Polytellurophenes with Properties Controlled by Tellurium-Coordination**

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The field of conjugated polymers is multidisciplinary and highly competitive given the potential for application in optoelectronic devices including transistors, light emitting diodes, and solar cells.[1] From a chemistry perspective, polythiophenes and thiophene-containing copolymers are arguably the most successful classes of conjugated polymers and have been the focus of the majority of research in this field.[2] Thiophene polymers, however, do face certain limitations and intense research is taking place to develop new polymers with improved properties. In recent years, polyselenophenes have been developed that have narrow HOMO–LUMO gaps,[3] high ambipolar charge transport characteristics,[4] and can be designed to undergo phase separation into nanostructures in the solid state.[5] All of these properties are desirable for optoelectronics, and although these studies are early and limited in number, they highlight the opportunities that arise when conjugated polymers are synthesized from heavier group 16 heterocycles.

Tellurophene, the heaviest known group 16 heterocycle, should prove even more useful for improving and tailoring optoelectronic properties. Specifically, tellurophene has a narrow HOMO–LUMO gap and thus polytellurophenes are predicted to have desirable light-absorption properties.[6] Tellurium is a metalloid with relatively large spin–orbit coupling, therefore polytellurophenes should have easily populated triplet excited states.[7] Indeed, there are some excellent examples of transition metal containing polymers that have these favorable properties.[8] Due to its metalloid nature, tellurium forms hypervalent coordination complexes,[9] which should enable supramolecular interactions that offer a means to further control structure and properties. Despite this promise and decades of conjugated polymer research, the solid state optoelectronic properties of well-defined polytellurophenes have not been described or investigated.

Polytellurophenes have only been reported in the literature a handful of times, and with very limited characterization data. Insoluble black powders formed from the oxidative polymerization of tellurophene were first described by Tsukagoshi and co-workers in 1985.[10] Similar results were reported in two papers by Ogura and co-workers in the mid 1990s using higher homologues of tellurophene as monomers,[11,12] as well as by Otsubo in 2000.[13] In 1995 the Wittig-condensation polymerization of tellurophene dialdehyde with a phenyl diphosphonium salt was reported by Kubo and co-workers.[14] In 1999 the synthesis and oxidative polymerization of 3-butylthiophene-tellurophene-3-butylthiophene was reported by Chan and co-workers.[15] The syntheses of Kubo and Chan are distinct because they are the only reports where soluble products were isolated. Most recently, in 2009, the synthesis and electrochemical polymerization of 3,4-dimethoxytellurophene was reported by Bendikov and co-workers.[16] This promising polytellurophene had markedly different properties than its selenium analog, however the authors noted that its identity was difficult to determine.

The fact that there are only a few reports in the 25-year history of polytellurophenes indicates that there are serious challenges associated with the synthesis of these potentially useful organic electronic materials. Palladium-catalyzed condensation polymerizations, which have proven to be one of the best methods for synthesizing well-defined conjugated polymers, have not been developed or described for tellurophenes. One significant obstacle is a lack of suitable monomers to carry out these syntheses. Herein we describe the synthesis of a novel, bifunctional tellurophene monomer, and a study that determines the conditions required to prepare polytellurophenes by solution-based palladium-catalyzed polymerization of this monomer. This synthesis prepares well-defined polytellurophenes that are stable, processable materials with distinct optoelectronic properties that can be controlled by coordination chemistry at their tellurium centers.

We first designed and carried out a synthetic route to prepare a dihalogenated bitellurophene monomer that is suitable for condensation polymerization reactions. Tellurophene was prepared by the method of Stephens and co-workers,[17] and converted to bitellurophene by treatment with *t*BuLi and copper(II) chloride at −78 °C by following a modified literature method (Figure 1).[11] To prepare the desired monomer for polymerization, bitellurophene must be halogenated at the 5 and 5′ positions. However, dihalotellurophenes are to our knowledge unknown compounds, likely due to difficulties associated with halogenating tellurophene heterocycles. Indeed, while several conditions for aromatic halogenation exist, most of these are not suitable for tellurophene. Specifically, tellurophene forms complexes with Br_2, and therefore conditions that require elemental bromine must be avoided. Acids must also be avoided

