

# Photoelectric Generation and Second-Order Nonlinear Optical Characters of the Dichromophore Dye Molecules

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Received: February 18, 1999; In Final Form: June 4, 1999

Centrosymmetric molecules can exhibit strong second-harmonic generation (SHG) by Langmuir–Blodgett (LB) technique. The macroscopic nonlinearity  $\chi^{(2)}$  of the monolayer film reaches  $245 \text{ pm V}^{-1}$  for 4,4'-di{1-[1-(*N,N'*-dioctadecaneamino)phenylethylpyridinium bromide]octyl}dipyridinium bromide (PMV<sub>8</sub>) and that for 4,4'-di{1-[1-(*N,N'*-dioctadecaneamino)phenylethylpyridinium bromide]propyl}dipyridinium bromide (PMV<sub>3</sub>) is  $184 \text{ pm V}^{-1}$ . Steady cathodic photocurrent is obtained upon excitation of the dyes incorporated into LB films deposited on an ITO electrode. The observed quantum yield of the photocurrent strongly depends on the applied electrode potential, concentration of the electron acceptor or donor, pH of the electrolyte, and the chemical structure of the dye congeners. The quantum yield reaches 4.73% for PMV<sub>8</sub>, while that for PMV<sub>3</sub> is 3.94%, under favorable conditions.

## Introduction

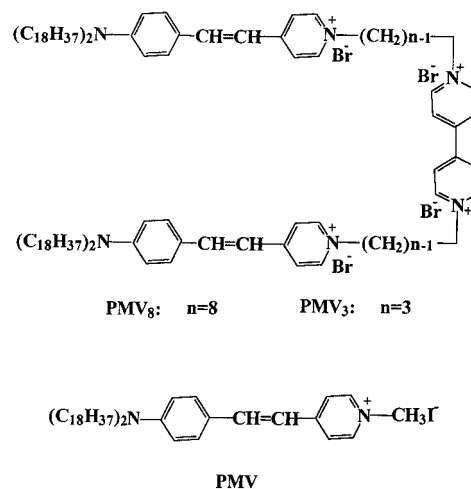
The study of the photosensitized charge injection in wide band gap semiconductors by adsorbed dyes has been initiated by the possible application to photoelectrochemical conversion of solar energy.<sup>1</sup> Our group has systematically studied the photoelectric conversion properties of some dye molecules with second-order nonlinear optical character and have found that the higher the molecular hyperpolarizability, the better the molecular photoelectric conversion efficiency.<sup>2–4</sup> It is known that hemicyanine is a good material in both second-order nonlinear optics<sup>5</sup> and photoelectric response,<sup>3</sup> and methyl viologen diiodide (MV<sup>2+</sup>) acts as a better electron acceptor in the photoelectrochemical system. We attempted to connect two hemicyanine chromophores with the viologen derivative as a bridge and expect to make charge separation easier and consequently to improve their second-harmonic generation (SHG) and photoelectric generation (PG) properties.

In this paper, we designed and synthesized centrosymmetric molecules 4,4'-di{1-[1-(*N,N'*-dioctadecaneamino)phenylethylpyridinium bromide]propyl}dipyridinium bromide (PMV<sub>3</sub>) and 4,4'-di{1-[1-(*N,N'*-dioctadecaneamino)phenylethylpyridinium bromide]octyl}dipyridinium bromide (PMV<sub>8</sub>). For comparison, *N*-methyl(*N,N'*-dioctadecaneamino)pyrenylethylpyridinium iodide (PMV) also was synthesized (Scheme 1). These dye molecules were successfully transferred onto ITO electrode by the LB technique. SHG and photoelectric conversion properties were studied. Mechanistic models for photocurrent generation under different conditions are proposed.

## Experimental Section

4-(Dioctadecaneamino)benzaldehyde was synthesized according to the method reported previously.<sup>6</sup> The viologen derivative was synthesized by reaction of dipyridine with 1,3-dibromopropane or 1,8-dibromooctane (Fluka) in absolute

## SCHEME 1



ethanol. 4,4'-Di[1-(4-methylpyridinium bromide)octyl]dipyridinium bromide was synthesized by reaction of 4,4'-di(1-brominoctyl)dipyridinium bromide with 4-methylpyridine in absolute ethanol. PMV<sub>8</sub> was synthesized by condensing 4,4'-di[1-(4-methylpyridinium bromide)octyl]dipyridinium bromide with an excess 4-(dioctadecaneamino)benzaldehyde in the mixture solvents of absolute ethanol and chloroform using piperidine as the catalyst. PMV<sub>3</sub> was synthesized following the same procedure as PMV<sub>8</sub>. PMV was synthesized by condensing 4-(dioctadecaneamino)benzaldehyde with 1,4-dimethylpyridinium iodide. During the entire synthesis process, the semifinished products were purified by recrystallization, and final products were purified by column chromatography under ambient conditions (eluent: chloroform–methanol, 10:1). The elemental analysis: Found for PMV<sub>8</sub>: C, 71.2; H, 9.5; N, 4.14%. Calc. for C<sub>124</sub>H<sub>208</sub>N<sub>6</sub>Br<sub>4</sub>: C, 70.83; H, 9.97; N, 4.0%. <sup>1</sup>H NMR

