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# Entropy-controlled thermal back-reaction of photochromic [2.2]paracyclophane-bridged imidazole dimer

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ABSTRACT

A [2.2]paracyclophane-bridged imidazole dimer having bulky 3′,4′,5′-triphenyl-1,1′:2′,1″-terphenyl substituents was synthesized and the photochromic properties were investigated. The half-life of the colored species generated by the UV irradiation of the parent imidazole dimer was 1.0 ms at 298 K in benzene. Although such bulky substituents are introduced on the imidazole dimer, the fast thermal back-reaction can be observed as found in other [2.2]paracyclophane-bridged imidazole dimers. Herein, enthalpy and entropy of the activation energies ($\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$, respectively) for the thermal back-reaction of the present molecule were compared with other [2.2]paracyclophane-bridged imidazole dimers in order to investigate the generality and the limitation of the molecular design of the photochromic imidazole dimer along with the correlation between bulkiness of the substituents and the rate constant of the thermal back-reaction. Finally, we referred to a new method for controlling the rate constant of the thermal back-reaction of [2.2]paracyclophane-bridged imidazole dimers.

## 1. Introduction

Considerable interest has been focused on organic photochromic molecules that change their color upon certain light irradiation and reverse to the initial species by either heating or irradiation with a specific wavelength of light [1–7]. In particular, thermally reversible photochromic molecules [8–11] attract much attention from a viewpoint of potential application for photochromatic eyewear and other photo-responsive materials which show photo-induced coloration upon UV light irradiation and the spontaneous thermal back-reaction in the dark.

We have recently developed a new type of photochromic molecule based on a [2.2]paracyclophane-bridged imidazole dimer [12–16] which shows instantaneous coloration upon exposure to UV light and a fast thermal back-reaction in the dark. The photochromic behavior of [2.2]paracyclophane-bridged imidazole dimer can be attributed to the photo-induced homolytic bond cleavage of the C–N bond between the imidazole rings and successive fast C–N bond formation in the dark. The back-reaction is induced only by the thermal activation, therefore [2.2]paracyclophane-bridged imidazole dimers can be classified into the T-type category of photochromic molecules [17–21]. The half-lives of the colored species of [2.2]paracyclophane-bridged imidazole dimers range from microseconds to milliseconds.

So far, we have succeeded to enhance the photosensitivity to the sunlight with introduction of electron-donating methoxy groups [13], and to achieve the acceleration of the thermal back-reaction [14]. We found that controlling the stability of the biradical state is effective in controlling the thermal bleaching rate for the photochromic [2.2]paracyclophane-bridged imidazole dimers. Moreover, we have also demonstrated that [2.2]paracyclophane-bridged imidazole dimers retain the fast photochromism even in a polymer matrix [15] and an organogel state [16]. In order to put photoactive materials into practical use, the excellent photoreactivity in various matrices are required from industry. From the viewpoint of photoresponsibility, the fast photochromism would be available for photochromatic materials. Hence, we consider the [2.2]paracyclophane-bridged imidazole dimer to be the most promising candidate for the fast light modulation, and the study of the photochromic properties of [2.2]paracyclophane-bridged imidazole dimer is of interest from the viewpoint of both science and technology. Herein, we have prepared a fast photochromic molecule bearing bulky substituents on the [2.2]paracyclophane-bridged imidazole dimer in order to

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investigate the generality and the limitation of the molecular design of the photochromic imidazole dimer along with the correlation between bulkiness of the substituents and the rate constant of the thermal back-reaction.

## 2. Experimental

### 2.1. General

All reactions were monitored by thin-layer chromatography using 0.2 mm E. Merk silica gel plates (60F-254). Column chromatography was performed on silica gel (Kanto Chemical Co., Silica Gel 60 N (spherical, neutral), 40–50 μm). All reagents were purchased from Tokyo Chemical Industry Co., Ltd., Wako Pure Chemical Industries, Ltd., Kanto Chemical Co., Inc., and were used without further purification. The NMR spectra were recorded on a JMN-ECP500A (JEOL) spectrometer, and the chemical shifts were quoted in ppm relative to tetramethylsilane. The FAB mass spectra were measured with MStation MS-700 (JEOL) spectrometer by using 3-nitrobenzyl alcohol as matrix.

