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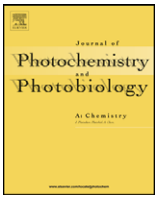

Transient spectra, kinetics and mechanism of Rhodamine 700 dye precursor photoreaction

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ABSTRACT

A new dye precursor (DP) molecule was synthesized and its photochromic, spectroscopic and kinetic properties were determined. This dye precursor yields the strongly fluorescent Rhodamine 700 dye when it is exposed to UV light. The ability to form a highly fluorescent dye was utilized in the fabrication of two-photon volumetric optical memory materials. The spectral characteristics, kinetics and photochemistry were measured and the photoreactions mechanism is proposed.

1. Introduction

Materials possessing functionality that can be activated by light-irradiation are of great importance because of their potential use in various applications such as drug delivery systems (DDS) [1,2], biological function imaging [3], printing [4] and optical data storage [5–8]. Among the types of functionality, fluorescence switching is one of the most desirable functions for volumetric optical data storage. The access of the stored data is achieved by measuring the fluorescence emitted by the fluorescing form of the photochromic material.

In the past decade or so we have developed a series of efficient and stable two-photon 3D recording materials using photochromic fluorescence compounds [9–12]. The write once read many (WORM) materials that we have synthesized and utilized as media to record and access information in 3D format were composed of two components: a photoacid generator (PAG) and a dye precursor (DP), both uniformly dispersed in a polymer host. The light-sensitive PAG produces acid molecules when exposed to light by either one UV photon (one-photon process) or two visible photons (two-photon process). The DP molecules are colorless and stable in neutral media, however a photoinduced acid will react with DP molecules to generate strongly colored, fluorescing molecules at the point, bit, where the laser pulses are focused. Several other groups have reported research on photoacid generators to modify dyes for optical data storage [13–16].

The novel DP molecules that we have utilized as a component for WORM media used to store, for the first time ever, 1 TB of data in a single DVD size disk [12] have the structure, shown in Scheme 1. This molecule was synthesized by treatment of Rhodamine 700 dye with base and determined that in the presence of acid restores the original structure of Rhodanine 700.

During the course of our research we also found that this dye precursor molecule possesses photochromic properties, namely it produces, reversibly, a fluorescent dye when exposed to UV light. In this paper we describe the synthesis, photochemistry, spectroscopic properties, kinetics and photoreaction mechanism of this DP material.

2. Experimental

Rhodamine 700 was a Lambdachrome laser dye. The other chemicals were Aldrich HPLC or spectral grade and used without further purification. Absorption and fluorescence spectra were measured using a Shimadzu UV-1601 spectrophotometer and a Shimadzu RF-5301PC spectrofluorophotometer respectively. Photoirradiation was carried out using a 150 W Xenon arc lamp (Oriel) or the 266 nm FHG, fourth harmonic, of a Continuum Surelite II laser.

Fluorescence quantum yields were measured relative to p-terphenyl standard with known quantum yield of 0.93 [17]. Photocoloration quantum yield, the ratio of photoinduced dye

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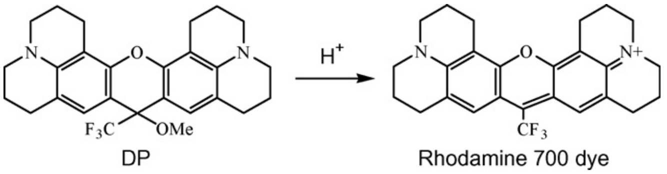


Scheme 1.

molecule number to the number of photons absorbed, was measured in 1 cm quartz optical cell excited by 266 nm laser pulses, generated by a Surelite II laser. To avoid possible thermal and nonlinear effects, the excitation beam diameter was 5 mm and the pulse energy ~1 mJ, while solutions were continuously stirred during the experiment. The number of absorbed photons was calculated from the pulse energy corrected for reflection and other energy loses. To insure that all excitation photons are absorbed the solutions optical density at 266 nm was 2.5. The number of photoinduced dye molecules was calculated from the absorption spectra measured immediately after excitation.

