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Photochromism induced aggregate-monomer interconversion and fluorescence switch of porphyrin with spiropyran

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ABSTRACT: A photo-induced fluorescence switch based on a novel mechanism was provided by physically mixed TPPS (tetra (4-phenylsulfonicacid) porphyrin) and SP (1-(*β*-carboxyethyl)-3, 3-dimethyl-5′-nitrospiro (indoline-2, 2′ [2H-1] benzopyran)). The ground state dipole moment of the open form (photomerocyanine, MC) is much larger than that of SP, thus it can induce the transformation of aggregated TPPS to its monomer, which is confirmed by UV–Vis absorption spectra, RLS spectra, and fluorescence lifetime. While TPPS aggregate has a fluorescence self-quenching phenomenon, its fluorescence was greatly enhanced after the formation of monomer. When the mixture was exposed to visible light, MC decayed back to SP, and consequently, TPPS monomer aggregated again, which resulted in its fluorescence turn off. Copyright © 2007 John Wiley & Sons, Ltd.

KEYWORDS: photochromism; spiropyran; switch

INTRODUCTION

Photochromic spiropyran has attracted tremendous research interests due to its potential application in information data storage and optical switches.[1–5] The basic principle is light-induced switch between its closed and open form, which is attended by changes in electronic properties. Taking advantage of this property, various fluorescence switches were implemented, and the most common mechanism exploited is fluorescence resonance energy transfer (FRET).[6,7] Gust *et al*. have covalently linked a spiropyran compound to a free-base (PH2) porphyrin, which has been an active field of research for several decades because of its involvement in many reactions of chemical and biological interest,[8,9] and found the fluorescence intensity of porphyrin can be controlled by light.[10] The reason is singlet energy transfer from porphyrin to the open form of spiropyran moiety, which results in about 10% quenching of fluorescence emitted by porphyrin.

This paper reports a novel mechanism of fluorescence switch, which is based on physically mixed tetra (4-phenylsulfonicacid)porphyrin (TPPS) and 1-(β-carboxy ethyl)-3, 3-dimethyl-5′-nitrospiro(indoline-2,2′[2H-1] benzopyran) (SP). TPPS is known to easily aggregate, and the polar zwitterionic open form of (photomerocyanine, MC) SP can induce the transformation of aggregated TPPS to its monomer, which resulted in the fluorescence enhancement of TPPS. On the other hand, with the restoration of SP upon visible light, TPPS aggregated again, and fluorescence returned back to its self-quenched state.

EXPERIMENTAL

TPPS were purchased from TCI, and used without further purification. SP was synthesized according to the literature.[11] A 500 W high-pressure mercury lamp was applied during UV irradiation. The UV–Visible absorption spectra were measured using a Perkin Elmer Lambda 35 UV/Vis spectrophotometer with the solution in quartz cuvettes having 1 cm pathlength. The steady-state fluorescence was carried out in a Hitachi F-4500 Fluorospectrometer. RLS spectra were obtained on the same instrument by synchronously scanning the excitation and emission wavelengths. The time resolved fluorescence was measured by a HORIBA NAES-1100 time resolved SpectroFluorometer.

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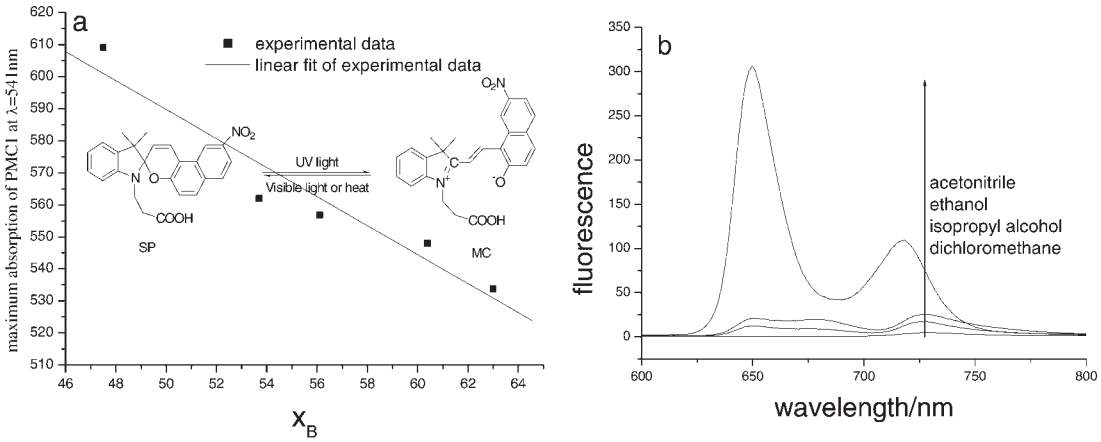

Figure 1. (a) Linear relationship between maximum absorption of MC and Brooker's parameter; inset is the photochromism of SP. (b) Fluorescence emission of TPPS in different polar solvents under the same concentration

