Dyes and Pigments, Vol. 39, No. 4, pp. 281–290, 1998
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Printed in Great Britain
PII: S0143-7208(98)00013-8 0143-7208/98/$—see front matter

Interaction of Squarylium Cyanine with Nanoparticle TiO_2 for Photoelectric Conversion

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(Received 16 January 1998; accepted 13 February 1998)

ABSTRACT

Three squarylium cyanine dyes with different attaching groups on the heterocyclic nitrogen atom were designed and synthesized. For 1,3-bis (N-3-sulfopropyl-3,3-dimethyl-2-methylene indolenine) squarylium cyanine pyridyl salt (Sq3), the apparent association constant of $3788\,mol^{-1}\,liter^{-1}$ *with nanoparticle* TiO_2 *was determined from the data of Sq3 fluorescence quenching by* TiO_2 *colloids, and the fluorescence lifetimes of Sq3 with or without* TiO_2 *were used to elucidate the kinetic information for the quenching process. ESR study provides direct evidence that electron injection from the excited singlet Sq3 to the conduction band of* TiO_2 *occurs. The Sq3-modified nanocrystalline* TiO_2 *electrode gives an overall photoelectric conversion efficiency of 2.17% and a top incident monochromatic photon-to-photocurrent conversion efficiency (IPCE) value of 6.2% at 650 nm. © 1998 Elsevier Science Ltd. All rights reserved*

Keywords: squarylium cyanine, nanoparticulate TiO_2 colloid, nanocrystalline TiO_2 electrode, electron injection, photoelectric conversion efficiency, incident monochromatic photon-to-photocurrent conversion efficiency.

1. INTRODUCTION

As an important class of functional materials, squarylium cyanines (Sqs) possess many advantages, e.g. stable structure, outstanding photoconductivity

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and small thermal conductivity, and they have, therefore extensive potential in organic solar cells, laser dyes, optical recording media, xerographic photoreceptors, nonlinear optical and imaging materials, etc. [1–3]. Moreover, the sharp and intense absorption of Sqs in the red visible region above 600 nm has made them potentially important in application for expanding the photoresponse of large bandgap semiconductors employed in photoelectrochemical solar cells.

In the present work, the sensitization of Sq to TiO_2 colloids in solution was carried out to provide information with respect to the interfacial electron injection process occuring at the semiconductor surface. Focus was made on the interaction kinetic rate and the detection of intermediates for the charge transfer process. The role of Sq in sensitizing nanocrystalline TiO_2 electrode is also presented.

2. EXPERIMENTAL

2.1 Materials

Sqs were synthesized according to the literature [4] and the chemical structures were shown in Fig. 1.

TiO_2 colloids in ethanol were prepared similar to a procedure employed earlier [5]. Titanium (IV) tetrachloride in anhydrous ethanol (10%, 2.3 mL) was injected by syringe into 100 mL of aqueous ethanol (1%), then kept

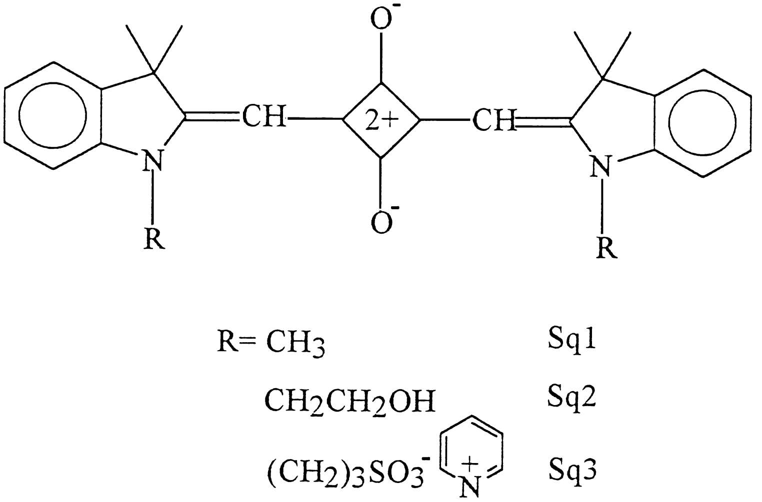

Fig. 1. Chemical structures of squarylium cyanine dyes.

stirring for 4 h. No stabilizing agents were used, and the colloidal suspensions of TiO_2 formed by this method were stable for several months. The fresh stock suspension, of concentration 0.02 mol/liter^{-1}, was diluted with ethanol to obtain the desired concentration of TiO_2 before experiments every time. The average particle size of colloidal TiO_2 for the present study was estimated to be *ca.* 5.0 nm from the absorption onset [6], which agrees with the results obtained by transmission electron microscopy (TEM).

