High Purity Isolation and Quantification of Semiconducting Carbon Nanotubes *via* Column Chromatography

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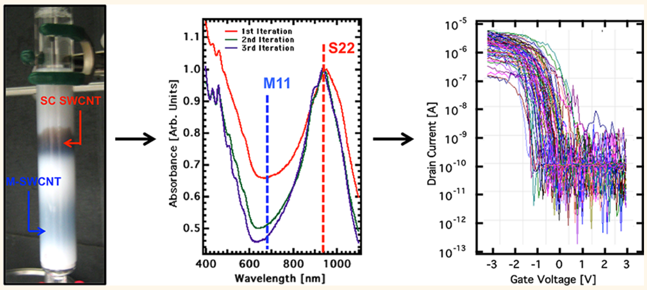
ABSTRACT The isolation of semiconducting carbon nanotubes (CNTs) to ultrahigh (ppb) purity is a prerequisite for their integration into high-performance electronic devices. Here, a method employing column chromatography is used to isolate semiconducting nanotubes to 99.9% purity. The study finds that by modifying the solution preparation step, both the metallic and semiconducting fraction are resolved and elute using a single surfactant system, allowing for multiple iterations. Iterative processing enables a far more rapid path to achieving the level of purities needed for high performance computing. After a single iteration, the metallic peak in the absorption spectra is completely attenuated. Although absorption spectroscopy is typically used to characterize CNT purity, it is found to be insufficient in quantifying solutions of high purity (>98 to 99%) due to low signal-to-noise in the metallic region of ultrahigh purity solutions. Therefore, a high throughput electrical testing method was developed to quantify the degree of separation by characterizing ∼4000 field-effect transistors fabricated from the separated nanotubes after multiple iterations of the process. The separation and characterization methods described here provide a path to produce the ultrahigh purity semiconducting CNT solutions needed for high performance electronics.



KEYWORDS: carbon nanotubes · sorting · purification · gel chromatography

While scaling down the size of silicon transistors has driven the microelectronics industry for the last 50 years, transistor performance has stalled in the past several generations and will be increasingly difficult going forward, thus allowing opportunities for introducing new materials.[1,2] Recent demonstrations of the performance of aggressively scaled (channel length < 10 nm) single-walled carbon nanotube field effect transistors (CNT-FETs),[3,4] along with numerous previous studies on CNT devices,[5−7] make them a leading candidate to replace silicon as the channel material in future (sub-10 nm technology node) high performance logic devices. As the sub-10 nm technology nodes will contain several billion transistors, the sorting of carbon nanotubes to many 9s purity is necessary for the integration of the material. In the absence of methods to directly synthesize the desired type of CNTs, sorting from solution is currently the most easily integratable option as most CNT placement methods proceed from solution. There are several key requirements for a sorting process targeted at high-performance computing, including (1) a process that sorts larger (>1.2 nm) CNTs to allow sufficient drive currents, (2) a process that is easily iterated to allow for approaching ppb purity levels, and (3) a process that leads to a narrow diameter distribution, and therefore a narrow band gap distribution so as to minimize variations in threshold voltage (V_t).

Several methods are described in the literature to sort semiconducting (sc-CNT) from metallic CNTs (m-CNT), including density gradient ultracentrifugation (DGU),[8] AC dielectrophoresis,[9] DNA-assisted separation,[10] selective polymer wrapping,[11,12] and column chromatography[13−16] (a nice review of several separation methods can be found in Hersam[17]). Each method can be effective and has its own set of advantages and disadvantages. Column

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chromatography, pioneered by Moshammer *et al*.,[13] is an especially simple, effective and scalable method for the sorting of carbon nanotubes. Essentially, the procedure initially involves sonicating the CNTs in an aqueous SDS solution. The solution is then sent through a column (containing Sephacryl-200 as the column media) where the metallic CNTs pass through and the semiconducting CNTs are retained at the top of the column. The semiconducting CNTs are then eluted *via* the addition of a second surfactant (typically sodium cholate). Moshammer *et al*. initially postulated that the separation mechanism was due to the sonication step producing a solution where the metallic CNTs are individualized and the semiconducting CNTs are left as small bundles. However, several studies since then have shown that the mechanism is likely dominated by selective adsorption of the semiconducting CNTs to the column media.[19−22]

