

A Mixed-Extractor Strategy for Efficient Sorting of Semiconducting Single-Walled Carbon Nanotubes

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Single-walled carbon nanotubes (SWNTs) have been widely studied for applications in electronics due to their high charge carrier mobility, mechanical flexibility, and compatibility with electronics.^[1–9] However, as-synthesized SWNTs are mixtures of semiconducting SWNTs (s-SWNTs) and metallic SWNTs (m-SWNTs), hindering their practical application in semiconductor-based electronics. Many methods (such as density gradient ultracentrifugation,^[10] gel chromatography,^[11] and aqueous two phase extraction^[12]) have been established to isolate s-SWNTs. Selective dispersion of s-SWNTs using conjugated molecules is considered as a very promising method for its simple procedures and high s-SWNT purity (99%).^[13–16] Furthermore, the sorted s-SWNTs are free from ions because they are directly dispersed in organic solvent, which facilitates the fabrication of thin film transistors (TFTs).^[17] This technology is thus considered to hold great promise for batch preparation of high purity s-SWNTs. However, the development of this separation technology is hindered by several problems. The most concerned problem is that the polymer wrapped on s-SWNT is hard to remove after separation, which is possible to be solved by designing supramolecular polymer^[18] or narrow bandgap polymer.^[19] Another problem is the low yield of the single extraction process for all the reported polymers, with the highest yield being 20%.^[16,20] Like other sorting methods, attaining high purity of s-SWNTs usually requires a complicated process, which inevitably results in low yield of s-SWNTs. The yield could be improved by increasing the concentration of conjugated molecules, extending the sonication time, or multiplying extraction processes, but at the expense of excess polymer contamination, reduced purity, shortened length, and

increased final cost. Therefore, it is important to establish a convenient method that increases the yield without affecting the product purity.

In the general sorting process, SWNT in solid powder form is first wrapped by the conjugated molecule, extracted to solution, and then stabilized by free conjugated molecules in solution.^[20] The conjugated molecule is defined as an extractor molecule. Dynamic mutual exchange which is the exchange between the individually dispersed state and the bundled state of the SWNTs is repeated during the sonication. The SWNTs are therefore isolated and recombined alternately and repeatedly until they are wrapped adequately by the conjugated molecules and stay isolated in solution.^[21] Among many factors that influence the separation, such as the type of solvent,^[22,23] molecular weight of polymers,^[24] and temperature,^[20] there is no doubt that the structure of the conjugated molecule plays a key role.^[25] Taking the molecular rigidity as an example, proper rigidity of the polymer backbone is required to form a stable wrapping structure around specific nanotubes,^[26] while the solubilization of more SWNTs requires molecules with higher flexibility. Chirality sorting has been realized by using rigid conjugated polymers such as PFH-A, poly[(9,9-dioctylfluorenyl-2,7-diyl)-co-(1,4-pyridyl)] (PFP), poly(9,9-dioctylfluorenyl-2,7-diyl) (PFO), poly[(9,9-dioctylfluorenyl-2,7-diyl)-co-(1,4-bipyridyl)] (PFBP) with relatively low yield.^[27,28] Nevertheless, molecules having low rigidity like vinyllogous tetrathiafulvalene–fluorene copolymer,^[29] metal-coordination polymers,^[30] and PDPP3T^[31] show strong dispersing power for SWNTs without giving good discrimination between the s-SWNTs and m-SWNTs. It is evident that if only one kind of extractor molecule is used, high selectivity and high yield of s-SWNTs are difficult to achieve simultaneously.

Here, we develop a strategy to introduce an enhancer molecule to help increase the yield of s-SWNT through cooperation between extractor and enhancer molecules, as illustrated in Figure 1a. The enhancer molecule has conjugated structure and can also act as extractor for s-SWNTs, but it has higher rigidity than the extractor molecule. Based on comprehensive analysis of the sorting mechanism of the mixed-extractor system composed of regioregular poly(3-dodecylthiophene)s (P3DDT)^[20] and poly[9-(1-octylonyl)-9H-carbazole-2,7-diyl] (PCO),^[32] we propose a general principle for designing a mixed-extractor system. Other groups of mixed-extractor chosen according to our principle also show enhanced sorting efficiency.

