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1. REPORT DATE (DD-MM-YYYY) 15/08/2012		2. REPORT TYPE		3. DATES COVERED (From - To) 05/15/2011-08/15/2012	
4. TITLE AND SUBTITLE Quantitative Separation of Single-Walled Carbon Nanotubes into Metallic and Semiconducting Fractions				5a. CONTRACT NUMBER	
				5b. GRANT NUMBER FA9550-09-1-0414	
				5c. PROGRAM ELEMENT NUMBER	
6. AUTHOR(S) Sun, Ya-Ping				5d. PROJECT NUMBER	
				5e. TASK NUMBER	
				5f. WORK UNIT NUMBER	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Clemson University Department of Chemistry Hunter Hall				8. PERFORMING ORGANIZATION REPORT NUMBER	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) Air Force Office of Scientific Research 875 N Randolph St Arlington, VA 22203 Dr. Charles Lee/RSA				10. SPONSOR/MONITOR'S ACRONYM(S)	
				11. SPONSOR/MONITOR'S REPORT NUMBER(S) AFRL-OSR-VA-TR-2012-1150	
12. DISTRIBUTION/AVAILABILITY STATEMENT DISTRIBUTION A: APPROVED FOR PUBLIC RELEASE					
13. SUPPLEMENTARY NOTES					
14. ABSTRACT Single-walled carbon nanotubes (SWNTs) are widely recognized as being broadly applicable to advanced materials and systems important to the Air Force. However, the nanotube production generally yields mixtures, which presents major barriers in harvesting metallic-SWNTs as the minor fraction (up to only 1/3) and also in obtaining highly pure semi-SWNTs (electronic applications, for example). Their post-production separation in sufficient quantities has proven to be very challenging. Our project is to build upon our previous discovery to achieve efficient and quantitative separation into metallic and semiconducting fractions and, as related, to have a fundamental understanding of the underlying selective and specific molecular interactions responsible for the separation. In this project we made significant progress in improving the separation reagents and process, and the characterization and evaluations (including those at the device level) of the separated nanotube samples. The results are published or submitted for publication.					
15. SUBJECT TERMS Carbon Nanotubes, Metallic, Semiconducting, Selective Interactions, Molecular Tweezers, Transparent Electrodes					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT		18. NUMBER OF PAGES
a. REPORT	b. ABSTRACT	c. THIS PAGE	U		19a. NAME OF RESPONSIBLE PERSON Ya-Ping Sun
U	U	U			19b. TELEPHONE NUMBER (Include area code) 864-656-5026

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Quantitative Separation of Single-Walled Carbon Nanotubes into Metallic and Semiconducting Fractions

FA9550-09-1-0414

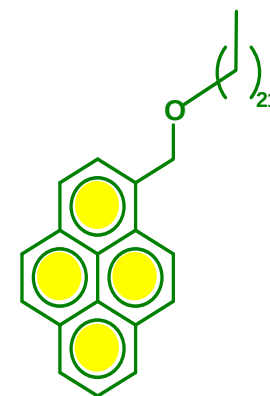
Ya-Ping Sun (Clemson University)

Single-walled carbon nanotubes (SWNTs) are widely recognized as being broadly applicable to advanced materials and systems important to the Air Force. However, the nanotube production generally yields mixtures, which presents major barriers in harvesting metallic-SWNTs as the minor fraction (up to only 1/3) and also in obtaining highly pure semi-SWNTs (electronic applications, for example). Their post-production separation in sufficient quantities has proven to be very challenging. Our project is to build upon our previous discovery to achieve efficient and quantitative separation into metallic and semiconducting fractions and, as related, to have a fundamental understanding of the underlying selective and specific molecular interactions responsible for the separation. In this project three discoveries or major advancements were made:

