

## NOTE

# End-group stannylation of regioregular poly(3-hexylthiophene)s

Luozheng Zhang<sup>1</sup>, Kazuhito Hashimoto<sup>1,2</sup> and Keisuke Tajima<sup>1,2</sup>

*Polymer Journal* (2012) 44, 1145–1148; doi:10.1038/pj.2012.84; published online 23 May 2012

**Keywords:** end group; *N,N,N',N'*-tetramethylethylenediamine; polythiophene; post-functionalization; Stille coupling; stannyl group

## INTRODUCTION

Polythiophenes have been intensively studied as semiconducting polymers for various applications such as in organic solar cells (OSCs)<sup>1</sup> and organic field-effect transistors.<sup>2</sup> To modify the intrinsic properties of polythiophenes, such as crystallinity and optoelectronic properties, and to improve their device performance, much work has been performed on the modifications of their side chains<sup>3</sup> and end groups.<sup>4,5</sup> Concerning these end groups, it has been reported that hydrogen-terminated regioregular poly(3-hexylthiophene) (P3HT) shows a slightly higher absorption coefficient, stronger photoluminescence, and more highly ordered interchain packing than bromine-terminated P3HT, resulting in better performance in OSCs. Cho *et al.*<sup>4</sup> reported that the surface energy of P3HT can be varied by the introduction of different end groups and that an improved phase separation of the active layer can be realized with a matched surface energy between P3HT and [6,6]-phenyl-C<sub>61</sub> butyric acid methyl ester, leading to enhanced photovoltaic efficiency.<sup>5</sup> Besides these simple modifications, end-group functionalization has been used for the initiation of polymerization, leading to the synthesis of various P3HT-based block copolymers.<sup>6,7</sup>

There are three possible strategies for functionalizing the end groups of P3HT: the quenching of polymerization with a functionalized quencher,<sup>8</sup> the initiation of polymerization with a functionalized initiator,<sup>9</sup> and the post-functionalization of purified polymer. The first two strategies rely on the chain-growth nature of Ni-catalyzed Grignard metathesis (GRIM) polymerization of P3HT, in which the Ni complex serves as the initiator and the growing P3HT chains have living ends during the reaction process. Although both the initiator and quencher methods are effective for introducing functionality into one of the ends, a prerequisite of both approaches is that target end groups should be chemically tolerant to Grignard reagents, thus limiting their applicability to a certain extent. On the other hand, even though the post-functionalization of purified P3HT has certain drawbacks, such as lower introduction rate and selectivity, it is free

from the limitations of functionalities and can be used to functionalize both ends of chains.<sup>10–12</sup> Taking advantage of this, reactive groups such as carboxylic acids<sup>10,11</sup> and aldehydes<sup>12</sup> have been introduced into the ends of P3HT by post-functionalization. However, this approach has been relatively less studied.

In this work, we studied the stannylation of the chain ends of P3HT by post-functionalization. As trialkylstannyl groups are key functionalities for Stille coupling with aryl bromides, the synthesis of stannylated P3HTs enables us to connect various  $\pi$ -conjugated moieties to chain ends by direct conjugation with P3HT.<sup>13</sup> This type of modification is particularly important for modifying the optoelectronic properties of P3HT, as end groups can have direct electronic coupling with P3HT through the conjugation. We found that both the end groups of P3HT can be successfully lithiated with *s*-butyllithium (*s*-BuLi) and stannylated with trimethyltin chloride (Me<sub>3</sub>SnCl); however, only mono-stannylated P3HT was formed through reactions with a Grignard reagent and Me<sub>3</sub>SnCl.

