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Evaluation of sensitizing ability of barbiturate-functionalized non-ionic cyanine dyes; application for photoinduced radical generation system initiated by near IR light

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Abstract

The sensitizing abilities of near infrared (near IR)-absorbing ionic (**D1**) and non-ionic (**D2** and **D3**) cyanine dyes in a photoinduced radical polymerization system were evaluated. The solubility in an organic solvent of non-ionic cyanine dyes is much higher than that of an ionic cyanine dye. The photoinduced radical polymerization system consists of a sensitizing dye (**D1**–**D3**), 2,4,6-tris(trichloromethyl)-*s*-triazine (TCT, as a radical genetrator), and a poly-functional acrylate monomer (DPHA) in the binder polymer. All dyes showed a sensitizing ability in the photoinduced radical polymerization systems by near IR light. Non-ionic cyanine dyes, **D2** and **D3**, showed a higher sensitizing ability than **D1**. From the IR and UV–vis studies, it was revealed that the high sensitizing ability of **D2** and **D3** is a result of an interaction between the dye and TCT in the polymer matrices, promoting the electron-transfer from the dyes to the TCT.

Keywords: Photopolymerization; Cyanine dye; Near IR; Photoinduced electron transfer

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1. Introduction

Much attention has been paid to the highly sensitive photoinduced polymerizing system in view of its applicability to imaging technologies [1,2]. Photopolymerization is mostly based on the radical polymerization of organic compounds such as vinyl monomers, oligomers, or polymers. Many studies have been devoted to the development of the photoinduced radical initiating system (photoinitiator). In this system, the excitation energy is transferred from the sensitizing dye to a radical generator. Thus, far we [3–7] and others [8–18] reported the behavior of UV and vis-sensitive photoinitiators.

In spite of the many examples of UV and vis-sensitive photoinitiators, there are only a few reports of photopolymerization that can be initiated by near infrared (near IR) light [19–27]. The use of near IR light is highlighted by its low photon energy. This enables us to operate the irradiation process under daylight, which is mostly composed of visible light. Cyanine dyes have evoked interest primarily because of their wide application field [28,29]. Moreover, its absorbing wavelength can be readily adjusted by changing the length of the conjugated methine chain. However, the solubility of cyanine dyes in an organic solvent is usually very poor, due to its ionic property as in near infrared-absorbing ionic (**D1)** shown in Fig. 1. For application of cyanine dyes to imaging technology, a high solubility in an organic solvent is required since the imaging technology requires an appropriate photosensitive layer thickness that is only satisfied by solution-based methods such as spin-coating wire-wound bar coating. In this

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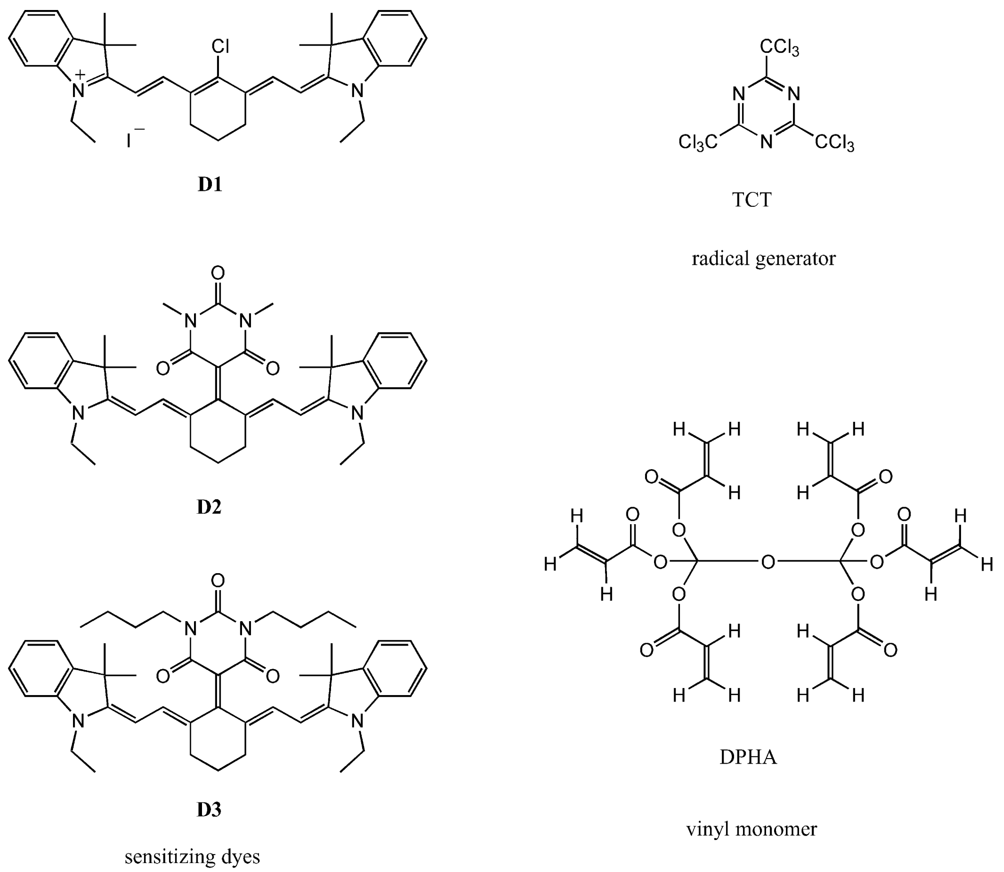


