Synthesis, Characterization, Photophysics, and Photosensitization Studies of Squaraine–Bipyridinium Diads

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Two squaraine-bipyridinium diads designed to study electron transfer between the squaraine chromophore and the bipyridinium group have been synthesized. The two diads, denoted as C_4Sq-By and $C_{12}Sq-By$, consist of amphiphilic squaraines covalently linked to a bipyridinium group by a trimethylene chain. The squaraine chromophores in the diads do not form charge-transfer complexes with the bipyridinium group in the ground state. Both C_4Sq-By and $C_{12}Sq-By$ show fluorescence yields about 100 times weaker than those of alkyl substituted squaraines, which is attributed to quenching by an intramolecular electron transfer from the excited squaraine chromophore to the bipyridinium; the intramolecular electron-transfer rate is estimated to be 4×10^{11} s⁻¹. Assuming the short lifetime for the undetectable transient produced is due to very fast back electron transfer to the radical cation of squaraine from the reduced bipyridinium ion, the rate of the back intramolecular electron transfer is estimated as $> 3 \times 10^{10}$ s⁻¹. The two diads synthesized in this work have been used as photocurrent enhancers for the monolayers of DSSQ (4-(distearylamino)phenyl-4'-(dimethylamino)phenylsquaraine). C_4Sq-By as a solution additive is 5 times more effective in sensitizing the cathodic photocurrent generation of the DSSQ monolayer-modified SnO₂ electrode compared to methylviologen. Analogously, C_{12} Sq-By is 3 times more effective in sensitizing the DSSQ monolayermodified SnO₂ electrode compared to 4-tetradecyl-4'-methylbipyridinium dichloride when it is incorporated upon spreading in the monolayer of DSSO. The increase in cathodic photocurrent generation efficiency is postulated to result from fast electron transfer from the excited squaraine to the bipyridinium group in the diad. The fast electron transfer facilitates electron separation in the photogeneration step and consequently increases the quantum efficiency of the cathodic photocurrent generation process.

Introduction

Squaraines have been the subject of many recent investigations both because of their unusual electronic structures as well as their properties as semiconductive and photogeneration materials in electrophotographic photoreceptors.¹ In photoreceptor applications, they are used as microcrystalline solids embedded in a polymer matrix. Excitation of the microcrystalline photoconductor leads to the formation of excitons, which formally dissociate into electron—hole pairs and subsequently are used in electrostatic imagings. Using aggregates formed in monolayers of 4-(distearylamino)phenyl-4'-(dimethylamino)phenylsquaraine (DSSQ), we modeled the photogeneration



process of squaraine using solution photoelectrochemical experiments.² For example, we observed generation of a cathodic photocurrent when a DSSQ aggregate-modified SnO_2 electrode was irradiated with visible light. The cathodic photocurrent generation was attributed to an electron transfer from the squaraine exciton to O_2 followed by a subsequent transfer of an electron from the conduction band of the SnO_2 electrode to the holes in the squaraine aggregates. Addition of electron acceptors, such as methylviologen, enhances the cathodic photocurrent generation under both ambient and deaerated conditions. On the other hand, electron donors, such as hydroquinone, quench the cathodic photocurrent in the ambient condition and make the photocurrent anodic when the electrolyte solution is deaerated.

Very recently, we³ studied electron transfer between the squaraine exciton and either an electron acceptor or a donor within a monolayer by incorporating either an amphiphilic donor or amphiphilic acceptor into the monolayer of DSSQ. From the effects of the concentration of the electron acceptor/donor on the intralayer electron-transfer process, we have been able to estimate the size of the squaraine exciton in the monolayer. Although transfer of an electron from the exciton of the squaraine aggregate to O₂ has been postulated in these studies, the thus-generated radical cation has not been detected in transient absorption experiments.⁴ In an attempt to gain further insight on the electron-transfer process, we synthesized two squaraine-bipyridinium diads, C₄Sq-By and C₁₂Sq-By (structures shown in Scheme 1), by covalently linking an amphiphilic squaraine group (with butyl or dodecyl chains) and a bipyridiniumyl group with a trimethylene chain. We report here a study on the aggregation and electrochemical, photophysical, and photoelectrochemical properties of these two diads. Interesting photosensitization results are obtained when the monolayers of stearic acid or DSSQ (on SnO₂ electrodes) are studied photoelectrochemically in the presence of C₄Sq-By and C₁₂Sq-By either in the electrolyte solution or in the monolayer. A photosensitization mechanism is proposed and discussed.

