Water Processable Polythiophene Nanowires by Photo-Cross-Linking and Click-Functionalization

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Supporting Information

ABSTRACT: Replacing or minimizing the use of halogenated organic solvents in the processing and manufacturing of conjugated polymer-based organic electronics has emerged as an important issue due to concerns regarding toxicity, environmental impact, and high cost. To date, however, the processing of well-ordered conjugated polymer nanostructures has been difficult to achieve using environmentally benign solvents. In this work, we report the development of water and alcohol processable nanowires (NWs) with well-defined crystalline nanostructure based on the solution assembly of azide functionalized poly(3-hexylthiophene) (P3HT-azide) and subsequent photo-cross-linking and functionalization of these NWs. The solution-assembled P3HT-azide NWs were successfully cross-linked by exposure to UV light, yielding good thermal and chemical stability. Residual azide units on the photo-cross-linked NWs were then functionalized with alkyne terminated polyethylene glycol (PEG–alkyne) using copper catalyzed azide–alkyne cycloaddition chemistry. PEG functionalization of the cross-linked P3HT-azide NWs allowed for stable dispersion in alcohols and water, while maintaining well-ordered NW structures with electronic properties suitable for the fabrication of organic field effect transistors (OFETs).

KEYWORDS: Solution-assembled nanowires, photo-cross-linking, click-functionalization, water processable organic electronics

Conjugated polymers have been evaluated extensively as the active component in cost-effective, lightweight, and flexible electronic devices due to their promising optoelectronic properties.1−3 Over the past decade, significant academic and industrial efforts have been devoted to the development of efficient organic electronic devices. As a result, conjugated polymer-based organic field effect transistors (OFETs) with charge carrier mobilities comparable to amorphous silicon have been demonstrated,4−8 and polymer solar cells have been fabricated with power conversion efficiencies that exceed the threshold for successful commercialization.9−11 Solution processing of high efficiency organic electronic devices, however, almost exclusively involves the use of halogenated solvents, such as chloroform and chlorobenzene.12−16 The toxicity, environmental impact, and high energy cost associated with these halogenated solvent-based processes make their use unsustainable.17,18 Furthermore, stricter regulation on the mass production of halogenated solvents,18 with the eventual goal of eliminating the use of these chemicals, strongly supports the need for the development of new electro-active materials and processes compatible with environmentally benign solvents. Despite the importance of, and growing interest in, “green” solvents for processing organic electronics, only limited success has been demonstrated to date.14−18

Solvents such as alcohols and water represent attractive alternatives to halogenated solvents due to reduced environmental impact, toxicity, and cost. In particular, the development of an aqueous platform for processing of organic electronics represents an important step toward the goal of sustainable device manufacturing. Prior to this work, two major strategies for the synthesis of water soluble conjugated polymers have been reported. One approach involves the incorporation of ionic moieties to the polymer backbone, which provide solubility in alcohols and water.19−21 These charged groups, however, can quench charge carriers and influence the energy level of the polymers, resulting in poor device performance
when these polymers are used in the active layer.\textsuperscript{15,17} In the second approach, conjugated polymers are synthesized with nonionic, hydrophilic pendant groups\textsuperscript{12,20,23} or hydrophilic blocks (i.e., polyethylene glycol, PEG).\textsuperscript{24,25} For example, Duan et al.\textsuperscript{12} recently synthesized alcohol-soluble, narrow band gap conjugated polymers functionalized with pendant amino groups and demonstrated their use as an active layer in PSCs. Despite their promising solubility characteristics, however, the presence of amino side groups in these conjugated polymers led to degradation of device performance. The introduction of bulky or extended hydrophilic side chains to improve aqueous solubility can also disturb the formation of a well-defined crystalline nanostructure, an important characteristic in determining the optoelectronic properties of many conjugated polymers.\textsuperscript{17,26} Ensuring the fidelity of well-ordered crystalline nanostructure after introduction of solubilizing groups is an important step toward achieving efficient green-solvent processable conjugated polymer devices.

