Enhancement of Second Harmonic Generation and Photocurrent Generation of a Novel Stilbazolium Dye Dimer in Langmuir−Blodgett Monolayer Films

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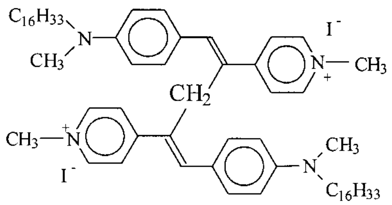
A novel amphiphilic stilbazolium dye dimer, bis{[1-(*N*-methyl-4-pyridinium)-2-(4-*N*-methyl-*N*-hexadecylaminophenyl)]ethenyl}methanediiodide (C_1BP) was synthesized, and (*E*)-*N*-methyl-4-[2-(4-*N*-methyl-*N*-hexadecylaminophenyl)ethenyl]pyridinium iodide (C_1P) as a standard for comparison was also synthesized. They were successfully transferred onto the semiconducting transparent indium−tin oxide (ITO) or quartz as H-aggregates by the Langmuir−Blodgett (LB) technique. This centrosymmetric dimer (C_1BP) can exhibit strong second-harmonic generation (SHG) by the LB method. The second harmonic susceptibility $\chi^{(2)}$ of the monolayer film reaches 167 pm V^{-1} for C_1BP and that for C_1P is 125 pm V^{-1}. The photoelectrochemistry of these dyes monolayer films was investigated in a traditional three-electrode cell. Steady cathodic photocurrent is obtained upon excitation of the dyes in LB films deposited on an ITO electrode. The observed photocurrent generation quantum yield strongly depended on the applied electrode potential, concentration of the redox couples in the electrolyte solution, and chemical structure of the dye congeners. The results show that the photocurrent generation property of the dimer is enhanced. The photocurrent generation quantum yield is 0.51% for C_1BP, while that for C_1P is 0.30%.

Introduction

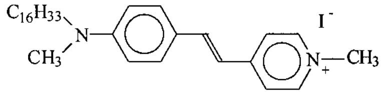
Because of rapid development of telecommunication techniques, there is growing interest in designing multiproperty molecule-based devices with conductivity, magnetism, and nonlinear optical response.[1−4] Our group has found that Langmuir−Blodgett films of some D-π-A conjugated systems appended with strong electron donors and acceptors not only show very good second harmonic generation but also exhibit good photoelectric conversion properties, which makes these dye films potentially useful as multifunctional organic materials.[5−9] Recently, our works indicate that better photocurrent generation of films can be observed when two or more chromophores are connected to one molecule by use of suitable bridges.[7−9]

As a part of the systematic study, herein we designed a novel stilbazolium dye dimer, bis{[1-(*N*-methyl-4-pyridinium)-2-(4-*N*-methyl-*N*-hexadecylaminophenyl)]ethenyl}methanediiodide (C_1BP) (Chart 1) connected

Chart 1. Molecular Structures of the Materials C_1BP and C_1P



C_1BP



C_1P

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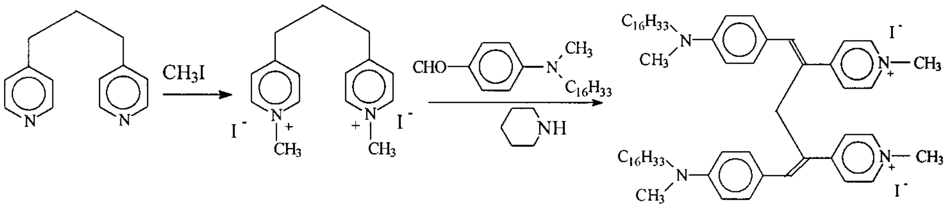
Scheme 1. Brief Synthetic Procedure for the C$_1$BP Molecule



with one CH$_2$ group. The dimer was successfully transferred onto an ITO electrode and quartz by LB technique. Second harmonic generation and photocurrent generation of C$_1$BP LB monolayer films were investigated. The possible mechanisms for photocurrent generation under different conditions are proposed. For comparison, the stilbazolium dye monomer (*E*)-*N*-methyl-4-[2-(4-*N*-methyl-*N*-hexadecylaminophenyl)ethenyl]pyridinium iodide (C$_1$P) was also synthesized and studied under the same conditions.