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Experimental Section

Materials. *N*-Methylaniline, 1,3-dibromopropane, *N*,*N*-dibutylaniline, potassium hexafluorophosphate, DMSO- d_6 , and 1-bromododecane were purchased from Aldrich. Potassium bicarbonate was from Baker, aluminum trichloride and sodium nitrate (electrolyte) were from Fisher, aniline was from Mallinck-rodt, and tributylorthoformate was from Lancaster. All these materials were used as received. The spreading solvent for the monolayer work was chloroform (HPLC, pentene stablized) and was purchased from Fisher. Distilled water was in-house deionized water purified by passing through a Millipore water purification system.

General Techniques. FAB-MS analysis of the squaraine compounds was performed at the Center for Mass Spectrometry at the University of Nebraska in Lincoln, Nebraska. NMR spectra were recorded on a GE NMR QE-300 spectrometer. Fluorescence emission spectra were recorded on a Spex Fluorolog spectrometer, and the spectral response was not corrected.

Monolayers of DSSQ, $C_{12}Sq-By$, and stearic acid were obtained by spreading chloroform solutions of the corresponding compound onto an aqueous subphase in a KSV 5000 film balance at room temperature (35 °C for DSSQ). Typical transfer ratios on hydrophilic SnO₂ substrates were 1.0 \pm 0.1. The aggregation of the squaraine chromophores in the Langmuir–Blodgett (LB) films was studied by absorption spectroscopy using a Hewlett-Packard 8452A diode array spectrophotometer.

The cyclic voltammograms of the squaraine diads were measured on an electrochemical analyzer, Model BAS 100B, from Bioanalytical Systems. Acetonitrile was used as solvent, and tetrabutylammonium perchlorate was used as the supporting electrolyte. The electrochemical cell consists of three electrodes, a platinum disk working electrode, a Ag/AgCl (KCl saturated) reference electrode, and a platinum wire auxiliary electrode. Photoelectrochemical experiments on various monolayer-modified SnO₂ electrodes were carried out as described elsewhere.²

Transient absorption experiments were performed on an inhouse apparatus using the 1064 nm fundamental pulse (25–35 ps at 10 Hz) of a mode-locked Nd:YAG laser (Continuum PY61C) as both pump and probe sources. The fundamental was passed through a computor-controlled variable optical delay line (Velmex) to achieve the desired delay between the pump and probe beams. The second harmonic wavelength of the laser (532 nm) was used as the excitation source. Raman shifting of

the 532 nm beam in acetone- d_6 was used to obtain the 600 nm excitation pulse used in this work. The excitation beam diameter was 2 mm. After the delay line, the fundamental pulse was focused into a 10 cm cell with quartz windows containing H₂O/ $D_2O(1:1)$ for white light continuum generation. The white light was then collimated and focused at one end of a 200 μ m fused silica optical fiber. It was split into two beams of equal intensity at the other end of the optical fiber by a cube beam splitter after passing through a polarization descrambler. One of the beams was used as reference, and the other was used as an interrogation beam. After the absorption of the transient was recorded, the two beams were then recollimated and focused at the end of a bifurcated fiber optic pair that was attached to a SPEX 270 monochromator. The spectra of the white light continuum for the sample and reference beams with and without excitation were detected after passing through the monochromator by a cooled dual diode array detector (Princeton Instruments ST121/DDA512), and the corresponding differential absorption spectra at the set delay time were calculated, displayed, and stored.