Ultrafast kinetics of the DP solutions were measured using the experimental systems described by us previously [18]. The experimental system consisted of a Tsunami (Spectra Physics) Ti:Sa femtosecond laser, amplified to emit 2 mJ, 150 fs, 267 nm third harmonic pulses, which were used for excitation. The picosecond range time-resolved spectra were obtained by excitation with a 266 nm, fourth harmonic, 35 ps pulse emitted by a Continuum Nd:YAG laser. The photoinduced transients were probed by delayed broad-spectrum super-continuum pulses, generated by passing fundamental wavelengths, 800 or 1064 nm, pulses through the cell with H_2O/D_2O mixture.

2.1. *Preparation of Rhodamine 700 dye precursor*

1 g of Rodamine 700 dye was dissolved in 50 ml of methanol and then a 0.2 M solution of potassium hydroxide in methanol was added dropwise under continuous stirring. After a white precipitate was formed and the blue color of the solution completely disappeared, the solvent was removed under vacuum. The product obtained was redissolved in 3:1 mixture of hexane/dichloroethane, filtered through fine Whatman filter paper and subsequently the solvent was removed by using a rotovapor under vacuum. The residue was recrystallized from ethanol yielding ~0.75 g of dye precursor white powder whose structure was confirmed by NMR and MS.

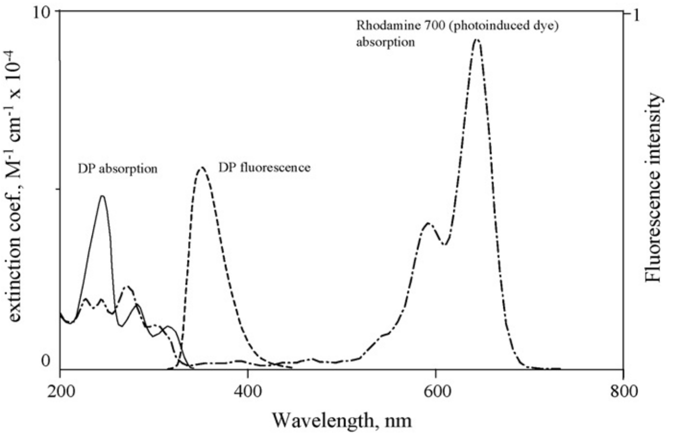


Fig. 1. Absorption and fluorescence spectra of DP and absorption spectra of the photoinduced dye and Rhodamine 700 in acetonitrile.

3. Results and discussion

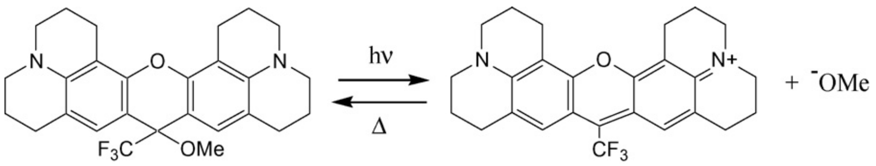
3.1. *Absorption and fluorescence properties*

The dye precursor is a neutral molecule soluble in most polar and non-polar organic solvents such as hexane, acetone, alcohols and acetonitrile. Fig. 1 shows the absorption spectra of DP in acetonitrile. This figure shows that this molecule absorbs in the UV region below 350 nm and also exhibits a slight red shift, few nanometers, in polar solvents such as acetonitrile and DMSO compared to non-polar hexane, which is shown in Table 1. The red shift in the absorption maximum with solvent polarity increase is indicative of π–π^* transition to the first excited state.

When excited with UV light DP molecules emit fluorescence whose spectra are also shown in Fig. 1. Fluorescence quantum yields were measured in various solvents and these data are listed in Table 1. The quantum yields were measured relative to p-terphenyl in cyclohexane used as a standard, which known to have $\phi = 0.93$ [17]. Table 1 shows that the fluorescence spectra display a red shift with increase in solvent polarity.

Table 1
Spectroscopic properties of DP in various solvents: absorption and fluorescence wavelength maxima; quantum yields of fluorescence and coloration photoreaction; rate constant of bleaching reaction of photoinduced dye.

