Supporting Information

for

Removable and Recyclable Conjugated Polymers for Highly Selective and High-Yield Dispersion and Release of Low-Cost Carbon Nanotubes

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1. Polymer Synthesis and Characterization

1.1 Materials and general methods

All reagents and starting materials were purchased from commercial sources and used without further purification. Thermal gravimetric analyses (TGA) were performed using a Mettler Toledo TGA/SDTA 851e at a heating rate of 10 °C/min under a nitrogen flow (20 mL/min). Gel permeation chromatography (GPC) was performed on Tosoh High-temperature EcoSEC (RI detector) at high-temperature of 180 °C using 1,2,4-tricholorobenzene (TCB) as eluent. Compounds **1** was purchased from Sigma-Aldrich.

Table S1. Price of commonly used polymers and SWNTs for sorting

Polymer/SWNT	Puriy[a]	Vendor	Price (USD)
Poly(9,9-di-n-dodecylfluorenyl-2,7-diyl) (PFDD)	99%	Sigma-Aldrich[b]	364.5/500mg
Regioregular poly(3-dodecylthiophene-2,5-diyl) (r-P3DDT)	99%	Sigma-Aldrich[c]	$642/g
RN020-SWNT	30%	Raymor Industries[d]	$10/g
RN220-SWNT	60~70%	Raymor Industries[d]	$45/g
AP-SWNT	30%	Carbon Solutions[e]	$35/g
P2-SWNTs	60%~70%	Carbon Solutions[e]	$280/g

[a] SWNT content purity contains both s-SWNTs and m-SWNTs.

[b] http://www.sigmaaldrich.com/catalog/product/aldrich/571660

[c] http://www.sigmaaldrich.com/catalog/product/aldrich/450650

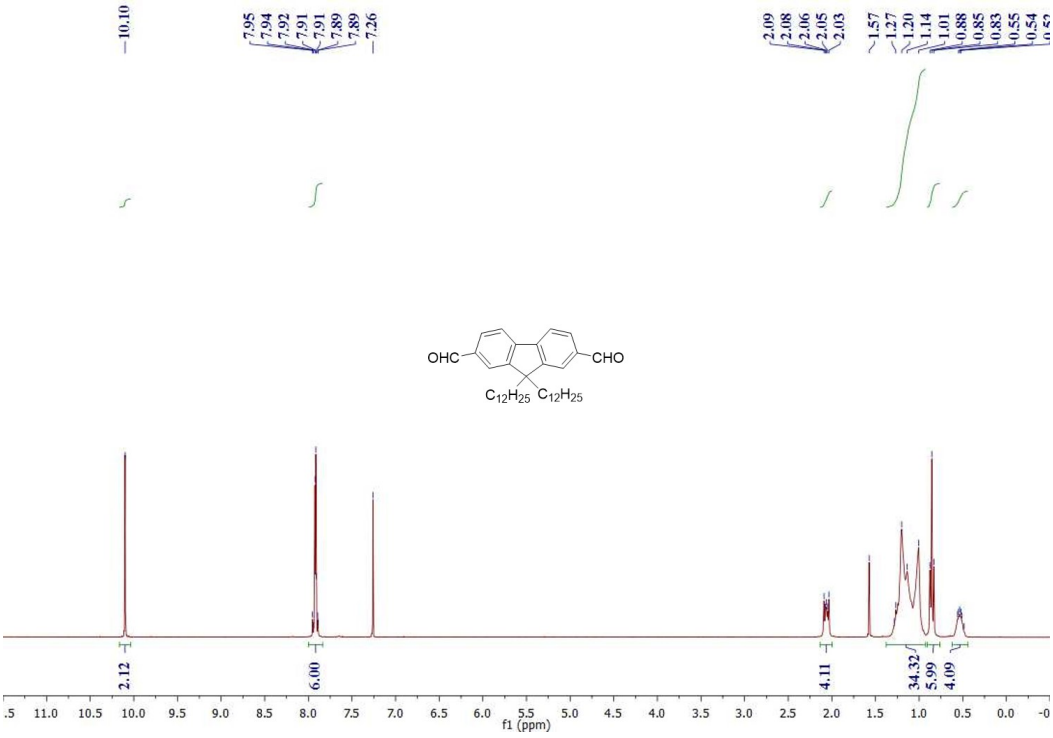
[d] http://raymor.com/our-products/plasmatubes/

