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# Photoelectric Conversion from a Hemicyanine Dye Containing Zinc Complex in a Langmuir–Blodgett Film

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# Photoelectric Conversion from a Hemicyanine Dye Containing Zinc Complex in a Langmuir–Blodgett Film

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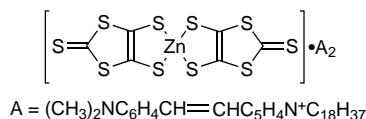
A cathodic photocurrent was obtained from a hemicyanine dye containing zinc complex;  $[(\text{CH}_3)_2\text{NC}_6\text{H}_4\text{CH}=\text{CHC}_5\text{H}_4\text{NC}_{18}\text{H}_{37}]_2\text{Zn}(\text{dmit})_2$  (where  $\text{dmit} = 4,5\text{-dimercapto-1,3-dithiole-2-thione}$ ), modified  $\text{SnO}_2$  electrode by Langmuir–Blodgett (LB) technology in a 1 M KCl electrolyte solution. The action spectrum conforms to the absorption spectrum very well indicating that the monomers on the surface of the electrode are responsible for the photocurrent generation. Some factors which may affect the observed photocurrent such as the bias voltage, the concentration of donor or acceptor in the electrolyte solution, pH value, and light intensity have been investigated. Data show that the quantum yield is 2-fold increased when a conductive zinc complex anion is used with the LB films to replace the  $\text{I}^-$  in the molecule of  $(\text{CH}_3)_2\text{NC}_6\text{H}_4\text{CH}=\text{CHC}_5\text{H}_4\text{NC}_{18}\text{H}_{37}\text{I}$ , so that this kind of compound can be evaluated as a promising photoelectric conversion material.

## Introduction

In biological systems, molecules organize themselves into complex functional entities with cooperating components of molecular dimensions. For instance, well-organized molecular assemblies in lipid bilayer membranes play an important role in the photosynthetic process of plants and bacteria.<sup>1</sup> As for photosynthesis, solar energy harvested by antenna pigments is funneled to spatial pairs in the reaction centers (RCs), where multistep electron transfer reactions proceed to separate electron-hole pairs far apart across the lipid bilayer membrane. To design an artificial photosynthetic molecular system for solar energy conversion,<sup>2</sup> it is of great interest to mimic the elaborate machinery for the light harvesting, the charge separation and catalytic multi-electron oxidation of water and reduction of  $\text{CO}_2$ . On the basis of the consideration of structure and function of the asymmetric spatial arrangement of electron donor and acceptor in the charge separation unit, a Langmuir–Blodgett (LB) film is one of the most appropriate artificial materials by which the spatial arrangement of the various functional moieties across the film can be constructed readily at molecular dimensions.

Hemicyanine dyes are a class of well-known nonlinear optical materials for their large second-order molecular hyperpolarizabilities.<sup>3</sup> The photochemical and photophysical properties of hemicyanine dyes have been studied extensively.<sup>4</sup> However, to our knowledge, the reports about their photoelectrochemical properties are very few

## Scheme 1. The Formula of SS



except for one,<sup>5</sup> where they doped a hemicyanine dye containing a large rare earth complex anion into a bilayer lipid membrane (BLM) system and obtained a considerable photocurrent.

The complex of a transition metal and sulfur-containing ligand,  $\text{dmit}$  ( $\text{H}_2\text{dmit} = 4,5\text{-dimercapto-1,3-dithiole-2-thione}$ ), is known as an electron acceptor which has been adopted in conductive LB films recently.<sup>6</sup> Since  $\text{Zn}(\text{dmit})_2$  was a good conductor in LB films,<sup>7</sup> in the present study, the photoelectrochemical properties of a hemicyanine containing  $\text{Zn}(\text{dmit})_2$  (SS, see Scheme 1) were studied by using a Langmuir–Blodgett technique to deposit SS on a  $\text{SnO}_2$  electrode and a high photocurrent was obtained when the film was illuminated. The quantum yield is about 0.9% in 1 M KCl electrolyte solution under  $-100$  mV bias voltage. Dependencies of the photocurrent on some factors which may affect the observed photocurrent were investigated, and a probable mechanism of the electron transfer for the present system will also be discussed.