D1

D2

D3

sensitizing dyes

TCT

radical generator

DPHA

vinyl monomer

Fig. 1. Molecular structures of sensitizing dyes (**D1**–**D3**), radical generator (TCT) and vinyl monomer (DPHA).

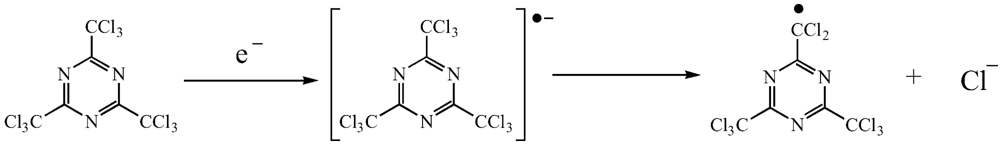
study, we focused on designing the cyanine dyes soluble in an organic solvent using strategically placed substituents.

The introduction of a substituent that is conjugated by a double bond at the center of a polymethine chain is critical strategy, because it removes the ionic property from the cyanine dyes as shown in Fig. 1. We synthesized the barbiturate-functionalized non-ionic cyanine dyes, **D2** and **D3**, and evaluated their sensitizing ability for application in the near IR light-induced radical generating system. We used 2,4,6-tris(trichloromethyl)-*s*-triazine (TCT) as the radical generator, which forms a radical by decomposition of its anion radical (Scheme 1) [32,33]. From the result of its sensitizing ability in a photoinduced radical polymerization system, the barbiturate-functionalized cyanine dye showed a high sensitizing ability in comparison to **D1**. Furthermore, it revealed that the barbiturate-substituted **D2** and **D3** effectively interacted with TCT, resulting in a high efficiency of the photoinduced electron transfer reaction and initiating a large amount of radicals.

2. Experimental

2.1. Materials

Sensitizing dyes **D1**–**D3** [32,33] and 2,4,6-tris(trichloromethyl)-*s*-triazine [34] were synthesized according to the literature methods. Polymethyl methacrylate (PMMA) and polyvinyl alcohol (PVA) were purchased from Wako Pure Chemical Industries Co., Ltd., and used without further purification. The poly-functional acrylate monomer, DPHA, was purchased from Nippon Kayaku Co., Ltd. All solvents were purified by distillation before use.



Scheme 1. Radical initiation from TCT.