RESULTS AND DISCUSSION

The design are based on the following grounds: first, MC shows negative solvatochromism (i.e., there is blue shift when the solvent polarity is increased), and good linear correlation was obtained between maximum absorption of MC and Brooker's parameter (Fig. 1a), implying that the major structure of MC is zwitterionic.[11,12] This leads to the ground state dipole moment of MC increase largely compared with that of SP.[13] Second, TPPS is easy to aggregate, which induces its fluorescence self-quenching.[14] What's most important is that the fluorescence intensity of TPPS is dependent on the solvent polarity, which means the higher the solvent polarity, the stronger the fluorescence intensity of TPPS is (Fig. 1b). The reason is that polar solvent is good for the solubility of water-soluble TPPS. Similarly, it can be anticipated that the formation of much higher polar MC could enhance the solubility of TPPS and consequently suppress the self-quenching phenomenon of TPPS. In addition, when MC converts back to SP, TPPS aggregates again, and the fluorescence should be turned off as a result.

Figure 2 displays the UV–Visible absorption spectra of the mixture in ethanol (the concentration of SP and TPPS were 8.30×10^{-5} and 2.24×10^{-5} mol L^{-1}, respectively) before and after UV irradiation, which is in good consistency with our expectation. The maximum absorption for the closed SP is at $\lambda = 340$ nm, and after 15 s UV irradiation, a new peak centered at $\lambda = 540$ nm appears, which is due to the zwitterionic MC. According to previous studies,[15] the peak centered at $\lambda = 415$ nm was attributed to S-band of molecular dispersed TPPS, and its Q-band is at $\lambda = 700$ nm. Besides that, the characteristic peak for its J-aggregate was detected at $\lambda = 490$ nm. It was obvious that after the formation of MC, the ratio of monomer to aggregate in terms of absorption intensity

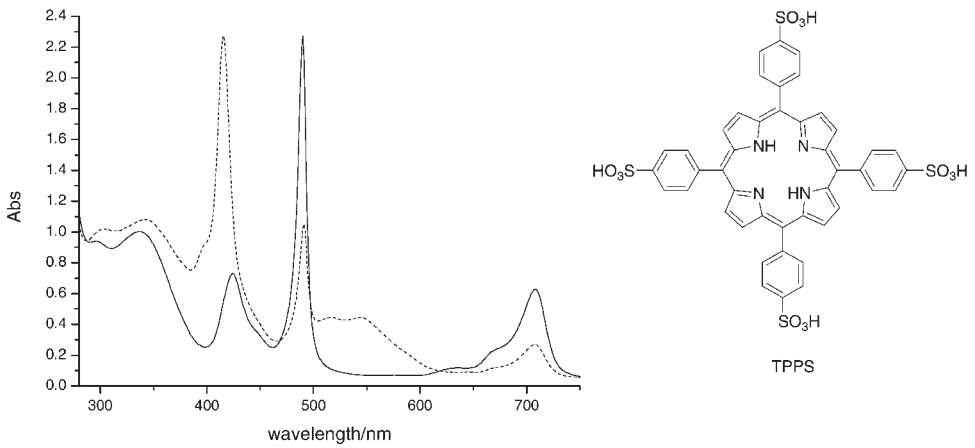

Figure 2. UV–Visible absorption spectra of the mixture before (solid line) and after (dashed line) 15 s UV irradiation, and the molecular structure of TPPS

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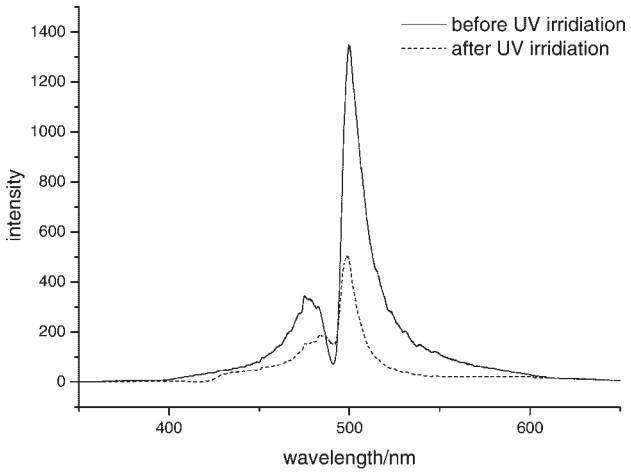

Figure 3. Resonance light scattering spectra of the mixture before (solid line) and after (dashed line) 15 s UV irradiation

Table 1. The fluorescence lifetimes of TPPS in ethanol at different concentrations

Concentration (Mol L^{-1})	τ (ns)	Amplitude
3.23×10^{-6}	$\tau_1 = 1.20$	0.22
	$\tau_2 = 10.8$	0.78
6.47×10^{-6}	$\tau_1 = 3.61$	0.78
	$\tau_2 = 13.7$	0.22
9.70×10^{-6}	$\tau_1 = 3.67$	0.91
	$\tau_2 = 15.4$	0.09
12.9×10^{-6}	$\tau = 4.28$	1

The excitation wavelength is $\lambda = 415$ nm and emission is recorded at $\lambda = 650$ nm.

increased from 0.32 to 2.16, indicating the TPPS conversion from aggregate to monomer.

