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Synthesis, Structure, and Electropolymerization of 3,4-Dimethoxytellurophene: Comparison with Selenium Analogue

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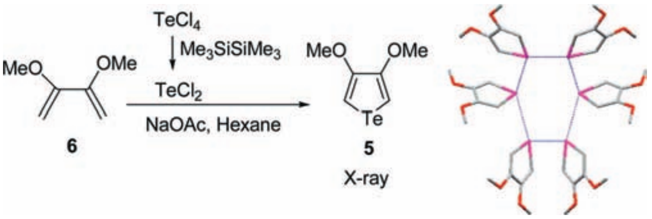
ABSTRACT



3,4-Dimethoxytellurophene (5) was synthesized via a new ring construction reaction. The crystal structure of 5 is characterized by unusually short Te···Te distances. The electropolymerization of 5 probably produces some amount of poly-5. Since the product was unstable under experimental conditions, a definitive assignment could not be made. However, the UV−vis spectrum recoded during electropolymerization of 5 shows an absorption peak at 679 nm with an onset at 820 nm (1.51 eV), closely matching the calculated band gap of poly-5.

Since the discovery of high conductivity in polyacetylene, significant efforts have been devoted to developing new families of conducting polymers.[1] Despite the diverse applications of conducting polymers in photovoltaic cells,[2] electrochromic devices,[3] chemical sensors,[4] microelectronic actuators,[5]organic light emitting diodes (OLEDs),[6] organic field effect transistors (OFETs),[7] nonlinear optics, etc., conducting polymer types are limited to polyacetylenes, polypyrroles, polyphenylenes, polythiophenes (**1**), poly(*p*-phenylene vinylene)s, and a few others.[1] Polythiophenes are the most studied conducting polymers.[1a,8] Recently, we have obtained the first highly conducting polyselenophene, namely poly(3,4-ethylenedioxyselenophene) (PEDOS),[9] and we have shown that polyselenophenes may even be superior to polythiophenes for some applications[10] while maintaining a low band gap, very high stability, and well-defined spectroelectrochemistry. Since the selenium atom is very similar to the sulfur atom, many properties of polyselenophenes (**2**) are similar to those of polythiophenes.

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(1) (a) *Handbook of Conducting Polymers*, 3rd ed.; Skotheim, T. A., Reynolds, J. R., Eds.; CRC Press:, Boca Raton, 2007. (b) *Handbook of Organic Conductive Molecules and Polymers*; Nalwa, H. S., Ed.; John Wiley & Sons: New York, 1997; Vol. 2.

(2) (a) Sariciftci, N. S.; Smilowitz, L.; Heeger, A. J.; Wudl, F. *Science* **1992**, *258*, 1474–1476. (b) Hoppe, H.; Sariciftci, N. S. *J. Mater. Res.* **2004**, *19*, 1924–1945.

(3) Dyer, A. L.; Reynolds, J. R. In *Handbook of Conducting Polymers: Theory, Synthesis, Properties and Characterization*, 3rd ed.; Skotheim, T. A., Reynolds, J. R., Eds.; CRC Press: Boca Raton, 2007; Chapter 20, pp 20.1−20.63.

(4) McQuade, D. T.; Pullen, A. E.; Swager, T. M. *Chem. Rev.* **2000**, *100*, 2537–2574.

(5) (a) Marsella, M. J.; Reid, R. J.; Estassi, S.; Wang, L. S. *J. Am. Chem. Soc.* **2002**, *124*, 12507–12510. (b) Jager, E. W. H.; Smela, E.; Inganäs, O. *Science* **2000**, *290*, 1540–1546.

(6) (a) Perepichka, I. F.; Perepichka, D. F.; Meng, H.; Wudl, F. *Adv. Mater.* **2005**, *17*, 2281–2305. (b) Ho, P. K. H.; Kim, J. S.; Burroughes, J. H.; Becker, H.; Li, S. F. Y.; Brown, T. M.; Cacialli, F.; Friend, R. H. *Nature* **2000**, *404*, 481–484.

(7) Katz, H. E. *Chem. Mater.* **2004**, *16*, 4748–4756.

(8) *Handbook of Oligo- and Polythiophenes*; Fichou, D., Ed.; Wiley-VCH: Weinheim, 1999.

(9) Patra, A.; Wijsboom, Y. H.; Zade, S. S.; Li, M.; Sheynin, Y.; Leitus, G.; Bendikov, M. *J. Am. Chem. Soc.* **2008**, *130*, 6734–6736.