Experimental Section

Materials. C$_1$BP was prepared by the process shown in Scheme 1.

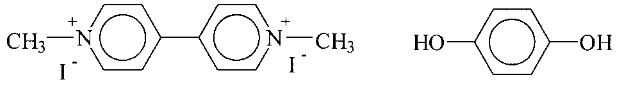
***N*-Methyl-*N*-hexadecylaniline.** *N*-Methylaniline (12 g) was reacted with 35 g of hexadecyl bromide in a mixture of 120 mL of toluene and 120 mL of 30% sodium hydroxide aqueous solution containing 0.2 g of *N*-hexadecyl-*N,N,N*-trimethylammonium bromide (as phase transfer catalyst) at 80 °C under stirring for at least 7 days. The toluene phase was washed with sodium chloride solution and then evaporated. The residue was purified on a silica gel column with pure petroleum ether and then a petroleum ether/ethyl acetate mixture as eluents: yield 84%, mp 52−53 °C.

***N*-Methyl-*N*-hexadecylaminobenzaldehyde.**[10] *N*-Methyl-*N*-hexadecylaniline (2.0 g) was added to 5 mL of DMF (freshly distilled). The mixture was cooled to 4 °C, and then 5 mL of POCl$_3$ was added dropwise to the mixture. This resulting mixture was kept stirring at room temperature for 1 h and then at 90 °C for 5 h. The reactant was purified on a silica gel column (petroleum ether/ethyl acetate mixture = 9:1 as eluent) after being neutralized to pH 7 with sodium hydroxide. A total of 0.24 g of target product was obtained: yield 12%, mp 54−55 °C.

1,3-(4-Pyridinium)propane diiodide was prepared according to the previous method reported.[11] The title dimer (C$_1$BP) was synthesized by condensing 120.5 mg of 1,3-(4-pyridinium)propane diiodide with 538.5 mg of 4-*N*-methyl-*N*-hexadecylaminobenzaldehyde in absolute ethanol, with piperidine as the catalyst. The product was purified by column chromatography on silica gel with a chloroform/methanol mixture (12:1) as the eluent: yield 48%, mp 223−225 °C. Anal. Calcd for $C_{63}H_{98}N_4I_2$: C, 64.96; H, 8.48; N, 4.81. Found: C, 65.25; H, 8.24; N, 5.15. ^{1}H NMR (300 MHz, CDCl$_3$): δ 0.88 (t, 6H, 2CH$_3$), 1.26 [m, 52H, 2(CH$_2$)$_{13}$], 1.69 (m, 4H, 2CH$_2$), 1.93 (m, 4H, 2CH$_2$), 3.10 (s, 2H, =CH−*CH$_2$*−CH=), 3.18 (s, 6H, 2N−CH$_3$), 3.42 (t, 4H, 2N−CH$_2$), 4.50 (s, 6H, 2N^{+-}CH$_3$), 7.01 (m, 4H, phenyl), 7.62 (d, 2H, phenyl), 7.77(d, 2H, phenyl), 7.96 (s, 2H, 2CH=),8.39(d, 2H, pyridyl), 8.77(d, 2H, pyridyl), 9.19 (m, 4H, pyridyl).

