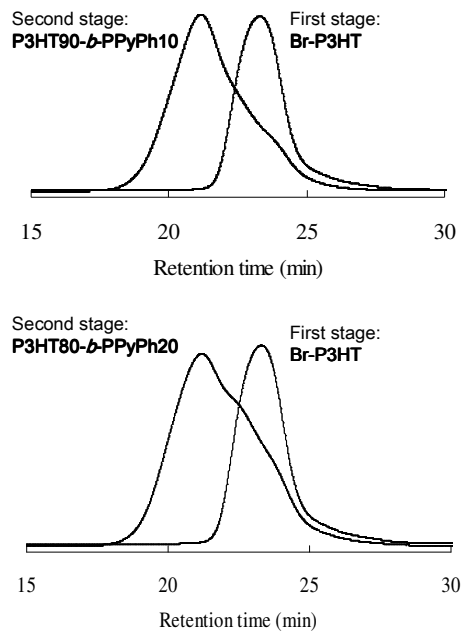


Figure 1. GPC traces of the first and second stages of the block copolymerization.

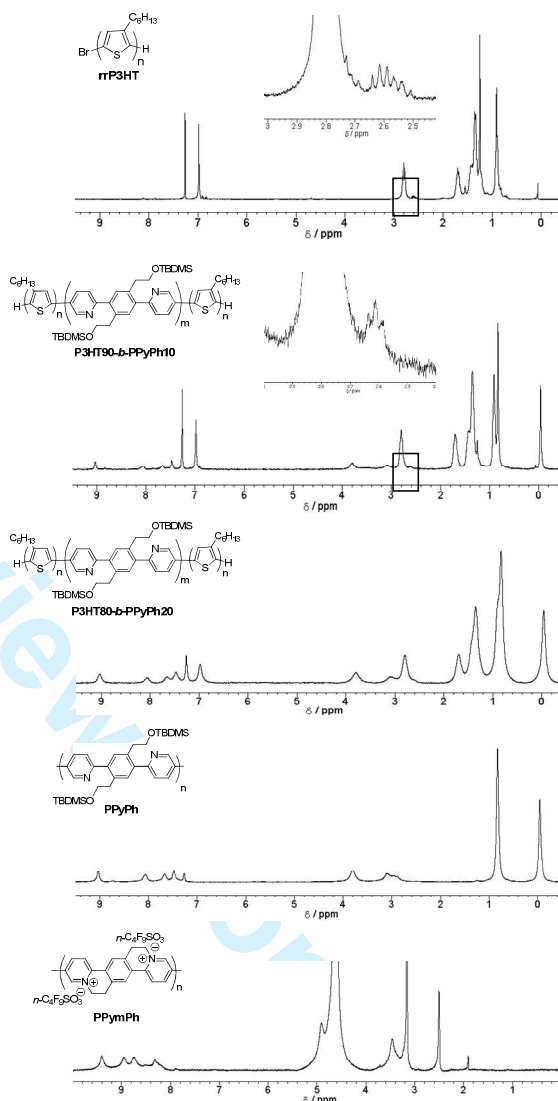


Figure 2. ^1H NMR spectra of **P3HT**, **P3HT-*b*-PPyPh**, **PPyPh** in CDCl_3 , and **PPymPh** in $\text{DMSO-}d_6/\text{D}_2\text{O}$. The regions shown in the boxes are expanded for clarity.

Optical Properties. The optical absorption spectra of the precursor block copolymers **P3HT-*b*-PPyPh**, and the corresponding homopolymers **P3HT** and **PPyPh** in dilute chloroform solution are shown in Figure 3a. The absorption spectra of precursor block copolymers are a superposition of those of the two polymer components, **P3HT** (an absorption maximum, $\lambda_{\text{max}} = 452 \text{ nm}$) and **PPyPh** ($\lambda_{\text{max}} = 319 \text{ nm}$), indicating no detectable ground state interaction between **P3HT** and **PPyPh** segments.

