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The photochromism of nitrospiropyran included in γ-cyclodextrin

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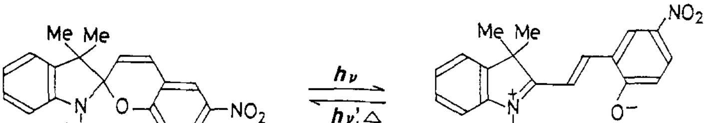
Summary

The inclusion compounds of 1',3',3'-trimethyl-6-nitrospiro-[2H,1-benzopyran-2,2'-indoline] (NSP) with γ-cyclodextrin (γ-CD), 2,3,6-O-permethylated γ-CD (γ-MCD), and naphthyl modified γ-CD (γ-NCD) showed normal photochromism in the solid state with high light sensitivity comparable with that of NSP dispersed in polymer matrices. This is in sharp contrast with NSP in the crystalline state, which is much less photosensitive. These results suggest that the host cavity offers a sufficient free volume for phototransformation of the guest molecule. The colored form of the inclusion compounds were found to be more stable both chemically upon prolonged UV irradiation and thermally in the dark as compared with that in a PMMA film.

Introduction

Organic photochromism is now under extensive investigation. Much attention has been focused on spirobenzopyran which is among popular photochromic compounds (1). The photochromic reaction of this family is the reversible heterolytic cleavage of the pyranyl C(spiro)-O bond, yielding a colored open (PMC) form upon exposure to UV light and colorless closed (SP) form by visible light irradiation or in the dark.



SP **PMC**

This photochromic reaction is significantly influenced by environmental factors such as polarity, viscosity or ionic impurity. The photochromic properties of spirobenzopyrans is not evaluated only in solutions (2), but also in polymer matrices (3) and organized media like liquid crystal (4), micells (5), liposomes (6), or Langmuir-Blodgett films (7). The main purposes of these studies are to regulate the photochromic reaction and/or the thermal reversion process and in turn to use this compound as a microenvironmental probe.

This paper describes the photochromism of 1',3',3'-trimethyl-6-nitrospiro[2H,1-benzopyran-2,2'-indoline] (NSP) included by γ-cyclodextrin (γ-

CD) and modified γ-CDs. The inclusion compounds showed normal photochromism in the solid state with high light sensitivity in sharp contrast with much less photosensitive NSP in the crystalline state.

Experimental

NSP (Tokyo Kasei Co. Ltd.) was purified by recrystallization from ethanol. γ-CD (Tokyo Kasei Co. Ltd.) was used as available. 6-O-(2-Naphthaleneacetyl)-γ-cyclodextrin (γ-NCD) was prepared according to ref (8) and the crude products were used without purification. Octakis(2,3,6-tri-O-methyl)-γ-cyclodextrin (γ-MCD) was kindly given by Prof. Odagiri of the Kumamoto Univ.

The inclusion compounds were obtained as precipitates by mixing an aqueous solution of γ-CDs (1×10^{-3} M;1 M = 1 mol dm^{-3}) and acetone solution of NSP (1×10^{-3} M). The slightly colored powders obtained were washed twice with water and then with methanol and dried in vacuo. The inclusion complexes thus obtained were hardly dissolved in both water and organic solvents.

For evaluating the photochromic property, the sample powder was applied on a white filter paper by pressing with a spatula. The amount of the sample applied was so small that the absorbance of the PMC in the visible region did not exceed 1.0 in the photostationary state. Poly(methyl methacrylate) (PMMA) films containing NSP (5 wt%) were prepared on glass plates from toluene solution using a spinner.

The absorption spectra and discoloration rate were measured by using a Shimadzu UV200 spectrophotometer equipped with an integrating sphere. The circular dichroic spectra were measured with a JASCO J-40 spectrophotometer. The irradiation was done with a 500 W high pressure Hg lamp through suitable combination of color glass filters.

Results and Discussion

Figure 1 shows X-ray diffraction patterns for the inclusion complex of NSP with γ-CD together with those for the host and guest crystals for the sake of comparison. It is clear that the inclusion complex is crystalline in nature, showing different crystalline structure from those of the two parent crystals. No further X-ray structural analysis was done, because we were not able to obtain the monocrystal of the inclusion complex.

