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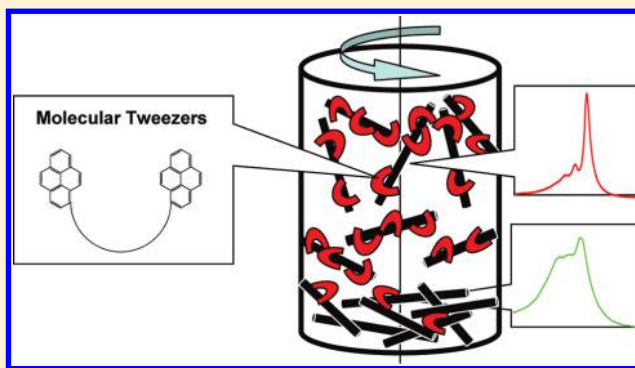
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# Facile and Effective Post-Production Separation of Single-Walled Carbon Nanotubes with Paired Aromatic Molecules: A Molecular Tweezers Approach

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**ABSTRACT:** As-produced single-walled carbon nanotubes (SWNTs) are mostly metallic and semiconducting mixtures. The population of semiconducting SWNTs in the as-produced mixtures is generally much higher than that of their metallic counterparts. Therefore, postproduction separation of metallic and semiconducting SWNTs is important to many potential uses of the nanotubes, especially those demanding higher electrical conductivity yet lower optical absorption. Because planar aromatic species are known to have somewhat different interactions with metallic and semiconducting SWNTs, in this work a molecule with a pair of planar aromatic moieties was specifically designed and synthesized to exaggerate the difference in its noncovalent functionalization and solubilization of the two types of nanotubes. As demonstrated, the molecule exhibited significant selectivity toward semiconducting SWNTs in the solubilization to allow the convenient harvesting of bulk metallic and semiconducting fractions in high purities. The results suggest that molecules with paired aromatic species or essentially molecular tweezers may represent a new class of agents for more effective and also relatively simple postproduction bulk separation of metallic and semiconducting SWNTs.



## INTRODUCTION

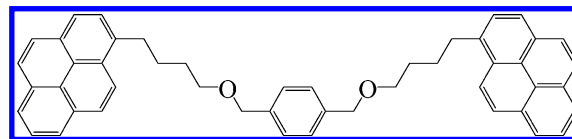
Single-walled carbon nanotubes (SWNTs) have been extensively investigated for their wide variety of potential applications, from serving as excellent electrical conductors for transparent electrodes in optoelectronic devices and other energy conversion systems,<sup>1–5</sup> to being used in field-emission transistors or for the harvesting of infrared photons in detectors or for hyperthermia cancer therapy.<sup>5,6</sup> However, as-produced SWNTs are mostly mixtures as an SWNT is either metallic or semiconducting. The population of semiconducting SWNTs in the as-produced mixtures is generally higher than that of their metallic counterparts, with a statistically predicted ratio of 2-to-1. Therefore, postproduction separation of metallic and semiconducting SWNTs is important to many potential uses of the nanotubes, especially those demanding higher electrical conductivity yet lower optical absorption.<sup>5</sup>

Significant effort and progress have been made in the development of methodologies for postproduction separation of metallic and semiconducting SWNTs.<sup>5,7–17</sup> These methods mostly explore differences between metallic and semiconducting SWNTs in loading molecular species such as DNA and surfactant or in interacting with various carefully selected or specifically designed molecules, so as to amplify the differences to allow subsequent applications of conventional separation techniques such as centrifugation. A well-established example is the supercentrifugation fractionation of SWNTs wrapped with

DNA or surfactant molecules.<sup>13,14</sup> For the approaches more relevant to this work, noncovalent interactions that are different between metallic and semiconducting SWNTs with the selected separation agents, such as amino molecules,<sup>8,12</sup> planar aromatic derivatives,<sup>10,11,18</sup> and other species,<sup>17</sup> have been used to impart significant solubility disparities between the nanotubes to enable subsequent relatively simple gravimetric separation.