P3DDT and PCO (Figure 1b) have both been reported as having good selectivity toward s-SWNTs. In a typical experiment, the concentration of both P3DDT and PCO is 0.5 mg mL⁻¹. HiPco SWNT powder is used with initial concentration of

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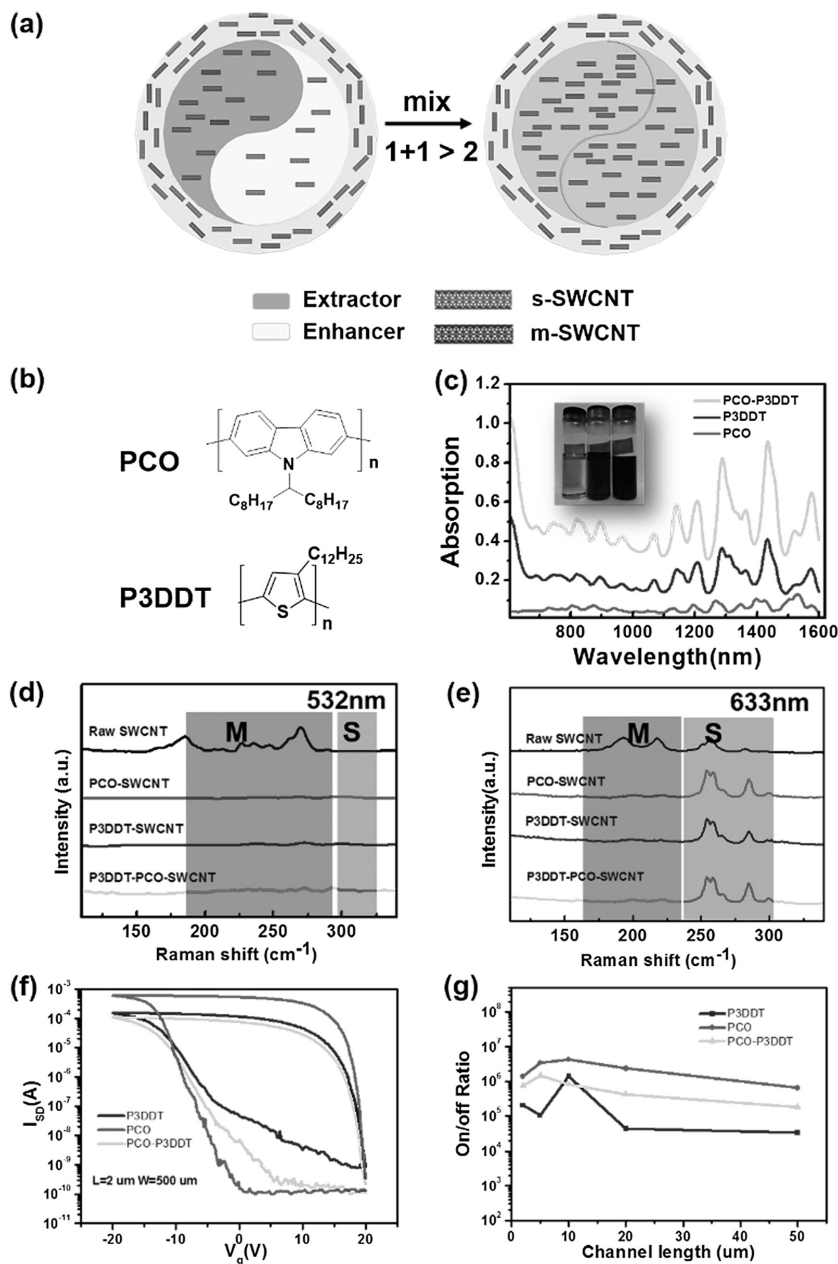