Figure 3b-c details the optical absorption spectra of dilute DMF solutions and thin films of pyridinium-based block copolymers **P3HT-*b*-PPymPh**, the corresponding homopolymers **P3HT** and

PPymPh. All of the thin films were made from the corresponding dilute DMF solutions. The absorption spectra of acceptor segments in block copolymers are significantly red-shifted relative to their respective precursors. This is in part a result of the ethylene bridges enforcing a planar conformation of the pyridinium-phenylene segment. Additionally, the solution absorption spectra of block copolymers are generally similar in shape to those of homopolymers **PPymPh** and **P3HT**. The weak absorption maximum of the **P3HT** donor block at 452 nm is overlapped by the stronger absorbing **PPymPh** ($\lambda_{\text{max}} = 403$ nm), and is only visible as a red-shift shoulder in the solution spectra. As expected the absorption spectra of thin films are significantly red-shifted relative to the solution absorption spectra. The absorption at $\lambda_{\text{max}} = 520$ nm results from a crystallization of the **P3HT** chains into a coplanar intrachain conformation. A longer wavelength shoulder of the donor segments at 550-700 nm and the red-shifted absorption maximum of acceptor segments around 420 nm are observed in the case of block copolymers, and are suggestive of intermolecular charge transfer interaction between donor and acceptor blocks.

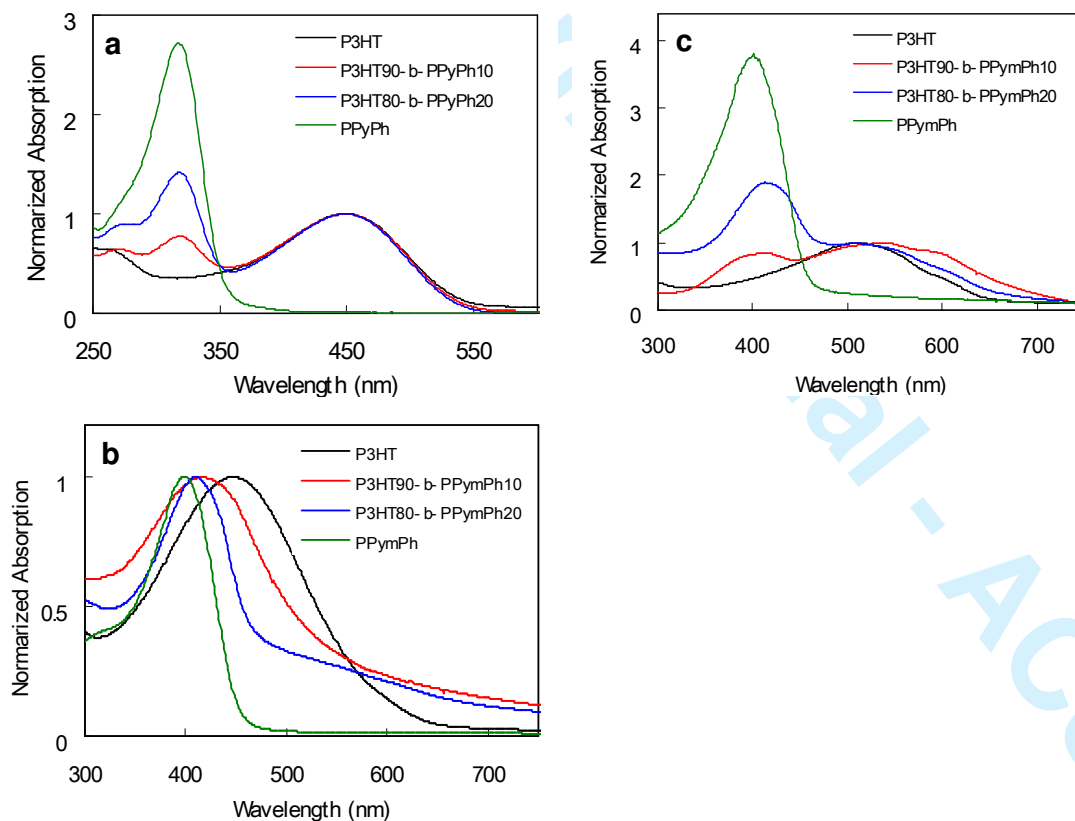


Figure 3. UV-vis absorption spectra of **P3HT**, **P3HT-*b*-PPyPh**, **PPyPh** in CHCl₃ solutions (a), **P3HT**, **P3HT-*b*-PPymPh**, **PPymPh** in DMF solutions (b), and as thin films on glass substrates (c).

