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Synthesis and Characterization of Coumarin-Based Spiropyran Photochromic Colorants

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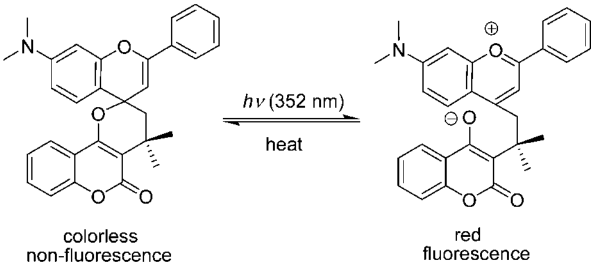
ABSTRACT



Two coumarin-based spiropyran derivatives were synthesized and characterized in two steps to explore their photochromic properties. Both prepared compounds are sensitive to UV light and change colors upon irradiation. The resulting photogenerated zwitterions revert to the original compounds while being heated. A new family of organic photochromic colorants is introduced.

Photochromism[1] refers to a reversible phototransformation of a chemical species between two forms having different absorption spectra. Compounds with photochromic properties may have a wide range of applications in the area of photonic materials[2] and optical memory devices.[3] The most well-known organic photochromic colorants include spiropyrans,[4] spirooxazines,[5] chromenes,[6] fulgides,[7] and diarylethenes.[8] While modifications of the existing photochromes may still generate compounds with unprecedented properties, development of new classes of organic photochromic dyes with novel molecular scaffolds as suitable materials for aforementioned applications remains desired. Recently, we reported a new family of photochromic colorants with a coumarin-based oxazabicycle as the molecular skeleton.[9] Here, we describe our efforts in the synthesis and characterization of two

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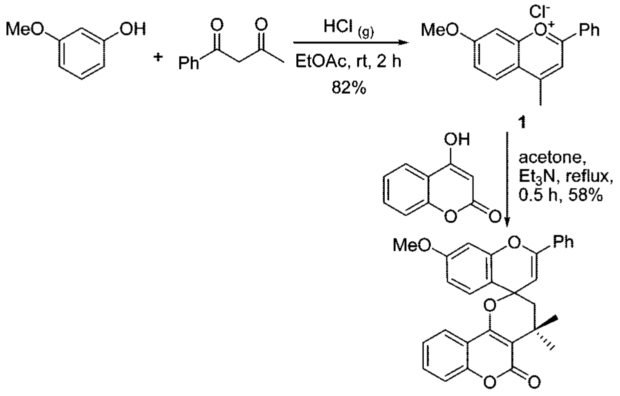
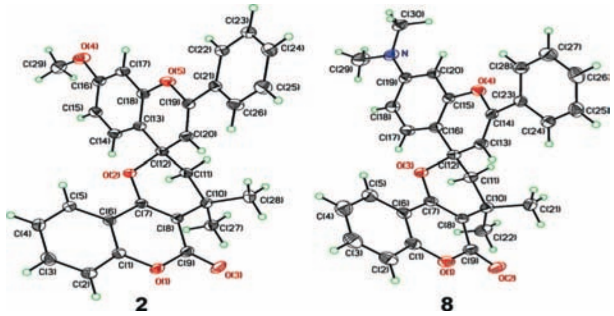
coumarin-based spiropyran derivatives and subsequent exploration of their photochemical properties. The photochemical interconversions between the ring-closed spiropyrans and the proposed photogenerated ring-opened zwitterionic species were investigated by UV−vis spectroscopy, conductivity, and fluorescence measurements.

Scheme 1



2

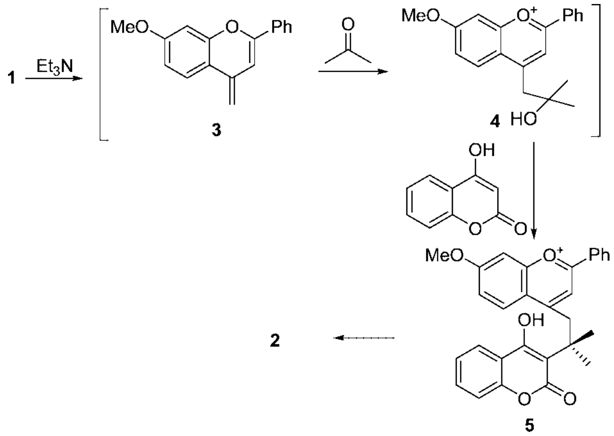
Scheme 1 shows the two-step preparation of coumarin spiropyran **2**. It started with an acid-mediated condensation[10] of *m*-methoxyphenol and benzoylacetone to form a green flavylium salt **1**, followed by a three-component coupling with 4-hydroxycoumarin in the presence of triethylamine in acetone under reflux conditions to afford the target compound **2**. The structure of **2** was confirmed by ^{1}H and ^{13}C NMR studies as well as by single-crystal X-ray diffraction analysis as presented in Figure 1, which clearly reveals a spiropyran skeleton. Scheme 2 depicts the proposed mechanism for this three-component reaction. It involved first deprotonation of flavylium salt **1** by triethylamine to give 7-methoxy-4-methylene-2-phenyl-4*H*-chromene (**3**) followed by reaction with acetone to afford the alcohol **4**. The subsequent coupling of **4** with coumarin yielded **5**. Final cyclization of **5** furnished the coumarin spiropyran **2**.



