# Control of the Association of Indolylfulgimide with Bis(acylamino)pyridine by Photochromism

**Tomoyuki Okuyama, Yayoi Yokoyama,† and Yasushi Yokoyama***

Department of Advanced Materials Chemistry, Graduate School of Engineering, Yokohama National University,
79-5 Tokiwadai, Hodogaya-ku, Yokohama, 240-8501

†Department of Home Economics, Faculty of Home Economics, Tokyo Kasei Gakuin University,
2600 Aihara-cho, Machida, Tokyo, 194-0292

(Received May 16, 2001)

While the association constant of the colored form of a thermally irreversible photochromic indolylfulgimide with 2, 6-bis (octanoylamino)pyridine in toluene at 21 °C was 156 ± 11 $\mathrm{mol^{-1}\,dm^3}$ through triplex hydrogen bonding, that of its colorless form, generated by visible-light irradiation, was increased to 885 ± 63 $\mathrm{mol^{-1}\,dm^3}$. This result was supported by PM3 semiempirical molecular–orbital calculations that the difference of the association constants between the *C*-form and the *E*-form was mainly due to differences in the structures and conformations of the imide moiety.

Photochromic compounds change their structures and electronic properties reversibly upon photoirradiation.[1–3] It is expected that the reversible changes of these properties can switch the functions of not only the photochromic molecules, themselves, but also the properties of the materials surrounding the photochromic molecules, by photoirradiation.

Fulgides are known to be the most studied thermally irreversible photochromic compounds throughout the 20th century.[4] Fulgimides, having the imide moiety instead of the acid anhydride moiety of fulgides, seem to be the most useful derivatives to attach an additional functional group to photochromic fulgide through the imide nitrogen atom.[5] Although a number of *N*-alkyl and *N*-aryl derivatives have been synthesized, the N–H imide was synthesized only as the synthetic intermediate.[5b]

Control of the association of guest chemical species with photochromic host fulgide derivatives by light has been demonstrated several times.[6,7] Other photochromic compounds possessing a crown-ether moiety, which can incorporate guest chemical species mainly with electrostatic interactions, have appeared frequently.[8] However, none has been studied so far to control the hydrogen-bonding ability of fulgide derivatives by photoirradiation.[9]

We report here on the control of the hydrogen-bonding ability of a thermally irreversible photochromic compound by photoirradiation, using an indolylfulgimide **1**, which can form triplex hydrogen bonds with a 2,6-bis(acylamino)pyridine.

## Results and Discussion

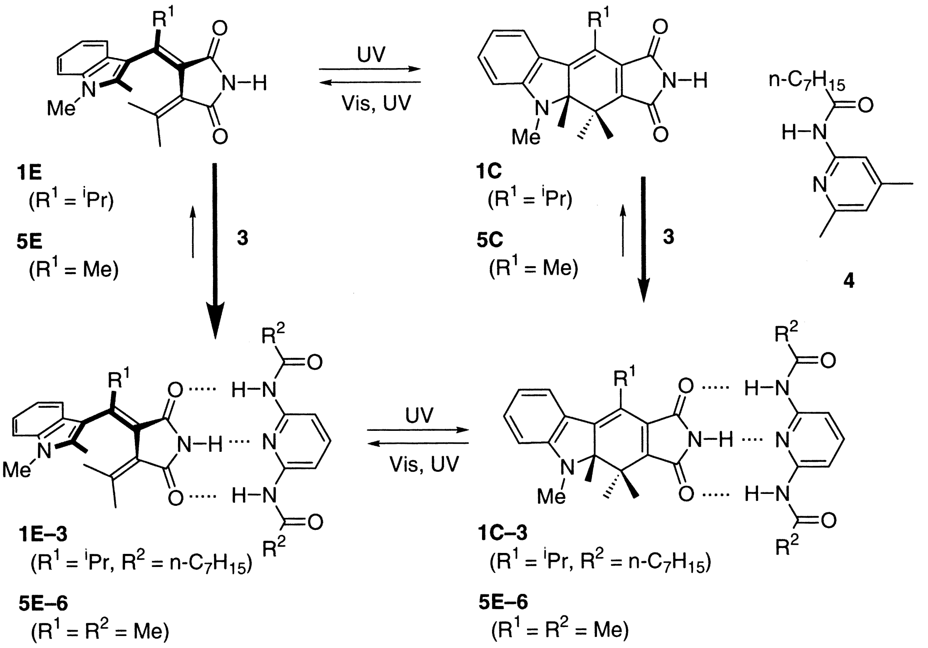
**Strategy of This Study.** The indolylfulgimide **1** can be easily prepared from the parent indolylfulgide **2**.[10] The isopropyl groups of **1** and **2** prohibit the formation of the *Z*-forms during UV-light irradiation due to steric congestion of the *Z*-forms. Because the imide group of **1** would work as an array of hydrogen-bond-acceptor, -donor, and -acceptor, an organic molecule possessing the complementary array of hydrogen-bond-donor, -acceptor, and -donor should have potential to associate with **1** through triplex hydrogen bonds.