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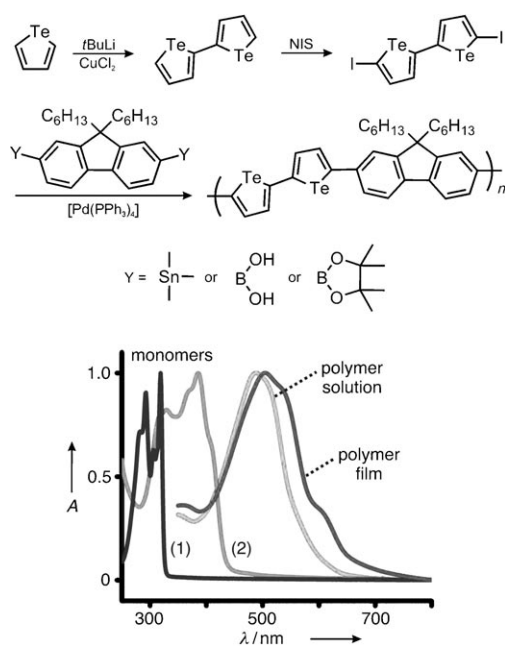
Figure 1. Top: Synthesis of 5,5′-diiodo-2,2′-bitellurophene and a general polymerization scheme. NIS = *N*-iodosuccinimide. Bottom: Absorbance spectra of the fluorene (1) and bitellurophene (2) monomers, and polymer solution and film.

because they are anticipated to lead to decomposition of the heterocycle. Based on these criteria, we selected *N*-iodosuccinimide (NIS) as the halogenating reagent because it does not require heating or the use of acids and is not a source of bromine. With some minor optimization of conditions, we could readily prepare the desired diiodobitellurophene monomer in 60% yield. Our initial attempts to brominate with *N*-bromosuccinimide (NBS) or iodinate with I_2/HIO_3 were unsuccessful, and show that the conditions for halogenating tellurophene are distinct from other heterocycles.

With the monomer in hand, we investigated a variety of commonly employed methods and conditions to prepare poly(bitellurophene-*alt*-9,9′-dihexylfluorene) copolymers using solution-based palladium-catalyzed polymerization (Table 1). This structure was chosen because the 9,9-dihexyl-fluorene comonomer was expected to improve processability. Because these polymerizations proceed by condensation, our main criterion for success was the percent conversion of the product. After each reaction, the polymers were isolated by

Table 1: Palladium-catalyzed polymerization conditions, product yields and molecular weights.

Fluorene functionality (Y)[a]	Solvent	Base	Yield [%][b]	M_n [kg mol^{-1}][c]
Sn(CH$_3$)$_3$	toluene	none	trace	n.d.[d]
B(OH)$_2$	THF	K$_2$CO$_3$	5.2	3.87
B(OH)$_2$	toluene	K$_2$CO$_3$	6.5	n.d.[d]
B(OR)$_2$	THF/MeOH	Bu$_4$N$^+$OH$^-$	18	2.70
B(OR)$_2$	toluene	K$_2$CO$_3$	32	3.14

[a] See Figure 1 for structures. [b] Yield after precipitation and extraction. [c] Measured in THF at room temperature. [d] Not determined.