Solvent	λ_{abs} (nm) (max)	λ_{fl} (nm) (max)	QY_{fluor}	$QY_{coloration}$	$k_{bleaching}$ (M^{-1} s^{-1})
DMSO	247, 284, 319	354	0.20 ± 0.04	0.047 ± 0.01	
Acetonitrile	246, 283, 317	351	0.20 ± 0.04	0.054 ± 0.01	
Methanol	246, 281, 315	349	0.06 ± 0.02	0.37 ± 0.05	550 ± 10
1-Propanol	246, 281, 313	345	0.12 ± 0.03	0.29 ± 0.05	2000 ± 5
1-Octanol	246, 280, 313	344	0.17 ± 0.04	0.17 ± 0.04	4000 ± 500
Hexane	246, 279, 312	336	0.20 ± 0.04	0	



Scheme 2.

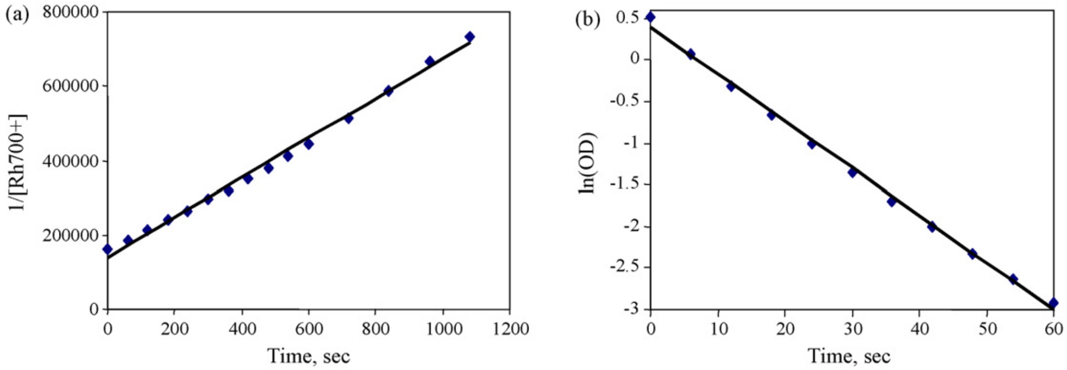


Fig. 2. Bleaching kinetics of the photoinduced dye in (a) methanol and (b) 10^{-4} M KOH/methanol solutions.

3.2. Photochromic properties

Solutions of DP in polar solvents were found to possess the following photochromic properties when exposed to UV light. The originally colorless solutions become colored. The absorption spectrum of the photoinduced colored product is identical to the absorption spectrum of Rhodamine 700 dye, Fig. 1; however, the initial coloration induced by UV light disappears. The bleaching rate that we measured was found to depend on solvent polarity, see Table 1. The DP also exhibits photochromic properties when it is dispersed in poly(2-hydroxyethyl methacrylate) films. Polymer films were made by casting from a solution of DP and poly(2-hydroxyethyl methacrylate) in methanol.

Based on the similarity of the absorption spectra between the photoinduced product and Rhodamine 700, we assume that the photochromic properties of the DP molecule may be described by photochemical reaction, shown in Scheme 2.

Light-induced C–O bond cleavage of the DP molecule leads to formation of a cation with Rhodamine 700-like structure and a nucleophilic MeO^- counter-anion. These cation and anion may recombine to form the original DP molecule. The bleaching kinetics in methanol, shown in Fig. 2a, show that the reaction follows second-order law that confirms the recombination of photoinduced cation and anion, which are formed in equal concentrations after C–O bond cleavage. In parallel with coloration and following the bleaching of DP in methanol solution we observed a decrease in DP fluorescence intensity, after UV exposure. This is followed by relaxation back to the original state with the same rate as the bleaching of the photoinduced 650 nm absorption band. Assuming the same extinction coefficient value for the photoinduced dye as 92,500 of the Rhodamine 700 [19], we have calculated the second-order rate constant of this recombination reaction in methanol solution to be equal to 550 $M^{-1}\,s^{-1}$. When the photoreaction of DP is conducted in 1.0×10^{-4} M solution of potassium hydroxide in methanol, the bleaching kinetics become pseudo-first-order due to excess of MeO^- anion concentration, see Fig. 2b. The bleaching rate constant calculated from these data yields practically the same value. However, in octanol solution, which is a much less polar solvent than methanol, the bleaching rate constant was measured to be $4 \times 10^3\,M^{-1}\,s^{-1}$ which is approximately seven times larger than rate constant in methanol. The relative increase in the bleaching rate constant in less polar solvents such as propanol and octanol compared to more polar methanol, see Table 1, is probably due to the stabilization of the cation–anion pair by polar solvent molecules.

