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Time-resolved fluorescence study on the photomerocyanine form of spiropyran and its derivative with azobenzene

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ABSTRACT

The excited state dynamics of the photomerocyanine (PMC) form originating from spirobenzopyran and the bi-functional photochromic compound spirobenzopyran–azobenzene (SpAz), containing typical photochromic molecules of spirobenzopyran (Sp) and azobenzene (Az), were investigated using picosecond time-resolved fluorescence measurements in solution at 200 and 285 K and in a PMMA polymer film at 298 K. While the fluorescence lifetimes of PMC were about twice as long as those of SpAz under all experimental conditions, both lifetimes showed similar strong dependence on viscosity rather than temperature. These results suggest that non-radiative decay to an intermediate state could be accompanied by a significant conformational change. The effect of the Az moiety in this relaxation process is also discussed. It is unlikely that an energy transfer from the PMC moiety to the Az moiety occurs. It was concluded that the PMC moiety in the bi-functional SpAz is independent from the Az moiety.

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1. Introduction

Light-induced reversible transformation between two isomers with different absorption spectra is referred to as photochromism [1]. Photochromic compounds have attracted much attention because of their potential for broad use in reversible information memory media [2]. Recent interest has also focused on bi-functional photochromic compounds that contain two photochromic moieties linked by specific spacers [3]. When each moiety can isomerize independently upon selective excitation at different wavelengths, four photoisomers could be arbitrarily introduced. This has the advantage of having increased digital codes in a single molecule. Our previous study examined a bi-functional photochromic compound, spirobenzopyran–azobenzene (SpAz), containing typical photochromic molecules of spirobenzopyran (Sp) and azobenzene (Az). We reported that the steady-state absorption spectral changes in SpAz by selecting specific irradiation wavelengths (300, 360 and 400 nm) indicated the production of three different photoisomers [3f,g]. Fig. 1 shows the photochromic reactions of Sp and SpAz irradiated by 360 nm light. In the case of UV-irradiated spiropyran, the spirocarbon–oxygen (C–O) bond of the colorless spiro isomer (SP-form) is broken, and subsequent isomerization leads to a colored open isomer referred to as the photomerocyanine isomer (PMC-form) [4]. The Az molecule can undergo *trans–cis*-photoisomerization under UV light irradiation [5]. Therefore, when SpAz is irradiated by 360 nm light, both the Sp and Az moieties isomerize as SP-*trans*Az-form → PMC-*cis*Az-form (PMCAz). It is well known that the PMC-form effectively returns to the SP-form by either thermal or light excitation [6]. Many studies have been carried out to investigate the excited state dynamics of the PMC-form by measuring time-resolved fluorescence [7] and transient absorption [8] under various solvent conditions. It was also found that some of observed spectroscopic behaviors could be attributed to isomerization among rotational isomers around the methine bridge, such as the *trans–trans–cis* (TTC) form and the *trans–trans–trans* (TTT) form in the excited state [8a–g]. In fluorescence measurements of PMC and PMCAz in toluene, we noticed that the fluorescent intensity of PMC was much larger than that of PMCAz, where 360 nm light was used not only for isomerization from the SP-form to the PMC-form, but also to excite the photoproduct PMC-form. The same measurement was carried out for mixing a solution of PMC and Az, resulting in almost the same fluorescent intensity as with PMC. Two explanations for this observation have been proposed. One is that excited states of PMC and PMCAz might have slightly different relaxation processes. The other is that in the case of PMCAz intra-molecular energy transfer from PMC to Az moieties can occur.

In this study, the excited state dynamics were studied by time-resolved fluorescence measurements on a picosecond time scale in order to discuss the photochemical properties of PMC and PMCAz. The fluorescence lifetimes of PMC were compared with those of PMCAz in toluene at 200 K and 285 K, and in PMMA film at 298 K.

