

Multifunctional Molecular Material Combining Photocurrent Generation and Second-Order Optical Nonlinearity in LB Monolayer Films[†]

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A novel amphiphilic stilbazolium dye, (*E*)-*N*-methyl-4-[2-(4-*N*-methyl-*N*-hexadecylaminophenyl) ethenyl]-2-isoquinolinium iodide (MHIQ), was synthesized. The dye was successfully transferred onto ITO electrode or quartz by the Langmuir-Blodgett (LB) technique. The second harmonic generation (SHG) and photocurrent generation properties of the LB film transferred under 35 mN/m of surface pressure were investigated. The broad absorption maximum of the LB monolayer of MHIQ at 434 nm is far away from the wavelength (532 nm) of resonant enhancement effect, and its second harmonic susceptibility $\chi^{(2)}$ is 167 pm/V, which means that the isoquinolinium is a good electron-accepting group. The photocurrent generation experiment shows that the photocurrent generation properties are dependent on the experimental conditions including bias voltage, redox couples and light intensity. By a light irradiation at 440 nm, the photocurrent generation quantum yields of the dye LB monolayer are 0.50% in 0.5 mol/L KCl electrolyte solution and 17.5% in 0.1 mol/L KI electrolyte solution with 0.01 mol/L I₂, respectively, indicating that the dye MHIQ is a good photoelectric conversion material.

Keywords multifunctional, photocurrent generation, LB film, second harmonic generation

Introduction

Molecular nonlinear optics (NLO) has attracted in-

creasing interest over the past ten years, because of their potential applications in various fields including telecommunications, optical data storage and processing and optical power limitation.^{1,2} It is well known that the push-pull chromophore, *i. e.* molecules combining an electron-donating group (D) and electron-accepting group (A) connected by a π conjugation system, is an ideal nonlinear optical material.³ In the previous publications, our group has found that Langmuir-Blodgett (LB) 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.⁴⁻⁹

As a type of D- π -A compounds, stilbazolium dyes have been the topic of many studies in the field of NLO. In general, NLO materials need low absorption in the range of double frequency in order to avoid the effect of resonant enhancement. Here, a novel amphiphilic D- π -A dye with the acceptor of isoquinolinium, (*E*)-*N*-methyl-4-[2-(4-*N*-methyl-*N*-hexadecylaminophenyl) ethenyl]-2-isoquinolinium iodide (MHIQ) was synthesized, and its maximum absorption peak is at 434 nm, which is far away from the wavelength (532 nm) of resonant enhancement effect. The second harmonic generation and photocurrent

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[†]Dedicated to Professor HUANG Yao-Zeng on the occasion of his 90th birthday.

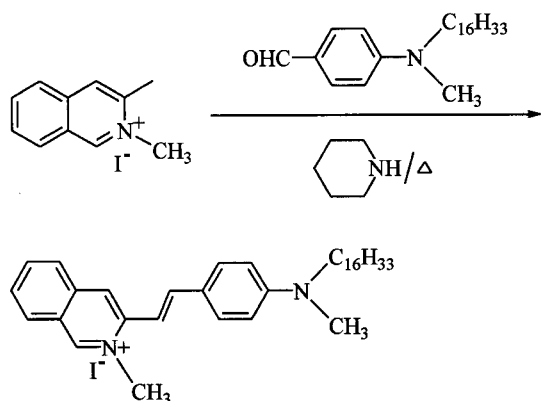
generation properties of **MHIQ** were investigated by the Langmuir-Blodgett (LB) technique.

Experimental

Materials

The synthesis of stilbazolium dye **MHIQ** has closely followed the aldol condensation strategy (in Scheme 1).¹⁰ **MHIQ** was synthesized by condensing 1,2-dimethyl isoquinolinium iodide with an equivalent mole of *N*-methyl-*N*-hexadecylaminobenzaldehyde¹¹ in absolute ethanol using piperidine as the catalyst. The product was purified by column chromatography on silica gel with a chloroform-methanol mixture (12:1) as eluent.

