

Supplementary Information (SI)

**Tandem Extraction Strategy for Separation of Metallic and
Semiconducting SWCNTs Using Condensed Benzenoid Molecules:
Effects of Molecular Morphology and Solvent**

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TEM images

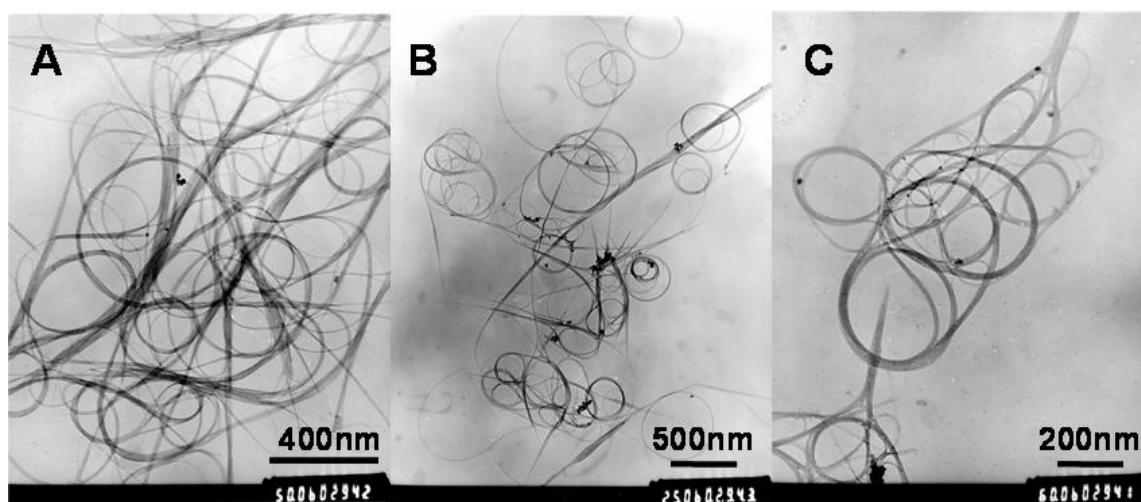


Fig. S1. TEM images of pristine SWCNTs (A), AN-S1 (B) and TMSEP-S1 (C) deposited on Cu TEM grids. All samples show high purity.

Dynamic light scattering (DLS) measurements

TABLE S1. Dynamic light scattering (DLS) mean diameters of different samples dispersed

in DMF using TMSEP as separation reagent.

Sample	Pristine SWCNT	S1	D1	S2	D2
DLS diameter (nm)	140	93	1286	116	2493

The DLS measurements were performed on a Brookhaven Instruments BI-200SM system (USA). The mean DLS diameters of the various samples were obtained using a model assuming that the solid contents existed as spherical particles. Therefore, the diameter values in Table S1 do not correspond to any specific physical parameter. However, the mean diameter values shall provide useful information helps to assess the nanotube aggregation states in various suspensions. The S1 and S2 solution were obtained according to the experimental procedure described in the main text (Fig. 3). For the pristine SWCNT, the sample was sonicated in DMF for 2h and then centrifugated under the same condition as that of the S1, S2 samples, and only the supernatant fraction were used in the DLS measurement. The suspension of D1 and D2 samples were prepared by sonicating the samples in DMF for 2h before the DLS measurement. DLS results indicate that the SWCNTs in the S1 and S2 samples are well dispersed and in a much less aggregated state than that of the starting materials and D1 and D2 samples. Very large mean diameters and wide size distributions were observed on both the D1 and D2 suspensions, which strongly suggest that there are many large bundles and aggregated particles in the two fractions.

