Chinese Chemical Letters Vol. 14, No. 6, pp 641 – 644, 2003
http://www.imm.ac.cn/journal/ccl.html

Enhancement of Photocurrent Generation of a Novel Stilbazolium Dye Dimer in LB Monolayer Films

Fu You LI[1], Xiao Rong ZOU[2], Chun Hui HUANG[1]*

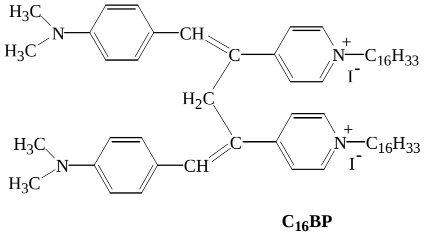
[1]State Key Laboratory of Rare Earth Materials Chemistry and Applications, Peking University - University of Hong Kong Joint Laboratory on Rare Earth Materials and Bioinorganic Chemistry, Peking University, Beijing 100871
[2]College of Aerospace and Material Engineering, National University of Defense Technology, Changsha, 410073

Abstract: A novel dye dimer, bis-{[1-(N-hexadecyl-4-pyridinium)-2-(4-N, N-dimethylamino-phenyl)] ethenyl}methane diiodide ($C_{16}BP$) was synthesized, and the photoelectrochemistry of the dye Langmuir-Blodgett monolayer modified ITO electrode was investigated. For comparison, the photoelectrochemistry of the monomer (E)-N-hexadecyl-4-[2-(4-N, N-dimethylaminophenyl) ethenyl] pyridinium iodide ($C_{16}P$) was also measured. The results show that the photocurrent generation property of the dimer is enhanced. The photocurrent generation quantum yield is 0.38% for $C_{16}BP$, while that for $C_{16}P$ is 0.23%.

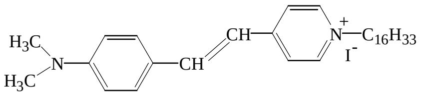
Keywords: Langmuir-Blodgett films, stilbazolium dye dimer, photocurrent generation.

Our group has found that Langmuir-Blodgett films of some D-π-A conjugated systems exhibit good photoelectric conversion properties[1]. Recently, our works indicated that the better photocurrent generation of LB films can be observed when two or more chromophores are connected to one molecule by using suitable bridges[2,3]. As a part of the systematic study, herein we designed a novel stilbazolium dye dimer, bis-{[1-(N-hexadecyl-4-pyridinium)-2-(4-N, N-dimethylaminophenyl)]ethenyl}methane diiodide ($C_{16}BP$) (**Scheme 1**) and the photocurrent generation of $C_{16}BP$ LB monolayer films modified ITO electrodes were investigated. For comparison, the dye monomer (E)-N-hexadecyl-4-[2-(4-N, N-dimethyl aminophenyl)ethenyl] pyridinium iodide ($C_{16}P$) was also studied under the same conditions.

Scheme 1 The molecular structures of the materials $C_{16}BP$ and $C_{16}P$



$C_{16}BP$



$C_{16}P$

Experimental

The dimer $C_{16}BP$ was synthesized by condensation of 1, 3-[di-(4-N-hexadecylpyridinium)] propane diiodide with 4-N, N-dimethylaminobenzaldehyde according to the literature method[4]. Details on the method used for surface pressure (π) – area (A) isotherm measurement and transfer process of monolayer films for $C_{16}BP$ and $C_{16}P$ were the same as described previously[2]. Here, the surface pressure of deposition is 25 mN/m. The photoelectrochemical properties for $C_{16}BP$ and $C_{16}P$ were carried out also by the previous method[2].

Results and Discussion

It can be seen from **Table 1** that the collapse pressures of $C_{16}BP$ and $C_{16}P$ are 34 and 37 mN/m, respectively, which reveals that the two dyes have good films formation properities. The limiting molecular area of $C_{16}BP$ and $C_{16}P$ are 1.16 and 0.65 nm^2, respectively, that is, the limiting area of $C_{16}BP$ is twice smaller than that of that of $C_{16}P$, therefore, we can conclude that the density of chromophores in $C_{16}BP$ LB films is higher than that of $C_{16}P$ and its inter-chromophoric distance is shorter than that of $C_{16}P$ in the films.

Table 1 The properties of $C_{16}BP$ and $C_{16}P$ LB films

	I^a nA cm^{-2}	I^b nA cm^{-2}	η^b %	No.(m) 10^{14} cm^{-2}	$I^{b'}$ nA $molecule^{-1}$	η^c %	P mN m^{-1}	A nm^2
$C_{16}BP$	~516	21.1	0.38	0.86	2.44×10^{-13}	1.34	34	1.16
$C_{16}P$	~335	14.2	0.23	1.54	9.2×10^{-14}	0.71	37	0.65

I: Photocurrent per square centimeter; η: External quantum yield; No.(m): Number of molecules /cm^2; $I^{b'}$: Photocurrent per molecule; A: Limiting area per molecule. P: Collapse pressures
a: 137.6 mW cm^{-2} white light, in 0.5 mol L^{-1} KCl_{aq}.
b: at 464 nm from a 137.6 mW cm^{-2} white light, in 0.5 mol L^{-1} KCl_{aq}.
c: at 464 nm from a 137.6 mW cm^{-2} white light, under -100 mV, in 0.5 mol L^{-1} KCl_{aq} containing 4 mmol L^{-1} MV^{2+}.

