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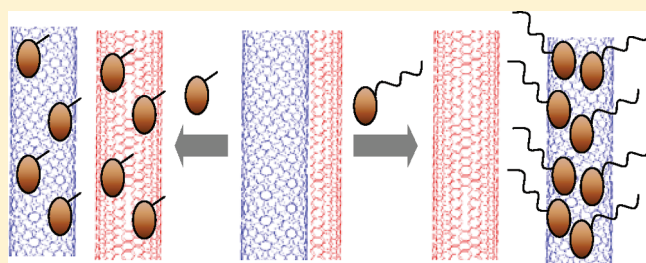
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Noncovalent Interactions of Derivatized Pyrenes with Metallic and Semiconducting Single-Walled Carbon Nanotubes

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ABSTRACT: Pyrene has been a popular molecular structure in the noncovalent functionalization of single-walled carbon nanotubes (SWNTs), and the selectivity between metallic and semiconducting SWNTs for the underlying interactions has been exploited for the postproduction metallic–semiconducting nanotube separation. Two pyrene derivatives, 1-pyreneacetic acid (PyAA) and 1-docosyloxymethylpyrene (DomP), which are hydrophilic and hydrophobic, respectively, were evaluated on their noncovalent interactions with SWNTs, as relevant to their selectivity and applicability to the postproduction separation. The results suggested that the interactions were not only dependent on molecular structures but also sensitive to solvent conditions and that a relatively lower solvent strength environment (solutions of less polar solvents) might be more favorable to the realization of the selectivity between interactions with metallic and semiconducting SWNTs. The surprising differences for the two pyrene derivatives in terms of their doping effects on the band gap transitions in semiconducting SWNTs are also reported and discussed.



INTRODUCTION

Single-walled carbon nanotubes (SWNTs), while grown mostly spontaneously in various productions, may be considered conceptually as being rolled from a graphene sheet into cylindrical structures.^{1,2} Depending on the chiral vector on which the rolling is based, an SWNT is either metallic or semiconducting.^{2,3} Statistically there are twice as many ways for rolling graphene sheet into a semiconducting SWNT as those for rolling the same sheet into its metallic counterpart, and therefore a metallic-to-semiconducting nanotube ratio of 1:2 should generally be expected in an as-grown mixture of SWNTs.

Metallic and semiconducting SWNTs differ not only in electrical conductivity but also in many other physical and chemical properties, including especially optical absorption and Raman spectroscopic characteristics, static polarizability, doping effects, and chemical reactivities. For example, semiconducting SWNTs are known to be extremely sensitive to electrical gating and capable of conductance changes by orders of magnitude under various electrostatic gate voltages.^{4,5} Conversely, metallic SWNTs are less sensitive to molecular adsorption and chemical gating, since charge transfer does not significantly affect the charge density at the Fermi level.⁴ In the widely pursued use of SWNTs in transparent conductive coatings to compete with the currently predominant indium tin oxide (ITO) technology,⁶ as a technologically important example, metallic SWNTs are required, as semiconducting SWNTs are more absorptive in visible/near-IR spectral regions, and thus their presence in the coatings is negative to the performance requirements for low electrical

resistivity and high optical transparency. Obviously, the availability of SWNTs that are either metallic or semiconducting is much desired by the research community, with significant effort and progress already made in the development of methodologies for harvesting metallic and semiconducting SWNTs postproduction.^{3,7–14}