Effects of the N-containing solvents and TMSEP adsorption on the Raman spectra of SWCNTs

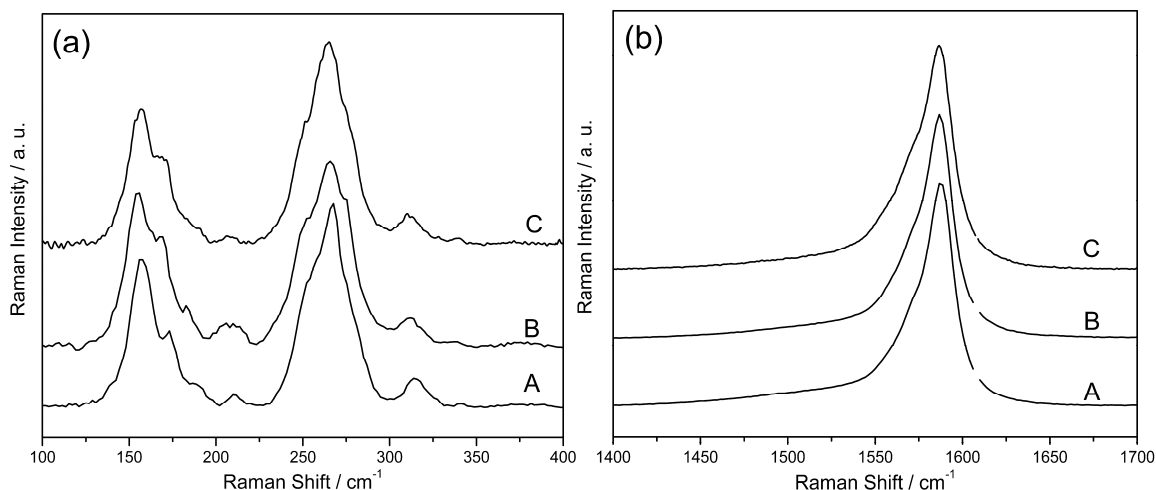


Fig. S2. RBM mode (a) and G band (b) of, supernatant (A) and deposition (B) samples obtained in pure NMP compared with the starting SWCNT sample(C).

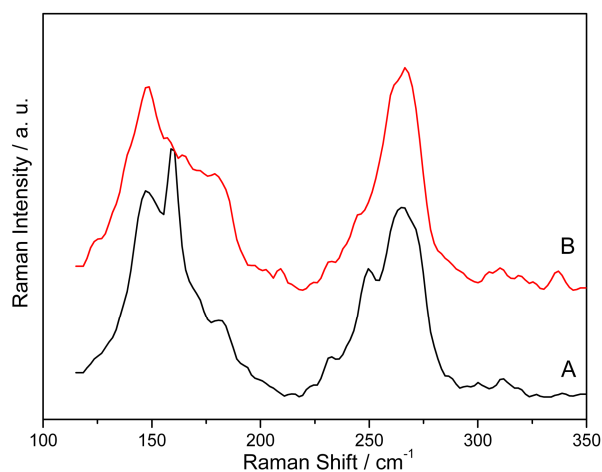


Fig. S3. Raman spectra of pristine SWCNT (A) and TMSEP modified SWCNT (B) under 532 nm excitation. Each spectrum reported herein represents an average of at least eight Raman spectra measured on different spots of same SWCNT sample.

Since amines have been reported to show selective adsorption on SWCNTs, it raises the question that whether the N-containing solvents have selectivity towards different SWCNTs. Hence, the effects of the N-containing solvents, including DMF and N-methyl-2-pyrrolidone (NMP), on the dispersibility of different types of SWCNTs were investigated. The SWCNTs were treated by a dispersion-centrifugation process in the pure solvents of DMF and NMP in

the absence of condensed benzenoid aromatic molecules. The supernatant and deposition parts were collected and examined by RRS at 532 nm (Fig. S2). Despite the small change in the peak shape, there is no obvious change in the intensity ratio of the met- and semi- bands in the RBM region. Meanwhile, no change in peaks shape in the G bands was observed. Fig. S2 confirms that the solvents, *ie.* DMF and NMP, used in this work have no ability in selectively dispersing SWCNTs. The M/S selectivity observed in this work is attributed solely to the selective adsorption of the condensed benzenoid molecules. Fig S3 shows that the adsorption of TMSEP onto the SWCNT surface does not cause significant change to the M/S ratio in the Raman spectra.

