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Studies on the Synergism of Benzoxazole Fluorescent Whitening Agents*

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ABSTRACT

The fluorescence spectra and fluorescence lifetimes of benzoxazole fluorescent whitening agents (FWAs) in DMF have been measured. The relationship between molecular structure and photophysical properties are discussed. The Dember photovoltages of FWAs adsorbed on a p-type silicon single crystal were also measured. It was found that there exists an interaction between two FWAs compounds; the synergism of the compounds was investigated by a study of energy transfer and charge carrier transfer.

INTRODUCTION

Studies of the synergistic effect between two fluorescent whitening agents (FWAs) are important for the application of these compounds. The synergistic effect is the observable or measurable enhancement of the effect of a combination of substances compared with that of the same amount of individual compounds. Several reports[1,2] on the synergistic effects of FWAs have been published and numerous patent applications have been disclosed and commercial products developed. However, these patents give only the composition of the products having synergistic effects, and they do not give an explanation of the mechanism of the synergistic effects.

The synergistic effects in silver halides emulsion systems, i.e. supersensitization, has been investigated more intensively.[3] The role of the supersensitizer is either to promote the ionization of the Frenkel exciton or to trap the

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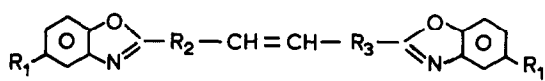
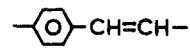
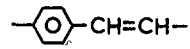
positive hole of the sensitizing dye, with final formation of the positive hole of the supersensitizer. Thus, recombination of a photoelectron injected into the conduction band of silver halide, and of the positive hole of the sensitizer, is prohibited. This has already been demonstrated in our previous investigations.[4] It was found that interaction between dyes is very important for supersensitization. Since the electronic energy levels of FWAs match each other, due to the similar chemical structures of the molecules, the mechanism of the synergistic effect of FWAs could be investigated by observation of energy transfer and charge carrier transfer. In this paper, the fluorescence spectra, lifetimes and Dember photovoltages of FWAs have been measured. The energy transfer and charge carrier transfer occurring in these systems are discussed in order to gain a viewpoint on the mechanism of the synergistic effect of FWAs.

EXPERIMENTAL

Sample preparation

The concentration of FWAs in DMF solution was $2{\cdot}053 \times 10^{-7}$M; this solution was used for measuring fluorescence spectra. Solid layer of FWAs adsorbed on the face (111) of a p-type Si single crystal piece (025 mm, 0·5 mm the thickness) were prepared to measure the Dember photovoltages.



FWAS	R_1	R_2	R_3
F_1	H		
F_2	Me		
F_4	H	–	
F_5	Me	–	
F_6	H	–	
F_7	Me	–	
F_8	Me	–	–

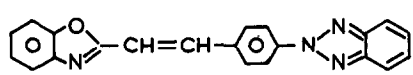
F_3 

Fig. 1. Chemical structures of FWAs used in the study.

Instrumentation

Absorption and fluorescence spectra measurements were made using a Shimadza UV-365 spectrophotometer and a Hitachi 850 fluorimeter, respectively. The fluorescence lifetime was measured by means of a single photon count technique (nanosecond resolved fluoresphotometer Horiba NES-1100). A block diagram of Dember effect measurable instruments has been shown in detail in Ref. 5. The light source (437A Nanopulser) used in the experiments gives a uniform exposure of 0·02 $\mu J/cm^2$ on the sample plane. The sample cell, amplifier and the scope were identical to those used previously.[5] The photovoltage data were stored on tape in a Hewlett-Packard HP 9825 and then transferred to an HP 9872B Plotter and exhibited.

The chemical structures of the fluorescent whitening agents studied in the paper are shown in Fig. 1.

RESULTS AND DISCUSSION

Fluorescence spectra

The fluorescence spectra of the samples are listed in Table 1.

The results show that introduction of a methyl group into the molecule ($R_1 = Me$) makes both the maximum excitation and emission wavelength red shifted and contributes to the increase in the fluorescence quantum yield. As a result, the fluorescence lifetime increases when R_1 is a methyl group.