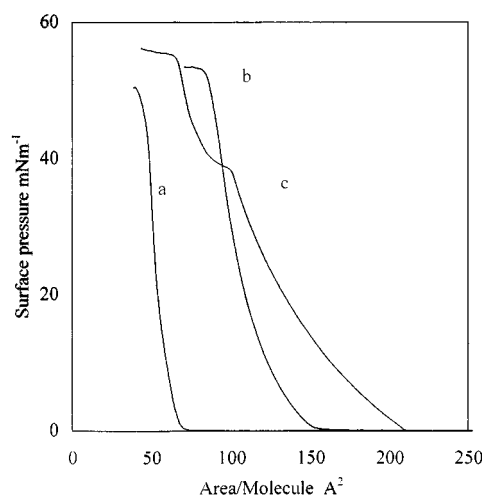
(CDCl<sub>3</sub>)  $\delta$  = 0.88 (t, 12H, 4CH<sub>3</sub>), 1.26 (m, 120H, 60 CH<sub>2</sub>), 1.68 (m, 8H, 4CH<sub>2</sub>), 1.95 (t, 16H, 8CH<sub>2</sub>), 3.19 (t, 8H, 4N-CH<sub>2</sub>), 3.44 (m, 8H, 4CH<sub>2</sub>), 4.68 (t, 4H, 2N<sup>+</sup>-CH<sub>2</sub>), 5.3 (t, 4H, 2N<sup>+</sup>-CH<sub>2</sub>), 6.63 (d, 4H, 2phenyl), 6.90(d, 2H, 2-CH=), 7.51-(d, 4H, 2phenyl), 7.53(d, 2H, 2CH=), 7.80 (d, 4H, 2pyridinyl), 9.00 (d, 4H, 2dipyridinyl), 9.10 (d, 4H, 2dipyridinyl). Mp. 64–66 °C. Elemental analysis: Found for PMV<sub>3</sub>: C, 70.16; H, 11.08; N, 4.52%. Calc. for C<sub>114</sub>H<sub>188</sub>N<sub>6</sub>Br<sub>4</sub>: C, 69.77; H, 9.66; N, 4.28%. <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  = 0.87 (t,12H, 4CH<sub>3</sub>), 1.25 (m, 120H, 60CH<sub>3</sub>), 1.60 (m, 8H, 4CH<sub>2</sub>), 3.31 (t,8H, 4N-CH<sub>2</sub>), 3.48 (m, 4H, 2-CH<sub>2</sub>-), 4.8 (t, 4H, 2N<sup>+</sup>-CH<sub>2</sub>), 5.0 (t, 4H, 2N<sup>+</sup>-CH<sub>2</sub>), 6.63 (d, 4H, 2phenyl), 6.79 (d, 2H, 2-CH=), 7.46 (d, 4H, 2phenyl), 7.54 (d, 4H, 2pyridinyl), 7.66 (d,2H, 2-CH=), 7.82 (d, 4H, 2pyridinyl), 8.75 (d, 4H, 2dipyridinyl), 9.29 (d, 4H, 2dipyridinyl). Mp. 79–80 °C. The elemental analysis: Found for PMV: C, 71.39; H, 11.80; N, 3.34%. Calc. for C<sub>50</sub>H<sub>87</sub>N<sub>2</sub>I: C, 71.23; H, 10.40; N, 3.32%. <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  = 0.88 (t, 6H, 2CH<sub>3</sub>), 1.26 (m, 60H, 30CH<sub>2</sub>), 1.60 (m,4H, 2CH<sub>2</sub>), 3.32 (t, 4H, 2N-CH<sub>2</sub>), 4.38 (s, 3H, 1N<sup>+</sup>-CH<sub>3</sub>), 6.62 (d, 2H, phenyl), 6.85 (d, 1H, 1-CH=), 7.52 (d, 2H, phenyl), 7.62 (d, 1H, 1-CH=), 7.82 (d, 2H, pyridinyl), 8.75 (d, 2H, pyridinyl). Mp. 198–199 °C. Methyl viologen diiodide (MV<sup>2+</sup>) was synthesized by reaction of 4,4'-dipyridyl with methyl iodide. Its identity was confirmed by <sup>1</sup>H NMR analysis. The electrolyte for the electrochemical experiment was KCl (AR). Hydroquinone (H<sub>2</sub>Q) (AR) was recrystallized from water before use. The spreading solvent used for film deposition was chloroform (AR).

