



## Fluorescence behavior of individual charge-transfer complexes revealed by single-molecule fluorescence spectroscopy: Influence of the host polymer matrix

Sadahiro Masuo<sup>1</sup>, Yasumasa Yamane, Shinjiro Machida, Akira Itaya\*

Department of Macromolecular Science of Engineering, Kyoto Institute of Technology, Matsugasaki, Sakyo-ku, Kyoto 606-8585, Japan

### ARTICLE INFO

#### Article history:

Received 17 August 2011  
Received in revised form 18 October 2011  
Accepted 15 November 2011  
Available online 23 November 2011

#### Keywords:

N-ethylcarbazole  
1,2,4,5-Tetracyanobenzene  
Charge-transfer fluorescence  
Single-molecule fluorescence spectroscopy  
Methacrylate polymers  
Polycarbonate

### ABSTRACT

Extremely pure polymer matrices were used for elucidating the fluorescence properties of singly isolated charge-transfer (CT) complexes formed between the donor N-ethylcarbazole and the acceptor 1,2,4,5-tetracyanobenzene. Simultaneous measurements (time traces of CT fluorescence intensities and lifetimes) using single-molecule fluorescence spectroscopy showed three patterns: (1) fluctuations in the fluorescence intensities and lifetimes seldom occurred, (2) the fluorescence intensities frequently fluctuated together with the lifetimes, or (3) in addition to the above fluctuations with time, blinking and/or off-states longer than 1 s were observed. For methacrylate polymers, both the degree of fluctuations in the CT fluorescence lifetimes and the percentage of the CT complexes showing off-states increased with the free volume of the host polymers. These results suggest that the degree of fluctuations in the relative geometrical arrangements of the donor and acceptor molecules is related to the availability of space in the host polymer, and that the free volume provides the necessary space for formation of non-fluorescent donor–acceptor geometries of the CT complexes and/or temporal dissociation of the CT complexes. Survival times of the CT fluorescence were also closely related with the free volume of the host polymers.

© 2011 Elsevier B.V. All rights reserved.

### 1. Introduction

Single-molecule fluorescence spectroscopy (SMS) has been applied to singly isolated molecules: a single fluorescent chromophore or multiple chromophores covalently linked to each other (e.g., multichromophoric dendrimers), single organic nanoparticles or -crystals and J-aggregates consisting of fluorescent chromophores, and single quantum dots [1–18]. Except for organic nano-particles and J-aggregates, systems formed by weak intermolecular interactions have been excluded from SMS studies. One such weak intermolecular interaction is a charge-transfer (CT) force resulting in the formation of CT complexes. It is widely known that certain CT complexes exhibit fluorescence [19]. Each CT complex is formed from two molecules, namely an electron donor and an acceptor, and thus differs from the above single molecules and multichromophoric molecules. Hence, fluorescent CT complexes are interesting research subjects for SMS. The CT fluorescence appears when the excited CT state returns to the ground state CT complex. That is, the CT fluorescence is approximately considered to be emission resulted from a charge-recombination process

in the excited CT state (charge-separated state). Recently, we investigated the fluorescence dynamics of singly isolated CT complexes formed between various monocarbazolyl and dicarbazolyl (Cz) donor compounds and the acceptor 1,2,4,5-tetracyanobenzene (TCNB) in an inert polymer, poly(methyl methacrylate) (PMMA), thin film [20,21].

The formation of CT interactions between Cz compounds and TCNB was investigated under an ensemble condition because the fluorescence properties of Cz:TCNB CT complexes and the electron transport properties of the corresponding neat solid films were revealed in detail compared with those of other CT systems in connection with the photoconductive properties of poly(N-vinylcarbazole) films [22–28]. In addition, since the Cz skeleton can be synthesized from purified tetrahydrocarbazole, it is possible to obtain very pure Cz compounds. The use of very pure compounds is indispensable for observing the fluorescence of isolated CT complexes in polymer matrices by SMS. A concentration of at least  $10^{-10}$  M is usually required for SMS, but since the formation of a CT complex is an equilibrium between separate donors and acceptors on the one hand and the complex on the other, the concentration of the donor and acceptor molecules is required to be much greater than  $10^{-10}$  M. Thus, both the donor and acceptor compounds have to be very pure in order to observe the fluorescence of such complexes at the single-molecule level. In particular, fluorescent contaminations absorbing at long wavelengths (488 nm for the present equipment) should be avoided.

\* Corresponding author. Tel.: +81 75 724 7832; fax: +81 75 724 7832.

E-mail address: [itaya@kit.ac.jp](mailto:itaya@kit.ac.jp) (A. Itaya).

<sup>1</sup> Present address: Department of Chemistry, School of Science and Technology, Kwansai Gakuin University, 2-1 Gakuen, Sanda, Hyogo 669-1337, Japan.

