

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/26749639>

Supramolecular Surface Modification and Solubilization of Single-Walled Carbon Nanotubes with Cyclodextrin Complexation

ARTICLE *in* CHEMISTRY - AN ASIAN JOURNAL · OCTOBER 2009

Impact Factor: 4.59 · DOI: 10.1002/asia.200900119 · Source: PubMed

CITATIONS

12

READS

27

4 AUTHORS, INCLUDING:



Bao-Hang Han

National Center for Nanoscience and Tech...

100 PUBLICATIONS 3,868 CITATIONS

SEE PROFILE

Supramolecular Surface Modification and Solubilization of Single-Walled Carbon Nanotubes with Cyclodextrin Complexation

Sheng-Zhen Zu,^[a] Xu-Xia Sun,^[a] Yuanqin Liu,^[b] and Bao-Hang Han*^[a]

Abstract: A novel approach to solubilize single-walled carbon nanotubes (SWCNTs) in the aqueous phase is described by employing supramolecular surface modification. We use cyclodextrin complexes of synthetic molecules that contain a planar pyrene moiety or a bent, shape-fitted triptycene moiety as a binding group connected through a spacer to an adamantane moiety that is accommodated in the cyclodextrin cavity. The binding groups attach to

the sidewalls of SWCNTs through a π - π stacking interaction to yield a supramolecular system that allows the SWCNTs to dissolve in the aqueous phase through the formed hydrophilic cyclodextrin shell. The black aqueous

Keywords: carbon nanotubes • cyclodextrins • fluorescence spectroscopy • Raman spectroscopy • triptycene

SWCNT solutions obtained are stable over a period of months. They are characterized through absorbance, static, and time-resolved fluorescence spectroscopy as well as Raman spectroscopy, TEM, and fluorescence-decay measurements. Furthermore, the shape-fitted triptycene-based system shows a pronounced selectivity for SWCNTs with a diameter of 1.0 nm.

Introduction

Since their discovery and characterization, carbon nanotubes (multiwalled in 1991,^[1] single-walled in 1993^[2]), one-dimensional nanoscale materials, have triggered a new field of promising interests, owing to their unique structure and physical and chemical properties.^[3] However, as-prepared carbon nanotube samples inevitably embed a large amount of metal catalysts, and consist of bundles of tens of nanotubes aggregated through van der Waals and π - π stacking interactions. After purification and debundling,^[4] the obtained carbon nanotubes (only small parts are individual tubes) are insoluble in most organic solvents and the solubility in water is even less. The difficulty in manipulating individual carbon nanotubes owing to the bundling and insol-

bility hampers the molecular-level studies and further device application of carbon nanotubes.

Much effort has been devoted to disperse carbon nanotubes in various potential solvents,^[5] such as several organic solvents or water through surface functionalization. Two kinds of approaches have been explored, covalent^[6] and noncovalent surface functionalization. The covalent functionalization has been investigated through a wide variety of reactions, however, covalent binding somewhat damages the electronic structure of the carbon nanotubes as it changes the linked carbon atoms from sp^2 -form into sp^3 -type.

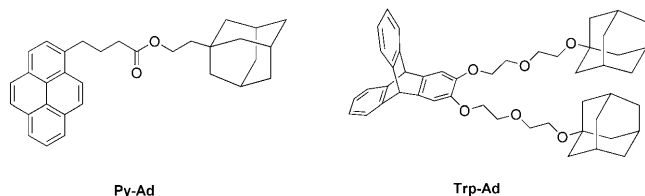
Noncovalent surface functionalization has so far employed various natural biopolymers, such as polysaccharides (Gum Arabic (a highly branched arabinogalactan polysaccharide: 70–80 % arabinogalactan, 20 % arabinogalactan-protein complex),^[7] starch,^[8] amylose,^[9] glycosylated polymers,^[10] schizophyllan and curdlan (β -1,3-glucans),^[11] alginic acid,^[12] water-soluble chitosan^[13]), peptide,^[14] DNA,^[15] green tea (catechins),^[16] natural lignosulfonate-based polyelectrolytes,^[17] artificial conjugate polymers,^[18] and pyrene-containing polymers.^[19] Many polyaromatic, especially small pyrene-based molecules and ions (electrolytes), have also been used as surface modifiers of carbon nanotubes.^[5c,18j,20,21,22] Through these efforts, solubilization/dispersion of carbon nanotubes has been solved to some extent. In some cases, a reasonable chirality- and/or diameter-selectivity has been achieved.^[18k,i,23]

[a] S.-Z. Zu, X.-X. Sun, Prof. B.-H. Han
National Center for Nanoscience and Technology
No. 11, Beiyitiao Zhongguancun Beijing 100190 (China)
Fax: (+86) 10-8254-5576
E-mail: hanbh@nanoctr.cn

[b] Y. Liu
Department of Chemistry
University of Toronto
80 St. George Street, Toronto, Ontario M5S 3H6 (Canada)

Supporting information for this article is available on the WWW under <http://dx.doi.org/10.1002/asia.200900119>.

In comparison with using polymeric molecules, using small molecules shows advantages in the noncovalent surface functionalization of carbon nanotubes when considering the ease in synthesis and solubilization. The approach presented herein employs a novel supramolecular surface-modification strategy. We used cyclodextrin complexes of synthetic bifunctional molecules (**Py-Ad** and **Trp-Ad** in Scheme 1) that contain a planar pyrene moiety or a bent,



Scheme 1. Synthetic bifunctional molecules.

shape-fitted triptycene moiety as a binding group connected through a spacer to an adamantane moiety that is accommodated in the cyclodextrin cavity. The binding groups attached to the sidewalls of single-walled carbon nanotubes (SWCNTs) through a π - π stacking interaction, yielding a supramolecular system that allowed SWCNTs to dissolve in the aqueous phase through the formed hydrophilic cyclodextrin shell (methylated β -cyclodextrin, bMCD; Figure 1 and Scheme S1 in the Supporting Information). We noticed that Ogoshi et al. recently reported the enhancement of water solubility of SWCNTs by cyclodextrin host-guest complexes with several anionic guest molecules through physical adsorption.^[24] Cyclodextrins are a type of cyclic oligosaccharide comprising several glucopyranose units.^[25] The sub-nanometer hydrophobic cavity can include a wide variety of organic molecules that are water insoluble, thus, making them “dissolve” in water through the help of the hydrophilic exterior surface of cyclodextrins. Herewith, the formation of cyclodextrin complexes with adamantane moieties in hydrophobic synthetic molecules **Py-Ad** or **Trp-Ad** can result in an amphiphilic species, in which the cyclodextrin complexes are the hydrophilic end, and the pyrene or triptycene moieties are the hy-

drophobic end. The hydrophobic ends attach to the sidewalls of SWCNTs through a π - π stacking interaction yielding a water-soluble supramolecular system in which SWCNTs are considered as a core, cyclodextrins as a corona or shell, and synthetic molecules **Py-Ad** or **Trp-Ad** as a linkage spacer through supramolecular interaction. The host-guest complexation of an adamantane moiety-cyclodextrin is reversible and the disassociation of the host-guest complexes can lead to a water-insoluble SWCNT system.

In previous studies, most small molecules employed as surface-modifiers of SWCNTs were planar. Since SWCNTs can be considered as cylinders of rolled-up graphene sheets, an optimum surface modifier to the sidewalls of SWCNTs should be a shape-fitted or bent molecule. However, few bent molecules have been used before as surface-modifiers of SWCNTs showing some diameter-selectivity or chirality selectivity.^[23d,26] Furthermore, Chen and co-workers have investigated the electrocatalytic properties for the sensitive detection of biological thiols through the attachment of triptycene orthoquinone on SWCNTs coated on a glassy carbon electrode.^[27] In our investigation, in addition to the planar pyrene moiety, we employed a triptycene moiety with a folding angle of 120° as a binder. The supramolecular surface functionalization yielded a nice dispersion/solubilization of the SWCNTs in aqueous solution and showed varied

