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# Cross-Linked Conjugated Polymer Fibrils: Robust Nanowires from Functional Polythiophene Diblock Copolymers

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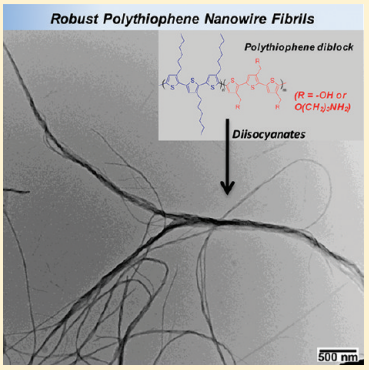
Supporting Information

**ABSTRACT:** A series of poly(3-hexyl thiophene) (P3HT)-based diblock copolymers were prepared and examined in solution for their assembly into fibrils, and post-assembly cross-linking into robust nanowire structures. P3HT-b-poly(3-methanol thiophene) (P3MT), and P3HT-b-poly(3-aminopropyloxymethyl thiophene) (P3AmT) diblock copolymers were synthesized using Grignard metathesis (GRIM) polymerization. Fibrils formed from solution assembly of these copolymers are thus decorated with hydroxyl and amine functionality, and cross-linking is achieved by reaction of diisocyanates with the hydroxyl and amine groups. A variety of cross-linked structures, characterized by transmission electron microscopy (TEM), were produced by this method, including dense fibrillar sheets, fibril bundles, or predominately individual fibrils, depending on the chosen reaction conditions. In solution, the cross-linked fibrils maintained their characteristic vibronic structure in solvents that would normally disrupt (dissolve) the structures.




**KEYWORDS:** polythiophene, self-assembly, fibril, nanowire

## INTRODUCTION

Conjugated polymers are of interest in organic photovoltaics (OPVs), because of their beneficial properties of low cost, ease of processability, and flexible design parameters.[1−3] OPV device performance depends critically on the polymer/nanocomposite morphology of the active layer, which ideally promotes efficient exciton formation, dissociation, and charge transport to the respective electrodes.[4,5] One potentially ideal active layer morphology would consist of an interpenetrating, bicontinuous network of donor and acceptor materials, having domain sizes of ∼10 nm (i.e., on the order of the exciton diffusion length).[6,7] Such morphologies depend on the miscibility of the donor and acceptor materials, and can be improved or disrupted upon application of solvent and/or thermal annealing procedures.[8] Poly(3-hexyl thiophene) (P3HT) and [6,6]-phenyl-C61-butyric acid methyl ester (PCBM) blends are widely studied in OPVs, because of a favorable combination of intrinsic materials performance, commercial availability, and ease of fabrication.[1,2,9] However, thin films of P3HT/PCBM composites microphase separate over time, giving large, crystalline aggregates of PCBM that diminish device performance.[10,11]

In recent years, compatibilizers have been examined for their ability to stabilize the morphology of bulk heterojunctions (BHJs) in solar cells. Compatibilizers serve to slow or prevent phase separation of the *p*-type (hole acceptor) and *n*-type (electron acceptor) components by reducing the interfacial energy of the system, thereby improving the thermal stability of the morphology.[12−14] Covalently substituted fullerene structures compatibilize P3HT/PCBM morphologies, as seen in P3HT-based block copolymers containing C-60 pendent groups (i.e., having several fullerene units per polymer chain),[15,16] and fullerene-terminated P3HT structures (i.e., having one fullerene per polymer chain).[17,18] In all cases, the fullerene functionalized compatibilizer stabilized the active layer of P3HT/PCBM-based solar cells, despite thermal annealing processes that diminished the performance of standard devices because of microphase separation.

Cross-linking the photoactive polymer in solar cells has also proven to stabilize device efficiency.[19−21] Hashimoto and co-workers[22] showed that thermally cross-linked poly(3-(5-hexenylthiophene) outperformed un-cross-linked P3HT/PCBM films, with PCE values about twice that of the un-cross-linked materials, following annealing at 150 °C for 600 h. Fréchet and co-workers[23] prepared a P3HT-r-poly(3-(6-bromohexyl)thiophene (P3BHT) copolymer, which cross-linked upon irradiation at 254 nm. Thermal annealing of cross-linked devices led to a minimal (∼10%) decrease in PCE over 50 h, while optical microscopy and atomic force microscopy (AFM) confirmed good film uniformity.

Preformed, highly crystalline assemblies of conjugated polymers are of interest for processing into devices in which desirable intermolecular interactions (i.e., $\pi-\pi$ stacking of polymer chains) responsible for charge transport are fixed from the outset.[24,25] Fibrils produced from conjugated polymers by solution assembly are highly crystalline and promise improvement over conventional thin-film processing in OPV devices.[26,27] Such fibrils offer efficient charge transport (i.e., hole mobility for *p*-type materials) along the polymer backbone and the fibril

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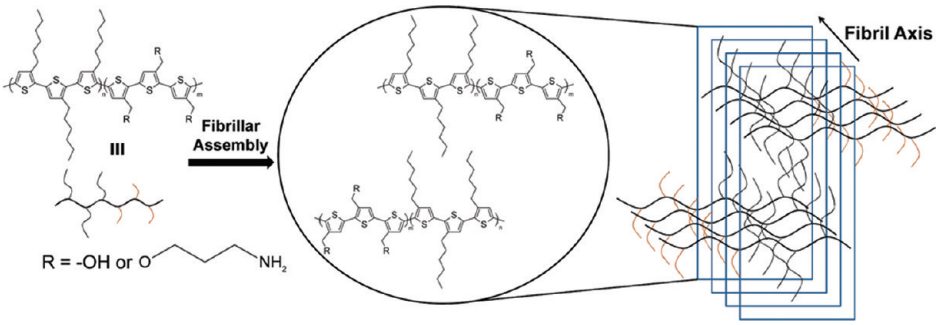


