Direct observation of *back energy transfer* in blue phosphorescent materials for organic light emitting diodes by time-resolved optical waveguide spectroscopy

H. Hirayama,¹ Y. Sugawara,¹ Y. Miyashita,¹ M. Mitsuishi,² and T. Miyashita²

¹Analysis Technology Center, Fujifilm Corporation, 210, Nakanuma, Minamishigara, Kanagawa, Japan

²Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, 2-1-1, Katahira, Aoba, Sendai 980-8577, Japan

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We demonstrate a high-sensitive transient absorption technique for detection of excited states in an organic thin film by time-resolved optical waveguide spectroscopy. By using a laser beam as a probe light, we detect small change in the transient absorbance which is equivalent to 10^{-7} absorbance unit in a conventional method. This technique was applied to organic thin films of blue phosphorescent materials for organic light emitting diodes. We directly observed the *back energy transfer* from emitting guest molecules to conductive host molecules. © 2013 American Institute of Physics. [<http://dx.doi.org/10.1063/1.4792838>]

Phosphorescent emitters in organic light emitting devices (OLEDs) have received considerable attention for flat panel devices and lighting devices because of the high theoretical limit of external quantum efficiency up to 20%, which is four times higher than that of fluorescence emitters.^{1–5} For practical use of full-color phosphorescent emitters (red, green, and blue), the development of blue emitters is the most challenging subject because an inefficient process of the back energy transfer (BET)^{6–11} occurs. The phosphorescent emitters in OLEDs usually consist of two kinds of molecules that are designed for the forward energy transfer (FET) from conductive host to phosphorescent guest molecules in excited states. The BET is an energy transfer process in the opposite direction from guest to host molecules, which increases inefficient non-radiative decay rate.

Although it is easy to avoid the possibility of the BET in red and green phosphorescent emitters, in blue emitters, the BET is believed to become a serious problem due to the lack of suitable host molecules, which should have higher triplet energy level than that of guest molecules. Some groups have studied the BET by observing the photoluminescence (PL) intensity or lifetime of guest molecules and indicated to be the serious inefficient process in blue emitters.^{9–11} However, despite the important process, no one has directly observed the host triplets generated by the BET. One of the reasons is experimental difficulty in the conventional optical transient absorption (TA) method for vacuum-deposited organic thin films. In general, the TA signal of excited states becomes much weaker than the static absorption signal of ground states due to the much smaller number of photo-excited molecules and the short lifetime (typically $\sim \mu\text{s}$). Moreover, a lot of organic molecules are quickly degraded by light irradiation, which requires shorter accumulation time in TA measurements. The lower excitation intensity is also required for the measurement of high density organic thin films made by vacuum deposition to avoid the lifetime change by non-linear effects like Triplet-Triplet annihilation. As a consequence, the detectable absorption signal of transient triplets becomes extremely small.

In this letter, we demonstrate a signal-enhanced TA technique combined with optical waveguide (OWG) spectroscopy.^{12,13} In this technique, the TA signal is enhanced more than a hundred times by multiple optical absorptions. The high sensitive technique enables to observe transient triplets of host molecules in the thin film made by vacuum deposition. Using this method, we directly observed BET in the host-guest system.

Figure 1 shows a basic experimental-setup. The sample was made on a quartz substrate enabling OWG mode propagation with a dimension of 0.2 mm thickness and 65 mm $\times$ 20 mm area. The end face of the long axis in the thin rectangular OWG substrate was tapered by 60° (inset of Fig. 1(a)) which allows the probe light to go through the inside of the OWG substrate and undergoes total reflections on the both top and bottom surfaces. The number of the reflections is calculated to be around 150 times, assuming parameters of the substrate thickness of 200 μm , the length

FIG. 1. (a) Schematic diagram of TA measurement using time-resolved OWG. CL is a cylindrical plano-concave lens. Inset: the principle of multiple total reflections by OWG substrate. (b) Absorption spectra of the p(nPMA-AMMA) monolayer measured by conventional transmission method (blue) and OWG spectroscopy (red).

