J Mater Sci (2007) 42:7678–7683
DOI 10.1007/s10853-007-1650-6

Photochemical behaviors during the photosensitization of colloidal TiO_2 particles by a newly synthesized multidentate squaraine

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Received: 19 January 2007 / Accepted: 1 March 2007 / Published online: 3 June 2007

Abstract A new squaraine dye Bis(4-*N*,*N*-dicarboxymethyl-2-hydroxyphenyl)squaraine (SQ) which could be used as organic photovoltaic materials, was synthesized, and its molecular structure was fully characterized by elemental analysis, IR, ^1H NMR and MS. SQ exhibits strong absorption band over 600–700 nm. Addition of TiO_2 colloids to the ethanol solution of SQ resulted in the increase of optical density, quenching of fluorescence and shortened fluorescence lifetime. The apparent association constant between the sensitizer and semiconductor as measured from the fluorescence quenching data, was 2427 M^{-1}. Fluorescence lifetime measurements gave the rate constant for the electron injection process from the excited singlet of SQ to the conduction band of TiO_2 nanoparticles as 2.55×10^{8} s^{-1}. In addition, SQ doped SiO_2 gel glass slices were prepared and characterized by absorption and emission spectra.

Introduction

Organic photovoltaic materials have been extensively investigated for their potential applications in low-cost, large-area solar cells [1–3]. Dye-sensitized solar cell has received considerable attention since Michael Gratzel et al. [4–9] reported the highly efficient ruthenium-complex sensitized colloidal TiO_2-based dye sensitized solar cell. However, the weak absorption in the red and IR region of the ruthenium bipyridyl complexes (absorption λ_{max}~550 nm) is still a factor restricting the photoelectric conversion efficiency of the cell [10, 11].

In order to search for better sensitizer to improve the photoelectric conversion efficiency of 'Gratzel solar cell', many efforts have been devoted to the design of dyes with strong absorption in > 600 nm spectral range. Recently, organic dyes, e.g. hemicyanines [12, 13], coumarines [14–16], and indolines [17], have been used in the sensitization of semiconductors. In contrast to ruthenium (II) complexes, the merits of organic dyes are obvious for their higher absorption coefficients and lower cost. While, these organic dyes have some disadvantages as photosensitizers. Firstly, some organic dyes (e.g. merocyanines) have relatively sharp absorption bands in the visible region, limiting the light harvesting. Secondly, the lifetime values of their singlet excited states are generally shorter than those of ruthenium bipyridyl complexes, which are not beneficial for ultrafast electron injection to semiconductors. In the latter case, it has been shown that photoactive compounds bearing carboxyl group as the substituent can interact with the TiO_2 surface and facilitate the electron injection to the conduction band of the semiconductor [9, 11].

To develop new organic sensitizers having strong absorption in far-red region, we focus our interest on squaraine dyes. Squaric acid, a photoactive compound with a specific aromatic system, is a neutral but charge-separated molecule that carries two positive charges within the four-member-ring framework. Its derivatives, squaraines, with good thermo stabilities, have strong extinction coefficients in the visible region [18–20]. In order to extend the absorption of sensitizer in visible light, herein, we

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synthesized the dialkylaminophenyl squaraine which had a donor–acceptor–donor (D–A–D) structure. Moreover, four carboxyl substituents were introduced on the squaraine molecule, which was expected to increase the coupling between the organic dye and TiO_2 colloids and lead to ultrafast electron transfer. In this study, we found that the photoelectrochemical parameters of SQ–TiO_2 system were efficiently improved. In order to compare with the sensitization behavior of SQ on TiO_2 nanoparticles surface, we have probed the photochemistry and photophysics of squaraine doped SiO_2 gel glass slices for the first time. The influence of SiO_2 gel network on molecule conformation and the stability of molecule excited state have been discussed.

