Molecular Structures of Colored Forms of Leuco Dye Colored by Phenolic Developers and the Correlation with Decolorable Toner Properties

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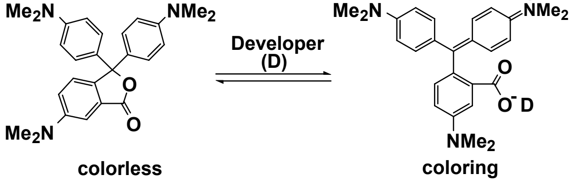
Abstract

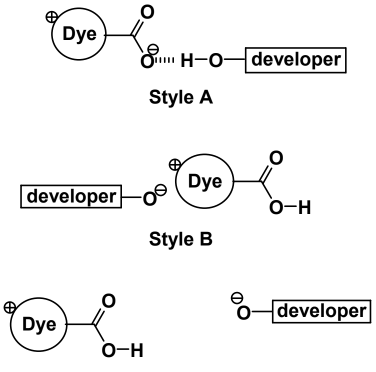
Although the recording system of the leuco dye and phenolic color developer has been employed in practical applications, the basis of colorless-to-coloring thermochromism had not been investigated, which prevented us from controlling the system. We have succeeded in isolating the six colored forms of a leuco dye colored by phenolic color developers and clarified the molecular structures by X-ray crystallography for the first time. It has been revealed that a leuco dye and phenolic developers combined with each other by the hydrogen bond between carboxylate moiety of a leuco dye and OH groups of developers. Correlation with decolorable toner properties and colored-form structures has been revealed; coloring property increases with an increase in the number of hydrogen bonds in colored forms, and erasing property increases with elongating hydrogen bond distance between the leuco dye and developers. Also, a feature of colored forms for toner with both high coloring and erasing properties has been suggested; expansion of hydrogen bond network between colored forms by relatively weak hydrogen bond.

Introduction

The recording system of the leuco dye and phenolic color developer has been employed in practical applications, e.g., thermosensitive recording paper and rewritable paper, owing to its colorless-to-coloring thermochromism [1]. Recently, we have succeeded in applying the system to toner for electrophotography and released a decolorable toner [2]. Images printed using the toner can be turned colorless by moderate heating and the same paper can be used repeatedly. LCA (Life Cycle Assessment) has demonstrated that, compared with using conventional toner, CO_2 emissions are sharply reduced by using decolorable toner [3]. However, compared with conventional toner, the optical density of decolorable toner has been insufficient until now, which prevents the widespread use of this technology. The recording system of the leuco dye and color developer is based on molecular structure change of leuco dye brought about by color developer: electron-donating leuco dye reacts with electron-accepting color developer, yielding a lactone ring-opened zwitterionic colored form (Equation 1). We assumed that the same reversible reaction as Equation 1 was achieved in the production process of decolorable toner and was dominated by colorless state, causing insufficient optical density. That is, a detailed understanding of the reversible reaction of Equation 1 is the key to controlling the system of the leuco dye and phenolic developer. However, product development preceded fundamental research and the basis of Equation 1 had not been clarified; even the molecular structure of colored form had not been confirmed [4]. As shown in Figure 1, colored form of the leuco dye and phenolic developer can take three possible styles of interaction from a viewpoint of developer location; developer combines with leuco dye by hydrogen bonding (Style A), developer exists around leuco dye as a counter anion and there is no fixed location for both dye and developer (Style B), and developer dissociates form leuco dye and freely exist (Style C). Although spectroscopic analyses had supported the Style A [5], there had been no direct evidence by X-ray crystallographic analysis.



