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Communication

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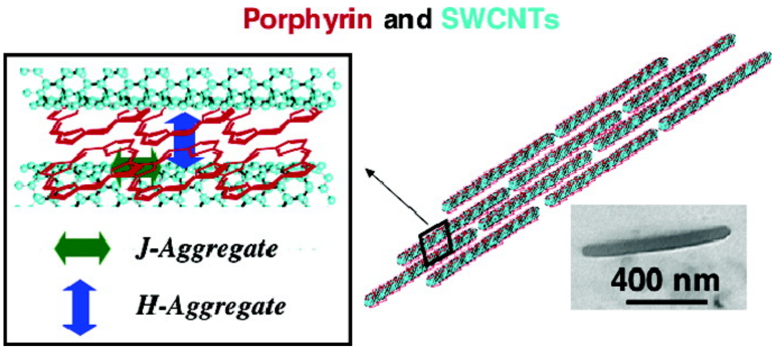

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Ordered Assembly of Protonated Porphyrin Driven by Single-Wall Carbon Nanotubes. J- and H-Aggregates to Nanorods

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Designing supramolecular assemblies based on single-wall carbon nanotubes (SWCNTs) has remained a challenge because of the problems associated with the dispersion in neat solvents and inability to control the molecular orientation in a desired fashion. Surface modification or covalent linkage of molecules often facilitates solubilization of SWCNTs but seldom favors the formation of an ordered assembly. Only under the influence of a dc electric field surfactant (tetraoctylammonium bromide or Nafion) capped SWCNTs can be assembled as linear bundles.[1] Fullerenes on the other hand undergo charge-transfer interactions with porphyrins and form supramolecular structures. The close contact between one of the electron-rich 6:6 bonds of the guest fullerene and the geometric center of the host porphyrin facilitates formation of ordered assemblies.[2,3]

SWCNTs have a characteristic curve-shaped surface that facilitates binding of larger organic molecules via noncovalent or hydrophobic interactions. Recent studies have shown that molecules such as porphyrin have an affinity to bind noncovalently with SWCNTs.[4] In fact, such interactions have facilitated separation of semiconductor and metallic type of SWCNTs.[4b] The obvious question is whether the interaction between porphyrin and SWCNTs can be modulated to achieve a supramolecular assembly. Of particular interest is the design of such composite assemblies for light energy harvesting applications. The SWCNTs can provide an ideal network to promote charge transfer in porphyrin-based systems and transport electrons to the collecting surface (e.g., photoelectrochemical cells).

Protonated porphyrins provide a convenient way to construct ordered molecular assemblies.[5] We report herein SWCNTs-driven aggregation of protonated porphyrin to produce supramolecular assemblies in the form of macroscopic bundles with specific spectroscopic fingerprints. The $\pi-\pi$ interaction between porphyrins and SWCNTs plays an important role to influence the orientation of protonated porphyrins, inducing J- and H-type aggregation effects on the SWCNTs surface.

The synthesis of 5,15-bis(3,5-di-*tert*-butylphenyl) porphyrin (H_2P) has been reported previously.[6] The purification procedure of SWCNTs (Nanocs Inc.) was adopted from the reported procedure.[7] The general strategy of constructing supramolecular assembly between H_2P and SWCNTs is shown in Figure 1. The first step involves binding of H_2P on the surface of SWCNTs. This is followed by van der Waals interaction to form aligned macroscopic rods. To facilitate $\pi-\pi$ interaction of protonated porphyrin and SWCNTs, we conducted these experiments in acidified THF. The binding of SWCNTs with the protonated form (H_4P^{2+}) in acidified THF solution is quite strong as it yields better solubility and stability of the suspension than one obtained with the unprotonated form (H_2P). Since the addition of a second proton is energetically favored, the observed protonated species are likely to be in the diacid form (H_4P^{2+}).

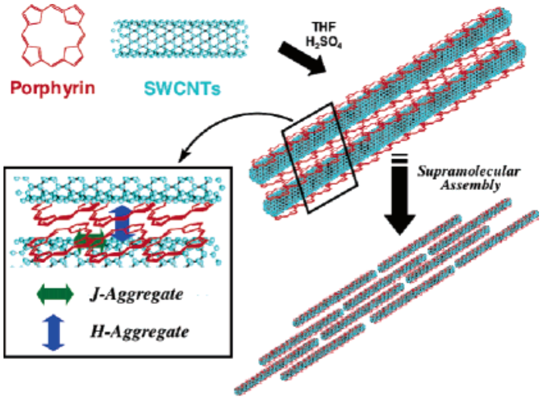

Figure 1. Illustration of supramolecular assembly between porphyrins and single-wall carbon nanotubes in this study.