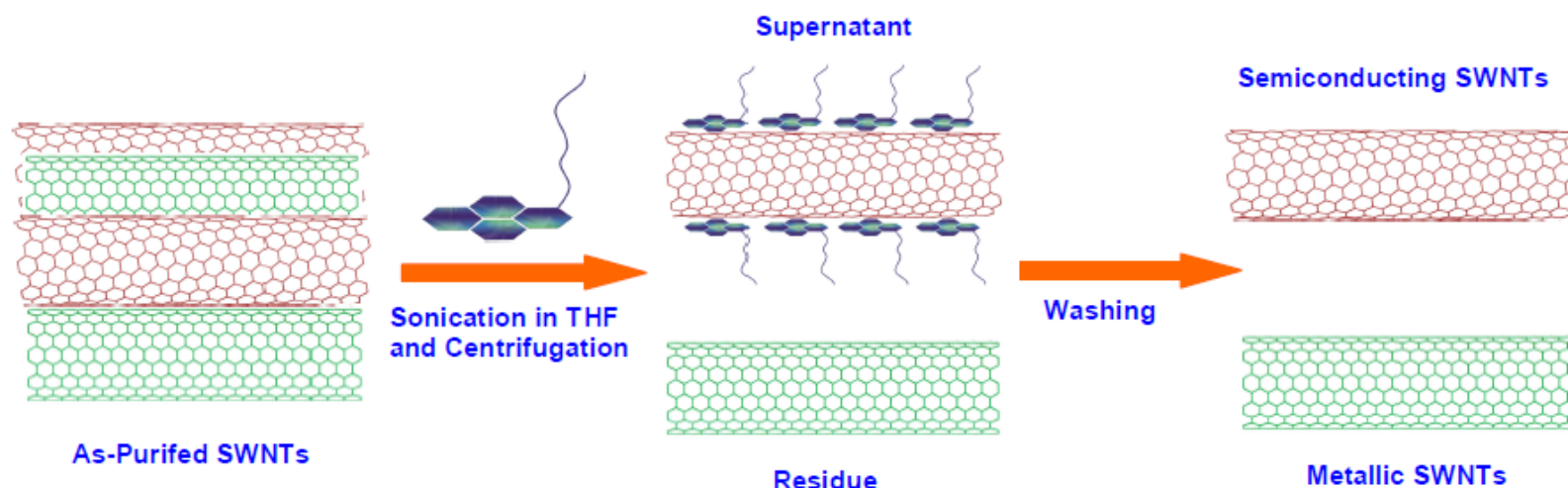
- (1) The development and validation of the “molecular tweezers” approach (separation agents based on molecules each containing more than one planar aromatic moiety), which represents a new and much improved platform for more effective and quantitative separation.
- (2) The recognition and experimental evaluation-confirmation on the role of solvent environment in the separation, thus more parameters to play with in pursuing more effective and efficient separation.
- (3) The development of an effective purification method for high-purity SWNTs, which not only facilitates the effective and efficient separation but also substantially improves the quality of the separated samples.

Toward Quantitative Bulk-Separation of Metallic & Semiconducting SWNTs

Our studies built upon our patented approach (U.S. Patent 7374685) to exploit the selectivity between metallic and semiconducting SWNTs in their interactions with planar aromatic molecules in solubilization. A molecule that was carefully validated as being excellent for the separation was DomP (pyrene with a long alkyl tail).



DomP



Scheme 1. The separation with DomP (pyrene with a long alkyl tail).

Features/Unique Advantages of the Approach/Method:

