

## Oligothiophene Functionalized Dimethyldihydropyrenes II: Electrochemical and Conductive Properties

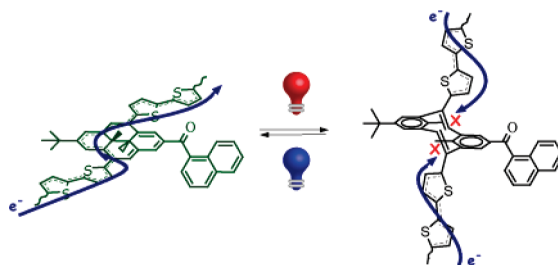
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Three different types of oligothiophene functionalized dihydropyrene photoswitches, (A) 2-naphthoyle-dimethyldihydropyrenes functionalized at the 4,9-positions with oligothiophenes, (B) benzodimethyldihydropyrenes functionalized at the 4-positions with oligothiophenes and the 10(11)-position with oligothiophenylcarbonyl groups, and (C) benzodimethyldihydropyrenes functionalized at the 4,5-positions with oligothiophenes, were studied with the goal of using the change in  $\pi$ -conjugation between the open and the closed forms of the dihydropyrene (DHP)–metacyclophane (CPD) switch to control electrical conductivity. UV–vis absorption studies were performed to measure the extent to which the attached thienyl oligomers were conjugated with the switch and the ability of the switch when opened or closed to affect conjugation. Of the three types of switches studied, those of type A showed the greatest effect. Solution cyclic voltammetry (CV) for the closed isomers indicated that the first few oxidation peaks were quasi-reversible, but that later ones were irreversible, leading to polymerization. Solution CV experiments on the open CPD form led to electrochemically induced closing to the DHP form. Conductivity studies were performed on undoped thin films of the A-type compound **4** and showed that opening the switch caused a decrease in electrical conductivity, and closing the switch caused an increase in electrical conductivity through the film. Doped films were studied by dual-electrode voltammetry and spectroelectrochemistry and showed that while doping led to an increase in the conductivity of the film it also led to the closing of the open form, preventing the conductivity of the open doped form from being measured.

### Introduction

The use of a photochromic compound to control electrical conductivity in conducting oligomers and polymers has received considerable interest in the development of electrically conducting optoelectronic molecular devices.<sup>1–4</sup> The properties found in conducting oligomers and polymers are

dependent on their  $\pi$ -conjugation, and so inserting a photochromic compound which can reversibly disrupt this  $\pi$ -conjugation has significant potential. Photochromic compounds based on the dithienylethene,<sup>4–11</sup> naphthopyran,<sup>12</sup>

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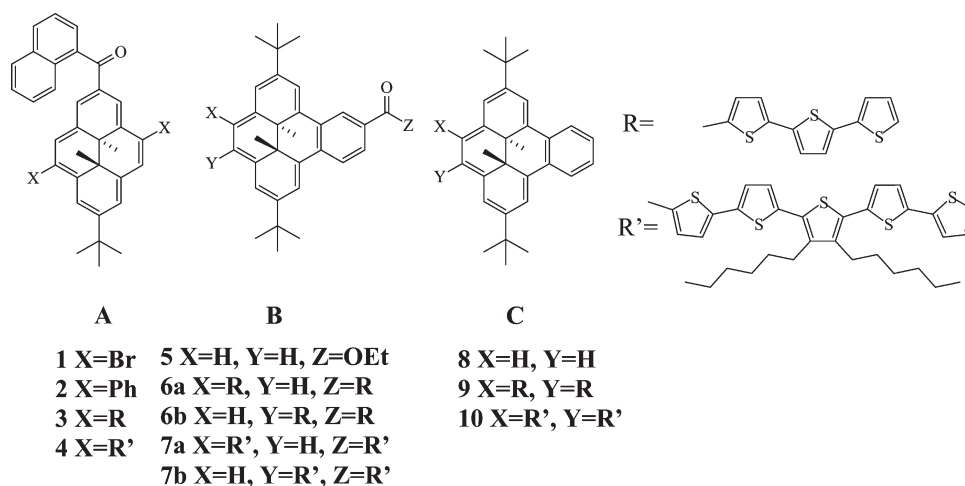
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**FIGURE 1.** Structure of photoswitches studied.

and spirobenzopyran<sup>13</sup> photochromes have been synthesized into conjugated oligomers and polymers and their properties studied. Irie showed that with the dithienylethene switch inserted into a poly(9,9-dialkylfluorene) that the conductivity of the closed form was 2.3 times that of the open form.<sup>7</sup> However, Irie and co-workers<sup>5</sup> also found with the dithienylethene switch and Ortica *et al.*<sup>12</sup> with the naphthopyran switch that as the conjugation length of the oligomers or polymer attached increased the photoswitching properties decreased. This was attributed in the dithienylethene case to intramolecular interactions between the dithienylethene switches.<sup>8</sup> These interactions could be minimized by using large twisted  $\pi$ -linkers but at the expense of the extended conjugation length.<sup>8</sup> Further complicating the result is the tendency for photostationary states to form, as they prevent experiments from being performed on the fully open and the fully closed forms of the switch. For example, the maximum conversion from the open to the closed form for the dithienylethene switch inserted into polyfluorene was only 10–14% in the solid state and 35–40% in solution.<sup>7</sup>

Less is known about the dimethyldihydropyrene (DHP) photoswitch despite the fact that it is an excellent candidate for studies on photoswitchable conjugated polymers for a number of reasons. DHP switches can be completely opened and closed,<sup>14</sup> and multiple switches attached through conjugated linkers can be opened and closed.<sup>15</sup> They are also rigid, exhibit excellent solubility in organic solvents, undergo small changes in dimensionality upon switching between the open and the closed form,<sup>16</sup> and new versions have recently been developed with greatly improved switching rates.<sup>14,17</sup> Consequently, the DHP switch is an attractive candidate for these studies. The goal of this research is to use these faster switching DHP switches inserted into thiophene oligomers and to use the disruption of  $\pi$ -conjugation when the switch is opened or closed to control electrical conductivity.

