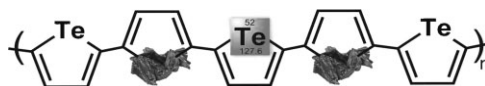


# Polytellurophenes

Ashlee A. Jahnke, Dwight S. Seferos\*

Will polytellurophenes bridge the gap between conjugated polymer and inorganic solid-state semiconductors? Polytellurophenes are a virtually unexplored class of conjugated polymer. In this paper, the synthetic methodologies that have been used to prepare polytellurophenes are chronicled. The properties of the resulting polymers are discussed and their potential for use as electronic materials is evaluated. It is far too early to know if these materials will lead to a useful class of thin-film semiconductors, however some key challenges associated with their synthesis and implementation are outlined. These challenges will need to be addressed as the conjugated polymer research community begins to utilize this area of the periodic table.



## Introduction

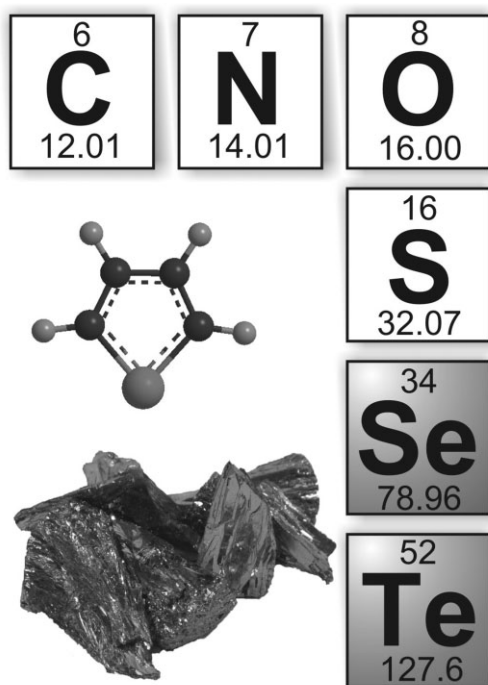
The field of conjugated polymers has evolved significantly over the past four decades. Early work primarily focused on insoluble materials, such as polyacetylene, that could be doped to form highly conductive films.<sup>[1–3]</sup> These materials were key to understanding the novel physical properties of conjugated polymers which opened a new direction in macromolecular research. As synthetic chemists began to work with physical chemists and physicists, new soluble derivatives were prepared, which further emphasized the unprecedented ability to tune properties by controlling macromolecular structure.<sup>[4,5]</sup> There are now numerous examples of stable, soluble polymer semiconductors that function as the active materials in a variety of optoelectronic devices including transistors, light emitting diodes, and photovoltaics.<sup>[6–8]</sup> Polymer semiconductors offer advantages over competing thin-film technologies in terms of production cost, processability, and weight that should make them ideal materials for certain electronic applications. The present challenge is to develop polymers that are stable and have high charge carrier mobility, ideally-positioned highest occupied molecular orbital (HOMO, valence) and lowest unoccupied molecular orbital (LUMO, conduction) levels, and a thin-film morphology that allows for desired optoelectronic and mechanical properties. Because polythiophenes and thiophene-containing copo-

lymers best fulfill all of these requirements, they are arguably the most successful classes of conjugated polymers thus far, and they have been the focus of the majority of research in this field.<sup>[9–23]</sup>

Thiophene polymers do face certain limitations however. Specifically, their optical band-gap (1.9 eV) is relatively large when compared to inorganic thin-film semiconductors such as CdTe (1.5 eV).<sup>[24]</sup> Polythiophenes also have modest charge carrier mobility ( $\approx 0.1 \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}$ ) when compared to their inorganic competitors ( $100\text{--}1\,000 \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}$ ).<sup>[25]</sup> In recent years, polyselenophenes have been developed in the search for polymers with improved properties, which now begins to meld the inorganic and organic worlds. The lower ionization potential of selenium leads to a polymer that has a lower band-gap (1.6 eV) than polythiophene.<sup>[26–28]</sup> The greater mass and polarizability of selenium is also expected to lead to improved charge transport characteristics. So far, polyselenophenes have similar hole mobilities, but improved electron mobilities when compared to polythiophenes.<sup>[29]</sup> Recently our group has shown that selenophene–thiophene block copolymers can be designed to undergo phase-separation into nanostructures in the solid-state, allowing both control of polymer morphology and optical properties without disrupting the conjugated backbone.<sup>[30]</sup> Although, these studies are early and limited in number, they highlight the potential when conjugated polymers are synthesized from heavier group-16 heterocycles.

