

Photoelectric Response from Two Amphiphilic Nitrobenzene Dyes with Alkoxy on a Monolayer-Modified ITO Electrode

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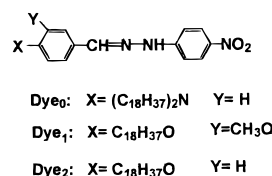
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Two amphiphilic nitrobenzene dyes 3-(CH₃O)-4-(C₁₈H₃₇O)-C₆H₃-CH=N-NH-C₆H₄-NO₂ (dye₁) and 4-(C₁₈H₃₇O)-C₆H₄-CH=N-NH-C₆H₄-NO₂ (dye₂) were synthesized and deposited on semiconducting transparent ITO electrodes by a Langmuir–Blodgett (LB) technique. The photocurrent generations have been studied in a conventional photoelectrochemical cell. Action spectra of the photocurrent generation are coincident with the absorption of the LB film-modified electrodes, indicating that the dye aggregates in the LB film are responsible for the photocurrent. Some factors which may affect the observed photocurrent, such as existence of O₂, concentration of MV²⁺ (methyl viologen) and H₂Q (hydroquinone), pH values, and the bias voltage, have been investigated. On the basis of experiments, mechanism models for the photocurrent generation under different conditions are proposed.

Introduction

The principle of second-harmonic generation indicates that the difference of the molecule dipole moment between the ground state and the excited state is one of the main factors for molecular hyperpolarizability.^{1,2} On the other hand, photoelectric response and charge dissociation are connected with the charge separation process,^{3,4} which also needs a large dipole moment in the excited state. So compounds that have good performance in the area of photoelectric conversion may also have excellent behavior in the aspect of second-order nonlinear optical character. For example, squaraine is a photoelectric conversion material which has been practically used in xerographic photoreceptors.⁵ Ashwell showed that this center symmetric molecule also has good second-order nonlinear optical character.⁶ In the past few years, we mainly studied some hemicyanine congeners and azopyridinium compounds with positive charge in the chromophore part.^{7–12} Recently we found that the amino nitrobenzene dye molecule (dye₀ shown in Chart 1) with electroneutral chromophores has a photoelectric response.¹³ As part of our systematic studies, the titled dye molecules 3-(CH₃O)-4-(C₁₈H₃₇O)-C₆H₃-CH=N-NH-C₆H₄-NO₂ (dye₁ shown in Chart 1) and 4-(C₁₈H₃₇O)-C₆H₄-CH=N-NH-C₆H₄-

Chart 1



NO₂ (dye₂ shown in Chart 1) are prepared in order to investigate their photoelectric conversion properties. One of the dyes (dye₂) had been reported by Lupo for its second-harmonic generation.¹⁴ Experimental results show as predicted that both dye₁ and dye₂ have good performance in the area of photoelectric conversion. They provide necessary experimental data for designing better photoelectric conversion materials.

