Photoregulation of Fluorescence in a Porphyrinic Dithienylethene Photochrome

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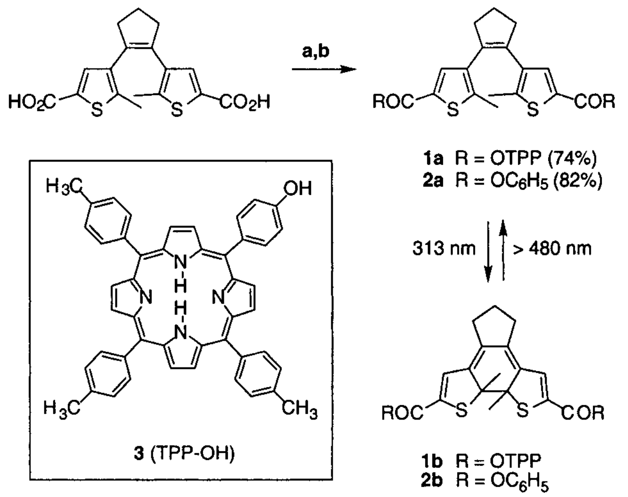
The appeal of the reversible photocyclization reactions of 1,2-dithienylethene derivatives as applied to photonic devices such as erasable memory media and optical switches lies in their being thermally irreversible, fatigue resistant, and easily monitored using UV−vis spectroscopy.[1] Applications in information processing most often hinge upon the ease of identifying both photochromic states by measuring the spectral changes close to the absorbances that trigger the photocyclization reactions. Despite its convenience and sensitivity, this detection method can ultimately result in the interconversion of the photochrome and concomitant loss of stored information. The destructive nature of tracking photochromism with UV−vis spectroscopy has encouraged the design of novel photochromic systems where information can be processed in a nondestructive manner.[2]

In many cases, the changes in the absorption spectra that occur during the photoisomerization reaction are accompanied by changes in other optical properties such as refractive index,[3] optical rotation[4,2c,e,f] and luminescence.[5,2b] Recording the changes in luminescence provides an alternative to UV−vis spectroscopy as a means to process stored information while minimizing the extent at which the information is erased during the detection event. An important condition must be met, however. The wavelengths of light used to produce the luminescence (excitation wavelengths, λ_{ex}) and the resulting emission wavelengths (λ_{em}) must reside outside the spectral regions where the photochromic reactions are induced. The ability to fine-tune the excitation wavelengths of porphyrins and the fact that they exhibit intense luminescence far into the visible region prompted us to investigate nondestructive information processing in porphyrin−dithienylethene hybrids.

We report herein the synthesis and optical characterization of a photochromic hybrid **1**, where porphyrin macrocycles are attached to the ends of the 1,2-bis(3-thienyl)cyclopentene backbone. The relationship between the luminescence intensity of the porphyrins and the state of the photoswitch (*open* or *closed*) is clearly illustrated and provides a novel information processing system. To the best of our knowledge, this is the first example of this type of porphyrinic photochrome.

Scheme 1[a]



[a] Reaction conditions: (a) $(COCl)_2$, DMF, CH_2Cl_2; (b) **3**, TEA, CH_2Cl_2 or phenol, NaH, benzene.

All photochromes used in these studies were prepared from readily available 1,2-bis(5-carboxy-2-methyl-3-thienyl)cyclopentene[6] as shown in Scheme 1. All new compounds were characterized by ^1H and ^{13}C NMR spectroscopy, UV−vis spectroscopy, and mass spectrometry. The absorption spectrum of bis(porphyrin) **1a** in the UV−vis region is essentially equivalent to the sum of the absorption spectra of the molecule's components (phenyl-functionalized photochrome **2a** and **3**) indicating there is little change in the ground state of either chromophore upon covalent linking. Irradiation[7] of **1a** at 313 nm resulted in an immediate increase in the adsorption intensity in the visible spectral region (500−625 nm) due to the appearance of the absorption bands of the *closed* isomer **1b** ($\lambda_{max} = 560$ nm for model photochrome **2b**) as shown in Figure 1. After 4 min of continuous irradiation (2×10^{-4} M, toluene-d_8), the photostationary state was reached and was identified by ^1H NMR spectroscopy as consisting of 69% of the closed isomer **1b**. The ease at which this photochemical ring closure occurs is impressive in light of the fact that porphyrins have been reported, on occasion, to inhibit photochromic processes.[8]