Synthesis of 1-(*p*-Didodecylaminophenyl)-2-hydroxycyclobutene-3,4-dione. Aniline (1 g, 10.7 mmol), 1-bromododecane (10.7 g, 43 mmol), potassium bicarbonate (10 g), iodine (0.18 g), and 100 mL of 1-butanol were added into a 250 mL roundbottom flask.⁵ The mixture was brought to reflux for 10 h. After the mixture was cooled to room temeprature, the solid in the mixture was removed by filtration and was washed with a small amount of 1-butanol. The filtrates were combined and the 1-butanol solvent was removed by evaporation under vacuum. The product was purified by column chromatography on silica gel using a mixture of hexane and ether as eluent. A colorless oil that was identified as *N*,*N*-didodecylaniline was isolated with a yield of 1.7 g (37%). NMR (ppm in CDCl₃): 1.02 (t, 6H), 1.42 (m, 36H), 1.72 (m, 4H), 3.37 (t, 4H), 6.77 (m, 3H), and 7.36 (t, 2H).

1-Chloro-2-(*p*-didodecylaminophenyl)cyclobutene-3,4-dione was then synthesized using the above aniline derivative according to the procedures described by Wendling et al.⁶ To a methylene chloride solution containing 0.62 g of squaric acid dichloride (4.1 mmol, freshly prepared according the procedure of De Selms and co-workers⁷) and 0.55 g of AlCl₃ (4.1 mmol) in 50 mL of CH₂Cl₂, *N*,*N*-didodecylaniline (1.7 g, 3.96 mmol) was introduced dropwise through a dropping funnel. After the addition was completed, the mixture was refluxed for 1 h. The solvent was removed and the product was purified by column chromatography on silica gel, affording a yellow solid identified as 1-chloro-2-(*p*-didodecylaminophenyl)cyclobutene-3,4-dione. This yellow solid was then dissolved in a mixture of ethanol and water (1:1). After a small quantity of concentrated hydrochloric acid was introduced, the mixture was refluxed for 1 h, resulting in a yellow solid suspension. The yellow solid was isolated by filtration and was washed throughly with water until the filtrate was neutral. It was then dissolved in chloroform and the residual water was removed by adding CaCl₂ into the chloroform solution, yielding pure 1-(*p*-didodecylaminophenyl)-2-hydroxycyclobutene-3,4-dione 0.9 g (43%) after removing the chloroform solvent.

Synthesis of 4-N-Methyl-N-(3-bromopropyl)aminophenyl-4'-(N',N'-dibutylamino)phenylsquaraine. The *N*-methyl-*N*-(3-bromopropyl)aniline used in the synthesis was synthesized by condensing *N*-methylaniline with 1,3-dibromopropane in 1-butanol in the presence of potassium bicarbonate and iodine.⁵ The yield was 70%. NMR (ppm in CDCl₃): 2.21 (m, 2H), 3.03 (s, 3H), 3.55 (m, 4H), 6.80 (m, 3H), and 7.38 (m, 2H).

4-*N*-Methyl-*N*-(3-bromopropyl)aminophenyl-4'-(N',N'-dibutylamino)phenylsquaraine was prepared by condensing 1-(dibutylamino)phenyl-2-hydroxycyclobutene-3,4-dione (0.48 g, 1.6 mmol, synthesized according to the procedure of Chen et al.⁸) with *N*-methyl-*N*-(3-bromopropyl)aniline (0.34 g, 1.48 mmol) in the presence of tributylorthoformate (1 mL) in about 50 mL of 1-butanol at reflux for 2 h.⁹ The progress of the synthesis was monitored by absorption spectroscopy. The product mixture was cooled in a refrigerator overnight. The solid product was isolated by filtration and was purified by washing first with 1-butanol and then ether. The yield was 0.28 g (37%). NMR (CDCl₃): 1.01 (t, 6H), 1.42 (m, 4H), 2.22 (m, 2H), 3.20 (s, 3H), 3.47 (t, 4H), 3.70 (t, 2H), 6.77 (m, 4H), and 8.41 (d, 4H).

