Photosensitized Electron Injection from an ITO Electrode to Trichromophore Dyes Deposited on Langmuir−Blodgett Films

Deng-Guo Wu, Chun-Hui Huang,* Liang-Bing Gan, Jie Zheng, Yan-Yi Huang, and Wen Zhang

State Key Laboratory of Rare Earth Materials Chemistry and Applications, Peking University−The University of Hong Kong Joint Laboratory on Rare Earth Materials and Inorganic Chemistry, Peking University, Beijing 100871, China
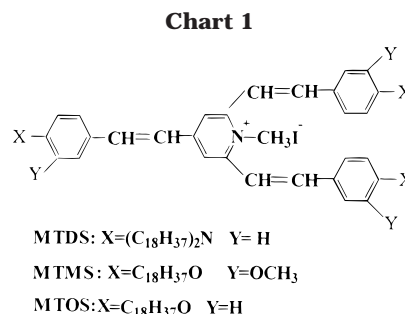
Two novel trichromophore amphiphilic dyes 1-methyl-2,4,6-tris[2-(3′-methoxy-4′-(octadecyloxy)phenyl)-ethenyl]pyridinium iodide (MTMS) and 1-methyl-2,4,6-tris[2-(4′-(octadecyloxy)phenyl)ethenyl]pyridinium iodide (MTOS) have been synthesized and successfully transferred on semiconducting transparent indium−tin oxide (ITO) electrodes by a Langmuir−Blodgett (LB) technique. The observed photocurrent strongly depends on the applied electrode potential, the presence of O_2, the concentrations of methyl viologen (MV^{2+}) and hydroquinone (H_2Q), and the pH of the electrolyte. Action spectra of the photocurrent generation are coincident with the absorption spectra of the LB film-modified ITO electrode, indicating that the dyes aggregated in the LB film are responsible for the photocurrent. Under favorable conditions the quantum yield are as high as 1.40% and 1.54% for the monolayer films of MTMS and MTOS, respectively. Models for the mechanism of photocurrent generation under different conditions are proposed.

Introduction

The potential of organic thin films for use in nonlinear and electrooptical applications has resulted in extensive research efforts directed toward improved design and understanding of these thin films.[1−8] Our group has systematically studied the photoelectric conversion properties of some monochromophore dye molecules.[9−11] Recently we found that the magnitude of increasing chromophores in one molecule, such as MTDS shown in Chart 1, can enhance efficiency of photocurrent conversion.[12] To further understand that the effects of the different molecular structures on the photocurrent generation and as a part of our systematic study, the titled dye molecules MTMS and MTOS (shown in Chart 1), in which there are six electron donors (MTMS) or three electron donors (MTOS) through three bridges connected with one acceptor, were designed and synthesized. By the LB technique, we successfully transferred the film floating on the water surface onto the ITO substrate.

In this contribution, we report an investigation of the photocurrent generation from trichromophore stilbazo-

Chart 1

MTDS: X=$(C_{18}H_{37})_2$N   Y= H

MTMS: X=$C_{18}H_{37}$O   Y=OCH_3

MTOS: X=$C_{18}H_{37}$O   Y=H

lium dye LB film-modified ITO electrodes. Mechanistic models for photocurrent generation under different conditions are proposed.

