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Synthesis and Photostability of Functional Squarylium Dyes

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ABSTRACT

Various symmetrical and unsymmetrical squarylium dyes have been synthesized and characterized with the aid of IR spectroscopy and solvatochromism. The photofading of squarylium dyes has been investigated in solution and in polyvinylbutyral (PVB) film with carbon arc Fade-Ometer. The photostability of squarylium dyes increases with the electron-withdrawing power of substituent groups at the indoline moiety. The rates of photofading of these dyes were remarkably suppressed in the presence of hydroxycarboxylic acid metal salt, while the addition of UV-absorber afforded little retardation of the rate of fading. © 1997 Elsevier Science Ltd

Keywords: squarylium dyes, photofading, functional dye, solvatochromism, organic photoreceptor, squaric acid.

INTRODUCTION

The synthesis of squarylium dyes is simple and has been reviewed several times in the literature [1, 2]. Because of the unique properties of squarylium dyes, many efforts to modify their chemical structure has been reported. Structural modification of squarylium dyes have been an active area of research since these dyes were found to be useful for xerographic application [3] and optical recording [4]. This class of cyanine dyes exhibit a sharp absorption with high extinction coefficient in solution in the red and near IR region (600–750 nm).

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Squarylium dyes are generally prepared by condensing one equivalent of squaric acid with two equivalents of various types of electron donating carbo cycles and heterocycles such as azulenes, [5] pyrroles [6], or heterocyclic methylene bases [7] in an azeotropic solvent.

Despite the relatively wide range of squarylium dyes now known, no electron withdrawing substituted dyes which exhibit a high light fatigue resistance have yet been reported.

In this paper we report on the synthesis, characteristics and photofading behaviour of some symmetrical and unsymmetrical squarylium dyes.

EXPERIMENTAL

Melting points were determined using an electrothermal IA 900 and are uncorrected. The visible and IR spectra were measured using Shimadzu UV-2100 and Nicolet Magna-IR 500 spectrophotometer, respectively. Elemental analysis were recorded on a Carlo Elba Model 1106 Analyzer.

Materials

Squaric acid was of reagent grade and was used without further purification. 2,3,3-Trimethylindolenine, 2-methylbenzothiazole, N,N-diethyl-m-aminophenol, 4-chlorophenylhydrazine hydrochloride and 3-methyl-2-butanone (Aldrich) were used without further purification. Organic solvents were reagent grade and used after distillation.

Synthesis of squarylium dyes and intermediates

2,3,3-trimethyl-5-chloroindolenine 1b

A mixture of 4-chlorophenylhydrazine hydrochloride (8 g, 44.6 mmol) and 3-methyl-2-butanone (4.6 g, 53.4 mmol) in 46 ml of ethanol containing 4.5 ml of 95% H_2SO_4 was refluxed for 5 h. After reaction, solvent was removed and 60 ml of 5% NaOH was added to the reaction mixture, which was then extracted with ether. The extract was concentrated by rotary evaporation and the resulting oily product collected and used in the next step without further purification. Yield 7.96 g (92.2%); Analysis: C, 66.40; H, 6.80; N, 7.48. $C_{11}H_{12}NCl$ requires: C, 68.22; H, 6.25; N, 7.25%.

2,3,3-trimethyl-5-nitroindolenine 1c

Commercially available 2,3,3-trimethylindolenine (11 g, 69 mmol) was nitrated with H_2SO_4–HNO_3 to give 2,3,3-trimethyl-5-nitroindolenine [8]. Yield 7.63 g (54%); Analysis: C, 63.47; H, 6.47; N, 15.21. $C_{11}H_{12}N_2O_2$ requires: C, 64.68; H, 5.92; N, 13.72%.

N-alkylation of 2,3,3-trimethylindolenine 2 (general method)
2,3,3-Trimethylindolenine (1.2 g 7.54 mmol) and methyl iodide (1.07 g, 7.54 mmol) were refluxed for 7 h in 70 ml of acetonitrile. After reaction, 1,2,3,3-tetramethylindolenium iodide *2a* was obtained in 67.8% yield (1.54 g) by filteration.

1,2,3,3-Tetramethyl-5-chloroindolenium iodide *2b*, 1,2,3,3-tetramethyl-5-nitroindolenium iodide *2c*, 2,3-dimethylbenzothiazolium iodide *10* were obtained using a similar procedure.