Tellurophene, the heaviest known group-16 heterocycle, is far less explored for the preparation of conjugated

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**Figure 1.** The transition down group-16 from sulfur to selenium to tellurium. Unlike sulfur and selenium, tellurium is a metalloid. The image is a picture of tellurium metal.

polymers (Figure 1). Polytellurophenes, however, do have potential advantages as polymer semiconductors. Specifically, tellurophene has a narrow HOMO–LUMO gap and thus polytellurophenes have been predicted to have red-shifted optical absorption properties.<sup>[31,32]</sup> Tellurium is a metalloid and forms strong Te–Te interactions.<sup>[33–36]</sup> Therefore, polytellurophenes should be capable of supramolecular interactions that lead to strong interchain electronic coupling and can further control the structure and properties. Despite this promise and decades of conjugated polymer research, the solid-state optoelectronic properties of well-defined polytellurophenes have only recently been studied. With only a handful of reports on polytellurophenes there is still limited information available about the properties of this potentially very useful class of compounds. In this paper, we describe the synthetic strategies that have been employed to prepare polytellurophenes, focusing on a recently developed palladium-catalyzed route that prepares well-defined polymers. We discuss how the optical properties of these polymers can be controlled post-polymerization, which is a distinct feature of this class of macromolecule. Finally, we outline the remaining challenges that face researchers in this multidisciplinary field that has the potential to combine the worlds of inorganic and polymeric electronic materials.



**Dwight S. Seferos** attended Western Washington University and completed a B.Sc. degree in 2001. He then attended graduate school at the University of California, Santa Barbara where he worked under the supervision of Guillermo Bazan on the synthesis and study of conjugated organic molecules. After completing a Ph.D. in 2006, Dwight moved to Northwestern University where he was an American Cancer Society Postdoctoral Fellow with Chad Mirkin. In 2009, Seferos launched his independent laboratory in the Chemistry Department at the University of Toronto where his group focuses on the optical and electronic properties of novel semiconducting polymers and nanomaterials.



**Ashlee A. Jahnke** received a B.Sc. in Chemistry from Texas A&M University in 2007 where she worked under the guidance of Professor François Gabbaï. She subsequently joined the research staff at Lynntech, Inc where her work focused on fullerene derivatives for use in photodynamic therapy applications. In 2009 she joined the research group of Professor Dwight Seferos at the University of Toronto to pursue her Ph.D. in polymers and materials chemistry. Her current doctoral research focuses on the synthesis, characterization, and application of novel polytellurophenes for organic electronics.

## Discussion

### Early Unsubstituted Polytellurophenes

The first synthesis of polytellurophene was reported by Tsukagoshi and coworkers in 1985.<sup>[37]</sup> The authors describe the oxidative polymerization of tellurophene (**1**, Figure 2) by exposing the monomer vapor to a film of FeCl<sub>3</sub> catalyst on a glass plate. Elemental analysis supported that poly(tellurophene) was indeed the product, but due to the insolubility of the polymer, neither NMR, IR, nor absorbance characterization were reported. The neutral polymer is nearly insulating ( $10^{-12} \text{ S} \cdot \text{cm}^{-1}$ ) while conductivity values as high as  $10^{-6} \text{ S} \cdot \text{cm}^{-1}$  are observed when the polymer is doped with I<sub>2</sub>. The doped polymer, however, has a much lower conductivity than doped poly(thiophene) or poly(selenophene), which is likely due to morphological differences between the thin films.

In the mid-1990 s, Ogura and coworkers reported the first galvanostatic polymerization of tellurophene and its higher homologs 2,2'-bitellurophene (**2**) and 2,2':5,2''-tertellurophene (**3**).<sup>[38]</sup> Although the main focus of the study is the synthesis and characterization of the monomers, the authors also performed electrochemical polymerization of all three. Polymerization of **1** yields a slightly conductive black powder ( $10^{-7} \text{ S} \cdot \text{cm}^{-1}$ ). Poly-**2** and poly-**3** give black

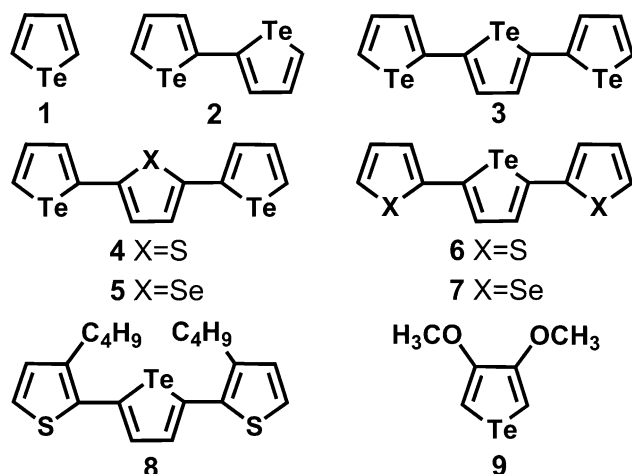


Figure 2. Structures of the tellurophene-containing monomers that have been polymerized by oxidative methods (chemical or electrochemical).

films rather than powders. One year later, Ogura again reported the polymerization of **1** and **2**.<sup>[39]</sup> Here, different polymerization conditions were tested by varying the solvent, supporting electrolyte, and polymerization current. The authors also report the chemical polymerization of **2** with a  $\text{FeCl}_3$  catalyst where they obtain a black polymer that is significantly less conductive than those previously reported for galvanostatic polymerization. Overall, these studies highlight the importance that reaction conditions and product solubility have on polymer properties.

