

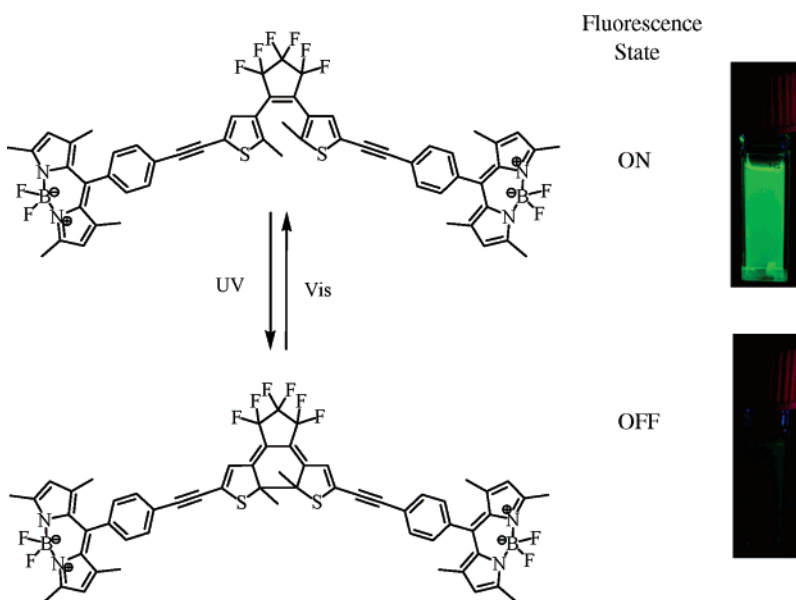
## Synthesis and Properties of Novel Fluorescent Switches<sup>†</sup>

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Received March 16, 2005



Photochromic dithienylethene moieties were covalently attached to fluorescent 4,4-difluoro-8-(4'-iodophenyl)-1,3,5,7-tetramethyl-4-bora-3a,4a-diaza-s-indacene (iodo-BODIPY) via a phenylacetylene linker. UV light induced isomerization of the photochrome results in significant decrease in fluorescence intensity. This fluorescence can be recovered with visible light. Steady-state fluorescence measurements demonstrate that the emission of the dye can be modulated by external light. An intramolecular energy transfer mechanism accounts for the fluorescence quenching in the UV light produced isomers.

### Background

Efficient light-driven molecular switching materials are targets of increasing interest for the electronics and optical memory devices industries.<sup>1–5</sup> Such materials can be obtained by combining a photochromic component with a unit possessing a given physical property to be modulated. In the ideal, the compound will undergo reversible light-induced photoisomerization to produce an isomer with a different absorption spectrum,<sup>6,7</sup> and this will be

accompanied by changes in the properties of the compound.<sup>3</sup> Certain dithienylethene derivatives, first described by Irie and Mohri,<sup>8</sup> are among the more promising candidates owing to highly efficient photoisomerization reactions, the thermal stability of both isomers, and excellent fatigue resistance. Octafluorocyclopentene derivatives in particular can be recycled thousands of times with no chemical change.<sup>4,8–10</sup> In the photochromic reaction, an open-ring hexatriene is converted reversibly to

<sup>†</sup> Contribution No. 553 from the Center for Photochemical Sciences.

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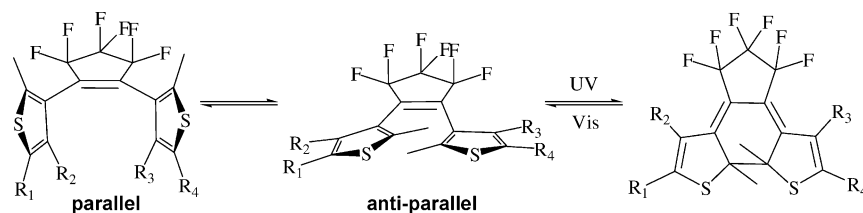
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SCHEME 1. Photoreaction of Dithienylethenes<sup>11</sup>

a closed-ring cyclohexadiene with UV light. This changes the absorption spectrum, as well as the geometrical and electronic structure of the product.<sup>10</sup> Though the opening isomer may exist in two conformations, antiparallel and parallel, photocyclization proceeds only from the antiparallel conformer.<sup>11</sup> The closed-ring isomer is converted back to the open-ring isomer following irradiation with a visible light (Scheme 1).