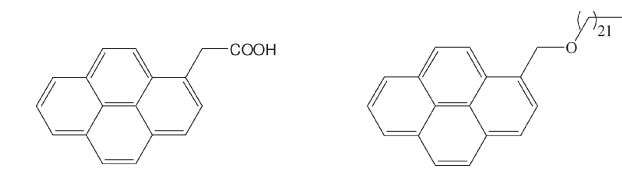
The noncovalent functionalization of SWNTs with planar aromatic molecules has been popular in the effort on introducing the nanotubes into solution. The selectivity in various degrees between metallic and semiconducting SWNTs in the noncovalent functionalization has been exploited for the postproduction separation.^{8,14–17} The interactions of aromatic molecules with nanotubes, on which the noncovalent functionalization and solubilization are based, are apparently dependent sensitively on the molecular structures as well as experimental conditions.³ In the work reported here we examined the structurally analogous pyrene derivatives, 1-pyreneacetic acid (PyAA) and 1-docosyloxymethylpyrene (DomP) illustrated in Scheme 1, on their significant differences in the noncovalent functionalization and solubilization of SWNTs, especially for what was manifested in the selectivity between metallic and semiconducting nanotubes in different solvent environments. The sharp contrast between the two pyrene derivatives in terms of doping effects on the electronic transitions associated with the van Hove

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Scheme 1. PyAA (left) and DomP (right)



singularity pairs in semiconducting SWNTs, reflecting significant differences in the underlying noncovalent interactions, is also highlighted and discussed.

RESULTS AND DISCUSSION

The pyrene derivative PyAA is hydrophilic, capable of noncovalently attaching to SWNTs in an aqueous solution. At a more basic pH (~ 12), the noncovalent functionalization was found to be nonselective between metallic and semiconducting SWNTs, so that the aqueous solubilization of the nanotubes as result of the functionalization was exploited for the removal of impurities from the nanotube sample to result in highly pure SWNTs.¹⁸ In this work, PyAA was used in aqueous solutions of lower pH values to functionalize SWNTs in the sample purified by the widely used nitric acid treatment,¹⁹ with the purpose of evaluating the selectivity for potentially metallic–semiconducting nanotube separation. At pH ~ 9 , for example, PyAA could similarly solubilize SWNTs, leaving behind residues containing few nanotubes (according to resonance Raman spectroscopy characterization) and mostly impurities, largely the same as the results obtained at pH ~ 12 .¹⁸ The aqueous supernatant (still pH ~ 9) was fractionated in various centrifugation fields, and the resulting sediments were characterized spectroscopically. The Raman G-band and RBM (radial breathing mode) band for the precipitates remained little changed from those of the prefunctionalization mixture (Figure 1), suggesting no significant enrichment of metallic SWNTs.

In aqueous solutions of even lower pH values, PyAA became much less soluble, making the functionalization and solubilization of SWNTs practically impossible. Thus, polar organic solvents were used for further evaluation on the selectivity of PyAA toward metallic or semiconducting SWNTs. In DMF, PyAA was still capable of noncovalently functionalizing and dispersing SWNTs, with the subsequent centrifugation to result in a more soluble fraction in the supernatant and the rest in the residue. As also shown in Figure 1 on a comparison of Raman spectra, the Raman G-band for the fraction in the residue from centrifugation exhibited some contribution of the Breit–Wigner–Fano (BWF) profile, which is known as characteristic of a sample enriched with metallic SWNTs,²⁰ and the corresponding G-band for the fraction in the supernatant was more symmetric, with the bandwidth narrower than that of the prepreparation mixture. These results suggested that the noncovalent functionalization by PyAA in DMF was somewhat selective toward semiconducting SWNTs, resulting in fractions enriched with either metallic or semiconducting SWNTs. While the selectivity was not high and the separation not effective, the significant difference between the results in aqueous and organic solutions pointed to a major role played by the solvent in the targeted separation of metallic and semiconducting SWNTs via

