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Supramolecular Peapods Composed of a Metalloporphyrin Nanotube and Fullerenes

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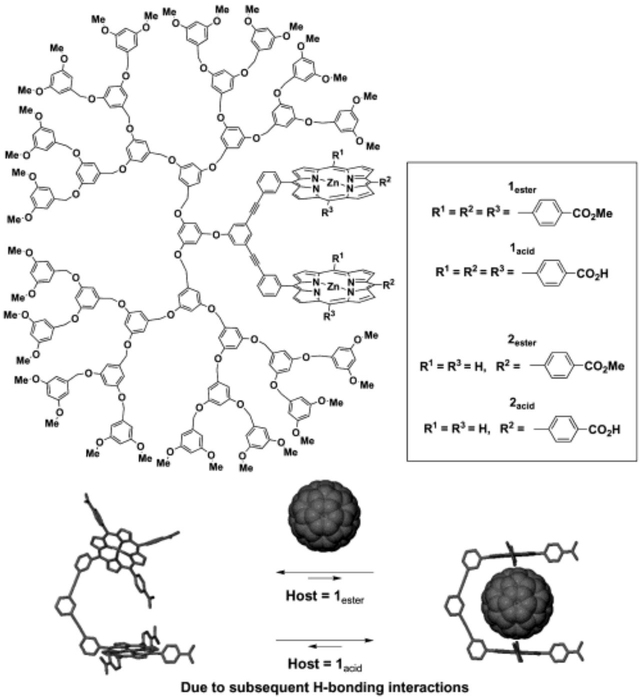
Recently, carbon nanomaterials such as fullerenes and carbon nanotubes have attracted considerable attention as potential components for the next-generation electronic nanodevices. From this point of view, an important challenge is to fabricate one-dimensional clusters of fullerenes. The first success was demonstrated in 1998 by the inclusion of C_{60} into a single-walled carbon nanotube.[1] Such "peapod"-like carbon nanocomposites[2] have also become of great interest, since electronic interactions between guest fullerenes and nanotube pods may generate unique physical properties.

Here we report the first example of "supramolecular peapods" composed of a linear zinc porphyrin nanotube and fullerenes such as C_{60} and C_{70} (Scheme 1). This achievement was demonstrated by the fullerene-triggered unidirectional supramolecular polymerization of an acyclic zinc porphyrin dimer having six carboxylic acid (CO_2H) functionalities (**1**$_{\mathbf{acid}}$).[3] **1**$_{\mathbf{acid}}$ also bears large [G4]-poly(benzyl ether) dendritic wedges, which are intended to overcome the solubility problem of carboxylic acid-appended metalloporphyrins and allow easier visualization by transmission electron microscopy (TEM).



We recently found that cyclic dimers of metalloporphyrins display very high affinities toward fullerenes and form stable inclusion complexes (e.g., $K_{\mathrm{assoc}} = 10^7-10^8$ M^{-1} with Rh^{III}; 10^5-10^7 M^{-1} with Zn) in solution.[4,5] On the other hand, the corresponding monomers do not interact with fullerenes under identical conditions. We also found that an acyclic zinc porphyrin dimer with methyl ester functionalities (**1**$_{\mathbf{ester}}$) hardly shows spectral changes associated with the metalloporphyrin−fullerene interaction. In sharp contrast, the corresponding carboxylic acid version (**1**$_{\mathbf{acid}}$),