Solution assembly of conjugated polymers into one-dimensional crystalline nanowires (NWs) represents an attractive route for processing of organic optoelectronic devices due to the excellent optoelectronic properties and long-range charge transport pathways offered by these well-organized structures with nanometer-scale cross-sectional dimensions.\textsuperscript{27–33} For example, conjugated polymer NWs have been used to enhance charge carrier mobility\textsuperscript{34–36} control bulk heterojunction morphology in solar cells,\textsuperscript{37–39} produce percolated conducting structures in blends with insulating polymers,\textsuperscript{40,41} and provide hybrid structures with inorganic semiconductors.\textsuperscript{42–44} Surface modification of preassembled conjugated polymer NWs with hydrophilic moieties would seem to represent a simple approach to achieve conjugated polymers that retained well-ordered crystalline nanostructures and good optoelectronic properties while allowing for subsequent processing from aqueous suspensions. For this strategy to succeed, maintaining stability (against both dissolution and aggregation) of the NWs during functionalization is a key challenge.

In this work, we present a strategy to chemically modify solution-assembled conjugated polymer NWs, based on azide-functionalized poly(3-hexylthiophene) (P3HT-azide), which allows for photo-cross-linking with UV light\textsuperscript{45,46} to provide stability and subsequent functionalization with alkyne-terminated molecules using click chemistry\textsuperscript{47,48} (Scheme 1). Photo-cross-linked P3HT-azide NWs are shown to be highly stable against temperature and solvent treatments, retaining their nanostructural integrity and electronic performance. These photo-cross-linked NWs are then successfully functionalized with alkyne-terminated PEG (PEG-alkyne) via the copper catalyzed cycloaddition reaction using residual azide units on the surfaces of the NWs. The resulting functionalized P3HT-PEG NWs can be stably dispersed in a variety of alcohols and water, while maintaining effective charge transporting nanostructures and electronic properties, enabling the processing of efficient OFETs from environmentally benign solvents—water and alcohols.

P3HT-azide copolymers were synthesized following a previously reported procedure.\textsuperscript{45,47,48} Random copolymerization of 3-(azidohexyl)thiophene and 3-hexylthiophene was conducted with feed ratios of 20 and 80 mol %, respectively. The actual content of 3-(azidohexyl)thiophene in the copolymer product was determined to be 21 ± 1 mol % using \textsuperscript{1}H NMR (Figure S1). The polymerization conditions were carefully optimized to yield highly regioregular P3HT with relatively high molecular weight; these characteristics allow the formation of crystalline NW structures with long-range charge transport pathways and optimal optoelectronic properties. The P3HT-azide copolymers were highly regioregular (>98%), as determined by \textsuperscript{1}H NMR, with a number-average molecular weight \((M_n)\) of 35 000 g/mol and dispersity \((D)\) of 1.4, relative to polystyrene stands, as measured using size exclusion chromatography (SEC).

Solution assembly of the P3HT-azide copolymer was induced by a mixed solvent method.\textsuperscript{39,50} Briefly, the addition of the poor solvent 1-butanol (BuOH, \(\delta = 11.30 \text{ cal}^{1/2} \text{ cm}^{-3/2}\)) to a solution of P3HT-azide in the good solvent tetrahydrofuran (THF, \(\delta = 9.52 \text{ cal}^{1/2} \text{ cm}^{-3/2}\)) drives growth of crystalline NWs. These solvents were chosen because they have low UV cut-offs (THF = 212 nm, BuOH = 215 nm), a critical consideration for azide photo-cross-linking. As the relative concentration of BuOH in the P3HT-azide solutions was increased, a progressive decline in the intensity of the absorption peak associated with dissolved P3HT \((\lambda = 450 \text{ nm})\) was observed by UV–vis spectroscopy. Simultaneously, vibrionic bands at 564 and 611 nm appeared and increased in intensity, indicating the \(\pi\)-electron delocalization of P3HT-azide chains associated with NW formation (Figure 1a).\textsuperscript{51} The optimal solvent composition for NW self-assembly was determined to be 7:1 (v/v) THF/BuOH. Under this condition, well-defined NWs were formed that had lateral dimensions of 18–20 nm and lengths of several micrometers, as visualized using transmission electron microscopy (TEM) (Figure 1c). Remarkably, incorporation of 20 mol % azide in the P3HT-azide copolymers does not appear to substantially disrupt the molecular packing or self-assembly of the copolymers, as well-defined NWs similar to those typically formed from P3HT homopolymers\textsuperscript{30,31,52} were obtained.

