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Backbone Photochromic Polymers Containing the Dimethyldihydropyrene Moiety: Toward Optoelectronic Switches

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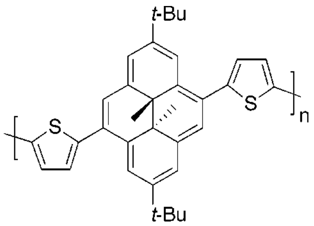
ABSTRACT



The design and synthesis of the first electrically conducting main chain photochromic conjugated polymer incorporating dimethyldihydropyrene is reported, as is the demonstration of the corresponding repeat unit as an optoelectronic redox switch.

Conjugated polymers (CPs) incorporating photochromic units can be classified as either side chain- or main chain-based systems depending on the respective placement of the photochromic unit.[1] With specific regard to electrically conducting CPs, the incorporation of photochromic units is of interest due to the potential of attenuating redox potentials and/or electrical conductivity as a function of absorbed light. Such photochromic CPs would be ideally suited for all-organic optoelectronic switching components of molecule-based devices.[2] Despite examples of photochromic CPs in the literature,[1,3,4] photochromic attenuation of conductivity has not yet been achieved. *In fact, definitive evidence of electrical conductivity in backbone photochromic CPs has not been reported*. Herein we report the design and synthesis of the first electrically conducting main chain photochromic CP incorporating dimethyldihydropyrene (DHP),[5] a photochrome that exhibits minimal conformational reorganization. The potential advantages of this latter fact are also discussed.

As illustrated most successfully by Lehn,[2] the dithienylethene (DTE) moiety is a reliable photochromic core for *solution state* switching devices. However, incorporation of DTE into the backbone of a CP for the purpose of achieving a *solid state* switching device has met with mixed results,[1,3,6] and electrical conductivity in such CPs has not yet been established. As a first step in our ultimate goal of preparing an electrically conducting optoelectronic switch, we focused on designing a system with three key features. First, switching of the photochromic unit should directly alter the effective conjugation length of the polymer. This prerequisite can be best understood by approximating a direct relationship between effective conjugation length and electrical conductivity.[7] Second, to help ensure electrical conductivity, the backbone of the polymer should, with the exception of the

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(1) Stellacci, F.; Bertarelli, C. T.; F.Gallazzi, M. C.; Zotti, G.; Zerbi, G. *Adv. Mater.* **1999**, *11*, 292−295.

(2) Gilat, S. L.; Kawai, S. H.; Lehn, J.-M. *Chem. Eur. J.* **1995**, *1*, 275−284.

(3) Yassar, A.; Moustrou, C.; Youssoufi, H. K.; Samat, A.; Guglielmetti, G.; F. *Macromolecules* **1995**, *28*, 4548−4553.

(4) Yassar, A.; Moustrou, C.; K.; Y. H.; Samat, A.; Guglielmetti, R.; Garnier, F. *J. Chem. Soc., Chem. Commun.* **1995**, 471−472.

(5) Mitchell, R. H. *Eur. J. Org. Chem.* **1999**, 2695−2703 and references therein.

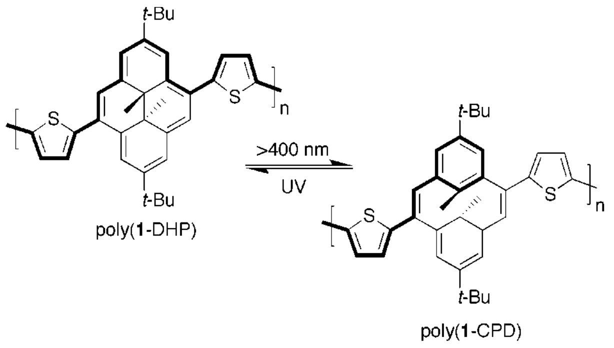
(6) Saika, T.; Irie, M.; Shimidzu, T. *J. Chem. Soc., Chem. Commun.* **1994**, 2123−2124.