Experimental Section

Materials. The title compound dye₁ was synthesized by condensing *p*-nitrophenylhydrazine with 3-methoxy-4-octadecyloxybenzaldehyde. The 3-methoxy-4-octadecyloxybenzaldehyde was from the corresponding *n*-iodidoalkane and vanillin. dye₂ was synthesized by condensing *p*-nitrophenylhydrazine with 4-octadecyloxybenzaldehyde. The 4-octadecyloxybenzaldehyde was from the corresponding *n*-iodidoalkane and 4-hydroxybenzaldehyde. Hexadecyltrimethylammonium bromide was used as the phase-transfer catalyst. The product was purified by column chromatography on silica gel with dichloromethane as eluent. Elemental analysis. Found for dye₁: C, 71.11; H, 9.24; N, 7.42. Calc for C₃₂H₄₉N₃O₄: C, 71.24; H, 9.09; N, 7.79. ¹H NMR (CDCl₃) δ: 0.88 (t, 3H, 1CH₃), 1.32 (m, 30H, 15CH₂), 1.87 (m, 2H, 1CH₂), 3.94 (m, 3H, 1CH₃O), 4.06 (m, 2H, 1CH₂O), 6.87 (d, 1H, phenyl-OCH₃), 7.07 (d, 1H, phenyl-OCH₃), 7.10 (d, 2H, phenyl-NO₂), 7.37 (d, 1H, phenyl-OCH₃), 7.75 (s, 1H, CH=N), 8.17 (d, 2H, phenyl-NO₂). Mp: 114–115 °C. Elemental analysis. Found for dye₂: C, 72.58; H, 9.15; N, 8.09. Calc for C₃₁H₄₇N₃O₃: C, 73.08; H, 9.09; N, 8.25. ¹H NMR (CDCl₃) δ: 0.88 (t, 3H, 1CH₃), 1.32 (m, 30H, 15CH₂), 1.81 (m, 2H, 1CH₂), 3.99 (t, 2H, 1CH₂O), 6.92 (d, 2H, phenyl-OCH₃), 7.09 (d, 2H, phenyl-OCH₃), 7.62 (d, 2H, phenyl-NO₂), 7.76 (s, 1H, CH=N), 8.17 (d, 2H, phenyl-NO₂). Mp: 112–113 °C. The spreading solvent used for film deposition

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was chloroform. The water subphase was in-house deionized water purified with an EASYpure RF compact ultrapure system ($R \sim 18 \text{ M}\Omega$). The electrolyte for the electrochemical experiment was KCl (AR). Hydroquinone (H_2Q) (AR) was recrystallized from water before use. Methyl viologen diiodide (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 with ethanol at least four times, and its identity was confirmed by ^1H NMR analysis.

Apparatus. C,H,N analyses of nitrobenzene dyes were performed by using a Carlo Erba 1106 elemental analyzer. ^1H NMR spectra were obtained by using a Bruker ARX 400. Electronic spectra were measured with a Shimadzu model 3100 UV-vis-NIR spectrophotometer. LB film-modified ITO electrodes were fabricated by using a model 622 NIMA Langmuir-Blodgett trough. The light source of the photoelectrochemical studied was a 500-W Xe arc lamp; the light beam was passed through a group of monochromatic filters (300–800 nm, Toshiba Co. Japan and Schott Co. USA) in order to get a given band-pass of light. The light intensity at each wavelength was calibrated with an energy and power meter (Scientech, USA).

LB Film Preparation. A solution of dye₁ (0.548 mg/mL in chloroform) or dye₂ (0.508 mg/mL in chloroform) was spread dropwise on the clean water subphase with a syringe at the subphase temperature $20 \pm 1^\circ\text{C}$. The chloroform was allowed to evaporate for 15 min, and the monolayer was then compressed. The substrate for monolayer deposition was transparent electrodes of indium-tin oxide (ITO)-coated borosilicate glass with a sheet resistance of $50 \Omega \text{ cm}^{-2}$. The ITO plates were cleaned with detergent and chloroform and then rinsed with pure water. To ensure the formation of a hydrophilic surface, the plate was immersed for 2 days in a saturated sodium methanol solution and then thoroughly rinsed with pure water under ultrasonication several times.

For deposition of the first monolayer, the ITO slide was immersed in the subphase; when the monolayer was formed and compressed to 25 mN m^{-1} , the slide was then raised at a rate of 4 mm/min. Only films having transfer ratios of 1.0 ± 0.1 were used in all experiments.

Photoelectrochemical and Electrochemical Measurements. A conventional glass three-electrode cell (30 mL capacity) having a flat window with a 0.38 cm^2 effective light irradiation area for illumination was used. The counter electrode was a polished Pt wire, and the reference was a saturated calomel electrode (SCE). All photoelectrochemical data were recorded with a model CH 600 voltammetric analyzer controlled by computer. Cyclic voltammetry (CV) experiments were performed on an EG&G PAR 273 potentiostat/Galvanostat with EG&G PAG 270 electrochemical software. The supporting electrolyte was an aqueous solution of 0.5 M KCl. Unless specified, oxygen was removed from the solutions by bubbling N_2 before every measurement.

