Light-Induced Electron Transfer on a Trichromophore Dye Modified ITO Electrode

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A novel trichromophore amphiphilic dye *N*-methyl-2,4,6-tri-(4-dioctadecylamino)stilbazolium iodide (P_3n) has been synthesized and successfully transferred on semiconducting transparent indium−tin oxide (ITO) electrodes by a Langmuir−Blodgett (LB) technique. Photocurrent generation was studied in a conventional photoelectrochemical cell. An action spectrum of the photocurrent generation is coincident with the absorption spectrum of the LB film-modified electrode, indicating that the dye aggregate in the LB film is responsible for the photocurrent. Some factors that may affect the observed photocurrent, such as the presence of O_2, the concentrations of methyl viologen (MV^{2+}) and hydroquinone (H_2Q), pH, and the bias voltage have been investigated. Models for the mechanism of light-induced electron transfer under different conditions are proposed.

Introduction

The study of photochemical and photophysical phenomena in organized assemblies is an area of considerable activity. Chlorophyll, porphyrin, and phthalocyanine pigments having a large π-conjugation effect in the molecules are classified as excellent photosynthesis materials in nature.[1] One found that if an electron donor and (or) acceptor is attached to those sensitizers, the quantum efficiencies can be efficiently enhanced.[2] Fujihira and co-workers have studied the relationship between the sensitizers and push−pull electron radicals by a Langmuir−Blodgett (LB) technique, and they found that only if the pushing radical-sensitizer-pulling radical is attached in a line can the quantum efficiencies of photoelectric conversion be the best.[3] Our group has systematically studied the photo-electric conversion properties of some dye molecules with second-order nonlinear optical character and has found that the higher the molecular hyperpolarizability, the better the molecular photoelectric conversion efficiency in the system of stilbazolium and its congeners.[4−6] Recently, our work also found that if two chromophores are connected through a suitable alkyl chain, it can obtain more than 2 times the photocurrent compared with the single chromophore.[7] As a part of our systematic study, we designed a novel dye molecule P_3n (Chart 1) in which there are three electron donors through three bridges connected by one acceptor. By a LB technique, we successfully transferred the molecule onto the indium−tin oxide (ITO) substrate.

In this paper, we report an investigation of the photocurrent generation from a trichromophore stilbazolium dye LB film modified ITO electrode. Mechanistic models for photocurrent generation under different conditions are proposed.
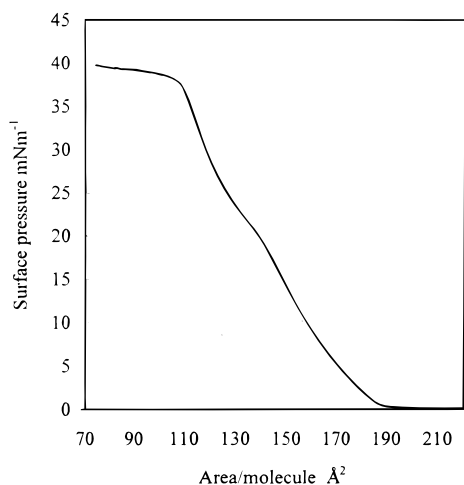
Experiment Section

Materials. The 4-dioctadecylaminobenzaldehyde was synthesized according to the previous method reported.[8] The *N*-methyl-2,4,6-trimethylpyridine iodide was synthesized by