The colorless form **1E** has the bismethylenesuccinimide moiety. Upon UV-irradiation, **1E** changes to the colored **1C**, which possesses the maleimide moiety. While the conjugation of π-system of the *E*-form is prevented by the steric congestion of the substituted bismethylenesuccinimide moiety, the planar *C*-form fully enjoys conjugation of the π-system.[10] In Addition, the structure, such as the planarity of imide moiety, particularly of the hydrogen-bond-forming sites, may differ substantially between **1C** and **1E**. Because the electronic as well as the steric properties of both isomers are thus different, the ability of association with other molecules may differ greatly. We chose 2,6-bis(octanoylamino)pyridine **3** and 2,4-dimethyl-6-octanoylaminopyridine **4** as counterparts of the hydrogen-bond-based association with **1**, and compared the results with that for **2** with **3** (Scheme 1).

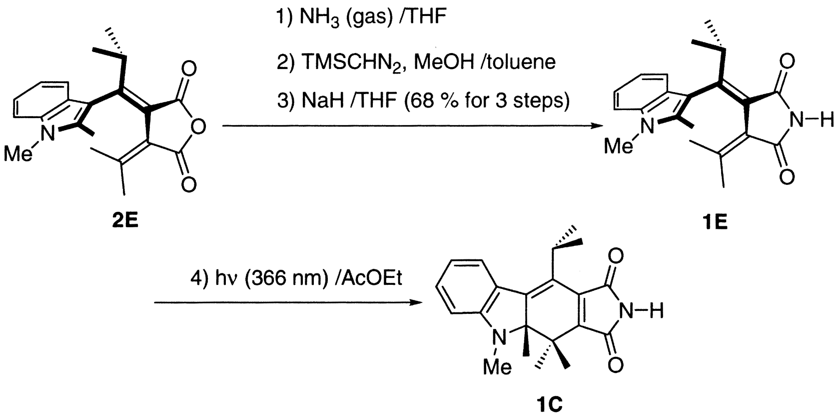
**Synthesis.** The synthesis of **1** was carried out as shown in Scheme 2. Ammonolysis of the indolylfulgide **2E**,[10] followed by esterification with (trimethylsilyl) diazomethane, afforded a position mixture of ester amides. The treatment of a mixture with sodium hydride afforded the indolylfulgimide **1E**. Its colored form **1C** was obtained from **1E** by 366-nm light irradiation in ethyl acetate.

Bis- and mono-octanoylaminopyridines **3** and **4** were synthesized by acylation of the corresponding di- and monoaminopyridines.

**Determination of Number of Associating Species.** When equal amounts of **1C** or **1E** and **3** were dissolved in $CDCl_3$, large downfield shifts of all of the N–H protons of fulgimide and acylpyridine were observed by the $^1H$ NMR spectra (Table 1). It is thus recognized that these N–H protons were involved in complexation. From the magnitude of the shift, the association constant of **1E** was supposed to be larger



Scheme 1.



Scheme 2. Synthesis of **1E** and **1C**.

Table 1. The Chemical Shifts of N–H Protons of **1** and **3** in $CDCl_3$

| | *C*-form | | *E*-form | |
|---|---|---|---|---|
| | $\delta_{N\text{–}H}$ (imide) | $\delta_{N\text{–}H}$ (amide) | $\delta_{N\text{–}H}$ (imide) | $\delta_{N\text{–}H}$ (amide) |
| **1** | 6.91 | | 7.90 | |
| **3** | | 7.52 | | 7.52 |
| Mixture | 8.18 | 7.88 | 9.88 | 8.52 |

than that of **1C**. On the other hand, little shift of the N–H protons of **3** was observed for a mixture of **2C** or **2E** and **3**, indicating that both **2C** and **2E** do not form stable complexes with **3**.

It seemed to be apparent that one molecule of **1** and one molecule of **3** formed triplex hydrogen bonds. To confirm this, a Job's plot[11] was examined for **1** and **3**. As shown in Figs. 1a and 1b, both **1C** and **1E** showed the largest deviation of absorption at 393 nm and 620 nm, respectively, when **1** and **3** are mixed in an equal amount in toluene at 21 °C. In addition, the change in spectra showed isosbestic points. These results proved that both **1C–3** and **1E–3** formed one-to-one complexes. Similar results were also obtained for the complexes of **1** and **4**.

**Association Constants.** The association constants of **1C** or **1E** and **3** or **4** were determined by Nagakura–Baba's method[12] using the shift of the absorption maximum wavelength in toluene according to the change in the ratio of fulgimide and acylaminopyridine. Table 2 lists the results.

The association constants of **3** are larger than that of **4**. This is a natural deduction that the triplex hydrogen bonding is stronger than the duplex hydrogen bonding.

The association constants of **1E** are larger than that of **1C**. An explanation for the difference is discussed later along with the results of MO calculations.