C, H, and N analyses of the compounds were performed by using a Carlo Erba 1106 elemental analyzer. <sup>1</sup>H NMR spectra were obtained by using Bruker ARX400. Electronic spectra were measured with a Shimadzu model 3100 UV-vis-near-IR spectrophotometer. SHG experiments were carried out in transmission with a Nd:YAG 1064 nm laser as incident fundamental light. The monolayers of PMV, PMV<sub>3</sub>, and PMV<sub>8</sub> were prepared by spreading on NIMA 622 Langmuir-Blodgett trough, and the temperature was kept constant at 20 ± 2 °C. Details on the method used for pressure ( $\pi$ )-area ( $A$ ) measurement and transfer process were the same as described previously.<sup>7</sup> Ultrapure water from a EASYpure RF system was used throughout ( $R \sim 18$  M $\Omega$ ). In all cases, the transfer ratio was close to 1.0 ± 0.1.

Photoelectrochemical measurements were carried out in 0.5 M KCl solution using the LB-modified ITO electrode, platinum wire, and Ag/AgCl electrode as working electrode, counter electrode, and reference electrode, respectively. The effective illuminated area of a flat window was 0.38 cm<sup>2</sup>. The light source used for the photoelectrochemical study was a 500 W Xe arc lamp; the light beam was passed through a group of filters (ca. 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). Cyclic voltammetry (CV) experiments were performed on an EG&GPAR 273 potentiostat/galvanostat with EG&GPAR 270 electrochemical software.

## Results and Discussion

**$\pi$ - $A$  isotherms and UV spectra.** The pressure-area isotherms of three dyes (PMV, PMV<sub>3</sub>, and PMV<sub>8</sub>) are given in Figure 1, which show that the collapses pressure of those molecules are larger than 50 mN m<sup>-1</sup>, indicating that they can form good monolayer film on water. The isothermal shapes of PMV and PMV<sub>3</sub> show similar trends with increasing pressure, and limiting area are 0.53 and 1.25 nm<sup>2</sup> molecule<sup>-1</sup>, respectively,



**Figure 1.** Surface pressure-area ( $\pi$ - $A$ ) isotherms of PMV (a) PMV<sub>3</sub> (b), and PMV<sub>8</sub> (c) at the air/water interface (20 ± 1 °C).

extrapolated from the  $\pi$ - $A$  curves under 30 mN m<sup>-1</sup>. The molecule area of PMV is equal to the congener (C<sub>16</sub>H<sub>33</sub>)<sub>2</sub>N-C<sub>6</sub>H<sub>4</sub>-CH=CH-C<sub>5</sub>H<sub>4</sub>N-CH<sub>3</sub>I reported (0.53 nm<sup>2</sup>).<sup>5</sup> When the surface pressure continues to be increased, the isotherm of PMV<sub>8</sub> shows a plateau-like region from 1.2 to 0.6 nm<sup>2</sup>, and the limiting area is 1.1 or 1.7 nm<sup>2</sup> molecule<sup>-1</sup>, extrapolated from the  $\pi$ - $A$  curve under 45 or 30 mN m<sup>-1</sup>, respectively (Table 1, A). The discrepancy between PMV<sub>3</sub> and PMV<sub>8</sub> is due to the alkyl chain length. The published value<sup>8</sup> of the viologen headgroup is 0.90 nm<sup>2</sup>. The values measured for the PMV<sub>3</sub> and the PMV<sub>8</sub> are slightly larger than that mentioned above. Owing to the fact that eight methylenes carbon chain can be folded when the surface pressure is increased, while one of the PMV<sub>3</sub> is not, we can suggest that the PMV<sub>3</sub> and PMV<sub>8</sub> are oriented as shown in Scheme 2 and the plateau region is attributed to the folding process of the eight methylenes chains.

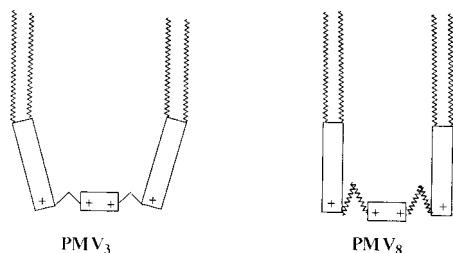
The spectra of dyes PMV, PMV<sub>3</sub>, and PMV<sub>8</sub> in LB films are similar but the broad absorption maximum of the charge-transfer band is blue-shifted by ca. 30 nm from the chloroform solution to LB films for the corresponding dye (Table 1,  $\lambda_{\text{max}}$ ), indicating the presence of H-aggregates in the films.<sup>9</sup> Data also show that  $\lambda_{\text{max(l)}}$  values successively blue shift from PMV to PMV<sub>8</sub>, by ca. 5 nm. This is not unusual, because alkyl chain has the ability of pushing the electron.