2 **8**

Figure 1. XRD structures of **2** and **8**.

Scheme 2



Upon ultraviolet (352 nm) irradiation, compound **2** changed from colorless to green within seconds. Figure 2 shows the UV−vis absorption spectra of **2** in methylene chloride with different irradiation times. With the increase of exposure time (352 nm), three new absorption bands with peak wavelengths around 400, 593, and 710 nm gradually increased, along with three isosbestic points (261, 323, and 368 nm). Although isolation and characterization of the photogenerated product proved to be difficult, it exhibits a green color, which corresponds to the chromophore of the green flavylium ion **1**. This observation prompted us to tentatively propose the ring-opened zwitterionic species **6** as the photogenerated product (Scheme 3). This proposed organic zwitterionic species **6** can cyclize back to **2** while being heated. In addition to imposing absorbance changes of spiropyran **2** in the visible region upon irradiation, the pronounced structural modifications associated with this photoinduced transformation translate also into significant dipole moment and molecular polarizability alterations. For instance, Figure 3 shows a linear relationship between the irradiation time and conductivity of **2** in acetonitrile at room temperature, indicating a proportional increase in conductivity when it is excited by UV light. However, increasing the concentration of **2** in acetonitrile without UV irradiation does not affect

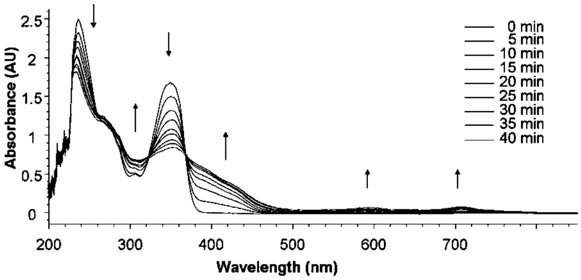


Figure 2. Absorption spectra of **2** (2.5×10^{-4} M in CH_2Cl_2) obtained with different exposure times (352 nm), 0−40 min, in 5 min increments.

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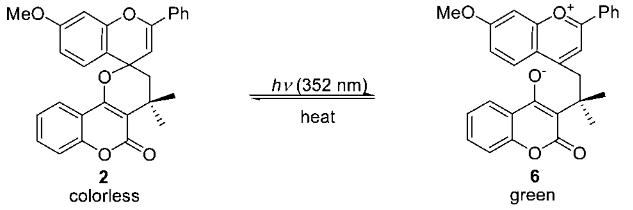
Scheme 3



the conductivity. This result not only provides the indirect evidence to support the zwitterionic structure of **6** but also suggests that conductivity may serve as a second output property of **2**, in addition to a distinct change in color.

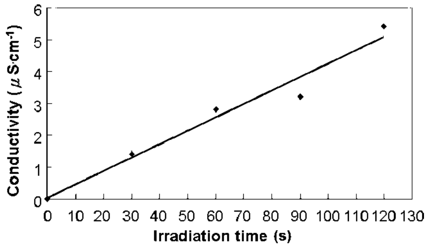
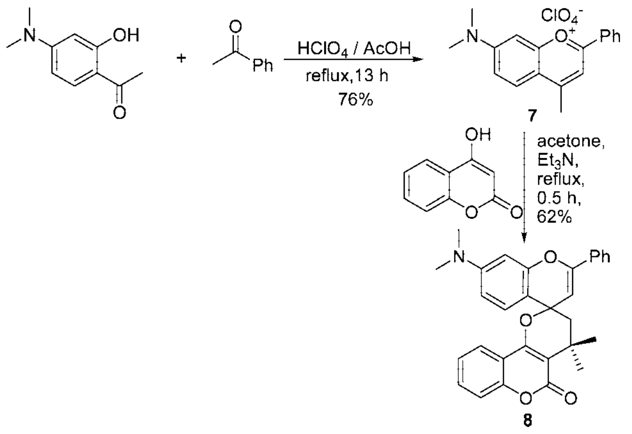


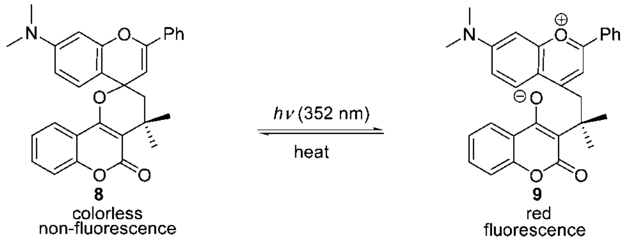
Figure 3. Time-dependent changes in conductivity of **2** (5 mM in MeCN) under UV light (352 nm).

