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Photoinduced Electron Transfer in a Dynamic Supramolecular System with Curved π-Structures

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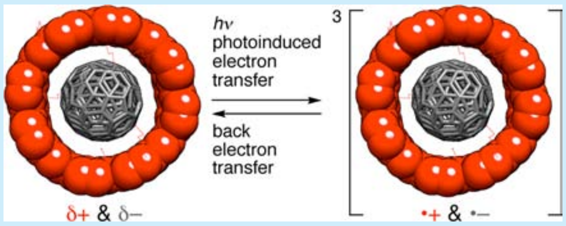
Ⓢ *Supporting Information*

ABSTRACT: Photoinduced electron-transfer processes in a carbonaceous supramolecular combination of a tubular host and a C_{60} guest were investigated with time-resolved transient absorption spectra upon laser flash photolysis. Following the formation of triplet charge-separated species via electron transfer from the host to the guest, a rapid back electron transfer proceeded to afford triplet C_{60}.



The structural chemistry of carbon nanotubes (CNT) started flourishing by the advent of synthetic tubular molecules of their segments.[1−3] These segmental models with molecular nature not only deepen the chemical understanding of CNT but also show unique characteristics due to their hoop-shaped structures. With our own tubular molecules, [4]cyclo-2,8-chrysenylenes ([4]CC), we recently demonstrated anomalous features of persistent tubular structures of sp^2-carbon networks in the field of supramolecular chemistry: the tubular structure was preorganized to accommodate fullerene guests with complementary spherical structures to afford the tightest host−guest complexes to date.[4] Furthermore, in the presence of such a tight association force, the nondirectional van der Waals nature allowed rapid dynamic motions for the guest in solution or even in the solid state.[4,5] We also revealed the atomic-level structures of the dynamic supramolecular system, so-called molecular peapods,[6,7] and recognizing the presence of smoothly curved structures with rich π-electrons, we became greatly interested in the electronic characters. In this Letter, we wish to report our first fundamental study on the electronic characteristics of the molecular peapod. We found that electronic interactions in the tube−sphere combination at the ground state are pronounced upon photoexcitation and revealed the details of the photoinduced electron-transfer (PET) reactions at the excited state by ultrafast time-resolved transient absorption spectroscopy. This first study on the PET dynamics in the curved π-systems will be of fundamental importance for the understanding of peapods in general.[6]

The first sign of photoinduced processes in the molecular peapod was noticed through titration experiments to derive the association constants.[4,8] Fluorescence of [4]CC was thus quenched upon encapsulation of C_{60}. To facilitate the analysis in polar media, we now added another entry of solvents for the encapsulation and carried out the titration experiments for the formation of (P)-(12,8)-[4]$CC_{2,8}{\supset}C_{60}$ in polar benzonitrile (PhCN) (Figure 1). As shown in Figure S1, the fluorescence of the host was effectively quenched in PhCN, and the association constant (K_a) was determined to be 1.0×10^{10} M^{-1} (25 °C; log K_a = 10.0). This value also confirmed the previous conclusion that the association constant of molecular peapods depends qualitatively on the solubility of C_{60}.[4]

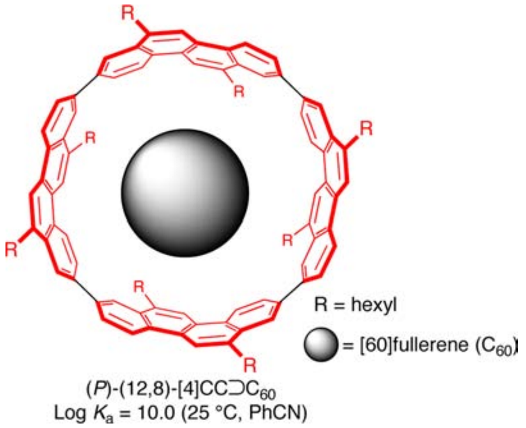


Figure 1. Molecular structure and association constant of (P)-(12,8)-[4]$CC_{2,8}{\supset}C_{60}$.