Experiment Section

Materials. 3-Methoxy-4-(octadecyloxy)benzaldehyde and 4-(octadecyloxy)benzaldehyde were synthesized according to the previous method reported.[13] 1-Methyl-2,4,6-trimethylpyridinium iodide was synthesized by reaction of 2,4,6-trimethylpridine (5 mL) and methyl iodide (2.4 mL) for 12 h at room temperature, and the product was purified by recrystallization in absolute ethanol. 1-Methyl-2,4,6-tris[2-(3′-methoxy-4′-(octadecyloxy)phenyl]ethenyl]pyridinium iodide (MTMS) was synthesized by condensing 1-methyl-2,4,6-trimethylpyridinium iodide (100 mg) with 3-methoxy-4-(octadecyloxy)benzaldehyde (460 mg) and refluxing with the complex solvents of absolute ethanol and chloroform for 3 weeks; hexahydropyridine was used as a catalyst. 1-Methyl-2,4,6-tris[2-(4′-(octadecyloxy)phenyl)ethenyl]pyridinium iodide (MTOS) was synthesized by condensing 1-methyl-2,4,6-trimethylpyridinium iodide (100 mg) with 4-(octadecyloxy)benzaldehyde (420 mg) as mentioned above. The products were purified by column chromatography on silica gel with chloroform and methanol (20:1) as eluent; the yield are ca. 25% and 30% for the MTMS and MTOS, respectively. Anal. Found for MTMS: C, 73.22; H, 9.82; N, 1.12. Calcd for $C_{87}H_{140}O_6NI$: C, 73.43; H, 9.92; N, 0.98. ${}^1H$ NMR ($CDCl_3$) (δ): 0.88 (t, 9H, $3CH_3$), 1.26 (m, 90H, $45CH_2$), 1.82 (d, 6H, $3CH_2$), 3.82 (t, 6H, $3CH_2O-$), 3.93 (t, 9H, $3CH_3O-$), 4.01 (s, 3H, N^+-CH_3), 6.63−

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6.65 (m, 3H, pyridinyl-CH=), 6.7 (d, 3H, 3CH=), 7.0 (d, 3H, phenyl-OCH$_3$),), 7.3 (d, 3H, phenyl-OCH$_3$), 7.7 (d, 3H, phenyl-OCH$_3$), 7.9 (s, 2H, pyridinyl). Mp: 170−172 °C. Anal. Found for MTOS: C, 74.88; H, 9.91; N, 1.09. Calcd for C$_{84}$H$_{134}$O$_3$NI: C, 75.69; H, 10.13; N, 1.05. ^{1}H NMR (CDCl$_3$) (δ): 0.88 (t, 9H, 3CH$_3$), 1.26 (m, 90H, 45CH$_2$), 1.77 (d, 6H, 3CH$_2$), 3.73 (t, 6H, 3CH$_2$O−), 3.86 (s, 3H, N$^+$−CH$_3$), 6.63−6.65 (m, 3H, pyridinyl-CH=), 6.7 (d, 6H, 3 phenyl), 6.9 (d, 3H, 3CH=), 7.6 (d, 6H, phenyl), 7.8 (s, 2H, pyridinyl). Mp: 172−174 °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$_2$Q) (AR) was recrystallized from water before use. The spreading solvent used for film deposition was chloroform. Water used as a subphase was in-house deionized water purified by an EASY pure RF compact ultrapure system ($R \sim 18$ MΩ).

Apparatus. C, H, and N analyses 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 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., U.S.A.) in order to obtain the given band-pass of light. The light intensity at each wavelength was calibrated by an energy and power meter (Scientech, U.S.A.).

LB Film Preparation. A solution of the MTMS or MTOS in chloroform was spread dropwise on 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 electrode of indium−tin oxide (ITO) coated borosilicate glass with a sheet resistance of 50 Ω cm^{-2}. The ITO plates were cleaned using the procedures described elsewhere.[13]

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 three-electrode glass 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). The action spectra of the photocurrent were obtained in a discontinuous way: for each data point, the wavelength was set to the appropriate value by certain filters and the current was allowed to relax to a stationary value during 10−30 s. All photoelectrochemical data were recorded by a model CH 600 voltammetric analyzer controlled by computer. Cyclic voltammetry (CV) experiments were performed on an EG&G PAR 273 potentiostat/galvanostat with an EG&G PAR 270 electrochemical software. The supporting electrolyte was an aqueous solution of 0.5 M KCl. The photocurrent data for each compound were obtained by, at least, four ITO electrodes fabricated independently. 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/molecule occupied by the dye at the air/water interface. Figure 1 shows two typical surface pressure−area π−A isotherms for the dyes MTMS and MTOS. The limiting area/molecule values are ca. 150 and 96.5 Å^2, respectively, extrapolated from the surface pressure versus the molecular area isotherm under 30 mN m^{-1} (Table 2, A). The limiting area/molecule of MTOS is about three times for compound C$_{18}$H$_{37}$OC$_6$H$_4$CH=CHC$_5$H$_4$NCH$_3$I at ca. 35 Å^2,[14]
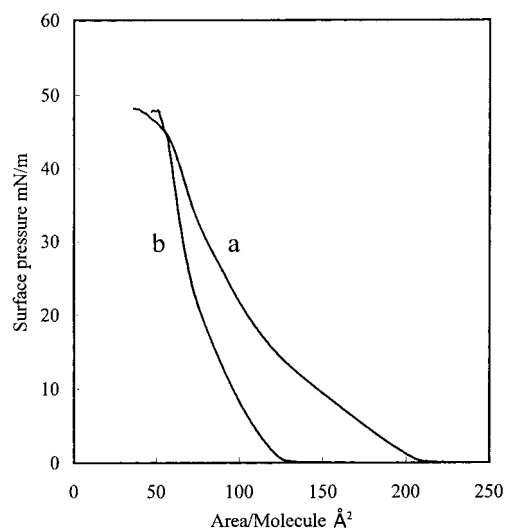

