

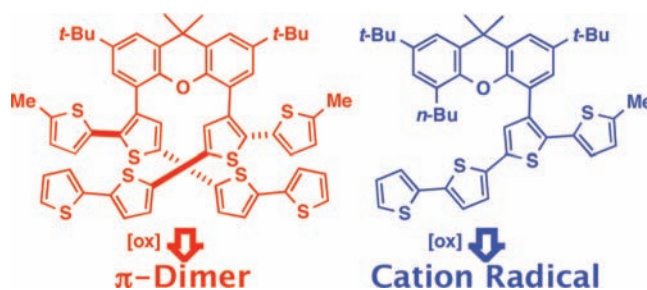
π -Dimer Formation in an Oligothiophene Tweezer Molecule

Ryo Takita,[†] Changsik Song, and Timothy M. Swager^{*}Department of Chemistry, Massachusetts Institute of Technology,
Cambridge, Massachusetts 02139

tswager@mit.edu

Received September 8, 2008

ABSTRACT



An oligothiophene tweezer molecule, which has two quaterthiophene moieties connected to create an electrochemically activated hinge, has been synthesized. Two-electron oxidation of the tweezer molecule produces an intramolecular π -dimer between the two oligothiophene moieties at room temperature as confirmed by UV–vis absorption, electrochemistry, and EPR experiments.

π -Dimers of cation radicals were proposed more than fifteen years ago to play a key role in electronic conduction of p-doped conjugated polymers, such as polythiophenes.¹ The pivotal work concerning π -dimers by Miller and Mann et al.² and the isolation of crystalline oligothiophene π -dimers^{2a,b,3,4} confirm the significance of bonding between π -aggregates in conducting polymers.^{2c}

Molecular actuators that convert an electrical stimulus into movement have a wide range of applications in medicine, microelectromechanical devices, and robotics.^{5,6} However, this potential remains largely unrealized, and new molecular mechanical frameworks are necessary to create highly efficient actuation. In pursuit of these materials, we have been interested in hinge structures, such as the calix[4]arene moiety.^{7–9} In addition to a mechanical framework, a

[†] Current Address: Institute for Chemical Research, Kyoto University, Uji, Kyoto 611-0011, Japan.

(1) Hill, M. G.; Mann, K. R.; Miller, L. L.; Penneau, J.-F. *J. Am. Chem. Soc.* **1992**, *114*, 2728.

(2) (a) Graf, D. D.; Campbell, J. P.; Miller, L. L.; Mann, K. R. *J. Am. Chem. Soc.* **1996**, *118*, 5480. (b) Graf, D. D.; Duan, R. G.; Campbell, J. P.; Miller, L. L.; Mann, K. R. *J. Am. Chem. Soc.* **1996**, *119*, 5888. (c) Miller, L. L.; Mann, K. R. *Acc. Chem. Res.* **1996**, *29*, 417.

(3) Yamazaki, D.; Nishinaga, T.; Tanino, N.; Komatsu, K. *J. Am. Chem. Soc.* **2006**, *128*, 14470.

(4) For other representative reports concerning the π -dimer of radical cations, see: (a) Bäuerle, P.; Segelbacher, U.; Gaudl, K.-U.; Huttenlocher, D.; Mehring, M. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 76. (b) Bäuerle, P.; Segelbacher, U.; Maier, A.; Mehring, M. *J. Am. Chem. Soc.* **1993**, *115*, 10217. (c) Zotti, G.; Berlin, A.; Pagani, G.; Schiavon, G.; Zecchin, S. *Adv. Mater.* **1994**, *6*, 231. (d) Cornil, J.; Brédas, J.-L. *Adv. Mater.* **1995**, *7*, 295. (e) Kingsborough, R. P.; Swager, T. M. *J. Am. Chem. Soc.* **1999**, *121*, 8825. (f) Brocks, G. *J. Chem. Phys.* **2000**, *112*, 5353. (g) Scherlis, D. A.; Marzari, N. *J. Phys. Chem. B* **2004**, *108*, 17791. (h) Picknolz, M.; dos Santos, M. C. *J. Mol. Struct. THEOCHEM* **2005**, *717*, 99.

(5) Yu, H.-H.; Swager, T. M. *IEEE J. Oceanic Eng.* **2004**, *29*, 692.