The focus of the preceding article<sup>18</sup> is on the synthesis and photochromic properties of oligothiophene functionalized dimethyldihydropyrenes, and this article will focus on the electrochemical and conductive properties.

## Results and Discussion

Compounds with three general structures were investigated (Figure 1): (A) dimethyldihydropyrene (DHP) switches with a naphthoyl group in the 2-position and functionalized on opposite sides of the switch (e.g., structure **2**), (B) benzodihydropyrene (BDHP) switches functionalized on opposite sides of the switch (e.g., structure **6a,b**, compounds **6** and **7** were isolated as inseparable ~3:1 mixtures of **6a/6b** and **7a/7b**), and (C) BDHP switches functionalized on the same side of the switch (e.g., structure **9**).

The mode of action hypothesized for how the DHP photoswitch will affect conductivity is through photo-switch-based disruption of the  $\pi$ -conjugation along the backbone of the conjugated oligomers, which will disrupt the pathway for electron flow. In particular, when a DHP molecule opens to its CPD form, a step is introduced in the molecule which interrupts the  $\pi$ -orbital overlap across the molecule (Figure 2).

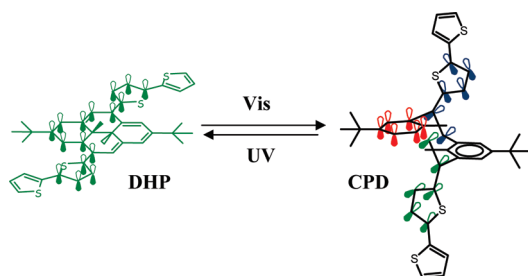
This change in the  $\pi$ -orbital overlap we hoped would lead to a large change in conductivity between the open and the closed forms.

**Solution Characterization. UV–Vis Absorption Studies of Conjugation Changes.** If the DHP-based photoswitch inserted into the backbone of conjugated oligomers and polymers is to affect the conductivity as hypothesized, then (1) the DHP switch should be conjugated with the oligomer or polymer into which it is inserted and (2) upon opening or closing the switch a change in the conjugation length should occur. UV–vis absorption studies were completed to determine how the three configurations (A, B, C) of the DHP switches met these criteria.

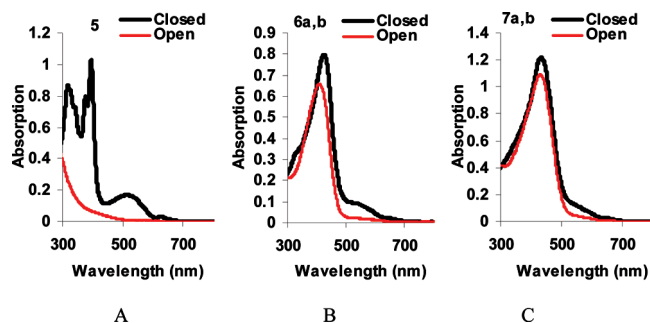
UV–vis spectroscopy is a useful tool for examining the extent to which  $\pi$ -electrons are conjugated as more extensive  $\pi$ -conjugation leads to a bathochromic shift in the UV–vis absorption and interruption of  $\pi$ -electron conjugation leads

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**FIGURE 2.** Schematic illustrating the disruption of  $\pi$ -conjugation from switching from the closed (DHP) form to the open (CPD) form of the switch.



**FIGURE 3.** Absorption spectra in cyclohexane illustrating the diminishing separation between the open and the closed forms with the addition of oligothiophenes and as the length of the oligothiophene increases for the BDHP series functionalized on opposite sides of the switch. (A) Compound **5**, (B) compound **6a,b**, and (C) compound **7a,b**.

to a hypsochromic shift in the UV–vis absorption. Adding oligothiophenes to the three dihydropyrene configurations (A–C) in their closed form led to two primary changes in the UV–vis absorption spectrum. First, the longest wavelength absorption characteristic of the dihydropyrene red-shifted consistent with conjugation into the thiophene ring system, as can be seen by comparing the closed form spectra in Figure 3 (for the BDHP **5**, **6a,b**, **7a,b** series) and from the data in Table 1 for all of the compounds. Second, a large peak appeared in the spectrum in the vicinity of 400–460 nm (Table 1). In Figure 3, this large peak is evident as the major feature of the spectra of **6a,b** and **7a,b** (parts B and C of Figure 3) near 430 nm, whereas the absorptions in this region for the non-oligothiophene containing **5** are characterized by much smaller extinction coefficients (Table 1). For comparison, the  $\lambda_{\text{max}}$  for comparable oligothiophenes appears at 355 nm (terthiophene)<sup>19</sup> and 396 nm (dihexyl functionalized quinquethiophene).<sup>20</sup> These UV–vis results indicate that there is extended conjugation from the oligothiophenes into the DHP switches.

Closer examination of the data in Table 1 shows that, while there is a significant bathochromic shift in the absorption of the closed forms upon the addition of the thienyl oligomers over switches with no thienyl oligomers, addition of the dihexyl quinquethienyl oligomers did not cause a

