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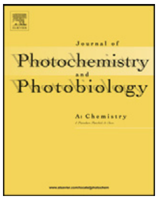

Time-resolved fluorescence study on the photomerocyanine form of spiropyran and its derivative with azobenzene

Kenji Kinashi[a,*], Yoko Ono[a], Yukito Naitoh[b], Akira Otomo[b], Yasukiyo Ueda[a]

[a] *Graduate School of Engineering, Department of Chemical Science and Engineering, Kobe University, 1-1, Rokko, Nada, Kobe 657-8501, Japan*
[b] *National Institute of Information and Communications Technology, Kobe Advanced ICT Research Center, Kobe 651-2492, Japan*

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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.

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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[*] Corresponding author. Tel.: +81 75 724 7809.
E-mail address: kinashi@kit.ac.jp (K. Kinashi).

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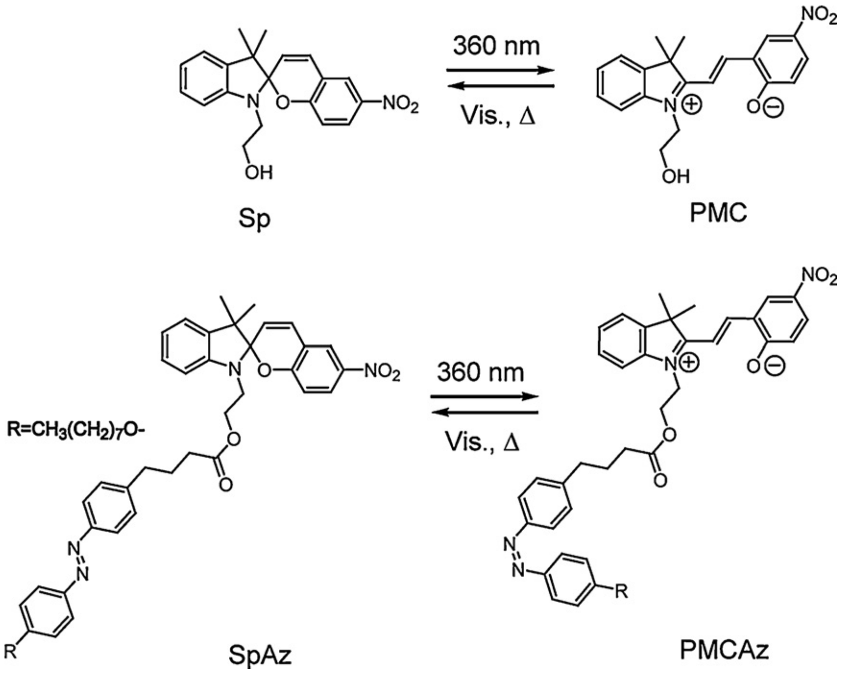

Fig. 1. Photochromic reactions from Sp to PMC and SpAz to PMCAz upon 360 nm excitation, and their back reactions. As the structure of the PMC-form, the most stable rotational isomer, the *trans–trans–cis* (TTC) form, around the methine bridge is described.

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