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Fluorescence quenching by the C_{60} guest involved PET reactions, and the photodynamics in (*P*)-(12,8)-[4]$CC_{2,8}\supset C_{60}$ were revealed by the time-resolved transient absorption spectra. The transient spectra recorded in deaerated PhCN upon femtosecond laser flash photolysis (λ_{ex} = 393 nm; fwhm = 130 fs) showed absorption maxima at 480 and 1072 nm (Figure 2a). The absorption band at 1072 nm was a diagnostic signature of an electron-transfer product from the guest, $C_{60}{}^{\bullet-}$,[9] and the decay time profile of this band obeyed first-order kinetics to afford the back electron-transfer rate constant (k_{BET}) of 6.7 × 10^8 s^{-1} and lifetime (τ) of the CS state to be 1500 ps. The other absorption band at 480 nm synchronously decayed at k = 6.5 × 10^8 s^{-1} and τ = 1600 ps (Figure S2) and was thus ascribed to the counterpart product from the donor, i.e., [4]$CC^{\bullet+}$. The electron paramagnetic resonance (EPR) spectrum of (*P*)-(12,8)-[4]$CC_{2,8}\supset C_{60}$ after photoirradiation indeed consisted of broad signals at g = 2.003 and a sharp signal at 2.0002 (Figure S3) which are assigned to [4]$CC^{\bullet+}$ and $C_{60}{}^{\bullet-}$, respectively.[10] Another characteristic signal was also observed at g = 4.25, which showed the presence of the triplet state of the radical ion pair. Thus, a triplet charge-separated (CS) state was generated via PET.[11]

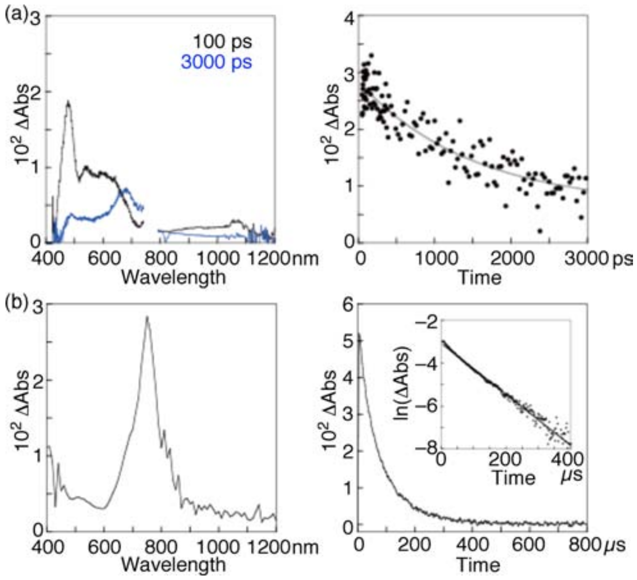

Figure 2. Transient absorption spectra of (*P*)-(12,8)-[4]$CC_{2,8}\supset C_{60}$ in deaerated PhCN at ambient temperature. The results of kinetics analysis are embedded in the decay profiles. (a) Left: Absorption spectra with peak signals at 480 and 1072 nm taken at 100 and 3000 ps after femtosecond laser flash excitation (λ_{ex} = 393 nm). [(*P*)-(12,8)-[4]$CC_{2,8}\supset C_{60}$] = 100 μM. Right: Decay profile of the signal at 1072 nm affording k_{BET} = 6.7 × 10^8 s^{-1} and τ = 1500 ps. See Figure S2 for the synchronous decay profile of the signal at 480 nm. (b) Left: Absorption spectrum with peak signals at 750 nm taken at 50 μs after nanosecond laser flash excitation (λ_{ex} = 420 nm). [(*P*)-(12,8)-[4]$CC_{2,8}\supset C_{60}$] = 25 μM. Right: Decay profile of the signal at 750 nm to give the rate of k_T = 1.2 × 10^4 s^{-1} and the lifetime of τ = 80 μs. Inset: First-order plot.