(*E*)-*N*-Methyl-4-[2-(4-*N*-methyl-*N*-hexadecylaminophenyl)ethenyl]pyridinium Iodide (C$_1$P). An absolute ethanol solution of 117.5 mg of *N*-methyl-4-methylpyridinium iodide was added to 179.5 mg of 4-*N*-methyl-*N*-hexadecylaminobenzaldehyde and 0.1 mL of piperidine. The mixture was refluxed for 8 h. After it was cooled to room temperature, the resulting precipitate was filtered and recrystallized from ethanol to give a red product: yield 80%, mp 207−208 °C. Anal. Calcd for $C_{31}H_{49}N_2I$: C, 63.33; H, 8.41; N, 4.76. Found: C, 63.85; H, 8.73; N, 5.13. ^{1}H NMR (300 MHz, CDCl$_3$): δ 0.88 (t, 6H, 2CH$_3$), 1.29 [m, 52H, 2(CH$_2$)$_{13}$], 1.60 (m, 2H, CH$_2$), 3.04 (s, 3H, N−CH$_3$), 3.38 (t, 2H, N−CH$_2$), 4.37 (s, 3H, N^{+-}CH$_3$), 6.67 (d, 2H, phenyl), 6.85 (d, 1H, CH=), 7.52 (d, 2H, phenyl), 7.59 (s, 1H, CH=), 7.82 (d, 2H, pyridyl), 8.77(d, 2H, pyridyl).

Chart 2. Molecular Structures of MV^{2+} and H$_2$Q



MV^{2+}

H$_2$Q

Methyl viologen diiodide (MV^{2+}, see Chart 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 (Beijing Chemical Factory, China). Hydroquinone (H$_2$Q, see Chart 2) (Beijing Chemical Factory, China) was recrystallized from water before use. EuCl$_3$·6H$_2$O was obtained by reaction of Eu$_2$O$_3$ with hydrochloric acid. The spreading solvent used for monolayer deposition was chloroform (Beijing Chemical Factory, China).

C, H, and N data for the compounds were obtained by using a Carlo Erba 1106 elemental analyzer. ^{1}H NMR spectra were measured on a Bruker ARX300 instrument. Electronic spectra in solution or on LB monolayer films were recorded on a Shimadzu model 3100 UV−vis−NIR spectrophotometer. Melting point was performed on an X4 micromelting point apparatus. The monolayers of C$_1$BP and C$_1$P were prepared by spreading corresponding dye solution on a NIMA 622 Langmuir−Blodgett trough. Water from a EASY pure RF system was used as a subphase ($R \sim 18$ MΩ·cm, pH ∼ 5.6). All experiments were carried out at a subphase temperature of 20 ± 1 °C. Details on the method used for pressure (π) area (A) measurement and transfer process were the same as described previously.[12] In all cases, the transfer ratios were close to 1.0 ± 0.1.

The second-harmonic generation (SHG) experiments were carried out in transmission with the laser beam (Nd:YAG, $\lambda = 1064$ nm) at an angle of 45° to the LB monolayer films. The SHG intensities were calibrated against a Y-cut quartz reference ($d_{11} = 0.5$ pm V^{-1}). The data of second-harmonic generation (SHG) from the LB monolayer films were analyzed by the general procedure described by Ashwell et al.[13]

Photoelectrochemical measurements were carried out in 0.5 M KCl solution with the LB monolayer-modified ITO electrode, platinum wire, and saturated calomel electrode (SCE) as working electrode, counterelectrode, and reference electrode, respectively. Effective illuminated areas of a flat window for C$_1$BP- and C$_1$P-modified ITO electrodes were 0.8 cm^2. 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. 400−800 nm, Toshiba Co., Japan, and Schott Co., Germany) in order to get a given band-pass of light. The light intensity at each wavelength was measured with an energy and power meter (Scientech Co.). Cyclic voltammetric (CV)

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Table 1. Properties of C_1BP and C_1P LB Films[a]

	I^b, nA cm^{-2}	I^c, nA cm^{-2}	η^c, %	no. (m), 10^{14} cm^{-2}	$I^{c'}$, 10^{-12} nA molecule^{-1}	I^d, nA cm^{-2}	η^d, %	$\chi^{(2)}$, pm V^{-1}	φ, deg	A, nm^2	$\lambda_{max(sol)}$, nm	$\lambda_{max(film)}$, nm
C_1BP	~780	30	0.51	1.47	5.30	132	2.44	167	32	0.68	513	462
C_1P	~546	22	0.30	2.86	1.91	91	1.24	125	29	0.35	503	460