Figure 1. Surface pressure−area isotherm of MTMS (a) and MTOS (b) at the air/water interface (20 ± 1 °C).

Table 1. CV Data for the Monolayer Modified ITO Electrode[a]

compds	E_{pa} (mV)	E_{pc} (mV)	ΔE_{pac}
MTDS	−384	−730	350
MTMS	−400	−700	300
MTOS	−380	−700	320

[a] E_{pa}: oxidation potential. E_{pc}: reduction potential. $\Delta E_{pac} = E_{pa} - E_{pc}$.

indicating that there are indeed three chromophores in the each molecule and three chromophore stilbazole radicals may be arranged on the substrate with a tilt angle. The limiting area/molecule of MTMS is larger than that of MTOS; this is because there is a methoxy radical on the third position of the phenyl ring.

It is known from Figure 1 that, before 20 mN m^{-1} surface pressure, the small solid-phase slope of the MTMS π−A curve may be due to larger hydrophilic character of the oxygen atoms than that in the MTOS molecule because there are six methoxy groups in MTMS while MTOS only has three methoxy groups. The second-harmonic generation (SHG) experiment shows that there are tilt angles 42 and 25 of the chromophores to normal of the substrate for the dyes MTMS and MTOS, respectively, which is similar to those obtained from films of the hemicyanine halides,[14] such as C$_{18}$H$_{37}$OC$_6$H$_4$CH=CH−C$_5$H$_4$NCH$_3$I (35°) and C$_{18}$H$_{37}$SC$_6$H$_4$CH=CHC$_5$H$_4$NCH$_3$I (26°).

The electronic absorption spectra of the MTMS and MTOS LB films are shown in Figure 2a,b, respectively. The λ_{max} occurs at ca. 420 and 393 nm, respectively, which are significantly blue-shifted (ca. 10−15 nm) from the absorption of the solution (the λ_{max} of the dyes in chloroform are at ca. 430 and 408 nm, respectively, in Figure 2c,d, suggesting the presence of H-aggregates[15] in the films).

Photocurrent Generation from Dye−ITO Electrode. A steady cathodic photocurrent ranging from 529 to 940 nA cm^{-2} (Table 2, condition 1) was obtained from the dye MTMS monolayer (transferred under 30 mN m^{-1} surface pressure) modified electrode when it was illuminated by a white light with 110 mW cm^{-2} light intensity and without any bias voltage in 0.5 M KCl

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Table 2. Photocurrent Generation *I* and Quantum Yield φ under Different Conditions[a]

compds	π (mN m^{-1})	condition 1 I (nA cm^{-2})	condition 2 I (nA cm^{-2})	condition 2 φ (%)	condition 3 I (nA cm^{-2})	condition 3 φ (%)	condition 4 I (nA cm^{-2})	condition 4 φ (%)	condition 5 I (nA cm^{-2})	condition 5 φ (%)	condition 6 I (nA cm^{-2})	condition 6 φ (%)	condition 7 I (nA cm^{-2})	condition 7 φ (%)	A (nm^2)
MTDS	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	1.54
MTMS		529~940	72.6	0.24	135.8	0.45	211.7	0.70	301.1	0.99	33.1	1.10	424.7	1.4	1.50
MTOS		346~362	53.4	0.42	69.7	0.55	116.5	0.92	148.3	1.18	171.5	1.36	194.8	1.54	0.96
MTDS	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	1.80
MTMS		447~697	49.2	0.16	85.8	0.28	151.6	0.50	179.4	0.59	204.6	0.67	293.7	0.97	2.00
MTOS		243~312	30.1	0.24	47.4	0.38	73.8	0.59	91.1	0.72	126.3	1.0	143.4	1.14	1.19

