Structure and solvent effect on the photostability of indolenine cyanine dyes

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Abstract

The structure and solvent effect on the photostability of a series of indolenine cyanine dyes have been investigated. It was found that the photostability did not increase with the increase of the central conjugated chain length and/or substituent groups on the heterocyclic ring. Using UV spectra data, we have found that the photostability of indolenine cyanine dyes in solution increased with increase of the $E_T(30)$ values of solvents. The rate of singlet oxygen formation, and β values in different solvents sensitized by the dye alone were measured using fluorescence spectra. Absolute photooxidation rate constants (k_r) are calculated, based on the determined β values and the decay rate of singlet oxygen (k_d). All these results well agreed with those obtained from UV spectra. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Solvent effect; Photostability; Cyanine dyes; Structure effect; Photooxidation

1. Introduction

In recent years, the emphasis in dye and pigment industry has shifted from traditional dyes and pigments to functional dyes for electro-optical applications [1–6]. Cyanine dyes, which were previously used as spectral sensitizer in photographic emulsions [7], are now of interest as photo-initiators in photo-polymerization [8] and potential sensitizers for photo dynamic therapy [9].

Indolenine cyanine dyes with different chain lengths of the central conjugated methine chain, are attractive mainly due to their ability to absorb light strongly from the blue to the near-infrared region [10]. Compared with other cyanine dyes, indolenine cyanine dyes have high solubility in solvents and have good thermal stability. Such properties could therefore be used as optical information recording materials. In the production process of optical discs, i.e. compact disc-recordable (CD-R) and digital versatile disc-recordable (DVD-R), dyes are usually deposited into a polymer substrate by a spin coating method. However, like any other cyanine dyes, indolenine cyanine dyes are prone to photophading in solution, though at a relatively slow rate [11–14]. Young [15] have reported that there are solvent effects on the photostability of dyes in dye-sensitized photooxidation reactions, and in addition, the photostability of cyanine dyes is strongly dependent on

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their chemical structure. To evaluate in appropriate solvent for the spin-coating of indolenine cyanine dyes and select materials suitable for optical recording media, both structure and solvent effect on the photostability of cyanine dyes are studied.

2. Experimental

2.1. Materials

All the solvents were of analytical grade and used without further purification. Cyanine dyes were obtained from Dr. T. Okazaki and M. Hayami of Japanese Research Institute for Photosensitizing Dyes, which we acknowledge with thanks. The chemical structure, together with their maximum absorption wavelengths (λ_{max}) of the cyanine dyes, are shown in Table 1. DPBF (1,3-diphenyl-isobenzofuran) was purchased from Acros and methylene blue was from Beijing Chemical Company, both of them are used as received.

2.2. Photophading of dyes

The accepted equation for dye-sensitized photooxidation reaction is a first-order reaction, viz., $D + {}^1O_2 \rightarrow DO_2$. Irradiation for the photooxidation of dyes was with a 500-W tungsten lamp and a cut-off filter was used which passed only light with wavelength longer than 400 nm. The oxidation rates of D-1 ~D-5 in acetonitrile and D-1 in different solvents were followed by monitoring the decrease in the absorption spectra on a Hitachi U-300 spectrophotometer. Solvents with values of $E_{T(30)}$ from 39.1 to 51.9 were selected to study the solvent effect on the photophading rate of the dyes.

2.3. Solvent effect on the rate of singlet oxygen formation sensitized by D-1

One-milliliter solutions of 10^{-5} mol/L 1,3-diphenylisobenzofuran (DPBF) and 9 ml of 10^{-4} mol/liter solutions of D-1 were mixed and part of them were then put into a spectro-fluorometric cell; DPBF was used as a standard compound for quenching ${}^1O_2$. The disappearance rate of DPBF (excitation 410 nm, emission 455 nm) was monitored by the decrease in the fluorescence intensity of it on a Hitachi F-4500 spectro-photometer every 2 min. Good first-order plots were obtained. Irradiation for the photooxidation in this experiment was with a 40-W lamp. During the irradiation period, the solution was bubbled with O_2. The distances between the lamp and samples was 2 meters.

2.4. Solvent effect on the β values and the rate constants for reaction of singlet oxygen with D-1

The experiments for the determination of the β values were similar to those of the rate constant of singlet oxygen formation in different solvents, the D-1 solution were replaced with a 10^{-5} mol/liter methylene blue (as photo-sensitizer) solution and a mixed solution of D-1 (10^{-4} mol/liter) and methylene blue (10^{-5} mol/liter). In both cases, the DPBF were used as standard compound to capture singlet oxygen (${}^1O_2$). The formation and quenching of singlet oxygen in these processes are outlined in Scheme 1 [15] where k_s and k_r are the rate constants of ${}^1O_2$ with DPBF and D respectively. K_d is the decay rate constant of singlet oxygen. Therefore, Stern–Volmer quenching plots were obtained for D-1 in each solvent. An inverse of the slope of these plots gave the β value directly.