CHART 1
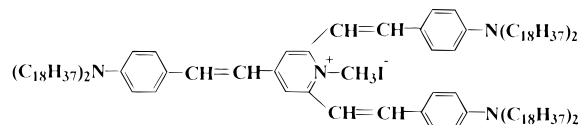
reaction of 2,4,6-trimethylpridine (5 mL) and iodic methyl (2.4 mL) for 12 h at room temperature, and the product was purified by recrystallization in absolute ethanol. *N*-Methyl-2,4,6-tri-(4-dioctadecylamine)stilbazolium iodide (P_3n) was synthesized by condensing *N*-methyl-2,4,6-trimethylpyridine iodide (53 mg) with 4-dioctadecylaminobenzaldehyde (410 mg) in refluxing complex solvents of absolute ethanol and chloroform for 3 weeks; hexahydropyridine was used as catalyst. The product was purified by column chromatography on silica gel with chloroform and methanol (20:1) as eluent, and the yield is ca. 25%. The elemental analysis is as follows. Found for P_3n: C, 79.44; H, 11.38; N, 2.61. Calcd for $C_{138}H_{245}N_4I$: C, 79.44; H, 11.79; N, 2.69. ^{1}H NMR (CDCl₃) δ: 0.86 (t, 18H, 6CH₃), 1.26 (m, 180H, 90CH₂), 1.57 (m, 12H, 6CH₂), 3.25 (t, 12H, 6CH₂N−), 4.04 (s, 3H, N⁺−CH₃), 6.46−6.52 (m, 3H, CH═), 6.55 (d, 6H, 3 phenyl), 6.92 (d, 3H, 3CH═), 7.52 (d, 6H, phenyl), 7.65 (s, 2H, pyridinyl). Mp, 199.9 °C. Methyl viologen diiodide (MV^{2+}) was synthesized by reaction of 4,4′-dipyridyl with methyl iodide. Its identity was confirmed by ^{1}H NMR analysis. The electrolyte for the electrochemical experiment was KCl (AR). Hydroquinone (H_2Q) (AR) was recrystallized from water before use. The spreading solvent used for film deposition was chloroform. The water subphase was in-house deionized water purified by an Easy pure RF compact ultrapure system (Barnstead Co.) ($R \approx 18$ MΩ).

Apparatus. C, H, N analysis of the compounds were performed by using a Carlo Erba 1106 elemental analyzer. ^{1}H NMR spectra were obtained by using a Brucker ARX 400. Electronic spectra were measured with a Shimadzu model 3100 UV−vis−NIR spectrophotometer. LB film modified ITO

Figure 1. Surface pressure—area isotherm of P$_3$n at the air/water interface (20 ± 1 °C).

Figure 2. (a) UV—vis absorption spectra of the P$_3$n LB film; (b) photocurrent action spectrum of the P$_3$n modified ITO electrode, upon irradiation with 464 nm light in 0.5 mol L^{-1} electrolyte solution with zero bias voltage. The intensities of different wavelengths are all normalized.

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 filters (300—800 nm, Toshiba Co., Japan, and Schott Co.) in order to get given band-pass of light. The light intensity at each wavelength was calibrated by an energy and power meter (Scientech).

LB Film Preparation. Solution of the P$_3$n in chloroform was spread dropwise onto the clean water subphase by syringe at a subphase temperature of 20 ± 1 °C. The chloroform was allowed to evaporate for 15 min, and the floating film was then compressed at a rate of 40 cm^2 min^{-1}. The substrate for monolayer deposition was transparent electrodes of indium—tin oxide (ITO) coated borosilicate glass with a sheet resistance of 50 Ω cm^{-2}. The ITO plates were cleaned by detergent and chloroform and then rinsed with pure water. To ensure the formation of the 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 monolayer, the ITO slide was first immersed in the subphase, when the monolayer was formed and compressed to 30 (or 10) mN m^{-1}. The slide was then raised at a rate of 4 mm min^{-1}. Only monolayer 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 by a model CH 600 voltammetric analyzer controlled by a computer. Cyclic voltammetry (CV) experiments were performed on an EG&G PAR 273 potentiostat/galvanostat with EG&G PAR 270 electrochemical software. The supporting electrolyte was an aqueous solution of 0.5 mol L^{-1} KCl. Unless specified, oxygen was removed from the solutions by bubbling N$_2$ before every measurement.

Results and Discussion

Characterization of LB Film and Dye—ITO Electrode. Surface pressure measurements on monolayers were used to determine the average values of the area per molecule occupied by the dye at the air/water interface. Figure 1 shows a typical surface pressure—area π—A isotherm for the dye P$_3$n. The
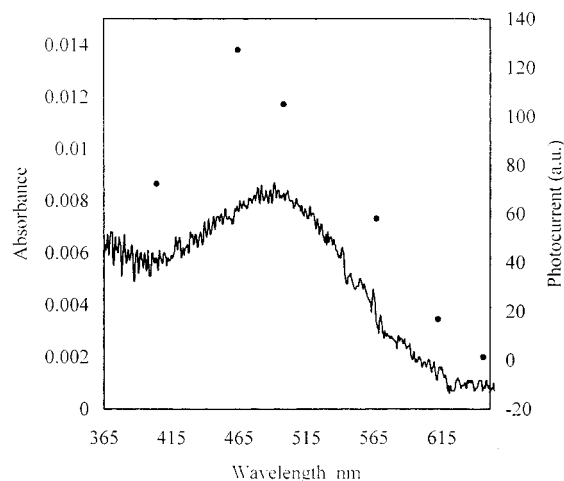
limiting area per molecule is ca. 154 Å^2, extrapolated from the surface pressure versus the molecular area isotherm under 30 mN m^{-1}. The value is about three times larger than that for compound (C$_{16}$H$_{33}$)$_2$N—C$_6$H$_4$—CH=CH—C$_5$H$_4$N—CH$_3$I, ca. 53 Å^2,[9] indicating that there are indeed three chromophores in the molecule and that the three chromophore stilbazolin radicals may be arranged on the substrate with a tilt angle. The second-harmonic generation (SHG) experiment shows that there is a tilt angle of 44° of the chromophores, relative to the normal of the substrate,[10] which is similar to that obtained from films of the hemicyanine halides.[9,11]

