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Effects of Fullerene Encapsulation on Structure and Photophysical Properties of Porphyrin-Linked Single-Walled Carbon Nanotubes

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Fullerene-encapsulating single-walled carbon nanotubes (C_{60}@SWNT) linked with porphyrins by a short bridge have been prepared for the first time. Steady state and time-resolved spectroscopies demonstrated the initial formation of an exciplex state, followed by a charge-separated state.

Because of the exceptional electronic, optical, and mechanical properties, single-walled carbon nanotubes (SWNT) have been explored as promising building blocks for artificial photosynthesis and photovoltaic devices.[1] Consequently, functionalizations of SWNT with photoactive molecules for the study of their excited state dynamics have become an active area of researches.[2-6] Among the photoactive components, porphyrins are stable electron-donors with a large extinction coefficient in the visible region and thereby have been widely employed in combination with SWNT.[2,3] Photophysical investigation on various noncovalently assembled porphyrin-SWNT hybrids, e.g., using π–π stacking and ionic interactions, by steady-state and time-resolved spectroscopic measurements has revealed the occurrence of electron transfer from the excited porphyrins to the SWNT.[2] In addition, porphyrin-SWNT composites covalently-linked by a flexible bridge have also shown photoinduced charge separation between the porphyrin and SWNT.[3] On the other hand, we proposed the evolution of an exciplex between porphyrin and SWNT when the two components were tethered by a short rigid phenylene spacer.[6] Photoelectrochemical measurements suggested that the exciplex decays directly to the ground state without generating the charge-separated state.[6] Therefore, the separation distance and spatial orientation between porphyrin and SWNT are crucial factors to control the relaxation processes from the excited states.

One of the fundamental approaches for controlling the electronic properties of SWNT is the inner space doping of suitable-sized organic molecules like fullerenes.[7] It is known that encapsulated fullerenes cause changes in the Fermi levels and band gap energies of SWNT.[8] When a suitable donor is combined with fullerene-encapsulated SWNT, i.e., fullerene peapods or C_{60}@SWNT, the enhanced electron-accepting character due to the ground state charge transfer (CT) interaction between C_{60} and SWNT can be supposed to promote the electron transfer from the excited donor molecule to the fullerene peapod.[9] Despite such intriguing properties of fullerene peapods, ternary nanohybrids of fullerene peapods with large π–aromatic molecules have yet to be prepared. As such, interactions between covalently linked peapods and large π–aromatic molecules in the ground and excited states have never been investigated. Herein, we report the first preparation and photophysical properties of fullerene peapods covalently functionalized[10] with porphyrins. To evaluate the effects of the fullerene encapsulation on the structure and photophysical properties, we chose the same short rigid phenylene spacer as that employed for the porphyrin-SWNT reference without C_{60} molecules.[6]

Encapsulation of C_{60} into open-ended SWNT (p-SWNT) with diameters of 1.3 – 1.6 nm was conducted by sublimation method (Fig. S1 in ESI).[5a,7b] Then, zinc porphyrin-linked fullerene peapod, C_{60}@SWNT-ZnP, was synthesized according to the two-step functionalization procedure as shown in Scheme 1 (see Experimental in ESI).[11] Briefly, surfactant-wrapped C_{60}@SWNT was reacted with *p*-iodophenyl diazonium salt in aqueous solution, followed by treatment with the in-situ generated diazonium salt in *o*-dichlorobenzene (ODCB) to yield pre-functionalized peapod with *p*-iodophenyl groups (C_{60}@SWNT-PhI). Then, Suzuki coupling reaction of C_{60}@SWNT-PhI with porphyrin boronic ester gave C_{60}@SWNT-ZnP. Transmission electron microscopy (TEM) measurements verified that the inner space of SWNT was still well-packed by the encapsulated C_{60} molecules after the modification of outer skeleton in the intensive conditions (Fig. S2 in ESI). Both C_{60}@SWNT-PhI

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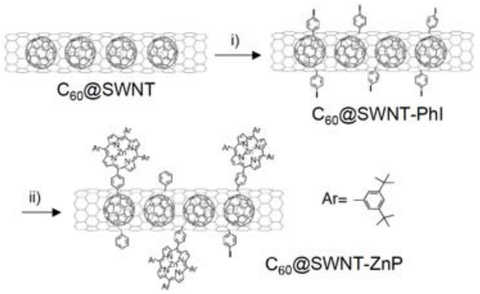
and C_{60}@SWNT-ZnP exhibited high solubility in common organic solvents including *N*,*N*-dimethylformamide (DMF), ODCB and toluene. The atomic force microscopy (AFM) image of C_{60}@SWNT-ZnP spin-coated on mica from DMF dispersion (Fig. S3 in ESI) revealed fibrous structures with an average diameter of 4.5 ± 1 nm, implying efficient debundling of C_{60}@SWNT by the bulky ZnP units.



