Light Emission Properties of Exciplex Formed in Polymer Thin Films

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Light emission from exciplex formed between a donor N,N'-bis(3-methylphenyl)-N,N'-diphenylbenzidine (TPD) and an acceptor 2-(4-biphenyl)-5-(4-tert-butyl-phenyl)-1,3,4-oxadiazole (PBD) was studied in an inert polymer films, when total molecular concentration was varied. Emission was composed of that from the donor and that from the exciplex. The exciplex emission spectral shape were found not to strongly depend on the concentration. Exciplex lifetime was found to be in the order of 10ns by the measurements with a ps excitation pulse source. Decay curve was well fitted by double exponential functions based on a simple model including the exciplex formation rate, and forward and reverse intersystem crossing processes.
Key words: exciplex, charge transfer, reverse intersystem crossing, OLED, dye laser

1. INTRODUCTION

One of the final targets of this study is to apply exciplexes formed in polymer films to optical amplification with very wide gain bandwidth. Since exciplex is an excited state delocalized on two adjacent molecules, its emission has large Stokes shift and broad spectral range. As confirmed recently by a Japanese group, these characteristics are preferable for tunable laser oscillation [1].

Additionally, exciplex is currently being actively studied for highly efficient OLEDs [2]. Usually, quantum efficiency of conventional OLED is limited to 25% due to spin statistics. Since the gap between the singlet and triplet states is so small in exciplexes that excitons can move back and forth between the two states via intersystem crossing (ISC) and reverse intersystem crossing (RISC), 100% of excitation can contribute to luminescence. That is due to small exchange interaction, or small singlet – triplet energy gap. This is the reason why so many studies of exciplex OLED are made now.

Exciplex state is considered to be a superposition of relaxed localized excited state and an intermolecular charge transferred state, and the detail might depend on material, environment, concentration and so on [3]. As exciplex can be formed with various types of compounds under various conditions, emission properties could be controlled by changing the combination, concentration and matrix polarity. Therefore, it is important to study the formation and decay processes of these states in various circumstances.

For thin-film solid-state laser application, we fabricated polymer films heavily doped with a typical donor and acceptor molecules to study the photoluminescence characteristics with conventional spectroscopy and time-resolved emission measurements. A simple model based on rate equations is also proposed to analyze their dynamics as described in the following parts.

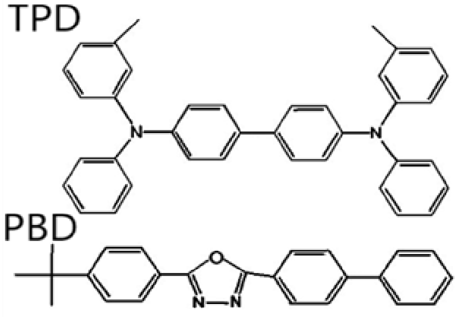

Fig. 1 Chemical structures of donor and acceptor materials used in this study.

2. EXPERIMENTAL

We chosed N,N'-bis(3-methylphenyl)-N,N'-diphenylbenzidine (TPD, Sigma-Aldrich) as a donor molecule, which is a representative material for OLEDs, and acceptor molecule 2-(4-biphenyl)-5-(4-tert-butyl-phenyl)-1,3,4-oxadiazole (PBD, Tokyo Chemical Industry). Equivalent amounts of two compounds were co-doped into PMMA (Sigma-Aldrich, MW:120,000) films prepared from chloroform solutions by spin-coating. The total weight ratio of small molecules was varied from 5 to 80% in order to control the intermolecular distance between the donor and acceptor to some extent. Molecular structures of the materials are shown in Fig. 1.

Absorption and fluorescence spectra (with Shimadzu 1800 and JASCO FP-6500, respectively) and temporal decay of light emission were measured. For the time-resolved study, ps light source of wavelength 375 nm semiconductor pulsed laser (LDH-P-C-375B, PicoQuest) was used, at which wavelength only donor molecules absorb photons. The repetition frequency was set to be 1 MHz and a pulse width was ~50 ps. A streak scope (C4334, Hamamatsu) was used for detection.