## EXPERIMENTAL PROCEDURE

### Synthesis

All the chemicals used were purchased from Aldrich, Wako Chemicals or Tokyo Chemical Industry and used without further purification, unless otherwise stated. All the glassware used was dried by heating before use. 2-Bromo-3-hexyl-5-iodothiophene was synthesized by following a reported procedure.<sup>14</sup>

### Poly(3-hexylthiophene) (Br-P3HT)

A typical procedure reported in the literature<sup>15</sup> was followed. To a 200-ml flask charged with 2-bromo-3-hexyl-5-iodothiophene (2.5 g, 6.7 mmol) and dry THF (67 ml), a solution of *i*-PrMgCl in THF (2 mol l<sup>-1</sup>, 3.35 ml) was added dropwise at 0 °C, and the resultant mixture was stirred for 30 min. After removing the mixture from the bath, a designated amount of Ni(dppp)Cl<sub>2</sub> catalyst (0.025–0.1 equiv. to monomer) was immediately added to the solution. After 30 min, the reaction was quenched with 5 mol l<sup>-1</sup> HCl aqueous solution. The organic layer was then extracted with CHCl<sub>3</sub> and

<sup>1</sup>Department of Applied Chemistry, School of Engineering, The University of Tokyo, Tokyo, Japan and <sup>2</sup>HASHIMOTO Light Energy Conversion Project, ERATO, Japan Science and Technology Agency (JST), Saitama, Japan

Correspondence: Prof. K Hashimoto or Dr K Tajima, Department of Applied Chemistry, School of Engineering, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, Japan.

E-mail: hashimoto@light.t.u-tokyo.ac.jp or k-tajima@light.t.u-tokyo.ac.jp

Received 20 January 2012; revised 11 April 2012; accepted 11 April 2012; published online 23 May 2012

washed three times with  $\text{NaHCO}_3$  aq and water, and then dried with  $\text{MgSO}_4$ . After removing the solvent by rotary evaporation, Br-P3HT was collected by sequential washing with MeOH and hexane (64%).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  6.98 (s, 1H), 2.80 (t, 2H), 1.71 (quint, 2H), 1.44 (m, 2H), 1.35 (t, 4H) and 0.92 (t, 3H).

### Bis-trimethylstannylated poly(3-hexylthiophene) ( $\text{Sn}_2$ -P3HT)

To a solution of Br-P3HT (30.3 mg, molecular weight ( $M_n$ ) = 5050, polydispersity index (PDI) = 1.11) in dry THF ( $3 \text{ g l}^{-1}$ ),  $N,N,N',N'$ -tetramethylethylenediamine (TMEDA) (120 equiv. to Br-P3HT, according to the  $M_n$  of Br-P3HT) and  $s\text{-BuLi}$  ( $1.05 \text{ mol l}^{-1}$  in cyclohexane/ $n$ -hexane, 100 equiv.) were added dropwise via a syringe at  $-78^\circ\text{C}$  under  $\text{N}_2$ . After 30 min,  $\text{Me}_3\text{SnCl}$  ( $1.0 \text{ mol l}^{-1}$  in THF, 200 equiv.) was injected in one portion. After stirring for

15 min, the reaction mixture was warmed to room temperature. After reaction for another 4 h, the mixture was poured into MeOH. The precipitate was collected by filtration and dried. Yield: 92%.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  6.98 (s, 1H), 2.80 (t, 2H), 1.71 (quint, 2H), 1.44 (m, 2H), 1.35 (t, 4H), 0.92 (t, 3H) and 0.40 (m, 18H).

### Mono-trimethylstannylated poly(3-hexylthiophene) (Sn-P3HT)

To a solution of Br-P3HT (48.3 mg,  $M_n = 5900$ , PDI = 1.09) in dry THF (16 ml) was added dropwise a solution of  $i\text{-PrMgCl}$  in THF ( $2 \text{ mol l}^{-1}$ , 0.1 ml, 25 equiv.) at room temperature under  $\text{N}_2$ . After 1 h, the solution was cooled to  $0^\circ\text{C}$  and  $\text{Me}_3\text{SnCl}$  solution ( $1.0 \text{ mol l}^{-1}$  in THF, 0.82 ml, 100 equiv.) was added dropwise. After stirring for 10 min, the reaction mixture was warmed to room temperature and stirred continuously overnight. The reaction was quenched by pouring the mixture into MeOH under sonication. Yield: 99%.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  6.98 (s, 1H), 2.80 (t, 2H), 1.71 (m, 2H), 1.44 (m, 2H), 1.35 (t, 4H), 0.92 (t, 3H) and 0.40 (m, 9H).

