

The Marriage of Metallacycle Transfer Chemistry with Suzuki–Miyaura Cross-Coupling To Give Main Group Element-Containing Conjugated Polymers

Gang He, Le Kang, William Torres Delgado, Olena Shynkaruk, Michael J. Ferguson, Robert McDonald, and Eric Rivard*

Department of Chemistry, University of Alberta, 11227 Saskatchewan Drive, Edmonton, Alberta, Canada T6G 2G2

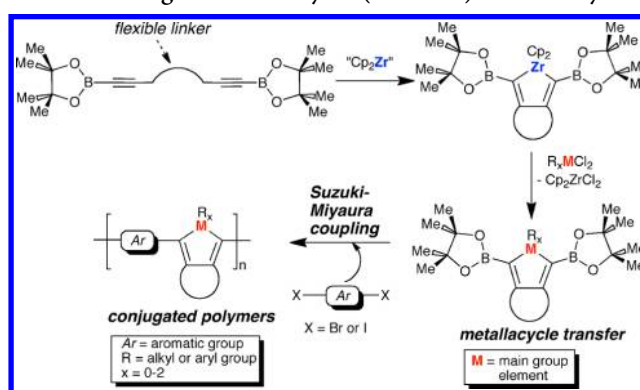
S Supporting Information

ABSTRACT: A versatile and general synthetic route for the synthesis of conjugated main group element-based polymers, previously inaccessible by conventional means, is reported. These polymers contain five-membered chalcogenophene rings based on S, Se, and Te, and we demonstrate that optoelectronic properties can be readily tuned via controlled atom substitution chemistry. In addition, regioregular hybrid thiophene–selenophene–tellurophene and selenophene–fluorene copolymers were synthesized to provide a further illustration of the scope of the presented metallacycle transfer/cross-coupling polymerization method.

Conjugated polymers have attracted considerable attention from the chemical community at large because of their widespread use in photovoltaics, polymer light-emitting diodes (PLEDs), and chemical sensing technologies.^{1–3} Moreover, polymers are amenable to various processing/manufacturing methods that are not readily translated to small-molecule-based systems. The emergence of cross-coupling C–C bond-forming methodologies has enabled the facile preparation of many organic-based conjugated polymers, but the construction of polymers featuring heavy inorganic elements as integral components has been much less studied.^{4,5} Herein we report a tandem synthetic strategy that combines the versatility of Suzuki–Miyaura cross-coupling with Zr-mediated metallacycle transfer chemistry (Scheme 1) to provide access to new polymeric frameworks containing inorganic rings such as selenophenes and tellurophenes. This general strategy represents a new addition to the ever-expanding synthetic toolkit available for the synthesis of functional polymeric materials.

At the onset, our goal was to devise a rapid method for generating selenophene- and tellurophene-containing polymers for photovoltaic applications.¹ Compared to their thiophene congeners, polyselenophenes and thiophene–selenophene copolymers are expected to have improved optoelectronic properties due to the presence of lower band gaps and deeper LUMO levels.⁵ Along these lines, Choi and co-workers have constructed high-performance thin-film transistors based upon selenophene copolymers,⁶ and the Seferos group has reported a series of elegant studies involving the construction of novel Se- and Te-based chalcogenophene block and alternate copolymers.^{5e,7} In each case, the incorporation of selenophene

Scheme 1. Combined Metallacycle Transfer/Cross-Coupling Route to Inorganic Heterocycle (Heterole)-Based Polymers

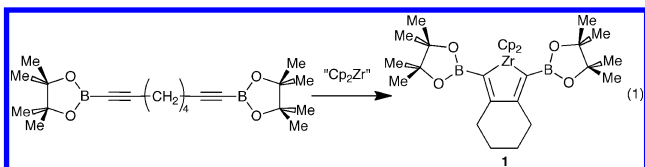


and tellurophene units led to a narrowing of the optical band gap relative to their ubiquitous sulfur-based counterparts. It should be noted that an efficient and high-yielding general route to these materials is desired in order to advance the study of these promising macromolecules.⁸