Experimental

Materials

Suspensions of colloidal TiO_2 were prepared according to Ref. [21]. The SQ doped SiO_2 gel slices were prepared as follow. Tetraethylorthosilicate, ethanol, water and catalytic amount of hydrochloric acid, were mixed at a stoichiometric molar ratio and stirred at room temperature for an hour, then, the ethanol solution of SQ was added and stirred for another 1 h in the pH range 6–7 to afford a transparent gel. The resulting gel was placed in a sealed container and dried for a week at room temperature. After that, the gel slices were heated in an oven below 150 °C for 3 h. Finally, the transparent SQ doped SiO_2 gel slices were obtained. All the solvents were of analytical grade and were purified before use. Figure 1 shows the chemical structure of the compound synthesized. The synthetic route of SQ is shown in Scheme 1.

Squaric acid **a** was prepared from hexachlorobutadiene and morpholine according to Ref. [22] via a one-pot method in the three-step reaction of substitution cyclization (intramolecular ‘2 + 2’ addition) and hydrolysis. SQ was synthesized by condensation of the 3-*N*, *N*-bis(2-carboxymethyl)aminophenol **b** with squaric acid in butanol., while **b** was obtained from the reaction between *m*-aminophenol and chloracetic acid. The target product was characterized by elemental analysis, IR, UV–vis, PL, ^1H NMR and MS.

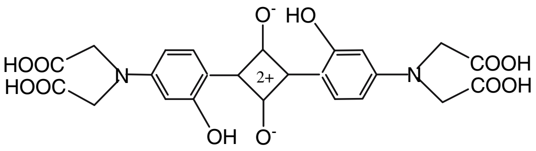


Fig. 1 Chemical structure of the target molecule

SQ: Greenish blue crystal, mp > 330 °C, Yield: 85%, Anal. Calcd (%) for $C_{24}H_{20}N_2O_{12}$: C, 54.54; H, 3.75; N, 5.30. Found (%): C, 54.59; H, 3.72; N, 5.80.υ max: 3600–2500 (br, –COOH and –OH), 1797 (s, C=O), 1623 (s, C=O), 1500, 1460 (s, Ar), 1213, 1159 (s, OCH_2) cm^{-1}. $\lambda_{max}^{EtOH}(\lg\varepsilon)$ 626.6 nm (5.35), $\delta_{^1H}$ (DMSO-d_6, ppm): 12.08 (4H, s, COOH), 11.68 (2H, d, ArOH), 7.90 (2H, d, ArH), 6.25 (4H, m, ArH), 4.08 (8H, m, NCH_2). M/Z (%): 528 (M^+, 20).

Instrumentation

Elemental analysis studies were carried out with a Carlo Erba 1106 elemental analyzer. IR spectra were recorded on a FX-IR 170SX infrared spectrophotometer with KBr pellet. UV–vis spectra were taken on a P-E Lambda 4B ultraviolet spectrometer. Photoluminescence (PL) spectra were measured on a Hitachi 850 fluorescence spectrophotometer. ^1H NMR spectra were recorded on a JNM-FX90G NMR spectrometer in $CDCl_3$. Quantum yields of fluorescence were measured by the relative method using optically dilute solution [23, 24]. MS spectra were recorded on a Finnigan-4510 mass spectrometer. Fluorescence lifetime measurements were performed on a Horiba NAES-1100 fluorescence spectrophotometer.