Photo-cross-linking of P3HT-azide NWs was carried out using solutions in quartz cuvettes under nitrogen atmosphere, with exposure to UV light \((\lambda = 254 \text{ nm}, 0.76 \text{ mW cm}^{-2}\) driving decomposition of azides into highly reactive nitrenes, which leads to cross-linking via C–H insertion.\textsuperscript{53} The conversion of azide groups was determined using Fourier transform infrared spectroscopy (FT-IR) by monitoring the reduction of the azide stretch at 2100 cm\textsuperscript{-1} (Figure S2). Figure 1b demonstrates the

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**Scheme 1. Schematic Illustration of Photo-Cross-Linking and Click-Functionalization of Solution-Assembled P3HT-Azide NWs**
The relative amount of residual azide units after different UV exposure times; the azide peak intensity decreases with extended UV irradiation, indicating the successful conversion of the azides in solution. Interestingly, the morphology of photo-cross-linked P3HT-azide NWs was unchanged, regardless of the extent of cross-linking, as shown using TEM (Figure 1d,e). Photo-cross-linked P3HT-azide NWs irradiated for 60 min (60% azide conversion, Figure 1d) and 120 min (90% azide conversion, Figure 1e) have a similar NW structure compared to the uncross-linked NWs. This photo-cross-linking method is particularly attractive both because it does not require the use of additional chemical reagents and because it avoids the extensive aggregation of NWs typically found except under very dilute conditions for previously reported chemical cross-linking methods.54−56

The thermal stability and solvent resistance of the photo-cross-linked P3HT-azide NWs were examined by monitoring the absorbance of vibronic bands in the UV−vis spectra (Figures S3−4). The relative intensity of the vibronic peak at 564 nm is plotted as a function of the solution temperature (Figure 2a) and volume equivalents of added chlorobenzene (CB) (Figure 2b). Increasing the temperature from 25 to 50 °C leads to complete dissolution of uncross-linked P3HT-azide NWs, as shown by the disappearance of the vibronic peaks. In contrast, the photo-cross-linked NWs retained significant absorption at 564 nm, with those irradiated for 60 min showing almost no reduction in intensity after thermal treatment, indicating a high degree of structural stability. A similar trend was observed with regards to solvent resistance. Addition of an equal volume of CB, which is one of the best solvents for P3HT, to the uncross-linked NWs resulted in complete dissolution, whereas NWs irradiated for 60 min retained nearly the original vibronic band peak intensity after addition of an equal volume of CB. Interestingly, only 60% azide conversion (60 min of UV irradiation) was sufficient to yield highly stable NWs, leaving 40% of residual azide groups available as reactive sites for further functionalization.

Table 1. OFET Characteristics of P3HT-Azide NWs Subjected to Different UV Exposure Times

<table>
<thead>
<tr>
<th>UV exposure time (min)</th>
<th>Hole mobility (cm² V⁻¹ s⁻¹)</th>
<th>on/off ratio</th>
<th>V_onset (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>7.7 ± 2.8</td>
<td>&gt;10³</td>
<td>−13.9 ± 10.9</td>
</tr>
<tr>
<td>10</td>
<td>6.5 ± 1.9</td>
<td>&gt;10³</td>
<td>2.7 ± 5.3</td>
</tr>
<tr>
<td>30</td>
<td>6.0 ± 1.5</td>
<td>&gt;10³</td>
<td>−1.8 ± 10.8</td>
</tr>
<tr>
<td>60</td>
<td>3.2 ± 0.9</td>
<td>&gt;10³</td>
<td>−9.6 ± 13.9</td>
</tr>
</tbody>
</table>

