Light-induced Electron Transfer on the Single Wall Carbon Nanotube Surrounded in Anthracene Dendron in Aqueous Solution

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Light illumination of single-wall carbon nanotubes (SWCNTs) dispersed with anthracene (An) dendrons afforded the accumulation of the reduced form of methyl viologen in the presence of a hole shifter. With the helps of the fluorescence lifetime and transient absorption measurements, the charge-separation process from the excited state of the hybrides of An dendrimer to SWCNT was confirmed.

Photoinduced electron-transfer processes mediated by carbon materials have attracted attention in view of the understanding photophysics with highly developed π-conjugated systems of carbon materials.[1] So far, a variety of π-conjugated carbon molecules such as fullerenes are reported as visible light active carbon materials.[2] Despite of such a considerable advances in the design of fullerene molecular systems, only a few studies are reported for the photochemistry of carbon nanotubes.[3]

In order to evaluate electronic properties of single-wall carbon nanotubes (SWCNTs), it is very important to disperse carbon nanotube in solution.[4a] Among the various methods for this aim, amphiphilic fullerodendrons with water-soluble carboxylate terminals were useful to disperse SWCNTs in water.[4b]

In the present study, we employed an amphiphilic poly(amidoamine) dendron containing anthracene moiety at the focal point and carboxylate groups at the terminals as shown in inset of Figure 1 (abbreviated as An(G2.5-COO$^-$)). When such dendrons are mixed with SWCNTs (Hipco) by sonication, we obtained homogeneous stable black solution. A TEM image of SWCNT/An(G2.5-COO$^-$) composite measured after evaporation of solvent shows slender fibrils (see SI).[7] This suggests that the aggregation of SWCNTs may be suppressed with the wrapping by An(G2.5-COO$^-$). The absorption spectrum of this solution is shown in Figure 1, which exhibits the weak van Hove transitions characteristic of the fuzzy SWCNTs.[5] The weak van Hove transitions support the formation of SWCNT/An(G2.5-COO$^-$) composite. The 390-nm band was attributed to the An moiety, which became broad by interaction with SWCNTs. In the present study, laser photolysis was performed with the 355, 400, and 532-nm lights. The 355 and 400-nm lights were absorbed predominantly by the An moiety and its tail, respectively, in addition to the broad absorption of SWCNTs. On the other hand, the 532-nm light exclusively excites SWCNTs.

The fluorescence spectrum of the An moiety shows the peak at 450 nm; the fluorescence intensity was decreased by mixing with SWCNTs accompanied by a considerable broadening as shown in Figure 2. To get more quantitative information, the fluorescence time profiles were measured as shown in inset of Figure 2. Acceleration of the fluorescence decay was observed by mixing with SWCNTs in agreement with the steady-state fluorescence intensity quenching.

From the curve-fitting of the fluorescence time profile with a biexponential fitting, the fluorescence lifetimes ($\tau_f(^1An^*)$) were evaluated to be 800 ps (60%) and 2500 ps (40%) for SWCNT/An(G2.5-COO$^-$). These values are shorter than the

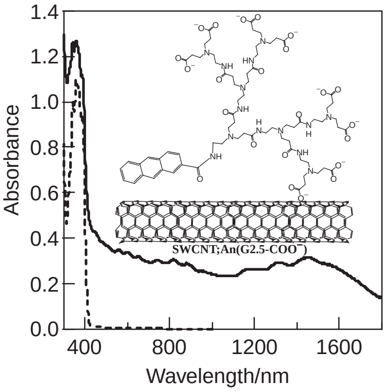

Figure 1. Steady-state absorption spectra of SWCNT;An(G2.5-COO$^-$) (solid line) and 0.05 mM An(G2.5-COO$^-$) (dash line) in D_2O. Inset: Model of molecular structure of SWCNT;An(G2.5-COO$^-$).

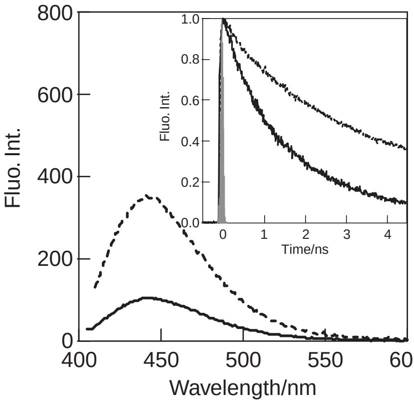

Figure 2. Steady-state fluorescence spectra of SWNT;An-(G2.5-COO$^-$) (solid line) and 0.05 mM An(G2.5-COO$^-$) (dash line) in D_2O; $\lambda_{ex} = 400$ nm. **Inset:** Fluorescence decays at 450 ± 20 nm.