Scheme 1 Brief synthetic procedure of **MHIQ**



MHIQ Yield 37%; m.p. 195—197 °C; ¹H NMR (CDCl₃, 300 MHz) δ : 0.87 (t, $J = 7.08$ Hz, 3H, CH₃), 1.24—1.30 (m, 26H, 13CH₂), 1.53—1.58 (m, 2H, CH₂), 2.93 (s, 3H, NCH₃), 3.25 (t, $J = 7.09$ Hz, 2H, NCH₂), 4.57 (s, 3H, N⁺CH₃), 6.64 (d, $J = 8.95$ Hz, 2H, phenyl), 7.56 (d, $J = 15.90$ Hz, 1H, CH=), 7.62 (d, $J = 8.95$ Hz, 1H, phenyl), 7.78 (d, $J = 15.90$ Hz, 1H, CH=), 7.95—7.99 (m, 2H, isoquinolyl), 8.24—8.29 (m, 2H, isoquinolyl), 8.87—8.93 (m, 2H, isoquinolyl). Anal. calcd for C₃₅H₅₁N₂I: C 67.08, H 8.20, N 4.48; found C 66.76, H 8.45, N 4.12.

Methyl viologen diiodide (MV²⁺) was synthesized by reaction of 4,4'-dipyridyl with methyl iodide. Its identity was confirmed by elemental analysis. The electrolyte for the electrochemical experiment was KCl (Beijing Chemical Factory, China). Hydroquinone (H₂Q) (Beijing Chemical Factory, China) was recrystallized from wa-

ter before use. The spreading solvent used for the monolayer deposition was chloroform (Beijing Chemical Factory, China).

C, H and N data of the compounds were obtained by using a Carlo Erba 1106 elemental analyzer. ¹H NMR spectra were measured by using a Bruker ARX400 spectrometer. 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.

A model 622 NIMA Langmuir-Blodgett (LB) trough was employed for the study. Water obtained from an EASY pure RF system was used as the subphase (R ~ 18 M Ω /cm, pH ~ 5.6). The substrates (ITO slide and quartz) were all hydrophilically pretreated as the previous methods.¹² A chloroform solution of 0.3 mg/mL **MHIQ** dye was spread drop-by-drop from a chloroform-cleaned glass microsyringe to the subphase surface [(20 \pm 1) °C]. After 15 min allowing the solvent to evaporate, the floating films were compressed at a ratio of 40 cm²/min and the surface pressure (π)-area (A) isotherms were recorded. For deposition of the first monolayer, the hydrophilically pretreated substrate was immersed in the subphase, and then the monolayer was formed at the surface pressure of 20 mN/m and transferred to the solid substrate with a pulling rate of 5 mm/min at 35 mN/m. Only the films with transfer ratios of (1.0 \pm 0.1) were used in the experiments.

Second harmonic generation (SHG) measurement

The SHG measurements were performed in transmission geometry using a *Y*-type quartz plate ($d_{11} = 0.5$ pm/V) as a reference and with a Q-switched Nd:YAG laser (1.064 μ m). A 1/2 λ plate and a Glan-Taylor polarizer were used to vary the polarization direction of the laser beam. The laser light, linearly polarized either parallel (p) or perpendicular (s) to the plane of incidence, was directed at an incidence angle of 45° onto vertically mounted sample. A set of 1.064 μ m filters and a monochromator were used to ensure that the signal detected by the photomultiplier was the second-harmonic radiation generated by the films. The average output signal was recorded on a digital storage oscilloscope (HP54510). All SHG data were average values of at least three individual measurements. The data of second-harmonic generation (SHG) from the LB monolayers were analysed by