Figure 2 shows the circular dichroic spectra of this inclusion complex dispersed in a transparent KBr pellet. Both SP and PMC exhibit a definite induced circular dichroism, supporting the formation of the inclusion com-

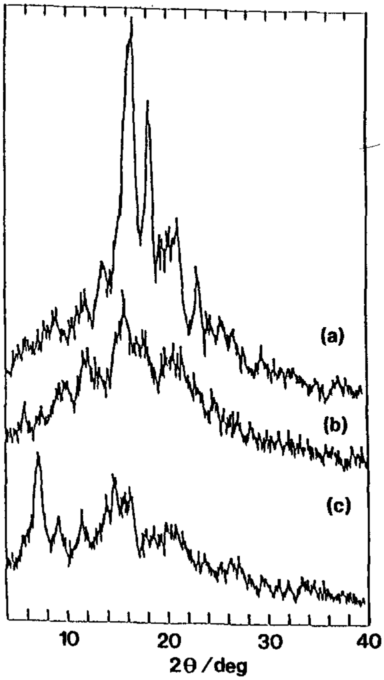


Fig. 1. The X-ray diffraction pattern of the solid powder: (a) NSP, (b) γ-CD, (c) the inclusion complex.

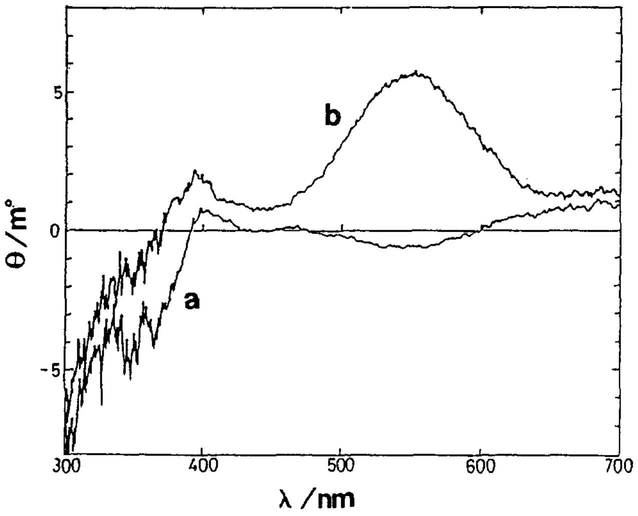


Fig. 2. The circular dichroic spectra of (a) SP and (b) PMC in γ-CD

plex. The absorption in the UV region shows negative circular dichroism, while the absorption of the PMC in the visible region shows positive circular dichroism. Based on the relationship between the rotational strength and relative direction of the transition moment of the guest and the molecular axis of the chiral host, it seems plausible that this inclusion complex has an axial configuration which means that the long axis of the guest is nearly parallel to the molecular axis of the host. The CPK molecular model suggests that the host can include the guest more deeply for less bulky benzopyranyl moiety than for indolyl moiety, though no evidence for molecular configuration has been obtained at this stage of investigation.

Table 1. The absorption maxima (λ_{max}) of PMC in the visible region and the half-life ($\tau_{1/2}$) upon to UV light

	λ_{max}/nm	$\tau_{1/2}$/min
γ-CD	555	90
γ-NCD	555	120
γ-MCD	590	150
PMMA	575	25

The absorption spectra of PMC were dependent on the property of matrices. The value of λ_{max} in the visible region increased in the order of γ-CD, PMMA, and γ-MCD. The results are listed in Table 1. The absorption spectrum in γ-NCD was identical to that in γ-CD. The matrix dependence of λ_{max} may reflect microenvironmental polarity: γ-CD is ascribable to alcohol (λ_{max} = 560 nm), while γ-MCD to hexane (λ_{max} = 590 nm). The half-width of this band for the inclusion complexes was broader than that for the absorption in solutios and in the PMMA film, suggesting the existence of various conformers of PMS in the inclusion complexes. We believe that there are few possibilities for molecular association of the pigment in these inclusion systems.