## Experimental Section

**Materials.** The synthesis of SS was reported elsewhere.<sup>8</sup> Methyl viologen diiodide ( $\text{MV}^{2+}$ ) was synthesized by reaction of 4,4'-dipyridyl with excess methyl iodide in refluxing ethanol for 6 h. The product was filtered and washed by ethanol at least four times and passed NMR analysis. The pure water was in-house deionized water purified by passing through a EASYpure RF compact ultrapure water system (Barnstead Co. USA). All other reagents were of analytical grade and were used without further purification except hydroquinone (HQ) recrystallized from water before use. AA represents ascorbic acid.

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**$\pi$ -A Isotherms and Film Deposition.** The monolayers of SS were formed by dropping its  $\text{CHCl}_3$  solution ( $\sim 0.5 \text{ mg/mL}$ ) on a pure water subphase ( $20 \pm 1^\circ \text{C}$ , pH 5.6) in a British NIMA Technology Langmuir-Blodgett Model 622 trough. Transparent  $\text{SnO}_2$  glass substrates with a lateral resistance of  $50 \Omega$  were hydrophilically pretreated. The LB films were fabricated by dipping the substrate into the aqueous subphase and raising at a rate of  $5 \text{ mm/min}$  with a moderate surface pressure at  $30 \text{ mN/m}$ . The multiple layers are deposited in Y-type mode. The up transfer ratios were about 1 and the down transfer ratios were about 0.90.

**Electrochemical Measurements.** A conventional three-electrode setup with a  $0.8 \text{ cm}^2$  effective contact area was used for all irradiation experiments. The film-modified  $\text{SnO}_2$  glass was used as a working electrode (WE), a Pt electrode as a counter electrode (CE), and a Ag/AgCl electrode as a reference electrode (RE). The electrolyte solution for the measurement of photocurrent was  $1 \text{ M KCl}$  aqueous solution. Other electrolyte solution for electrochemical measurement was the "Brinton-Robinson" buffer solution (pH 2–10) containing  $1 \text{ M KCl}$ . All measurements were made at room temperature on a Model 600 Voltammeter Analyzer (CH Instruments, USA). The different concentrations of donor or acceptor in electrolyte solution are obtained by adding solid sample into the solution directly.

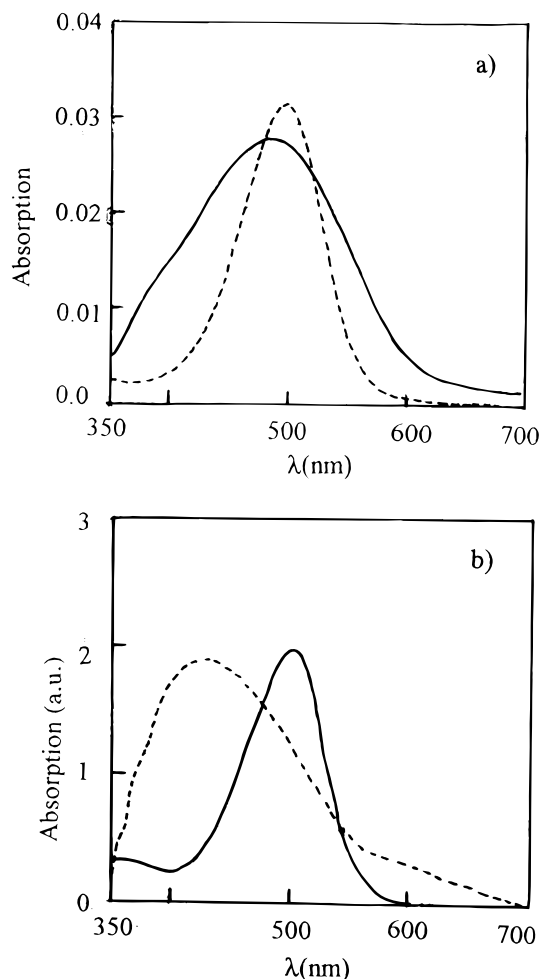
**Photochemical Experiments.** A 500 W xenon lamp (Ushio Electric, Japan) was used as the excitation source for the photochemical experiments. Different wavelengths were obtained by using various filters with a certain bandpass, for instance, the absorption centered at  $450 \text{ nm}$  (Toshiba KL-45, Japan) with a half bandpass of  $15 \text{ nm}$ . The intensity of the incident beam was checked by a Model LM-91 Photopower meter (National Institute of Metrology, Beijing, China). The IR light was filtered for all the experiments with a Toshiba IRA-25S filter (Japan).