Table 2. Optical and Electrochemical Properties of **P3HT**, **P3HT-*b*-PPymPh**, and **PPymPh**.

polymer	λ_{\max} (nm)	λ_{onset} (nm)	$E_g^{\text{opt a}}$ (eV)	$E_{\text{red}}^{\text{b}}$ (V)	$E_{\text{red}}^{\text{onset b}}$ (V)	E_{ox}^{b} (V)	$E_{\text{ox}}^{\text{onset b}}$ (V)	$E_g^{\text{el c}}$ (eV)	EA ^d (eV)	IP ^e (eV)
P3HT	516	653	1.9	-	-	1.24	0.73	-	3.2	5.1
P3HT90-<i>b</i>-PPymPh10	416, 530	672	1.8	-0.94	-0.61	1.15	0.71	1.3	3.8	5.1
P3HT80-<i>b</i>-PPymPh20	421, 546	704	1.8	-0.81, -1.56	-0.44	1.04	0.71	1.2	4.0	5.1
PPymPh	407	470	2.6	-0.83, -1.51	-0.45	-	-	-	4.0	6.6

^a E_g^{opt} : Optical band gap estimated from the band edge (λ_{onset}) of the absorption spectra. ^b E_{red} , $E_{\text{red}}^{\text{onset}}$, E_{ox} , $E_{\text{ox}}^{\text{onset}}$: Formal and onset reduction and formal and onset oxidation potentials (vs SCE). ^c E_g^{el} : Electrochemical band gap estimated from the onset reduction and oxidation potentials. ^d EA: Electron affinity obtained based on $\text{EA} = E_{\text{red}}^{\text{onset}} + 4.4$ (eV) for **P3HT-*b*-PPymPh**, **PPymPh** and $\text{EA} = \text{IP} - E_g^{\text{opt}}$ for **P3HT**. ^e IP: Ionization potential calculated from $\text{IP} = \text{EA} + E_g^{\text{opt}}$ (eV) for **PPymPh** and $\text{IP} = E_{\text{ox}}^{\text{onset}} + 4.4$ (eV) for **P3HT**, **P3HT-*b*-PPymPh**.

Electrochemical Properties. The oxidation and reduction potentials of thin films of pyridinium-based conjugated D-A block copolymers **P3HT-*b*-PPymPh** and their respective precursors **P3HT-*b*-PPyPh** were determined by cyclic voltammetry in CH₃CN (vs SCE), as shown in Figure 4 and summarized in Table 2. Figure 4a-d presents the cyclic voltammograms of **P3HT**, **P3HT90-*b*-PPymPh10**, **P3HT80-*b*-PPymPh20**, and **PPymPh**, respectively. The reduction potentials of **P3HT-*b*-PPymPh** and **PPymPh** are significantly more positive relative to their respective precursors. This is attributed to the highly electrophilic pyridinium rings. All of the pyridinium-containing polymers **P3HT-*b*-PPymPh** and **PPymPh** showed reversible viologen-like redox behavior,¹¹ and the donor-acceptor

