

# Soft-Lithography Patterning of Functionalized Regioregular Polythiophenes<sup>†</sup>

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Poly(3-(6-thiohexyl)-4'-dodecyl-2,2'-bithiophene) (**1**) was successfully synthesized by postpolymerization functionalization of poly(3-(6-bromohexyl)-4'-dodecyl-2,2'-bithiophene) (**12**). 3-(6-Bromohexyl)-4'-dodecyl-2,2'-bithiophene (**10**), a key intermediate in the synthesis of polymer **12**, was synthesized via Stille coupling of 2-bromo-3-(bromohexyl)thiophene (**8**) and 2-trimethylstannyl-4-dodecylthiophene (**9**) in 30% isolated yield. Microstructure patterns of poly(3-(6-thiohexyl)-4'-dodecyl-2,2'-bithiophene) (**1**) were fabricated on a gold-coated glass slide through microcontact printing and microtransfer molding techniques. Circuit patterns of poly(3-hexylthiophene)s were constructed from a patterned silicon wafer via capillary force lithography methodology.

## Introduction

Polymeric integrated circuits are rapidly growing in importance as the realization of thin, flexible, and inexpensive electronic circuits is just over the horizon. Potential applications of polymeric integrated circuits range from low-end, high-volume microelectronics such as smart labels to fully electronic newspapers. Regioregular polyalkylthiophenes have great potential in the fabrication of polymeric integrated circuits due to their high conductivity and their ease of processibility.

One method to fabricate devices from regioregular polythiophenes is to cast films of polythiophenes and then photochemically remove photolabile side chains through a mask, which leads to insoluble polythiophenes in a circuit pattern.<sup>1a</sup> Using this method, fully patterned, all-organic thin film transistors, on glass, have been produced using poly(3,4-ethylenedioxythiophene).<sup>1b</sup> Although photolithography is the dominant technology in manufacturing microdevices, it is not universally suitable within the area of organic microelectronics. Methods such as ink jet printing and soft lithography are rather inexpensive methods and may be more well-suited for nonplanar surfaces. Soft-lithography techniques include micromolding in capillaries (MIMIC),<sup>2</sup> microtransfer molding ( $\mu$ TM),<sup>3</sup> microcontact printing ( $\mu$ CP),<sup>4</sup> and capillary force lithography (CFL)<sup>5</sup> that have been mainly developed by the Whitesides group and can be used to fabricate conducting polymer based microcircuitry.

Other than stamping methods, Mirkin has pioneered a direct-write dip-pen nanolithography (DPN) method to deliver alkanethiols from an atomic force microscope (AFM) tip to a solid substrate of interest via capillary forces.<sup>6</sup> This method can be used to write conducting polymers directly onto substrates.<sup>7</sup> Poly-3,4-ethylene-

dioxythiophene lines have been written directly on insulating or semiconducting surfaces through electrochemical polymerization of 3,4-ethylenedioxythiophene directly underneath the AFM tip. However, ideally conducting polymers bearing thiol groups could be used to deliver ordered conducting polymers to surfaces using DPN methods.

Here, we report the synthesis of soluble regioregular polyalkylthiophenes bearing thiol-terminated side chains and the use of these polymers in fabricating device-like structures by soft-lithography methods. The thiol-containing polythiophenes can form strong gold–sulfur bonds when exposed to a gold surface and can be used to form microstructures through  $\mu$ CP and  $\mu$ TM techniques. We also demonstrate the efficient construction of ordered microstructures of regioregular poly(3-hexylthiophene) on glass substrates through capillary force lithography.

## Results and Discussion

Well-defined  $\pi$ -stacking of regioregular polyalkylthiophenes has been shown to be essential for the high conductivity of the bulk polymer.<sup>8</sup> Polybithiophenes, functionalized with alternating thiol-terminated and unfunctionalized alkyl side chains, are desirable for the formation of well-ordered structures on gold surfaces. The strong bonding of the thiol-terminated side chains with the gold surface is expected to provoke an energetically stable anti conformation of adjacent thiophene rings (Figure 1). It has been reported that this lamellar arrangement would allow the most compact packing.<sup>9,10</sup>

Our target polymer, poly(3-dodecyl-3'-hexylthiol-5,2'-bithiophene) (**1**), could not be directly synthesized from 3'-(6-thiohexyl)-4-dodecyl-5-bromo-2,2'-bithiophene (**2**) or its thiol-protected derivatives **3** and **4** (Chart 1). These sulfur-containing molecules were found to be incompatible with our polymerization methods.<sup>13</sup> Specifically, we observed that the addition of thiol derivatives **5**, **6**, or **7** (analogues of **2–4**) to a THF solution of 5-chlorozinc-2-bromo-3-hexylthiophene and Ni(dppp)Cl<sub>2</sub> would quench the polymerization, perhaps due to catalyst poisoning. It

<sup>†</sup> Part of the *Langmuir* special issue dedicated to David O'Brien.