**Figure 1.** Schematic of P3HT-b-P3RT diblock copolymer fibril formation (R = $CH_2OH$ or $CH_2O(CH_2)_3NH_2$).

axis, as a multiaxial transport media. Jenekhe and co-workers[28] have used unannealed poly(3-butyl thiophene) (P3BT) nanowire/PCBM blends to fabricate devices with ~3.3% PCE, which is an order-of-magnitude increase over devices from standard P3BT/PCBM thin films. Field-effect hole mobilities of the nanowire/PCBM blend measured $8 \times 10^{-3}$ $cm^2/(V\ s)$, compared to $3.8 \times 10^{-5}$ $cm^2/(V\ s)$ for standard P3BT/PCBM thin films. Highly crystalline P3BT nanowires have higher hole mobility based on their multiaxial conjugation pathways, and the nanowires provide a scaffold toward an interpenetrating network with PCBM, with length scales of ~10 nm (i.e., on order of exciton diffusion length). Additional studies by Jenekhe and co-workers[29] revealed a solvent-induced crystallization of polythiophene-based diblock copolymers, giving nanowires from P3BT-b-poly(3-octyl thiophene) (P3OT). Guillerez and co-workers[30] investigated the difference between P3HT/PCBM blends in thin films and fibrils in solar cells. PCE values of ~3.6% were obtained when using P3HT fibrils, compared to <1% for unannealed P3HT thin films. Thus, the deposition of preformed, highly crystalline assemblies precludes the need for annealing, which may be advantageous in many circumstances, including application in thin, flexible solar cells where polymer substrates, such as poly(ethylene terephthalate) (PET), are used.

Despite their inherent advantages, P3HT fibrils present their own processing difficulties, because of their instability to thermal annealing, and dissolution (i.e., going back to free polymer) in solvents useful for device fabrication. Motivated by the promise of these fibrillar strucutres, and the challenge of their current limitations, we sought to design a reliable cross-linking method to produce robust structures from such solution assemblies. Specifically, we describe the synthesis, solution assembly, and cross-linking of P3HT-b-poly3-MT (where M = $CH_2OH$), and P3HT-b-P3AmT (where Am = $CH_2O(CH_2)_3NH_2$). Both the hydroxyl and amino functionalized diblock copolymers were seen to form fibrillar assemblies, by first dissolving the polymer in a favorable solvent (chloroform), then adding a nonfavorable solvent (dichloromethane (DCM)). We surmise that the P3HT block forms a crystalline fibril core (noting the ~15−25-nm fibril width typical of P3HT fibrils of these molecular weights), with the hydroxyl and amine functional blocks decorating the fibril exterior. Reaction of these functionalized fibrils with 1,6-hexanediisocyanate provided a route to fix the fibril structures by cross-linking. Based on reagent concentration and relative ratios of fibril to cross-linker, a variety of structures were produced, ranging from individual fibrils to dense sheets. To our knowledge, this is the first reported solution cross-linking of P3HT-based fibrils, exploiting functionality integrated into the fibrillar design by way of the block copolymer precursors. Figure 1 illustrates this fibril formation, and the use of the reactive functionality for cross-linking.

## RESULTS AND DISCUSSION

Scheme 1 shows the synthesis of P3HT-b-P3MT and P3HT-b-P3AmT diblock copolymers. P3HT-b-P3MT (polymer **9**) was prepared by deprotecting the tetrahydropyran (THP)-protected precursor **8**, while P3HT-b-P3AmT (polymer **12**) was prepared from alkyl bromide precursor **10**. In both cases, the P3HT block was synthesized first by GRIM, followed by chain extension with THP thiophene **2** or bromo-3-propyloxymethylthiophene **4**, to give diblock copolymers **8** and **10**, respectively. Each of the diblock structures was synthesized with P3HT as the major block, aiming to promote crystallization into fibrils, while also providing the reactive functionality needed for performing chemistry on the assembled structures.

Table 1 provides molecular weight data for the diblock copolymers obtained, typically in the range of 10−16 kDa, with polydispersity index (PDI) values of 1.4−1.6, as estimated by gel permeation chromatography (GPC). In each case, the P3HT block was the major component (~70−85 mol %). The relative block ratios (molar monomer equivalent) were calculated by $^1H$ NMR spectroscopy, comparing the signal intensity of the P3HT methylene group (adjacent to the thiophene ring) at 2.70 ppm to the same methylene of the P3MT (4.80 ppm) and P3AmT (4.50 ppm) blocks. For example, for entry 4 of Table 1, a 9200 g/mol P3HT was extended to a 11 600 g/mol diblock structure with THP-thiophene (**2**), followed by THP−ether deprotection to yield the primary alcohol.

Poly(3-THP)thiophene (**8**) was deprotected by stirring a 0.40 mM THF solution of polymer in 0.33 M HCl in THF at 60 °C for 5 h. Fourier transform infrared (FT-IR) spectroscopy of P3HT-b-P3MT (**9**) revealed a broad hydroxyl signal centered at ~3307 $cm^{-1}$, and $^1H$ NMR spectroscopy confirmed the absence of the THP protons (1.25−1.5 ppm, 3.5−3.7 ppm, and 4.5−4.7 ppm), while the methylene adjacent to the thiophene ring shifted to 4.8 ppm. P3HT-b-P3AmT (**12**) copolymers were obtained by reacting P3HT-b-P3BPT (**10**) with potassium phthalimide in chlorobenzene at 125 °C for 24 h, followed by conversion to the free amine by stirring in a THF solution of hydrazine at room temperature for 5 h. FT-IR spectroscopy of P3HT-b-P3AmT showed the expected amine stretch at 3414 $cm^{-1}$, and $^1H$ NMR spectroscopy showed a signal for the methylene adjacent to the amine at 2.85 ppm (shifted from the protected precursor at 3.40 ppm).