With UV exposure times of 0, 30, 60, and 90 min, NWs were fabricated in a top-contact, bottom-gate geometry. The surface of a highly n-doped Si wafer with a thermally grown SiO₂ (300 nm Cₛ = 10 nF cm⁻²) was modified with an octadecyltrime-thoxysilane (OTS) monolayer following a literature procedure.27 Gold electrodes were deposited with a channel length of 50 μm and a channel width of 1000 μm. Without cross-linking, P3HT-azide NWs exhibited a hole mobility of 7.7 × 10⁻³ cm² V⁻¹ s⁻¹, which agrees with previously reported hole mobilities of highly ordered P3HT films.35,36 We observed similar hole mobilities of 6.5 × 10⁻³ cm² V⁻¹ s⁻¹ and 6.0 × 10⁻³ cm² V⁻¹ s⁻¹ for P3HT-azide NW devices that had been subjected to 30 and
60 min of photo-cross-linking, respectively. While degradation in performance was observed for devices exposed to further irradiation (hole mobility of $3.2 \times 10^{-3}$ cm$^2$ V$^{-1}$ s$^{-1}$ at 90 min), devices cross-linked for 60 min showed similar mobility and transistor characteristics as uncross-linked devices (Figure S5), demonstrating that photo-cross-linking of azide-functionalized conjugated polymers is an effective route to produce stable NWs that retain their electronic properties.

A distinct advantage of the P3HT-azide system is that residual azide groups on the photo-cross-linked NWs can be subsequently functionalized with alkyne-terminated molecules by copper catalyzed azide-alkyne cycloaddition. We chose PEG as a model system for functionalization because of its excellent aqueous solubility (Figure 3a). Alkyne-terminated monomethyl ether PEG (PEG-alkyne, $M_n = 3.0$ kg/mol, $D = 1.05$, Figure S6a), was synthesized following a modified literature procedure (Scheme S1). Fidelity of the alkyne end-group of the PEG-alkyne was confirmed by MALDI-TOF (Figure S6b) and $^1$H NMR (Figure S7) analyses. PEG-alkyne was then coupled to photo-cross-linked P3HT-azide NWs in a 7:1 THF/BuOH solution in the presence of a CuBr catalyst. Following the click reaction, the azide peak disappeared from the FT-IR spectrum, indicating complete reaction of residual azides with PEG-alkyne (Figure S8). Excess PEG-alkyne was removed by centrifugation, and the resulting product was treated with CupriSorb to remove residual copper. TEM images (Figure 3b) revealed that P3HT-PEG NWs retained essentially the same morphology as pristine P3HT-azide NWs. In contrast, functionalization of uncross-linked P3HT-azide NWs with PEG led to an almost complete destruction of NW structure, as evidenced by a dramatic decrease in the intensity of the vibronic bands in UV–vis spectra (Figure S9) and a loss of NW morphology in TEM images (Figure 3c). To determine the areal density of PEG chains on the P3HT-PEG NWs, we adopt the monoclinic structural model of P3HT crystals of Brinkmann et al. which gives an area per thiophene unit of 0.15 nm$^2$ along the NW surfaces, corresponding to (100) crystal planes. However, only half of these have alkyl chains facing toward the nanowire surface, yielding an areal density of 3.3 nm$^{-2}$. Since 21 mol % of hexyl units are initially azide functionalized, and 60% of these are consumed during cross-linking, the areal chain density of remaining azides, and therefore grafted PEG chains, is calculated to be 0.28 nm$^{-2}$. This is several times larger than the surface overlap density estimated for 3 kg/mol PEG chains, $(1/(\pi \times R_g^2)) \approx 0.08$ nm$^{-2}$, with radius of gyration $R_g \approx 2$ nm, suggesting that the grafted PEG layer may provide effective steric stabilization of the NWs in polar solvent environments.