precipitation and purified by successive Soxhlet extraction in acetone and chloroform. All chloroform fractions were analyzed by NMR and absorbance spectroscopy (see Supporting Information). While all the tested conditions have been shown to yield thiophene copolymers in high yield, we found that the conditions required to polymerize tellurophene were much more specific. A Stille-type polymerization with a trimethylstannane-functionalized fluorene unit in toluene gave mainly starting material and very little polymer, indicating that iodinated tellurophenes react relatively poorly under Stille-type conditions. Suzuki polymerization in THF and 2 M aqueous K$_2$CO$_3$, with a boronic acid-functionalized fluorene unit, resulted in a slightly improved 5.2% yield after extraction. A Suzuki coupling with the same fluorene unit in toluene and 2 M aqueous K$_2$CO$_3$ using a phase-transfer agent also gave a similarly low yield (6.5%). At this point, it was assumed that the bitellurophene monomer could be sensitive to the boronic acid functionality and we switched to a boronic ester-functionalized fluorine monomer. Suzuki polymerization of the boronic ester fluorene in THF/MeOH with tetrabutylammonium hydroxide gave an improved 18% yield, however, the solubility of the diiodobitellurophene monomer in THF/MeOH is visibly poor, even at polymerization temperatures. The very best method for palladium-catalyzed condensation of 5,5′-diiodo-2,2′-bitellurophene is a biphasic Suzuki reaction with a boronic ester-functionalized fluorene unit carried out in toluene and 2 M aqueous K$_2$CO$_3$ using a phase-transfer agent (Aliquat 336). This is likely due to functional group tolerance and improved solubility of the reactants. Polymer yield after precipitation, washing, and extraction is 32% under optimized conditions.

The obtained polymers have desirable properties with respect to solubility and processability, which is a major concern for polytellurophenes. The chemical structure of poly(bitellurophene-*alt*-9,9′-dihexylfluorene) was verified by ^{1}H NMR spectroscopy. The number-average molecular weight (M_n) of the highest yielding synthesis was 3.1 kg mol^{-1} ($M_n/M_w = 1.2$), determined by gel permeation chromatography (GPC) in THF compared with polystyrene standards. Poly(bitellurophene-*alt*-9,9′-dihexylfluorene) is soluble in common organic solvents such as THF, chloroform, and chlorobenzene, giving brightly colored solutions. The optical properties of the polymer have large bathochromic shifts relative to the monomer starting materials, indicating intra-chain electronic delocalization (Figure 1). The absorption maximum of the polymer in chloroform is 488 nm, compared to 385 nm for the bitellurophene monomer, which shows the electronic delocalization between the metalloid bitellurophene unit and carbon-based fluorene unit. Importantly, all obtained polymers have a nearly identical absorption profile, indicating this profile is characteristic of their chromophore (Supporting Information).

Solutions of the polymer can be cast into stable films for solid-state optical characterization. The absorption maximum of the film is red-shifted to 506 nm. The red-shift that is observed when going from solution to film is indicative of increased order in the solid state. Additionally, the absorption profile of the film possesses shoulders at 540 and 610 nm suggesting further organization and π-stacking in the solid

state. This observation is important because it provides evidence that inter-chain electronic delocalization is occurring in these polymers.

We next set out to test whether the metalloid nature of tellurophene leads to new ways of controlling optoelectronic properties. Other groups have shown the utility of controlling the properties of conjugated polyelectrolytes by the choice of their counter-ions,[18] and controlling the properties of electron-deficient conjugated polymers by the addition of Lewis acids.[19] In the case of tellurophene, reports in the literature have indicated that it forms a coordination complex with molecular bromine where one equivalent of Br_2 adds to Te.[20] Intrigued by the possibility of using Te-coordination to control properties, we set out to study the changes in optical absorption when the polymer is treated with molecular bromine. Solutions of polymer (ca. $0.01\ mg\,mL^{-1}$ in $CHCl_3$) were titrated with a solution of molecular bromine in chloroform. After the addition of only 0.1 equivalent of Br_2 (per Te, based on the GPC molecular weight) the onset of absorption shifts significantly from 624 to 727 nm (Figure 2 a). After the addition of approximately 0.4 equivalents of Br_2, the reaction appears to reach an end-point, where the polymer λ_{max} reaches 552 nm and a visible color change from orange to purple is observed (Figure 2 c). For reference, Br_2 has a λ_{max} at 410 nm and no appreciable absorption beyond 575 nm (Supporting Information). The observation that the end-point is reached before one equivalent of Br_2 is consumed is likely due to systematic error associated with polymer molecular weight determination rather than incomplete bromine coordination of the polymer. In general, GPC tends to overestimate the molecular weight of rigid-rod polymers.[21] Evidence for complete bromination after addition is supported by GPC measurements. The GPC-determined M_n of the brominated polymer is $4.7\ kg\,mol^{-1}$, corresponding to a weight increase of 46% or the addition of approximately 2 Br_2 per repeat unit. The specificity of the coordination reaction was supported by control experiments performed using poly(bitellurophene-*alt*-9,9′-dihexylfluorene) and I_2 or poly(bithiophene-*alt*-9,9′-dioctylfluorene) and Br_2 under analogous conditions which did not lead to an observable change in the absorbance spectra, confirming selectivity for Te and Br_2 (Supporting Information).