[a] I, photocurrent per square centimeter; η, external quantum yield; no.(m), number of molecules per square centimeter; $I^{c'}$, photocurrent per molecule; $\chi^{(2)}$, second-order susceptibility; φ, tilt angle relative to the normal line on the substrate; A, limiting area per molecule; $\lambda_{max(sol)}$, absorption maximum of electric spectrum in chloroform solution; $\lambda_{max(film)}$, absorption maximum of electric spectrum for LB film. [b] Under irradiation of 137 mW cm^{-2} white light for $C_1BP$and C_1P, in 0.5 M KCl electrolyte solution under ambient conditions. [c] Under monochromized irradiation at 464 nm from a 137 mW cm^{-2} white light for C_1BP and C_1P, in 0.5 M KCl electrolyte solution under ambient conditions. [d] Under monochromized irradiation at 464 nm from a 137 mW cm^{-2} white light for C_1BP and C_1P, under −100 mV and in 0.5 M KCl solution under ambient conditions containing 5 mM $EuCl_3$ and 4 mM MV^{2+}.

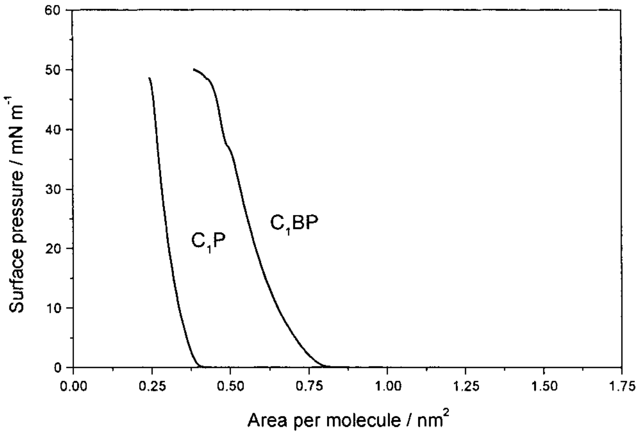

Figure 1. Surface pressures versus area isotherms of C_1BP and C_1P dyes at the air/water interface (20 ± 1 °C).

experiments (sweep rate = 100 mV s^{-1}) were performed on an EG&G PAR 273 potentiostat/galvanostat with EG&G PAR 270 electrochemical software. Oxygen was removed from the electrolyte solution by bubbling N_2 before every measurement.

Results and Discussion

Properties of LB Monolayer Films. The amphiphilic styryl dyes were characterized by the measurement of their surface pressures−area isotherms in the monolayer on the subphase. It can be seen from Figure 1 that the collapse pressures of C_1BP and C_1P are 47 and 48 mN m^{-1}, respectively, which reveals that the two dyes have good film formation properties. But the limiting molecular areas of C_1BP and C_1P are different. The limiting molecular areas of C_1BP and C_1P are 0.68 and 0.35 nm^2, respectively; that is, the limiting area of C_1BP is smaller than that twice that for C_1P, which is in agreement with the fact that C_1BP is a dimer derivative of C_1P. At the same time, we can conclude that the density of chromophores in C_1BP LB films is higher than that of C_1P and that the interchromophoric distance is shorter than that in the C_1P assembly.