Results and discussion

Absorption characteristics of SQ

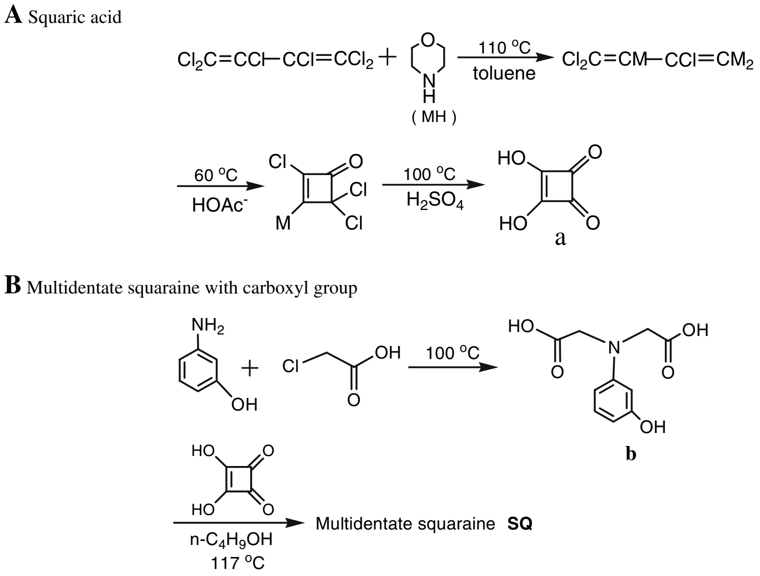
SQ exhibits an intense absorption band in the visible region with a maximum at 620 nm, making it good candidate for sensitization. The relationship between absorption spectra of SQ in ethanol and the concentration of colloidal TiO_2 are shown in Fig. 2. With the addition of TiO_2, the optical density of sensitizer increases, the absorption spectrum is broadened and the maximum is red shifted by about 15 nm. Interaction with the surface hydroxyl groups of colloidal TiO_2 leads to broadening of the absorption bands of SQ (up to $\lambda \approx 670$ nm). These changes indicate that there is an interaction between SQ and TiO_2 colloids with the help of strong anchoring group of carboxyl, which changes the electronic state of SQ.

As reported earlier [25], the protonation equilibria makes that the surface of TiO_2 is polarized (reaction 1 and 2),

$$TiOH_2^+ = TiOH + H^+ \quad pK_a = 4.95 \tag{1}$$

$$TiOH = TiO^- + H^+ \quad pK_a = 7.8 \tag{2}$$

And the point of zero charge $pH_{pzc} = 1/2(4.95 + 7.8) = 6.4$. The pH value of SQ with four carboxylic acid groups must



Scheme 1 Synthetic route of multidentate squaraine

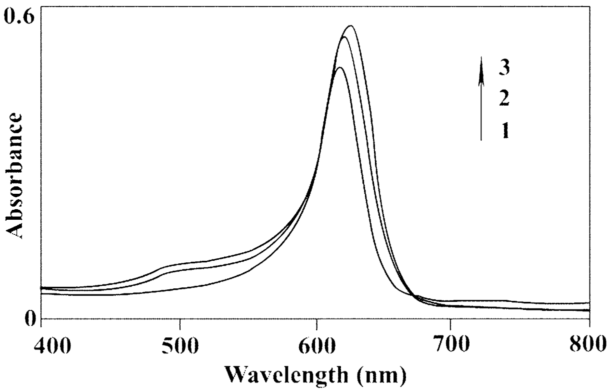


Fig. 2 Absorption spectra of SQ (2.0×10^{-6}mol L^{-1}) in ethanol at various concentrations of TiO_2 (mol L^{-1}): (1) 0, (2) 8×10^{-4}, (3) 2×10^{-3}

be lower than pH_{pzc}. Therefore, the SQ dye, with high polarity, is also easily adsorption onto the TiO_2 colloids due to an electrostatic interaction.

The absorption band in the visible region (635–660 nm), corresponding mainly to the addition of TiO_2, is used to determine the association constant. The apparent association constant determined by the Benesi-Hildebrand method [26] is 2320 M^{-1}.

Fluorescence quenching by colloidal TiO_2

Addition of TiO_2 colloids to the ethanol solution of SQ results in the quenching of its fluorescence emission. Figure 3 shows the effect of the concentration of TiO_2 colloids on the fluorescence emission spectrum of SQ.