Results and Discussion

Characterization of LB Films and Dye-ITO Electrodes. Surface pressure measurement on the monolayer was used to determine the average value of the area per molecule occupied by the dye at the air-water interface. Figure 1 shows two typical surface pressure-area (π - A) isotherms for dye₁ and dye₂. The limiting areas per molecule are 0.33 and 0.29 nm^2 for dye₁ and dye₂, respectively. The former is reasonably larger than the latter, since dye₁ has one more alkoxy at the 3-position. The limiting area per molecule for dye₂ is fairly in agreement with the value 0.28 nm^2 reported by Lupu.¹⁴ It can be clearly seen that there is a platform in each π - A curve, indicating that the dye molecules reorient on the water surface after 20 mN m^{-1} of surface pressure, since the nitrobenzene molecule has two hydrophilic radicals (NO_2 and NH).

The λ_{max} values of the LB films of dye₁ and dye₂ in UV-vis absorption spectra are peaked at 432 and 433 nm while the λ_{max} values of the corresponding dyes in chloroform are at 406 and 401 nm, respectively (Table 2, $\lambda_{\text{max}}^{\text{f}}$ and

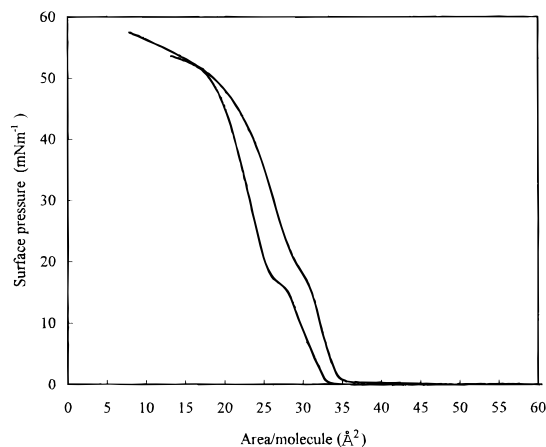


Figure 1. Surface pressure-area isotherms of dye₁ and dye₂ at the air-water interface ($20 \pm 1^\circ\text{C}$).

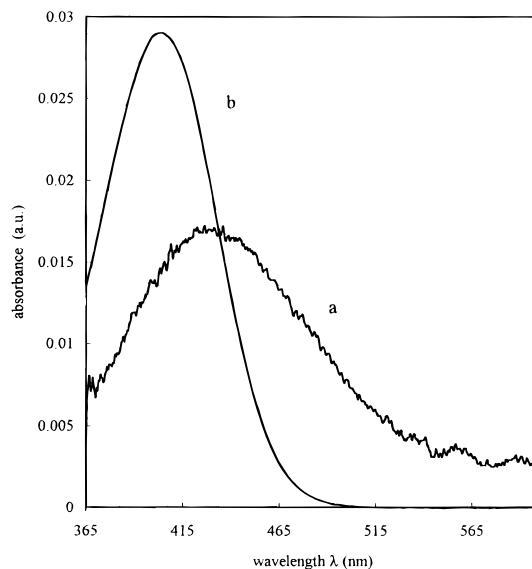


Figure 2. Absorption spectroscopy of dye₁ on an ITO substrate (a) and in chloroform solution (b).

$\lambda_{\text{max}}^{\text{f}}$), indicating that the aggregation of the dyes' chromophores is a J-aggregate.¹⁵ Figure 2 is the absorption spectra of dye₁ on an ITO substrate and in chloroform solution.