Irradiation of the closed isomer **1b** at wavelengths greater than 480 nm[7] resulted in the rapid ring-opening photoreaction and the regeneration of the original absorption spectrum corresponding to **1a**. The reversible photoisomerization reaction was also verified by monitoring the changes in the ^1H NMR spectrum where typical upfield shifts for the thiophene C−H signals and downfield shifts for the methyl thiophene signals were observed.[9]

The presence of the porphyrins' Soret absorption bands centered at 420 nm allows for this chromophore to be selectively irradiated in a region of the spectrum where the 1,2-(dithienyl)cyclopentene photochromic fragment of **1a** is transparent.[10] The luminescence

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[6] The 1,2-bis(5-carboxy-2-methyl-3-thienyl)cyclopentene photochrome was synthesized from the known 1,2-bis(5-chloro-2-methyl-3-thienyl)cyclopentene, see: Lucus, L. N.; van Esch, J.; Kellogg, R. M.; Feringa, B. L. *J. Chem. Soc., Chem. Commun.* **1998**, 2313. See Supporting Information for details.

[7] Standard lamps used for visualizing TLC plates (Spectroline E-series, 470 $\mu W/cm^2$) were used to carry out the ring-closing reaction of **1a** to **1b** and **2a** to **2b**. The ring-opening reactions were carried out using the light of a 150 W tungsten source that was passed through a 480 nm cutoff filter to eliminate higher energy light.

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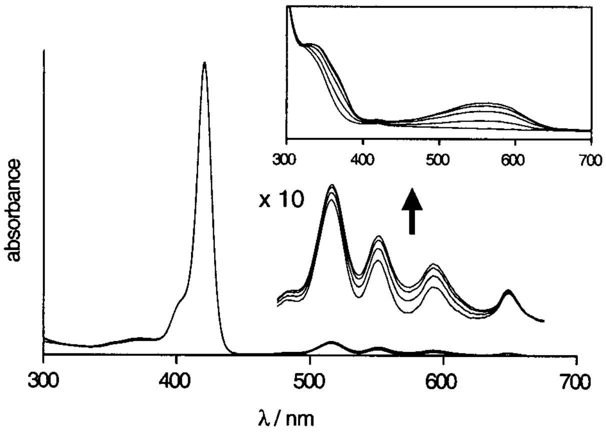

Figure 1. Changes in the UV−vis absorption spectra of a toluene solution of **1a** (2 × 10^{-6} M) upon irradiation with 313 nm light. Irradiation periods are 0, 10, 30, and 50 s. The inset shows the changes for **2a** under similar conditions.

of the porphyrin macrocycles in **1a** and **1b** greatly depends on the state of the 1,2-(dithienyl)cyclopentene photoswitch. In the *open* form (**1a**), the porphyrins display significant fluorescence intensity at 655 nm when excited at 430 nm.[11] When the photocyclization reaction was carried out by irradiating **1a** at 313 nm, the nonfluorescent[12] *closed* form **1b** was produced. Back irradiation at wavelengths greater than 480 nm regenerated **1a** and restored the original emission spectrum. The intensity of the porphyrins' fluorescence is conveniently regulated by toggling between **1a** and **1b** by alternate irradiation at 313 nm and greater than 480 nm (Figure 2), clearly demonstrating that the hybrid **1** can act as a system for reversible data processing using fluorescence as the detection method.