Preparation of symmetrical squarylium dyes 4a–4c (general method)
Squaric acid (0.68 g, 6 mmol) and 12 mmol of the methylene base *2a*, *2b* or *2c* were heated under reflux for 3 h in a mixture of 60 ml of n-butanol/benzene (4:1/v:v) containing 3 ml of quinoline. Water was removed azeotropically using a Dean–Stark trap. The reaction mixture was cooled to room temperature. The precipitated crude product were separated by filtration and washed with n-hexane. Yields and physical properties are shown in Table 1.

Preparation of unsymmetrical squarylium dyes 12, 13
Two unsymmetrical squarylium dyes *12*, *13* were prepared from the cyclobutenedione precursor *9* with *10* and *11* using previously described procedures [9]. Yields and physical properties of these unsymmetrical squarylium dyes are shown in Table 1.

Photofading behaviour in solution and in polyvinylbutyral (PVB) film

Solutions of dye (4.5×10^{-6} mol/l) in $CHCl_3$, with (1.5×10^{-6} mol/l) and without additive, were prepared. These solutions (35 ml) were placed in pyrex

TABLE 1
Physical Properties, Elemental Analysis Data for Squarylium Dyes

Dye	*Yield (%)*	*λ_{max} (nm)*	*$\Delta\lambda$ (nm)*	*ε^a ($\times 10^{-5}$)*	*M.p. (°C)*	*Analysis (%) Found/Calc*		
						C	*H*	*N*
4a	61	633	—	3.21	>300	79.03	6.86	6.70
						79.21	6.64	6.60
4b	77	639	+6	5.09	>300	68.26	5.32	5.64
						68.16	5.31	5.67
4c	92	665	+32	3.04	>300	65.03	5.34	9.91
						65.35	5.09	10.81
12	69	648	+15	6.01	285–287	73.24	5.39	6.82
						72.43	5.35	6.76
13	61	637	+4	3.10	218–220	74.59	6.81	6.69
						74.97	6.77	6.73

[a] Measured in $CHCl_3$.

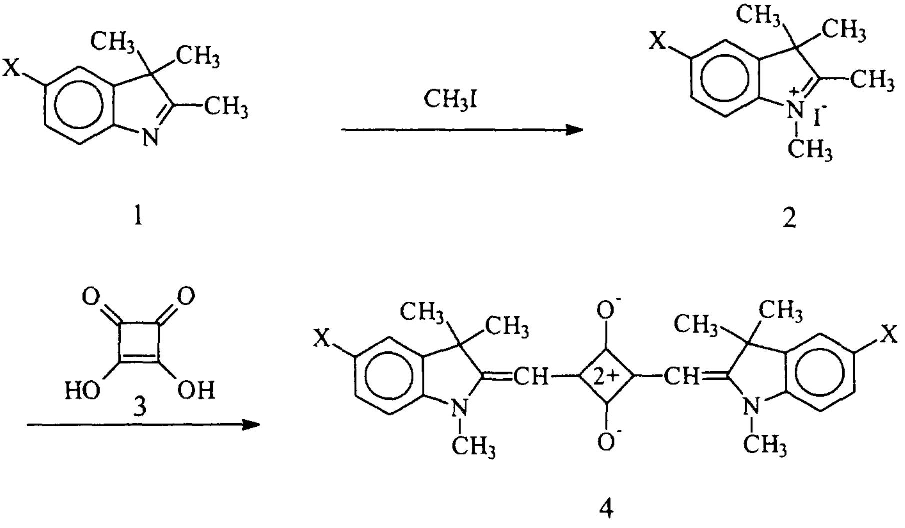
glass tubes. The solutions were then irradiated with a 5 kW carbon arc Fade-Ometer (Shimadzu Fadetester CF-20N). The absorption spectra were measured before and after irradiation and relative % photofading (conversion) determined at the absorption maximum of each of the dyes.

0.1 mmol of the appropriate squarylium dyes were dissolved in a mixture comprising 5 g of polyvinylbutyral (PVB) and 100 g of methylene chloride. The resulting dispersion was cast with a thickness of about 7 μm on a slide glass and dried at 80°C for 5 h. The relative percentage fading was determined as described above.