**Spectroscopic Measurement.** The UV-vis spectra were recorded on a Shimadzu UV-3100 spectrometer (Japan).

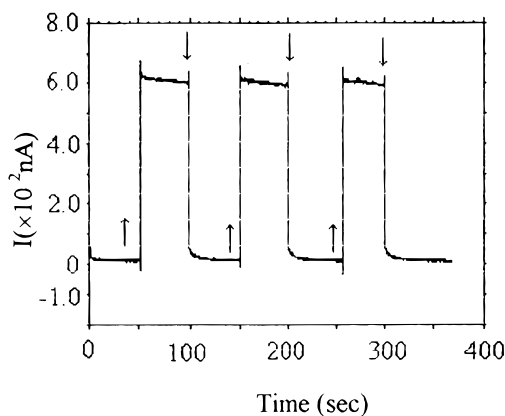
## Results and Discussion

**Characterization of SS- $\text{SnO}_2$  Electrode.** Figure 1a shows the absorption spectra of SS in  $\text{CHCl}_3$  solution and on a  $\text{SnO}_2$  substrate. From it, one can see that the maximum absorption of SS in  $\text{CHCl}_3$  centers at  $495 \text{ nm}$ , which may be attributed to the  $\pi \rightarrow \pi^*$  transition band of the hemicyanine chromophores. The absorption peak blue-shifts to  $480 \text{ nm}$  when SS is transferred onto  $\text{SnO}_2$  electrodes; the shift is very small and the absorption position is typical for hemicyanine monomer species.<sup>9</sup> Comparing the two absorption spectra, SS on  $\text{SnO}_2$  electrodes shows a broader absorption. This may be due to the different environments of the two states. In comparison, the absorption spectra of an iodide compound with the same hemicyanine cation as SS,  $(\text{CH}_3)_2\text{NC}_6\text{H}_4\text{-CH=CH-C}_5\text{H}_4\text{N}^+\text{C}_{18}\text{H}_{37}\text{I}^-$  (SI) in  $\text{CHCl}_3$  solution and in LB films are also studied and shown in Figure 1b. It can be seen that the absorption maximum of SI in LB film further blue-shifts to about  $415 \text{ nm}$ , the peak position lies between those of the typical H-aggregate ( $405 \text{ nm}$ )<sup>9</sup> and the monomer. This indicates that the replacement of the iodide anion in hemicyanine can substantially reduce the H-aggregation formation tendency, because the large zinc complex can act as both counterion and spacer, in agreement with our earlier studies.<sup>3,8</sup>

**Photocurrent Generation from a SS- $\text{SnO}_2$  Electrode.** A steady cathodic photocurrent ranging from  $450$  to  $830 \text{ nA}$  can be obtained from the SS monolayer modified electrode when it is irradiated by white light under  $40 \text{ mW/cm}^2$  light intensity in  $1 \text{ M KCl}$  electrolyte solution. Through tens of times switching on and off, the photo-



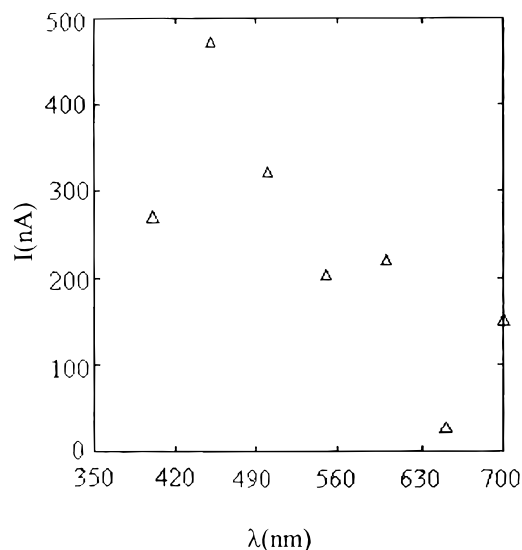
**Figure 1.** (a) Absorption spectra of SS in  $\text{SnO}_2$  electrode (—) and in  $\text{CHCl}_3$  solvent (---). (b) Absorption spectra of SI in  $\text{SnO}_2$  electrode (---) and in  $\text{CHCl}_3$  solvent (—).



