Effect of MCl_2 (M = Hg, Zn, Cu) subphase on photoinduced electron transfer in a pyrazinium styryl dye Langmuir–Blodgett film

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An amphiphilic heteroaromatic styryl dye, 2-(4-dihexadecylaminostyryl)-1,5-dimethylpyrazinium iodide (I) was synthesized. Its Langmuir–Blodgett films fabricated from different subphases, namely pure water (Ia), 10^{-5} M CuCl₂ (Ib), 10^{-5} M ZnCl₂ (Ic) and 10^{-5} M HgCl₂ (Id), were characterized by UV-Vis spectra and XPS measurements. The photoelectrochemistry of these film-modified conducting transparent indium–tin oxide (ITO) electrodes was investigated on a traditional three-electrode cell. The experimental data indicated that the films fabricated from different subphases have distinctive photoelectric responses. Under ambient conditions (0.5 M KCl), the quantum yields of photoelectric conversion were 0.03, 0.05, 0.06, and 0.1% for films Ia, Ib, Ic and Id, respectively. The effects of factors such as bias voltage, methylviologen (MV²⁺), and hydroquinone (H₂Q) on the photocurrent generation were also investigated. Based on the experimental data, a possible mechanism of photoinduced electron transfer in this system is proposed.

Introduction

Photoinduced electron transfer (PET) in films is a central process relative to natural photosynthesis,¹ and also plays an important role in materials science.² In recent years, our group have found that Langmuir-Blodgett (LB) films of many dyes, such as hemicyanine with an electron donor- π electron conjugation bridge-electron acceptor (D- π -A) structure not only have good non-linear optical properties, but also exhibit good photoelectric conversion properties.³⁻⁷ Further investigations indicated that the properties of the conjugation bridge,³ the electron donor or acceptor⁴ and the number of chromophore⁵⁻⁷ all have great effects on photocurrent generation from such dye LB films. However, less attention has been paid to the subphase effect. A possible reason is that dye acceptor moieties such as pyridinium and quinolinium cations could not coordinate with the metal ions in the subphase. To explore the subphase effect, we designed an amphiphilic dye, 2-(4-dihexadecylaminostyryl)-1,5-dimethylpyrazinium iodide (I). A pyrazinium cation was introduced as the acceptor group because the external N atom on the pyrazinium cation could readily donate an electron to metal ions of CuCl₂ or ZnCl₂ and form zwitterionic complexes with these metal salts.⁸ In this work, the photoelectric conversion properties of LB films of this dye I fabricated from different subphases such as ZnCl₂, CuCl₂ and HgCl₂ were studied. Distinctive photoelectric responses from the films fabricated from different sub-phases were observed.

Experimental

Materials

2-(4-Dihexadecylaminostyryl)-1,5-dimethylpyrazinium iodide (I) was synthesized as shown in Scheme 1: 1,2,5-trimethylpyrazinium iodide was condensed with 4-dihexadecylaminobenzaldehyde (1:1 molar ratio) and the product was purified by column chromatography on silica gel with a mixed eluent of chloroform, light petroleum (bp 30–60 °C) and methanol (1:1:1); mp: 147 °C. Its structure was confirmed by using elemental analysis and ¹H NMR. Found: C, 68.4, H 9.81; N, 5.11. Calculated for $C_{46}H_{80}N_3I$: C, 68.9; H, 9.99; N, 5.24%. ¹H NMR (CDCl₃): δ 0.879 (t 6H, 2CH₃), 1.26 (m 52H, 26CH₂), 1.62 (t 4H, 2CH₂), 2.29 (S, 3H, CH₃), 3.34 (t 4H, 2CH₂-N), 4.55 (s 3H, R₃-N⁺-CH₃), 6.71 (d 1H, -CH=CH), 6.76 (d 1H, -CH=CH), 6.94 (s, 1H, Py-H) 7.46 (s, 1H, Py-H), 7.61 (d, 2H, Ar-H), 7.74 (d 2H, Ar-H).