[e] http://carbonsolution.com/products

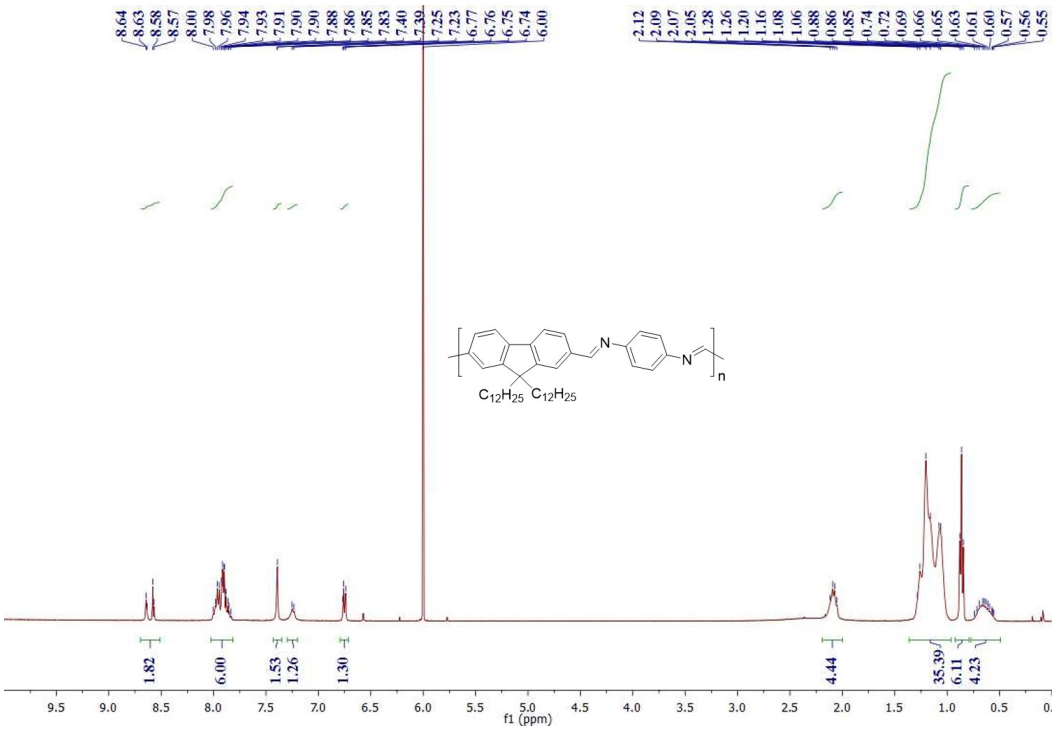
1.2 Polymer synthesis

9,9-didodecyl-9H-fluorene-2,7-dicarbaldehyde (**F-CHO**)[1]: To a 100 mL round bottom flask, compound **1** (3 g, 4.54 mmol) and ethyl ether (40 mL) was added. n-BuLi (2.5 M, 4.54 mL, 11.4 mmol) was added at −78 °C. After stirring at −78 °C for 30 min, dry DMF (1.16 g, 15.9 mmol) was added dropwise at −78 °C. The mixture was allowed to warm up to room temperature and stir for 1 h. Then the mixture was quenched with HCl (50 mL, 1 M aqueous solution). The aqueous layer was extracted with dichloromethane (3 × 50 mL). The combined extracts were washed with distilled water, dried over anhydrous Na_2SO_4. After removal of the solvents under reduced pressure, the residue was purified via chromatography with silica (eluent: hexane/dichloromethane = 4/1 to 1/1) to afford **F-CHO** as an off-white solid. Yield: 2.23 g (88%). ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 10.10 (s, 2H), 8.00–7.84 (m, 6H), 2.13–2.00 (m, 4H), 1.38–0.93 (m, 36H), 0.85 (t, J = 6.8 Hz, 6H), 0.62–0.44 (m, 4H).

Polymerization for **PF-PD:** To a Schlenk tube (100 mL), **F-CHO** (800 mg, 1.43 mmol), *p*-phenylenediamine (154.8 mg, 1.43 mmol), *p*-toluenesulfonic acid (PTSA) (13.6 mg, 0.0715 mmol, 5 mol%), anhydrous $CaCl_2$ (200 mg), and anhydrous toluene (50 mL) were added under nitrogen atomsphere. The internal drying agent anhydrous $CaCl_2$ was employed to remove the generated H_2O and thereby increase the molecular weight of the polymers. The tube was then sealed under nitrogen atomsphere. The mixture was stirred for 48 h at 110 °C. After completion, dry K_2CO_3 (20 mg) was added to neutralize the mixture and the mixture was stirred at 110 °C for 30 mins. Then the mixture was filtered through a nylon filter and washed with toluene to remove the drying agent and any insoluble salts. After removing the solvent in vacuum, the polymer was collected to afford a yellow solid (890 mg, yield 99%). ^{1}H NMR ($C_2D_2Cl_4$, 400 MHz, ppm): δ 8.64–8.57 (m, 2H), 8.00–7.83 (m, 6H), 7.40–7.23 (m, 2H), 6.77–6.74 (m, 2H), 2.12–2.05 (m, 4H), 1.28–1.06 (m, 36H), 0.88–0.85 (t, J = 6.8 Hz, 6H), 0.69–0.55 (m, 4H). Molecular weight from HT-GPC, M_w: 15,580 Da, PDI: 2.19.



^{1}H NMR spectrum of F-CHO in $CDCl_3$ at 298K.