Simultaneous measurements (time traces of CT fluorescence intensity and lifetime) showed three patterns in the PMMA films: (1) fluctuations in the fluorescence intensities and lifetimes seldom occurred, (2) the fluorescence intensities fluctuated frequently together with the lifetimes, and (3) in addition to the second pattern, blinking or off-states (off-times longer than 1 s) were observed. The third characteristic was detected for only 1.7% of the complexes (one CT complex among 60) in the monocarbazolyl-*N*-ethylcarbazole (ECz) CT system and 20–30% in the dicarbazolyl- and monocarbazolyl-*N*-isopentylcarbazole CT systems. The time traces with frequent fluctuations often showed off-states. We attributed the fluctuations in the fluorescence intensities and lifetimes of the isolated CT complexes to changes in the relative geometrical arrangements of the Cz donor and the TCNB acceptor and/or changes in the local environment around the individual CT complexes leading to changes in, e.g., local polarity. Both the frequency of the fluctuations in intensities and lifetimes and the frequency of off-states were related to the chemical structure of the carbazolyl compounds. Because Cz donor chromophores with a small degree of freedom are less able to adapt to positional fluctuations of the smaller TCNB acceptor molecules in CT complexes, the off-states were thought to arise mainly from formation of non-fluorescent donor-acceptor geometries of the CT complexes and/or temporal dissociation of the CT complexes in the inert polymer film during measurement.

In the present work, we investigated the effect of the host polymer matrix on the fluorescence behavior of isolated individual CT complexes formed between ECz and TCNB to reveal the origin of the appearance of the fluctuations and long-off states (off-times longer than 1 s). We used PMMA, poly(ethyl methacrylate) (PEMA), poly(*n*-propyl methacrylate) (PnPrMA), poly(*n*-butyl methacrylate) (PnBuMA), polycarbonate (PC), and a dextrin derivative as host polymers. With respect to the methacrylate polymers (PMMA, PEMA, PnPrMA, and PnBuMA), an increase in the side-chain length results in greater mobility of the main chain and a decrease in the glass transition temperature due to the fact that the side groups hinder packing of the chains in the films, which results in an increase in the free volume. Although values for the permeability coefficient of oxygen gas are unknown for PnPrMA and PnBuMA films, such values for these polymers are expected to be larger than those of PMMA and PEMA because of the increase in free volume of the polymers in the films. As aforementioned, blinking or off-states were observed only for one among 60 ECz:TCNB CT complexes in PMMA films [21]. However, when other polymer matrices were used, the off-states were observed more frequently.

## 2. Experimental

The ECz was the same as the material used previously [20,21]. It was synthesized from purified Cz, recrystallized, and further purified by zone refining and vacuum sublimation. TCNB was purified by recrystallization and vacuum sublimation. The structures of ECz and TCNB are shown in Fig. 1. PMMA and PEMA purchased from Aldrich (secondary standard) were used as host polymers without further purification. PnPrMA was thermally polymerized in a degassed glass tube from rigorously purified *n*-propyl methacrylate, which was distilled under reduced pressure after removal of added inhibitor by a usual method, and was further purified by vacuum distillation. PnBuMA purchased from Polymer Source was used without further purification. Very pure PC and a dextrin derivative with the chemical structure shown in Fig. 1 were supplied by Sumika Styron Polycarbonate Limited and Nissan Chemical Industries Limited, respectively, and were used without further purification. No fluorescence was observed from spin-coated films of these polymers under the present experimental conditions. The

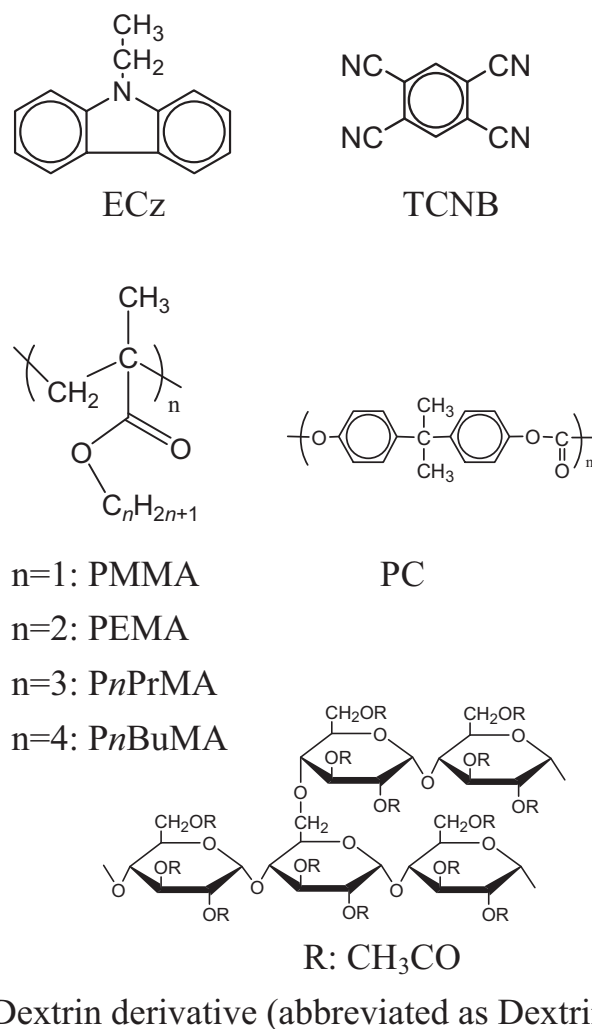


Fig. 1. Chemical structures of the ECz donor, TCNB acceptor, and the polymers used as host matrices.

chemical structures of the host polymers and their physical properties are shown in Fig. 1 and Table 1, respectively. The physical properties of the dextrin derivative (abbreviated as Dextrin) are unknown. This polymer was used, however, because of the observation of characteristic fluorescence properties for CT complexes formed in Dextrin films, as shown later.

Chloroform solutions containing 1 wt% host polymers (PMMA, PEMA, PnPrMA and PC), ECz, and TCNB were spin-coated (at 3000 rpm for 90 s) onto cleaned cover glasses. For the Dextrin polymer, ethyl lactate was used as a solvent. For these polymers, the concentrations of ECz and TCNB in the spin-coated thin films were  $5.0 \times 10^{-4}$  M each.