Based on Scheme 1, the rate of photo-oxidation reaction at low concentration can be given by the following equation: $d[D]/dt = k_f \cdot k_r[D]/k_d$, where k_f is the rate of formation rate of singlet oxygen. As $k_d/k_r = \beta$, and β values can be obtained for D-1 in various solvent from the slope of first-order plots the absolute rate constant, k_r, are then obtained by dividing these values into the decay rate constant of singlet oxygen.
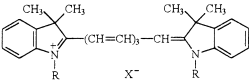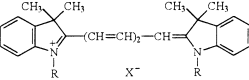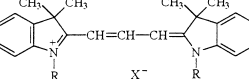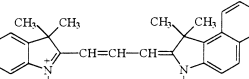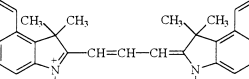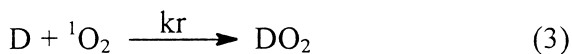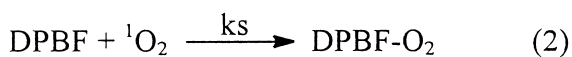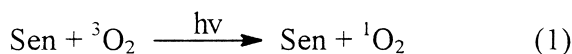
3. Results and discussion

3.1. Photophading of dyes in acetonitrile

According to the photooxidation mechanism of dye, the rate of photooxidation can be expressed as:

$$-d[D]0/dt = k_r[D][{}^1O_2].$$

Table 1
Structure of the indolenine cyanine dyes and λ_{max} in methanol

Abbreviation	Structure	λ_{max} (nm)
D-1		741
D-2		637
D-3		546
D-4		566
D-5		586

$$\text{Sen} + {}^3\text{O}_2 \xrightarrow{\text{hv}} \text{Sen} + {}^1\text{O}_2 \qquad (1)$$

$$\text{DPBF} + {}^1\text{O}_2 \xrightarrow{\text{ks}} \text{DPBF-O}_2 \qquad (2)$$

$$\text{D} + {}^1\text{O}_2 \xrightarrow{\text{kr}} \text{DO}_2 \qquad (3)$$

$${}^1\text{O}_2 \xrightarrow{\text{kd}} {}^3\text{O}_2 \qquad (4)$$

Scheme 1. The processes of formation and quenching of singlet oxygen.

When $[{}^1\text{O}_2]$ is constant, the following equation can be obtained:

In $[D]_0/[D]_t = Kt$, where $K = k_r[{}^1\text{O}_2]$.

The photophading rate constant (K) of the dyes can be obtained from the slope of the Stern–Volmer quenching plots. Fig. 1 shows the photostability of solutions of dyes having different chemical structures.
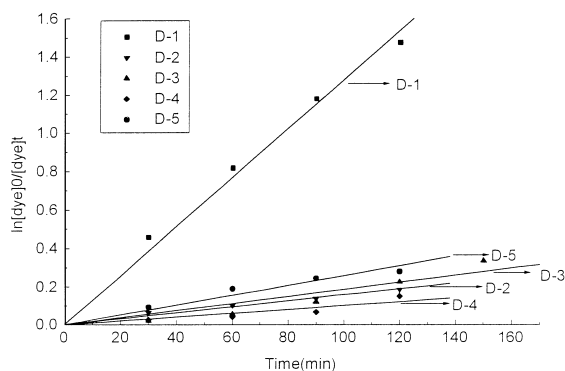

Fig. 1. Effect of chemical structure on the lightfastness of dyes in acetonitrile solutions.

The linear relationship between $\ln [D]_0/[D]_t$ and t indicates they are all first-order kinetic reactions. The slope of these plots indicate the photophading rate constant of D-1 is much larger than that of

the others; this is because it has a longer central conjugated chain length. When the methine chain length is lower, the photostability of the dyes greatly increased. However, as the methine chain length was further decreased, the photostability of the dyes did not increase very much, but tended to be constant. This may be due to the increasing difficulty for the attack of $^1O_2$ to the methine chain, tending to be constant when the methine length decreased to a certain degree. In addition, the substitutant groups do not have affect much on influence the electronic structure and the methine chain length of the dyes, and hence on the photostability of the dyes.

The photo-quenching rate constant (K) of D-1 in solvents with various $E_T(30)$ values are recorded in Table 2. We can concluded from Table 2 that the photostability increases with the increasing $E_T(30)$ of the solvents. To further understand the solvent effect on the photostability of dyes, the following results are reported.