Extended periods of continuous irradiation (1 h) of a toluene solution of the photostationary state of **1** (2 × 10^{-6} M) with 430 nm light resulted in an increase (∼45%) in the emission intensity at 655 nm and a corresponding decrease in absorption intensity in the visible region (500−625 nm).[13] Decomposition of the photochrome can be ruled out as a cause of these spectral changes as the resulting solutions could be taken through several photochromic cycles reproducing the original UV−vis and fluoresence spectra. The spectral changes are, therefore, indicative of partial cycloreversion of **1b** to **1a**. It is unlikely that this partial ring-opening is due to the *closed* isomer **1b** absorbing light at this wavelength. This is supported by the fact that the parent photochrome **2b** displayed no observable changes in the UV−vis spectrum when irradiated at 430 nm under identical conditions.

This phenomenon was also directly observed by ^{1}H NMR spectroscopy. In this experiment, a mixture of the partially closed isomers of both **1b** and **2b** were irradiated at 430 nm. After 15 h of continuous irradiation **1b** was almost completely converted to its *open* isomer **1a**, while a minimal amount of **2b** was converted to **2a**. In light of these results, a more probable explanation for the ring-opening reaction of **1b** at 430 nm is that the porphyrins are acting as light-harvesting antennae, channeling their excited-state energy toward the photochromic center. The result of this process is the photochemical regeneration of **1a**. The extent of ring-opening is significantly less for **2b** as would be expected because the porphyrins' excited-state energy, in this case, must be transferred to photochrome **2b** through a diffusion-controlled intermolecular process. It is obvious that this process will not be able to compete significantly with its intramolecular counterpart. The interesting photochemical characteristics displayed by **1** are strikingly similar to those found in natural light harvesting systems, where the role of the porphyrins includes acting as antennae to collect and deliver their excited state energies to the reaction centers where photochemistry ultimately takes place. Systems of this type are appealing for applications where selective irradiation of one photochrome in the presence of another is desirable. The precise nature and mechanism of this process is under investigation and the results will be reported in due time.

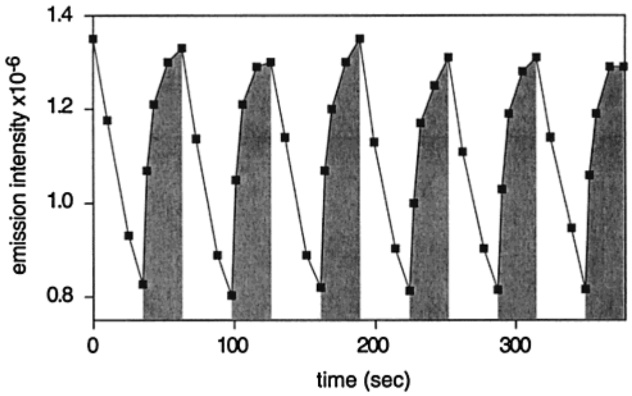

Figure 2. Modulated emission signal of a toluene solution of 1 (2 × 10^{-6} M) during alternating irradiation at 313 (unshaded areas) and >480 nm (shaded areas). All spectra were run in deoxygenated toluene (λ_{ex} = 430 nm, λ_{em} = 655 nm).

We have shown that the combination of porphyrins and dithienylethenes have potential in the area of optical information processing. We are currently optimizing the system by electronically fine-tuning both the porphyrin and dithienylethene chromophores.

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Supporting Information Available: Synthesis and characterization of compounds **1** and **2** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(10) This claim is based on a comparison of the absorption spectra of model compounds **2a**, **2b**, and **3**.

(11) The monochromator of the fluorescence spectrophotometer (1 mm slit) was employed (65-W Xenon lamp).

(12) The *closed* form **1b** was isolated in 98% purity (2% residual *open* isomer **1a**, see Supporting Information). This sample displayed 2−3% fluorescence intensity relative to **1a** (λ_{excit} = 430 nm, λ_{em} = 655 nm) indicating that **1b** is nonfluorescent.

(13) See Supporting Information.