**SHG Properties.** The data of second-harmonic generation (SHG) from the LB films were analyzed by the general procedure described by Ashwell et al.<sup>13</sup> The higher intensity is obtained for the PMV<sub>8</sub> film deposited on quartz under 45 mN m<sup>-1</sup>. The optimum signal is higher than the SHG from monolayer films of the more commonly reported donor-( $\pi$ -bridge)-acceptor (D- $\pi$ -A) dyes.<sup>5</sup> For example, the macroscopic nonlinearity  $\chi^{(2)}$  value of the similar hemicyanine (C<sub>16</sub>H<sub>33</sub>)<sub>2</sub>N-C<sub>6</sub>H<sub>4</sub>-CH=CH-C<sub>5</sub>H<sub>4</sub>N-CH<sub>3</sub>I is 146 pm V<sup>-1</sup>, while the  $\chi^{(2)}$  value of the PMV, PMV<sub>3</sub>, or PMV<sub>8</sub> is 176, 184 or 245 pm V<sup>-1</sup>, respectively (Table 1). The tilt angle  $\varphi$  of the chromophores to the normal of the film surface changes from 30° to 35°, which agrees with the similar compounds.<sup>5,11</sup> It is known that PMV<sub>3</sub> and PMV<sub>8</sub> have a center of symmetry in the molecules, but they cannot yield SHG according to the principle of second-harmonic nonlinear optics; but the measurement of SHG shows that the two dyes have stronger signal than the PMV. This fact indicates the LB method can offer the opportunity to orient chromophores which would normally tend to centrosymmetry.<sup>12</sup> In order to understand the effect of the surface pressure on SHG, we chose PMV<sub>8</sub> to determine SHG

**TABLE 1: Experimental Data of PMV, PMV<sub>3</sub> and PMV<sub>8</sub><sup>a</sup>**

	$I^a$ (nA cm <sup>-2</sup> )	$I^b$ (nA cm <sup>-2</sup> )	$\eta^b$	$I^c$ (nA cm <sup>-2</sup> )	$\eta^c$	$\chi^{(2)}$ (pm V <sup>-1</sup> )	$\varphi$ (deg)	$A$ (nm <sup>2</sup> )	$\pi$ (nM m <sup>-1</sup> )	$\lambda_{\max(l)}$ (nm)	$\lambda_{\max(s)}$ (nm)
PMV	1345–1562.6	300.3	1.44	480.5	2.21	176	31	0.53	30	520	487
PMV <sub>3</sub>	1044–1428	251.6	2.46	402.6	3.94	184	36	1.25	30	515	483
PMV <sub>8</sub>	1535–2063.1	372.6	2.96	596.2	4.73	245	30	1.10	45	511	480

<sup>a</sup>  $I$ , photocurrent;  $\eta$ , quantum yield;  $\chi^{(2)}$ , macroscopic nonlinearity value;  $\varphi$ , tilt angle;  $A$ , area/molecule;  $\lambda_{\max}$ , maximum wavelength (l and s present solution and film, respectively);  $\pi$ , deposited pressure. (a) irradiation under 110 mW cm<sup>-2</sup> white light, in 0.5 M KCl electrolyte solution containing 1 mM MV<sup>2+</sup>. (b) irradiation under -100 mV, in 0.5 M KCl electrolyte solution containing solvated O<sub>2</sub> and 1 mM MV<sup>2+</sup>, at 464 nm. (c) irradiation under -100 mV, pH = 2, solvated O<sub>2</sub> and 5 mM MV<sup>2+</sup>, at 464 nm.

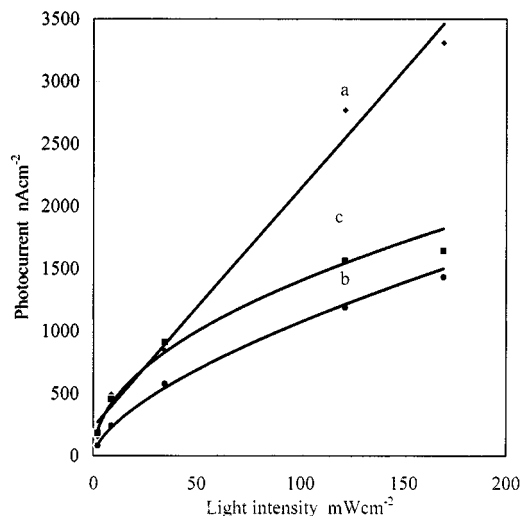
**SCHEME 2**

in different depositing pressure. Experiment found that when the PMV<sub>8</sub> monolayer was deposited under 10 mN m<sup>-1</sup>, the tilt angle  $\varphi$  is 40°, which is larger than that (30°) under 45 mN m<sup>-1</sup> as we predict.  $\chi^{(2)}$  value is only 106 pm V<sup>-1</sup>, that is, less than half of the value (245 pm V<sup>-1</sup>) under 45 mN m<sup>-1</sup>. This is because  $\chi^{(2)}$  depends not only on the molecular nonlinearity but also on the orientation of the chromophores and the ordering of the films. It is also worth noting that the sequence of resonant enhancement is PMV > PMV<sub>3</sub> > PMV<sub>8</sub>, while the sequence of  $\chi^{(2)}$  is PMV < PMV<sub>3</sub> < PMV<sub>8</sub>, so the enhancement of SHG should be attributed to the structure effect of the molecules.