Synthesis of 4-*N*-Methyl-*N*-(*N*'-methyl-N"-(4,4'-bipyridiniumyl)-3-propyl)aminophenyl-4"-dibutylaminophenylsquaraine Bromide Iodide (C₄Sq-By). There was first prepared 4-*N*-methyl-*N*-(4-(4-pyridyl)pyridiniumyl)-3-propylaminophenyl-4'-(dibutylamino)phenylsquaraine by reacting 4-(*N*methyl-*N*-(3-bromopropyl)amino)phenyl-4'-(dibutylamino)phenylsquaraine (0.2 g, 0.39 mmol) with 1.2 g (7.82 mmol) of 4,4'-bipyridyl in 40 mL of acetonitrile at reflux for 2 days. After the solvent was removed, excess bipyridyl was removed by extracting with benzene repeatedly. The pure desired squaraine product was obtained in 69% yield (0.18 g). NMR (DMSO d_6): 0.88 (t, 6H), 1.26 (m, 4H), 1.53 (m, 4H), 2.33 (m, 2H), 3.12 (s, 3H), 3.53 (t, 4H), 3.75 (t, 2H), 4.71 (t, 2H), 6.68 (m, 4H), 8.06 (m, 2H), 8.11 (m, 4H), 8.63 (m, 2H), 8.81 (d, 2H), and 9.25 (d, 2H).

C₄Sq-By was then prepared by reacting the above squaraine product (0.03 g, 0.045 mmol) with 2 mL of methyl iodine in 10 mL of acetonitrile at room temperature for 2 days. After the solvent was removed, the product was purified by column chromatography on celullose using acetonitrile as eluent, affording 10 mg of C₄Sq-By (27%). NMR (CD₃CN): 0.96 (t, 6H), 1.39 (m, 4H0, 1.93 (m, 4H0, 2.42 (m, 2H), 3.11 (s, 3H), 3.50 (t, 4H), 3.71 (t, 2H), 4.40 (s, 3H), 4.74 (t, 2H), 6.88 (m, 4H), 8.15 (m, 4H), 8.35 (d, 4H), and 8.90 (d, 4H). FAB-MS: 602.3 (M⁺). Maximum absorption (in CHCl₃): 636 nm $(3.1 \times 10^5 \text{ M}^{-1} \text{ cm}^{-1})$.

Synthesis of 4-*N*-Methyl-*N*-(*N*'-methyl-*N*"-(4,4'-bipyridiniumyl)-3-propylaminophenyl-4"-(didodecylamino)phenylsquaraine Bromide and Iodide (C_{12} Sq-By). The titled compound was synthesized analogously to C_4 Sq-By. NMR



Figure 1. Absorption spectrum of C₄Sq-By in acetonitrile.

(CD₃CN): 0.87 (t, 6H), 1.27 (m, 32H), 1.93 (m, 4H), 2.12 (m, 4H), 2.40 (m, 2H), 3.10 (s, 3H), 3.49 (t, 4H), 3.70 (t, 2H), 4.39 (s, 3H0, 4.69 (t, 2H), 6.85 (m, 4H), 8.15 (m, 4H), 8.30 (m, 4H), 8.85 (m, 4H). FAB-MS: 826.6 (M+). Maximum absorption: 636 nm $(3.1 \times 10^5 \text{ M}^{-1} \text{ cm}^{-1})$.

The PF₆ salt of C_{12} Sq-By, C_{12} Sq-By/PF₆, could be prepared by an ion exchange process using KPF₆ and C_{12} Sq-By in acetonitrile. The spectroscopic properties of C_{12} Sq-By/PF₆ were found to be identical with those of the bromide iodide compound.