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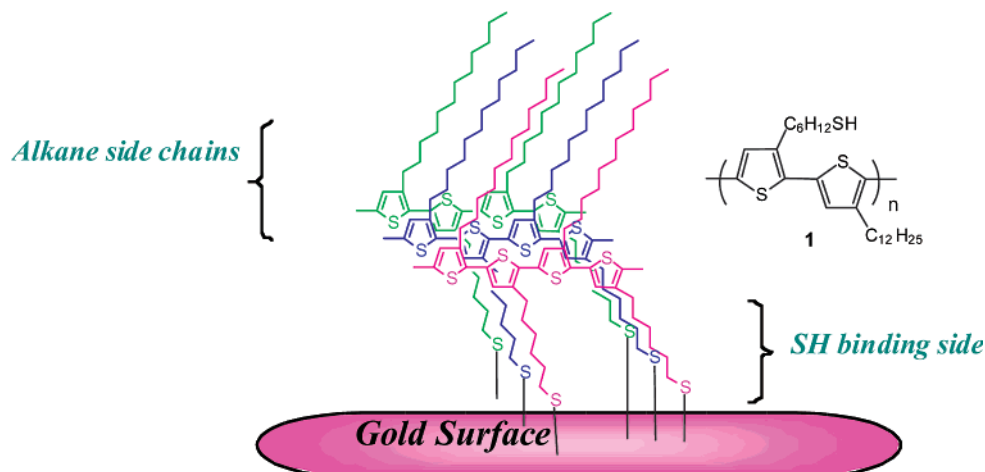
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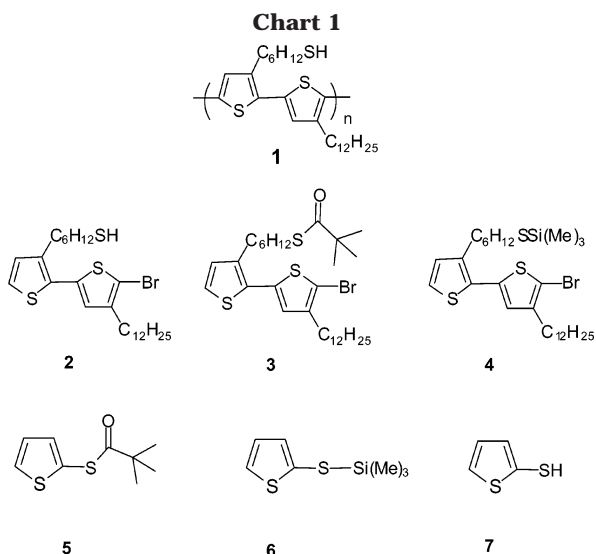
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**Figure 1.** Desired surface structure of a SAM on gold comprised of an alternating alkyl/thioalkyl motif.



has been reported that the synthesis of a regioregular poly(3-alkylthiophene) in which the alkyl group contains a thioether functionality produced a polymer that was not soluble in chloroform, THF, and xylene, and the molecular weight was found to be less than 5K Da.<sup>11</sup> Therefore, we have found that using a postpolymerization functionalization method that we developed for synthesizing a poly(3-alkylthiophene) bearing adjacent carboxylic acid and amine-terminated alkyl chains<sup>12</sup> can be applied to make poly(3-alkylthiophene) bearing thiol-terminated side chains.

**Monomer Synthesis.** For a postpolymerization functionalization approach, we first synthesized the functionalized polymer, poly(3-(6-bromo-hexyl)-4'-dodecyl-2,2'-bithiophene (**12**)) (Scheme 1). We synthesized the bithiophene derivative, 3-(6-bromo-hexyl)-4'-dodecyl-2,2'-bithiophene (**10**), through Stille coupling of 2-bromo-3-(bromo-hexyl)thiophene (**8**) and 2-trimethylstannyl-4-dodecylthiophene (**9**) in 30% isolated yield. Bromination of 3-(6-bromo-hexyl)-4'-dodecyl-2,2'-bithiophene (**10**) with *N*-bromosuccinimide resulted in a mixture of 2-mono- and 2,5'-dibrominated products. However, treating **10** with 1,3-dibromo-5,5-dimethylhydantoin in THF at 0 °C gave >99% of the monobrominated product **11** in 83% isolated yield. 3'-(6-Bromo-hexyl)-4-dodecyl-5-bromo-2,2'-bithiophene (**11**) was then polymerized using conditions previously

reported<sup>13</sup> to afford polymer **12** in 30% yield after washing with methanol and hexanes. This polymer was found to be 98% regioregular by <sup>1</sup>H NMR analysis.<sup>13</sup> Heating poly(3-(6-bromo-hexyl)-4'-dodecyl-2,2'-bithiophene (**12**)) at reflux in THF with excess potassium thioacetate led to >99% substitution of the alkylbromide side groups with thioacetate producing poly(3-(6-thioacetylhexyl)-4'-dodecyl-2,2'-bithiophene (**13**)) in 80% yield after washing with methanol and hexanes. Figure 2 illustrates the <sup>1</sup>H NMR spectral changes for these postpolymerization functionalizations.

For the <sup>1</sup>H NMR spectrum of polymer **12** (Figure 2a), the triplet at  $\delta$  3.4, assigned as the terminal methylene group alpha to the bromine, shifts upfield to  $\delta$  2.9 in Figure 2b, which is consistent with thioacetate substitution. In addition, the singlet at  $\delta$  2.3 is assigned as the acetate methyl group of polymer **13**. Our attempts at simple hydrolysis of the thioacetate functionality with NaOH in THF/water (10:1 v/v) resulted in an insoluble precipitate. Disulfides are known to form in an oxygen atmosphere in the presence of a small amount of base; hence, it would seem plausible that the insoluble precipitate is a disulfide-cross-linked polymer. Liberation of the thiol functionality was ultimately achieved through reduction of the thioacetate group with LiAlH<sub>4</sub> and led to the soluble product, poly(3-(6-thiohexyl)-4'-dodecyl-2,2'-bithiophene (**1**)). As shown in Figure 2c, the singlet assigned as the acetate methyl group vanishes after this reduction and is consistent with the cleavage of the acetyl protecting group. The quartet corresponding to the thiol-bound methylene group at  $\delta$  2.5 is consistent with literature chemical shifts of analogous alkane thiols.<sup>14</sup> It also suggests that the proton of the thiol group does not exchange with other sulfur atoms. Exposure of **1** to an oxygen atmosphere also leads to an insoluble polymer, again, due to cross-linking of the thiol functionality. However, polymer **1** remains stable for months in THF at -15 °C under a nitrogen atmosphere.

