Charge transfer dynamics of 9-arylcarbazole studied by femtosecond transient absorption spectroscopy

Takamoto, Kazuya; Ueno, Yoshifumi; Ohta, Kaoru; Akimoto, Seiji; Matsubara, Ryosuke;
Tominaga, Keisuke

2020

Takamoto, K., Ueno, Y., Ohta, K., Akimoto, S., Matsubara, R., & Tominaga, K. (2020). Charge transfer dynamics of 9-arylcarbazole studied by femtosecond transient absorption spectroscopy. Proc. Of the 7th Asian Spectroscopy Conference (ASC 2020).
doi:10.32655/ASC_8-10_Dec2020.68

<https://hdl.handle.net/10356/144427>

https://doi.org/10.32655/ASC_8-10_Dec2020.68

Charge Transfer Dynamics of 9-Arylcarbazole Studied by Femtosecond Transient Absorption Spectroscopy

Kazuha Takamoto¹, Yoshifumi Ueno¹, Kaoru Ohta^{1,2}, Seiji Akimoto¹, Ryosuke Matsubara¹, and Keisuke Tominaga^{1,2}

¹Graduation School of Science and ²Molecular Photoscience Research Center, Kobe University, 1-1 Rokkodai, Nada, Kobe, Hyogo 657-8501, Japan

E-mail: 209s208s@stu.kobe-u.ac.jp

Abstract

In chemistry it is important to understand reaction mechanisms in solutions at a molecular level because most chemical reactions occur in solutions. Intramolecular charge transfer (ICT) in solutions is one of the most basic reactions, and the reaction mechanism of ICT is influenced by not only solute-solvent interactions but also geometrical change of solute molecule. 3,6-Bis(dimethylamino)-9-(4-cyanophenyl)carbazole (BANCC, Figure 1(a)) consists of an electron donor of the carbazole unit and an acceptor of the cyanophenyl unit, which are connected by a single bond^[1]. In order to elucidate the ICT reaction mechanism of BANCC, we performed real time observation of the reaction process in various organic solvents by femtosecond transient absorption (TA) spectroscopy.

A pump pulse of 400 nm and a probe pulse of white light were generated from the output of a Ti:sapphire regenerative amplifier. The samples were excited at 400 nm under the magic angle condition, and transient spectra were recorded with femtosecond time resolution by multichannel detectors after dispersing the probe pulse by prisms. We also performed measurements on 3,6-bis(dimethylamino)carbazole (BAC, Figure 1(a)), a molecule of the electron donor part of BANCC.

The absorption spectra of BANCC show two bands at 340 nm and 390 nm with no solvent dependence. These spectral features are the same as those of BAC. On the other hand, the fluorescence spectra of BANCC show a red shift as the solvent polarity increases, while those of BAC are less solvent-dependent. This result suggests that the excited state of BANCC is the ICT state with a large dipole moment. Figure 1(b) displays observed TA spectra of BANCC in dimethylsulfoxide (DMSO) following excitation at 400 nm. A band emerges at 680 nm immediately after photoexcitation, and a new band rises at 550 nm together with decay of the band at 680 nm. Because the band at 680 nm is similar to the observed TA spectra of BAC, it is considered that the carbazole unit is locally excited by photoexcitation followed by charge transfer to the cyanophenyl group.

Furthermore, a peak of the band at 550 nm shows a blue shift with a time constant of ~3 ps, which is similar to the solvation time of DMSO. The time constants of the blue shift in other solvents also show values close to the solvation times of these solvents. This suggests that the static and dynamic properties of the solvent have an effect on the ICT reaction. In presentation, we show the spectral features of the TA spectra in detail and discuss the molecular mechanism of the ICT reaction.

Keywords: intramolecular charge transfer, femtosecond transient absorption spectroscopy, solvation dynamics

References:

- [1] R. Matsubara *et al.*, "9-Aryl-3-aminocarbazole as an Environment- and Stimuli-Sensitive Fluorogen and Applications in Lipid Droplet Imaging," *J. Org. Chem.*, **84**, 5535-5547 (2019).

Figure 1. (a) Molecular structures of BANCC and BAC. (b) TA spectra of BANCC in DMSO.