**TABLE 1.** UV–Vis Absorption Peaks and Molar Absorptivity in Cyclohexane

| switch type | parent  | R = Ph  | R = Th <sub>3</sub>                             | R = Th <sub>5</sub>                             |
|-------------|---|---|---|---|
| A           | <b>1<sup>a</sup></b>                            | <b>2</b>  | <b>3</b>  | <b>4</b>  |
|             | $\lambda_{\text{max}}/\text{nm}$ ( $\epsilon$ ) | $\lambda_{\text{max}}/\text{nm}$ ( $\epsilon$ ) | $\lambda_{\text{max}}/\text{nm}$ ( $\epsilon$ ) | $\lambda_{\text{max}}/\text{nm}$ ( $\epsilon$ ) |
|             | 670 (325)                                       | 676 (640)                                       | 703 (1600)                                      | 703 (1600)                                      |
|             | 604 (1440)                                      |   |   |   |
|             | 527 (13300)                                     | 537 (13700)                                     | 568 (16200)                                     | 566 (18900)                                     |
| 412 (39600) | 419 (49800)                                     | 456 (78200)                                     | 459 (81800)                                     |   |
|             |   | open form                                       |   |   |
|             | 303 (20100)                                     | 307 (27800)                                     | 446 (43100) sh                                  | 434 (63300)                                     |
|             |   |   | 388 (56800)                                     |   |
| B           | <b>5</b>  | <b>6a,b</b>                                     | <b>7a,b</b>                                     |   |
|             | 630 (650)                                       | 647 (1700)                                      | 655 (1850)                                      |   |
|             | 513 (4060)                                      | 526 (8400)                                      |   |   |
|             | 395 (24900)                                     | 426 (69300)                                     | 433 (99500)                                     |   |
|             |   | open form                                       |   |   |
|             | 251 (30600)                                     | 407 (57100)                                     | 431 (89200)                                     |   |
| C           | <b>8<sup>24</sup></b>                           | <b>9</b>  | <b>10</b>                                       |   |
|             | 504 (7000)                                      | 510 (6630)                                      | 554sh (5380)                                    |   |
|             | 388 (35000)                                     | 407 (69800)                                     | 412 (103000)                                    |   |
|             |   | open form                                       |   |   |
|             |   |   | 380 (53900)                                     | 408 (83800)                                     |

<sup>a</sup>In dichloromethane.

significant additional shift over that of the terthienyl substituted compounds, especially for **4** versus **3** and **7** versus **6**. This is consistent with the expectation that, as  $\pi$ -conjugation increases, the absorption spectrum will progressively shift less with each unit addition.<sup>21,22</sup> The  $\pi$ -conjugation of the terthienyl substituted compounds is already sufficiently extended that only a small additional shift is observed in the more extended dihexyl quinquethienyl substituted compounds. Also, because the addition of dihexyl groups in the  $\beta$ -position is known to distort the backbone of oligothiophenes reducing the extent of  $\pi$ -conjugation,<sup>23</sup> the magnitude of the bathochromic shift on going from a terthienyl to a quinquethienyl containing one of these dihexyl groups in the  $\beta$ -position is expected to be small.

Irradiation of freshly prepared solutions of the closed samples with visible light (490 nm long-pass filter) led to the opening of the switch as seen by a change in color from dark red-brown for the BDHP-based photoswitches or green-brown for the thienyl functionalized DHP-based photoswitches to the orange yellow color of the open form. More quantitatively, fully opening the switches by irradiation led to a decrease in the peak or shoulder of the lowest energy absorption in the spectral range of 500–700 nm, as can be seen for compounds **5**, **6a,b**, and **7a,b** in Figure 3 and the **4**, **7a,b**, and **10** series in Figure 4 (see also Table 1). As the length of the oligothiophenes attached to the photoswitch increased, a smaller separation was observed between the long-wavelength absorption onset for the open versus closed forms (Figure 3). This indicates that the ability of the photoswitch to change the effective  $\pi$ -conjugation decreased as the length of the oligothiophenes increased.

The position of the oligothiophenes on the photoswitch was also a factor. The DHP-based photochromes with oligothiophenes attached directly to the switch showed the

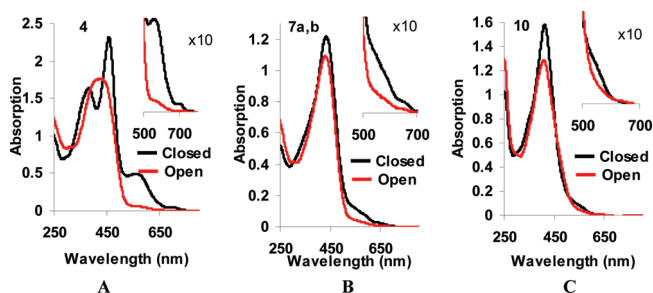
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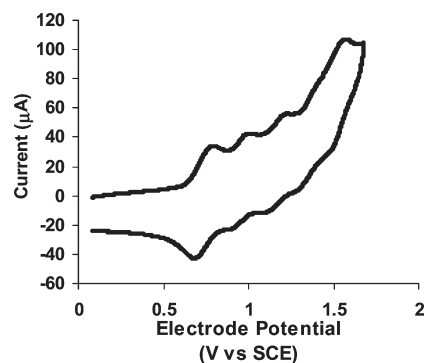
**FIGURE 4.** UV-vis absorption of the open and closed forms of (A) **4**, (B) **7a,b**, and (C) **10** in cyclohexane. Inset: an expansion of the 500–700 nm region.

biggest difference in the UV-vis absorption between the open and the closed forms (e.g., Figure 4A). The BDHP switch with oligothiophenes attached directly to the switch on one side, but cross conjugated on the other, showed less of a difference in the absorption between the open and the closed form (Figure 4B). The BDHP switch with oligothiophenes attached on the same side, which limits the ability for the oligothiophenes to be coplanar with the switch, showed almost no change in the absorption spectrum between the open and the closed forms for the quinquethienyl functionalized version (Figure 4C).

On the basis of the UV-vis data, the DHP-based photoswitches **3** and **4** with oligothiophenes attached directly to the switch showed the most potential for being able to control conductivity. These compounds had extended conjugation between the thiophene oligomers and the switch, and the opening and closing of the switch had the largest impact on the effective conjugation length.