^{1}H NMR spectrum of polymer PF-PD in $C_2D_2Cl_4$ at 298K

1.3 Thermal stability of polymer

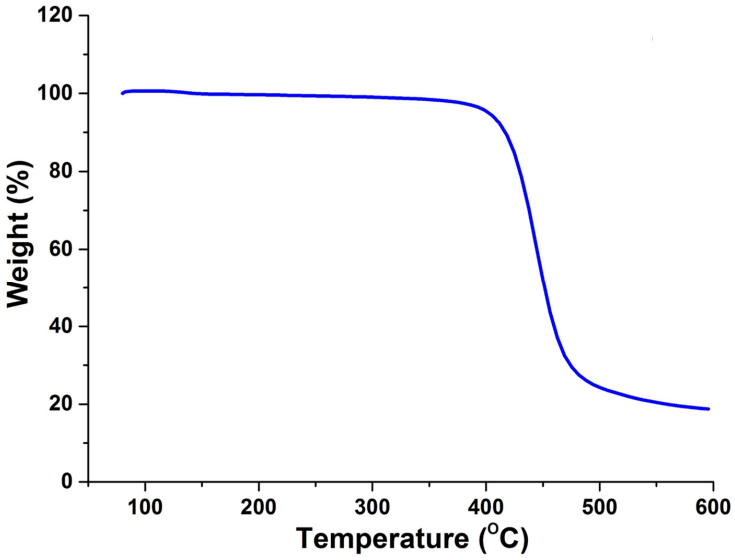
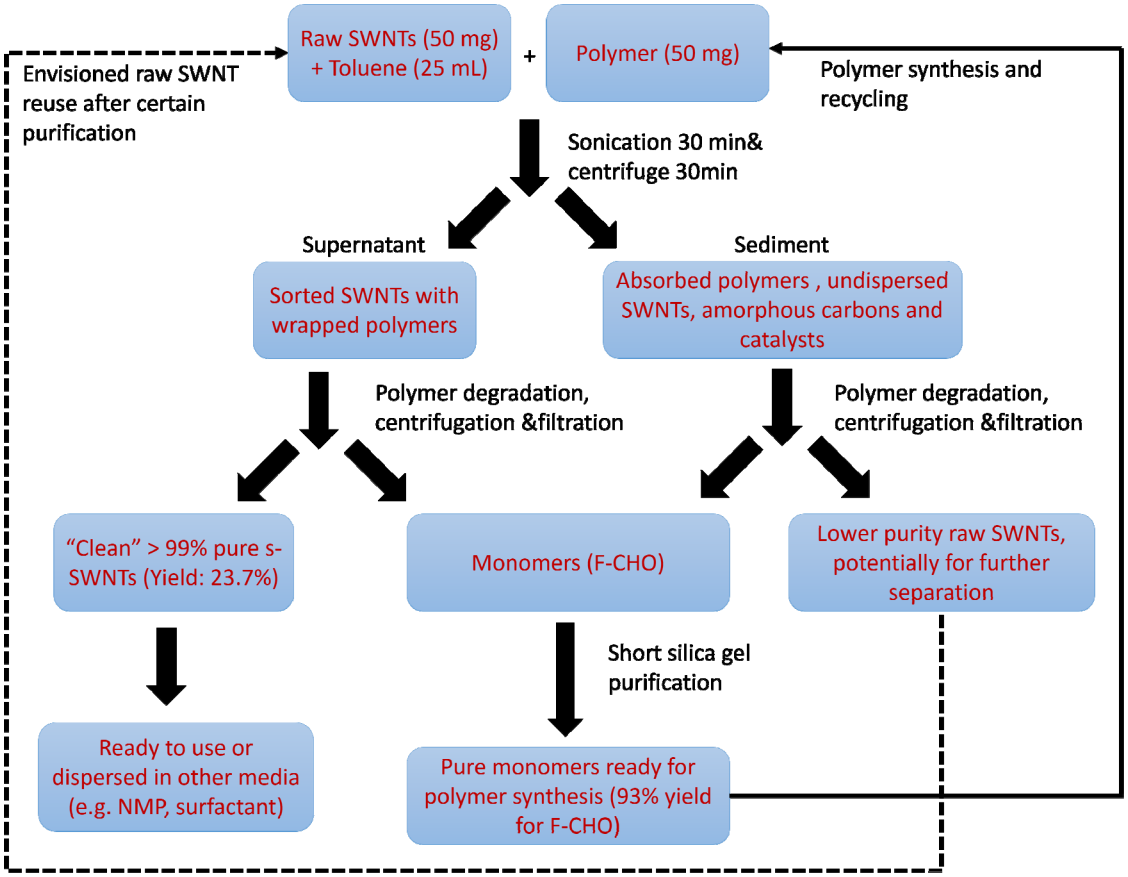


Figure S1. Thermogravimetric analyses (TGA) of PF-PD (5% loss, 400 °C).

2. Selective Dispersion, Release and Recycling



Scheme S1. Summary of the experimental procedures used in this study.

2.1 Selective dispersion and determination of sorting yield

50 mg of PF-PD and 50 mg of raw SWNTs (RN-020) were mixed in 25 mL of toluene and ultrasonicated for 30 min at an amplitude level of 50% (Cole Parmer ultrasonicator 750 W) while externally cooled with a dry ice bath (Scheme S1). The solution was then centrifuged at 17 000 rpm (22 000 g) for 30 min at 16 °C. 80 % of the supernatants (20 mL) was collected. Absorption spectroscopy revealed a peak absorption of A = 2.486 at λ = 939 nm for a d = 1 cm cuvette (Figure 2b in the paper).

To remove the wrapping polymers, a small amount of TFA (20 μL) and 1 drop of water were added to the sorted SWNT solution. SWNT precipitates were formed after depolymerization. The solution was bath sonicated for 30 mins to complete the hydrolysis reaction. Then the mixture was centrifuged at 17 000 rpm for 5 min to

sediment the SWNTs. The sediment was finally filtered through a 0.2 μm pore-size PTFE membrane, washed with toluene 3 times (20 mL), and dried in vacuum at 60 °C. All the filtrates were collected for polymer recycling. A SWNT film was formed on the membrane after filtration. Weighting the SWNT film gives a total mass of 1.41 mg. Thus the SWNT concentration of the sorted solution (20 mL) was calculated to be 0.0705 mg/mL.

