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Cis/Trans Isomerization of Thioindigo Derivatives Adsorbed on Silica Gel Modified with Octadecyl Groups

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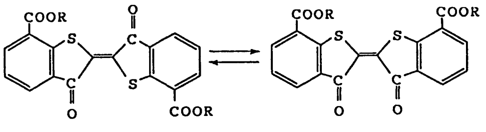
Synopsis. A photochromic behavior based on the cis/trans isomerization of thioindigo derivatives (**I**) adsorbed on alkylated silica gel is described. The reversible cis/trans isomerization of **I** in the adsorbed state can be induced by irradiation, and the signal is read out as fluorescence. The thermal cis-to-trans isomerization of **I** adsorbed on modified silica gel is extremely slow, compared with that obtained on untreated silica gel.

The use of silica gel, alumina, and zeolite as a support for photoreactive compounds has received attention recently.[1,2] Part of this interest is derived from the fact that the reactivity of many compounds adsorbed onto inorganic supports is vastly different from that in solution. Physicochemical perturbations on the photoreactivity are those introduced by adsorption as well as inclusion or intercalation. Our interest lies in the study of the effective reversible photoisomerization of photochromic dyes on the solid surface. In the earlier paper, we reported the photoreversible isomerization and the promoted thermal cis-to-trans conversion of a thioindigo dye adsorbed on silica gel when dipped in cyclohexane.[3] When the dye is in strong adhesion with silica gel, it scarcely undergoes photoisomerization, suggested by the earlier experiment. We assume that weakening such strong interaction will lead to the facile photoisomerization on the solid surface as well as in hydrophobic solvent.

We describe here the photochemical behavior and thermal kinetics of the 7,7′-substituted thioindigo dyes (**1a**—**1g**) adsorbed on alkylated silica gel obtained by the diffuse reflection method. The photochromic properties of (**I**) adsorbed on alkylated silica gel have also been compared with those of (**I**) on untreated silica gel and in solution.



trans-(I) cis-(I)

R= $(CH_2CH_2O)_m$-C_nH_{2n+1}

(Ia) m=1 n=1, (Ib) m=1 n=4, (Ic) m=0 n=12, (Id) m=1 n=12,
(Ie) m=2 n=12, (If) m=3 n=12 (Ig) m=4 n=12

Scheme 1.

Experimental

General. UV spectra were obtained by using a Hitachi UV-3410 spectrophotometer and an Ohtsuka Denshi MCPD-100 spectrophotometer. The fluorescence of the trans thioindigo dyes was detected through a color filter by a Shimadzu RF-5000 fluorescence spectrophotometer. The solvents (cyclohexane and chloroform) used in taking the spectra were spectroanalytically pure. Diglyme was purified by distilling it twice under reduced pressure before use. Seven kinds of thioindigo dyes (**1a**—**1g**) used in the experiments of adsorption and isomerization were synthesized by the esterification of 7,7′-bis(chlorocarbonyl)thioindigo with the corresponding alcohols.[4] HRMS for dyes (**I**) produced were as follows, (**1a**), HRMS Calcd for $C_{24}H_{20}O_8S_2$: M, 500.0600, Found: *m*/*z* 500.0590; (**1b**), HRMS Calcd for $C_{30}H_{32}O_8S_2$: M, 584.1539, Found: *m*/*z* 584.1537; (**1c**), HRMS Calcd for $C_{42}H_{56}O_6S_2$: M, 720.3518, Found: *m*/*z* 720.3511; (**1d**), HRMS Calcd for $C_{46}H_{64}O_8S_2$: M, 808.4043, Found: *m*/*z* 808.4033; (**1e**), HRMS Calcd for $C_{50}H_{72}O_{10}S_2$: M 896.4567, Found: *m*/*z* 896.4542; (**1f**), HRMS Calcd for $C_{54}H_{80}O_{12}S_2$: M 984.5091, Found: *m*/*z* 984.5109. Calcd for $C_{58}H_{88}O_{14}S_2$, (1g): C, 64.90; H, 8.26%. Found for (1g): C, 64.38; H. 8.10%. Silica gel (silica gel 70 Plate-Wako/glass plate) used as adsorbent was activated by heating in an oven at 120 °C for 3 h. Alkylated silica gel was prepared by the reaction of octadecyltrichlorosilane (ODS) with activated silica gel in a mixture of chloroform and carbon tetrachloride. Silica gel/glass plates used in these experiments were cut in the size of 10×20 mm.[5] Dyes were anchored on ODS-modified silica gel from the diglyme-water solution (95:5 v/v, 1.0×10^{-5} mol dm^{-3}) and on untreated silica gel from chloroform solution (1.0×10^{-5} mol dm^{-3}). The electronic spectra of I adsorbed on untreated silica gel were obtained by the immersion method in cyclohexane and the fluorescence spectra, by the diffuse reflection method through a color filter (Toshiba color filter O-55) by scanning with excitation light (535 nm). Trans-to-cis and cis-to-trans isomerization of I adsorbed on ODS-modified silica gel were performed by irradiating with 535 nm and 480 nm light, respectively. The light source was a 150 W Xe lamp equipped with RF-5000 spectrophotometer.