2.2. Instrumentations

Absorption spectra in the vis and near-IR regions were measured using a JASCO V-570 UV/vis spectrophotometer. IR spectra of the films were measured using a JASCO FT/IR-410 spectrophotometer. The redox potentials of the dyes and TCT in N_2-saturated acetonitrile were measured by cyclic voltammetry using a HOKUTO DENKO HABF1510m. The Ag/Ag^+ electrode was used as the reference electrode. 0.1 M tetrabutylammonium tetrafluoroborate was used, as the supporting electrolyte and the sample concentration was 0.05 M for each measurement. The CV voltammograms were recorded by scanning from −2.0 to +2.0 V at scan rates of 100 mV s^{-1}. For the irreversible system, the redox potential data were taken equal to the half-peak potentials. All potentials are listed versus the standard calomel electrode (SCE) in Table 1.

2.3. Preparation of PMMA film of dyes for spectral measurement

PMMA films containing **D1**–**D3** for the absorption measurement and IR spectra were typically prepared in the following manner. **D1**–**D3** with or without TCT was dissolved in 10 wt.% PMMA in chloroform. This solution was coated on a glass plate by a spin-coating method (1000 rpm). The solvent was removed by air-drying for 30 min. The PMMA film was peeled from the glass plate then further dried in a vacuum. The thickness of the prepared film was about 5 μm and the concentration of the sensitizing dye was ca. 10 mmol dm^{-3} in PMMA.

2.4. Preparation of photopolymer plate

The polymer solution was initially prepared by dissolving the poly-functional acrylate monomer and alkali-soluble binder polymer (copolymers of methyl methacrylate and methacrylic acid; 1:9 by mol) (DPHA: the binder polymer = 1:1 by weight) in a mixture of cyclohexanone and 2-methoxyethanol (9:1 by weight) (the presence of these DPHA and the binder polymer does not effect the initial process of the electron transfer between the excited cyanine dye and TCT). The sensitizing dye and TCT (2:5 by weight) were dissolved in the polymer solution (dye: TCT: DPHA = ca. 1: 3.3: 35 by mol). This solution was coated on the aluminum plate with a wire-wound bar, then dried in an oven at 70 °C for 2 min. The thickness of the photosensitive layer was ca. 5 μm. The concentration of the sensitizing dye and TCT were about 40 and 130 mmol dm^{-3}, respectively. To prevent a reaction with oxygen, the obtained plate was further coated with a 5 wt.% PVA aqueous solution followed by drying in oven for 2 min.

Table 1
Optical, redox and energetic data of **D1**–**D3**

	$\lambda_a(CH_3CN)$ (nm)	λ_a(PMMA) (nm)	E_{ox} (V)	E_{red} (V)	ΔG_{et} (kcal mol^{-1})
D1	778	790	+0.45	−0.64	−8.6
D2	747	758	+0.28	−0.95	−13.9
D3	747	757	+0.27	−0.94	−14.1

2.5. Evaluation of sensitivity of the photopolymer plate by light irradiation

Photosensitivity of the photopolymer plate was evaluated from the minimum light energy dose required to make an insoluble image in an aqueous alkali developer solution. Irradiation was carried out using a xenon lamp (USHIO UI-501C; 500 W) through a Narumi Co., Ltd., grating spectrograph to provide selective irradiation in the wavelength region between 680 and 980 nm. After a 5 min irradiation, the uncured part was removed by immersing the coatings in an aqueous alkali developer (1% Na_2CO_3 aqueous solution) for 30 s and washing with water. The sensitivity (S [mJ cm^{-2}]) was obtained from the polymerized part on the plate. The obtained sensitivity was reduced to the photon number (M [einstein cm^{-2}]) for photochemical evaluation at the desired wavelength.

3. Results and discussion

3.1. Solubility of sensitizing dyes ***D1–D3****, and their optical and redox properties*

The solubility of the sensitizing dye is a particularly important factor aspect when evaluating candidates for use in a polymer matrix, since the most desirable processing of these materials is solution-based methods such as spin-coating and wire-wound bar coating as described in the introduction. The absence of ionic properties for **D2** and **D3** drastically enhanced their solubilities in a less-nonpolar organic solvent such as chloroform. The saturated concentration of **D1** is about 40 mmol dm^{-3}, whereas that of **D2** and **D3** is 170 and 110 mmol dm^{-3}, respectively. This result shows that the non-ionic cyanine dye is superior to the ionic cyanine dye regarding solubility, thus allowing us to make a highly concentrated photosensitive layer.

