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A new model system for studying excited states of dye aggregates of photographic color paper

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Abstract

As a new model system of dye-containing oil droplet of color paper, the dispersion of dye-containing oil droplet in water was successfully prepared by reprecipitation method, and was used for the analysis of photo-excited states of dyes used for color image formation in silver halide color photography. This model was applied to analysis of photo-excited states of yellow dye aggregates of 1,1-dioxo-1,2,4-benzothiadiazine series. It was found that the lightfastness of the yellow dye of this series is controlled by the degree of aggregation and the lifetime of S_1 state of the aggregate. Based on the finding, we have succeeded in improvement of lightfastness of the dye by sterically hindering the aggregation and reducing the lifetime of the excited state.

Keywords: Dye aggregates; Lightfastness; Organic nanoparticle; Reprecipitation method

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1. Introduction

Silver halide color photographic system is constituted such that silver halide grains acting as a light sensor, and oil droplets comprising image-forming dye precursor (hereafter referred to as "coupler") and high-boiling solvent (alkyl phthalate- or alkyl phosphate derivatives, hereafter referred to as "oil") are together dispersed in gelatin layers (Fig. 1). The silver halide grains (AgX) exposed to blue, green, and red light, respectively oxidize the base compound of a developer, and the oxidized developer reacts with respective couplers to form yellow, magenta (reddish violet), and cyan (blue green) dyes to create a color image [1]. Since the size of the silver halide crystal is several hundred nanometers while the amorphous oil droplet is as small as *ca.* 100 nanometers, the silver halide color photographic system can be regarded as a kind of functional nano-material.

Acylacetanilides, pyrazoline-5-ones, and phenol derivatives have so far been used as yellow coupler, magenta coupler, and cyan coupler, respectively. However, we have coped with the improvement of color reproduction and storage stability of dyes and have succeeded in developing novel skeletons of 1,1-dioxo-1,2,4-benzothiadiazine, 1*H*-pyrazolo[1,5-*b*][1,2,4]triazole, and 1*H*-pyrrolo[1,2-*b*][1,2,4]triazole derivatives as yellow, magenta, and cyan couplers, respectively (Fig. 2). These couplers have been introduced in certain color paper and reversal films which have realized overwhelming differentiation in quality [2].

The greatest issue in introduction of the 1,1-dioxo-1,2,4-benzothiadiazine yellow coupler having the high molar extinction coefficient ε (Scheme 1), excellent color hue and storage stability against heat and humidity of the derived dye was the improvement in lightfastness. That is, there was a problem that while the yellow dye derived from a 1,1-dioxo-1,2,4-

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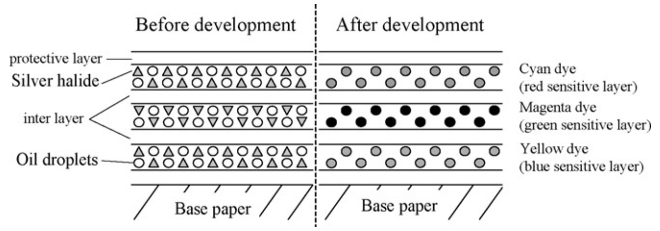


Fig. 1. Schematic illustration of layer composition of photographic color paper. Left figure represents before development and right figure represents after development.