### 2.2. Laser flash photolysis experiments

The laser flash photolysis experiments were carried out with a Unisoku TSP-1000 time-resolved spectrometer. A continuum Minilite II Nd:YAG (Q-switched) laser with the third harmonic at 355 nm (ca. 8 mJ per 5 ns pulse) was employed for the excitation light. The probe beam from an OSRAM HLX64623 halogen lamp was guided with an optical fiber scope to be arranged in an orientation perpendicular to the exciting laser beam. The probe beam was monitored with a Hamamatsu R2949 photomultiplier tube through a spectrometer (Unisoku MD200).

### 2.3. Syntheses

#### 2.3.1. Synthesis of 1,2-bis(3′,4′,5′-triphenyl-[1,1′:2′,1″-terphenyl]-4-yl)ethane-1,2-dione (2)

2,3,4,5-Tetraphenylcyclopenta-2,4-dienone (676 mg, 1.76 mmol) was poured into the *o*-xylene (8.0 mL) solution of 1,2-bis(4-ethynylphenyl)ethane-1,2-dione **1** (150 mg, 0.581 mmol) [22]. Then, the resulting mixture was heated under reflux at 170 °C for 17 h under $N_2$ atmosphere. The crude mixture was purified by silica gel column chromatography using $CH_2Cl_2$/hexane = 2/3 as eluent to give a yellow powder of **2** (390 mg, 0.402 mmol, 69% yield). $^1H$ NMR (500 MHz, DMSO-$d_6$) δ: 7.67 (d, $J = 7.9$ Hz, 4H), 7.46 (s, 2H), 7.40 (d, $J = 8.6$ Hz, 4H), 7.16 (m, 10H), 6.96–6.82 (m, 30H); Found FAB-MS: *m/z* [M + $H^+$] 972.0; $C_{74}H_{51}O_2$ requires 971.4.

#### 2.3.2. Synthesis of 3′,4′,5′-triphenyl-1,1′:2′,1″-terphenyl-substituted [2.2]paracyclophane-bridged bisimidazole (3)

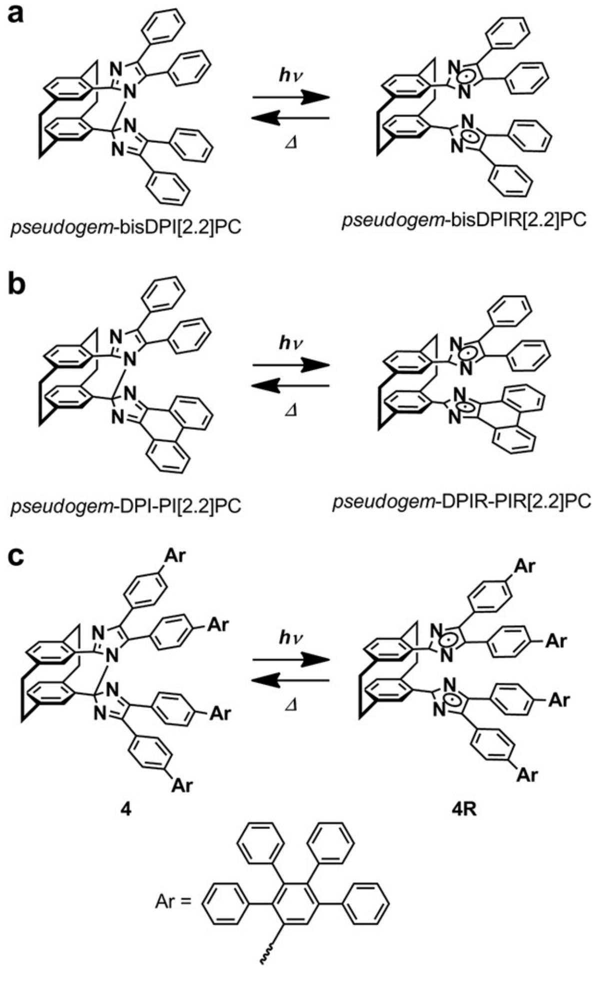
Compound **2** (407 mg, 0.419 mmol), [2.2]paracyclophane-4,13-carbaldehyde (50 mg, 0.189 mmol) and ammonium acetate (136 mg, 1.76 mmol) were dissolved in chloroform (0.9 mL). The mixture was degassed by freeze–pump–thaw method. The resulting solution was heated under reflux at 110 °C for 36 h. After cooled to room temperature, the mixture was washed with water and dried over $Na_2SO_4$. The crude mixture was purified by silica gel column chromatography using $CH_2Cl_2$ as eluent to give a white powder **3** (108 mg, 0.050 mmol, 27% yield). $^1H$ NMR (500 MHz, $CDCl_3$-$d_1$) δ: 8.91 (s, 2H), 7.47 (d, $J = 13.5$ Hz, 3H), 7.18–7.05 (m, 26H), 6.94–6.63 (m, 77H), 4.30 (t, $J = 6.0$ Hz, 1H), 4.06 (d, $J = 8.6$, 1H), 3.18(s, 2H), 3.13 (s, 4H); mp > 300 °C; Found FAB-MS: *m/z* [M + $H^+$] 2166.0; $C_{166}H_{117}N_4$ requires 2165.9.