Kinetics for Thermal Cis-to-Trans Isomerization of Dyes (I). The trans isomers of **I** on untreated silica gel (dipped in cyclohexane) or on ODS-modified silica gel were converted to the corresponding cis isomers upon irradiation with filtered light (λ>540 nm). Thermal isomerization of the cis-isomers adsorbed on untreated silica gel was followed spectrophotometrically in cyclohexane by increasing the trans isomers, whereas the thermal conversion of the cis isomers adsorbed on ODS-modified silica gel was measured according as the fluorescent intensity of the trans isomers at 577 nm (E_x=535 nm).

Results and Discussion

A solution of **I** in chloroform has the intense absorption band (for example, log ε=4.10 at 537 nm for the trans isomer of **1g**) (Fig. 1) and has the clear-cut emission band (E_m=578 nm, E_x=535 nm for the trans

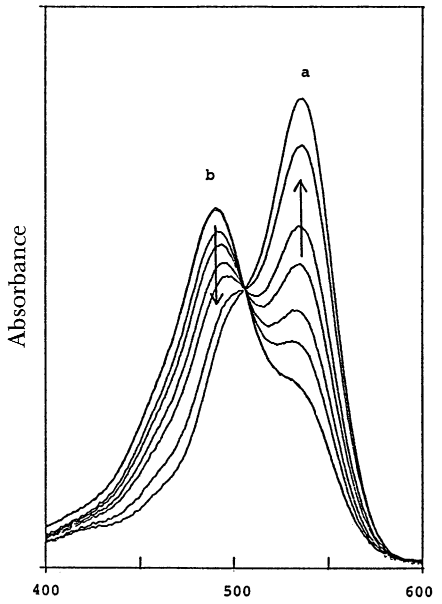


Fig. 1. Absorption spectra of **1g** in $CHCl_3$; (a) *trans*-**1g**, (b) *cis*-**1g**. The thermal cis-to-trans isomerization is shown by the arrow.

isomer of **1g**). The transformation from the trans form to the cis form of **I** was instantaneous when irradiated with 540 nm light ($\log\varepsilon=4.0$ at 490 nm for the cis isomer of **1g**). The fluorescence spectrum of the trans isomer was found, whereas no such spectrum for the cis isomer was observed. The photochromic phenomenon was observed only in case of dyes (**I**) adsorbed on untreated silica gel dipped in cyclohexane,[3] but no photoisomerization occurred when in the dry state. The absorption of **I** adsorbed on untreated silica gel was observed in longer wavelength ($\lambda_{max}=548$ nm for the trans isomer of **1g**), also the fluorescence appeared at the longer wavelength region (590—600 nm). Since the absorption is based on the π-π^* transition, the red shift suggests that the dye adsorbed on untreated silica gel is placed in the more polar surroundings.

Unfortunately, we failed to get the electronic spectrum of **I** because of less uptake by modified silica gel. Thus, the presence of **I** adsorbed on ODS-modified silica gel was confirmed by the fluorescence of the trans isomer.[6] The fluorescence spectra of the trans isomers were obtained as emmision at 577 nm by excitation of 535 nm light (Fig. 2), which is in agreement with that of the trans isomer in chloroform. On exposure to 535 nm light the fluorescent intensity of *trans*-**I** adsorbed on ODS-modified silica gel was gradually reduced (Fig. 2. a→b→c), reversely upon irradiation with 480 nm light, the fluorescent intensity was recovered (Fig. 2. c→a). The variation of fluorescence intensity of the trans isomer is demonstrated by repeated irradiation at 535 nm and 480 nm (Fig. 3), which may correspond to on-off signal of information. Untill now we could not determine the quantum yield for the trans-to-cis and cis-to-trans isomerization, because we did not know the absorption coefficients of adsorbed **I**. However, their ratios ($\phi_{t\to c}/\phi_{c\to t}$) were estimated to be in the range of 0.2—0.3 (0.29 for **1g**) from their fluorescent intensity of photostationary state and values of $\varepsilon_t/\varepsilon_c$ of dyes in chloroform, by using the equation $[cis]/[trans]=(\phi_{t\to c}/\phi_{c\to t})(\varepsilon_t/\varepsilon_c)$.