Electrochemical Properties of the Dyes. To estimate the redox potentials of the excited-state dye and discuss the mechanism of photocurrent generation, cyclic voltammetry (CV) studies were carried out. A typical voltammogram for dye₁ is shown in Figure 3. A monolayer of dye on ITO was used as working electrode in a 0.5 M KCl aqueous solution. The pH of the electrolyte solution was adjusted to about $\text{pH} \sim 2$ with a dilute HCl solution in an acidic system. It can be seen from Figure 3 that the CV curve was shifted toward the positive voltage in an acidic medium compared with that in a neutral medium. The reduction peak was shifted about 179 mV while the oxidation peak was only shifted about 85 mV. The positive shift of the reduction peak indicates that a proton takes part in the redox reaction and that the reduction reaction takes place more easily in an acidic medium than in a neutral medium.¹⁶ The electrochemical experimental data for dye₀, dye₁, and dye₂ are given in Table 1 for comparison purposes. Table 1 shows that there

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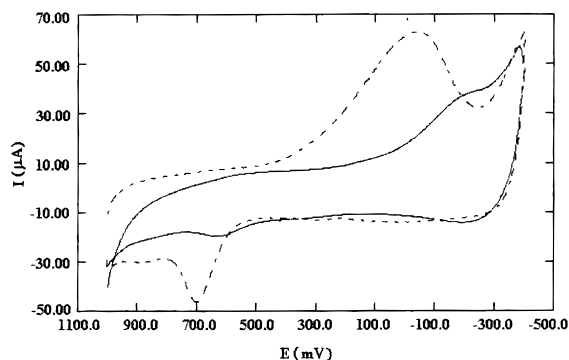


Figure 3. Cyclic voltammogram of the dye₁ monolayer-modified ITO substrate as working electrode in a 0.5 M KCl aqueous solution: (—) neutral solution; (---) pH ~ 2 solution; sweep rate = 100 mV/s.

Table 1. Cyclic Voltammetric Experimental Data of the Dyes (mV)

	Epa ^a	Epc ^a	Epa ^b	Epc ^b	ΔEpa ^c	ΔEpc ^d
dye ₀	800	-350	830	-220	32	130
dye ₁	620	-210	700	-31	85	179
dye ₂	669	-163	735	-83	66	80

^a Neutral medium (0.5 M KCl solution). ^b Acidic medium (pH ~ 2, 0.5 M KCl). ^c ΔEpa = Epa^a - Epa^b. ^d ΔEpc = Epc^a - Epc^b.

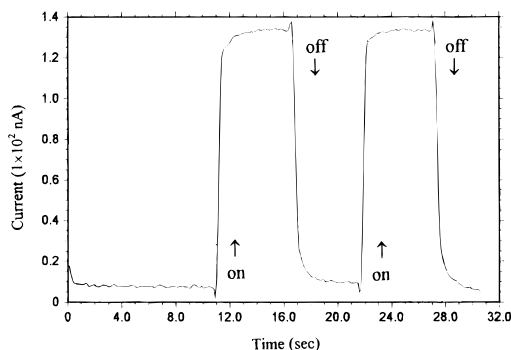


Figure 4. Photocurrent generation from the dye₁ monolayer-modified ITO electrode upon irradiation with a white light at 110 mW/cm² (↑, light switching on; ↓, light switching off).

are similar electrochemical characters for the dye congeners. A relatively smaller redox potential change is observed for dye₂ from acidic medium to neutral medium.

Photocurrent Generation from the Dye-ITO Electrode. A steady cathodic photocurrent ranging from 80 to 140 nA/cm² was obtained from the dye₁ monolayer-modified electrode when the dye-ITO electrode was illuminated by white light with a 110 mW/cm² light intensity and without any bias voltage in a 0.5 M KCl electrolyte solution. The photoelectric response was very stable when switching on and off for many times, as shown in Figure 4. Figure 5 shows the action spectrum of the cathodic photocurrents for dye₁. The spectrum responses coincide with those of the absorption spectrum (Figure 2), suggesting that the aggregate of the dye in the LB film is responsible for the photocurrent generation. dye₂ has similar behavior. About a 44.8 nA/cm² photocurrent can be obtained for dye₁ under 1.14 × 10¹⁶ photons/cm²·s at 464 nm irradiation by white light of 110 mW/cm² through a band-pass filter (KL45 + GG420) in a 0.5 M KCl electrolyte solution with zero bias voltage. The 44.8 nA/cm² photocurrent means that the quantum yield is about 0.21% for the monolayer dye₁-modified electrode (the absorbance