1 block copolymers **P3HT-*b*-PPymPh** displayed reversible ambipolar redox properties as evident from
2 the areas and close proximity of the anodic and cathodic peaks. As expected, an oxidation wave was
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4 observed in the cyclic voltammogram of the **P3HT**-containing polymers, **P3HT** and **P3HT-*b*-PPymPh**,
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6 at the formal potentials between 1.04 and 1.24 V, while no oxidation wave was observed for **PPymPh**
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8 that lacked **P3HT** blocks. Also **P3HT-*b*-PPymPh** and **PPymPh** exhibited similar reduction behavior
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10 between -0.81 to -1.56 V. The onset reduction and oxidation potentials of the block copolymers **P3HT-*b*-**
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12 **PPymPh** were from -0.61 to -0.44 V and 0.71 V (vs. SCE), respectively, from which we estimated an
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14 electron affinity (EA, LUMO level) of 3.8 to 4.0 eV ($EA = E_{\text{red}}^{\text{onset}} + 4.4$) and an ionization potential (IP,
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16 HOMO level) of 5.1 eV ($IP = E_{\text{ox}}^{\text{onset}} + 4.4$).¹³ Interestingly, the EA values are higher than those
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18 estimated with the same method for most conventional polyheterocycles,¹⁴ and are comparable to well
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20 known electron transporters PCBM (4.2 eV)^{1b} or BBL (4.0 eV),¹⁵ as well as homopolymer **PPymPh** (4.0
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22 eV).⁹

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28 An electrochemically reversible charge trapping behavior was observed in the CVs of **P3HT80-*b*-**
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30 **PPymPh20** with 20 mol% of acceptor moieties (Fig. 4c and 4e). Scanning the reductive and oxidative
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32 regions separately results in reversible redox behavior, as shown in Fig. 4e. The cyclic voltammogram
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34 shows six peaks A-F in the potential range between -1.7 and 1.1 V (vs. SCE, Fig. 4c and 4e). The
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36 position of peak A corresponds to the reported oxidation potential of **P3HT** donor moiety, and the
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38 positions of the C-F and D-E couples are in agreement with the doping and undoping potentials of
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40 poly(pyridinium phenylene) **PPymPh**. In the range from -0.8 to 1.1 V, mainly the A-B couple is
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42 observed, whereas scanning in the range -1.7 to 0.3 V gives rise only to the C-F and D-E couples (Fig.
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44 4e). These observations indicate that the A-B couple is primarily related to the oxidation and reduction
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46 of the **P3HT** donor blocks, whereas the C-F and D-E couples are related to the reduction and oxidation
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48 of the **PPymPh** acceptor blocks. Similar charge trapping phenomena have been observed in other
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50 thiophene- or Ru(bpy)₃-based polymers.¹⁶ The charge trapping is most apparent in **P3HT80-*b*-**
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52 **PPymPh20** and is not clearly present for **P3HT90-*b*-PPymPh10**. The lower content of the **PPymPh**
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54 units in the latter limit the interchain interactions between the electroactive pyridinium ions that are
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suspected to give rise to charge trapping. The unusually large potential difference between the A and B peaks suggests the occurrence of a particular chemical interaction after the oxidation of the thiophene ring that prevents reduction at the thermodynamic potential.