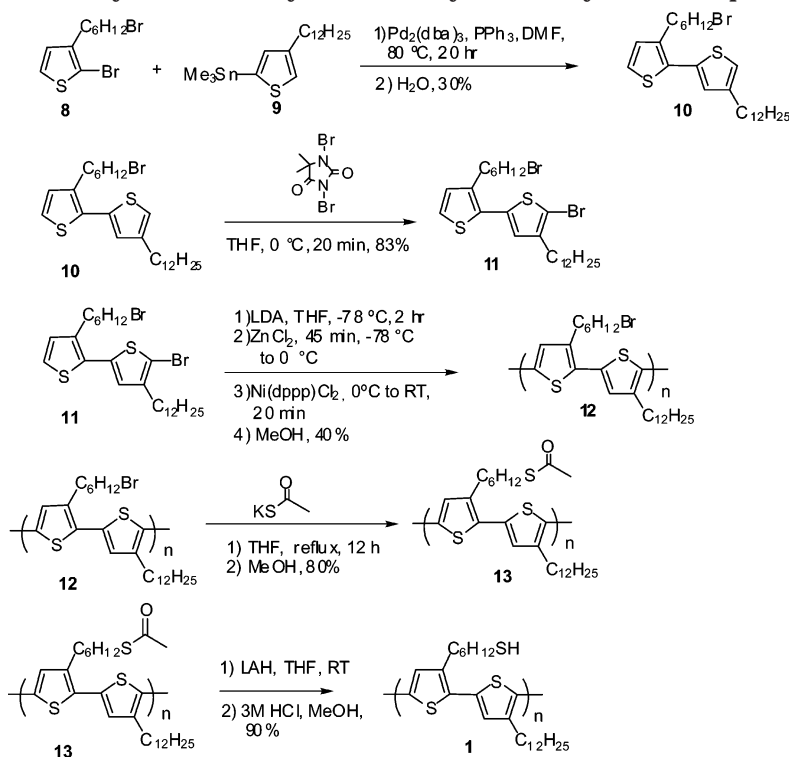
The deposition of poly(3-(6-thiohexyl)-4'-dodecyl-2,2'-bithiophene (**1**)) onto a gold surface was investigated by observation of the UV-vis absorption of a gold-coated glass slide before and after immersion in a THF solution of **1**. For this experiment, a glass slide was sputter-coated with gold and was analyzed by UV-vis to obtain a "blank"

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**Scheme 1. Synthesis of Poly(3-(6-thiohexyl)-4'-dodecyl-2,2'-bithiophene (1))**

reading. The slide was then immersed in a THF solution of **1** and was allowed to stand overnight. This slide was washed with chloroform to remove any nonadsorbed polymer. Figure 3 represents the UV-vis absorbance difference spectrum of the dipped and undipped gold slide. The observed  $\lambda_{\max}$  of 526 nm for polymer **1** is consistent with that reported for poly(3-dodecylthiophene) in the solid state.<sup>13</sup> This indicates that poly(3-(6-thiohexyl)-4'-dodecyl-2,2'-bithiophene (**1**)) can be coated onto gold surfaces via the formation of sulfur-gold bonds.

**Preparation of Stamps.** A 2000 mesh transmission electron microscopy (TEM) grid and a patterned silicon wafer were used as the master stamps for  $\mu$ CP and  $\mu$ TM, respectively, of the poly(3-(6-thiohexyl)-4'-dodecyl-2,2'-bithiophene (**1**)). The same patterned silicon wafer was used as the master stamp for capillary force lithography. These master stamps were placed in a plastic Petri dish. The poly(dimethylsiloxane) (PDMS) stamps were made by pouring a 10:1 ratio (w/w or v/v) mixture of Sylgard 184 and a Sylgard curing agent (Dow Corning Corp.) into the Petri dish. After curing for 2 days at room temperature, a polymer was formed that molded to the TEM grid and silicon wafer. Each master stamp was separated from the PDMS polymer, and the peeled sections were washed several times with ethanol and hexane and air-dried for 5 min before being used in a stamping process.

