Fluorescence Properties of Individual Charge-transfer Complexes in Polymer Films Revealed by Single Molecule Fluorescence Spectroscopy

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This is the first report of fluorescence dynamics of singly isolated charge-transfer (CT) complexes in a polymer film. It was suggested that relative geometrical structures of donor and acceptor molecules change during the measurement and that microenvironment around individual CT complexes is different.

Recently, single molecule fluorescence spectroscopy is applied for elucidating various phenomena concerning with functionality of materials induced by photoexcitation.[1] Photoconductivity is one of such phenomena. Fluorescence properties of charge-transfer (CT) complexes in the solid state have received considerable attention in connection with the photoconductive properties. In particular, when poly(*N*-vinylcarbazole) (PVCz) films are doped with an electron acceptor, a CT complex is formed between the carbazolyl (Cz) chromophore and the acceptor, and both sensitization of the photocurrent in the corresponding CT absorption region and CT fluorescence are observed. Since radiative processes of CT fluorescence is competitive with carrier photogeneration process, electric-field effect on the steady-state CT fluorescence of PVCz films doped with 1,2,4,5-tetracyanobenzene (TCNB) and dynamics of the CT fluorescence have been investigated.[2,3] In addition, photoinduced charge separation, recombination, and hole-transfer processes in PVCz/TCNB and Cz-dimeric compounds/TCNB amorphous solid films have been investigated by transient absorption spectroscopy.[4–6]

The above studies have been carried out for the ensemble of CT complexes in solid films. In the present letter, we focus on isolated CT complexes formed between *N*-ethylcarbazole (ECz) and TCNB in inert solid films, because this CT system is similar to PVCz/TCNB and their Cz-dimeric compounds/TCNB amorphous solid systems, whose fluorescence properties are revealed well compared to others. The present work is one of the basic approaches to clarifying properties of CT complexes in solid films with single molecular level.

To observe fluorescence of a single molecule in polymer matrixes, the concentration of 10^{-10} M is required usually. Since CT complex formation is equilibrium between donor/acceptor and the CT complex, concentration of donor and acceptor molecules is required to be very large compared to 10^{-10} M. Thus, very high purity of both donor and acceptor compounds is required. In particular, contamination of fluorescent compounds showing absorption in longer wavelengths (488 nm for the present equipment) should be avoided. Hence, ECz was synthesized from tetrahydrocarbazole which was purified by recrystallization, and the final product was recrystallized and subsequently purified by zone refining. TCNB was also purified by recrystallization and the following vacuum sublimation. Poly(methyl methacrylate) (PMMA) was used as a host polymer.

The fluorescence properties of individual CT complexes were measured using a sample-scanning confocal microscope, whose details are described elsewhere.[7] All measurements were performed under nitrogen atmosphere at room temperature.

Absorption and fluorescence of ECz/TCNB in PMMA films show broad spectra with a peak at ca. 475 and 580 nm, respectively (Figure S1).[8] The CT absorption and fluorescence are mainly due to a 1:1 complex because ECz is distributed homogeneously in PMMA films and does not form a dimer that leads to excimer upon excitation. A decay time of the CT fluorescence was ca. 40 ns for ensemble measurement (Figure S2),[8] which is very long compared with the decay time constant of the photoinduced charge-separated state in ECz:TCNB toluene solution (3.6 ns).[4]

Figure 1 shows fluorescence intensity images of various sample films. As aforementioned, the concentration of 10^{-10} M is required usually for measuring single molecule fluorescence. Few bright spots are observed for 0.1 M sample of ECz and 0.01 M sample of TCNB, which indicates that the present ECz and TCNB are very pure and do almost not contain compounds showing fluorescence in longer wavelengths. For ECz (0.1 M)/TCNB samples, many bright spots are observed compared to ECz and TCNB samples. The number of bright spots decreases with a decrease in TCNB concentration, although the number of very bright spots almost never changes. This result means that almost all of the bright spots are attributed to the fluorescence of individual CT complexes, although the brightness of the spots is low because of its very low fluorescence yield. This is supported by the fact that the fluorescence disappears stepwise

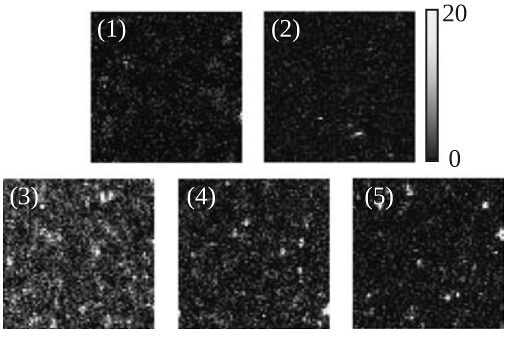

Figure 1. Representative fluorescence intensity images. (1) ECz (0.1 M), (2) TCNB (0.01 M), (3) ECz (0.1 M)/TCNB (2.0×10^{-5} M), (4) ECz (0.1 M)/TCNB (1.0×10^{-5} M), (5) ECz (0.1 M)/TCNB (1.0×10^{-6} M) in PMMA. The image scales are $10 \times 10\,\mu m^2$. The resolution is 70×70 pixels with an integration of 10 ms/pixel. The laser fluence is 800 nW.