We have modified this method to achieve a process that is easily iterative and developed a high throughput characterization method that can quantify the separation precisely. The key results of this work are (a) a modified solution preparation that allows for elution of both metallic and semiconducting CNTs using a single surfactant solution and concentration, thus allowing for iterative processing; (b) the effect of the pore size, which is critical to achieve effective separation; (c) UV−vis−NIR spectroscopy is only effective in characterizing purities up to ∼98% and that high-throughput electrical characterization is necessary to effectively characterize the degree of separation in a highly purified CNT solution; and (d) the achievement of purity of ∼99.9% that is verified electrically after three iterations of the process. The combination of iterative processing and high-throughput electrical characterization are promising pathways to achieve the level of purity necessary for high-performance logic.

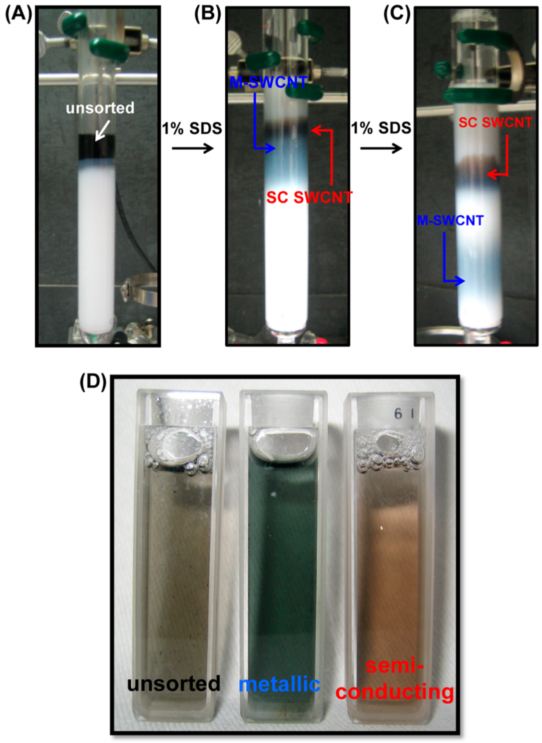

Figure 1. Images of the separation process when the CNT solution is (a) initially loaded (b) beginning to move down the column while forming two distinct bands and (c) near the bottom of the column where a large separation between the bands is observed. The images and labels show how the sc-CNTs move more slowly in the column than the m-CNTs while eluting with the same surfactant mixture. An image of the unsorted, metallic, and semiconducting fractions after separation is shown in panel d.

RESULTS AND DISCUSSION

Carbon nanotubes produced *via* an arc-discharge method (Hanwha Nanotech) were used in this study due to their high quality and relatively large diameters (∼1.4 nm). For high performance computing, smaller diameter CNTs do not produce enough drive current to be implemented.[18] This study found that the CNT/SDS solution preparation method is a key step in yielding a process where the separation is achieved using one surfactant. The CNTs are first sonicated in a 1% SDS aqueous solution in a concentration of 1 mg/mL using a horn-type sonicator. The solution is then purified using a step-gradient centrifugation step[8] where a high density solution (0.25% SDS in 45% Iodixinol) is layered underneath the CNT solution and then centrifuged (a schematic of this process is in the Supporting Information). Upon centrifugation, a layer of highly purified CNTs sediments to the middle of the tube; while larger bundles and other impurities sediment to the bottom of the tube due to their different buoyant densities. It is important to note that this process does not sort the CNTs by electronic type (evidence by the absorption spectrum and black color of the solution), it is a step analogous to typical high speed centrifugation used to initially purify CNT solutions in preparation for further processing. The advantage of using the stop layer is the formation of much denser, highly pure solutions (see Supporting Information). The authors found that the lower concentration of SDS used in the stop layer (0.25% *versus* 1%) is critical to achieving a separation process where the CNTs both separate and elute in the same surfactant. The impact of this subtle difference in the surfactant concentration will be the subject of future studies.