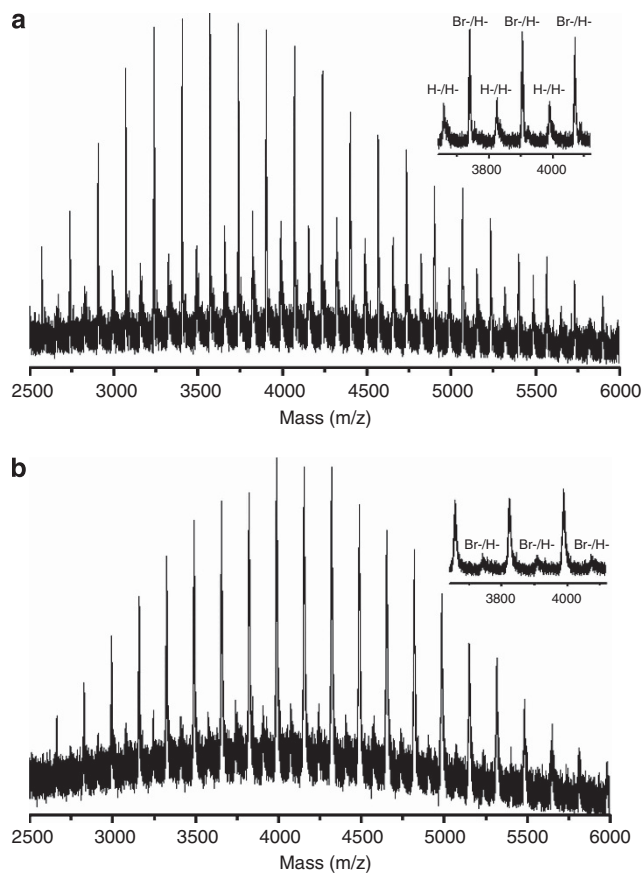
### Material characterization

$^1\text{H}$  NMR spectra in  $\text{CDCl}_3$  were measured on a JEOL Alpha FT-NMR spectrometer equipped with an Oxford superconducting magnet system (500 MHz). Matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF-MS) was carried out in the reflection ion mode on an Applied Biosystems BioSpectrometry Workstation model Voyager DE-STR spectrometer using dithranol as the matrix and  $\text{CHCl}_3$  as the solvent. Gel permeation chromatography (GPC) was performed at  $40^\circ\text{C}$  using a Shimadzu Prominence system equipped with a UV detector and  $\text{CHCl}_3$  as the eluent. The sample solution in  $\text{CHCl}_3$  was passed through a polytetrafluoroethylene filter (pore size:  $0.2 \mu\text{m}$ ) before injection.

### RESULTS AND DISCUSSION

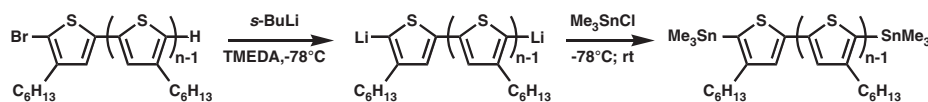
Regioregular P3HT was synthesized according to the literature through the GRIM polymerization method.<sup>15</sup>  $\text{Ni}(\text{dppp})\text{Cl}_2$  catalyst was added in one portion, and the reaction mixture was quenched with 5 M HCl aq in order to attain a small PDI and to avoid the dimerization of living P3HT chains,<sup>16</sup> respectively. The number averaged  $M_n$  of P3HT determined by GPC was 5600 with a PDI of 1.08 when the amount of  $\text{Ni}(\text{dppp})\text{Cl}_2$  was 0.05 equiv. to the monomer. The MALDI-TOF-MS profile of the product is shown in Figure 1a, in which most of the end groups can be assigned to P3HT with Br-/H- end groups, and only a small fraction with the H-/H- end groups was observed (ca. 24% by peak intensity). Thus, the product is denoted Br-P3HT hereafter.

