

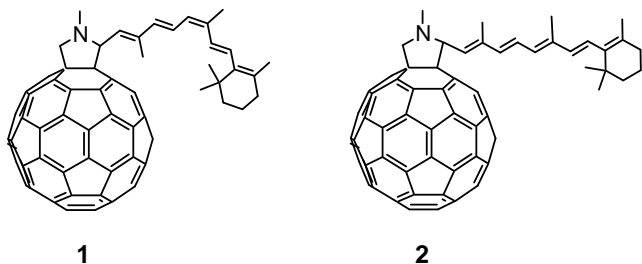
Photoinduced Electron Transfer Reaction in 9-*cis*-Retinyl-C₆₀ Dyad

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Intramolecular photoinduced electron and/or energy-transfer processes in donor-acceptor linked molecules have attracted considerable interests in the studies of the light-energy conversion systems. Recently, fullerene-donor dyads have been studied due to their unique photophysical and photochemical properties. Since C₆₀ has a low reduction potential, it acts as a good electron acceptor. Retinyl polyenes play important roles in visual and photosynthetic systems due to their ability to photo responsibility. Furthermore, in the view of transient absorption spectroscopy, the intense and sharp absorption band of retinyl cation is good spectral probe in the visible region. Recently, Yamazaki et al. have investigated *all-trans*-retinyl-C₆₀ dyad (**2**) by time-resolved absorption and fluorescence techniques.[1] They demonstrated that **2** shows microsecond-timescale charge recombination in polar

Figure 1. Structure of 9-*cis*-retinyl-C₆₀ (**1**) and *all-trans*-retinyl-C₆₀ (**2**)



solvents. In the present study, we newly synthesized 9-*cis*-retinyl-C₆₀ (*c-ret*-C₆₀, **1**) as a structural isomer of **2** and investigated its photoinduced charge separation.

1 was synthesized by the same method reported previously.

1 shows oxidation and reduction at 0.46 and -1.06 V vs Fc/Fc⁺, respectively. From fluorescence lifetime measurements, charge separation in **1** was indicated in polar solvents. The quantum yields of charge separation are estimated to be 0.40 and 0.60 in benzonitrile (BN) and *N,N*-dimethylformamide (DMF), respectively, by using *N*-methylpyrrolidino-

fullerene as a reference.

Picosecond transient absorption measurements were carried out using 388 nm laser, which excites predominately *c-ret*-moiety. From the spectra, the *c-ret* cation radical (absorption band is observed around 620 nm) was generated within 10 ps in polar solvents. Furthermore, since the *c-ret* cation radical generates immediately after laser irradiation in DMF, **1** forms charge transfer complex in DMF due to *cis*-conformation of **1** and strong polarity of DMF. This finding was supported by UV-vis spectra. Rate constants of charge recombination from singlet-charge separated-state are $2.5 \times 10^{10} \text{ s}^{-1}$ and $9.5 \times 10^{10} \text{ s}^{-1}$ in

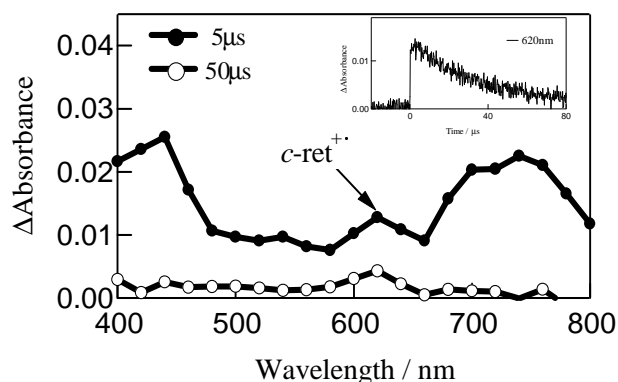


Figure 2. Transient absorption spectra of **1** (in BN, 532 nm laser excitation)

BN and DMF, respectively.

From nanosecond transient absorption measurements by 532 nm laser, rate constant of charge recombination of the charge separated-state with triplet character was $9.3 \times 10^7 \text{ s}^{-1}$, which correspond to lifetime 43 μs in BN. The equilibrium among charge separated-state (*c-ret*⁺·-C₆₀⁻·), triplet excited state of *c-ret*-moiety (^{3*}*c-ret*-C₆₀), and C₆₀-moiety (*c-ret*-^{3*}C₆₀) was suggested by its transient absorption spectrum (figure 2).

In the transient absorption spectrum using 355 nm laser, which excites mainly *c-ret*-moiety, the absorption intensity of the *c-ret*-cation radical increased.

In conclusion, we found that new compound **1** shows long-time charge-separated state; lifetime of the radical-ion pair was as long as 43 μs in BN. This lifetime of the radical-ion pair was due to the equilibrium between charge-separated state and triplet-excited states.

References

- [1] M. Yamazaki, Y. Araki, M. Fujitsuka, O. Ito, *J. Phys. Chem. A*, **2001**, *105*, 8615.