the general procedure described by Ashwell *et al.*¹³

Photoelectrochemical measurements

Photoelectrochemical measurements were carried out in 0.5 mol/L KCl solution using the LB monolayers-modified ITO electrode, platinum wire and saturated calomel electrode (SCE) as working electrode, counter electrode and reference electrode, respectively. Effective illuminated area of a flat window for MHIQ modified ITO electrodes was 0.8 cm². The light source used for the photoelectrochemical study was a 500 W Xe arc lamp, and the light beam was passed through a group of filters (*ca.* 350–800 nm, Toshiba Co., Japan, and Schott Co. Germany) in order to get a given bandpass of light. The light intensity at each wavelength was measured with an energy and power meter (Sciencetech Co., USA). Cyclic voltammetric (CV) experiments (sweep rate = 100 mV/s) were performed on an EG&GPAR 273 potentiostat/galvanostat with EG&GPAR 270 electrochemical software. Oxygen was removed from the electrolyte solution by bubbling N₂ before every measurement.

Results and discussion

Properties of LB monolayer films

The amphiphilic styryl dye was characterized by the measurement of their surface pressure-area (π - A) isotherm in the monolayer on the subphase. It can be seen from Fig. 1 that the collapse pressure of MHIQ is 44.1 mN/m, which reveals that the dye has good film formation property at the interface of water/air. The limiting molecular area of MHIQ is 0.60 nm², extrapolated from the π - A curve under 35 mN/m.

The broad absorption maximum of the charge-transfer band of MHIQ in chloroform solution is 445 nm (Fig. 2). Comparing the electronic spectrum of LB film on the ITO electrode (Fig. 2) with that in the chloroform solution, λ_{\max} blue shift of 11 nm can be observed for MHIQ, which results from the extended dipole interactions between the chromophores. The blue shift suggests the formation of H-aggregates on the ITO LB films for MHIQ.¹⁴

SHG properties

The second harmonic susceptibility $\chi^{(2)}$ for MHIQ

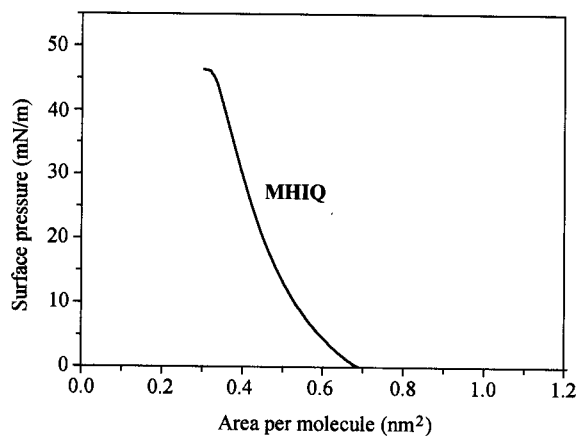


Fig. 1 Surface pressure versus area isotherm of MHIQ at the air/water interface [(20 ± 1) °C].

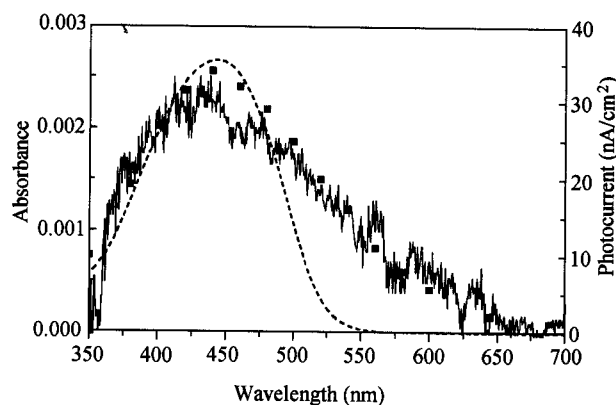


Fig. 2 UV-vis absorption spectrum of MHIQ in chloroform solution (--) and in LB monolayers (—), and the action spectrum of the cathodic photocurrents for MHIQ-ITO (■). The photocurrent intensities of different wavelengths are all normalised.