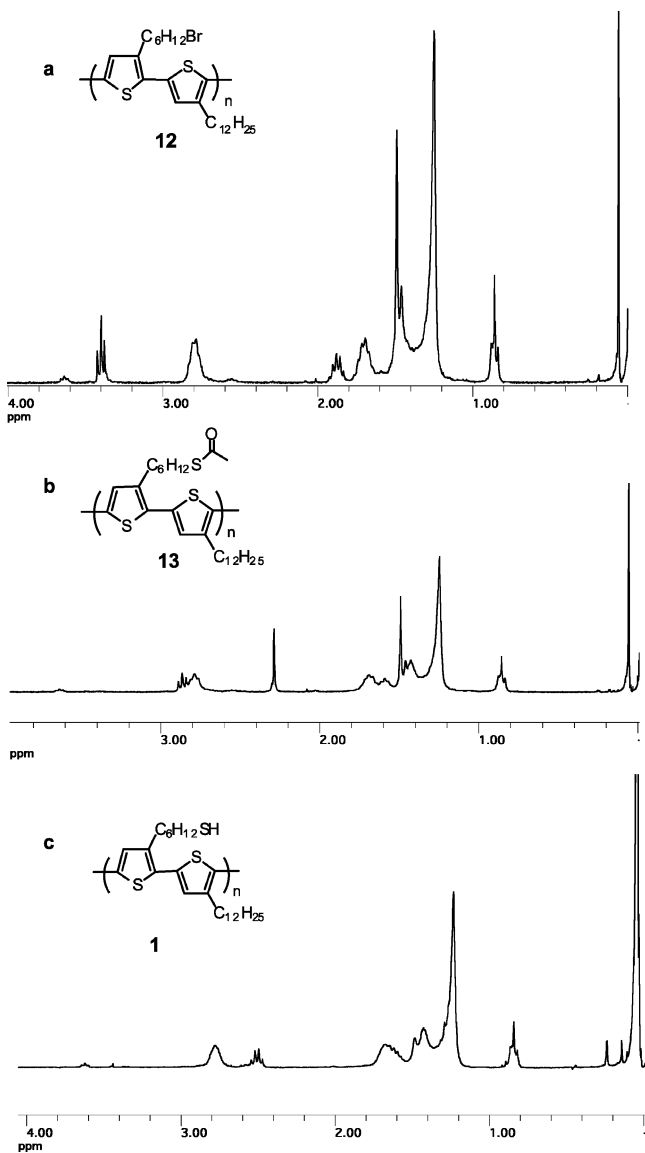
**$\mu$ CP of Poly(3-(6-thiohexyl)-4'-dodecyl-2,2'-bithiophene (**1**)).** Poly(3-(6-thiohexyl)-4'-dodecyl-2,2'-bithiophene (**1**)) was dissolved in THF/chloroform (1:1, v/v) to make a 1 mM solution which would be used as the "ink" for microcontact printing. One drop of this ink was placed on the PDMS stamp surface (made from the 2000 mesh TEM grid), and the liquid was air-dried for 20 s. The stamp was then gently placed on a gold-coated glass slide. Light pressure was applied by hand to ensure the contact between the stamp and the substrate. The stamp was removed after 10 s of contact, and the surface was washed with chloroform. This patterned surface was examined by scanning electron microscopy (SEM).

Figure 4 shows an image of microstructures of poly(3-(6-thiohexyl)-4'-dodecyl-2,2'-bithiophene (**1**)) patterned on a gold surface with THF/chloroform (1:1 v/v) as the ink solvent. The white regions are polymer **1** and are 13  $\mu$ m on a side. AFM analysis of the patterned gold surface indicates that the relief is > 100 nm, which is not consistent with a self-assembled monolayer (SAM). As the polymer is deposited on the surface, we believe that surface adsorption is occurring, but cross-linking in the oxygen atmosphere of the stamping process helps to form aggregates of **1**, hence the large height of the patterned polymer. Therefore, microcontact printing of **1** forms patterned aggregates of conductive polymers instead of SAMs. The diffusion of the ink and the swelling of the PDMS stamps due to chloroform incorporation could affect the resolution of the pattern. Delamarche et al. have reported that the ultimate limit of microcontact printing was restricted by the range and type of diffusive phenomena that occur when molecules were transferred to a surface.<sup>15</sup> Higher molecular weight alkanethiols, such as eicosanethiol, were found to form more accurately printed SAMs than a lower molecular weight alkanethiol, such as dodecanethiol. Since our molecular weights are reasonably high, the swelling of the stamps by chloroform is our major loss of resolution in this process. The technique of microcontact printing of **1** might be improved by using stiffer stamps such as "hard" PDMS made by Schmid et al.<sup>16</sup>

**$\mu$ TM of Poly(3-(6-thiohexyl)-4'-dodecyl-2,2'-bithiophene (**1**)).** A chloroform solution of poly(3-(6-thiohexyl)-4'-dodecyl-2,2'-bithiophene (**1**)) was cast on the surface of a PDMS mold, patterned from a silicon wafer. The solution filled the gaps in the stamp, and excess solution was removed by scraping the stamp with a flat PDMS block. This mold, filled with polymer solution, was then placed on the surface of a gold-coated glass slide and was allowed

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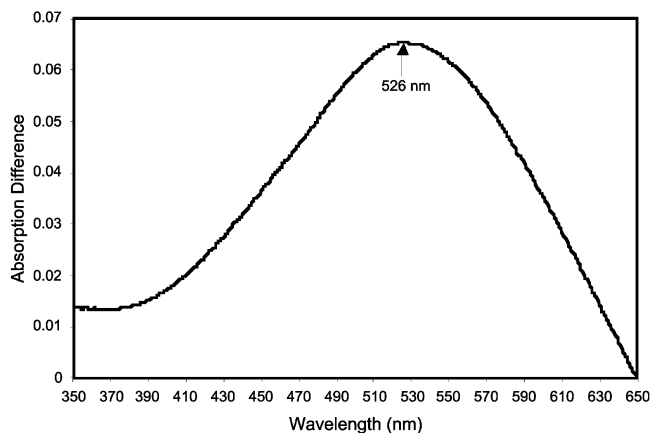
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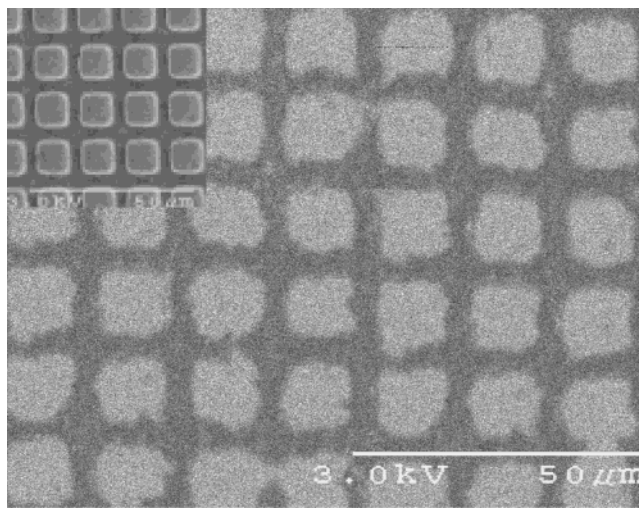
**Figure 2.**  $^1\text{H}$  NMR spectra of postpolymerization functionalization of poly(3-hexylbromo-3'-dodecyl-5,2'-bithiophene): (a) poly(3-(6-bromohexyl)-4'-dodecyl-2,2'-bithiophene) (**12**); (b) poly(3-(dodecyl-3'-hexylthiolacetate)-5,2'-bithiophene) (**13**); (c) poly(3-(6-thiohexyl)-4'-dodecyl-2,2'-bithiophene) (**1**).