(10) Li, M.; Patra, A.; Sheynin, Y.; Bendikov, M. *Adv. Mater.* **2009**, *21*, ASAP (http://dx.doi.org/10.1002/adma.200802259).

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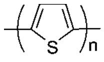
However, the properties of the tellurium atom, being the next member of group VI, are significantly different from those of selenium.[11,12] Indeed, the electronegativity of sulfur is 2.58 and of selenium is 2.55, while the electronegativity of tellurium is 2.10 (according to the Pauling scale). Tellurium is a metal and has significantly higher polarizability than sulfur and selenium. After much research on tetrathiafulvalene (TTF) and tetraselenafulvalene (TSF) and their derivatives, extensive studies were undertaken on tetratellurafulvalene (TTeF) and its derivatives due to expectations of enhanced dimensionality as a result of Te···Te intermolecular contacts.[13] Parent polytellurophene (**3**) and any substituted polytellurophenes are practically unknown;[14] however, they are expected to have properties significantly different from those of polyselenophenes and polythiophenes. No spectroscopic studies or experimental band gap evaluations of polytellurophenes have been reported. The band gap of polytellurophenes is expected to be lower than the band gap of polyselenophenes and polythiophenes.[15] The lack of research on polytellurophenes is most probably due to the unavailability of suitable synthetic methodologies for the preparation of substituted tellurophene-based monomeric precursors.[12] Consequently, very few substituted tellurophenes with accessible 2,5-positions are known.[16]



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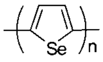

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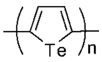

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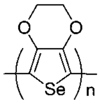
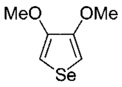


PEDOS



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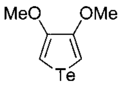

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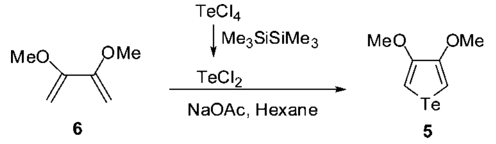
Inspired by the high stability, lower band gap, and promising properties of PEDOS[9] and its derivatives,[10] we decided to extend our study to polytellurophenes. Here, we describe a new and simple one step synthetic method to construct a tellurophene ring, specifically, 3,4-dimethoxytellurophene (**5**), and we present its crystal structure, DFT calculations, and electropolymerization. Throughout, comparison is made with 3,4-dimethoxyselenophene (**4**).[9,17]

Synthesis of suitable tellurophene monomers is the crucial first step toward developing conjugated oligo- and polytellurophenes. To prepare a tellurophene core, we first developed a new and efficient synthetic strategy for the preparation of **5**. Our synthetic methodology is based on a ring-closure addition−elimination reaction between 2,3-dimethoxy-1,3-butadiene (**6**) and $TeCl_2$[18] in the presence of NaOAc in hexane at room temperature (Scheme 1). This type of ring-closure reaction was recently developed by von Kieseritzky et al.[19] to form a thiophene ring and by us to form a selenophene ring.[9]

Scheme 1. Synthesis of 3,4-Dimethoxytellurophene (**5**)



3,4-Dimethoxytellurophene (**5**) is a colorless solid with a low melting point that is stable at room temperature. No visual degradation was observed while storing it for 1 year at 4 °C. Single crystals of **5** were grown from a mixture of chloroform and hexane by slow evaporation at 4 °C (Figure 1). Only a few crystal structures of tellurophene derivatives are reported in the literature.[14b,16c,20,21] The crystal structure of **5** consists of a planar tellurophene ring bearing in-plane methoxy substituents. It does not indicate any π-π interactions (the molecules are not stacked on top of each other, being completely slipped without overlap between the layers). However, it does reveal specific Te···Te interactions (Figure 1), which function as the dominant force driving crystal packing. The Te···Te distance is 3.80−4.04 Å, which is approximately 0.3−0.5 Å shorter than twice the van der Waal distance of Te (4.30 Å). The tendency of **5** to form multiple clusters reflects the more metallic character of tellurium, as compared to S and Se. To the best of our knowledge, this is the shortest Te···Te distance reported in tellurophene derivatives; distances of around 4.06−4.10 Å were previously found in benzo[*c*]tellurophene crystals,[16c] which is about 0.2 Å longer than the Te···Te distance in **5**. A strong Te···Te interaction should be important for applications of tellurophene containing compounds as organic electronic materials.