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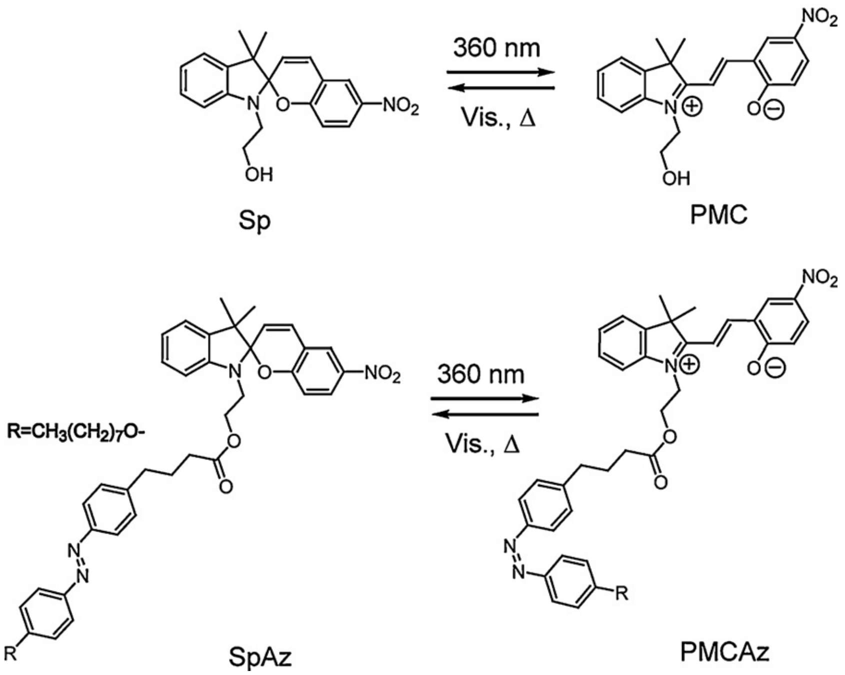

Fig. 1. Photochromic reactions from Sp to PMC and SpAz to PMCAz upon 360 nm excitation, and their back reactions. As the structure of the PMC-form, the most stable rotational isomer, the *trans–trans–cis* (TTC) form, around the methine bridge is described.

This is the first attempt to explore how the bulky Az can influence the excited state dynamics of PMC in a bi-functional photochromic compound.

2. Experimental

Time-resolved fluorescence spectra and decay profiles of the PMC-form were measured using a picosecond streak camera system (Hamamatsu C4334). As an excitation light source, a regeneratively amplified Ti:sapphire laser system (Spectra Physics Hurricane; 100 fs pulse width, 1 mJ per pulse at 800 nm and repetition rate of 1 kHz) with two optical parametric amplifiers (OPAs) (Spectra Physics OPA 800C) was used. The fourth harmonic outputs of the idler and signal waves from two OPAs, $4\omega_i$ (545 nm), were selected for excitation to the first and higher electronic excited states of the PMC-form, respectively. These excitation lasers passed through an interference filter to reduce unnecessary components in the OPA output and through a neutral density filter to attenuate the laser power before a sample cell. The fluorescence obtained was passed through a high-pass dielectric multilayer filter to cut the laser scatter and focused into a 150 mm monochromator (Acton) for detection by the streak camera. Unfortunately, the time-resolved fluorescence spectra in toluene at 200 K yielded an ambiguous change due to imperfect reduction in the shorter wavelength region of scattered lights by the excitation laser into a cryostat. The synthesis of Sp and SpAz has been described previously [3f,g]. Compounds were dissolved in toluene (conc. 3.5×10^{-5} M) of the highest spectroscopic grade (Nacalai Tesque) without further purification. The PMC-form was obtained by irradiation of 360 nm output from a Xe lamp with an optical filter (300 W; Asahi spectra MAX-301). For SpAz, this irradiation also caused a *trans* to *cis* isomerization of the Az moiety with high efficiency. Since the PMC-form in toluene is easily returned to the initial SP-form due to poor thermal stability after several minutes at 298 K, two types of temperature-controlled experiments were performed. In the first, a sample cell (fused silica, 1 mm path length) was placed in a cryostat (Oxford OptistadDN) set at 200 K using liquid nitrogen, wherein it was able to maintain the PMC-form coloration during the fluorescence lifetime measurement. In the other experimental setup, a sample flow system using a PTFE diaphragm pump (Cole-Parmer Instrument Co.) with a cold ice-NaCl bath was applied. The surface temperature of the sample cells was set slightly above the dew point (ca. 285 K) so as not to hold mist conditions. After a sample bottle and pump, two flow cells, with 1 cm path length for the Xe lamp (360 nm) and 1 mm for the excitation laser, were connected with a Teflon tube. Off-focus lamp irradiation was started 10 min before measuring the time-resolved fluorescence to ensure sufficient PMC-form was present and this was continued through the end of the measurement. In order to compare the dynamics in solution, samples in PMMA films containing 4 wt% Sp or SpAz at 298 K were also examined. Three minutes of irradiation with 360 nm light of the PMC-form with a lifetime of 100 min at 298 K was determined to be sufficient to measure the fluorescence lifetime.