Here, we report the synthesis of a molecule with a pair of planar aromatic moieties (Scheme 1) specifically designed to

**Scheme 1.** 1,1'-Bis-purenebutyoxyl-*p*-xylene (bis-pyrene)



exaggerate the difference between metallic and semiconducting SWNTs in the noncovalent functionalization and solubilization. As demonstrated, the molecule exhibited significant selectivity toward semiconducting SWNTs in the solubilization to allow the convenient harvesting of bulk metallic and semiconducting

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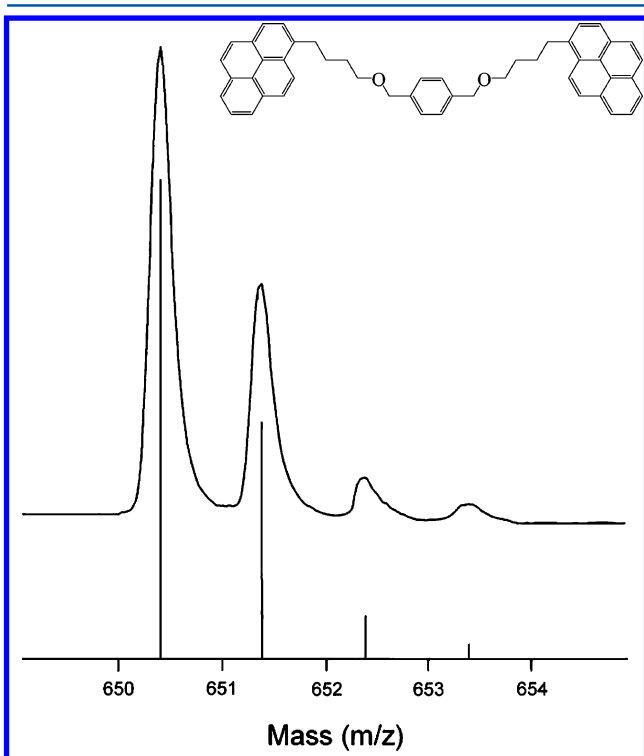
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fractions of high purities. The results suggest that molecules with paired aromatic species or essentially molecular tweezers may represent a new class of agents for more effective and also relatively simple postproduction bulk separation of metallic and semiconducting SWNTs.

## RESULTS AND DISCUSSION

The molecule containing a pair of planar aromatic moieties was designed such that it would be able to noncovalently functionalize and solubilize SWNTs with selectivity toward the semiconducting ones. Because the simple pyrene derivative 1-docosyloxymethyl-pyrene (DomP) was found to exhibit these desired functions and selectivity,<sup>11,18,19</sup> the bis-pyrene structure shown in Scheme 1 was selected for its resembling a pair of DomP, with more structural flexibility around the pyrene moiety for better solubility characteristics. It also contributed to the selection of the molecule because of its relatively straightforward synthesis. Briefly, 1-pyrenebutanol was reacted with anhydrous sodium hydride for the conversion to alkoxide, which was then coupled with 1,1'-dibromo-*p*-xylene in dry THF to form the bis-pyrene compound (Scheme 1) in good yield (70% in terms of the purified sample). The molecular structure was characterized in terms of <sup>1</sup>H and <sup>13</sup>C NMR measurements, and confirmed unambiguously by the matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) MS results (Figure 1).



**Figure 1.** Observed MALDI-TOF MS trace for the bis-pyrene (in 2,5-dihydroxybenzoic acid matrix) is compared with the prediction (Chemdraw 8.0) reflecting isotope compositions.