Hydroquinone (H₂Q), KCl, methyl iodide and other reagents were all of analytical reagent grade and were used as received. Water (resistivity 18 M Ω) was purified by passing de-ionized water through an easy pure RT Compact ultrapure water system (Barnstead). To prepare methylviologen diiodide



Scheme 1 Synthesis of dye I.



Fig. 1 Surface pressure–area isotherms of dye I on pure water (a) and subphases: 10^{-5} M HgCl₂ (b), CuCl₂ (c) and ZnCl₂ (d): (Temperature: 20 ± 1 °C).

 (MV^{2+}) , 4,4-bipyridyl was reacted with an excess of methyl iodide in refluxing ethanol for 6 h and the product was filtered and washed with ethanol at least four times. Its identity was confirmed from its ¹H NMR spectrum.

Apparatus

UV-Vis spectra were recorded by using a Shimadzu UV-3100 spectrometer. Films were formed and deposited on indium-tin oxide (ITO) electrodes by using a Langmuir trough (Nima Technology, Model 622). X-ray photoelectron spectra (XPS) were measured with a VG (Winsford, Cheshire, UK) ESCA LAB 5 Multitechniques photoelectron spectrometer and Al was used as the target of the X-ray source.



Fig. 2 Absorption spectra of the dye in chloroform (A), ethanol (B) and monolayer (C).



Fig. 3 Absorption spectra of the films Ia, Ib, Ic and Id on the ITO substrate.

LB film formation

A sample of I in chloroform solution (0.34 mg ml⁻¹) was spread on water or another subphase at 20 ± 1 °C. After the evaporation of the solvent for 15 min, the monolayer was compressed at the rate of 50 cm² min⁻¹ and then transferred, at a rate of 2.5 mm min⁻¹ (vertical dipping) under a surface pressure of 25 mN m⁻¹, on to transparent electrodes of ITOcoated borosilicate glass (resistance 250 Ω). To ensure the formation of a hydrophilic surface, the plate was immersed for 2 d in a saturated solution of sodium methylate in methanol and then thoroughly rinsed with pure water under ultrasonication several times. Films with a transfer ratio of *ca*. 1.0 \pm 0.1 were used in the experiments.

Photoelectrochemical and electrochemical measurements

A 500 W Xe arc lamp was used as the light source in the photoelectrochemical studies and various filters (ca. 300-800 nm) were used to obtain different wavelengths. The intensity of light was measured with a Light Gauge Radiometer (Coherent, Santa Clara, CA, USA). A conventional glass three-electrode cell with the film-fabricated ITO electrode as the working electrode, a polished Pt wire as the counterelectrode, and saturated calomel electrode (SCE) as the reference electrode were used in the measurements. The supporting electrolyte was an aqueous solution of 0.5 M KCl in the photoelectrochemical studies and 0.1 M KCl in the electrochemistry experiments. All experimental data were recorded using a model CH 600 voltammetric analyzer controlled by a computer. In the electrochemical measurements, the solution was deoxygenated by bubbling nitrogen for at least 15 min. The effective illuminated area of the working electrode was 1 cm² in all photoelectrochemistry experiments.

Results and discussion

Characterization of LB films

1. Formation of Langmuir-Blodgett films. Surface pressure vs. area isotherms of dye I on the different subphases were distinctive. As shown in Fig. 1(a), the limiting area of an isotherm obtained from a pure water subphase is 76 Å², and the corresponding collapse pressure is 34 mN m^{-1} . When ZnCl_2 , CuCl₂ and HgCl₂ were added to the subphase at levels up to 10^{-5} M, the limiting areas for monolayers (Fig. 1(b), (c) and (d), respectively] increased to about 81 $Å^2$ and the collapse pressures were enhanced to about 38-42 mN m⁻¹ for the isotherms. It is known that the limiting area values for simple long-chain carboxylic acids are in the range 18-25 Å² per molecule,9 hence the larger values obtained for the dye suggest that the large bulky head group determines the packing density in the monolayers. The experimental data indicated that the addition of metal salts to the subphase could have some effect on the alignment of the dye molecules, and is favorable for film formation by increasing the collapse pressure.