Quantum yields of DP transformation from the colorless to colored dye form in various solvents were measured by excitation with 266 nm laser light and calculating the ratio of photoinduced dye molecules to the number of photons absorbed. The values of the quantum yields listed in Table 1 show that in acetonitrile solution the coloration efficiency is significantly lower than the one in alcohols. As mentioned above, photocoloration of DP solutions leads to decrease in fluorescence intensity (at the ~350 nm maximum), which in alcohol solutions recovers almost completely to the original value shortly after bleaching. However, in acetonitrile solutions the fluorescence intensity decreases and does not return back to the original value after similar excitation conditions. The absorption spectrum of DP is also restored after bleaching in alcohol solutions, while in acetonitrile the change is irreversible. Those data indicate that some irreversible decomposition process occurs during coloration of DP in acetonitrile. The same behavior was observed in other aprotic solvents, such as DMSO and DMF. In lower polarity

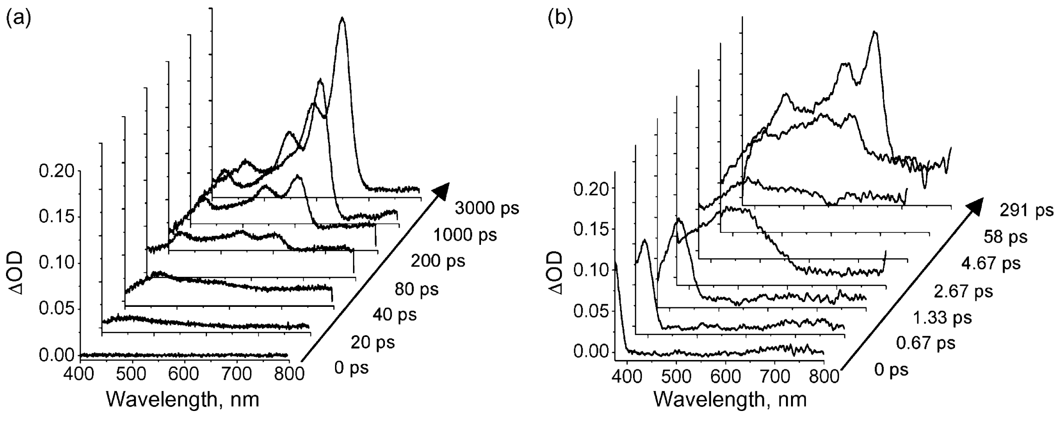


Fig. 3. Transient absorption spectra of DP/methanol solutions measured after 266 nm excitation with (a) 35 ps and (b) 150 fs laser pulses.

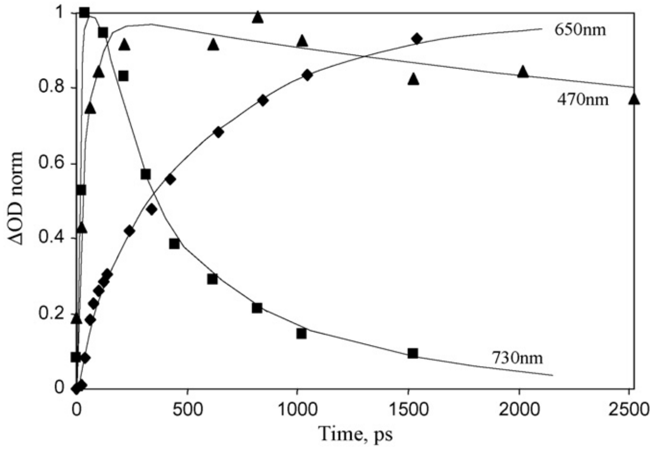


Fig. 4. Formation and decay kinetics of transients in DP/methanol solution after excitation with 266 nm, 35 ps laser pulse.