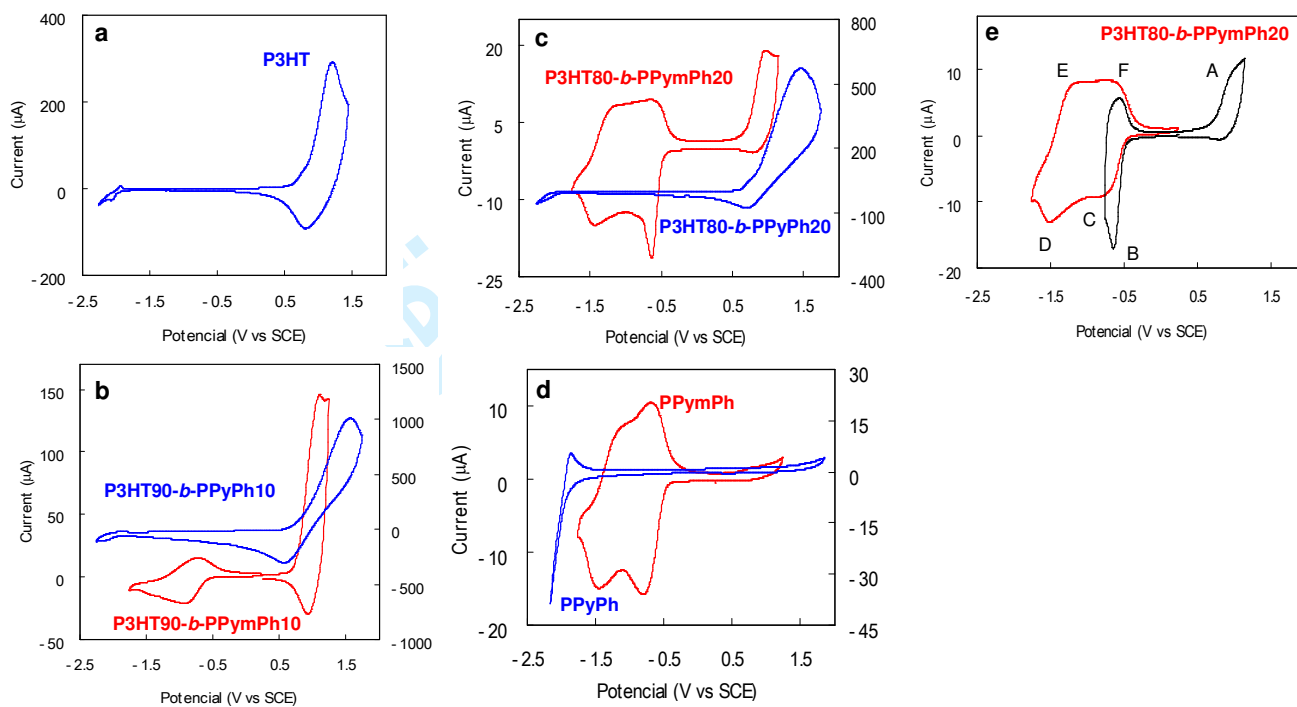


Figure 4. Cyclic voltammograms of drop-cast films of (a) P3HT, (b, c, e) P3HT-*b*-PPymPh, (d) PPymPh and the corresponding precursors on a Pt button electrode in CH₃CN with 0.1 M TBAPF₆ as a supporting electrolyte.

Morphology. The morphology of P3HT-*b*-PPymPh block copolymer thin films was investigated by using transmission electron microscopy (TEM). Figures S1a-b (See the Supporting Information) present TEM morphology images of dropcast thin films of P3HT-*b*-PPymPh with the block molar ratio of 90:10 and 80:20. Films of P3HT80-*b*-PPymPh20 block copolymer with the block ratio of 80:20 (Figure S1b) form nanosized spherical aggregates with a diameter of roughly 10-30 nm. In the case of P3HT90-*b*-PPymPh10 block copolymers with the block ratio of 90:10 (Figure S1a) the morphology changes and is most consistent with previously reported nanofiber-like structures of P3HT blocks also having a