In 1988, Fagan and co-workers reported the synthesis of a wide range of main group element (M) heterocycles via metallacycle transfer from readily available zirconacyclopentadienes in high yield.⁹ Later, Tilley reported the direct synthesis of zirconacyclopentadiene-containing polymers from the reaction of rigid aryl-spaced diynes [e.g., $\text{MeC}\equiv\text{CSiMe}_2(\text{C}_6\text{H}_4)\text{SiMe}_2\text{C}\equiv\text{CMe}$] with sources of “ Cp_2Zr ” ($\text{Cp} = \eta^5\text{-C}_5\text{H}_5$).^{10–12} Despite the promise of this method, there are challenges associated with replacing all of the Cp_2Zr groups along the polymer backbone with main group elements to give air-stable conjugated polymers, although successful examples are known.¹¹ Furthermore, obtaining regioregular substitution about the heterole rings can also be difficult.¹³

In line with the targets presented in Scheme 1, we sought to develop a zirconacycle precursor containing pinacolborane (BPin) cross-coupling groups at the 2 and 5 positions of the ZrC_4 ring. The desired zirconacycle **1** was prepared by reacting the known pinacolborane-capped diyne $(\text{PinB})\text{C}\equiv\text{C}(\text{CH}_2)_4\text{C}\equiv\text{C}(\text{BPin})$ ¹⁴ with in situ-generated “ Cp_2Zr ” in tetrahydrofuran (THF), as outlined in eq 1. Zirconacycle **1** was isolated as an air- and moisture-sensitive red crystalline solid in

Received: March 3, 2013



65% yield, and the X-ray structure of **1** is shown in Figure 1. Despite the presence of hindered BPin groups at flanking

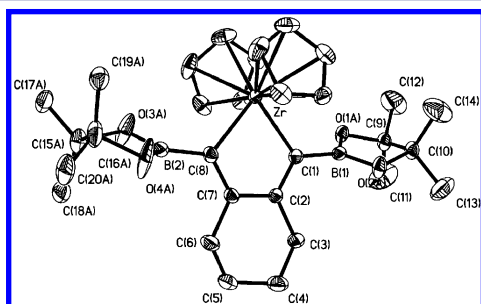
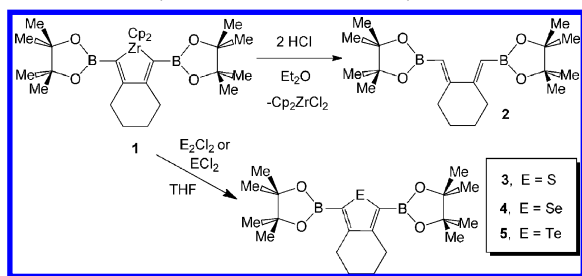


Figure 1. Molecular structure of **1** with thermal ellipsoids presented at the 30% probability level. H atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Zr–C(1), 2.245(3); Zr–C(8), 2.249(4); C(1)–B(1), 1.535(5); C(8)–B(2), 1.544(5); C(1)–Zr–C(8), 79.62(13); Zr–C(1)–C(2), 109.8(2); Zr–C(8)–C(7), 109.5(2).

positions about the zirconacycle, the Zr center in **1** appeared to have sufficient steric accessibility to allow for productive metallacycle transfer chemistry with halides of main group elements.

As anticipated, zirconacycle **1** is a progenitor to various main group element-containing heterocycles (Scheme 2). For future

Scheme 2. Synthesis of Heterocyclic Polymer Precursors 2–5 via Metallacycle Transfer Chemistry