LB monolayer films deposited on quartz under 35 mN/m is 163 pm/V. The tilt angle φ of MHIQ in LB monolayer film is 32°, which agrees with the similar compounds.¹⁵ In our experiment the wavelength of resonant enhancement is 532 nm, and $\Delta\lambda_{\max}$ ($\Delta\lambda_{\max}$ stands for 532 nm — $\lambda_{\max(\text{film})}$) for MHIQ is 98 nm, which shows the effect of resonant enhancement is small. Therefore, the large $\chi^{(2)}$ of MHIQ is mainly due to its structural factor. This result shows that the 2-isoquinolinium is a good electron-accepting group.

Here, the second harmonic susceptibility $\chi^{(2)}$ (163 pm/V) of MHIQ is larger than that (126 pm/V) of the typical hemicyanine dye, (*E*)-*N*-methyl-4-[2-(4-*N*-methyl-*N*-hexadecylaminophenyl) ethenyl] pyridinium io-

dide (C_1P).¹⁶ What should be emphasized is that ($\Delta\lambda_{\max}$ ($\Delta\lambda_{\max}$ stands for $532\text{ nm} - \lambda_{\max(\text{film})}$) for **MHIQ** (98 nm) is larger than that (72 nm) of C_1P , that is, the effect of resonant enhancement of **MHIQ** is smaller than that of C_1P . Therefore, the dye **MHIQ** is a better nonlinear optical material than the typical one.

Photoelectric conversion properties (PEC)

A steady cathodic photocurrent was obtained from the **MHIQ** monolayer films modified ITO electrode (denoted as **MHIQ**-ITO) in 0.5 mol/L KCl solution by illumination of 137 mW/cm white light. The photoelectric response of **MHIQ**-ITO was very stable when switching on and off many times. The action spectrum of the cathodic photocurrent for **MHIQ**-ITO (Fig. 2) is similar to the absorption spectrum of it, suggesting that the **MHIQ** monolayer films are responsible for photocurrent generation. About 30 nA/cm photocurrent can be obtained for **MHIQ**-ITO by a 440 nm light irradiation which corresponds to an intensity of 3.48×10^{15} photons/(s·cm²), in 0.5 mol/L KCl electrolyte solution with zero bias voltage. The quantum yield is about 0.51% for **MHIQ** LB monolayer film modified ITO electrode (the absorbance of the monolayer films is about 0.46% at 440 nm).

Dependence of photoelectric conversion on experimental conditions

It is well known that the experimental conditions affect largely photocurrent generation. (1) In the range of +150—-150 mV, a linear relationship was found between photocurrent and bias voltage (Fig. 3), indicating that the photocurrent flows in the same direction as the applied negative voltage. (2) It can be seen from Fig. 4 that the equation for the dependence of the photocurrent (i_{ph}) on light intensity (I) for **MHIQ**-ITO electrode is $i_{\text{ph}} = 5.32 I$ ($R^2 = 0.988$). Comparing these equations with Donovan equation¹⁷ $i_{\text{ph}} = KI^m$, it can be seen that m is 1 for **MHIQ**, indicating that the unimolecular recombination of separated charge relaxation process occurs in the LB monolayers for **MHIQ** system. (3) The effects of electron donor (H_2Q) and acceptors (MV^{2+} and O_2) and inert gas (N_2) on the cathodic photocurrent for **MHIQ**-ITO (Table 1) show that the electron acceptors sensitize the cathodic photocurrent and that the electron donor and inert gas quench it (even reverse it).⁸ Fig. 5 is a plot of the

