

## Selective Interactions of Porphyrins with Semiconducting Single-Walled Carbon Nanotubes

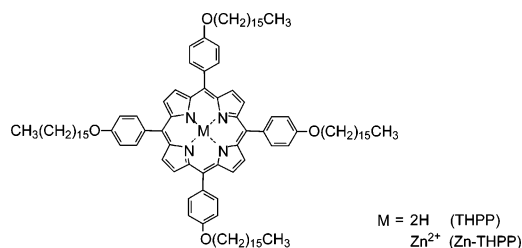
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Single-walled carbon nanotube (SWNT) samples produced via various techniques are generally mixtures of metallic and semiconducting SWNTs,<sup>1</sup> which correspond to different electrical conductivities and other related properties. These properties are important to a variety of technological applications of SWNTs including, for example, the electrical conductivity and charge dissipation in polymeric/carbon nanocomposites and thin films.<sup>2,3</sup> The enrichment of metallic over semiconducting SWNTs or vice versa in a nanotube sample, toward a complete separation of the two different kinds of SWNTs, has attracted much recent attention.<sup>4,5</sup> In this communication, we report on the selectivity of a derivatized porphyrin toward semiconducting SWNTs in presumably noncovalent interactions,<sup>6</sup> resulting in significantly enriched semiconducting SWNTs in the solubilized sample and predominantly metallic SWNTs in the residual solid sample according to Raman, near-IR absorption, and bulk conductivity characterizations.

The SWNT sample was produced in Professor A. M. Rao's laboratory (Physics Department, Clemson University) by using the arc-discharge method. It was purified via oxidative acid treatment according to an established procedure.<sup>7,8</sup> 5,10,15,20-tetrakis(hexadecyloxyphenyl)-21*H*,23*H*-porphyrin (THPP) was synthesized by coupling *p*-hexadecyloxybenzaldehyde with pyrrole in glacial acetic acid, followed by column chromatography separation and structural characterizations.



In a typical noncovalent solubilization experiment, a purified SWNT sample (100 mg) was added to a solution of THPP in chloroform (10 mg/mL, 20 mL), and the mixture was sonicated (Fisher Scientific FS20, 70 W, 42 kHz) for 48 h. After the removal of chloroform on a rotary evaporator, the solid mixture was extracted repeatedly with hexanes, coupled with vigorous centrifuging (~3100g) for 20 min, to remove free THPP. Then, THF (10 mL) was added to the solid sample to dissolve the THPP-attached SWNTs. Upon vigorous centrifuging for 10 min, the solid residue was collected and then used to go through the same noncovalent solubilization procedure again (note: the third repeat was tried, but no further solubilization was observed). The unfunctionalized SWNT sample largely free from the porphyrin was obtained as the

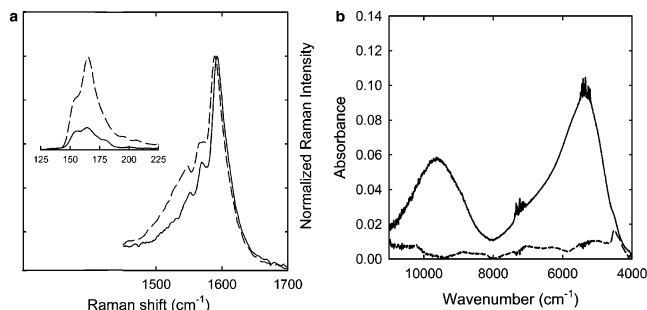
final solid residue (39 mg, denoted as "free-SWNT" sample). The soluble THPP-SWNT samples from the two repeated experiments were combined, followed by a complete evaporation of the solvent THF. The removal of THPP from the combined soluble sample was accomplished via washing the sample with acetic acid, coupled with vigorous centrifuging, resulting in the recovery of insoluble SWNTs (denoted as "recovered-SWNT" sample). The results from scanning electron microscopy analyses show that the two samples are largely similar. To ensure a rigorous comparison between the free-SWNT and recovered-SWNT samples in subsequent spectroscopy and conductivity characterizations, both solid-state samples were thermally treated under the same experimental condition of 800 °C for 14 h in a nitrogen atmosphere.