Resonance light scattering (RLS) results provide further evidence for the above conversion. It is known that RLS revealed the existence of excitonically coupled (delocalized) electronic transition, and thus it is a valuable technique for detecting and characterizing extended aggregates of chromophores.[16–18] Figure 3 shows the RLS spectra of the mixture before and after UV irradiation. The stronger RLS signal at $\lambda = 500$ nm is associated with the J-band, and the weaker RLS intensity at $\lambda = 475$ nm is ascribed to the H-band transitions. In contrast to the large scattering before UV irradiation, the intensity of both the J and H band was reduced to less than half of its original intensity after UV irradiation, which implies that the TPPS molecules transformed to a less aggregated state upon UV irradiation and the corresponding ones were released into the solution.

Aggregate to monomer conversion was also supported by time resolved fluorescence studies. The mixture in the closed form of SP displays biexponential decay, and the major component of the decay (0.79) is the species of short lifetime (3.6 ns). In contrast, when the mixture was irradiated with UV light, the major decay (0.70) is the species of long lifetime (11.2 ns). Though the open form of SP is luminescent, its decay is within ps time region,[10] which cannot be detected under our experimental conditions (the detection limit is 0.2 ns). Thus, the biexponential decay species is from TPPS and is not related to SP. This change is in accordance with the following experimental results. As mentioned above, it is easy for porphyrin to aggregate and increasing concentration means more TPPS in the aggregated state. As can be seen in Table 1, with the increase of concentration, the shorter lifetime species gradually dominates. Therefore, the long lifetime one corresponds to the monomer of TPPS, while the short lifetime species is associated with aggregate ones.[15] Accordingly, it is due to disassembling of TPPS aggregate, the lifetime of excited state was prolonged after UV irradiation.

So far, we can conclude with confidence that the MC can induce the monomer formation of TPPS from aggregate as expected. The results of Fig. 4 show the fluorescence spectra of the mixture before and after UV irradiation. Apparently, before UV irradiation, the fluorescence intensity of TPPS is very small due to aggregation-induced fluorescence self-quenching as mentioned above. After UV irradiation, however, the emission at $\lambda = 650$ nm is enhanced as large as more than three times. Furthermore, when the mixture was irradiated by visible light, the emission intensity came back to that before UV irradiation. In addition, the fluorescence change (70%) is much larger than the one reported by Gust (10%). Thus, this behavior can be applied as a fluorescence switch.

Concentration effect was further investigated to gain more insight into the system. When the concentration of TPPS was less than a certain value (1.00×10^{-5} mol L^{-1}), TPPS were molecularly dispersed even at SP form. On the

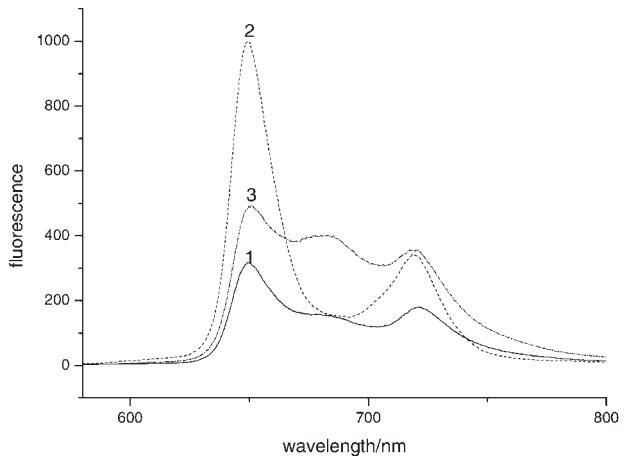

Figure 4. Emission spectra of the SP and TPPS mixture before (line 1), after 15 s UV irradiation (line 2), and then after 15 s visible light irradiation (line 3). All samples were excited at $\lambda = 415$ nm

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other hand, when it was larger than 1.00×10^{-4} mol L^{-1}, the transformation between MC and SP was largely suppressed with increasing TPPS concentration. Thus, 8.30×10^{-5} mol L^{-1} is an optimized value, wherein the transformation is efficient between aggregate and monomer, that is, the fluorescence change is the largest. Considering that the concentration for SP (8.30×10^{-5} mol L^{-1}) is nearly three times higher than that for TPPS, SP can be regarded as a solvent. Consequently, the interaction between MC and TPPS is similar to the interaction between a solvent and its solute, which is essentially responsible for the MC-induced transformation between monomer and aggregate.

CONCLUSION

In summary, a fluorescence switch was elaborately designed and realized in the mixture of TPPS and SP, and the working principle is interconversion of TPPS between aggregate and monomer, induced by the photochromic reaction of SP and MC. It is a novel mechanism which is different from the one reported by Gust. What's more, the fluorescence change (70%) is much larger than the one reported by Gust (10%).

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