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Photostabilization of organic thermochromic pigments: Action of benzotriazole type UV absorbers bearing an amphoteric counter-ion moiety on the light fastness of color formers

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Abstract

Color formers are extensively used in information recording systems or thermochromic systems for textiles, but their light fastness properties are poor. The improvement of light fastness is therefore being sought at the present time. Various kinds of stabilizers have been synthesized to prolong the life of colored species derived from color formers. The retarding effect of these compounds towards photofading was investigated on cellulose. It was found that the UV absorbers bearing the groups capable of acting as an amphoteric counter-ion play a very important role in improving the light fastness of colorants for imaging and data recording systems. Zinc and nickel 5-(2-benzotriazolyl)-2,4-dihydroxybenzoates and the derivatives have been proposed as effective stabilizers against the fading of color formers.
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Keywords: Color former; Photofading; Improvement; Benzotriazole; UV absorber; Counter-ion

1. Introduction

The chemistry of color formers has recently become of importance, particularly in connection with the rapid development of information recording systems and thermochromic systems for a diverse range of applications [1–3]. Thermal recording systems using heat-sensitive paper have been widely used in facsimiles, word-processors, printers and point of sale labels, because of its workable properties. Furthermore, a heat-sensitive recording method has been used in prepaid cards. These information recording systems have recently become more common in our daily life [1]. In the systems, the image is recorded by the color-forming reactions upon heating. This process is an intermolecular acid–base equilibrium reaction. Thus, the coloration occurs when basic color formers react with acidic developments, e.g. bisphenol-A [2].

In addition, the color formers are also employed in the making of thermochromism. Examples of the use of these materials include temperature indicator for children's food by color change plastic mugs, indicator stripes on beer to indicate correct chilling, and on milk cartons to indicate that they have been refrigerated. In the novelty area, logos on mugs and printed textiles such as ski wear or promotional T-shirts are common uses. Such pigments are actually composites formulated from three components, the color former, an acidic catalyst and a non-polar co-solvent medium. The thermochromism centers around the interaction of color former and developer which occurs in a low-melting hydrophobic medium: the color of pigment changes when heated above its melting point and returns instantaneously on cooling and solidification [3]. But, functional dyes of this type gradually fade and so improved light fastness is currently being sought [1].

In previous papers [4–8], the photofading behaviors of Crystal Violet lactone and related compounds were examined in solution and in the adsorbed state. Zinc or nickel salts of 1-hydroxy-2-naphthoic acid and its derivatives afforded more

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marked improvements in the light fastness of color formers than did ordinary stabilizers. It was found that the amphoteric counter-ion effect plays a very important role in the photostability of color formers. Moreover, a benzophenone type UV absorber with attached amphoteric counter-ion residues was presented in a subsequent paper [9]. New functional UV absorbers provided an enhanced photochemical stability. Therefore, it is of interest to prepare the different types of UV absorbers capable of acting as the amphoteric counter-ion (X–A–Y) in complex II with color former (see Scheme 1).

In this paper, the influence of benzotriazole type UV absorbers containing an amphoteric counter-ion moiety on the photofading behavior of color formers was investigated on cellulose, and a novel approach for improving the light fastness of colorants for imaging and data recording systems is now reported.

2. Experimental

2.1. Materials

2,2-Bis(4-hydroxyphenyl)propane (bisphenol-A), nickel dimethyldithiocarbamate (NMC), 2-hydroxybenzophenone (HBP), 2-(2-benzotriazolyl)-*p*-cresol (BTC) and the chloride of Crystal Violet (**7**) were purchased from Tokyo Chemical Ind. Co., Ltd. Cellulose TLC plates (0.1 cm thickness) were purchased from Merk Co., Ltd. Tetrachlorophthalic acid mono(ethylene glycol ester) zinc salt (PEG-Zn), Crystal Violet lactone (**1**), 3-(*N*-ethylisobutylamino)-6-methyl-7-anilinofluoran (**3**) and 3-diethylamino-7,8-benzofluoran (**5**) were obtained from a commercial source. All 2-[(2-nitrophenyl)-azo]phenol derivatives employed in this research were prepared by diazotization of 2-nitroaniline and the subsequent coupling reaction with 2,4- or 2,6-dihydroxybenzoic acid ethyl ester or 2,4,6-trihydroxybenzoic acid ethyl ester. The desired hydroxyphenylbenzotriazoles were synthesized by reaction of the corresponding azo compounds with thiourea-*S*,*S*-dioxide and sodium hydroxide in a mixture of 2-propanol and water (1:1, vol./vol.) according to procedures described [10]. These compounds were purified by appropriate methods until chromatographically pure and identified by ^{1}H NMR, mass, IR and elemental analyses. Metal carboxylates were prepared and purified as described previously [5].