Table 1 shows the data of UV−vis spectra of C_1BP and C_1P. λ_{max} values of C_1BP and C_1P in chloroform solution are 513 and 503 nm, respectively. When two D-π-A chromophores are linked together by a methylene group to form a C_1BP molecule, the intramolecular and intermolecular interactions between two D-π-A chromophores exist for C_1BP in chloroform solution, whereas only intermolecular interactions exist for C_1P in chloroform solution. Furthermore, the interchromophoric distance in C_1BP is shorter than that in the C_1P assembly, which means that the interaction between π-orbitals of chromophores in C_1BP becomes stronger than that of chromophores in C_1P. Therefore, λ_{max} of C_1BP in chloroform is 10 nm red-shifted compared with that of C_1P. Upon comparison of their electronic spectra in LB monolayer films with those in chloroform (in Table 1, λ_{max}), blue shifts of 51 and 43 nm can be observed for C_1BP and C_1P, respectively, indicating that H-aggregates formed in the monolayer films for C_1BP and C_1P.[14]

SHG Properties. The second harmonic susceptibilities $\chi^{(2)}$ for C_1BP and C_1P LB monolayer films deposited on quartz at 30 mN m^{-1} are 167 and 125 pm V^{-1}, respectively. The tilt angles φ of C_1BP and C_1P LB monolayer films are 29° and 32°, respectively, which is in agreement with the values for similar compounds.[15,16] It is known that C_1BP has a center of symmetry in the molecule when the two chomophores take the trans configuration relative to the CH_2 group (as shown in Chart 1), and that cannot yield SHG according to the principle of second-harmonic nonlinear optics. In the solution, this molecule spends most of the time with noncentrosymmetric configurations due to molecular rotation, but the dipolar moment is not large because the two D-π-A chromophores in one C_1BP molecule take mostly a partial trans form relative to the CH_2 group. In the interface of water/air, the chromophores take almost the same orientation due to the existence of the hydrophobic tails and the hydrophilic heads. Therefore, the C_1BP molecule has to take a noncentrosymmetric configuration, and the dipolar moment in LB film is enlarged; then the large second harmonic response is generated. This fact indicates that the LB technique can offer the opportunity to make the hydrophobic tails take the same direction, which favors the noncentrosymmetric configuration.[17]

It must be pointed out that λ_{max} of C_1BP in chloroform is red-shifted by 10 nm compared with that of C_1P, but λ_{max} values of C_1BP and C_1P in LB films are 462 and 460 nm, respectively. Therefore, the resonant enhancement effect of C_1BP is almost the same as that of C_1P. However, the data show that $\chi^{(2)}$ of C_1BP is about 1.34 times larger than that of C_1P, so the enhancement of the SHG property of C_1BP should be contributed to the structure factor (that is, the shorter intermolecular distance) when the two chromophores are tightened together with an alkyl bridge.

Photoelectric Conversion Properties. A steady cathodic photocurrent was obtained from the C_1BP and

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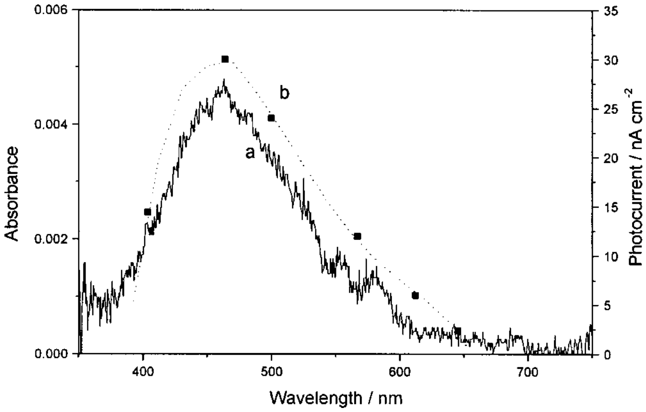

Figure 2. (a) UV−Vis absorption spectrum of C_1BP in LB monolayers and (b) action spectrum of the cathodic photocurrents. The intensities of different wavelengths are all normalized.