2.2 Instruments

Absorption spectra were recorded on a Hitachi-557 spectrometer and fluorescence spectra on a Hitachi-850 spectrofluorometer. Fluorescence lifetimes were obtained with a Horiba NAES-1100 time-correlated single-photon counting fluorometer. Spin-trapped electron paramagnetic resonance (ESR) spectra were taken with a Brucker Model ESP 300E ESR spectrometer equipped with a Quanty-Ray Nd(YAG laser system and a computer for data acquisition and instrument control.

2.3 Photoelectrochemical measurement

The signalling apparatus (Model DCD-1), constant potentiometer (Model 551) and recording instrument (Model 3036X-Y) were equipped with the recording of the photocurrent–photovoltage characteristic curve, while a 250 W tungsten halogen lamp served as a light source, the normal intensity of incident light being 75 mW cm^{-2}. In the photocurrent action spectrum measurement, monochromatic irradiation was generated with a 500 W Xenon lamp and a high intensity grating monochromator (Model WDG-1). A digital electric flow meter (Model 179) was employed for measuring the short-circuit (I_{sc}). All the measurements were performed at room temperature.

3. RESULTS AND DISCUSSION

3.1 Spectral properties of Sqs

Both the absorption and emission spectra of Sqs showed single peaks in the red visible region with rather small Stokes' shifts (10 to 20 nm). The absorption band exhibited negative solvatochromism, i.e. a blue shift of the absorption maximum with increasing solvent polarity, which can be illustrated by interactions between the dye molecule and the solvent to stabilize the ground state. Compared to normal cyanines, the ground states of ionic squarylium cyanines have much more polar character than those of the excited states, so the increase of solvent polarity is beneficial in lowering the energy of the ground states relative to the excited states of the dye molecules [7]. With changes in the substituents on the heterocyclic nitrogen atom, the absorption spectra were bathochromic shifted in the order: $(CH_2)_3SO_3{-}Py^+ > CH_2\ CH_2OH > CH_3$. Furthermore, the powerful light-harvesting capacity of Sqs (molar extinction coefficient ε up to 10^5 (mol/liter)$^{-1}$cm^{-1}) indicates a high value in solar energy utilization, especially for extending the photoresponse into the longer-wavelength region above 600 nm.

In the experimental system, due to the weak competitive adsorption ability on TiO_2 compared with ethanol, Sq1 and Sq2, with an attaching methyl and hydroxyethyl group on the heterocyclic nitrogen atom, respectively, could not be close enough to TiO_2 surface to inject an electron into the TiO_2 conduction band within the short excited singlet lifetime of the dyes (below 2 ns in ethanol). However, Sq3 could be adsorbed on the TiO_2 surface, because of the strong electrostatic attraction force between Sq3 with the negatively charged substituent and the positively charged TiO_2 particles in acidic medium.

3.2 Interaction between Sq3 and TiO_2 colloids

3.2.1 Absorption characteristics of the Sq3–TiO_2 system

The spectral absorption changes of Sq3 with increasing concentration of TiO_2 colloids in ethanol are shown in Fig. 2. Sq3 had an intense absorption band peaking at 635 nm in ethanol; during addition of TiO_2 colloid, the absorption maximum remained nearly constant, but the optical density (O.D.) of Sq3 decreased.

3.2.2 Fluorescence quenching by colloidal TiO_2

Addition of TiO_2 colloids to a solution of Sq3 resulted in quenching of its fluorescence, as shown in Fig. 3.

Since intersystem crossing efficiency of Sq3 is quite low [8], participation of the triplet excited state of Sq3 in the charge injection process can be ruled out. Thus, electron injection from the excited singlet state of Sq3 to TiO_2 conduction band may occur.