The photochemical change in the structure from **1C** to **1E** induced a dramatic change in the association constant. When **1C** (concentration $1.0 \times 10^{-3}$ mol $dm^{-3}$) and **3** ($1.0 \times 10^{-3}$

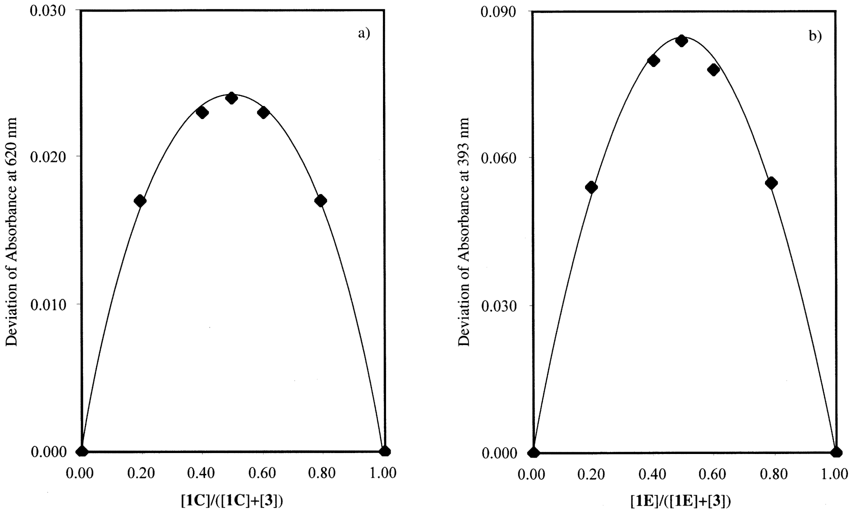


Fig. 1. Job's plots of a) **1C** and **3** and b) **1E** and **3** at 21 °C. The sum of concentration of **1** and **3** was kept at $4.76 \times 10^{-4}$ mol dm$^{-3}$.

Table 2. Association Constants $K_a$ of **1** with Guest Molecules in Toluene at 21 °C

| | *C*-form | *E*-form |
|---|---|---|
| **1** and **3** | 156 ± 11 | 885 ± 63 |
| **1** and **4** | 62 ± 12 | 132 ± 3 |

Table 3. Absorption Spectral Data of **1C** and **1E** in Toluene at 21 °C

| | $\lambda_{max}$/nm ($\varepsilon_{max}$/mol$^{-1}$ dm$^3$ cm$^{-1}$) | |
|---|---|---|
| | *C*-form | *E*-form |
| **1** | 543 (5650) | 362 (4700) |
| **1** with **3** | 560 (5570) | 372 (5400) |
| **1** with **4** | 550 (5380) | 364 (5180) |
| **2** | 574 (6180) | 385 (4790) |
| **2** with **3** | 574 (6040) | 385 (4830) |

mol dm$^{-3}$) are present in a toluene solution at 21 °C, the ratio of free **3** (not complexing with **1C**) is calculated to be 88%. When the solution is irradiated by visible light to change all **1C** to **1E**, the ratio of free **3** should become 64%. Similarly, when **1** (concentration $1.0 \times 10^{-2}$ mol dm$^{-3}$) and **3** ($1.0 \times 10^{-2}$ mol dm$^{-3}$) are present, the ratio of free **3** is calculated to be 54% and 28% when the fulgimide takes the form of **1C** or **1E**, respectively. Thus, the concentration of free chemical species, such as **3**, that forms triplex hydrogen bonds with the fulgimide **1**, can be altered by photoirradiation.

Contrary to the results for **1** and **3** or **4**, almost no spectral change was observed for the combination of **2** and **3**, indicating again that there was little interaction between **2** and **3**.

**Spectral Properties of 1 in the Absence and Presence of Guest.** The UV-vis spectroscopic properties of **1** in the absence and presence of **3** or **4**, and of **2** in the absence and presence of **3** are shown in Table 3. The absorption maximum of isomers of **1** are 20 to 30 nm shorter than those of corresponding isomers of **2**. It is explained that because the carbonyl groups of imides are less electron-withdrawing than the carbonyl groups of acid anhydrides, the nature of intramolecular charge transfer for **1** is weakened.

Even in the presence of 100 eq of **3**, **2** showed little change compared to the spectrum without **3**. This demonstrates that there is little electronic interaction between **2** and **3** in toluene. It seems that they can never form stable duplex hydrogen bonds because of the repulsion of the lone pairs of anhydride oxygen of **2** and pyridine nitrogen of **3**.

To the contrary, in the presence of **3** (100 eq) or **4** (830 eq), **1** exhibited a certain bathochromic shift of absorption. The shift was larger for **3**, forming triplex hydrogen bonds, than **4**, forming duplex hydrogen bonds. Because the electron-withdrawing ability of the carbonyl groups of **1** was increased by the hydrogen bonds, the absorption maximum of **1** shifted to a longer wavelength.

**Photochromic Properties of 1 in the Absence and Presence of Guest.** Similar to the indolylfulgide **2** possessing an isopropyl group, **1** showed a photochromic reaction that does not involve the formation of the *Z*-isomer in toluene. All of the quantum yields of **1** are larger than **2**. However, the ratio **1C**/**1E** is smaller than **2C**/**2E** at the photostationary state of 405-nm light irradiation, because of the largeness of the molar-absorption coefficient of **1C** compared to **1E** at 405 nm.

The photoreaction of **1** in the presence of an excess amount of **3** (100 eq) or **4** (830 eq) was carried out in toluene. The quantum yields of photoreactions are summarized in Table 4.