to stand for 1 day. The mold was peeled away, and the substrate was washed with chloroform and examined by SEM. The SEM image indicates that  $\mu\text{TM}$  of **1** is able to reproduce the microstructure of the patterned silicon wafer (Figure 5). A thin film of polymer was formed between the substrate and the raised features (indicated by the arrow in Figure 5) due to the polymer residue on the stamp surface. The same phenomenon was also reported by Zhao et al., where they reported the patterning of UV-curable polyurethane on silver through  $\mu\text{TM}$ .<sup>17</sup> We have tried to pattern poly(3-hexylthiophenes) (with no thiol functionality) on glass slides and gold surfaces through  $\mu\text{TM}$ ; however, no pattern could be observed after the substrate was washed with chloroform. These results suggest that both the chemical binding between appropriately substituted polymers and substrates and their subsequent cross-linking are essential to construct stable microstructures from polythiophenes using  $\mu\text{TM}$  techniques.

**Capillary Force Lithography for Poly(3-hexylthiophene).** Capillary force lithography has been widely



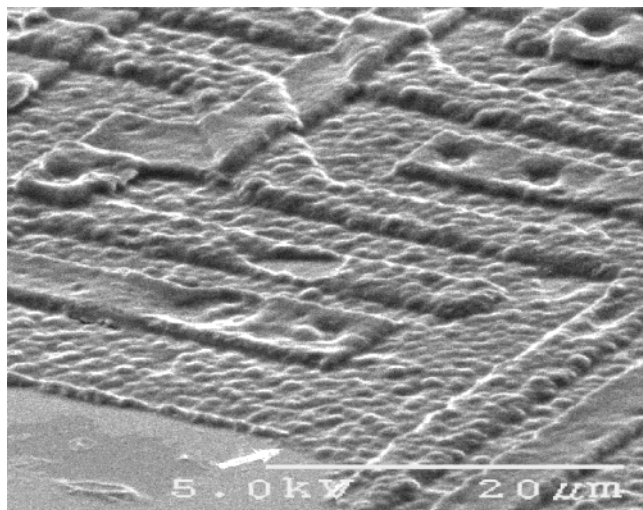
**Figure 3.** UV-vis spectrum of poly(3-(6-thiohexyl)-4'-dodecyl-2,2'-bithiophene) (**1**) on a gold-coated glass substrate with gold background subtracted.  $\lambda_{\text{max}} = 526$  nm is consistent with that reported for poly(3-dodecylthiophene).



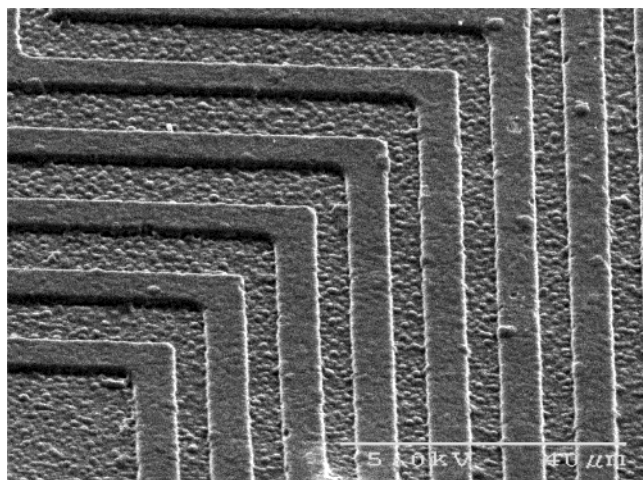
**Figure 4.** SEM image of a patterned gold surface of poly(3-(6-thiohexyl)-4'-dodecyl-2,2'-bithiophene) (**1**) by microcontact printing. Square-shaped structures represent positive surface relief and are  $13\ \mu\text{m}$  on a side. Inset: SEM of the PDMS stamp used in the process.

used in the patterning of polymeric materials.<sup>17</sup> The wetting of the wall of a PDMS stamp by a melted polymer can lower the total free energy of the system, which leads to the filling of the mold by capillary forces, ultimately filling the gaps in the stamp. Poly(3-hexylthiophene) ( $M_n = 9800$ ,  $DP = 1.3$  from gel permeation chromatography (GPC)) was analyzed by differential scanning calorimetry (DSC), and the melting point was found to be  $223\ ^\circ\text{C}$ . A  $5\ \mu\text{m}$  polymer film was coated onto a glass slide, and a PDMS mold was placed on the polymer surface. The mold was pressed against the substrate to ensure that there were no small gaps or air bubbles between the mold and the polymer surface. The film and the mold were heated to  $250\ ^\circ\text{C}$  for 1.5 h under a nitrogen atmosphere. The film was then cooled to room temperature, and the mold was removed from the surface. The SEM image of patterned poly(3-hexylthiophene) indicated that capillary force lithography is able to accurately reproduce the pattern of the silicon master (Figure 6). Since the thickness of the polymer film ( $5\ \mu\text{m}$ ) is larger than the depth of the gaps on the stamp ( $2\ \mu\text{m}$ ), the polymers completely filled the mold and residual polymer remained on the substrate as shown in Figure 7. The patterned film was doped with iodine for 12 h, and a four-point probe conductivity of  $4\ \text{S}/\text{cm}$  was measured.

