

Ultrafast Intramolecular Charge Transfer Process of Asymmetric 9,9'-Bianthryl derivative in Ionic Liquid

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Abstract: Femtosecond transient absorption spectroscopy revealed that initial ultrafast charge transfer process of asymmetric 10-cyano-9,9'-bianthryl in ionic liquid occurs in the sub-100 femtosecond domain which is much faster than that of symmetric 9,9'-bianthryl.

OCIS codes: (300.0300) Spectroscopy; (300.6530) Spectroscopy, ultrafast

1. Introduction

Room temperature ionic liquid (IL) is a molten organic salt which is expected to be a new type of organic solvent for chemical synthesis, electrolytes in batteries and solar cells, etc [1]. Normal polar solvent molecules possess a constant electric dipole moment and act as dielectrics. Solvation dynamics of normal polar solvent is considered to be governed by the rotational motion of solvent molecules. Meanwhile in ILs, positive and negative charges can move independently in principle. Hence, IL is expected to exhibit a solvation dynamics different from those of normal polar solvents. In this study, we have carried out femtosecond transient absorption (TA) spectroscopy and compared charge transfer (CT) process of an asymmetric bianthryl derivative, 10-cyano-9,9'-bianthryl (CBA) to that of symmetric 9,9'-bianthryl (BA) in IL, *N,N*-diethyl-*N*-methyl-*N*-(methoxyethyl)ammonium tetrafluoroborate (DemeBF₄) and also in acetonitrile (ACN), the molecular structures of which are shown in Fig. 1. Because BA is a symmetric molecule with no electric dipole moment, while asymmetric CBA is bipolar, solvation structure in the ground state is considered to be different. It is expected that pre-solvation structure of IL affects the CT process differently for the two compounds due to the highly viscous and heterogeneous nature of IL.

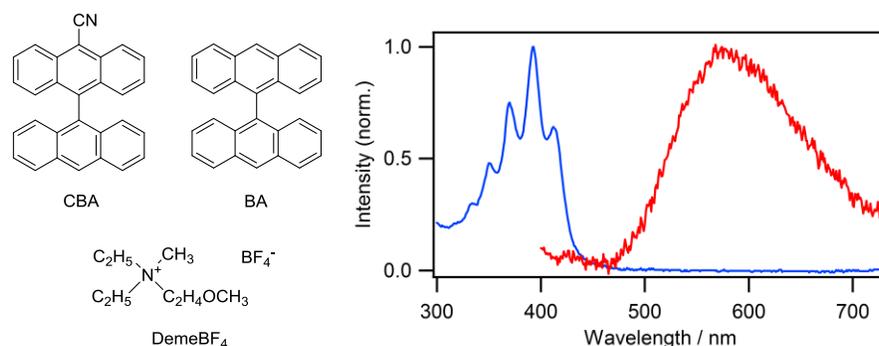


Figure 1. Molecular structures of 10-cyano-9,9'-bianthryl (CBA), 9,9'-bianthryl (BA) and *N,N*-diethyl-*N*-methyl-*N*-(methoxyethyl)ammonium tetrafluoroborate (DemeBF₄), and absorption (blue curve) and emission spectra (red curve) of CBA in DemeBF₄.

2. Experimental method

The laser system used in this work has been described in detail previously [2]. A pair of non-collinear optical parametric amplifiers (NOPA) was pumped by a regeneratively amplified femtosecond Ti:Sapphire laser with 1 kHz repetition rate. The pulse centered at ca. 840 nm generated from one of the NOPA was converted into the second harmonic at 420 nm which was utilized as a pump pulse (pulse duration: 30 fs). White-light supercontinuum was generated from a 1 mm thick CaF plate by focusing the beam centered at ca. 1000 nm generated from the other NOPA. The signal and the reference pulses were detected with multichannel diode array systems connected to a personal computer. Spectra were calibrated numerically for the group velocity dispersion based on optical Kerr measurement between the pump pulse and the white-light continuum. CNBA was synthesized and purified according to the reported method [3]. The sample solution was placed in a rotating cell with a thickness of 0.1 mm and the concentration was adjusted to obtain absorbance of ca. 1.0 at the absorption maximum.

