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Photostabilization of organic thermochromic pigments. Part 2: Effect of hydroxyarylbenzotriazoles containing 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; improvement of light fastness is therefore being sought. Various kinds of stabilizer were synthesized in an attempt 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 hydroxyarylbenzotriazoles bearing groups that are capable of acting as amphoteric counter-ions play an important role in improving the light fastness of colorants for imaging and data-recording systems. Both zinc and nickel 3-(2-benzotriazolyl)-2-hydroxy-1-naphthoates and derivatives are proposed as effective stabilizers against the fading of color formers.

Keywords: Information; Thermochromism; Light fastness; Stabilization; Amphoteric counter-ion; Metal salts

1. Introduction

The chemistry of color formers has recently become the focus of great interest, 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, etc. because of their workable properties; in addition, a heat-sensitive recording method has been used in prepaid cards. In these information-recording systems, which have recently become more common in our daily life [1], the image is recorded by color-forming reactions upon heating. This process is an intermolecular acid–base equilibrium reaction in which coloration occurs when basic color formers react with acidic developer, e.g. bisphenol-A [2].

The color formers are also employed in 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. These pigments are composites formulated from three components, namely the color former, an acidic catalyst and a non-polar co-solvent medium. The thermochromism involved, centers around the interaction of the color former and developer which occurs in a low-melting hydrophobic medium: the color of the pigment changes when heated above its melting point and returns instantaneously on cooling and solidification [3]. However, 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 both the solution and adsorbed states. The zinc or nickel salts of 1-hydroxy-2-naphthoic acid and its derivatives afforded more marked improvements in the light fastness of

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color formers than did ordinary stabilizers. It was found that the amphoteric counter-ion plays a very important role in the photostability of color formers. Moreover, a benzophenone or benzotriazole type UV absorbers with attached amphoteric counter-ion residues were presented in subsequent papers [9,10]. New functional stabilizers provided an enhanced photochemical stability. Therefore, it is of interest to prepare the naphthalene derivatives of benzotriazole type UV absorbers capable of acting as the amphoteric counter-ion (X–A–Y) in a complex (**II**) with color formers (see Scheme 1).

In this paper, the influence of naphthalene derivatives containing an amphoteric counter-ion moiety, upon 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-(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 Merck Co., Ltd. Tetrachlorophthalic acid mono(ethylene glycol ester)zinc salt (PEG-Zn), Crystal Violet lactone (**1**), 3-diethylamino-7,8-benzofluoran (**3**) and 3-(*N*-ethylisobutylamino)-6-methyl-7-anilinofluoran (**5**) were obtained from a commercial source. 5-(2-Benzotriazolyl)-2,4-dihydroxybenzoic acid (**12a**) and the metal salts (**12b**,**c**) were synthesized according to the procedure described previously [10]. All [(2-nitrophenyl)azo]-naphthol derivatives employed in this research were prepared by diazotization of 2-nitroaniline and the subsequent coupling reaction with 2-hydroxy-1-naphthoic or 2-hydroxy-3-naphthoic acid or 3,5-dihydroxy-2-naphthoic acid. The desired hydroxyarylbenzotriazoles 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 v/v) according to procedures described [11]. 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.

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

According to the procedure described previously [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 v/v) with or without additive (4×10^{-2} mol dm^{-3}) such as carboxylic acids, metal salts, or BTC, was prepared in the presence of bisphenol-A (54.8 mg), and then stirred at 80 °C for 1 h.

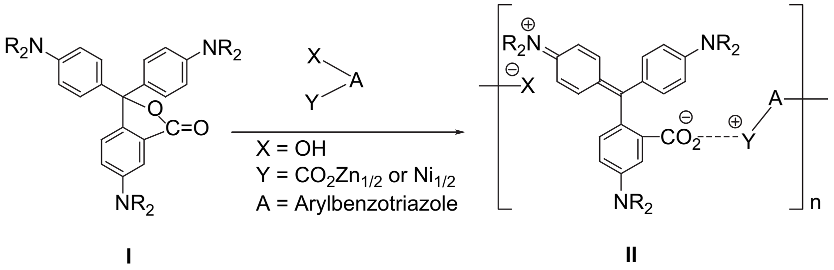
Portions of the solution (1×10^{-2} cm^3) were spotted on cellulose TLC plates held at a distance of approximately 5 cm from a 100 W high-pressure mercury lamp (Ushio Electric Inc., UM-102 type) and exposed to light ($\lambda > 300$ nm) in air; the apparatus was kept at 30 ± 2 °C. After irradiation for 3 h, the plates were developed with 60% acetic acid. The spot of the 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**, employing irradiation times of 5 h in the cases of **3** and **5**, and 23 h in the case of **7**.