The formulas of dye **7** and these materials are shown in Figs. 1 and 2.

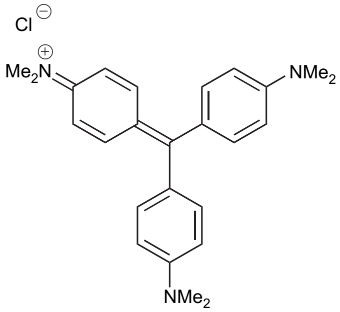


Fig. 1. Chemical structure of dye **7**.

2.2. General procedure for photofading of color formers and related dye

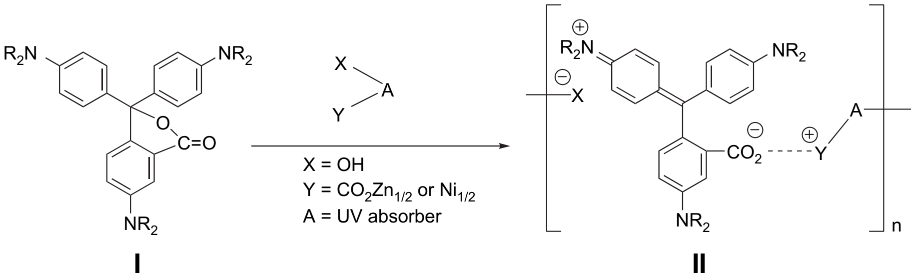
According to the procedure described in the previous papers [5–9], a solution of **1** (8×10^{-3} mol dm^{-3}) in 10 cm^3 of a mixture of pyridine and water (4:1, vol./vol.) with or without additive (4×10^{-2} mol dm^{-3}) such as carboxylic acids, metal salts, HBP or BTC, was prepared in the presence of bisphenol-A (54.8 mg), and then stirred at 80 °C for 1 h.

Portions of the solutions (1×10^{-2} cm^3) were spotted on cellulose. TLC plates were held at a distance of approximately 5 cm from the light source (100 W high-pressure mercury lamp: Ushio Electric Inc., UM-102 type) and exposed to light ($\lambda > 300$ nm) in air. The apparatus was kept at 30 ± 2 °C. After irradiation for 3 h, the plates were developed with 60% acetic acid. The spot of separated color was scanned using a Shimadzu thin-layer chromatoscanner (CS-920 type). The percentage conversion was calculated by comparison with unirradiated color. A similar procedure was also used for dyes **3**, **5** and **7**. The irradiation times were 5 h in the case of **3** or **5**, and 23 h in the case of **7**.

3. Results and discussion

3.1. Effect of functional UV absorbers on the photofading of Crystal Violet lactone

Dye **1** is a chromogenic compound in its colorless form. Acidic catalysts, e.g. acidic clay, open the lactone ring, thereby allowing a violet triarylmethane dye (**2**, λ_{max} 605 nm) to form, as illustrated in Scheme 2 [2]. The dye



Scheme 1.