(1)



Style A

Style B

Style C

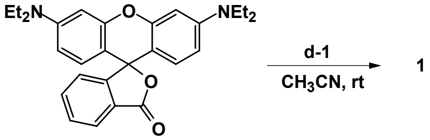
Figure 1. *Possible styles of interaction between the leuco dye and phenolic developer in colored form.*

Recently, we have succeeded in isolating the colored forms of a leuco dye colored by phenolic developers and revealed the molecular structures by X-ray crystallography for the first time. Applying the results to the study of decolorable toner, the correlation with the toner properties has been revealed and a feature of colored-form structure providing toner with both high coloring and erasing properties has been suggested.

Experimental section

Preparation and isolation of colored forms

Colored forms **1**–**6** were obtained as air-stable red crystals by the reaction of rhodamine B base and phenolic developers **d-1**–**d-6** in acetonitrile at room temperature, respectively (Equation 2), and the single crystals suitable for X-ray crystallographic analysis were grown by slow evaporation of acetonitrile solutions [6]. We have selected rhodamine B base as a leuco dye because the colored forms had been reported as metal complexes and salts [4-a, b]. Molecular structures of phenolic developers **d-1**–**d-6** are shown in Figure 2.



rhodamine B base

(2)

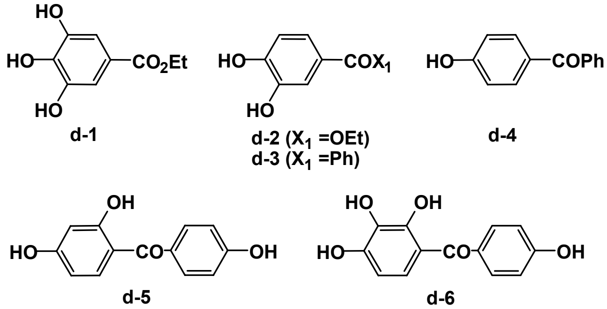


*Figure 2. Phenolic developers for colored form **1**–**6**.*

Measurement of optical density and erase ability of decolorable toner

Coloring and erasing properties of decolorable toner were evaluated by optical density and erasability, respectively. Optical density was measured by colorimeter of color difference formula CR-300 (KONICA MINOLTA) in reflection mode. That is, the higher the optical density, the higher the coloring property. Erasability was defined as Equation 3, where ODer and ODor are given by subtracting optical density of blank paper from those of ghost image after heat-erasing and original image, respectively. That is, the smaller the erasability, the higher the erasing property.

$$\text{erasability} = \text{ODer} / \text{ODor} \qquad (3)$$

Results and discussion

Molecular structures of colored forms

The molecular structures of **1**–**6** were determined by X-ray crystallography and Figure 3 shows the molecular structure of colored form **1** **[7]**. The lactone ring of a leuco dye opened and the benzene ring was almost perpendicular to the xanthene moiety. Bond distances of C–NEt$_2$, 1.352(4) and 1.357(4) Å, were intermediate between those of C$_{\mathrm{aryl}}$–NR$_2$ (C$_{\mathrm{aryl}}$: aromatic carbon atom, R: alkyl group) single bond (1.371 Å) and C$_{\mathrm{aryl}}$=NR double bond (1.346 Å) [8]. The geometry around N atom combined with xanthene moiety was almost planer with the sum of bond angles 359.9 °. Also, C–C bond distances in the xanthene moiety, 1.355–1.430 Å, were intermediate between those of alkane (1.53 Å) and alkene (1.322 Å) [8]. These results show that the double bonds in the xanthene moiety conjugate. The bond distances of C14–O2 and C14–O3 were 1.237 Å and 1.268 Å, intermediate between those of typical C=O bond (1.305 Å) and C–OH bond (1.226 Å) of carboxylic acid [8]. From this result it is suggested that, in colored forms negative charge delocalizes over carboxylate moiety. Table 1 shows O(H)–O bond distances and O–H–O bond angles consisting of carboxylate moiety of a leuco dye and phenolic OH groups of a developer. Each value in Table 1 is classified as that of typical hydrogen bond [9]. The same results are obtained in other colored forms.