Results and Discussion

Synthesis and Characterization of C₄Sq-By and C₁₂Sq-**By**. The synthetic path for C_4Sq-By and $C_{12}Sq-By$ is given in Scheme 1. The entire synthesis is dictated by our ability to purify the intermediates and the final products. For example, we attempted to synthesize C₄Sq-By by condensing the covalently linked aniline-bipyridinium derivative with the corresponding "half squaric acid". Although C₄Sq-By was formed and detected spectroscopically and chromatographically, we failed to isolate any pure material in this study. The synthetic route in Scheme 1, although not the shortest, offers the advantage that each intermediate is amenable to purification. Both C₄Sq-By and C₁₂Sq-By are characterized by proton NMR and FAB mass spectrometric analysis. In the absorption spectra, both compounds exhibit sharp and intense absorption very typical of that of the monomer of squaraine (Figure 1).¹⁰ The absorption maxmium is at 636 nm in dilute acetonitrile solution, and the molar extinction coefficient is 3.1×10^5 cm⁻¹ M^{-1} . The absorption data suggest that there is no ground state interaction between the squaraine chromphore and the bipyridinium group in C₄Sq–By and C₁₂Sq–By.

The lack of any ground-state charge transfer interaction between the squaraine chromophore and the bipyridinium group in C₄Sq–By and C₁₂Sq–By is also supported by the cyclic voltammetry (CV) data. Figure 2 depicts a cyclic voltammogram of C₄Sq–By in acetonitrile. The redox potentials are basically the combination of the two chromphores in the diads, with the oxdiation potential at 0.71 and 1.04 V vs Ag/AgCl, attributable to the squaraine chromophore,¹¹ and the reduction potential at -0.4 V vs Ag/AgCl is attributable to the bipyridinium group.¹²

Aggregation Studies. Unlike alkyl substitued squaraines, which are readily soluble in chloroform, C_4Sq-By is insoluble in chloroform and $C_{12}Sq-By$ is only slightly soluble in choroform, forming a mixture of monomer and blue-shifted



Potential (mV) (vs. Ag/AgCl)

Figure 2. Cyclic voltammogram of C₄Sq-By in acetonitrile.



Figure 3. Surface pressure—area compression isotherm of a monolayer of C_{12} Sq-By on water.

aggregates (530 nm) in diluted chloroform solution. A good organic solvent found for C₄Sq-By and C₁₂Sq-By is acetonitrile probably because of the ionic bipyridinium groups in the diads. The low solubility of C₄Sq-By in chloroform has limited our LB film work to C12Sq-By. Figure 3 shows the surface pressure-area compression isotherm for the monolayer of C_{12} Sq-By on water. The monolayer is stable with practically no hysteresis. The limiting molecular area is 57 Å²/molecule, and it corresponds to the cross-sectional area of two hydrocarbon chains,13 suggesting that C12Sq-By lies vertically along the long molecular axis on the water surface. Figure 4 shows the absorption spectra of the monolayers of C₁₂Sq-By when they are transferred to hydrophilic glass substrates at varying surface pressures. At very low surface pressure, e.g., 2 mN/m, C12Sq-By exists as squaraine monomers in the monolayer. As the surface pressure increases, the monomers of C₁₂Sq-By (655 nm) are in an equilibrium with the blue-shifted aggregates (530 nm) in the monolayer. This is very characteristic for a number of squaraine monolayers, and the results have been summarized in an earlier publication.¹⁴ We concluded earlier that the squaraine chromophores tend to aggregate as a supramolecular unit, such as the tetramer, without forming a dimer as an



Figure 4. Absorption spectra of transferred monolayers of $C_{12}Sq-By$ on glass substrates as a function of the transferring surface pressure.

TABLE 1: Fluorescence Quantum Yields of C_4Sq-By and $C_{12}Sq-By$

squaraine	solvent	quantum yield
C_4Sq-By C_4Sq-By/PF_6 $C_{12}Sq-By$ bis(4-(octadecylamino)phenyl)- squaraine	acetonitrile acetonitrile acetonitrile chloroform	$\begin{array}{c} 1 imes 10^{-3} \\ 1 imes 10^{-3} \\ 1.2 imes 10^{-3} \\ 0.84^a \end{array}$

^a Reference 16.

intermediate. We have also shown that this aggregation behavior is a result of the unique stabilization energy for the supramolecular structure in the squaraine aggregates.¹⁵ At higher surface pressures, e.g., > 25 mN/m, only the blue-shifted aggregates are formed.