For different volume ratios of F_1 and F_2 in a DMF solution of equal total concentration ($7{\cdot}587 \times 10^{-6}$ M), fluorescence lifetimes are listed in Table 2.

TABLE 1
Fluorescence Spectral Data of Samples[a]

Samples	λ_{ex}^{max} (*nm*)	λ_{em}^{max} (*nm*)	Φ (%)[a]	τ_f (*ns*)
F_1	379	423·7	79	0·844
F_2	378	436	89	0·994
F_4	384	447	86	0·903
F_5	389	455	87	1·04
F_6	368	432	86	0·806
F_7	371	434	88	0·969

[a] λ_{ex}^{max} and λ_{em}^{max} are the maximum wavelengths of excitation and emission respectively; Φ is the fluorescence quantum yield and τ_f is the fluorescence lifetime.

TABLE 2
Fluorescence Lifetime τ_f

Samples $F_1:F_2$ *by volume*	*5:0*	*4:1*	*3:2*	*2:3*	*1:4*	*0:5*
τ_f (ns)	0·90	0·956	0·942	1·01	0·919	0·914

Note: Excited at 375 nm, monitored at 435 nm.

From these experiments, the fluorescence lifetime of the synergistic system F_1/F_2 decayed by single-component kinetics, and was greater than that of the individual systems. It can be concluded that a synergistic effect takes place for an F1:F2 system, and that an energy transfer process exists between F_1 and F_2. This energy transfer process is attributed mainly between single excited states. The similarity between the electronic energy levels, due to the similar chemical structures, meets the necessary condition of energy transfer.

Dember photovoltage measurements

Under pulsed light exposure, the product of the number and diffusion length of free electrons is unequal to that of the number and diffusion length of free holes. Therefore the net charge-length difference results in a Dember photovoltage. A piece of the p-type Si single crystal used as substrate in the experiments is a 'hole source'. The influence on the diffusion of charge carriers results from the interaction between FWAs. The results are shown in Figs 2 and 3.

Compared with the decay curves of the Dember photovoltage (Figs 2 and 3), it is apparent that the decay of the synergistic systems is faster than that of individual systems, regardless of the light excitation of FWAs. The half-decay times of the photovoltage are listed in Table 3.

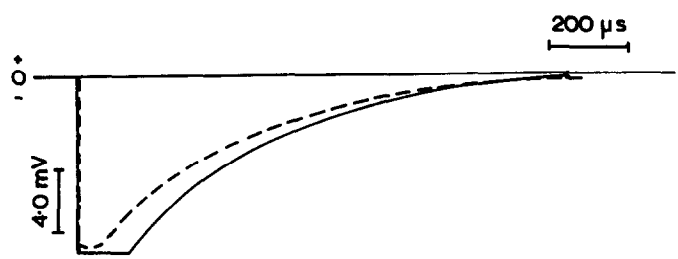


Fig. 2. Dember effect of F_1(a) and $F_1 + F_2$(b) systems with Si facing light (——) (a), ------ (b)).

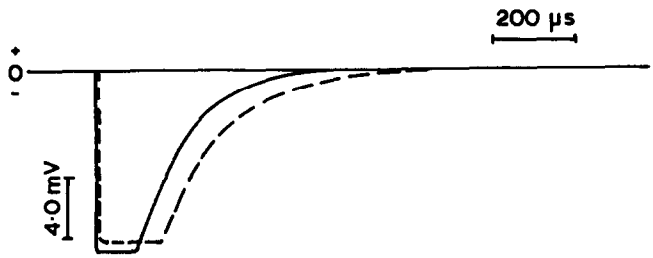


Fig. 3. Dember effect of F_1(a) and $F_1 + F_2$(b) systems with FWAs facing light (—— (a), ------ (b)).

The data listed in Table 3 show that the difference between $\tau_{1/2}$ of a single FWA and of the synergistic FWAs is not apparent when the FWA is facing light, but the difference between the $\tau_{1/2^*}$s is evident when the p-type Si is facing light. Regardless of the condition of exposure, there is a trend that the decay of photovoltage on the synergistic systems is faster than that of individual systems. This implies that there exists an interaction between the FWAs.