3. Results and discussion

3.1. Effect of hydroxyarylbenzotriazoles on the photofading of Crystal Violet lactone

Dye **1** is a chromogenic compound in its colorless form; acidic catalysts, such as 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 derived from the color former generally has poor light fastness, and an improvement of the property is requested.

A number of different types of UV stabilizers have been previously suggested for stabilization of dyes, but only four fundamentally different classes have achieved commercial significance, namely, derivatives of 2-hydroxybenzophenone, phenyl esters, substituted cinnamic acid derivatives and hydroxyphenylbenzotriazoles. The latter type of compound, which is used in this work, protect the dye by preferentially absorbing the harmful UV radiation and converting it into heat energy by means of rapid tautomerism (see Scheme 3) [12].



Scheme 1.

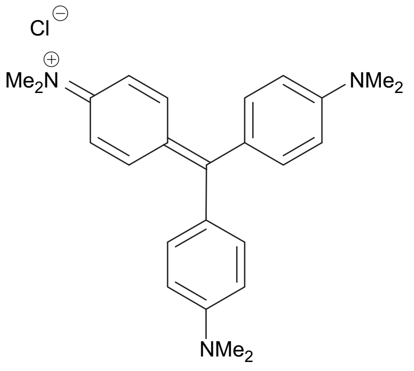
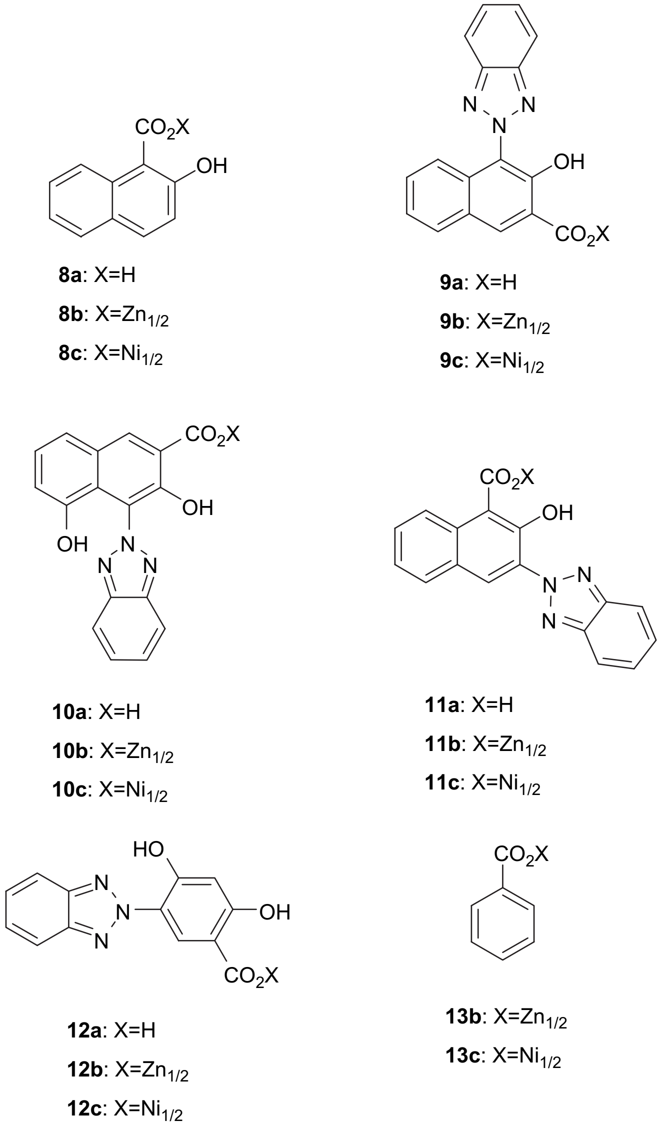


Fig. 1. Chemical structure of dye **7**.