The optical density at 939 nm was used to calculate the absorbance coefficient (ε, mL mg^{-1} cm^{-1}) via Beer-Lambert law: $A = OD_{939} = \varepsilon lc$, where l is the path length (cm) of the cuvette and c is the SWNT concentration (mg/mL). To obtain the calibration curve for absorbance coefficient (ε), we prepared s-SWNT solutions with different concentrations by dispersing the sorted s-SWNTs to PF-PD polymer solutions. Figure S2b shows the calibration curve. Based on the curve, we can calculate the absorbance coefficient to be 35.3 mL mg^{-1} cm^{-1}, consistent with a recently reported value of 34.9 mL mg^{-1} cm^{-1} for similar type of s-SWNTs.[2]

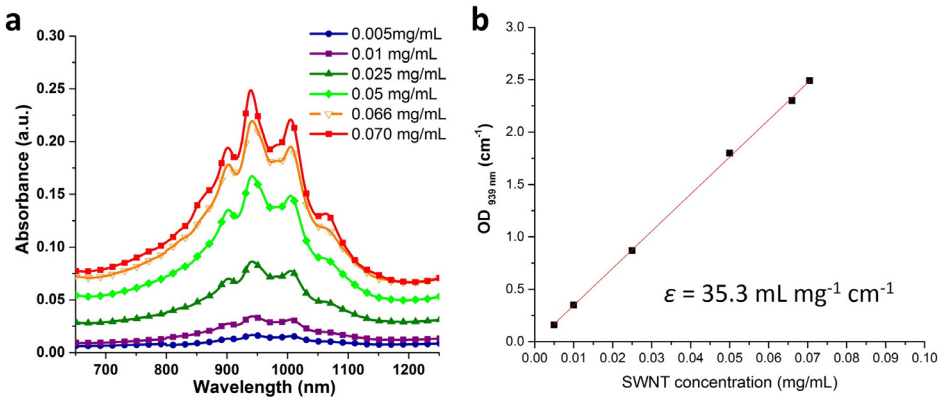


Figure S2. (a) Absorption spectra of sorted s-SWNTs dispersed in PF-PD/toluene solutions. (b) Optical density at 939 nm for six different s-SWNT concentrations. The linear regression line (red) shows an absorbance coefficient of 35.3 mL mg^{-1} cm^{-1}.

The yield of PF-PD sorted SWNTs was based on the semiconducting SWNT content of the raw samples. The SWNT content in the raw samples was provided by the vendor (Raymor Industries Inc., http://raymor.com/our-products/plasmatubes/), which is 30% estimated by thermogravimetric analysis. Because the raw SWNTs are produced by plasma torch process, the semiconducting and metallic tubes are statistically produced with a ratio of 2:1. Thus the s-SWNT content in the raw samples is estimated to be 20%.

For example, for polymer/SWNT = 5 mg:5 mg, the optical density at 939 nm of the solution (25 mL) is 0.334. With the absorbance coefficient (ε = 35.3 mL mg^{-1} cm^{-1}), the s-SWNT amount in the solution can be calculated to be 0.334/35.3×25=0.237 mg. Since the s-SWNT content in the raw samples is 20%. Thus the yield can be calculated to be 0.237/(5 × 20%) = 23.7%.

2.2 Polymer removal and recycling

The sediment produced in the sorting process contains amorphous carbon, m-SWNTs, and undispersed s-SWNTs, which absorbed a significant amount of polymers (about 1/2 to 2/3 of the conjugated polymers were absorbed). To recycle these polymers, 20 mL acetone, a small amount of TFA (20 μL) and 1 udrop of water were added. The mixture was sonicated for 30 mins in a bath sonicator and centrifuge at 17 000 rpm for 15 mins to wash the SWNT sediments. Repeating the washing step twice. Then the sediments were removed by filtration.

All the filtrates from the above steps were combined for polymer recycling (Scheme S1). After removal of the solvents under reduced pressure, the yield of the monomer (F-CHO) was first determined by absorption spectroscopy based on the absorbance coefficient (ε) of F-CHO. The absorbance coefficient (ε) was determined by measuring the optical density of F-CHO absorption peak at 341 nm, which was calculated to be 61.4 mL mg^{-1} cm^{-1} using Beer-Lambert law: $A = OD_{341} = \varepsilon lc$. For a 50 mg polymer, the amount of the degraded monomer (F-CHO) was calculated to be 43.5 mg, corresponding to a yield of 98.6%.

The monomer was purified via short flash chromatography (eluent: hexane/dichloromethane = 1/1), yielding the pure F-CHO (41.1 mg, yield: 93%). The structure of the monomer was confirmed by ^{1}H NMR, which can be used for polymerization as described in the synthesis part. We did not attempt to collect and purify the *p*-phenylenediamine co-monomer as it is readily available commercially at low cost.