2. UV-Vis spectra. Fig. 2 shows the UV-Vis spectra of the dye under the different conditions (in chloroform and ethanol and as an LB monolayer). Several conclusions can be obtained from experimental data. First, compared with the UV-Vis spectrum of I in chloroform (curve A), the maximum absorption of the I film fabricated from pure water subphase is blue shifted from 555 to 512 nm (curve C), which results from the intermolecular dipole–dipole interaction of chromophores and indicates the formation of "H" aggregates on the substrates.¹⁰ Second, the maximum wavelength of dye I in ethanol solution (strongly polar solvent) (curve B) is also blue shifted from 555 nm in chloroform solution to 532 nm, which suggests that the dipole moment in the excited state is smaller than that in the ground state, and photoinduced charge



XPS spectra of $Hg4f_{7/2}$ in $HgCl_2$ on the ITO electrode and Fig. 4 film Id.



Fig. 5 Photocurrent generation from Id-ITO electrode upon irradiation with white light at 113 mW cm⁻² in 0.5 M KCl solution.



Fig. 6 Action spectrum of the cathodic photocurrent for film Id. The intensities of the photocurrent at the different wavelengths were all normalized

Table 1 Photoelectric conversion property data for films Ia, Ib, Ic and Id

separation between the donor and acceptor parts could take place in the excited state.11

Fig. 3 the shows UV-Vis spectra of the dye films fabricated from different subphases. It can be seen that the maximum wavelength for all the films is about 512 nm, but the absorption of the monolayers varies with the different subphases. Compared with the absorption of film Ia fabricated from pure water, the absorption of the films is enhanced about 1.8, 2.3 and 2.7 times for films Ib, Ic and Id, respectively. Such a difference in absorption for the films could be attributed to the interaction between metal salts in the subphases and the dye molecules.

3. XPS measurements. To clarify further this interaction between the dye molecules and metal salts in the subphases, XPS was used to study the binding energies of metals (Cu, Zn, and Hg). Several conclusions can be drawn from data. First, it can be seen from Fig. 4 that organic film Id fabricated from $HgCl_2$ subphase contains characteristic peaks of Hg $4f_{7/2}$, but the binding energy of Hg $4f_{7/2}$ is shifted from 100.1 eV for pure HgCl₂ (curve HgCl₂) on the ITO electrode to 101.8 eV for film Id. Second, the shifts in binding energy are also observed for films **Ib** and **Ic**. The binding energy of $Cu 2p_{3/2}$ is shifted from 935.1 eV for pure CuCl₂ on the ITO electrode to 932.7 eV for film Ib. The binding energy of Zn $2p_{3/2}$ is shifted from 1023.3 eV for pure ZnCl₂ on the ITO electrode to 1022.0 eV for film Ic. These shifts in binding energy suggested that the coordination environment of the metal ions changed when they interacted with the dye molecules. The XPS data are in agreement with a report that 1,2,5-trimethylpyrazinium iodide could readily coordinate with CuCl₂ or ZnCl₂ and form zwitterionic complexes.8

Photocurrent generation from the dye-ITO electrodes

To understand the effect of different subphases on the photoinduced electron transfer in dye I LB films, the photocurrent responses in the films fabricated from different subphases were studied. Steady cathodic photocurrents flowed instantly when the different film-modified ITO electrodes were illuminated by white light of 113 mW cm⁻², and fell as soon as irradiation was terminated. The photoelectric responses were very stable even after switching on and off many times. Fig. 5 shows a typical example of the experiments. The average values (obtained from eight samples for each type of film) are 57, 161, 275 and 482 nA cm⁻² for films Ia, Ib, Ic and Id, respectively. The photocurrent action spectra for the films were obtained by illuminating the dye-fabricated ITO electrodes under light of different wavelengths. For example, Fig. 6 shows the action spectrum of film Id, which is coincident with its absorption spectrum on ITO electrodes (Fig. 3). About a 10 nA anodic photocurrent was generated when a blank ITO electrode was irradiated. These results indicate that photoinduced electron transfer took place, and the aggregates on the different films were responsible for the generation of photocurrents. The photoelectric conversion properties for the films are given in Table 1. It can be seen that under illumination by monochro-

