
*Communication***Photochromic dye-sensitized solar cells**

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Abstract: We report the fabrication and characterization of photochromic dye sensitized solar cells that possess the ability to change color depending on external lighting conditions. This device can be used as a “smart” window shade that tints, collects the sun’s energy, and blocks sunlight when the sun shines, and is completely transparent at night.

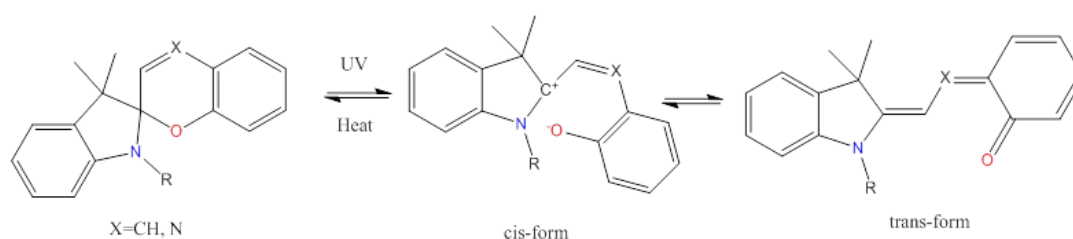
Keywords: DSSC; dye sensitized solar cell; photochromatic; spiro

1. Introduction

Solar power is the largest renewable energy resource, and the demand for higher solar power capacity is increasing every year. In urban areas, considerable surface areas of the sides and windows of buildings are not utilized for light absorption. These surface areas can be covered with solar cells that are completely transparent and colorless at night and function similar to photochromic sunglasses, to provide for the best view. The cells act as window shades during the day by tinting the glass and absorbing a section of the visible range of sunlight to generate electric power.

There are a few classes of organic compounds that exhibit this photochromic property—diarylethenes [1–4], azas [5], spiropyrans [6,7,8], and spirooxazines [9,10]. Spiropyran and its derivatives with the spirooxazines are among the most studied organic compounds in this group, with high stability and broad visible light absorption, so these compounds were chosen for study in this work.

Both spiropyrans and spirooxazines have the same mechanism of color change. When in the dark, these compounds have a closed ring conformation, which breaks into an extended chain conformation when exposed to UV light. In the closed spiro form, the two conjugated systems are separated by an sp^3 -hybridized carbon. Once opened into the merocyanine form, they are connected to form an extended π system, allowing for the absorption of visible light. They can then relax back into the closed ring structure with time and ambient heat (Scheme 1) [11]. The rate of this transformation is retarded when the compounds are trapped in a rigid solid matrix such as a polymer system. However, the transformation occurs when the compounds are provided with physical space for their molecular expansion [10].



Scheme 1. Mechanism of spiropyran/spirooxazine color change.

With this in mind, we absorbed spiropyrans and spirooxazines onto a thin and transparent mesoporous titanium dioxide photoanode, to act as the sensitizer in a dye-sensitized solar cell (DSSC) [12]. Originally discovered in 1991 by Grätzel, DSSCs have exhibited remarkable robustness, with a wide variety of sensitizers, substrates, electrolytes, and electrodes [13–16]. Organometallic-based dyes, such as the ruthenium-based N719 dye, have been used widely [17], as well as many organic cells that avoid the use of rare earth metals [18,19,20].

In this work, we report the fabrication and characterization of DSSCs, with the sensitizing unit being composed of a spiropyran moiety. This cell exhibits the ability to change color depending on ambient light conditions, and therefore it has the potential to be used as a solar cell to be installed on windows. In the process of preparing this publication, we noticed the recent publication of a DSSC based on another photochromic compound with a similar concept, so the references are cited here [21,22].

2. Materials and Method

The solar cells were prepared according to the procedure described previously [23]. A titanium dioxide paste was purchased from Solaronix (Ti-Nanoxide T/SP). The paste was then doctor bladed onto FTO glass (Hartford Glass, 7 Ω/\square) and sintered at 500 $^{\circ}\text{C}$ for 1 h and cooled to 80 $^{\circ}\text{C}$, at which point it was immersed in the respective dye solutions (0.5 mM in methanol) for 48 h. Next, the photoanode was rinsed with ethanol and dried. The cell was completed by sandwiching an electrolyte solution consisting of 0.5 M lithium iodide (Aldrich 99.9%) and 0.05 M iodine (Aldrich 99%) in an acetonitrile together with the photoanode and a counter electrode. The cathode was prepared by spin coating 50 μL of a 5 mM solution consisting of chloroplatinic acid hydrate (Aldrich, 99.9%) in 2-propanol (Aldrich, 99%) onto