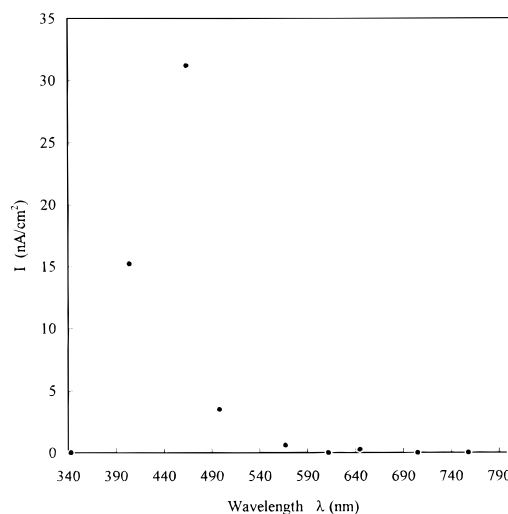


Figure 5. Action spectrum of the cathodic photocurrents for dye₁ (The photocurrents and the intensities of different wavelengths are all normalized).

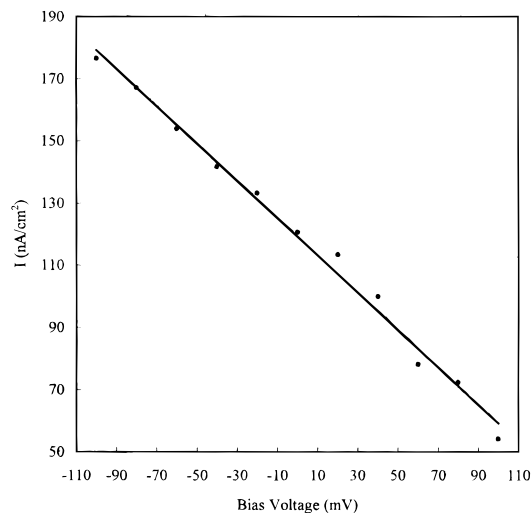


Figure 6. Relationship between photocurrent and bias voltage for dye₁.

ratio of the film is about 1.16% for dye₁ under the incident light at 464 nm) (Table 2, I^a and φ^a).

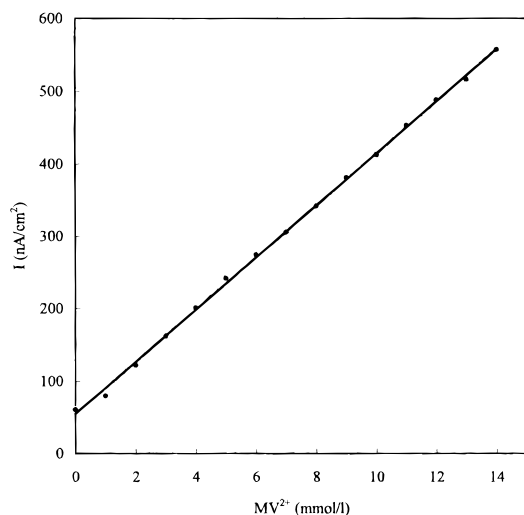
Effect of Bias Voltage. The observation of cathodic photocurrent indicates that electrons flow from the electrode through the LB film to the electrolyte solution. To further prove the electron-transfer process between the ITO electrode and the LB film, the effect of bias voltage was investigated. The relationship between bias voltage (vs SCE) and the photocurrent values for dye₁ is shown in Figure 6. With the increasing of negative bias to the electrode, an increment of cathodic photocurrent can be seen and *vice versa*. When a -100 mV bias voltage was applied to the electrode, the photocurrent obviously became larger than that generated without any bias voltage. In this case the quantum yield reached about 0.32% (Table 2, φ^c). This may result from the applied negative voltage, which has the same polarity as the photocurrent.