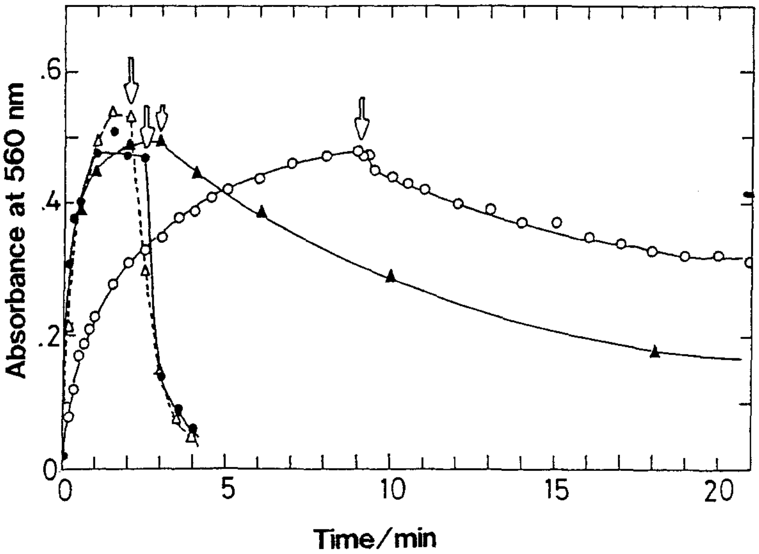


Fig. 3. The photochromic response of NSP: (●) in γ-CD, (▲) in γ-MCD, (△) in PMMA film, and (○) in the crystalline state. The UV light was turned on at time zero. The arrows show the turn-off of the UV light and subsequent turn-on of the visible light.

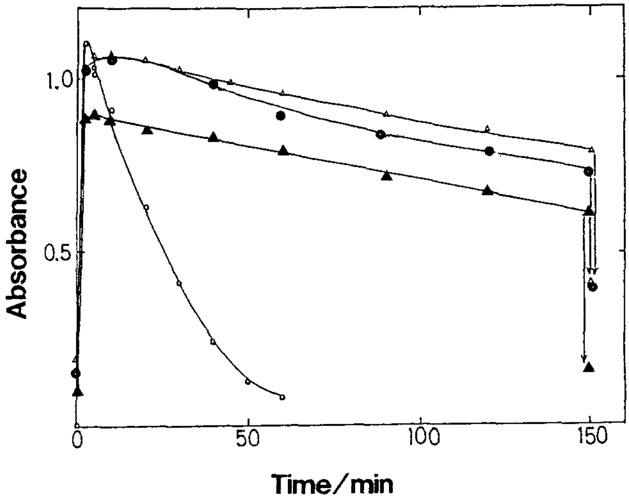


Fig. 4. The photodurability evaluation of NSP upon exposure to the UV light: (●) in γ-CD, (△) in γ-NCD, (▲) in γ-MCD, and (○) in PMMA. The arrows indicate the discoloration brought about reversibly by the visible light irradiation.

Figure 3 shows the absorbance changes of the inclusion complexes at λ_{max} of PMC upon exposure to UV light and subsequently to visible lights. The UV irradiation of the inclusion complex gives rise to PMC with comparable yield to that obtained for the PMMA film. The reversion to SP by the visible light irradiation occurs with high efficiency except for γ-MCD, for which the colored form is relatively stable, and discolored eventually after prolonged irradiation. This is in sharp contrast with much less photoresponsive NSP in the crystalline state. The high performance of photochromic reaction of the inclusion complexes in the solid state can be carried out owing to sufficient free volume supplied by the host cavity.

Figure 4 shows photodurability evaluation of NSP in various matrices upon exposure to the UV light. It is remarkable that the absorbance in the visible region hardly decreases for the inclusion complexes upon prolonged irradiation. This is partly due to irreversible coloration of the samples. Upon UV irradiation, the samples became yellowish or light brownish eventually and could not be discolored by subsequent irradiation with the visible light. The irreversible absorption may arise from fatigue reactions whatever they are. The contribution of the absorption due to reversible coloration was evaluated by subtracting the absorption of irreversible components from the total absorption. The values of the half-life ($\tau_{1/2}$) for the reversible component are listed in Table 1. It is clear that the inclusion by γ-CDs improve the fatigue resistance of the photochromic guest molecule. Recent studies on the photochromic mechanism of NSP in solutions indicate that there are various routs to fatigue, which include photodegradation mainly through the triplet state, photooxydation, discoloration by acidic degradation products, and molecular association in less polar solvents (2). γ-CDs may interrupt some of them to protect the guest from fatigue. The effect appears greatest for γ-MCD in which the irreversible coloration is much less. It seems unlikely that the fatigue is dependent on the environmental polarity of the inclusion complex as in the case of solutions. The naphthyl moiety is a triplet quencher of NSP and convenient for elongating $\tau_{1/2}$. γ-NCD may has such an additional effect.