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(11) *The Chemistry of Organic Selenium and Tellurium Compounds*; Patai, S., Rappoport, Z., Eds.; John Wiley & Sons: New York, 1986.

(12) Petragnani, N. *Tellurium in Organic Synthesis*, 2nd ed.; Academic Press: London, 2007.

(13) (a) Bendikov, M.; Wudl, F.; Perepichka, D. F. *Chem. Rev.* **2004**, *104*, 4891–4945. (b) Otsubo, T.; Takimiya, K.; Aso, Y. *Phosphorus Sulfur* **2001**, *171*, 231–253. (c) McCullough, R. D.; Kok, G. B.; Lerstrup, K. A.; Cowan, D. O. *J. Am. Chem. Soc.* **1987**, *109*, 4115–16. (d) Wudl, F.; Aharon-Shalom, E. *J. Am. Chem. Soc.* **1982**, *104*, 1154–6.

(14) Electrochemical polymerization of tellurophene and 2,2′-bitellurophene has been claimed to produce polytellurophene (**3**). However, the measured conductivities were very low (up to 10^{-6} S/cm), and no characterization was reported. See: (a) Sugimoto, R.; Yoshino, K.; Inoue, S.; Tsukagoshi, K. *Jpn. J. Appl. Phys.* **1985**, *24*, L425–L427. (b) Otsubo, T.; Inoue, S.; Nozoe, H.; Jigami, T.; Ogura, F. *Synth. Met.* **1995**, *69*, 537–538.

(15) Salzner, U.; Lagowski, J. B.; Pickup, P. G.; Poirier, R. A. *Synth. Met.* **1998**, *96*, 177–189.

(16) (a) Huang, Z.; Lakshmikantham, M. V.; Lyon, M.; Cava, M. *J. Org. Chem.* **2000**, *65*, 5413–5415. (b) Discordia, R. P.; Dittmer, D. C. *Tetrahedron Lett.* **1988**, *29*, 4923–4926. (c) Pittelkow, M.; Reenberg, T. K.; Nielsen, K. T.; Magnussen, M. J.; Solling, T. I.; Krebs, F. C.; Christensen, J. B. *Angew. Chem., Int. Ed.* **2006**, *45*, 5666–5670.

(17) Dian, G.; Merlet, N.; Barbey, G. *J. Electroanal. Chem.* **1987**, *238*, 225–237.

(18) $TeCl_2$ (or a synthetic equivalent of $TeCl_2$) was prepared from $TeCl_4$ and $Me_3SiSiMe_3$, according to the procedure described in the literature: Paul, R. C.; Arneja, A.; Narula, S. P. *Inorg. Nucl. Chem. Lett.* **1969**, 1013–1015. A similar procedure was used in: Tokitoh, N.; Sadahiro, T.; Hatano, K.; Sasaki, T.; Takeda, N.; Okazaki, R. *Chem. Lett.* **2002**, 34–35.

(19) von Kieseritzky, F.; Allared, F.; Dahlstedt, E.; Hellberg, J. *Tetrahedron Lett.* **2004**, *45*, 6049–6050.

(20) (a) Dabdoub, M. J.; Justino, A.; Guerrero, P. G. *Organometallics* **1998**, *17*, 1901–1903. (b) Zukerman-Schpector, J.; Dabdoub, M. J.; Dabdoub, V. B.; Pereira, M. A. *Acta Crystallogr.* **1992**, *C48*, 767. (c) Fanfani, L.; Nunzi, A.; Zanazzi, P. F.; Zanzari, A. R.; Pellinghelli, M. A. *Cryst. Struct. Commun.* **1972**, *1*, 273–278. (d) Inoue, S.; Jigami, T.; Nozoe, H.; Otsubo, T.; Ogura, F. *Tetrahedron Lett.* **1994**, *35*, 8009–8012.