The absorption spectra of the sensitizing dye **D1**–**D3** in acetonitrile are shown in Fig. 2. All dyes have a π–π* absorption band in the 600–800 nm region. The absorption spectra of **D2** and **D3** are almost identical and their absorption maxima are shorter than that of **D1** by 30 nm. The absorption property of **D1** in the near IR region is imparted by the ionic nature of the dipole diamidine structure. In spite of the lack of an ionic property, the absorption maxima of **D2** and **D3** are notably not very far from **D1**. This implies the contribution of the zwitterionic structure in **D2** and **D3** (Scheme 2) [35–37]. This zwitterionic structure is attributed to the strong electron withdrawing effect of the barbiturate substituent.

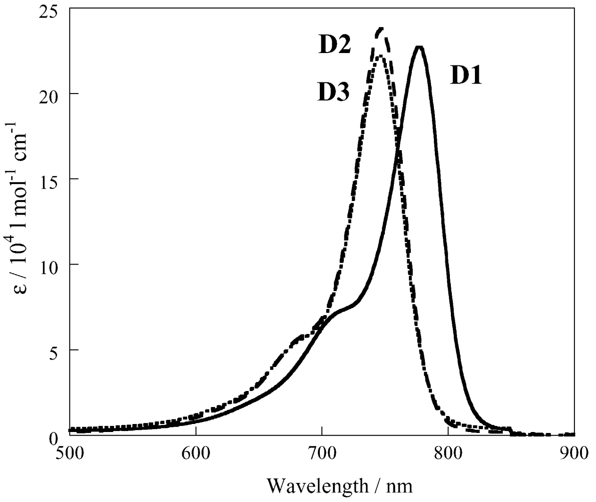


Fig. 2. Absorption spectra of sensitizing dyes **D1** (solid), **D2** (dotted), and **D3** (dashed line) in acetonitrile.

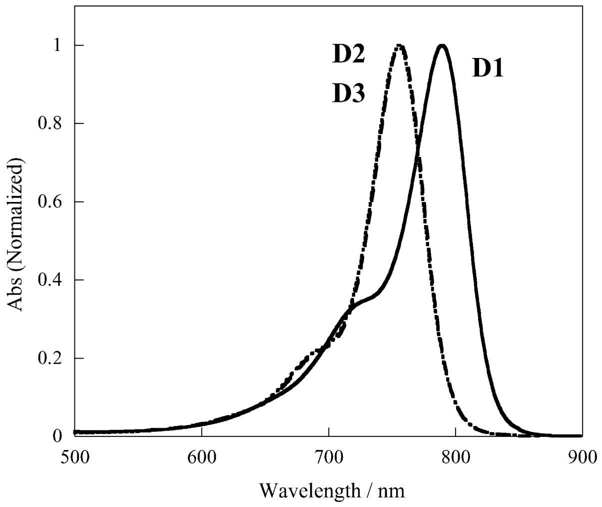


Fig. 3. Normalized absorption spectra of sensitizing dyes **D1** (solid), **D2** (dotted), and **D3** (dashed line) in PMMA film.

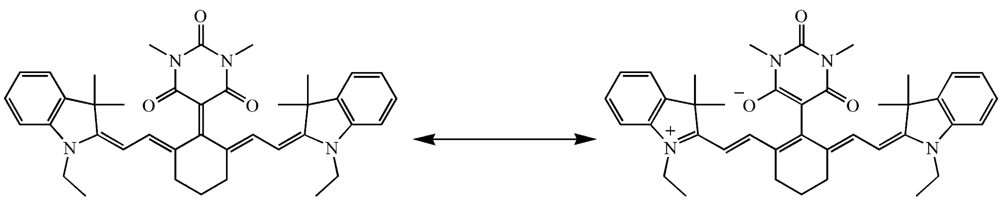
Fig. 3 shows the absorption spectra of dyes embedded in the PMMA film. Although the absorption maxima red-shifted about 10 nm and are slightly broadened compared to those in acetonitrile, the shape of the absorption spectra in the PMMA film is similar to those in acetonitrile. The absorption spectra of these dyes in the PMMA film did not show a concentration dependence in the range from 1.3×10^{-2} to 8.3×10^{-4} mol dm^{-3}. This result demonstrates that the red-shift in the absorption spectrum of the film is not caused by aggregation of the dye, but might be due to the usual solvent effect. The absence of any aggregation is useful for a sensitizing dye of photosensitive layer since a homogeneous photosensitive layer is easily obtained, which is a very important property for industrial materials.