10.1021/ol006293i CCC: $19.00

photochromic unit, mimic that of an established CP. Third, the photochromic component of the polymer should be chosen on the basis of its ability to undergo a *minimal conformational change* during a switching cycle. This last prerequisite may allow switching to occur in the solid state with greater ease.

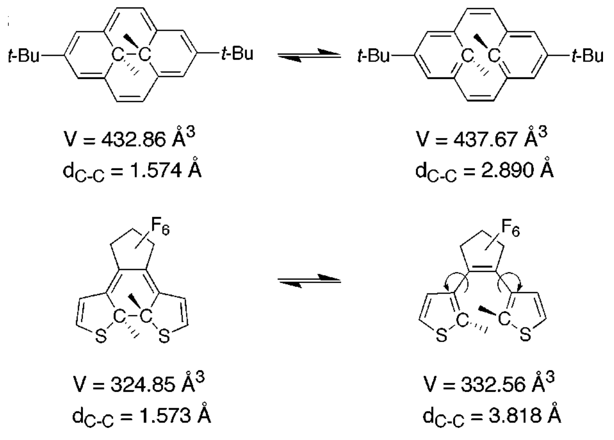
On the basis of the aforementioned prerequisites, poly(**1**), a thiophene−DHP copolymer, was selected as the system of choice. As noted with bold face in Scheme 1, the established photochemical DHP−cyclophanediene (CPD) interconversion directly impacts the conjugation length of poly(**1**) by switching between the fully conjugated poly(**1**-DHP) to the cross-conjugated poly(**1**-CPD). Copolymerization with bithiophene was chosen in an effort to impart onto the system the established electrical conductivity and stability of oligothiophenes.

Scheme 1



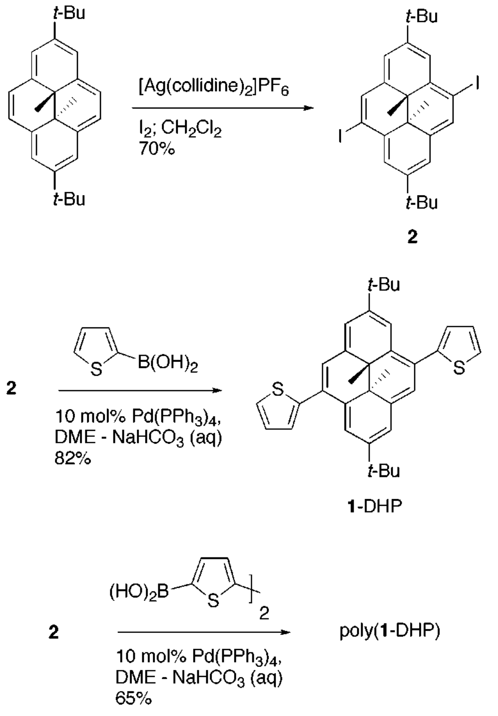
One attractive feature of the DHP photochrome is its ability to serve as a more rigid DTE analogue. Specifically, although both DHP and DTE undergo similar electrocyclic ring opening/closure processes during photochromic switching, DTE possesses the greater degree of conformational freedom, with allowed rotation about the two thienyl−perfluorocyclopentenyl bonds (note arrows in Scheme 2). Modeling[8] at the MMFF level was used to assist in quantifying the differences in dimensional changes between the two photochromes. The change in overall molecular volume (*V*) and the change in distance between the two carbons that undergo hybridization interconversion during a switching cycle ($d_{\mathrm{C-C}}$) were determined, and the results are shown in Scheme 2. In both cases, DHP undergoes the smaller dimensional perturbation, exhibiting less than half the volume change of DTE (1.11% versus 2.37%). As alluded to above, conformationally restricted photochromic moieties (such as DHP) may facilitate solid state device operation. As a first step toward testing this concept, the synthesis of a DHP-based backbone photochromic CP was pursued.