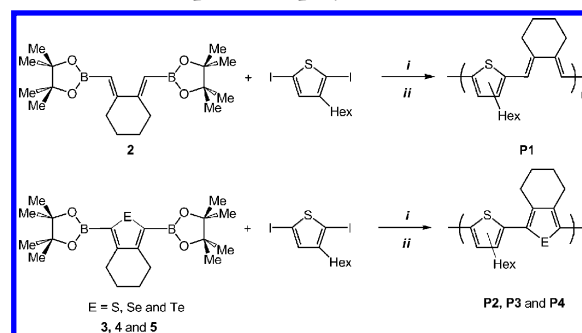


comparative studies, the butadiene-linked monomer **2** was first synthesized as an air-stable colorless solid in 77% yield by adding an aqueous HCl solution to **1**.¹⁶ The thiophene heterocycle **3** was then prepared via pre-established metallacycle transfer chemistry using S_2Cl_2 as the chalcogen source. We found that the heavier Se congener **4** (yellow solid) was best generated from the reaction of **1** with metastable $SeCl_2$.¹⁷ Initially we attempted to generate the tellurophene monomer **5** using “ $TeCl_2$ ” (prepared from $TeCl_4$ and $Me_3SiSiMe_3$)¹⁸ as a tellurium delivery agent, but no reaction between this reagent and **1** was observed. We speculated that the lack of reactivity was due to the poor solubility of “ $TeCl_2$ ” in THF, and therefore, we treated **1** with the soluble 2,2′-bipyridyl-sequestered tellurium dihalide adduct $bipy\cdot TeCl_2$.¹⁹ Gratifyingly, this reaction afforded **5** in a moderate 55% yield as green-yellow crystals. In contrast to previously reported polytellurophene precursors (e.g., diiodobitellurophene),^{7a} **5** exhibits considerable

thermal stability in the solid state (mp = 180–181 °C) and solution, thus expanding the temperature regime that can be accessed during the subsequent polymerization chemistry. Characterization of the pinacolborane-containing monomers **2–5** was accomplished by 1H , ^{11}B , and $^{13}C\{^1H\}$ NMR spectroscopy; single-crystal X-ray crystallography (see Figures S2–S5 in the Supporting Information),¹⁵ elemental analysis, UV–vis spectroscopy, and thermogravimetric analysis (TGA).

Given the successful synthesis of **2–5**, we were eager to explore Suzuki–Miyaura cross-coupling methodologies to incorporate conjugated diene and chalcogenophene units into polymeric structures. To begin, we combined **2–5** with 2,5-dibromo-3-hexylthiophene to afford a series of hybrid butadiene–thiophene (**P1**) or heterole–thiophene (**P2–P4**) copolymers using $Pd(PPh_3)_4$ as a catalyst and nBu_4NF as a phase-transfer agent. Although productive cross-coupling was observed, the molecular weights obtained were only 2–3 kg/mol. The $Pd_2(dba)_3/[HP^tBu_3]BF_4$ catalyst system (Scheme 3) used in

Scheme 3. Synthesis of the Hybrid Butadiene–Thiophene and Heterole–Thiophene Copolymers P1–P4^a



^aConditions: (i) $Pd_2(dba)_3$, $[HP^tBu_3]BF_4$, $K_2CO_3(aq)$, THF, 70 °C, 24 h; (ii) toluene, 70 °C, 24 h.

conjunction with 2,5-diiodo-3-hexylthiophene^{20,21} gave the target regiorandom polymers with higher number-average molecular weights (M_n) of 3.57–6.51 kg/mol (relative to polystyrene in THF). The synthesis of polymers containing tellurophene repeat units (**P4**) is noteworthy^{Se,7} and could be due to the higher thermal stability of the bis(BPin)-substituted reagent **5**, which enabled efficient cross-coupling to transpire at 70 °C in THF/toluene for 3 days. It should be mentioned that hybrid S/Se and S/Te oligochalcogenophenes related to **P3** and **P4** have been prepared in small quantities via electropolymerization and/or oxidative polymerization routes, and optical properties similar to those of our systems were noted (vide infra).^{5d,22} Our route remains attractive because it offers a high degree of control over the polymer composition. As a result of the versatile nature of Suzuki–Miyaura cross-coupling, the chemistry described above could be readily applied to the synthesis of various heterole–aryl copolymers simply by altering the nature of the aryl dihalide and BPin-grafted heterole being copolymerized.^{8,23}

Figures 2 and S11¹⁵ show the UV–vis data for polymers **P1–P4**. A general red shift of the optical absorption profiles upon moving from the polythiophene (**P2**) to the selenophene (**P3**) and tellurophene (**P4**) hybrids was observed, consistent with a progressive decrease in optical band gap (E_g). Interestingly, the butadiene-linked polymer **P1** showed a longer absorption wavelength (E_g = 2.36 eV in solution) relative to those in **P2–P4**;²⁴ therefore, monomer **2** could be a useful building block for the construction of new conjugated polymer systems.²⁵