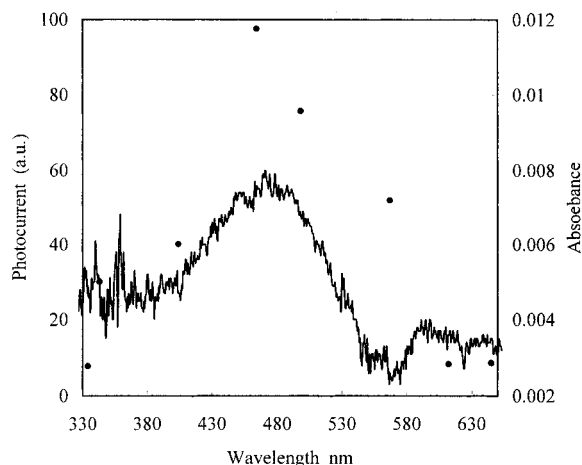
**Photocurrent Generation on Dye-Modified ITO Electrodes.** The principle of second-harmonic nonlinear optics requires that the molecule has a large difference of the dipole moment between the ground and excited states. On the other hand, photocurrent generation and charge dissociation are connected with the charge separation process, which also requires a large dipole moment in the excited state. In order to obtain a better understanding of the relationship between the SHG and the photoelectric conversion, the photoelectric properties of above three dyes were investigated in detail.

**Light Intensity Dependence of the Photocurrent.** Figure 2 shows the intensity dependence of the photocurrent measured at a zero bias potential versus SCE for PMV, PMV<sub>3</sub>, and PMV<sub>8</sub> LB films on ITO electrode, in 0.5 M KCl electrolyte solution containing 1 mM MV<sup>2+</sup>. The equations are (a)  $y = 19.1x + 231.6$ , (b)  $y = 56.3x^{0.64}$ , and (c)  $y = 97.6x^{0.68}$  for PMV, PMV<sub>3</sub>, and PMV<sub>8</sub>, respectively. It was pointed out that the photocurrent,  $i$ , 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>13</sup> Comparing these equations with the generally used form,  $i = KI^m$ , it is known that  $m$  is 1, 0.64, and 0.68 for PMV, PMV<sub>3</sub>, and PMV<sub>8</sub>, respectively, indicating that the separated charge loss process occurs in the dye LB films under unimolecular recombination for PMV system and occurs in both of the above recombination processes for PMV<sub>3</sub> and PMV<sub>8</sub> systems.

**Dependence on Redox Concentration and Photocurrent Generation.** A steady cathodic photocurrent was obtained from the dyes monolayer-modified ITO electrode in 0.5 M KCl solution containing 1 mM MV<sup>2+</sup> as an electron carrier by illumination of 110 mW cm<sup>-2</sup> white light. The agreement between the action spectra and absorption of the PMV<sub>8</sub> in 365–



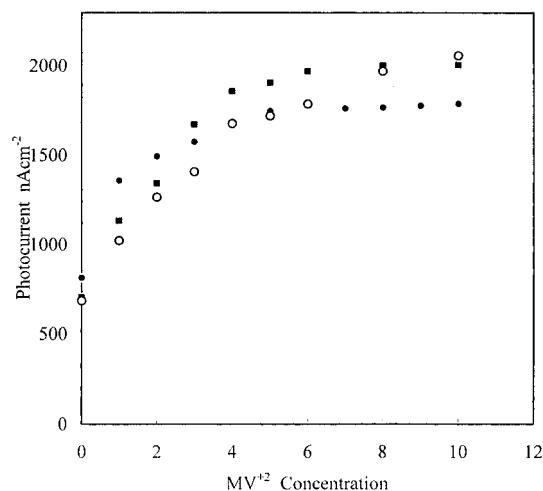
**Figure 2.** Light intensity dependence of the photocurrent measured versus SCE for three electrodes in 0.5 M KCl electrolyte solution containing 1 mM MV<sup>2+</sup> under ambient condition without bias voltage: (a) PMV; (b) PMV<sub>3</sub>; (c) PMV<sub>8</sub>.