The radical initiating mechanism of a near IR cyanine dye and TCT system starts from an electron transfer, which is from the excited state of the cyanine dye to the ground state of TCT, giving a TCT anion radical. Subsequently a TCT anion radical easily decomposes to give a dichloromethylene-triazine radical and a chlorine anion (Scheme 1) [30,31]. In order to estimate the efficiency of the photoinduced electron transfer reaction between the dye **D1**–**D3** and TCT, we measured the redox potentials of the dyes and TCT in acetonitrile, and calculated the free energy changes for the electron transfer reactions (ΔG_{et}) using the Rehm–Weller equation [38]. The first oxidation potentials of the dyes are summarized in Table 1. The oxidation and reduction potentials of the non-ionic dye are both lower compared to **D1** due to the presence of barbiturate functionality. This was supported by the reduction potential of the barbiturate functionalized cyanine dye that is close to that of 1,3-dimethylbarbituric acid ($E_{\mathrm{red}} = -1.01$ V versus SCE). These values and the excitation energy of the dyes are used for the calculation of ΔG_{et}. The electron acceptor, TCT, has one irreversible reduction potential at −0.83 V (versus SCE). The calculated ΔG_{et} values are also listed in Table 1. Negative values of ΔG_{et} are obtained, indicating the feasibility of the photoinduced electron transfer reaction from the excited dye to TCT.

*3.2. Sensitivity measurement in photopolymer plate containing **D1**–**D3** and TCT*

The above optical and redox data show the possibility of the near IR-induced electron transfer reaction between the sensitizing dye and TCT, which may occur in a polymer matrix. In the next stage of our investigation, we prepared a photopolymer plate containing a sensitizing dye (**D1**–**D3**), TCT and a poly-functional vinyl monomer to investigate the sensitivity of the photopolymer plate.

The photopolymer plate was irradiated by a xenon lamp through the grating spectrograph. After irradiation for 5 min, the photopolymer plate was developed using alkali-developer solution. Surprisingly, the polymeric part appeared as an image in all the photopolymer plates which were irradiated with



Scheme 2. Neutral (left) and zwitterionic (right) structures of **D2**.

near IR light. A photopolymer plate that shows sensitivity to near IR light is rare [16,19–27].

From the image of the plates, we obtained the maximum sensitivities and their wavelengths. These results are summarized in Table 2. The $M_{\max}$ value shows the minimum photon number to initiate the photoinduced radical polymerization reaction in the photosensitive layer. The photopolymer plate containing **D2** showed the lowest $M_{\max}$ value. The maximum sensitivity of **D2** is two times higher than that of **D1**. This result is consistent with the result of ΔG_{et}. This indicates that the efficiency of the photoinduced electron transfer from the cyanine dye to TCT is the dominant factor determining the sensitivity.

3.3. *Efficiency of radical generation from TCT in PMMA film*

The results from the above experiment showed that the sensitizing ability of **D2** to drive photopolymerization is the highest among the three examined dyes. Furthermore, the difference in the sensitizing ability strongly depends on the electron transfer from the dye to the radical generator, TCT. Assuming that the sensitized anion radical of TCT quantitatively decomposed into free radical species that initiate the radical polymerization, the sensitizing ability of dye can be also evaluated by the decomposition of TCT.

The mechanism of the radical generation of TCT starts from the decomposition of its anion radical by cleavage of the C–Cl bond, producing a chloride anion and a dichloromethylene-triazine radical (Scheme 1). From this mechanism, the amount of generated radicals should be proportional to the decomposition of TCT. To estimate the decomposition percentage of TCT by the dye-sensitization, we prepared a PMMA film containing only a sensitizing dye and TCT (2:5 by weight) then irradiated by near IR light. This PMMA film corresponds to the photoinduced radical generating system of the photopolymer plate.