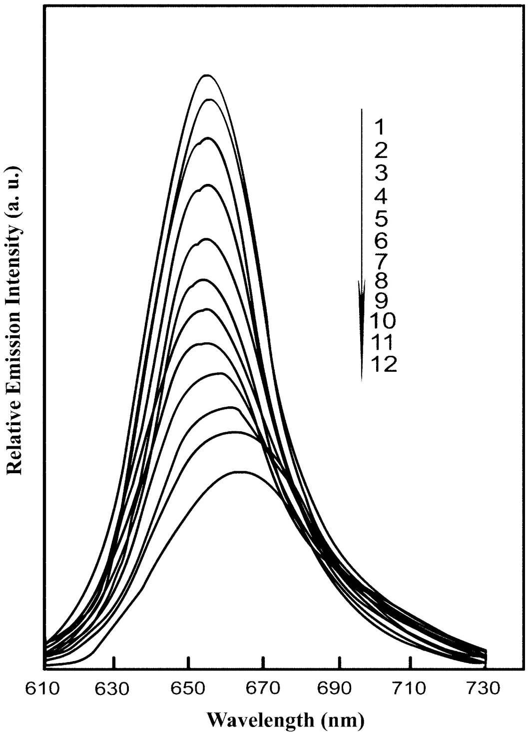


Fig. 3 Fluorescence spectra of SQ (3.0×10^{-6}mol L^{-1}) in ethanol at various concentration of TiO_2 (λ_{Ex} =600 nm) [TiO_2](mol L^{-1}): (1) 0, (2) 2.0×10^{-5}, (3) 3.3×10^{-5}, (4) 1.3×10^{-4}, (5) 2.0×10^{-4}, (6) 2.7×10^{-4}, (7) 3.3×10^{-4}, (8) 4.0×10^{-4}, (9) 4.7×10^{-4}, (10) 5.3×10^{-4}, (11) 6.0×10^{-4}, (12) 6.7×10^{-4}

Nearly 90% of the emission of SQ (3.0×10^{-6}mol L^{-1}) can be quenched when the concentration of TiO_2 is 6.7×10^{-4}mol L^{-1}. This marked quenching behavior is attributed to the strong adsorption of the sensitizer on TiO_2 colloidal particles, which leads to the electron injection from the excited singlet of SQ to the conduction band of semiconductor. The oxidation potential of SQ is around –1.6 V (versus normal hydrogen electrode (NHE)), determined from cyclic voltammetry and the excitation energy, whereas the energy level of the conduction band of TiO_2 is around –0.5 V (versus NHE) [27]. Naturally, this provides favorable energetics for the electron injection process.

The participation of TiO_2 in the quenching process is further analyzed by considering the equilibrium between adsorbed and non-adsorbed molecules of SQ with an apparent association constant of K_{app} (reaction 3).

$$\mathrm{SQ} + \mathrm{TiO_2} \xrightleftharpoons{K_{app}} [\mathrm{SQ} \cdots \mathrm{TiO_2}] \tag{3}$$

As shown earlier, the observed quantum yield (Φ_f) of the sensitizer in a colloidal TiO_2 suspension can be related to the fluorescence yields of non-adsorbed (Φ_f^0) and adsorbed (Φ_f') molecules of the sensitizer by the equation

$$\Phi_f = (1 - \alpha)\Phi_f^0 + \alpha\Phi_f' \tag{4}$$

where α is the degree of association between TiO_2 and SQ. At relatively high TiO_2 concentrations, α can be equated to ($K_{app}[TiO_2]/1 + K_{app}[TiO_2]$). Then Eq. 4 can be simplified to

$$\frac{1}{\Phi_f^0 - \Phi_f} = \frac{1}{\Phi_f^0 - \Phi_f'} + \frac{1}{K_{app}(\Phi_f^0 - \Phi_f')[\mathrm{TiO_2}]} \tag{5}$$