3. Results and discussion

3.1. Steady-state absorption and fluorescence properties

Fig. 2 shows the UV–visible absorption spectral changes for Sp, Az, and SpAz in toluene before and after 360 nm light irradiation. It can be seen that the spectrum for SpAz is almost equal to the sum of the Sp and Az spectra. The spectral changes and band assignments are indicated in our previous reports [3f,g]. Briefly, the absorption intensity at 350 nm decreased, and that at 450 nm increased as a result of photoisomerization from *trans*- to *cis*-form by UV light irradiation (Fig. 2b). In the case of Sp and SpAz, newly appeared broad absorption bands centered at 585 and 610 nm are assigned to the PMC-form (Fig. 2a and c). The intensity of their corresponding UV bands is partly reduced. This indicates that the PMC-form also has an absorption band of around 360 nm. When PMC and PMCAz in toluene were excited with 545 nm light, pale-red emission (λ = 580–700 nm for PMC, λ = 600–730 nm for PMCAz) was observed as shown in Fig. 2d. When the PMC-form was excited with 360 nm light, fluorescence spectra were shaped similar to that with 545 nm excitation, and almost no peak shift was observed. The steady state absorption and fluorescence spectra in toluene at

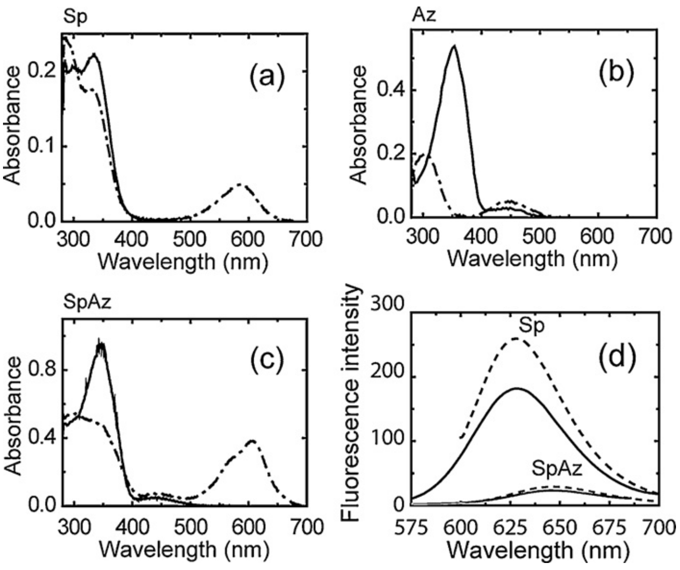

Fig. 2. Absorption spectral change of (a) Sp, (b) Az and (c) SpAz in toluene (conc. 3.5×10^{-5} M); initial state (solid line) and the photostationary state (broken line) upon 360 nm excitation. (d) Fluorescence spectra of PMC and PMCAz upon 360 nm (solid line) and 545 nm (broken line) excitations at 285 K.

285 K and PMMA film at 298 K are quite similar. It is noteworthy that the fluorescence intensity of PMC was much larger than that of PMCAz, however the absolute fluorescence quantum yield of PMC ($\Phi = 0.10$) was almost same as that of PMCAz ($\Phi = 0.087$) [9].