* All of the photocurrent data (except for condition 1) were obtained under 464 nm (MTDS) or 404 nm (MTMS and MTOS) irradiation monochromatized from a white light of 110 mW cm^{-2} through a band-pass filter (KL45 + GG420 for MTDS or KL40 + WG360 + IRA − 25S for MTMS and MTOS). Condition 1: irradiation under a white light of 110 mW cm^{-2}. Condition 2: irradiation under monochromatized light. Condition 3: −100 mV bias voltage. Condition 4: 5 mM MV^{2+}. Condition 5: 5 mM MV^{2+} and −100 mV bias voltage. Condition 6: pH ca. 2, 5 mM MV^{2+}, oxygen saturated. Condition 7: pH ca. 2, 5 mM MV^{2+}, oxygen saturated, and −100 mV bias voltage.
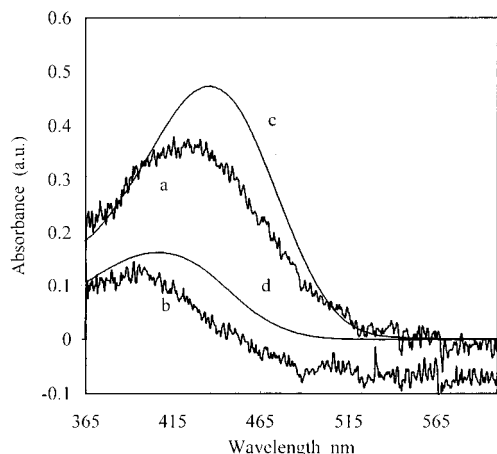

Figure 2. UV−vis absorption spectra of the (a) MTMS and (b) MTOS LB monolayer films deposited under 30 mN m^{-1} and (c, d) in CHCl$_3$ solution for MTMS and MTOS, respectively.
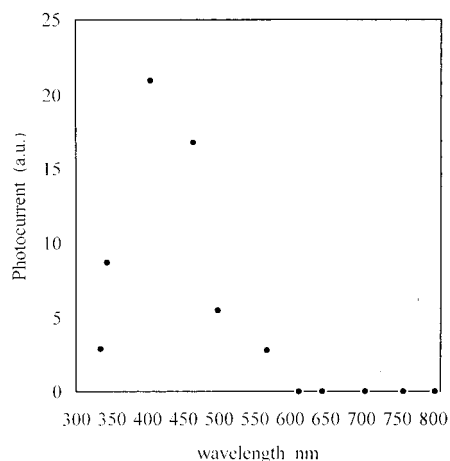

Figure 3. Photocurrent action spectrum of the MTMS−ITO electrode, upon irradiation with a 404 nm light in 0.5 M KCl electrolyte solution with zero bias voltage. The intensities of different wavelengths are all normalized.
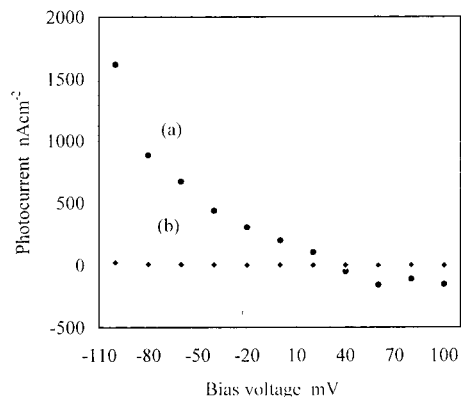

Figure 4. Photocurrent vs bias voltage for the LB film of the dye MTMS−ITO electrode in 0.5 M KCl aqueous solution (a) upon irradiation with a 110 mW cm^{-2} white light and (b) with dark current (unirradiation)

mN m^{-1} surface pressure irradiated by a 404 nm light with the intensity of 1.14×10^{16} photons cm^{-2} s^{-1} in 0.5 M KCl electrolyte solution under zero bias voltage. The quantum yields φ are about 0.24 and 0.42% for the monolayer dye MTMS and MTOS modified electrodes, respectively (Table 2, condition 2) (the absorbance ratio of the films are about 1.66% and 0.69% for the dyes MTMS and MTOS, respectively, under the incident light of 404 nm).