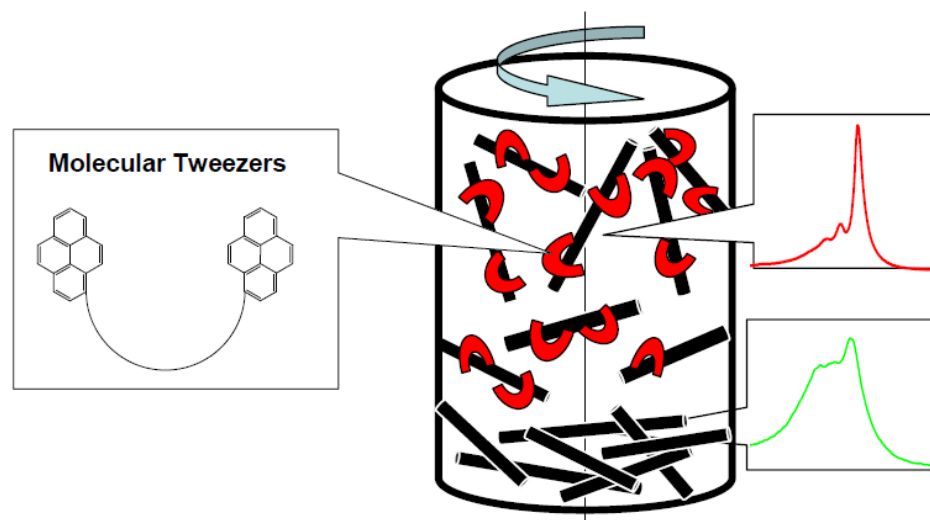
- Targeted to/suitable for bulk-separation (sub-gram quantity in lab already), amenable to scale-up;
- Particularly good for the high-performance arc-discharge/laser SWNTs;
- “Splitting” the sample into fractions, thus no/little sample losses, and no damages to the separated nanotubes;
- High nanotube purity and semiconducting or metallic purity can be achieved;
- No waste in terms of the separation agents (>95% recycled);
- Relatively simple procedures and operation, and potentially developed into continuous separation;
- For fundamental understanding of the non-covalent interactions-functionalization of SWNTs.

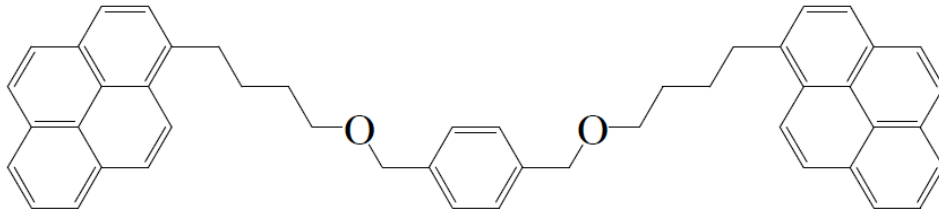
“Molecular Tweezers” Approach

Why it is better than DomP?

The use of DomP was successful to obtain reasonably pure metallic SWNTs and purer semiconducting SWNTs, especially with two separation cycles. However, the selectivity in DomP interactions with SWNTs is not high, which makes the separation processing more demanding or even somewhat tricky in terms of controlling the experimental conditions.