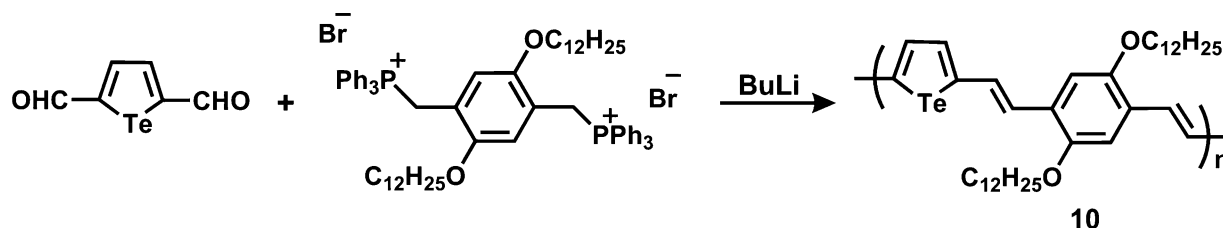
The first tellurophene copolymer was reported by Otsubo and coworkers in 2000 using chemical oxidation and electrochemical polymerization of hybrid terchalcogenophenes (**4–7**).<sup>[40]</sup> These authors report more extensive studies of tellurophene homologs and their polymerizations. The small HOMO–LUMO energy gaps of these monomers compared to thiophene monomers are demonstrated by voltammetric studies. Upon electrochemical polymerization, poly(terchalcogenophenes) **4** and **5** have much lower conductivities than **6** and **7**. The relative reaction rates of bitellurophene, biselenophene, and bithiophene are 5 to 3 to 2, respectively. Thus, it was concluded that poor solubility rather than slow reactivity prevents high degrees of polymerization in polytellurophenes. This report is the first to demonstrate that in order to realize the true potential for tellurophene containing polymers as conductive materials, further development of syntheses that lead to high molecular weight soluble polytellurophenes are needed.

### Stoichiometric Synthesis of Soluble Polytellurophenes

In 1999, Chan and coworkers reported the synthesis and oxidative polymerization of 2,5-bis(3-butyl-2-thienyl)telluro-

phene (**8**).<sup>[41]</sup> This report is one of only three examples of a soluble tellurophene-containing polymer and the only soluble example with an entirely chalcogenophene polymer backbone. The centrosymmetrical monomer unit **8** results in a regioregular polymer (with tail-to-tail linkages), and the butyl side-chains provide for solubility. The polymerization was carried out by solution-based chemical oxidation using  $\text{FeCl}_3$ . Under these conditions the polymer is obtained in 70% yield and is slightly soluble in chloroform, allowing for characterization data that could not be obtained for the previous insoluble examples. The polymer  $^1\text{H}$ NMR spectrum has two singlets in the aromatic region at  $\delta$  7.60 ppm (tellurophene protons) and 6.98 ppm (thiophene proton). The number average molecular weight ( $\bar{M}_n$ ) of this polymer is  $3.0 \text{ kg} \cdot \text{mol}^{-1}$  and the polydispersity (PDI) is 1.21 as determined by gel permeation chromatography (GPC) in tetrahydrofuran (THF). Absorption maxima are 484 and 493 nm for the solution ( $\text{CHCl}_3$ ) and film of the polymer, respectively. These maxima are significantly red-shifted when compared to the absorption maximum of the monomer (279 nm) indicating extension of the conjugation length. The band-gap energy is 1.71 eV based on the onset of absorption and is narrow compared to poly(3-alkylthiophenes). Thermogravimetric analysis shows that the iodine and  $\text{FeCl}_3$  doped polymers decompose at lower temperatures than the neutral polymer. However, the  $\text{FeCl}_3$  doped tellurophene polymer is more stable than doped polythiophene at  $110^\circ\text{C}$ . The iodine-doped polymer achieves promisingly high conductivities ( $0.42 \text{ S} \cdot \text{cm}^{-1}$ ) with an  $\text{I}_2$  intake of 120 wt.-%. These results highlight the importance of solubility and solid-state morphology for the conductivity of polytellurophenes, and demonstrate the potential use of polytellurophenes as semiconducting materials.

In 1995, the first reported non-oxidative polymerization was carried out by Wittig condensation of tellurophenedialedehyde with a phenyl diphosphonium salt.<sup>[42]</sup> The reaction (Figure 3) gives a red polymer in 65% yield that is soluble in both chloroform and THF. The polymer has an  $\bar{M}_n$  of  $7.0 \text{ kg} \cdot \text{mol}^{-1}$ , which was determined by GPC versus polystyrene standards.  $^1\text{H}$  NMR spectroscopy revealed multiplets in the aromatic region ( $\delta$  7.5–6.5 ppm) corresponding to the vinylene and aromatic/heterocyclic protons. An absorption band at  $935 \text{ cm}^{-1}$  is observed by infrared spectroscopy and is attributed to the C–H bending of the *trans*-vinylene, confirming the formation of a poly(arylenevinylene). The absorption spectrum of the polymer solution (THF) has an absorption maximum at 500 nm and an optical band-gap of 2.2 eV. Cyclic voltammetry (CV) revealed that the polymer has an oxidation potential of 0.69 V (vs.  $\text{Ag}/\text{AgCl}$ ). Third-order susceptibility measurements indicate that the polymer is effective as a nonlinear optical material. The polymer also has excellent stability and can be cast into films that are stable when stored for 45 d at room temperature in air.