The electronic absorption spectra of the P$_3$n LB film is shown in Figure 2a. The λ_{max} occurs at ca. 500 nm, which is significantly blue-shifted from the chloroform solution (λ_{max} = 520 nm), suggesting the presence of H-aggregates[12] in the film.

Photocurrent Generation from Dye—ITO Electrode. A steady cathodic photocurrent ranging from 1300 to 1700 nA cm^{-2} (Table 1, condition 1) was obtained from the dye P$_3$n monolayer (transferred under 30 mN m^{-1} surface pressure) modified electrode when it was illuminated by white light with 110 mW cm^{-2} light intensity and without any bias voltage in 0.5 mol L^{-1} KCl electrolyte solution. The photoelectric response was very stable when switching on and off many times. The action spectrum of the cathodic photocurrents for the dye monolayer transferred under 30 mN m^{-1} surface pressure is also shown in Figure 2b. The spectrum responses coincide with the absorption spectrum of the dye films, suggesting that the aggregate of the dye in the LB film is responsible for the photocurrent generation. About 117 nA cm^{-2} photocurrent can be obtained for the dye P$_3$n transferred under 30 mN m^{-1} surface pressure irradiated by a 464 nm light with an intensity of 1.14 × 10^{16} photons cm^{-2} s^{-1} in 0.5 mol L^{-1} KCl electrolyte solution with zero bias voltage. The quantum yield φ is about 0.41% for the monolayer dye P$_3$n modified electrode (Table 1, condition 2) (the absorbance ratio of the film is about 1.6% for the dye under an incident light of 464 nm).

Table 1 shows that the photocurrent generated from the LB film deposited under 10 mN m^{-1} is lower than that from the LB film deposited under 30 mN m^{-1}. About 16% of the limiting area per molecule is reduced when the surface pressure is increased from 10 to 30 mN m^{-1}, while 70% photocurrent can be increased under irradiation of light of 464 nm. It may be

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TABLE 1: P$_3$n Photocurrent Generation I and Quantum Yield φ under Different Conditions^a

deposition pressure mN m^{-2}	condition 1 I nA cm^{-2}	condition 2 I nA cm^{-2}	φ %	condition 3 I nA cm^{-2}	φ %	condition 4 I nA cm^{-2}	φ %	condition 5 I nA cm^{-2}	φ %	condition 6 I nA cm^{-2}	φ %	condition 7 I nA cm^{-2}	φ %
30	1336−1705	117	0.41	202.8	0.69	345.7	1.2	368.9	1.3	475.9	1.63	600.3	2.1
10	700−970	69.2	0.24	109.1	0.37	172.4	0.59	184.4	0.63	234.2	0.80	243.2	0.83

^{a} All the photocurrent data (except condition 1) were obtained under 464 nm irradiation monochromatized from white light of 110 mW cm^{-2} through a band-pass filter (KL45+GG420). Condition 1: irradiation under a white light of 110 mW cm^{-2}. Condition 2: irradiation under monochromatized light at 464 nm. Condition 3: under −100 mV bias voltage. Condition 4: under 5 mmol L^{-1} MV^{2+}. Condition 5: under 5 mmol L^{-1} MV^{2+} and −100 mV bias voltage. Condition 6: under pH ca. 2 and 5 mmol L^{-1} MV^{2+} and oxygen-saturated. Condition 7: under pH ca. 2 and 5 mmol L^{-1} MV^{2+}, oxygen-saturated, and −100 mV bias voltage.
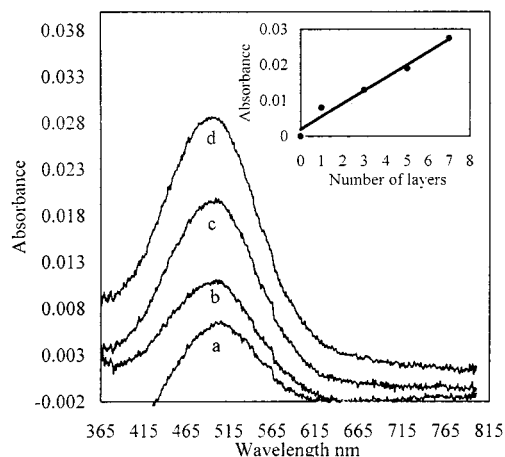