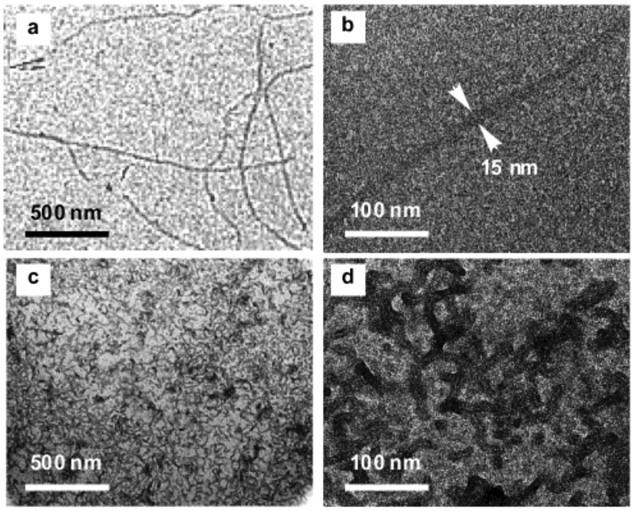
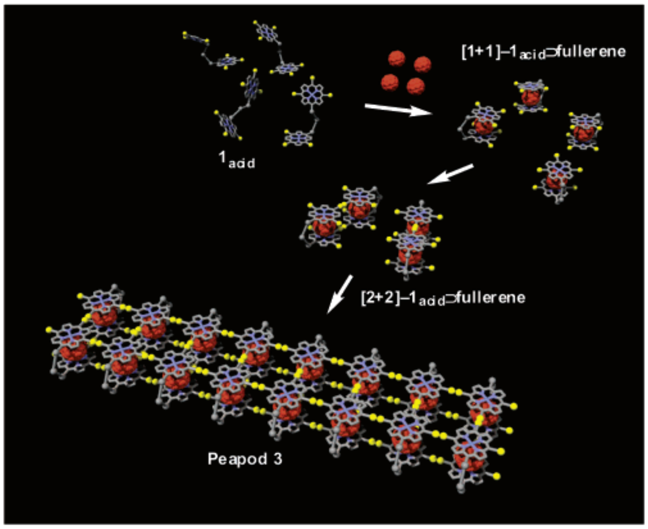


Figure 1. TEM micrographs of (a,b) **1**$_{\mathbf{acid}}$ with C_{60} and (c,d) **1**$_{\mathbf{acid}}$ alone. Samples were cast from TCE after being heated once at 120 °C, followed by incubation at 40 °C for 4 days, and stained with RuO_4.

Scheme 1. One-Dimensional Supramolecular Polymerization of Acyclic Zinc Porphyrin Dimer **1**$_{\mathbf{acid}}$ Directed by a π-Electronic Interaction with Fullerenes



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though acyclic, exhibited notable spectral changes, similar to those observed for the inclusion complexation. Typically, a 1,1,2,2-tetrachloroethane (TCE) solution of a mixture of $\mathbf{1_{acid}}$ (1.2×10^{-5} M) and C_{60} (2.4×10^{-5} M) was heated once at 120 °C and then allowed to stand at 40 °C for 4 days. TEM observation of the resulting mixture showed the presence of very long (>1 μm) fibers with a uniform diameter of 15 nm (Figure 1a,b). A virtually identical TEM micrograph was observed when C_{70} was used in place of C_{60}.[3] On the other hand, $\mathbf{1_{acid}}$ alone (1.2×10^{-5} M) without C_{60}, under conditions otherwise identical to those described above, gave a heavily entangled, irregular assembly (Figure 1c,d).

A TCE solution of $\mathbf{1_{acid}}$ (1.2×10^{-6} M) showed exciton-coupled split Soret absorption bands at 427.8 and 435.6 nm,[3] indicating a twisted or tilted geometry of the two zinc porphyrin chromophores.[6] On the other hand, upon titration with C_{70}, the exciton coupling gradually disappeared to give a less intensified Soret absorption band at 428.2 nm.[3] This spectral change, together with the TEM micrographs (Figure 1), suggests that zinc porphyrin dimer $\mathbf{1_{acid}}$, upon interaction with fullerenes, adopts a parallel and eclipsed conformation, to form hydrogen-bonded [2 + 2] inclusion complexes having four CO_2H functionalities on each side ($[2+2]-\mathbf{1_{acid}}\supset$fullerene) (Scheme 1). The inclusion complexes can then be polymerized unidirectionally via the dimerization of the CO_2H side groups, to afford fullerene-included "peapods" **3** with a zinc porphyrin nanotube. The diameter of **3**, as estimated from a molecular model with the dendritic envelope, is 12 nm, which agrees well with that observed by TEM (Figure 1b).