#### 2.3.3. Synthesis of 3′,4′,5′-triphenyl-1,1′:2′,1″-terphenyl-substituted [2.2]paracyclophane-bridged imidazole dimer (4)

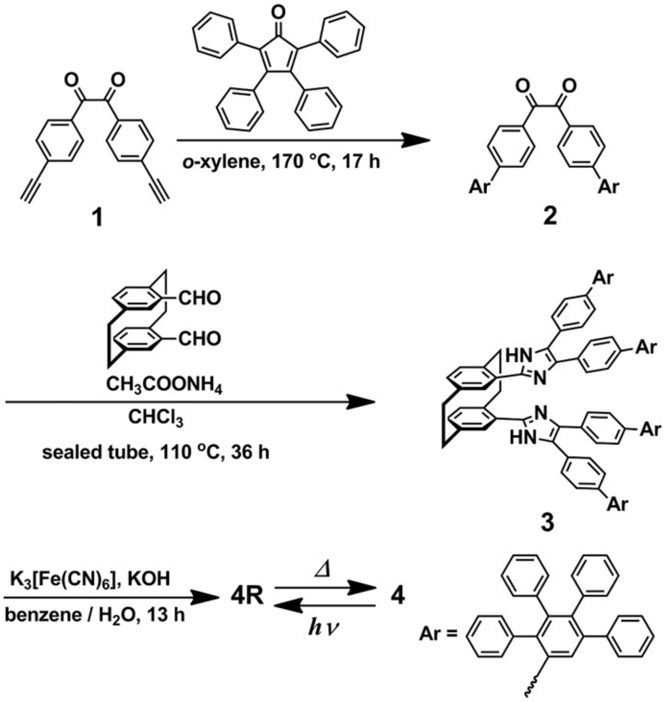
All manipulations were carried out with the exclusion of light. Compound **3** (28 mg, 0.0129 mmol) was dissolved in benzene (4.1 mL) and $K_3[Fe(CN)_6]$ (202 mg, 0.614 mmol) aqueous solution containing KOH bilayer and the solution was stirred for 13 h. After the reaction was completed, the reaction product was extracted with benzene (5 mL), and then washed with water (2 × 10 mL). The crude mixture was purified by silica gel column chromatography using $CH_2Cl_2$ as eluent to give a white powder **4** (20 mg, 0.00670 mmol, 72% yield). $^1H$ NMR (500 MHz, $CDCl_3$-$d_1$) δ: 7.57 (s, 1H), 7.53 (s, 1H), 7.48 (s, 1H), 7.22–7.15 (m, 16H), 7.05–6.68 (m, 81H), 6.61–6.54 (m, 4H), 6.42 (dd, $J = 18.5$ and 8.0 Hz, 2H), 4.43 (t, $J = 10.0$, 1H), 3.24–2.89 (m, 7H); mp > 220 °C; Found FAB-MS: *m/z* [M + $H^+$] 2164.0; $C_{166}H_{115}N_4$ requires 2163.9.