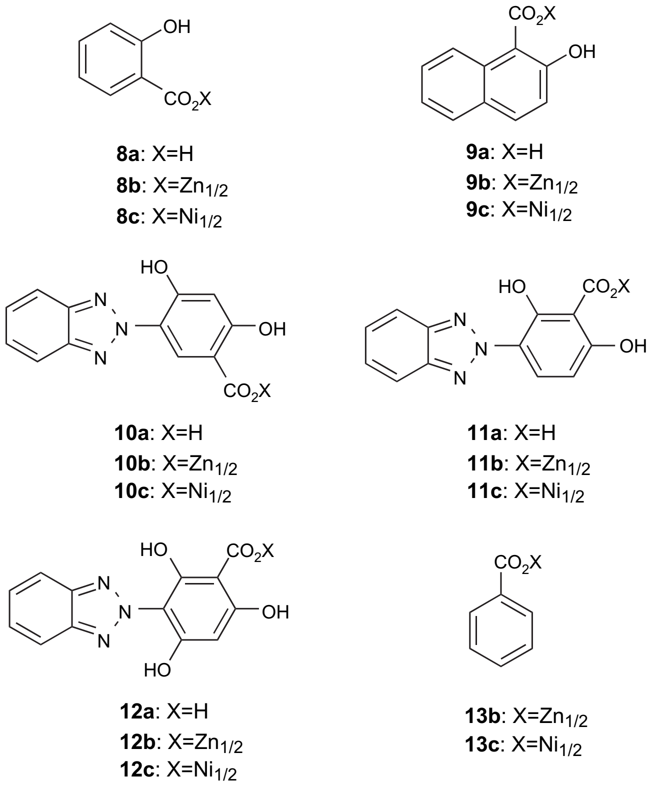
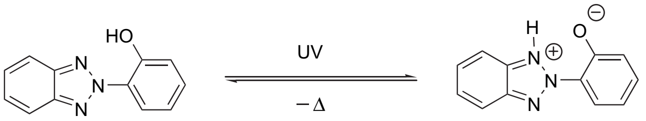


Fig. 2. Various stabilizers used in the present study.

derived from the color former generally has a poor light fastness, and an improvement of the property is requested.

A number of different types of UV stabilizer compounds have been previously suggested for stabilization of dyes, but only four fundamentally different classes have achieved commercial significance. These are the derivatives of 2-hydroxybenzophenone, phenyl esters, substituted cinnamic acid derivatives, and hydroxyphenylbenzotriazoles. The latter type of compound, which is used in this work, protects the dye by preferentially absorbing the harmful UV radiation and converting it into heat energy by means of rapid tautomerism (see Scheme 3) [11].

In previous studies [5–8], the effect of various counter-ions on the photofading of color materials derived from color formers was studied on cellulose plate or heat-sensitive recording paper. It was found that the amphoteric counter-ion effect

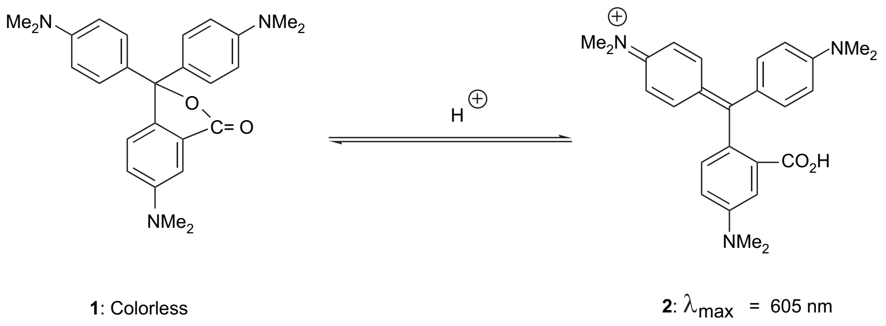


Scheme 3.

plays a very important role not only in the photostability but also in the image stability of color formers. It is therefore of interest to investigate benzotriazole type UV absorber containing a built-in amphoteric counter-ion moiety as a means of improving the light fastness of phthalide type color former. Various types of related stabilizers were prepared, and the effectiveness of these compounds was examined on cellulose plate. The influence of various additives on the photofading of dye **2** on cellulose was examined in air on exposure to filtered radiation ($\lambda > 300$ nm) from a 100 W high-pressure mercury lamp, and the results are shown in Table 1.