The solution assembly of fibrils, starting from functional polythiophenes **9** and **12**, was accomplished by diluting a 10 mg/mL


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**Scheme 1**

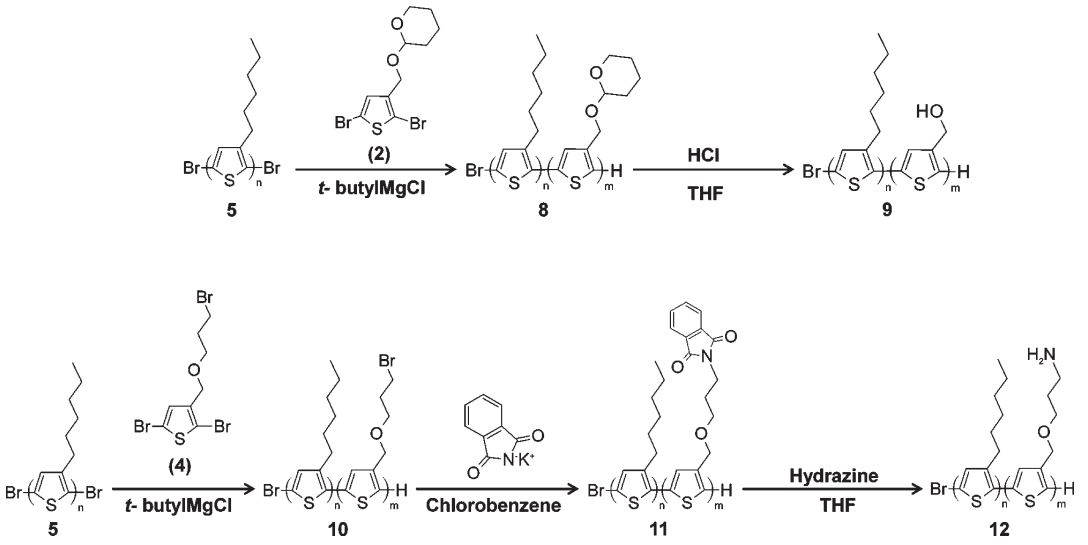


**Table 1. Molecular Weights of P3HT-b-P3THPT, P3HT-b-P3MT, P3HT-b-P3(BPT), and P3HT-b-P3(AmT) Diblock Copolymers**

| | | Molecular Weight (g/mol) | | | |
|---|---|---|---|---|---|
| entry | polymer | $M_{n(Theor.)}$[a] | $M_{n(Exper.)}$[b] | PDI[b] | P3HT:P3RT weight ratio[c] |
| 3 | **8** | 15 000 | 12 450 | 1.40 | 3:1 |
| 4 | **8** | 10 000 | 11 600 | 1.45 | 4:1 |
| 4[d] | **9** | | 10 750 | 1.40 | 4:1 |
| 5 | **10** | 15 000 | 16 150 | 1.40 | 5:1 |
| 7 | **10** | 15 000 | 11 550 | 1.60 | 4:1 |
| 7[e] | **11** | | 12 050 | 1.50 | 4:1 |
| 7[d] | **12** | | 10 250 | 1.55 | 4:1 |

[a] From the monomer:catalyst ratio. [b] Estimated by GPC against PS standards. [c] Calculated from $^1$H NMR spectroscopy. [d] Deprotected polymer. [e] Intermediate polymer.

chloroform solution of polymer with dichloromethane. The fibril solutions were aged (allowed to stand) for 24 h to promote polymer crystallization, as monitored by the increase in relative intensities of the vibronic bands (peaks at 530, 560, and 610 nm), and freely dissolved polymer (460 nm) in the ultraviolet-visible light (UV−vis) spectra. As seen in Figure 2B, the relative intensities of these signals indicates that ∼95% of P3MT and ∼70% P3AmT are integrated into the polymer assembly, compared to ∼55% for pure P3HT (12 000 g/mol, PDI = 1.30).[30] The particularly high degree of interchain association observed for P3HT-b-P3MT (**9**) is attributed to the influence of hydrogen bonding available from the functional block. The transition from free polymer to fibrils was studied by varying the $CHCl_3$:$CH_2Cl_2$ ratio and observing the growth of the vibronic bands with poorer solvent quality (see Figure 2A). Fibril assemblies begin to form at a $CHCl_3$:$CH_2Cl_2$ ratio of 1:1, with predominately fibril solutions forming at ratios of >1:5.

Reaction of the functionalized fibrils with 1,6-diisocyanatohexane was performed at room temperature, in a 1:7 $CHCl_3$:$CH_2Cl_2$ mixture for P3MT copolymers, or a 1:11 $CHCl_3$:$CH_2Cl_2$ mixture for P3AmT copolymers. Under these conditions, P3HT-b-P3MT fibrils cross-linked in 8 h, while the more nucleophilic amine groups of P3HT-b-P3AmT led to faster cross-linking (<30 min). The stability of the cross-linked assemblies was tested at various

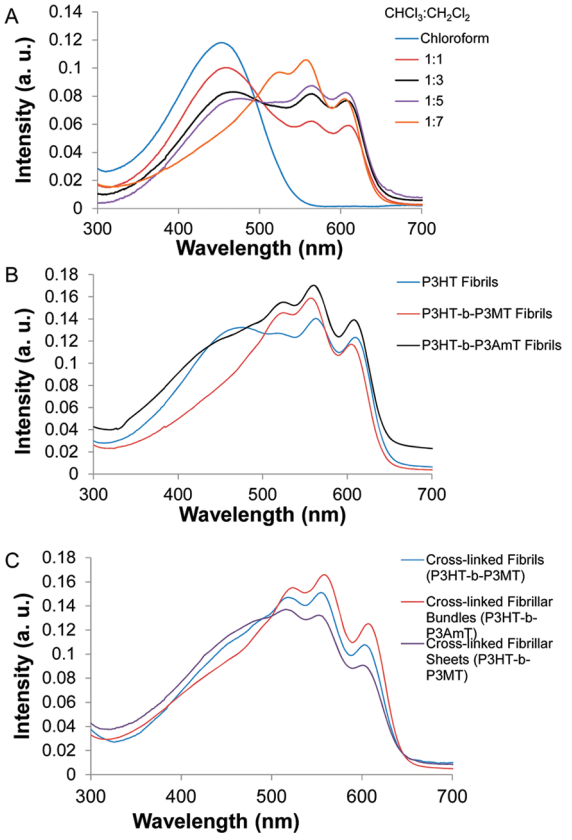


**Figure 2.** UV−vis absorption spectra: (A) P3HT-b-P3MT at various $CHCl_3$:$CH_2Cl_2$ ratios; (B) fibrillar P3HT, P3HT-b-P3MT, and P3HT-b-P3AmT in 1:7 or 1:11 $CHCl_3$:$CH_2Cl_2$; and (C) cross-linked fibrillar sheets, bundles, and independent fibrils in chloroform.


