

*rillum rubrum*<sup>18</sup> indicate that Ni is not present within the Fe-S cubane core since there was no evidence for Ni-Fe interactions. Further description of the linkage "X" between Ni and iron and the structure of this complex will require comparison of the properties of biomimetic models with those of CODH and further analyses of the properties of CODH.

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## Blocked Photochromism of Diarylethenes

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Photochromic molecules with a clasp, which undergo photoisomerization only when the clasp is freed by a switch molecule, were synthesized. Photochromism has attracted renewed interest because of the recent development of fatigue-resistant compounds. A classical photochromic molecule, 6-nitrospirobenzopyran, loses its photochromic property after 30-50 coloration/decoloration cycles, while several newly synthesized molecules can maintain performance through more than 10<sup>4</sup> repetitions of the cycle.<sup>1-4</sup> Among the molecules, 1,2-diarylethenes containing heterocyclic rings have the potential ability for many applications owing to an additional characteristic, namely, the thermal stability of both isomers.<sup>5</sup> Besides fatigue resistance and thermal irreversibility, a property that is strongly desired but still lacking in existing photochromic molecules is gated photochemical reactivity.<sup>6</sup> Gated reactivity is the property that irradiation with any wavelength causes no molecular change, while a photoreaction occurs when another external stimulation, such as an electric field or chemicals, is present.<sup>7</sup> We designed and synthesized chemical-gated molecules by introducing substituents that have hydrogen-bonding ability into the 1,2-diarylethenes.

1,2-Bis(2-methylbenzo[*b*]thiophen-3-yl)perfluorocyclopentene derivatives with carboxyalkyl groups at the 6 and 6' positions, **1** and **2**, were synthesized.<sup>8</sup> The perfluorocyclopentene moiety is

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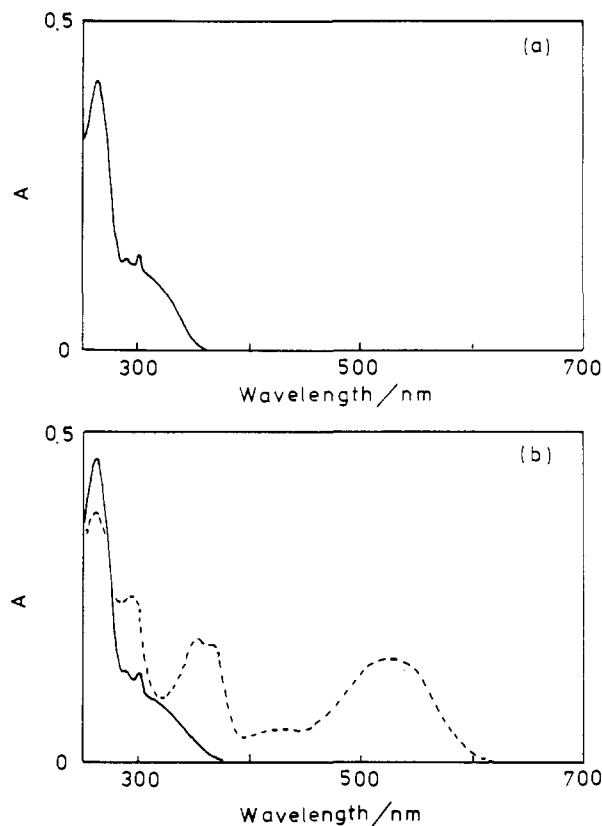
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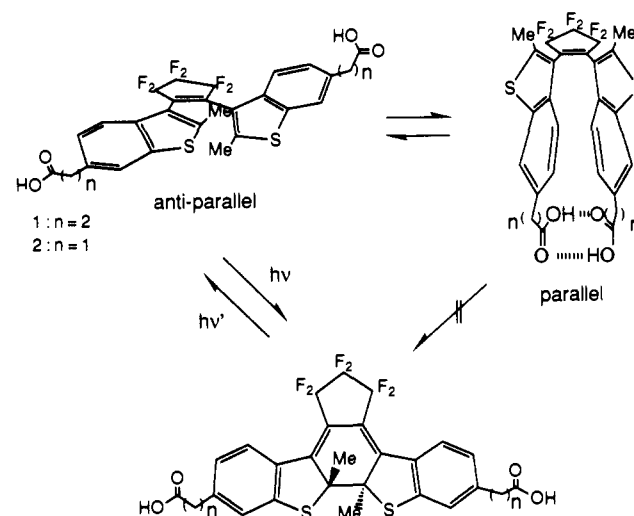
(7) Recently, a chemical-gated photochromic molecule was reported. Yokoyama, Y.; Yamane, T.; Kurita, Y. *J. Chem. Soc., Chem. Commun.* **1991**, 1722.

(8) **1**: mp 105-106 °C; <sup>1</sup>H-NMR (270 MHz, C<sub>2</sub>D<sub>5</sub>OD) δ 2.16 (3 H, s), 2.47 (3 H, s), 2.55 (2 H, t), 2.60 (2 H, t), 2.92 (2 H, t), 3.01 (2 H, t), 7.07 (1 H, d, *J* = 8.06 Hz), 7.29 (1 H, d, *J* = 8.06 Hz), 7.44 (1 H, d, *J* = 8.06 Hz), 7.56 (1 H, d, *J* = 8.06 Hz), 7.50 (1 H, s), 7.60 (1 H, s). Anal. Calcd for C<sub>29</sub>H<sub>22</sub>O<sub>4</sub>S<sub>2</sub>F<sub>6</sub>: C, 56.85; H, 3.62. Found: C, 56.78; H, 3.72. **2**: mp 219.5-220.5 °C; <sup>1</sup>H-NMR (270 MHz, C<sub>2</sub>D<sub>5</sub>OD) δ 2.21 (3 H, s), 2.49 (3 H, s), 3.62 (2 H, s), 3.71 (2 H, s), 7.14 (1 H, d, *J* = 8.18 Hz), 7.34 (1 H, d, *J* = 8.18), 7.50 (1 H, d, *J* = 8.18 Hz), 7.61 (1 H, d, *J* = 8.18 Hz), 7.59 (1 H, s), 7.69 (1 H, s). Anal. Calcd for C<sub>27</sub>H<sub>18</sub>O<sub>4</sub>S<sub>2</sub>F<sub>6</sub>: C, 55.48; H, 3.10. Found: C, 55.56; H, 3.46.



**Figure 1.** Absorption spectra of **1** ( $2.5 \times 10^{-5}$  mol/L) (—) upon irradiation with 313-nm light in (a) cyclohexane and (b) ethanol; the absorption band around 525 nm (---) is due to the closed-ring form.

## Scheme I



effective in increasing the durability of the molecules.<sup>1a</sup> The photochromic reaction of the 1,2-diarylethenes belongs to a 1,3,5-hexatriene to cyclohexadiene type reaction. According to the Woodward-Hoffmann rule based on  $\pi$ -orbital symmetries, a conrotatory cyclization is brought about by light.<sup>9</sup> When the aryl groups are heterocyclic five-membered rings, the molecule has two conformations, with the two rings in mirror and  $C_2$  symmetries,<sup>3,7</sup> and the conrotatory cyclization can proceed only from the conformation with the rings in  $C_2$  symmetry. This means that the photocyclization is prohibited if the heterocyclic rings are fixed to the mirror symmetry, or parallel orientation, while

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