The fate of the triplet CS state was tracked by a subsequent transient absorption spectrum upon nanosecond laser flash photolysis (λ_{ex} = 420 nm). As shown in Figure 2b, the transient absorption spectrum showed an intense band at 750 nm, which was a diagnostic signal of the triplet excited state of the guest (${}^3C_{60}{}^*$). The decay profile afforded a rate constant (k_T) of 1.2 × 10^4 s^{-1} and lifetime (τ) of 80 μs.

The overall picture of the energetics for the photoexcitation processes has been completed by the analysis with cyclic voltammetry (CV). The voltammograms of (*P*)-(12,8)-[4]$CC_{2,8}\supset C_{60}$, (*P*)-(12,8)-[4]$CC_{2,8}$ and C_{60} are shown in Figure 3.

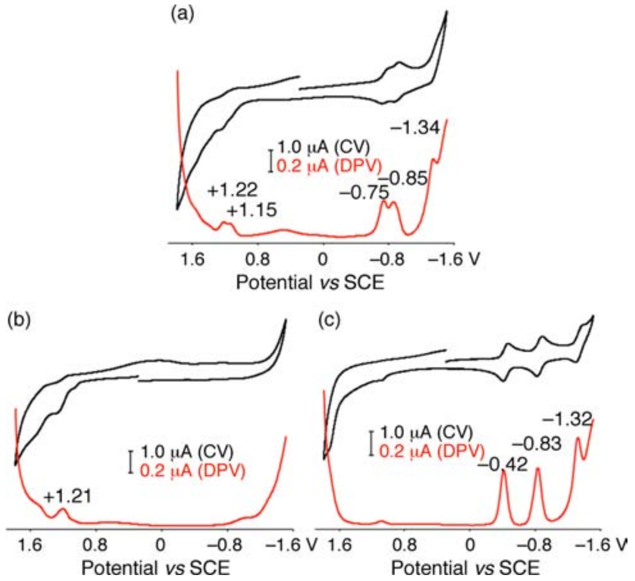

Figure 3. Cyclic voltammograms (CV) and differential pulse voltammograms (DPV) in deaerated PhCN at ambient temperature. Conditions: [Specimen] = 200 μM, [Bu_4NPF_6] = 100 μM, scan rate = 100 mV s^{-1} (CV) and 4 mV s^{-1} (DPV), working and counter electrodes = Pt, Reference electrode = Ag/$AgNO_3$. CVs and DPVs of (a) (*P*)-(12,8)-[4]$CC_{2,8}\supset C_{60}$, (b) (*P*)-(12,8)-[4]$CC_{2,8}$, and (c) C_{60}.

The CS state energy was determined from the difference of the first redox potentials in (*P*)-(12,8)-[4]$CC_{2,8}\supset C_{60}$ to afford the value 1.90 eV. The energy of the singlet excited state of [4]CC host (^{1}[4]CC*; * denotes the excited state) was determined from the average of the absorption and fluorescence energies (λ_{max} = 417 nm and λ_{fl} = 450 nm) to be 2.87 eV.[3] On the other hand, the energy of the singlet excited state of C_{60} (${}^1C_{60}{}^*$) is known to be 1.99 eV.[12] Thus, photoinduced electron transfer to form the charge-separated state in the supramolecular complex is energetically favorable because the energy of the CS state is lower than the excited state of both of the components. The energy diagram of the photodynamic processes is summarized in Figure 4.[13] The photodynamic processes associated with the fluorescence quenching was thus revealed as follows: After photoexcitation of the [4]CC host, a rapid PET reaction

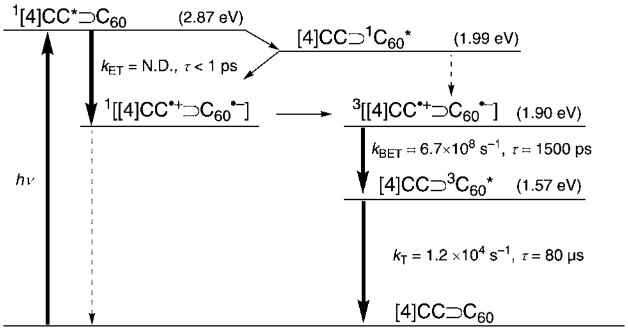

Figure 4. Energetics of photodynamic processes in (*P*)-(12,8)-[4]$CC_{2,8}\supset C_{60}$. The bold arrows show the pathway confirmed by the present study, and the broken arrow shows a potential minor pathway.