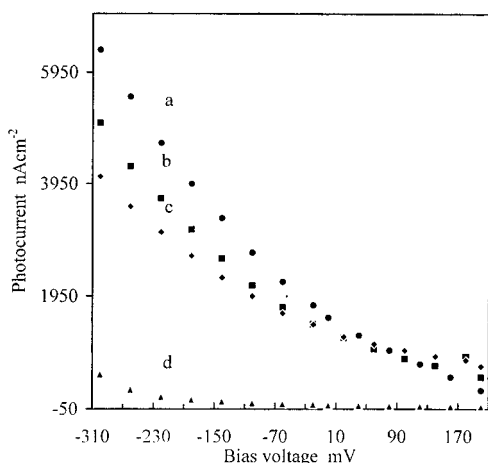
**Figure 3.** UV-vis absorption spectrum (—) and action spectrum (●) for PMV<sub>8</sub> monolayer on ITO electrode. Photocurrent measured at 464 nm without bias voltage. The intensities of different wavelengths are all normalized.

600 nm as an example for the dye congeners was shown in Figure 3, indicating that the aggregate of the dye in the LB film is responsible for photocurrent generation.

Figure 4 shows a plot of the photocurrents versus the concentration of acceptor (MV<sup>2+</sup>), illuminated by 110 mW cm<sup>-2</sup> white light and without any bias voltage, in 0.5 M KCl electrolyte solution. At low concentration the magnitude of the photocurrent is observed to show an increase with the concentration of the MV<sup>2+</sup> and then levels off when the concentration is higher than 5 mM. At these high concentrations the electron transfer depends only on the concentration of surface generated holes. Experiment found that solvated oxygen is favorable to



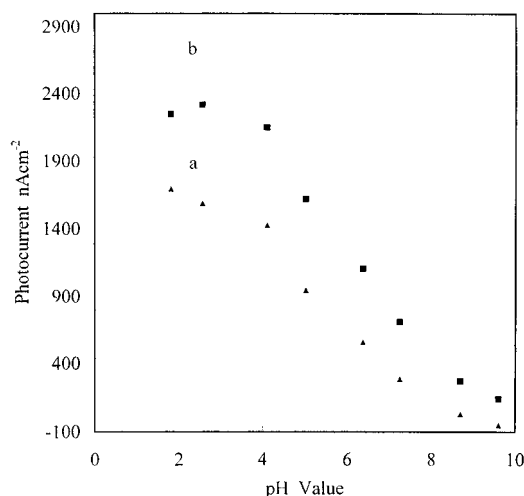
**Figure 4.** Dependence of the photocurrent on the concentration of MV<sup>2+</sup> under ambient conditions: (○) for PMV; (■) for PMV<sub>3</sub>; (●) for PMV<sub>8</sub>.



**Figure 5.** Photocurrent vs bias voltage for PMV<sub>8</sub> (a), PMV<sub>3</sub> (b), and PMV (c) LB films-ITO electrodes in 0.5 M KCl aqueous solution containing 1 mM MV<sup>2+</sup>, under ambient conditions, upon irradiation with a 110 mW cm<sup>-2</sup> white light; (d) dark current.

cathodic photocurrent because it acts as an electron acceptor through the formation of a superoxide anion radical. If the H<sub>2</sub>Q was added into the electrolyte solution, the photocurrent was quickly decreased, even the concentration of the H<sub>2</sub>Q is 0.1 mM, indicating that the H<sub>2</sub>Q is unfavorable to the production of a cathodic photocurrent in the system.

**Photocurrent Voltage Measurements.** The dependence of the photocurrent on the applied bias potential is an important character for a photocurrent cell. Figure 5 shows the photocurrent voltage curves for PMV, PMV<sub>3</sub>, and PMV<sub>8</sub> modified ITO electrodes. Comparing curves (a), (b), and (c) with curve (d), the dark current is meagre, indicating that the current is generated by the light-sensitized dye molecules. When a negative bias voltage is applied to the ITO electrode the cathodic photocurrent is increased with increasing applied bias potential and vice versa. This can be attributed to an enhancement of the rate constant for charge transfer or an efficient dissociation of electron-hole pairs. When 1 mM MV<sup>2+</sup> and O<sub>2</sub> are presented in the electrolyte solution, ca. 300, 252, and 373 nA cm<sup>-2</sup> photocurrent was obtained for the three dyes under -100 mV bias voltage at 464 nm irradiation with a  $1.14 \times 10^{16}$  photons cm<sup>-2</sup> s<sup>-1</sup> light intensity. In this case, the quantum yields reach ca. 1.44, 2.06, and 2.96% for PMV, PMV<sub>3</sub>, and PMV<sub>8</sub>, respectively (the corresponding absorbance ratio of the films



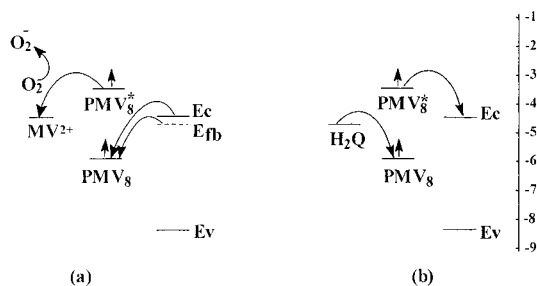
**Figure 6.** Effect of pH on PMV<sub>8</sub>-ITO electrode photocurrent in Britton-Kobison buffer solution containing 0.5 M KCl under ambient conditions, upon irradiation with 110 mW cm<sup>-2</sup> white light: (a) without bias voltage, (b) under -100 mV.

are ca. 1.14, 0.56, and 0.69 for incident light at 464 nm), (Table 1, I<sup>b</sup>, η<sup>b</sup>). Open circuit photopotentials are 0.52, 0.35, and 0.28 V; short circuit photocurrents are 1.31, 1.35, and 1.58 μA for PMV, PMV<sub>3</sub>, and PMV<sub>8</sub>, respectively.