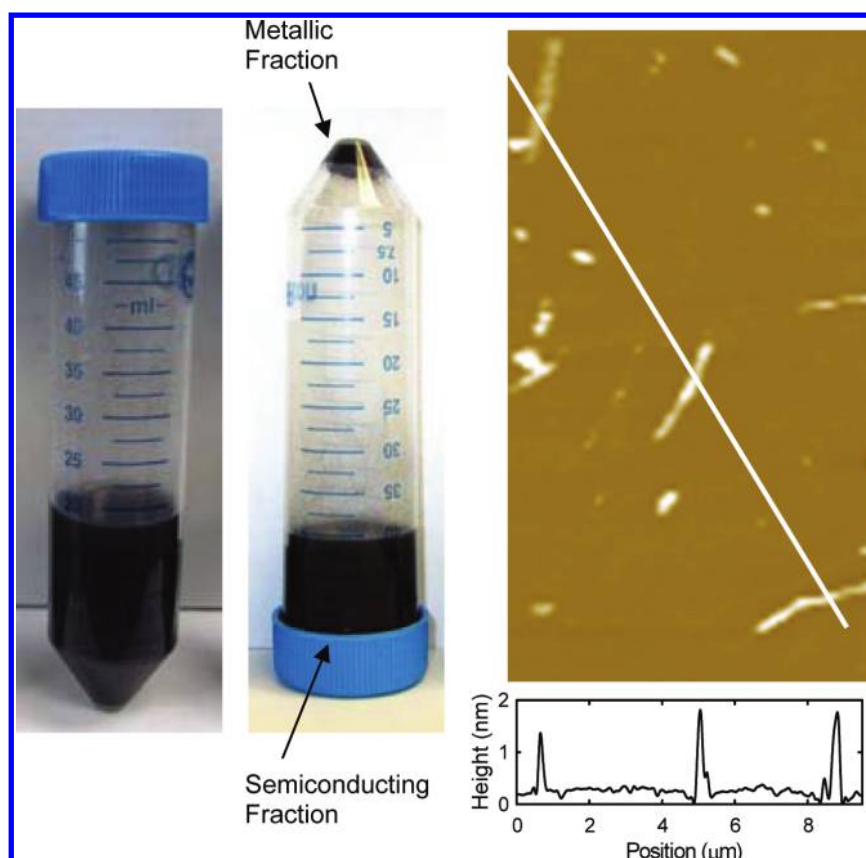
The bis-pyrene compound was used to noncovalently functionalize purified SWNTs in a mixture of dry THF and toluene (80/20, v/v) to form a relatively stable dispersion (Figure 2). A specimen was prepared from the dispersion for atomic force microscopy (AFM) analyses, and individualized SWNTs were found in the images (Figure 2). In a centrifuging

field, however, the dispersion could be fractionated by using different *g* values. The first fraction was obtained as the sediment at 1000 *g* centrifugation (Figure 2), the middle fraction in relatively much smaller quantity as the sediment at the subsequent 2000*g* centrifugation, and the remaining supernatant as the last fraction. The three fractions thus obtained were washed thoroughly to remove the bis-pyrene for recycling, resulting in three solid-state samples of the fractionated SWNTs.

The first and last fractions, accounting for about 32% and 62% of the starting purified nanotube sample prefractionation, were dispersed in DMF for optical absorption measurements. Shown in Figure 3 are their absorption spectra to 1300 nm right before the solvent cutoff, thus covering the spectral region for *S*<sub>22</sub> (the transition associated with the second pair of van Hove singularity in the electronic density of states in semiconducting SWNTs,<sup>20</sup> centered at ~1015 nm for arc-discharge produced nanotubes used in this study). The nearly absent *S*<sub>22</sub> absorption in the first fraction and the strong band for the last fraction indicated that the first and last fractions were significantly enriched with metallic and semiconducting SWNTs, respectively. With the starting purified nanotube sample prefractionation containing 1/3 metallic and 2/3 semiconducting SWNTs (Figure 3), the calculation based on *S*<sub>22</sub> absorptions of the nanotube samples well-dispersed in DMF suggested the semiconducting content of only about 8% in the first fraction and 97% in the last fraction. Therefore, about 94% of the starting purified nanotube sample was separated in such a relatively simple single-step process into highly enriched metallic SWNTs and nearly pure semiconducting SWNTs demonstrating the effectiveness in terms of the molecular tweezers approach for the postproduction bulk separation of metallic and semiconducting SWNTs.