The purified CNT solution is then loaded into a column (as shown in Figure 1a) packed with Sephacryl-200 (copolymer based column chromatography medium) that was previously flushed with an aqueous 1% SDS solution. As the CNT solution fully enters the column, an additional 1% SDS solution is added to the column to push the CNTs through. After several minutes of elution, the black band differentiates into a red and blue band as the CNTs start moving through the column as seen in Figure 1b. As the material continues to pass through the column, the red band moves much more slowly as the blue band pulls ahead; leading to a large differentiation. When the material is near the bottom of the column, the two materials are clearly separated with the blue (metallic) band eluting first and the red (semiconducting) band eluting last (Figure 1c). The solutions are collected as two separate fractions—a metallic (blue) fraction and a semiconducting (red) fraction. Typically, the first 2−3 mL of the red band is discarded as the later part of that band is of higher purity. Figure 1d is an image of the unsorted CNT solution (brown/black), the metallic fraction (blue/green) and the semiconducting fraction (red). This elution of both bands is in contrast to the previously described method where the semiconducting CNTs are trapped in the column and only elute after the addition of a sodium cholate solution,[13] in which case the sodium cholate must be replaced with SDS (which can be difficult) in order to repeat the process. Liu *et al.*[16] described a method where a larger concentration (5% *versus* 2%) of SDS elutes the semiconducting CNTs; although this method uses a single surfactant, the concentrations are different and reducing the concentration back to 1% would be required before iterating the process. The method described here employs a single-surfactant solution, and concentration allows one to simply reload the separated material into the column to achieve a higher degree of separation.

The effect of pore size of the column media was also examined to determine the effect it has on the quality of the separation. Figure 2a contains UV−vis−NIR absorption spectra for separation runs using Sephacryl-100, 200, and 300 as the separation media, where the usable molar mass ranges are 10^3 to 10^4 g/mol (100), 5×10^3 to 2.5×10^5 g/mol (200) and 10^4 to 1.5×10^6 g/mol (300), respectively. In all three cases, the CNTs showed some degree of separation using a single surfactant. This is a surprising result as the molar mass range for the CNTs ($d \approx 1.4$ nm and $L \approx 500$ nm) is $\sim 5 \times 10^5$ g/mol with the bundled semiconducting CNTs being several times larger than that. This result suggests that the separation mechanism is complex and that the resolution is a result of a combination of selective adsorption and the materials traveling at different speeds through the pores.[14,19−22] As evidenced in Figure 2a, the separation using Sephacryl-200 (red curve) had the highest efficiency where the metallic peak (labeled M11) was completely attenuated. The other two semiconducting fractions, despite some enrichment, still had a substantial M11 peak remaining. The data presented from here forward were all obtained using Sephacryl-200 as the separation media.

UV−vis−NIR spectra of the initial, unsorted material (black), the metallic fraction (blue), and the semiconducting fraction (red) are shown in Figure 2b. The two key optical transitions are the second optical transition of the semiconducting CNTs (S22) and the first optical transition of the metallic CNTs (M11). The ratio of these two peaks is an indication of the level of purity. The unsorted fraction gives a spectrum typical of purified CNTs suspended in an aqueous SDS solution. The metallic fraction shows a very strong M11 peak, while the S22 region is clearly diminished. It is important to note that the separation method was not optimized to isolate metallic CNTs and that further development on this front would likely lead to even higher purity metallic fractions. The semiconducting fraction, shown as a red curve, exhibits the opposite features where the S22 peak is quite strong and the M11 is completely attenuated. These spectra were obtained after a single pass through the column. The high degree of semiconducting enrichment after this single pass indicates the effectiveness and ease that this process affords.