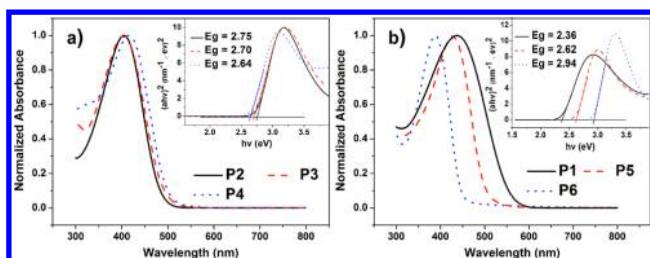
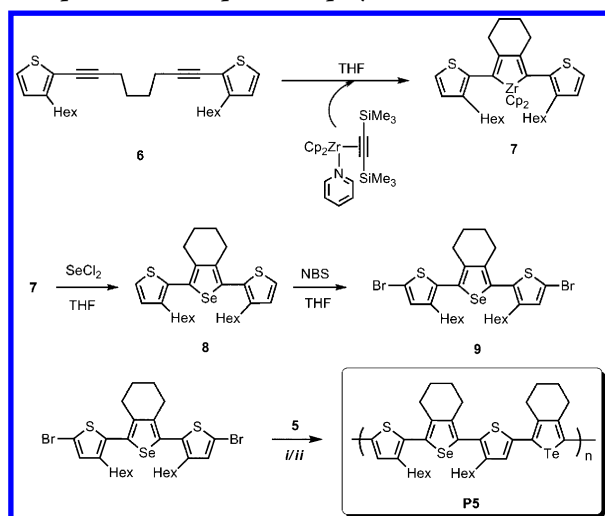


Figure 2. Absorption spectra of (left) **P2**–**P4** and (right) **P1**, **P5**, and **P6** in THF; extrapolated optical band gaps (E_g) are shown as insets.²⁴

The polymers also showed high thermal stabilities ($T_{\text{dec}} = 300$ – 350 °C by TGA; Figure S12),¹⁵ while clearly resolved melting temperatures (T_m) were observed at 212–227 °C (Figure S14). Weak luminescence (orange-red) by polymers **P2** and **P3** was noted, but the tellurophene analogue **P4** was nonemissive.²⁶

As noted, polymers **P1**–**P4** have regio-irregular structures, which may limit their use in optoelectronic devices.^{1,2} To install solubilizing hexyl groups at regiospecific sites along a polymer backbone, the procedure outlined in Scheme 4 was developed.

Scheme 4. Synthesis of Regioregular Thiophene–Selenophene–Tellurophene Copolymer **P5**^a



^aConditions: (i) $\text{Pd}_2(\text{dba})_3$, $[\text{HP}^t\text{Bu}_3]\text{BF}_4$, $\text{K}_2\text{CO}_3(\text{aq})$, THF, 70 °C, 24 h; (ii) toluene, 70 °C, 48 h.

Specifically, the thiophene-capped diyne **6** was first reacted with $\text{Cp}_2\text{Zr}(\text{py})(\text{Me}_3\text{SiCCSiMe}_3)$ ²⁷ to give zirconacycle **7** as a hexanesoluble orange-red solid (see Figure S6 for its crystallographically determined structure).¹⁵ Replacement of the Cp_2Zr unit in **7** by Se followed by selective bromination of the thiophene residues using *N*-bromosuccinimide (NBS) afforded the regioregular thiophene–selenophene monomer **9** as a yellow oil. The direct Suzuki–Miyaura copolymerization of **9** with tellurophene **5** led to the formation of the novel regioregular thiophene–selenophene–tellurophene copolymer **P5** ($M_n = 4.30$ kg/mol; PDI = 1.62) in 69% yield (Scheme 4).

Further evidence for the structural composition of **P5** was obtained via MALDI–TOF mass spectrometry (Figure 3a), which gave the expected spectral pattern in line with the assigned structure (repeat unit of m/z 750.11). To the best of our knowledge, **P5** is the first example of a conjugated polymer containing three different chalcogenophenes (S, Se, and Te) as part of a single polymer repeat unit. Consistent with the

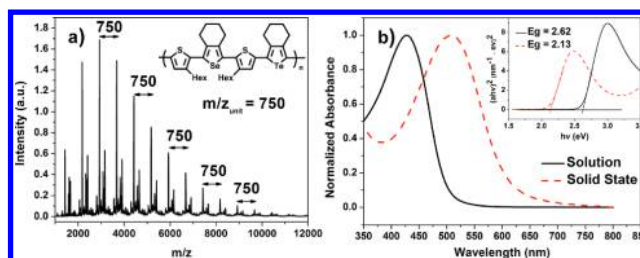
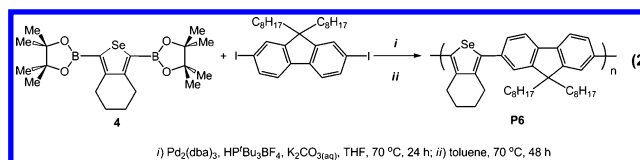