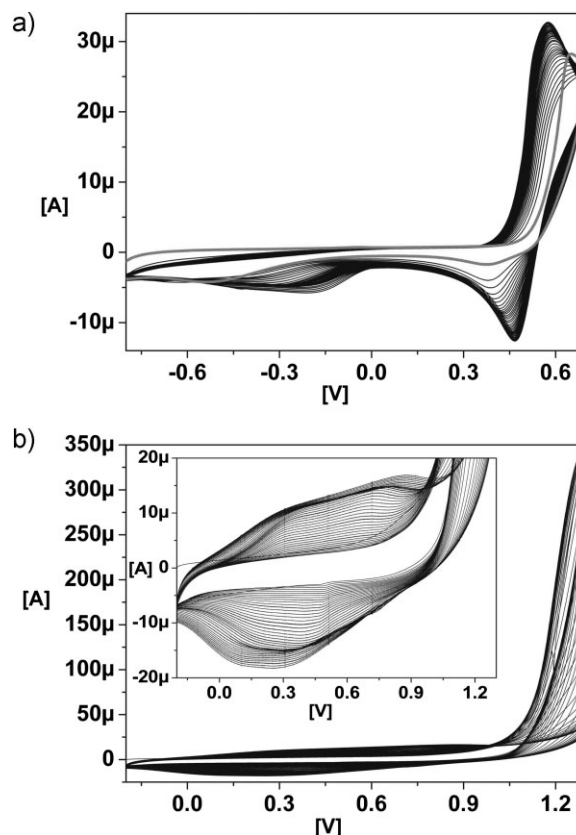


■ Figure 3. Reaction scheme for the Wittig condensation polymerization.

### Substituted Polytellurophenes

In 2009, the synthesis and electrochemical polymerization of 3,4-dimethoxytellurophene (**9**) was reported by Bendikov and coworkers.<sup>[43]</sup> This promising polytellurophene is the first example of a substituted tellurophene homopolymer, and the authors present the first spectroscopic and experimental band-gap evaluations of a tellurophene homopolymer. The novel monomer **9** was synthesized and studied by X-ray crystallography, density functional theory (DFT) calculations, and electrochemical methods. The crystal structure reveals Te–Te interactions (3.80–4.04 Å) that are shorter than the van der Waals distance of tellurium (4.30 Å) and act as a driving force for crystal packing. These crystals show the strong intermolecular interactions of Te-containing heterocycles, which are not observed in the thiophene and selenophene analogs, and may have a significant influence on the properties of tellurophene containing organic materials. The electrochemical properties of **9** were investigated by CV, which shows that this monomer has two oxidation peaks at 0.60 and 0.95 V (vs. Ag/AgCl, Figure 4). Oxidation occurs at lower potentials than either the selenophene or thiophene analog, which is expected based on the previously reported data<sup>[38]</sup> and the lower ionization potential of tellurophene (8.27–8.40 eV) versus selenophene (8.77–8.95 eV) or thiophene (8.86 eV).

When **9** is subjected to repeated CV cycles, the formation of an insoluble, powdered product is observed. This contrasts with the formation of stable films observed under the same conditions for the selenophene analog. To further understand the electropolymerization of **9**, in situ time-resolved spectroelectrochemical measurements were obtained (Figure 5). Using ITO as the working electrode at a constant potential, the formation of three absorption maxima are observed at 378, 522, and 679 nm after the polymerization has taken place. The band-gap (1.51 eV) determined from the onset of absorption is very close to the calculated value (1.64 eV) for poly-**9**. However, electrochemical doping, which should be visualized by an absorption peak in the near IR region, is not observed for poly-**9**. The authors speculate that poly-**9** is not stable under doping conditions. The formation of poly-**9** is supported by the