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intervals following diisocyanate addition, by diluting aliquots in chloroform and observing their absorption by UV−vis spectroscopy. The cross-linking was considered complete when it was sufficient to stabilize the assemblies in chloroform (i.e., when the fibril vibronic absorption was maintained), and, at a critical cross-linking density, the fibrils were seen to segregate to the fluid/air interface. The cross-linked fibril solutions were dried by rotary evaporation, suspended in THF, and centrifuged to separate fibrils from free polymer. Physical evidence of successful cross-linking was given by the observed stability of the assemblies in THF and chloroform (even after sonication), because we observed these solvents to disassemble un-cross-linked fibrils. UV−vis spectroscopy showed the assemblies to maintain their vibronic bands (530, 560, 610 nm) in chloroform (Figure 2C), and FT-IR spectroscopy indicated formation of the expected urethane and urea groups. For P3HT-b-P3MT, infrared (IR) signals associated with carbamate functionality were seen (3339 $cm^{-1}$ N−H bond, 1023 $cm^{-1}$ C−O bond, and 1617 $cm^{-1}$ C═O bond), while the urea-containing cross-linked P3HT-b-P3AmT showed an N−H stretch at 3414 $cm^{-1}$ and a C═O stretch at 1647 $cm^{-1}$.

Transmission electron microscopy (TEM) analysis was used to image fibrils, following drop-casting onto copper grids (see Figures 3A and 3B), where fibril widths were observed to vary from ∼15−25 nm, with lengths ranging from ∼0.5 to 5.0 $\mu$m. TEM images of cross-linked fibrillar materials were obtained on samples prepared at different concentrations and relative amounts of polymer and diisocyanate. Interestingly, variation of these parameters led to distinctly different morphologies. For example, as shown in Figures 3C and 3D, sheetlike materials on the length scale of 2−50 $\mu$m were obtained by cross-linking P3HT-b-P3MT fibrils in 1:7 $CHCl_3$:$CH_2Cl_2$, at 75 mM of hydroxyl or amine groups and 70 mM of diisocyanate. Under these concentrations, it is evident that significant intrafibril and interfibril cross-linking occurs, yielding more densely packed fibrils with interconnected microscale sheets. Performing the cross-linking chemistry at lower polymer concentration (45 mM of functional group and 30 mM of diisocyanate) gave less-dense fibrillar bundles, as seen in the TEM image of Figures 3E and 3F. These bundles range from 0.5 $\mu$m to 10 $\mu$m in diameter, and they contain individual fibrillar strands ∼15−85 nm thick. Even lower reactant concentrations (30 mM of functional group and 15 mM of isocyanate) gave predominantly individual fibrils, likely resulting from primarily intrafibril cross-linking among reactive groups along the long axis of the $\pi$-stacked polythiophene structure, as shown in Figures 3G and 3H. To test their long-term stability, the assemblies were stored in chloroform for 6 months, and despite long exposure to a favorable solvent, the assemblies maintained their structural integrity (see Figures S3-A, S3-B, and S3-C in the Supporting Information). A 10 mg/mL chloroform solution of fibrils was dropcast onto a glass slide and annealed at 150 °C under vacuum for 1 h to test thermal stability. The cross-linked assemblies were rinsed off the slide with chloroform and they were observed to retain their original nanowire morphologies, again as monitored by the presence of the vibronic bands in the UV−vis spectra, as well as TEM images (see Figure S3-D in the Supporting Information). Despite extended periods of time in a favorable solvent, and thermal annealing, the cross-linked assemblies maintained their structural integrity (see Figures S3-A, B, C, and D in the Supporting Information), indicating the production of stable and robust fibrillar materials.

In summary, we have described a synthesis of P3HT-based diblock copolymers that form well-defined fibrils in solution, and that contain reactive functionality that provides a viable route for fibril cross-linking in solution. The hydroxyl and amine-functionalized polythiophene copolymers can be processed to yield assemblies over a range of length scales. The robust assemblies maintained their integrity over time (at least 6 months), and the properties and performance of these materials in devices is under evaluation.