	$I^a/nA \text{ cm}^{-2}$					<i>φ</i> ^{<i>a</i>} (%)	
Films	KCl ^b	Bias ^c	MV^{2+d}	H_2Q^e	$MV^{2+} + bias^{f}$	KCl ^b	$MV^{2+} + bias^{f}$
Ia Ib Ic Id	57 161 275 482	163 326 586 1137	136 274 652 758	-160 -412 -498 -620	372 696 1115 1823	0.03 0.05 0.06 0.1	0.13 0.17 0.21 0.37

Ia, film fabricated from pure water subphase; Ib, film fabricated from 10^{-5} M CuCl₂ subphase; Ic, film fabricated from 10^{-5} M ZnCl₂ subphase; Id, film fabricated from 10^{-5} HgCl₂. ^{*a*} *I*-photocurrent and φ = photoelectric conversion efficiency under irradiation with 498 nm monochromated light with an intensity of 6.14×10^{15} photons cm⁻¹ in 0.5 M KCl solution. ^{*b*} Ambient conditions. ^{*c*} -200 mV bias voltage. ^{*d*} 1 mg ml⁻¹ MV^{2+} . $^{\circ}$ 0.1 mg ml⁻¹ H₂Q in 0.5 M KCl solution. f -200 mV bias voltage and 1 mg ml⁻¹ MV²⁺ in 0.5 M KCl solution.



Fig. 7 Relationship between MV^{2+} concentration and photocurrents under ambient conditions (113 mW cm⁻² white light, 0.5 M KCl solution) for film Id.

mated 498 nm light with an intensity of 6.14×10^{15} photon cm⁻² s⁻¹, the efficiencies of photoelectric conversion are 0.03, 0.05, 0.06 and 0.1% for films Ia, Ib, Ic and Id, respectively. Compared with film Ia, the quantum efficiencies can be enhanced about 1.6, 2.0 and 3.3 times for Ib, Ic and Id, respectively, by just changing the component of the subphase from H₂O to CuCl₂, ZnCl₂ and HgCl₂ respectively.

Some factors in photoinduced electron transfer

The observed cathodic photocurrents indicate that the photogenerated electrons flow from the films to solution. In order to explore this process in detail, the different factors affecting these processes were investigated as follows.

First, to study electron transfer between the ITO electrode and LB films, the effect of bias voltage was investigated. All the cathodic photocurrents increased with the potential of the working electrode more negative than the SCE electrode for all the films (shown in Table 1), and vice versa, indicating that photocurrents flow in the same direction as the applied negative voltage. Such a negative voltage on the ITO electrode can form a strong electric field within the LB films (ca. 3 nm), which can accelerate electron transfer from the ITO electrodes to the holes in the aggregates, and then from films to accep-



Fig. 8 Cyclic voltammetric graphs of the blank ITO and **Ib** filmmodified ITO electrode (0.1 M KCl, sweep speed = 100 mV s^{-1}).

Table 2 HOMO and LUMO energy levels (eV) for films Ia, Ib, Ic and Id

Ib^l

-5.57

tors in the solution, leading to the enhancement of cathodic photocurrents.¹²

Second, to investigate the electron transfer between the excited aggregates and the electron acceptors or donor in the solution, the effect of a typical electron acceptor, methyl-viologen (MV^{2+}), on the photocurrent generation from the films was investigated. The cathodic photocurrents for all the films increased with the addition of MV^{2+} to the solution (shown in Table 1), because the strong electron acceptor MV^{2+12} could accept electrons from the film and accelerate the rate of electron transfer from the film to the solution, leading to the enhancement of the cathodic photocurrents. As an example, Fig. 7 shows the dependence of the photocurrent for the **Id** film on the concentration of MV^{2+} in solution.