When dye **2** adsorbed on cellulose was exposed for 3 h to filtered radiation, it showed 84% conversion, while in the presence of 2-hydroxybenzoic acid (**8a**) or 2-hydroxy-1-naphthoic acid (**9a**) showed 70 and 72% conversion, respectively. These carboxylic acids are incapable of acting as amphoteric counter-ions, and so had little influence on the rate of photofading. However, the addition of zinc salts to these acids (**8b**, **9b**) in the photofading system markedly retarded the fading. A similar stabilization effect was also observed in the presence of nickel salts (**8c**, **9c**). The retardation effect provided by these compounds (**8b**, **c**, **9b**, **c**) was significantly better than those of the monofunctional zinc and nickel benzoates (**13b**, **c**), and the conventional stabilizers, PEG-Zn and NMC. Such an enhanced photochemical stability may be due to the contribution of an intermolecular amphoteric counter-ion effect, since these metal salts had little influence on the rate of photofading of dye **7** which contains no lactone ring [5].

Moreover, the influence of UV absorbers on the photofading of dye **2** was also examined on cellulose. When 2-(2-benzotriazolyl)-*p*-cresol (BTC), benzotriazole type UV absorber, or 2-hydroxybenzophenone (HBP), benzophenone type UV absorber, was added to the photofading system, dye **2** showed 43 and 66% conversion, respectively. A similar stabilizing effect also observed in the presence of 5-(2-benzotriazolyl)-2,4-dihydroxybenzoic acid (**10a**), while the inhibiting effect against the fading of dye **2** was small. On the contrary,



Scheme 2.

Table 1
Effect of various additives on the photostability of colorants on cellulose

Additive[a]	Conversion (%)	
	2	**7**
None	84	61 (68)[f]
8a	70	–
8b	20	65[f]
8c	17	53[f]
9a	72	–
9b	40	68[f]
9c	19	58[f]
10a	48	–
10b	9	47
10c	7	45
13b	82	57
13c	62	37
BTC[b]	43	33
HBP[c]	66	35
PEG-Zn[d]	82	–
NMC[e]	64	–

[a] For key, see Fig. 2.

[b] 2-(2-Benzotriazolyl)-*p*-cresol.

[c] 2-Hydroxybenzophenone.

[d] Tetrachlorophthalic acid mono(ethylene glycol ester) zinc salt.

[e] Nickel dimethyldithiocarbamate.

[f] Exposed for 24 h.

when the zinc 5-(2-benzotriazolyl)-2,4-dihydroxybenzoate (**10b**) was added to the photofading system, dye **2** showed only 9% conversion. The nickel salt (**10c**) gave a far more efficient protecting effect against the fading of dye **2** under the condition employed. Such an enhanced photochemical stability may be caused by combined function of amphoteric counter-ion effect such as **14** and UV absorbing ability by UV absorber, since these salts had little influence on the fading of dye **7** which contains no lactone ring [5] (see Scheme 4).

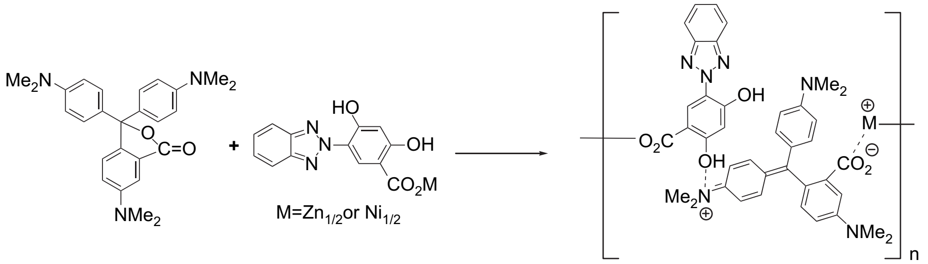
The process of formation of complex **14** is now being studied and will be reported later. Further, the retardation effects afforded by the nickel salts were generally superior to those of the zinc salts. Since the contribution of singlet oxygen to the photofading of Crystal Violet lactone has been proposed in recent years [12], this may result from the singlet oxygen quenching effects caused by nickel salts [5]. This hypothesis is supported by the fact that the retardation effect given by NMC, well-known singlet oxygen quencher [13], is slightly superior to that of PEG-Zn, a conventional stabilizer for color former. Consequently, these observations suggest that the introduction of the groups capable of acting as an amphoteric counter-ion into UV absorber plays a very important role in the photostabilization of phthalide type color formers.