The polymer–bromine adduct is a stable material that can be isolated as a solid. Bromine treatment, however, could lead

to polymer degradation and that could cause the observed changes in the optical properties. To test for polymer degradation we examined the reversibility of Br_2 addition. For this experiment, the bromine adduct was prepared and isolated by concentration, then redissolved and cast into a film. Films of the bromine adduct have significantly red-shifted optical properties (Figure 2 b, curve 2) relative to the parent polytellurophene film (Figure 2 b, curve 1). Interestingly, the absorption profile of these films lacks the shoulders that are observed in the parent polymer, possibly indicating less order in the film. This is likely due to the inclusion of bromine, which disrupts the molecular packing that is observed in the parent polymer. Remarkably, upon annealing at 150 °C, the absorption profile of the film returns to the identical spectrum of the non-brominated polymer (Figure 2 b, curve 3). This observed reversibility of bromine addition provides support that the polymer is not degraded after bromine treatment, and provides evidence that a coordination species is formed.

In addition to the observed changes in solid-state optical properties, we also observe a significant change in the HOMO and LUMO positions. Here, the polymer HOMO level was estimated based on the onset of the first oxidation peak (Supporting Information) and the LUMO level was estimated from the HOMO level and the optical band-gap. Accordingly, the HOMO level of the parent polytellurophene is positioned at -5.28 eV and shifts to -5.40 eV upon bromine addition. The LUMO level of the parent polytellurophene is positioned at -3.50 eV and shifts to -3.78 eV upon bromine addition. Overall, bromine coordination appears to shift the polymer molecular orbitals (MOs) to more low-lying levels. This indicates that these classes of polymers not only have coordination-tunable absorption properties, but that the relative MO energy positions can be controlled by changing the coordination state at their Te centers.

Based on what is known about the supramolecular chemistry of tellurophene, bromine coordination in the polymer was anticipated. It is not obvious, however, why coordination leads to a red-shift in polymer optical properties, and why the relative positions of the frontier orbitals shift to more low-lying levels. To understand how tellurium–bromine interactions lead to the observed changes in optical and electronic properties we performed a series of density functional theory calculations (B3LYP-LANL2DZ). In all calculations we used the basic polymer repeat units, which are useful for predicting trends in the MO energy levels of conjugated copolymers.[22] We will first discuss the calculated geometry of the repeat units. For the parent tellurophene polymer, the calculated geometry optimizes to one that is similar to the sulfur analog (Supporting Information). For the bromine
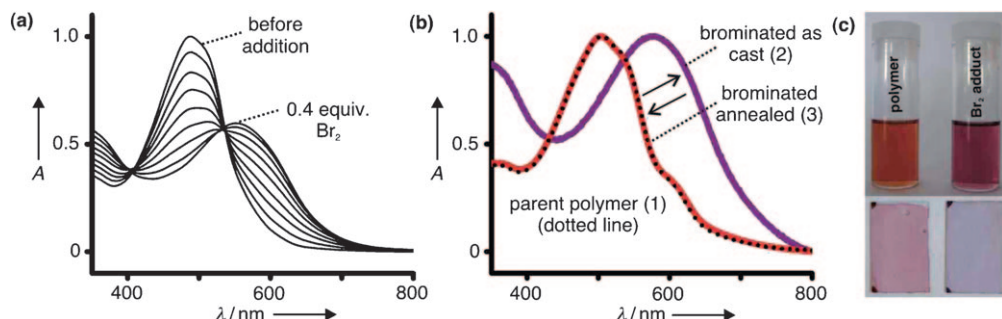