**Solution Cyclic Voltammetry.** The electrochemical behavior of the photoswitches was explored by studying one compound from each of the three major switch types and all with the same oligothiophene side chain (**4**, **7ab**, and **10**). The switch **6ab** was also studied so that when compared with **7ab** the influence of chain length could be investigated. Finally, switch **1** was studied as a control for comparison to the oligothiophene containing switches. Solution cyclic voltammetry experiments were performed using dichloromethane (DCM) as the solvent and tetrabutylammonium hexafluorophosphate (TBAPF<sub>6</sub>) as the electrolyte salt. In their closed forms, all of the compounds containing oligothiophenes showed a series of redox waves at positive potential corresponding to sequential oxidation of the photoswitch. Figure 5 shows a representative voltammogram for **4**, and the positions of the anodic and cathodic peak potential,  $E_{pa}$  and  $E_{pc}$ , respectively, and the apparent reduction potential  $E^{o'} = (E_{pa} + E_{pc})/2$  for all of the compounds are reported in Table 2. The term apparent reduction potential  $E^{o'}$  is used because only in a few cases was the  $E_{pa} - E_{pc}$  near the ideal 60 mV limit for a thermodynamically reversible redox process at the 250 mV/s scan rate used. Separations larger than the ideal 60 mV limit increase the uncertainty in determining the true reduction potential.

The observed separation between  $E_{pa}$  and  $E_{pc}$  increased in going from the redox wave at the least positive potential to that at the most positive potential. Over the potential range studied, the non-thiophene containing switch **1** showed only



**FIGURE 5.** Cyclic voltammogram of **4** collected at 0.25 V/s in a 0.1 M TBAPF<sub>6</sub> dichloromethane solution cycling from 0.1 to 1.7 V vs SCE.

**TABLE 2.** Summary of Results from Cyclic Voltammetry at 0.25 V/s of ~1 mM Samples of **4**, **7a,b**, **6a,b**, **10**, and **1** in 0.1 M TBAPF<sub>6</sub> Dichloromethane Solutions<sup>a</sup>

| compound  | $E_{pa}$<br>(V vs SCE) | $E_{pc}$<br>(V vs SCE) | $E^{o'}$<br>(V vs SCE) |
|---|------------------------|------------------------|------------------------|
| NpCO-DHP-(Th <sub>5</sub> ) <sub>2</sub> <b>4</b>   | 0.80                   | 0.69                   | 0.74                   |
|   | 1.01                   | 0.89                   | 0.95                   |
|   | 1.24                   | 1.09                   | 1.17                   |
|   | 1.58                   | 1.27                   | 1.43                   |
| Th <sub>3</sub> CO-BDHP-Th <sub>3</sub> <b>7a,b</b> | 0.59                   | 0.51                   | 0.55                   |
|   | 0.97                   | 0.84                   | 0.91                   |
|   | 1.21                   | 1.06                   | 1.14                   |
|   | 1.51                   | 1.43                   | 1.47                   |
| Th <sub>3</sub> CO-BDHP-Th <sub>3</sub> <b>6a,b</b> | 0.54                   | 0.48                   | 0.51                   |
|   | 0.74 <sup>b</sup>      |                        |                        |
|   | 0.97                   | 0.84                   | 0.91                   |
|   | 1.28                   | 1.16                   | 1.22                   |
| BDHP-(Th <sub>5</sub> ) <sub>2</sub> <b>10</b>      | 0.55                   | 0.49                   | 0.52                   |
|   | 0.77 <sup>b</sup>      |                        |                        |
|   | 0.95                   | 0.82                   | 0.89                   |
|   | 1.32                   | 1.06                   | 1.19                   |
| NpCO-DHP-Br <sub>2</sub> <b>1</b>                   | 1.15                   | 1.06                   | 1.11                   |

<sup>a</sup>Data are for the closed form of the photoswitches except where noted. <sup>b</sup>Observed if the sample was first opened with visible light.

a single redox wave at a relatively large positive potential illustrating the substantial electroactivity imparted by the oligothiophene side chains.

The most positive redox waves involved polymerization of the thiophene side chains. Repeated cycling beyond the first three oxidation peaks for **4** and the first two oxidation peaks for **6a,b** and **7a,b** led to an increase in the current in subsequent cycles, as shown in Figure 6B for **4**. Cycling over the full range of Figure 6B also resulted in the deposition of an insoluble black film on the electrode, which is consistent with the formation of an electroactive polymer film.<sup>25</sup> In contrast, stable cycling without the observation of film deposition occurred if the potential range was restricted to the first three redox waves, as shown in Figure 6A.

Complete electrochemical characterization of the open forms was not possible due to rapid electrochemical closing, as has been observed with other classes of photoswitches.<sup>10,26</sup>

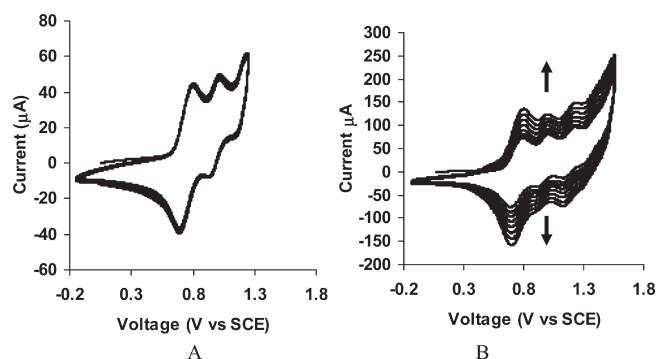
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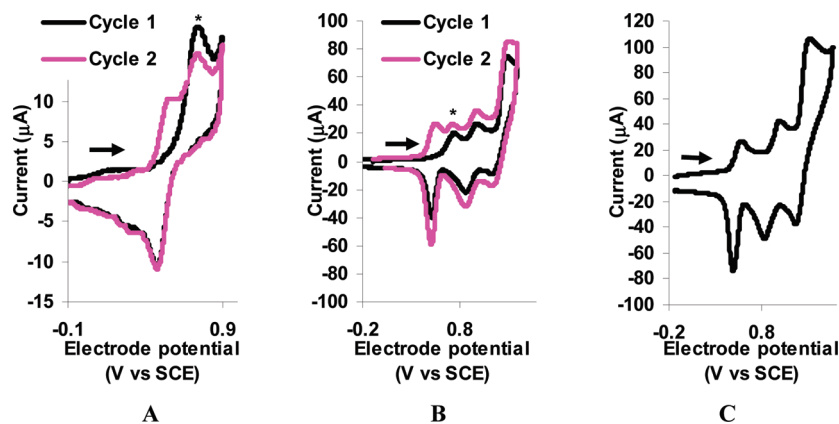
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During electrochemical cycling of the open forms, the solution in the vicinity of the electrodes changed from the orange-yellow color characteristic of the open forms to the dark red-brown or green-brown characteristic of the closed forms. The closing was also evident from the forms of the observed voltammograms. With compound **6a,b** as an example, Figure 7 shows voltammograms for this compound collected over a limited potential range (Figure 7A) and over the same potential range (Figure 7B) used for the closed form (Figure 7C). The limited range of Figure 7A focuses attention on the closing process and is discussed first. The single anodic peak observed on the initial cycle is distinct from and occurs at a more positive potential ( $E_{pa} = 0.74$  V vs SCE) than the first anodic wave of the closed form ( $E_{pa} = 0.54$  V vs SCE). The corresponding cathodic peak, however, occurs at the same potential as for the first redox wave of the *closed* form. This suggests that the switch closes rapidly upon initial oxidation so that its re-reduction is not directly observed even at scan rates up to 1 V/s. Rather, only a cathodic wave corresponding to the closed form of the switch is observed. The formation of the closed form of the switch was also clearly evident upon subsequent cycling. On the second cycle, the initial oxidation wave of the closed form grew in at  $E_{pa} = 0.54$  V vs SCE, leading to the observed two anodic peaks. Again,