Numerous studies have demonstrated the potential of these compounds in recording media, where certain properties can be changed by means of the photochromic dithienylethene moiety.<sup>4,9,12–18</sup> Among other outputs, fluorescence emission is considered to be one of the most attractive owing to its ease of detection and the cheap fabrication of devices in which it is detected. In designing fluorescence photoswitching materials, is it essential to provide a nondestructive readout capability;<sup>10</sup> i.e., the energy of the light used to detect the difference between open- and closed-ring isomers should not change the structures of the molecules.<sup>16,19</sup> Many examples have closely approached this concept.<sup>12,20–23</sup> Although a large family of derivatized dithienylethenes exhibits good reversibility in fluorescence intensity, most of the reported examples have relatively small quantum yields of fluorescence.<sup>11,20–22,24</sup> However, a high quantum yield of fluorescence of the open-ring isomer is achieved in a system containing two dithienylethene units connected by 9,10-bis(2-phenylethynyl)anthracene, where the anthracene moiety acts as an emitting component.<sup>14</sup> The isolated photoproduct of UV irradiation, in which only one of dithienylethene moieties undergoes a photochromic reaction, exhibits very weak fluorescence. The fluorescence can be recovered after exposure to the visible light. The fluorescence quantum yields for the open- and closed-ring isomers are 0.83 and less than 0.001, respectively.<sup>14</sup> Even though the fluorescence can be effectively switched in this compound, the isomerization reaction proceeds with low yield, and the photoproduct needs to be isolated. An outstanding result has been achieved by connection of a dithienylethene moiety to bis(phenylethynyl)an-

thracene via an adamantyl spacer.<sup>25,26</sup> Although the effective switching of fluorescence at a single-molecule level has been attained in this system, the synthetic route is rather tedious.

## Results and Discussion

A series of fluorescent switches **1–3** (Scheme 2) containing photochromic dithienylethene units linked to derivatized 4,4-difluoro-4-bora-3a,4a-diaza-*s*-indacene (BODIPY dye)<sup>27</sup> was synthesized. The latter were first prepared by Treibs and Kreuzer in 1968<sup>28,29</sup> and have found numerous applications in molecular biology<sup>27,30</sup> as well as in the development of molecular devices.<sup>31,32</sup> The attractive properties of these dyes include high molar extinction coefficients, high fluorescence quantum yields, insensitivity to solvent polarity and pH, and a tunable emission range.<sup>33,34</sup> Our approach in designing efficient fluorescence switches is based on the fact that the emission of the BODIPY dye<sup>27,29</sup> overlaps significantly with the absorption of the closed-ring isomer of the dithienylethene photochromic moiety,<sup>35</sup> thus allowing an energy transfer to occur, which will lead to a strong fluorescence quenching.<sup>36</sup>

Target compounds **1–3** were synthesized from 4,4-difluoro-8-(4'-iodophenyl)-1,3,5,7-tetramethyl-4-bora-3a,4a-diaza-*s*-indacene and dithienylethenes **4** and **5** by Sonogashira coupling using Pd<sub>2</sub>(dba)<sub>3</sub>.<sup>37</sup> Two-fold excess of iodo-BODIPY was allowed to react with **4** to afford switch **1**, while for switch **2**, iodo-BODIPY was added along with iodobenzene to dithienylethene **4**. The molecular structures of switches **1–3** were confirmed by electrospray ionization time-of-flight mass spectrometry, as well as by NMR spectroscopy. The target compounds are soluble