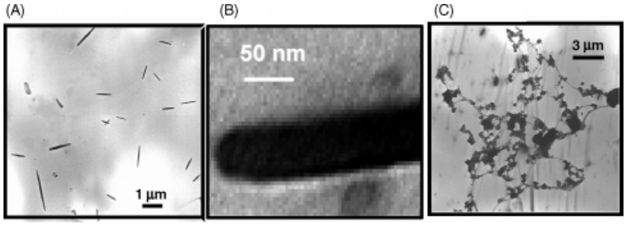

Figure 2. (A) and (B) Transmission electron microscope (TEM) images of the $H_4P^{2+}-$SWCNTs composite prepared in acidified THF. (C) TEM image of the H_2P-SWCNTs composite prepared in THF without acidification.

The ordered assembly of SWCNTs$-H_4P^{2+}$ was obtained by the following procedure. A quantity of 1 mg of purified SWCNTs was added to 0.2 mM solution of porphyrin in THF containing 1.0% H_2SO_4 (v/v). The suspension was sonicated for 1 h at room temperature, followed by centrifugation of the suspension for 30 min at 10 000 rpm to separate the SWCNTs$-H_4P^{2+}$ composite. The solid was resuspended in acidified THF with sonication (1 h) and centrifuged again to wash out any unbound porphyrin. The solid was resuspended in acidified THF. The suspension of SWCNTs$-H_4P^{2+}$ was stable for carrying out spectroscopic and microscopic measurements.

TEM images of SWCNTs and porphyrin composites prepared in THF with and without acidification are shown in Figure 2. The two representative images of the H_4P^{2+} and SWCNTs composite (A and B in Figure 2) show that these fully grown rod structures are 40−60 nm in diameter and 0.5−3.0 μm in length. Judging from the molecular size of porphyrins and SWCNTs, it is evident that H_4P^{2+}-bound SWCNTs undergo linear assembly to yield large rod-like structures. The reproducibility of obtaining rods of similar shape

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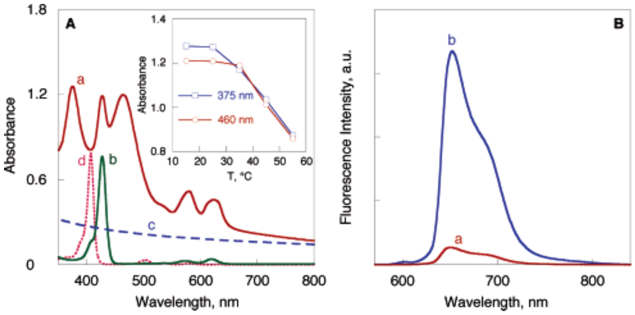

Figure 3. (A) Absorption spectra in THF of (a) 0.17 mM H_4P^{2+} and SWCNTs after a centrifugation, (b) 0.017 mM H_4P^{2+}, (c) SWCNTs, and (d) 0.017 mM H_2P. The inset shows the temperature dependence of absorbance at 375 and 460 nm corresponding to the aggregation peaks. (B) Fluorescence spectra in THF of (a) SWCNTs$-H_4P^{2+}$ composite after centrifugation and redispersion and (b) 0.17 mM H_4P^{2+}. Excitation wavelength is 425 nm.

shows the importance of SWCNTs in driving the supramolecular assembly into well-defined cylindrical structures. In the absence of acid, the interaction between H_2P and SWCNTs is rather weak, and we fail to see an ordered assembly structure in the TEM (C in Figure 2). As a result of this weak interaction, we observe isolated clusters of H_2P clusters.[8a] In addtion, the TEM image of the SWCNTs$-H_4P^{2+}$ composite is totally different from that of the H_4P^{2+} cluster (S1) of spherical shape. This drastic difference in forming ordered structure of H_4P^{2+} and SWCNTs versus random clustering of H_2P and SWCNTs is attributed to the strong intermolecular interaction between porphyrin moieties or ordered aggregation effects in the protonated form. Closely packed H_4P^{2+} molecules on SWCNTs not only induce aggregation on the surface of SWCNTs, but also induce aggregation of porphyrin-bound carbon nanotubes to form macroscopic rods. Controlled aggregation of oppositely charged porphyrins has been shown to yield tubular structures.[8b]