In earlier 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 plays a very important role not only in the photostability but also in the image stability of color formers. Recently it has been found that benzotriazole UV absorbers containing a built-in amphoteric counter-ion moiety are able to secure a more marked improvement in the light fastness of color formers than are conventional stabilizers [10]. It was therefore considered of interest to further investigate hydroxyarylbenzotriazoles bearing an amphoteric counter-ion effect 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-hydroxy-1-naphthoic acid (**8a**) showed 72% conversion. This carboxylic acid is incapable of acting as an amphoteric counter-ion, and so had little influence on the rate of photofading. However, the addition of zinc salt of this acid (**8b**) in the photofading system moderately retarded the fading. A marked stabilization effect was observed in the presence of nickel salt (**8c**). The retardation effect provided by these compounds (**8b**,**c**) was significantly better than those of the monofunctional zinc and nickel benzoates (**13b**,**c**), and of the conventional stabilizers, PEG-Zn and NMC. Such an enhanced photochemical stability may be due to the



8a: X=H
8b: X=$Zn_{1/2}$
8c: X=$Ni_{1/2}$

9a: X=H
9b: X=$Zn_{1/2}$
9c: X=$Ni_{1/2}$

10a: X=H
10b: X=$Zn_{1/2}$
10c: X=$Ni_{1/2}$

11a: X=H
11b: X=$Zn_{1/2}$
11c: X=$Ni_{1/2}$

12a: X=H
12b: X=$Zn_{1/2}$
12c: X=$Ni_{1/2}$

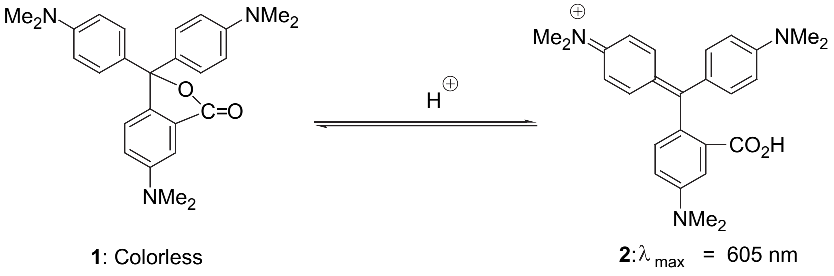
13b: X=$Zn_{1/2}$
13c: X=$Ni_{1/2}$

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

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

Additive[a]	Conversion (%)	
	Dye **2**	Dye **7**
None	84	61(68)[f]
8a	72	–
8b	40	68[f]
8c	19	58[f]
9a	39	–
9b	39	50
9c	10	44
10a	23	–
10b	0	33
10c	0	33
11a	48	–
11b	38	38
11c	0	28
12a[b]	48	–
12b[b]	9	47
12c[b]	7	45
13b	82	57
13c	62	37
BTC[c]	43	33
PEG-Zn[d]	82	–
NMC[e]	64	–

[a] For key see Fig. 2.
[b] Proposed in a preliminary paper [10].
[c] 2-(2-Benzotriazolyl)-*p*-cresol.
[d] Tetrachlorophthalic acid mono(ethylene glycol ester)zinc salt.
[e] Nickel dimethyldithiocarbamate.
[f] Exposed for 24 h.



Scheme 2.

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 hydroxyarylbenzotriazoles, synthesized in this study, on the photofading of dye **2** was also examined on cellulose. When 2-(2-benzotriazolyl)-*p*-cresol (BTC), well-known UV absorber, was added to the photofading system, dye **2** showed 43% conversion. Similar stabilizing effect was also observed in the presence of 1-(2-benzotriazolyl)-2-hydroxy-3-naphthoic acid (**9a**) or 3-(2-benzotriazolyl)-2-hydroxy-1-naphthoic acid (**11a**), while 4-(2-benzotriazolyl)-3,5-dihydroxy-2-naphthoic acid (**10a**) showed higher inhibition against the fading of dye **2**. Such a high photochemical stability may be attributed to the introduction of further hydroxyl group associated with UV absorbing ability.

