

FEMTOSECOND TRANSIENT SPECTROSCOPIC STUDY ON AQUEOUS ORGANIC NANOCOLLOIDS

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Solid-state organic compounds are expected to show photophysical processes and photochemical reactions different from those of molecules in solutions because of restricted molecular motions in a crystalline lattice and of the electronic interactions between the neighboring excited-state molecules. In order to investigate such processes directly by a femtosecond pump-probe spectroscopy, we chose to study organic nanoparticles dispersed in water, because such aqueous nanocolloids having the 100-nm size can be excited uniformly and allow us to use the conventional solution-phase techniques. In the presentation, we introduce excited-state relaxation dynamics of several organic nanocolloids such as fullerene-C₆₀, diarylethenes, and quinacridone by using femtosecond transient absorption spectroscopy.

Here, we described the results of the fullerene-C₆₀ nanoparticles (nC60).[1] We have prepared the nC60 (mean size: 50 nm) dispersed in water with the laser fragmentation method, and examined dependences of the excited-state relaxation process on excitation density and wavelength. Figure 1a shows the transient absorption spectra at 0.1 and 1 ps after a femtosecond 350-nm pulse excitation (100 fs FWHM). At low excited-state density (0.14 mJ cm⁻² pulse⁻¹), the relaxation from the intermolecular charge-transfer (CT) excited state to the locally excited S₁ state and/or excimer state was directly and firstly observed in C₆₀ solids, and its intrinsic lifetime of 0.35 ps was found. After that, the S₁ state decayed to excimers and/or directly to the ground state in a few tens of ps time region, but no triplet state was observed even at 500 ps (Figure 1b). This decay time was shortened by 10-100 times compared to those of solid C₆₀ thin film and molecular solution. The shortened decay time was not due to the increased rate of the intersystem crossing to the triplet state, but to quenching by trapped sites in the nanoparticles and/or by water molecules at the surface of the nanoparticle.

On the other hand, at high excited-state density (1.4 mJ cm⁻² pulse⁻¹), the transient spectral band shape at 0.1 ps was different compared to that at the low density (Figure 1a). The new transient band around 750 nm immediately after the excitation was observed. Because the femtosecond dense excitation created a number of excited molecules at the same time in nanoparticle and excited molecules were neighboring each other, the interaction between neighboring CT excited states was generated. The interaction disappeared through the charge recombination of geminate charge pair or between different intermolecular charge pairs with a lifetime of 0.45 ps, and the isolated S₁ molecule and/or ground state molecules at the same time. In addition, the decay profiles of the S₁ state were independent of the fluence (Figure 1b), indicating that the singlet-singlet annihilation process hardly took place in nC60 in water different from the solid C₆₀ thin film.

[1] Y. Ishibashi, et al, Phys. Chem. Chem. Phys., **2018**, 20 958 - 966.

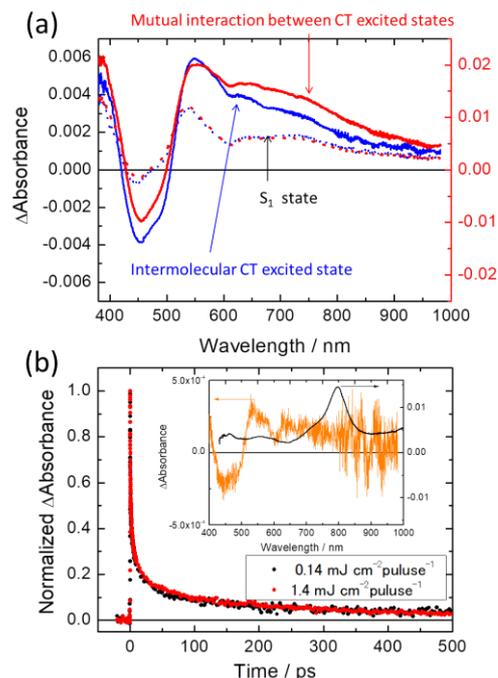


Figure 1. (a) Comparison of transient absorption spectra of nC60 in water by a fs 350-nm pulse excitation at the fluence of 0.14 (blue) and 1.4 (red) mJ cm⁻² pulse⁻¹; 0.1 ps (solid) and 1 ps (dotted). (b) Normalized time profile of transient absorbance at 540 nm at the fluence of 0.14 (blue) and 1.4 (red) mJ cm⁻² pulse⁻¹. Inset is the transient absorption spectrum of nC60 at 500 ps (black), together with that of C₆₀ in toluene (orange).