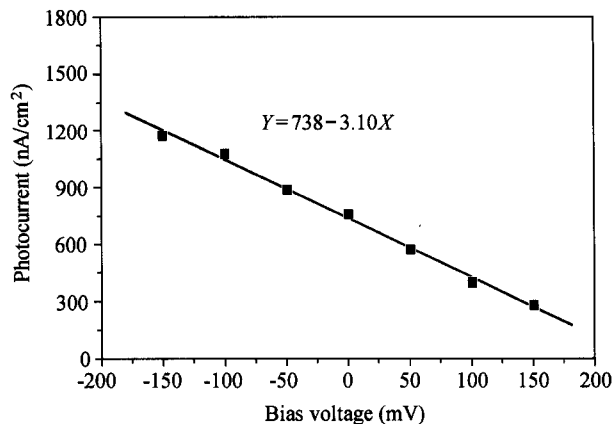


Fig. 3 Photocurrent versus bias voltage for **MHIQ**-ITO in 0.5 mol/L KCl aqueous solution under ambient conditions, upon irradiation of 137 mW/cm² white light.

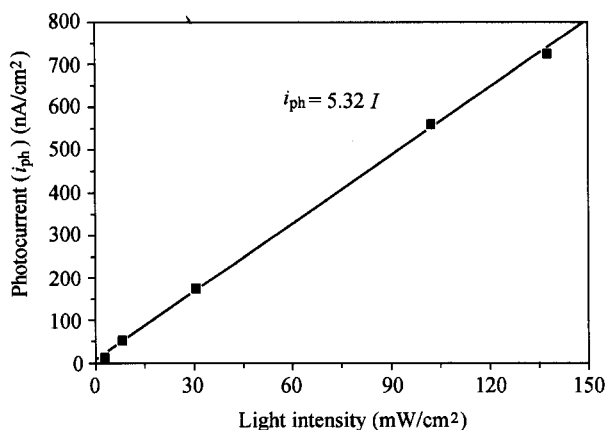


Fig. 4 Dependence of the photocurrent on light intensity for **MHIQ**-ITO in 0.5 mol/L KCl electrolyte solution under ambient condition without bias voltage.

cathodic photocurrent for **MHIQ**-ITO versus the concentration of MV^{2+} illuminated by the white light of 30.5 mW/cm and without any bias voltage, in 0.5 mol/L KCl electrolyte solution. The cathodic photocurrent increased gradually with increasing the concentration of MV^{2+} and leveled off at 10.0 mmol/L. This means that MV^{2+} acts as a relay in accepting electrons from the **MHIQ** assemblies and therefore increases the concentration of electrons involved in the electron transfer process. Under favorable conditions (-100 mV, dissolved O_2 , 10 mmol/L MV^{2+}), a photocurrent of 84 nA/cm for **MHIQ** was obtained under the irradiation at 440 nm, and the corresponding quantum yield is 1.43%. When the photocurrent generation of **MHIQ**-ITO electrode in 0.1 mol/L KI electrolyte solution with 0.01 mol/L I_2 , about 1030 nA/cm

Table 1 Effect of donors and acceptors on the photoelectric conversion properties of **MHIQ**-ITO

Donor/ acceptor	Conc. (mmol/L)	Photocurrent (nA/cm ²) ^a		
		Ambient	N ₂ degassed	O ₂
MV ²⁺	0	146	51	173
	10	304	152	385
H ₂ Q	0	168	58	189
	4	-502 ^b	-640 ^b	-415 ^b

^a Irradiation under 30.5 mW/cm² white light for **MHIQ**-ITO in 0.5 mol/L KCl solution. ^b “-” stands for anodic photocurrent.

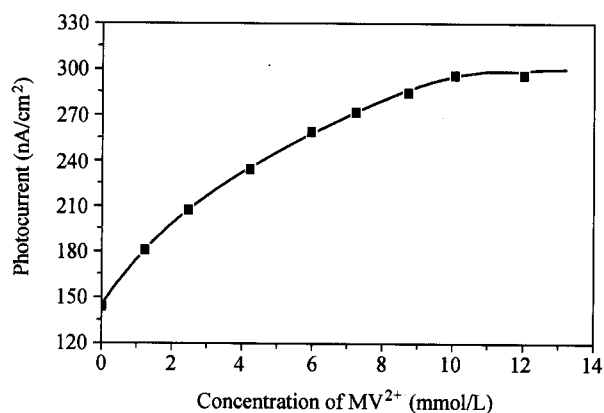


Fig. 5 Dependence of the photocurrent on the concentration of MV²⁺ under ambient conditions without bias voltage for **MHIQ**-ITO upon irradiation of 30.5 mW/cm² white light.

cathodic photocurrent can be obtained for **MHIQ** by a 440 nm light irradiation with zero bias voltage, and then a much more large quantum yield (17.5%) can be obtained.