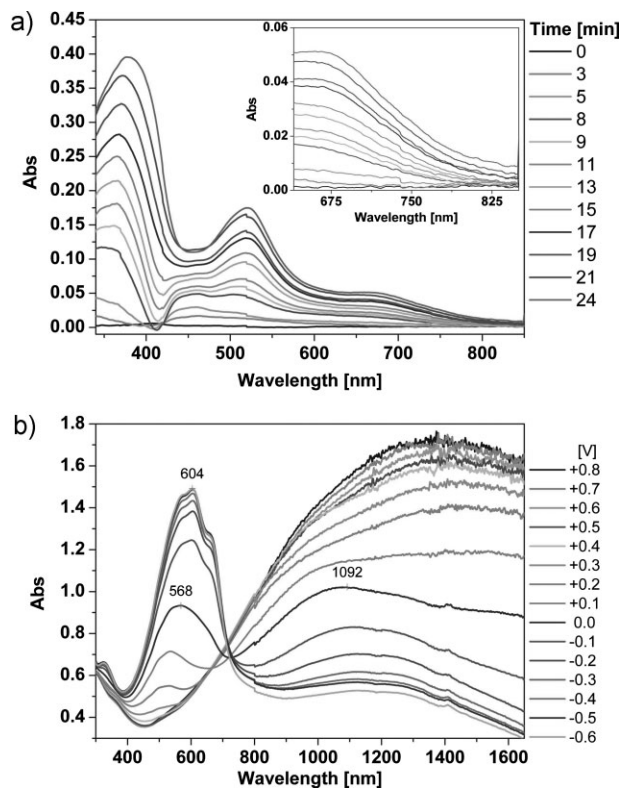
■ Figure 4. Cyclic voltammogram of (a) **9** and (b) its selenium analog on a Pt button electrode at  $100 \text{ mV} \cdot \text{s}^{-1}$  in  $\text{LiClO}_4/\text{ACN}$ , versus Ag/AgCl,  $\text{Fc}/\text{Fc}^+ = 0.37 \text{ V}$ . Adapted with permission from ref.<sup>[43]</sup> Copyright 2009, American Chemical Society.

spectroelectrochemical data and DFT calculations as well as by direct comparison with the selenophene analog.

### Palladium-catalyzed Synthesis of Soluble Polytellurophenes

Palladium-catalyzed condensation polymerizations have proven to be one of the best methods for synthesizing well-defined conjugated polymers but had not been previously

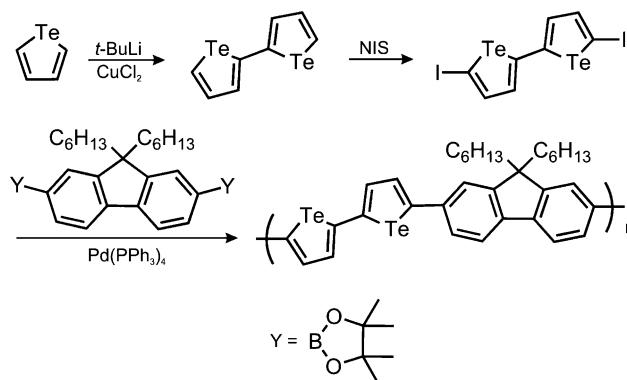




**Figure 5.** (a) In situ time-resolved absorption spectra of the material obtained by electropolymerization of **9** at a constant potential (1.4 V) using ITO as the working electrode in dichloromethane/TBAPF<sub>6</sub>. (b) Spectroelectrochemistry of the selenium analog polymer as a function of applied potential between -0.6 and +0.8 V in propylene carbonate/LiClO<sub>4</sub>. Adapted with permission from ref.<sup>[43]</sup> Copyright 2009, American Chemical Society.

described for tellurophenes. One significant obstacle was a lack of suitable monomers to carry out these types of polymerizations for tellurophenes, however, we have recently described the synthesis of a bifunctional tellurophene monomer as well as a study that determines the conditions required to prepare polytellurophenes by solution-based palladium-catalyzed conditions using this monomer.<sup>[44]</sup>

First, a dihalogenated bitellurophene monomer that is suitable for condensation polymerization reactions was prepared. Tellurophene, and subsequently bitellurophene, are prepared by following modified literature methods (Figure 6).<sup>[38,45]</sup> In order to obtain the desired monomer for polymerization, bitellurophene must be halogenated at the 5 and 5' positions. Symmetric dihalotellurophenes were previously unknown compounds, likely due to the difficulties associated with halogenating tellurophene heterocycles. While several conditions for aromatic halogenation exist, most of these are not suitable for tellurophene. Specifically, tellurophene forms complexes with Br<sub>2</sub>, and therefore conditions that require elemental bromine must



**Figure 6.** Synthesis of 5,5'-diiodo-2,2'-bitellurophene and subsequent Suzuki polymerization to form poly(bitellurophene-*alt*-9,9'-dihexylfluorene). Adapted with permission from ref.<sup>[44]</sup> Copyright 2010, John Wiley and Sons, Inc.

be avoided. Conditions that require heating and acids must also be avoided because they lead to decomposition of the heterocycle. We found that *N*-bromosuccinimide, commonly used to halogenate thiophene and selenophene, does not work for tellurophene. With this knowledge, *N*-iodosuccinimide was selected as the halogenating reagent because it does not require heating or acids and is not a source of bromine. After optimization of conditions, we can readily prepare the desired diiodobitellurophene monomer in 60% yield.