Figure 3. (a) MALDI–TOF mass spectrum of **P5**. (b) UV–vis absorption spectra of **P5** in THF solution and as a film.

presence of a regioregular material, **P5** displays a single thiophene-bound hydrogen environment in the ^1H NMR spectrum. **P5** exhibited an absorption maximum at 429 nm in THF (Figure 2b), which was red-shifted by ca. 10 nm relative to the S/Te hybrid copolymer **P4**. When films of **P5** were cast, the absorption maximum became broader and was red-shifted by ca. 80 nm relative to that in solution, suggesting an increase in conjugation in the solid state (Figure 3b). Moreover considerable tailing of the absorption to 750 nm in films of **P5** was noted.^{7c} Like the polytellurophene **P4**, the S–Se–Te terpolymer **P5** was not luminescent. Further manipulation of the structure of **P5** via side-group placement/annealing should lead to improved optoelectronic characteristics; we are currently in the process of evaluating the charge carrier mobilities of **P5** and its related regioregular polychalcogenophenes.

The general synthetic route shown in Scheme 1 could be further applied to construct fluorene–chalcogenophene copolymers, such as the Se analogue **P6** (eq 2). The absorption



maximum of this polymer (389 nm) is significantly hypsochromically shifted relative to those **P1**–**P5**, consistent with the behavior of other blue-emitting polyfluorenes found in the literature.²⁸ Accordingly, **P6** is luminescent in the blue spectral region with $\lambda_{\text{em}} = 458$ nm, a property that is highly desirable for PLEDs. We are actively exploring **P6** and related systems to this end in our laboratory.

In conclusion, we have reported a highly efficient and modular synthetic route to conjugated polymers featuring heterole units with tunable atomic composition. To illustrate this concept, we synthesized a number of S-, Se- and Te-containing polymers with varying compositions and optoelectronic properties. This combination of Zr-mediated ring-forming chemistry with Suzuki–Miyaura cross-coupling should provide access to an immense range of new polymer classes via judicious selection of the heterole and aryl cross-coupling partners. Future work will involve extending this synthetic concept to include conjugated materials containing new inorganic heterocycles.²³

■ ASSOCIATED CONTENT

Supporting Information

Experimental details; crystallographic data for **1**–**5** and **7** (CIF); and UV–vis, fluorescence, DSC, TGA, and MALDI data for the new polymers. This material is available free of charge via the Internet at <http://pubs.acs.org>.

■ AUTHOR INFORMATION

Corresponding Author

erivard@ualberta.ca

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was supported by the Natural Sciences and Engineering Research Council (NSERC) of Canada, the Canada Foundation for Innovation, and Alberta Innovates-Technology Futures (New Faculty Award to E.R.). We thank William Ramsay and Jason Brandt for their initial investigations of metallacycle transfer chemistry.