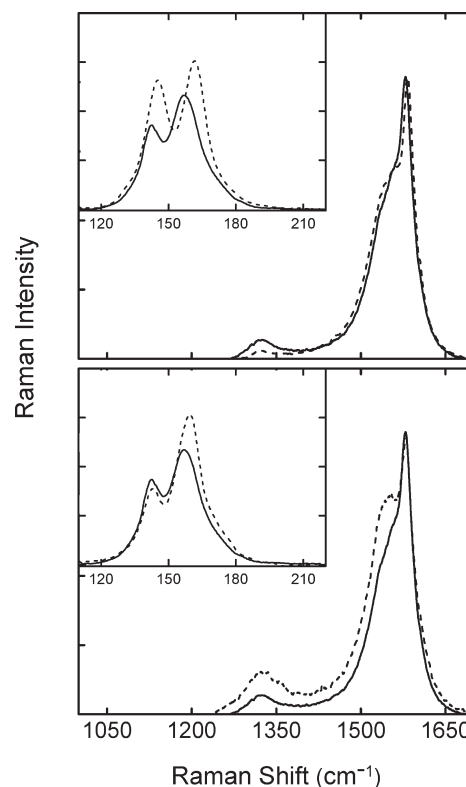


Figure 1. Raman spectra (G-band and RBM-band in the inset) of the purified SWNTs (—) are compared with those of the precipitated samples (---) in the PyAA functionalization in aqueous solution (pH ~ 9 , upper) and in DMF (lower).

the noncovalent functionalization by the pyrene derivative. It seems reasonable to rationalize that the tougher requirement for aqueous solubilization of the extremely hydrophobic nanotubes probably overwhelms the relatively weaker differences in pyrene–nanotube interactions between metallic and semiconducting SWNTs, thus essentially no separation in basic aqueous solutions.¹⁸ The same rationale may be applied to the observed real yet relatively less effective metallic–semiconducting separation in DMF. As an extrapolation, noncovalent functionalization by the pyrene derivative in less polar organic solvents should be favorable to more effective metallic–semiconducting separation. In those solvents (such as THF), however, the solubility of PyAA is not high enough for the noncovalent functionalization and solubilization. The pyrene derivative with a long alkyl tail (DomP, Scheme 1) is more suitable to those solvent conditions.⁸

As reported previously,¹⁸ the lack of selectivity for PyAA in the noncovalent functionalization between metallic and semiconducting SWNTs in a basic aqueous solution could be exploited for removing residual metal catalysts and carbonaceous impurities from the nanotube sample. In addition, the purification with PyAA may also serve another important purpose of making the highly pure nanotube sample more suitable for the metallic–semiconducting separation. Generally in the solubilization of SWNTs through various noncovalent or covalent functionalization reactions, there is always a portion of the sample that is insoluble under whatever conditions, as found, for example, in sequentially repeated functionalization reactions with the same nanotube sample.²¹ The composition of this “special” insoluble portion of the sample may be complex, though

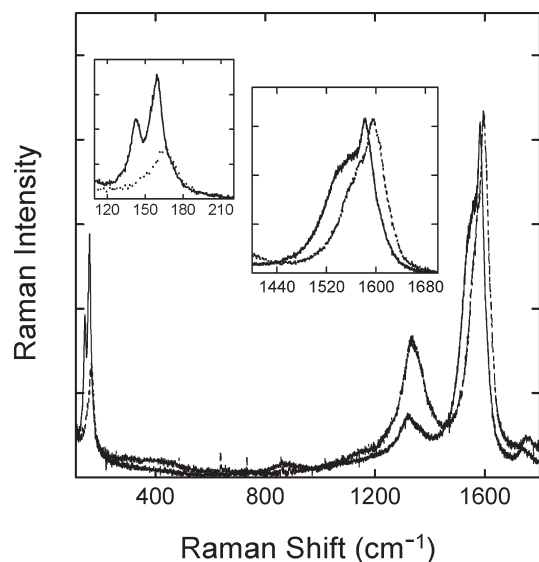


Figure 2. Raman spectra (expanded G-band and RBM-band in insets) of the separated metallic (—) and semiconducting (---) SWNTs from the DomP separation of a highly pure nanotube sample.

it does contain mostly SWNTs according to Raman and other characterization results. While the reasons behind these SWNTs being obviously different in their response to functionalization agents and solubilization reaction conditions are not so clear, logical speculations might include the bundling of nanotubes in such a way that morphologically prevents their being accessed by the functionalization agents or the presence of some intertwining or even cross-linking between the nanotubes. Regardless, a negative consequence of such a special portion of the sample to the postproduction separation based on preferential solubilization of semiconducting SWNTs is that these never-soluble nanotubes, a mixture of metallic and semiconducting, would remain in the residue to interfere with the mass balance of the separation. Therefore, beyond the sample purification reported previously,¹⁸ the PyAA noncovalent functionalization and solubilization in basic aqueous solution also eliminated the always-insoluble portion from the nanotube sample to yield highly pure SWNTs that could be “split” into metallic and semiconducting fractions in the postproduction separation.