Effect of Electron Donor and Acceptors. Figure 7 presents the dependence of the photocurrent on the MV²⁺ concentration for dye₁. It is seen that the photocurrent increases along with the MV²⁺ concentration. For comparison with the effect of oxygen on the photocurrent, the photocurrent was measured both under ambient conditions and in the absence of oxygen (N₂ gas was used to

Table 2. π -A, Photocurrent, and UV-vis Spectral Data of the Dyes^b

	π (mN m ⁻¹)	A (nm ²)	I^a (nA cm ⁻²)	φ^a (%)	I^b ($\times 10^{-13}$ nA/ molecule)	I^c (nA cm ⁻²)	φ^c (%)	I^d (nA cm ⁻²)	φ^d (%)	I^e (nA cm ⁻²)	φ^e (%)	λ_{\max}^f (nm)	λ_{\max}^g (nm)
dye ₀	23	0.45	49.7	0.24	2.2	62.1	0.30			120.6	0.58	430	450
dye ₁	25	0.33	44.8	0.21	1.5	67.9	0.32	68.9	0.33	104.5	0.49	406	432
dye ₂	25	0.29	42.6	0.25	1.2	69.1	0.40	61.3	0.35	91.4	0.53	401	433

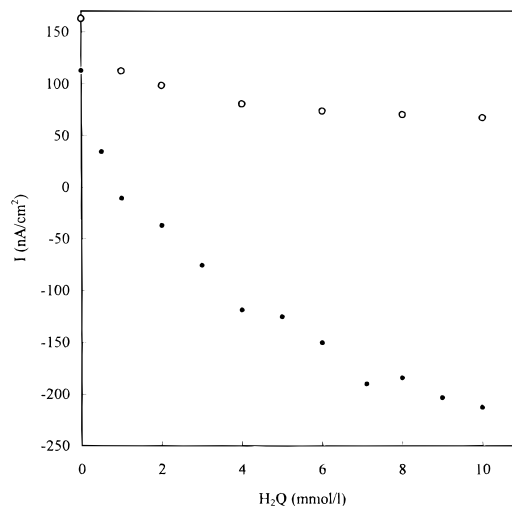
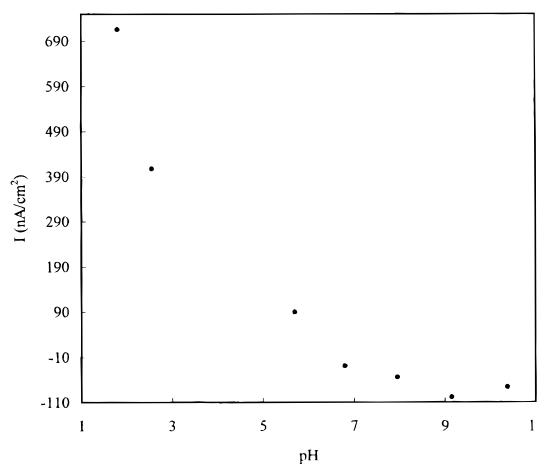
^a I , photocurrent; φ , quantum yield under light irradiation in the absence of oxygen. ^b Photocurrent of a dye molecule. ^c Under -100 mV bias voltage and light irradiation in the absence of oxygen. ^d Under oxygen saturation and light irradiation. ^e Under pH ~ 2 , 5 mmol/L MV²⁺, oxygen saturated, -100 mV bias voltage, and light irradiation. ^f In chloroform solution. ^g On ITO substrate. ^h All of the photocurrent data were obtained under 464 nm irradiation monochromatized from a white light of 110 mW/cm² through a band-pass filter (KL45+GG420).

**Figure 7.** Relationship between MV²⁺ concentration and photocurrent generation for dye₁.

degas O₂ in the electrolyte solution). Data indicate that the quantum yield is higher in the presence of oxygen. For example, if the electrolyte solution measured was saturated with oxygen by bubbling oxygen, the photocurrent obviously increased about 50% in magnitude compared with that generated in the absence of oxygen (Table 2, I^c), indicating that O₂ is a favorable factor in the electron-transfer process because it acts as an electron acceptor through the formation of a superoxide anion radical.¹⁷