3.2. Improvement of the light fastness of fluoran dyes

Fluoran dyes **3** and **5** together with dye **1** are extensively used for technical reproduction, e.g. business forms for resisters or computers, or thermochromic systems for textiles. The colored materials **4** and **6** derived from color formers **3** and **5** showed black color (λ_{max} 446 and 586 nm) and red color (λ_{max} 490, 522 and 555 nm), respectively, as illustrated in Scheme 5, but their light fastness properties are as poor as dye **1** [1].

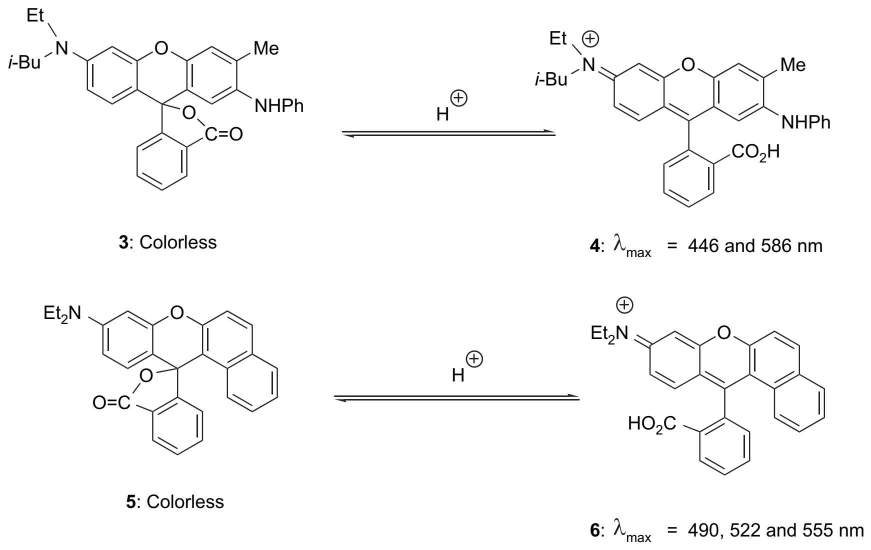
In Section 3.1, it was found that metal hydroxyarylcarboxylates were highly effective for photostabilizing the colored material derived from Crystal Violet lactone. In particular, functional UV absorbers (**10b**, **c**) were effective in preventing fading. Following this, it was considered to further investigate the protecting effects of these stabilizers in connection with improving the light fastness of fluoran dyes. The influence of various stabilizers on the photofading of fluoran dyes was examined using dyes **4** and **6** in the same manner as above, and the results are shown in Table 2. When dye **4** on cellulose was exposed for 5 h to filtered radiation, it showed 86% conversion, while in the presence of 2-hydroxybenzoic acid (**8a**) or 2-hydroxy-1-naphthoic acid (**9a**) showed 63% conversion, respectively. These behaviors may be supported by the fact that the carboxylic acids, such as 2-hydroxybenzoic acid, capable of forming intramolecular hydrogen bonds gave little protection against the fading of color formers in solution and on silica gel [14]. However, the rate of photofading was efficiently suppressed by adding 2-hydroxybenzoic acid zinc salt (**8b**) or 2-hydroxy-1-naphthoic acid zinc salt (**9b**). A similar stabilizing effect was also observed in the presence of these nickel salts (**8c**, **9c**). Such an effective photochemical stability may be due to the contribution of amphoteric counter-ions as well as the case of dye **1**.

On the other hand, dye **4** showed 27% conversion by adding **10a**, which must be capable of acting as an UV absorber. The protecting effect was superior to that of BTC or HBP, good UV absorber. The use of **10b** or **10c** further showed higher inhibition against the fading of dye **4**. Nevertheless, these stabilizers behaved in a very slightly inferior way to **8b** or **8c**. This phenomenon may be attributed to inhibition of the amphoteric



1 **14**

Scheme 4.