The synthetic route of bis-stannylated P3HT ( $\text{Sn}_2$ -P3HT) is shown in Scheme 1. The end groups of Br-P3HT were successively lithiated with  $s\text{-BuLi}$  and stannylated with  $\text{Me}_3\text{SnCl}$ . First, we followed a report<sup>17</sup> in which the end groups of P3HT were converted to carboxyl groups by the lithiation of P3HT in the absence of TMEDA, the subsequent deactivation of residual  $s\text{-BuLi}$  at an elevated temperature and treatment with  $\text{CO}_2$ . However, this reaction procedure yielded neither mono-stannylated P3HT (Sn-P3HT) nor  $\text{Sn}_2$ -P3HT as

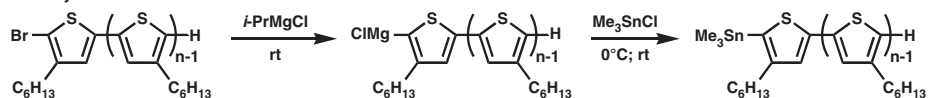


**Figure 1** MALDI-TOF-MS profiles of (a) Br-P3HT ( $M_n = 5600$  and PDI = 1.08, by GPC) and (b) stannylated P3HT. Insets: magnified images of largest-fraction region. Observed mass of Br-P3HT: (Br-/H-) 3572, 3738, 3905; (H-/H-) 3657, 3824, 3991. Calculated mass: (Br-/H-) 3572.8, 3739.1, 3905.3; (H-/H-): 3660.2, 3826.5, 3992.7.