It can also be seen from Table 2 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}. This may be due to the difference of magnitude of the active molecules per area in the LB films.

Bias Voltage Dependence of Electron Injection. For clarity of description, the dye MTMS is selected as a representative to discuss below, since it exhibits the better photocurrent conversion properties of the two dyes. To understand the behavior of electron injection within the LB film, the photocurrent dependence on the bias voltage was investigated; the relationship between the bias voltage and the photocurrent is shown in Figure 4. It is noteworthy that the photocurrent shows a nonlinear dependence on the applied bias voltage; e.g. when the negative bias voltage was applied to the ITO electrode, a slow initial rise is followed by an increase of the cathodic photocurrent up to a potential of −40 mV. Above −40 mV a fast increase is obtained. In our previous systems studied, bias voltage dependence of the photocurrent shows a linear relationship under lower bias voltage (ca. ±100 mV); only for multilayer films (ca. 20 layers) reported can one see the nonlinear phenomenon under higher voltage.[16] The phenomenon found here in a dye monolayer film is really rare. This cannot be attributed to an enhancement of the rate

electrolyte solution. While under the same conditions that for MTOS is ranging from 346 to 362 nA cm^{-2} .The photoelectric response was very stable when switching on and off for many times. Upon change of the excitation wavelength, a photocurrent action spectrum of the MTMS monolayer (transferred under 30 mN m^{-1}) is obtained with a maximum at 404 nm, as shown in Figure 3, which is coincident with the absorption spectrum of the corresponding dye film (Figure 2 a), suggesting that the aggregate of the dye in the LB film is responsible for the photocurrent generation. About 73 nA cm^{-2} photocurrent can be obtained for the dye MTMS transferred under 30
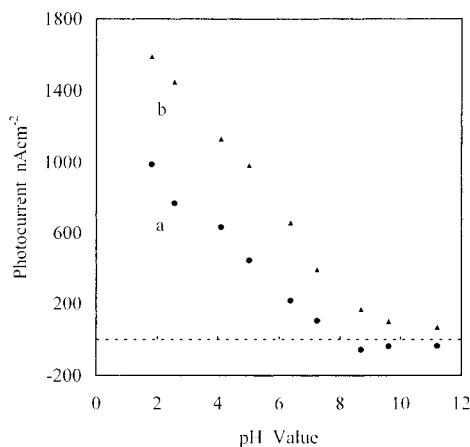
Figure 5. Effect of pH on the MTMS−ITO electrode photocurrent in a Britton−Kobinson buffer solution containing 0.5 M KCl electrolyte solution, upon irradiation with a 110 mW cm⁻² white light: (a, ●) under zero bias voltage; (b, ▲) under −100 mV.

constant for the initial charge transfer. It can be readily attributed to a more efficient dissociation of electron−hole pairs.[16] When the bias voltage was 40 mV, the anodic and cathodic spikes were observed upon starting and stopping the illumination, respectively. After 60 mV the photocurrent was a pure anodic response.

The dark current as a function of applied potential is shown in Figure 4b. It shows that the current does not change with the changing of bias voltage without irradiation, indicating that the current is generated by the light-sensitized dye molecules.

Effect of the Electronic Acceptors and Donor. To understand the flow direction of electron through the LB film, the effects of the electronic acceptors and donor on the dye-sensitized ITO electrode were investigated. Experiment result shows that MV^{2+} concentration and dissolved oxygen (by bubbling oxygen in the electrolyte solution) can increase the cathodic photocurrent, indicating that electrons flow from the ITO electrode to the electrolyte solution through the LB film. The increase of the photocurrent upon the admission of air suggests that photocurrents are generated by the interaction between excitons and oxygen, leading to the formation of mobile holes and superoxide anions.[16,17] If H_2Q was added into the electrolyte solution, the photocurrent quickly decreased, indicating that H_2Q is unfavorable to the production of a cathodic photocurrent in the system.