The PMMA film is irradiated by a xenon lamp (>540 nm) for 20 s then measured by IR spectroscopy. The irradiation of the PMMA film decreases the absorption intensity at 694 cm^{-1} derived from the C–Cl stretching mode of TCT. Fig. 4 is a plot of the percentage of decomposed TCT as a function of the irradiation time. A comparison of the decomposition percentage for a 300 s irradiation reveals a clear difference between the ionic and non-ionic dyes. The percentage of the decomposed TCT sensitized by **D2** is almost the same as **D3**, and two times greater than that by **D1**. This result agrees with the sensitivity of the photopolymer plate.

Table 2
Sensitivity of photopolymer plate irradiated by xenon lamp

	$S_{\max}$ ($\mathrm{mJ\,cm^{-2}}$) ($\lambda_{\max}$/nm)	$M_{\max}$ (10^{-7} einstein cm^{-2})
D1	32.9 (827)	2.27
D2	13.1 (823)	0.90
D3	20.8 (813)	1.41

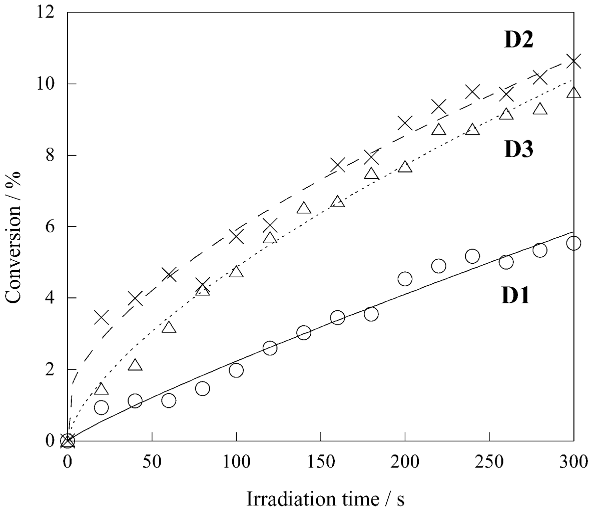


Fig. 4. The plot shows the conversion of TCT by dye-sensitization in PMMA film as a function of irradiation time (**D1**: circles; **D2**: crosses; **D3**: triangle symbols).

During the irradiations the absorption bands of **D1**–**D3** were decreased. Several products were generated and we tried to isolate them but do not have succeeded to determine their structures.

The initial 50 s irradiation of this plot reveals the specific behavior of the decomposition of TCT. In the **D2**-containing film, TCT decomposed with a very high efficiency during the initial 20 s, and then the efficiency is almost parallel to that of the **D1**-containing film. Similarly, in the case of the **D3**-containing film, TCT decomposed with a high efficiency during the initial 120 s, and then the efficiency is also parallel to that of the **D1**-containing film. Thus, the decomposition of TCT in PMMA films of **D2** and **D3** contain two distinct processes. In the rigid matrix, the distance between the electron donor and the acceptor is quite important for the photoinduced electron transfer reaction, because the diffusion of a molecule is significantly inhibited in comparison to a solution and the static electron transfer is a predominant role. The efficient decomposition during the initial stage of the irradiation implies that the photoinduced electron transfer reaction preferentially occurs due to the closeness of the electron donor and the acceptor in the PMMA film.

3.4. *Interaction of dye and TCT in polymer film*

The above experiment implies the static electron transfer of **D2** and **D3** with TCT in the PMMA film though the quenching radii between them were not determined by nonfluorescent **D2** and **D3**. However, the interactions between the dyes and TCT were observed in the ground state. Fig. 5 shows the absorption spectral change of **D2** involved in the PMMA film by adding various amounts of TCT. As the amount of TCT increased, the absorption maxima of the dyes in the PMMA film red-shift and are slightly broadened. In acetonitrile solution, however, this effect is not observed in the same