Photophysics of C12Sq-By and C4Sq-By. Both C4Sq-By and C₁₂Sq-By fluoresce in the visible region, and the emission spectra are typical of the monomer of an alkylated squaraine.¹⁰ The fluorescence emission maxima and the fluorescence quantum yield data are summarized in Table 1. In comparsion with the fluorescence yields of alkyl substitued squaraines,^{10,16} the fluorescence quantum yields for C₄Sq-By and C12Sq-By are about 100 times lower. Since both absorption and electrochemical data indicate that there is no groundstate interaction between the squaraine chromophore and the bipyridinium group, we attribute the significant decrease in fluorescence yield to fluorescence quenching by electron transfer from the excited squaraine chromphore to the bipyridinium group. The radiative decay rate of squaraine was estimated to be $4 \times 10^8 \text{ s}^{-1.16}$ From the quantum yield data in this work, the rate of the intramolecular electron-transfer process can be estimated to be 4 \times 10¹¹ s⁻¹.

As noted earlier, one of the objectives of this work was to study the electron-transfer reaction between the squaraine chromophore and the bipyridinium group and the kinetics of resulting transients. The transient absorption spectrum for C_4 Sq-By is given in Figure 5. The monomer absorption at 638 nm is bleached and recovers very rapidly. Unfortunately, the reduced bipyridinium radical cation, which should absorb at around 605 nm,¹⁷ was not observable. The lack of a detectable transient may be due to spectral overlapping between the bleached peak and the reduced bipyridinium radical cation, or more likely to the very rapid back electron recombination between the squaraine radical cation and the reduced bipyridinium radical cation. Kinetic analyses of peaks observed in the transient experiment suggest that the transient, if formed,



Figure 5. Transient absorption spectra of C_4Sq–By in acetonitrile $([C_{12}Sq-By]=3.5\times10^{-6}~M)$



Figure 6. Effect of adding C₄Sq-By in the electrolyte (1 M NaNO₃) on the action spectra of the cathodic photocurrent generation of a DSSQ monolayer-modified SnO₂ electrode: (a) 1 M NaNO₃ as electrolyte; (b) 3.9×10^{-7} M of C₄Sq-By/PF₆ added to (a); (c) modified electrode in (b) recovered and rinsed and then the photocurrent measured according to conditions in (a).

must have a lifetime shorter than 30 ps. If the radical cation of the squaraine chromophore is indeed formed, the rate of the intramolecular charge recomination should be $> 3 \times 10^{10}$ s⁻¹.

Photoelectrochemical Studies. Although $C_{12}Sq$ -By forms stable monolayers on water and the films are transferrable to hydrophilic substrates, e.g., SnO₂ electrodes, with essentially unit efficiency, we have been unable to study the photoactivity of the LB film-modified electrode in solution photoelectrochemical experiments because the monolayer respreads on the water surface when the electrode is introduced to the aqueous electrolyte solution.

In this work, we use C₄Sq-By and C₁₂Sq-By as photocurrent enhancers for the DSSQ monolayers in solution photoelectrochemical experiments. Previously, we reported that when methylviologen was added to the electrolyte solution (1 M NaNO₃) in a photoelectrochemical cell, we observed a slight increase in cathodic photocurrent generation for the DSSQ monolayer-modified SnO₂ electrode.² The photocurrent enhancement was attributed to the electron transfer from the squaraine exciton to methylviologen. Here, we introduced C₄Sq-By/PF₆ (3.9 × 10⁻⁷ M) into the electrolyte solution instead. We observed a drastic increase (×5) in the cathodic photocurrent generation (Figure 6). Since fluorescence and transient experiments suggest that electron transfer from the



Figure 7. (a) Action spectra of a stearic acid monolayer-modified SnO_2 electrode as sensitized by adding C_4Sq-By/PF_6 in the electrolyte (1 M NaNO₃). (b) Absorption spectrum of the recovered stearic acid layer.

excited squaraine to the bipyridinium group is extremely fast, we suggest that the squaraine chromophore in C_4Sq-By is incorporated into the aggregates of DSSQ on the monolayer-modified electrode. The presence of C_4Sq-By in the DSSQ aggregate facilitates charge separation, leading to the increase in the cathodic photocurrent generation. This interpretation is supported by the action spectrum in Figure 6 (curve c). The observation of significant photocurrent for the recovered modified DSSQ electrode indicates that C_4Sq-By/PF_6 is incorporated into the aggregates of DSSQ in the first photoelectrochemical experiment.