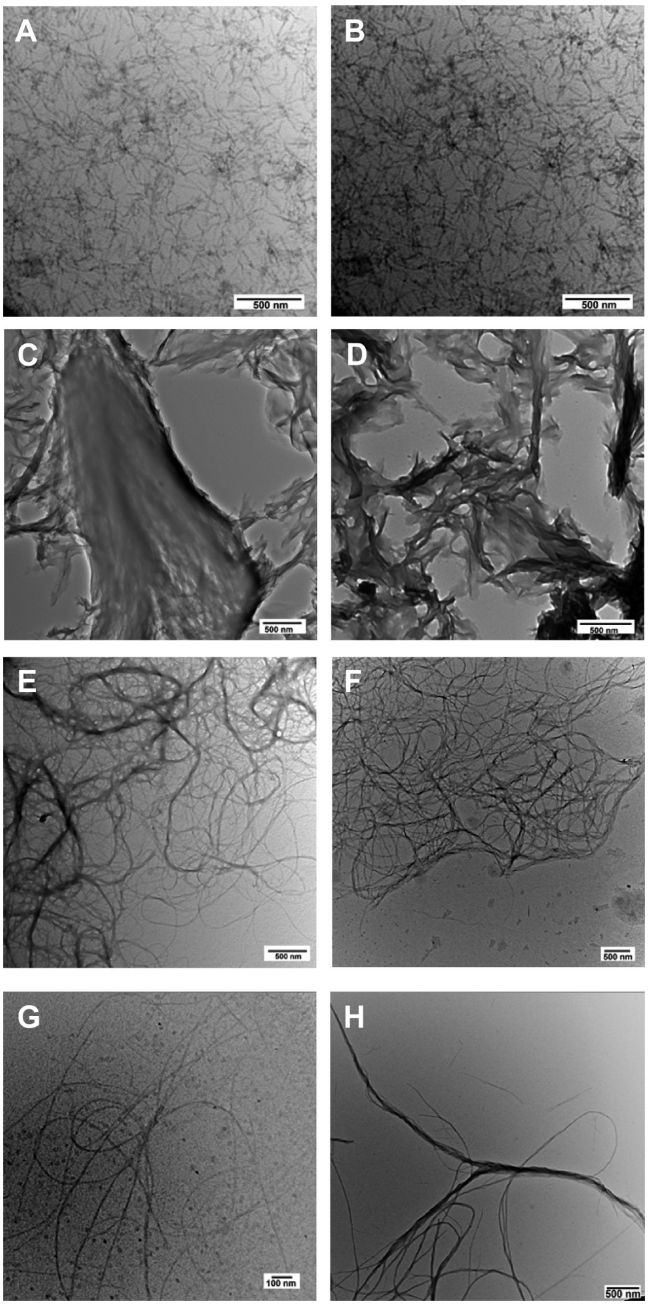


**Figure 3.** Transmission electron microscopy (TEM) images of (A) P3HT-b-P3MT fibrils, (B) P3HT-b-P3AmT fibrils, (C) P3HT-b-P3MT cross-linked fibrillar sheets, (D) P3HT-b-P3AmT cross-linked fibrillar sheets, (E) P3HT-b-P3MT cross-linked bundles of fibrils, (F) P3HT-b-P3AmT cross-linked bundles of fibrils, (G) P3HT-b-P3MT cross-linked discrete fibrils, and (H) P3Ht-b-P3AmT cross-linked discrete fibrils.

## EXPERIMENTAL SECTION

**Materials.** Tetrahydrofuran (THF) was dried over sodium/benzophenone under nitrogen and freshly distilled before use. Chloroform


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(99%, from Fisher Scientific) was used as received. 3-Thiophene methanol (99%, from Aldrich), 3-bromothiophene (97%, from Alfa Aesar), and 1-bromohexane (98%, from Aldrich) were all used as received. *N*-bromosuccinimide (NBS) (99%, from Acros Organics) was recrystallized in water; triethyl amine (TEA) was dried over calcium hydride under nitrogen and freshly distilled before use. 3-Bromothiophene (97%, from Alfa Aesar), 3,4-dihydro-2H-pyran (DHP) (98%, from Aldrich), 1,6-diisocyanatohexane (98%, from Aldrich), *p*-toluene sulfonic acid (98.5%, from Aldrich), *tert*-butyl magnesium chloride (2.0 M in diethyl ether, from Aldrich), 3-bromopronol (98%, from Aldrich), potassium phthalimide (99%, from Aldrich), and [1,3-bis-(diphenylphosphino)propane]-dichloronickel(II) (99%, from Aldrich) were all used as-received. All other chemicals were purchased from Aldrich Chemicals and used as-received.

**Techniques.** $^1$H NMR spectra were recorded on a Brüker Model Spectrospin 400 system, using the residual proton resonance of the solvent as the internal standard. Molecular weights of the polymers were estimated using GPC with chloroform as the eluent, using a polystyrene standard with a refractive index detector. UV−vis absorption spectra were obtained from a Shimadzu Model 1601 UV spectrometer. TEM images were taken from JEOL Model 100CX and 2000FX systems.

**Synthesis.** *Synthesis of 2,5-Dibromo-3-thiophenemethanol (**1**).* 3-Thiophenemethanol (5 g, $4.38 \times 10^{-2}$ mol) was dissolved in THF (40 mL) in a dry 100-mL round-bottomed flask (RBF). The flask was degassed with nitrogen for 15 min before being sealed under a nitrogen atmosphere. NBS (15.59 g, $8.76 \times 10^{-2}$ mol) was gradually added to the reaction mixture over a 10-min period, and the reaction was run at room temperature overnight. The solution was run through a plug of Celite 545 filter powder to remove residual NBS, then the THF was removed via rotary evaporation. The product was dissolved in diethyl ether and then rinsed sequentially with 1 M sodium hydroxide solution and water. The organic layer was concentrated and the product was run through a silica gel column with an eluent of hexane:ethyl acetate (80:20), collecting the third active spot seen by thin-layer chromatography (TLC). The solvent was removed by rotary evaporation to yield the product (10.0 g, 85% yield) as a white solid. $^1$H NMR (400 MHz, $CDCl_3$, $\delta$, ppm): 4.60 (s, 2H) and 6.70 (s, 1H). $^{13}$C NMR (400 MHz, $CDCl_3$, $\delta$, ppm): 58.89, 109.11, 111.43, 130.38, 141.26.

*Synthesis of 2,5-Dibromo-3-tetrahydropyranoxymethylthiophene (**2**).* 2,5-Dibromo-3-thiophenemethanol (5 g, $1.84 \times 10^{-2}$ mol), *p*-toluene sulfonic acid ($3.53 \times 10^{-2}$ g, $1.84 \times 10^{-4}$ mol), and dichloromethane were added to a dry 100-mL RBF that was equipped with a $N_2$ inlet. 3,4-Dihydro-2H-pryan (2.08 mL, $2.3 \times 10^{-2}$ mol) was added dropwise to the solution over a 5-min period, and the reaction was run at room temperature for 6 h. The solution was dried by rotary evaporation and run through a silica gel column with a hexane/ethyl acetate (80:20) solvent combination as the eluent. The first UV active spot was collected, dried by rotary evaporation to yield the product (5.36 g, 82% yield) as a clear liquid. $^1$H NMR (400 MHz, $CDCl_3$, $\delta$, ppm): 1.25−1.50(m, 6H), 3.50(d, 1H), 3.70(d, 1H), 4.60 (d, 1H), 4.75(d, 1H), 4.80(s, 1H), 6.85 (s, 1H). $^{13}$C NMR (400 MHz, $CDCl_3$, $\delta$, ppm): 19.03, 25.21, 30.21, 61.88, 62.90, 97.71, 109.74, 110.90, 130.79, 139.11.