Next, a variety of commonly employed solution-based palladium-catalyzed polymerization conditions were examined to prepare the target poly(bitellurophene-*alt*-9,9'-dihexylfluorene). This copolymer structure was chosen because the 9,9'-dihexylfluorene comonomer was expected to improve solubility. While all the tested conditions have been shown to give thiophene copolymers in high yield, we found that the conditions required to polymerize tellurophene are much more specific. For example, a Stille-type polymerization with a trimethylstannane functionalized fluorene unit in toluene gives mainly starting material and very little polymer, indicating that iodinated tellurophenes react relatively poorly under Stille-type conditions. Suzuki polymerizations with a boronic acid functionalized fluorene unit result in low yields. This is likely due to monomer sensitivity to the boronic acid functionality. We, therefore, revised the synthesis to incorporate a boronic ester functionalized fluorene, and chose to carry out subsequent polymerizations in toluene which allowed higher reaction temperatures and improved solubility of reactants. Accordingly, a biphasic Suzuki reaction with a boronic ester functionalized fluorene unit carried out in toluene and 2 M aqueous K<sub>2</sub>CO<sub>3</sub> using a phase-transfer agent (Aliquat 336) affords poly(bitellurophene-*alt*-9,9'-dihexylfluorene) in 32% isolated yield after precipitation, washing, and extraction.

The obtained polytellurophenes have desirable properties with respect to solubility and processability. The chemical structure of poly(bitellurophene-*alt*-9,9'-dihexylfluorene) is verified by  $^1\text{H}$  NMR. The  $\overline{M}_n$  of the highest yielding synthesis is  $3.1 \text{ kg} \cdot \text{mol}^{-1}$  (PDI = 1.2), determined by 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 7). 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. The solutions can be cast into stable films for solid-state optical characterization. The absorption maximum of the film is shifted to 506 nm, which 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  $\pi$ -stacking in the solid state. This observation is important because it provides evidence of inter-chain electronic delocalization which is important for solid-state electronic materials.

### Coordination-controllable Optoelectronic Properties

Using the palladium-catalyzed route to polytellurophenes, test batches of 50 mg of stable polymer can be prepared. Experiments were then designed to test whether the metalloid nature of these polymers lead to new ways of controlling optoelectronic properties. It has been shown

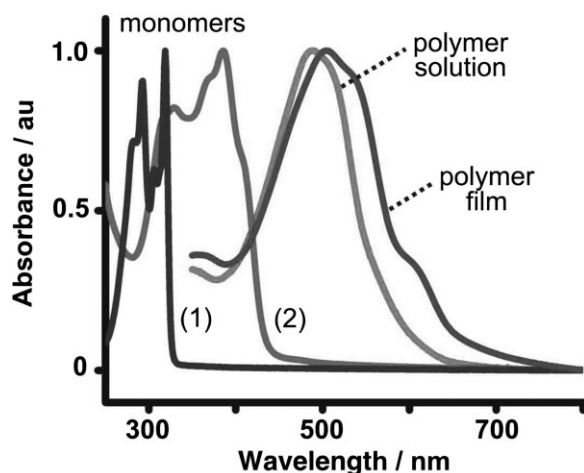


Figure 7. Absorbance spectra of the fluorene (1) and bitellurophene (2) monomers and polymer solution and film. Adapted with permission from ref.<sup>[44]</sup> Copyright 2010, John Wiley and Sons, Inc.

that the properties of conjugated polyelectrolytes can be controlled by the choice of their counter-ions,<sup>[46,47]</sup> and the properties of electron-deficient conjugated polymers can be controlled by the addition of Lewis acids.<sup>[48,49]</sup> This tunability is useful for determining structure–property–function relationships and is also important for synthesizing materials with designer properties. In the case of tellurophene, reports in the literature have indicated that Te-containing heterocycles form a coordination complex with molecular bromine where one equivalent of  $\text{Br}_2$  adds to Te.<sup>[50,51]</sup> To test whether polytellurophenes would be capable of such interactions, solutions of polymer were prepared ( $\approx 0.01 \text{ mg} \cdot \text{mL}^{-1}$  in  $\text{CHCl}_3$ ) and titrated with solutions of molecular bromine. After the addition of only 0.1 equiv. of  $\text{Br}_2$  (per Te, based on the GPC molecular weight) the onset of absorption shifts significantly from 624 to 727 nm (Figure 8). After the addition of  $\approx 0.4$  equiv. of  $\text{Br}_2$ , the reaction appears to reach an end-point, where the polymer absorption maximum reaches 552 nm and a visible color change from orange to purple is observed. The observation that the end-point is reached before 1 equiv. of  $\text{Br}_2$  is added 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