**FIGURE 6.** Electrochemical polymerization of **4** on a glassy carbon electrode in a 0.1 M TBAPF<sub>6</sub> dichloromethane solution. (A) No polymerization is observed when cycling four times through the first three oxidation peaks (−0.15 to 1.25 V vs SCE, 0.5 V/s). (B) Polymerization is observed when cycling 10× beyond the first three oxidation peaks (−0.14 to 1.6 V vs SCE, 0.5 V/s).



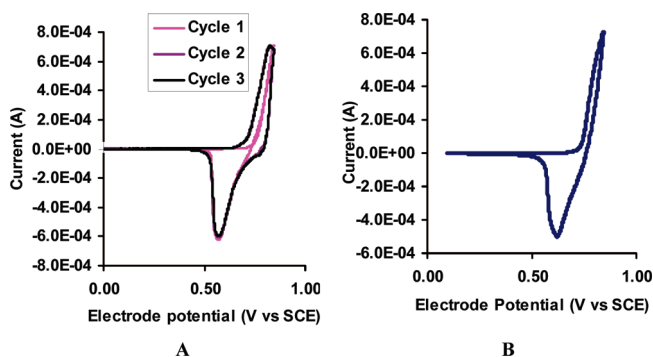
**FIGURE 7.** Cyclic voltammetry of **6a,b** at 0.25 V/s. (A) Cycling the open form from −0.1 to 0.9 V. (B) Cycling the open form between 1.4 and −1.5 V. (C) Closed form, cycling from −0.1 to 1.6. The asterisk (\*) indicates the peak from the open form. The arrow indicates the scan direction.

only a single cathodic peak characteristic of the closed form was observed over this limited cycling range. The expanded voltammogram of Figure 7B further confirms electrochemical closing. Aside from the differences in the first anodic wave just discussed, the voltammograms of the open and closed forms over the wider potential range of Figure 7B are very similar. The slight increase in current between the first and second cycles is consistent with deposition of an electroactive polymer, as previously discussed for the closed form.

The voltammograms for the open form of **10** was similar to that for **6ab**. As with **6ab**, initial oxidation of the open form of **10** occurred at a more positive potential and led to closing of the switch. For both compounds **4** and **7ab**, electrochemical closing was evident from an observed color change, but the voltammogram of the initially open state appeared nearly identical to that of the closed state. The first oxidation wave, which initiated closing, is apparently characterized by very nearly the same reduction potential for that of the closed form. This is consistent with the extended conjugation in **4** and **7ab**, due to the geometrical arrangement of the thiophene side chains in the former and the longer side chains in the latter, relative to **6ab**.

The above results indicate that, while electrochemical characterization of the closed form of all three types of switches studied (A, DHP with oligothiophenes on opposite sides; B, BDHP switch with oligothiophenes on opposite sides; and C, BDHP switch with oligothiophenes on the same side of the switch) could be obtained, rapid electrochemical induced closing prevented complete electrochemical characterization of the open form of these switches.

**Solid-State Characterization.** A primary goal of this work is to demonstrate modulation of conductivity by action of the photoswitch. To explore this possibility, the solid-state electrochemistry, conductivity, and absorptivity of solid-state thin films of compound **4** were investigated in detail. Of all of the compounds, **4** had the most potential to be able to control electrical conductivity as it had extended conjugation from the oligothiophenes into the switch and the largest difference in conjugation between the open and the closed forms. As will be shown below, compound **4** also exhibited stable electrochemical cycling in the solid state, whereas the voltammograms for solid films of **7a,b** and **10** changed substantially upon cycling (see the

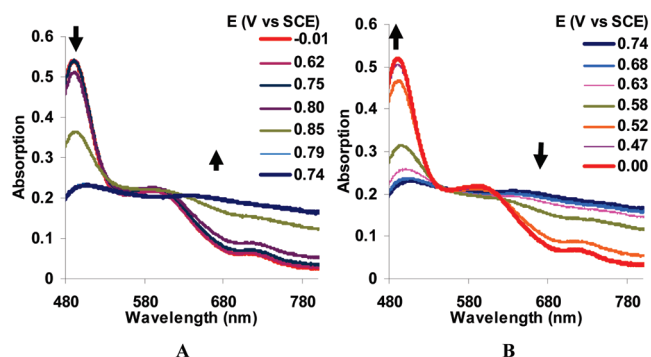


**FIGURE 8.** Thin film cyclic voltammetry of **4** on an indium tin oxide coated glass slide. (A) Three cycles of the closed form scanning from 0 to 0.85 V vs SCE at 0.01 V/s. (B) Scanning the open form from 0.1 to 0.84 V vs SCE at 0.01 V/s while continuously irradiating with light.