1 similar diameter.¹⁷ The latter nanoscopic morphology presents advantages for the design of efficient
2 bulk heterojunction solar cell devices when considering the short exciton diffusion lengths of organic
3 semiconductors. These results demonstrate that the covalent binding of **P3HT** donor and **PPymPh**
4 acceptor segments controls the scale length of nanostructural formation and may allow us to optimize
5 bulk heterojunction photovoltaic cells. Device measurements of these new block copolymers are
6 underway. Since the role of counterions complicates these applications as we indicated in our earlier
7 paper,⁹ significant experimentation is needed to understand this new class of organic photovoltaic
8 devices using polyelectrolytes.
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21 **X-Ray Diffraction Measurement.** X-ray diffraction (XRD) measurements were performed on thin
22 films of **P3HT-*b*-PPymPh** with the block ratio of 90:10 and 80:20, and on **P3HT** and **PPymPh**
23 homopolymers for reference to analyze the molecular packing and orientations of block copolymers
24 (Figure 5). Thin film samples were prepared by drop-casting polymer solutions in chloroform for **P3HT**
25 and in DMF for **P3HT-*b*-PPymPh** and **PPymPh**. The **P3HT** film showed characteristic diffraction
26 peaks at 2θ of 5.22, 10.59 and 15.82° consistent with its lamellar structure and a lattice constant of 1.69
27 nm for the (h00) plane.¹⁸ The thin film of the **PPymPh** homopolymer showed a weaker diffraction peak
28 at 7.95° that may correspond to weak ordering in a lamellar structure with an interlayer distance of ca
29 1.1 nm. This is smaller than that of the **P3HT** homopolymer, which is consistent with the shorter side
30 chains of **PPymPh**. Additionally, the XRD diffraction patterns of the block copolymers with 10 and 20
31 mol% **PPymPh** are different. It appears that the copolymer with 10 mol% **PPymPh** (trace b) displays
32 the features of **P3HT** homopolymers while the copolymer with 20 mol% **PPymPh** (trace c) displays the
33 features of **PPymPh**. This indicates that **P3HT** or **PPymPh** segments in the rigid rod-rod block
34 copolymers form a layered crystalline structure with strong orientations similar to the corresponding
35 homopolymers.
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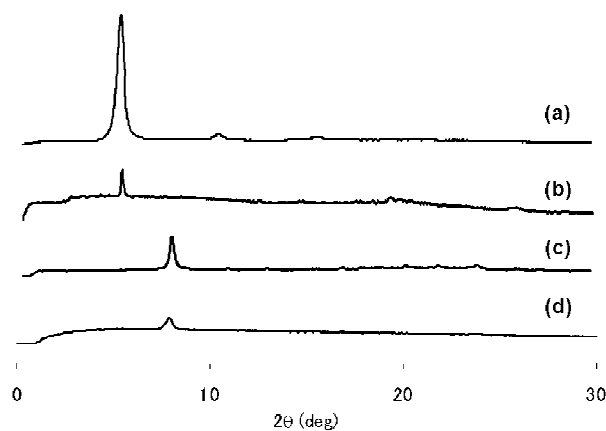


Figure 5. XRD spectra for (a) **P3HT**, (b) **P3HT90-*b*-PPymPh10**, (c) **P3HT80-*b*-PPymPh20**, and (d) **PPymPh**.

Conclusion. We have prepared new conjugated crystalline–crystalline donor–acceptor block copolymer semiconductors with regioregular poly(3-hexylthiophene) as a donor block and poly(pyridinium phenylene) as an acceptor block within the backbone. These materials are synthesized by the Grignard metathesis method of **P3HT**, a Yamamoto-type cross-coupling copolymerization and cyclization sequence. The conjugated block copolymers are soluble in organic solvents and display broad optical absorption bands over the visible spectrum. These materials have high electron affinities (LUMO levels) of 3.8–4.0 eV for the acceptor components, useful ionization potentials (HOMO levels) of 5.1 eV for the donor components, reversible ambipolar redox behavior, and unique charge trapping behavior. Additionally, these block copolymers demonstrated nanodomains of ca. 20 nm in diameter, which matches the expected exciton diffusion lengths. The combination of these properties qualifies **P3HT-*b*-PPymPh** as promising functional materials for nanostructured bulk heterojunction photovoltaic devices.

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Supporting Information Available. TEM images and experimental details of the block copolymers. This material is available free of charge via the Internet at <http://pubs.acs.org>.

References and Notes.