■ REFERENCES

- (1) (a) Yu, G.; Gao, J.; Hummelen, J. C.; Wudl, F.; Heeger, A. J. *Science* **1995**, *270*, 1789. (b) Helgesen, M.; Søndergaard, R.; Krebs, F. C. *J. Mater. Chem.* **2010**, *20*, 36. (c) Hou, J.; Chen, H.-Y.; Zhang, S.; Chen, R. I.; Yang, Y.; Wu, Y.; Li, G. *J. Am. Chem. Soc.* **2009**, *131*, 15586. (d) Li, C.; Liu, M.; Pschirer, N. G.; Baumgarten, M.; Müllen, K. *Chem. Rev.* **2010**, *110*, 6817. (e) Chen, J.; Cao, Y. *Acc. Chem. Res.* **2009**, *42*, 1709. (f) Park, S. H.; Roy, A.; Beaupré, S.; Cho, S.; Coates, N.; Moon, J. S.; Moses, D.; Leclerc, M.; Lee, K.; Heeger, A. J. *Nat. Photonics* **2009**, *3*, 297.
- (2) (a) Friend, R. H.; Gymer, R. W.; Holmes, A. B.; Burroughes, J. H.; Marks, R. N.; Taliani, C.; Bradley, D. D. C.; Dos Santos, D. A.; Brédas, J. L.; Lögdlund, M.; Salaneck, W. R. *Nature* **1999**, *397*, 121. (b) Akcelrud, L. *Prog. Polym. Sci.* **2003**, *28*, 875. (c) Choi, M.-C.; Kim, Y.; Ha, C.-S. *Prog. Polym. Sci.* **2008**, *33*, 581.
- (3) (a) Thomas, S. W., III; Joly, G. D.; Swager, T. M. *Chem. Rev.* **2007**, *107*, 1339. (b) Jäkle, F. *Chem. Rev.* **2010**, *110*, 3985. (c) Hong, V.; Lam, J. W. Y.; Tang, B. Z. *Chem. Commun.* **2009**, *45*, 4332. (d) Zhu, C.; Liu, L.; Yang, Q.; Lv, F.; Wang, S. *Chem. Rev.* **2012**, *112*, 4687.
- (4) (a) Beaujuge, P. M.; Fréchet, J. M. J. *J. Am. Chem. Soc.* **2011**, *133*, 20009. (b) Jahnke, A. A.; Seferos, D. S. *Macromol. Rapid Commun.* **2011**, *32*, 943.
- (5) (a) Heeney, M.; Zhang, W.; Crouch, D. J.; Chabinyc, M. L.; Gordyev, S.; Hamilton, R.; Higgins, S. J.; McCulloch, I.; Skabara, P. J.; Sparrowe, D.; Tierney, S. *Chem. Commun.* **2007**, 5061. (b) Patra, A.; Wijsboom, Y. H.; Zade, S. S.; Li, M.; Sheynin, Y.; Leitus, G.; Bendikov, M. *J. Am. Chem. Soc.* **2008**, *130*, 6734. (c) Das, S.; Zade, S. S. *Chem. Commun.* **2010**, *46*, 1168. (d) Chu, T.-Y.; Lu, J.; Beaupré, S.; Zhang, Y.; Pouliot, J.-R.; Wakim, S.; Zhou, J.; Leclerc, M.; Li, Z.; Ding, J.; Tao, Y. *J. Am. Chem. Soc.* **2011**, *133*, 4250. (e) Jahnke, A. A.; Djukic, B.; McCormick, T. M.; Buchaca Domingo, E.; Hellmann, C.; Lee, Y.; Seferos, D. S. *J. Am. Chem. Soc.* **2013**, *135*, 951.
- (6) Ha, J. S.; Kim, K. H.; Choi, D. H. *J. Am. Chem. Soc.* **2011**, *133*, 10364.
- (7) (a) Jahnke, A. A.; Howe, G. W.; Seferos, D. S. *Angew. Chem., Int. Ed.* **2010**, *49*, 10140. (b) Hollinger, J.; Jahnke, A. A.; Coombs, N.; Seferos, D. S. *J. Am. Chem. Soc.* **2010**, *132*, 8546. (c) Gibson, G. L.; McCormick, T. M.; Seferos, D. S. *J. Am. Chem. Soc.* **2012**, *134*, 539. (d) Hollinger, J.; DiCarmine, P. M.; Karl, D.; Seferos, D. S. *Macromolecules* **2012**, *45*, 3772.
- (8) Salzner, U.; Lagowski, J. B.; Pickup, P. G.; Poirier, R. A. *Synth. Met.* **1998**, *96*, 177.
- (9) (a) Fagan, P. J.; Nugent, W. A. *J. Am. Chem. Soc.* **1988**, *110*, 2310. (b) Fagan, P. J.; Nugent, W. A.; Calabrese, J. C. *J. Am. Chem. Soc.* **1994**, *116*, 1880.
- (10) (a) Mao, S. S. H.; Tilley, T. D. *J. Am. Chem. Soc.* **1995**, *117*, 5365. (b) Mao, S. S. H.; Tilley, T. D. *Macromolecules* **1997**, *30*, 5566. (c) Lucht, B. L.; Mao, S. S. H.; Tilley, T. D. *J. Am. Chem. Soc.* **1998**, *120*, 4354.