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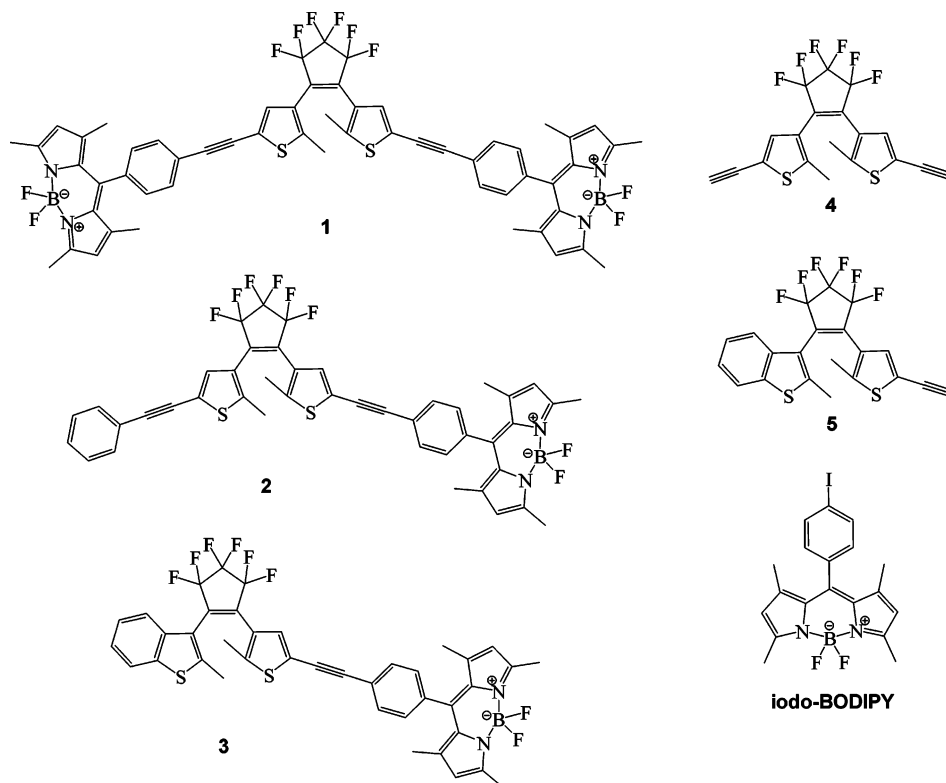
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## SCHEME 2. Molecular Structures of Switches 1–3 and Their Precursors

TABLE 1. Molar Absorption Coefficients ( $\epsilon$ ), Quantum Yields of Fluorescence ( $\Phi_f$ ), and Lifetimes ( $\tau$ ) of 1–3, and Iodo-BODIPY

compd	$\lambda_{\max}$ , nm ( $\epsilon/10^4$ , $M^{-1} \text{ cm}^{-1}$ )	$\Phi_f$	$\tau$ , ns
1 <sup>a</sup>	503 (13.1), 315 (5.8), 279 (4.3)	0.27 ± 0.02	1.3 ± 0.1
2 <sup>a</sup>	503 (10.3), 312 (6.0), 280 (4.5)	0.32 ± 0.02	1.3 ± 0.1
3 <sup>a</sup>	503 (8.9), 312 (3.5), 260 (3.3), 229 (4.7)	0.34 ± 0.03	1.3 ± 0.1
iodo-BODIPY <sup>b</sup>	500 (4.7)	0.64 ± 0.02	3.0 ± 0.1

<sup>a</sup> Measured in hexane,  $\lambda_{\text{exc}} = 488$  nm (for quantum yield),  $\lambda_{\text{exc}} = 480$  nm (for lifetime),  $\lambda_{\text{em}} = 518$  nm. <sup>b</sup> Measured in  $\text{CHCl}_3$ ,  $\lambda_{\text{exc}} = 488$  nm.<sup>38</sup>

in most organic solvents and can be purified by preparative TLC on neutral alumina.

All three target compounds 1–3 have a characteristic sharp absorption maximum at 503 nm in hexane, Figure 1, originating from the BODIPY moiety. Interestingly, the absorption peaks in 1–3 do not shift upon covalent linkage of the dye to the photochromic dithienylethenes, and their positions remain unchanged compared to that of iodo-BODIPY itself. This means that attachment of the dye to the dithienylethene entity results in negligible distortion of its optical properties.

The photochemical and optical properties of 1–3 have been investigated and are reported in Table 1. The quantum yields of fluorescence are approximately half that of iodo-BODIPY, though still remaining relatively high. Attachment of the dye to a dithienylethene unit apparently provides an additional pathway for deactivation of its fluorescence. Also, the lifetimes of target compounds are half that of iodo-BODIPY, though the molar extinction coefficients are significantly higher.