Figure 3. UV−vis absorption spectra of the P$_3$n multilayer films. Number of layers: (a) 1, (b) 3, (c) 5, (d) 7. Inset shows a linear relationship between the absorbance at 500 nm and the number of monolayers transferred under 30 mN m^{-1} surface pressure.

due to the difference of magnitude of the active molecules per area in the LB films.

A linear relationship between the absorbance at 500 nm and the number of monolayers transferred was observed (Figure 3), indicating that there are no interactions between the layers that significantly affect the extinction coefficient. However, the photocurrent first increases as the the number of layers increases, and after three layers it levels off and then gradually decreases. The reason is that the film resistance increases as the number of layers is increased, since there are some long hydrocarbon chains in the P$_3$n molecule, indicating the presence of a competitive process between the number of active molecules and the film resistance.

Electrochemical Properties of the Dye. To estimate the redox potentials of the excited-state dye and to discuss the mechanism of photocurrent generation, CV studies were carried out. Typical voltammograms of the P$_3$n films transferred under 30 mN m^{-1} are shown in Figure 4. Monolayer dye−ITO was used as a working electrode in 0.5 mol L^{-1} KCl aqueous solution. The reduction and oxidation potentials of the couples dye/dye^{-} and dye^{-}/dye are −730 and −384 mV vs SCE, respectively, in a neutral medium. The difference between the anodic and cathodic peak potentials (ΔE_p = 350 mV) are larger than the ideal value (60 mV), indicating slow kinetics of the couple.[13] Figure 4 shows that the cathodic current is ca. 370 μA, while its anodic current is only 25 μA, indicating that there is an irreversible chemical reaction on the electrode. Experimental results show that the cathodic current is decreased successively as the number of sweeps increases, while the anodic current does not, which agrees with the fact that the redox wave is irreversible. A weak reduction peak, ca. 45 μA, was obtained when the pH of the electrolyte solution was adjusted to ca. pH 2 with dilute HCl solution in an acidic medium (inset of Figure
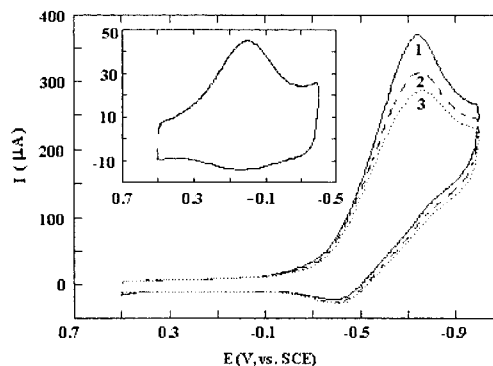

Figure 4. CV of the P$_3$n monolayer transferred under 30 mN m^{-1} surface pressure on ITO substrate as working electrode in 0.5 mol L^{-1} KCl aqueous solution. Curves 1−3 is the number of sweeps, and the inset shows CV in pH ca. 2 solution. Sweep rate = 100 mV s^{-1}
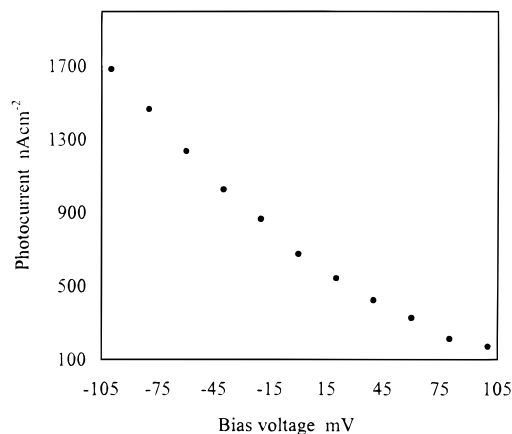
Figure 5. Photocurrent vs bias voltage for LB film of dye P$_3$n on ITO electrode in 0.5 mol L^{-1} KCl aqueous solution upon irradiation with a 110 mW cm^{-2} white light.