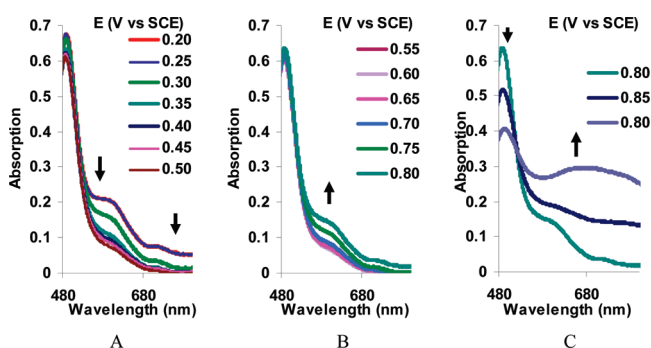
Supporting Information). For these reasons, studies on thin solid films focused on compound **4**. In regards to electrochemical studies on solid films, one of the limitations found for oligothiophene functionalized DHP compounds is that they tend to be somewhat soluble in all the common organic solvents used as electrolytes, which limits the ability to electrochemically study these compounds in the solid state.<sup>16</sup> Fortunately, we found that the addition of dihexyl functional groups to the thiophene oligomers attached to the switch (e.g., in compounds **4**, **7a,b**, and **10**) resulted in these compounds being completely insoluble in acetonitrile-based electrolytes.

For conductivity studies, it is typical to study electrochemically oxidized or doped samples in order to take advantage of the large increase in conductivity that occurs upon doping. The rapid electrochemically induced closing observed in the solution CV experiments, however, is a concern because it suggests that it may not be possible to access the doped form of the open switch. Moving from solution to the solid state has a potential to affect the kinetics of the closing process. Consequently, the electrochemistry of thin solid films was studied to explore any differences from the solution results. The absorption spectrum of the film was simultaneously monitored (spectroelectrochemistry) to better follow any changes in the state of the photoswitch. Conductivity studies were then performed on the doped state using dual-electrode voltammetry and then on the undoped state using a simple two-electrode measurement.

**Thin Film Cyclic Voltammetry Spectroelectrochemistry.** Thin film samples of **4** were studied using saturated tetramethylammonium tetrafluoroborate (TMABF<sub>4</sub>) acetonitrile solutions as electrolyte. To enable simultaneous spectral characterization, indium tin oxide coated glass slides were used as electrodes. After an initial break in cycle (Figure 8A, cycle 1), the film could be cycled repeatedly with little change in the cyclic voltammogram (Figure 8A, cycles 2 and 3). The scan range was restricted to the first redox wave to minimize complications due to polymerization, as accompanied the more positive redox waves in the solution studies. After cycling over the range shown in Figure 8A, the film could be redissolved in an appropriate nonpolar solvent, supporting the absence of substantial polymerization. The separation between the observed anodic ( $E_{pa} = 0.83$  V vs SCE) and cathodic ( $E_{pc} = 0.57$  V vs SCE) peaks under the conditions



**FIGURE 9.** Spectroelectrochemistry of a thin film of the closed form of **4** on an ITO coated glass slide at 0.01 V/s in a TMABF<sub>4</sub>/ACN solution. (A) Increasing the voltage from  $-0.01$  to  $0.85$  and back to  $0.74$  V vs SCE, (B) decreasing the voltage from  $0.74$  to  $0$  V vs SCE (arrows indicate the direction of absorption change).



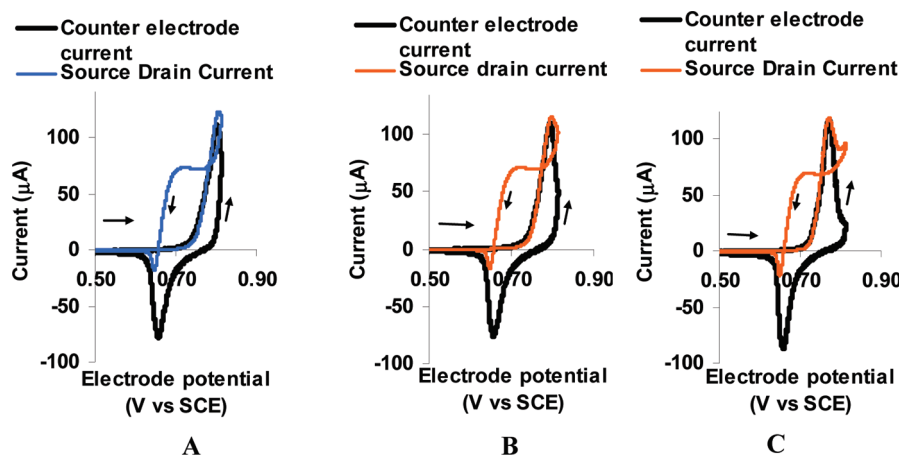
**FIGURE 10.** Spectroelectrochemistry of **4** under continuous illumination at 0.01 V/s on an ITO coated glass slide in a TMABF<sub>4</sub>/ACN solution. (A) Photo-opening of the initially closed form of **4** due to illumination as the voltage was swept from  $0.2$  to  $0.5$  V vs SCE. (B) Electrochemically induced closing of **4** as the voltage was swept from  $0.55$  to  $0.8$  V vs SCE. (C) Doping of **4** as the voltage was swept from  $0.80$  to  $0.85$  and back to  $0.80$  V vs SCE.

of Figure 8A was large and strongly dependent on scan rate, indicating substantial kinetic limitations. Although the separation between  $E_{pa}$  and  $E_{pc}$  was observed to decrease upon slowing the scan rate, a significant separation was still observed even at  $0.5$  mV/s. The slow oxidation of thin films of **4** is most likely related to low permeability of the electrolyte ions into the film.