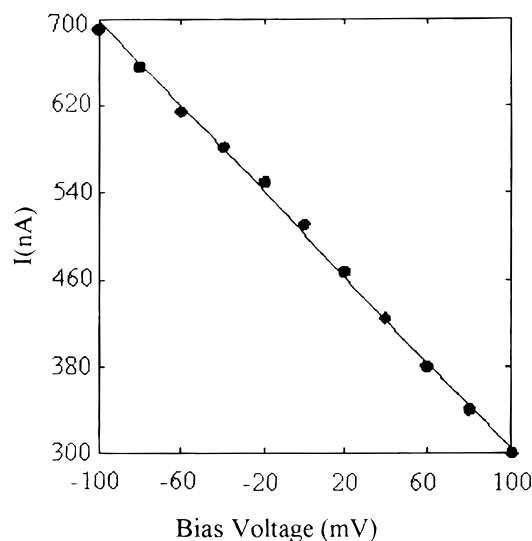
**Figure 2.** Photocurrent generation from SS- $\text{SnO}_2$  electrode upon irradiation of white light at  $40 \text{ mW/cm}^2$  ( $\uparrow$  represents light switching on and  $\downarrow$  represents light switching off).

electric response was very stable as shown in Figure 2. About  $472 \text{ nA}$  photocurrent can be obtained under  $1.8 \times 10^{16} \text{ photons/cm}^2\cdot\text{s}$  at  $450 \text{ nm}$  in  $1 \text{ M KCl}$  electrolyte solution with zero bias voltage. The attainment of  $472 \text{ nA}$  photocurrent means that the quantum yield, which is cited per absorbed photon, is about  $0.68\%$  for the monolayer SS modified electrode (the absorbance ratio of the film is about  $5\%$  for the incident light at  $450 \text{ nm}$ ). As a comparison, the SI modified  $\text{SnO}_2$  electrode only generates about  $315 \text{ nA}$  and the corresponding quantum yield is about  $0.35\%$  at the same condition. The quantum yield

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**Figure 3.** Action spectrum of SS-SnO<sub>2</sub> electrode. The intensities of different wavelengths were all normalized.

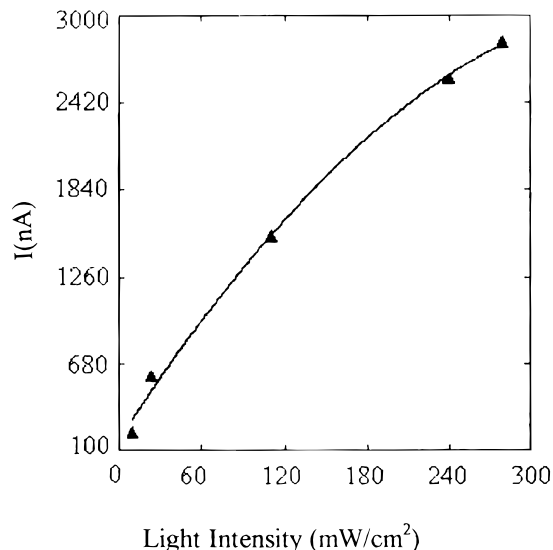


**Figure 4.** Effluence of bias voltage to the photocurrent generation from SS-SnO<sub>2</sub> electrode under an irradiation of 40 mW/cm<sup>2</sup>.

is raised about 2-fold with presence of zinc complex in the hemicyanine system.

Figure 3 shows the SS-SnO<sub>2</sub> electrode action spectrum. The most effective region of the wavelength centers at 450 nm which corresponds to the monomer absorption of SS in the SnO<sub>2</sub> electrode, indicating that the monomer of SS in the LB film may be responsible for the photocurrent generation.

**Effect of Bias Voltage and Light Intensity.** The observation of cathodic photocurrent indicates that electrons flow from the electrode through the LB film to the electrolyte solution. To further prove the electron-transfer process between the SnO<sub>2</sub> electrode and the LB film, the effect of bias voltage was investigated. The relationship between bias voltage ( $\sim$ Ag/AgCl) and the photocurrent values is shown in Figure 4. With the increasing of negative bias to the electrode, an increment of cathodic photocurrent can be seen and vice versa. When  $-100$  mV bias voltage was applied to the electrode, about 620 nA photocurrent can be obtained at 450 nm, indicating that the quantum yield reaches about 0.9%. That may result from the applied negative voltage which is the same polarity to the photocurrent forming a strong electric field



**Figure 5.** Dependence of photocurrent generation from SS-SnO<sub>2</sub> electrode with the irradiated light intensities (white light was used).

within the LB film ( $\sim 30$  Å) and such strong electric field may accelerate the photoinduced separation or induce the formation of charge separation and decrease the probability of the charge recombination of being trapped on the way before they reach their target electron acceptors.