C_1P monolayer film-modified ITO electrode in 0.5 M KCl solution by illumination of 137 mW cm^{-2} white light (see Table 1, I^b). To discuss conveniently, C_1BP is given as an example for discussion. The photoelectric response of C_1BP was very stable when it was switched on and off many times. The action spectrum of the cathodic photocurrent for C_1BP (see Figure 2b) is similar to the absorption spectrum, suggesting that the C_1BP monolayer films are responsible for photocurrent generation. About 30 nA cm^{-2} photocurrent can be obtained for C_1BP by a 464 nm light irradiation, which corresponds to an intensity of 3.48 × 10^{15} photons cm^{-2} s^{-1}, in 0.5 M KCl electrolyte solution with zero bias voltage. The quantum yield is about 0.51% for C_1BP LB monolayer films modified electrode (in Table 1, η^c) (the absorbance of the monolayer films is about 0.46% at 464 nm), while that for C_1P is 0.30%.

Correlation between Molecular Structure and PEC Property. Because the number of active moieties per unit area in the LB monolayer films is an important factor contributing to the photoelectric conversion (PEC) performance, here we use the photocurrent per chromophore as the data for comparison. To discuss conveniently, we assume that C_1BP contains two D-π-A chromophores. Taking the limiting molecular area into account, one can get molecular numbers per square centimeter [Table 1, no.(m)] of 1.47 × 10^{14} and 2.86 × 10^{14} for C_1BP and C_1P, respectively. Consequently, the chromophore numbers per square centimeter for C_1BP and C_1P are 2.94 × 10^{14} and 2.86 × 10^{14}, respectively. Furthermore, with reference to the photocurrent per square centimeter, one can see that photocurrents per one chromophore for C_1BP and C_1P are 2.65 × 10^{-12} and 1.91 × 10^{-12} nA chromophore^{-1} (Table 1, $I^{c\prime}$), respectively. Therefore, the photocurrent generated by one C_1BP molecule [5.30 × 10^{-12} nA (one C_1BP molecule)$^{-1}$] is 1.4 times as large as the photocurrent generated by two C_1P molecules (2 × [1.91 × 10^{-12} nA (two C_1P molecules)$^{-1}$]). That is, the photocurrent per dimer is larger than double the photocurrent per monomer in LB films. Therefore, C_1BP performs better in photocurent generation than C_1P does, which is due not only to the higher density of C_1BP but also to the dimerization of the chromophores.

Dependence of PEC on Experimental Conditions. It is well-known that the experimental conditions affect photocurrent generation. Here, in 0.5 M KCl electrode solution, C_1BP−ITO as an example was investigated. (1) In the range of +150 to −150 mV, a linear relationship was found between photocurrent and bias voltage (see Figure 3), indicating that the photocurrent flows in the same direction as the applied negative voltage. (2) It can be seen from Figure 4 that the equations of dependence of the photocurrent (i_{ph}) on light intensity (I) for C_1BP and C_1P−ITO electrode are $i_{ph} = 25.0I^{0.70}$ and $i_{Ph} = 3.80I$ ($R^2 = 0.988$), respectively. By comparison of these equations with the Donovan equation,[18] $i_{ph} = KI^m$, it can be seen that m is 0.70 for C_1BP and 1 for C_1P, indicating that the unimolecular recombination of separated charge relaxation process occurs in the LB monolayers for the C_1P system and both unimolecular recombination and bimolecular recombination processes occur simultaneously for the C_1BP system. (3) The effects of electron donor (H_2Q and N_2) and acceptor (MV^{2+} and Eu^{3+}) on the cathodic photocurrent for C_1BP (as an example, shown in Table 2) and C_1P show that electron acceptors sensitize the cathodic photocurrent and electron donors quench it (even reverse it). Figure 5 is a plot of the photocurrent for C_1BP versus the concentration of $EuCl_3$, illustrated by the white light at 137 mW cm^{-2} and without any