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 CV method provides a measurement of the energy of the HOMO. The oxidation peak potential is 0.92 V for **MHIQ**, and the energy level of the excited state for **MHIQ** LB monolayer film is -5.66 eV (0.92 V vs. SCE) on the absolute scale. With reference to UV-Vis spectrum of **MHIQ** LB monolayer film, the $\lambda_{\max(\text{film})}$ is 434 nm corresponding to a band gap of 2.86 eV. Therefore, the energy level of the ground state for **MHIQ** LB monolayer film is -2.80 eV on the absolute scale. 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,¹⁸ respectively. Reduction potential of MV²⁺ is -4.51 eV (-0.23 V vs. SCE),¹⁹ and oxidation potential of H₂Q is -4.61 eV (-0.13 V vs. SCE),¹⁸ on the absolute scale. Then, an energy level diagram for **MHIQ** can be constructed as shown in Fig. 6, which describes the mechanism for photosensitization of the ITO electrode.

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 O₂ and MV²⁺ in electrolyte solution, electron transfers from the excited state of **MHIQ** to the electron acceptor, subsequently the electrons of ITO conduction band inject into the hole re-

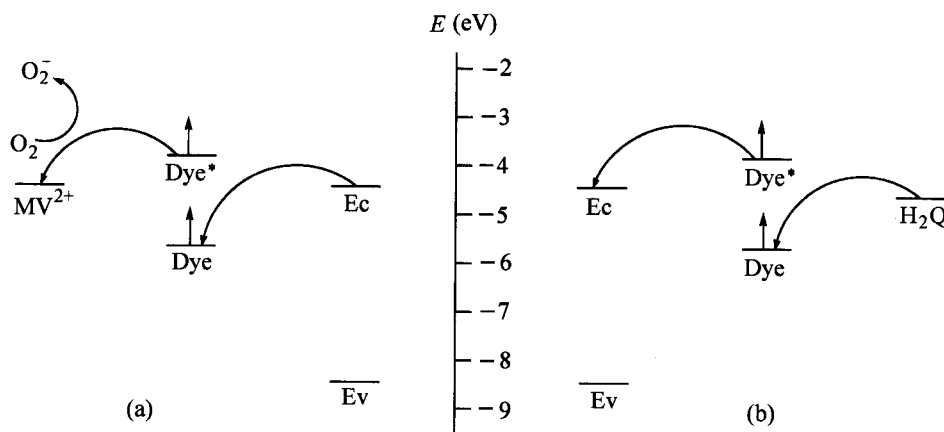


Fig. 6 Mechanism of electron transfer of the dye **MHIQ** on ITO electrode in different conditions. (a) Cathodic photocurrent; (b) anodic photocurrent. Dye and Dye* present the ground state and the excited state of the dye **MHIQ**, respectively.

siding in the dye molecules. Thus, cathodic photocurrent is generated. On the contrary, if there are strong electron donors in the system, such as H₂Q, it will exhibit a reduced photocurrent and even reverse the direction of photocurrent.

Conclusions

In the present system, the broad absorption maximum of the MHIQ LB film at 434 nm, is far away from the wavelength (532 nm) of resonant enhancement effect, and its second harmonic susceptibility $\chi^{(2)}$ is 163 pm/V. The photocurrent generation experiment shows that the dye MHIQ has good photocurrent generation property. Therefore, it can be concluded that the dye MHIQ is a good multifunctional molecular based material bearing photocurrent generation and second-order optical nonlinearity properties.

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