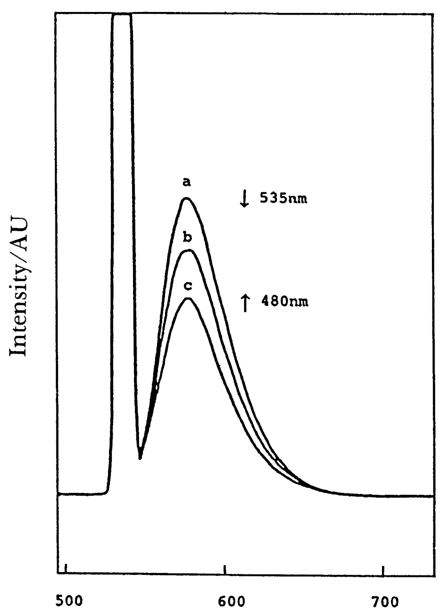


Fig. 2. Fluorescence spectra of **1g** adsorbed on ODS-modified silica gel; ↓: upon irradiation at 535 nm, ↑: upon irradiation at 480 nm. E_x=535 nm, E_m=577 nm.

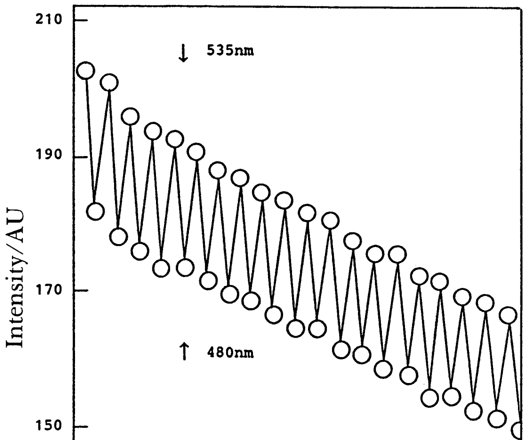


Fig. 3. Repetition characteristics of **1g** adsorbed on ODS-modified silica gel by alternate irradiation at 535 and 480 nm. E_x=535 nm, E_m=577 nm.

The cis isomer, thermodynamically less stable, can be thermally or catalytically converted to the trans-isomer. The surface of ordinary silica gel is characterized by the presence of silanol groups having the acidic property, which enhanced the isomerization.[3]

The thermal isomerization of **I** dissolved in chloroform proceeded at the relatively lower rate (for example, $k(20\,°\mathrm{C})=1.52\times10^{-6}\,\mathrm{s}^{-1}$ for **1g**), whereas the thermal isomerization of **I** adsorbed on untreated silica gel (dipped in cyclohexane) occurred quite rapidly ($k(20\,°\mathrm{C})=4.0\times10^{-3}\,\mathrm{s}^{-1}$). This is because of the characteristic effect of silanol groups. Hence, one can expect the retardation of thermal isomerization by protecting the silanol group on silica gel. The rate of thermal isomerization of **I** adsorbed on such silica gel was reduced (for example, $k(20\,°\mathrm{C})=1.28\times10^{-6}\,\mathrm{s}^{-1}$ for **1g**).

The dyes (**I**) are strongly adsorbed on untreated silica gel from chloroform solution by chemisorption owing to hydrogen bond and dipole-dipole interaction, which shifts the $\lambda_{\max}$ of both absorption spectrum and the fluorescent spectrum to the longer wavelength, $\lambda_{\max}=548$ nm and $\lambda_{\max}=600$ nm respectively, for **1g**. In contrast, the adsorption of **I** on ODS-modified silica gel is supposed to be physical adsorption because the fluorescent wavelength of **I** adsorbed on ODS-modified silica gel was almost the same as that of **I** dissolved in chloroform. Though there is no significant difference for the spectral data, the facile interconversion and the retarded dark reaction of (**1a**—**1g**) used, the amount of dyes (**I**) adsorbed on ODS-modified silica gel varied depending upon R groups. Amongst the dyes (**1f**) and (**1g**) showed the most favorable adsorption, judging from their relative fluorescent intensity (Table 1). On adsorption, octadecyl group on silica gel may fit the hydrophobic dodecyl group linked to the flexible oxyethylene chain. Finally, the thioindigo dyes adsorbed on ODS-modified silica gel were reversibly isomerized in the dry state upon irradiation and the thermal stability of the cis isomers were gained.

Table 1. Relative Fluorescent Intensity of Dyes (**1a**—**1g**) Adsorbed on ODS-Modified Silica Gel from Diglyme-Water (95 : 5 v/v, 1.0×10^{-5} mol dm^{-3}). $E_x=535$ nm, $E_m=577$ nm

Dyes	Fluorescent intensity	
	AU	Rel. ratio
1a	231.2±14.9	1.2
1b	235.0±20.5	1.2
1c	190.6±1.9	1.0
1d	249.5±13.1	1.3
1e	356.1±42.8	1.9
1f	496.7±47.7	2.6
1g	448.0±42.6	2.4

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