(21) The crystal structure of **5** shows similarity in bond lengths and bond angles with previously known tellurophene derivatives bitellurophene[14b] and 4,7-dimethoxybenzo[*c*]tellurophene.[16c]

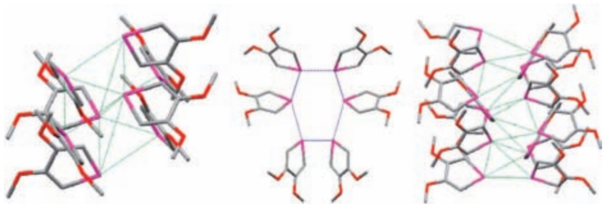
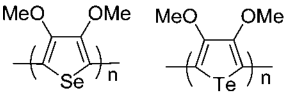


Figure 1. (Left) stacks viewed along *X* axis, (middle) a chained Te-aggregate viewed along Y axis, (right) view along *Z* axis.

For comparative purposes, single crystals of **4** were grown by slow evaporation of a solution of **4** in a mixture of chloroform and hexane at 4 °C. Compound **4** shows Se⋯Se interactions in chained aggregates along the Z-axis (Figure S2, Supporting Information). The Se⋯Se distance is 3.78 Å, which is similar to twice the van der Waal distance of Se (3.80 Å), so that weak Se⋯Se contacts are observed in contrast to the strong Te⋯Te contacts in **5**.



Poly-**4** Poly-**5**

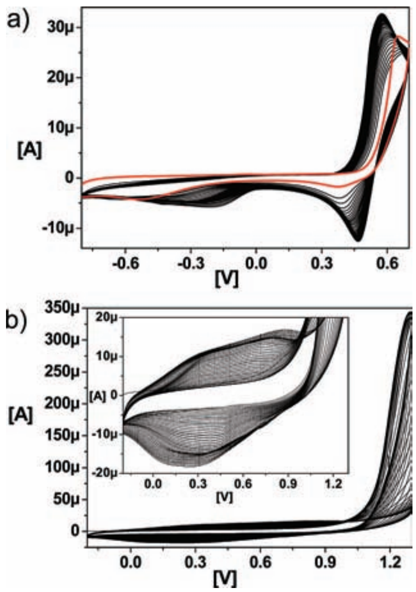


Figure 2. Cyclic voltammogram of (a) **5** (first cycle is shown in red) and (b) **4** on a Pt button electrode at 100 mV/s in $LiClO_4$/ACN, vs Ag|AgCl wire, Fc/Fc$^+$ = 0.37 V.

The electrochemical properties of **5** were investigated by cyclic voltammetry (CV). The monomer presents an oxidation peak at 0.60 V (vs Ag|AgCl wire) in CV measurements (Figure 2a). A second oxidation peak at 0.95 V is also observed (Figure S5, Supporting Information). By comparison, the first oxidation peak of the selenium analogue **4** is at 1.23 V, with a second oxidation peak at 1.67 V (Figure S4, Supporting Information).

The first and second oxidation potentials of 3,4-dimethoxythiophene are at even higher potentials of 1.36 and 1.85 V, respectively, under similar conditions. This is consistent with the previously reported oxidation potential of tellurophene (1.54 V originally reported,[20d] 1.37 V after recalibration to the conditions used in this paper), which is significantly lower than the potential of thiophene (2.1 V under the conditions used in this paper). The first ionization potentials of tellurophene (8.27−8.40 eV) are also significantly lower than those of selenophene (8.77−8.95 eV) and thiophene (8.86 eV).[22] Under repeated CV cycles, **5** produces mainly undefined products, presumably oligomers, with some insoluble material, which does not form a well-defined film on the electrode. By contrast, the smooth growth of poly-**4** on the surface of the Pt electrode was observed under repeated CV scans of **4** (Figure 2b). Unlike **5**, electropolymerization of compound **4** produces stable films on a Pt electrode.

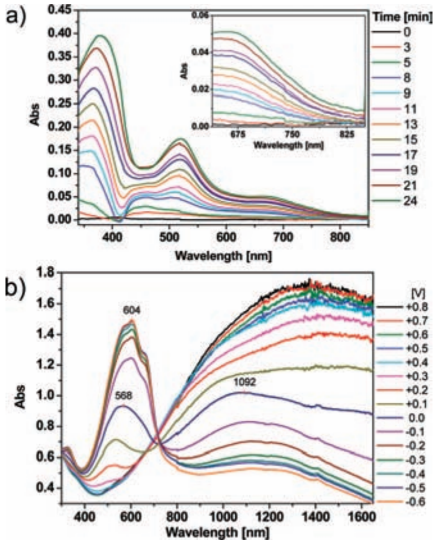


Figure 3. (a) In situ time-resolved UV−vis spectra of the material obtained by electropolymerization of **5** at a constant potential (1.4 V) using ITO as the working electrode in dichloromethane/$TBAPF_6$. (b) Spectroelectrochemistry of poly-**4** as a function of the applied potential between −0.6 and +0.8 V in propylene carbonate/$LiClO_4$.