Irradiation of 1–3 in hexane with 254 nm light led to new bands at 610, 603, and 550 nm, respectively, assigned to the corresponding closed-ring isomers. The changes in the absorption spectra after photoreaction

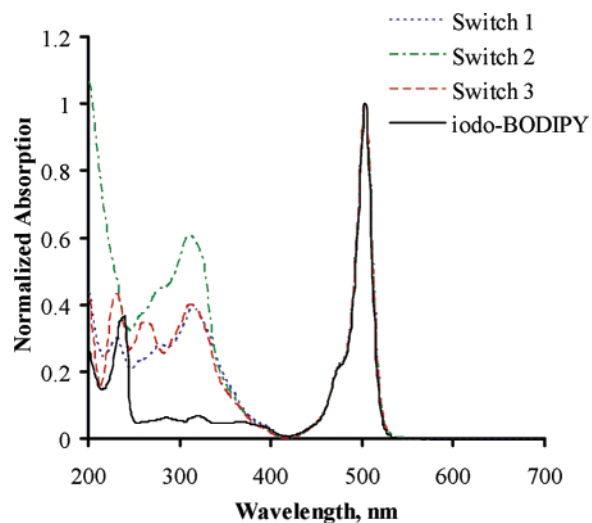
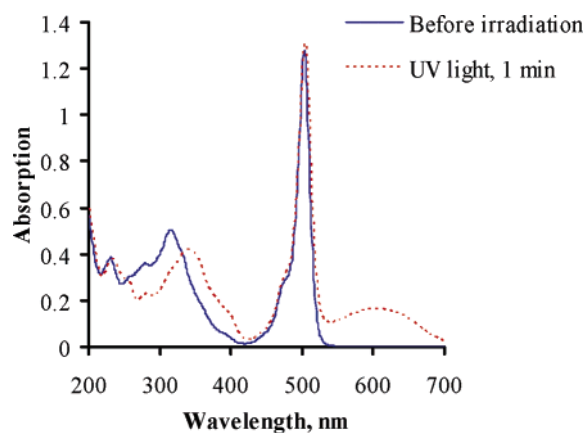


FIGURE 1. Normalized absorption spectra of compounds 1–3 and iodo-BODIPY in hexane.

result from the extended  $\pi$ -conjugation of the closed-ring isomers, Figure 2. For each compound, the photostationary state was reached after 1 min of irradiation and the



**FIGURE 2.** Absorption spectral changes of **1** ( $9.8 \times 10^{-6}$  M in hexane) before (solid line) and after (dotted line) irradiation with UV light.

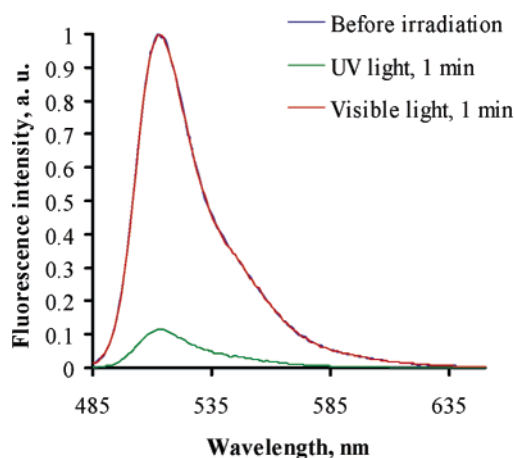
**TABLE 2. Degree of Photoconversion, Quantum Yields of Photocyclization ( $\Phi_{\text{cycl}}$ ) Reaction, and Quantum Yields of Fluorescence ( $\Phi_{\text{fl}}$ ) for Closed-Ring Isomers of 1–3**

compd	degree of photoconversion <sup>a</sup>	$\Phi_{\text{cycl}}^b$	$\Phi_{\text{fl}}$ (closed) <sup>c</sup>
<b>1</b>	0.96	0.32	0.02
<b>2</b>	0.95	0.28	0.04
<b>3</b>	0.81	0.25	0.08