RESULTS AND DISCUSSION

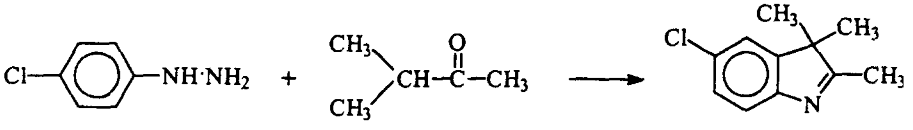
Synthesis and structure elucidation of squarylium dyes

Symmetrical squarylium dyes are normally synthesized by condensation of squaric acid *3* and electron rich aromatic or heteroaromatic compounds. The general procedures to prepare the symmetrical squarylium dyes are shown in Scheme 1. 2,3,3-Trimethyl-5-chloroindolenine *1b* was synthesized from 4-chlorophenyl hydrazine and 3-methyl-2-butanone in 92% yield.



a : X = H
b : X = Cl
c : X = NO_2

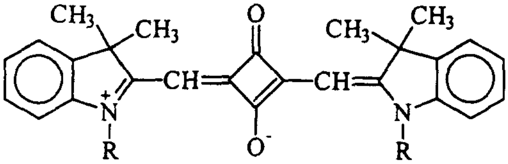
Scheme 1



5 6 1b

2,3,3-Trimethylindolenine *1a* in conc. sulphuric acid was nitrated with mixed acid to give 2,3,3-trimethyl-5-nitroindolenine *1c*. Reaction of *1a* with methyliodide in acetonitrile give *2a*, and similar reaction of *1b* and *1c* with methyliodide gave the corresponding *2a* and *2c*. A mixture of *2a* and squaric acid *3* in n-butanol/benzene (4:1/v:v) containing a small amount of quinoline as catalyst was refluxed for 3 h to give the symmetrical dye *4a*. Dyes *4b* and *4c* were obtained by similar reaction (Scheme 1). Absorption spectra and analysis data are shown in Table 1.

The effect of substituents on the absorption spectra of the squarylium dyes, compared with the parent dye *4a* was evaluated by the $\Delta\lambda$ value. Introduction of an electron-accepting group such as chlorine into dye *4a* produced a 6 nm red shift (dye *4b*). However, substitution by strong electron-accepting group such as nitro produced a large bathochromic shift of 32 nm in dye *4c*. As dyes derived from squaric acid, two different resonance type structure, *4-I* and *4-II*, is possible.



4-I

The IR spectra (Fig. 1) of the squarylium dyes *4a*–*4c* show no $C=O$ stretching at $\sim 1700\,\mathrm{cm}^{-1}$. Instead, strong absorption bands at $\sim 1600\,\mathrm{cm}^{-1}$ are observed and they are attributable to the $C\overset{\cdots}{=}C$ stretching in the four-membered ring and the phenyl ring. The absence of any $C=O$ stretching in a strong indication of extensive bond delocalization in the four-membered ring of the squarylium dye structure *4-I*.

If the dye molecules possess a strong dipole, a polar solvent lowers the energy of the ground state more than that of the excited state, and the solvent thus produces a hypsochromic shift (negative solvatochromism) [10]. Dimroth *et al.* have suggested that the transition energy for pyridinium-N-phenoxide betain dye, expressed in kcal/mol, be used as a polarity parameter [10]. This quantity is referred to as the E_T value. UV–Vis spectral data of the