The strong adsorption of Sq3 on colloidal TiO_2 particles resulted in an equilibrium between the adsorbed and unadsorbed molecules of the sensitizer and TiO_2 colloids in solution, with an apparent association constant K_{app} (eqn (1)).

$$\mathrm{Sq3} + \mathrm{TiO_2} \overset{K_{app}}{\rightleftharpoons} [\mathrm{Sq3\text{-----}TiO_2}] \tag{1}$$

On the basis of eqn (1), the observed fluorescence yield (ϕ_f) of the sensitizer in a colloidal TiO_2 solution can be correlated to the fluorescence yields of

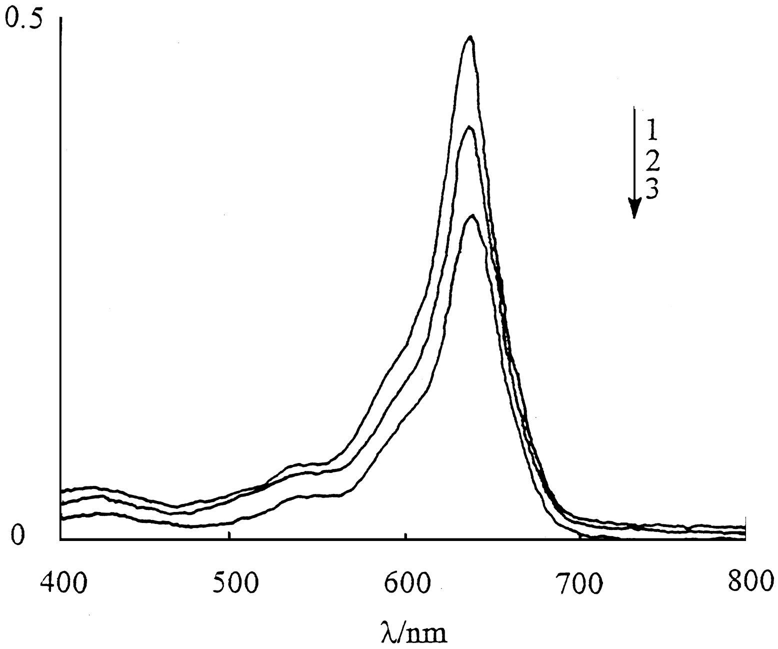

Fig. 2. Absorption spectra of 2.0×10^{-6} mol liter^{-1} Sq3 in ethanol [TiO_2] (mol liter^{-1}): (1)0, (2) 8×10^{-4}, (3) 2×10^{-3}.

unadsorbed ($\phi_f^o = 0.03$) and adsorbed (ϕ_f') molecules of the sensitizer by eqn (2) [9]

$$\frac{1}{\phi_f^0 - \phi_f} = \frac{1}{\phi_f^0 - \phi_f'} + \frac{1}{K_{\text{app}}\left(\phi_f^0 - \phi_f'\right)[\text{TiO}_2]} \tag{2}$$

The experimental results in Fig. 3 showed a linear dependence of $1/\phi_f^o - \phi_f)$ on the reciprocal concentration of TiO_2 colloids as indicated in Fig. 4. The values of K_{app} and ϕ_f', as determined from the slope and intercept of this plot, were 3788 mol^{-1} liter and 0.01, respectively.

3.2.3 Fluorescence lifetime measurement

The fluorescence lifetimes of Sq3 were measured in the presence or absence of TiO_2 colloids. The experimental data showed that the Sq3 molecules adsorbed on the TiO_2 surface had a significantly shorter excited singlet lifetime than Sq3 without TiO_2 colloids in solution. Assuming that the observed decrease in the fluorescence lifetime is entirely due to the electron injection process from excited singlet Sq3 to the conduction band of TiO_2, and that the rate constants for other radiative and nonradiative decay processes of Sq3 associated with TiO_2 colloids remain the same as in neat solvent, the