In situ time-resolved spectroelectrochemical measurements of the electropolymerization of **5** at a constant potential (1.4 V vs Ag|AgCl wire, Fc/Fc$^+$ = 0.37 V)[23] using ITO as the working electrode are shown in Figure 3a. The absorbance in the visible region increases gradually with time over a period of about 30 min. The UV−vis spectrum reveals three well-separated absorption maxima at 378, 522, and 679 nm. These three peaks were consistently observed in different experiments using slightly different electrochemical setups. The intensity of the

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(22) Lias, S. G.; Bartmess, J. E.; Liebman, J. F.; Holmes, J. L.; Levin, R. D.; Mallard, W. G. Ion Energetics Data. In *NIST Chemistry WebBook*; LinstromP. J., Mallard, W. G., Eds.; NIST Standard Reference Database No. 69; National Institute of Standards and Technology: Gaithersburg, MD, http://webbook.nist.gov(retrieved Nov 20, 2008).

(23) Electropolymerization of **5** on ITO using a potential of less than 1.4 V did not lead to any UV−vis−NIR spectral changes.

peak at 679 nm relative to other peaks was different under different conditions. This indicates that the peak at 679 nm corresponds to chemical species which is not associated with the peaks at 378 and 522 nm. The absorption at 679 nm with an onset at 820 nm (1.51 eV) fits very nicely with the calculated band gap of poly-**5** (see discussion below for DFT calculations which support such an assignment).[24] The strong absorption peaks at 378 and 520 nm compared to that at 679 nm indicate that electropolymerization of **5** mainly produces oligomers with, probably, a small amount of polymer which is unstable over longer periods of time. If poly-**5** is indeed observed in Figure 3a, then it should undergo electrochemical doping, which was not observed, as evident from the absence of absorption in the near IR region of the spectra. Most probably, poly-**5** is unstable under doping due to the easy release of a Te cation from the cation radical of the tellurophene ring by breaking a Te−C bond.[25] For comparison, the spectroelectrochemistry of poly-**4** film obtained on an ITO electrode is shown in Figure 3b. The spectroelectrochemically measured band gap of poly-**4** (assigned as the onset of the $\pi-\pi^*$ transition) is 1.71 eV (725 nm). This value is 0.20 eV higher than the onset assigned to poly-**5**. For comparison, the band gap of poly(3,4-dimethoxythiophene) is 1.85 eV.[26] The color of poly-**4** ranges from deep-blue in the neutral state to transmissive gray in the doped-state. The films are highly stable during spectroelectrochemical measurements between −0.6 V and +0.8 V.

Geometries and electronic structures of poly-**4** and poly-**5** were calculated using the hybrid density functional theory at the B3LYP level combined with the periodic boundary conditions (PBC) method as implemented in the Gaussian 03[27] program. Lan2dz and BasisSet-I[28] basis sets were used.[29] The optimized geometries of poly-**4** and poly-**5** have a planar backbone, and their inter-ring bond distances are 1.433 and 1.431 Å, respectively (at B3LYP/Lan2dz). Calculated frontier orbital energies and band gaps for poly-**4** and poly-**5** are given in Table 1. The calculated (B3LYP/Lan2dz) band gap of poly-**5** is 1.64 eV, which is 0.16 eV lower than the calculated band gap of poly-**4** (1.80 eV) (Table 1). The measured (from the onset on the $\pi-\pi^*$ transition, Figure 3a) band gap for poly-**5** is 1.51 eV, which is in excellent agreement with the calculated value (1.64 eV), especially considering the difference between measured and calculated values for poly-**5** (0.13 eV) is practically the same as the difference between measured and calculated values for poly-**4** (0.09 eV).[24] Using a larger basis set (BasisSet-I,[28] which is of similar quality to 6-31G(d)) gives similar results (Table 1).