All of the quantum yields of the photoreactions of **1** were decreased in the presence of **3** or **4**. They decreased more in

Table 4. Quantum Yields of Photoreactions of **1** and **2** in Toluene at 21 °C

| | 405-nm light | | Visible light | *C*:*E*[a] |
|---|---|---|---|---|
| | $\Phi_{EC}$ | $\Phi_{CE}$ | $\Phi_{CE}$ | |
| **1** | 0.62 | 0.52 | 0.11[b] | 68:32 |
| **1** with **3** | 0.46 | 0.34 | 0.060[b] | 78:22 |
| **1** with **4** | 0.58 | 0.36 | 0.11[b] | 78:22 |
| **2** | 0.23 | 0.31 | 0.054[c] | 81:19 |
| **2** with **3** | 0.41 | 0.65 | 0.061[c] | 76:24 |

a) At photostationary state of 405-nm light irradiation.
b) 554-nm light irradiation. c) 608-nm light irradiation.

the case of **3**. We have previously clarified that the introduction of an electron-donating substituent on the indole ring of the indolylfulgide made the quantum yields smaller.[13] Because the formation of the hydrogen bonds on carbonyl groups enhanced their electron-withdrawing ability, it imposed a similar effect on **1C** and **1E** to reduce the quantum yields.

While it has been concluded that **2** does not form a complex with **3**, the quantum yields of the photoreactions of **2** in the presence of **3** are much larger than that in the absence of **3**. It has been well documented that the quantum yields become smaller when the polarity of the media, which is measured by dielectric constants for example, increases;[14] thus, the observed change is not due to a change in the polarity. Because the spectral change of **2** upon the addition of **3** was small, an unexpected interaction between **2** and **3** may be working.

**Semiempirical MO Calculation.** PM3 semiempirical molecular orbital calculations[15] were carried out to assess the association constants of **5** with **6**, which are the model molecules of **1** and **3**, respectively. The change in the heat-of-formation before and after complexation proved that, whereas the stabilization by complexation of **5C** with **6** is $-11.8$ kJ mol$^{-1}$, that of **5E** with **6** is $-18.1$ kJ mol$^{-1}$. The results are summarized in Table 5. It is in good accordance with the magnitude of the observed association constants, when the entropy terms of non-complexed and complexed forms of **5C**, **5E**, and **6** are neglected (or cancelled). The calculated association constants for them at 25 °C are also listed in Table 6, and the PM3-optimized structures of the complexes are shown in Fig. 2.

Table 7 gives the electron density of the atoms that participate in the formation of hydrogen bonds (Chart 1). As can be deduced from Table 7, the origin of the difference of association constants is not an electronic effect, because only a little difference in electron density was found for the atoms concerning the hydrogen bonds.

Instead, a notable change of planarity of the imide group was observed, as proved by the dihedral angles of the imide moiety, as shown in Table 8. As for the **5C–6** complex, the dihedral angles of two O–C–N–H moieties of **5C** are substantially twisted in opposite helicity to each other. On the other hand, in the **5E–6** complex, the hydrogen-bond-relating groups lie almost in one plane. Because the C(3)–C(4) bond is a single bond, it can rotate to adjust the position of the relevant atoms to be suitable for the hydrogen bonding. Therefore, while the arrangements of the atoms composing each hydrogen bond of **5C–6** are apparently doglegged, those of **5E–6** lie in almost straight lines.

Table 5. PM3-Calculated Difference of Heat-of-Formation Values of **5** and **6** and the Complexes

| | *C*-form | *E*-form |
|---|---|---|
| $\Delta H$ of **5**/kJ mol$^{-1}$ | $-119.4$ | $-116.9$ |
| $\Delta H$ of **6**/kJ mol$^{-1}$ | $-261.2$ | |
| ($\Delta H$ of **5** + $\Delta H$ of **6**)/kJ mol$^{-1}$ | $-380.6$ | $-378.1$ |
| $\Delta H$ of complex/kJ mol$^{-1}$ | $-392.4$ | $-396.2$ |
| $\Delta\Delta H$/kJ mol$^{-1}$ | $-11.8$ | $-18.1$ |

Table 6. Comparison of PM3-Calculated and Observed Association Constants $K_a$

| | $K_a$ | |
|---|---|---|
| | *C*-form | *E*-form |
| **5** and **6** (calculated)[a)] | 117 | 1483 |
| **1** and **3** (observed)[b)] | 156 ± 11 | 855 ± 63 |

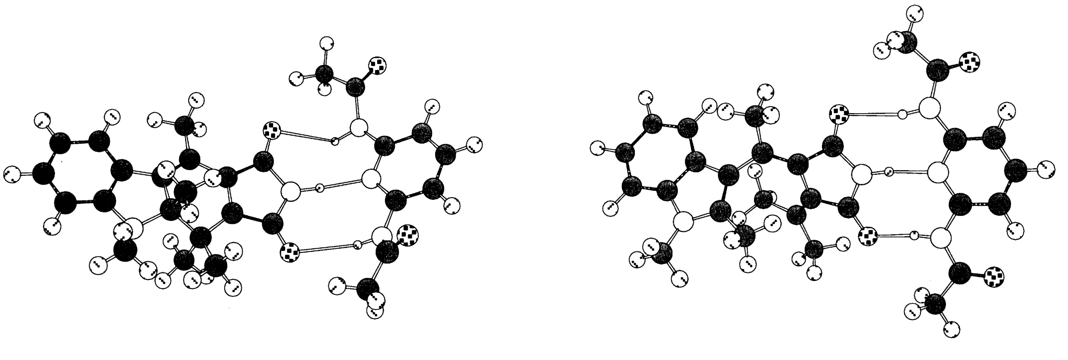
a) At 25 °C. b) At 21 °C.