Effect of pH Value. The acid or base character of the medium has a strong effect on the photocurrent generation. In the present case, the effect of pH value was investigated in a Britton−Kobinson buffer solution containing 0.5 M KCl. Figure 5a shows that the cathodic photocurrent generated from the MTMS-modified ITO electrode was quickly increased when the pH value was decreased under zero bias voltage. To understand the bias voltage dependence of pH value, the photocurrent change with pH value was also determined under −100 mV as shown in Figure 5b. Data show that the change tendency of the photocurrent under −100 mV is coincident with that under zero bias voltage, except the photocurrent is larger under −100 mV than that at the corresponding pH value of zero bias voltage, indicating that an acidic medium is favorable to the cathodic photocurrent generation.

It is worthy to note that, at pH > 8, the photocurrent has no obvious variation when the pH values were changed
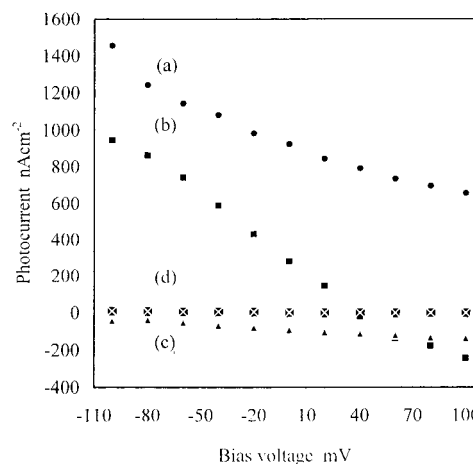

Figure 6. Photocurrent vs bias voltage plot for the MTMS−ITO electrode under different pH values: (a) pH ca. 1.81 (●); (b) pH ca. 6.37 (■); (c) pH ca. 9.67 (▲); (d) dark current as a function of applied potential under pH ca. 9.67 (×).

under bias voltage either 0 or −100 mV, respectively (Figure 5a,b). To further confirm this observation, and more clearly understand the effect of pH and bias voltage on the photocurrent generation, the bias voltage dependence of photocurrent was measured at three different pH values, that is, pH 1.81, 6.37, or 9.6 as shown in Figure 6. Figure 6c shows that the bias voltage has little effect on the photocurrent in an alkaline medium in this system. This may be due to the following two reasons: One is of dye molecules losing their activity in the alkaline medium, resulting in that they cannot sensitize the semiconducting ITO electrode to generate photocurrent. Another reason may the contribution to the damage of the molecules. This is supported by the fact that after the system undergoes an alkaline medium measurement, only ca. 50−60% photocurrent can be regenerated when the identical MTMS−ITO electrode is determined again under an acidic medium. The small anodic current signal observed may be the intrinsic character of the ITO electrode in the alkaline medium. This viewpoint is supported by Figure 6d; e.g. the current of the MTMS film has no obvious difference upon irradiation, comparing with the dark current, so increasing pH is unfavorable to the cathodic photocurrent generation.

It also can be seen from Figure 6a,b that the difference of the photocurrent between pH ca. 1.81 and pH ca. 6.37 becomes larger under the positive bias voltage than that under the negative bias voltage. This may be caused by the decreased electrolyte pH leading to an anodic shift of flat-band potential at an acidic medium,[18,19] which cancels out the negative effect of the positive bias voltage on the cathodic photocurrent, resulting in the different tendency under same bias voltage as shown in curves a and b. Under favorable conditions, e.g. pH ca. 2, in the presence of O_2 and 5 M MV^{2+}, with −100 mV bias voltage, then photocurrents of ca. 424.7 and 194.8 nA cm⁻² were obtained under 404 nm irradiation, and the corresponding quantum yields are 1.40 and 1.54% for MTMS and MTOS, respectively (Table 2, condition 7).