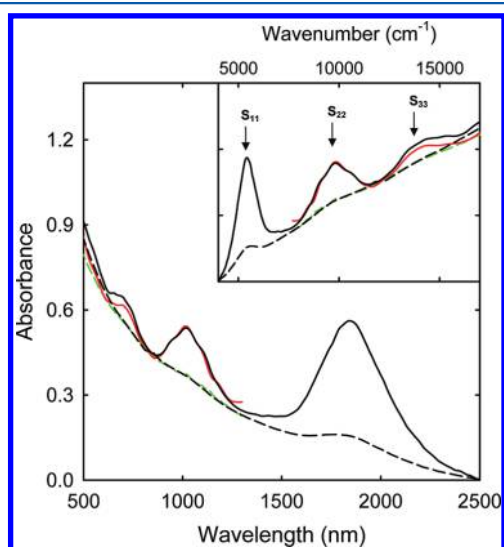
Also shown in Figure 3 are absorption spectra of the same nanotube fractions in solid-state thin films, extending the spectral range to cover the *S*<sub>11</sub> absorption band (the transition associated with the first van Hove singularity pair in semiconducting SWNTs). For the *S*<sub>22</sub> absorption band of the semiconducting fraction in DMF dispersion, the Beer's law calculation yielded an absorptivity of 5.8 (g/L)<sup>-1</sup> cm<sup>-1</sup> or 70 *M*<sub>Carbon</sub><sup>-1</sup> cm<sup>-1</sup> (where *M*<sub>Carbon</sub> denotes molar concentration in terms of nanotube carbon) at the *S*<sub>22</sub> band peak (1015 nm, Figure 3). By assuming the value unchanged from the DMF dispersion to the nanotube film, the absorptivity for the *S*<sub>11</sub> band was estimated as 11.8 (g/L)<sup>-1</sup> cm<sup>-1</sup> or 142 *M*<sub>Carbon</sub><sup>-1</sup> cm<sup>-1</sup> at the peak (1840 nm, Figure 3). Whereas in general agreement with those from processing multiple sets of experimental results reported by different laboratories,<sup>21,22</sup> these *S*<sub>11</sub> and *S*<sub>22</sub> absorptivity results should be considered as being more accurate because they were obtained from direct measurements of nearly pure semiconducting SWNTs.

Results from resonance Raman characterization of the first and last fractions were consistent with their being substantially enriched with metallic and semiconducting SWNTs, respectively. As compared in Figure 4, the G-band (peaking around 1590 cm<sup>-1</sup>) for the first fraction is much broader than that for the starting purified nanotube sample, characteristic of the Breit–Wigner–Fano (BWF) feature exhibited by metallic SWNTs.<sup>23</sup> However, the G-band for the last fraction is much narrower (Figure 4), consistent with the removal of metallic SWNTs from the prefractionation mixture to yield nearly pure semiconducting SWNTs.

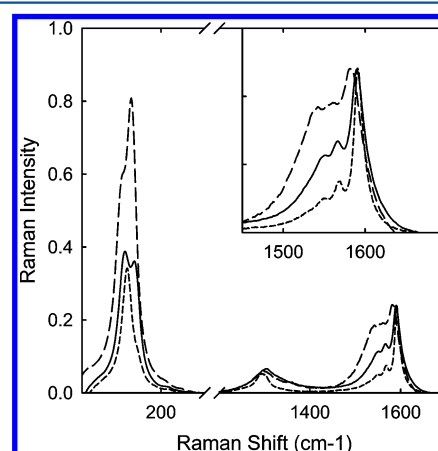


**Figure 2.** Left: Photographs showing SWNTs solubilized by the bis-pyrene in the THF–toluene mixture (80/20, v/v) before (left tube) and after (residue and supernatant, right tube) centrifugation at 1000g. Right: AFM image on a specimen prepared from the dispersion in the left tube, with the nanotubes featured in the height analysis on the order of submicrometer length.

The middle fraction in relatively much smaller quantity was apparently a mixture closer to the pre-separation purified sample. Its collection in a higher centrifuging field after the first fraction was necessary to make the last fraction purer in



**Figure 3.** Optical absorption spectra of the separated metallic (dashed lines, green: in DMF dispersion and black: in solid-state thin film) and semiconducting (solid lines, red: in DMF dispersion and black: in solid-state thin film) fractions. The same spectra on the wavenumber scale are shown in the insert, with the  $S_{11}$ ,  $S_{22}$ , and  $S_{33}$  peaks marked.



**Figure 4.** Raman spectra (785 nm excitation, with the G-band region featured in the insert) of the pre-separation SWNTs (solid line), and the separated metallic (long dashed line) and semiconducting (short dashed line) fractions.

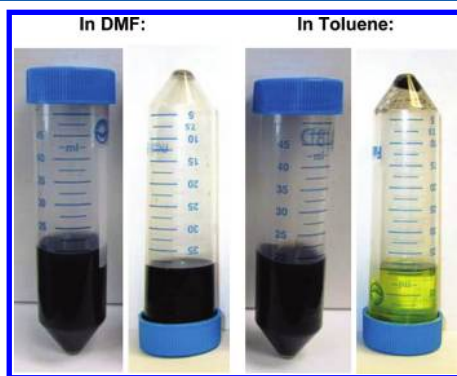
semiconducting SWNTs. The sample could be further separated or recycled (mixed with purified nanotube samples for the same fractionation experiments).