Figure 2. a) Solution absorbance spectra before and after addition of bromine. b) Solid state absorption spectra of parent polymer film, brominated polymer film, and brominated polymer film after annealing. c) Photographs of solutions and films of polymer before and after bromine addition.

adduct (which contains one equivalent of Br$_2$ per tellurophene heterocycle) the calculated geometry optimizes to a conformation with bromines in a pseudo-axial geometry relative to the tellurophene ring. While this geometry appears unusual, it is consistent with crystallographic data for tellurium-containing heterocycles that are bonded to two halogen atoms.[23] Our attempts to grow crystals of brominated bitellurophene were all unsuccessful due to the very low solubility of this model compound. However, vibronic energy calculations performed on optimized geometries give real (as opposed to imaginary) values for these bond types and provide additional confidence in the calculations (Supporting Information).

Once the optimized geometries were found, frontier molecular orbital calculations were used to estimate the spacing and position of the HOMOs and LUMOs (Figure 3). For the repeat unit of the parent polymer, the calculated HOMO–LUMO gap is 3.18 eV. For the bromine adduct, the
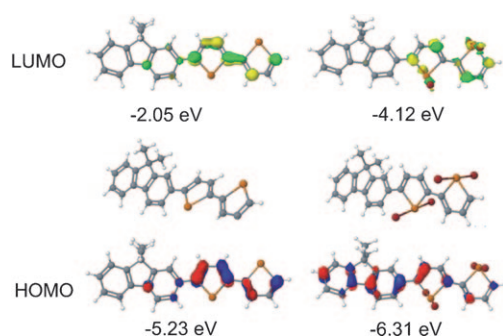

Figure 3. Calculated energies of the frontier orbitals (LUMO and HOMO) and electron distribution of the tellurophene polymer repeat unit and its brominated adduct. A representative image of the optimized geometry is positioned between the two frontier orbitals. Gray C, white H, orange Te, red Br.

gap narrows by approximately 1 eV to 2.19 eV, which is consistent with the observed red-shift in optical properties. Interestingly, the predicted MO levels of the bromine adduct are much more low-lying than the parent polymer repeat unit, and support the trends observed in the electrochemical measurements. The LUMO energy surface of the bromine adduct is strongly associated with the heterocyclic fragment, and the HOMO is strongly associated with the fluorene unit. On the other hand, the parent polymer repeat unit has a relatively symmetric energy distribution in the HOMO and LUMO. Overall, these energy surface calculations show that bromine coordination leads to an intramolecular charge-transfer complex, which is not present in the parent polymer. Charge-transfer complexes are known to lead to both narrow HOMO–LUMO gaps and low-lying energy levels.[2k–o] The fact that a charge-transfer complex can be switched on and off through coordination chemistry is a distinct and previously unknown property for these polytellurophenes.

In conclusion, we have synthesized a novel dihalogenated tellurophene monomer, and used this monomer to prepare well-defined polytellurophenes under palladium-catalyzed condensation conditions. This is the first report where polytellurophenes have been prepared by these methods. Using biphasic Suzuki-type chemistry, we can isolate these previously unreported polytellurophenes in greater than 30% yield. We believe that our monomer and polymer synthesis are significant advances that will open the door for research on well-defined conjugated polymers that incorporate tellurophene. The general lack of characterization on these types of polymers cannot be overstated. In the case of the polymers reported here, we have found that they are stable compounds with clearly defined optical properties. Evidence for both intra-chain and inter-chain electronic delocalization is observed. Importantly, due to their metalloid nature, the properties of these polymers can be reversibly controlled by treatment with a coordinating species, which appears to act on their Te centers and changes the electronic distribution within their π-conjugated system. This feature is not only new and interesting, but potentially very useful. It indicates that a single class of polytellurophene can be used for applications that require different HOMO–LUMO gaps and/or positions, such as both n-type and p-type semiconductors, or as both donor-type and acceptor-type materials. This will lead to new opportunities in polymer optoelectronics that are based on the distinct chemistry of tellurophene.