Scheme 2



Compound **1**[9] was prepared by further elaboration of the reported di-*tert*-butyldimethyldihydropyrene synthesis (Scheme 3).[5] Thus, iodination of the 4 and 9 positions of di-*tert*-butyldimethyldihydropyrene with Ag(collidine)$_2$PF$_6$−I$_2$ afforded a mixture of the 4,9-isomer, compound **2**, and the 4,10-isomer. The two isomers are readily distinguished by ^{1}H NMR, and the mixture could be easily separated via crystallization to afford compound **2** in 70% yield. Palladium-catalyzed cross-coupling of **2** with thiophene boronic acid afforded compound **1**-DHP in 82% yield as a red solid. This

Scheme 3



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(7) Skotheim, T. A.; Elsenbaumer, R. L.; Reynolds, J. R. *Handbook of Conducting Polymers*, 2 ed.; Marcel Dekker: New York, 1998.

(8) Titan V 1.0.1, Wavefunction Inc., 18401 Von Karman Ave., Irvice, CA 92715, Schrödinger, Inc., 1500 SW First Avenue, Suite 1180, Portland, OR 97201.

(9) ^{1}H NMR (CDCl$_3$): −3.62 (6H, s); 1.63 (18H, s); 7.31 (dd, 2H); 7.54 (dd, 2H); 7.57 (bd, 2H); 8.51 (bs, 2H); 8.58 (bs, 2H); 9.06 (bs, 2H). ^{13}C NMR (CDCl$_3$): 14.05; 31.80; 120.25; 121.68; 125.31; 125.73; 125.98; 126.99; 128.22; 133.62; 144.66. HRMS (EI): C$_{34}$H$_{36}$S$_2$ calcd 508.2240; found 508.2239. UV (cyclohexane) $\lambda_{\max}$: 361 nm; 401 nm; 499 nm.

same strategy could be readily modified to support polymerization by substituting thiophene boronic acid with the bifunctional cross-coupling component, bithiophene diboronic acid. Poly(**1**) was recovered in 65% yield as a low molecular weight polymer with $n \approx 5$ as determined by MALDI.[10] Although n is low, the monomer itself is large, and the average polymer chain thus possesses ca. 80 contiguous sp^2 carbons along its backbone. Most importantly, the low M_w did not preclude electrical conductivity, vide infra. Also of note is the fact that Kumada coupling, a traditionally successful route to polythiophenes, was unsuccessful in preparing poly(**1**). We are currently attempting to optimize our polymerization conditions.

Central to our efforts was the demonstration of electrical conductivity in poly(**1**). The relative conductivity (drain current) as a function of oxidation state (gate voltage) was determined according to the transistor experiment reported by Wrighton.[11] The resulting window of electrical conductivity (drain current > 0) is shown in Figure 1 and establishes the first definitive example of electrical conductivity in a backbone photochromic CP. Of note is the fact that the conductivity observed for poly(**1**-DHP) contrasts the reported lack of electroactivity in analogous DTE-based polymers prepared by electrochemical methods.[6]

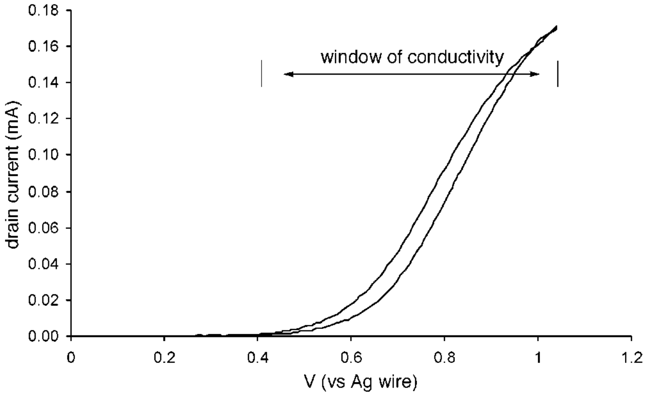

Figure 1. Relative conductivity (reported as drain current) of poly(**1**) *(thin film)* as a function of oxidation state (gate voltage). A current greater than zero indicates electrical conductivity in poly(**1**). Measurement was made in 0.1 M $TBAPF_6$/MeCN at a sweep rate of 25 mV/s and an offset potential of 50 mV.