Fluorescence emission is considered to be one of the most attractive signal outputs of switching materials owing to its high sensitivity, easy detection and low-cost procedure.[11] In an effort to integrate both photochromic and fluorescent functions into this coumarin-based spiropyran system, we introduced an *N*,*N*-dimethylamino group onto the 4*H*-chromene ring to increase the emission intensity of the photogenerated zwitterionic species. The designed compound **8** was prepared by the similar procedure as that of **2**, except that the starting materials *m*-methoxyphenol and benzoylacetone were replaced with 4-*N*,*N*-dimethylamino-2-hydroxyacetophenone[12] and acetophenone, respectively (Scheme 4). The crystal structure of **8** is depicted in Figure 1, which confirms a desired *N*,*N*-dimethylamino group at the 7-position of 4*H*-chromene moiety.

Scheme 4



Scheme 5



Upon ultraviolet irradiation (352 nm), the spiropyran **8** changed from colorless to red (Scheme 5). With the increase of exposure time (352 nm), a new absorption band with the peak wavelength around 520 nm gradually increased, along with a clear isosbestic point at 274 nm (Figure 4). The absorbance at 520 nm, which resembles to the chromophore of the red flavylium ion **7**, showed a smooth, continuous growth and reached a plateau in approximately 80 min, indicating the stationary conversion to the proposed zwitterionic species **9**. Figure 5 shows the fluorescence spectra of the nonfluorescent **8** obtained with different exposure times (352 nm) in methylene chloride. To our delight, the emission intensity increases with the increase of irradiation time. The zwitterionic species **9** is indeed fluorescent as expected. When heated at 90 °C in toluene, this photogenerated ring-opened form **9**thermally decays away with the disappearance of the 520 nm band with the reverse rate constant of 2×10^{-4} s^{-1}, along with the decrease of emission intensity (see

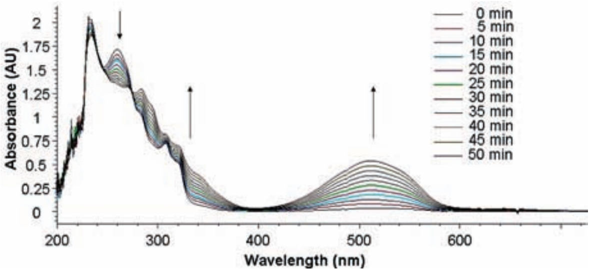


Figure 4. Absorption spectra of **8** (6.1×10^{-5} M in CH_2Cl_2) obtained with different exposure times (352 nm), 0−50 min, in 5 min increments.

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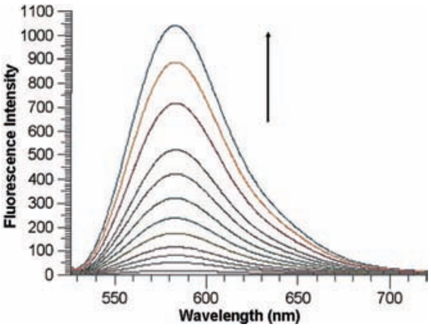

Figure 5. Emission spectra of **8** (1.5×10^{-6} M in CH_2Cl_2) obtained with different exposure times (352 nm), 0−55 min, with 5 min increments.

the Supporting Information for details). Upon UV irradiation of the colorless product, the photoproduct turned red again with the appearance of the 520 nm band characteristic for **9**. Although the photochromic interconversion between **8** and **9** is currently limited to four cycles due to the occurrence of side reactions, the photochromic property of these spiropyrans can presumably be modulated or fine-tuned by incorporating different substituents on the 4*H*-chromene or coumarin moieties.

To gain further insight to this light-induced ring-opening mechanism, the molecular simulation of **8** utilizing the density function theory (DFT) method at the B3LYP/6-31G* level[13] was carried out. According to the calculation, the electron density of HOMO is mainly located on the *N*,*N*-dimethylamino-4*H*-chromene moiety. Conversely, the electron density is transferred to the coumarin group in the LUMO (Figure 6). The net change of the electron density during the HOMO → LUMO transition upon UV irradiation is expected to cause the C−O bond weakening and consequently cleavage, leading to the colored ring-opened zwitterionic species **9**.

In summary, two coumarin-based spiropyran derivatives were efficiently synthesized in a two-step, three-component reaction to study their photochromic properties. We have demonstrated that the absorption property of **2** and the emission property of **8** can be controlled by UV irradiation. The present work introduces a new molecular scaffold with photochromic property. Further investigations for the development of more sophisticated systems based on the same molecular skeleton for colorimetric or fluorescent ion-sensing and other applications are in progress in our laboratory.

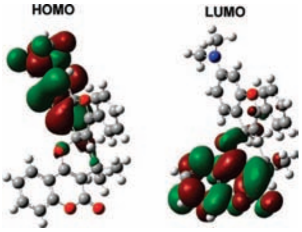

Figure 6. HOMO/LUMO of **8**.

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Supporting Information Available: Synthesis of compounds **2** and **8**, experimental details, and additional spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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