*Synthesis of 2,5-Dibromo-3-bromomethylthiophene (**3**).* 2,5-Dibromo-3-bromomethylthiophene (**3**) was synthesized utilizing a procedure developed by Tan et al.[31] with minor modifications. Compound **2** (5 g, $1.84 \times 10^{-2}$ mol) and dry methylene chloride (100 mL) were added to a 250-mL RBF that was sealed under a nitrogen atmosphere. The solution was placed in an ice bath and stirred for 20 min. Phosphorus tribromide (1.73 mL, $1.84 \times 10^{-2}$ mol) was added dropwise to the solution over a 15-min period. The reaction was run at room temperature for 5 h and then quenched with a 10% sodium bicarbonate solution. The organic solution was passed through a plug of Celite 545, rinsed with water, and then dried over magnesium sulfate. The solution was filtered and dried using rotary evaporation to yield the product (5.8 g, 94% yield) as a light yellow solid. $^1$H NMR (400 MHz, $CDCl_3$, $\delta$, ppm): 4.80 (s, 2H) and 6.80 (s, 2H). $^{13}$C NMR (400 MHz, $CDCl_3$, $\delta$, ppm): 24.18, 111.19, 111.58, 130.28, 137.12.

*Synthesis of 3-(3-bromopropyl)oxymethylthiophene (**4**).* 2,5-Dibromo-3-bromomethylthiophene (5 g, $1.49 \times 10^{-2}$ mol) was dissolved in THF (20 mL) in a dry 100-mL RBF. Potassium *tert*-butoxide (1.75 g, $1.56 \times 10^{-2}$ mol), *tert*-butanol (10 mL), and 3-bromopropanol (2.20 g, $1.58 \times 10^{-2}$ mol) were added to the solution, and the reaction was run at 40 °C for 8 h. The solution was dried by rotary evaporation and run through a silica gel column with a hexane/ethyl acetate (75:25) solvent combination as the eluent. The second UV-active spot was collected and dried by rotary evaporation to yield the product (4.10 g, 70% yield) as a light yellow liquid. $^1$H NMR (400 MHz, $CDCl_3$, $\delta$, ppm): 2.20 (m, 2H), 3.50 (t, 2H), 3.60 (t, 2H), 4.55 (s, 2H) and 6.8 (s, 1H). $^{13}$C NMR (400 MHz, $CDCl_3$, $\delta$, ppm): 30.56, 32.77, 66.82, 67.82, 110.19, 111.43, 130.81, 139.21.

*Synthesis of 3-hexylthiophene.* 3-Hexylthiophene was synthesized following a procedure developed by Urien et al.[32] Magnesium turnings (1.47 g, $6.05 \times 10^{-2}$ mol) and diethyl ether (100 mL) were added to a flame-dried two-necked RBF that was equipped with an addition funnel and $N_2$ inlet. The flask was packed in ice and flushed with nitrogen before being sealed under a nitrogen atmosphere. 1-Bromohexane (8.55 mL, $6.05 \times 10^{-2}$ mol) and diethyl ether (50 mL) were mixed and added to the addition funnel, where they were added dropwise to the reaction flask over a 30-min period, after which the reaction was run for 2 h at room temperature. 3-Bromothiophene (5.73 mL, $6.05 \times 10^{-2}$ mol), [1,3-bis(diphenylphosphino)propane]-dichloronickel(II) (3.28 g, $6.05 \times 10^{-3}$ mol), and diethyl ether (200 mL) were mixed in a two-necked RBF that was equipped with a septum and nitrogen input. The flask was placed in a dry ice/acetone bath and the 1-bromomagnesium-hexane solution was cannulated into the flask. The reaction was allowed to stir for 15 min in the dry ice/acetone bath and then run overnight at room temperature. The reaction was quenched with 1 M HCl solution and extracted with water, keeping the organic layer. The solvent was removed by rotary evaporation, yielding the crude product (8.60 g, 85% yield) as a color liquid; no further purification took place. $^1$H NMR (400 MHz, $CDCl_3$, $\delta$, ppm): 0.80 (t, 3H), 1.25−1.50 (m, 8H), 2.50 (t, 2H), 6.75 (d, 1H), 6.90 (s, 1H), 6.80 (d, 1H). $^{13}$C NMR (400 MHz, $CDCl_3$, $\delta$, ppm): 14.14, 22.70, 29.10, 30.34, 30.61, 31.77, 119.75, 125.00, 128.21, 143.13.

*Synthesis of 2,5-Dibromo-3-hexylthiophene.* Crude 3HT (5 g, $2.98 \times 10^{-2}$ mol) and THF (40 mL) were added to a 100-mL RBF that was degassed for 15 min and then sealed with nitrogen. NBS (10.60 g, $5.96 \times 10^{-2}$ mol) was gradually added over 10 min, and the reaction was run at room temperature for 4 h. The reaction was run through a plug of Celite 545 filter powder and the solvent was removed by rotary evaporation. The crude product was distilled, with **6** (8.5 g, 88% yield) being collected at 135 °C as a colorless oil. $^1$H NMR (400 MHz, $CDCl_3$, $\delta$, ppm): 0.80 (t, 3H), 1.25−1.50 (m, 8H), 2.50 (t, 2H), 6.85 (s, 1H). $^{13}$C NMR (400 MHz, $CDCl_3$, $\delta$, ppm): 14.40, 22.88, 29.09, 29.76, 30.00, 31.87, 108.21, 110.60, 131.16, 143.18.