If H₂Q is added into the electrolyte solution under N₂ bubbling, the cathodic photocurrent will quickly decrease and become the anodic photocurrent. H₂Q is a strong electron donor which can quench the excited dye aggregate and change the direction of electron injection.¹⁸ If the H₂Q is added into the system in the presence of oxygen, the cathodic photocurrent will slowly decrease and come to a platform. In this case, the anodic current will not occur as shown in Figure 8, indicating that O₂ and H₂Q undergo competitive processes in the direction of electron injection. The electronic donate-accept between H₂Q and O₂ will weaken the quenching effect of H₂Q on the excited dye aggregate, so the process of generating the anodic photocurrent cannot be observed in the presence of oxygen.

Effect of pH Values. The effect of pH values on the photocurrent of the monolayer was investigated in Britton-Kobinson buffer solution containing 0.5 M KCl. Figure 9 presents the effect of pH values on the photocurrent for dye₁. It is seen that the photocurrent is quickly decreased with increasing pH value, indicating that an acidic medium is favorable for the cathodic photocurrent

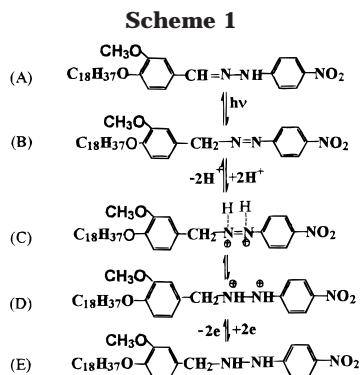
**Figure 8.** Dependence of the photocurrent on the H₂Q concentration for dye₁: (○) under ambient condition; (●) in the absence of oxygen.**Figure 9.** Effect of pH values on the photocurrent in Britton-Kobinson buffer solution for dye₁.

while an alkaline medium is not. This may result from nitrogen atoms (=N-NH-) in the dye molecule combining with hydrogen ions and making positive-charged dyes. These positively charged dye molecules easily accept an electron and are favorable for generating cathodic photocurrent. Under favorable conditions, such as pH ~ 2 , the presence of O₂, 5 mmol/L of MV²⁺, and a -100 mV bias voltage, about 105 nA/cm² of photocurrent can be obtained under a 464 nm irradiation, and the quantum yield is 0.49% (Table 2, I^e and φ^e).

Molecule Structure and Photoelectric Response. The experimental data of dye₀, dye₁, and dye₂ are given in Table 2 for comparison. It can be seen that the pulling electron groups (electron acceptor) of those dyes are identical (NO₂) while the pushing electron groups (electron donors) are not. In terms of the ability of the pushing

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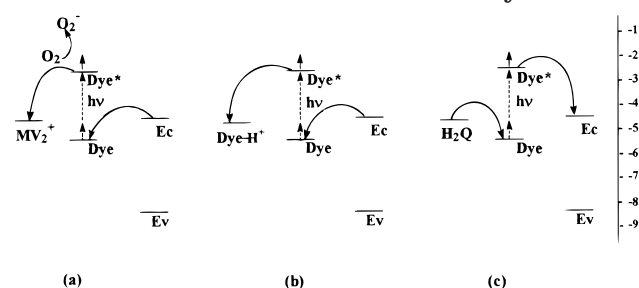
electrons, the sequence is $R_2N \rightarrow (RO)_2 \rightarrow RO$, so the push-pull electron ability is expected to be $dye_0 > dye_1 > dye_2$. Experimental results show that the photocurrent generation per molecule is coincident with this rank (Table 2, *I^b*). The photocurrent generation from a unit area has a similar sequence, but the difference is very small (Table 2, *I^c*). This may be due to the limiting area of the dye molecules decreasing, resulting in the number of molecules per unit area increasing successively from dye_0 to dye_2 (Table 2, *A*). The quantum yield or photocurrent is a macroscopic magnitude; besides molecular structure, it depends on many other factors, such as the limiting area per molecule and the absorbance of the film. The response ability of the molecules changes with changing extraneous conditions, such as the presence of donors or acceptors in the system, the bias voltage, and the pH values, so a complicated sequence appears between molecular structure and photocurrent generation or quantum yield under different conditions (Table 2, *c*, *d*, and *e*).