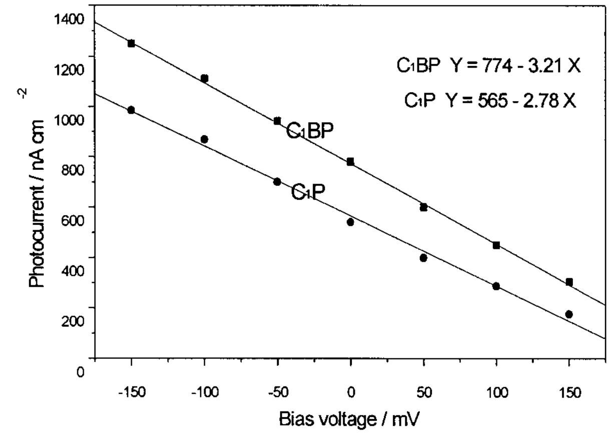

Figure 3. Photocurrent versus bias voltage for C_1BP and C_1P LB films−ITO electrodes in 0.5 M KCl aqueous solution under ambient conditions, upon irradiation of 137 mW cm^{-2} white light.

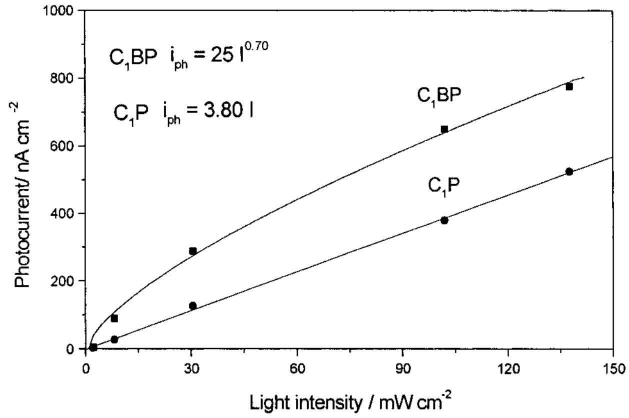

Figure 4. Dependence of the photocurrent on light intensity for C_1BP and C_1P electrodes in 0.5 M KCl electrolyte solution under ambient condition without bias voltage.

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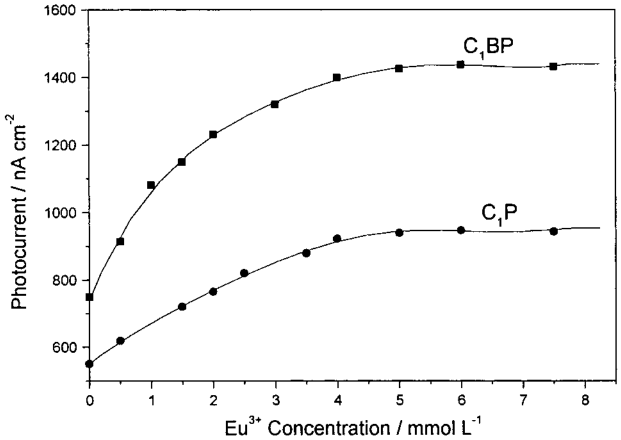


Figure 5. Dependence of the photocurrent on the concentration of $EuCl_3$ under ambient conditions without bias voltage for C_1BP and C_1P monolayer upon irradiation with 137 mW cm^{-2} white light.

Table 2. Effect of Donors and Acceptors on the Photoelectric Conversion of C_1BP–ITO Electrode

donor/ acceptor	concn, mM	photocurrent,[a] nA cm^{-2}	
		ambient	N_2 degassed
MV^{2+}	0	764	480
	4	2085	1512
Eu^{3+}	0	788	494
	5	1435	975
H_2Q	0	758	476
	5.4	−1835[b]	−2620[b]

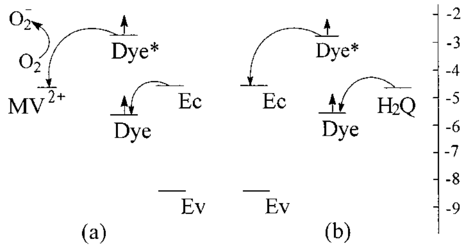
[a] Irradiation under 137 mW cm^{-2} white light for C_1BP in 0.5 M KCl electrolyte solution. [b] Negative value stands for anodic photocurrent.

bias voltage, in 0.5 M KCl electrolyte solution. The cathodic photocurrent increased gradually with increasing concentrations of $EuCl_3$ and leveled off at 5.0 mM. This means that $EuCl_3$ acted as a sensitizer in accepting electrons from the C_1BP assemblies and therefore increased the concentration of electrons involved in the electron-transfer process.