DomP is structurally similar to PyAA, except for a long alkyl tail which makes the molecule more soluble in organic solvents, including those that are less polar. In the noncovalent functionalization, DomP is selective toward semiconducting SWNTs, thus an excellent agent for postproduction separation of SWNTs into metallic and semiconducting fractions.^{22–24} Experimentally, the separation is such that the DomP-functionalized semiconducting SWNTs are solubilized in an organic solvent like THF, leaving in the residue metallic SWNTs. As a result, the separation is sensitive to the nanotube sample purity, as impurities may interfere with the noncovalent functionalization of SWNTs by DomP and the distribution of the impurities between the two separated fractions is not predictable. In this work, the highly pure sample of SWNTs from the PyAA purification was used for the DomP separation. In the separation experiment, about two-thirds of the nanotube sample could be solubilized by DomP into THF as the fraction in the supernatant, leaving behind the other fraction in the residue. Upon the removal of DomP, the two fractions from the supernatant and residue were

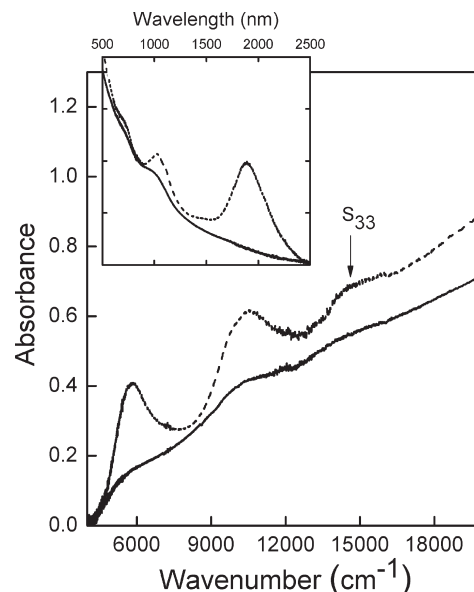


Figure 3. Optical absorption spectra (on wavenumber scale, with the same on wavelength scale in the inset) for neat nanotube films of the separated metallic (—) and semiconducting (---) SWNTs.

found to be dominated by semiconducting and metallic SWNTs, respectively, according to results from resonance Raman (Figure 2) and near-IR optical absorption (Figure 3) characterizations. The noncovalent nature in the DomP functionalization of SWNTs was confirmed by the fact that DomP could be washed off the nanotubes and recovered quantitatively (according to the quantitative NMR characterization). The separated nanotubes after the removal of DomP molecules were morphologically similar to the pre-separation highly pure sample, as suggested by electron microscopy results (Figure 4).¹⁸

For the separated semiconducting fraction, the observed absorption spectrum consists of a weak feature around 700 nm ($14\,300\text{ cm}^{-1}$) in addition to the prominent S_{11} and S_{22} bands (Figure 3). The assignment of this absorption feature is of significant interest because this is the region where M_{11} absorption is expected (thus potential contradiction to the notion that the fraction is dominated by semiconducting SWNTs).²⁵ However, a more likely assignment for the weak feature is S_{33} absorption, which according to literature results is strongly dependent on the nanotube diameter. Shown in Figure 5 are collections of literature data on the nanotube diameter dependencies of the S_{33} and M_{11} absorption bands.^{26–28} The S_{33} and M_{11} are both higher in energy for smaller diameter SWNTs, with the absorptions gradually red-shifting with increasing nanotube diameters. However, the S_{33} obviously red-shifts faster than does the M_{11} , with the two absorption bands apparently converging at about $14\,500\text{ cm}^{-1}$ (690 nm) for SWNTs of around 1.4 nm in diameter (Figure 5). Interestingly, the arc discharge-produced SWNTs used in this work for postproduction separation are rather narrowly distributed in diameter, with an average diameter of 1.4 nm according to the Raman radial breathing mode (Figure 2). Therefore, it is understandable that the S_{33} and M_{11} absorptions appeared in the same wavelength region for the separated metallic and semiconducting arc-discharge SWNTs. On the basis of the estimated peak positions in the absorption spectrum of the separated semiconducting SWNTs (Figure 3),