The change in the absorption spectrum accompanying the voltammogram in Figure 8A, cycle 2, is shown in Figure 9. Electrochemical oxidation of a film of the closed form of **4** produced a broad increase in the absorption above  $530$  nm and a bleach of the large absorption below  $530$  nm (Figure 9A). This broad increase in the absorption is typical for doped oligo- and polythiophenes.<sup>27</sup> Reduction of the film back to its neutral form gave back the initial UV–vis absorption (Figure 9B).

The thin film voltammetry of the open form was studied by illuminating and then initiating the potential scan nearly simultaneously. The change in the absorption spectrum accompanying the voltammogram in Figure 8B is shown in Figure 10. The potential scan was started in a region where the film was not electroactive, so in the early parts of the scan,

(27) Furukawa, Y. *J. Phys. Chem.* **1996**, *100*, 15644–15653.

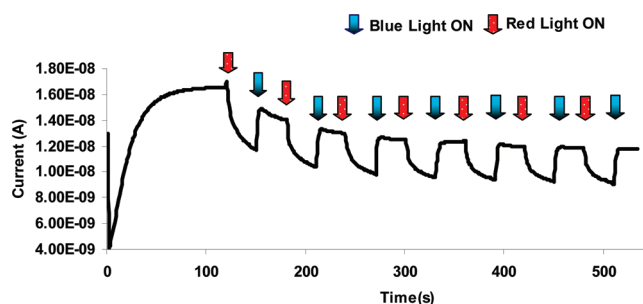


**FIGURE 11.** Cyclic voltammetry scanning of **4** from 0.49 to 0.81 V vs SCE at 0.02 V/s. (A) An initially closed sample. (B) An initially open sample (after 1 min visible light irradiation). (C) Film under continuous illumination during the experiment. Arrows indicate scan direction.

the photoinduced opening could be followed spectroscopically, as shown in Figure 10A. Opening of **4** was observed by the decrease in the absorption in the region of 540–800 nm. As the CV reached the oxidation peak, the film began to electrochemically close as seen by the increase in the absorption from 540 to 800 nm (Figure 10B). The film then doped, in a similar fashion as was seen during the cyclic voltammetry scan of the initially photochemically closed sample (Figure 10C).

**Dual-Electrode Voltammetry.** From the spectroelectrochemistry results, it is clear that some electrochemically induced closing is occurring during the electrochemistry experiment. Dual-electrode voltammetry experiments were performed to see if enough of the switches remained open to have an effect on the conductivity of the film in the doped state. A thin film of **4** was spin coated onto a gold interdigitated electrode, and TMABF<sub>4</sub> in acetonitrile was used as the electrolyte. In the dual-electrode experiment, a three-electrode cyclic voltammetry (CV) experiment was conducted using one side of the interdigitated gold electrode as the working electrode (also termed the source), a platinum wire as the counter electrode, and a Ag/Ag<sup>+</sup> reference electrode. During this CV experiment, a 25 mV offset potential was applied between the source fingers and the so-called drain fingers that make up the other half of the interdigitated electrode. The current at the counter electrode,  $I_C$ , and the source–drain current,  $I_{SD}$ , were measured. The latter has contributions from both electrochemical doping/undoping of the material, which also contributes to the counter electrode current, and current due to the material becoming conductive.

Figure 11 shows the results of the dual-electrode voltammetry experiments on **4** in its initially closed state, initially open state, and under continuous illumination (490 nm long-pass filter). The  $I_C$  and  $I_{SD}$  are different shapes due to the contribution of a conductivity current to the latter. As the film is swept positive from the initial value of 0.49 V vs SCE, both  $I_{SD}$  and  $I_C$  rise in a similar manner due to the oxidation or doping of the film. Upon sweep reversal at 0.81 V vs SCE, the  $I_C$  drops and then becomes negative as re-reduction of the film occurs. The  $I_{SD}$  upon reversal, however, remains near a constant positive value, signaling that the film has been

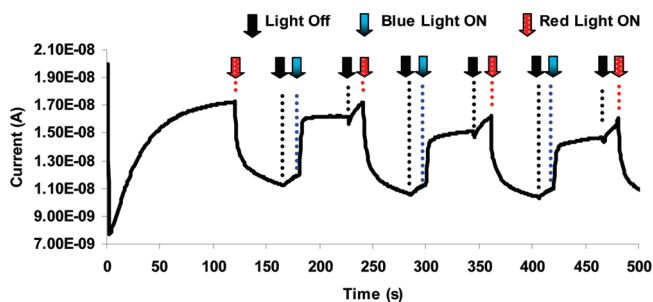


**FIGURE 12.** Opening and closing of the DHP switch **4** under vacuum on an interdigitated electrode using red and blue light while applying 30 V across the fingers of the electrode.

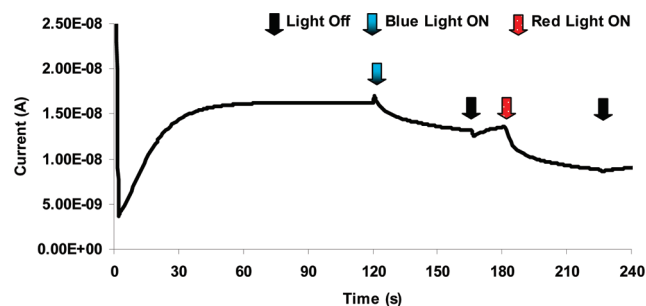
doped to its highly conductive state. As re-reduction of the film occurs, the  $I_{SD}$  drops back to near zero, consistent with conversion back to the undoped state. There is little difference in the behavior between the dual-electrode voltammograms of the initially open and closed states, as well as with that under continuous illumination (490 nm long-pass filter) to drive opening of the switch. This result indicates that either opening the switch has little or no effect on the electrical conductivity through a doped film or the open form of the switch electrochemically closes as observed in the solution phase experiments.