From these results, it has been revealed that a leuco dye and phenolic developers combine with each other by the hydrogen bond between the carboxylate moiety of a leuco dye and OH groups of developers, described as Style A in Figure 1.

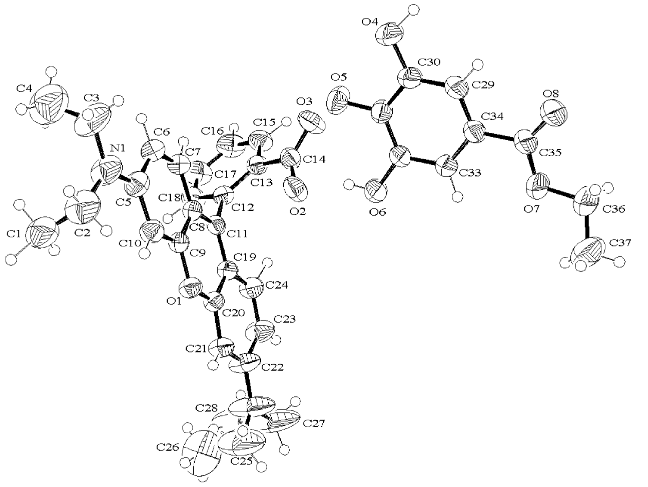


*Figure 3. ORTEP drawing of colored form **1**. Crystal data for **1** (293 K): triclinic; P1̄ (no. 2), Z = 2, R = 8.34%, wR =15.15%.*

Table1 Geometrical parameters for hydrogen bond in 1.

	O3(H)O5	O2(H)O6
O(H)–O distances /Å	2.581(3)	2.603(3)
O–H–O angles /°	159.17	147.40

The basis of colored forms, hydrogen bonding between carboxylate moiety of a leuco dye and OH groups of developers is common among **1**–**6**. Detailed features, the number and the position of hydrogen bonds and existence of other interactions vary among **1**–**6**, as shown in Figure **4**. In colored form **4**, whose developer has only one OH group, a leuco dye combines with a developer by one hydrogen bond. This result shows that one hydrogen bond is enough to hold a colored form. In colored forms **1**–**3**, whose developers have OH groups on 3 and 4-positions successively, hydrogen bonds are formed at two carboxylate oxygen atoms. In colored form, negative charge delocalizes over two carboxylate oxygen atoms. Therefore, for stabilizing colored forms it is more effective to form hydrogen bonds at two carboxylate oxygen atoms. Colored form **1** has its own feature, namely, two colored forms dimerize by the hydrogen bonds between the third OH groups and carbonyl groups of developers. In colored forms **5** and **6**, whose developers have OH groups on two aromatic rings, two carboxylate oxygen atoms form hydrogen bonds with OH groups on two aromatic rings, respectively. In colored form **5**, OH groups on two aromatic rings combine with different leuco dye molecules, respectively, and hydrogen bond network expands infinitely. In colored form **6**, two leuco dyes and two developers combine alternately, providing a cyclic structure. Also colored forms **5** and **6** have a common feature, namely, OH group on 2-position forms intramolecular hydrogen bond with carbonyl group. This result shows that OH group on 2-position does not form hydrogen bond with leuco dye when developer has carbonyl group on 1-position.