## 3. Results and discussion

A fast photochromic molecule having bulky 3′,4′,5′-triphenyl-1,1′:2′,1″-terphenyl substituents on the [2.2]paracyclophane-bridged imidazole dimer has been designed (Scheme 1). Compound **4** was synthesized in three steps from 1,2-bis(4-ethynylphenyl)ethane-1,2-dione (Scheme 2). After introduction of pentaphenyl moieties via Diels–Alder reaction in 69% yield, bis (pentaphenyl) substituted benzil derivative **2** was reacted with [2.2]paracyclophane-4,13-dicarbaldehyde to form the bisimidazole **3** in 27% yield. The resulting bisimidazole **3** was oxidized with $K_3[Fe(CN)_6]$ under base



Scheme 1.



**Scheme 2.**

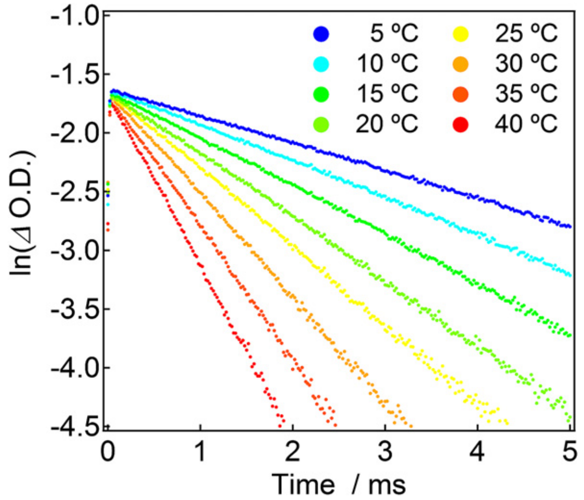


**Fig. 2.** First-order kinetic profiles of colored species of **4**, monitored at 400 nm in degassed benzene ($1.95 \times 10^{-5}$ M). The measurements were performed in the temperature range from 278 to 313 K.

condition to afford the bis(pentaphenyl) substituted [2.2] paracyclophane-bridged imidazole dimer **4** in 72% yield.

Although the thermal back-reaction is too fast to recognize the photochromic color change in solution at room temperature, the deceleration of the thermal back-reaction at low temperature makes it possible to increase the concentration of the colored species of **4** and the photochromic color change from colorless to green is detectable even by the human eye. The transient vis–NIR absorption spectra of **4** at 298 K in degassed benzene were measured by a nanosecond laser flash photolysis experiment (Fig. 1).

For the sake of checking the solid state reactivity, that is required from the aspect of industrial application, a nanosecond laser flash photolysis experiment was also performed for the amorphous phase on a glass substrate (Fig. S3) [23–28]. Certain bulky substituents cause steric hindrance on the imidazole rings and consequently the efficient molecular motion necessary to the configuration change in the photochromic reaction would be suppressed [29,30], however the present molecule showed reversible and efficient photochromic reaction upon UV light irradiation even in solid state as well as in solution. These tolerant photochromic properties of [2.2] paracyclophane-bridged imidazole dimer **4** have stimulated further studies in fast photo-switching materials.

In order to investigate the effect of bulky 3′,4′,5′-triphenyl-1,1′:2′,1″-terphenyl substituent on the photochromic properties in solution, the transient vis–NIR absorption spectra of **4** were analyzed in detail, and the thermal back-reaction was compared with *pseudogem*-bisDPI[2.2]PC (Scheme 1a) as a reference compound which had no bulky substituents on each imidazole ring. The half-life of the colored species **4R** was 1.0 ms at 298 K in benzene while that of *pseudogem*-bisDPI[2.2]PC was 33 ms under the same conditions. As well as the colored species of *pseudogem*-bisDPI[2.2]PC, the thermal recombination of the photo-induced **4R** obeys first-order kinetics over