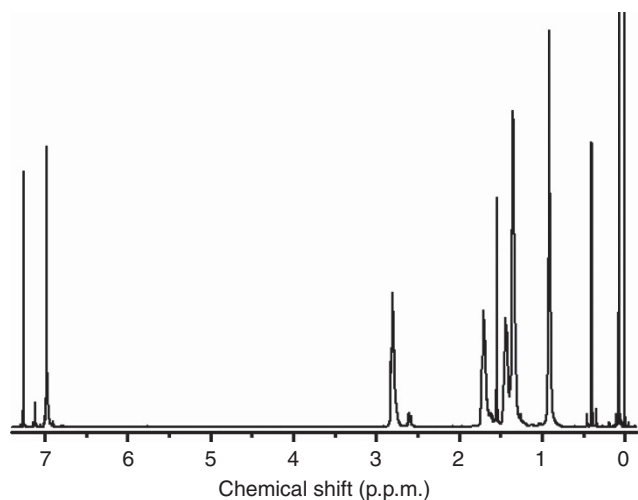
#### Bis-stannylation



#### Mono-stannylation



**Scheme 1** Synthetic schemes for  $\text{Sn}_2$ -P3HT and Sn-P3HT. rt, room temperature.

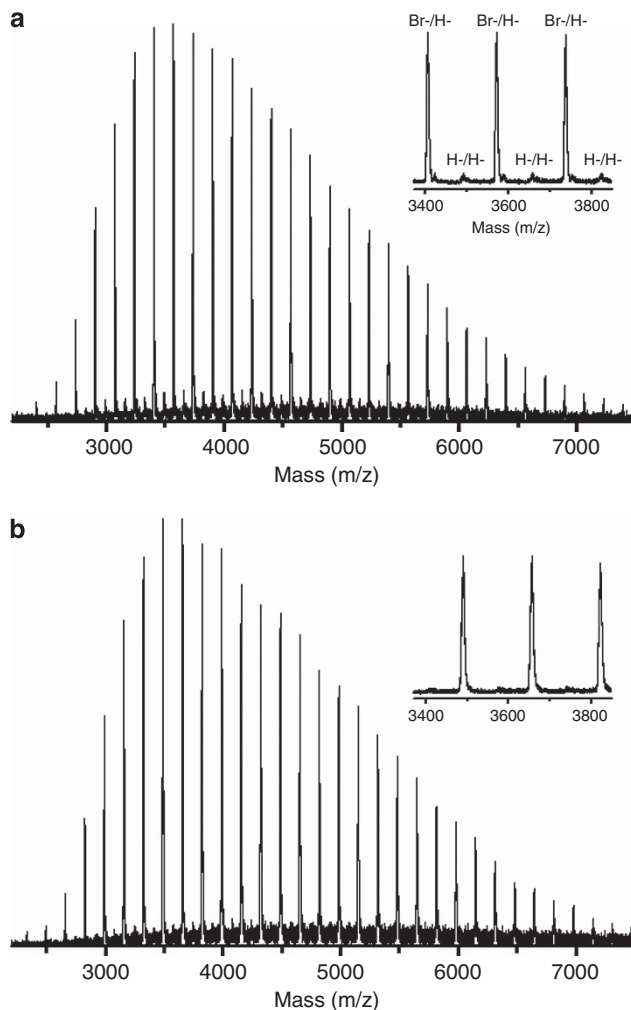


**Figure 2**  $^1\text{H}$  NMR spectrum of  $\text{Sn}_2\text{-P3HT}$  ( $M_n=5050$ , conversion of end groups: 81.4%).

confirmed from the  $^1\text{H}$  NMR spectra, even when a large excess (300 equiv.) of  $\text{Me}_3\text{SnCl}$  was added. Note that the reaction mixture exhibited a purple color at  $-78^\circ\text{C}$ , indicating that most of the P3HT aggregated at such a low temperature (a THF solution of P3HT at room temperature is orange). This could decrease the reactivity of the end groups. TMEDA has been reported to enhance the polarity of alkyllithium species or to break them into smaller clusters, leading to higher reactivity and faster metalation.<sup>18,19</sup> Thus, we have conducted the lithiation of P3HT in the presence of TMEDA. The  $^1\text{H}$  NMR spectrum recorded after stannylation shows that the addition of TMEDA to the lithiation process resulted in the formation of stannylated P3HT (see Figure 2 for a typical  $^1\text{H}$  NMR spectrum), as indicated by the presence of a characteristic  $-\text{CH}_3$  peak at  $\delta = 0.40$  in the  $\text{Me}_3\text{Sn}-$  group. It should be emphasized here that this is the first synthesis of P3HT-based stannylated compounds.

In the MALDI-TOF-MS profile (Figure 1b), there are two series of peaks of which the minor series (ca. 12% by peak intensity) could be assigned to the residual starting P3HT with the  $\text{Br-}/\text{H-}$  end group. The major peak series (ca. 88%) could be derived from stannylated P3HT, as shown in the  $^1\text{H}$  NMR spectrum. Compared with the spectrum of the starting material (Figure 1a), the unimodal peak distribution of the major peak series shifted to higher molecular weight as a whole, which suggests the attachment of stannyl groups to the ends. However, it is difficult to distinguish  $\text{Sn}_2\text{-P3HT}$  from  $\text{Sn-P3HT}$  and P3HT with both ends protonated (denoted as  $\text{H}_2\text{-P3HT}$ ) in the MALDI-TOF-MS profile, as their molecular weights are too close. For example, the calculated mass of  $\text{Sn}_2\text{-P3HT}$  with  $n = 23$  is 4152, whereas that of  $\text{Sn-P3HT}$  with  $n = 24$  is 4156 and that of  $\text{H}_2\text{-P3HT}$  with  $n = 25$  is 4159.