To gain insight into possible changes in the molecular packing of P3HT-azide NWs following PEG functionalization, wide-angle X-ray scattering (WAXS) of cross-linked P3HT-azide and P3HT-PEG NWs was performed (Figure 4a). Photo-cross-linked P3HT-azide NWs exhibited two distinct peaks with d-spacings of 1.69 and 0.37 nm, consistent with literature values for the distance between polythiophene backbones separated by interdigitated side chain (100) and π–π stacking distance (010), respectively. After PEG functionalization, the distances between adjacent P3HT-azide chains were essentially unchanged at 1.69 and 0.37 nm, indicating that the molecular packing within P3HT-azide NWs, a critical factor in determining optoelectronic properties, was not altered by surface functionalization with PEG-alkyne. We can conclude that P3HT-azide NWs provide an excellent platform for adding diverse functionality on the surface of NWs using facile click chemistry, while the molecular packing structure of the NWs can be preserved due to photo-cross-linking.

To determine the effect of PEG functionalization on the electrical performance of NWs, OFET devices were fabricated by casting films using 7:1 THF/BuOH as a solvent. Devices based on P3HT-PEG NWs showed shifted threshold voltages, and device operation became hysteric (Figure S10), which might be a result of the polarity of the PEG side chains that can induce p-type doping in the active layer. In addition, the ability of PEG chains to coordinate cationic species, particularly Li$^+$, K$^+$, and Na$^+$, could yield higher levels of salt impurities in films of the functionalized polymers, further affecting performance. While the hole mobility for P3HT-PEG NWs ($7.2 \times 10^{-4}$ cm$^2$ V$^{-1}$ s$^{-1}$) was reduced by an order of magnitude relative to that for the UV-cross-linked NWs, it remained 2 orders of magnitude larger than that for uncross-linked P3HT NWs functionalized with PEG ($4.3 \times 10^{-6}$ cm$^2$ V$^{-1}$ s$^{-1}$), clearly demonstrating that photo-cross-linking of P3HT-azide NWs provide sufficient stability to allow additional functionality to be added to the NW surface while largely preserving structural and electronic properties.

Figure 4b–d shows the structure of P3HT-PEG NWs dispersed in a variety of polar solvents. To demonstrate the suitability of these functionalized NWs for processing using environmentally benign solvents, suspensions in 7:1 THF/BuOH were centrifuged to isolate the P3HT-PEG NWs, followed by dispersion in BuOH (δ = 11.30 cal$^{1/2}$ cm$^{-3/2}$), MeOH (δ = 14.28 cal$^{1/2}$ cm$^{-3/2}$), and water (δ = 23.50 cal$^{1/2}$ cm$^{-3/2}$). In all cases, P3HT-PEG NWs formed dispersions that were stable against aggregation, while nonfunctionalized P3HT-azide NWs remained highly aggregated. To demonstrate the potential of these materials for organic electronics processed from high polarity solvents, OFET devices were prepared from P3HT-PEG NWs suspended in each solvent. The hole mobilities for devices based on P3HT-PEG NWs dispersed in...
BuOH, MeOH, and water were found to be $6.5 \times 10^{-4}$, $5.7 \times 10^{-4}$, and $2.1 \times 10^{-4}$ cm$^2$ V$^{-1}$ s$^{-1}$, respectively (Figure 4e, Figures S11 and S12). The slightly lower mobility of the water-based device was most likely a result of high surface tension, which resulted in a relatively nonuniform film. It should be noted, however, that this is the first demonstration of a water-processed P3HT-based organic electronic device, thus demonstrating the excellent potential of P3HT-azide for formation of stable and functional NW structures. Furthermore, the extension of this approach to conjugated polymers with inherently higher mobilities than P3HT may provide a future route to water-processable NW structures with even more attractive electronic properties.