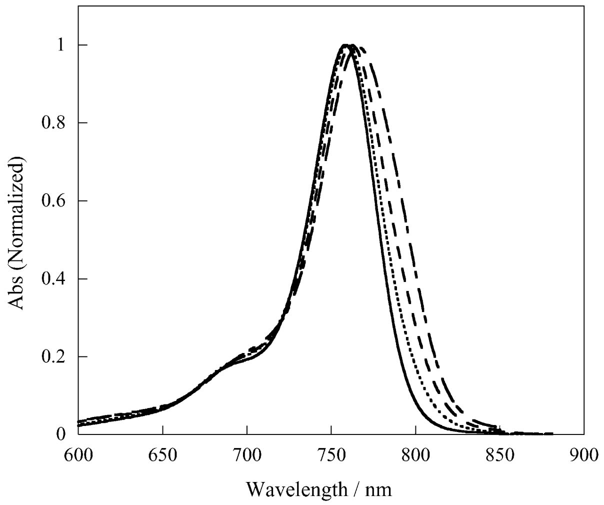


Fig. 5. Normalized absorption spectral change of **D2** (20 mmol dm^{-3}) in PMMA film adding variable amount of TCT ([TCT]/[**D2**] = 0 (solid), 7 (dotted), 35 (dashed), 144(dotted dash lines)).

concentration ratio because the interaction is too weak to be observed in solution.

Fig. 6 illustrates the plots of the shift in the absorption maxima of the dyes with various amounts of TCT in the PMMA films as a function of the molar ratio of adding TCT. The shifts in the absorption maxima of **D2** and **D3** are greater than that of **D1**, indicating that TCT more strongly interacted with the barbiturate-functionalized **D2** and **D3** than with **D1**. As these interactions are corresponding to the difference of the oxidation potentials between the dyes, the interaction between the barbiturate-functionalized cyanine dye and TCT is most likely an aromatic electron donor-acceptor interaction [39–42]. Especially, this interaction for **D2** is much higher than **D3**, which is explained by the difference in the substitution at the nitrogen atom in the barbiturate.

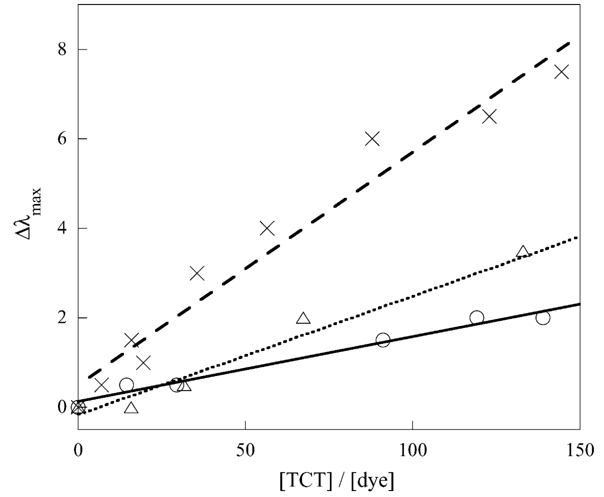


Fig. 6. Influence of adding TCT on absorption maxima of **D1** (solid line and circles), **D2** (dashed line and crosses), and **D3** (dotted line and triangles) (20 mmol dm^{-3}, respectively) in PMMA film.

Thus, the photoinduced radical generation of the cyanine dye–TCT system in the PMMA film is summarized as follows: The static electron transfers are occurred between TCT and the dyes. Especially, in the case of barbiturate-functionalized cyanine dyes, the electron donor-acceptor interaction in the ground state is observed and this interaction could induce the high efficient decomposition.

4. Conclusion

Using the near IR absorbing cyanine dye as a sensitizer, we could obtain a photopolymer plate that shows a high sensitivity to near IR light. The non-ionic cyanine dyes were found to be especially useful as a near IR sensitizer in the multi-components photoinitiation system because of high efficiency of the photoinduced electron transfer reaction. The high efficiencies of the sensitization of **D2** and **D3** in the polymer matrices are partly responsible for the interaction with TCT. From an industrial view, non-ionic cyanine dyes have advantages over ionic cyanine ones because they are soluble in organic solvents, thereby facilitating the solution-based preparation of the photopolymer plate.

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