The fluorescence properties of individual CT complexes were measured using the same system as reported previously [20,21] that was based on a sample-scanning confocal fluorescence microscope consisting of an inverted microscope (TE2000, Nikon) equipped with an oil-immersion objective (Nikon, 100 $\times$ , 1.3 N.A.) and an avalanche single photon counting module (APD) (SPCM-AQR-14, PerkinElmer). The laser and detector systems used were also the same as reported [20,21]. The excitation laser wavelength, power, and repetition rate were 488 nm, 0.34 kW/cm<sup>2</sup>, and 8 MHz, respectively. All measurements were performed under nitrogen at room temperature.

As previously reported for the PMMA system [20,21], in fluorescence intensity images, few bright spots were observed both

**Table 1**  
Physical properties of polymer films used as host matrices.

Polymers	$T_g^a$ [K]	Free volume [nm <sup>3</sup> ]	Permeability coefficient of oxygen gas <sup>a</sup> [cm <sup>3</sup> (STP) cm/(cm <sup>2</sup> s Pa)]	Refractive index <sup>a</sup>
PMMA	378	0.079 <sup>b</sup>	$1.16 \times 10^{-14}$	1.490
PEMA	338	0.088 <sup>b</sup>	$8.89 \times 10^{-14}$	1.485
PnPrMA	308	0.091 <sup>b</sup>	–	1.484
PnBuMA	293	0.099 <sup>b</sup>	–	1.483
PC	417	0.109 <sup>c</sup>	$1.05 \times 10^{-13}$	1.550
Dextrin	–	–	–	–

<sup>a</sup> [44].

<sup>b</sup> At 295 K [45].

<sup>c</sup> At 300 K [46].

for 0.1 M sample of ECz only and for 0.01 M samples of TCNB only, which indicated that the present ECz and TCNB were very pure and did almost not contain compounds showing fluorescence in longer wavelengths.

### 3. Results and discussion

#### 3.1. Simultaneous measurement of the time traces of the fluorescence intensities and lifetimes of singly isolated CT complexes

Before measuring the fluorescence of the isolated CT complexes under a single-molecule condition, absorption and fluorescence spectra and fluorescence lifetimes of the CT complexes under an ensemble condition were measured for cast films with high concentrations of donor and acceptor molecules. These results are given in the Supporting Information.

To assure observation of singly isolated CT complexes, dilute ( $5.0 \times 10^{-4}$  M) samples of ECz donor and TCNB acceptor molecules were prepared. It was impossible to detect the fluorescence of singly isolated CT complexes in PnBuMA thin films under the present single-molecule conditions, although it was observed under an ensemble condition (see Supporting Information). This difference is most probably attributed to the presence of dynamic equilibria between association of the donors and acceptors and dissociation of the CT complexes in PnBuMA films, because the glass transition temperature ( $T_g$ ) of PnBuMA is very close to room temperature, which was the measurement temperature. This dynamic equilibrium makes it impossible to observe the fluorescence of singly isolated CT complexes fixed in PnBuMA films. This situation is never found for single molecules and is a distinctive feature of CT complexes, which exist in equilibrium with the two molecules from which they are formed.

Typical results of simultaneous measurements (time traces of fluorescence intensities and lifetimes) of ECz:TCNB CT complexes in PEMA and Dextrin thin films are shown in Fig. 2 (1–3) and (4–6), respectively. The fluorescence intensity decreased suddenly in a single step to the background level, which is attributed to the scattering of excitation laser light. This single-step decrement corresponds to photo-bleaching of the CT complex, indicating that the observed signal can be attributed to individual CT complexes. The fluorescence intensities were very low: approximately twice to three times and three to five times the intensity of the background for PEMA and Dextrin systems, respectively. Although the fluorescence intensity in the Dextrin system is larger than those in the other polymer systems, the CT fluorescence spectrum is observed in a long wavelength region compared to the other polymer systems (Fig. S1 in Supporting Information). Considering both wavelength dependence of photon detection efficiency of the APD detector (SPCM-AQR-14, PerkinElmer) and the detector sensitivity of the fluorescence spectrometer, the fluorescence intensity in the Dextrin system is not necessarily large. In any event, the overall low fluorescence intensities are probably due to the small absorption

coefficients of the CT complexes and their low fluorescence quantum yields.