The effect of oxygen on the electron transfer process was also investigated. When O_2 was removed from the solution by bubbling N_2 , the cathodic photocurrents decreased gradually and reached stable values until saturation of N_2 in the solution, because it could act as an electron acceptor to form a superoxide anion radical,¹² and accelerate the electron transfer from the film to the solution. When H_2Q was added to the solution, the cathodic photocurrents for the four films decreased so quickly that they became anodic photocurrents (shown in Table 1). The experimental results indicated that the presence of a strong electron donor is unfavorable to cathodic photocurrent generation.¹²

Mechanism of photoinduced electron transfer in the film modified ITO electrodes

It is known that photoinduced electron transfer involves electron transfer within the different energy levels.¹²⁻¹⁴ In order to elucidate the detailed mechanism of electron transfer under the different conditions, cyclic voltammetric studies (sweep rate = 100 mV s⁻¹) were carried out in neutral 0.1 M KCl solution to estimate the redox potentials of the films on the ITO electrode. For example, it can be seen from Fig. 8 that there is no peak in the range 0-1.2 V for the blank ITO electrode, but an irreversible oxidation potential peak was observed when film Ib modified the ITO electrode. Under the same conditions, the oxidation potentials of the dve-dve⁺ couples for the films are 0.798 V ($Ia-Ia^+$), 0.828 V ($Ib-Ib^+$), 0.858 (Ic-Ic⁺) and 0.903 V (Id-Id⁺) vs. SCE (shown in Table 2). Hence the HOMO energy levels available for donating electron are estimated to be -5.54, -5.57, -5.60 and -5.64eV for films Ia, Ib, Ic and Id, respectively. The band gaps are 518 nm (2.39 eV) for all films and the LUMO energy levels available for accepting electrons can be obtained as -3.15, -3.18, -3.21 and -3.25 eV for Ia, Ib, Ic and Id, respectively, on the absolute scale. The conduction band $E_{\rm c}$ and valence band E_v of the ITO electrode are known to be *ca*. -4.5 and -8.3 eV on an absolute scale, respectively.¹² The reduction potential of MV^{2+} is about -4.51 eV, and the oxidation potential of H_2Q is -4.61 eV on the absolute scale.¹² Thus a mechanism could be proposed as shown in the Scheme 2. When the dye aggregates are excited, the direction of photocurrents is dependent not only on the excited dye aggregates, but also on the nature of the redox couples around the electrode in the solution. For example, a cathodic photocurrent is generated through the following process: the dye aggregates

Id^d

- 5.64

-3.25

2.39(518 nm)

ITO

-8.3

-4.5

3.82(325 nm)

LUMO -3.15 -3.18 Band gap 2.39(518 nm) 2.39(518 nm)

^{*a*} Ia: film fabricated from pure water. ^{*b*} Ib: film fabricated from 10^{-5} M CuCl₂ subphase. ^{*c*} Ic: film fabricated from 10^{-5} M ZnCl₂ subphase. ^{*d*} Id: film fabricated from 10^{-5} M HgCl₂ subphase. The energy level of the dyes were obtained from the oxidation potentials from the cyclic voltammetry of the dye monolayers in 0.1 M KCl solution (sweep rate = 100 mV s^{-1}). ^{*e*} Values cited from ref. 12.

Ic

-5.60

-3.21

2.39(518 nm)

Ia

-5.54

Energy level

номо



Scheme 2 Mechanism of photoinduced electron transfer in the dye films under the different conditions.

are excited by absorbing light energy, and electrons transfer from the excited aggregates to the electron acceptors such as O_2 or MV^{2+} in the solution, and subsequently electrons from the conduction band of the ITO electrode are injected into the holes residing in the dyes aggregates. Under optimum conditions (1 mg ml⁻¹ MV^{2+} , -200 mV), the quantum efficiency for films Ia, Ib, Ic and Id can reach 0.13, 0.17, 0.21 and 0.37%, respectively. The strong electron donor H₂Q in the solution can donate electrons to quench the excited aggregates,^{12,13} as a result of the formation dye anion radicals, which can inject electrons into the conduction band of the ITO electrode, leading to anodic photocurrent generation.