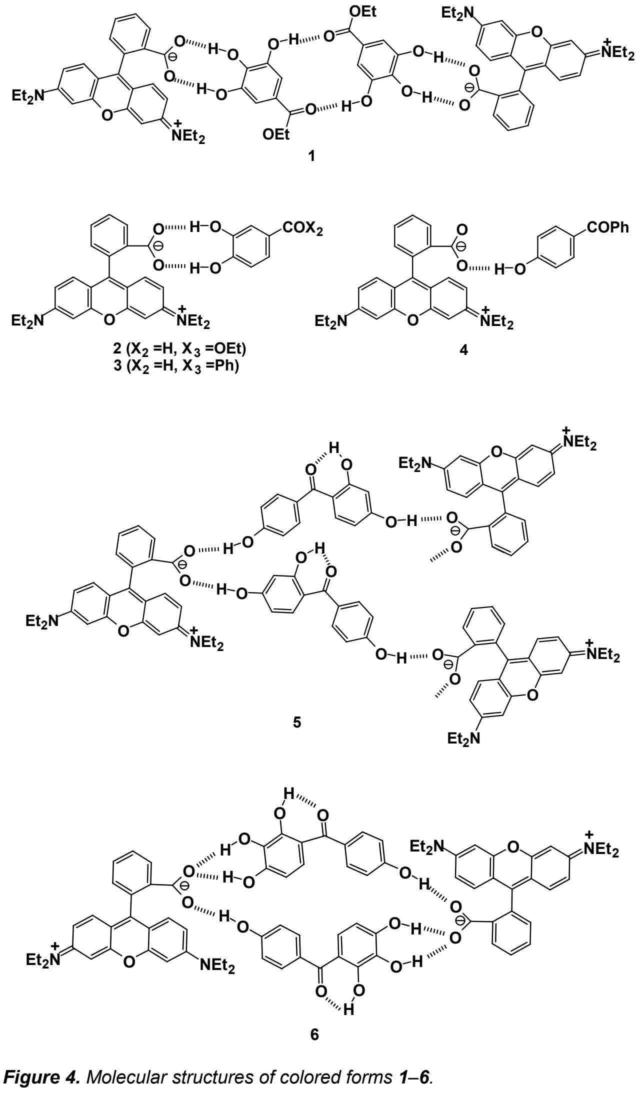


*Figure 4. Molecular structures of colored forms **1–6**.*

Application to toner properties

Correlation between toner properties and colored-form structures

We prepared decolorable toner corresponding to colored forms **1**–**6** and clarified their optical density and erasability, respectively. For measurement of optical density and calculation of erasability, see the experimental section. Table 2 shows selected structural parameters of colored forms **1**–**4**, in which a leuco dye and a developer simply combine, and the corresponding toner properties. The number of hydrogen bonds is that per leuco dye molecule, and distance of hydrogen bond is the average of those between the leuco dye and developer.

Table 2 Toner properties and structural parameters.

	1	2	3	4
The number of hydrogen bonds	3	2	2	1
Distance of hydrogen bond /Å	2.592	2.589	2.551	2.479
Optical density	0.98	0.90	0.89	0.61
Erasability	0.082	0.084	0.092	0.106

From Table 2, the following two features are clarified. First, optical density of toner increases with an increase in the number of hydrogen bonds. This result is explained as follows: the stability of colored form increases with an increase in the number of hydrogen bonds, and colorless-to-coloring equilibrium reaction of leuco dye proceeds toward coloring direction, resulting in the higher optical density. Second, erasability of toner decreases with elongating hydrogen bond distance. In other words, erasing property increases with elongating hydrogen bond distance. The principle of color erasing of decolorable toner is cleavage of bonding between the leuco dye and developers. Thus the correlation between erasing property and bond distance is reasonable.

A feature of colored form for toner with both high coloring and erasing properties

Among six colored forms, colored form **1** has the highest coloring and erasing properties. Colored form **1** has its own feature, namely, colored forms dimerize by the hydrogen bonds between developers. From this result, we assumed that expansion of hydrogen bond network by the hydrogen bond between developers was the key to both high coloring and erasing properties, and compared the toner properties with colored form **5**, in which hydrogen bond network expanded by the hydrogen bond between the leuco dye and developer. Table 3 shows optical density and erasability of toners **1** and **5**, corresponding to colored forms **1** and **5**, respectively. Optical density of toner **5** is as high as that of toner **1**. This result suggests that expansion of hydrogen bond network among colored forms is important for high optical density of toner, owing to improvement of colored-form stabilization (refer to previous paragraph). On the other hand, erasing property of toner **5** is low compared with that of toner **1**. Figure 5 shows hydrogen bond distances in colored forms **1** and **5**. As shown in Figure 5, the hydrogen bond distance between developers is shorter than those between the leuco dye and developer. From these results, it is suggested that the hydrogen bond between developers does not lower erasing property because the bond strength is relatively weak.