- (1) (a) Gunes, S.; Neugebauer, H.; Sariciftci, N. S. *Chem. Rev.* **2007**, *107*, 1324–1338. (b) Thompson, B. C.; Freché, J. M. J. *Angew. Chem., Int. Ed.* **2008**, *47*, 58-77.
- (2) Kraft, A.; Grimsdale, A. C.; Holmes, A. B. *Angew. Chem., Int. Ed.* **1998**, *37*, 402-428.
- (3) (a) *Electrochromism: Fundamentals and Applications*; Monk, P. M. S., Mortimer, R. J., Rosseinsky, D. R., Eds.; VCH: Weinheim, 1995. (b) Sapp, S. A.; Sotzing, G. A.; Reynolds, J. R. *Chem. Mater.* **1998**, *10*, 2101-2108.
- (4) (a) Swager, T. M. *Acc. Chem. Res.* **1998**, *31*, 201-207. (b) McQuade, D. T.; Pullen, A. E.; Swager, T. M. *Chem. Rev.* **2000**, *100*, 2537-2574.
- (5) (a) Allard, S.; Forster, M.; Souharce, B.; Thiem, H.; Scherf, U. *Angew. Chem. Int. Ed.* **2008**, *47*, 4070-4098. (b) Murphy, A. R.; Freché, J. M. J. *Chem. Rev.* **2007**, *107*, 1066-1096.
- (6) (a) Granstrom, M.; Petritsch, K.; Arias, A. C.; Lux, A.; Andersson, M. R.; Friend, R. H. *Nature (London)* **1998**, *395*, 257-260. (b) Jenekhe, S. A.; Yi, S. *Appl. Phys. Lett.* **2000**, *77*, 2635-2637. (c) Kietzke, T.; Egbe, D. A. M.; Hrhhold, H.-H.; Neher, D. *Macromolecules* **2006**, *39*, 4018-4022.
- (7) (a) Babel, A.; Jenekhe, S. A. *J. Am. Chem. Soc.* **2003**, *125*, 13656-13657. (b) Zhan, X.; Tan, Z.; Domercq, B.; An, Z.; Zhang, X.; Barlow, S.; Li, Y.; Zhu, D.; Kippelen, B.; Marder, S. R. *J. Am. Chem.*

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55
56
57
58
59
60

Soc. **2007**, *129*, 7246-7247. (c) Letizia, J. A.; Salata, M. R.; Tribout, C. M.; Facchetti, A.; Ratner, M. A.; Marks, T. J. *J. Am. Chem. Soc.* **2008**, *130*, 9679-9694. (d) Usta, H.; Facchetti, A.; Marks, T. J. *J. Am. Chem. Soc.* **2008**, *130*, 8580-8581.

(8) (a) Sommer, M.; Lindner, S. M.; Thelakkat, M. *Adv. Funct. Mater.* **2007**, *17*, 1493-1500. (b) Lindner, S. M.; Hüttner, S.; Chiche, A.; Thelakkat, M. Krausch, G. *Angew. Chem. Int. Ed.* **2006**, *45*, 3364-3368. (c) Tu, G.; Li, H.; Forster, M.; Heiderhoff, R.; Balk, L. J.; Scherf, U. *Macromolecules* **2006**, *39*, 4327-4331. (d) Sommer, M.; Lang, A. S.; Thelakkat, M. *Angew. Chem. Int. Ed.* **2008**, *47*, 7901-7904.

(9) Izuhara, D.; Swager, T. M. *J. Am. Chem. Soc.* **2009**, *131*, 17724-17725.

(10) (a) Loewe, R. S.; Ewbank, P. C.; Liu, J.; Zhai, L.; McCullough, R. D. *Macromolecules* **2001**, *34*, 4324-4333. (b) Iovu, M. C.; Sheina, E. E.; Gil, R. R.; McCullough, R. D. *Macromolecules* **2005**, *38*, 8649-8656.

(11) Michaelis, M.; Hill, E. S. *J. Gen. Physiol.* **1933**, *16*, 859-873.

(12) (a) Lyapkalo, I. M.; Webel, M.; Reißig H.-U. *Eur. J. Org. Chem.* **2002**, 1015-1025. (b) Sugiura, H.; Takahira, Y.; Yamaguchi, M. *J. Org. Chem.* **2005**, *70*, 5698-5708.

(13) Li, Y.; Ding, J.; Day, M.; Tao, Y.; Lu, J.; D'iorio, M. *Chem. Mater.* **2004**, *16*, 2165-2173.