M/S ratio calculation

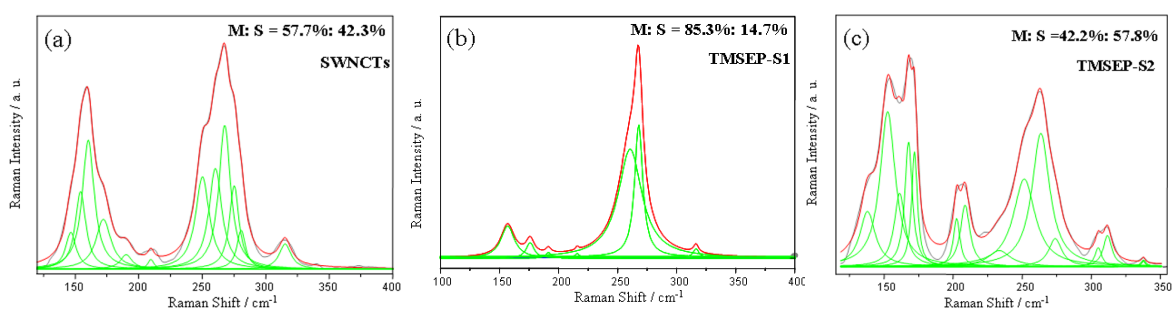


Fig. S4. M/S ratio calculation of pristine SWCNTs (a), TMSEP-S1 obtained in DMF (b) and TMSEP-S2 in CHCl₃ (c). The RBM bands were fitted using multiple Lorentz peaks.

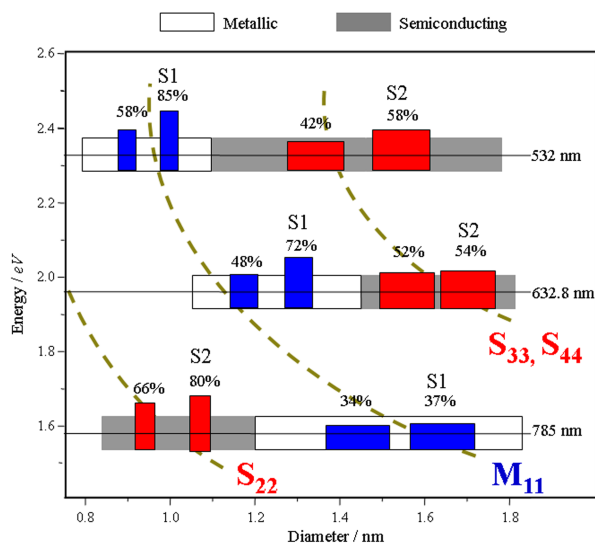


Fig. S5. Separation efficiency map of met- and semi-SWCNTs extracted by TMSEP, based on the RRS spectra under multi-wavelength excitation.

TABLE S2. Abundance of met- and semi- SWCNTs* in the produced samples using AN, TMSEP, PBA as separation reagents in different solvents, as measured from the Raman spectra under 532 nm excitation.

	AN		TMSEP		PBA	
	met- ^a	semi- ^b	met- ^a	semi- ^b	met- ^a	semi- ^b
DCB	68.1%	42.3%	57.8%	43.7%		
CHCl ₃	72.2%	42.3%	74.6%	57.8%		
NMP	69.4%	46.9%	80.3%	51.0%	60.6%	42.3%
DMF	79.3%	43.7%	85.3%	46.9%	58.4%	52.1%

*When measured under the same condition, the abundance of the met- and semi- SWCNTs in the starting materials were found to be 57.8% and 42.2%, respectively.

^a S1 samples (supernatant from the first extraction process).

^b S2 samples (supernatant from the second extraction process).