3. Result and discussion

The absorption and emission spectra of CBA in DemeBF₄ exhibits large Stokes shift due to the intramolecular CT reaction. The TA spectra of CBA in DemeBF₄ and that in ACN excited by a femtosecond laser pulse at 420 nm are shown in Fig. 2a and 2b. Immediately after the photoexcitation, LE state absorption can be seen at 520 nm and a new band at 680 nm rapidly arises in both systems. We attribute this spectral change to the CT reaction. In other words, intramolecular CT occurs within ca. 0.1 ps. DemeBF₄ is a significantly viscous IL with a viscosity of 590 cP which requires a few nanoseconds for the solvation dynamics to accomplish. The time scale of the CT is ultra-short compared to the diffusive solvation while it is comparable to that of intramolecular nuclear organization or "inertial response" of the solvation. In normal solvents, inertial response is considered to be induced by the microscopic free-rotation of solvent molecules in the vicinity of the solute, while in IL, small distance free-translation of ions can also contribute.

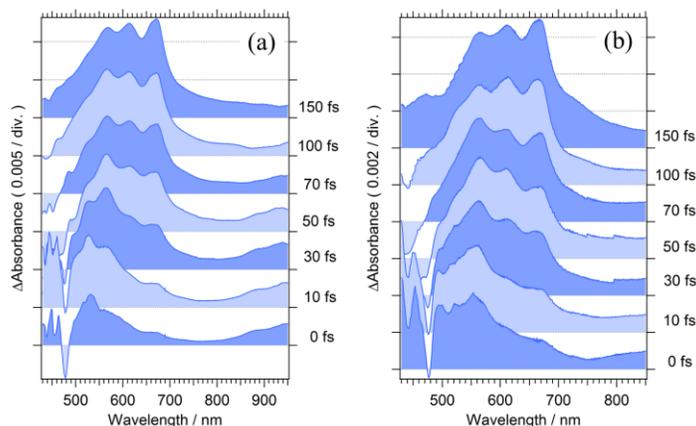


Figure 2. Femtosecond transient absorption (TA) spectra of CBA in (a) DemeBF₄ and (b) in ACN excited at 420 nm.

In the time range of 150 fs and longer, TA spectrum of CBA in DemeBF₄ broadens and new peaks at 560 and 710 nm appears. This spectral change could be due to structural relaxation such as the twisting of the central bond connecting the two anthryl moieties. Because the twisting involves motion of large anthryl groups, it is expected to be viscosity dependent. The time-dependence of the differential absorbance (Δ abs) shown in Fig. 3 was monitored at wavelengths of 670 nm and 710 nm which corresponds to the absorption peaks of the initially formed CT state and the structurally relaxed conformer, respectively. At 670 nm, it can be seen that the CT state is formed with an ultrashort time constant of 50–60 fs which is nearly solvent independent. At 715 nm, it is clear that the rise of Δ abs in DemeBF₄ ($\tau = 69$ ps) is much slower than that in ACN ($\tau = 370$ fs), indicating solvent viscosity dependence of the structural relaxation as expected. It is concluded that CT occurs faster than the diffusive solvation, and subsequently structural relaxation takes place.

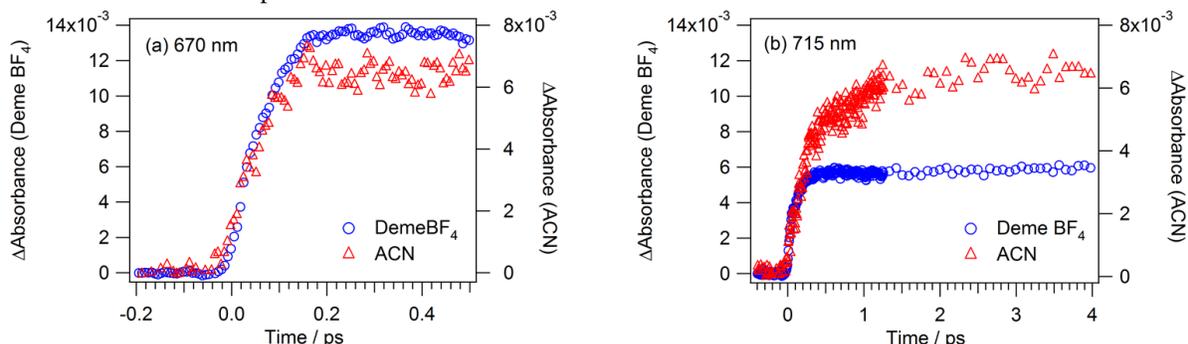


Figure 3. Time evolution of the differential absorbance of CBA in DemeBF₄ (blue circles) and in ACN (red triangles) at (a) 670 nm and (b) at 715 nm. The vertical axis is adjusted in a way that the signals in both solvents overlap at 670 nm.

4. References

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