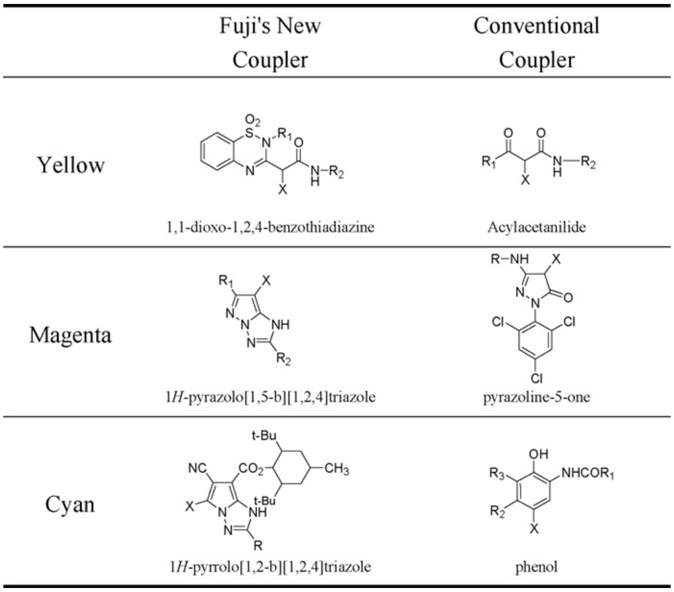
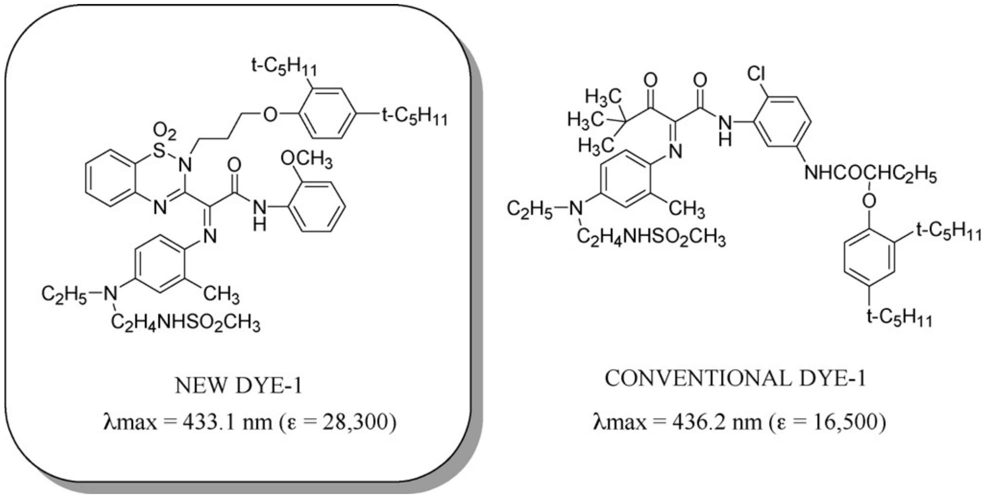


Fig. 2. New- and conventional coupler skeletons of photographic color paper.

benzothiadiazine coupler is as light-resistant as conventional acylacetanilide dyes in a dilute solution (*e.g.* 10^{-5} mol/L), the lightfastness suffers drastic drop in the concentration range corresponding to the oil droplets in color paper (0.5–5 mol/L). Thus elucidation of the controlling factors of fading reaction by analysis of photo-excited state of the highly concentrated dye was indispensable for improvement of lightfastness of the novel yellow dye.

Since the ε of the 1,1-dioxo-1,2,4-benzothiadiazine type yellow dye is 28,000 $\mathrm{cm^{-1}\,M^{-1}}$, the optical density (*e.g.* OD = 1) on spectrometric measurement with the concentration of the color paper (0.5–5 mol/L) should require a cell having the light pass length of 0.1–1 μm, which is by no means realistic. For this reason, the analytical studies made on photo-excited states of highly concentrated system have been very few, and as far as we know, there has been published a few papers, for example, (1) investigation of dependence of light fading reaction on wavelength and light intensity using a film sample wherein a photographic dye and an oil was dispersed in gelatin [3], and (2) preparation of polydiacetylene nanocrystals using reprecipitation method [4] devised as a method to prepare organic nanoparticles, to investigate the size and thermal relaxation process of the nanocrystals [5].

Preparation of the film in the former procedure requires such troublesome processes as emulsification and coating, and also necessitates use of large amounts around 10 g of dye and oil. Thus the method is inappropriate during the developing stage of exploration of the optimal chemical structure which requires a fast cycle of dye preparation and evaluation. So far known preparative methods of organic nanoparticles as have been quoted in the latter paper include reprecipitation, evaporation method in an inert gas [6], and laser ablation [7], as well as sol-gel process based on pH change [8]. Evaporation and laser ablation necessitate such specific devices as a special evaporating apparatus and laser system, and so have the demerit of inapplicability to organic compounds which are unstable under heat and laser light. The sol-gel process utilizing pH change cannot be applied to the dyes of the present study which have no particular dissociating groups. On the other hand, the merits of reprecipitation method are that it needs no special equipment and that it allows easy preparation of nanoparticles even from just a few milligrams of the sample. In addition, there exists an abundance of parameters for size control, which permits reproducible



Scheme 1. Structures of yellow dyes and absorption properties in ethyl acetate.

preparation of the nanoparticles [9]. Therefore we judged that this method is best suited to preparation of the analytical model of this study.

In the present paper, we report successful construction of excellent analytical model of such highly concentrated aggregation system as the oil droplets of color papers by using reprecipitation method [4], and the analytical result of the relationship between structure of the 1,1-dioxo-1,2,4-benzothiadiazine yellow coupler and lightfastness of the derived dye.