[1] a) B. C. Thompson, J. M. J. Fréchet, *Angew. Chem.* **2008**, *120*, 62–82; *Angew. Chem. Int. Ed.* **2008**, *47*, 58–77; b) G. Yu, J. Gao, J. C. Hummelen, F. Wudl, A. J. Heeger, *Science* **1995**, *270*, 1789–1791; c) H. Sirringhaus, P. J. Brown, R. H. Friend, M. M. Nielsen, K. Bechgaard, B. M. W. Langeveld-Voss, A. J. H. Spiering, R. A. J. Janssen, E. W. Meijer, P. Herwig, D. M. de Leeuw, *Nature* **1999**, *401*, 685–688.

[2] a) C. R. G. Grenier, W. Pisula, T. J. Joncheray, K. Müllen, J. R. Reynolds, *Angew. Chem.* **2007**, *119*, 728–731; *Angew. Chem. Int. Ed.* **2007**, *46*, 714–717; b) R. D. McCullough, *Adv. Mater.* **1998**, *10*, 93–116; c) I. Osaka, R. D. McCullough, *Acc. Chem. Res.* **2008**, *41*, 1202–1214; d) J. Liu, E. Sheina, T. Kowalewski, R. D. McCullough, *Angew. Chem.* **2002**, *114*, 339–342; *Angew. Chem. Int. Ed.* **2002**, *41*, 329–332; e) Q. F. Wang, R. Takita, Y. Kikuzaki, F. Ozawa, *J. Am. Chem. Soc.* **2010**, *132*, 11420–11421; f) A. Yokoyama, R. Miyakoshi, T. Yokozawa, *Macromolecules* **2004**, *37*, 1169–1171; g) H. A. Bronstein, C. K. Luscombe, *J. Am. Chem. Soc.* **2009**, *131*, 12894–12895; h) H. Xin, F. S. Kim, S. A. Jenekhe, *J. Am. Chem. Soc.* **2008**, *130*, 5424–5425; i) Q. Zhang, A. Cirpan, T. P. Russell, T. Emrick, *Macromolecules* **2009**, *42*, 1079–1082; j) J. Mattu, T. Johansson, S. Holdcroft, G. W. Leach, *J. Phys. Chem. B* **2006**, *110*, 15328–15337; k) S. A. Jenekhe, L. Lu, M. M. Alam, *Macromolecules* **2001**, *34*, 7315–7324; l) M. Svensson, F. Zhang, S. C. Veenstra, W. J. H. Verhees, J. C. Hummelen, J. M. Kroon, O. Inganäs, M. R. Andersson, *Adv. Mater.* **2003**, *15*, 988–991; m) J. C. Bijleveld, M. Shahid, J. Gilot, M. M. Wienk, R. A. J. Janssen, *Adv. Funct. Mater.* **2009**, *19*, 3262–3270; n) J. Hou, H.-Y. Chen, S. Zhang, R. I. Chen, Y. Yang, Y. Wu, G. Li, *J. Am. Chem. Soc.* **2009**, *131*, 15586–15587; o) E. Bundgaard, F. C. Krebs, *Sol. Energy Mater. Sol. Cells* **2007**, *91*, 954–985.

[3] a) M. Heeney, W. Zhang, D. J. Crouch, M. L. Chabinyc, S. Gordeyev, R. Hamilton, S. J. Higgins, I. McCulloch, P. J. Skabara, D. Sparrowe, S. Tierney, *Chem. Commun.* **2007**, 5061–5063; b) A. Patra, Y. H. Wijsboom, S. S. Zade, M. Li, Y. Sheynin, G. Leitus, M. Bendikov, *J. Am. Chem. Soc.* **2008**, *130*, 6734–6736.

[4] Z. Chen, H. Lemke, S. Albert-Seifried, M. Caironi, M. M. Nielsen, M. Heeney, W. M. Zhang, I. McCulloch, H. Sirringhaus, *Adv. Mater.* **2010**, *22*, 2371–2375.

[5] J. Hollinger, A. A. Jahnke, N. Coombs, D. S. Seferos, *J. Am. Chem. Soc.* **2010**, *132*, 8546–8547.