(14) Kulkarni, A. P.; Tonzola, C. J.; Babel, A.; Jenekhe, S. A.; *Chem. Mater.* **2004**, *16*, 4556-4573, and references therein.

(15) While EA 4.0 eV has been reported for BBL, it is noteworthy that BBL was processed by strong acid, rather than common solvents: Alam M. M.; Jenekhe, S. A. *Chem. Mater.* **2004**, *16*, 4647-4656.

(16) (a) Zotti, G.; Schiavon, G.; Zecchin, S. *Synth. Met.* **1995**, *72*, 275-281. (b) Zhu, S. S.; Kingsborough, R. P.; Swager, T. M. *J. Mater. Chem.* **1999**, *9*, 2123-2131. (c) Zhou, Z.; Maruyama, T.;

1 Kanbara, T.; Ikeda, T.; Ichimura, K.; Yamamoto, T.; Tokudab, K. *J. Chem. Soc., Chem. Commun.* **1991**,
2 1210-1212.
3

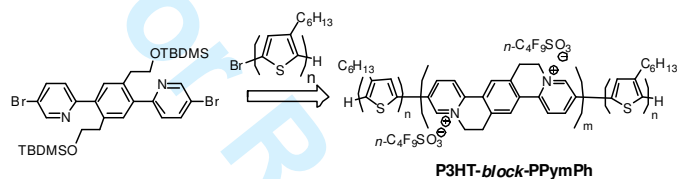
4
5
6 (17) Tao, Y.; McCulloch, B.; Kimc, S.; Segalman, R. A. *Soft Matter*, **2009**, *5*, 4219–4230.
7

8
9 (18) (a) Merlo, J. A.; Frisbie, C. D. *J. Phys. Chem. B* **2004**, *108*, 19169-19179. (b) Berson, S.; De
10 Bettignies, R.; Bailly, S.; Guillerez, S. *Adv. Funct. Mater.* **2007**, *17*, 1377-1384.
11
12
13
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For Table of Contents Use Only

Poly(3-Hexylthiophene)-*block*-Poly(Pyridinium Phenylene)s: Block Polymers of P- and N-Type Semiconductors

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Poly(3-Hexylthiophene)-*block*-Poly(Pyridinium Phenylene)s: Block Polymers of P- and N-Type Semiconductors

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Instrumentation. Transmission Electron Microscopy (TEM) analysis was performed using a JEOL 200CX operating at 200 kV. Samples for the morphological investigation were prepared by drop-casting and thermally annealing at 130 °C. The films were cast from *N,N*-dimethylformaldehyde (DMF) solutions onto NaCl freshly cleaved from a single crystal ingot. The films were then floated onto water and placed on a copper TEM grid.

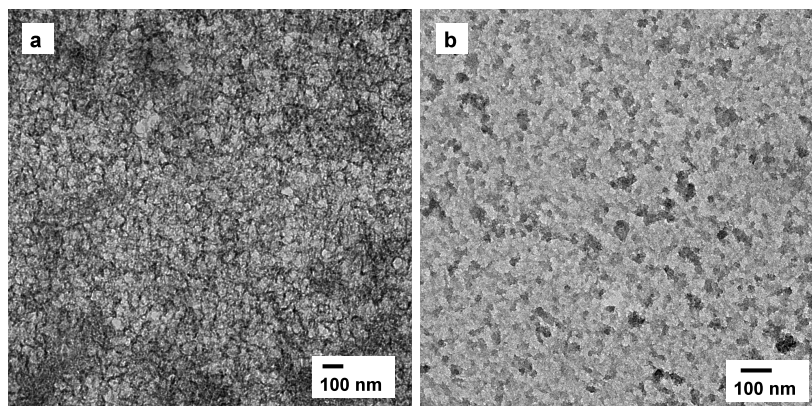


Figure S1. TEM images of the self-assembled structures of (a) **P3HT90-*b*-PPymPh10** and (b) **P3HT80-*b*-PPymPh20**.