2. Experimental

2.1. Samples

The yellow dyes of the 1,1-dioxo-1,2,4-benzothiadiazine series as well as the oils were synthesized according to the process previously reported [10]. The substituents were appropriately varied to examine the substituent effect on lightfastness. Wako special grade acetone was used for preparation of nanoparticles by reprecipitation method, and extra-pure water from the extra-pure water preparing equipment Milli-Q Advantage made by Millipore was used as the poor solvent.

The film sample was prepared by coating the gelatin dispersion of a 1,1-dioxo-1,2,4-benzothiadiazine yellow dye dissolved in an oil on cellulose triacetate base (hereafter referred to as dye-dispersion film). The details were the same as those described in the previously reported paper [3]. The average size of the oil droplets comprising the yellow dye and oil in the dye-dispersion film was *ca*. 100 nm. The dye concentration was varied by varying the ratio of the dye weight to the volume of the oil used. For example, the notation "oil:dye = 2:1" means that 1 g of dye dissolved in 2 mL of oil has been dispersed in gelatin. For information, "oil:dye = 2:1" corresponds to *ca*. 1 mol/L concentration.

2.2. Spectroscopic study

Measurement of the electronic absorption spectrum was conducted by a UVPC-2400 spectrophotometer from Shimadzu. The fluorescence spectrum was measured by a Fluorolog3 type fluorescence spectrophotometer from HORIBA, with adjusting the optical density of the sample to 0.2–0.3 so as to avoid re-absorption and other undesirable influences. The fluorescence intensity was normalized by the number of excited photons. For kinetic study of azomethine dye's excited states, we built a sub-picosecond dynamics measurement system. This system is provided with wavelength-tunable excitation light and the time resolution of our system is 300 fs, and the lower limit of detection is 2×10^{-4} AU. The size of nano-particles was measured by LB-550 dynamic light scattering equipment from HORIBA.

2.3. Preparation of a new model system of dye aggregates

The oil droplet analyzing model was typically prepared through reprecipitation method by the following procedure. Five milligrams of the dye and 5 μL of the oil were dissolved in 10 mL of acetone, a good solvent for these solutes. A 100 μL portion of this solution was injected into 10 mL of vigorously stirred extra-pure water (controlled to 20 degrees centigrade) using a micro-syringe, to give a dispersion of nano-particles comprising the yellow dye and the oil. Examination of the influence of the acetone remaining in the liquid dispersion on absorption- and fluorescent spectra revealed that the presence or absence of acetone had little influence on the spectra, and as a result we did not take any step, such as heating, to eliminate acetone. The details were the same as those described in the previously reported paper [4]. The dye concentration in the nano-particles was adjusted by varying the ratio of the dye weight to the oil volume.

3. Results and discussion

3.1. Verification of the new model system

The dispersion of the nano-particles comprising the dye and the oil prepared by reprecipitation was almost free from influence of light scattering and thus was optically transparent and barely distinguishable from a dilute solution (Fig. 3). The absorption- and fluorescent spectra of the liquid yellow dye dispersions described in Fig. 3(a) are shown in Fig. 4. As has been anticipated from the appearance of the dispersion, no elevation of the baseline of the absorption spectrum due to light scattering was observed.

We could also successfully adjust the optical density of the nano-particle dispersion (hereafter referred to as oil droplet

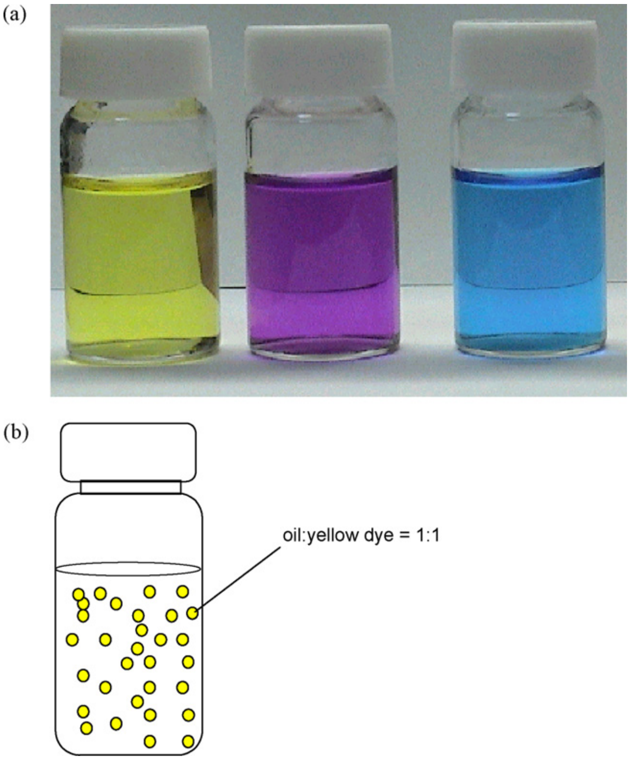


Fig. 3. (a) Photographs of dispersion liquid of the nano-particles comprising the yellow, magenta and cyan dyes and the oil prepared by reprecipitation method. (b) Schematic illustration of dispersion liquid of the nano-particles comprising the yellow dye and the oil.