FTO glass (Hartford Glass, $15 \Omega/\gamma$) and annealing at 400°C for 40 min. The cells were assembled using standard published procedures [24]. The photoanode thickness, determined by SEM was $13 \mu\text{m}$ (see Supporting Information). The solar cells were tested with a Gamry Reference 600 potentiostat, using a 300 W Xe lamp and 0.25 cm^2 mask, filtered to 1.5 AM (100 mW cm^{-2}). It should be noted that the efficiencies of the DSSCs were lower than what is reported for state-of-the-art DSSC and there are several reason. Firstly, our DSSCs contain no additives to boost performance. For instance, with the addition of 4-*tert*-butylpyridine (TBP), previous work has shown that DSSCs achieve efficiencies of 8.5% but without TBP cell efficiency drops to 3.7% [25]. Secondly, our fabricated DSSCs did not contain a compact TiO_2 layer in between the photoanode and FTO, which is known to improve performance by reducing the number of reaction sites for the recombination of triiodide with electrons on the bare FTO. Adding a compact layer has been shown to improve efficiency by up to 33.3% [26]. Third, they did not contain a scattering layer, which can enhance the efficiency by up to 30% [27], mainly by improving light harvest efficiency, thereby improving J_{sc} . Fourth, the DSSC here did not undergo a TiCl_4 post-treatment of the TiO_2 layer, which normally improves the current density by roughly 18% without affecting the open-circuit voltage [28]. The additives and other treatments are optimized for ruthenium based DSSCs and not for this novel class of photochromic dyes. By not including these enhancements, we are isolating and only comparing the effect of the dye molecule on the performance of the DSSC without any unwanted interference.

The first attempted photochromic solar cell was made using the compound known as “Oxford Blue,” (1) shown in Figure 1. This spirooxazine is a product of Keystone Inc. (Chicago, IL), and can be prepared according to an existing procedure [29].

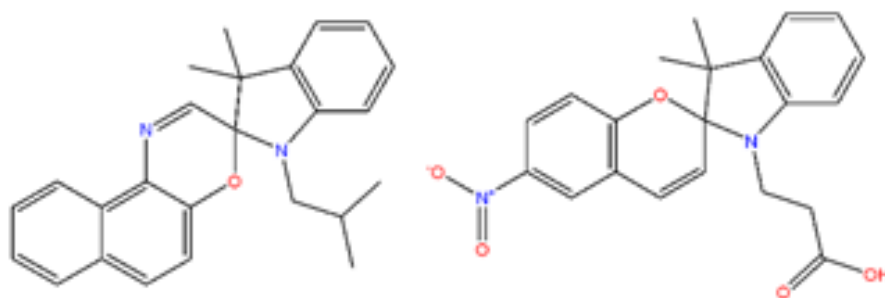


Figure 1. Left: 1-isobutyl-3,3-dimethylspiro[indoline-2,3'-naphtho[2,1-b][1,4]oxazine] (1); Right: 3-(3',3'-dimethyl-6-nitrospiro[chromene-2,2'-indolin]-1'-yl)propanoic acid (2).

In our first approach, the TiO_2 layer on the FTO anode on the glass was soaked in a dye solution of CH_3CN for 48 h. Then the glass was rinsed with methanol twice and dried before a measurement was made. As is seen in Figure 1, the photocurrent is very small at around 0.08 mA/cm^2 . Diffusion of 1 due to the lack of an anchoring group to bind to the TiO_2 photoanode is a likely cause for the low current. We believe that most of the dye was rinsed off the TiO_2 surface and therefore, little photocurrent was generated when the device was exposed to sunlight.

The lack of an anchoring group necessitated the use of a spray-coated epoxy polymer layer to minimize molecular diffusion [30]. In a modified approach, the dye solution was dropped on the TiO₂ layer and dried after the solvent was evaporated. A thin, uniform layer of the dye was noticeable on the TiO₂ that changed to a blue color when the coating is exposed to sunlight (Figure 2). To avoid the diffusion of the dye into the electrolyte solution, a thin layer of epoxy polymer in ether was spray coated on the top of the dye film. After the epoxy layer was solidified, a DSSC device was prepared for photocurrent test. The results were similar to those without using the epoxy coating. We believe that the epoxy coating limited mass transport of the triiodide/iodide redox couple and the dye was unable to regenerate itself. Furthermore, the low efficiency is expected because the epoxy layer cannot completely block the diffusion of the dye into the electrolyte. This was evidenced from the gradual color change of the electrolytes and the loss of the capability to generate electricity of the cell. Therefore, modifications were deemed necessary to improve efficiency. The main issue seen before was absorption to the surface, so a modified form was chosen with carboxylic acid functionality that can adhere to the titanium dioxide substrate (Figure 1). Therefore, compound 2 was synthesized according to an existing procedure [11,31].