To test the hypothesis, we prepared a modified electrode containing a monolayer of pure stearic acid on the SnO₂ substrate. When this modified electrode is introduced into the photoelectrochemical cell containing 1 M NaNO3 as electrolyte solution, no photocurrent was observed. On the other hand, when C₄Sq-By/PF₆ (1.2×10^{-6} M) is added to the electrolyte solution, a cathodic photocurrent (600 nA/cm²) was recorded. The action spectrum for the cathodic photocurrent peaks at 530 nm (Figure 7, curve a), suggesting that a blue-shifted aggregate of the squaraine chromphore is responsible for the observed photocurrent. Analysis of the recovered stearic acid-modified SnO₂ electrode after the photoelectrochemical experiment by absorption spectroscopy reveals the presence of squaraine in the stearic acid monolayer (absorption maximum at 650 nm corresponding to the monomer of the squaraine chromphore, Figure 7, curve b). The result suggests that C_4Sq-Py/PF_6 is adsorbed and incorporated in the stearic acid monolayer during the photoelectrochemical experiment. In water, the squaraine chromophores form the blue-shifted aggregates due to hydrophobic interactions,⁸ and this aggregate produces the cathodic photocurrent observed in Figure 7. When the stearic acid monolayer is removed from the electrolyte solution, the aggregate breaks apart and the stearic acid layer exhibits a visible absorption corresponding to the monomer of the squaraine chromophore.

We³ recently introduced amphiphilic electron acceptors 4-tetradecyl-4'-methylbipyridinium dichloride and 4-octadecyl-4'-methylbipyridinium dichloride in the monolayers of DSSQ. We observed intralayer electron transfers when the mixed monolayers are studied in photoelectrochemical experiments. Although we have been unable to study the photoactivity of the monolayer of C₁₂Sq-By directly, we are able to incorporate it into the monolayer of DSSQ. At a 1:10 ratio (C₁₂Sq-By: DSSQ), we find that C₁₂Sq-By is 3 times more effective in sensitizing the cathodic photocurrent compared to a mixed monolayer containing 4-tetradecyl-4'-methylbipyridinium di-



Figure 8. Cathodic photocurrent generation action spectra for various DSSQ-modified SnO₂ electrodes in solution photoelectrochemical experiments: (a) C_{12} Sq-By incorporated in the DSSQ monolayer at a 1:10 ratio and 1 M NaNO₃ used as electrolyte; (b) 7.9×10^{-7} M of C_4 Sq-By/PF₆ added into the 1 M NaNO₃ electrolyte solution; (c) the electrolyte solution in (b) deaerated by nitrogen.

chloride. For instance, the maximun photocurrent observed for the C_{12} Sq-By sensitized electrode is 1500 nA/cm² (Figure 8, curve a) whereas one that is sensitized by 4-tetradecyl-4'methylbipyridinium dichloride is only about 500 nA/cm² under similar conditions.³ We attribute the higher sensitization efficiency for the C12Sq-By-sensitized electrode to the very fast intramolecular electron transfer from the squaraine chromphore to the bipyridinium group. This is because the squaraine chromophore in C₁₂Sq-By is part of the squaraine aggregate in the monolayer-modified electrode and the presence of C12Sq-By facilitates charge separation in the photogeneration step. A further increase in cathodic photocurrent generation, as high as 2600 nA/cm², was obtained when C_4Sq-Py/PF_6 is added into the electrolyte solution (Figure 8, curve b). This corresponds to a quantum yield of 1.5% for the squaraine monolayer-modified SnO₂ electrode.