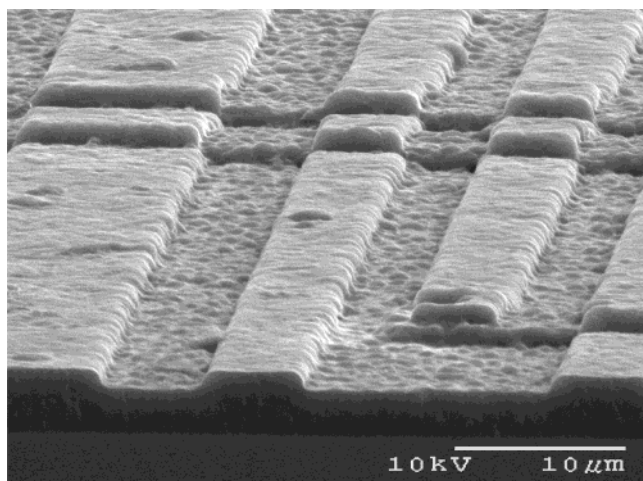
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**Figure 5.** SEM image of microtransfer-molded poly(3-(6-thiohexyl)-4'-dodecyl-2,2'-bithiophene) (**1**). The raised structures are features transferred from the PDMS mold, whereas the white arrow indicates residual polymer **1** deposited by the molding technique.



**Figure 6.** SEM image of patterned regioregular poly(3-hexylthiophene) by capillary force lithography.



**Figure 7.** Edge profile SEM image of regioregular poly(3-hexylthiophene) patterned by capillary force lithography indicating that the polymer has filled the cavities of the stamp.

**Conclusions.** Regioregular poly(3-(6-thiohexyl)-4'-dodecyl-2,2'-bithiophene) (**1**) was synthesized using our postpolymerization functionalization method, and micro-

patterns of this polymer were constructed through microcontact printing and microtransfer molding techniques. Capillary force lithography was employed to fabricate micropatterns of poly(3-hexylthiophene). Our studies have shown that regioregular polythiophene can be reproducibly deposited onto different substrates with desirable patterns, which could provide a simple and inexpensive method for the fabrication of complex organic microcircuits.

### Experimental Section

**General Information.** Commercial chemicals, purchased from Aldrich Chemical Co., Inc., were used without further purification unless noted otherwise. All reactions were performed under nitrogen, using either flame-dried or oven-dried glassware. Tetrahydrofuran and diisopropylamine were dried over Na/benzophenone-ketyl and calcium hydride, respectively, and freshly distilled prior to use. Unless noted otherwise, concentration of reaction mixtures through removal of solvents was accomplished by rotary evaporation at ca. 35 Torr (water aspirator). Flash chromatography was performed with silica gel (40  $\mu\text{m}$ , 60  $\text{\AA}$  mesh) purchased from J. T. Baker.  $^1\text{H}$  NMR spectra were recorded on an IBM Bruker FT300 spectrometer operating at 300 MHz. All NMR samples were dissolved in  $\text{CDCl}_3$ , unless otherwise stated. GPC measurements were carried out on a Waters 2690 separation module, equipped with two 5  $\mu\text{m}$  Phenogel columns connected in series (guard, 1000, and 100  $\text{\AA}$ ), and a Waters 2487 dual  $\lambda$  absorbance UV detector. Analyses were performed at 30  $^\circ\text{C}$  using chloroform as the eluent, and the flow rate was 1.0  $\mu\text{L}/\text{min}$ . Calibration was based on polystyrene standards obtained from Polymer Standards Service. Gas chromatography–mass spectrometry (GC–MS) analysis was performed on a Hewlett-Packard 59970 GC–MS workstation with a Hewlett-Packard fused silica capillary column cross-linked with 5% phenyl-methylsilicone as the stationary phase. Elemental analyses were performed by Midwest Microlab, Indianapolis, IN. Optical spectroscopy was performed at room temperature (RT) on a Perkin-Elmer Lambda 900 UV/vis/near-IR spectrometer. Glass transition and melting temperatures were measured by DSC on a Perkin-Elmer DSC-4 differential scanning calorimeter with a heating rate of 10  $^\circ\text{C}/\text{min}$ . SEM analyses were performed on a Hitachi S-2460N workstation. Gold-coated glass substrates were prepared using a Pelco SC-6 sputter coater. The film thickness of the substrate was 80 nm.

**2-Trimethylstannyl-4-dodecylthiophene (9).** Dodecylthiophene (40 g, 0.158 mol) was dissolved in 400 mL of dry THF. The solution was cooled to  $-78$   $^\circ\text{C}$ , and *tert*-BuLi (102.7 mL, 0.158 mol) was added dropwise. The solution was stirred for 1 h; then trimethylstannyl chloride (174 mL, 0.174 mol) was added and the solution was stirred for 2 more hours at room temperature. Water (50 mL) was added, and mixture was extracted with  $\text{Et}_2\text{O}$  (3  $\times$  50 mL). The organic extracts were washed with water (3  $\times$  50 mL) and  $\text{NaHCO}_3$  (aq) (2  $\times$  50 mL). The organic layer was dried over anhydrous  $\text{MgSO}_4$ , and the removal of solvent yielded a yellow oil. Kugelrohr distillation at 160–170  $^\circ\text{C}$  and 0.2 Torr gave 40.1 g (61%) of 2-trimethylstannyl-4-dodecylthiophene (**9**) as a colorless liquid.  $^1\text{H}$  NMR  $\delta$  7.17 (s, 1H), 6.99 (s, 1H), 2.63 (t,  $J$  = 7.32 Hz, 2H), 1.61 (p,  $J$  = 7.33 Hz, 2H), 1.25 (m, 18H), 0.87 (t,  $J$  = 6.59 Hz, 3H).