Mechanistically, the bis-pyrene must be more selective toward attaching and solubilizing semiconducting SWNTs, more so than a molecule like DomP with only a single pyrene moiety.<sup>11</sup> As a result, the less functionalized and solubilized metallic SWNTs could be preferentially precipitated in a relatively weak centrifuging field. Again in comparison with



DomP or the like, the molecular tweezers approach to use a functionalization agent containing a pair of planar aromatic moieties apparently amplifies the selectivity in the noncovalent functionalization and associated solubilization between metallic and semiconducting SWNTs, enabling their separation in a facile process to yield purer metallic SWNTs and nearly pure semiconducting SWNTs.

As the separation was associated with the difference in solubilization between metallic and semiconducting SWNTs by the bis-pyrene, it was obviously dependent on the solvent environment. For example, in neat DMF or neat toluene, the same fractionation process resulted in nearly no changes in the metallic-to-semiconducting ratio in various fractions. The former is known as an excellent solvent for dispersing SWNTs, so that the centrifugation of the dispersion in DMF (even at 3000g) yielded essentially no precipitation (Figure 5).



**Figure 5.** Photographs on the solubilization of SWNTs by the bis-pyrene in DMF before (left tube) and after (right tube) centrifugation at 3000 g and in toluene before (left tube) and after (right tube) centrifugation at 1000 g.

Toluene has a lower solvent strength and more nanotube-phobic, in which the noncovalent functionalization and solubilization of SWNTs by the bis-pyrene were apparently less effective, so that in the centrifuging field of 1000g essentially no nanotubes remained in the supernatant (Figure 5). Therefore, the balance of solubility characteristics with the use of a solvent mixture in this study was more effective. Whereas in principle other solvents or solvent mixtures might be coupled with different centrifuging fields to yield similar or even somewhat better separation results, the improvements are probably limited as the purities in the separated samples discussed above are already high. Nevertheless, the solvent effects may help the understanding and exploitation of noncovalent interactions of molecular tweezers-like species with nanotubes and the obvious selectivity between metallic and semiconducting SWNTs.

Carbon nanotubes are characterized by their extended  $\pi$ -networks, with which strong interactions by planar aromatic molecules are logically expected and to a significant extent supported by available experimental and computational results. It is probably no surprise that the  $\pi$ - $\pi$  interactions with carbon nanotubes are dependent on the electronic structures of the nanotubes. In solution-phase carbon nanotubes are probably also polarized to the extent that there are localized charges on surface (which may be facilitated or enhanced by the presence of surface defects), responsible for complexation with the planar aromatic moieties. Such polarization effect and consequently the complexation may be different between

metallic and semiconducting SWNTs. The results presented here suggest that the different electronic structures between the two kinds of SWNTs do manifest themselves in the  $\pi$ - $\pi$  interactions and complexation with planar aromatic species and that the difference can be amplified with the use of molecules containing paired aromatic moieties (molecular tweezers). As reported above, a valuable exploitation of the enhanced selectivity in such interactions is for the more efficient postproduction separation of metallic and semiconducting SWNTs to yield metallicity-wise pure or purer nanotube samples. Beyond the separation, however, the same enhanced selectivity from the use of molecular tweezers may find other applications such as more effective noncovalent functionalization and debundling of SWNTs or in sensors and other nanotube-based devices.

## EXPERIMENTAL SECTION

**Materials.** The nanotube samples (arc-discharge production) were acquired from Carbon Solutions ("AP-SWNT", carbonaceous purity 40–60%) or produced in house. 1-Pyrenebutanol and 1,1'-dibromo-*p*-xylene were purchased from Aldrich. Nitric acid (HNO<sub>3</sub>) was obtained from Fisher Scientific, concentrated hydrochloric acid (HCl, 37%), anhydrous sodium hydride (NaH, 60% in oil), sodium hydroxide (NaOH), and anhydrous sodium sulfate (Na<sub>2</sub>SO<sub>4</sub>) from Acros, and tetrahydrofuran (THF), toluene, ethyl acetate, and dimethyl formamide (DMF) from Mallinckrodt. The organic solvents were distilled prior to use. Membrane filters (PVDF, 0.22  $\mu$ m pore size) were supplied by Fisher Scientific. Water was deionized and purified by being passed through a Labconco WaterPros water purification system.