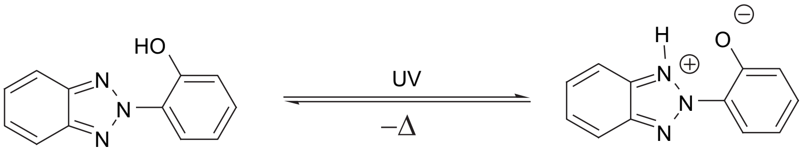
On the other hand, when zinc 1-(2-benzotriazolyl)-2-hydroxy-3-naphthoate (**9b**) or 3-(2-benzotriazolyl)-2-hydroxy-1-naphthoate (**11b**) was added to the photofading system, dye **2** showed 39 and 38% conversion, respectively. The retarding effects provided by these additives were inferior to that of zinc 5-(2-benzotriazolyl)-2,4-dihydroxybenzoate (**12b**) proposed in a preliminary study [10]. These findings suggest that a simple extension of the π-conjugated ring system might not necessarily be a useful modification improving the light fastness of phthalide type color formers because such an extension may inhibit the amphoteric counter-ion effects (see Scheme 1). This hypothesis may be supported by the fact that these salts showed apparent inhibition against the fading of dye **7** which contains no lactone ring. However, it is noteworthy that nickel salt (**11c**) completely suppressed the fading. Furthermore, the addition of zinc 4-(2-benzotriazolyl)-3,5-dihydroxy-2-naphthoate (**10b**) in the photofading system perfectly stopped the fading. A similar stabilizing effect was also observed in the presence of nickel salt (**10c**). In addition, 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 [13], 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 [14], is slightly superior to that of PEG-Zn, a conventional stabilizer for color former.

3.2. *Effect of functional UV absorbers on the light fastness of fluoran dyes*

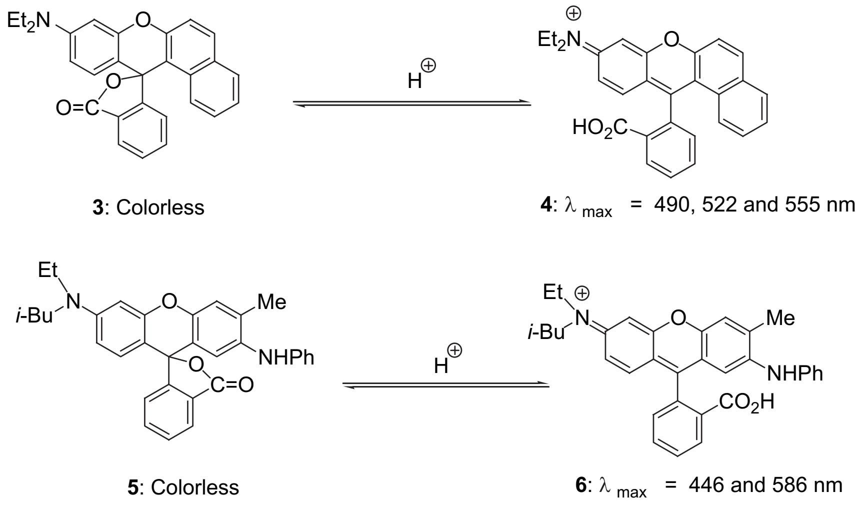
Fluoran dyes **3** and **5** together with dye **1** are extensively used for technical reproduction, e.g. business forms for resisters or computers, or thermochromic systems for textiles. The colored materials **4** and **6** derived from color formers **3** and **5** showed red color (λ_{max} 490, 522 and 555 nm) and black color (λ_{max} 446 and 586 nm), respectively, as illustrated in Scheme 4, 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 hydroxyarylbebzotriazoles (**10b**,**c**, **11c**) 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 87% conversion, while in the presence of 2-hydroxy-1-naphthoic acid (**8a**) showed 66% conversion. This behavior may be supported by the fact that the carboxylic acids, such as 2-hydroxybenzoic acid, capable of forming intramolecular hydrogen bonds gave a little protection against the fading of color formers in solution and on silica gel [15]. However, the rate of photofading was efficiently suppressed by adding 2-hydroxy-1-naphthoic acid zinc salt (**8b**). A similar stabilizing effect was also observed in the presence of nickel salt (**8c**). Such an effective photochemical stability



Scheme 3.