**3-Hexylbromothiophene.** To a 500-mL three-necked round-bottom flask equipped with stirring was added 3-bromothiophene (30 g, 0.18 mol) followed by syringe addition of dry hexane (250 mL). The flask was chilled to  $-40$   $^\circ\text{C}$ , and the solution was stirred for 10 min. *n*-BuLi (72 mL, 0.18 mol) was added dropwise via syringe, and stirring was continued for 10 min. THF (15 mL) was added dropwise via syringe. The solution was stirred for 1 h. The cooling bath was removed, and the reaction mixture was allowed to warm to  $-10$   $^\circ\text{C}$ . Dibromohexane (110 mL, 0.72 mol) was added neat in one portion, and the solution slowly warmed to room temperature. The solution was stirred for 2 h; then water (20 mL) was added and the mixture was extracted with  $\text{Et}_2\text{O}$  (3  $\times$  20 mL). The combined organic extracts were washed with water (3  $\times$  20 mL) and dried ( $\text{MgSO}_4$ ). Removal of solvent under reduced pressure afforded a yellow oil. Distillation of the crude product gave 24.7 g of a colorless oil (56%).  $^1\text{H}$  NMR  $\delta$  7.22 (dd,  $J$  = 5.13,

2.93 Hz, 1H), 6.92 (d,  $J = 5.13$  Hz, 1H), 6.90 (s, 1H), 3.40 (t,  $J = 6.59$  Hz, 2H), 2.64 (t,  $J = 7.33$  Hz, 2H), 1.86 (p,  $J = 7.32$  Hz, 2H), 1.65 (p,  $J = 7.32$  Hz, 2H), 1.5 (m, 2H), 1.2 (m, 2H). Elemental analysis (%): C, 48.38 (calculated 48.59); H, 6.04 (calculated 6.12); Br, 32.32 (calculated 32.32).

**2-Bromo-3-(bromohexyl)thiophene (8).** In a 500-mL single-necked flask, equipped for stirring, 3-bromohexylthiophene (27.39 g, 0.11 mol) was dissolved in a mixture of THF (135 mL) and acetic acid (135 mL). *N*-Bromosuccinimide (23.7 g, 0.13 mol) was added to the solution in one portion, and the solution was stirred for 1 h. The solution was then extracted with Et<sub>2</sub>O (3 × 50 mL), and the combined organic extracts were washed with water (3 × 50 mL) and NaHCO<sub>3</sub> (aq) (2 × 50 mL). The organic layer was dried (MgSO<sub>4</sub>), and the removal of solvent under reduced pressure gave a yellow oil. Distillation (120 °C, 0.05 Torr) gave 25.2 g of a colorless oil (70%). <sup>1</sup>H NMR δ 7.17 (d,  $J = 5.86$  Hz, 1H), 6.77 (d,  $J = 5.86$  Hz, 1H), 3.39 (t,  $J = 6.59$  Hz, 2H), 2.57 (t,  $J = 8.06$  Hz, 2H), 1.85 (p,  $J = 8.33$  Hz, 2H), 1.61 (m,  $J = 8.33$  Hz, 2H), 1.51 (m, 2H), 1.39 (m, 2H). Elemental analysis (%): C, 36.83 (calculated 36.83); H, 4.29 (calculated 4.33); S, 9.82 (calculated 9.83); Br, 49.07 (calculated 49.01).

**3-(6-Bromohexyl)-4'-dodecyl-2,2'-bithiophene (10).** To a three-necked 250-mL round-bottom flask equipped for stirring and reflux was added 2-bromo-3-hexylbromothiophene (**8**, 10 g, 30.6 mmol) followed by anhydrous DMF (150 mL) which was added via syringe. This mixture was degassed with dry nitrogen for 20 min. Triphenylphosphine (1.6 g, 6.12 mmol) and tris-(dibenzylidene-acetone)dipalladium(0) (1.4 g, 1.53 mmol) were added in one portion to the reaction mixture followed by purging with nitrogen for 2 min. The reaction flask was immersed in an 80 °C oil bath, and the reaction mixture was stirred for 20 min. 1-Trimethylstannyl-4-dodecylthiophene (**9**, 12.7 g, 30.6 mmol) was added in two portions, via pipet, followed by a nitrogen purge for 2 min. The reaction mixture was allowed to stir for 20 h. The reaction flask was removed from the oil bath and allowed to cool to RT. The mixture was filtered, and the filtrate was extracted with hexanes (3 × 50 mL). The combined organic extracts were washed with water (3 × 50 mL) and brine (1 × 50 mL) and dried (Na<sub>2</sub>SO<sub>4</sub>). The solvent was removed under reduced pressure (35 Torr) to give a dark brown oil that was flash chromatographed (silica gel, hexanes). Removal of solvent afforded 4.5 g (9 mmol, 30%) of **10** as a colorless oil.  $R_f$  (hexanes) = 0.38. <sup>1</sup>H NMR δ 7.13 (d,  $J = 5.13$  Hz, 1H), 6.91 (s, 1H), 6.88 (d,  $J = 5.13$  Hz, 1H), 6.86 (s, 1H), 3.37 (t,  $J = 6.59$  Hz, 2H), 2.74 (t,  $J = 7.69$  Hz, 2H), 1.83 (p,  $J = 7.3$  Hz, 2H), 1.63 (t,  $J = 7.3$  Hz, 4H), 1.47–1.17 (m, 24H), 0.87 (t,  $J = 6.59$  Hz, 3H).