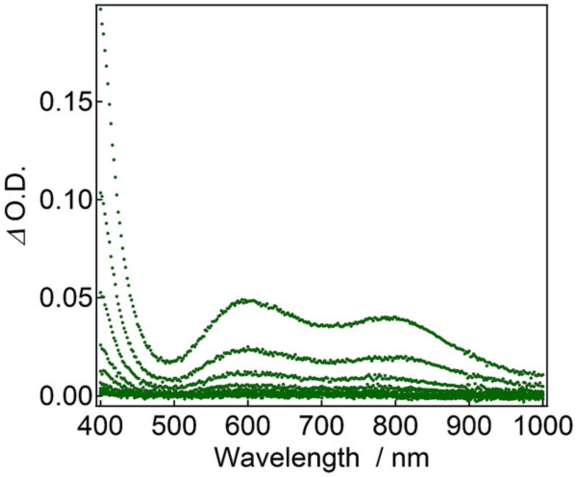


**Fig. 1.** Transient vis–NIR absorption spectra of colored species of **4** at 298 K in degassed benzene ($1.95 \times 10^{-5}$ M; light path length: 10 mm). Each of spectra was recorded at 1 ms intervals after excitation with nanosecond laser pulse (excitation wavelength, 355 nm; pulse width, 5 ns; power, 8.1 mJ/pulse).

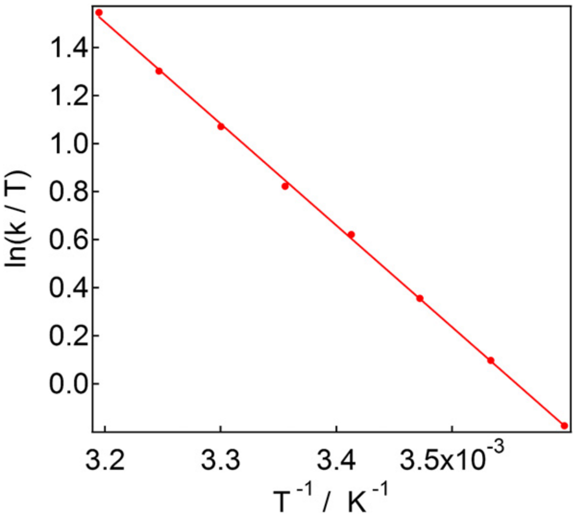


**Fig. 3.** An Eyring plot for the thermal back-reaction of colored species of **4** in degassed benzene ($1.95 \times 10^{-5}$ M).

**Table 1**
Kinetic parameters associated with the thermal back-reaction at 298 K in benzene.

| Compound | $k$ s$^{-1}$ | $\Delta H^{\ddagger}$ kJ mol$^{-1}$ | $\Delta S^{\ddagger}$ J K$^{-1}$ mol$^{-1}$ | $\Delta G^{\ddagger}$ kJ mol$^{-1}$ |
|---|---|---|---|---|
| Compound **4** | $6.78 \times 10^{2}$ | 35.2 | −72.4 | 56.8 |
| *Pseudogem*-bisDPI[2.2]PC | $2.06 \times 10^{1}$ | 59.8 | −19.1 | 65.5 |
| *Pseudogem*-DPI-PI[2.2]PC | $1.96 \times 10^{4}$ | 35.4 | −44.1 | 48.6 |

the temperature range from 278 to 313 K as shown in Fig. 2. The enthalpy and entropy of activation energies ($\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$, respectively) for the thermal back-reaction of **4** were estimated from an Eyring plot over the same temperature range (Fig. 3).