Scheme 1. Preparation of C_{60}@SWNT-ZnP. i) 4-Iodobenzenediazonium tetrafluoroborate, SDBS, H_2O, room temperature, 2 h, then *p*-iodoaniline, isopentyl nitrite, ODCB, 65 °C, 4 h; ii) 5-(pinacolboryl)-10,15,20-tris(3,5-di-*tert*-butylphenyl)porphyrinato zinc(II), $Pd(PPh_3)_4$, Cs_2CO_3, DMF, 105 °C, 24 h.

X-ray photoelectron spectroscopy (XPS) measurements corroborated the covalent functionalizations of C_{60}@SWNT (Fig. S4 in ESI). The functionalization ratio of C_{60}@SWNT-ZnP was estimated to be one ZnP unit per 300 carbons of nanotube sidewall (details of the estimation are in ESI). This corresponds to one ZnP unit at each nanotube length of 3 - 4 nm. Taking into account a size of the porphyrin (1.8 nm, Fig. S5 in ESI), the ZnP molecules would not interact directly with each other on the peapod. Moreover, the same two-step functionalization using p-SWNT yielded p-SWNT-ZnP with the functionalization ratio of one ZnP unit per 400 sidewall carbons (Fig. S4), which largely agrees with the ratio of C_{60}@SWNT-ZnP. The influence of the C_{60} encapsulation on the sidewall reactivity was not significant. Resonant Raman spectra of C_{60}@SWNT-ZnP, C_{60}@SWNT-PhI, and C_{60}@SWNT also support the surface modification on the C_{60}@SWNT (Fig. S6 in ESI).

Fig. 1a displays UV-vis absorption spectra of C_{60}@SWNT-ZnP, C_{60}@SWNT-PhI, and 5-phenyl-10,15,20-tris(3,5-di-*tert*-butylphenyl)porphyrinatozinc(II) (ZnP-ref) in DMF. C_{60}@SWNT-ZnP exhibits a moderate Soret band at around 428 nm and weak Q bands at around 560 and 599 nm, in addition to the broad structureless absorption of the C_{60}@SWNT extending into the NIR region. This provides unambiguous evidence for the presence of the ZnP on the C_{60}@SWNT. The Soret band of C_{60}@SWNT-ZnP was broadened and red-shifted by 425 nm compared with that of ZnP-ref, suggesting that there is weak electronic communication between the ZnP and C_{60}@SWNT in the ground state. Upon excitation of C_{60}@SWNT-ZnP and ZnP-ref at the Soret band, where the absorbance of the porphyrin was adjusted to be identical, the emission intensity from the ZnP unit on the C_{60}@SWNT decreased drastically relative to that of ZnP-ref (Fig. 1b). Such efficient quenching of the porphyrin excited singlet state (^{1}ZnP*) is indicative of a strong interaction between the ^{1}ZnP* and C_{60}@SWNT. Note here that analogous absorption broadening and fluorescence quenching were also observed in the spectra of p-SWNT-ZnP (Fig. S7 in ESI).[6]

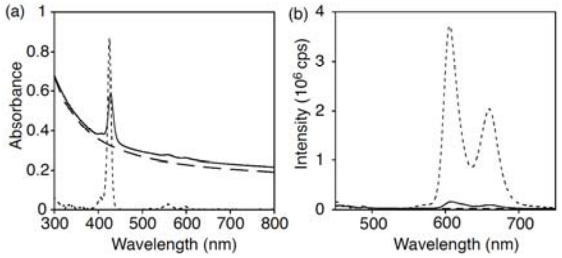


Fig. 1. (a) UV-vis absorption and (b) fluorescence spectra of C_{60}@SWNT-ZnP (solid line), C_{60}@SWNT-PhI (dashed line), and ZnP-ref (1.6 μM for (a) and 0.3 μM for (b), dotted line) in DMF. For the excitation, the absorbance of the porphyrin moiety was adjusted to be identical at the peak position of the Soret band.