(6) For a recent review of general molecular machines and conjugated polymer actuators, see: (a) Kay, E. R.; Leigh, D. A.; Zerbetto, F. *Angew. Chem., Int. Ed.* **2007**, *46*, 72. (b) Smela, E. *Adv. Mater.* **2003**, *15*, 481. See also: (c) Marsella, M. J. *Acc. Chem. Res.* **2002**, *35*, 944. (d) Liu, Y.; Flood, A. H.; Bonvallet, P. A.; Vignon, S. A.; Northrop, B. H.; Tseng, H.-R.; Jeppesen, J. O.; Huang, T. J.; Brough, B.; Baller, M.; Magonov, S.; Solares, S. D.; Goddard, W. A.; Ho, C.-M.; Stoddart, J. F. *J. Am. Chem. Soc.* **2005**, *127*, 9745. (e) Marsella, M. J.; Rahbarnia, S.; Wilmot, N. *Org. Biomol. Chem.* **2007**, *5*, 391.

(7) (a) Yu, H.-H.; Xu, B.; Swager, T. M. *J. Am. Chem. Soc.* **2003**, *125*, 1142. (b) Yu, H.-H.; Pullen, A. E.; Büschel, M. G.; Swager, T. M. *Angew. Chem., Int. Ed.* **2004**, *43*, 3700.

(8) Song, C.; Swager, T. M. *Org. Lett.* **2008**, *10*, 3575.

(9) (a) Scherlis, D. A.; Marzari, N. *J. Am. Chem. Soc.* **2005**, *127*, 3207. (b) Casanovas, J.; Zanuy, D.; Alemán, C. *Angew. Chem., Int. Ed.* **2006**, *45*, 1103. (c) Alemán, C.; Zanuy, D.; Casanovas, J. *J. Org. Chem.* **2006**, *71*, 6952. (d) Zauny, D.; Alemán, C. *Chem.–Eur. J.* **2007**, *13*, 2695.

thermodynamic driving force for the conformational change is needed, and we have targeted the chemical bonding in π -dimers to produce movement and/or large changes in mechanical modulus. Recently, intramolecular π -dimer formation at room temperature in well-defined oligothiophene dimers was reported by the groups of Otsubo¹⁰ and Collard.¹¹ These demonstrations of effective π -dimer formation at room temperature suggest that the integration of this property into molecular actuators could be fruitful if the π -dimer bonding interactions drive a conformational change capable of producing mechanical motion. Herein, we report oligothiophene tweezer molecules designed to behave as a molecular mechanical hinge and afford π -dimer species by chemical or electrochemical oxidation.

Our actuator design is based on π -dimer formation in tweezer molecules as illustrated in Figure 1. Oligothiophene



Figure 1. Schematic illustration of a molecular actuation triggered by a π -dimer formation of oligothiophene moieties connected with electronically inactive hinge parts.

moieties, connected with electronically inactive hinges, are expected to display reduced molecular length upon oxidation as a result of the formation of π -dimers.^{5,12} We have developed tweezer molecules **2a** and **2b** (Figure 2b,c) as the model segments for such actuating molecules, which are available in five steps from commercially available 4,5-dibromo-2,7-di-*tert*-butyl-9,9-dimethylxanthene by repeating palladium-catalyzed cross-couplings and halogen introductions.^{13,14} A reference compound **1**, with only one quaterthiophene moiety, was also prepared in a similar sequence.¹³

Compounds **1** and **2a** displayed similar UV-vis absorbance (396 and 397 nm, respectively) in their neutral state (Figure 2a,b). Upon one-electron oxidation of **1** with $\text{Et}_3\text{O}\cdot\text{SbCl}_6$ ^{15,16} in CH_2Cl_2 at room temperature, the growth of two new signals (663 and \sim 1100 nm) was observed, attributed to the cation radical **1**⁺, and is concomitant with

(10) (a) Sakai, T.; Satou, T.; Kaikawa, T.; Takimiya, K.; Otsubo, T.; Aso, Y. *J. Am. Chem. Soc.* **2005**, *127*, 8082. (b) Satou, T.; Sakai, T.; Kaikawa, T.; Takimiya, K.; Otsubo, T.; Aso, Y. *Org. Lett.* **2004**, *6*, 997.

(11) Knoblock, K. M.; Silvestri, C. J.; Collard, D. M. *J. Am. Chem. Soc.* **2006**, *128*, 13680.