The linear relation of the Eyring plot gave $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ by means of standard least-squares analysis, and the values for **4** were 35.2 kJ mol$^{-1}$ and −72.4 J K$^{-1}$ mol$^{-1}$, respectively. Therefore, the free energy barrier ($\Delta G^{\ddagger} = \Delta H^{\ddagger} - T\Delta S^{\ddagger}$) was 56.8 kJ mol$^{-1}$ at 298 K in benzene, while $\Delta H^{\ddagger}$, $\Delta S^{\ddagger}$, $\Delta G^{\ddagger}$ values for *pseudogem*-bisDPI[2.2]PC were 59.8 kJ mol$^{-1}$, −19.1 J K$^{-1}$ mol$^{-1}$ and 65.5 kJ mol$^{-1}$ at 298 K in benzene, respectively. The estimated values of thermodynamic parameters and the rate constants are listed in Table 1. The rate constant of the thermal back-reaction of **4** was accelerated only 33 times compared with that of *pseudogem*-bisDPI[2.2]PC at 298 K in benzene [12], while that of another reference compound, *pseudogem*-DPI-PI[2.2]PC (Scheme 1b) was accelerated 950 times under the same conditions. Following standard Marcus theory, an increase in the change in Gibbs energy, $\Delta G^{0}$, between the reactant and the product would lead to a decrease in the free energy of activation, $\Delta G^{\ddagger}$, and consequently, the rate constant for the thermal back-reaction would be accelerated. Thus, Marcus theory gave us a crucial insight into controlling the rate of the radical recombination reaction. We have considered that Gibbs energy $\Delta G^{0}$ of the thermal back-reaction could be enlarged by destabilizing the colored species, and thus designed *pseudogem*-DPI-PI[2.2]PC, with a [2.2]paracyclophane moiety that couples diphenylimidazole and phenanthroimidazole groups [14]. The steric repulsion between the rigid phenanthroimidazole group and the phenyl rings facing each other should destabilize the biradical state (*pseudogem*-DPIR-PIR[2.2]PC), whereas the rotational motion along the C—C single bond between the imidazole group and the phenyl ring in *pseudogem*-bisDPIR[2.2]PC should relax the steric hindrance between the phenyl rings facing each other. Since it was expected that the steric repulsion between the phenanthroimidazole groups introduced on one side of the geminal position of [2.2]paracyclophane should enhance the destabilization of the biradical state, and accelerate the thermal back-reaction of *pseudogem*-DPI-PI[2.2]PC. It should be noted that the overall free energy $\Delta G^{\ddagger}$ for **4** was significantly different from that of *pseudogem*-DPI-PI[2.2]PC, while the activation enthalpy $\Delta H^{\ddagger}$ for **4** was almost same to that of *pseudogem*-DPI-PI[2.2]PC. Therefore, the significant difference of overall free energy $\Delta G^{\ddagger}$ was attributed to the large negative entropy $\Delta S^{\ddagger}$ for **4**. The bulky 3′,4′,5′-triphenyl-1,1′:2′,1″-terphenyl units would bring about this large negative entropy. Considering the molecular structures of **4** and **4R**, a large nuclear configuration change in the transition state would be expected because the bulky units could form a variety of conformations along the phenyl—phenyl single bonds in the biradical state while only small number of limited conformations in the sterically-restricted transition state is allowed. Therefore the radical recombination process of **4** is considered to be entropically very unfavorable. An entropic effect is occasionally found in a variety of chemical reactions [31–39] and the present case could also be applied to the entropic effect.

## 4. Conclusion

We have prepared a fast photochromic molecule having bulky substituents on the [2.2]paracyclophane-bridged imidazole dimer in order to investigate the generality of the molecular design of the photochromic imidazole dimer. Compound **4** showed a relatively slow thermal back-reaction compared with *pseudogem*-DPI-PI[2.2]PC at 298 K in benzene. In order to investigate the fast photochromism in detail, the thermodynamic parameters for the thermal back-reaction of **4** were also estimated from an Eyring plot over the temperature range from 278 to 313 K. Interestingly, the relatively slow thermal back-reaction of **4** was the contribution of a large negative $\Delta S^{\ddagger}$. A certain bulky substituent would prevent fast biradical recombination mainly by the large $\Delta H^{\ddagger}$ derived from steric hindrance, however, in the present case the activation enthalpy $\Delta H^{\ddagger}$ for **4** was almost the same as that of *pseudogem*-DPI-PI[2.2]PC and the significant difference of overall free energy $\Delta G^{\ddagger}$ was attributed to the large negative entropy $\Delta S^{\ddagger}$ for **4**. Considering the molecular structure if a certain substituent which has a variety of conformations is introduced on the [2.2]paracyclophane-bridged imidazole dimer, the molecular conformations would be restricted in the transition state compared to the biradical state. Such a molecular reconfiguration process is considered to be entropically very unfavorable; therefore in this case the rate constant of the thermal back-reaction would be decreased mainly by the contribution of the activation entropy. In this study, we showed that it was possible to control the rate constants of the thermal back-reaction of photochromic [2.2]paracyclophane-bridged imidazole dimer derivatives by both enthalpy and/or entropy effects. We believe that the systematic control of the thermal back-reaction of thermally reversible photochromic compounds makes it possible to realize the custom-made molecular design.

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## Appendix. Supplementary material

NMR and MS spectra of compounds and the thermal decay profile of amorphous phase of **4** were included in the Supplementary materials.

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.dyepig.2011.04.009.

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