**Measurements.** Bench-top centrifuge (Fisher Scientific Model 228), homogenizer (PowerGen 125), and bath sonicator (VWR Model 250D) were used in the nanotube purification and separation experiments. Optical absorption spectra were recorded on Shimadzu UV-3100 and UV-3600 spectrophotometers. Raman spectra were obtained on a Renishaw Raman spectrometer equipped with a 50 mW diode laser source for 785 nm excitation. Atomic force microscopy (AFM) imaging was carried out in the acoustic AC mode on a Molecular Imaging PicoPlus system equipped with a multipurpose scanner and a NanoWorld Pointprobe NCH sensor. The height profile analysis was assisted by using the SPIP software distributed by Image Metrology.

**1,1'-Bis-pyrenebutyoxyl-*p*-xylene (bis-pyrene).** A mixture of 1-pyrenebutanol (1 g, 3.65 mmol) and anhydrous NaH (60% in oil, 0.888 g, 36.5 mmol) in dry THF (100 mL) was prepared, and the mixture was heated to 60 °C for 1 h under nitrogen atmosphere. Upon its being cooled to room temperature, a solution of 1,1'-dibromo-*p*-xylene (480 mg, 1.85 mmol) in dry THF (50 mL) was added dropwise. The resulting mixture was refluxed at 70 °C for 48 h under nitrogen purging, and then cooled back to room temperature. The solvent was removed on a rotary evaporator, and the residue was extracted with chloroform and then filtered. The chloroform solution was washed with water (4  $\times$  25 mL), and the organic layer was collected and dried with anhydrous sodium sulfate. Upon filtration and solvent evaporation, the resulting yellow oil-like sample was purified on a silica gel column with hexane as eluent. The bis-pyrene was obtained as a light-yellow solid sample (840 mg, 70% yield). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz):  $\delta$  8.25–8.23 (d, 2H), 8.14–8.12 (d, 4H), 8.08–8.04 (m, 4H), 8.02–8.00 (d, 4H), 7.98–7.94 (t, 2H),

7.84–7.82 (d, 2H), 7.28 (s, 4H), 4.47 (s, 4H), 3.52–3.49 (t, 4H), 3.35–3.33 (t, 4H), 1.95–1.92 (m, 4H), 1.81–1.78 (m, 4H) ppm.  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz):  $\delta$  137.97, 136.92, 131.52, 131.01, 129.85, 128.71, 127.85, 127.61, 127.37, 127.25, 126.62, 125.85, 125.16, 125.12, 124.88, 124.73, 123.57, 72.84, 70.21 33.40, 29.87, 28.55 ppm. MALDI-TOF: 650 ( $\text{M}^+$ ).

**SWNTs and Separation.** The as-produced samples of SWNTs were purified in terms of an established procedure involving nitric acid treatment. Briefly, a sample (1 g) was heated at 300 °C with air in a furnace for 30 min, and 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 oven for 12 h.

An as-purified SWNT sample (100 mg) was added to a solution of the bis-pyrene in dry THF-toluene (80/20, v/v, 10 mg/mL, 20 mL). The mixture was homogenized and sonicated until appearing homogeneous. Upon centrifugation at 1000g for 30 min, the sediment was collected as the first fraction. The supernatant was further centrifuged at 2000g for 30 min to collect the sediment as the middle fraction, and the remaining supernatant after solvent removal was designated as the last fraction. All fractions were refluxed in THF, followed by repeated washing with THF until no bis-pyrene was detected in the washing solution. The bis-pyrene molecules from washing the fractions were harvested for recycling.

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### Notes

The authors declare no competing financial interest.