The recovered-SWNT sample is enriched in semiconducting SWNTs, while the free-SWNT sample contains predominantly metallic SWNTs. Their Raman spectra obtained with 785 nm (1.58 eV) excitation exhibit different features (Figure 1a).<sup>9–11</sup> According to the widely cited work of Dresselhaus and co-workers,<sup>9</sup> while semiconducting and metallic SWNTs may have different tangential mode G-bands, the difference is not expected to be obvious for the arc-produced SWNTs used in this work with the 785 nm excitation. The recent results and analyses by Papadimitrakopoulos and co-workers on laser ablation-produced SWNTs reaffirmed such a conclusion (Figure 4 in ref 5). As shown in Figure 1a, however, the G-band of the free-SWNT sample is broader and more unsymmetric than that of the recovered-SWNT sample, indicative of substantial enrichment in metallic SWNTs (Breit-Wigner-Fano line shape).<sup>9–11</sup> The Raman features in the radial breathing mode region are also consistent with an enrichment of metallic SWNTs in the free-SWNT sample.<sup>5</sup>

The significant separation of semiconducting nanotubes (in recovered-SWNT sample) from metallic nanotubes (in free-SWNT sample) is made more evident by a quantitative comparison of the near-IR absorption spectra. The spectra shown in Figure 1b were obtained by measuring (Thermo-Nicolet Nexus 670) the thermally treated solid-state samples of the same quantity under the same experimental conditions. No surfactant or other dispersion agents were used in the preparation of the specimens for measurements to avoid even the remote possibility of any doping effects. For the semiconducting recovered-SWNT sample, the near-IR absorption spectrum contains significant bands at ~5390 cm<sup>-1</sup> (1855 nm, 0.67 eV) and ~9710 cm<sup>-1</sup> (1030 nm, 1.19 eV), corresponding to transitions associated with the first (S<sub>11</sub>) and second (S<sub>22</sub>) pairs, respectively, of van Hove singularities in the electronic density of states for semiconducting SWNTs.<sup>12</sup> On the other hand, the absorption of the metallic free-SWNT sample is negligible over the near-IR region.<sup>13</sup> The results suggest that most of the semiconducting SWNTs in the starting sample ended up in the

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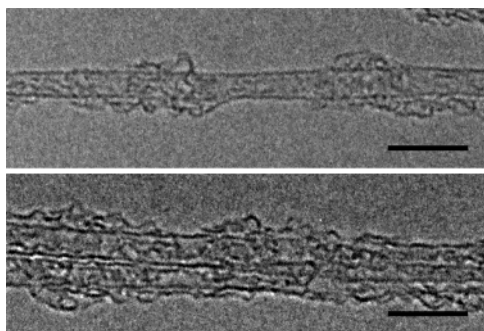


**Figure 1.** (a) Raman spectral features (785 nm excitation) and (b) near-IR absorption spectra of the semiconducting recovered-SWNT (—) and metallic free-SWNT (---) samples after the same thermal treatment.

recovered-SWNT sample, namely that the porphyrin interactions were selective toward semiconducting SWNTs.

The bulk electrical conductivities of the free-SWNT and recovered-SWNT samples (thermally treated under the same conditions, as described above) are very different. In a comparative conductivity evaluation, the two samples were pressed separately into pellets of approximately 9 mm × 3 mm × 1 mm in dimension. Results from the classical four-probe conductivity measurements under ambient conditions show that the bulk conductivities of the two samples differ by more than two-orders of magnitude, 1.1 S/cm for the metallic free-SWNT vs 0.007 S/cm for the semiconducting recovered-SWNT.

To examine the effects of the nanotube on the THPP species on the surface, the soluble THPP-SWNT sample in solution was characterized by <sup>1</sup>H NMR (data not shown). The NMR signals of THPP are significantly broadened upon the attachment to SWNTs, which is likely due largely to the significantly reduced mobility of the THPP species.<sup>14</sup> Consistent with the NMR results it seems that the porphyrin ring is probably bound to the SWNT surface, leaving long alkyl chains to wiggle around in solution. Such a picture is supported by the high-resolution TEM results, which show soft materials on the surfaces of individual nanotubes (Figure 2).<sup>15</sup>



**Figure 2.** High-resolution TEM images (scale bars = 5 nm) of the soluble THPP-SWNT sample.

The interactions of THPP with SWNT are apparently specific to the porphyrin free base, hindered upon the chelation of a metal cation. For example, the Zn-THPP was used in the place of THPP under the same experimental conditions, but no interaction leading to the solubilization of SWNTs was observed. The negative results with the use of metalloporphyrins also suggest that the selectivity toward semiconducting SWNTs reported above is associated with THPP, not fragments of decomposed THPP, because porphyrins with and without the center-chelated metal share similar decomposition patterns.<sup>16</sup>

In summary, the derivatized porphyrin THPP selectively interacts with and solubilizes semiconducting SWNTs, resulting in the “extraction” of most of the semiconducting SWNTs from the

starting purified nanotube sample. Mechanistically, we suspect that the semiconducting and metallic SWNTs have significantly different surface properties. A speculation is that a semiconducting SWNT is more like a conjugated macromolecule with the nanotube surface properties conceptually similar to those found in radical ion pairs, thus amenable to interactions with the free-base porphyrin molecules.<sup>17</sup> Since the porphyrin is readily prepared and largely recoverable from the extraction experiment, the reported procedure may become an effective and convenient method for the separation of semiconducting SWNTs from metallic SWNTs.

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**Supporting Information Available:** Additional figures (PDF). This material is available free of charge via Internet at <http://pubs.acs.org>.

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