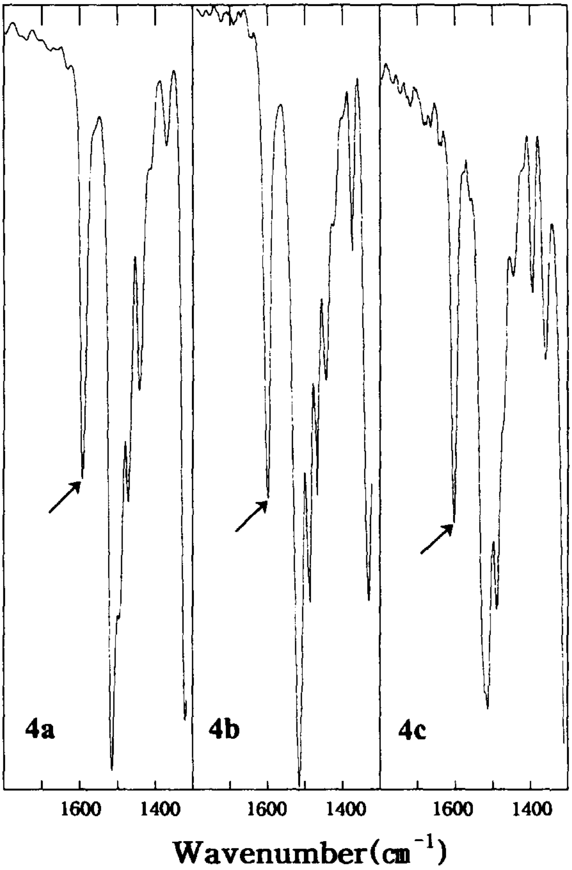


Fig. 1.

squrylium dye *4a* and the E_T value of the solvents used are listed in Table 2. In this present work, reasonably linear plots were obtained on plotting λ_{max} versus the solvent parameter E_T (Fig. 2). As the solvent polarity increased, a hypsochromic shift was observed (i.e, negative solvatochromism). The negative solvatochromism indicated that the structure of the squarylium dye is more polar structure *4-I*.

It is known that reaction of squaric esters with a methylene base leads to mono substituted ester *7*. Compound *7* was reacted with *2a* to give the monosubstituted squaric ester *8*. This ester was hydrolyzed by 40% NaOH and subsequent protonation with HCl afforded the monosubstituted squaric acid *9* [9].

Condensation of *10* and *11* with *9* can be achieved by heating the components in a similar manner described above to give unsymmetrical squarylium dyes *12* and *13*. Reaction procedure and results are summarized in Scheme 2

TABLE 2

λ_{max} of the Squarylium Dye *4a* in Various Solvent and E_T Values

Solvent	$E_T(kcal mol^{-1})$	$\lambda_{max}(nm)$
Methanol	55.4	624
Ethanol	51.9	627
1-Butanol	50.2	630
Acetonitrile	45.6	628
Acetone	42.2	630
Dichloromethane	40.7	633
Chloroform	39.1	632
Tetrahydrofuran	37.4	636
1,4-Dioxane	36.0	635
Benzene	34.3	639

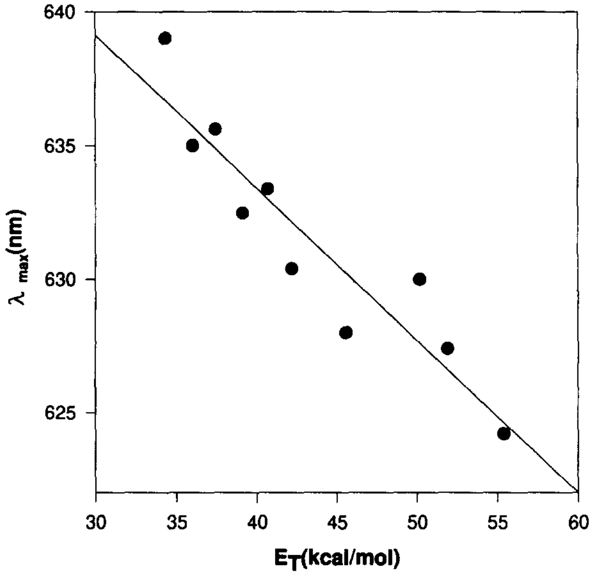
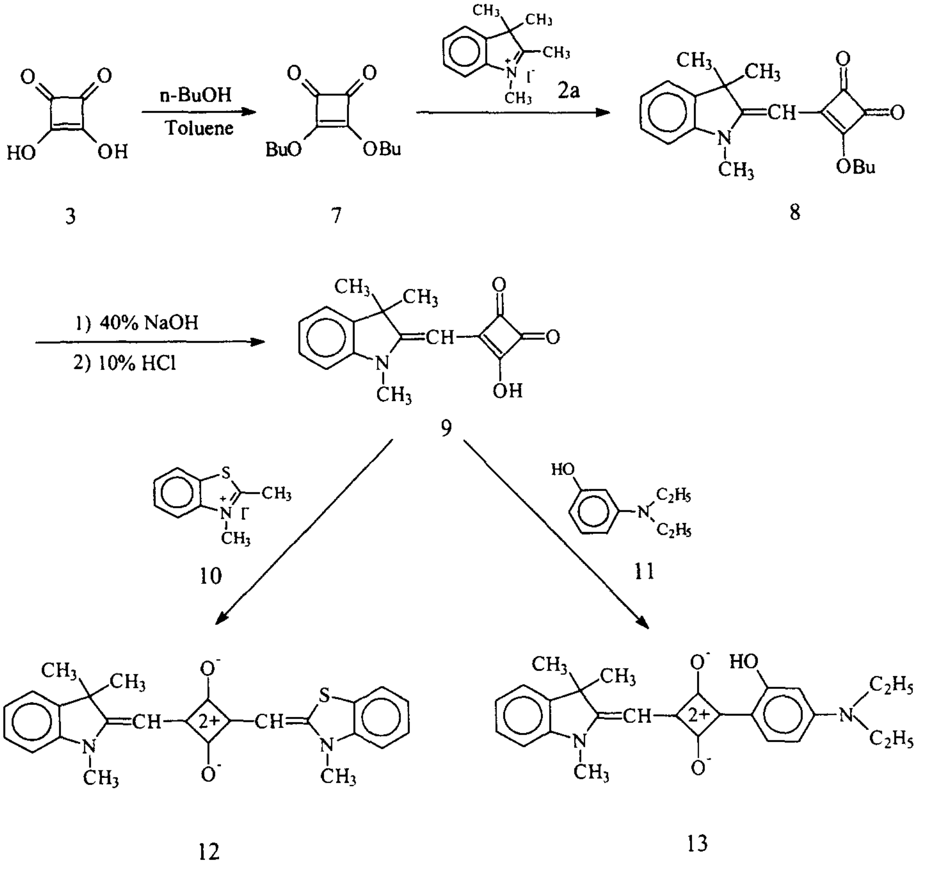