(12) The reported distances in X-ray crystal structure of π -dimers are 3.47 Å (in ref 2a) and ca. 3.0 Å (in ref 3). In the neutral state, the distance of two oligothiophenes in **2a** is estimated to be 4.2–4.5 Å from the X-ray structure of a synthetic intermediate **S5** (see Supporting Information).

(13) For details, see Supporting Information.

(14) While the structure of **2a** is illustrated as an *anti*-isomer in terms of two quaterthiophene moieties in Figure 2b, it was revealed by VT ¹H NMR experiments that **2a** is in the equilibrium between *anti*- and *syn*-isomers at room temperature. For details, see Supporting Information.

(15) (a) Rathore, R.; Kumar, A. S.; Lindeman, S. V.; Kochi, J. K. *J. Org. Chem.* **1998**, *63*, 5847. (b) See ref 8.

(16) An excess amount of the oxidant (up to ca. 10 equiv per oligothiophene moiety) was necessary for the complete oxidation under ambient atmosphere.

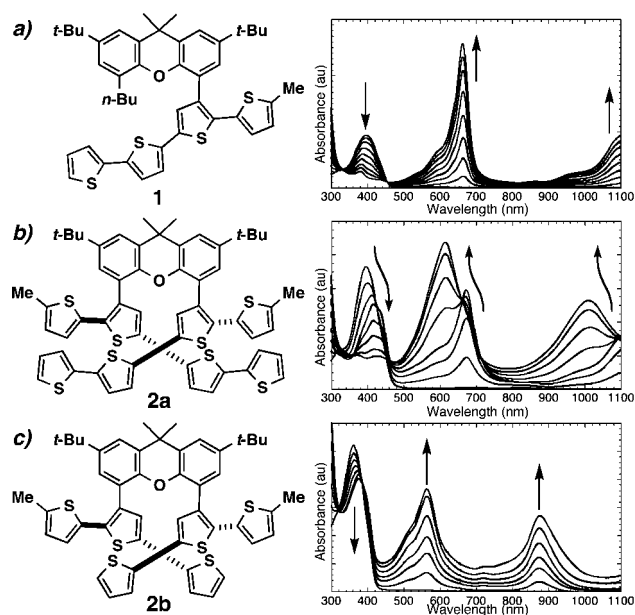


Figure 2. Structures of **1** (a), **2a** (b), and **2b** (c) and UV-vis spectra with oxidation in CH_2Cl_2 by $\text{Et}_3\text{O}\cdot\text{SbCl}_6$ at room temperature under air.

the disappearance of the original band at 396 nm. Two-electron oxidation does not occur under these conditions. The overall behavior of **2a** with oxidation is notably different from **1**. The initial oxidation of only one quaterthiophene to give **2a**⁺ closely parallels the spectral characteristics observed for **1** and displays new bands at 673 and $>$ 1100 nm, as well as a decrease in the 417 nm band. However, the second one-electron oxidation to give **2a**²⁺ triggered the appearance of new absorbance maxima at 615 and 1011 nm. The similarity of these changes with previous reports^{2,3,10,11} suggests that a π -dimer is formed. In contrast, the two terthiophenes of **2b** do not form a π -dimer (Figure 2c), and the peaks associated with the terthiophene cation radicals at 563 and 875 nm did not change during the oxidation process. This result suggests that quaterthiophenes are more effective at π -dimer formation, which is in agreement with previous experimental^{2c} and theoretical data.^{4g}

Effective π -dimer formation is further supported by electrochemical and EPR measurements. The cyclic voltammogram (CV) of **1** (Figure 3a) displays two quasi-reversible, one-electron oxidation processes.¹⁷ On the other hand, **2a** afforded quasi-reversible processes at potentials similar to those of **1** that are split into two one-electron oxidation peaks. The doubling of the number of redox waves is further resolved in the differential pulse voltammograms (Figure 3b). In the case of **2a**, first one-electron oxidations of the two quaterthiophene moieties occurred at 0.30 and 0.45 V, whereas the quaterthiophene in **1** was oxidized at 0.43 V. The lower oxidation potential for the initial oxidation to produce **2a**⁺ suggests that the proximate neutral quaterthiophene has a stabilizing effect, by forming a mixed-valence compound, and indeed we also see a red-shift in the absorption bands of **2a**⁺ relative to those for **1**⁺ (Figure

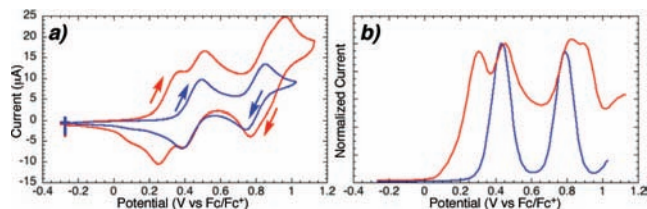


Figure 3. Cyclic voltammograms (CV, a) and differential pulse voltammograms (b) of **1** (blue line) and **2a** (red line) recorded in CH₂Cl₂ (ca. 2 mM) on a Pt button electrode with 0.1 M tetrabutylammonium hexafluorophosphate as a supporting electrolyte with a scan rate of 100 mV/s.