*Synthesis of Poly(3-hexylthiophene) (P3HT) (**5**).* 3HT (1.00 g, $3.05 \times 10^{-3}$ mol) and THF (20 mL) were added to a dry 100-mL two-necked RBF that was equipped with a condenser and an $N_2$ inlet. *Tert*-butyl magnesium chloride (1.52 mL (2 M sol.), $3.05 \times 10^{-3}$ mol) was added to the solution and the reaction was refluxed for 2 h. The flask was cooled to room temperature and [1,3-bis(diphenylphosphino) propane]-dichloronickel(II) (Ni(dppp)$Cl_2$) ($2.75 \times 10^{-2}$ g, $5.08 \times 10^{-5}$ mol) was added. The polymerization was allowed to proceed at room temperature for 15 min and then it was quenched with methanol (20 mL). The polymer was precipitated in methanol, isolated by centrifugation, purified by sequential Soxhlet extractions using methanol, hexane, and chloroform, respectively. The chloroform fraction was dried to yield the final polymer (350 mg, 68% yield) as a deep purple

solid. $M_n$ = 9700 g/mol, polydispersion index (PDI) = 1.30, as compared to polystyrene standards. $^1$H NMR (400 MHz, $CDCl_3$, $\delta$, ppm): P3HT — 0.85(t, 3H), 1.25−1.70(m, 8H), 2.70(t, 2H), 7.00(s, 1H). $^{13}$C NMR (400 MHz, $CDCl_3$, $\delta$, ppm): 14.32, 22.84, 29.45, 29.65, 30.69, 31.88, 128.77, 130.64, 133.85, 140.05. P3HT: $M_n$ = 10 000 g/mol, PDI = 1.20.

*Synthesis of P3HT-b-P3RT Diblock Copolymers (where R = tetrahydropyranoxymethyl (PTHPT) (**8**) or 3-bromopropylmethyloxymethl (P3BPT) (**10**)).* Standard diblock copolymer synthesis involves the formation of the Grignard derivative of each monomer, as previously outlined. 3HT was polymerized first as outlined previously; this synthesis typically goes to 99% conversion within 10 min, and then the Grignard derivative (**2** or **4**) is cannulated into the P3HT flask. The second block is polymerized for 1 h, after which it is quenched with methanol (20 mL). The polymer is precipitated in methanol and centrifuged, with the polymer being collected after the solvent is decanted off. The polymer was purified by sequential Soxhlet extractions using methanol, hexane, and chloroform. The chloroform fraction was dried to yield the final polymer as a deep purple solid. Polymerizations were carried out as previously outlined with the following monomer ratios, yielding the following polymer samples: 3HT (2.00 g, 6.14 × $10^{-3}$ mol), 3THPT (7.28 × $10^{-1}$ g, 2.04 × $10^{-3}$ mol) with those equivalents of the Grignard reagent, and Ni(dppp)$Cl_2$ (4.75 × $10^{-2}$ g, 8.77 × $10^{-5}$ mol) yielded 65% yield (3:1 weight ratio, $M_n$ = 12 500 g/mol, PDI = 1.40). 3HT (2.00 g, 6.13 × $10^{-3}$ mol), 3THPT (5.46 × $10^{-1}$ g, 1.54 × $10^{-3}$ mol), and Ni(dppp)$Cl_2$ (5.54 × $10^{-2}$, 1.02 × $10^{-4}$ mol) yielded 70% yield (4:1 weight ratio, $M_n$ = 11 500 g/mol, PDI = 1.40). $^1$H NMR (400 MHz, $CDCl_3$, $\delta$, ppm): P3HT — 0.85 (t, 3H), 1.25−1.70 (m, 8H), 2.70 (t, 2H), 7.00 (s, 1H). $^{13}$C NMR (400 MHz, $CDCl_3$, $\delta$, ppm): 14.32, 22.84, 29.45, 29.65, 30.69, 31.88, 128.77, 130.64, 133.85, 140.05. P3THPT — 1.25−1.50(m, 6H), 3.50(m, 1H), 3.70(m, 1H), 4.50(m, 1H), 4.75(m, 1H), 4.80(s, 1H), 7.00(s, 1H). $^{13}$C NMR (400 MHz, $CDCl_3$, $\delta$, ppm): P3THPT — 19.05, 25.20, 30.31, 61.88, 62.90, 97.70, 129.21, 130.75, 133.50, 136.62. 3HT (2.00 g, 6.14 × $10^{-3}$ mol), 3BPT (7.86 × $10^{-1}$ g, 2.00 × $10^{-3}$ mol) with those equivalents of the Grignard reagent, and Ni(dppp)$Cl_2$ (4.16 × $10^{-2}$ g, 7.68 × $10^{-5}$ mol) yielded 62% yield (3:1 weight ratio, $M_n$ = 12 000 g/mol, PDI = 1.55). 3HT (2.00 g, 6.13 × $10^{-3}$ mol), 3BPT (6.02 × $10^{-1}$ g, 1.54 × $10^{-3}$ mol), and Ni(dppp)$Cl_2$ (5.54 × $10^{-2}$, 1.02 × $10^{-4}$ mol) yielded 69% yield (4:1 weight ratio, $M_n$ = 11 500 g/mol, PDI = 1.40). 3HT (2.00 g, 6.13 × $10^{-3}$ mol), 3BPT (4.81 × $10^{-1}$ g, 1.23 × $10^{-3}$ mol), and Ni(dppp)$Cl_2$ (4.15 × $10^{-2}$, 7.66 × $10^{-5}$ mol) yielded 72% yield (5:1 weight ratio, $M_n$ = 16 000 g/mol, PDI = 1.40). $^1$H NMR (400 MHz, $CDCl_3$, $\delta$, ppm): P3HT — 0.85(t, 3H), 1.25−1.70(m, 8H), 2.70(t, 2H), 7.00(s, 1H). $^{13}$C NMR (400 MHz, $CDCl_3$, $\delta$, ppm): 14.32, 22.84, 29.45, 29.65, 30.69, 31.88, 128.77, 130.64, 133.85, 140.05. P3BPT — 2.20(m, 2H), 3.40(m, 2H), 3.50(m, 2H), 4.65(m, 1H), 7.00(s, 1H). $^{13}$C NMR (400 MHz, $CDCl_3$, $\delta$, ppm): P3BPT — 30.55, 32.77, 66.81, 67.82, 129.32, 131.01, 133.69, 137.48.