Fig. 2.

and Table 1. Smaller bathochromic shifts of 4 nm and 15 nm were obtained in dyes *12* and *13* compared with the parent dye *4a*.

Photofading of squarylium dyes

Squarylium dyes synthesized by the above procedure are often found to exhibit high dark-conductivity and low charge-acceptance values in xerographic devices [11]. The number of organic materials showing both good photogeneration and good transport properties is limited.



Scheme 2

To improve the characteristics of organic photoreceptors, a multilayer structure was developed in which a thin charge generation layer (CGL) is put into intimate contact with a thicker charge transport layer (CTL). The photogeneration of charge carrier occurs in the thin (about 0.1 ~ 3 μm) CGL layer, comprising the photoconducting materials such as squarylium dyes dispersed in a polymeric binder, usually a polyvinylbutyral (PVB).

The characteristics of dyes *4a–4c*, *12* and *13* with respect to organic photoconductor (OPC) properties are under investigation and will be reported separately. The stability of dyes and pigments to light in both solution and polymeric media encompasses a number of problems of technological interest and importance. The above problems are normally solved by two approaches. The first involves the development of dye structures that are capable of dissipating the absorbed light energy, while the second involves the incorporation of appropriate additives into the dyed (or pigmented) medium.

In this present work, the photofading behavior of squarylium dyes in solution and on a polyvinylbutyral (PVB) film was investigated and the effect of a metal complex is also discussed.

As shown by Fig. 3, a chloroform solution containing squarylium dyes excessively faded on exposure to carbon arc light. The order of photostability is as follows.

$$4c > 4b > 13 > 4a > 12$$

Introduction of an electron accepting groups such as chloro and nitro into the parent dye *4a* afforded considerable protection against fading.

If a similar behavior was also observed in the photofading of these dyes on the PVB film (Fig. 4), the order of photostability becomes:

$$4c > 13 > 4b > 4a > 12$$

Oda and Kitao observed a significant increase in the photostability of colour formers on adding metal carboxylates [12]. The influence of a metal carboxylate on the photofading of dye *4b* in solution was investigated and shown in Fig. 5. A solution of the squarylium dye *4b* faded considerably.