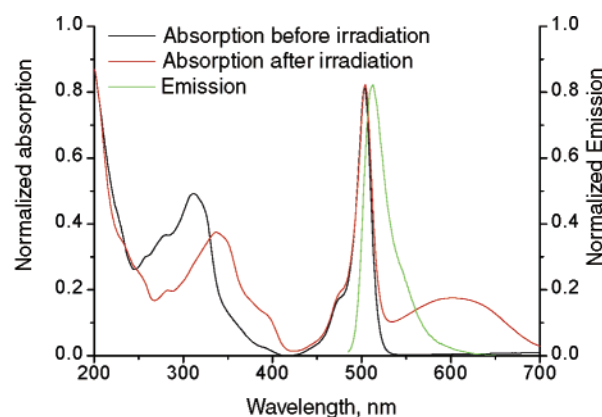
<sup>a</sup> Determined from the corresponding  $^1\text{H}$  NMR spectrum in  $\text{CD}_2\text{Cl}_2$  at room temperature. <sup>b</sup> Determined by potassium ferrioxalate actinometry at 254 nm light. Standard deviation of the experimental error:  $\pm 2\%$ .<sup>39</sup> <sup>c</sup> Measure at a photostationary state after 1 min irradiation with 254 nm light and corrected for the presence of residual open-ring isomers.

solution changed from yellow to dark-blue for **1** and **2**, and from yellow to pink for **3**. When the resulting solutions were irradiated with visible light ( $\lambda > 500$  nm) for 1 min the absorption spectra reverted to their original shapes with isosbestic points at 333 nm, 330 nm and 322 nm for **1**, **2** and **3**, respectively. Also, upon irradiation with visible light all three solutions changed colors back to yellow. The intensity of the sharp absorption peak at 503 nm, characteristic of the presence of a BODIPY moiety, did not change throughout the experiments. The conversion of **1** to the closed-ring isomer was as high as 96% at the photostationary state. Table 2 summarizes data on the degree of photoconversion, as well as on the quantum yields for the photocyclization reactions and the quantum yields of fluorescence for closed-ring isomers of 1–3.

The changes during the isomerization reaction between open- and closed-ring forms of 1–3 were followed by measuring the fluorescence spectra of both forms. Fluorescence measured after the first UV irradiation cycle showed a drastic decrease in intensity dropping to less than 11%, 19%, and 49% of the initial value for **1**, **2**, and **3**, respectively. The recovered fluorescence intensity after the first irradiation with visible light was 100%, 87%, and 100% for **1**, **2**, and **3**, respectively. The fluorescence intensity decrease and recovery for **1** is demonstrated in Figure 3. We carried out more than 20 irradiation cycles repeatedly for each compound in order to study fatigue resistance of the new switches. After 20 cycles, the recovered fluorescence was 88% for **1**, 80% for **2**, and 100% for **3**. The observed quenching of fluorescence that



**FIGURE 3.** Fluorescence spectra of **1** ( $3.0 \times 10^{-6}$  M in hexane,  $\lambda_{\text{exc}} = 480$  nm) before irradiation, at the photostationary state after UV light irradiation, and after visible light irradiation.



**FIGURE 4.** Write-read-erase wavelengths for compound **2** ( $7.9 \times 10^{-6}$  M in hexane,  $\lambda_{\text{exc}} = 480$  nm).

occurs in corresponding closed-ring isomers in the new switches 1–3 is ascribed, as expected, to the efficient intramolecular energy transfer from excited BODIPY moiety to the closed-ring forms of dithienylethene units.

The separated wavelengths of writing, reading, and erasing cycles (Figure 4) can allow control of the fluorescence intensity in a reversible manner without causing destruction in readout capability. Since the excitation wavelength (480 nm) used to measure the emission spectra is close to the range of visible light that triggers cycloreversion reaction, we performed control experiments on **2** to see if the excitation light might initiate ring-opening reaction. A solution of **2** in hexane was irradiated with 254 nm light for 2 min, followed by 10 min irradiation with 480 nm light. After each cycle, the emission spectra were taken and compared. Control experiments demonstrated a negligible effect on the emission spectra after irradiation at the excitation wavelength, which means that we do not produce open-ring isomers when taking emission spectrum of UV irradiated solution.

## Conclusions

The novel fluorescent photoswitching materials 1–3 have been synthesized and studied. Covalently linking

BODIPY dyes to photochromic dithienylethenes allows formation of new photoswitches that are highly emissive as open-ring isomers and in which the fluorescence is significantly quenched in closed-ring isomers. Moreover, photoconversion to closed-ring isomers proceeds with high efficiency. Intramolecular energy transfer from the dye to the closed-ring form of dithienylethenes is suggested to be the mechanism of fluorescence quenching that takes place after photochromic reaction. Switching of fluorescence is reversible and can be repeated many times without significant loss of its intensity. Ongoing investigations on the response time of the systems to external light and kinetic experiments are the subjects of future reports. The performance of the new photoswitches, when incorporated in a polymer matrix, is also under investigation.