The maximum absorption wavelengths λ_{max} of $C_{16}BP$ and $C_{16}P$ in chloroform solution are 510 and 501 nm, respectively. λ_{max} of $C_{16}BP$ in chloroform is 9 nm red-shifted comparing with that of $C_{16}P$, indicating that the interaction between π-orbit of chromophores in $C_{16}BP$ became stronger than that of $C_{16}P$. This result agreed with that the inter-chromophoric distance in $C_{16}BP$ is shorter than that in $C_{16}P$ assembly. Comparing their electronic spectra of LB monolayer films with those in chloroform, blue-shifts of 51 and 43 nm could be observed for $C_{16}BP$ and $C_{16}P$, respectively, indicating that H-aggregates formed in the monolayer films for $C_{16}BP$ and $C_{16}P$[5].

A steady cathodic photocurrent was obtained from $C_{16}BP$ and $C_{16}P$ monolayer films modified ITO electrode in 0.5 mol L^{-1} KCl solution by illumination of 137.6 mW cm^{-2} white light (see **Table 1**, I^a). For convenience, $C_{16}BP$ is given as an example for discussion. The photocurrent action spectrum of $C_{16}BP$ is similar to its absorption spectrum, suggesting that the $C_{16}BP$ monolayer films are responsible for photocurrent generation. About 21.1 nA cm^{-2} photocurrent can be obtained for $C_{16}BP$ by a 464 nm light irradiation (3.48×10^{15} photons cm^{-2} s^{-1}), in 0.5 mol L^{-1} KCl electrolyte solution with zero bias voltage. The quantum yield is about 0.38% for $C_{16}BP$ (in **Table 1**, η^b) (the absorbance of the monolayer films is about 0.43% at 464 nm), while that for $C_{16}P$ is 0.23%.

Because the number of active moieties per unit area in the LB monolayer films is an important factor contributing to the PEC performance, here we use the photocurrent per chromophore as the data for comparison. We assume that $C_{16}BP$ contains two D-π-A chromophores of discussion. Taking the limiting molecular area and photocurrent per unit area into account, one can see that photocurrents per chromophore for $C_{16}BP$ and $C_{16}P$ are 1.22×10^{-13} and 9.2×10^{-14} nA chromophore^{-1} (**Table 1**, $I^{b\prime}$), respectively. That is, the photocurrent per dimer is larger than double of the photocurrent per monomer in LB films. Therefore, $C_{16}BP$ performs better in photocurent generation than $C_{16}P$ does. It is not only due to the higher density of $C_{16}BP$ but also due to the dimerization of the chromophores.

It is well known that the experimental conditions affect photocurrent generation. Here, we take $C_{16}BP$-ITO as an example and investigate in 0.5 mol L^{-1} KCl electrode solution. (1) In the range of +150 mV ~ -150 mV, linear relationship was found between photocurrent and bias voltage, indicating that the photocurrent flows in the same direction as the applied negative voltage. (2) The equations of dependence of the photocurrent (i_{ph}) on light intensity (I) for $C_{16}BP$-ITO and $C_{16}P$-ITO electrodes are $i_{ph} = 16.4\ I^{0.75}$ and $i_{Ph} = 4.11\ I$ (R^2 =0.98), respectively. (3) The effects of electron donor (hydroquinone H_2Q and N_2) and acceptor (methyl viologen diiodide MV^{2+}) on the cathodic photocurrent for $C_{16}BP$ and $C_{16}P$ showed that electron acceptors sensitize the cathodic photocurrent, but electron donors quench it. From the result of above experiments, we can propose that the mechanism of the photocurrrent generation for these dye systems is intramolecular electron-transfer reaction.

Under favorable conditions (–100 mV, dissolved O_2, and 4 mmol L^{-1} MV^{2+}), a photocurrent of 74.5 nA cm^{-2} for $C_{16}BP$ was obtained under the irradiation at 464 nm, the quantum yield was 1.34%. Under the same conditions, the quantum yield of $C_{16}P$ was 0.71% (see **Table 1**, I^c, η^c).

Conclusions

It can be seen from **Table 1** that in the present systems the photocurrent generation quantum yield η under the same conditions has the sequence: $C_{16}BP > C_{16}P$. The experimental results of photocurrent generation showed that the dimer $C_{16}BP$ exhibited photocurrent per $C_{16}BP$ molecule (2.44×10^{-13} nA molecule^{-1}) twice larger than the monomer $C_{16}P$ did (9.2×10^{-14} nA molecules^{-1}). The further studies of the reason for this interesting phenomenon are in progress.

Acknowledgments

The authors thank the State Key Project of Fundamental Research (G1998061308, 2002AA 3024030) and the National Natural Science Foundation of China (20023005) and China Postdoctoral Science Foundation for financial support of this work.

References

1. C. H. Huang, F. Y. Li, Y. Y. Huang, *Ultrathin Films for Opticisc and Electronics* (in Chinese), Peking University Press, Beijing, **2001**.
2. F. Y. Li, J. Zheng, Y. Y. Huang, *et al.*, *Chem. Mater.*, **2001**, *13*, 192.
3. D. G. Wu, C. H. Huang, Y. Y. Huang, *et al*., *J. Phys. Chem. B*, **1999**, *103*, 7130.
4. H. W. Gibson, F. C. Bailey, *J. Chem. Soc., Perkin Trans. II,* **1976**, 1575.
5. D. G. Whitten, *Acc. Chem. Res.*, **1993**, *26*, 502.

Received 16 May, 2002