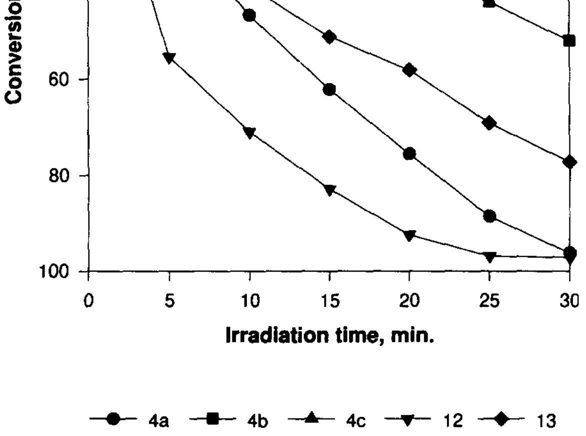


Fig. 3.

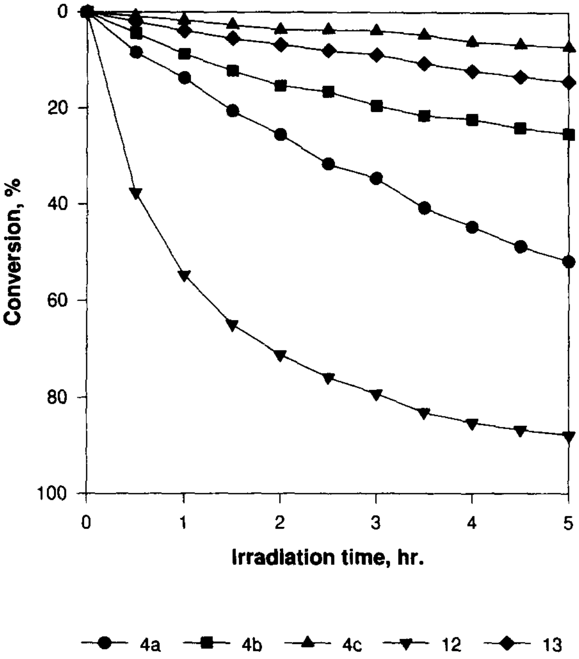

Conversion, %
0
20
40
60
80
100
0
1
2
3
4
5
Irradiation time, hr.
4a
4b
4c
12
13

Fig. 4.

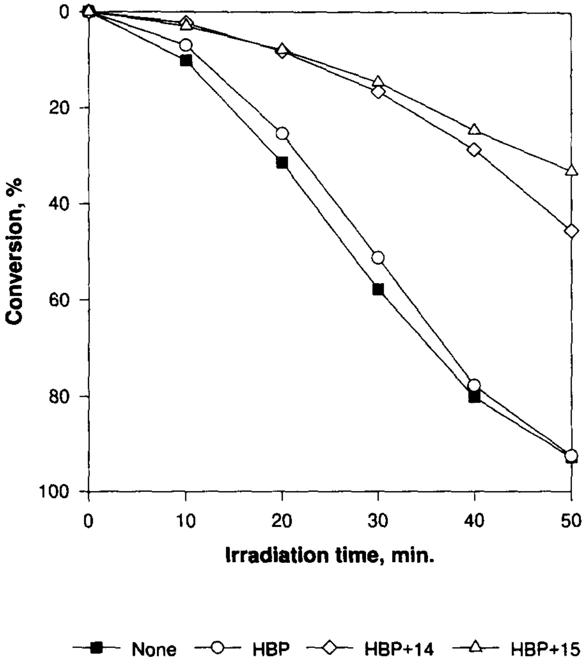
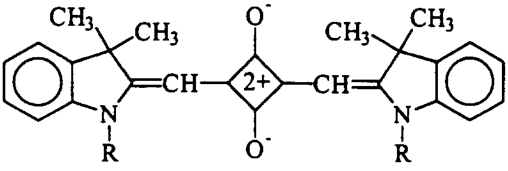

Conversion, %
0
20
40
60
80
100
0
10
20
30
40
50
Irradiation time, min.
None
HBP
HBP+14
HBP+15

Fig. 5.



4-II

Auto-oxidation reaction of dyes is generally evoked by UV radiation and retarded by the addition of a UV absorber such as 2-hydroxy benzophenone (HBP). In the present work, the addition of HBP afforded little protection against the fading of dye *4b*. However, the addition of various metal complex of hydroxy carboxylic acid, i.e. *14*, *15*, on the photofading of dye *4b* together with HBP, considerably retarded the rate of photofading of dye *4c*. This behavior suggests that the addition of a single UV absorber such as HBP is not very beneficial for the protection of the fading of *4b*, but that the combined use of HBP and a metal carboxylate affords a significent suppressing effect on that fading.

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