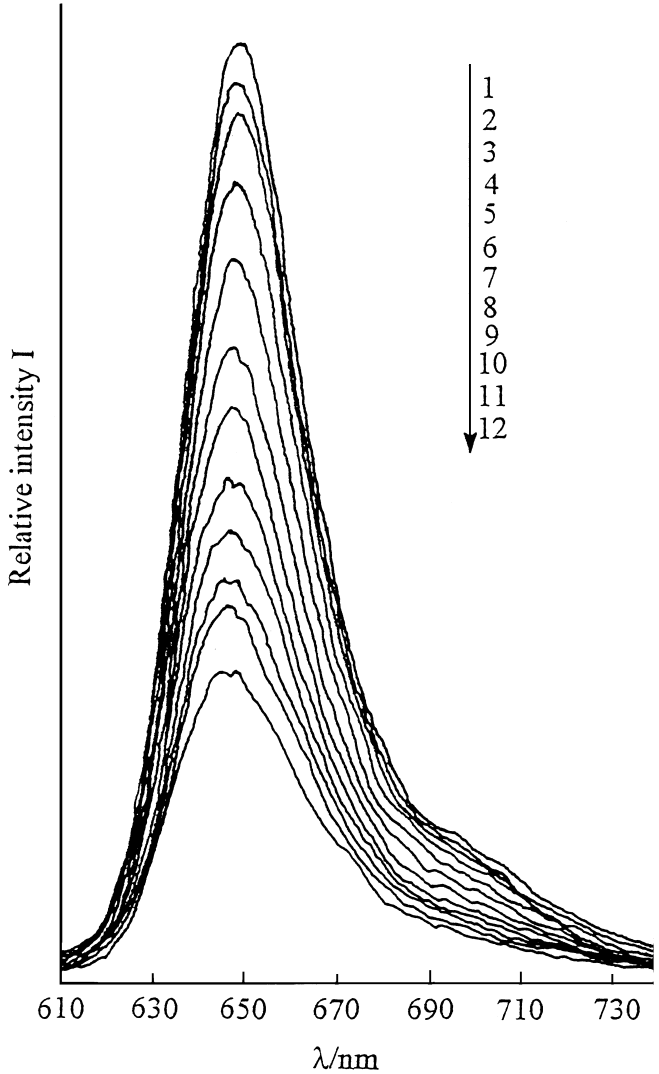

Fig. 3. Fluorescence spectra of 1.0×10^{-6} mol liter^{-1} Sq3 in ethanol at various concentration of TiO_2 ($\lambda_{Ex} = 600$ nm) [TiO_2] (mol liter^{-1}): (1)0; (2)$1.7\times10-5$; (3)3.3×10^{-5}; (4)1.0×10^{-4}; (5)1.7×10^{-4}; (6)2.3×10^{-4}; (7)3.0×10^{-4}; (8)3.7×10^{-4}; (9)4.3×10^{-4}; (10)5.0×10^{-4}; (11)5.7×10^{-4}; (12)7.0×10^{-4}.

observed fluorescence lifetime of Sq3 associated with TiO_2 (τ_{ads}) can be expressed by eqn (3) [9].

$$1/\tau_{\mathrm{ads}} = 1/\tau + K_{\mathrm{et}} \tag{3}$$

where τ is the fluorescence lifetime of Sq3 without TiO_2 colloids in ethanol, and K_{et} is the specific rate constant of the charge injection process.

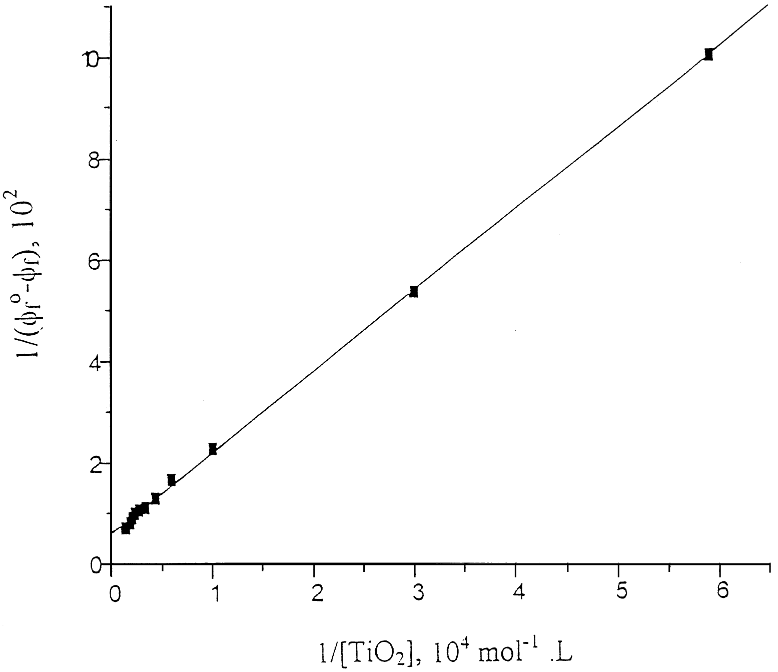

Fig. 4. The dependence of $1/(\phi_f^o - \phi_f)$ on the reciprocal concentration of TiO_2.