2.3 Raman and PLE characterization of sorted SWNTs

Raman spectroscopy was carried out at 2.33 eV (532 nm), 1.93 eV (638 nm) and 1.58 eV (785 nm) excitations at ×100 magnification and 1-μm spot size. The peak positions were

calibrated with the Si line at 521 cm^{-1}. To compare peak intensities of pristine and sorted SWNTs, their G^+ peaks were normalized to the same intensity. The Raman peaks can be assigned to metallic or semiconducting SWNTs according to the Raman Kataura plot. The PLE spectra of various SWNT samples in toluene were taken using Horiba Fluorolog-3 system. Several strong peaks are assigned according to the theoretical prediction by Weisman *et al.*[3]

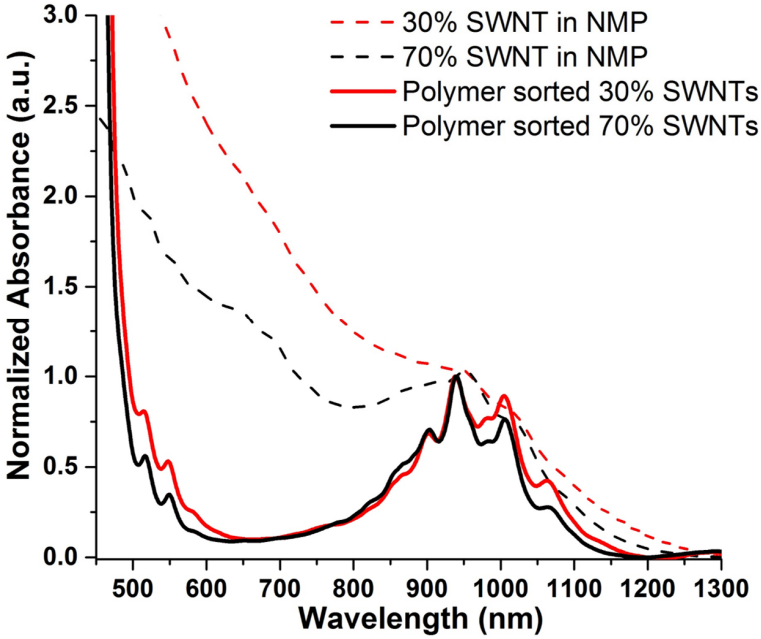


Figure S3. Comparison for using different purity SWNTs under the same sorting conditions (polymer/SWNT ratio = 1:1).

As-produced 30% SWNTs (RN-020, 10 USD/g) and semi-purified SWNT (RN-220, 60~70% purity, 45 USD/g) were purchased from Raymor Industries Inc. (http://raymor.com/our-products/plasmatubes/). Semi-purified SWNTs display obviously higher SWNT contents than as-produced raw SWNTs, as shown by their NMP dispersed solutions. After PF-PD sorting, 30% SWNTs showed a ϕ value of 0.407 and a yield of 23.7%, while 70% SWNTs showed a ϕ value of 0.408 and a yield of 19.8%. The yield calculation was based on the s-SWNT amounts of the total mass of raw SWNTs (for RN-020, the s-SWNTs amount is 20%; for RN-220, the s-SWNT amount is 46%). Therefore, compared with 70% semi-purified SWNTs, 30% raw SWNTs showed very similar selectivity and even higher yield.

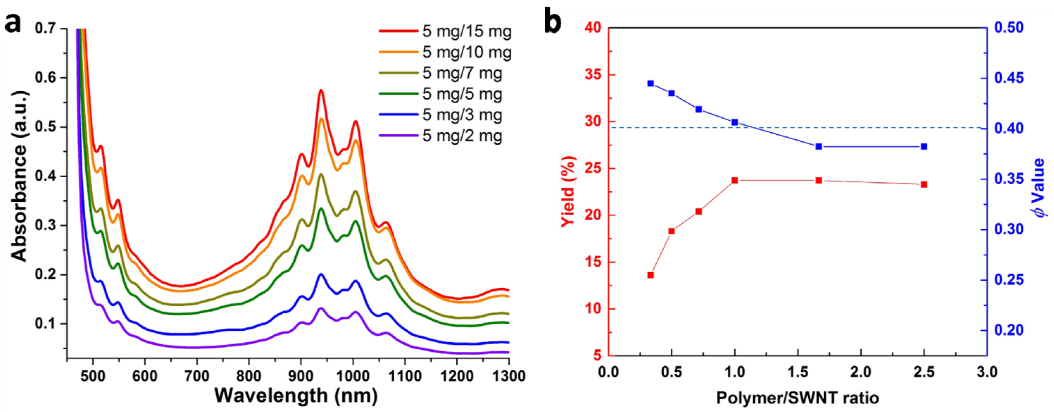


Figure S4. (a) Absorption spectra of raw SWNTs (30% purity) dispersed by PF-PD using different polymer/SWNT ratios. (b) Plot of yields and ϕ values for different polymer/SWNT ratios. Higher SWNT contents give lower yield but higher selectivity.