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## REFERENCES

- (1) Gruner, G. *J. Mater. Chem.* **2006**, *16*, 3533.
- (2) Cao, Q.; Rogers, J. A. *Adv. Mater.* **2009**, *21*, 29.
- (3) Sgobba, V.; Guldi, D. M. *Chem. Soc. Rev.* **2009**, *38*, 165.
- (4) Kumar, A.; Zhou, C. *ACS Nano* **2010**, *4*, 11.
- (5) Lu, F.; Mezzani, M. J.; Cao, L.; Sun, Y.-P. *Langmuir* **2011**, *27*, 4339.
- (6) Kam, N. W. S.; O'Connell, M.; Wisdom, J. A.; Dai, H. *Proc. Natl. Acad. Sci. U. S. A.* **2005**, *102*, 11600.
- (7) Krupke, R.; Hennrich, F.; Lohneysen, H.; Kappes, M. M. *Science* **2003**, *301*, 344.
- (8) Chattopadhyay, D.; Galeska, I.; Papadimitrakopoulos, F. *J. Am. Chem. Soc.* **2003**, *125*, 3370.
- (9) Zheng, M.; Jagota, A.; Strano, M. S.; Santos, A. P.; Barone, P.; Chou, S. G.; Diner, B. A.; Dresselhaus, M. S.; McLean, R. S.; Onoa, G. B.; Samsonidze, G. G.; Semke, E. D.; Usrey, M.; Walls, D. J. *Science* **2003**, *302*, 1545.
- (10) Li, H.; Zhou, B.; Gu, L.; Wang, W.; Fernando, K. A. S.; Kumar, S.; Allard, L. F.; Sun, Y.-P. *J. Am. Chem. Soc.* **2004**, *126*, 1014.
- (11) Wang, W.; Fernando, K. A. S.; Lin, Y.; Mezzani, M. J.; Veca, L. M.; Cao, L.; Zhang, P.; Kimani, M. M.; Sun, Y.-P. *J. Am. Chem. Soc.* **2008**, *130*, 1415.
- (12) (a) Maeda, Y.; Kimura, S.; Kanda, M.; Hirashima, Y.; Hasegawa, T.; Wakahara, T.; Lian, Y.; Nakahodo, T.; Tsuchiya, T.; Akasaka, T.; Lu, J.; Zhang, X.; Gao, Z.; Yu, Y.; Nagase, S.; Kazaoui, S.; Minami, N.; Shimizu, T.; Tokumoto, H.; Saito, R. *J. Am. Chem. Soc.* **2005**, *127*, 10287. (b) Maeda, Y.; Kanda, M.; Hashimoto, M.; Hasegawa, T.; Kimura, S.; Lian, Y.; Wakahara, T.; Akasaka, T.; Kazaoui, S.; Minami, N.; Okazaki, T.; Hayamizu, Y.; Hata, K.; Lu, J.; Nagase, S. *J. Am. Chem. Soc.* **2006**, *128*, 12239.
- (13) (a) Arnold, M. S.; Green, A. A.; Hulvat, J. F.; Stupp, S. I.; Hersam, M. C. *Nat. Nanotechnol.* **2006**, *1*, 60. (b) Hersam, M. C. *Nature* **2009**, *460*, 186.
- (14) Fantini, C.; Jorio, A.; Santos, A. P.; Peressinotto, V. S. T.; Pimenta, M. A. *Chem. Phys. Lett.* **2007**, *439*, 138.
- (15) Moshhammer, K.; Hennrich, F.; Kappes, M. M. *Nano Res.* **2009**, *2*, 599.
- (16) Voggu, R.; Rao, K. V.; George, S. J.; Rao, C. N. R. *J. Am. Chem. Soc.* **2010**, *132*, 5560.
- (17) Tange, M.; Okazaki, T.; Iijima, S. *J. Am. Chem. Soc.* **2011**, *133*, 11908.
- (18) Anilkumar, P.; Fernando, K. A. S.; Cao, L.; Lu, F.; Yang, F.; Song, W.; Sahu, S.; Qian, H.; Thorne, T. J.; Anderson, A.; Sun, Y.-P. *J. Phys. Chem. C* **2011**, *115*, 11010.
- (19) Fernando, K. A. S.; Lin, Y.; Wang, W.; Kumar, S.; Zhou, B.; Xie, S.-Y.; Cureton, L. T.; Sun, Y.-P. *J. Am. Chem. Soc.* **2004**, *126*, 10234.
- (20) Chiang, I. W.; Brinson, B. E.; Smalley, R. E.; Margrave, J. L.; Hauge, R. H. *J. Phys. Chem. B* **2001**, *105*, 1157.
- (21) Zhao, B.; Itkis, M. E.; Niyogi, S.; Hu, H.; Zhang, J.; Haddon, R. C. *J. Phys. Chem. B* **2004**, *108*, 8136.
- (22) Tian, L.; Mezzani, M. J.; Lu, F.; Kong, C. Y.; Cao, L.; Thorne, T. J.; Sun, Y.-P. *ACS Appl. Mater. Interfaces* **2010**, *2*, 3217.
- (23) Jorio, A.; Pimenta, M. A.; Filho, A. G. S.; Saito, R.; Dresselhaus, G.; Dresselhaus, M. S. *New J. Phys.* **2003**, *5*, 139.