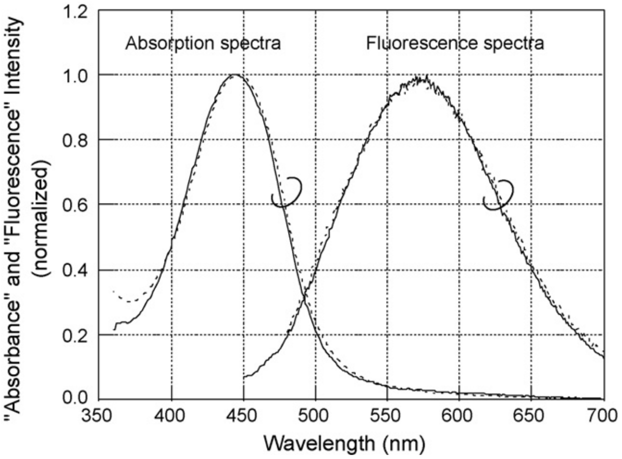


Fig. 4. Absorption- and fluorescence spectra of highly concentrated environment of NEW DYE-1. Solid line: spectra of the oil droplet model, broken line; spectra of dye-dispersed film.

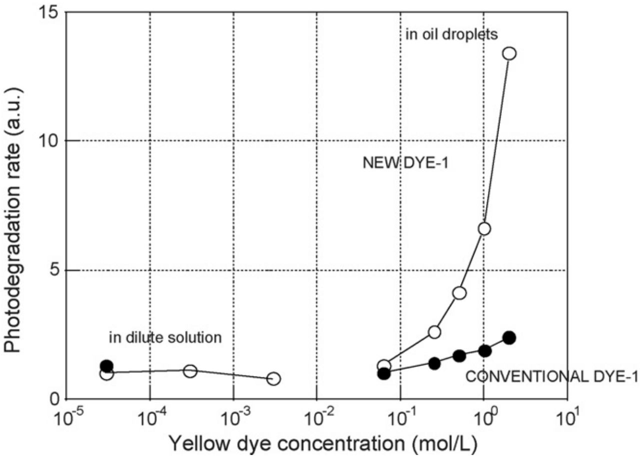


Fig. 5. Concentration dependence of lightfastnes of NEW DYE-1 (closed circle) and CONVENTIONAL DYE-1 (open circle). Structures of these dyes are shown in Scheme 1.

model) within the range of optical density not exceeding 2 in a general purpose cell having 1 cm long optical path, keeping dye concentration in the nano-particles as high as that in the oil droplets of the color paper (0.5–5 mol/L). The dispersion was stable enough to allow various spectrophotometric measurements for more than 1 month without addition of a disperser such as surfactant. By optimizing the preparative conditions, we could attain the particle size of 90 nm (number averaged particle size determined by dynamic light scattering) which was almost the same as that of the droplets in color paper. In addition, since preparation of the oil droplet model by reprecipitation method requires only a small amount of dye, i.e. several milligrams, and only simple operation, this proved to be the best preparative technique of analytical models for evaluation of a variety of dyestuff samples with small amounts, as is exemplified by exploration study of the optimal structure.

Fig. 4 demonstrates the result of measurement of absorption- and fluorescence spectra of high concentration of NEW DYE-1, a 1,1-dioxo-1,2,4-benzothiadiazine yellow dye (oil:dye = 2:1, *ca.* 1 mol/L). The outstanding coincidence of the spectra in an oil droplet model and a dye-dispersion film was a proof of successful preparation of amorphous dye/oil nano-particles in the oil droplet model. Thus, the dispersion of amorphous nano-particles prepared by reprecipitation method was confirmed to be useful as an oil droplet model of color paper.

3.2. *Lightfastness and spectroscopic features*

Fig. 5 shows dependence of the lightfastness of NEW DYE-1 on dye concentration. As is demonstrated, it has the lightfastness equal to or greater than that of conventional acylacetanilide dye (CONVENTIONAL DYE-2) when the concentration is as low as 1×10^{-5} mol/L, while the stability rapidly drops in the region of high concentration corresponding to the practical concentration (0.5–5 mol/L).