If the observed quenching is due to the association of SQ with TiO_2 colloids, one would expect a linear dependence of $1/(\Phi_f^0 - \Phi_f)$ on the reciprocal concentration of TiO_2 colloids with an intercept equal to $1/(\Phi_f^0 - \Phi_f')$ and a slope equal to $1/(\Phi_f^0 - \Phi_f')K_{app}$. Indeed the linearity of the double reciprocal plot shown in Fig. 4 confirms this behavior. The values of K_{app} and Φ_f' as determined from this plot are 2427 M^{-1} and 0.006, respectively. The well matched value of K_{app} with the value of 2320 M^{-1}, determined independently by the Benesi-Hildebrand method, highlights the validity of the assumption proposed for the association between SQ and TiO_2 colloids.Φ_f^0 is determined to be 0.058 following the relative method and optically dilute solutions. Then, the fluorescence quenching efficiency is $\eta = (\Phi_f^0 - \Phi_f')/\Phi_f^0 = 89.7\%$. The large value of K_{app} indicates a strong interaction between the sensitizer and the semiconductor colloids. And it well supports that the incorporating carboxyl group can lead to a special affinity to adsord onto the surface of TiO_2 colloids and build up suitable electric coupling between the excited state of photosensitizer and the conduction band of semiconductor, which is necessary for observing an efficient electron injection process. Fluorescence Lifetime Measurements To probe the mechanism of fluorescence quenching by the TiO_2 colloids, we further measured the fluorescence lifetime of SQ. It has been shown that the sensitizer molecules adsorption on the TiO_2 surface had a much shorter excited singlet lifetime than that in homogeneous solution, and this decrease in lifetime can be correlated with the charge injection process. The fluorescence decay for SQ in 6.7 × 10^{-4}mol $L^{-1}$$TiO_2$ suspension and the calculated decay curve (fitted to a two-exponential decay) are shown in Fig. 5. The fluorescence lifetimes of the two components of SQ adsorbed on TiO_2 colloid and non-adsorbed SQ in EtOH are 2.03 and 4.20 ns, respectively. The fluorescence lifetime decrease suggests the effective electron injection from SQ attaching carboxyl group to the conduction band of TiO_2 particles.

If we assume the observed decrease in fluorescence lifetime is entirely due to the electron injection process and the other radiative and non-radiative decay processes of SQ

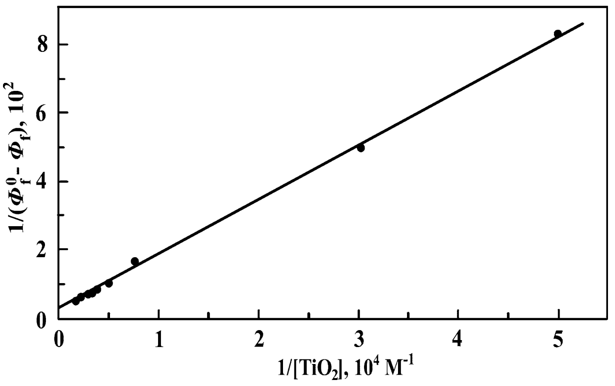


Fig. 4 Dependence of $1/(\Phi_f^0 – \Phi_f)$ on the reciprocal concentration of TiO_2

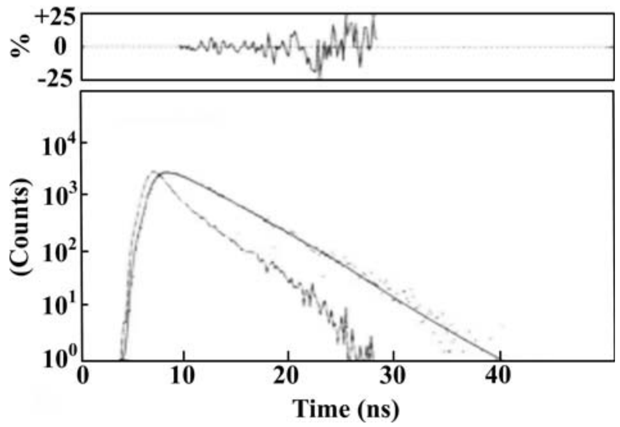


Fig. 5 Fluorescence decay and normalized instrument response curves for a deaerated sample of SQ (3.0 × 10^{-6}mol L^{-1}) in TiO_2 (6.7 × 10^{-4} mol L^{-1})/ethanol suspension, λ_{Ex} = 600 nm, λ_{Em} = 655 nm, T_1 = 2.03 ns, T_2 = 4.20 ns

associated with TiO_2 colloid occur at the same rate as in neat solvent, one can correlate the observed lifetimes by the following expression.