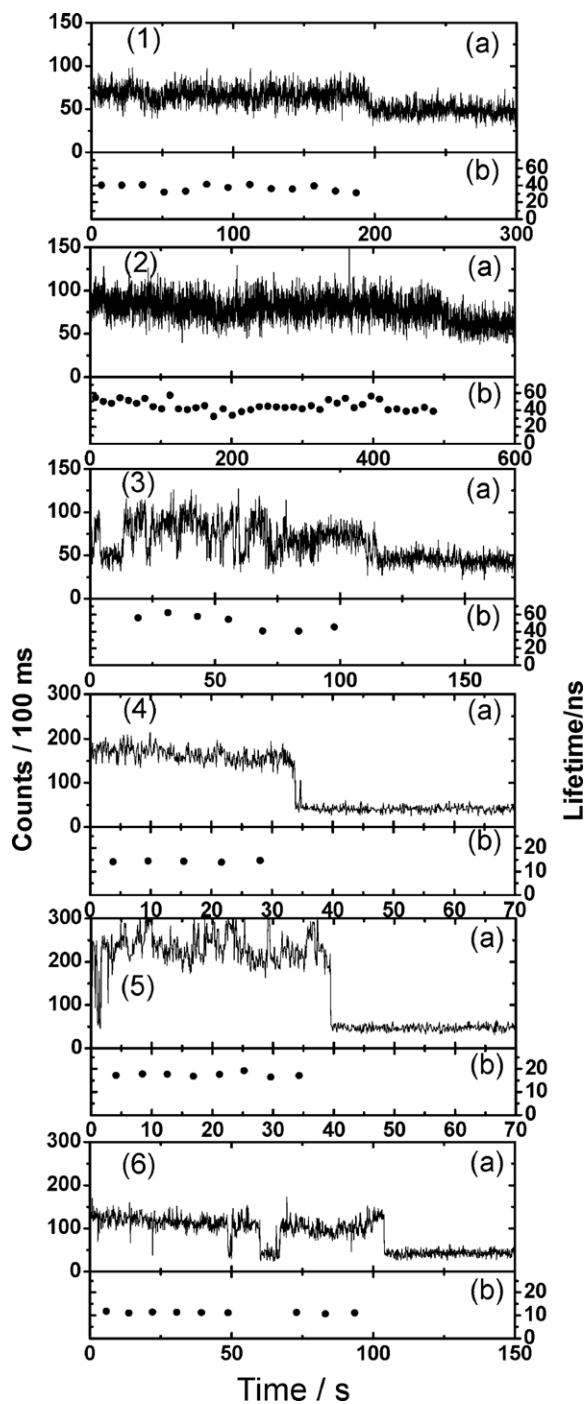
Decay curves built from every 10,000 photons were fitted to a double-exponential function with two decay times, as was reported for ECz:TCNB in PMMA [21]. That is, one decay time was very short and corresponded to an instrument response function. This fast decay component is due to the scattering of excitation laser light and contributes to the aforementioned background counts (Supporting Information). The slow decay times (lifetimes) are plotted against measurement time in Fig. 2(b).

#### 3.2. Fluctuation of CT fluorescence intensities and lifetimes

As is the same in the PMMA system [21], three patterns were observed in the time traces of fluorescence intensities and lifetimes for CT complexes in PEMA and Dextrin. (1) Fluctuations in the fluorescence intensities and lifetimes seldom occurred (Fig. 2 (1 and 4)), (2) the fluctuations occurred frequently with time (Fig. 2 (2 and 5)), and (3) in addition to fluctuations in the fluorescence intensities and lifetimes with time, blinking and/or off-states longer than 1 s (we have called an off-time longer than 1 s an off-state) were observed (Fig. 2 (3 and 6)).

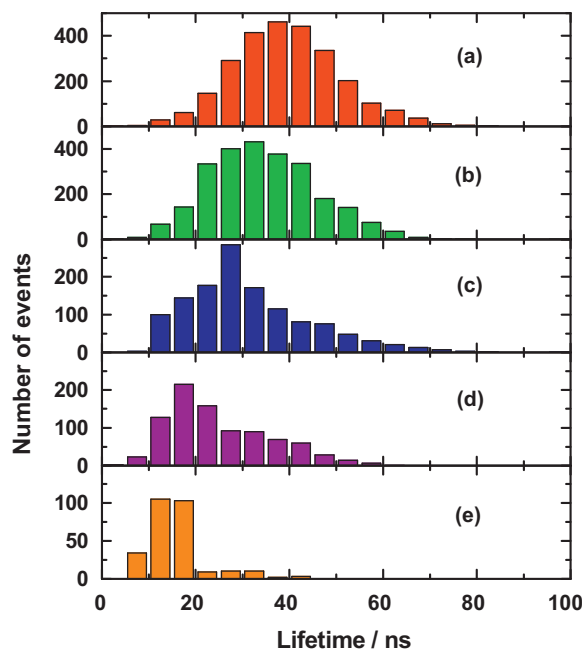
To investigate in detail these behaviors for the PEMA system, 85 individual CT complexes were analyzed, of which 25 showed very few fluctuations, 52 showed frequent fluctuations with time, and 8 showed both off-states and fluctuations. That is, the fluorescence intensity of 61% of the CT complexes fluctuated very frequently together with the lifetime, while 9% showed off-states in addition to the fluctuation. In the Dextrin system, on the other hand, 66% of CT complexes showed very few fluctuations of the fluorescence intensity, while 24% showed off-states in addition to the fluctuation. The same three patterns in the time traces of fluorescence intensities and lifetimes were observed also for the other polymer systems. The numbers of isolated CT complexes observed were 60, 53, 53, and 58 for the PMMA, PnPrMA, PC, and Dextrin systems, respectively.

It is difficult to evaluate the fluctuation of the fluorescence intensity because there is no clear criterion for discriminating the intensities. Thus, we used CT fluorescence lifetimes. To clarify the frequent fluctuation of CT fluorescence lifetimes, histograms of lifetimes obtained from isolated CT complexes in all host polymer systems are shown in Fig. 3. As mentioned above, these lifetimes were obtained by fitting the decay curves built from every 10,000 photons. The lifetimes of each system were distributed within a time region spanning a few tens of nanoseconds, except for the Dextrin system. The lifetimes of the Dextrin system were shorter than those of the other polymer systems. As previously reported [21], frequent fluctuations of CT fluorescence intensities and lifetimes with time (the distribution of the lifetimes) are most likely attributed to changes in the relative geometrical arrangements of the ECz donors and TCNB acceptors in the complexes and/or changes in the local environments around the individual CT complexes, e.g., local variations in polarity, during measurement.