3. RESULSTS AND DISCUSSIONS

Absorption spectra gave similar features to those obtained by the addition of the donor and the acceptor's spectra, showing that no charge-transfer complex was formed in the ground states.

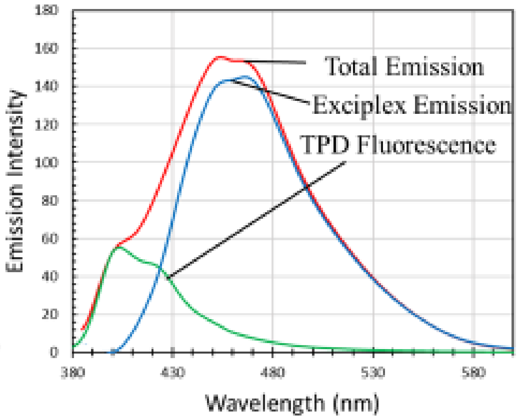

Fig. 2 Emission spectrum of the sample with 40wt% molecules in film, and two spectra obtained with SVD analysis.

In conrast, new and strong emission peaks were observed on the longer wavelength side in fluorescence spectra as shown in Fig. 2. The position of the new peaks, apparently caused by exciplex formation, red-shfted as molecular concentation incresed up to 40%, while no further shift was observed over the concentration above.

Assuming that spherical shaped molecules were dispersed homogeneously in the matrix, intermolecular distance can be estimated. And the critical concentration was estimated to be 50%, above which the intermolecular distance was almost zero. The change in the spectal shapes could be explained by the dependence of excplex formation probability on the concentration.

Spectra were sucessfully decomposed into two components with the method of singular value decomposition (SVD) [4,5]. For the samples with concentration from 10% to 80%, the resultant emission spectra were able to be reproduced by linear combination of two spectral components assigned to TPD and exciplex emission. The results suggests that exciplex emission spectrum, therefore basic exciplex structure does not depend on the concentration. In other words, only single type of the exciplex are involved in the all samples except for the ones where the dye concentration is dilute.

Fig. 2 gives the emssion spectrum of 40% sample and the two components derived by SVD, for example. From the weight ratio of two components, we could estimate the exciplex formation ratio, however, the details will be given elsewhere.

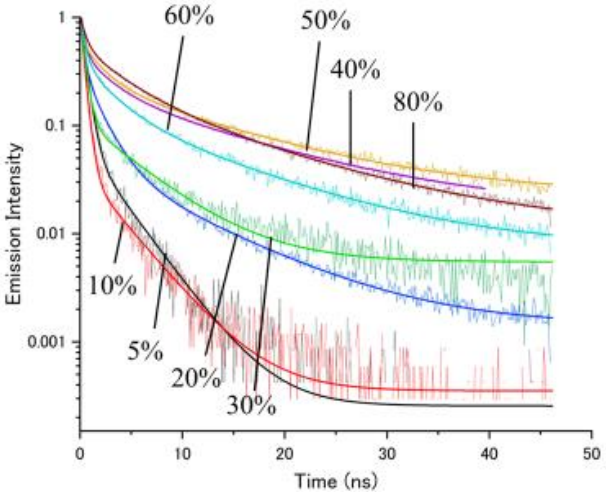

Fig. 3 Results of emission decay curves of TPD-PBD thin films at various concentrations.

Figure 3 shows the curves of the temporal decay obtained by the integration over the entire wavelength region (360 to 580 nm). The results can be well fitted by double exponential functions as depicted. Fast decay in low concentration sapmples reflected the dominance of the donor emission, while highly concentrated case gave much slower decay due to exciplex emission. Curve featutes varied in a complex way, but these would be roughly classified into two types with boundary around 30 ~ 40% concentration. These results also suggest that the temporal behavior strongly relates to the inermolecular distance in film samples.