Although much work is still needed to clarify the reasons for the effect of subphases on photocurrent generation from the films, one possible reason in the present system is that metal ions could affect the energy levels of the ground or excited states of the films by coordination interaction between the metal ions and the acceptor part of the dye. As shown in Scheme 2, changes in energy levels of the ground and excited states of the films may affect the electron transfers between the ITO electrode, dye aggregates and the acceptors or donor in the solution.

Conclusions

An organic styryl amphiphilic dye, 2-(4-dihexadecylaminostyryl)-1,5-dimethylpyrazinium iodide (I), was synthesized. Experimental data indicate that there is a strong interaction between metal salts such as $CuCl_2$, $ZnCl_2$ and $HgCl_2$ in the subphases and the dye molecules at the interface. The photoelectric conversion properties of the dye films fabricated from subphases containing metal are obviously better than those of a film fabricated from pure water. The experimental results may provide a new way to improve the photoelectric response from such dye LB films. Studies on the reasons for this interesting phenomenon are still in progress.

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References

- (a) Topics in Current Chemistry, ed. J. Mattay, Springer, Berlin, 1991, vol. 159; (b) T. Pfannschmidt, A. Nilsson and J. F. Allen, Nature (London), 1999, **397**, 625; (c) G. Steinberg-Yfrach, J.-L. Rigaud, E. N. Durantini, A. L. Moore, D. Gust and T. A. Moore, Nature (London), 1998, **392**, 479.
- 2 U. Bach, D. Lupo, P. Comte, J. E. Moser, F. Weissortel, J. Salbeck, H. Spreiitzer and M. Grätzel, *Nature (London)*, 1998, 395, 583.
- 3 W. S. Xia, C. H. Huang, L. B. Gan and C. P. Luo, J. Phys. Chem., 1996, 100, 15525.
- 4 A. D. Liang, J. Zhai, C. H. Huang, L. B. Gan, Y. L. Zhao, D. J. Zhou and Z. D. Chen, J. Phys. Chem. B, 1998, 102, 1424.
- 5 D. G. Wu, C. H. Huang, L.-B. Gan and J. Zheng, *Langmuir*, 1999, 15, 7276.
- 6 D. G. Wu, C. H. Huang, L.-B Gan, W. Zhang, J. Zheng, H. X Luo and N. Q. Li, J. Phys. Chem. B, 1999, 103, 4377.
- 7 D. G. Wu, C. H. Huang, Y.-Y. Huang and L. B. Gan, J. Phys. Chem. B, 1999, 103, 7130.
- 8 W. L. Darby and L. M. Vallarino, Inorg. Chim. Acta, 1983, 75, 65.
- 9 (a) J. Glazer and A. E. Alexander, Trans. Faraday Soc., 1951, 47, 401; (b) B. Asgharian and D. A. Cadenhead, J. Colloid Interface Sci., 1990, 134, 522.
- 10 D. G. Whitten, Acc. Chem. Res., 1993, 26, 502.
- 11 Ph. Hebert, G. Baldacchino, Th. Gustavsson and J. C. Mialocq, J. Photochem. Photobiol. A, 1994, 84, 45.
- 12 Y. S. Kim, K. Liang, Y. Law and D. G. Whitten, J. Phys. Chem., 1994, 98, 984.
- 13 A. Vaes, M. V. D. Auweraer, P. Bosmans and F. C. D. Schryver, J. Phys. Chem. B, 1998, 102, 5451.
- 14 K.-Y. Law, *Chem. Rev.*, 1993, **93**, 449, and reference cited therein.