Subsequently we examined the concentration dependence of the absorption- and fluorescence spectra of NEW DYE-1 in the oil droplet model and found that both spectra suffered red shift in the practical concentration region where deterioration of light stability had been observed (Fig. 6). The red shift was notable particularly in the fluorescence spectrum, which exhibited some 60 nm shift in practical concentration (oil:dye = 2:1, *ca.* 1 mol/L) with reference to the dilute solution (1×10^{-5} mol/L). The red shift of the fluorescence spectrum corresponding to the increase of dye concentration in the oil droplets suggests influence of dye aggregation and self-absorption. Since we measured the fluorescence spectrum of the liquid dispersion having optical density not higher than 0.2 in order to eliminate the influence of self-absorption, and since the red shifts of dispersions may differ according to the dye structure even if optical density is the same (Fig. 11), we assumed that the main factor causing the red shift should be due to aggregation of the dye, and the extent of red shift could be a measure of aggregation. The shifting is observed only at very high concentration, suggesting week interaction between the dye molecules.

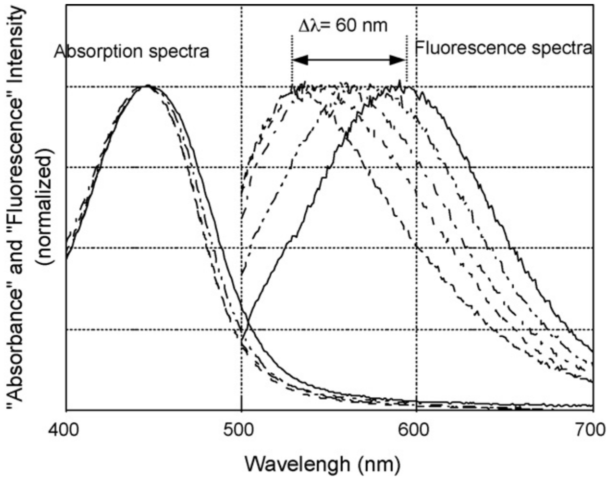


Fig. 6. Concentration dependence of absorption- and fluorescence spectra of NEW DYE-1 measured by the model system. From the shorter wavelength, dye concentrations are 0.05 mM (dilute solution), oil/dye = 3.5:1, oil/dye = 2.0:1, oil/dye = 0.8:1, oil/dye = 0.1:1, respectively.

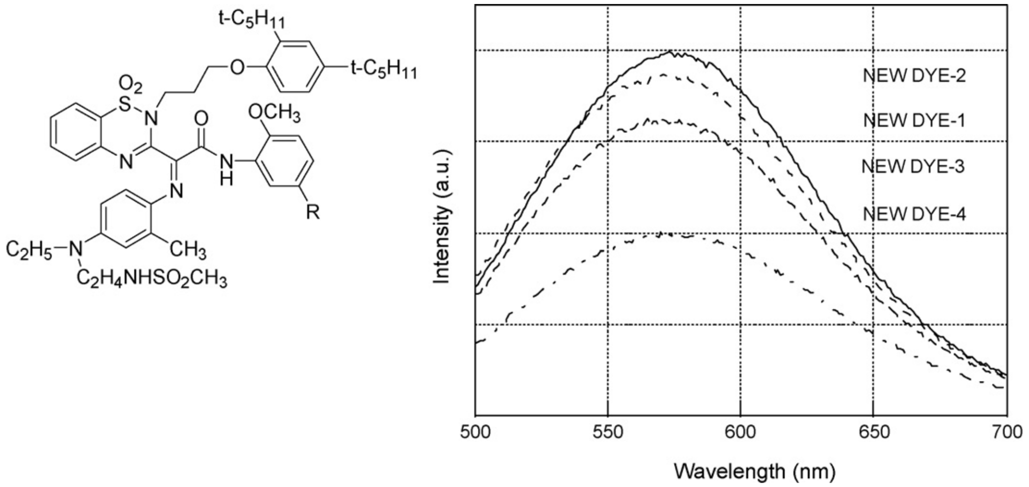


Fig. 7. Fluorescence intensity of the new yellow dye aggregates measured in the model system. Structures of substituent R: DYE-1; –H, DYE-2; –Cl, DYE-3; –CH_3, DYE-4; –OCH_3, respectively.

Fig. 7 shows the comparison of fluorescence spectra of four 1,1-dioxo-1,2,4-benzothiadiazine yellow dyes (NEW DYE-1, NEW DYE-2, NEW DYE-3, and NEW DYE-4) each carrying different substituent R. The maximum fluorescence absorption wavelengths of these novel yellow dyes are almost the same, but the fluorescence intensity (normalized on the number of excitation photon), *i.e.* the relative quantum yield of the fluorescence, was found to be different depending on the substituent structures. In addition, it was found that the higher relative quantum yield of the fluorescence of these dyes gave the poorer lightfastness (data omitted).