3.2. Time-resolved fluorescence measurements

Fig. 3 shows typical examples of fluorescence decay profiles for PMC and PMCAz upon 545 nm excitation under three different experimental conditions. The profiles were obtained by accumulation over a 20 nm range around the peak of the fluorescence spectra. These profiles were fitted to mono- or bi-exponential convoluted with the instrument response.

The experimental conditions such as irradiation wavelength, temperature and matrix were also changed, and the detailed excited state dynamics was investigated. The best-fit time constants and average lifetimes of the profiles in various conditions are summarized in Table 1. One characteristic of profiles is that the average time constants in toluene at 285 K (Fig. 3a) are approximately 10–15 times faster than those at 200 K (Fig. 3b), and those in PMMA film at 298 K (Fig. 3c). The large difference in time constants in toluene at 200 K and 285 K appeared to be ascribable to temperature-dependent vibrational and rotational isomer distributions, where the PMC-form, which has several rotational isomers centered on the methine bridge, are considered herein with TTC (Fig. 1) being the most stable conformation [10]. Additionally, the lifetimes in toluene at 200 K and in PMMA at 298 K show the same behavior. Therefore, the lifetimes derived from the excited state greatly depend on the matrix conditions. According to literature [11], the viscosity of toluene at 200 K (ca. 3.0×10^{-3} Pa s) is almost 5 times larger than that at 285 K (ca. 6.5×10^{-4} Pa s). This indicates that the rate constant of the non-radiative process could be directly influenced, not by the thermal barrier but by the viscosity of the medium. The increased lifetimes are thus related to the increased viscosity of the medium. The other interesting characteristic is the approximately 2 times faster fluorescence decays of PMCAz com-

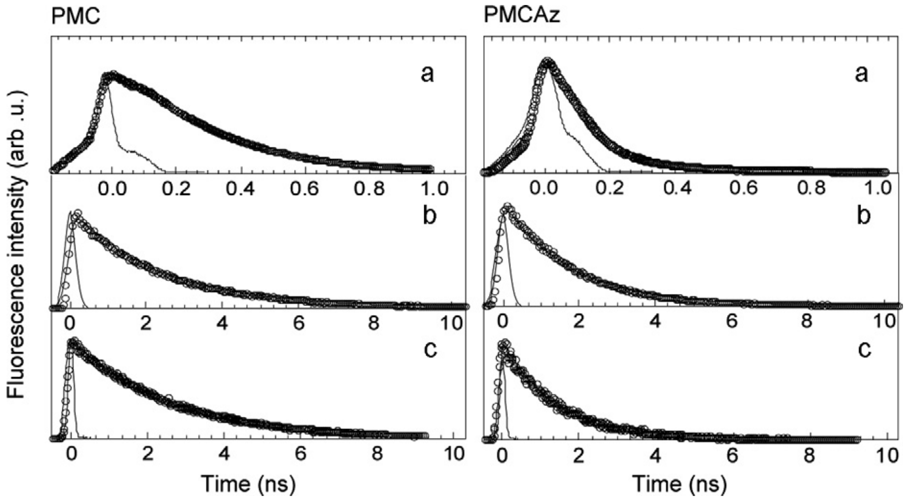

Fig. 3. Fluorescence decay profiles of PMC and PMCAz on 545 nm excitation in (a) toluene at 285 K, (b) toluene at 200 K, and (c) PMMA film at 298 K along with the instrument response. The solid lines represent the best fit to the data by convolution of instrument response with mono- or bi-exponential. The best fit time constants are summarized in Table 1. The listed time constants indicate two significant features.

Table 1
The best-fit time constants and average lifetimes of the decay profiles of the S_1 state for PMC and PMCAz in toluene and PMMA films.