The Dember effect of the p-type Si alone is shown in Fig. 4. Compared with Figs 2 and 3, the adsorption of FWAs on the p-type Si results in a negative signal, which can be attributed mainly to the slow diffusion of holes. When the FWAs are facing light, the excitation of the FWAs produces a small amount of electrons, which are able to recombine with the holes from the Si phase.

For synergistic systems, the interaction between two FWAs will produce more electrons, which increases the recombination with holes and makes the decay of the photovoltage more rapid. However this charge is not obvious, due to a large amount of holes in the p-type Si, relative to which the amount of electrons excited in the FWAs is small. Thus, $\Delta\tau\tau_{1/2} = \tau_{1/2}^{F_1+F_n} - \tau_{1/2}^{F_n}$ is small as shown in Table 3.

With the p-type Si facing light, the difference, $\Delta\tau_{1/2^*} = {}^{*F_1+F_n}_{1/2} - \tau^{*}_{1/2^*}{}^{F_n}$ is very apparent. The influence on hole diffusion is clearly demonstrated in these experiments. The synergistic combination of FWAs results in the

TABLE 3
Half-Decay Time of the Photovoltage

Samples	F_1	F_1+F_2	F_4	F_1+F_4	F_5	F_1+F_5	F_6	F_1+F_6	F_7	F_1+F_7	F_8	F_1+F_8
$\tau_{1/2}$ (μs)	68	62	96	96	88	72	58	58	72	70	100	38
$\tau^{1/2}{}_*$ (μs)	246	228	236	234	212	204	190	186	296	244	164	—

Note: $\tau_{1/2}$ for FWAs excited by light; $\tau^{1/2}{}_*$ for Si facing light and FWAs not excited by light.

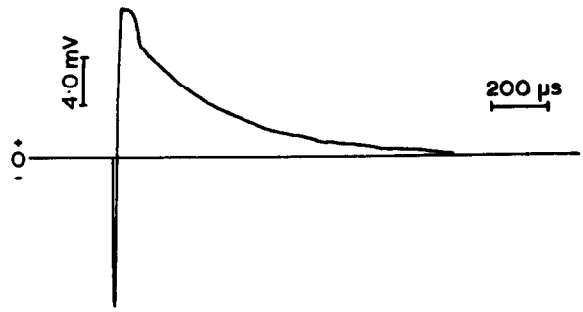


Fig. 4. Dember effect of Si (ρ).

shortening of hole lifetime. An interaction exists between two FWAs, regardless whether there is light excitation or not.

The structure of the F_3 compound is different from the other FWAs. The synergistic combination of F_1 and F_3 gives a different Dember photovoltage, as shown in Fig. 5.

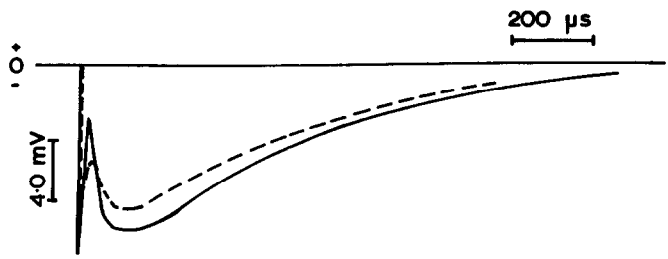


Fig. 5. Dember effect of (a) and F3/Si and (b) $F_1 + F_3$/Si systems with Si facing light (—— (a), - - - - - - (b)).

CONCLUSIONS

Synergism of benzoxazole fluorescent whitening agents (FWAs) has been investigated. Energy transfer between the excited singlet states of the FWAs was observed.

Interaction exists between two FWAs, regardless whether there is light excitation or not. This interaction influences the diffusion of charge carriers in the systems, especially for holes.

The synergistic effect of benzoxazole FWAs takes place mainly by the energy transfer between the FWAs. Charge carrier transfer processes were not evident in the experiments carried out by us.

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