**Dependence on pH Values.** In order to understand the effect of the acid or base character of the medium on the photocurrent generation, the effect of pH value on the photocurrent generation was investigated in a Britton-Robinson buffer solution, containing 0.5 M KCl. Figure 6 shows that the cathodic photocurrent generated from PMV<sub>8</sub>-modified ITO electrode was quickly increased when pH value was decreased under zero bias voltage (Figure 6a). The photocurrent changed with pH value was also determined under -100 mV as shown in Figure 6b. 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 than that at the corresponding pH value of zero bias voltage. This is attributed to the fact that an acidic medium can lead to an anodic shift of the flat-band potential of the ITO electrode. Under favorable conditions, e.g. pH ca. 2, in the presence of O<sub>2</sub> and 5 M MV<sup>2+</sup>, with -100 mV bias voltage, a photocurrent of 596.2 nA cm<sup>-2</sup> for the PMV<sub>8</sub> was obtained under 464 nm irradiation; the quantum yield is 4.73%, while under the same conditions, the quantum yields are 2.21% and 3.94% for PMV and PMV<sub>3</sub>, respectively (Table 1, I<sup>c</sup>, η<sup>c</sup>).

**Electrochemical Properties of the Dyes.** In order to estimate the redox potentials of the excited-state dye and to discuss the mechanism of photocurrent generation, CV studies were carried out. The electrochemical properties of the three dye molecules were determined in 0.5 M KCl aqueous solution, the monolayer dye-ITO used as working electrode. Oxygen was removed from the electrolyte solution by bubbling N<sub>2</sub> before every measurement. Cyclic voltammetry of PMV, PMV<sub>3</sub> and PMV<sub>8</sub> monolayer films on ITO electrodes shows similar shape, indicating that the electrochemical behavior of the LB films on the ITO electrode is identical for these dyes. The oxidation peak potentials are 1.15, 1.10, and 1.19 V for PMV, PMV<sub>3</sub>, and PMV<sub>8</sub>, respectively.

**Mechanism of Photocurrent Generation.** In order 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 oxidation potential data obtained from the CV, together with the monolayer optical excitation, an energy level diagram can be constructed as shown

**SCHEME 3: Schematic Diagram Showing Electron Transfer Processes<sup>a</sup>**

<sup>a</sup> (a) Cathodic photocurrent; (b) anodic photocurrent.  $PMV_8$  and  $PMV_8^*$  present the ground state and excited state of the dye  $PMV_8$ , respectively;  $E_{fb}$  presents an anodic shift of flat-band potential in the acidic medium.

in Scheme 3 that describes the thermodynamics for spectral sensitization of the ITO electrode. The oxidation peak potential for the dye  $PMV_8$  (as an example) provides a measure of the energy of the HOMO. An estimate for the energetic level of the dye-excited state can be obtained by subtracting the energy for excitation light of the monolayer from its oxidation potential value. Calculated in this manner, the oxidation potential for the excited state will correlate with the ability of the photoexcited dye to inject electrons into the ITO conduction band. From the electron affinity the conduction band (Ec) and valence band (Ev) edges of ITO electrode surface are estimated to be ca.  $-4.5$  eV and  $-8.3$  eV,<sup>14</sup> respectively. The energy levels of the excited state and ground state for the dye  $PMV_8$  film transferred under  $45 \text{ mN m}^{-1}$  are assumed to be  $-5.93$  eV ( $1.19$  V vs SCE) and  $-3.35$  eV on the absolute scale, respectively, with reference to oxidation potential of  $1.19$  V (vs SCE) and band gap of  $2.58$  eV ( $480$  nm). Reduction potential of  $MV^{2+}$  is  $-4.51$  eV ( $-0.23$  V vs SCE),<sup>15</sup> and oxidation potential of  $H_2Q$  is  $-4.61$  eV ( $-0.13$  V vs SCE)<sup>15</sup>, respectively, on the absolute scale.

It can be seen from the Scheme 3 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 cathodic photocurrent because 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.