In addition, the lengths of the hydrogen bonds, particularly H(2)–O(2), are considerably shorter for **5E–6** than that for **5C–6**. Table 9 gives the distances between X and H in X···H–N (X = N or O) in **5E–6** and **5C–6**. This implies that the hydrogen bonds in **5E–6** are stronger than that in **5C–6**.

Thus, the results obtained by MO calculations strongly support the experimentally observed results that the association constant of **1E–3** is larger than that of **1C–3**.

## Conclusion.

A new indolylfulgimide **1** forms a triplex hydrogen bonding one-to-one complex with the bis(acylamino)pyridine **3**. The absorption maximum wavelength of the *E*- and *C*-forms of **1** showed bathochromic shifts when they formed complexes with **3**. The stability of complex **1E–3** is larger than that of **1C–3**. The difference in the stability is not due to the electronic nature of the isomers, but due to the structural difference, particularly the difference between the more flexible bismethylene-



a) **5C** - **6** Complex b) **5E** - **6** Complex

Fig. 2. PM3-optimized structures of **5C–6** and **5E–6** complexes.

Table 7. PM3-Calculated Electron Density of Atoms at Binding Site of **5** and **6**

| | **6** | **5C** | | **5E** | |
|---|---|---|---|---|---|
| | | **5C** Only | Complex | **5E** Only | Complex |
| C(1) | | 0.3006 | 0.3183 | 0.3046 | 0.3226 |
| C(2) | | 0.3017 | 0.3206 | 0.3050 | 0.3264 |
| N(1) | | −0.0934 | −0.1580 | −0.0747 | −0.1358 |
| O(1) | | −0.3056 | −0.3439 | −0.3417 | −0.3718 |
| O(2) | | −0.3075 | −0.3470 | −0.3447 | −0.3960 |
| H(1) | | 0.1174 | 0.1843 | 0.1145 | 0.1873 |
| N(2) | −0.1684 | | −0.1794 | | −0.1784 |
| N(3) | 0.0409 | | 0.0213 | | 0.0089 |
| N(4) | 0.0409 | | 0.0327 | | 0.0211 |
| H(2) | 0.0823 | | 0.1015 | | 0.1453 |
| H(3) | 0.0823 | | 0.0928 | | 0.0973 |

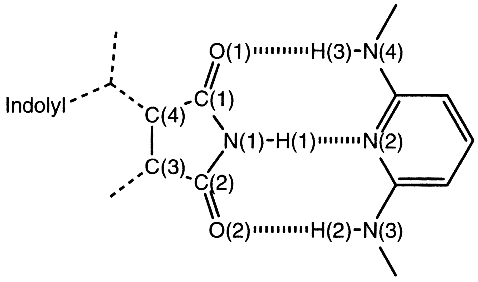


Chart 1. Atom numbering of hydrogen-bonding site.

Table 8. PM3-Calculated Dihedral Angles of Imide Moiety of Complexes **5**

| | **5C** | **5E** |
|---|---|---|
| O(1)–C(1)–N(1)–H(1) | 3.66 | 12.01 |
| H(1)–N(1)–C(2)–O(2) | 7.24 | −13.65 |
| O(1)–C(1)–N(1)–C(2) | −179.97 | −176.76 |
| C(1)–N(1)–C(2)–O(2) | −178.85 | 177.60 |

Table 9. PM3-Calculated Bond- and Hydrogen-Bond-Lengths of 5 and **6**

| | **6** | *C*-form | | *E*-form | |
|---|---|---|---|---|---|
| | | **5** | Complex | **5** | Complex |
| N(1)–H(1) | | 0.995 | 1.027 | 0.995 | 1.028 |
| N(3)–H(2) | 1.000 | | 0.999 | | 1.000 |
| N(4)–H(3) | 1.000 | | 0.999 | | 1.015 |
| H(1)–N(2) | | | 1.864 | | 1.829 |
| H(2)–O(2) | | | 2.440 | | 1.822 |
| H(3)–O(1) | | | 2.567 | | 2.494 |

succinimide in **1E** and the less flexible disubstituted maleimide (or dihydrophthalimide) in **1C**. Because the association constants change dramatically, the concentration of the free bis(acylamino)pyridine in solution can be controlled by photoirradiation.