Substituting the values of τ (1.22 ns) and τ_{ads} (0.94 ns) into eqn (3), the K_{et} value is $2.4\times10^8\,s^{-1}$.

3.2.4 ESR study on sensitization of Sq3 to TiO_2 nanoparticles

As a convenient and efficient method to detect radical intermediates, spin-trapped electron paramagnetic resonance (ESR) spectroscopic technology has been extensively applied in studying the mechanism of spectral sensitization [10, 11].

The ESR spectrum was recorded after 532 nm laser steady state excitation on the Sq3/TiO_2 solution under N_2-saturated condition, and a strong ESR signal (Fig. 5, curve 1, $g = 1.958$) was observed, which provides direct evidence of an interfacial electron transfer process between Sq3 and TiO_2 nanoparticles (eqn (4)).

$$(TiO_2\text{-----}Sq3(S_o))\xrightarrow{hv}(TiO_2\text{-----}Sq3^*(S_1))\xrightarrow{K_{et}}Sq3^{+\cdot}+TiO_2(e) \qquad (4)$$

A series of reference experiments were carried out to confirm the origin of the ESR signal in curve 1. Sq3 or colloidal TiO_2 alone gave no ESR signal, either without or with, 532 nm laser steady state irradiation (Fig. 5, curve 3,4,5,6). The signal for the Sq3/TiO_2 solution was not observed without

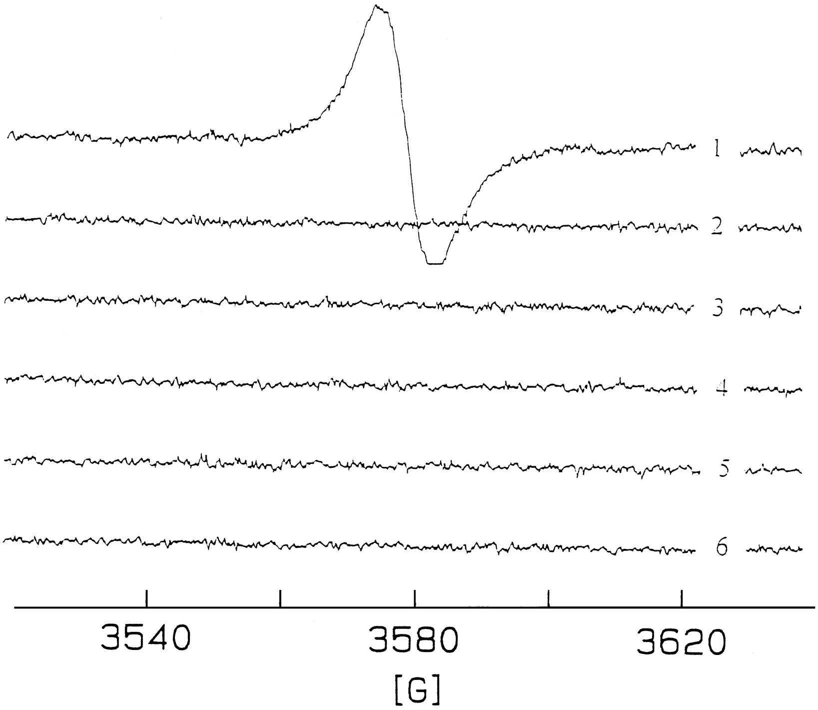

Fig. 5. The ESR spectra for samples of (1) 1.0×10^{-4} mol liter^{-1} Sq3 + 1.0×10^{-2} mol liter^{-1} colloidal TiO_2 in ethanol under 523 nm steady-state laser irradiation; (2) 1.0×10^{-4} mol liter^{-1} Sq3 + 1.0×10^{-2} mol liter^{-1} colloidal TiO_2 in ethanol without irradiation; (3) 1.0×10^{-4} mol liter^{-1} Sq3 in ethanol under 532 nm steady-state laser irradiation; (4)1.0×10^{-4} mol liter^{-1} Sq3 in ethanol without irradiation; (5) 1.0×10^{-2} mol liter^{-1} colloidal TiO_2 in ethanol with irradiation; (6) 1.0×10^{-2} mol liter^{-1} colloidal TiO_2 in ethanol without irradiation.

irradiation (Fig. 5, curve 2). Therefore, the ESR signal in curve 1 can only be attributed to the electron injection process from singlet excited Sq3 to TiO_2 particles, generating two transient components: Sq3 cation radical and surface trapped electron (eqn (4)), both of which, in theory, are paramagnetic centers producing the ESR signal. However, the lifetime of the former is so short (~ps) [12] that it is impossible to detect its signal under steady state ESR measurement; therefore the signal belongs to the latter, which is consistent with the result in the literature [13]. Thus the present ESR data verify the essential process of sensitization.