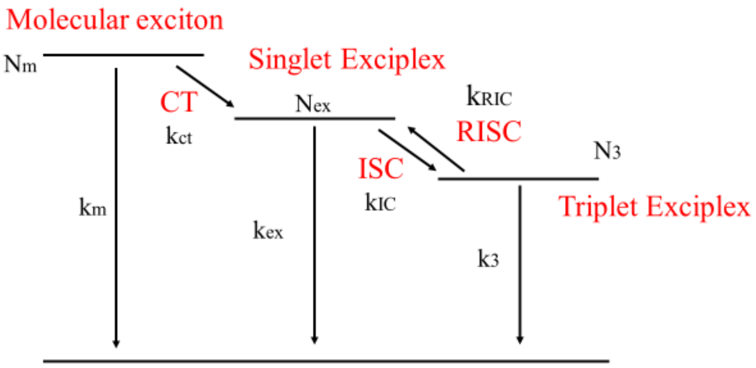

Fig. 4 Model diagram of exciplex formation and relaxation processes.

In order to analyze decay behavior, we made a simple model as shown in Fig. 4. In this model, we consider the molecular exciton as the initial state which is populated with a δ-function pump pulse. Light emissive singlet exciplex forms via CT process with the rate of k_{ct}. Exciplex emission occurs just after the formation or after round-trips to triplex exciplex state through ISC and RISC processes. Because the energy gap between the singlet and the triplet exciplex states would be so small that the back-and-force rates should be kept into account. The relaxation rates (addition of emissive and non-emissive processes) to the ground state from the three excited states are given by k_m, k_{ex}, and k_3 as summarized in the figure. k_3 was neglected in our analysis.

Population of the excited molecules, singlet exciplex and triplet exciplex are expressed by N_m, N_{ex}, and N_3, respectively. Based on this scheme, the following equation were derived. Notice that the latter three k's include both emissive and non-emissive rates inseparable from our experiments.

$$\frac{dN_m}{dt} = -(k_m + k_{ct})N_m \tag{1a}$$

$$\frac{dN_{ex}}{dt} = k_{ct}N_m - (k_{ex} + k_{IC})N_{ex} + k_{RIC}N_3 \tag{1b}$$

$$\frac{dN_3}{dt} = k_{IC}N_{ex} - (k_{RIC} + k_3)N_3 \tag{1c}$$

The solution to the equations is given as below. We only show N_{ex}, since this corresponds to the value proportional to the emission intensity. It composed of the particular solution (the last term), and two general solution terms. Explicit forms of coefficients C's and the rate constants (or inversed time constants) λ's are omitted here.

$$N_{ex} = C_+e^{\lambda_+t} + C_-e^{\lambda_-t} + \frac{k_{CT}(-(k_m + k_{CT}) + k_3 + k_{RIC})}{(\lambda_+ + k_m + k_{CT})(\lambda_- + k_m + k_{CT})}e^{-(k_m+k_{CT})t} \tag{2}$$

The coeffients of the last term is usually negative which appears as the time rag of the emission due to exciplex formation. Actually, its time constant will be shorter than our experimental resolution, making it possible to consider the results would be double expoential being consistent with experiments. Numerical consideration based on the model is now in progress.

4 SUMMARY AND CONCLUSION

In order to study the characteristics of exciplex formed in polymer matrix, we fabricated thin films heavily doped with typical donor TPD and typical acceptor PBD, both of which are popularly employed in OLED devices. Formed exciplex gave emission composed of emission from TPD and the exciplex. By decomposing the spectra into two components, it was found that a single type of exciplex is involved. The exciplex formation probability was estimated and it was close to unity when the total small molecular concentration was above 50%. Decay behavior also qualitatively changed aroud 40% as a boundary, although double exponential fitting was well suited to both cases. Further analysis is now in progress based on a simple model.

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