## Experimental

**General.** $^1$H NMR spectra were recorded with a JEOL JNM-EX-270 (270 MHz) spectrometer in $CDCl_3$. The signals are expressed as parts per million down field from tetramethylsilane, used as an internal standard ($\delta$ value). Splitting patterns are indicated as s, singlet; d, doublet; t, triplet; quint, quintet; m, multiplet. IR spectra were measured using a Perkin-Elmer 1650 FT-IR spectrometer. Low- and high-resolution mass spectra were taken with a JEOL JMS AX-500 mass spectrometer. UV-vis spectra were recorded on a JASCO Ubest-50 UV-vis spectrophotometer. The emission line of 405 nm of a 500 W high-pressure mercury lamp (Ushio Electric) was separated by filters (5-cm water filter, Toshiba UV-35, V-44, and KL-40 glass filters). Monochromatic light beams of the visible region were taken out from a 500 W xenon lamp (Ushio Electric) using filters (554 nm; 5-cm water filter and Toshiba Y-47, IRA-25S, and KL-56 glass filters. 608 nm; 5-cm water filter and Toshiba O-58, IRA-25S, and KL-60 glass filters). The irradiation-light intensity was determined by a photometer (IL-1350, International light Inc.) with a detector (SED038 for 405-, 554-, and 608-nm lights), calibrated with tris(oxalato)ferrate (III) chemical actinometer. The silica-gel column chromatographic separation was carried out with a Merck Kieselgel 60 (230–400 mesh) with a mixture of ethyl acetate and hexane as an eluent. Analytical thin-layer chromatography was performed on Merck pre-coated silica gel 60 F-254, 0.25-mm thick TLC plates. All of the synthetic reactions were carried out under a dry nitrogen atmosphere. Tetrahydrofuran (THF) was freshly distilled from benzophenone ketyl, and diethyl ether and dichloromethane were distilled from $CaH_2$ immediately before use. The calculations were done with PM3 in the CAChe system ver. 3.7 (CAChe Scientific, Inc.) on compounds **5E**, **5C**, and **6**. Calculations were performed on model molecules to reject the local minima due to the rotation of 2-propyl and octanoyl groups.

**Synthesis of (*E*)-3-[1-(1,2-Dimethyl-3-indolyl)-2-methylpropylidene]-4-isopropylidene-2,5 (3*H*,4*H*)-furandione (2).** The synthesis of **2** was described previously.[10]

**Synthesis of Amide Ester 8.** Through a stirred solution of the fulgide **2** (403 mg, 1.19 mmol) in tetrahydrofuran (30 mL) was bubbled $NH_3$ gas at −78 °C until **2** was completely consumed; the mixture was allowed to warm to room temperature while stirring was continued for 2 h. After the solvent was removed in vacuo, the residue was dissolved in toluene (7 mL). To this solution was added methanol (2.0 mL) and (trimethylsilyl)diazomethane (1.60 mmol, 0.8 mL of 2.0 mol $dm^{-3}$ solution in hexane) at room temperature. The mixture was stirred for 1 h, and the solvent was removed in vacuo. The residue was purified by column chromatography to give **8** (316 mg, 72% for 2 steps). Mp 190–190.5 °C. IR (KBr) 3166, 1696, 1664, 1372 $cm^{-1}$. $^1H$ NMR (270 MHz, $CDCl_3$) $\delta$ 1.03 (3H, d, $J = 6.60$ Hz), 1.09 (3H, d, $J = 6.93$ Hz), 1.68 (3H, s), 1.95 (3H, s), 2.15 (3H, s), 3.05 (3H, s), 3.53 (1H, m), 3.65 (3H, s), 5.35 (1H, s), 6.81 (1H, s), 6.98 (1H, t, $J = 6.93$ Hz), 7.01 (1H, t, $J = 7.59$ Hz), 7.09 (1H, d, $J = 7.92$ Hz), 7.21 (1H, d, $J = 9.57$ Hz).

**Synthesis of 3-[1-(1,2-Dimethyl-3-indolyl)-2-methylpropylidene]-4-isopropylidene-2,5 (3*H*,4*H*)-pyrroledione (1E).** To a stirred suspension of NaH (69.0 mg, 1.72 mmol) in 30 mL THF at 0 °C was added a THF (10 mL) solution of **8** (316 mg, 0.817 mmol). The mixture was stirred over night at room temperature. The reaction mixture was extracted with ethyl acetate, and the organic layer was washed with water and then brine, and dried over anhydrous $Na_2SO_4$. The drying agent was removed by filtration, and the solvent was removed in vacuo. The residue was purified by column chromatography to give **1E** (275 mg, 95%). Mp 181–182 °C. IR (KBr) 3162, 1736, 1702, 1577, 1335 $cm^{-1}$. $^1H$ NMR (270 MHz, $CDCl_3$) $\delta$ 0.93 (3H, s), 0.95 (3H, d, $J = 6.93$ Hz), 1.40 (3H, d, $J = 8.16$ Hz), 2.07 (3H, s), 2.10 (3H, s), 3.66 (3H, s), 4.26 (1H, m), 7.14 (3H, m), 7.48 (1H, d, $J = 7.41$ Hz), 7.90 (1H, s). MS (EI, 70 eV) *m*/*z* 336 ($M^+$, 100), 321 ($(M - CH_3)^+$, 7). Found: *m*/*z* 336.1845. Calcd for $C_{21}H_{24}N_2O_2$: M, 336.1838.