The peak oxidation potential, $E_{p,a}$, of monomer **1** in solution was found to be very close to that of adsorbed thin films of poly(**1**) (ca. 0.58 V, as determined by square wave voltammetry), thus implicating similar effective redox centers for both. Recording multiple CVs of adsorbed poly(**1**) films was not possible due to its partial or complete solubility in all organic electrolyte solutions tested. Apparently, the *tert*-butyl and methyl groups of the DHP moiety prevent the strong intermolecular attractive forces traditionally associated with planar polyaromatic hydrocarbons. Consistent with the similar redox potentials is the relatively small red shift observed in the UV−vis spectra upon going from **1** to poly(**1**) (average $\Delta\lambda_{max} = 35$ nm). Such results might be expected for polymers (such as poly(**1**)) that are composed of monomeric units already possessing a large π-system and small HOMO−LUMO gap. Furthermore, X-ray crystallography of **1** has revealed an approximate 45° twist of the thiophene rings relative to the DHP core. Both of these factors are likely to contribute to the fact that poly(**1**) appears to possess a similar effective conjugation length to that of compound **1**. We note that the UV−vis spectrum does broaden somewhat upon going from **1** to poly(**1**).

The photochromic properties of **1** are shown in Figure 2 and clearly illustrate that **1**-DHP to **1**-CPD interconversion occurs. With regard to the rate of switching, the parent unsubstituted DHP switches rather slowly to CPD, due to a low photochemical quantum yield of $\phi = 0.02$ (lower in the presence of oxygen). Since addition of certain conjugating groups such as acetyl or nitro increases this quantum yield 10 to 20 times,[5] we had hoped that the thiophene groups of **1** would do likewise. Indeed, the rate of switching of **1**-DHP is increased over its parent. However, the increase was not as much as we had hoped, and certainly not as much as for the benzo compound **3**, where the quantum yield not only exceeds that of its parent but is also unaffected by oxygen and is thus an excellent switch.[5] Since poly(**1**) has many DHP moieties to open, each with a low quantum yield (and switching rate), it appears to open more slowly than **1** itself. Although somewhat disappointing, this fact does not imply an inherent flaw in DHP-based backbone photochromic CPs. Indeed, preliminary studies of thienyl-appended compound **4** (Figure 3) indicate significantly enhanced switching rates as compared to those of **1**.[12]

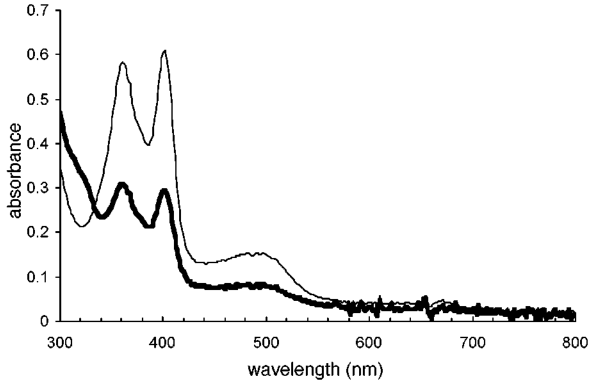

Figure 2. UV−vis spectra showing the conversion of **1**-DHP to **1**-CPD (ca. 1.2 × 10^{-5} M in MeCN). Narrow trace represents **1**-DHP prior to irradiation; bold trace represents enrichment with **1**-CPD via irradiation with >400 nm light.