Scheme 5.

counter-ion effect by bulky substituents in dye **3** and benzotriazole moiety in stabilizer. Similar enhanced photochemical stability was also achieved in the case of dye **6**. When dye **6**, adsorbed on cellulose, was exposed for 5 h to filtered radiation ($\lambda > 300$ nm) and air, it showed 87% conversion, and in the presence of **8a** and **9a** showed 66% conversion, respectively. When BTC or HBP was added to the system, dye **6** still showed 63 and 60% conversion, respectively. However, the use of **10b**, **c** afforded a higher degree of protection against the fading of dye **6**. Accordingly, these results indicate that a single use of UV absorber is not very beneficial for stabilizing the color former, but that the combined use of an amphoteric counter-ion effect and UV absorber plays a very important role in the stabilization of color former.

3.3. Influence of amphoteric counter-ion moiety on the photochemical stability of color formers

In Section 3.2, it was predicted that UV absorbers possessing an amphoteric counter-ion effect, like complex **14** in Scheme 4, impart more improvement in the light fastness properties of color formers than conventional stabilizers. Therefore, UV absorbers bearing different type of amphoteric counter-ion moiety, e.g. **11b**, **c** or **12b**, **c**, were here prepared, and their effectiveness examined using dye **2** in the same manner as above. The results are shown in Table 3. When dye **2** on cellulose plate was exposed for 3 h to filtered light ($\lambda > 300$ nm), it showed 84% conversion, and in the presence of 3-(2-benzotriazolyl)-2,6-dihydroxybenzoic acid (**11a**) or 3-(2-benzotriazolyl)-2,4,6-trihydroxybenzoic acid (**12a**) showed 37 and 27% conversion, respectively. The retardation effect provided by these compounds was almost equal or little superior to that of BTC. However, the use of zinc 3-(2-benzotriazolyl)-2,6-dihydroxybenzoate (**11b**) or zinc 3-(2-benzotriazolyl)-2,4,6-trihydroxybenzo-ate (**12b**) showed higher inhibition against the fading of dye **2** compared with **11a**, **12a** or carboxylic acids and the metal salts (**8a**–**c**, **9a**–**c**).

Table 2
Effect of various stabilizers on the photofading of fluoran dyes

Additives[a]	Conversion (%)	
	4	**6**
None	86	87
8a	63	66
8b	14	41
8c	14	38
9a	63	66
9b	20	41
9c	9	37
10a	27	37
10b	18	12
10c	17	11
BTC	36	63
HBP	30	60

[a] For key, see Fig. 2 and Table 1.

Table 3
Effect of various stabilizers on the photofading of colorants on cellulose

Additive[a]	Conversion (%)	
	2	**7**
None	84	61 (68)[b]
8a	70	–
8b	20	65[b]
8c	17	53[b]
9a	72	–
9b	40	68[b]
9c	19	58[b]
11a	37	–
11b	12	43
11c	0	25
12a	27	–
12b	0	31
12c	0	28
BTC	43	33

[a] For key, see Fig. 2 and Table 1.
[b] Exposed for 24 h.

In particular, the use of **12b** completely retarded the rate of photofading of dye **2** under the condition herein described. Furthermore, it is noteworthy that the addition of these nickel salts (**11c**, **12c**) also perfectly stopped the fading of dye **2**. Such an excellent degree of protection against the fading of dye **2** may be caused by combined function of bifunctional amphoteric counter-ions effect such as **15** and/or **16**, and UV absorbing ability by UV absorbers, since these salts had little influence on the fading of dye **7** which contains no lactone ring [5] (see Scheme 6).

Similar behavior was observed in the case of fluoran dyes **3** and **5**, and the results are shown in Table 4.