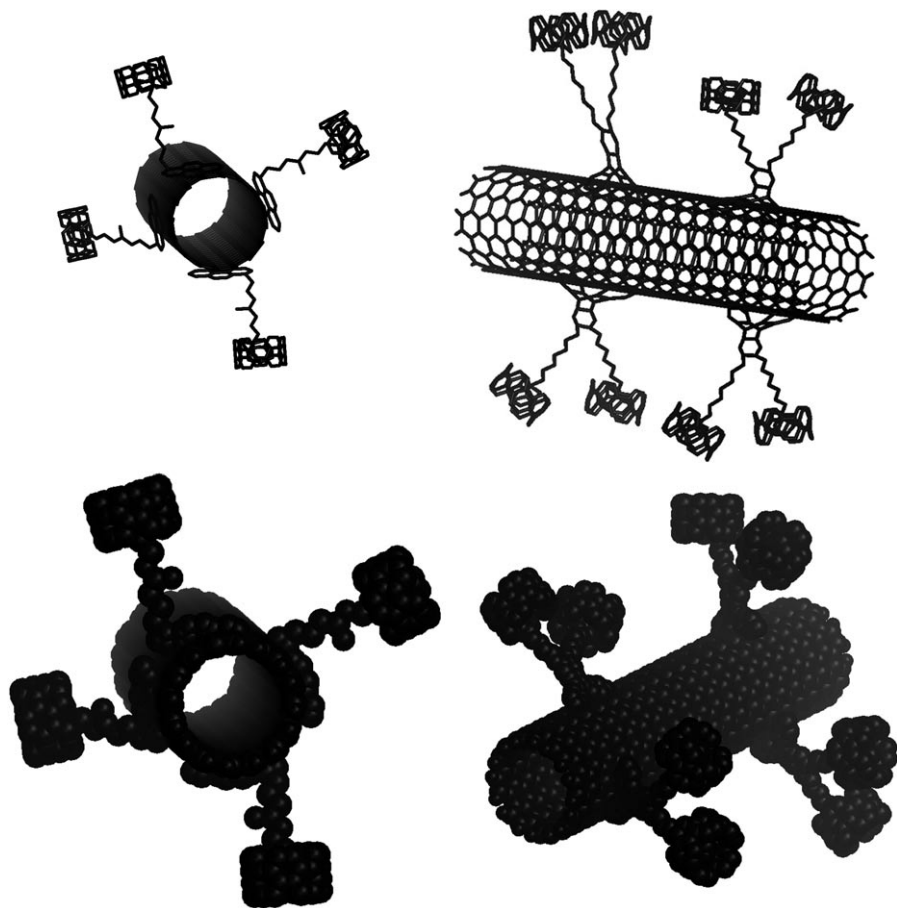


Figure 1. Schematic illustration of supramolecular complexes of SWCNT~Py(Trp)-Ad~bMCD

selectivity for bent aromatic binding groups based upon the diameter of carbon nanotubes. The resulting individual or small bundled carbon nanotube dispersion or solution was stable over a period of months. The concentration of the carbon nanotubes present in the aqueous solution was increased. These features (water soluble and debundled) make it possible to investigate the carbon nanotubes at a molecular level for possible device applications as well as for application in biological systems.

Results and Discussion

Preparation of aqueous SWCNT solution: Figure 2 shows the formation of an aqueous SWCNT solution through supramolecular surface modification: SWCNT~Py~Ad~

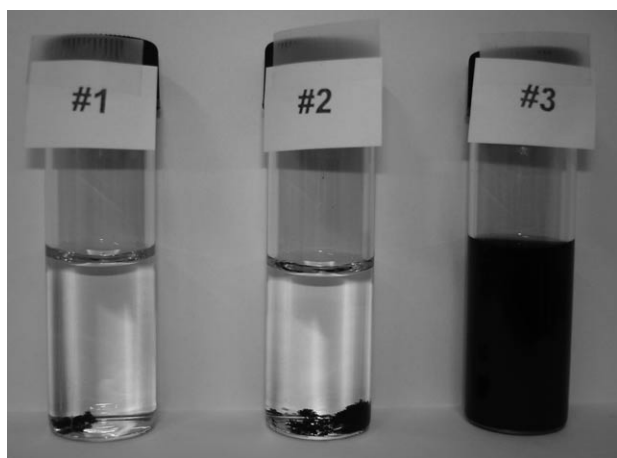


Figure 2. Photograph of three aqueous samples: 1) SWCNTs; 2) SWCNTs+bMCD; 3) SWCNTs+Py~Ad+bMCD.

bMCD system (3), and SWCNT suspension in water (1) and SWCNTs in aqueous bMCD solution (2) as control experiments. The photograph was taken about 2 months after the preparation of the samples, and the black aqueous SWCNT~Py~Ad~bMCD solution was stable for more than ten months. This indicates that the supramolecular system was formed as schematically illustrated in Figure 1, that is, hydrophobic pyrene groups attached onto the sidewalls of the SWCNT (core), and the adamantane groups formed inclusion complexes with cyclodextrin (water-soluble corona/shell), which led to solubilization of the SWCNTs in the aqueous phase.

The SWCNTs used in our investigation were purified and shortened from pure high-pressure carbon monoxide (HiPco) SWCNTs according to previously reported procedures.^[28,29] The treatment did not influence the inherent structure of SWCNTs, that is, the quality of the SWCNTs was still high based on the Raman spectroscopic investigation.^[29,30] The treated SWCNTs readily suspended in aqueous alkaline solution owing to the carboxylic acid groups on both ends and the defected sites of the carbon nanotubes. In

our investigation, we dispersed the treated SWCNTs directly in aqueous solution at pH 8.0–11.0. However, the aqueous SWCNT suspension (obtained through sonication of SWCNTs in water) was stable only for a short time and sedimentation of solid SWCNTs occurred after several hours. Centrifugation sped up the procedure to yield solid SWCNTs and a clear aqueous supernatant solution in which no or little SWCNTs were dispersed. A control experiment of the SWCNT suspension is shown in the photograph in Figure 2 (sample 1).

The synthetic hydrophobic compounds **Py~Ad** and **Trp~Ad** are almost insoluble in water. However, they slightly dissolved in an aqueous solution of methylated β -cyclodextrin through the accommodation of an adamantane moiety into the cyclodextrin cavity. It is well known that β -cyclodextrin specifically forms a very stable complex with adamantane since adamantane's rigid spherical skeleton is the best shape/size to fit into the β -cyclodextrin cavity and thus leads to a strong van der Waals interaction between the host and the guest.^[31] Upon addition of SWCNTs, ultrasonication of the mixture for 1–3 h resulted in a good dispersion of the SWCNTs and a black solution or suspension formed. After centrifugation at 14 000 g, a macroscopically homogeneous solution was obtained in the supernatant (Figure 2, sample 3).

A second control experiment is shown as sample 2 in Figure 2 in which the mixture of SWCNTs and bMCD in water were processed by using ultrasonication and centrifugation with identical procedures (samples 1, 2, and 3 were processed in the same batch). We were not able to disperse SWCNTs in the aqueous bMCD solution, indicating that solely methylated β -cyclodextrin can not solubilize SWCNTs.

To confirm the formation of the supramolecular system, we added 1-adamantane-ethanol to the aqueous SWCNT~Py~Ad~bMCD solution. Upon addition, we found that the color of the black solution immediately lightened into a light grey within several minutes; in the meantime, black precipitates formed at the bottom of the container. Given this, it seems that 1-adamantane-ethanol formed inclusion complexes competitively with cyclodextrin and excluded the part of **Py~Ad** of the SWCNT~Py~Ad~bMCD supramolecular system, which resulted in the formation of a water-insoluble SWCNT~Py~Ad species. This phenomenon revealed the host–guest complexation of adamantane moieties with cyclodextrins in the SWCNT~Py~Ad~bMCD supramolecular system in an aqueous solution. This phenomenon also confirmed the reversible complexation of adamantane moieties with cyclodextrins. On the basis of this phenomenon, we tried to transfer the SWCNT species from the aqueous phase to the organic phase (1-adamantane-ethanol solution in chloroform). However, no phase transfer of SWCNTs was observed. We obtained solid SWCNT precipitates at the interface, which may arise from the difficulty in the phase transfer of sub-micrometer-scale SWCNT species and the tendency of SWCNT~Py~Ad complexes to assemble.

TEM images: As seen from the photograph in Figure 2, the black SWCNT~Py~Ad~bMCD solution is a macroscopically homogeneous solution. However, microscopically it is heterogeneous with the SWCNTs surrounded by a hydrophilic cyclodextrin shell, as shown in Figure 1, and as such, stably disperse in the aqueous phase. This was revealed by TEM images of the above SWCNT solution presented in Figure 3. We observed many individual or debundled carbon

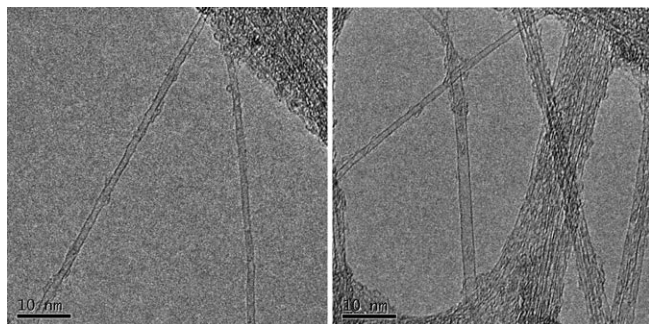


Figure 3. TEM images of the aqueous SWCNT solution (SWCNTs+Py~Ad+bMCD)

nanotubes on the carbon film that was coated on the copper grids. However, the corona/shell of cyclodextrin complexes can not be observed through TEM owing to their low electron density. The images showed a nice dispersion of debundled SWCNTs in an aqueous SWCNT solution.