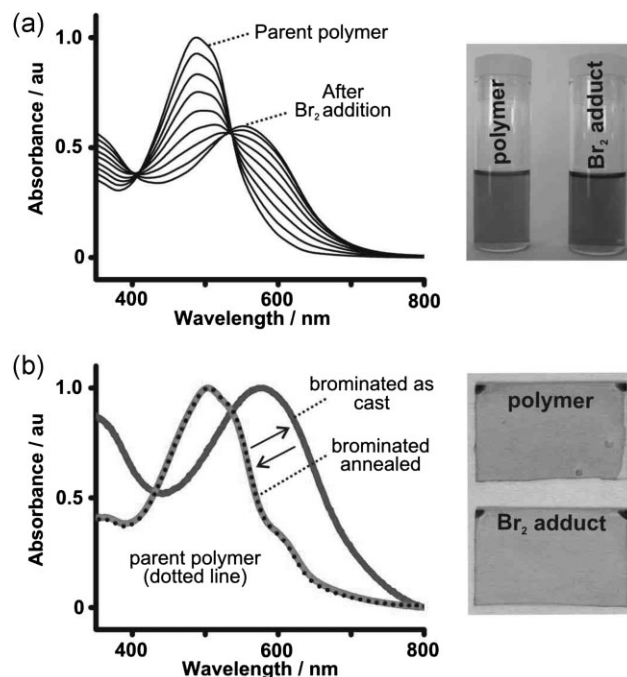


Figure 8. (a) Solution absorbance spectra and photographs of solutions before and after addition of bromine. (b) Solid state absorption spectra of polymer film before bromine addition, after bromine addition, after annealing, and photographs of films. Adapted with permission from ref.<sup>[44]</sup> Copyright 2010, John Wiley and Sons, Inc.

molecular weight of rigid-rod polymers.<sup>[52]</sup> Evidence for complete bromination after addition is supported by relative GPC measurements. The GPC-determined  $\overline{M}_n$  of the brominated polymer is  $4.7 \text{ kg} \cdot \text{mol}^{-1}$ , corresponding to a relative weight increase of 46% or the addition of  $\approx 2 \text{ Br}_2$  per repeat unit. The specificity of the coordination reaction was supported by control experiments performed using poly(bitellurophene-*alt*-9,9'-dihexylfluorene) and  $\text{I}_2$  or poly(bithiophene-*alt*-9,9'-dioctylfluorene) and  $\text{Br}_2$  under analogous conditions which did not lead to an observable change in the absorbance spectra, confirming selectivity for Te and  $\text{Br}_2$ .

To test for polymer degradation after  $\text{Br}_2$  addition, we examined the reversibility of this reaction. For this experiment, the bromine adduct was prepared and isolated by concentration. Films of the bromine adduct have significantly red-shifted optical properties relative to the parent polytellurophene film (Figure 8). The absorption profiles of these films lack the shoulders that are observed in the parent polymer, which could indicate that there is less order in the solid state. This is likely due to the inclusion of bromine, which disrupts the molecular packing that is observed in the parent polymer. Upon annealing at  $150^\circ\text{C}$ , the absorption profile of the film returns to the identical spectrum of the non-brominated polymer. This observed reversibility of bromine addition provides evidence that the polymer is not degraded after bromine treatment, and supports the hypothesis that a coordination species is formed.

In addition to the observed changes in solid-state optical properties, significant changes in the HOMO and LUMO positions are observed when the polymer is treated with bromine. Here, the HOMO level was estimated from electrochemistry based on the onset of the first oxidation peak, while 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  $-5.28 \text{ eV}$  and shifts to  $-5.40 \text{ eV}$  upon bromine addition. The LUMO level of the parent polytellurophene is positioned at  $-3.50 \text{ eV}$  and shifts to  $-3.78 \text{ eV}$  upon bromine addition. Overall, bromine coordination appears to shift the polymer molecular orbitals (MOs) to more low-lying levels. This indicates that this class of polymers not only has coordination-tunable absorption properties, but that the relative MO energy positions can be controlled by changing the coordination state at the Te centers.

To understand how tellurium–bromine interactions change the optical and electronic properties of the polymer, a series of density functional theory calculations (B3LYP-LANL2DZ) were performed (Figure 9). In all calculations the basic polymer repeat units, which are useful for predicting trends in the MO energy levels of conjugated copolymers, were used.<sup>[53]</sup> The calculated geometry of the parent polytellurophene repeat unit optimizes to one that is similar to the sulfur-based analog. For the bromine adduct

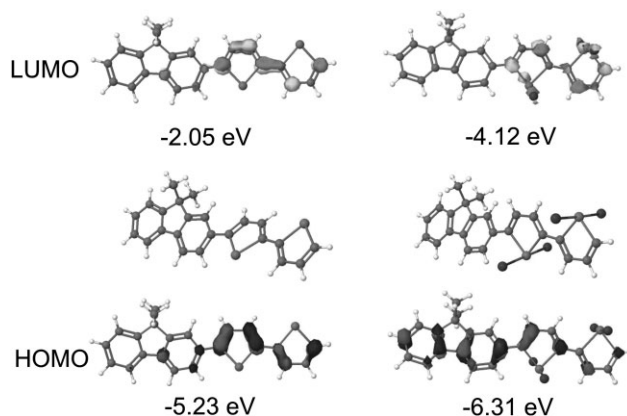


Figure 9. Calculated energies of the frontier orbitals (LUMO and HOMO) and electron distribution of the tellurophene polymer repeat unit and its brominated adduct. A representative image of the optimized geometry is shown in the middle. Adapted with permission from ref.<sup>[44]</sup> Copyright 2010, John Wiley and Sons, Inc.