The estimated photocurrent generation efficiency for the DSSQ-C₁₂Sq-By monolayer electrode and the estimated rate constant of 3×10^{11} s⁻¹ for return electron transfer in the C₁₂Sq-By diad allow estimation of the rate constant for the interfacial electron transfer between the monolayer and the electrode (and/or monolayer-oxygen) be in the range (2–5) $\times 10^9$ s⁻¹. We assume in these calculations that the return electron transfer rate is the same in the LB film as in solution and that the photocurrent generation efficiency is limited only by return electron transfer. Consequently, the estimated rate constants may be taken as lower limits. In any event, our estimate is in the same range compared to that of the electron transfer rate constants from excited states of J-aggregate of cyanine dyes to AgBr microcrystals, which were reported to be 10^9-10^{10} s⁻¹ by Tani et al.¹⁸ and Muenter et al.¹⁹

It is worth pointing out that when the electrolyte solution in the above C_{12} Sq-By photosensitization experiment is deaerated with nitrogen, the cathodic photocurrent is attenuated significantly (Figure 8, curve c). The results indicate that molecular oxygen is still vital in the photocurrent generation process even in the presence of the bipyridinium groups. We suspect that although the bipyridinium groups may faciliate charge separation, charge recombination may occur if the photogenerated radical cation and anion are not removed from the recombination range. Molecular oxygen likely serves as an electron shuttle to remove the photogenerated charge pair out of the recombination range. The results seem to indicate that, in the absence of an electron acceptor, molecular oxygen plays a dual role in the cathodic photocurrent generation process. It creates as well as separates the photogenerated charges.

Summary and Remarks

This work reports the synthesis of two squaraine—bipyridinium diads. Both absorption and electrochemical results indicate that there is no intramolecular ground-state charge-transfer interaction between the squaraine chromophore and the bipyridinium group. In the fluorescence emission spectra, a significant decrease in fluorescence yield was observed for the diads. The low fluorescence yield was attributed to fluorescence quenching due to intramolecular electron transfer. From the radiative rate constant, the forward intramolecular electron-transfer rate is estimated to be $4 \times 10^{11} \text{ s}^{-1}$. In the transient absorption experiment, no long-lived transient was detected and any transient, if formed, should have a lifetime shorter than 30 ps. This leads to an estimated return electron-transfer rate of $> 3 \times 10^{10} \text{ s}^{-1}$.

C₁₂Sq-By was shown to form stable monolayers on water, and the monolayers are transferrable to hydrophilic substrates with nearly unity efficiency. Photoelectrochemical experiments with the monolayer-modified electrode of C₁₂Sq-By were unsuccessful because the monolayer was found to respread on the water surface. However, we have been able to study both C₄Sq-By and C₁₂Sq-By as sensitizers in photoelectrochemical experiments involving the monolayer-modified electrodes of DSSQ. We found that C_4Sq-By/PF_6 is a much more effective sensitizer in the electrolyte solution compared to methylviologen. Evidence is provided that C₄Sq-By is incorpoated into the monolayer of DSSQ. The incorporated C₄Sq-By serves as a site for charge separation because of the fast intramolecular electron transfer between the excited squaraine chromophore and the bipyridinium group. Similarly, C₁₂Sq-By is a more effective sensitizer compared to 4-tetradecyl-4'-methylbipyridinium dichloride in the monolayer of DSSQ. Again, the improved effectiveness in sensitization for C₁₂Sq-By can be attributed to the fast electron transfer between the excited squaraine chromphore and the bipyridinium group, which facilitates the charge generation.

This work also demonstrates that molecular oxygen is essential to the cathodic photocurrent generation process even in the presence of electron acceptors such as the bipyridinium group. We hypothesize that oxygen plays a dual role in the cathodic photocurrent generation process. It facilitates the charge generation step and then serves as an electron shuttle to move the generated charge pairs out of the recombination range.

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