**Conclusions.** In this work, we have demonstrated a platform for producing chemically and thermally stable, functionalized conjugated polymer NWs that facilitate device processing with high polarity and environmentally benign solvents. Copolymers based on P3HT and containing 20 mol % azide-functionalized thiophene units undergo crystallization-driven solution assembly into NWs similar to those of P3HT homopolymers. Irradiation with 254 nm UV light drives cross-linking, with a conversion of 60% of azide units providing excellent stability against both thermal and solvent treatments. Surface modification of cross-linked NWs with PEG-alkyne using the residual azide groups allowed for the stable dispersion of functionalized NWs in alcohols and water, enabling processing of P3HT-based OFET devices from environmentally benign solvents. We anticipate that this approach to highly stable and functionalized NWs will provide a valuable and flexible tool for the processing of other types of conjugated polymer-based devices, including photovoltaics and sensors.

**Methods. Preparation of Solution-Assembled P3HT-Azide NWs.** P3HT-azide was first dissolved in tetrahydrofuran (THF) at 10 mg/mL with heating and sonication. The solution was then passed through a PTFE syringe filter (0.45 μm), and 1-butanol (BuOH) was slowly added into the solution with vigorous stirring to induce homogeneous nucleation of the NWs. The resulting solution with a concentration of 1 mg/mL and a THF/BuOH volume ratio of 7:1 was aged for 48 h with stirring at room temperature.

**Photo-Cross-Linking and Click-Functionalization.** P3HT-azide NW solutions were placed in a quartz cuvette under nitrogen atmosphere and exposed to UV light ($\lambda$ = 254 nm) from a low power hand-held lamp (UVP UVGL-25, 0.76 mW cm$^{-2}$), with gentle stirring. For the click reaction, all procedures were performed under nitrogen atmosphere to avoid oxidation of the Cu catalyst. After photo-cross-linking, an excess amount of PEG-alkyne (1.5 eq, 0.015 mmol, 35 mg) was added to the 60 min photo-cross-linked P3HT-azide NW solution (10 mL, 0.01 mmol of azide units). Next, a solution containing 10 mg of CuBr (0.07 mmol) and 14.55 μL of PMDETA (0.07 mmol) in 1 mL of 7:1 THF/BuOH was prepared, and then 0.14 mL (1 eq, 0.01 mmol) of this CuBr/PMDETA solution was added into the P3HT-azide and PEG-alkyne solution to initiate the click reaction. Prepared solutions were stirred overnight at 40 °C. Afterward, CupriSorb (1 mg) was added to remove the copper catalyst, and then excess PEG-alkyne was removed by the centrifugation. Collected suspensions of P3HT-PEG NWs

**Figure 4.** (a) X-ray scattering of photo-cross-linked P3HT-azide NWs and P3HT-PEG NWs. TEM images of P3HT-PEG NWs dispersed in (b) BuOH, (c) MeOH, and (d) water, with insets showing a lack of dispersion for P3HT NWs (left) and excellent dispersion for P3HT-PEG NWs (right). (e) Hole mobilities measured for OFET devices prepared from P3HT-PEG NWs dispersed in various solvents (7:1 THF/BuOH, BuOH, MeOH, and water) were compared.
were redispersed in THF/BuOH, BuOH, MeOH, or water at a concentration of 1 mg/mL.

**Electronic Device Fabrication and Measurement.** OFET devices were fabricated on heavily doped n-type silicon wafers with a 300 nm thick thermally grown SiO₂ layer (C = 10 nF cm⁻²) as the substrate and dielectric. The surface of Si/SiO₂ substrates was then modified with OTS self-assembled monolayer (SAM) as previously reported.57 The contact angle on the hydrophobic OTS-modified wafer with D.I. water droplet was found out to be >10⁶°. The OTS-treated substrates were washed sequentially with toluene, acetone, and isopropyl alcohol and dried under a nitrogen stream. Suspensions containing 1 mg/mL of photo-cross-linked P3HT-azide NWs in 7:1 THF/BUOH or P3HT-PEG NWs isopropyl alcohol and dried under a nitrogen stream. The electrical performance was measured in a N₂-filled glovebox using a Keithley 4200 SCS and Micromanipulator 6150 probe station.

**REFERENCES**