Absorption spectroscopy: As the binding moieties (pyrene and triptycene) are polyaromatic organic entities, they absorb light in the ultraviolet region. Thus, we can spectroscopically monitor and characterize the formation of the supramolecular SWCNT solution. When **Py~Ad** dissolved in aqueous bMCD solution, the characteristic pyrene absorption shown in Figure 4 indicated the presence of pyrene groups in the aqueous phase. When the treated SWCNTs were sonicated in aqueous Py~Ad~bMCD solution, the absorption intensity of the pyrene peaks in the su-

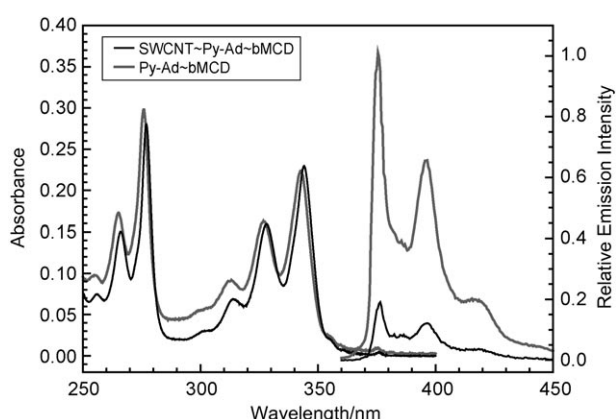


Figure 4. Absorption spectra and fluorescence spectra of aqueous SWCNT~Py~Ad~bMCD and Py~Ad~bMCD solutions. Optical cell length = 1.0 mm.

pernatant solution after centrifugation was enhanced significantly.^[32] This indicates that the concentration of pyrene moieties in the aqueous SWCNT~Py~Ad~bMCD solution was much larger than that in the aqueous Py~Ad~bMCD solution. The solubility of amphiphilic Py~Ad~bMCD complexes in water is limited. The formation of a ternary supramolecular SWCNT~Py~Ad~bMCD system improved the apparent concentration of pyrene moieties in the solution. The hydrophobic pyrene moieties attached onto the side-walls of the SWCNTs to form SWCNT~cyclodextrin complexes with core-shell/corona or micelle-like structures. As the exterior surface of the corona cyclodextrin complexes is hydrophilic, more **Py~Ad** compounds were dissolved in the aqueous solution in the form of ternary supramolecular complexes, which resulted in a much-enhanced pyrene UV absorbance. Furthermore, the pyrene absorption peaks were at 277, 328, and 345 nm, respectively, which are about 2 nm red-shifted compared with those of **Py~Ad** in aqueous bMCD solution. This indicates the π - π stacking interaction between the planar pyrene moieties and sidewalls of SWCNTs. This is consistent with those results observed by other researchers for pyrene and carbon nanotube systems.^[20c,21a,b]

A similar phenomenon was observed for the case of **Trp~Ad**. The absorbance of the triptycene moiety in aqueous SWCNT~Trp~Ad~bMCD solution was also enhanced as compared with that in Trp~Ad~bMCD solution, indicating a supramolecular surface modification of SWCNTs by Trp~Ad~bMCD complexes. Furthermore, we observed that the triptycene absorption peak (approximately 290 nm) in the SWCNT~Trp~Ad~bMCD system did not show any obvious shift, but broadened compared with that in Trp~Ad~bMCD, indicating that triptycene moieties attached to SWCNT side-walls.

The ultraviolet absorption of the binding groups (pyrene and triptycene) in the synthetic compounds **Py~Ad** and **Trp~Ad** confirmed their presence in the black aqueous SWCNT solution as surface-attaching modifiers on the sidewalls of SWCNTs through π - π stacking interactions. As SWCNTs themselves absorb light in the Vis/NIR region, we can obtain the absorption information of carbon nanotube in aqueous solution in this region. The Vis/NIR spectra of the black SWCNT solutions (SWCNT~Py~Ad~bMCD and SWCNT~Trp~Ad~bMCD) are shown in Figure 5. The characteristic van Hove singularities of SWCNTs in the range of 400–1300 nm demonstrated that the electronic properties of the nanotubes have not been profoundly disturbed.^[18h] The line widths of the van Hove singularities are related to the size of the SWCNT bundles. As compared with the well-resolved sharp peaks of the individual isolated tubes wrapped by surfactant sodium dodecylsulfonate (SDS),^[18h] peptides,^[14a] and DNA,^[15c,f,g] the peaks corresponding to the van Hove transitions in aqueous SWCNT~Py~Ad~bMCD and SWCNT~Trp~Ad~bMCD solutions were broader. This implies some bundling but it is comparable to or better resolved than most other results reported for water-soluble carbon nanotubes.^[8,18i,20c,24,33]

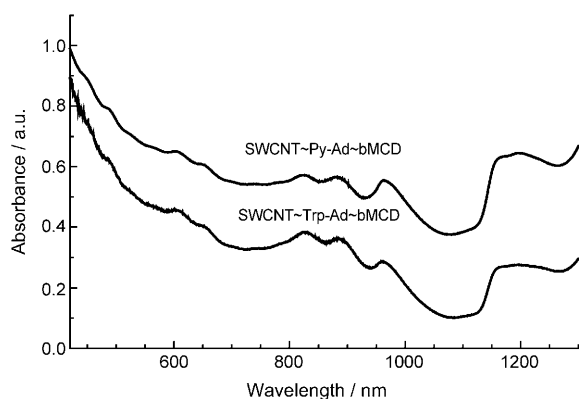


Figure 5. Vis/NIR absorption spectra of aqueous SWCNT~Trp~Ad~bMCD and SWCNT~Py~Ad~bMCD solutions.

It was reported that the concentration of SWCNTs in aqueous solution can be calculated/estimated from the absorbance at approximately 500 nm.^[34] Despite the difference in the aqueous SWCNTs solution between our systems and those in the references, we roughly estimated the concentration of SWCNTs in our aqueous SWCNT solutions based on the absorbance in Figure 5. The concentration of SWCNTs in aqueous SWCNT~Py~Ad~bMCD solution is about 0.040 mg mL⁻¹ (40 mg L⁻¹). This is a reasonable value as we prepared the aqueous SWCNTs solution by mixing 1.0 mg SWCNTs in aqueous Py~Ad~bMCD solution (12 mL). This indicates that approximately 50 wt% of the feeding SWCNTs were extracted into the solution by the Py~Ad~bMCD complex. The concentration of SWCNTs in aqueous SWCNT~Trp~Ad~bMCD solution is about 0.025 mg mL⁻¹ (25 mg L⁻¹). The concentration of SWCNTs in our aqueous solution is comparable to those of most other reported systems that are solubilized by small molecules^[18i,j,34] and polymers,^[10,11] although smaller than those systems solubilized by polyethylene glycol and surfactant SDS.^[35]

From the absorption spectra of both the binding groups and the SWCNTs in the UV/Vis/NIR region, we demonstrated their presence within the aqueous SWCNT solution and the attachment of binding groups on the SWCNT sidewalls through π - π stacking interactions. The weight percentages of Py~Ad~bMCD and Trp~Ad~bMCD in SWCNT~Py~Ad~bMCD and SWCNT~Trp~Ad~bMCD hybrids were both approximately 48 wt% by thermogravimetric analysis (TGA) measurements (see the Supporting Information), which further confirmed the binding groups on the SWCNTs.

Fluorescence spectroscopy: As mentioned above, the binding moieties (pyrene and triptycene) are polyaromatic organic entities and they not only absorb light, but also emit fluorescence upon a suitable excitation. When aqueous Py~Ad~bMCD or SWCNT~Py~Ad~bMCD solution was excited at 343 nm, characteristic pyrene-monomer fluorescence emission was observed in both aqueous solutions. The monomer emission peaks were centered at 377 and 396 nm and the excimer peak was very low and located at 415 nm

(Figure 4). Furthermore, when the as-prepared Py~Ad~bMCD and SWCNT~Py~Ad~bMCD solutions with distinctly different pyrene concentrations (the ratio of absorbance of these two solutions is about 6.2) were identically diluted in the same ratio, we found that the fluorescence intensity of pyrene moieties in aqueous SWCNT~Py~Ad~bMCD solution was only less than twice that in aqueous Py~Ad~bMCD solution. This indicates that the fluorescence emission in aqueous SWCNT~Py~Ad~bMCD solution was significantly quenched owing to the π - π stacking interaction of pyrene with SWCNT sidewalls.^[18a, 19c, e, 20c, 21b, c, 23a, 36]

The phenomenon of fluorescent emission of pyrene groups quenched by carbon nanotubes has been qualitatively reported by several groups.^[20c, 21b, c] However, to the best of our knowledge, there was little quantitative measurement performed so far.^[19c] Herein, the quantum yields of the binding moiety in aqueous Py~Ad~bMCD and SWCNT~Py~Ad~bMCD solutions were quantitatively investigated. We obtained the quantum yield ratio of these two solutions, rather than the quantum yield of these two solutions based on an additional reference substance. Aqueous SWCNT~Py~Ad~bMCD and Py~Ad~bMCD solutions (showed about a same absorbance at the excitation wavelength, that is, 345 nm) were diluted and their fluorescence emission measured. The absorbance and fluorescence spectra of aqueous Py~Ad~bMCD and SWCNT~Py~Ad~bMCD solutions are shown in Figure 4. The fluorescence quantum yields were calculated according to the following equation [Eq. (1)].^[37]

$$Y_U = \frac{Y_R \times A_R \times F_U}{A_U \times F_R} \quad (1)$$

In Equation (1), Y_U , F_U , and A_U denote the fluorescence quantum yield, the integral fluorescence intensity, and the absorbance of the unknown sample, respectively. Y_R , F_R , and A_R denote the fluorescence quantum yield, the integral fluorescence intensity, and the absorbance of the reference sample, respectively.