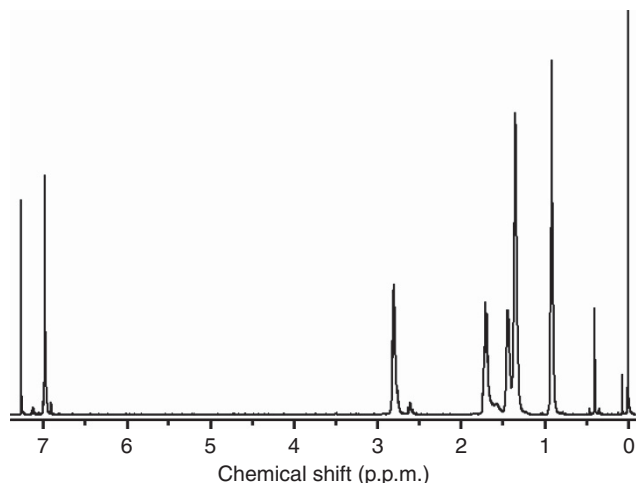
To evaluate the conversion of  $\text{Me}_3\text{Sn}-$  groups quantitatively, the percentage of  $\text{Me}_3\text{Sn}-$  groups in the final product is estimated by calculating the integrated areas of the peaks at  $\delta = 2.80$  ( $-\text{CH}_2-$  next to the thiophene ring in the main chain), 2.60–2.56 ( $-\text{CH}_2-$  next to the thiophene ring at the chain ends) and 0.40 ( $-\text{CH}_3$  in  $\text{Me}_3\text{Sn}-$ ) in  $^1\text{H}$  NMR spectra.<sup>20</sup> The conversion from either  $\text{Br-}$  or  $\text{H-}$  ends to  $\text{Me}_3\text{Sn}-$  was 59% as estimated from the  $^1\text{H}$  NMR spectrum, and the amounts of  $\text{H-}$  and  $\text{Br-}$  end groups in the product were about 35 and 6%, respectively, as estimated from MALDI-TOF-MS profile based on the assumption that there is no degradation of  $\text{C-Sn}$  and  $\text{C-Br}$  bonds during the MALDI-TOF-MS measurements. This estimation suggests that the major peaks of MALDI-TOF-MS in Figure 1b are from the



**Figure 3** MALDI-TOF-MS profiles of (a)  $\text{Br-P3HT}$  ( $M_n=5900$  and  $\text{PDI}=1.09$  by GPC) and (b) mono-stannylated P3HT. Insets: magnified images of largest-fraction region. Observed mass after mono-stannylation: ( $\text{Me}_3\text{Sn-}/\text{H-}$ ) 3490, 3656, 3822. Calculated mass: ( $\text{Me}_3\text{Sn-}/\text{H-}$ ) 3490.4, 3656.7, 3823.0.

mixture of  $\text{Sn}_2\text{-P3HT}$ ,  $\text{Sn-P3HT}$  and  $\text{H}_2\text{-P3HT}$ . When the  $M_n$  of P3HT was changed from 2500 to 9200, the conversion of the chain ends to  $\text{Me}_3\text{Sn-}$  after stannylation varied between 59 and 72%, suggesting that  $M_n$  of P3HT has weak influence on the conversion.

The reaction conditions were analyzed to achieve a maximum conversion of  $\text{Me}_3\text{Sn}-$  groups. First, the amounts of TMEDA and *s*-BuLi were optimized in the ranges of 10–120 and 50–100 equiv., respectively, to increase the conversion of the reaction. We found that the conversions were in the range of 57–73% and not very sensitive to the amount of TMEDA or *s*-BuLi. Next, the effect of reaction temperature was investigated. Although it was presumed that TMEDA functions to enhance the activity of BuLi, it has also been reported that TMEDA can stabilize lithiated products.<sup>21</sup> To confirm this, the lithiation duration was elongated from 1 h to 3 h with 120 equiv. of TMEDA and 100 equiv. of *s*-BuLi. In this case, no formation of  $\text{Me}_3\text{Sn}-$  groups was observed in the final product, suggesting that the lithiated product is of low stability even at  $-78^\circ\text{C}$ . In view of this instability of lithiated P3HT, the lithiation duration was shortened from 1 h to 30 min. As a result, a much improved conversion of 81% was obtained, as calculated from the peak intensities of the  $^1\text{H}$  NMR spectrum in



**Figure 4**  $^1\text{H}$  NMR spectrum of Sn-P3HT ( $M_n=5900$ , conversion of end groups: 74%).

Figure 2, suggesting that the presence of TMEDA in the reaction can stabilize lithiated P3HT, thus improving stannylation conversion.

