

Detailed Analysis of Emitting Processes of Emitters for OLED using Time-resolved Vibrational Spectroscopy

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ABSTRACT

We investigated the light emitting processes of thermally activated delayed fluorescence (TADF) emitters for OLED in terms of structural dynamics using time-resolved infrared vibrational spectroscopy. As a result, we found the strong correlation between TADF activity and structural change upon intersystem crossing.

1 INTRODUCTION

Knowing the mechanism of light emission is important for developing efficient and durable organic emitters. Between photo- or electrical excitation and light emission, there are many processes on a time scale ranging from femtosecond (10^{-15} s) to nanosecond (10^{-9} s). To understand these processes, changes in charge distribution and molecular structure should be tracked in this wide time range. For this purpose, we propose time-resolved infrared vibrational spectroscopy (TR-IR) systems particularly for obtaining structural information in the emission processes, which complements time-resolved photo-luminescence spectroscopy (TR-PL).

Infrared vibrational spectroscopy is one of the common tools for analyzing materials. This is not only because it is nondestructive, remote, and in-situ analytical methods but also because a complicated vibrational spectrum contains rich electronic and structural information on a molecule, so-called fingerprint of a molecule. TR-IR takes over these features besides ultrahigh temporal resolution; however, TR-IR is not so popular for analyzing photofunctional materials for now. Thus, we have developed TR-IR systems applicable to a wide variety of photofunctional materials and unveiled many important dynamical processes in the materials: organic semiconductors [1,2], transition metal complexes [3,4], electron transfer processes in supramolecules [5], photoactive liquid crystals [6]. Recently, we have applied this system to exploring mechanisms of light emitting processes of thermally activated delayed fluorescence (TADF) materials for OLED [7-9], and revealed the correlation between structural dynamics and TADF activities.

2 EXPERIMENT

TR-IR spectra were measured by the pump-probe method using a Ti:sapphire chirped pulse amplifier (pulse duration = 120 fs, wavelength = 800 nm). The tunable mid-

infrared probe pulse was generated by the combination method between the optical parametric amplification (OPA) and difference frequency generation from a part of the amplifier output. The probe pulse passed through a sample was dispersed by a 19-cm polychromator and detected with a 64-channel linear mercury-cadmium-telluride (MCT) IR detector array. The specifications of our system are below: temporal resolution: 100 fs, temporal range: 100 fs - 10 ms, probe range: 1000 cm^{-1} - 4000 cm^{-1} , available pump energy: 266 nm - 2500 nm, sensitivity: $\Delta\text{abs} < 10^{-5}$, sample temperature: 20 K - 400 K, measurable samples: solution, thin film, crystal, etc.

The TR-IR spectra were analyzed by quantum chemical calculations using Gaussian package. The calculation condition: functional, basis set, and solvent effect, was optimized by comparison between the observed and calculated TR-IR spectra.

3 RESULTS AND DISCUSSION

Carbazole-benzonitrile (Cz-BN) derivatives are the first pure organic emitters which achieved nearly 100 % PL quantum yield by a TADF process. Nevertheless, the mechanism of light emitting process is still elusive and there is a poor design strategy for desired high-performance emitters. Thus, we have investigated the detailed photoexcited processes using TR-IR [7,8].

Fig. 1 shows one example of the TR-IR spectra: 1 mM o-3CzBN (3,4,5-tri(9H-carbazole-9-yl)benzonitrile) in CH_3CN . Fig. 1a compares the TR-IR spectrum at 100 ns after photoexcitation and the calculated difference spectrum between the triplet excited state (T_1) and ground state (S_0). Because these spectra are in good agreement with each other, we assigned the spectrum at 100 ns to T_1 , which is consistent with TR-PL spectra. Fig. 2b shows the temporal evolution from 2 ns to 200 ns in a part of TR-IR spectrum. Considering that the intersystem crossing (ISC) rate ~ 15 ns, the spectral change from 2 ns to 200 ns indicates that a large structural change occurs in a course of ISC. We carried out these measurements systematically for various Cz-BN derivatives and found that a large structural change between S_1 and T_1 suppresses TADF activity [7]. This result indicates that the potential shape between S_1 and T_1 should be considered to design TADF activity in addition to the highly electronic states.

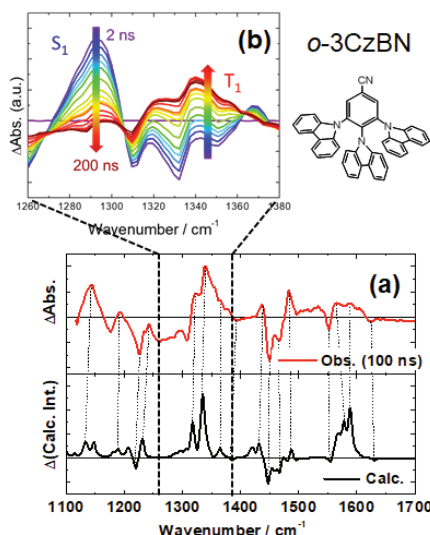


Fig. 1. (a) TR-IR and calculated spectra of o-3CzBN in CH₃CN solution, (b) Temporal evolution of TR-IR spectra

The light emitting processes are affected by their environments, so that we also measured TR-IR spectra in different solutions, in a solid phase, and in a thin film. Fig. 2 shows the TR-IR spectra of powder of o-3CzBN in a KBr pellet. We found little spectral change upon photoexcitation as well as no spectral change at 1 ns and 50 ns, indicating that the structural change observed in a solution is strongly suppressed in a solid phase probably due to inter-molecular interactions.

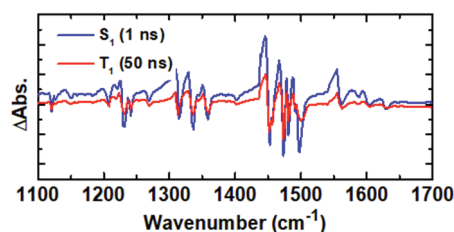


Fig. 2. TR-IR spectra of powder of o-3CzBN in a KBr pellet

4. CONCLUSIONS

We revealed the structural changes in carbazole-benzonitrile derivatives in various solutions upon photoexcitation using time-resolved infrared vibrational spectroscopy. Also, we found that the structural changes are suppressed in a solid in some cases. These structural dynamics are a key for understanding TADF processes in OLED emitters.

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