The quantum yield of pyrene moieties in aqueous SWCNT~Py~Ad~bMCD solution was found to be only approximately 7.5% of that in aqueous Py~Ad~bMCD solution. This demonstrates that the quantum efficiency of the pyrene moiety was largely decreased owing to the π - π stacking interaction between the pyrene moieties and SWCNT sidewalls in aqueous SWCNT~Py~Ad~bMCD solution.

The fluorescence spectra and quenching phenomenon were also observed in the case of Trp~Ad. When excited at approximately 290 nm, the Trp~Ad~bMCD solution showed fluorescence emission with a peak centered at around 330 nm. Similarly, the fluorescence emission of the SWCNT~Trp~Ad~bMCD solution was largely quenched. It was found that the quantum yield of the triptycene moiety in the SWCNT~Trp~Ad~bMCD system was about 15% of that in the Trp~Ad~bMCD system.

The above fluorescence spectroscopic investigation further confirmed the noncovalent surface modification of polyaromatic binding groups (pyrene and triptycene) on the sidewalls of SWCNTs through the fluorescence quenching caused by π - π stacking interactions with SWCNTs. As for the pyrene species, it can be considered that there are free pyrene moieties in the Py-Ad~bMCD complex form and bound pyrene moieties attached on the SWCNT sidewalls in the SWCNT solution from a thermodynamic viewpoint. However, from the overall fluorescent emission measurement, we were not able to tell the fluorescence contribution from free or unbound pyrene moieties, and we also wanted to know more about the bound pyrene moieties in the SWCNT solution. Considering these concerns, quenching experiments were designed and conducted by employing a general quencher, that is, nitrite. The fluorescence spectra of a series of solutions containing the pyrene species at a constant concentration (approximately 4.5×10^{-7} M) and nitrite at various concentrations have been measured. We found that the relative fluorescence intensity of pyrene moieties in the Py-Ad~bMCD system gradually decreased upon the addition of nitrite (see Figure 6). In contrast, the decrease in

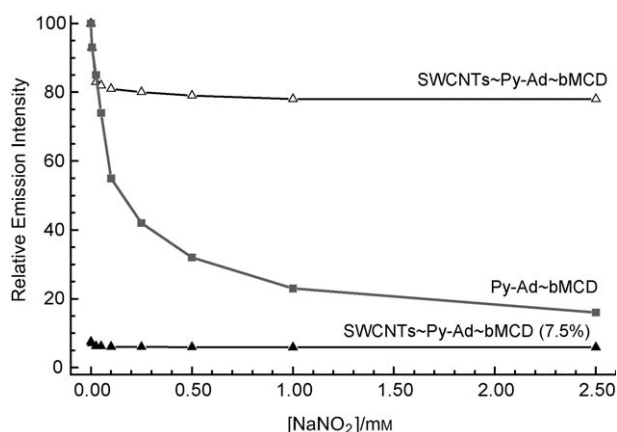


Figure 6. The changes in relative fluorescence intensity of Py-Ad~bMCD (■) and SWCNT~Py-Ad~bMCD (▲; △ = without consideration of quantum yield ratio 7.5%) solutions upon addition of quencher NaNO₂. (excitation at 343 nm)

the relative fluorescence intensity of pyrene moieties in the SWCNT~Py-Ad~bMCD system was comparable to that in the Py-Ad~bMCD system at low concentrations of nitrite. However, when the concentration of nitrite was larger than 50 times that of the pyrene moieties, the decrease in the relative emission intensity got much smaller, that is, more quencher did not, at least to any significant extent, influence the emission behavior of the pyrene in the system. This could be obviously seen when the quantum yield ratio of 7.5% was not considered (△, Figure 6).

The pyrene moieties in the Py-Ad~bMCD system can be considered to be totally free and accessible to the quencher nitrite. Therefore, the fluorescence intensity of pyrene moieties in the Py-Ad~bMCD system showed a constant de-

crease upon an increase in the quencher concentration. From the thermodynamic viewpoint, there should be a small amount of free pyrene moieties in the Py-Ad~bMCD complex form in the aqueous SWCNT~Py-Ad~bMCD solution. Besides the free and accessible pyrene moieties, the bound pyrene moieties attaching on the sidewalls of SWCNTs might be inaccessible to the quencher species owing to the shell of the cyclodextrin complex. To determine whether the bound pyrene moieties are accessible and how many of the fluorophores are inaccessible, we employed a modified Stern–Volmer plot to analyze the fluorescence quenching results.^[38] The Stern–Volmer plot ($\frac{I_0}{I} \sim [Q]$, where I_0 and I represent the fluorescence intensity of the fluorophores in the absence and presence of quencher, respectively, $[Q]$ signifies the concentration of quencher) is a widely accepted model to analyze fluorescence-quenching data. When considering both accessible and inaccessible fluorophores to quenchers, the modified Stern–Volmer plot ($\frac{I_0}{I_0 - I} \sim \frac{1}{[Q]}$) was developed. From the intercepts of the modified Stern–Volmer plot, the populations of accessible fluorophores can be estimated. It was found that all pyrene moieties (approximately 100%) in aqueous Py-Ad~bMCD solution are accessible to quencher nitrite, whereas about 80% of the initial fluorescence of pyrene moieties in aqueous SWCNT~Py-Ad~bMCD solution are inaccessible to nitrite quencher. This part of the inaccessible pyrene moieties must be bound to the sidewalls of SWCNTs and shielded by the shell of the cyclodextrin complex. The part of the accessible pyrene moieties that contributed approximately 20% of the initial fluorescence might include free pyrene moieties in the Py-Ad~bMCD form and a small part of the bound pyrene moieties as the quantum yield of the pyrene moieties in aqueous SWCNT~Py-Ad~bMCD solution is only 7.5% of that in aqueous Py-Ad~bMCD solution. Similarly, it also indicated that the apparent quantum yield of 7.5% of the pyrene moieties in aqueous SWCNT~Py-Ad~bMCD solution included a considerable contribution from the free pyrene moieties in the Py-Ad~bMCD complex form.

To further confirm the presence of free pyrene moieties in aqueous SWCNT~Py-Ad~bMCD solution, we investigated aqueous Py-Ad~bMCD and SWCNT~Py-Ad~bMCD solutions by using time-resolved fluorescence spectroscopy. From the fluorescence decay measurements of Py-Ad~bMCD solution, we observed the lifetime of pyrene moieties (about 130 ns), which is very close to the lifetime of pyrene in methanol that we measured. For the case of the aqueous SWCNT~Py-Ad~bMCD solution (pyrene-moiety concentration approximately 5×10^{-7} M), the decay profile obtained showed the same slope as that in the aqueous Py-Ad~bMCD solution, except for the initial drop region (Figure 7). These results absolutely demonstrated the presence of free pyrene moieties in the Py-Ad~bMCD complex form in aqueous SWCNT~Py-Ad~bMCD solution and its dominant role in emission. The initial drop might be a result of the contribution of bound pyrene moieties on SWCNT sidewalls and light scattering of SWCNTs. When adding large amounts of nitrite (15 mM) to the SWCNT solution,

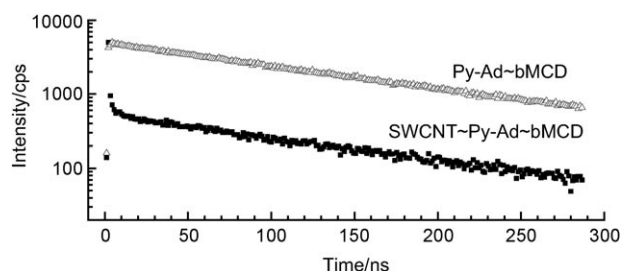


Figure 7. Fluorescence decay profiles of Py-Ad~bMCD (Δ) and SWCNT~Py-Ad~bMCD (\blacksquare) solutions.

we observed a component with a lifetime of about 20 ns, which was considered to be bound pyrene moieties in aqueous SWCNT~Py-Ad~bMCD solution.