## Experimental Section

The synthetic procedure of 3,3'-(3,3,4,4,5,5-hexafluoro-1-cyclopentene-1,2-diyl)bis[5-ethynyl-2-methylthiophene] (**4**) has previously been reported.<sup>9</sup> 4,4-Difluoro-8-(4'-iodophenyl)-1,3,5,7-tetramethyl-4-bora-3a,4a-diaza-s-indacene (iodo-BODIPY) has previously been reported and was synthesized according to the published procedure.<sup>40,41</sup> 3-Bromo-2-methyl-5-trimethylsilyl-ethynylthiophene and 3-(2,3,3,4,4,5,5-heptafluorocyclopenten-1-yl)-2-methylbenzo[*b*]thiophene have been synthesized and characterized previously.<sup>9,42</sup>

**3-(2-[5-Ethynyl-2-methylthien-3-yl]-3,3,4,4,5,5-hexafluorocyclopenten-1-yl)-2-methylbenzo[*b*]thiophene (**5**).** The synthesis was carried out according to the published procedure.<sup>43</sup> A solution of 3-bromo-2-methyl-5-trimethylsilyl-ethynylthiophene (154 mg, 568  $\mu$ mol) in dry THF (15 mL) was cooled to  $-78$  °C under argon atmosphere. A hexane solution of *n*-butyllithium (0.23 mL of 2.5 M solution in hexane) was added, and the mixture was stirred for 1 h. 3-(2,3,3,4,4,5,5-Heptafluorocyclopenten-1-yl)-2-methylbenzo[*b*]thiophene (193 mg, 568  $\mu$ mol) was added. The reaction mixture was stirred for 1 h at  $-78$  °C, after which it was allowed to warm to room temperature. After an additional stirring during 1 h, the mixture was diluted with THF and washed with dilute hydrochloric acid (1% v/v) and water. The organic phase was extracted with dichloromethane, and the solvent was evaporated. To deprotect the acetylene group, the residue was dissolved in a solution of NaOH in methanol/THF (4:1 v/v) and stirred for 1 h. The reaction mixture was diluted with dichloromethane, washed with water, extracted with dichloromethane, and dried over Na<sub>2</sub>SO<sub>4</sub>. After removal of the solvent, the product was purified by silica gel preparative TLC eluting with dichloromethane/hexane (1:2) to yield **5** (68 mg, 153  $\mu$ mol,

27%). **5**: mp = 75–77 °C; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  = 1.87, (s, 3H), 2.27, (s, 3H), 3.31 (s, 1H), 7.19 (s, 1H), 7.33 (m, 2H), 7.52 (d, *J* = 7.5 Hz, 1H), 7.74 (dd, *J* = 6.9, 1.8 Hz, 1H); FTIR (solid state, cm<sup>-1</sup>) 3303, 2923, 2106, 1269, 1135, 1269, 757, 656; HRMS (EI) *m/z* = 442.0273 (M<sup>+</sup>), calcd *m/z* = 442.0285.

**General Procedure for the Preparation of 1–3.** Pd<sub>2</sub>(dba)<sub>3</sub> (8 molar %, where **6** is 100 molar %) and AsPh<sub>3</sub> (80 molar %) were added to an argon-purged solution of dithienylethene and 4,4-difluoro-8-(4'-iodophenyl)-1,3,5,7-tetramethyl-4-bora-3a,4a-diaza-s-indacene **6** in Et<sub>3</sub>N/toluene (4:1 v/v). For **1**, 2-fold excess of iodo-BODIPY **6** was allowed to react with **4**. For **2**, iodo-BODIPY **6** was added along with iodobenzene to react with dithienylethene **4** in 1:1:1 ratio. For **3**, dithienylethene **5** was reacted with iodo-BODIPY **6** in a 1:1 ratio. The resulting mixture was stirred for 20 h at 45 °C. The solvent was evaporated, and the residue was filtered through a short plug of neutral alumina eluting with dichloromethane. After removal of the solvent under reduced pressure, the product was purified by neutral alumina preparative TLC using a mixture of hexane and ethyl acetate (5:1 v/v); additional neutral alumina preparative TLC was performed using a mixture of hexane and benzene (1:1 v/v) to remove residual AsPh<sub>3</sub> and yielded **1–3** as red-orange solids (yields 34–42%).