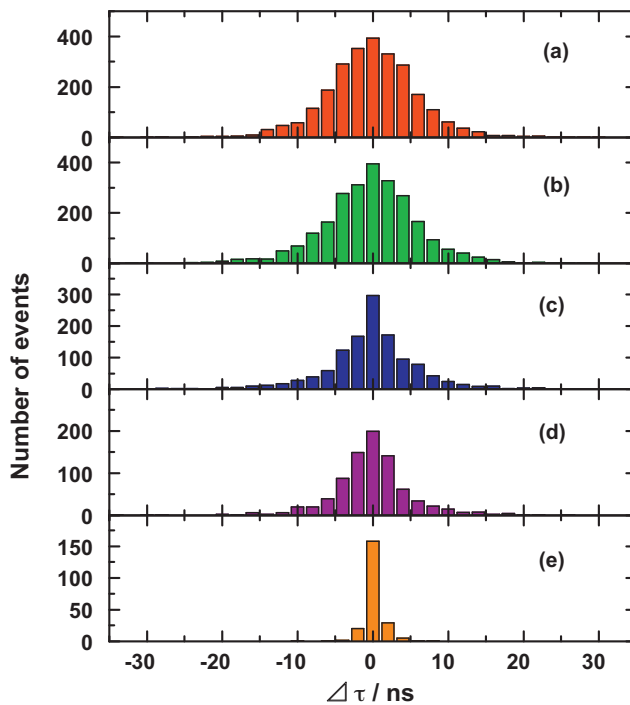
**Fig. 2.** Typical time traces of fluorescence intensities (a) and lifetimes (b) of ECz:TCNB CT complexes. Ca. 30 counts/100 ms are due to the background. Lifetimes were obtained by fitting decay curves built from every 10,000 photons. (1–3): In PEMA and (4–6): in Dextrin host polymers. The concentrations of ECz chromophore and TCNB were  $5.0 \times 10^{-4}$  M each. (1) and (4): Both fluorescence intensity and lifetime seldom fluctuated. (2) and (5): The fluorescence intensities and lifetimes fluctuated together with time. (3) and (6): In addition to fluctuation in the fluorescence intensity and lifetime with time, blinking and/or long off-states were observed. In PMMA, this last pattern was observed for only one out of 60 CT complexes.

The average values (average lifetimes:  $\tau_{av}$ ) were calculated for lifetimes obtained for every 10,000 photons, and were 39.5, 34.7, 31.4, 25.0, and 15.9 ns for the PMMA, PEMA, PnPrMA, PC, and Dextrin systems, respectively. In order to quantitatively estimate the degree of fluctuation in the lifetimes, we calculated the difference



**Fig. 3.** Histograms of fluorescence lifetimes obtained from isolated ECz:TCNB CT complexes in (a) PMMA, (b) PEMA, (c) PnPrMA, (d) PC, and (e) Dextrin thin films. Because the CT complexes showed fluctuations in their lifetimes during the measurements, lifetimes obtained from every 10,000 photons were plotted. The concentrations of the ECz chromophore and TCNB were  $5 \times 10^{-4}$  M each.

$\Delta\tau$  between the lifetimes obtained from two consecutive sets of 10,000 photons in the time traces of the lifetimes. Histograms of the lifetime-differences  $\Delta\tau$  are shown in Fig. 4. The standard deviations for the histograms were 6.16, 6.55, 6.31, 5.43, and 1.57 for the PMMA, PEMA, PnPrMA, PC, and Dextrin systems, respectively. The ratios  $\Delta\tau/\tau_{av}$  of these lifetime-differences  $\Delta\tau$  to their average



**Fig. 4.** Histograms of the lifetime-difference ( $\Delta\tau$ ) between lifetimes obtained from consecutive sets of 10,000 photons: (a) PMMA, (b) PEMA, (c) PnPrMA, (d) PC, and (e) dextrin thin films.

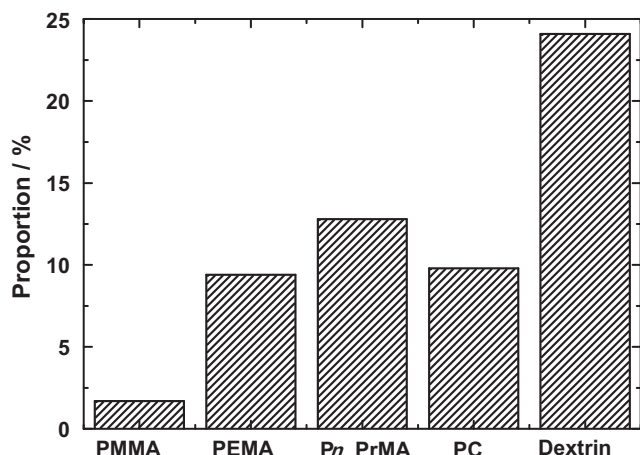


Fig. 5. Percentage of the CT complexes showing off-states longer than 1 s in various host polymer films.

lifetimes  $\tau_{av}$  were 0.156, 0.189, 0.201, 0.217, and 0.0987 for the PMMA, PEMA, PnPrMA, PC, and Dextrin systems, respectively. It is reasonable to consider the relative value  $\Delta\tau/\tau_{av}$  as a parameter representing the degree of fluctuation of the lifetimes. Although the difference in the value of the ratios is small, this order corresponds to the order of the free volume of the host polymers except for Dextrin, whose free volume is unknown. Therefore, the fluctuations in the relative geometrical arrangements of the ECz donors to the TCNB acceptors in the host polymers with large free volumes occur frequently compared to those in polymers with small free volumes. This result suggests that the degree of fluctuation in the relative geometrical arrangements of the donor to acceptor molecules is related to the availability of free space in the host polymer. The Dextrin system is unusual because of its exceptionally high CT fluorescence intensity and short average fluorescence lifetime. The origin of these properties is not clear at the present stage.