The static and time-resolved fluorescence spectroscopic investigation revealed that the binding groups attached on the sidewalls of SWCNTs result in significant fluorescence quenching. The results showed that most pyrene species existed in the bound state and were inaccessible to the quencher. The results also showed that there was a small amount of free-pyrene moieties in the Py-Ad~bMCD complex form in the SWCNT solution that were accessible to quencher and yielded considerable contribution to the fluorescence emission in the SWCNT~Py-Ad~bMCD system.

Raman spectra analysis: We have characterized the obtained SWCNT~Py/Trp-Ad~bMCD ternary supramolecular systems by using absorption and fluorescence spectroscopy techniques in the above sections. The above spectroscopic measurements are mainly based on the light-absorbing polyaromatic binding groups (pyrene and triptycene). In this section, we will analyze the ternary supramolecular SWCNT solution based on the electronic and vibrational properties of SWCNTs by using Raman spectroscopy. We will also demonstrate that diameter selectivity resulted from the supramolecular surface modification of SWCNTs by the planar pyrene and bent, shape-fitted triptycene moieties. Raman spectroscopy has been demonstrated to be an important technique for characterization of SWCNTs owing to the strong resonant Raman enhancement of the scattering cross-section and a photo-selective response of the radial breathing mode (RBM) with respect to tube diameters.^[39]

Resonant Raman spectra of the SWCNT systems were measured with the solution samples and dried solid samples. Similar spectra were obtained with both the solution samples and dried solid samples. Since the background from water in the solution samples is not easy to be reasonably subtracted/calibrated, dried solid samples were employed by the Raman spectra measurement.

When preparing the SWCNT samples for Raman spectra measurement employing a centrifuge, the solid SWCNTs sedimented from the aqueous SWCNT suspension can not be employed to prepare a control sample with supernatant-involved identical procedures to those for preparing the SWCNT~Py-Ad~bMCD or SWCNT~Trp-Ad~bMCD samples. We employed the SWCNT~SDS sample as a con-

trol and observed almost identical resonant Raman spectra for the SWCNT~SDS sample and pristine SWCNT sample.

Figure 8 shows characteristic resonant Raman spectra of the SWCNT~SDS, SWCNT~Py-Ad~bMCD, and SWCNT~Trp-Ad~bMCD samples: *G*-bands at 1560–

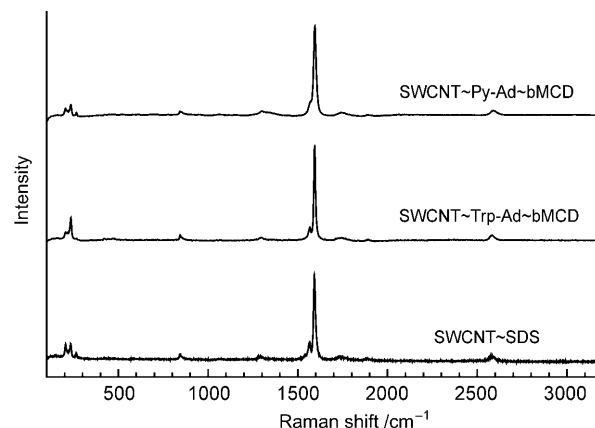


Figure 8. Resonant Raman spectra of SWCNT~Py-Ad~bMCD, SWCNT~Trp-Ad~bMCD, and SWCNT~SDS samples (excited at 785 nm, centrifugation at 88 500 g).

1600 cm^{-1} , *D*-bands centered at 1295 cm^{-1} , and RBM sections at 120–350 cm^{-1} . The solid carbon nanotube samples were sitting on an oxidized silicon substrate that provided contributions to the Raman spectra at 841 cm^{-1} .

The disorder-induced *D*-mode was caused by vacancies, substitutional heteroatoms, sp^3 defects (covalent modification), finite-size effects, and even bending. The *D*-mode was observed for all our SWCNT samples but its intensity was weak and did not show any obvious change upon surface modification, indicating that a small number of sp^3 hybridized carbons existed within the nanotube framework and the influence of the supramolecular surface modification on *D*-bands was limited.

As seen in Figure 9a, when compared with the SWCNTs control sample, the Raman spectrum of SWCNT~Trp-Ad~bMCD sample showed a similar Raman spectrum at the *G*-bands. In contrast, the SWCNT~Py-Ad~bMCD sample showed a slightly different spectrum, that is, the *G*⁺ component decreased slightly and changed into a shoulder peak. This indicates the supramolecular surface modification of SWCNT sidewalls by the binding groups. As 633 nm radiation excites Raman spectra of both metallic and semiconducting carbon nanotubes,^[40] the Raman spectra were obtained through excitation at 633 nm with a laser, which showed similar changes (Figure 9b). The line shape of the SWCNT~SDS sample, which was almost identical to that of the clean HiPco SWCNTs, indicated that the sample is a mixture of semiconducting and metallic carbon nanotubes. The resonance Raman spectrum of the SWCNT~Py-Ad~bMCD sample exhibited a Lorentzian line-shape feature in the *G*-band region, suggesting some enrichment of semiconducting SWCNTs in aqueous solution,^[39] which is consistent

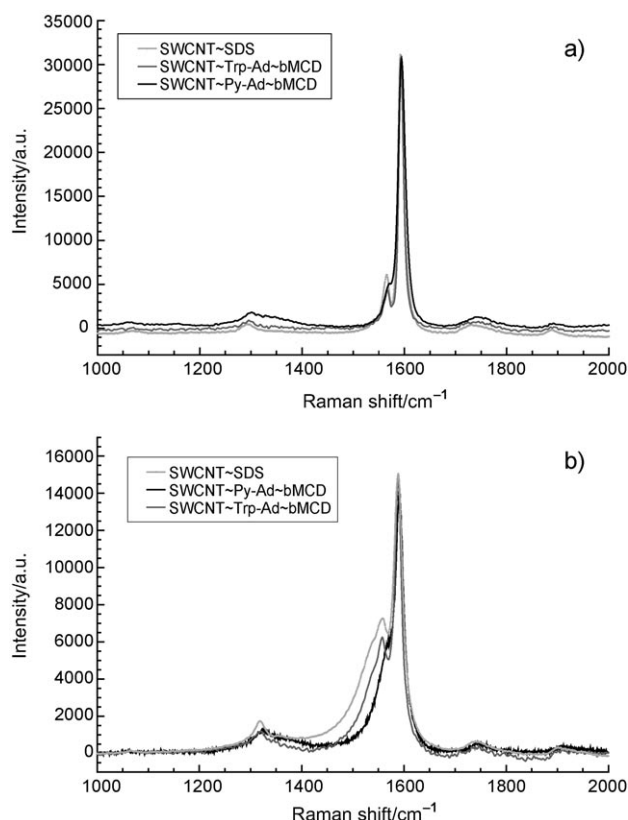


Figure 9. Resonant Raman spectra of SWCNT~Py~Ad~bMCD, SWCNT~Trp~Ad~bMCD, and SWCNT~SDS samples (excited at 785 nm (a) and 633 nm (b), centrifugation at 88 500 g).

with results reported previously.^[18] Furthermore, in the Raman spectra of SWCNT~Py~Ad~bMCD and SWCNT~Trp~Ad~bMCD samples, the G^+ component was shifted upfield by about 3 nm and 2 nm, respectively, indicating that the π - π stacking interaction between the pyrene and triptycene moieties and SWCNT sidewalls.^[22a,39]

When excited with a 785 nm laser, we observed several peaks centered at 205.4, 216.4, 236.2, and 265.9 cm^{-1} in the RBM section for the SWCNT samples centrifuged at 88 500 g (Figure 10, trace a, b, and c), corresponding to SWCNTs of 1.17, 1.10, 1.00, and 0.88 nm in diameter calculated according to the following equation [Eq. (2)]:^[18i,39c,41]

$$\omega_{\text{RBM}} = \frac{223.5}{d_t} + 12.5 \quad (2)$$

In Equation (2), ω_{RBM} represents the RBM frequency, d_t signifies the nanotube diameter, the constants 223.5 and 12.5 are taken from literature.^[42]

From the intensity of the RBM peaks, we observed that SWCNT~Trp~Ad~bMCD system (Figure 10, trace c) showed a remarkable selectivity for SWCNTs with a diameter of 1.00 nm, whereas the intensities for the other components with 1.17, 1.10, and 0.88 nm in diameter decreased significantly as compared with the SWCNT~SDS system

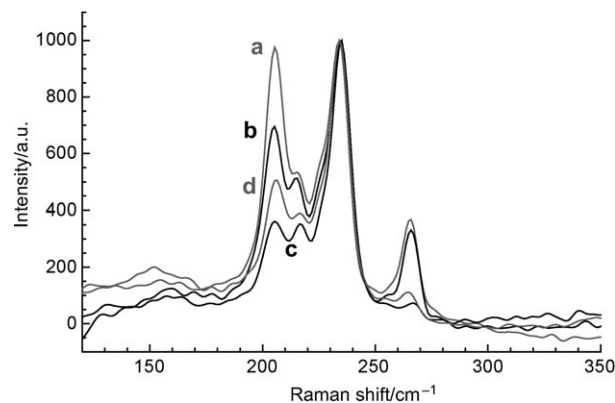


Figure 10. Resonant Raman spectra of a) SWCNT~SDS, b) SWCNT~Py~Ad~bMCD, and c) SWCNT~Trp~Ad~bMCD samples centrifuged at 88 500 g, and d) SWCNT~Trp~Ad~bMCD sample centrifuged at 14 000 g (excited at 785 nm)

(Figure 10, trace a). We did not, however, observe any evidence of diameter selectivity in the SWCNT~Py~Ad~bMCD system (Figure 10, trace b).