of 65 mm, the refractive index of 1.47 (at $\lambda = 400$ nm), and the incident angle of 45° . So the signal enhancement was predicted more than double digits. The sample was excited with a nano-second pulsed laser (pulse width: 4–6 ns, wavelength: 266 nm or 415 nm, pulse energy: 1 mJ/pulse, repetition rate: 10 Hz). The beam was expanded with a cylindrical plano-concave lens to irradiate the sample area where the probe light passed through. We used two types of probe light sources as the situation demands. For the measurement of the transient absorption spectra, we used a Xe lamp. A He-Ne laser (633 nm) was used for the time decay measurement. The detectors were a photo diode array for Xe lamp measurements in spectrum domain at specific delay time and a photo diode with digital oscilloscope for laser measurements in time domain at the wavelength of probe light.

To confirm signal enhancement by OWG, we performed simple measurements of static absorption by the two absorption techniques: the conventional method (single transmission) and the OWG method (multiple reflections). As a test sample, we used a p(nPMA-AMMA) (the copolymer of 9-anthrylmethyl methacrylate (AMMA, 10 mol. %) with neopentyl methacrylamide (nPMA)) Langmuir-Blodgett (LB) monolayer,¹² which has very weak absorption, to prevent signal saturation by strong enhancement of the OWG method. Figure 1(b) shows static absorption spectra of the LB film on OWG substrate by the two methods. The OWG signal has much larger intensity and better S/N ratio than those of a conventional method. The enhancement factor reached around 300 times, which was consistent with the predicted value calculated from multiple reflection times.

We now turned to time-resolved measurements. First, we carried out the measurement of the vacuum-deposited film composed of single host material to ensure the potential of the OWG for the detection of the very small TA signal of host triplets. The sample was the 4,4'-bis N-carbazolyl-2,2'-biphenyl (CBP) film, which was evaporated at 5×10^{-3} Pa on the OWG substrate with the thickness of 20 nm and the area of 15×60 mm². Figure 2(a) shows the TA spectrum of the CBP film at 5 μ s after optical excitations with a nanosecond laser at 266 nm, probed with Xe lamp. The absorption peak around $\lambda = 633$ nm was attributed to T_1 - T_n absorption of CBP which was confirmed by a conventional TA measurement for CBP in dichloromethane solution (not shown here). Figure 2(b) shows the time profile at 633 nm in the TA

FIG. 2. (a) TA spectrum of the CBP film (20 nm) monitored at 5 μ s after the excitation of the nanosecond laser at 266 nm. Inset: chemical structure of CBP. (b) Time profile of transient absorption at 633 nm of the CBP film (20 nm) under 266 nm nanosecond laser excitation. Inset: the baseline noise of the time profile.

spectrum. The non-radiative decay had a lifetime of $\tau_{CBP_{only}} = 93 \mu$ s fitted by single exponential function, which was longer than that of CBP triplet in dichloromethane solution (lifetime = 40 μ s). This may indicate that the motion of the CBP molecule in solution facilitates the excited state relaxation. The background noise level of the data in Fig. 2(b) was ΔOD of 10^{-5} . This was corresponding to detectable ΔOD of 10^{-7} in a conventional TA technique because the signal enhancement by OWG was more than 100 times.

Next, we tried to observe the BET in a host-guest composite film. The host and guest materials were CBP and bis(4,6-difluorophenylpyridinato-N,C2) picolinateiridium (Flrpic), respectively. The film was made by vacuum co-deposition with doping concentration of Flrpic of 2.5 wt. %, area of 15×60 mm², and thickness of 20 nm. The absorption spectra of each material in dichloromethane are shown in Fig. 3(a). Selective photo-excitation for the guest material is possible at 415 nm. Nanosecond laser irradiation was performed at 415 nm, which ensures generation of the host triplets by BET from photo-excited guests. Figure 3(b) shows a TA spectrum of the composite film probed by Xe lamp. In the spectrum, two kinds of transient signal were observed; one was the strong negative signal of the emission from Flrpic triplets at the wavelength range of 450 nm–620 nm, the other was the weak positive signal of absorption by CBP triplets at the range of 620 nm–700 nm. Though the intensity level of the absorption is close to the noise level, we can clearly confirm the positive signal by data smoothing (inset of Fig. 3(a)).