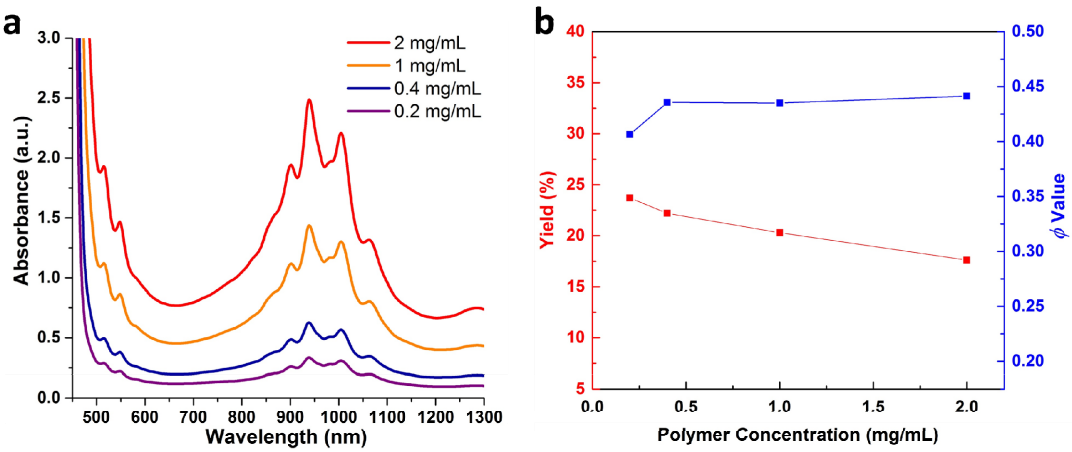


Figure S5. (a) Absorption spectra of raw SWNTs (30% purity) dispersed by PF-PD using different polymer concentrations (polymer/SWNT ratio = 1:1). Spectra were taken in a 1 cm path length cuvette. (b) Plot of yields and ϕ values for different polymer/SWNT concentrations. Higher concentrations give slightly lower yield but provide higher throughput for large-scale production.

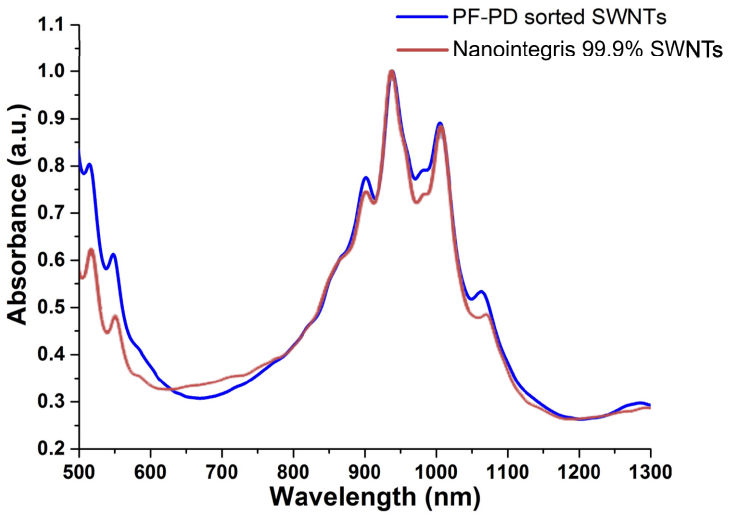


Figure S6. Purity comparison of the s-SWNTs dispersed by PF-PD with commercially available 99.9% pure s-SWNTs from Nanointegris (the spectrum was adapted from the company website: http://www.nanointegris.com/en/IsoSol-S100). PF-PD sorted s-SWNTs with similar tube diameters showed better selectivity as indicated by the "deep valley" in the M_{11} region (600~760 nm).