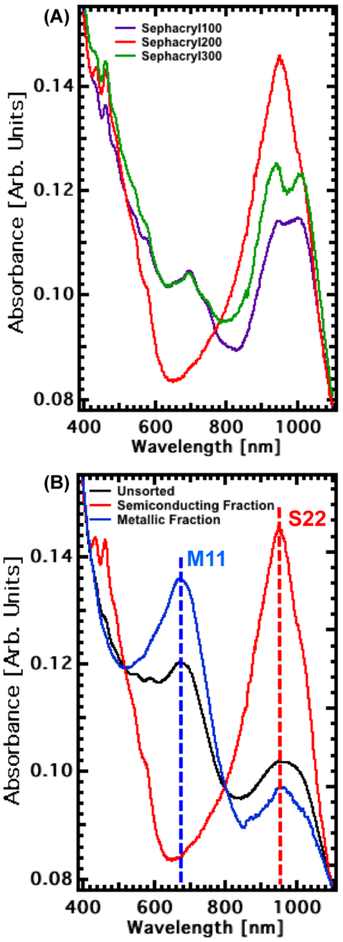

Figure 2. (a) UV−vis−NIR spectrum of the semiconducting fraction after passing the CNT solutions through three different column mediums, including Sephacryl-100 (purple), 200 (red), and 300 (green). The pore size of the columns increases with increasing number. The data indicates that Sephacryl 200 yields the highest semiconducting purity. (b) UV−vis−NIR spectrum of the unsorted (black), semiconducting fraction (red), and metallic fraction (blue) after passing through a Sephacryl-200 column.

Since only a single surfactant is used, iterative separation is easily performed. One simply takes the semiconducting fraction, sonicates it, and then passes it through the column again. UV−vis−NIR spectra of the semiconducting fraction after one, two, and three iterations is shown in Figure 3a as red, green, and purple curves, respectively.

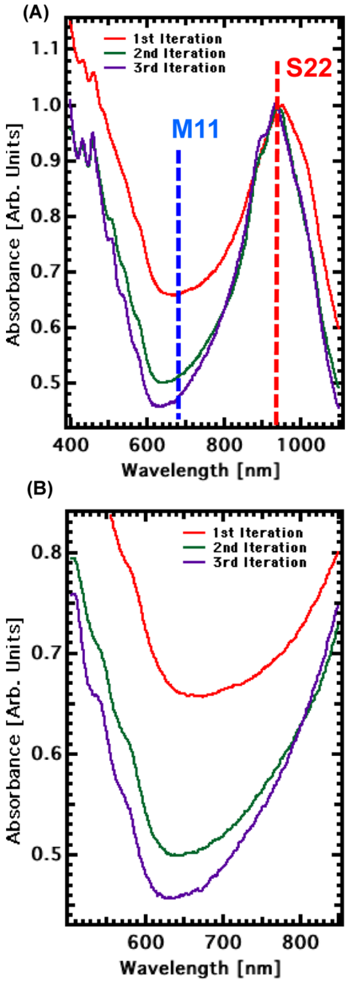

Figure 3. (a) UV−vis−NIR spectrum of the semiconducting fraction after the first (red), second (green), and third (purple) iteration showing both the S22 and M11 regions. In both cases, the M11 region is completely attenuated. (b) A close-up of the M11 section in the UV−vis−NIR spectrum of panel a.

At first glance, the spectra (especially the second and third iteration) look very similar. One key feature is that the S22 region is slightly blue-shifted after each iteration, indicating a preference for smaller diameter tubes in the semiconducting fraction. This is an indication that the diameter distribution is narrower after separation. Another feature is that the background is lower after every iteration. Although the lower background may indicate a higher degree of purity, which would indeed agree with the data, the authors find that the background level also greatly depends on how free of graphitic impurities the solution is. Figure 3b is a zoomed in view of the M11 region of the three spectra. All three curves show complete attenuation of the metallic region. It would be impossible to gain an accurate measurement of purity by integrating the S22 and M11 peaks due to the near-zero signal of the M11 region. Although we assume the purity has improved after every iteration, it is impossible to measure the improvement using currently available optical techniques. It is important to note that the concentration does decrease with each iteration and a concentration step may need to be performed after several iterations. This result illustrates how difficult it is to quantify the separation efficiency in materials of very high purity.