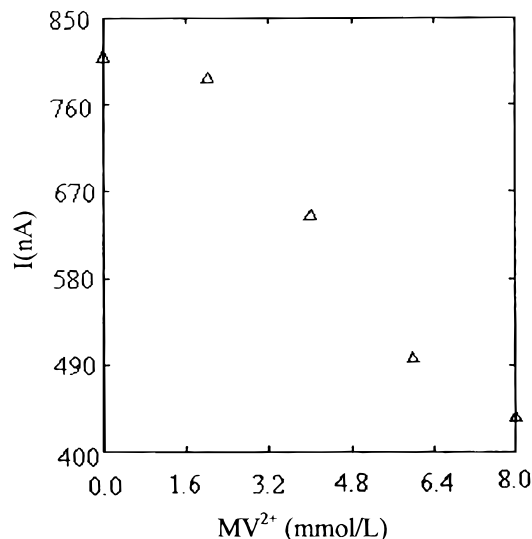
Figure 5 shows the dependencies of the incident light intensity and the observed photocurrent. It was pointed out that the measured signal,  $i$ , has a dependence on light intensity,  $i = kI^m$ , where  $m = 1$  is the characteristic of unimolecular recombination and  $m = 1/2$  is the characteristic of bimolecular recombination.<sup>10</sup> From Figure 5, it can be seen that  $m = 2/3$  and  $k = 66$  for the present SS-SnO<sub>2</sub> electrode. So the relationship between photocurrent and light intensity (white light) for the SS-SnO<sub>2</sub> electrode indicates that the separated charge loss process occurring in the SS-LB film contains both of the above recombination processes.

**Effect of Electron Donor and Acceptor.** From the former results, we know that the electrons flow from the electrode to the 1 M KCl electrolyte solution through the LB film probably by a tunneling mechanism. Water molecules are the only possible electron acceptors in 1 M KCl electrolyte solution. Generally, the addition of electrolyte acceptor viologen (MV<sup>2+</sup>) to the electrolyte solution helps increase the cathodic photocurrent, so the behavior with the SS-SnO<sub>2</sub> electrode is unusual. The photocurrent decreases with the addition of MV<sup>2+</sup> into the electrolyte solution as shown in Figure 6. The addition of the well-known electron donor ascorbic acid (AA) into the 1 M KCl electrolyte solution also produces an unexpected result. The cathodic photocurrent increases instead of decreasing. Very low concentration ( $\leq 2$  mol/L) of AA makes the photocurrent raise from 830 to 1100 nA (increasing about 30% in magnitude, the photocurrent is an average value from four independent experiments). More AA added to the electrolyte solution does not enhance the photocurrent as shown in Figure 7. However, hydroquinone (HQ) can quench the photocurrent sharply at first and then reach a saturate state with the addition of HQ to the electrolyte solution as shown in Figure 8.

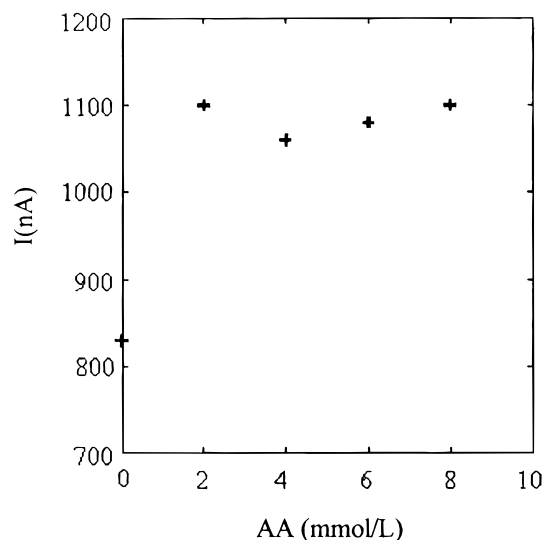
O<sub>2</sub> often acts as an electron acceptor through the formation of superoxide anion radical.<sup>11</sup> When we used

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**Figure 6.** Dependence of photocurrent generation from SS-SnO<sub>2</sub> electrode with the concentrations MV<sup>2+</sup> in 1 mol/L KCl electrolyte solution at 40 mW/cm<sup>2</sup> irradiation.