We also found that faster centrifugation enhanced the diameter selectivity of the SWCNT~Trp~Ad~bMCD system.^[43] The intensities of the peaks at 205.4, 216.4, and 265.9 cm^{-1} of the samples prepared through centrifugation at 14 000 g (Figure 10, trace d) are larger than those at 88 500 g (Figure 10, trace c), indicating that the selectivity for the component with a diameter of 1.00 nm over the others decreased owing to the slower centrifugation. However, we did not observe this effect in the SWCNT~Py~Ad~bMCD system. Furthermore, no influence was observed for the G-bands for all the SWCNT solutions.

Tromp et al. reported that pentacene-based molecular tweezers showed diameter-selectivity in toluene, whereas smaller anthracene-maleimide adducts did not work.^[23d] However, possessing similar dimension to anthracene-maleimide adducts, our triptycene binder showed strong surface modification ability and nice diameter selectivity. Chen and co-workers successfully attached triptycene orthoquinone on SWCNTs that were coated on a glassy carbon electrode.^[27] This is reasonable when considering that the driving force for triptycene-SWCNT sidewall interactions is much stronger in aqueous solution than in nonpolar organic solvents. Further, as compared with the anthracene-maleimide adduct, our triptycene binder possesses a much larger conjugate π system that was revealed through the UV absorbance and fluorescence emission (UV absorption peak at approximately 290 nm for Trp and approximately 270 nm for anthracene-maleic anhydride adducts).

The resonant Raman spectroscopy analysis of our ternary supramolecular SWCNT system demonstrated that the sidewalls of SWCNTs were surface modified by the polyaromatic binding groups through strong π - π stacking interaction. Modification by triptycene moieties led to diameter selectivity for SWCNTs with a diameter of 1.00 nm, and diameter selectivity was enhanced with faster centrifugation.

Conclusions

A novel approach to solubilize SWCNTs in the aqueous phase has been described by employing supramolecular surface modification. We used cyclodextrin complexes of synthetic molecules that contain a planar pyrene moiety or a bent, shape-fitted triptycene moiety as a binding group. This moiety is connected through a spacer to an adamantane moiety that is accommodated in the cyclodextrin cavity. The binding groups are attached to the sidewalls of SWCNTs through strong π - π stacking interaction, yielding a supramolecular system that made SWCNTs dissolve in the aqueous phase owing to the hydrophilic cyclodextrin shell. It was characterized through absorbance, static, and time-resolved fluorescence spectroscopy, Raman spectroscopy, and TEM. The results confirmed the strong π - π stacking interaction between the binding moieties (pyrene or triptycene) and the sidewalls of the SWCNTs, yielding stable aqueous SWCNT solutions. In aqueous SWCNT~Py~Ad~bMCD solution, fluorescence quenching and decay measurements revealed that a small amount of free pyrene moieties in the Py~Ad~bMCD complex form exist in the SWCNT solution that are accessible to quencher species, whereas most of the bound pyrene moieties on SWCNT sidewalls are inaccessible to quencher species. The shape-fitted triptycene-based system showed a pronounced selectivity for cylindrical SWCNTs with a diameter of 1.0 nm.

Experimental Section

Commercial reagents were used as received, unless otherwise stated. Methylated β -cyclodextrin (bMCD) was obtained from Wacker Chem. Single-walled carbon nanotubes were purchased from Carbon Nanotechnologies, Inc. (16200 Park Row, Houston TX 77084), and treated by using reported procedures.^[28,29] The bifunctional molecules **Py~Ad** and **Trp~Ad** were synthesized according to similar procedures reported previously (see the Supporting Information).

Preparation of aqueous SWCNT~Py~Ad~bMCD and SWCNT~Trp~Ad~bMCD solution: An alkaline solution at pH 8.0 was prepared by dissolving NaOH in pure water (Milli-Q, 18 M Ω cm) and used throughout our investigation except when indicated otherwise. Aqueous SWCNT~Py~Ad~bMCD solution was prepared by sonicating 12 mL of solution containing treated HiPco SWCNTs (1.0 mg), **Py~Ad** (4.6 mg, 0.01 mmol) and bMCD (131.0 mg, 0.10 mmol). Sonication was performed for about 1–3 h by using a KQ-100DB ultrasonicator with a 100 W input energy and the temperature was maintained at 20–30 °C. The sonicated samples were then centrifuged at different rates (14000 and 88500 g) for 30 min and the supernatants were used for all analyses. SWCNT~Trp~Ad~bMCD dispersion was prepared similarly by using treated HiPco SWCNTs (1.0 mg), **Trp~Ad** (7.3 mg, 0.01 mmol), and bMCD (261.0 mg, 0.20 mmol).

Control experiments: Several dispersions were prepared through identical procedures to the above preparation except without the addition of Py~Ad/Trp~Ad or Py~Ad/Trp~Ad, and bMCD. SWCNT~SDS dispersion was prepared by stirring 0.25 mg of SWCNTs in aqueous SDS (20 mg) solution (10 mL) at room temperature overnight, and subsequent processing with the above identical procedures.

Absorption spectra were obtained using a Perkin–Elmer Lambda 900 UV/Vis/NIR spectrophotometer and quartz cells with 1-cm or 1-mm path length. Photoluminescence spectra were obtained using a Perkin–Elmer LS55 luminescence spectrometer. Fluorescence decay profiles of the solu-

tions at 23 °C were recorded by using a nanosecond time-correlated single-photon-counting system from IBH. Each solution was placed in a quartz cell and excited with a NanoLED (λ_{ex} = 340 nm). An emission monochromator (385 \pm 16 nm) and two cut-off filters (346 nm and 370 nm) were used to minimize the amount of scattered light from the sample entering the detector. Data collected until 5000 or 10000 counts were accumulated in the maximum channel. The instrumental response function was obtained by using a degassed ludox solution as a standard. The supernatants (centrifuged at 88500 g) were diluted 10-fold with pure water, and 2- μ L volumes were dropped onto a copper grid (3.00 mm, 200 mesh, coated with carbon film). Samples were placed in a desiccator to dry for 24 h prior to TEM imaging. HRTEM images were acquired by using an FEI TECNAI G2 F20 transmission electron microscope at an accelerating voltage of 200 kV. Aqueous SWCNT~Py~Ad~bMCD or SWCNT~Trp~Ad~bMCD solution (2 μ L, centrifuged at 14000 or 88500 g) was spotted on a silicon substrate and allowed to dry in a desiccator overnight prior to analysis. Raman spectra of solid samples were obtained with a Renishaw inVia Raman spectrometer equipped with a charge-coupled device (CCD) detector. The laser excitation was provided by a regular model laser operating at 633 and 785 nm with 5% output power by using a 10 \times objective lens and a 25 μ m slit. The laser beam was focused on the substrate (approximately 1 μ m) and the exposure time is 10 s. Wavenumber calibration was carried out by using the line at 520.5 cm⁻¹ of the silicon wafer. Each curve is the average result of the signals coming from 10 different positions in the samples. Thermogravimetric analyses were performed on a Pyris Diamond TG/DTA instrument (5 °C min⁻¹, air). The samples were prepared by filtrating the SWCNT~Py~Ad~bMCD solution and SWCNT~Trp~Ad~bMCD solution carefully and dried in the vacuum oven before use.

Acknowledgements

The financial supports of the Ministry of Science and Technology of China (National Basic Research Program, grant no. 2007CB808000) and of National Science Foundation of China (grant no. 20672025) are acknowledged. We thank Dr. M. Antonietti at MPI KG for his insightful discussion, Dr. M. Winnik at the University of Toronto for his helpful discussion, and Dr. G. Guerin for reading our manuscript. Z.S.Z. thanks Mr. Tian-Long Zhang for his assistance with the quantum yield measurements.