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(10) ^{1}H NMR ($CDCl_3$): −3.52 (s); −3.72 (s); 1.62 (s); 1.68 (s); 7.26 (m); 7.46 (m); 7.64 (m); 8.52 (bm); 8.61 (bm); 9.18 (bm). ^{13}C NMR ($CDCl_3$): 15.30; 31.84; 120.58; 121.98; 124.01; 124.24; 125.26; 127.94; 128.42; 128.86; 130.87; 133.64; 147.23. UV (cyclohexane): λ_{max} 386 nm; 435 nm; 540 nm.

(11) Kittlesen, G. P.; White, H. S.; Wrighton, M. S. *J. Am. Chem. Soc.* **1984**, *106*, 7389.

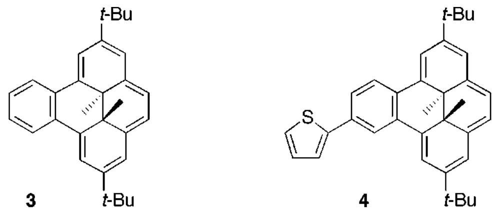

Figure 3. Depicting compound **3** and its 2-thienyl analogue, compound **4**.

Although solid state studies of optoelectronic conductivity switches fabricated from poly(**1**) are currently precluded by both solubility factors and slow switching rates (vide supra), demonstration of an optoelectronic redox switch based on **1** can be readily demonstrated.[1,2,13] Thus, a MeCN solution of compound **1**-DHP was irradiated (>400 nm) until a mixture of **1**-DHP and **1**-CPD was obtained. Square wave voltammetry was then used to probe the anodic activity within a window of 0 to 0.75 V. Note that only **1**-DHP is electroactive within this window ($E_{p,a}$ = ca. 0.58 V vs Ag°). The response for this initial state (defined as the "off" state) is shown in Figure 4a. The sample was then subjected to UV irradiation (365 nm) until the solution UV−vis spectra indicated complete conversion back to the **1**-DHP form. Square wave voltammetry was again used to probe anodic activity of the solution. As expected, the increased concentration of **1**-DHP resulted in a greater current associated with the anodic wave ("on" state, see Figure 4b).

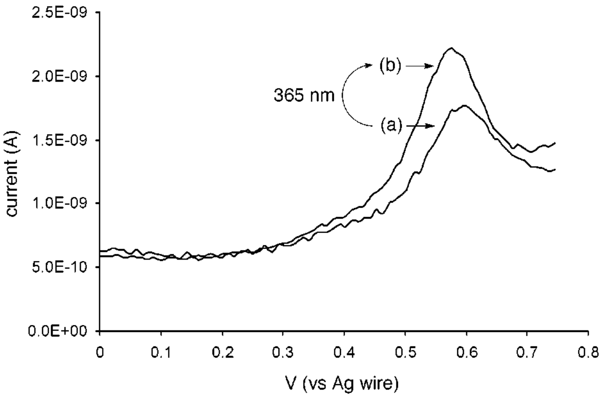

Figure 4. Demonstration of an optoelectronic redox switch based on **1** (ca. 1.2 × 10^{-5} M in MeCN): (a) mixture of **1**-DHP and **1**-CPD; (b) conversion of mixture to **1**-DHP via irradiation with 365 nm light. Peak current ($E_{p,a}$) corresponds to oxidation of **1**-DHP. Square wave voltammetry measurements were made in 0.1 M $TBAPF_6$/MeCN with a frequency of 10 Hz, step potential of 0.01 V, and amplitude of 0.02 V.

The similarity in the redox characteristics for both **1** and poly(**1**) should be re-emphasized here, as it is anticipated that similar optoelectronic redox switching in poly(**1**) would directly affect conductivity by perturbing both the number of carrier species (oxidation state, see Figure 4) and their mobility (effective conjugation length, see Scheme 1).[7] Studies directed at modifying the design of **1** and its corresponding polymer such that they meet the requirements of a rapid optoelectronic conductivity switch in the solid state are currently underway and will be the subject of future reports.

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(13) Kawai, S. H.; Gilat, S. L.; Ponsinet, R.; Lehn, J.-M. *Chem. Eur. J.* **1995**, *1*, 285−293.