Sample	Solvent of matrix	Temperature (K)	λ_{ex}[a] (nm)	λ_{fl} (nm)	τ_1[b] (ps)	τ_2[b] (ps)	$\langle\tau\rangle$[c] (ps)
PMC	Toluene	285	545	640–660	60 ± 6 (39.2%)	320 ± 9 (60.8%)	218
	Toluene	200	545	640–660	2370 ± 15 (100%)	–	–
	PMMA	298	545	640–660	2417 ± 29 (100%)	–	–
PMCAz	Toluene	285	545	640–680	63 ± 3 (93.5%)	899 ± 72 (6.5%)	117
	Toluene	200	545	640–680	1787 ± 16 (100%)	–	–
	PMMA	298	545	640–680	1292 ± 18 (100%)	–	–

[a] λ_{ex} is the excitation wavelength.
[b] τ_1 and τ_2 are the first and second components of the decay profiles, respectively.
[c] $\langle\tau\rangle$ is the average lifetime including both components.

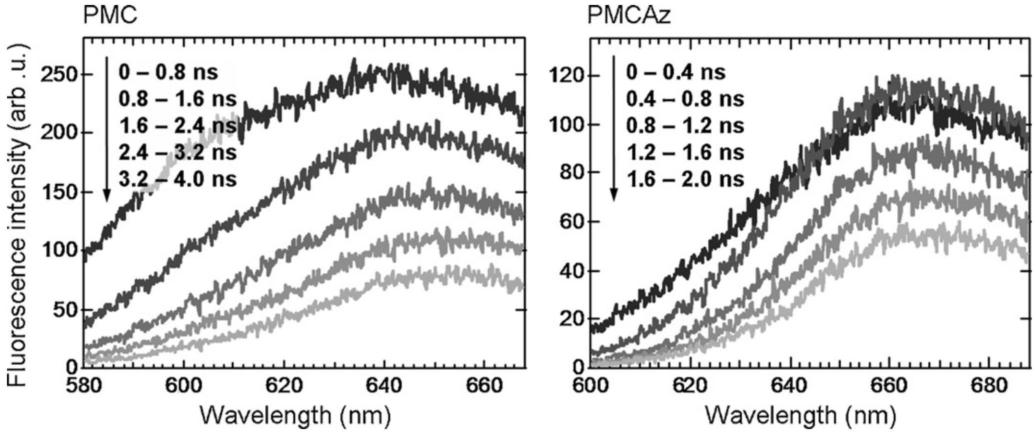

Fig. 4. Time-resolved fluorescence spectra were accumulated in the same time interval for PMC and PMCAz in PMMA films upon 545 nm excitation. Clear spectral changes are observed in the early stages.

pared to those of PMC under all experimental conditions, with the contributions of longer components (τ_2) being less than 10%. In the case of PMC, the contribution of longer components is extremely large, >50%. Bi-exponential fluorescence decays in toluene at 285 K suggest that the intermediate state might be in equilibrium with the excited singlet state of the PMC-form. Thus, a metastable intermediate state would also reform into the initial lowest excited singlet state (S_1) of the PMC-form. As a result, the lifetime of the longer component could be attributed to fluorescence from reformed S_1. As a result, the fluorescence decay fitted the mono-exponential in toluene at 200 K and in PMMA film at 298 K. The results indicate that the excited state dynamics are controlled by the solvent viscosity rather than the internal distributions. However, the excited state dynamics of PMCAz are complicated, hence it was impossible to explain these based on only the decay profiles since the lifetime, which is constructed from several independent rate constants, does not depend on the fluorescence intensity or external environment. Here, we propose a new non-radiative decay pathway to an intermediate state via the excited state with a rate of k_{im}.

In general, the fluorescence lifetime, τ_{fl}, is expressed as the sum of the various rate relaxation paths, as below [12],

$$\tau_{\mathrm{fl}} = \frac{1}{(k_{\mathrm{fl}} + k_{\mathrm{ic}} + k_{\mathrm{isc}} + k_{\mathrm{im}})}$$