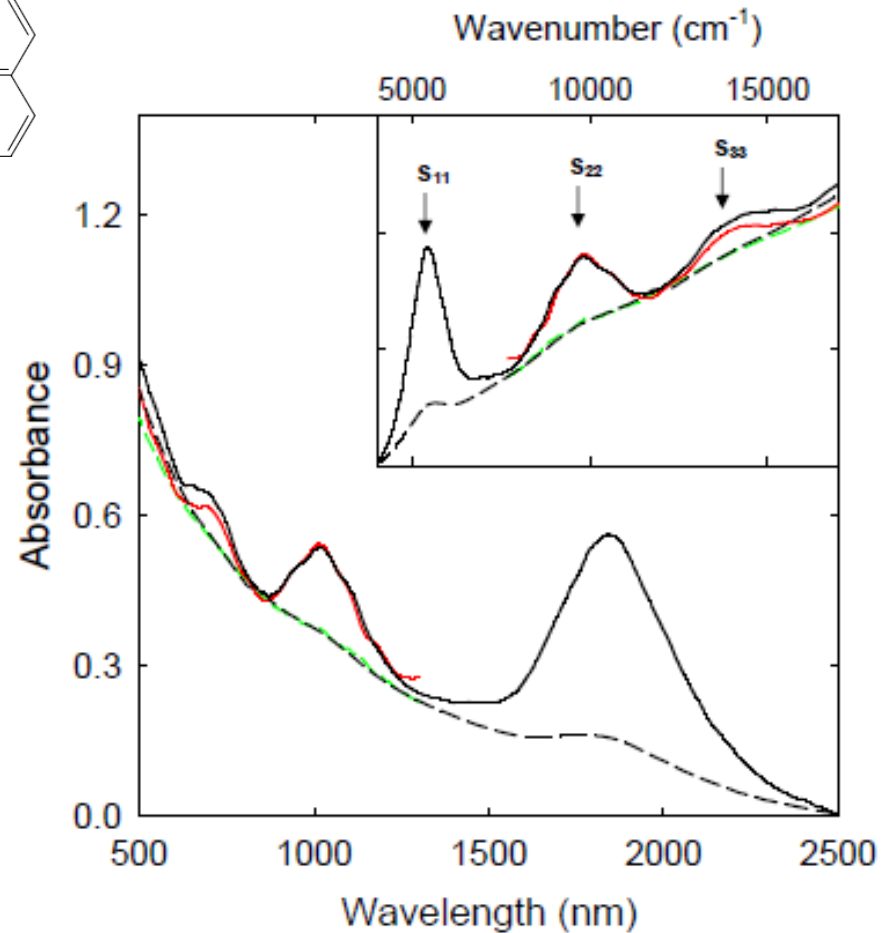
The idea with the use of paired aromatic moieties or “molecular tweezers” is to enhance the selectivity found in the use of DomP, thus not only to allow significantly improved separation (metallic fraction purity of 92% and semiconducting fraction purity of 97%), but also to make separation process more straightforward.

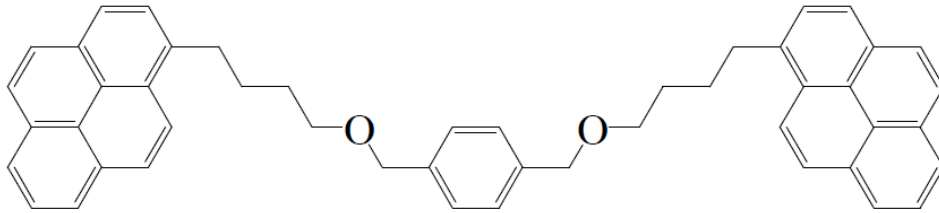




Bis-pyrene – the “molecular tweezers”

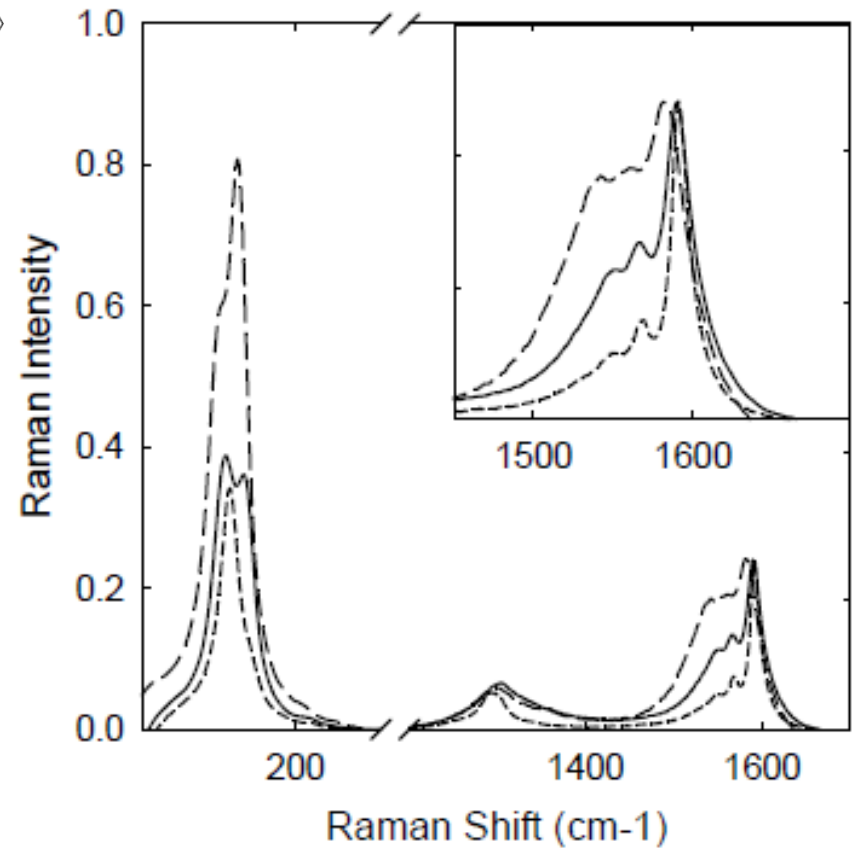
Optical absorption spectra of the separated metallic (dashed lines, green: in DMF dispersion and black: in solid-state thin film) and semiconducting (solid lines, red: in DMF dispersion and black: in solid-state thin film) fractions. The same spectra on the wavenumber scale are shown in the inset, with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