4). The potential is −7 mV vs SCE. The positive shift of the reduction peak indicates that the proton is involved in the redox reaction and that the reduction reaction takes place more easily in an acidic rather than in a neutral medium.[14] Note that those CV data refer to the dye in the LB film on an ITO semiconducting electrode, not to the dye in solution.

Bias Voltage Dependence of Electron Injection. To understand the effect of bias voltage on electron injection, the relationship between bias voltage and photocurrent generation is investigated. The photocurrent is increased as the applied negative bias voltage is increased (Figure 5). About 203 nA cm^{-2} photocurrent can be obtained at −100 mV, and under irradiation of light of 464 nm, the quantum yield reaches ca. 0.69% (Table 1, condition 3). This can be readily attributed to an acceleration in the rate of charge separation, resulting in an increasing proportion of the electron−hole pair separation occurring within the LB film. This increase in magnitude could
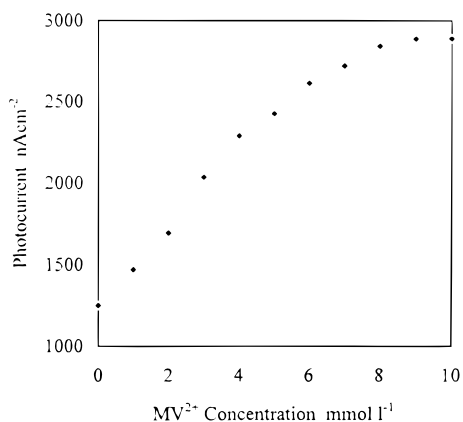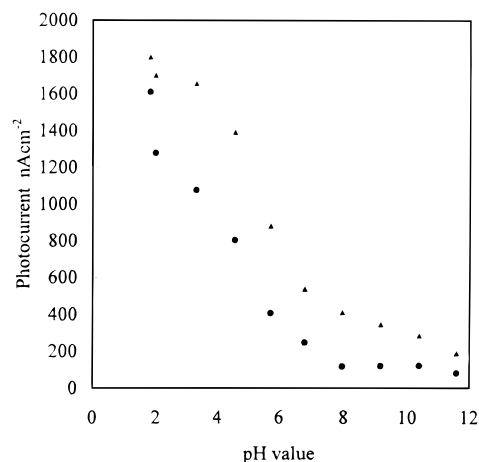
Figure 6. Dependence of the photocurrent on the MV^{2+} concentration upon irradiation with a 110 mW cm^{-2} white light in 0.5 mol L^{-1} KCl aqueous solution.

Figure 7. Effect of pH on the photocurrent in Britton−Kobinson buffer solution (●) under zero bias voltage and (▲) under −100 mV in 0.5 mol L^{-1} KCl electrolyte solution upon irradiation with a 110 mW cm^{-2} white light.

be attributable, at least in part, to an increase of the yield for electron injection from the ITO conduction band to the HOMO of the dye at negative bias.

Effect of Electron Donors and Acceptors. Figure 6 shows the dependence of the photocurrent on MV^{2+} concentration. It is seen that the photocurrent increases with increasing MV^{2+} concentration, then it levels off when the MV^{2+} concentration is larger than ca. 8 mmol L^{-1}. If the electrolyte solution was saturated by bubbling oxygen, the photocurrent would be noticeably increased by ca. 50%, indicating that O_2 is a favorable factor in the electron-transfer process because it acts as an electron acceptor through the formation of a superoxide anion radical.[14] If H_2Q was added to the electrolyte solution, the photocurrent would quickly decrease and become an anodic current, though the H_2Q concentration is 0.1 mmol L^{-1}, indicating that the presence an electron donor is unfavorable to production of a cathodic photocurrent in the system. According to the Franck−Condon principle, the only possibility under these circumstances is electron transfer between the ITO electrode and dye* (excited state) in the LB film. Electrons flow from the ITO semiconductor to the HOMO of the dye in the LB films, and the excited state loses electrons to the electrolyte, the dye* acting as an electron transporter. Whatever factors cause this to occur, as long as they can improve the electron transporting ability, they may enhance the photocurrent. MV^{2+}, for example, can accept electrons from the excited state, and it increases the cathodic photocurrent. H_2Q, which donates electrons to the HOMO of the dye, prohibits the flow of electrons from ITO to the HOMO of the dye, thus resulting in a reduced photocurrent and even reversing the electron flow.