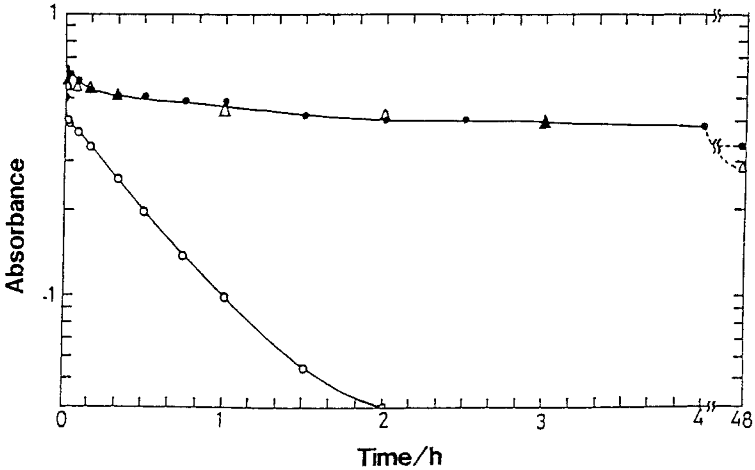


Fig. 5. The thermal discoloration of PMC in the dark at room temperature: (●) in γ-CD, (△) in γ-MCD, and (○) in PMMA film.

Figure 5 shows thermal discoloration in the dark. The colored form of the inclusion complex is significantly stable in the dark. This may be the consequence that the configuration of the colored form has a good fit with the host cavity. Thus, NSP in the inclusion complex is stabilized spatially in the host cavity for both SP and PMC configurations.

Conclusively, the inclusion complexes of NSP with γ-CDs showed normal photochromism in the crystalline solid state, being chemically and thermally stable. These inclusion complexes can be used as insoluble photochromic pigment with considerably high photodurability.

References

1. Bertelson R-C (1971) Photochromic processes involving heterolytic cleavage. In: Brown G-H (ed.) Photochromism. Wiley-Interscience, New York.
2. (a) Sakuragi M, Aoki K, Tamaki T, Ichimura, K, Aoki K (1990) Bull Chem Soc Jpn 63: 74, (b) Tamaki T, Sakuragi M, Ichimura K, Aoki K (1989) Chem Phys Letters 161: 23
3. (a) Horie K, Tsukamoto M, Mita I (1985) Eur Polym J 21: 805, (b) Kryszewski M, Nadolski B, North A-M, Pethrick R-A (1980) J Chem Soc Faraday Trans II 76: 351
4. (a) Ramesh V, Labes M-M (1987) J Am Chem Soc 109: 3228, (b) Cabrera I, Krongauz V, Ringsdorf H (1988) Mol Cryst Liq Cryst 155: 221
5. Tazuke S, Kurihara S, Yamaguchi H, Ikeda T (1987) J Phys Chem 91: 249
6. (a) Sunamoto J, Iwamoto K, Mohri Y, Kominato T (1982) J Am Chem Soc 104: 5502, (b) Nadolski B, Uznanski P, Kryszewski M (1984) Makromol Chem Rapid Commun 5: 327, (c) Seki T, Ichimura K (1989) J Colloid Interface Sci 129: 353
7. (a) Polymeropoulos E-E, Mobius D (1979) Ber Bunsenges Phys Chem 83: 1215, (b) Morin M, LebLanc R, Gruda I (1980) Can J Chem 58: 2038, (c) Ando E, Miyazaki J, Morimoto K, Nakahara H, Fukuda K (1985) Thin Solid Films 133: 21
8. Ueno A, Tomita Y, Osa T (1983) Chem Lett: 1635

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