proceeds to afford the triplet CS species at 1.90 eV. The energy of the triplet excited state of C_{60} ($^3C_{60}$*: 1.57 eV) is lower than that of the CS state (1.90 eV), facilitating the fast BET reaction of 6.7×10^8 s^{-1} to afford C_{60}* in the complex. As is the case of naked C_{60}, the triplet C_{60} survives with a relatively long lifetime (80 μs) and, finally, relaxes to the ground state at the rate of 1.2×10^4 s^{-1}.

Other interesting characteristics indicated by the voltammetry analysis were the effects of the complexation on the host and the guest at the ground states. Thus, the oxidation potentials of [4]CC shifted by −60 mV (from +1.21 V to +1.15 V), and the first reduction potentials of C_{60} shifted by −330 mV (from −0.42 to −0.75 V) upon encapsulation. The negative shifts of the potentials, for both the oxidation of the host and reduction of the guest, show a ground state communication in the complex and indicate the presence of partial charge transfer from the [4]CC host and the C_{60} guest at the ground state. The large negative shift of −330 mV in the C_{60} guest is, in passing, among the largest values recorded in supramolecular systems of C_{60} and is probably caused by less solvation of $C_{60}^{\bullet -}$ and also by efficient electronic communications in the complex at the ground state.[14,15] Albeit a static view, a preliminary theoretical investigation with the DFT method on the complex indicated the presence of partial charge transfer (0.06 electrons) from the host to the guest at the ground state. The accompanying shifts in the frontier orbital levels upon complexation were +170 meV for $\mathrm{LUMO}_{\mathrm{guest}}$ and +50 meV for $\mathrm{HOMO}_{\mathrm{host}}$, which explains the negative shifts of the redox potentials of the C_{60} guest and the [4]CC host, respectively. Further theoretical studies including the dynamics behaviors are currently ongoing.

Finally, we consider the preceding relevant results of infinite single-wall CNT (SWNT) peapods by taking into account the results obtained in this study. It has been reported that fullerene-encapsulating sites in peapods with single-wall CNTs (SWNTs) act as quantum wells in the one-dimensional system of SWNTs to modulate the band characteristics,[16] which may indicate that the fundamental characters of the finite systems may be, surely with great care on the applicability, extrapolated to the infinite systems. As a device application, a field-effect transistor (FET) of peapods comprising infinite SWNTs and C_{60} was reported by Li and co-workers.[17] Their observation of an increased hole density in SWNT FET upon peapod formation indeed correlates well with the partial charge transfer process from the host to the guest at the ground state in this study. Interestingly, Li further observed that the threshold voltage in the peapod FET shifted back toward the negative voltage upon photoirradiation and suggested an excess BET reaction from C_{60} to SWNT as its potential origin. Although the observation of the rapid BET reaction in our finite system may correlate well with this proposal, we may suggest that the triplet-coupled nature of the CS species from the photoexcitation could also act as a hole trap in the p-type FET and that such spin correlations in SWNT peapods may deserve further studies in the future.

In summary, we studied the fundamental photodynamics of the molecular peapod with curved π-structures. Despite the dynamic structures of the peapod,[4,5] the PET processes were not hampered, and the photodynamics followed the energetics derived from the static molecular components. The tight and effective contacts between host and guest with highly delocalized π-systems may play a central role in such unique PET systems, and the detailed correlations of energetics, kinetics, and molecular dynamics will be studied in the near future. Experimental investigations for control over energetics, for instance, with other molecular peapods of both host and guest variants, are also of immediate interest.[4,18] The observation of triplet-coupled CS species led us to an interesting proposal of spin correlations in SWNT peapods and may stimulate further studies along this line.

■ ASSOCIATED CONTENT

Supporting Information

Materials, methods and additional data. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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