The use of a Grignard reagent instead of *s*-BuLi can lead to the functionalization of only one end of P3HT (Scheme 1) owing to the selectivity of the thiophene to be brominated at the 2-position. A similar reaction was reported for the synthesis of monocarboxylated P3HT.<sup>11</sup> The MALDI-TOF-MS profiles of Br-P3HT and the product (Figure 3) show that Br- groups were completely removed and almost only one series of peaks could be observed after the mono-stannylation. The NMR spectrum of the product (Figure 4) clearly demonstrates that  $\text{Me}_3\text{Sn}$ - groups were successfully attached to the chain ends. The conversion of Br- ends to  $\text{Me}_3\text{Sn}$ - groups in the product is estimated to be 74%. The rest of the polymer should be  $\text{H}_2$ -P3HT formed by the quenching of the unreacted Grignard end of P3HT.

## CONCLUSION

By choosing the reaction conditions, the end groups of regioregular P3HT were either bis- or mono-stannylated by post-functionalization. Both stannylated P3HTs are expected to be useful in Stille coupling for the synthesis of P3HT-based materials. For example, electron or energy acceptor groups could be attached to either one or both ends of P3HT through  $\pi$ -conjugation.<sup>12</sup> This could lead to novel optoelectronic polymer materials with precisely controlled structures.

## ACKNOWLEDGEMENTS

We thank Dr Yue Zhang, Dr Chunhe Yang and Dr Erjun Zhou for helpful discussion. This work was supported in part by the JST-ERATO HASHIMOTO Light Energy Conversion Project and the Global COE Program (Chemistry Innovation through Cooperation of Science and Engineering) of MEXT, Japan. LZ Zhang thanks the Ministry of Education of China for financial support through the Japanese Government (MONBUKAGAKUSHO: MEXT) Scholarship for research student.