- [1] S. Iijima, *Nature* **1991**, 354, 56–58.
- [2] S. Iijima, T. Ichihashi, *Nature* **1993**, 363, 603–605.
- [3] a) Carbon Nanotubes (Eds.: M. S. Dresselhaus, G. Dresselhaus, Ph. Avouris), *Top. Appl. Phys.* **2001**, 80, 1–425; b) Special Issue on Carbon Nanotubes (Ed.: R. C. Haddon), *Acc. Chem. Res.* **2002**, 35, 997–1113; c) M. Terrones, *Annu. Rev. Mater. Sci.* **2003**, 33, 419–501.
- [4] a) H. Hu, B. Zhao, M. E. Itkis, R. C. Haddon, *J. Phys. Chem. B* **2003**, 107, 13838–13842; b) C. A. Furtado, U. J. Kim, H. R. Gutierrez, L. Pan, E. C. Dickey, P. C. Eklund, *J. Am. Chem. Soc.* **2004**, 126, 6095–6105.
- [5] a) D. Tasis, N. Tagmatarchis, V. Georgakilas, M. Prato, *Chem. Eur. J.* **2003**, 9, 4000–4008; b) A. Hirsch, O. Vostrowsky, *Top. Curr. Chem.* **2005**, 245, 193–237; c) H. Murakami, N. Nakashima, *J. Nanosci. Nanotechnol.* **2006**, 6, 16–27.
- [6] a) A. Hirsch, *Angew. Chem.* **2002**, 114, 1933–1939; *Angew. Chem. Int. Ed.* **2002**, 41, 1853–1859; b) R. K. Saini, I. W. Chiang, H. Peng, R. E. Smalley, W. E. Billups, R. H. Hauge, J. L. Margrave, *J. Am. Chem. Soc.* **2003**, 125, 3617–3621; c) K. Balasubramanian, M. Burghard, *Small* **2005**, 1, 180–192.
- [7] R. Bandyopadhyaya, E. Nativ-Roth, O. Regev, R. Yerushalmi-Rozen, *Nano Lett.* **2002**, 2, 25–28.
- [8] A. Star, D. W. Steuerman, J. R. Heath, J. F. Stoddart, *Angew. Chem.* **2002**, 114, 2618–2622; *Angew. Chem. Int. Ed.* **2002**, 41, 2508–2512.
- [9] O.-K. Kim, J. Je, J. W. Baldwin, S. Kooi, P. E. Pehrsson, L. J. Buckley, *J. Am. Chem. Soc.* **2003**, 125, 4426–4427.