Infrared spectroscopy of a mixture of $\mathbf{1_{acid}}$ and C_{60}, cast from a TCE solution on a CaF_2 plate, showed a C=O stretching vibration at 1688 cm^{-1} assignable to a dimeric form of CO_2H, without any shoulder at 1725 cm^{-1} due to monomeric CO_2H.[3] Although ^1H NMR spectroscopy of the mixtures of $\mathbf{1_{acid}}$ and fullerenes was less informative due to significant spectral broadening, an acyclic dimer with two CO_2H groups ($\mathbf{2_{acid}}$), in combination with C_{70},[3] gave reasonable support for the fullerene-directed conformational change of $\mathbf{1_{acid}}$. A TCE-d_2 solution of $\mathbf{2_{acid}}$ (1.5×10^{-3} M) at 20 °C showed zinc porphyrin meso-H and bridging aromatic *o*-H/*p*-H (Ar-*o*-H/Ar-*p*-H) at δ 10.16 and 7.14/7.23 ppm. Upon mixing 5 equiv of C_{70} with $\mathbf{2_{acid}}$, the meso-H and Ar-*p*-H signals shifted upfield to δ 9.99 and 7.09 ppm, respectively, whereas the Ar-*o*-H signal showed a downfield shift (δ 7.33 ppm). By reference to the ^1H NMR spectral feature of a covalent cyclic dimer with phenylene-ethynylene spacers, this spectral change can be attributed to a relative rotation of the two zinc porphyrin moieties of $\mathbf{2_{acid}}$ upon interaction with C_{70}.[7] Thus, $\mathbf{2_{acid}}$, upon interaction with C_{70}, kinetically forms a U-shaped pseudoinclusion complex ($[1+1]-\mathbf{2_{acid}}\supset C_{70}$) as a temporary product, which is then trapped by dimerization to give thermodynamically favored $[2+2]-\mathbf{2_{acid}}\supset C_{70}$ (Scheme 1). Inclusion complex $[2+2]-\mathbf{2_{acid}}\supset C_{70}$, thus formed, is unable to be polymerized because of the absence of free CO_2H side groups, thereby affording the well-resolved ^1H NMR spectrum. As expected, such a fullerene-induced spectral change was only very small for the methyl ester version of $\mathbf{2_{acid}}$ ($\mathbf{2_{ester}}$),[3] due to the absence of any subsequent events to stabilize temporarily formed $[1+1]-\mathbf{2_{ester}}\supset C_{70}$.

The inclusion of fullerenes within the supramolecular zinc porphyrin nanotube was also supported by ^{13}C NMR spectroscopy using ^{13}C-enriched C_{60}.[3] At −40 °C, a TCE-d_2 solution of a 1:2 mixture of $\mathbf{1_{acid}}$ and C_{60} showed a broad signal at δ 139.6 ppm, assignable to included C_{60} (Figure 2), in addition to a sharp signal due to free C_{60} (δ 143.0 ppm).[4a] As estimated from the half-width values of the signals, relaxation time T_2 of the signal due to included C_{60} (0.018 s) was only 18% of that of free C_{60} (0.097 s), indicating a highly constrained motion of C_{60} in the tubular space. Upon heating, the signal due to included C_{60} gradually shifted to a lower magnetic field and appeared to coalesce at 60 °C with the signal due to free C_{60}.[3] Such a high coalescence temperature has never been observed for C_{60} complexed with nonpolymerizable, linear cyclic dimers of porphyrins.[4b,7] Therefore, the peapod architecture, once formed, considerably lowers the complexation/decomplexation dynamics of guest fullerenes.

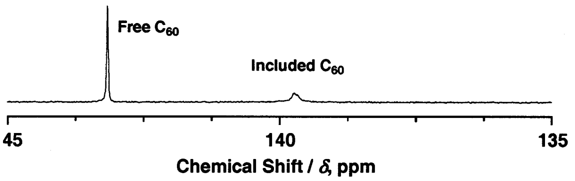

Figure 2. ^{13}C NMR spectrum of a 1:2 mixture of $\mathbf{1_{acid}}$ and ^{13}C-enriched C_{60} in TCE-d_2 at −40 °C.

In conclusion, we have demonstrated the first example of "supramolecular peapods" consisting of a hydrogen-bonded zinc porphyrin nanotube and fullerenes, by the fullerene-directed one-dimensional supramolecular polymerization of an acyclic zinc porphyrin dimer bearing six carboxylic acid functionalities ($\mathbf{1_{acid}}$). The peapods are thermally stable and characterized by their untangled, discrete architectures with very high aspect ratios. These new π-electronic nanocomposite materials may serve as potential components for photoelectronic devices.

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Supporting Information Available: Synthetic procedures and spectral data of **1** and **2**; TEM of $\mathbf{1_{acid}}/C_{60}$ and $\mathbf{1_{acid}}/C_{70}$; selected UV−vis, IR, ^1H NMR spectra, and DLS profiles of **1** and **2** with fullerenes (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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