- Zhao, G. J., He, Y. J. & Li, Y. F. 6.5% efficiency of polymer solar cells based on poly(3-hexylthiophene) and indene-C(60) bisadduct by Device Optimization. *Adv. Mater.* **22**, 4355–4358 (2010).
- Wei, Q. S., Miyayoshi, S., Tajima, K. & Hashimoto, K. Enhanced charge transport in polymer thin-film transistors prepared by Contact Film Transfer method. *ACS Appl. Mater. Interfaces* **1**, 2660–2666 (2009).
- Cho, C. H., Kang, H., Kang, T. E., Cho, H. H., Yoon, S. C., Jeon, M. K. & Kim, B. J. Controlling side-chain density of electron donating polymers for improving their packing structure and photovoltaic performance. *Chem. Commun.* **47**, 3577–3579 (2011).
- Kim, Y. *et al.* Effect of the end group of regioregular poly(3-hexylthiophene) polymers on the performance of polymer/fullerene solar cells. *J. Phys. Chem. C* **111**, 8137–8141 (2007).
- Kim, J. S., Lee, Y., Lee, J. H., Park, J. H., Kim, J. K. & Cho, K. High-Efficiency Organic Solar Cells Based on End-Functional-Group-Modified Poly(3-hexylthiophene). *Adv. Mater.* **22**, 1355–1360 (2010).
- Iovu, M. C. *et al.* Conducting regioregular polythiophene block copolymer nanofibrils synthesized by reversible addition fragmentation chain transfer polymerization (RAFT) and nitroxide mediated polymerization (NMP). *Macromolecules* **40**, 4733–4735 (2007).
- Radano, C. P., Scherman, O. A., Stingelin-Stutzmann, N., Müller, C., Breiby, D. W., Smith, P., Janssen, R. A. & Meijer, E. W. Crystalline-crystalline block copolymers of regioregular poly(3-hexylthiophene) and polyethylene by ring-opening metathesis polymerization. *J. Am. Chem. Soc.* **127**, 12502–12503 (2005).
- Jeffries-El, M., Sauve, G. & McCullough, R. D. *In-situ* end-group functionalization of regioregular poly(3-alkylthiophene) using the Grignard metathesis polymerization method. *Adv. Mater.* **16**, 1017–1019 (2004).
- Bronstein, H. A. & Luscombe, C. K. Externally Initiated Regioregular P3HT with Controlled Molecular Weight and Narrow Polydispersity. *J. Am. Chem. Soc.* **131**, 12894–12895 (2009).
- Liu, J. S. & McCullough, R. D. End group modification of regioregular polythiophene through postpolymerization functionalization. *Macromolecules* **35**, 9882–9889 (2002).
- Lohwasser, R. H. & Thelakkat, M. Synthesis and Characterization of Monocarboxylated Poly(3-hexylthiophene)s via Quantitative End-Group Functionalization. *Macromolecules* **43**, 7611–7616 (2010).
- Lim, H., Huang, K. T., Su, W. F. & Chao, C. Y. Facile Syntheses, Morphologies, and Optical Absorptions of P3HT Coil-Rod-Coil Triblock Copolymers. *J. Polym. Sci. A Polym. Chem.* **48**, 3311–3322 (2010).
- Zhang, L. Z., Tajima, K. & Hashimoto, K. Low Bandgap polymers based on regioregular oligothiophenes linked with electron accepting anits. *Macromolecules* **44**, 4222–4229 (2011).
- Yokoyama, A., Miyakoshi, R. & Yokozawa, T. Chain-growth polymerization for poly(3-hexylthiophene) with a defined molecular weight and a low polydispersity. *Macromolecules* **37**, 1169–1171 (2004).
- Zhang, Y., Tajima, K., Hirota, K. & Hashimoto, K. Synthesis of all-conjugated diblock copolymers by quasi-living polymerization and observation of their microphase separation. *J. Am. Chem. Soc.* **130**, 7812–7813 (2008).
- Miyakoshi, R., Yokoyama, A. & Yokozawa, T. Synthesis of poly(3-hexylthiophene) with a perty narrower polydispersity. *Macromol. Rapid Commun.* **25**, 1663–1666 (2004).
- Lohwasser, R. H., Bandara, J. & Thelakkat, M. Tailor-made synthesis of poly(3-hexylthiophene) with carboxylic end groups and its application as a polymer sensitizer in solid-state dye-sensitized solar cells. *J. Mater. Chem.* **19**, 4126–4130 (2009).
- Natori, I. Anionic polymerization of 1,3-cyclohexadiene: Reactivity of poly(1,3-cyclohexadienyl)lithium. *Macromol. Chem. Phys.* **207**, 2215–2221 (2006).
- Rutherford, J. L., Hoffmann, D. & Collum, D. B. Consequences of correlated solvation on the structures and reactivities of RLi-diamine complexes: 1,2-addition and alpha-lithiation reactions of imines by TMEDA-solvated *n*-butyllithium and phenyllithium. *J. Am. Chem. Soc.* **124**, 264–271 (2002).
- Iovu, M. C., Sheina, E. E., Gil, R. R. & McCullough, R. D. Experimental evidence for the quasi-‘living’ nature of the Grignard metathesis method for the synthesis of regioregular poly(3-alkylthiophenes). *Macromolecules* **38**, 8649–8656 (2005).
- Stanetty, P., Koller, H. & Mihovilovic, M. Directed ortho-lithiation of phenylcarbamic acid 1,1-dimethylethyl ester (N-Boc-aniline). revision and improvements. *J. Org. Chem.* **57**, 6833–6837 (1992).