Figure 3(c) shows the time profile of TA at 633 nm (blue line) and 500 nm (red line). At 633 nm, we clearly observe the transient decay of CBP triplets generated by BET from Flrpic triplets excited by the selective photo-excitation. The laser probing is very effective for avoiding the disadvantage

FIG. 3. (a) Normalized absorption spectra of CBP and Flrpic in dichloromethane solution. (the inset is the molecular structure of Flrpic.) (b) TA spectrum for the Flrpic:CBP composite film (20 nm) at 1 μ s after nanosecond laser excitation at 415 nm. Inset: smoothed line for the data surrounded with a dashed circle. (c) Time profiles of phosphorescence of Flrpic detected at 500 nm (red, multiplied with -1) and transient absorption of the CBP (blue) detected at 633 nm.

FIG. 4. Estimated energy flow diagram and quantum efficiencies for the CBP:Flrpic composite film under selective photo-excitation of Flrpic. The arrows show photo-excitation (blue), intersystem crossing in Flrpic (dashed black), the cycle process (orange), decay from Flrpic (green), and decay from CBP (red), respectively. The dashed arrows show non-radiative processes. The solid arrows show one-photon processes.

of OWG, which is inefficient coupling of the probe light due to the incident loss at the small entrance width ($230 \mu\text{m} = 200 \mu\text{m}/\sin(60^\circ)$) of the substrate's edge. The lifetime was $\tau_{\text{CBP}} = 28 \mu\text{s}$ by single exponential fitting. This is the direct observation of the BET in host-guest system for OLED emitter layer.

The efficiencies of $\phi_{\text{nr}(\text{CBP})}$ and $\phi_{\text{FET}(\text{CBP})}$ can be calculated by the two lifetimes of CBP triplet excitons measured in the CBP film and the CBP-Flrpic composite film. The efficiencies are $\phi_{\text{nr}(\text{CBP})} = k_{\text{nr}(\text{CBP})}/(k_{\text{nr}(\text{CBP})} + k_{\text{FET}(\text{CBP})}) = 0.30$ and $\phi_{\text{FET}(\text{CBP})} = 1 - \phi_{\text{nr}(\text{CBP})} = 0.70$, where $k_{\text{nr}(\text{CBP})}$ and $k_{\text{FET}(\text{CBP})}$ are the thermal relaxation rate of CBP triplet ($= 1/\tau_{\text{CBPonly}} = 1/93 \mu\text{s}^{-1}$) and the FET rate from CBP T_1 to Flrpic T_1 in the composite film ($k_{\text{nr}(\text{CBP})} + k_{\text{FET}(\text{CBP})} = 1/\tau_{\text{CBP}} = 1/28 \mu\text{s}^{-1}$), respectively.¹⁴

The strong negative signal around 500 nm in Fig. 3(b) was assigned to the phosphorescence of Flrpic.⁹ The phosphorescence decay curve had two lifetime components of $\tau_{\text{FI-1}} = 1.9 \mu\text{s}$ and $\tau_{\text{FI-2}} = 27 \mu\text{s}$ (the amplitudes are $A_{\text{FI-1}} = 0.12$, $A_{\text{FI-2}} = 0.018$, respectively) fitted by double exponential function (Fig. 3(c)) and the ratio of the phosphorescence intensities of the two components becomes $(\tau_{\text{FI-1}}A_{\text{FI-1}})/(\tau_{\text{FI-2}}A_{\text{FI-2}}) = 0.23/0.49 = 0.47$. The lifetime of the slow component was equivalent to that of CBP triplets ($\tau = 28 \mu\text{s}$). This indicates that the majority of Flrpic triplets decays radiatively with the lifetime of $\tau_{\text{FI-1}} = 1.9 \mu\text{s}$ and the rest decays radiatively or non-radiatively with the lifetime of $\tau_{\text{FI-2}} = 27 \mu\text{s}$ through the multiple recycling process between CBP and Flrpic T_1 levels.