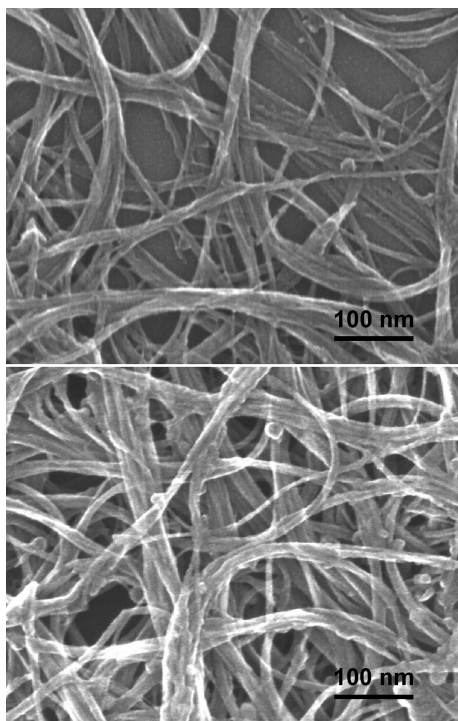


Figure 4. S-TEM (in the SE mode) images of the separated metallic (upper) and semiconducting (lower) SWNTs.

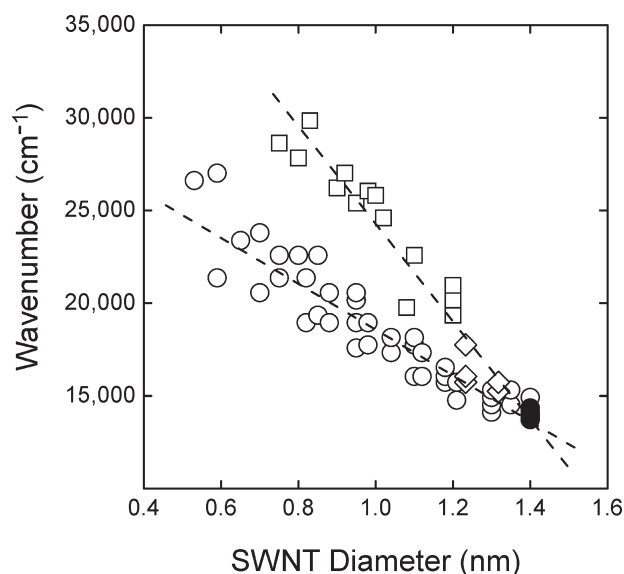


Figure 5. Dependencies of S_{33} (\square) and M_{11} (\circ) band energies on SWNT diameters (data from refs 26–28). The S_{33} value for the nanotube diameter of 1.4 nm (\bullet) is also marked in Figure 3.

the energy gaps for S_{22} – S_{11} and S_{33} – S_{22} are around 4600 and 4200 cm^{-1} , respectively.