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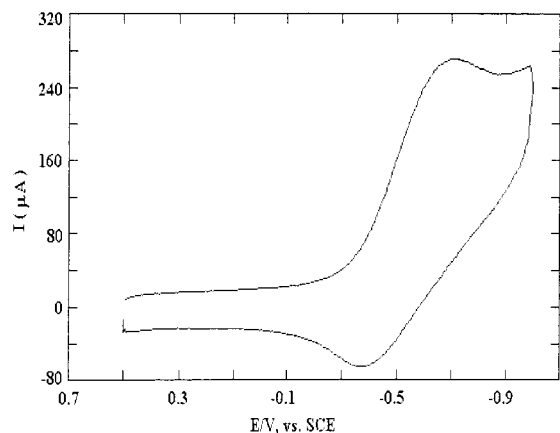
Figure 7. CV of the MTMS monolayer transferred under 30 mN m^{-1} surface pressure on the ITO substrate as a working electrode in 0.5 M KCl aqueous solution. Sweep rate = 100 mV s^{-1}.

Electrochemical Properties of the Dyes. CV studies were carried out for discussing the mechanism of the photocurrent generation. Typical voltammograms of the MTMS films transferred under 30 mN m^{-1} are shown in Figure 7. Monolayer dye–ITO was used as a working electrode in 0.5 M KCl aqueous solution. The scan rate was 100 mV s^{-1}. The reduction and oxidation potentials of the couples dye/dye$^-$ and dye$^-$/dye are −700 and −400 mV vs SCE, respectively. It can be seen from Figure 7 that the cathodic current is ca. 273.3 μA, while its anodic current is only 65.5 μA, indicating that there is an irreversible chemical reaction on the electrode. The electrochemical experimental data for MTDS, MTMS, and MTOS are given in Table 1 for comparison purposes. Table 1 shows that there are similar electrochemical characters for the dye congeners.

Effect of the Molecule Structure. The experimental data for dye MTMS and MTOS films transferred under 30 and 10 mN m^{-1} are given in Table 2; for comparison, the experimental data for the MTDS also are given in the Table 2. It can be seen that the electron-withdrawing groups (electron acceptor) of those dyes are identical (pyridinium cation) while the electron-releasing group (electron donors) are different. In terms of the ability of the pushing electrons, the sequence is R$_2$N → (RO)$_2$ → RO, so the push–pull electron ability is expected to be of the order MTDS > MTMS > MTOS. Experimental results show that the photocurrent generation per molecule values are 1.8×10^{-12}, 1.1×10^{-12}, and 0.52×10^{-12} nA/molecule for the MTDS, MTMS, and MTOS transferred under 30 mN m^{-1} and condition 2, respectively, which are fairly coincident with what we have predicted. Although the limiting areas of the dye molecules decreased successively from MTDS to MTOS, the photocurrent generation values from a unit area still have a similar sequence under other experimental conditions (see Table 2), indicating that the push–pull electron ability of those dye molecules plays an important role in photocurrent generation.

To compare the change of photocurrent under difference surface pressures, the photocurrent was also determined under 10 mN m^{-1}. The experimental data also are shown in Table 2. Comparing the data obtained from the film transferred under 30 and 10 mN m^{-1}, one can find that the photocurrent follows a similar sequence under the same experimental conditions from MTDS to MTOS, except the value is smaller under 10 mN m^{-1} than that under 30 mN m^{-1}. But the quantum yield does not follow a sequence similar to that for the photocurrent; this it is
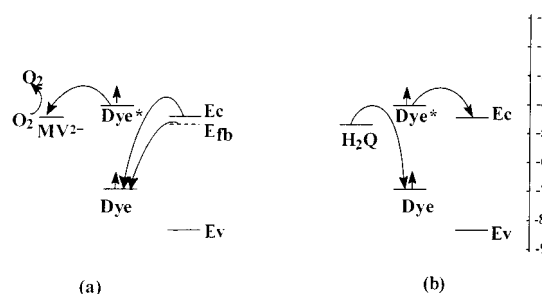
[a] Dye and dye* represent the ground state and excited state of the dye MTMS, respectively. E_{fb} represents an anodic shift of flat-band potential in the acidic medium.

due to the difference of the absorbance ratio of the dye monolayer films as mentioned above.