- [10] X. Chen, G. S. Lee, A. Zettl, C. R. Bertozzi, *Angew. Chem.* **2004**, *116*, 6237–6242; *Angew. Chem. Int. Ed.* **2004**, *43*, 6111–6116.
- [11] M. Numata, M. Asai, K. Kaneko, A.-H. Bae, T. Hasegawa, K. Sakurai, S. Shinkai, *J. Am. Chem. Soc.* **2005**, *127*, 5875–5884.
- [12] Y. Liu, P. Liang, H. Y. Zhang, D. S. Guo, *Small* **2006**, *2*, 874–878.
- [13] a) H. Yang, S. C. Wang, P. Mercier, D. L. Akins, *Chem. Commun.* **2006**, 1425–1427; b) Y. Liu, Z.-L. Yu, Y.-M. Zhang, D.-S. Guo, Y.-P. Liu, *J. Am. Chem. Soc.* **2008**, *130*, 10431–10439.
- [14] a) V. Zorbas, A. Ortiz-Acevedo, A. B. Dalton, M. M. Yoshida, G. R. Dieckmann, R. K. Draper, R. H. Baughman, M. Jose-Yacamán, I. H. Musselman, *J. Am. Chem. Soc.* **2004**, *126*, 7222–7227; b) B. Wegenhart, L. Tan, M. Held, M. Kieliszewski, L. Chen, *Nanoscale Res. Lett.* **2006**, *1*, 154–159.
- [15] a) M. Zheng, A. Jagota, E. D. Semke, B. A. Diner, R. S. McLean, S. R. Lustig, R. E. Richardson, N. G. Tassi, *Nat. Mater.* **2003**, *2*, 338–342; b) M. Zheng, A. Jagota, M. S. Strano, A. P. Santos, P. Barone, S. G. Chou, B. A. Diner, M. S. Dresselhaus, R. S. McLean, G. B. Onoa, G. G. Samsonidze, E. D. Semke, M. Usrey, D. J. Walls, *Science* **2003**, *302*, 1545–1548; c) N. Nakishima, S. Okuzuno, H. Murakami, T. Nakai, K. Yoshikawa, *Chem. Lett.* **2003**, *32*, 456–457; d) M. Zheng, B. A. Diner, *J. Am. Chem. Soc.* **2004**, *126*, 15490–15494; e) M. Zheng, E. D. Semke, *J. Am. Chem. Soc.* **2007**, *129*, 6084–6085; f) Y. Noguchi, T. Fujigaya, Y. Niidome, N. Nakashima, *Chem. Eur. J.* **2008**, *14*, 5966–5973; g) Y. Noguchi, T. Fujigaya, Y. Niidome, N. Nakashima, *Chem. Phys. Lett.* **2008**, *455*, 249–251.
- [16] G. Nakamura, K. Narimatsu, Y. Niidome, N. Nakashima, *Chem. Lett.* **2007**, *36*, 1140–1141.
- [17] a) Y. Liu, L. Gao, S. Zheng, Y. Wang, J. Sun, H. Kajiu, Y. Li, K. Noda, *Nanotechnology* **2007**, *18*, 365702; b) Y. Liu, L. Gao, J. Sun, *J. Phys. Chem. C* **2007**, *111*, 1223–1229.
- [18] a) B. Z. Tang, H. Xu, *Macromolecules* **1999**, *32*, 2569–2576; b) M. J. O'Connell, P. Boul, L. M. Ericson, C. Huffman, Y. Wang, E. Haroz, C. Kuper, J. M. Tour, K. D. Ausman, R. E. Smalley, *Chem. Phys. Lett.* **2001**, *342*, 265–271; c) A. Star, J. F. Stoddart, D. Steuerman, M. Diehl, A. Boukai, E. W. Wong, X. Yang, S. W. Chung, H. Choi, J. R. Heath, *Angew. Chem.* **2001**, *113*, 1771–1775; *Angew. Chem. Int. Ed.* **2001**, *40*, 1721–1725; d) A. Star, J. F. Stoddart, *Macromolecules* **2002**, *35*, 7516–7520; e) J. Chen, H. Liu, W. A. Weiner, M. D. Halls, D. H. Waldeck, G. C. Walker, *J. Am. Chem. Soc.* **2002**, *124*, 9034–9035; f) C. A. Mitchell, J. L. Bahr, S. Arepalli, J. M. Tour, R. Krishnamoorti, *Macromolecules* **2002**, *35*, 8825–8830; g) A. Star, Y. Liu, K. Grant, L. Ridvan, J. F. Stoddart, D. W. Steuerman, M. R. Diehl, A. Boukai, J. R. Heath, *Macromolecules* **2003**, *36*, 553–560; h) M. S. Strano, C. A. Dyke, M. L. Usrey, P. W. Barone, M. J. Allen, H. Shan, C. Kittrell, R. H. Hauge, J. M. Tour, R. E. Smalley, *Science* **2003**, *301*, 1519–1522; i) H. Paloniemi, T. Äärilä, T. Laiho, H. Liuke, N. Kocharova, K. Haapakka, F. Terzi, R. Seeber, J. Lukkari, *J. Phys. Chem. B* **2005**, *109*, 8634–8642; j) Y. Tomonari, H. Murakami, N. Nakashima, *Chem. Eur. J.* **2006**, *12*, 4027–4034; k) R. Chen, B. Wang, Y. Chen, L. J. Li, *Nano Lett.* **2007**, *7*, 3013–3017; l) A. Nish, J. Y. Hwang, J. Doig, R. J. Nicholas, *Nat. Nanotechnol.* **2007**, *2*, 640–646.
- [19] a) F. J. Gómez, R. J. Chen, D. Wang, R. M. Waymouth, H. Dai, *Chem. Commun.* **2003**, 190–191; b) X. Lou, R. Daussin, S. Cuenot, A. S. Duwez, C. Pagnoulle, C. Detrembleur, C. Bailly, R. Jérôme, *Chem. Mater.* **2004**, *16*, 4005–4011; c) W. Z. Yuan, J. Z. Sun, Y. Dong, M. Häussler, F. Yang, H. P. Xu, A. Qin, J. W. Y. Lam, Q. Zheng, B. Z. Tang, *Macromolecules* **2006**, *39*, 8011–8020; d) P. G. Holder, M. B. Francis, *Angew. Chem.* **2007**, *119*, 4448–4451; *Angew. Chem. Int. Ed.* **2007**, *46*, 4370–4373; e) D. Wang, W. X. Ji, Z. C. Li, L. Chen, *J. Am. Chem. Soc.* **2006**, *128*, 6556–6557.
- [20] a) R. J. Chen, Y. Zhang, D. Wang, H. Dai, *J. Am. Chem. Soc.* **2001**, *123*, 3838–3839; b) N. Nakashima, Y. Tomonari, H. Murakami, *Chem. Lett.* **2002**, 638–639; c) T. Ogoshi, Y. Takashima, H. Yamaguchi, A. Harada, *J. Am. Chem. Soc.* **2007**, *129*, 4878–4879; d) K. A. S. Fernando, Y. Lin, W. Wang, S. Kumar, B. Zhou, S. Y. Xie, L. T. Cureton, Y. P. Sun, *J. Am. Chem. Soc.* **2004**, *126*, 10234–10235.
- [21] a) D. M. Guldi, G. M. A. Rahman, N. Jux, N. Tagmatarchis, M. Prato, *Angew. Chem.* **2004**, *116*, 5642–5646; *Angew. Chem. Int. Ed.* **2004**, *43*, 5526–5530; b) D. M. Guldi, G. M. A. Rahman, N. Jux, D. Balbinot, U. Hartnagel, N. Tagmatarchis, M. Prato, *J. Am. Chem. Soc.* **2005**, *127*, 9830–9838; c) C. Ehli, G. M. A. Rahman, N. Jux, D. Balbinot, D. M. Guldi, F. Paolucci, M. Marcaccio, D. Paolucci, M. Melle-Franco, F. Zerbetto, S. Campidelli, M. Prato, *J. Am. Chem. Soc.* **2006**, *128*, 11222–11231; d) V. Sgobba, G. M. A. Rahman, D. M. Guldi, N. Jux, S. Campidelli, M. Prato, *Adv. Mater.* **2006**, *18*, 2264–2269; e) J. S. Kavakka, S. Heikkinen, I. Kilpeläinen, M. Mattila, H. Lipsanen, J. Helaja, *Chem. Commun.* **2007**, 519–521; f) M. Á. Heranz, C. Ehli, S. Campidelli, M. Gutiérrez, G. L. Hug, K. Ohkubo, S. Fukuzumi, M. Prato, N. Martín, D. M. Guldi, *J. Am. Chem. Soc.* **2008**, *130*, 66–73.
- [22] a) J. Zhang, J. K. Lee, Y. Wu, R. W. Murray, *Nano Lett.* **2003**, *3*, 403–407; b) N. Nakashima, *Sci. Technol. Adv. Mater.* **2006**, *7*, 609–616.
- [23] a) A. Kukovecz, T. Pichler, R. Pfeiffer, C. Kramberger, H. Kuzmany, *Phys. Chem. Chem. Phys.* **2003**, *5*, 582–587; b) A. Ortiz-Acevedo, H. Xie, V. Zorbas, W. M. Sampson, A. B. Dalton, R. H. Baughman, R. K. Draper, I. H. Musselman, G. R. Dieckmann, *J. Am. Chem. Soc.* **2005**, *127*, 9512–9517; c) Z. B. Zhang, S. L. Zhang, *J. Am. Chem. Soc.* **2007**, *129*, 666–671; d) R. M. Tromp, A. Afzali, M. Freitag, D. B. Mitzi, Z. Chen, *Nano Lett.* **2008**, *8*, 469–472.
- [24] T. Ogoshi, M. Ikeya, T. A. Yamagishi, Y. Nakamoto, A. Harada, *J. Phys. Chem. C* **2008**, *112*, 13079–13083.
- [25] a) W. Saenger, *Angew. Chem.* **1980**, *92*, 343–361; *Angew. Chem. Int. Ed. Engl.* **1980**, *19*, 344–362; b) *Comprehensive Supramolecular Chemistry: Cyclodextrins, Vol. 3* (Eds.: J. Szejtli, T. Osa), Pergamon, Oxford, UK, **1996**; c) G. Wenz, B. H. Han, A. Müller, *Chem. Rev.* **2006**, *106*, 782–817.
- [26] a) X. Peng, N. Komatsu, S. Bhattacharya, T. Shimawaki, S. Aonuma, T. Kimura, A. Osuka, *Nat. Nanotechnol.* **2007**, *2*, 361–365; b) X. Peng, N. Komatsu, T. Kimura, A. Osuka, *J. Am. Chem. Soc.* **2007**, *129*, 15947–15953.
- [27] K. Gong, X. Zhu, R. Zhao, S. Xiong, L. Mao, C. Chen, *Anal. Chem.* **2005**, *77*, 8158–8165.
- [28] a) Y. Liu, A. Adronov, *Macromolecules* **2004**, *37*, 4755–4760; b) Y. Liu, Z. Yao, A. Adronov, *Macromolecules* **2005**, *38*, 1172–1179.
- [29] W. Zhao, C. Song, P. E. Pehrsson, *J. Am. Chem. Soc.* **2002**, *124*, 12418–12419.
- [30] Raman spectra showed that there is no obvious difference in the intensity ratio of D-band and G-band between the pristine and treated SWCNT samples, suggesting that the high quality of the treated SWCNTs. This was also supported by the NIR absorption spectra of aqueous SWCNT solution where the van Hove features of SWCNTs are retained.
- [31] a) W. C. Cromwell, K. Bystrom, M. R. Eftink, *J. Phys. Chem.* **1985**, *89*, 326–332; b) M. R. Eftink, M. L. Andy, K. Bystrom, H. D. Perlmutter, D. S. Kristol, *J. Am. Chem. Soc.* **1989**, *111*, 6765–6772.
- [32] The concentrations of pyrene moieties in the obtained aqueous Py-Ad-bMCD and SWCNT-Py-Ad-bMCD solutions were estimated to be about 8.2×10^{-5} M and 5.1×10^{-4} M, respectively, according to the extinction coefficient of pyrene in methanol ($\sim 5.0 \times 10^4$ M⁻¹ cm⁻¹).
- [33] a) J. Chen, C. P. Collier, *J. Phys. Chem. B* **2005**, *109*, 7605–7609; b) D. Wang, L. Chen, *Nano Lett.* **2007**, *7*, 1480–1484; c) A. Ikeda, Y. Tanaka, K. Nobusawa, J. I. Kikuchi, *Langmuir* **2007**, *23*, 10913–10915; d) L. Y. Yan, Y. F. Poon, M. B. Chan-Park, Y. Chen, Q. Zhang, *J. Phys. Chem. C* **2008**, *112*, 7579–7587.
- [34] A. Ikeda, K. Hayashi, T. Konishi, J. Kikuchi, *Chem. Commun.* **2004**, 1334–1335.
- [35] a) J. Amiran, V. Nicolosi, S. D. Bergin, U. Khan, P. E. Lyons, J. N. Coleman, *J. Phys. Chem. C* **2008**, *112*, 3519–3524; b) Z. Sun, V. Nicolosi, D. Rickard, S. D. Bergin, D. Aherne, J. N. Coleman, *J. Phys. Chem. C* **2008**, *112*, 10692–10699.
- [36] a) V. Georgakilas, K. Kordatos, M. Prato, D. M. Guldi, M. Holzinger, A. Hirsch, *J. Am. Chem. Soc.* **2002**, *124*, 760–761; b) D. M. Guldi, G. M. A. Rahman, F. Zerbetto, M. Prato, *Acc. Chem. Res.* **2005**, *38*, 871–878.

- [37] a) J. N. Demas, G. A. Crosby, *J. Phys. Chem.* **1971**, 75, 991–1024; b) R. F. Kubin, A. N. Fletcher, *J. Lumin.* **1982**, 27, 455–462.
- [38] J. R. Lakowicz, *Principles of Fluorescence Spectroscopy*, 3rd ed., Springer, Singapore, **2006**.
- [39] a) M. S. Dresselhaus, G. Dresselhaus, *Adv. Phys.* **1981**, 30, 139–326; b) T. Enoki, M. Endo, M. Suzuki, *Graphite Intercalation Compounds and Applications*, Oxford University Press, New York, **2003**; c) M. S. Dresselhaus, G. Dresselhaus, R. Saito, A. Jorio, *Phys. Rep.* **2005**, 409, 47–99.
- [40] a) R. Krupke, F. Hennrich, H. Löhneysen, M. M. Kappes, *Science* **2003**, 301, 344–347; b) D. Chattopadhyay, I. Galeska, F. Papadimitrakopoulos, *J. Am. Chem. Soc.* **2003**, 125, 3370–3375.
- [41] a) G. Gouadec, P. Colomban, *Prog. Cryst. Growth Charact. Mater.* **2007**, 53, 1–56; b) M. S. Dresselhaus, G. Dresselhaus, A. Jorio, A. G. S. Filho, M. A. Pimenta, R. Saito, *Acc. Chem. Res.* **2002**, 35, 1070–1078; c) R. Saito, H. Kataura, *Top. Appl. Phys.* **2001**, 80, 213–247.
- [42] S. M. Bachilo, M. S. Strano, C. Kittrell, R. H. Hauge, R. E. Smalley, R. B. Weisman, *Science* **2002**, 298, 2361–2366.
- [43] M. S. Arnold, A. A. Green, J. F. Hulvat, S. I. Stupp, M. C. Hersam, *Nat. Nanotechnol.* **2006**, 1, 60–65.

Received: May 8, 2009

Published online: August 17, 2009