Noncovalent functionalizations of SWNTs with planar aromatic molecules are commonly attributed to interactions similar to π – π stacking found in many aromatic systems. The interactions typically have significant effects on the nanotube π electronic structure, resulting in decreased or even diminished band gap electronic transitions, which is referred to in

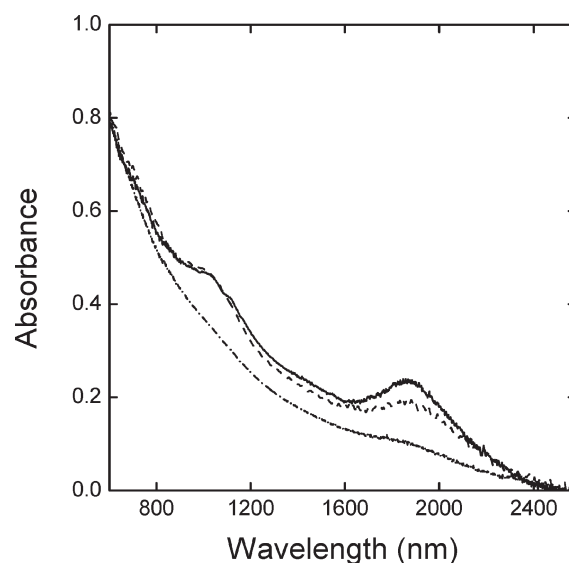


Figure 6. Optical absorption spectra in films of semiconducting SWNTs functionalized by DomP (– · –) and PyAA (—: from basic aqueous solution; ---: from DMF solution).

the literature as the nanotube surface doping effect.^{29,30} For the DomP functionalization of the separated semiconducting SWNTs in THF, the effect on both S_{11} and S_{22} bands was obviously extreme, essentially diminishing the absorptions in THF solution and also in the thin film made from the solution (Figure 6).³¹ The effect was reversible, however, with both S_{11} and S_{22} absorption bands restored upon the removal of DomP from the nanotube surface.^{25,31}

The doping effect associated with the PyAA functionalization was clearly different. As compared in Figure 6, both S_{11} and S_{22} absorption bands in thin films prepared from the basic aqueous solution or DMF solution of PyAA-functionalized semiconducting SWNTs were largely preserved, suggesting that there was no significant doping effect. The observation, readily producible in repeated experiments, was somewhat surprising as stronger interactions with the nanotubes were expected for PyAA (capable of solubilizing both metallic and semiconducting SWNTs).¹⁸ Nevertheless, a rationalization on the results might be that the functionalization action of PyAA for nanotube solubilization was driven more significantly by the solvent conditions, due less to π – π stacking-like interactions that induce the doping effect. Alternatively, the strong effect with DomP might be attributed to possible secondary functionalization of the complex-like configuration of pyrenes-on-nanotube by the long alkyl chain. Further investigations with more variations of planar aromatic molecules and solvent and other experimental conditions are required for an improved understanding of the doping effect.

In summary, the noncovalent interactions of the derivatized pyrenes (representing more broadly planar aromatic molecules) with SWNTs are apparently complex, depending not only on molecular structures but also on solvent conditions. Consequently, the selectivity of such interactions between metallic and semiconducting SWNTs is similarly or more affected, which further complicates the use of the selectivity for metallic–semiconducting nanotube separation. However, the complications also bring opportunities, enabling potentially exploitations of the different molecular structures and experimental conditions

for more effective separation and harvesting of purer metallic and/or semiconducting SWNTs. The results from this work seem to suggest that the selectivity in pyrene–nanotube interactions is relatively weak between the metallic and semiconducting SWNTs, so that an environment of relatively lower solvent strength (less polar solvents) should be more favorable to the realization of the selectivity. These findings may provide some guidance in the further pursuit of postproduction bulk separation of metallic and semiconducting SWNTs by using planar aromatic molecules as fully recyclable separation agents.

EXPERIMENTAL SECTION

Materials. The SWNT samples (arc-discharge production) were produced in house or acquired from Carbon Solutions, Inc. (“AP-SWNT”, carbonaceous purity 40–60%). 1-Pyreneacetic acid (PyAA) and pyrene methanol were purchased from Aldrich. Nitric acid was obtained from Fisher Scientific, concentrated hydrochloric acid (HCl, 37%) and sodium hydroxide (NaOH) from Acros, and tetrahydrofuran (THF), ethyl acetate, and dimethylformamide (DMF) from Mallinckrodt. The organic solvents were distilled prior to use. Membrane filters (PVDF, 0.22 μm pore size) were supplied by Fisher Scientific. Water was deionized and purified by being passed through a Labconco WaterPros water purification system.