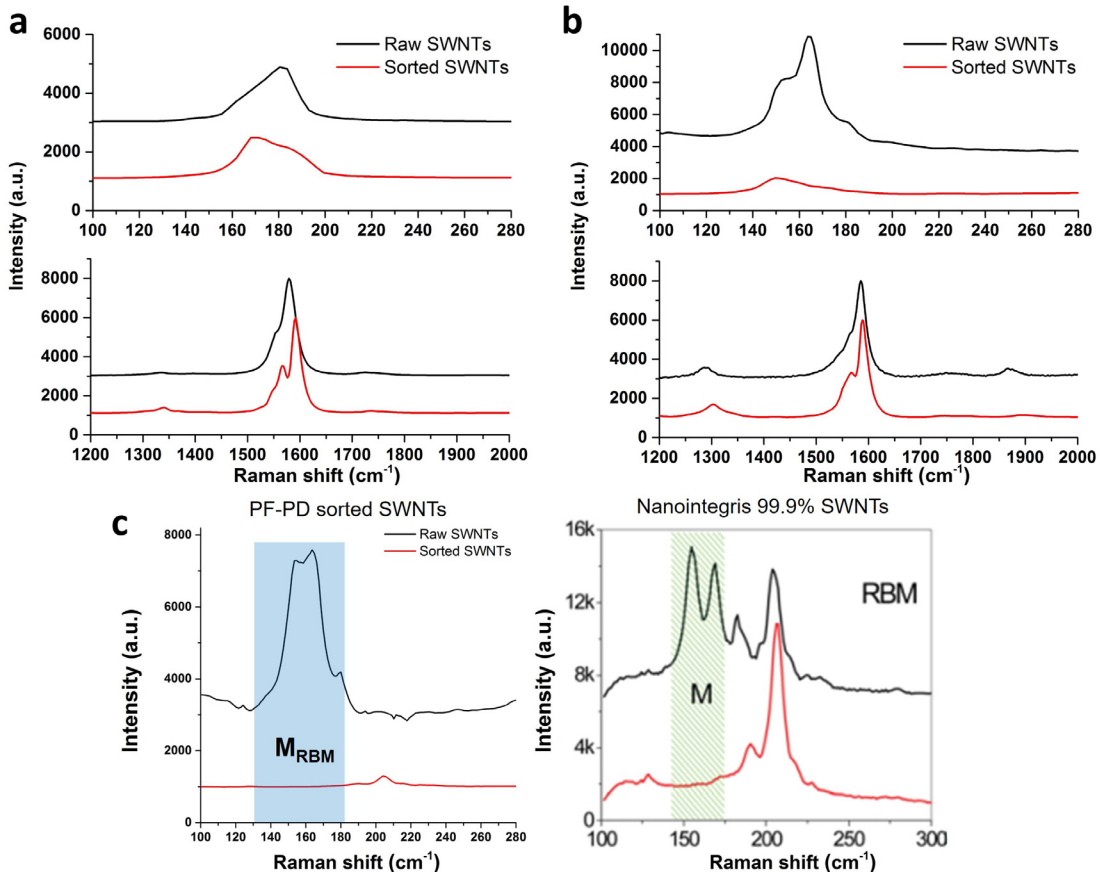


Figure S7. Raman spectra of pristine SWNTs and SWNTs sorted by polymer PF-PD, excited using (a) 532 nm and (b) 638 nm lasers. Under 532 nm and 638 nm excitations, several RBM peaks of s-SWNTs were observed in the range of 150−200 cm^{-1} in the pristine SWNTs. After sorting, some peaks remained and the relative peak intensity also changed, indicating that the polymer prefers to disperse certain chiralities of s-SWNTs. (c) Raman spectrum (785 nm) comparison of PF-PD sorted s-SWNTs (left) and the 99.9% pure s-SWNTs from Nanointegris (right) (the Raman spectrum was adapted from the company website: http://www.nanointegris.com/en/IsoSol-S100). For the commercial 99.9% pure s-SWNTs, some metallic peaks in the range of 140~180 cm^{-1} can still be observed; however, for PF-PD sorted SWNTs, the metallic peaks can hardly be detected. This result also indicates the higher purity for PF-PD sorted s-SWNTs.

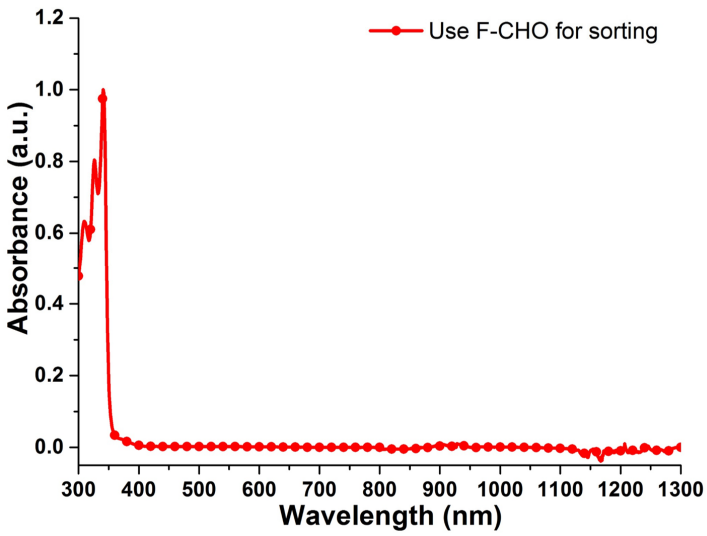


Figure S8. Absorption spectra of the solution using monomer F-CHO for dispersion. No SWNT absorption was detected, indicating that the monomer cannot disperse any SWNTs.

3. Device Fabrication and Characterization

Short channel device fabrication and characterization. Diluted SWNT solutions (20 times) were drop-casted on thermally grown SiO_2 (36nm)/Si wafer, wait 20 seconds, then gradually ramp spin speed to 3000 RPM until the surface is dry. Removal of wrapping polymers from SWNTs was carried out by rinsing with toluene containing a small amount (0.1 % v/v) of TFA and rapid thermal annealing (RTA) of wafer for 15 min in N_2 at 500°C. Palladium (30 nm) as metal contact was defined by traditional photolithography process using an ASML 5500 Stepper. Using a chuck to globally bias the wafer as a gate, the electrical behavior of the carbon nanotubes was measured using an Agilent 4156C. Since most of the sorted tubes exhibited tube lengths in the range of 0.5 to 2 μm (Figure S10), the short channel devices used here will short if there are m-SWNTs bridging directly across the channel.

TFT fabrication and characterization. The drain and source electrodes for bottom-contact device electrodes were fabricated on a highly doped 4 in. silicon wafer with 300 nm SiO_2 by photolithography. A bilayer of Cr (3 nm) and Au (25 nm) was deposited by

thermal evaporation as the source-drain electrodes, followed by a lift-off process in acetone. The SWNT networks were fabricated by drop-casting the polymer sorted SWNT solutions and then rinsed with toluene containing a small amount (0.1 % v/v) of TFA to remove polymer residues, then dried with nitrogen flow, and annealed at 200 °C for 20 min. Toluene rinsing was used to degrade and remove the polymer residues. Annealing lead to better tube-tube junctions and improved source/drain contacts. The evaluations of the FETs were carried out in atmosphere on a probe stage using a Keithley 4200 SCS as parameter analyzer. The carrier mobility, μ, was calculated from the data in the saturated regime (V_{DS} = –40V). Devices with different channel lengths of 5, 10, 20 and 30 μm were fabricated and tested.