Fig. 8 shows the result of measurement of transient response with regard to the S_1–S_n absorption of NEW DYE-1 and NEW DYE-4, using our own sub-picosecond dynamics measurement system. While the S_1 lifetime of NEW DYE-1 was *ca.* 120 ps, that of NEW DYE-4 having lower relative fluorescent quantum yield was *ca.* 40 ps, about one third, giving good correlation between the relative fluorescent quantum yield and the lifetime of fluorescence. Since the natural radiation lifetimes of NEW DYE-1,2,3, and 4 are estimated to be almost the same because these dyes have the same skeleton, it is highly probable that the relative fluorescent quantum yield and the lifetime of fluorescence showed good correspondence.

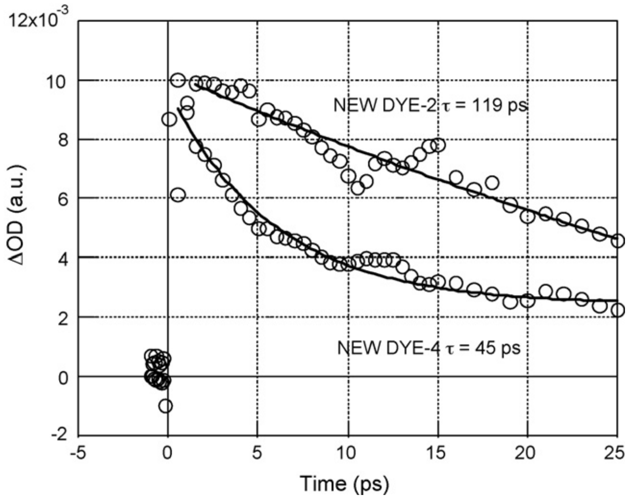


Fig. 8. S_1 lifetime of the new yellow dye aggregates measured in the model system with our sub-picosecond dynamics measurement system. Structures of dyes are same as in Fig. 7.

The quantum yield of intersystem crossing from S_1 to T_1 of 1,1-dioxo-1,2,4-benzothiadiazine yellow dye has been known to be very low because the dye exhibits neither phosphorescence even when cooled to the temperature of liquid nitrogen nor triplet-derived transient absorption [11,12]. Therefore, the lightfastness of the dye is supposedly influenced by the property of S_1 state. The lightfastness of the yellow dye deteriorates with increasing dye concentration in the oil droplets (Fig. 5) accompanied with red shift of the fluorescence spectrum (Fig. 6), and the S_1 lifetime depends on the substituent structure (Fig. 7) so that the longer S_1 lifetime gives inferior lightfastness of the dye as long as the maximal intensity of fluorescence emission is alike (NEW DYE-1, NEW DYE-2, NEW DYE-3, NEW DYE-4). Based on these facts we have postulated that “the stronger aggregation and the longer S_1 lifetime will give rise to the lower lightfastness”.

In order to verify this postulate, we examined the relationship between the degree of aggregation and the lightfastness, as well as that between the S_1 lifetime and the lightfastness. The fluorescence properties were measured in the oil droplet model system, and the lightfastness was evaluated in the color paper. We used the magnitude of red shift ($\Delta\lambda$) with reference to a dilute solution (2×10^{-5} mol/L) as an index of the degree of aggregation.

$$\begin{aligned}\Delta\lambda = {} & \text{(maximum wavelength of fluorescence emission at} \\ & \text{practical concentration}^{*}) - \text{(maximum wavelength of} \\ & \text{fluorescence emission in dilute solution}^{**}) \qquad (1)\end{aligned}$$

*Determined in the oil droplet model prepared by reprecipitation method (oil:dye = 2:1, *ca.* 1 mol/L).