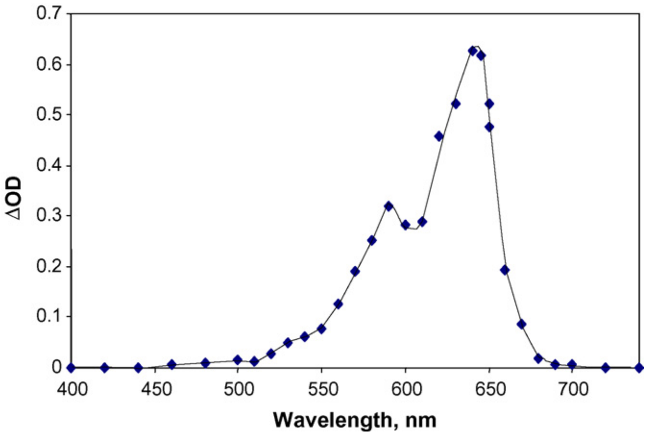


Fig. 5. Transient absorption spectrum of DP/methanol solution measured 100 ns after excitation with 266 nm, 6 ns laser pulse.

solvents, such as THF, hexane, UV exposure of DP solutions leads only to irreversible decomposition of DP molecules rather than coloration.

3.3. Time-resolved spectra and kinetics

Fig. 3a shows transient absorption spectra of DP solution in methanol after excitation with 266 nm, 35 ps laser pulses. The transient spectrum consists of a broad absorption band that covers the region from 400 nm to 800 nm and a wide maximum at ~450 nm that is formed after excitation. At ~60 ps after excitation two new absorption bands located at 580 and 645 nm appear and continue to grow with a rise-time of ~0.5 ns, Fig. 4. These two peaks correspond in shape and wavelength exactly to the absorption maxima of Rhodamine 700 dye and therefore strongly indicate that the rate of its appearance corresponds to the rate of formation of this dye, which is also the final product of this photoreaction. The rise-time of this dye product corresponds also to the decay time of the transient absorption at 730 nm, Fig. 4, where, as shown in Fig. 1, Rhodamine 700 does not absorb. These spectra and kinetics suggest that the 730 nm transient is precursor of Rhodamine 700 dye. The absorption band at 470 nm decays with much slower rate than the rise of absorption at 645 nm, Fig. 4, therefore this transient cannot be precursor of the Rhodamine 700 dye, but rather a lower quantum yield side product formed in a parallel reaction path. The 470 nm absorption band was also found to almost completely disappear after 100 ns. The spectra of the species formed after 100 ns correspond to absorption of Rhodamine 700, are shown in Fig. 5.

The proposal that the transient absorption, at 470 nm, belongs to a side reaction product is also confirmed by the transient absorption spectra measured in acetonitrile solutions, where the decomposition process is efficient. These spectra show similar behavior as in methanol solutions, however, the intensity of transient absorption at 470 nm relative to Rhodamine 700 maxima, at 580 and 645 nm, is much more intense than the one measured in methanol, Fig. 6a. The rise of the 645 nm absorption band and the decay of the 730 nm absorption band in acetonitrile also proceed simultaneously, Fig. 6b, but this decay lifetime was measured to be 3 ns, which is slower by factor of 6 than the lifetime measured in methanol. This behavior may be explained if we assume that a radical pair is formed after the C–O bond cleavage of the excited DP molecules, followed by electron transfer. The broad transient absorption spectra with a wide maximum at ~450 nm and a long tail in the 730 nm range, observed ~20–60 ps after pulse excitation, Fig. 3, could be due to the $DP^{\bullet}$ radical. We believe that the primary photochemical process is the formation of singlet-excited state DP molecules, DP^*. However, our data cannot clearly identify this species strictly from the spectra evolution from this electronically excited state to the radical. The uncertainty lies on the fact that the spectrum maybe hidden, owing to the fact that these spectra are broad and overlap extensively. Transient absorption spectra of DP in methanol solution, measured after excitation by 266 nm, 150 fs laser pulses, reveal that 400 nm transient is formed in a time equal to the excitation pulse duration and decays within ~2 ps, Fig. 3b. The observed spectra evolution is also complicated by the probe beam dispersion [18]. The transient absorption at 730 nm appears to grow with the same ~2 ps rise-time as the decay of the transient absorption at 400 nm, Fig. 7, that