Measurements. A Fisher Scientific centrifuge (Model 228) and homogenizer (PowerGen 125) and VWR bath sonicator (Model 250D) were used in the purification and separation experiments. Thermogravimetric analysis (TGA) was carried out on a Mettler-Toledo TGA/SDTA851e instrument or a TA Instruments Q500 TGA analyzer. Electron microscopy images were obtained in the SE mode on a Hitachi HD-2000 scanning transmission electron microscope. Optical absorption spectra were recorded on Shimadzu UV-3100 and UV-3600 spectrophotometers. Raman spectra were obtained on a Jobin Yvon T64000 Raman spectrometer equipped with a Melles-Griot He–Ne laser (35 mW) for 632.8 nm excitation, a triple monochromator, a liquid-nitrogen-cooled symphony detector, and an Olympus BX-41 microscope for sampling.

Sample Purification. The as-produced samples of SWNTs were purified in terms of an established procedure involving nitric acid treatment.¹⁹ Briefly, a sample (1 g) was heated at 300 °C with air in a furnace for 30 min, then suspended in aqueous nitric acid (2.6 M, 500 mL), and refluxed for 24 h. The mixture back at room temperature was centrifuged to retain the residue, followed by repeated washing with deionized water until neutral pH. The purified sample was recovered by removing water and drying in a vacuum for 12 h.

For further purification with PyAA,¹⁸ an above purified sample (150 mg) and PyAA (200 mg) were mixed in an aqueous NaOH solution (0.1 M, 100 mL) with homogenization for 30 min and then sonicated for 12 h. The resulting suspension was centrifuged at 1400g for 30 min to retain the dark-colored supernatant. For the precipitation of nanotubes, the supernatant was acidified with aqueous HCl to pH \sim 3. Upon filtration with a PVDF membrane filter (0.22 μm pore size), the nanotube sample was washed with deionized water and ethyl acetate in repeated dispersion–centrifugation cycles and then refluxed in ethyl acetate for 12 h. The purified SWNTs were precipitated and collected (105 mg), and from the solution PyAA was recovered

nearly quantitatively. TGA results suggested that the purity in the nanotube sample was higher than 95%.¹⁸

Separation with PyAA. A purified nanotube sample (150 mg) was added to an aqueous PyAA solution (pH \sim 9, 100 mL). The mixture was homogenized for 30 min and then sonicated for 24 h, followed by centrifuging at 3000g for 30 min to collect the precipitate. It was washed with dilute acid solution, refluxed in THF for 24 h, and then washed repeatedly with THF until no PyAA was detected in the washing solution.

For separation in organic solvent, a purified nanotube sample (150 mg) was added to a solution of PyAA in dry DMF (150 mg, 60 mL). The mixture was homogenized for 30 min and sonicated for 24 h, followed by centrifuging at 50000g to collect the precipitate. It was refluxed in THF for 24 h and then washed repeatedly with THF until no PyAA was detected in the washing solution.

Separation with DomP. DomP (Scheme 1) was synthesized and fully characterized as previously reported.^{23,31} In the separation, a purified nanotube sample (150 mg) was added to a solution of DomP in dry THF (10 mg/mL, 60 mL), and the mixture was homogenized for 1 h and sonicated for 24 h, followed by centrifuging at 1400g for 15 min. The supernatant was collected, and the residue was used for another round of the same separation. After two repeats, the three supernatants were combined and evaporated to remove THF for the soluble fraction and the final residue as the other fraction. Both fractions were washed repeatedly with THF, refluxed in THF for 24 h, and then washed repeatedly with THF again to ensure a complete removal of DomP from the samples.

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