**Synthesis of the Colored-Form Fulgimide 1C.** A stirred solution of **1E** (275 mg, 0.817 mmol) in 70 mL ethyl acetate was irradiated with 366-nm light from a high-pressure mercury lamp for 4 h. After the solvent was removed in vacuo, the residue was purified by column chromatography to afford **1C** (104 mg, 38%). Mp 183–184 °C. IR (KBr) 3192, 1762, 1712, 1598, 1550 $cm^{-1}$. $^1H$ NMR (270 MHz, $CDCl_3$) $\delta$ 1.16 (3H, d, $J = 6.93$ Hz), 1.23 (3H, s), 1.24 (3H, s), 1.48 (3H, d, $J = 6.93$ Hz), 1.73 (3H, s), 2.85 (3H, s), 3.54 (1H, sept, $J = 7.13$ Hz), 6.54 (1H, d, $J = 8.25$ Hz), 6.73 (1H, t, $J = 7.59$ Hz), 6.91 (1H, s), 7.22 (1H, t, $J = 7.59$ Hz), 7.52 (1H, d, $J = 7.59$ Hz),. MS (EI, 70 eV) *m*/*z* 336 ($M^+$, 24), 321 ($(M - CH_3)^+$, 3), 145 (100). Found: *m*/*z* 336.1847. Calcd for $C_{21}H_{24}N_2O_2$: M, 336.1838

**Synthesis of 2,6-Bis(octanoylamino)pyridine (3).** To a stirred solution of 2,6-diaminopyridine (545 mg, 4.99 mmol) in 100 mL $CH_2Cl_2$ at room temperature was added octanoyl chloride (1.79 g, 11.0 mmol) and triethylamine (1.26 g, 12.5 mmol). The mixture was stirred over night at room temperature. After the reaction mixture was extracted with $CH_2Cl_2$, the organic layer was washed with water and brine, and dried over $Na_2SO_4$. The solvent was removed in vacuo, and the residue was purified by column chromatography, to give **3** (1.65 g, 91%). Mp 107–107.5 °C. IR (Nujol) 3318, 1667, 1467 $cm^{-1}$. $^1H$ NMR (270 MHz, $CDCl_3$) $\delta$ 0.88 (6H, t, $J = 6.93$ Hz), 1.32 (16H, m), 1.70 (4H, m), 2.37 (4H, t, $J = 7.25$ Hz), 7.52 (2H, s), 7.70 (1H, t, $J = 7.91$ Hz), 7.90 (2H, d, $J = 7.92$ Hz). MS (EI, 70 eV) *m*/*z* 361 ($M^+$, 47), 235 (100).

**Synthesis of 2,4-Dimethyl-6-octanoylaminopyridine (4).** The synthesis of **4** (90% yield) was done from 2-amino-4, 6-dimethylpyridine by a similar method to prepare **3**. Mp 50.5–51 °C. IR (Nujol) 3095, 1704, 1611 $cm^{-1}$. $^1H$ NMR (270 MHz, $CDCl_3$) $\delta$ 0.87 (3H, t, $J = 6.93$ Hz), 1.29 (8H, m), 1.70 (2H, m), 2.31 (3H, s), 2.37 (2H, t, $J = 7.25$ Hz), 2.40 (3H, s), 6.73 (1H, s), 7.88 (1H, s), 8.23 (1H, s). MS (EI, 70 eV) *m*/*z* 248 ($M^+$, 14), 122 (100).

**Job's Method.** Solutions of mixtures of **1C** or **1E** and **3** in toluene were prepared to measure the change in the absorption spectra by association. The sum of the concentrations of **1** and **3** was kept at $4.76 \times 10^{-4}$ mol $dm^{-3}$, and the concentration of **1** was changed from 0 to $4.76 \times 10^{-4}$ mol $dm^{-3}$. The absorbance of the *C*-form or *E*-form was then read at 620 or 393 nm, respectively, for every solution, where the change in absorbance of **1** by the association was the largest. The change in absorbance was then plotted for the ratio [**1**]/([**1**] + [**3**]), as shown in Fig. 1.

**Nagakura–Baba Method.** Toluene solutions of **1** ($2.00 \times 10^{-4}$ mol $dm^{-3}$) and **3** ($1.00 \times 10^{-3}$, $2.00 \times 10^{-3}$, $1.00 \times 10^{-2}$, and $2.00 \times 10^{-2}$ mol $dm^{-3}$) were prepared. In a quartz cell (path length 1 cm for UV-vis spectrometer), 1 ml of a solution of **1** and 1 mL of each of the solutions of **3** were mixed, and the mixture was stirred for 5 min. UV-vis spectra were measured for these solutions.

The relationship between the association constants, the concentration of guest molecule, and the absorbance at the designated wavelength is

$$K_a = [\mathrm{b}_1 (D_0 - D_2) + b_2 (D_1 - D_0)]/b_1 b_2 (D_2 - D_1),$$

where $D_0$ is the absorbance of **1**; $D_1$ and $D_2$ are the absorbance of **1** in the presence of guest molecule with the concentration $b_1$ and $b_2$, respectively. The association constant, $K_a$, can be calculated for a combination of $b_1$ and $b_2$. The average value for several different combinations of $b_1$ and $b_2$ was determined (Table 2).