### 3.3. Off-state of CT fluorescence

The mechanism for blinking and off-states of single organic molecules have been discussed, with several proposed depending on the timescale of the off-time, such as triplet blinking [29,30], molecular reorientation [31], spectral diffusion [32], conformational change [33,34], intramolecular electron transfer [35], and intermolecular CT between the excited state of the molecule and traps present in the surrounding environment [36–41]. Even if the off-time could be attributed to intermolecular interactions, these off-times resulted from the excited state of single molecules. The present systems are CT complexes formed between electron donor and acceptor molecules, and specifically between two molecules. In our previous paper, hence, the mechanism for Cz:TCNB CT complexes was considered to be different from those for single molecules [21].

In the methacrylate polymers, the percentage of the CT complexes showing off-states (the probability of observation of (3)) is in the order PnPrMA (12.8%) > PEMA (9.4%) > PMMA (1.7%), as shown in Fig. 5. This order corresponds with the order of the free volumes of the polymers (Table 1). In the previous manuscript, we attributed the off-state observed for CT fluorescence to temporary dissociation of the CT complexes formed between two molecules, a phenomenon that is never observed with single molecules, and/or formation of non-fluorescent donor–acceptor geometries of the CT complexes [21]. According to this assumption, when a CT complex exists in a polymer matrix with a large free volume, a large change

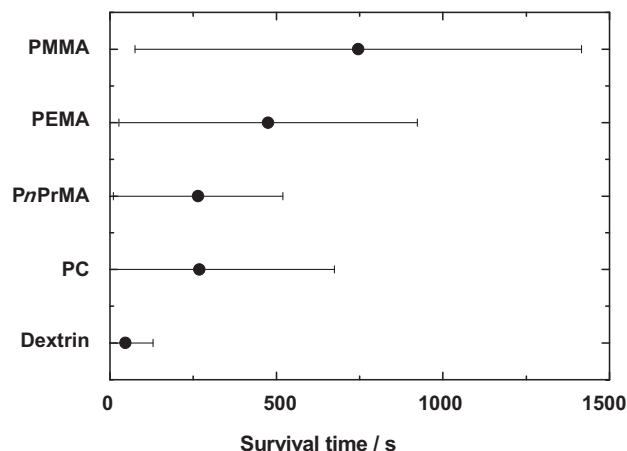


Fig. 6. Average survival times and their standard deviations for isolated ECz:TCNB CT complexes in various host polymer films.

in the relative geometrical arrangement of the ECz donor and TCNB acceptor in the complex is possible within the polymer matrix, thereby inducing various relative geometrical arrangements. The formation of the various relative geometrical arrangements probably results in an increase in the formation of non-fluorescent donor–acceptor geometries of the CT complexes and/or in an increase in the temporal dissociation of the CT complexes. That is, the large free volume provides space for temporary dissociation of the CT complexes and/or for formation of non-fluorescent donor–acceptor geometries of the CT complexes.

Vacha et al. have reported that blinking behavior of single cyanine dye molecule in polymer matrices is correlated with free volume in the polymers [42]. For PMMA and PEMA with higher  $T_g$  than the measuring temperature, fraction of dye molecules showing the blinking in PMMA films was smaller than that in PEMA films. They proposed an explanation that a conformational change of the dye molecule in PEMA with large free volume is easier than that in PMMA with small free volume. This result also supports the above explanation.

De Schryver et al. reported that single-molecule conformational changes can probe the local free volume in amorphous polymer films [43]. A dye molecule in PnBuMA films was investigated by following the time traces of fluorescence intensities and lifetimes of the dye at 292 K (smaller than the  $T_g$  in PnBuMA). For five molecules of the 92 molecules studied, the reversible change between flat and twisted conformations of the molecule was observed. This reversible process was attributed to the dynamic structural disorder of the matrix. Hence, the reversible behavior observed in the present system is probably attributed to the dynamic structural disorder of the matrix.

### 3.4. Survival times of CT complexes

Fig. 6 shows average survival times (the time when the single-step decrement due to photo-bleaching of the isolated CT complex occurred during measurement) and their standard deviations for isolated ECz:TCNB CT complexes in the host polymer thin films. In the methacrylate polymer system, average survival times decreased in the order PMMA > PEMA > PnPrMA. This order is opposite to the one for the free volumes of the polymers (Table 1) and for the percentage of CT complexes showing off-states (Fig. 5). That is, the average survival time for the PnPrMA film with both the largest free volume and the largest percentage of CT complexes showing off-states is shortest among these three polymers. For this observation, the following two interpretations are proposed. One is that the large free volume induces a change in the temporal dissociation

of the CT complexes to their permanent dissociation, which is observed as photo-bleaching. That is, the systems with a large percentage of CT complexes showing off-states tend to show short survival times. The other is that photo-oxidation reaction between excited CT complexes and oxygen induces photo-bleaching of the CT fluorescence. This explanation is supported by the following observation under an ensemble condition: when CT fluorescence of very thin films containing CT complexes was measured under aerated conditions, the CT fluorescence intensity obtained with the second scan was smaller than that with the first scan, while this decrement was never observed under nitrogen. It is known that permeability coefficients of oxygen gas are larger in polymers with large free volumes than in those with small free volumes (see Table 1, although the data for PnPrMA was not found). Hence the photo-oxidation of CT complexes in PMMA, which has a small free volume, hardly occurs compared with that in PnPrMA, which has a large free volume. Both the free volume and the permeability coefficient of oxygen gas in PC are larger than those in PEMA. These greater properties are probably the reason why the average survival time of the CT fluorescence in PC is smaller than that in PEMA and nearly equal to that in PnPrMA.