As high-purity semiconducting CNTs are required for high-performance computing, a high throughput method was developed to quantify, *via* electrical testing, the semiconducting fraction. A large array of FET (field-effect transistor) structures were fabricated on a highly doped Si substrate with a 10 nm thermally grown SiO_2 layer. Since the CNTs dispersed in SDS tend to contain some small bundles, the separated CNT solution is then diluted to the appropriate concentration with a 1% sodium cholate solution. The addition of sodium cholate, followed by sonication, helps to isolate the bundled CNTs yielding a higher percentage of individual CNTs for electrical testing.[23] The CNTs were randomly deposited on the surface from solution at a concentration of $\sim$0.5 CNT/μm^2. An array of source and drain contacts (0.5 nm Ti/15 nm Pd/20 nm Au) were then fabricated, *via* e-beam lithography, metal deposition, and lift-off; this resulted in several thousand devices per chip (shown in Figure 4a). This yields approximately 20−30% of devices where a single nanotube spans the source and drain contact. The low yield, controlled by the density of the CNT solution, helps prevent devices with several CNTs spanning the source and drain. A device with a CNT spanning the source and drain is shown in Figure 4c. The device layout was designed to be compatible with a semiautomated probe station to allow for high throughput characterization. The I_d *vs* V_{gs} curves of the devices are measured, and the number of metallic *versus* semiconducting devices are simply counted. A set of subthreshold curves ($V_{ds} = -0.5$ V) from one chiplet (approximately 150 devices) is shown in Figure 4b. This particular area showed no metallic devices, which can be identified based on the ratio of on-current to off-current in the subthreshold curve (a metallic nanotube would have an on/off current ratio < 100). The average on-current of the devices is $\sim$2 μA (at V_{ds} of -0.5 V) with an on/off current ratio of $\sim 10^5$; performance characteristics that are in agreement with previous reports of nanotubes with similar diameter and of high-quality. We conclude there is no loss in performance due to the separation process. As is typical of CNT devices, there is a large variation in on-current and V_t; previous studies describe the mechanisms of device−device variability along with methods to decrease the variability.[24]

Table 1 is the aggregated data from this study. The unsorted fraction yielded a semiconducting purity of 55.2% after measurement of 1213 devices. A metallic CNT was defined as a device with a current-modulation of less than 10^2. A total of 2634 devices were measured from the semiconducting fraction after one iteration where 2588 were semiconducting, giving a semiconducting yield of 98.3 ± 0.3%. After the second iteration, another set of chips produced 3823 working devices where 21 were semiconducting giving a semiconducting yield of 99.5 ± 0.1%. The third iteration of the separation

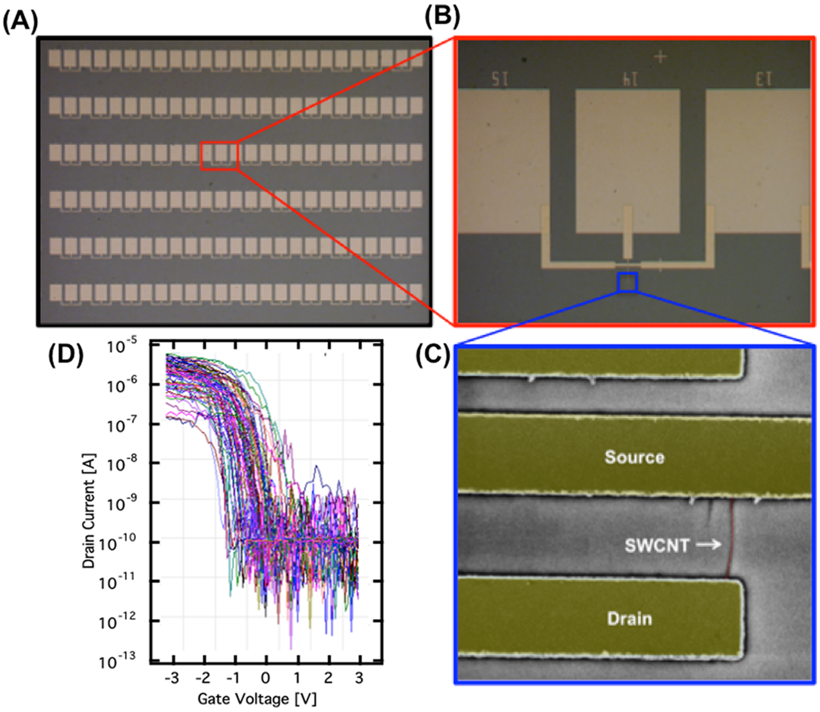

Figure 4. Optical microscope images of the device array (a) and an individual device (b). The array is designed to be compatible with a semiautomated probe station. (c) A SEM image of an individual device showing a single CNT spanning the source and drain. (d) Subthreshold I_d-V_{gs} curves of a section of a chip (approximately 150 devices).