According to the Franck–Condon principle, the only possibility under these circumstances is electron transfer between the ITO substrate and  $PMV_8^*$  within the LB film. In the presence of some electron acceptors such as  $O_2$  and  $MV^{2+}$  in electrolyte or in acidic medium, electrons transfer from the excited state of  $PMV_8^*$  to the electron acceptor, and subsequently the electrons of ITO conduction band inject into the hole residing in the dye aggregate.<sup>15</sup> Thus, cathodic photocurrent was generated. 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. When  $H_2Q$  donates electron to the hole of the ground-

state dye aggregate,<sup>15</sup> the generated anion radical can transfer an electron to the ITO conduction band, resulting in a reduced photocurrent or an anodic photocurrent. The same mechanisms for  $PMV_3$  and  $PMV$  were followed when they are excited and photocurrent is generated.

**Conclusion**

From Table 1, one can conclude that the sequence of SHG  $\chi^{(2)}$  is  $PMV_8 > PMV_3 > PMV$  and the quantum yield of the photocurrent has similar sequence for the three dye molecules, indicating that there is a relationship between SHG and PG. Comparing the  $PMV_8$  with the  $PMV$ , due to having no 4,4'-dipyridinium cations in the  $PMV$  molecule, the photocurrent becoming small is rational. Because the viologen derivative is led into the  $PMV_8$  or  $PMV_3$ , it makes the excited-state electron separate from the electron–hole pairs more efficient by than that in the  $PMV$ . Comparing the  $PMV_3$  with the  $PMV_8$ , due to the tensile stress of the alkyl chain between the two chromophores, it makes the two chromophores to be not well aligned in the  $PMV_3$ , compared with the  $PMV_8$ . On the other hand, the decrease of active molecules per unit is another reason, for the limiting area of the  $PMV_3$  is larger than that of  $PMV_8$ . In short, when two hemicyanine chromophores are connected with the viologen derivative of an eight-methylene chain, it not only enhances the SHG signal of the molecules within the LB films but also increases quantum yield of the photoelectric conversion on ITO electrode. The reason for this phenomenon is quite interesting and not quite clear yet at the present stage; more work in this respect is in progress.

**Acknowledgment.** The project is financially supported by climbing program and NNSFC (No. 29671001).

**References and Notes**

- (1) Roberts, G. *Sensors Actuators* **1984**, *4*, 131.
- (2) Xia, W. S.; Huang, C. H.; Zhou, D. J. *Langmuir* **1997**, *13*, 80.
- (3) Xia, W. S.; Huang, C. H.; Ye, X. Z.; Luo, C. P.; Gan, L. B.; Liu, Z. F. *J. Phys. Chem.* **1996**, *100*, 2244.
- (4) Lang, A. D.; Zhai, J.; Huang, C. H.; Gan, L. B.; Zhao, Y. L.; Zhou, D. J.; Chen, Z. D. *J. Phys. Chem. B* **1998**, *102*, 1424.
- (5) Bubeck, C.; Laschewsky, A.; Lupo, D.; Neher, D.; Ottenbreit, P.; Paulus, W.; Prass, W.; Ringsdorf, H.; Wegner, G. *Adv. Mater.* **1991**, *3*, 54.
- (6) Wu, D. G.; Huang, Y. Y.; Huang, C. H.; Gan, L. B. *J. Chem. Soc., Faraday Trans.* **1998**, *94*, 1411.
- (7) Wu, D. G.; Huang, C. H.; Gan, L. B.; Huang, Y. Y. *Langmuir* **1998**, *14*, 3783.
- (8) Cotton, T. M.; Kim, J. H.; Uphaus, R. A. *Microchem. J.* **1990**, *42*, 44.
- (9) Mooney, W. F.; Brown, P. E.; Russell, J. C.; Costa, S. B.; Pedersen, L. G.; Whitten, D. G. *J. Am. Chem. Soc.* **1984**, *106*, 5659.
- (10) Ashwell, G. J.; Jackson, P. D.; Crossland, W. A. *Nature* **1994**, *368*, 438.
- (11) Huang, C. H.; Wang, K. Z.; Xu, G. X.; Zhao, X. S.; Xie, X. M.; Xu, Y.; Liu, Y. Q.; Xu, L. G.; Li, T. K.; *J. Phys. Chem.* **1995**, *99*, 14397.
- (12) Ashwell, G. J.; Jefferies, G.; Hamilton, D. G.; Lynch, D. E.; Roberts, M. P. S.; Bahra, G. S.; Brown, C. R. *Nature* **1995**, *375*, 385.
- (13) Donovan, K. J.; Sudiwala, R. V.; Wilson, E. G. *Mol. Cryst. Liq. Cryst.* **1991**, *194*, 337.
- (14) Sereno, L.; Silber, J. J.; Otero, L.; Bohorquez, M. D. V.; Moore, A. L.; Moore, T. A.; Gust, D. *J. Phys. Chem.* **1996**, *100*, 814.
- (15) Kim, Y. S.; Liang, K.; Law, K. Y.; Whitten, D. G. *J. Phys. Chem.* **1994**, *98*, 984.