**3'-(6-Bromohexyl)-4-dodecyl-5-bromo-2,2'-bithiophene (11).** To a 250-mL round-bottom flask equipped for stirring was added **10** (2.0 g, 4.0 mmol) via pipet followed by THF (150 mL) added via syringe. The reaction flask was purged with nitrogen for 2 min and then was immersed in a 0 °C bath. Stirring was continued for 15 min followed by addition of 5,5-dimethyl-1,3-dibromohydantoin (0.64 g, 2.2 mmol) in five portions over a period of 5 min. The reaction mixture was stirred for 20 min, and then water (50 mL) was added in one portion and stirring was continued for 10 min. The heterogeneous mixture was extracted with ether (3 × 50 mL), and the combined organic extracts were washed with water (3 × 50 mL) and brine (1 × 50 mL) and dried (Na<sub>2</sub>SO<sub>4</sub>). The solvents were removed under reduced pressure (35 Torr) to give a yellow oil which was flash chromatographed (silica gel, hexanes) to give **11** as light-yellow oil (1.9 g, 83%).  $R_f$

(hexanes) = 0.2. <sup>1</sup>H NMR δ 7.14 (d,  $J = 5.13$  Hz, 1H), 6.88 (d,  $J = 5.13$  Hz, 1H), 6.76 (s, 1H), 3.37 (t,  $J = 6.59$  Hz, 2H), 2.70 (t,  $J = 7.70$  Hz, 2H), 1.84 (p,  $J = 6.59$  Hz, 2H), 1.61 (p,  $J = 6.59$  Hz, 4H), 1.52–1.2 (m, 24H), 0.87 (t,  $J = 7.32$  Hz, 3H).

**Poly(3-(6-bromohexyl)-4'-dodecyl-2,2'-bithiophene (12)).** To a three-necked 100-mL round-bottom flask equipped for stirring was added diisopropylamine (6 mmol) followed by the addition of THF (25 mL) via syringe. The reaction flask was chilled to –70 °C, and stirring was continued for 10 min. *n*-BuLi (2 mL, 5 mmol) was added via syringe, and the solution was stirred for 1.5 h. 3'-(6-Bromohexyl)-4-dodecyl-5-bromo-2,2'-bithiophene (**11**, 2.88 g, 5 mmol) was added in one portion via syringe. The mixture was stirred for 2 h at –78 °C. Anhydrous ZnCl<sub>2</sub> beads (0.7 g, 5 mmol) were added in one portion, and the reaction was stirred until all ZnCl<sub>2</sub> had dissolved. The cooling bath was removed, and the mixture was warmed to –5 °C followed by addition of Ni(dppp)Cl<sub>2</sub> (14 mg, 0.025 mmol). The mixture was allowed to warm to RT, and the reaction mixture was stirred for 20 min and quenched with methanol (100 mL). The polymer precipitate was washed with methanol, followed by hexanes in a Soxhlet extractor. The polymer then was dissolved by Soxhlet extraction into chloroform. Removal of the chloroform under reduced pressure (35 Torr) followed by drying under a vacuum (1 Torr) afforded 1.0 g (40%) of 98% head-to-tail coupled poly(3-(6-bromohexyl)-4'-dodecyl-2,2'-bithiophene (**12**). <sup>1</sup>H NMR δ 6.96 (s, 1H), 6.957 (s, 1H), 3.39 (t,  $J = 6.59$  Hz, 2H), 2.78 (m, 4H), 1.88 (p,  $J = 6.59$  Hz, 2H), 1.66 (p,  $J = 6.59$  Hz, 4H), 1.49–1.25 (m, 22H), 0.87 (t,  $J = 7.32$  Hz, 3H) (Mn = 31 420, DP = 1.94 by GPC).

**Poly(3-(6-thioacetylhexyl)-4'-dodecyl-2,2'-bithiophene (13)).** To a three-necked 100-mL round-bottom flask equipped for stirring was added poly(3-(6-bromohexyl)-4'-dodecyl-2,2'-bithiophene (80 mg, 0.16 mmol). THF (50 mL) was added via syringe, and potassium thioacetate (931 mg, 8 mmol) was added in one portion. The solution was heated to reflux, and the mixture was stirred overnight. The reaction was quenched in methanol (200 mL). The solid polymer was washed with methanol, followed by hexanes in a Soxhlet extractor. After extraction, 330 mg (80%) of polymer **13** was obtained. <sup>1</sup>H NMR δ 6.96 (s, 1H), 6.95 (s, 1H), 2.88 (t,  $J = 7.33$  Hz, 2H), 2.50 (t,  $J = 7.33$  Hz, 4H), 2.26 (s, 3H), 1.88 (p,  $J = 6.59$  Hz, 2H), 1.66 (p,  $J = 6.59$  Hz, 4H), 1.49–1.25 (m, 22H), 0.87 (t,  $J = 7.32$  Hz, 3H) (Mn = 31 260, DP = 1.95 by GPC).

**Poly(3-(6-thiohexyl)-4'-dodecyl-2,2'-bithiophene (1)).** To a three-necked 100-mL round-bottom flask equipped for stirring was added poly(3-(6-thioacetylhexyl)-4'-dodecyl-2,2'-bithiophene) (98.4 mg, 0.2 mmol). THF (50 mL) was added via syringe, and after the polymer had dissolved, a THF solution of LiAlH<sub>4</sub> (1 mL, 1 mmol) was added via syringe. The mixture was stirred for 30 min and was quenched in methanol (100 mL). The polymer precipitate was washed with methanol, followed by hexanes in a Soxhlet extractor. After extraction, 81 mg (90%) of polymer **1** was obtained. <sup>1</sup>H NMR δ 6.96 (s, 1H), 6.957 (s, 1H), 2.77 (m, 4H), 2.50 (q,  $J = 7.32$ , 6.6 Hz, 2H), 1.68–1.25 (m, 28H), 0.86 (t, 3H) (Mn = 29 880, DP = 1.92 by GPC).

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