The average survival time of the Dextrin system is very short, and the percentage of the CT complexes showing off-states is very large (Fig. 5). In addition, as mentioned above, the system is unusual because of its exceptionally high CT fluorescence intensity and short average fluorescence lifetime. Fluorescence properties of isolated CT complexes in the Dextrin system and the PMMA system are both extremes, as shown in Figs. 3–6. Although the physical properties of the Dextrin polymer are unknown, other factors such as polarity may also contribute to the fluorescence properties.

#### 4. Conclusions

Extremely pure polymer matrices that do not emit upon excitation with 488 nm laser light were used to investigate the fluorescence properties of singly isolated ECz:TCNB CT complexes. Three patterns were observed for the time traces of the fluorescence intensities and lifetimes obtained from singly isolated CT complexes: (1) fluctuations in the fluorescence intensities and lifetimes seldom occurred, (2) the fluorescence intensity fluctuated frequently together with the lifetime, and (3) in addition to the above fluctuation with time, blinking and/or off-states longer than 1 s were observed. In methacrylate polymers, both the degree of fluctuation of the CT fluorescence lifetimes and the percentage of the CT complexes showing off-states increased with the free volume of the host polymers. These results suggest that the degree of fluctuation in the relative geometrical arrangements of donor to acceptor molecules is related to the availability of space in the host polymer, and that larger free volumes provide greater space for formation of non-fluorescent donor–acceptor geometries of the CT complexes and/or temporal dissociation of the CT complexes. In addition, the survival times of the CT fluorescence are also closely related to the free volumes of the host polymers. The present information was hidden in the ensemble measurements because of the process of averaging, and was discovered only when using SMS.

#### Acknowledgements

This work was partly supported by JSPS KAKENHI (No. 21550012). We would like to thank Sumika Styron Polycarbonate Limited and Nissan Chemical Industries Limited for supplying the samples of very pure polycarbonate (PC) and dextrin derivative, respectively.

#### Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jphotochem.2011.11.005.