Scheme 4.

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 49% conversion by adding **9a**, which must be capable of acting as an UV absorber. The protecting effect was superior to that of BTC, good UV absorber. The use of **9b** or **9c** further showed higher inhibition against the fading of dye **4**. Such a high degree of protection against the fading of dye **4** was also observed in the presence of other metal salts (**10b**,**c**). The protecting effects provided by dihydroxy derivatives (**10a**–**c**) was apparently superior to those of monohydroxy derivatives (**9a**–**c**). This finding indicates that the introduction of a further hydroxyl group in the position responsible for UV absorbing function is very useful for retarding the fading of dye **4** as well as in the case of dye **2**. Nevertheless, when **11a** was added to the photofading system, dye **4** still showed 77% conversion. Similar incomplete protection has also been observed on addition of **11b**. This fact may predict that the introduction of benzotriazolyl group in β-position of naphthalene ring influences to a lesser extent the protecting effect against the fading of benzofluoran type color former. In contrast the suppressing effect conferred by **11c** was nearly equal to that of other nickel salts (**9c**, **10c**). This high protection may result from the singlet oxygen quenching effect caused by nickel salt since the contribution of singlet oxygen to the photofading of fluoran dyes has been proposed in recent years [7].

On the contrary, sufficient photochemical stability was achieved in the case of dye **6**. When dye **6**, adsorbed on cellulose, was exposed for 5 h to filtered light, it showed 86% conversion, and in the presence of **8a** showed 63% conversion. When BTC was added to the photofading system, dye **6** still showed 36% conversion. Similar incomplete protection has also been observed in the presence of **9a** or **11a**. This fact suggests that the application of simple UV absorbers is not necessarily useful for improving the light fastness of color formers. However, the use of **11b**,**c**, which showed lower inhibition against fading of dye **4** compared with **12b**,**c**, almost completely or completely suppressed the rate of photofading of dye **6** under the conditions herein described. Such a difference of protecting effect might be attributed to the chemical structure of color formers. The retardation effects provided by the metal salts (**11b**,**c**) were significantly better than that of **12b**,**c**. Such an excellent degree of protection against the fading of dye **6** may be dependent on promoted amphoteric counter-ion effect by extension of the π-conjugated ring system.

Nevertheless, the suppressing effects imparted by **9b**,**c** were inferior to that of **12b**,**c**. This suggests that the introduction of benzotriazolyl group in α-position of the naphthalene ring is not necessarily a useful modification for photostabilization of fluoran dyes. Moreover, dye **6** showed 22% conversion by adding **10a**, and the protecting effect was apparently superior to that of **9a**, **11a** or **12a** as well as in the case of dye **2**. The addition of zinc salt (**10b**) in the photofading system remarkably retarded the fading, and similar enhanced photochemical stability was also achieved with nickel salt (**10c**). These

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

Additive[a]	Conversion (%)	
	Dye **4**	Dye **6**
None	87	86
8a	66	63
8b	41	20
8c	37	9
9a	49	43
9b	34	40
9c	26	25
10a	39	22
10b	25	7
10c	19	4
11a	77	34
11b	62	3
11c	25	0
12a	37	27
12b	12	18
12c	11	17
BTC	63	36

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

retardation effects conferred by the metal salts (**10b**,**c**) were superior to that of **12b**,**c**.

Consequently, these results demonstrate that the benzotriazole type UV absorbing compounds containing an amphoteric counter-ion moiety can be applied as effective stabilizers against the photofading of color formers, especially nickel complexes are effective.

4. Conclusions

The chemistry of color formers has recently become important, particularly in connection with the rapid development of information-recording systems and thermochromic systems for a diverse range of applications.

In this study, the influence of various naphthalene derivatives of benzotriazole type UV absorbers capable of acting as amphoteric counter-ions on the photostability of color materials derived from color formers has been investigated on cellulose. The use of UV absorbing compounds was not very beneficial for improving the light fastness of color formers. But a series of hydroxyarylbenzotriazoles bearing a built-in amphoteric counter-ion moiety afforded an excellent degree of protection against the photofading of color formers. The functional UV absorbing compounds discovered in this study may be applied as effective stabilizers against photofading of color formers.

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