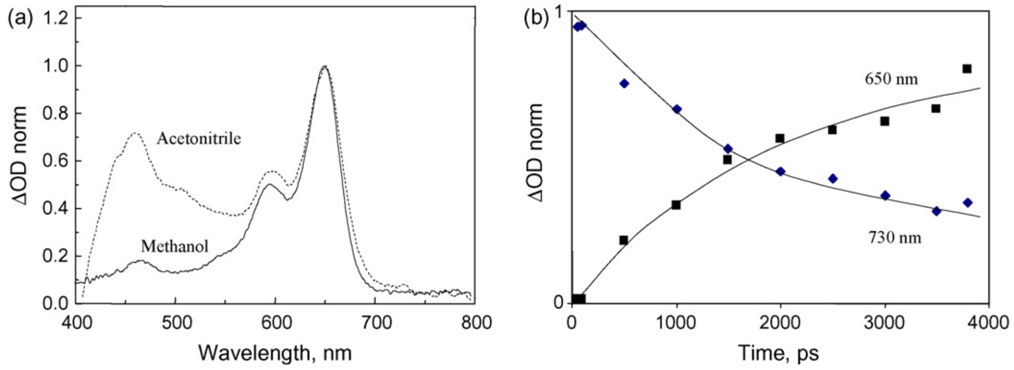


Fig. 6. (a) Transient absorption spectra measured 4 ns after excitation of DP in methanol and acetonitrile and (b) kinetics measured at 650 and 730 nm in acetonitrile.

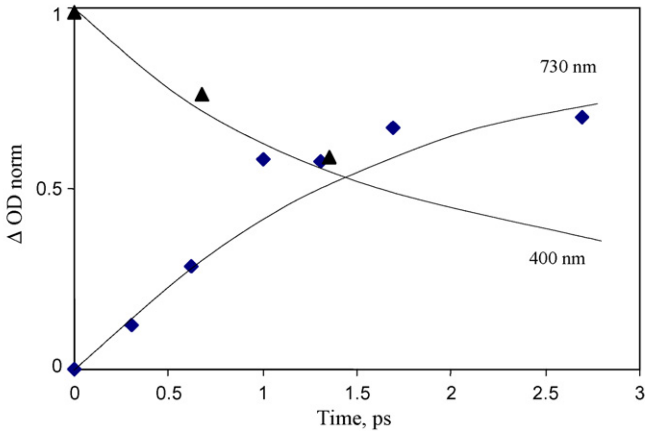
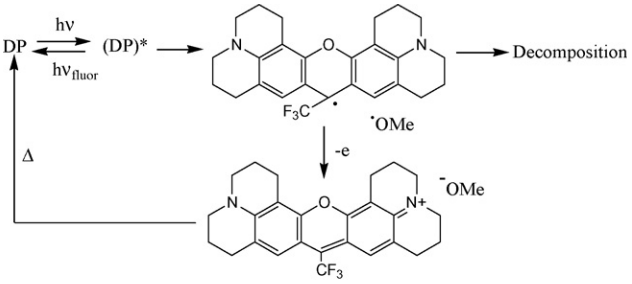


Fig. 7. Formation and decay kinetics of transients measured at 400 and 730 nm after excitation of DP/methanol solution with a 266 nm, 150 fs laser pulse.



Scheme 3.

may be attributed to the transition from the singlet-excited state to radical pair. The radicals formed react further resulting in:

(1) recombination that will form the original molecule,
(2) decomposition,
(3) hydrogen abstraction from solvent,
(4) electron transfer that will lead to the formation of the dye.

In methanol more effective hydrogen abstraction and/or electron transfer will decrease the DP$^\bullet$ radical lifetime and consequently depress its recombination and decomposition that should lead to increase in the quantum yield of dye formation. In contrast aprotic solvents such as acetonitrile will increase the DP$^\bullet$ radical lifetime and consequently increase the probability of its recombination and decomposition, resulting in a lower dye formation quantum yield. In fact, the measured sixfold faster decay rate of DP$^\bullet$ radical in methanol compared to acetonitrile correlates very well with the dye formation quantum yields measured in the same solvents, which is found to be also sixfold higher in methanol than in acetonitrile, see Table 1.

Taking into account the above considerations, we propose the following scheme for the photoreaction mechanism of DP molecule, shown in Scheme 3.

4. Conclusion

We have synthesized a novel photochromic dye precursor molecule that generates a strongly fluorescent Rhodamine 700 dye. Its spectral properties and photoreaction kinetics were measured and the photoreaction mechanism is determined. The photocoloration proceeds from the singlet-excited state of DP molecule via C–O bond cleavage and formation of a radical pair, followed by electron transfer that leads to the formation of Rhodamine 700 structure.

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