Under favorable conditions (−100 mV, dissolved O_2, 2 mM MV^{2+}, and 4 mM Eu^{3+}), a photocurrent of 132 nA cm^{-2} for C_1BP was obtained under the irradiation at 464 nm; the quantum yield is 2.44%. Under the same conditions, the quantum yield of C_1P is 1.24% (see Table 1, I^d and η^d).

Mechanism of Photoelectric Conversion. To elucidate the mechanism of photoinduced electron-transfer process for the cathodic and anodic photocurrent, the energy levels of the relevant electronic states must be estimated. The oxidation peak potential for the dyes measured by the CV method provides a measurement of the energy of the highest occupied molecular orbital (HOMO). The oxidation peak potentials are 0.75 and 0.67 V for C_1BP and C_1P, respectively, and the energy levels of the excited state for C_1BP and C_1P LB monolayer films are −5.49 eV (0.75 V vs SCE) and −5.41 eV (0.67 V vs SCE) on the absolute scale, respectively. With reference to UV−vis spectra of C_1BP and C_1P LB monolayer films, their $\lambda_{\max(\mathrm{film})}$ are 462 and 460 nm and their band gaps are 2.68 and 2.70 eV, respectively. Therefore, the energy levels of the ground state for C_1BP and C_1P LB monolayer films are −2.81 and −2.71 eV on the absolute scale, respectively. 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,[19] respectively. The reduction potential of MV^{2+} is −4.51 eV (−0.23 V vs SCE),[20] the reduction potential of Eu^{3+} is −4.39 eV (−0.35 V vs SCE), and the oxidation potential of H_2Q is −4.61 eV(−0.13 V vs SCE),[19] on the absolute scale. Then, an energy level diagram for C_1BP and C_1P can be constructed, and that for C_1BP is shown in Scheme 2 only for clarity, which describes the mechanism for photosensitization of the ITO electrode.

Scheme 2. Mechanism of Electron Transfer of the Dye on ITO Electrode under Different Conditions[a]



[a] (a) Cathodic photocurrent; (b) anodic photocurrent. Dye and dye* represent the ground state and the excited state of the dye C_1BP, respectively.

It can be known from energy levels that the direction of the photocurrent depends not only on the dye sensitized by the light but also on the nature of the redox couple in the aqueous phase surrounding the electrode. In the presence of some electron acceptors, such as O_2, MV^{2+}, and Eu^{3+} in electrolyte solution, electron transfer occurs from the excited state of C_1BP to the electron acceptor, and subsequently the electrons of ITO conduction band inject into the hole residing in the dye molecules. Thus, cathodic photocurrent is generated. On the contrary, if there are strong electron donors in the system, such as H_2Q, it will exhibit a reduced photocurrent and even reverse the direction of photocurrent.

Conclusions

It can be seen from Table 1 that in the present systems the second harmonic generation susceptibility $\chi^{(2)}$ and photocurrent generation quantum yield η have the same sequence under the same conditions: $C_1BP > C_1P$. The experimental results of photocurrent generation show that the dimer C_1BP exhibits photocurrent per C_1BP molecule (5.30×10^{-12} nA molecule^{-1}) twice as large as the monomer C_1P does (1.92×10^{-12} nA molecule^{-1}) when they are deposited on ITO electrodes at 30 mN m^{-1} by the LB technique. It is an interesting phenomenon in dimer and monomer molecules. Thorough studies of the reason for this interesting phenomenon are in progress.

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