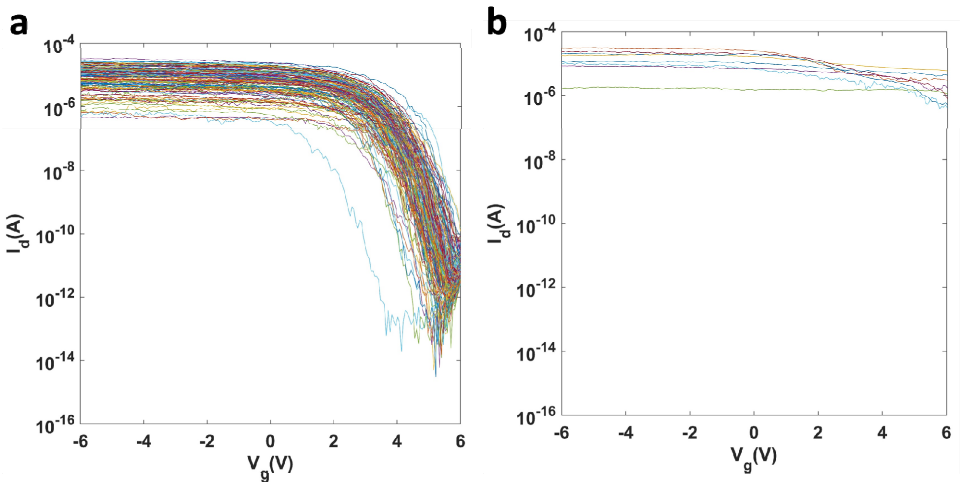


Figure S9. Short-channel device (500 nm) characterization of PF-PD sorted SWNTs. Transfer characteristics of (a) 182 semiconducting devices; (b) 8 shorted devices.

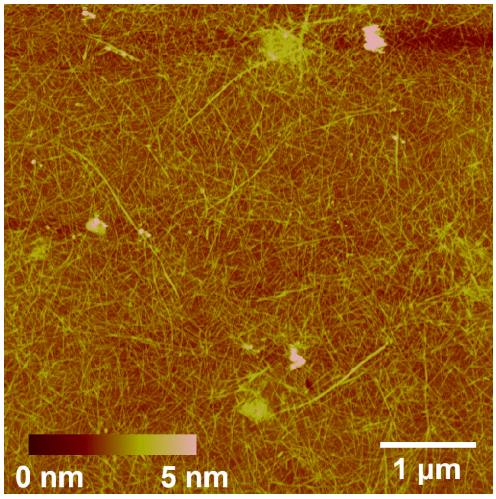


Figure S10. AFM height images of SWNT network fabricated by drop-casting and rinsed with toluene containing a small amount (0.1 % v/v) of TFA.

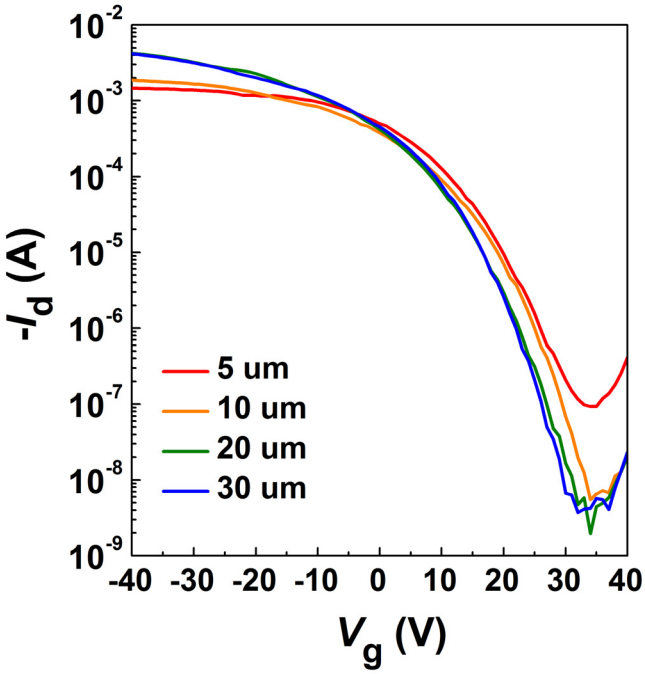


Figure S11. Transfer characteristics of TFT devices with different channel lengths. 10, 20 and 30 μm devices showed high on/off ratios >10^6; 5 μm devices showed slightly lower on/off ratios of 10^4–10^5. Compared to the unsorted raw SWNTs with on/off ratios lower than 10, the high on/off ratios further confirmed the high purity of the sorted s-SWNTs.

4. References

(1) Xu, J.; Takai, A.; Kobayashi, Y.; Takeuchi, M. *Chem. Commun.* **2013**, *49*, 8447.

(2) Mistry, K. S.; Larsen, B. A.; Blackburn, J. L. *ACS Nano* **2013**, *7*, 2231.

(3) Weisman, R. B.; Bachilo, S. M. *Nano Lett.* **2003**, *3*, 1235.