When dye **4**, adsorbed on cellulose, was exposed for 5 h to filtered light, it showed 86% conversion, and in the presence of **11a** and **12a** showed 25 and 20% conversion, respectively. The retardation effect provided by **11a** or **12a** was somewhat superior to that of BTC, but the extent of protection against the fading of dye **4** was small. On the contrary, the addition of these zinc salts (**11b**, **12b**) in the photofading system remarkably retarded the fading, and similar enhanced photochemical stability was also achieved with the nickel salts (**11c**, **12c**). Such a higher degree of protection by these metal salts (**11b**, **c**, **12b**, **c**) was also recognized against the fading of dye **6**. As a rule, the retardation effects conferred by the metal salts (**11b**, **c**, **12b**, **c**) were superior to that of **10b**, **c**. The promoted stability may be a result of the contribution of bifunctional amphoteric counter-ions such as **15** and/or **16** in Scheme 6. The process of formation of complex **15** or **16** is now being studied and will be reported later. Consequently, these results demonstrate that the benzotriazole type UV absorbers containing an amphoteric counter-ion moiety can be applied as effective stabilizers against the photofading of color formers, and particularly nickel complexes are effective.

Table 4
Effect of various stabilizers on the photofading of fluoran dyes

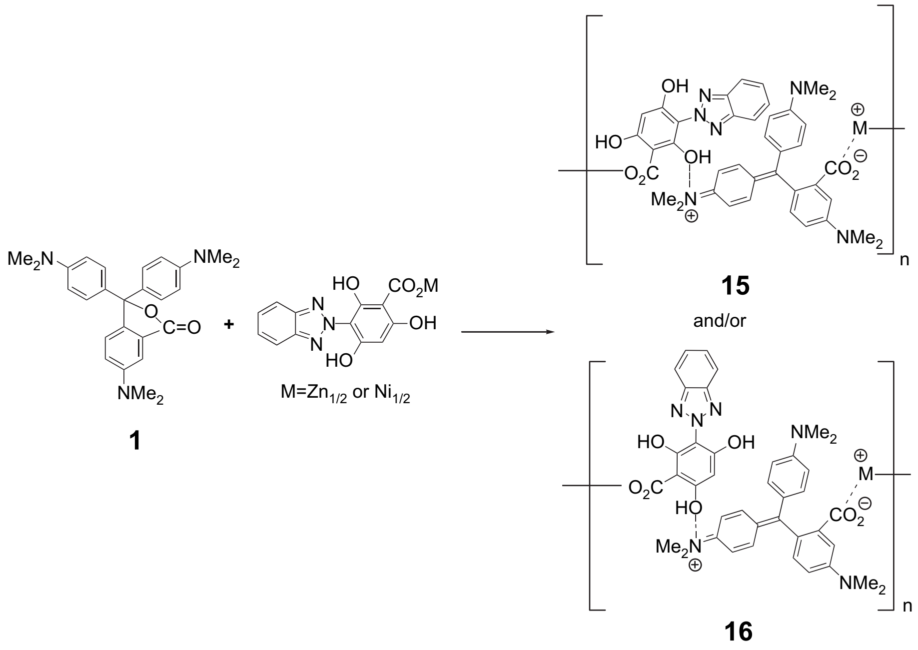
Additives[a]	Conversion (%)	
	4	**6**
None	86	87
8a	63	66
8b	14	41
8c	14	38
9a	63	66
9b	20	41
9c	9	37
11a	25	67
11b	16	8
11c	7	7
12a	20	57
12b	10	6
12c	8	0
BTC	36	63

[a] For key, see Fig. 2 and Table 1.

4. Conclusions

While the contribution of counter-ions to the photofading of cationic dyes has been previously investigated by several workers, there is no study pertaining to the use of counter-ions as a means of improving the light fastness of color formers.

In this study, the influence of various UV absorbers capable of acting as amphoteric counter-ions on the photostability of color materials derived from color formers has been examined on cellulose. The use of conventional UV absorbers was not very beneficial for improving the light fastness of color formers. But a series of UV absorbers bearing a built-in amphoteric counter-ions moiety afforded an excellent degree of



Scheme 6.

protection against the photofading of color formers. The functional UV absorbers discovered in this study may be applied as effective stabilizers against photofading of color formers.

Acknowledgement

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