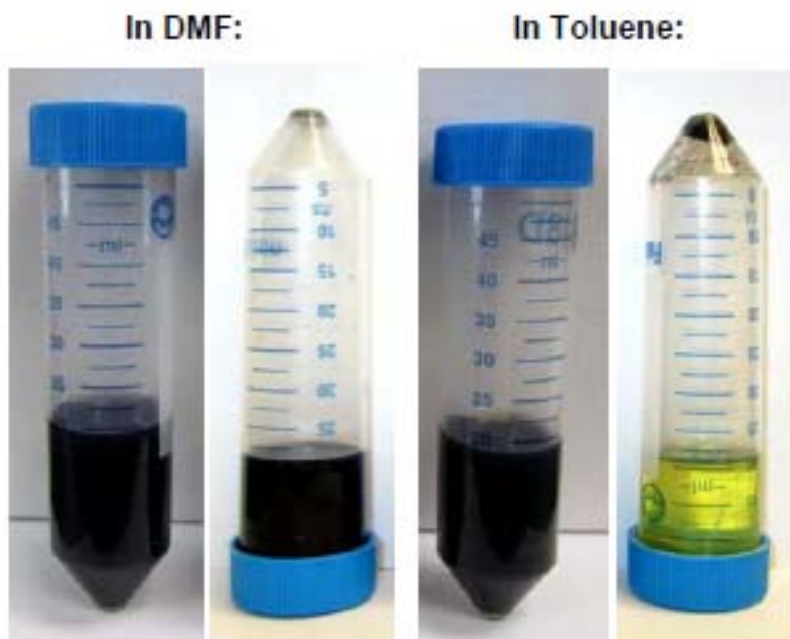
Bis-pyrene – the “molecular tweezers”

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



Solvent Effects on the Selectivity and Separation:

Mechanistically, the separation method exploits the selectivity between metallic and semiconducting SWNTs in their interactions with planar aromatic molecules. The selectivity in interactions is solvent dependent, less selective in more SWNT-philic solvents such as DMF, and more selective in a less SWNT-philic solvent like THF (even better in THF-toluene mixture, but not at all in pure toluene). For example, with the bis-pyrene as the separation agent, no separation in DMF because everything remains in solution and thus no precipitates, and neither in toluene because everything precipitated out of the solution – see the photos below. Therefore, a THF-toluene mixture (80/20, v/v) was used for the successful separation.



Photographs on the solubilization of SWNTs by the bis-pyrene in DMF before (left tube) and after (right tube) centrifugation at 3,000 *g* and in toluene before (left tube) and after (right tube) centrifugation at 1,000 *g*.