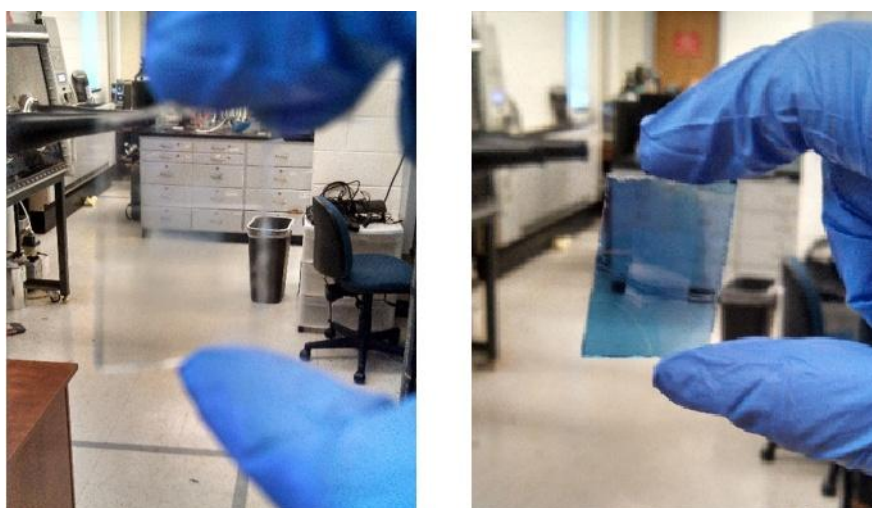


Figure 2. Color change of the dye on the TiO₂ film before (left) and after (right) exposure to sunlight.

Table 1. Solar cell performance.

Dye	J_{sc} (mA/cm ²)	V_{oc} (mV)	Fill Factor (%)	η (%)
N719	4.12	760	63	1.9
(1)	0.08	208	41	0.007
(2)	0.10	490	55.9	0.028

The solar cell using dye (2) was transparent through most of the visible region, which was the goal of this overall project (Figure 2). The solar cell based on dye (2) showed a

significant improvement with a conversion efficiency (Table 1) of 0.028%, 4 times greater than dye (1), with the reference cell using N-719 [32] achieving a conversion efficiency of 1.9% under the same conditions (Figure 3). We were unable to do IPCE of dye (1) and (2) due to the low current values. This indicates a usable efficiency from the carboxylic attachment to the titanium dioxide substrate. As a comparison, we fabricated a dye-free, bare TiO_2 DSSC which showed no clear J-V behavior (Figure 4s).

Although the efficiency is much improved, it is still very low. Most of the losses come from a reduction in the short circuit current and a decrease in the open circuit voltage. The low photocurrent can be partially attributed to a low absorption of solar radiation as seen in Figure 3. It is also possible that the HOMO and LUMO of the dyes are not well aligned with the conduction band of TiO_2 and the redox potential of iodide/triiodide. Poor alignment would make charge injection inefficient and also limit dye regeneration. Furthermore, it is known that the open-circuit voltage is determined by the difference between the redox potential and the TiO_2 fermi energy level. Since not many electrons are generated, the fermi energy level is closer to the valence band rather than the conduction band of TiO_2 . This decreases the energy difference between the fermi level and the redox potential and can be a possible reason for the lower open-circuit voltage seen in dyes (1) and (2).

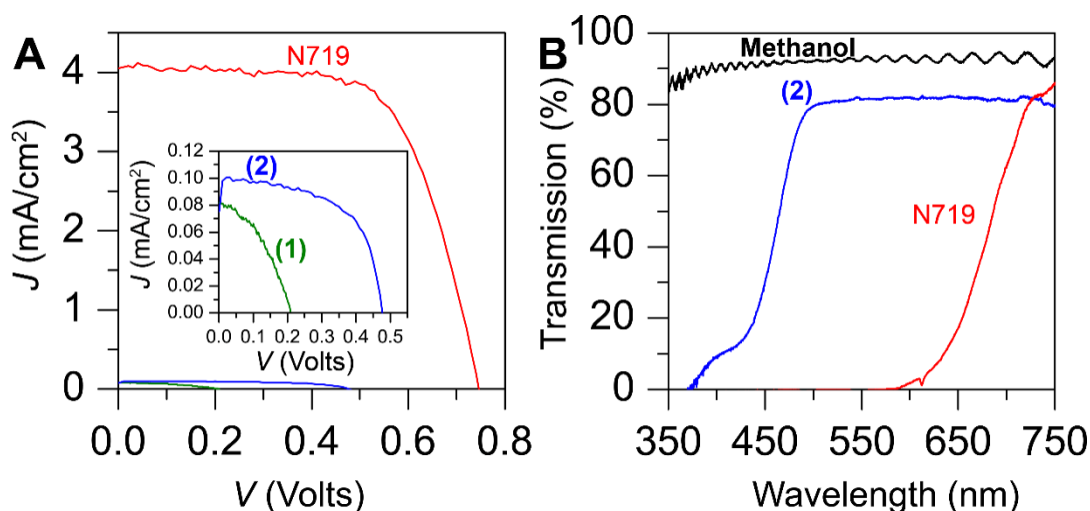


Figure 3. (A) J-V behaviour for DSSCs fabricated using N719 (red), dye 1 (green), dye 2 (blue). (B) UV-vis absorption comparing dye 2 and a reference N719 dye solution.

3. Conclusion

We have successfully synthesized and assembled photochromic dye-sensitized solar cells using a spiropyran moiety as the light-sensitizing compound. This compound showed color changes which allow for diurnal variability, making it potentially useful as a solar panel for windows. We believe that the photochromic dyes can be modified to obtain a higher photocurrent by taking better advantage of the solar spectrum and by more effectively injecting excited electrons into the TiO_2 photoanode.

Conflict of Interest

The authors declare no conflict of interest in this paper.

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