Table3 Toner properties of toner 1 and 5.

	toner 1	**toner 5**
optical density	0.98	0.98
erasability	0.082	0.094

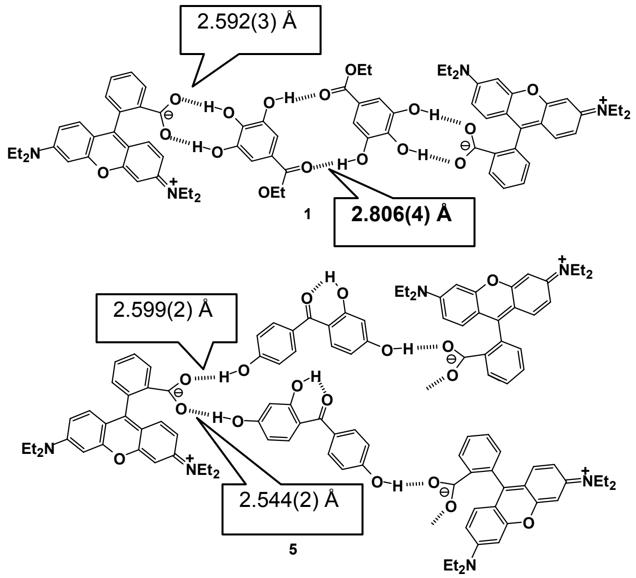


*Figure 5. Comparison of hydrogen bond distances of colored form **1** and **5**.*

Conclusion

We have succeeded in isolating the six colored forms of a leuco dye colored by phenolic color developers and clarified the molecular structures by X-ray crystallography for the first time. It has been revealed that a leuco dye and phenolic developers combined with each other by the hydrogen bond between carboxylate moiety of a leuco dye and OH groups of developers. Correlation with decolorable toner properties and colored-form structures have been clarified; coloring property increases with an increase in the number of hydrogen bonds per leuco dye molecule, and erasing property increases with elongating hydrogen bond distance between the leuco dye and developers. Also, a feature of colored-form structure for toner with both high coloring and erasing properties has been suggested; expansion of hydrogen bond network between colored forms by relatively weak hydrogen bond.

This study elucidates the basis of the leuco dye and phenolic developer system and is applicable to material design at the molecular level.

Acknowledgement

We gratefully acknowledge Professor Z. Mizuguchi of Yokohana National University for his helpful advice and discussion. We are also grateful to Mr. T. Umeki of Sumika Chemical Analysis Service, Ltd. for help with X-ray crystallographic analysis.

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[7] X-ray crystallographic studies were carried out on a Rigaku RAXIS RAPID diffractometer with graphite monochromated Cu-Kα radiation (λ = 1.54187 Å). Single crystals were mounted on top of a glass fiber by gluing. The data were corrected for Lorenz and polarization effects. The structures were solved by direct methods using SIR92. Refinement was carried out by full-matrix least squares methods against F for colored forms **1**–**4** and **6**, against F^2 (SHELXL-97) for colored form **5**. Hydrogen atoms of ethyl groups were placed in geometrically calculated positions and others were located by difference Fourier syntheses for colored forms **1**, **2**, and **5**. For colored forms **3**, **4**, and **6**, all hydrogen atoms were placed in geometrically calculated positions.

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Author Biography

Yumiko Sekiguchi has been a researcher at Corporate Research & Development Center, Toshiba Corporation, since 2004. She received a BSc degree and an MSc degree from Tohoku University in 2002 and 2004, respectively. Her current research interests are leuco dye chemistry and decolorable ink and toner technology.