where k_{fl}, k_{ic}, and k_{isc} are the rate constants of fluorescence, internal conversion, and intersystem crossing, respectively. These substance-specific rate constants are not influenced by solvent temperature and viscosity. On the other hand, the introduced k_{im} was assumed to be a precursor, dependent on solvent temperature and viscosity, of the ring closure reaction known as an effective relaxation for the isomers centered at the methane bridge. A number of studies on this intermediate state have been carried out. Hobley et al. proposed a “perpendicular state” as the intermediate state, where perpendicular is an analogy to loosening the C=C bond in the ethylene bridge [8b]. This intermediate state is probably *cis* or twisted at the central methine bond, because the methine bond can easily twist with low activation energy [8b–d]. From the above equation, k_{im} assumes that the intermediate in thermal equilibrium depends on the external environment involving free volume or viscosity of the medium that imposes a rotational restriction on the central methine bond. Thus, the fluorescence lifetimes in toluene at 200 and 285 K suggest that fluorescence and non-radiative processes are competing in the S_1 state. Interestingly, the obtained fluorescence decay profiles of PMC are in close agreement with previously reported data [7,8b,c]. The previous reports also indicate that a higher fluorescence quantum yield was observed at a lower temperature [13]. Therefore, the proposed intermediate state would be formed via a non-radiative process which involves significant structural relaxation because the significant contribution to the longer component for PMC indicates that S_1 of PMC could be more easily set in equilibrium with the intermediate state than PMCAz. In other words, it was suggested that the structural relaxation of PMCAz was prevented in both matrices by the bulky Az moiety and the viscosity of the medium, and consequently, the inhibitory factor for the relaxation of PMC is only the viscosity of the medium. In addition, the intermediate state was identified using the time-resolved fluorescence spectra measurements of PMC and PMCAz in the PMMA films, as shown in Fig. 4. The time resolved fluorescence spectra of PMC shows a long-wavelength spectral shift within about 0–2.0 ns. Experimental proof for the existence of several PMC-forms was obtained by the photochemical reaction carried out in rigid media at low temperatures [12]. Therefore, the red-shifted fluorescence was generated from some geometric arrangements of the PMC-form. The intermediate state then thermally relaxes to the excited state of the other conformations. The conformation of the PMC-form possesses a central chain of three carbon–carbon bonds. Thus, by the three associated dihedral angles, eight geometric arrangements of this chain may be recognized ($2^3 = 8$ possible conformations). As for the reason for decreasing static fluorescent intensity of PMCAz, the contribution of k_{ic} became larger than that of PMC since the excited state of PMCAz was thermally unstable owing to the bulky Az moiety. Also, energy transfer from the PMC moiety to the Az moiety in PMCAz is another possible reason for the different intensities of the static fluorescence spectra. The independence of the PMC moiety in PMCAz was also investigated. Since the absorption band of the Az moiety is in the region <500 nm, the energy of 545 nm light cannot be absorbed by the Az moiety. However, 360 nm light has sufficient energy to transfer to the Az moiety. Thus, the lifetimes for PMCAz at 360 nm excitation were compared to that at 545 nm excitation. The results were $\tau_1 = 61$ ps (92%) and $\tau_2 = 724$ ps (8%) for 360 nm excitation (*cis*-Az moiety) and $\tau_1 = 63$ ps (94%) and $\tau_2 = 899$ ps (6%) for the 545 nm excitation (*trans*-Az moiety). Similar values were obtained for the main component (τ_1). From this result, it is unlikely that an energy transfer from the PMC moiety to the Az moiety could occur. Therefore, it was concluded that the PMC moiety is independent from the Az moiety.

4. Conclusions

Fluorescence dynamics of PMC and PMCAz were examined under three different sets of experimental conditions. The fluorescence lifetimes heavily depended on the viscosity of the medium. The results suggest that the non-radiative process from S_1 of the PMC-form is closely related to structural relaxation. Comparison of the lifetimes of PMC and PMCAz indicated significant dynamics. The non-radiative process from the S_1 of the PMC-form to the intermediate state in PMCAz occurred more easily than that in PMC. One possible consideration is that the bulky Az moiety in PMCAz seems to inhibit the non-radiative process. Moreover, it is unlikely that energy transfer from PMC moiety to Az moiety could occur.

It is concluded that SpAz has four clear digital codes and that there is potential for using it for the fabrication of multi-addressable systems and molecular switching for optical memories.

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