2). The higher potentials of the second one-electron oxidation waves of the quaterthiophenes of **2a** compared to **1** (0.79 V) reflect the stabilizing effect of the π -dimer formation (at 0.83 V) and increased Coulombic repulsion by the formation of tetracation species (at 0.89 V).

EPR measurements upon oxidation by Et₃O·SbCl₆¹⁸ provided an additional confirmation of a π -dimer for **2a**²⁺. Under argon atmosphere, increasing the oxidant from 1.5 to 5 equiv increased the EPR intensity of the cation radical **1**^{•+} (Figure 4a); in agreement, an absorbance band at 666 nm was observed in the UV–vis spectrum of the diluted EPR sample (Figure 4b). When 10 equiv (i.e., 5 equiv per quaterthiophene moiety) of Et₃O·SbCl₆ was added to a solution of **2a**, the EPR intensity was diminished relative to the intensity obtained with 3 equiv of the oxidant (Figure 4c). With 3 equiv of the reagent, the absorbance bands at 413 and 674 nm in the UV–vis spectrum of the diluted EPR sample (Figure 4d, dashed line) imply that **2a**^{•+} was generated. Further addition of the oxidant (10 equiv) increased the amount of the spinless π -dimer **2a**²⁺, the formation of which is supported by the absorbance at 617 nm, and therefore

(17) Cyclic voltammogram of **2b** showed an irreversible process, probably due to lack of the stabilization effect of the π -dimer and/or rather unstable radical cation of terthiophene under these conditions.

(18) EPR experiments were performed in nondegassed dry dichloromethane using quartz tubes sealed by a rubber septum under Ar atmosphere. One-electron oxidation of each quaterthiophene moiety occurred with ca. 5 equiv of Et₃O·SbCl₆ under these conditions.

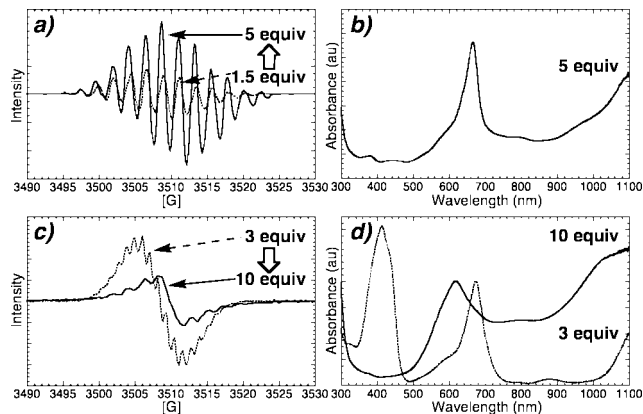


Figure 4. EPR and UV–vis spectra of (a,b) **1** with 1.5 (dashed line) and 5 (solid line) equiv of Et₃O·SbCl₆ and (c,d) **2a** with 3 (dashed line) and 10 (solid line) equiv of Et₃O·SbCl₆ at room temperature under Ar.

reduced the EPR intensity. Thus, UV–vis, electrochemistry, and EPR unequivocally demonstrate that **2a** forms a stable π -dimer upon oxidation by two electrons.

In conclusion, we have synthesized a new tweezer hinge molecule with quaterthiophene moieties that displays π -dimers at room temperature upon oxidation. Molecular and polymeric actuators containing this segment are the subjects of ongoing research.

Acknowledgment. This work was supported by the Office of Naval Research. We thank Dr. Peter Müller (Massachusetts Institute of Technology) for X-ray crystallography and Dr. Kazunori Sugiyasu (Massachusetts Institute of Technology) for valuable discussions. R.T. thanks a JSPS Postdoctoral Fellowship for Research Abroad.

Supporting Information Available: Experimental details and characterization of the products. This material is available free of charge via the Internet at <http://pubs.acs.org>.

OL8020995