#### References

- [1] F.C. De Schryver, T. Vosch, M. Cotlet, M. Van der Auweraer, K. Müllen, J. Hofkens, *Acc. Chem. Res.* 38 (2005) 514.
- [2] S. Masuo, T. Vosch, M. Cotlet, P. Tinnefeld, S. Habuchi, T.D.M. Bell, I. Oesterling, D. Beljonne, B. Champagne, K. Müllen, M. Sauer, J. Hofkens, F.C. De Schryver, *J. Phys. Chem. B* 108 (2004) 16686.
- [3] P. Tinnefeld, J. Hofkens, D.P. Herten, S. Masuo, T. Vosch, M. Cotlet, S. Habuchi, K. Müllen, F.C. De Schryver, M. Sauer, *ChemPhysChem* 5 (2004) 1786.
- [4] P. Tinnefeld, K.D. Weston, T. Vosch, M. Cotlet, T. Weil, J. Hofkens, K. Müllen, F.C. De Schryver, M. Sauer, *J. Am. Chem. Soc.* 124 (2002) 14310.
- [5] S. Masuo, A. Masuhara, T. Akashi, M. Muranushi, S. Machida, H. Kasai, H. Nakanishi, H. Oikawa, A. Itaya, *Jpn. J. Appl. Phys.* 46 (2007) L268.
- [6] A.J. Gesquiere, T. Uwada, T. Asahi, H. Masuhara, P.F. Barbara, *Nano Lett.* 5 (2005) 1321.
- [7] R. Yasukuni, T. Asahi, T. Sugiyama, H. Masuhara, M. Sliwa, J. Hofkens, F.C. De Schryver, M. Van der Auweraer, A. Herrmann, K. Müllen, *Appl. Phys. A* 93 (2008) 5.
- [8] S. Masuo, T. Tanaka, S. Machida, A. Itaya, *Appl. Phys. Lett.* 92 (2008) 233114/1.
- [9] I.G. Scheblykin, A. Yartsev, T. Pullerits, V. Gulbinas, V. Sundstrom, *J. Phys. Chem. B* 111 (2007) 6303.
- [10] P.F. Barbara, A.J. Gesquiere, S.J. Park, Y.J. Lee, *Acc. Chem. Res.* 38 (2005) 602.
- [11] A.J. Gesquiere, S.J. Park, P.F. Barbara, *J. Am. Chem. Soc.* 127 (2005) 9556.
- [12] P. Kumar, T.H. Lee, A. Mehta, B.G. Sumpter, R.M. Dickson, M.D. Barnes, *J. Am. Chem. Soc.* 126 (2004) 3376.
- [13] C.W. Hollars, S.M. Lane, T. Huser, *Chem. Phys. Lett.* 370 (2003) 393.
- [14] J. Yu, D.H. Hu, P.F. Barbara, *Science* 289 (2000) 1327.
- [15] T. Huser, M. Yan, L.J. Rothberg, *Proc. Natl. Acad. Sci. U.S.A.* 97 (2000) 11187.
- [16] E. Lang, A. Sorokin, M. Drechsler, Y. Malyukin, J. Köhler, *Nano Lett.* 5 (2005) 2635.
- [17] S.A. Empedocles, D.J. Norris, M.G. Bawendi, *Phys. Rev. Lett.* 77 (1996) 3873.
- [18] M. Nirmal, B.O. Dabbousi, M.G. Bawendi, J.J. Macklin, J.K. Trautman, T.D. Harris, L.E. Brus, *Nature* 383 (1996) 802.
- [19] N. Mataga, Y. Murata, *J. Am. Chem. Soc.* 91 (1969) 3144.
- [20] S. Masuo, T. Endo, Y. Yamane, S. Machida, A. Itaya, *Chem. Lett.* 37 (2008) 916.
- [21] S. Masuo, Y. Yamane, T. Endo, S. Machida, A. Itaya, *J. Phys. Chem. C* 113 (2009) 11590.
- [22] M. Yokoyama, S. Shimokihara, A. Matsubara, H. Mikawa, *J. Chem. Phys.* 76 (1982) 724.
- [23] A. Itaya, A. Egawa, Y. Umehara, H. Sakai, H. Masuhara, *Polymer* 35 (1994) 3149.
- [24] H. Miyasaka, T. Moriyama, S. Kotani, R. Muneyasu, A. Itaya, *Chem. Phys. Lett.* 225 (1994) 315.
- [25] T. Ueda, R. Fujisawa, H. Fukumura, A. Itaya, H. Masuhara, *J. Phys. Chem.* 99 (1995) 3629.
- [26] A. Itaya, T. Kitagawa, T. Moriyama, T. Matsushita, H. Miyasaka, *J. Phys. Chem. B* 101 (1997) 524.
- [27] K. Watanabe, T. Asahi, H. Masuhara, *J. Phys. Chem.* 100 (1996) 18436.
- [28] K. Watanabe, T. Asahi, H. Masuhara, *J. Phys. Chem. B* 101 (1997) 5131.
- [29] W.T. Yip, D.H. Hu, J. Yu, D.A. Vanden Bout, P.F. Barbara, *J. Phys. Chem. A* 102 (1998) 7564.
- [30] F. Köhn, J. Hofkens, R. Gronheid, M. Van der Auweraer, F.C. De Schryver, *J. Phys. Chem. A* 106 (2002) 4808.
- [31] W.P. Ambrose, P.M. Goodwin, J.C. Martin, R.A. Keller, *Phys. Rev. Lett.* 72 (1994) 160.
- [32] H.P. Lu, X.S. Xie, *Nature* 385 (1997) 143.
- [33] K.D. Weston, P.J. Carson, H. Metiu, S.K. Buratto, *J. Chem. Phys.* 109 (1998) 7474.
- [34] K.D. Weston, S.K. Buratto, *J. Phys. Chem. A* 102 (1998) 3635.
- [35] T.D.M. Bell, A. Stefan, S. Masuo, T. Vosch, M. Lor, M. Cotlet, J. Hofkens, S. Bernhardt, K. Müllen, M. Van der Auweraer, J.W. Verhoeven, F.C. De Schryver, *ChemPhysChem* 6 (2005) 942.
- [36] J.N. Clifford, T.D.M. Bell, P. Tinnefeld, M. Heilemann, S.M. Melnikov, J. Hotta, M. Sliwa, P. Dedecker, M. Sauer, J. Hofkens, E.K.L. Yeow, *J. Phys. Chem. B* 111 (2007) 6987.
- [37] E.K.L. Yeow, S.M. Melnikov, T.D.M. Bell, F.C. De Schryver, J. Hofkens, *J. Phys. Chem. A* 110 (2006) 1726.
- [38] M. Haase, C.G. Huebner, E. Reuther, A. Herrmann, K. Müllen, T. Basche, *J. Phys. Chem. B* 108 (2004) 10445.
- [39] J. Schuster, F. Cichos, C. von Borczyskowski, *Appl. Phys. Lett.* 87 (2005) 051915.
- [40] J.P. Hoogenboom, E.M.H.P. van Dijk, J. Hernandez, N.F. van Hulst, M.F. García-Parajó, *Phys. Rev. Lett.* 95 (2005) 097401.
- [41] R. Zondervan, F. Kulzer, S.B. Orlinskii, M. Orrit, *J. Phys. Chem. A* 107 (2003) 6770.
- [42] K. Suzuki, S. Habuchi, M. Vacha, *Chem. Phys. Lett.* 505 (2011) 157.
- [43] R.A.L. Vallee, M. Cotlet, M. Van der Auweraer, J. Hofkens, K. Müllen, F.C. De Schryver, *J. Am. Chem. Soc.* 126 (2004) 2296.
- [44] J. Brandrup, E.H. Immergut (Eds.), *Polymer Handbook*, 3rd ed., John Wiley & Sons, Inc., 1989.
- [45] D. Kilburn, G. Dlubek, J. Pionteck, M.A. Alam, *Polymer* 47 (2006) 7774.
- [46] J. Kristiak, J. Bartos, K. Kristiakova, O. Sausa, P. Bandzuch, *Phys. Rev. B* 49 (1994) 6601.