This work was supported by a Grant-in-Aid for Scientific Research on Priority Area (A) "Molecular Synchronization for Design of New Materials System" (No. 11167235) from The Ministry of Education, Science, Sports and Culture.

## References

1 "Photochromism: Molecules and Systems," ed by H. Dürr and H. Bouas–Laurent, Elsevier, Amsterdam (1990).

2 "Applied Photochromic Polymer Systems," ed by C. B. McArdle, Blackie, Glasgow (1992).

3 "Organic Photochromic and Thermochromic Compounds," ed by J. C. Crano and R. Guglielmetti, Kluwer Academic/Plenum Publishers, New York (1999), Vols. 1 and 2.

4 Y. Yokoyama, *Chem. Rev.*, **100**, 1717 (2000).

5 a) R. J. Hart, H. G. Heller, and K. J. Salisbury, *J. Chem. Soc., Chem. Commun.*, **1968**, 1627. b) I. Cabrera, A. Dittrich, and H. Ringsdorf, *Angew. Chem., Int. Ed. Engl.*, **30**, 76 (1991). c) J. Walz, K. Ulrich, H. Port, H. C. Wolf, J. Wonner, and F. Effenberger, *Chem. Phys. Lett.*, **213**, 321 (1992). d) I. Willner, S. Rubin, J. Wonner, F. Effenberger, and P. Bäuerle, *J. Am. Chem. Soc.*, **114**, 3150 (1992). e) R. Matsushima and H. Sakaguchi, *J. Photochem. Photobiol. A: Chem.*, **108**, 239 (1997).

6 Z. Guo, G. Wang, Y. Tang, and X. Song, *Liebigs Ann. Chem.*, **1997**, 941.

7 Y. Yokoyama, T. Ohmori, T. Okuyama, Y. Yokoyama, and S. Uchida, *Mol. Cryst. Liq. Cryst.*, **344**, 265 (2000).

8 Selected examples: Azobenzene: S. Shinkai, T. Minami, Y. Kusano, and O. Manabe, *J. Am. Chem. Soc.*, **105**, 1851 (1983); F. Würthner and J. Rebek, Jr., *Angew. Chem., Int. Ed. Engl.*, **34**, 446 (1995). Thioindigo: M. Irie and M. Kato, *J. Am. Chem. Soc.*, **107**, 1024 (1985). Spiropyran: M. Inouye, M. Ueno, and T. Kitao, *J. Am. Chem. Soc.*, **112**, 8977 (1990); H. Sasaki, A. Ueno, J. Anzai, and T. Osa, *Bull. Chem. Soc. Jpn.*, **59**, 1953 (1986); K. Kimura, T. Yamashita, and M. Yokoyama, *J. Chem. Soc., Chem. Commun.*, **1991**, 147. Malachite Green: K. Kimura, R. Mizutani, M. Yokoyama, R. Arakawa, G. Matsubayashi, M. Okamoto, and H. Doe, *J. Am. Chem. Soc.*, **119**, 2062 (1997); Diarylethene: a) M. Takeshita and M. Irie, *J. Org. Chem.*, **63**, 6643 (1998). b) S. H. Kawai, *Tetrahedron Lett.*, **39**, 4445 (1998); Dihydroindolyzine: H. Dürr, T. Thome, C. Kranz, H. Kilburg, S. Bollmenn, B. Braun, K.-P. Janzen, and E. Blasius, *J. Phys. Org. Chem.*, **5**, 689 (1992); Anthracene dimer: J. H. R. Tucker, H. Bouas-Laurent, P. Marsau, S. W. Riley, and J.-P. Desvergne, *Chem. Commun*,. **1997**, 1165; Chromene: M. T. Stauffer, D. B. Knowles, C. Brennan, L. Funderburk, and F.-T. Lin, *Chem. Commun.*, **1997**, 287.

9 For thermally reversible spiropyran, one excellent example has been reported: M. Inouye, K. Kim, and T. Kitao, *J. Am. Chem. Soc.*, **114**, 778 (1992).

10 a) S. Uchida, S. Yamada, Y. Yokoyama, and Y. Kurita, *Bull. Chem. Soc. Jpn.*, **68**, 1677 (1995). b) Y. Yokoyama, Y. Shimizu, S. Uchida, and Y. Yokoyama, *J. Chem. Soc., Chem. Commun.*, **1995**, 785.

11 P. Job, *Ann. Chim. Phys.*, **9**, 113 (1928).

12 a) S. Nagakura, *J. Am. Chem. Soc.*, **80**, 520 (1958). b) H. Baba, *Bull. Chem. Soc. Jpn.*, **31**, 169 (1958).

13 Y. Yokoyama, T. Tanaka, T. Yamane, and Y. Kurita, *Chem. Lett.*, **1991**, 1125.

14 Y. Yokoyama, H. Hayata, H. Ito, and Y. Kurita, *Bull. Chem. Soc. Jpn.*, **63**, 1607 (1990).

15 J. J. P. Stewart, *J. Comput. Chem.*, **10**, 209, 221 (1989).