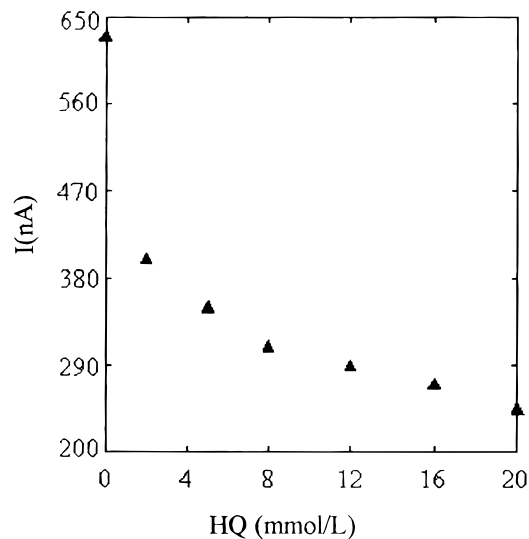


**Figure 7.** Dependence of photocurrent generation from SS-SnO<sub>2</sub> electrode with the concentrations AA in 1 mol/L KCl electrolyte solution at 40 mW/cm<sup>2</sup> irradiation.

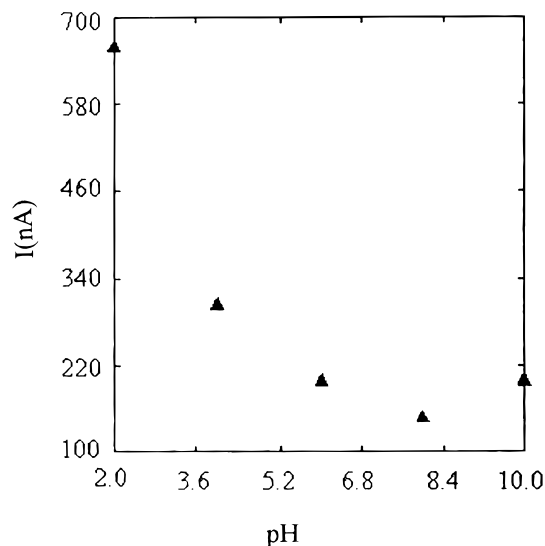
O<sub>2</sub> to saturate electrolyte solution, the photocurrent can be raised about 25% in magnitude compared with that under ambient condition. However, when N<sub>2</sub> gas was used to degas O<sub>2</sub> in the electrolyte solution, the photocurrent decreased. The decrease ratio of the photocurrent is about 50%, indicating that O<sub>2</sub> is a helpful factor in the electron transfer process, but is not the only one. The molecule itself may play an important role in the electron transfer process in the present system.

**Effect of pH Value.** In order to optimize conditions for the photoresponse, the effect of different pH values on the photocurrent was investigated. Figure 9 shows the results we obtained. With the pH value decreased from alkaline to acidic condition, the photocurrent increases. From the latter discussion, we know that the photochemical activity (photoisomerization) increases with SS in acidic condition. Thus more photochemically active molecules in the electrode participate in the photochemical reaction, resulting in a larger photocurrent in acidic condition than that in neutral and alkaline conditions.

**Mechanism of Photocurrent Generation from the SI-SnO<sub>2</sub> Electrode.** It has been reported<sup>4</sup> that most hemicyanine dyes undergo a facile *trans* → *cis* photoisom-



**Figure 8.** Dependence of photocurrent generation from SS-SnO<sub>2</sub> electrode on hydroquinone in 1 mol/L KCl electrolyte solution upon irradiation of 40 mW/cm<sup>2</sup>.



**Figure 9.** Effect of different pH values in B-R electrolyte solution containing 1 mol/L KCl electrolyte solution on the photocurrent generated from SS-SnO<sub>2</sub> electrode under irradiation of 40 mW/cm<sup>2</sup>.

erization process upon irradiation. We found that the cation of the title compound, (CH<sub>3</sub>)<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>CH=CH-C<sub>5</sub>H<sub>4</sub>N<sup>+</sup>C<sub>18</sub>H<sub>37</sub> (SI), can undergo a *trans* → *cis* photoisomerization with a very low quantum yield in ethanol solution upon irradiation at 500 nm. When SI is in the acidic condition, a facile photoisomerization can be observed readily. The larger quantum yield in acidic condition suggests that the photochemical reaction can take place more easily. Since aromatic chromophores have  $\pi$ -electrons which may facilitate the electron transfer reaction between donors and acceptors linked by them as a bridge,<sup>12</sup> a photoinduced tautomerism as shown in Scheme 2 may take place. This process was supported by other work and calculations.<sup>13</sup>

Upon irradiation, state "A" absorbs energy from excitation light and produces an electron-hole pair in the

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