$$1/\tau_{ads} = 1/\tau + k_{et} \quad (6)$$

Where τ and τ_{ads} are the lifetimes of the sensitizer in ethanol and adsorbed on to the TiO_2 surface and k_{et} is the spectific rate of the electron injection process. The value of k_{et} obtained upon substitution of the values of τ 4.20 ns and τ_{ads} 2.03 ns in Eq. 6 is 2.55×10^8 s^{-1}. This is similar to the reported value of quinizarin complexed with TiO_2 clusters [28].The solvent environment and the energetics of the excited sensitizer can affect the rate of the charge injection process.

Absorption and fluorescence spectra of SQ doped SiO_2 gel glass slices

In order to compare with the sensitization behaviors of SQ on TiO_2 nanoparticles surface, SQ doped SiO_2 gel slices were prepared by special sol–gel process and characterized by means of UV and fluorescent spectroscopic technology.

The absorption and emission spectra of SQ–SiO_2 gel slices (Figs. 6, 7 respectively) are very different from those of SQ–TiO_2 system, including peak shape and position as well as emission intensity. The visible absorption peak at 620 nm in ethanol solution (Fig. 2) disappears, however a broad absorption band appeares in ultraviolet region, with a maximum at 230 nm and a shoulder peak around 330 nm. Both of them are gradually intensed and broadened with the increase of the concentration of SQ. And the absorption spectra cover the whole range from 200 nm to 500 nm. The difference between the spectra of SQ in solution and SiO_2 gel slices can be explained by the formation of hydrogen bond and the quantum size localization effect of SiO_2 gel network. In ethanol solution, the squaraine molecules are roughly planar and adopt the *trans* conformation, although slightly intramolecular rotation along the C–C single bond between phenyl rings and the central C_4O_2 unit exists. In contrary, in SiO_2 gel slices, the molecule conformation of SQ is twisted, because of the effects of the limitation of SiO_2 nanometer gel network, strong hydrogen bonding between carboxylic acid groups and SiO_2 and large molecule spacer, which disrupts the whole conjugated plan and leads to the decrease of electron delocalization (π-system decrease), conjugated energy and the increase of transition energy. That may be the reason for the visible absorption peak disappeared and ultraviolet absorption appeared.

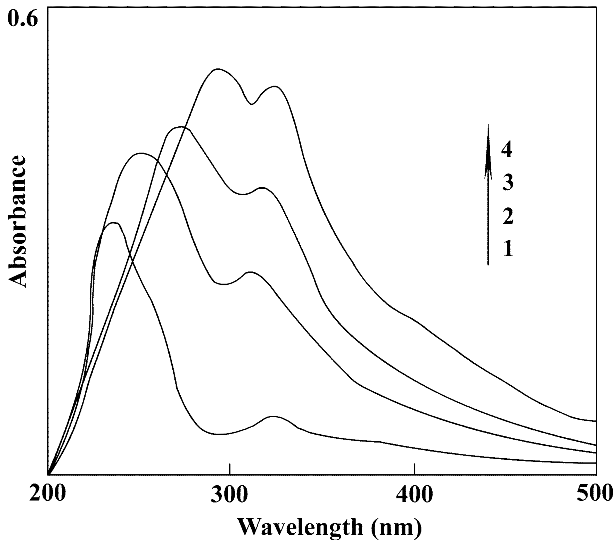


Fig. 6 Absorption spectra of SQ doped SiO_2 gel slices. [SQ] (mol L^{-1}): (1) 1.0×10^{-4}, (2) 2.0×10^{-4}, (3) 3.0×10^{-3}, (4) 4.0×10^{-4}