For comparison of photocurrent conversation efficiency between the single chromophore and trichromophores, dye molecule C$_{18}$H$_{37}$OC$_6$H$_4$CH=CHC$_5$H$_4$N$^+$CH$_3$I$^-$ monolayer transferred under 30 mN m^{-1} was determined. A ca. 88–91 nA cm^{-2} photocurrent can be obtained under a white light irradiation of 110 mW cm^{-2} (condition 1), and only ca. 10 nA cm^{-2} photocurrent can be obtained at 404 nm (condition 2). If this is compared with the trichromophore molecule MTOS, one can find that photocurrent is about four times for the trichromophore molecule compared to that for the single chromophore molecule, indicating that magnitude of increasing chromophore can enhance efficiency of photocurrent conversion.

Mechanism of Photocurrent Generation from the Dye–ITO Electrode. To examine the mechanism of light sensitization for the cathodic and anodic photocurrent, the energies of the relevant electronic states must be estimated. Using the reduction potential data obtained from Table 1, together with the monolayer optical excitation, an energy level diagram can be constructed as shown in Scheme 1 that describes the thermodynamics for spectral sensitization of the ITO electrode. The reduction potential for the dye MTMS (as an example) provides a measure of the energy of the LUMO. An estimate for the energetic level of the dye ground state can be obtained by subtracting the energy for excitation light of the monolayer from its reduction potential value. Calculated in this manner, the reduction potential for the ground state will correlate with the ability of the photoexcited dye to accept electrons from the ITO conduction band. From the electron affinity the conduction band (E_c) and valence band (E_v) edges of ITO electrode surface are estimated to be ca. −4.5 and −8.3 eV[20] respectively. The levels of the excited state and ground state for the dye MTMS film transferred under 30 mN m^{-1} are assumed to be −4.04 eV (−0.70 V vs SCE) and −6.99 eV on the absolute scale, respectively, with reference to the reduction potential of −0.70 V (vs SCE) and band gap of 2.95 eV (420 nm). The reduction potential of MV^{2+} is −4.51 eV (−0.23 V vs SCE)[21] and the oxidation potential of H$_2$Q is −4.61 eV (−0.13 V vs SCE),[21] respectively, on the absolute scale.

It can be seen from Scheme 1 that, in the presence of redox couples, if the system is favorable to electron donation it will exhibit anodic photocurrent, while if there are electron acceptors in the aqueous phase it will exhibit

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(21) Kim, Y. S.; Liang, K.; Law, K. Y.; Whitten, D. G. *J. Phys. Chem.* **1994**, *98*, 984.

cathodic photocurrent. This is beecause 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.

The cathodic photocurrent 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[21] in the presence of some electron acceptors, such as O_2 and MV^{2+}, or in an acidic medium in an electrolyte solution. If there are strong electron donors in the system, 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,[21] resulting in an anodic photocurrent.

Conclusions

(1) Two novel trichromophore amphiphilic dyes were designed and synthesized, and the characterizations of their photoelectric conversion were investigated by the LB film technique.

(2) The experiment shows that when the electron-withdrawing groups are identical, the stronger the ability of the releasing electron of the electron-releasing group, the higher the quantum yield for the photoelectric conversion of the material. For example, when the electron acceptor is pyridinium, since the sequence of the ability of releasing electron is $R_2N > (RO)_2 > RO$, this results that the photocurrent generation values of the MTDS, MTMS, and MTOS molecules are 1.8×10^{-12}, 1.2×10^{-12}, and 0.52×10^{-12} nA/molecule.

(3) The efficiency of the photocurrent response is increased with increasing number of chromophores in one molecule. For instance, the photocurrent generation of the MTOS molecule is 4-fold larger than that for $C_{18}H_{37}OC_6H_4CH=CHC_5H_4N^+CH_3I^-$.

(4) The magnitude of the active molecule/unit area can be increased as the surface pressure of the LB film is increased, resulting in that the quantum yield of the photocurrent generation is enhanced. When the surface pressure is 30 mN m^{-1}, for example, the quantum yields of the MTDS, MTMS, and MTOS molecules are 2.1, 1.4, and 1.54%, respectively, while their corresponding quantum yields are 0.83, 0.97, and 1.14% when the surface pressure is 10 mN m^{-1}.