**Data for 3,3'-(3,3,4,4,5,5-hexafluoro-1-cyclopentene-1,2-diyl)bis[5-(2-(4-[(3,5-dimethyl-2*H*-pyrrol-2-ylidene- $\kappa$ N)-(3,5-dimethyl-1*H*-pyrrol-2-ylato- $\kappa$ N)difluoroboron]methyl)phenyl)-1-ethynyl)-2-methylthiophene] (**1**):** mp = 150–152 °C; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  = 1.42 (s, 12H), 1.97 (s, 6H), 2.56 (s, 12H), 5.99 (s, 4H), 7.30 (s, 2H), 7.31 (d, *J* = 8.1 Hz, 4H), 7.65 (d, *J* = 8.1 Hz, 4H); MS (MALDI) *m/z* = 1060.20 (M<sup>+</sup>), calcd *m/z* = 1060.30; HRMS (QToF) *m/z* = 1061.3141 (M + H<sup>+</sup>), calcd *m/z* = 1061.3112; UV–vis (hexane)  $\lambda_{\max}$ , nm ( $\epsilon$ ) = 279 (43 000), 315 (58 000), 503 (131 000).

**Data for 2-methyl-3-(2-[5-(2-phenyl-1-ethynyl)-2-methylthien-3-yl]-3,3,4,4,5,5-hexafluorocyclopenten-1-yl)-5-(2-[4-[(3,5-dimethyl-2*H*-pyrrol-2-ylidene- $\kappa$ N)-(3,5-dimethyl-1*H*-pyrrol-2-ylato- $\kappa$ N)difluoroboron]methyl]phenyl)-1-ethynyl)thiophene (**2**):** mp = 113–115 °C; <sup>1</sup>H NMR (300 MHz, MeOD)  $\delta$  = 1.46 (s, 6H), 1.99 (s, 3H), 2.00 (s, 3H), 2.49 (s, 6H), 6.08 (s, 2H), 7.29 (s, 1H), 7.35 (s, 1H), 7.39 (m, 5H), 7.51 (m, 2H), 7.71 (d, *J* = 8.4 Hz, 2H); HRMS (QToF) *m/z* = 815.2003 (M + H<sup>+</sup>), calcd *m/z* = 815.1972; UV–vis (hexane)  $\lambda_{\max}$ , nm ( $\epsilon$ ) = 280 (45 000), 312 (60 000), 503 (103 000).

**Data for 3-(2-[5-(2-[4-[(3,5-dimethyl-2*H*-pyrrol-2-ylidene- $\kappa$ N)-(3,5-dimethyl-1*H*-pyrrol-2-ylato- $\kappa$ N)-difluoroboron]methyl]phenyl)-1-ethynyl)-2-methylthien-3-yl]-3,3,4,4,5,5-hexafluorocyclopenten-1-yl)-2-methylbenzo[*b*]thiophene (**3**):** mp = 219–221 °C; <sup>1</sup>H NMR (300 MHz, CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$  = 1.44 (s, 6H), 1.94 (s, 3H), 2.34 (s, 3H), 2.51 (s, 6H), 6.03 (s, 2H), 7.25 (s, 1H), 7.31 (d, *J* = 8.4 Hz, 2H), 7.34 (m, 2H), 7.53 (d, *J* = 7.2 Hz, 1H), 7.62 (d, *J* = 8.4 Hz, 2H), 7.78 (dd, *J* = 6.9, 1.8 Hz, 1H); HRMS (QToF) *m/z* = 765.1817 (M + H<sup>+</sup>), calcd *m/z* = 765.1816; UV–vis (hexane)  $\lambda_{\max}$ , nm ( $\epsilon$ ) = 229 (47 000), 260 (33 000), 312 (35 000), 503 (89 000).

**Acknowledgment.** T.A.G. and D.V.K. are thankful for the fellowships from the McMaster Endowment.

**Supporting Information Available:** Synthesis of iodo-BODIPY; <sup>1</sup>H NMR, IR, UV, and emission spectra; irradiation experiments. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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