3.3 Photosensitization of Sq3 on nanocrystalline TiO_2 electrode

To investigate the Sq3-photosensitization on the nanocrystalline TiO_2 electrode, the Sq3-modified nanocrystalline TiO_2 working electrode was incorporated in a thin-layer regenerative solar cell equipped with a Pt/SnO_2

counter electrode and using 0.5 mol liter^{-1} KI-0.05 mol liter^{-1} I_2 in propylene carbonate (PC)-ethylene carbonate (EC) solution (V:V = 2:8) as redox electrolyte for photoelectrochemical measurements.

Figure 6 demonstrates the photocurrent action spectrum of the Sq3-modified nanocrystalline TiO_2 electrode. The incident monochromatic photon-to-photocurrent conversion efficiency (IPCE), defined as the number of electrons injected by the excited dye in the external circuit divided by the number of incident photons, is observed from the short-circuit photocurrents recorded at various excitation wavelengths by means eqn (5) [14]

$$IPCE(\%) = \frac{I_{sc}}{I_{\mathrm{inc}}} \times \frac{1240}{\lambda} \times 100 \tag{5}$$

where I_{sc} is the short-circuit photocurrent (A cm^{-2}), I_{inc} is the incident light intensity (W cm^{-2}) and λ is the excitation wavelength (nm).

As seen in Fig. 6, the Sq3-modified nanocrystalline TiO_2 electrode can extend the photocurrent response of TiO_2 electrode from the UV region below 400 nm into the red visible region above 600 nm. The photocurrent action spectrum of Sq3-modified electrode resembles well the absorption spectrum of Sq3 (Fig. 2), which indicates that the photocurrent is generated by the injection of electrons from the adsorbed excited Sq3 molecules into the conduction band of the large bandgap semiconductor TiO_2. The electrode gives the *IPCE* performance mainly in the 600–700 nm range, with the top value of 6.2% at 650 nm, and an overall photoelectric conversion efficiency up to 2.17%.

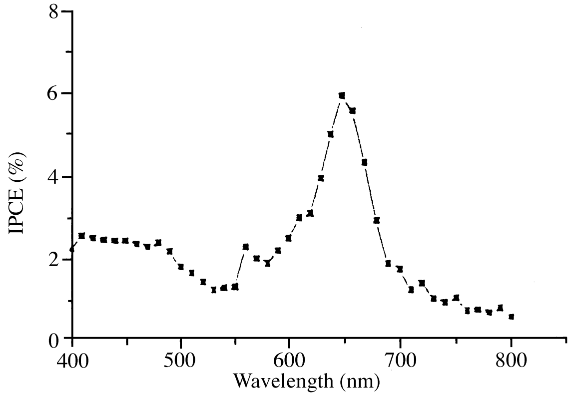

Fig. 6. The photocurrent action spectrum of the Sq3-sensitized nanocrystalline TiO_2 electrode.

4. CONCLUSION

Three squarylium cyanine dyes with different groups on the heterocyclic nitrogen atom were synthesized and their adsorption ability on TiO_2 surface increased in the order Sq3 > Sq2 > Sq1. The photosensitizing property of Sq3, 1,3-bis (N-3-sulfopropyl-3,3-dimethyl-2-methylene indolenine) squarylium cyanine pyridyl salt, was investigated by characterizing the interaction between Sq3 and TiO_2 colloids. The spectroscopic measurements indicated that Sq3 was capable of injecting electrons from its excited singlet states into the conduction band of TiO_2 nanoparticles, while adsorption of the Sq3 dye on the nanocrystalline TiO_2 electrode could convert red visible light above 600 nm into electrical energy. The top *IPCE* value of 6.2% at 650 nm and photoelectric conversion efficiency of 2.17% were obtained.

ACKNOWLEDGEMENTS

The work was supported by the National Natural Science Foundation of China (Projects: 59790050 and 29572072). We are grateful to the research group of Professor Xu-rui Xiao for the photoelectrochemical measurement.

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