The direct observation of the lifetime of host triplets enables us to have quantitative analysis for the BET efficiency $\phi_{\text{BET}(\text{FI})}$ and the two final quantum efficiencies of Φ_{FI} from Flrpic T_1 to S_0 and Φ_{CBP} from CBP T_1 to S_0 ($\Phi_{\text{FI}} + \Phi_{\text{CBP}} = 1$). For the analysis, we assume four conditions as follows; (i) the intersystem crossing efficiency of Flrpic is $\phi_{\text{ISC}} = 1$, (ii) the decay processes from Flrpic involve only $\phi_{\text{r}(\text{FI})}$ and $\phi_{\text{BET}(\text{FI})}$ ($\phi_{\text{r}(\text{FI})} + \phi_{\text{BET}(\text{FI})} = 1$), (iii) the decay paths from CBP are only $\phi_{\text{nr}(\text{CBP})}$ and $\phi_{\text{FET}(\text{CBP})}$ ($\phi_{\text{nr}(\text{CBP})} + \phi_{\text{FET}(\text{CBP})} = 1$), (iv) $\phi_{\text{nr}(\text{FI})}$ is negligible. In these assumptions, Φ_{FI} can be written using the formula of infinite geometrical series as

$$\begin{aligned} \Phi_{\text{FI}} &= \Phi_{\text{FI-1}} + \Phi_{\text{FI-2}} = \phi_{\text{r}(\text{FI})} \\ &+ \sum_{k=1}^{\infty} \left(\phi_{\text{BET}(\text{FI})} \phi_{\text{FET}(\text{CBP})} \right)^k \phi_{\text{r}(\text{FI})} \\ &= \sum_{k=0}^{\infty} \left(\phi_{\text{BET}(\text{FI})} \phi_{\text{FET}(\text{CBP})} \right)^k \phi_{\text{r}(\text{FI})}, \end{aligned} \quad (1)$$

where $\Phi_{\text{FI-1}}$ and $\Phi_{\text{FI-2}}$ are the first decay from Flrpic T_1 to S_0 and slow decay after BET and FET, respectively, and k is the coming and going number of energy between CBP T_1 and Flrpic T_1 . Φ_{CBP} can be also written as

$$\Phi_{\text{CBP}} = \sum_{k=0}^{\infty} \left(\phi_{\text{BET}(\text{FI})} \phi_{\text{FET}(\text{CBP})} \right)^k \phi_{\text{BET}(\text{FI})} \phi_{\text{nr}(\text{CBP})}. \quad (2)$$

From Eqs. (1) and (2), the BET efficiency can be written as¹⁵

$$\phi_{\text{BET}(\text{FI})} = \{ \phi_{\text{FET}(\text{CBP})} (1 + \Phi_{\text{FI-1}}/\Phi_{\text{FI-2}}) \}^{-1}. \quad (3)$$

By approximation of $\Phi_{\text{FI-1}}/\Phi_{\text{FI-2}} \sim (\tau_{\text{FI-1}}A_{\text{FI-1}})/(\tau_{\text{FI-2}}A_{\text{FI-2}})$, the BET efficiency was obtained as $\phi_{\text{BET}} = 0.97$. The final radiative and non-radiative quantum efficiencies were also calculated as $\Phi_{\text{FI}} = 0.09$ and $\Phi_{\text{CBP}} = 0.91$, respectively. Figure 4 shows the consequent energy flow with the estimated quantum efficiencies for the selective excitation of Flrpic in the composite film.

In conclusion, we demonstrated high-sensitive measurements of energy dynamics in organic thin films using time-resolved optical waveguide spectroscopy. This approach allows us to monitor the minute change in the transient absorbance ($\sim 10^{-7}$) in vapor-deposited thin films. We directly observed the BET from T_1 level of guest (Flrpic) to T_1 level of host (CBP) in a blue phosphorescent material for OLEDs. From the result, we quantitatively estimated the inefficiency of BET, which is one of the most important problems for applying blue phosphorescent materials to OLEDs.

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