If indeed the SWCNTs surface is responsible for assembling H_4P^{2+} in an orderly fashion, we should be able to monitor the intermolecular interactions between the porphyrin moieties with absorption changes. Figure 3A shows the absorption spectra in acidified THF solution of H_4P^{2+} in the presence (spectrum a)[9] and absence (spectrum b) of SWCNTs solution. The SWCNTs suspension in acidified THF solution (spectrum c) and the unprotonated H_2P in THF (spectrum d) are also shown. The Soret band of H_2P with absorption maximum at 407 nm shifts to 427 nm upon protonation. At relatively low concentrations ($<$0.02 mM), the protonated porphyrin exists in the monomeric form.[10] Upon binding to the SWCNTs surface, we observe splitting of the Soret bands and Q-bands. Such a band splitting phenomenon is commonly associated with the J- and H-type aggregation effects.[5] Comparison of spectrum a with that of spectrum b in Figure 3A shows the appearance of two new bands with maximum peaks at 375 and 460 nm, corresponding to the H- and J-type aggregations, respectively.[5,11] In addition, a small fraction of H_4P^{2+} that escapes intermolecular interaction contributes to the monomer peak. The appearance of the low energy Soret band at 460 nm (J-type) is diagnostic of exciton coupling of the Soret band.[12]

We checked the stability of the aggregate by recording the absorption spectrum of the SWCNTs$-H_4P^{2+}$ composite at different temperatures. The aggregates bound to the SWCNTs surface are stable up to 308 K.[13] At higher temperatures, the aggregation bands disappear (inset, Figure 3A) with the emergence of the monomer band. Upon decreasing the temperature, we can reestablish the aggregation bands. The disappearance of aggregation bands at higher temperature is an indication of weakened intramolecular interactions and/or dissociation of H_4P^{2+} from the SWCNTs surface.

We measured the fluorescence spectrum of the SWCNTs$-H_4P^{2+}$ composite in comparison with that of H_4P^{2+} alone (Figure 3B). The fluorescence intensity of the SWCNTs$-H_4P^{2+}$ composite is much smaller than that of H_4P^{2+} (92% of the emission is quenched). This shows additional deactivation pathways for the porphyrin excited state arising from the interaction between H_4P^{2+} and SWCNTs in the supramolecular composite and/or aggregated state. It is important to note that both protonation of the porphyrin and the substituents group on the porphyrin ring play an important role in attaining the ordered assemblies.[14]

In conclusion, we have succeeded in achieving ordered assembly of protonated porphyrin in the form of J- and H-type aggregates on the SWCNTs surface. This unusual molecular aggregation phenomenon driven by SWCNTs further assembles in the form of linear bundles. This simple method of designing supramolecular assembly could pave the way for developing light harvesting assemblies and optoelectronic devices.

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Supporting Information Available: TEM image of H_4P^{2+} clusters (S1) and absorption spectra of H_2P in the protonated and unprotonated forms (S2 and S3), absorption spectra of SWCNTs$-H_4P^{2+}$ composite (S4). This material is available free of charge via the Internet at http://pubs.acs.org.

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(9) After centrifugation, 85% porphyrin was found to remain in the supramolecular composite by way of neutralizing the solution and the recording absorption spectrum. The absorption features of spectrum a in Figure 3A were retained even after three cycles of suspension and centrifugation. The H_4P^{2+} did not leach out into the solution in subsequent centrifugation.

(10) Because of aggregation effects the absorption spectrum of a high concentration of H_4P^{2+} (0.17 mM) in THF is different from that of a low concentration of H_4P^{2+} (0.017 mM) in THF. At a low concentration, the counterion for H_4P^{2+} is HSO_4^-. See: Supporting Information Figures S2 and S3.

(11) Upon increasing the concentration of H_4P^{2+}, the absorbance due to the aggregation bands at 375 and 460 nm increases as more H_4P^{2+} molecules are accommodated on the SWCNT surface (see Supporting Information Figure S4).

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(13) At low temperature (~5 °C) the suspension is stable for a week or more.

(14) When a porphyrin with additional substitution (viz., protonated 5,10,15,-20-bis(3,5-di-*tert*-butylphenyl)porphyrin) was employed with SWCNTs, no aggregation effects or ordered assembly structures were observed.

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