**Determined in ethyl acetate solution of dye (2×10^{-5} mol/L).

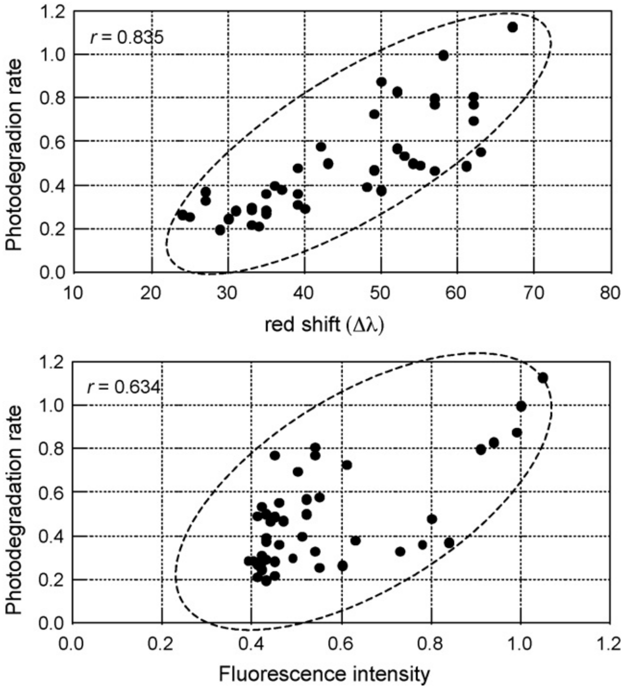


Fig. 9. Correlations between lightfastness of the new yellow dyes and fluorescence properties: (a) red shift and (b) fluorescence intensity.

Since determination of the S_1 lifetimes (τ_s) of a number of dyes by sub-picosecond dynamics measurement system was extremely difficult, these values were substituted by relative fluorescent quantum yields (ϕ'_{fl}).

As is shown in Fig. 9, a weak correlation was observed between $\Delta\lambda$ and lightfastness ($r = 0.835$) as well as between ϕ'_{fl} and lightfastness ($r = 0.634$). In contrast, since no correlation was observed between $\Delta\lambda$ and ϕ'_{fl} (data omitted), we attempted multiple regression between $\Delta\lambda$ and ϕ_{fl} on some 50 dyes and found that fluorescence properties measured in the model system were in good correlation with the lightfastness evaluated in the photographic color paper, as indicated in Fig. 10 ($r = 0.949$). This clarified that the main controlling factor of the lightfastness of 1,1-dioxo-1,2,4-benzothiadiazine yellow dye is the degree of aggregation and the S_1 lifetime of the aggregate. Thus we deduced that the higher tendency for aggregation and the longer S_1 lifetime of the aggregate should lead to lower lightfastness.

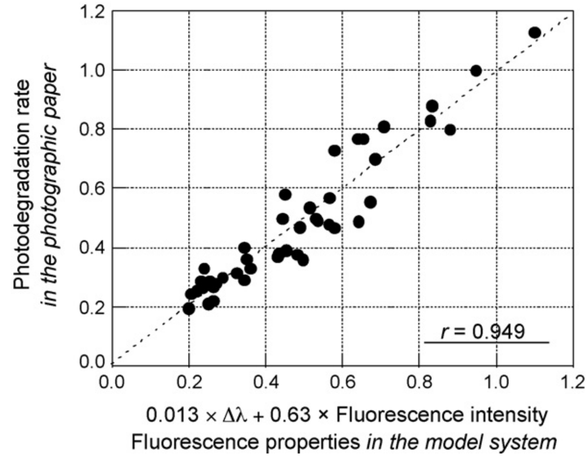


Fig. 10. Multiple regression between red shift and fluorescence intensity on some 50 new yellow dyes.

3.3. Improvement of lightfastness

Since the controlling factor of the lightfastness of the 1,1-dioxo-1,2,4-benzothiadiazine yellow dye was inferred to be the degree of aggregation and the S_1 lifetime of the aggregate, "suppression of aggregation" and "reduction of the S_1 lifetime of the aggregate" are considered to be effective to improve the lightfastness. Specifically, (1) suppression of aggregation by introduction of steric hindrance and (2) intramolecular quenching of the S_1 state by electronic effect of substituents were studied in the hope of effective improvement of lightfastness.

Fig. 11 shows the relationship between the structure of substituent and fluorescence spectrum. Introduction of a bulky substituent shifts the fluorescence to shorter wavelength with reduced $\Delta\lambda$, thus suggesting achievement of expected suppression of aggregation by introduction of a sterically hindering moiety.