Mechanism of Photocurrent Generation from the Dye-ITO Electrode. To discuss the mechanism of photocurrent generation, the UV-vis spectral change of the dyes was measured in chloroform solution under irradiation at 464 nm, and the experimental results show that no detectable spectral changes were observed after 1 h of irradiation, indicating that the conjugate effect of the dyes is basically no change before and after irradiation. According to this fact, it is concluded that there is no trans \rightarrow cis photoisomerization taking place in this system under such conditions. A photoinduced tautomerism as shown in Scheme 1 may take place in the present system (dye_1 was chosen as an example). Upon irradiation, state A absorbs energy from the excitation light and undergoes a tautomerism involving an intramolecular shift of a hydrogen atom between alternative binding sites to form state B. In an acidic medium, state B may accept protons to become state C, which is an electron acceptor and is favorable for generating cathodic photocurrent. This process is coincident with the phenomenon of photocurrent generation in an acidic medium. State C and state D belong to the resonance structure which accepts electrons to become state E. This is in agreement with CV experiments.

The direction of the photocurrent generation is shown in Scheme 2. It can be seen that the direction of the photocurrent depends not only on the dye sensitized by light but also on the nature of the redox couple in the aqueous phase surrounding the electrode. In the presence of redox couples favoring electron donation, the photocurrent exhibited an anodic photocurrent, while with electron acceptors in the aqueous phase it exhibited a cathodic photocurrent.

To examine the mechanism of light sensitization for the cathodic and anodic photocurrent, the energies of the

Scheme 2. Schematic Diagram Showing Electron-Transfer Processes for Dye₁^a



^a Arrows indicate the electron flow. (a and b) Cathodic photocurrent; $dye-H^+$ represents the state of dye_1 which combines with H^+ ions in an acidic medium. (c) Anodic photocurrent.

relevant electronic states must be estimated. From the electron affinity the conduction band (E_c) and valence band (E_v) edges of the ITO electrode surface are estimated to be ca. -4.5 eV and -8.3 eV,¹⁹ respectively. The levels of the dye are assumed to be -5.36 eV (0.62 V vs SCE) and -2.49 eV on the absolute scale (dye_1 as an example), respectively, with reference to the oxidation potential 0.62 V (vs SCE) and the band gap 2.87 eV (432 nm). The reduction potential of dye_1 in the acidic medium is -4.71 eV (-0.03 V vs SCE), the reduction potential of MV^{2+} is -4.51 eV (-0.23 V vs SCE),¹⁸ and the oxidation potential of H_2Q is -4.61 eV (-0.13 V vs SCE)¹⁸ on the absolute scale.

The cathodic photocurrent probably involves an electron transfer from the excited dye aggregate to the electron acceptor with a subsequent electron transfer from the conduction band of the ITO electrode to the hole residing in the dye aggregate¹⁸ in the presence of some electron acceptors, such as O_2 , MV^{2+} , and the acidic medium in the system.

In the presence of strong electron donors such as H_2Q , the quenching of the excited dye aggregate becomes energetically favorable. As a result of the electron-transfer quenching, an anion radical of the dye aggregate is formed. The generated anion radical can transfer an electron to the conduction band of the ITO substrate with a subsequent electron transfer from the H_2Q to the hole of the ground-state dye aggregate,¹⁸ resulting in an anodic photocurrent.

Conclusions

The experimental results suggest that the mechanism of cathodic photocurrent from the dye-ITO electrode involves the formation of excited-state tautomerism. This state accepts an electron from the conductive band of the ITO electrode and transfers the electron to the electrolyte solution through the LB film. The mechanism is supported by studying the effect of bias voltage, the addition of the donor and acceptors, and pH value on the photocurrent generation. The quantum yields are 0.49% and 0.53% for dye_1 and dye_2 , respectively, under some favorable conditions. This series of dyes is easy to synthesize and stable enough to form LB films, so they are a set of promising materials for energy conversion.

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