To get insights into the interaction in the excited state, we monitored the porphyrin emission decays of C_{60}@SWNT-ZnP and ZnP-ref by time-correlated single-photon counting (TCSPC) technique (Table S1 in ESI). The fluorescence decay of ZnP-ref was analyzed by a single component with a lifetime (τ) of 2.0 ns, which is in good agreement with the literature value reported for analogous zinc tetraphenylporphyrins.[12] On the other hand, the fluorescence decay curve of C_{60}@SWNT-ZnP was fitted by a fast major component ($\tau <$ 70 ps) and a slow minor component (τ = 1.9 ns). These imply the occurrence of ultrafast quenching of ^{1}ZnP* by the C_{60}@SWNT, which is beyond the time resolution of the present TCSPC system (ca. 70 ps). The minor component may stem from the impurity or degradation of C_{60}@SWNT-ZnP during the measurement. Similar quenching of ^{1}ZnP* was also seen in the spectrum of p-SWNT-ZnP (Table S1).[6]

To shed light on the ultrafast process, the femtosecond pump-probe transient absorption measurements were performed for p-SWNT-ZnP, p-SWNT-PhI, C_{60}@SWNT-ZnP and C_{60}@SWNT-PhI with a laser excitation at 420 nm where both the ZnP and the nanotube moieties were excited. Transient absorption component spectra of p-SWNT-ZnP showed negative signal in the full range of the measurement (500 – 1100 nm) with a lifetime (τ) of 0.3 ps (Fig. S8 in ESI). This signal can be assigned to the ground state photobleaching due to the SWNT absorptions of M_{11} (the lowest transitions between van Hove singularities in the valence and conduction bands of metallic SWNT) and S_{22} (the second lowest transitions in semiconducting SWNT).[13,14] The spectrum of p-SWNT-PhI also exhibited similar negative signal (Fig. S8). Additionally, a broad and featureless positive absorption band in the visible region emerged in the spectra of p-SWNT-ZnP with τ of > 1 ns. We have already shown that the photoelectrochemical device based on similar porphyrin-SWNT composites linked by the same phenylene spacer revealed no photocurrent response by the porphyrin absorption, ruling out the possibilities of electron and energy transfer from the excited porphyrin to the SWNT.[6] Therefore, this broad and featureless absorption in the visible region can be assigned to the exciplex state comprised of the ZnP and SWNT.[15]

The absorption changes recorded upon the excitation of C_{60}@SWNT-ZnP at 420 nm (Fig. 2 and Fig. S9 in ESI) differ from those of p-SWNT-ZnP. In addition to the negative signal of the ground state photobleaching of the C_{60}@SWNT moiety (Fig. S10 in ESI), the exciplex absorption appeared, but the lifetime (τ = 24 ps) was much shorter than that of p-SWNT-ZnP (τ = 1073 ps). Furthermore, an additional long-lived component (τ > 2 ns) with two minima at 560 and 600 nm emerged (Fig. S11 in ESI). Importantly, the third component exhibited weak positive absorption in the 650 – 750 nm region. Considering the similarity between this band and that of one-electron oxidized ZnP,[12] we can assign it as the charge-separated state. In contrast with p-SWNT-ZnP, where the resultant exciplex decayed without forming the charge-separated state, C_{60}@SWNT-ZnP evolves to the porphyrin radical cation and the radical anion of the fullerene peapod after the exciplex formation. The energy level of the charge-separated state would become lower than that of the exciplex state by the inclusion of the fullerene molecules. It should be noted here that no clear signals for C_{60} radical anion at 1080 nm[16] are visible. This may be rationalized by no occurrence of the consecutive electron transfer from exterior frame of SWNT to the encapsulated C_{60} or low molar absorption coefficient of C_{60} radical anion at 1080 nm. The differences in the photodynamics of C_{60}@SWNT-ZnP and p-SWNT-ZnP highlight the effect of fullerene encapsulation on the electronic communications between the SWNT and ZnP in the excited state.

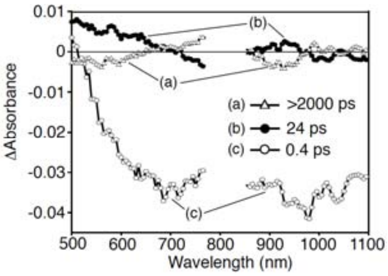


Fig. 2. Spectra of decay components obtained by three-exponential global fit of the transient absorption data of C_{60}@SWNT-ZnP in DMF. The sample was excited at 420 nm. The fitted time constants are displayed in the figure.

In summary, we have prepared a porphyrin-C_{60}@SWNT composite covalently fixed with a short rigid phenylene spacer for the first time. The porphyrin-C_{60}@SWNT ternary composite disclosed the initial formation of the exciplex state prior to the charge-separated state, whereas the porphyrin-SWNT binary composite with the same phenylene spacer revealed the formation of the exciplex state solely. Our results exemplify that the encapsulation of C_{60} into SWNT inner space have large impacts on the excited-state interactions between porphyrin and SWNT. These results obtained here demonstrate that the inner space doping of SWNT will have considerable merit for tuning the electronic properties of SWNT in the hybrid materials with photoactive molecules for the applications in artificial photosynthesis and solar energy conversion.

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