3.2. Solvent effect on β value and absolute photo-oxidation rate constant

First of all, the formation rate of singlet oxygen in different solvent, should be varied from each other. Fig. 2 shows the decrease of fluorescence intensity of DPBF, which corresponds with the formation rate of singlet oxygen sensitized by D-1. The formation rate constants were also collected in Table 2.

The values were determined by the method proposed by Young et al. [15]. In order to get simplified first-order kinetics, a very low concentration of

the standard compound (DPBF) for quenching the singlet oxygen was used. Thus, a typical Stern–Volmer relationship results in: $S_0/S_D = 1 + (k_d/k_r)[D]$, and a Stern–Volmer plot of S_0/S_D vs $[D]$ results in a slope of $k_d/k_r = \beta$. The life-time of singlet oxygen in a specific media is constant, so the absolute photo-reaction rate constant can be calculated from the obtained β values in various solvents. The β values and the absolute photooxidation rate constant for D-1 in a series of solvents are reported in Table 2.

From Table 2, the following results can be easily concluded.

1. the decay rate of singlet oxygen increased with the increase of the $E_T(30)$ values of the solvents, in the mean time, the formation rate of singlet oxygen decreased;
2. as the $E_T(30)$ values of solvents increased, the values and the absolute photooxidation rate constant increased. Each of these factors can result in a higher photostability of dyes in a solvent with higher $E_T(30)$ values, as shown by the K values in Table 2. There is an excellent relationship between the increasing of $E_T(30)$ values of solvent and the decreasing rate of the photooxidation reaction for D-1 in all solvents studied. Also, as expected, the faster the rate of reaction (the larger the rate constant) of dyes with singlet oxygen, the smaller is the solvent effect. The solvent effect changes from a relative small ratio of 217:167 for D-1 in chloroform and acetonitrile with change of $E_T(30)$ value of 6.5, to 167:10.3 for D-1 in acetonitrile and alcohol with change of $E_T(30)$ value of 6.3.

Table 2
β values and some rate constants in a series of solvents with various $E_T(30)$ values

Solvents	Chloroform	Acetonitrile	Alcohol	Diacetone alcohol
$E_T(30)$	39.1	45.6	51.9	–
$k_d \times 10^{-4}\,s^{-1}$)	1.7[a]	3.3[a]	8.3[a]	–
k_f (liter/mol s)[b]	a[b]	11.7	4.0	0.68
K ($\times 10^{-6}\,s^{-1}$)	217	167	10.3	2.5
β ($\times 10^5$)	–	3.84	12.7	29.0
k_r ($\times 10^{-8}$ liter/mols)	–	8.59	6.53	

[a] Ref. [16].
[b] The fluorescence intensity of DPBF decreased so fast that we could not get a good relationship between $\ln[F]_0/[F]_t$ and t to calculate the k_f.
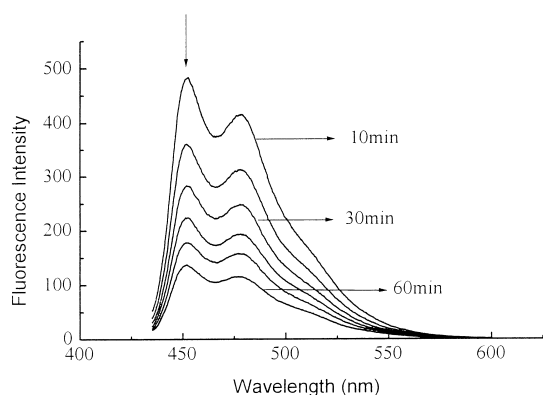
Fig. 2. The decrease of fluorescence intensity of DPBF in acetonitrile, containing D-1 as sensitizer.

Since the $E_T(30)$ value and k_d of diacetone alcohol have not been determined at present, the absolute reaction rate constant (k_r) cannot be calculated and compared with that in other solvents. Nevertheless, from the results that D-1 exhibits highest stability in diacetone alcohol, we can tentatively assume that the $E_T(30)$ value of diacetone alcohol is a little higher than that of alcohol. In addition, the solubility of the indolenine cyanine dyes in diacetone alcohol is higher than any other solvents studied here. All these properties indicates that diacetone alcohol is a good solvent for the preparation of dye media films by the spin coating method.

4. Conclusions

The photostability of indolenine cyanine dyes increased with the decrease of its polymethine length when it is longer than di-methine dyes. Substituents on the terminal cyclic ring do not have much affect on the photostability of the dyes. The photostability of the dyes in solution can be much affected by the polarity of the solvents. The larger the $E_T(30)$ of the solvents, the smaller is the absolute photo-oxidation reaction rate (k_r) and the formation rate of singlet oxygen (k_f).

Acknowledgements

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