[6] a) Y. Narita, I. Hagiri, N. Takahashi, K. Takeda, *Jpn. J. Appl. Phys. 1* **2004**, *43*, 4248–4258; b) Y. Narita, K. Takeda, *Jpn. J. Appl. Phys. 1* **2006**, *45*, 2628–2642.

[7] Y. Shao, Y. Yang, *Adv. Mater.* **2005**, *17*, 2841–2844.

[8] a) F. Guo, Y.-G. Kim, J. R. Reynolds, K. S. Schanze, *Chem. Commun.* **2006**, 1887–1889; b) G. L. Schulz, S. Holdcroft, *Chem. Mater.* **2008**, *20*, 5351–5355; c) J. M. Nelson, P. Nguyen, R. Petersen, H. Rengel, P. M. Macdonald, A. J. Lough, I. Manners, N. P. Raju, J. E. Greedan, S. Barlow, D. Ohare, *Chem. Eur. J.* **1997**, *3*, 573–584.

[9] P. C. Srivastava, S. Bajpai, C. Ram, R. Kumar, J. P. Jasinski, R. J. Butcher, *J. Organomet. Chem.* **2004**, *689*, 194–202.

[10] R.-I. Sugimoto, K. Yoshino, S. Inoue, K. Tsukagoshi, *Jpn. J. Appl. Phys. 2* **1985**, *24*, L425–L427.

[11] S. Inoue, T. Jigami, H. Nozoe, T. Otsubo, F. Ogura, *Tetrahedron Lett.* **1994**, *35*, 8009–8012.

[12] T. Otsubo, S. Inoue, H. Nozoe, T. Jigami, F. Ogura, *Synth. Met.* **1995**, *69*, 537–538.

[13] S. Inoue, T. Jigami, H. Nozoe, Y. Aso, F. Ogura, T. Otsubo, *Heterocycles* **2000**, *52*, 159–170.

[14] H. Saito, S. Ukai, S. Iwatsuki, T. Itoh, M. Kubo, *Macromolecules* **1995**, *28*, 8363–8367.

[15] S. C. Ng, H. Ding, H. S. O. Chan, *Chem. Lett.* **1999**, *28*, 1325–1326.

[16] A. Patra, Y. H. Wijsboom, G. Leitus, M. Bendikov, *Org. Lett.* **2009**, *11*, 1487–1490.

[17] D. P. Sweat, C. E. Stephens, *J. Organomet. Chem.* **2008**, *693*, 2463–2464.

[18] a) R. Yang, H. Wu, Y. Cao, G. C. Bazan, *J. Am. Chem. Soc.* **2006**, *128*, 14422–14423; b) R. Yang, A. Garcia, D. Korystov, A. Mikhailovsky, G. C. Bazan, T.-Q. Nguyen, *J. Am. Chem. Soc.* **2006**, *128*, 16532–16539.

[19] a) C.-J. Yang, S. A. Jenekhe, *Chem. Mater.* **1991**, *3*, 878–887; b) G. C. Welch, R. Coffin, J. Peet, G. C. Bazan, *J. Am. Chem. Soc.* **2009**, *131*, 10802–10803.

[20] a) E. H. Braye, W. Hübel, I. Caplier, *J. Am. Chem. Soc.* **1961**, *83*, 4406–4413; b) J. D. McCullough, *Inorg. Chem.* **1975**, *14*, 2285–2286.

[21] S. Holdcroft, *J. Polym. Sci. Pol. Phys.* **1991**, *29*, 1585–1588.

[22] N. Blouin, A. Michaud, D. Gendron, S. Wakim, E. Blair, R. Neagu-Plesu, M. Belletête, G. Durocher, Y. Tao, M. Leclerc, *J. Am. Chem. Soc.* **2008**, *130*, 732–742.

[23] a) J. D. McCullough, *Inorg. Chem.* **1975**, *14*, 1142–1146; b) M. Abe, M. R. Detty, O. O. Gerlits, D. K. Sukumaran, *Organometallics* **2004**, *23*, 4513–4518.