(which contains one equivalent of  $\text{Br}_2$  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.<sup>[54,55]</sup> Once the optimized geometries were found, MO calculations were used to estimate the band gap and positions of the HOMOs and LUMOs. For the repeat unit of the parent polymer, the calculated HOMO–LUMO gap is  $3.18 \text{ eV}$ . For the bromine adduct, the gap narrows by  $\approx 1\text{--}2.19 \text{ eV}$ , 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 of the bromine adduct is strongly associated with the heterocyclic unit, 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.<sup>[9,12,17,22,23]</sup> The fact that a charge-transfer complex can be switched on and off through coordination chemistry is a distinct and was a previously unknown property for these polytellurophenes. This indicates that a single class of polytellurophenes can be used for applications that require different HOMO–LUMO gaps and relative positions, such as both donor-type and acceptor-type materials or as both electron-type or hole-type semiconductors.

## Conclusion and Outlook

We have described the state-of-the-art in the synthesis and characterization of polytellurophenes. Tellurophene has a narrow HOMO–LUMO gap and desirable light absorption properties that give rise to great potential for future applications in optoelectronics. Tellurium's metalloid properties and ability to form supramolecular complexes allow for controlling the solid-state and optoelectronic properties through intermolecular interactions and/or coordinating species that act on their Te centers. Perhaps the most significant challenge that is holding back this field is lack of synthetic methodologies to prepare monomers suitable for mild and efficient polymerizations. The halogenated monomer synthesis and development of the palladium-catalyzed polymer synthesis offer a significant advance for future well-defined conjugated polymers that incorporate tellurophene units. Currently however, there are no reports of polytellurophenes with molecular weights that are comparable to their thiophene analogs ( $10 \text{ kg} \cdot \text{mol}^{-1}$  or greater). This is critical because molecular weight has a significant influence on properties.<sup>[56–58]</sup> As a library of tellurophene monomers is developed, and polymerization methods optimized, we anticipate that the floodgates will open, allowing for the synthesis of a myriad of high molecular weight polytellurophenes with desirable and controllable properties.

Another parameter that is expected to be critical as one moves toward new heterocycles is the side-chain, which is crucial for solution processability. For many years the hexyl side-chain in poly(3-hexylthiophene) (P3HT) was thought to lead the best optoelectronic devices. Recently the Jenekhe group reinvestigated what was thought to be a long proved theory, and remarkably, have shown that poly(3-butylthiophene) devices have comparable efficiencies with P3HT when processing is optimized.<sup>[19]</sup> As researchers begin to explore tellurophene polymers in more detail, thorough investigations will be needed to determine how the side-chain influences stability and solid-state properties. As stable and processable polymers become available, the next key step will be to incorporate them into optoelectronic devices.

At the time of the preparation of this paper, polytellurophenes have not been demonstrated to function as active materials in optoelectronic devices. In polyselenophene devices, work thus far has led to efficiencies that are similar to or lower than polythiophene analogs. For example, a recent report on poly(3-hexylselenophene) (P3HS) solar cells has shown that this materials has a better short-circuit current (due to better spectral response), yet poorer fill factor (due to poorer charge transport in a P3HS-electron acceptor blend) than (P3HT).<sup>[59]</sup> The result is a slightly decreased efficiency (2.7% for P3HS and 3.0% for P3HT) under analogous conditions. Researchers are cautioned not

to draw conclusions about these polymers prematurely. Polythiophenes have benefited from many years of processing and post-process optimization studies. The optimization of morphology, microphase separation, and electrical contacts through solvent processing, molecular weight, PDI, regioregularity, and annealing have resulted in steadily improved polythiophene devices over the years.<sup>[60–62]</sup> As new tellurophene (and selenophene) polymers are developed, detailed studies that determine how solvent processing and annealing affect performance will need to be undertaken so that optimization can be achieved.

For now, two paradigms exist in the race for low-cost, lightweight, thin-film semiconductors. On one hand, polymer semiconductors offer tremendous potential in terms of production costs, mechanical durability, and ease of installation, however typical semiconducting polymers have poor electronic and optical properties relative to their inorganic counterparts. For example, the best laboratory-scale polymer photovoltaic devices have modest efficiencies; to date, the best are in the 6–7% range.<sup>[23,63–66]</sup> On the other hand, inorganic thin-film semiconductors such as cadmium telluride or copper indium gallium diselenide are superior semiconductors with laboratory photovoltaic device efficiencies that are as high as 20%, yet they require more material (films are typically ten times thicker than polymers) and their cost (environmental or production-wise) is likely to be greater.<sup>[67]</sup> This paper has discussed a possible third paradigm. Polymeric materials that incorporate judiciously selected “heavy” elements in an atom economical way. Will such polymers serve to bridge the gap between these two competing thin-film technologies? Only with extensive synthetic, characterization, and device fabrication and testing efforts will we know the answer to this question, which may just give us the best of two worlds.

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