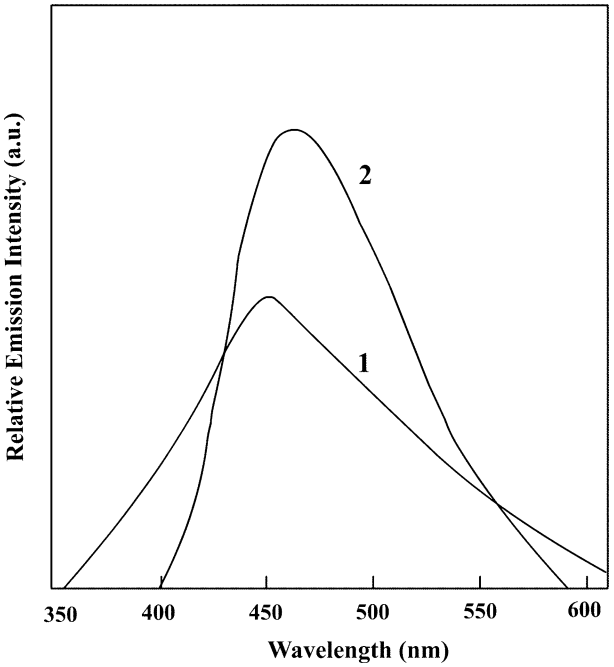


Fig. 7 Fluorescence spectra of SQ doped SiO_2 gel slices: (1) without thermal treatment, (2) after being annealed at 150 °C for 3 h

After SQ–SiO_2 gel slices being annealed at 150 °C for 3 h, the absorption peak is red shifted and intensed with the increase of concentration of SQ. This is similar to the quantum size effect of microcrystallite-doped semiconductor, whose optical absorption edge moves to longer wave lengths with increasing doped ratio [29]. After thermal treatment, the solvents (H_2O, EtOH) are removed from SiO_2 gel network, resulting in enhancement of the rotational freedom of SQ, as well as molecule conjugated plan and conjugated energy. Therefore, the absorption spectrum is red shifted due to the decrease of transition energy.

In ethanol solution, SQ has an emission peak at 655 nm (Fig. 3), while in SiO_2 gel slices, it exhibits a significant broad emission peak (350–600 nm) with a maximum at 440 nm. After being annealed at 150 °C for 3 h, the maximum is red shifted to 460 nm. The fluorescence emission intensity of SQ in SiO_2 network was enhanced up to decades-fold relative to that in solution. Different from that in soft solvent medium, in rigid SiO_2 network structure, the molecule conformation of SQ is intensely distorted, which leads to the enhancement in excited state energy level and the energy gap between ground-state and excited-state. As a result, the emission peak is blue shifted. At the same time, the restriction to the rotation freedom of dye molecule which can consume the excited state energy is beneficial to the stability of excited state molecule. The decreasing rate of non-radiative decay process brings about an increase in the fluorescence quantum yield and fluorescence intensity. That is similar to the fluorescence enhancement of squaraine complexation with β-cyclodextrin [30].As mentioned above, the intrinsic properties of substrate materials can remarkably influence the photochemical and photophysical behaviors.

Conclusion

A new multidentate squaraine dye bearing carboxyl groups was synthesized and successfully used as photosensitizer. SQ exhibits extended absorption into the visible region with the addition of TiO_2 colloids, making it good candidate as the sensitizer of the ‘‘Gratzel solar cell’’. Sensitizer bearing carboxylic acid functions as anchoring groups can more strongly absorb onto the surface of semiconductor. The fluorescence emission of SQ can be efficiently quenched by TiO_2 colloids attributing to the electron injection from the excited singlet of SQ to the conduction band of semiconductor, which are supported by the apparent association constant of K_{app} and the measurement of the fluorescence lifetime. The rigid SiO_2 gel network can make the excited state of SQ molecule more stable, which causes obvious enhancement in fluorescence intensity and quantum yield in comparison with surface active SQ–TiO_2 system.

Acknowledgements This work was supported by the key foundation of education ministry of China (project No. 105142).

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