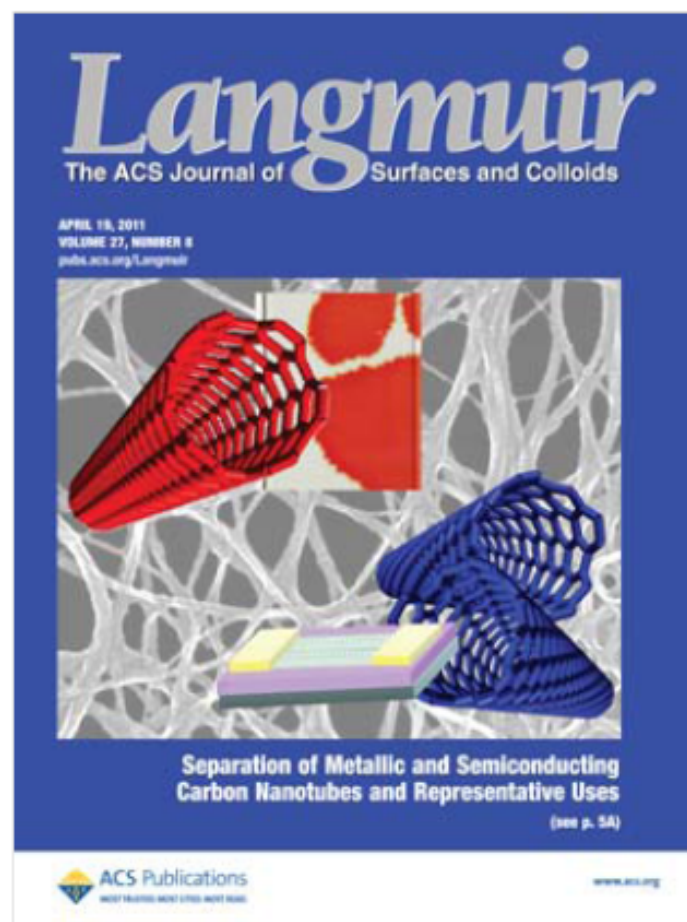
Metallic/Semiconducting Single-Walled Carbon Nanotubes (SWNTs)

Feature Article and Cover Story

- ❑ We were invited by the American Chemical Society Journal *Langmuir* to prepare a feature article to highlight our method and progress and to build upon that for a critical review of the field;
- ❑ Upon the peer-review and acceptance of the article, the Journal decided that the field and work are very important and should be featured as the journal cover (see attached); The response from the relevant scientific community has been overwhelmingly positive and encouraging;
- ❑ We thank AFOSR and Dr. Charles Lee for making all of these possible and for the continuing support.

Langmuir, **2011**, 27 (8) Cover – Published 4/19/2011

Cover image by Ya-Ping Sun. Single-walled carbon nanotubes (SWNTs), extensively investigated for their superior properties and application potentials, are either metallic or semiconducting (statistically 1:2 in population ratio), which are distinctively different in electrical conductivity and many other aspects. The available bulk production methods generally yield mixtures of metallic and semiconducting SWNTs, despite continuing effort on metallicity-selective nanotube growth. We highlight significant advances and major achievements in the development of post-production separation methods, which are now capable of harvesting separated metallic and semiconducting SWNTs from different production sources, with sufficiently high enrichment and quantities for satisfying at least the needs in research and technological exploration. We also present some representative uses of the separated nanotubes, such as metallic SWNTs for transparent conductive electrodes widely applicable in optoelectronic systems and their semiconducting counterparts for nanoscale sensors, field-effect transistors, and other device nanotechnologies. For more information, see “Separated Metallic and Semiconducting Single-Walled Carbon Nanotubes: Opportunities in Transparent Electrodes and Beyond” by Fushen Lu, Mohammed J. Meziani, Li Cao, and Ya-Ping Sun on pages 4339-4350.



Publications Acknowledging AFOSR Support

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