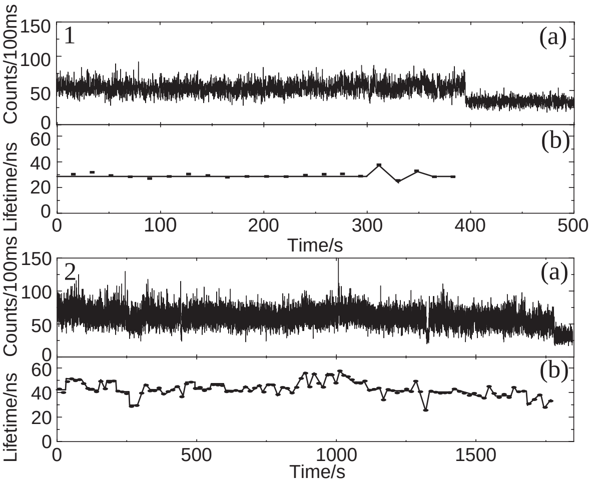

Figure 2. Typical time traces of (a) fluorescence intensity and (b) lifetimes, which were obtained by fitting to the decay curves built from every 10000 photons. (1) Both fluorescence intensity and lifetime seldom fluctuate. (2) The fluorescence intensity and lifetime fluctuate frequently together with time. Both of the concentrations of ECz and TCNB are 5.0×10^{-4} M. The counts/100 ms of ca. 30 is due to background.

during the measurement of time trace of the fluorescence intensity (vide infra). The very bright spots are assigned to impurity emission because of their very short lifetime and short survival time (vide infra).

To assure observation of singly isolated CT complexes, dilute samples of donor and acceptor were prepared (5.0×10^{-4} M). Typical two results of simultaneous measurements (time traces of fluorescence intensity and lifetime) for single spots of ECz/TCNB in PMMA films are shown in Figure 2. The fluorescence intensity decreases suddenly stepwise to the background level that is attributed to the scattering of the excitation laser light. This stepwise decrement means photobleaching of the CT complex, which indicates that the observed signal can be attributed to a single CT complex. We notice that the fluorescence intensities are very low and are comparable to the intensity of the background level. This is most probably due to the small absorption coefficient of the CT complex and its low fluorescence quantum yield.[8]

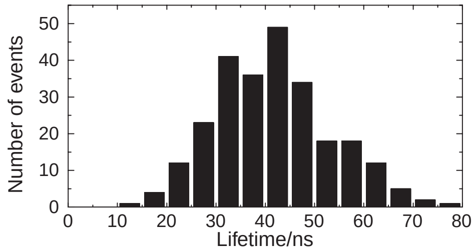

Figure 3. Histogram of fluorescence lifetime obtained from 60 isolated ECz/TCNB complexes. Because of the change of lifetime during the measurement, individual lifetimes which fluctuated with time were counted. Both of the concentrations of ECz and TCNB are 5.0×10^{-4} M.

Decay curves built from 10000 photons were able to be fitted to a double-exponential function with two decay times (Figure S3).[8] One decay time is very fast and corresponds to an instrumental response function. This fast decay component is due to the scattering of the excitation laser light and contributes to the background counts as aforementioned. The slow decay times (lifetimes) are plotted in Figure 2b. The fluorescence intensity and lifetime fluctuate together with time. One can recognize two patterns for time traces of the fluorescence intensity and lifetimes. One is that the fluctuation seldom occurs. The other is that the fluctuation occurs frequently with time. To investigate these behaviors in detail, 60 individual CT complexes were measured. 42 CT complexes showed a few or less fluctuations, and 18 complexes showed many fluctuations with time. Namely, 30% of CT complexes showed that the fluorescence intensity fluctuates very frequently together with the lifetime. This phenomenon is most likely to be attributed to a change of relative geometrical structures of ECz donor and TCNB acceptor in CT complex and/or a change of microenvironments around individual CT complexes during the measurement. We notice that the fluorescence of single CT complexes shows long survival times. In 60 CT complexes, the longest survival time was 31 min. These long survival times seem to be characteristic of the fluorescence of singly isolated CT complexes. In addition, these long survival times were able to be used for discriminating between impurity and CT fluorescence.

Figure 3 shows a histogram of lifetimes obtained from 60 isolated CT complexes. Most of the lifetimes distribute from 20 to 65 ns and the average lifetime is 40 ns. This average lifetime is close to the lifetime measured for ensemble of CT complexes ($\tau_{1/e} = 39.0$ ns, mean lifetime: $\langle\tau\rangle = 43.3$ ns) (Figure S2).[8] This distribution of the lifetimes is most likely to be attributed to difference in microenvironments around individual CT complexes; for example, micropolarity and/or the difference in relative geometrical structures of ECz donor and TCNB acceptor.

In conclusion, fluorescence dynamics of single isolated CT complexes in solid matrixes was investigated for the first time. It was suggested that relative geometrical structures of ECz donor and TCNB acceptor molecules change during the measurement and that microenvironment around individual CT complexes is different. The above information can be revealed using single molecule fluorescence spectroscopy but not using ensemble measurement.

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8 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/.

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