TABLE 1

solution	total device no.	no. metallic devices	% semiconducting
unsorted	1213	543	55.2 ± 2.0%
iteration 1	2634	46	98.3 ± 0.3%
iteration 2	3823	21	99.5 ± 0.1%
iteration 3	4212	6	99.9 ± 0.1%

process produced a yield of 99.9 ± 0.1% where 4212 devices were measured with only 6 being metallic. It is important to note that the fabrication method does not guarantee that there is only one CNT per channel and that some channels may have more than one (although SEM indicates only a small number of devices (*ca.* 1−2%) have more than one CNT). Devices with more than one nanotube would underestimate the level of purity, so the numbers shown here represent the lower bound in possible values. The key message here is that the absorption spectra is not sufficient to quantify the degree of separation and is limited to purities of *ca.* 98−99% as the metallic region in the absorption spectra was completely attenuated in all three of the cases measured here. If higher purities are required, methods such as the one described here will need to be used to quantify the level of purity. The data also illustrate the high degree of separation that is possible using a chromatographic approach. Future work will include mechanistic studies and further iterations to push toward ever-higher purities as required for high performance electronics.

CONCLUSIONS

Herein, a method was described to purify semiconducting CNTs and quantify the separation using high-throughput electrical characterization. The method is simple and scalable and allows for multiple iterations. The effect of pore size in the column media was found to have a profound effect on the separation quality. Absorption spectroscopy alone is not sufficient to quantify the degree of separation above 98−99%. To circumvent this problem, an electrical test bed was fabricated where the measurement was automated to allow for high-throughput testing. Upon a third iteration, 4206 out of 4212 devices were found to be semiconducting, producing a yield of 99.9%. The solution preparation step in the method is critical and easily affords for multiple iterations and provides a path to many 9s purity as required for high-performance logic.

METHODS

CNT Solution Preparation. A 1 mg/mL solution of CNTs (Hanhwa Nanotech) in a 1% aqueous SDS (Sigma Aldrich) was prepared *via* horn sonication (99%, 1 s pulse, 20 min). The solution was then purified using a step gradient ultracentrifugation step. For the purification, 6 mL of a 0.25% SDS in 45% Iodixdinol (Sigma Aldrich) solution was prepared and layered below 6 mL of the CNT solution in a 12 mL centrifuge tube. The layered solution is then centrifuged for 15 h at 41k rpm using a Beckman Culter Opitma L-100 XP ultracentrifuge equipped with a swinging bucket type rotor. A schematic of this process is shown in the Supporting Information. The purified CNT solution sediments at the interface of the two layers while the graphitic impurities and large bundles settle to the bottom of the centrifuge tube. The purified CNT solution is then removed *via* pipet and diluted 1:1 with a 1% aqueous SDS solution prior to loading on the column.

Chromatography. A column is prepared by loading a 25 mm diameter glass chromatography column with a Sephacryl-200 slurry so that the column is roughly 20 cm long (Sigma Aldrich). The column is flushed with a 1% SDS solution several times. The CNT solution (5 mL) is then added to the column and is allowed to pass through the column using only gravity (*i.e.*, no N_2 back pressure). Although one can use back pressure to speed-up the process, the resolution of the bands will suffer. Once the solution is fully into the column, more 1% SDS solution (total of *ca.* 100 mL) is added and is continually added until all of the CNTs (now separated) pass through the column. Typical elution times are 30 min for the metallic fraction and 90 min for the semiconducting fraction. Fractions of the solution are collected in small glass vials and characterized using a UV−vis−NIR absorption spectrometer (Perkin-Elmer Lamda 950).

Electrical Testing. Prior to CNT deposition, the CNT solution is diluted with a 1% sodium cholate solution (typically 1:20) and sonicated for 20 min in a bath sonicator. The CNT solution is deposited onto a heavily p-doped silicon wafer containing 10 nm of thermally grown SiO_2 by placing a few drops on the substrate, allowing it to stand for several minutes and then blown dry with a nitrogen gun. The substrate is then gently rinsed with methanol to remove excess surfactant. Source and drain electrodes and pads are then patterned using e-beam lithography, developed and then fabricated by depositing 0.2 nm Ti/15 nm Pd/20 nm Au. Following lift-off, the chip is placed in a semiautomated probe station for testing. A metallic CNT is defined as a device with less than 10^2 on/off current ratio.

Conflict of Interest: The authors declare no competing financial interest.

Supporting Information Available: A schematic of the initial centrifugation process. This material is available free of charge via the Internet at http://pubs.acs.org.

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