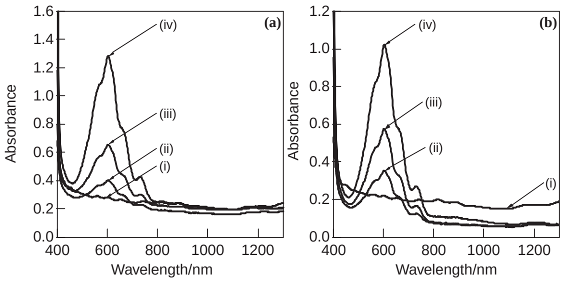

Figure 3. Steady-state absorption spectra observed after the repeated laser light irradiations of SWNT;An(G2.5COO$^-$) in the presence of 0.5 mM MV^{2+} in Ar-saturated D_2O; (a) 355 nm and (b) 532 nm; [BNAH] = (i) 0, (ii) 0.2, (iii) 0.3, and (iv) 0.5 mM.

value (4600 ps (100%)) of free An(G2.5-COO$^-$) in D_2O. From the shorter component, $\tau_f(^1An^*)$, quenching rate ($k_q(^1An^*)$) and quantum yield ($\Phi_q(^1An^*)$) were calculated to be 1.3×10^9 s^{-1} and 0.86, respectively. These values suggest that efficient quenching of $^1An^*$ occurs within the composite. Probably, charge separation may be the main origin of the fluorescence quenching.

Further experiments were conducted with the aid of methyl viologen dication (MV^{2+}) as an electron mediator and electron pool and 1-benzyl-1,4-dihydronicotinamide (BNAH) as a hole shifter. On addition of MV^{2+} and BNAH to the SWCNT/An-(G2.5-COO$^-$) solution, new absorption bands appeared after the repeated laser-light irradiations as shown in Figure 3. New absorption peak appearing at 600 nm was attributed to the radical cation of methyl viologen ($MV^{\bullet+}$), as a result of electron trapping. With the BNAH concentrations, an increase of $MV^{\bullet+}$ was observed. The maximal $MV^{\bullet+}$ concentrations were evaluated to be 0.075 and 0.065 mM with 355- and 532-nm laser light irradiations, respectively, which correspond to the 15 and 13% conversions. Without BNAH, appreciable accumulation of $MV^{\bullet+}$ was not observed. It is notable that almost the same $MV^{\bullet+}$ was observed with UV light and visible light irradiation, in which the former light excites the An moiety, whereas the latter light excites SWCNT of SWCNT/An(G2.5-COO$^-$).

Furthermore, the nanosecond transient absorption spectra were observed by 355-nm laser irradiation of SWCNT/An-(G2.5-COO$^-$) as shown in Figure 4.[7] The absorption band appeared at 740 nm with shoulder at 950 nm, which can be attributed to the $An^{\bullet+}$ moiety.[6a] After the decay of the $An^{\bullet+}$ moiety and recovery of the depletion due to the An emission, a long lived transient absorption band appeared in the 450–500 nm region. This band is attributed to the triplet excited state of the An moiety,[6b] which may be generated via intersystem crossing in competitive with charge separation via $^1An^*$. As a counter part of the $An^{\bullet+}$ moiety, absorptions of the electron trapped on SWCNTs may be hidden in Figure 4.

These transient spectra support the generation of $SWCNT^{\bullet-}/An^{\bullet+}$(G2.5-COO$^-$). From the time profile at 740-nm of the $An^{\bullet+}$ moiety, charge-recombination rate was calculated to be 1.0×10^6 s^{-1} ($\tau_{RIP} = 1000$ ns). When both MV^{2+} and BNAH were added, the most of the transient absorption bands disappeared, leaving the rise of $MV^{\bullet+}$ at 600 nm.[7] This indicates that an electron migrates from $SWCNT^{\bullet-}$ to MV^{2+}, generating $MV^{\bullet+}$, whereas a hole shifts from $An^{\bullet+}$ to BNAH, generating $BNAH^{\bullet+}$. From the observed time profiles, it was revealed that these hole-shift and electron migration take place very fast near the diffusion controlled limit.[7] In the case of 532-nm laser light excitation, broad transient absorption bands were observed in the visible and NIR regions,[7] which were also quenched by the addition of MV^{2+} and BNAH, leaving $MV^{\bullet+}$. Thus, the accumulation of $MV^{\bullet+}$ may be caused by direct photoelectron ejection from SWCNTs to MV^{2+} in addition to the charge separation between attached An moiety.

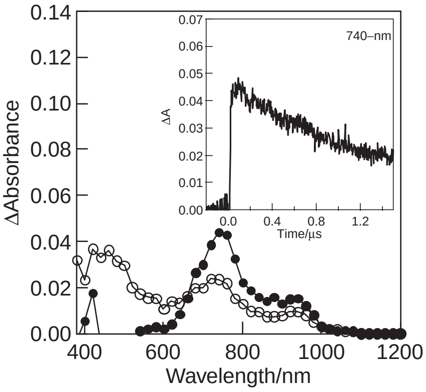

Figure 4. (a) Nanosecond transient absorption spectra of SWCNT;An(G2.5-COO$^-$) in D_2O observed by 355-nm laser irradiation; (●) 100 ns and (○) 1000 ns. Inset: Absorption time profile.

In conclusion, we have demonstrated photosensitized electron-transfer, electron-migration, and hole-shift processes of SWNT/An(G2.5-COO$^-$) in the presence of MV^{2+} and BNAH. As reasons for the accumulating $MV^{\bullet+}$, generation of $SWNT^{\bullet-}$/$An^{\bullet+}$(G2.5-COO$^-$) and direct photoejection with UV and visible light illuminations, respectively, were proposed.

References and Notes

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7 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journal/chem-lett/index.html.