- (11) (a) Lucht, B. L.; Buretea, M. A.; Tilley, T. D. *Organometallics* **2000**, *19*, 3469. (b) Hay, C.; Hissler, M.; Fischmeister, C.; Rault-Berthelot, J.; Toupet, L.; Nyulászi, L.; Réau, R. *Chem.—Eur. J.* **2001**, *7*, 4222. (c) Jiang, B.; Tilley, T. D. *J. Am. Chem. Soc.* **1999**, *121*, 9744. (d) Morisaki, Y.; Aiki, Y.; Chujo, Y. *Macromolecules* **2003**, *36*, 2594. (e) Zhou, W.-M.; Tomita, I. *J. Inorg. Organomet. Polym.* **2009**, *19*, 113.
- (12) For reports concerning the preparation and nature of “Cp₂Zr” (generated from the reaction of Cp₂ZrCl₂ with 2 equiv of “BuLi in THF”), see: (a) Negishi, E.; Cederbaum, F. E.; Takahashi, T. *Tetrahedron Lett.* **1986**, *27*, 2829. (b) Negishi, E.; Takahashi, T. *Acc. Chem. Res.* **1994**, *27*, 124. (c) Dioumaev, V. K.; Harrod, J. F. *Organometallics* **1997**, *16*, 1452.
- (13) Miller, A. D.; McBee, J. L.; Tilley, T. D. *J. Am. Chem. Soc.* **2008**, *130*, 4992.
- (14) Gandon, V.; Leca, D.; Aechtner, T.; Vollhardt, K. P. C.; Malacria, M.; Aubert, C. *Org. Lett.* **2004**, *6*, 3405.
- (15) See the Supporting Information for full details.
- (16) Thanedar, S.; Faron, M. F. *J. Organomet. Chem.* **1982**, *235*, 65.
- (17) Maaninen, A.; Chivers, T.; Parvez, M.; Pietikäinen, J.; Laitinen, R. S. *Inorg. Chem.* **1999**, *38*, 4093.
- (18) Patra, A.; Wijsboom, Y. H.; Leitus, G.; Bendikov, M. *Org. Lett.* **2009**, *11*, 1487.
- (19) Dutton, J. L.; Farrar, G. J.; Sgro, M. J.; Battista, T. L.; Ragogna, P. J. *Chem.—Eur. J.* **2009**, *15*, 10263.
- (20) Cross-coupling was also investigated with 2,5-dibromo-3-hexylthiophene, but lower molecular weights ($M_n \approx 3$ kg/mol) were obtained.
- (21) Haid, S.; Mishra, A.; Uhrich, C.; Pfeiffer, M.; Bäuerle, P. *Chem. Mater.* **2011**, *23*, 4435.
- (22) Ng, S. C.; Ding, H.; Chan, H. S. O. *Chem. Lett.* **1999**, *28*, 1325.
- (23) To date, five-membered heteroles containing a variety of main group elements (e.g., B, Ga, Al, Si, Ge, Sn, P, Bi, S, Se, and Te) have been prepared via metallacycle transfer chemistry (see ref 9 for details).
- (24) Eckhardt, H.; Shacklett, L. W.; Elsenbaumer, R. L. *J. Chem. Phys.* **1989**, *91*, 1303.
- (25) The presence of the fused cyclohexyl side groups in P1–P6 may lead to undesired twisting of the polymer backbone. Fortunately, the reported synthetic procedure should enable the synthesis of polymers bearing less encumbered cyclopentyl and cyclobutyl side groups.
- (26) (a) Perepichka, I. F.; Perepichka, D. F.; Meng, H.; Wudl, F. *Adv. Mater.* **2005**, *17*, 2281. (b) Polytellurophenes are generally nonemissive in solution. For a recent report of solid-state phosphorescence, see: Lapkowski, M.; Motyka, R.; Suwinski, J.; Data, P. *Macromol. Chem. Phys.* **2012**, *213*, 29.
- (27) Rosenthal, U.; Ohff, A.; Baumann, W.; Tillack, A.; Görls, H.; Burlakov, V. V.; Shur, V. B. *Z. Anorg. Allg. Chem.* **1995**, *621*, 77.
- (28) Zeng, G.; Yu, W.-L.; Chua, S.-J.; Huang, W. *Macromolecules* **2002**, *35*, 6907.