Table 1. HOCO^a and LUCO^b Energies and Band Gaps of Poly-**4** and Poly-**5** Calculated at PBC/B3LYP/Lanl2dz (Values Using the PBC/B3LYP/BasisSet-I[28] Are Given in Parentheses)

polymers	HOCO^a (eV)	LUCO^b (eV)	band gap (eV)
poly-**4**	−4.12 (−3.96)	−2.32 (−2.07)	1.80 (1.89)
poly-**5**	−3.93 (−3.76)	−2.28 (−2.09	1.64 (1.67)

^{a} Highest occupied crystal orbital. ^{b} Lowest unoccupied crystal orbital.

To summarize, we have constructed a tellurophene ring by a new cycloaddition reaction and have presented the synthesis and characterization of stable 3,4-dimethoxytellurophene (**5**). The crystal structure of **5** is characterized by unusually short Te···Te distances. An in situ spectroelectrochemical study of the electropolymerization of **5** probably indicates that some amount of poly-**5** is produced, as evident from the absorption peak at 679 nm with an onset at 820 nm (1.51 eV). Although we do not have considerable experimental evidence to strongly support that poly-**5** is among the products formed, our supposition of poly-**5** formation on the basis of the spectroelectrochemical data is corroborated by DFT calculations. These calculations show that both the measured and calculated band gaps of poly-**5** are about 0.2 eV lower than those of its selenophene analogue, poly-**4**. If formed, poly-**5** is unstable under conditions at which its selenium analogue is very stable, which reveals very significant differences between polytellurophene and polyselenophene, in contrast to the smaller differences observed between polyselenophenes and polythiophenes.

Acknowledgment. We are grateful to Prof. Norihiro Tokitoh of Kyoto University for providing the synthetic procedure for TeCl$_2$ and to Alex Banaru for help with the X-ray structure discussion. We thank the Israel Science Foundation and the Helen and Martin Kimmel Center for Molecular Design for financial support. M.B. is the incumbent of the Recanati career development chair and a member ad personam of the Lise Meitner-Minerva Center for Computational Quantum Chemistry and acknowledges DuPont for a Young Professor Award.

Supporting Information Available: Experimental procedures, spectral data, CIF files, electrochemistry data, details of calculations, and the complete citation for ref.[27] This material is available free of charge via the Internet at http://pubs.acs.org.

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(24) We note that such a long wavelength absorption might also originate from a cation radical of **5**. Although we cannot rule out this possibility, it seems unlikely since we do not see any absorption in the near-IR region which would originate from cation radicals of oligomers of **5**. Also, the calculated (TDB3LYP/BasisSet-I[28]) spectra of the cation radical of **5** (from 400 nm to NIR) have a strong absorption at 427 nm and a weaker absorption at 1300 nm, which are very different from the observed spectra in Figure 3a. Furthermore, the calculated spectra of the cation radical of a dimer of **5** (medium intensity absorption at 640 nm and strong, about 8 times larger absorption at 416 nm) do not match with the spectra in Figure 3. Similar calculations on the bithiophene cation radical produce calculated UV spectra that are in excellent agreement with its experimental UV spectra. See: Salzner, U. *J. Chem. Theor. Comput.* **2007**, *3*, 1143–1157.

(25) The instability of doped poly-**5** is also supported by instability of positively charged **5**, since we were not able to obtain the MS data for **5** using either ESI of FD techniques.

(26) (a) Szkurlat, A.; Palys, B.; Mieczkowski, J.; Skompska, M. *Electrochim. Acta* **2003**, *48*, 3665–3676. (b) Zotti, G.; Zecchin, S.; Schiavon, G.; Groenendaal, L. B. *Chem. Mater.* **2000**, *12*, 2996–2005.

(27) All calculations were performed using the Gaussian 03 program. Frisch, M. J., et al. *Gaussian 03*, Revision C.02; Gaussian, Inc.: Wallingford, CT, 2004. See the Supporting Information for details.

(28) Peterson's basis sets with small-core relativistic pseudopotentials (cc-pVDZ-PP, see Peterson, K. A.; Figgen, D.; Goll, E.; Stoll, H.; Dolg, M *J. Chem. Phys.* **2003**, *119*, 11113.) were used for tellurium and selenium atoms, while all other atoms were calculated using the 6−31G(d) basis set. We call this basis set BasisSet-I. Band gap calculation for poly-**4** using the B3LYP/6−31G(d) gives practically the same results as with the B3LYP/BasisSet-I (Table S4, Supporting Information).

(29) The calculated (with both B3LYP/Lan2dz and B3LYP/BasisSet-I) bond lengths and bond angles in **5** are in excellent agreement with the experimental values (see the Supporting Information, Table S2).