Effect of pH Value. The effect of pH value on the photocurrent generation was investigated in a Britton−Kobinson buffer solution containing 0.5 mol L^{-1} KCl. Figure 7 shows that the photocurrent decreases rapidly with increasing pH value. To understand the bias voltage dependence of pH value, the photocurrent was also determined under −100 mV. The change tendency of the photocurrent under the different pH is coincident with that under zero bias voltage, except the photocurrent is larger than that at the corresponding pH value of zero bias voltage, indicating that an acidic medium is favorable for the production of a cathodic photocurrent while the alkaline medium is not. This may result from the acidic medium being able to decrease the flat band potential of the electrode.[16] On the other hand, the nitrogen of aminobenzenes in the title compound P_3n can combine with H$^+$ ion in an acidic system; it may accept protons to became HP_3n^+, $H_2P_3n^{2+}$ or $H_3P_3n^{3+}$, which is an

electron acceptor and thus assists generation of a cathodic photocurrent, so the protons play twofold roles in the system. Under favorable conditions, e.g., pH ca. 2, in the presence of O_2 and 5 mmol L^{-1} MV^{2+}, with −100 mV bias voltage, a photocurrent of ca. 600 nA cm^{-2} was obtained under 464 nm irradiation; the quantum yield is 2.1% (Table 1, condition 7), which is the biggest quantum yield in all stilbazolin pigments so far.[6] The open-circuit voltage was 0.675 V for the P_3n monolayer film.

Mechanism of Photocurrent Generation from the Dye−ITO Electrode. For the mechanism of light sensitization for some semiconductors, both energy and electron transfer were assumed to be possible. Van der Auweraer et al. reported that light sensitization of anodic and cathodic photocurrents belonged to the mechanism of energy transfer.[17] To elucidate the mechanism for the cathodic and anodic photocurrent in this system, the energies of the relevant electronic states must be estimated. 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 and −8.3 eV,[18] respectively. The lowest levels available to accept an electron and the first excited singlet state for the dye P_3n film transferred under 30 mN m^{-1} are assumed to be −4.01 eV (−0.73 V vs SCE) and −6.49 eV on an absolute scale, respectively, with reference to a reduction potential of −0.73 V (vs SCE) and band gap of 2.48 eV (500 nm). The reduction potential of the dye P_3n in an acidic medium is −4.733 eV (−0.007V vs SCE), the reduction potential of MV^{2+} is −4.51 eV (−0.23V vs SCE),[19] and the oxidation potential of H_2Q is −4.61 eV (−0.13 V vs SCE),[19] respectively, on an absolute scale.

The direction of photocurrent generation are shown in Scheme 1. 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 anodic photocurrent, while with electron acceptors in the aqueous phase it exhibited cathodic photocurrent.

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 aggregate[19] in the presence of some electron acceptors, such as O_2, MV^{2+}, and the acidic medium in the monolayer film system.

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SCHEME 1: Schematic Diagram Showing Electron Transfer Processes of (a) Cathodic Photocurrent and (b) Anodic Photocurrent[a]

(a)   (b)
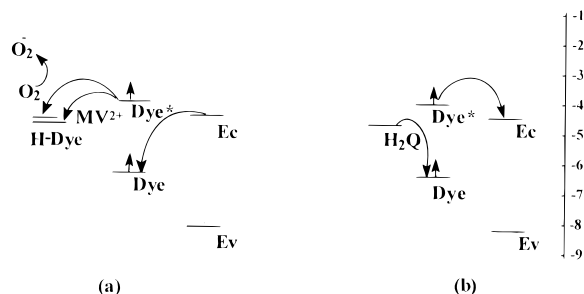
[a] Dye and dye* represent the ground state and excited state of the dye P_3n, respectively. H−Dye represents the state of the dye P_3n that combines with H^+ ions in the acidic medium.

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 energy-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,[19] resulting in an anodic photocurrent.

Conclusions

A novel trichromophore amphiphilic dye was designed and synthesized. The mechanism of light-induced electron transfer was proposed. The open-circuit voltage is 0.675 V for the monolayer film. The quantum yield is 2.1% under favorable conditions.

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