**Undoped Conductivity.** The lack of change in the conductivity observed in the doped samples and the likelihood that it was due to rapid closing of the doped form prompted investigation of the undoped form. An undoped thin film of **4** was spin coated onto an interdigitated gold electrode; 30 V was applied across the fingers of the electrodes, and the resulting current was measured. After a preliminary stabilization period in the dark for 120 s, an alternating sequence of 30 s periods of red light (490 nm long-pass filter), which completely opens the switch, and blue light (BG6 band-pass filter, 310–510 nm), which partially closes the switch, was applied. Upon application of the red light, which opens the switches, the current decreased, and on application of the blue light, which closes the switches, the current increased (Figure 12). The direction of the observed current changes on application of the red and blue light is consistent with the





**FIGURE 13.** Applying 15 s of darkness between red and blue light irradiations.



**FIGURE 14.** Irradiating a film of **4** under vacuum with blue light followed by red light.

hypothesis that opening the switch will lead to a decrease in conductivity due to the disruption of  $\pi$ -conjugation.

To support the conclusion that the changes in conductivity observed in the film are a result of the opening and the closing of the switches, and not simply due to a photocurrent, two control experiments were performed. In the first control experiment, 15 s periods of darkness were introduced between the application of the red and the blue light. As can be seen in Figure 13, on removal of the light, no dramatic shift in the current is observed, as would be expected if the changes in conductivity were due to a photocurrent. Instead, during the periods of darkness applied after irradiating with the red or the blue light, the current gradually increases, which is consistent with thermal closing of the switches. The current can increase in the dark after application of the blue light because the blue light does not fully close the switch but instead leads to a photostationary state with a population of open switches that can thermally close.

A second control experiment was conducted that makes use of the photostationary state that occurs when the blue light is applied to demonstrate that the changes in the conductivity of the film are a result of photoswitching. Applying the blue light to a fully closed sample leads to a drop in the current, as shown in Figure 14. This drop in the current can be understood as the result of some of the switches opening due to the photostationary state that occurs when the blue light is applied. Application of the red light after the blue light leads to a further decrease in the current as the rest of the switches open. Thus, irradiating a fully closed film with blue light leads to a decrease in the current, and irradiating an open film with the same blue light leads to an increase in the current. This bidirectional movement in the current when the blue light is applied indicates that the current changes observed are a result of

photoswitching rather than from a photocurrent. Although the conductivity changes observed are not large, we believe that they are not caused by artifacts and do represent conductivity changes due to photoswitching.

## Conclusions

Three different types of oligothiophene functionalized DHP photoswitches were studied with the objective of using the change in  $\pi$ -conjugation when the switches are opened or closed to control electrical conductivity. UV-vis and cyclic voltammetry experiments were performed, which indicated that the oligothiophenes were conjugated with the switches and that the switches could be used to control  $\pi$ -conjugation. From these studies, the 2-naphthoyldimethyldihydropyrene functionalized in the 4,9-positions with oligothiophenes was selected for conductivity studies as it showed the greatest ability to affect  $\pi$ -conjugation, and as a thin film, it was more electrochemically stable than the other compounds tested. Thin film conductivity studies indicated that some control over electrical conductivity could be obtained in the undoped state, that is, as a semiconductor. Opening the switch caused a decrease in the conductivity, and closing the switch led to an increase in the conductivity. The sample could be cycled repeatedly between the open and the closed forms. When doping was employed to achieve much higher conductivities, the switch was found to be electrochromic, and only the closed form was then stable and accessible. Doping could thus be used to dramatically increase the conductivity of thiophenes with dihydropyrenes inserted, but then switching of the dihydropyrene is not possible.

## Experimental Procedures

Compounds were synthesized as reported previously.<sup>18</sup> Dichloromethane was dried by distillation from calcium hydride. Acetonitrile was dried by distillation from  $P_2O_5$ . Solution cyclic voltammetry experiments were performed using a potentiostat interfaced to a personal computer. All measurements were conducted in oven-dried glass cells cooled under a flow of argon. The working electrode was glassy carbon; the counter electrode was a platinum wire, and the reference electrode was a silver wire. Ferrocene was used as the internal standard (0.46 V vs SCE). TBAPF<sub>6</sub> was recrystallized three times from 95% ethanol and dried at 80 °C for 24 h prior to use. Sample concentrations of ~1 mM in 100 mM TBAPF<sub>6</sub> were used. Tetramethylammonium tetrafluoroborate (TMABF<sub>4</sub>) was recrystallized from water and dried in vacuo at 80 °C for 5 days. Thin film cyclic voltammetry was performed with a potentiostat using either an indium tin oxide coated glass slide or a gold interdigitated electrode as the working electrode, a coiled platinum wire as the counter electrode, and a non-aqueous Ag(s)/Ag<sup>+</sup> reference electrode. The gold interdigitated electrodes used in the dual-electrode experiments and the undoped conductivity measurements consisted of 21 interpenetrating gold fingers 2.5 mm in length with a gap spacing between the fingers of 7 to 10  $\mu$ m. The reference electrode was prepared from a 3 mm diameter glass tube with a Vycor frit at one end. It was filled with TMABF<sub>4</sub>(sat)/0.005 M AgNO<sub>3</sub>/ACN and was referenced against a commercial SCE. Films were prepared by either drop coating or spin coating from 5 to 10 mg/mL solutions in dichloromethane. Dual-electrode electrochemistry was performed with a potentiostat and a source measure unit under computer control. The undoped conductivity measurements were performed under vacuum,



using a semiconductor parameter analyzer with 30 V applied across the fingers of the interdigitated electrodes. Samples were irradiated using a tungsten–halogen white light source with either a 490 nm long-pass filter or a BG6 band-pass filter (310–510 nm). Spectroelectrochemistry was performed using a diode array spectrophotometer connected via a fiber optic cable. Solution UV–vis experiments were performed on a UV–vis spectrophotometer. Solution visible light opening experiments were performed using a 500 W household tungsten–halogen lamp (8500 lm) as the light source with a 490 nm long-pass filter.

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**Supporting Information Available:** Spectroelectrochemistry data for compounds **7a,b** and **10**. This material is available free of charge via the Internet at <http://pubs.acs.org>.