*Synthesis of P3HT-b-poly(3-methanol thiophene) (P3MT) (**9**).* P3HT-b-P3THPT (10 500 g/mol, 3.00 × $10^{-1}$ g, 3.00 × $10^{-5}$ mol) was dissolved in THF (75 mL) in a 100-mL RBF. HCl (2 mL, 2.50 × $10^{-2}$ mol) was added and the solution was heated at 60 °C for 5 h. Sodium bicarbonate (5 g, 5.59 × $10^{-2}$ mol) was added to the solution and it was stirred for 30 min. The solution was run through a plug of Celite 545 filter aid and dried by rotary evaporation. The solid was purified by Soxhlet extraction with methanol and chloroform as the solvents. The chloroform fraction was dried down to yield the final product as a deep purple solid (2.45 × $10^{-1}$ g, 91% yield). $M_n$ = 15 100 g/mol, PDI = 1.60. $^1$H NMR (400 MHz, $CDCl_3$, $\delta$, ppm): P3MT — 4.80(s, 1H), 7.00(s, 1H). $^{13}$C NMR (400 MHz, $CDCl_3$, $\delta$, ppm): P3MT — 58.89, 129.22, 130.80, 133.52, 136.68.

*Synthesis of P3HT-b-poly(3-phthalimide thiophene) (P3PhT) (**11**).* P3HT-b-P3BPT (**10**) (11 500 g/mol, 5.00 × $10^{-1}$ g, 4.35 × $10^{-5}$ mol) was dissolved in chlorobenzene (50 mL) in a 100-mL RBF. Potassium phthalimide (7.92 × $10^{-1}$ g, 4.35 × $10^{-3}$ mol) was added and the solution was heated at 125 °C for 24 h. The resulting phthalimide containing polymer **11** was precipitated in methanol and dried to yield the desired polymer (4.55 × $10^{-1}$ g, 87% yield) as a deep purple solid. P3PhT — $^1$H NMR (400 MHz, $CDCl_3$, $\delta$, ppm): 2.35 (m, 2H), 3.20(m, 2H), 3.50(m, 2H), 4.65(m, 1H), 7.00(s, 1H). $^{13}$C NMR (400 MHz, $CDCl_3$, $\delta$, ppm): 24.96, 30.54, 66.80, 67.81, 123.42, 129.34, 131.02, 132.96, 133.68, 133.87, 137.46, 168.37.

*Synthesis of P3HT-b-poly(3-aminopropyloxymethylthiophene) (P3AmT) (**12**).* **11** (4.55 × $10^{-1}$g , 3.79 × $10^{-5}$ mol) was dissolved in THF (20 mL), hydrazine (1.48 × $10^{-1}$ g, 4.35 × $10^{-3}$ mol) was added, and the reaction was run at room temperature for 5 h. The reaction was quenched with methanol and dried by rotary evaporation. The resulting polymer underwent sequential Soxhlet extractions using methanol and chloroform, respectively. The chloroform fraction was dried by rotary evaporation to yield the desired polymer (3.75 × $10^{-1}$ g, 90% yield). P3AmT — $^1$H NMR (400 MHz, $CDCl_3$, $\delta$, ppm): 2.30(m, 2H), 2.90(m, 2H), 3.50(m, 2H), 4.65(m, 1H), 7.00(s, 1H). $^{13}$C NMR (400 MHz, $CDCl_3$, $\delta$, ppm): 30.63, 41.16, 66.81, 67.82, 129.31, 131.04, 133.65, 137.48.

**Solution Preparation.** Fibrils formation was done under an $N_2$ atmosphere and in darkness. To induce aggregation, a respective amount of dichloromethane (7 mL for **9**, 11 mL for **12**) was added to the P3HT-b-P3MT or P3HT-b-P3AmT solution (10 mg/mL) in chloroform.

**Assembly Cross-Linking Procedure.** P3HT-b-P3RT (10 mg, 9.5 × $10^{-7}$ mol (**9**) or 1.0 × $10^{-6}$ mol (**12**)) was dissolved in $CHCl_3$ (1 mL) in a 20-mL vial. $CH_2Cl_2$ (7 or 11 mL) was added to the solution and fibril formation was allowed to proceed overnight. Cross-linked assemblies were achieved with the following concentrations (expressed as relative ratios) of polymer functional group:TEA:1,6-diisocyanatohexane in 1:7/11 $CHCl_3$:$CH_2Cl_2$: polymer sheets (75 mM of the hydroxyl/amine functional group:70.0 mM:70.0 mM); bundles of fibrils (45 mM:35.0 mM:30.0 mM); and predominantly isolated fibrils (30 mM:20.0 mM:15.0 mM). Once cross-linking was achieved, the solutions were dried by rotary evaporation, suspended in THF, and isolated by centrifugation.

TEM analysis was performed on self-assembled structures of P3HT-b-P3MT and P3HT-b-P3AmT in chloroform/dichloromethane solvent mixtures, and in chloroform for cross-linked assemblies (1 mg/mL). Samples were drop-cast on a carbon-coated copper grid, and the solution was allowed to evaporate on the TEM grid under ambient conditions. UV−vis spectroscopy was carried out with 0.1 mM sample solutions.

## ■ ASSOCIATED CONTENT

**Supporting Information.** Characterization of the molecular weights and photophysical properties of the polymers is included. This information is available free of charge via the Internet at http://pubs.acs.org/.

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