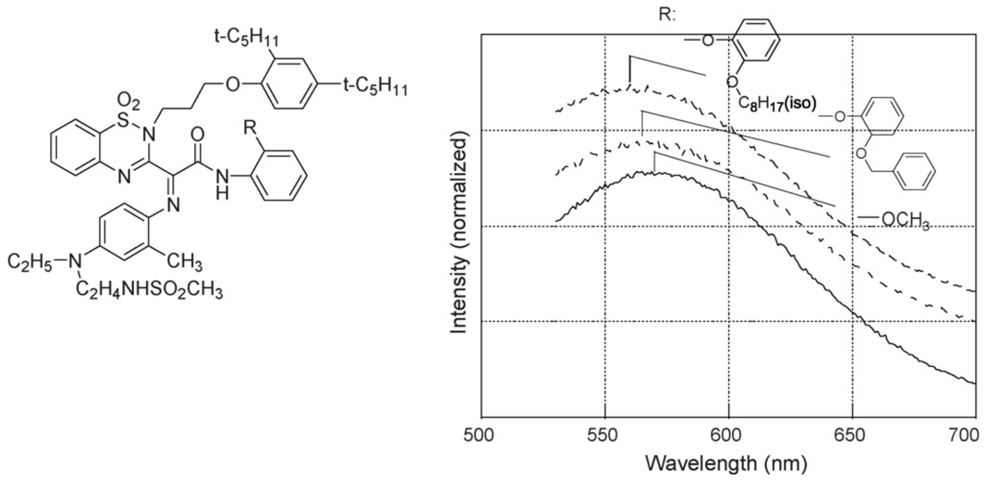


Fig. 11. Steric effects caused by bulky substituent on fluorescence spectra. Dye concentration of dispersions is oil/dye = 1:1.

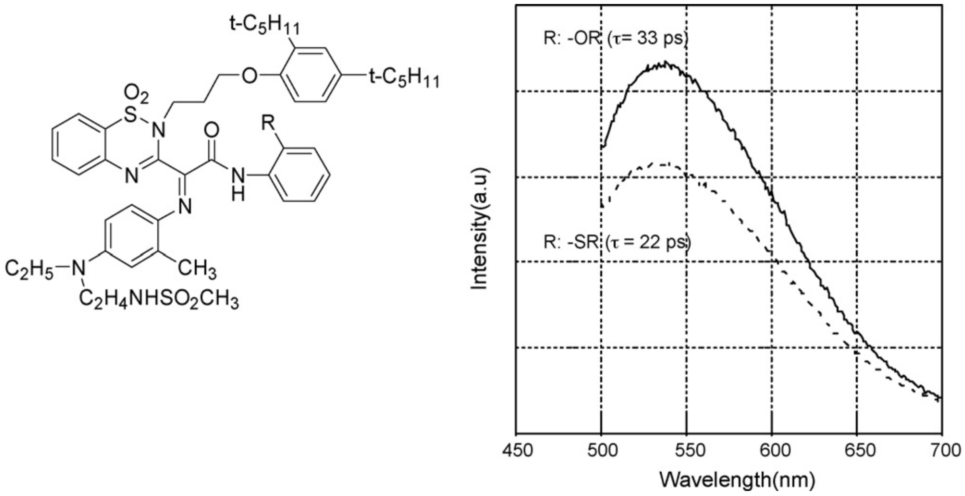


Fig. 12. Effect of S atom on fluorescence spectra.

Subsequently we studied the relationship between substituent and intensity of fluorescence. As shown in Fig. 12, introduction of a thioether moiety reduced the fluorescence intensity and shortened S_1 lifetime with little change of the maximum fluorescence wavelength. Also, as is shown in Fig. 7, introduction of an electron-donating group proved to reduce the fluorescence intensity accompanied with little change of the maximum fluorescence emission wavelength. We speculate that the change of S_1 lifetime of the aggregate brought about by the substituent is due to quenching of S_1 state of the aggregate, promoted by charge separation and recombination within the novel yellow dye owing to electronic effect of the substituent.

By optimizing the substituents to maximize steric-hindrance-assisted suppression of aggregation and electronic-effect-assisted quenching of S_1, we could successfully improve the lightfastness of 1,1-dioxo-1,2,4-benzothiadiazine yellow dye of practical concentration to compete or exceed the light-resistant level of conventional acylacetanilide yellow dyes. This enabled us to introduce the 1,1-dioxo-1,2,4-benzothiadiazine yellow coupler into our color paper, FUJICOLOR “EVER-BEAUTY PAPER TYPE II for LASER”.

4. Conclusion

By means of reprecipitation method dye-containing oil droplet dispersion in water was prepared, and was proven to be useful as the easy-handling model of color paper where dye-containing oil droplets were dispersed in a film. Using this model, analysis of photo-excited state in highly concentrated system became possible. Thereby we succeeded in clarifying the controlling factor of the lightfastness of 1,1-dioxo-1,2,4-benzothiadiazine yellow dye by using the oil droplet model, and thus in improvement of the lightfastness up to the targeted level within a short period. This enabled us to successfully introduce the novel yellow coupler in our color paper, FUJICOLOR “EVER-BEAUTY PAPER TYPE II for LASER”.

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