Figure 1. a) Schematic illustration of enhanced sorting of s-SWNT by mixed-extractor system. b) The chemical structure of PCO and P3DDT. c) Absorption spectra of s-SWNTs sorted by PCO/P3DDT mixed-extractor system, PCO, and P3DDT. The inset is an optical image of the corresponding solution of s-SWNTs, showing PCO, P3DDT, and mixed-extractor system from left to right. d,e) Raman regions of raw SWNT and s-SWNT sorted by PCO, P3DDT, and mixed-extractor excited by 532 and 633 nm. The RBM regions corresponding to metallic (M) and semiconducting (S) SWNTs are shaded. f) Typical transfer characteristic of TFTs ($L = 2 \mu\text{m}$, $W = 500 \mu\text{m}$) fabricated with s-SWNTs sorted by P3DDT, PCO, and mixed-extractor system. g) Plot of on/off ratio ($I_{\text{on}}/I_{\text{off}}$) versus channel length for TFTs fabricated with s-SWNT sorted by P3DDT, PCO, and mixed-extractor. The drain-source voltage used is 1.0 V.

0.25 mg mL⁻¹ for all solutions. SWNT solutions dispersed by mixed-extractor P3DDT/PCO, P3DDT, and PCO are denoted as P3DDT/PCO-SWNT, P3DDT-SWNT, and PCO-SWNT, respectively. Absorption spectra are collected to evaluate the dispersion efficiency. Previous reports have demonstrated that almost

all impurities including amorphous carbon and catalyst particles could be removed,^[15] which is confirmed by the nearly horizontal baseline in the absorption spectrum. Under this circumstance, the absorption value is directly related to the concentration of SWNTs in the solution (see details in Figure S4 in the Supporting Information, the concentration of s-SWNTs is linear with the concentration of polymer). For accurate evaluation, the peak area A is used to assess the concentration of sorted s-SWNTs. Specifically, the integral area of S_{11} peaks of sorted s-SWNTs are calculated by Equation (1)

$$A = \sum_{n=1}^n \int_{a_n}^{b_n} H d \quad (1)$$

where λ_{a_n} and λ_{b_n} represent the initial and final wavelengths of each peak in the absorption spectra, respectively, and H represents the absorption value at each wavelength of the peak. When each extractor molecule is used individually, the yield of s-SWNTs is linearly dependent on the concentration of the molecule (see details in Figure S4, Supporting Information). When the two extractor molecules are mixed, the S_{11} peak areas of P3DDT/PCO-SWNT ($A_{\text{P3DDT/PCO}}$) is much higher than the sum of S_{11} peak area of P3DDT-SWNT (A_{P3DDT}) and PCO-SWNT (A_{PCO}) Figure 1c. We use enhancement factor Ω to assess enhancement of yield, calculated by Equation (2)

$$\Omega = \frac{A_{\text{En/Ex}}}{A_{\text{En}} + A_{\text{Ex}}} \quad (2)$$

where $A_{\text{En/Ex}}$, A_{En} , and A_{Ex} represent the integral area of S_{11} peaks of s-SWNTs sorted by mixed-extractor, enhancer molecule, and extractor molecule, respectively. The Ω of P3DDT/PCO system is 1.92, which indicates that the dispersion yield of s-SWNTs has been significant enhanced by mixing of PCO and P3DDT. To further confirm the high yield, absolute yield for PCO-P3DDT system is estimated and found to reach about 40.5% for a single process when sonication time is 30 min and the concentration for PCO and P3DDT is 0.5 mg mL⁻¹ (see details in the Supporting Information). Furthermore, the P3DDT/PCO-SWNTs have peak positions

similar with P3DDT-SWNTs, but have higher intensities for these peaks.

The M_{11} absorption of m-SWNTs ranges from 400 to 600 nm, which overlaps with the absorption of P3DDT, so it is hard to obtain information directly about the content of

m-SWNTs from the absorption spectra. High temperature annealing has been applied to remove P3DDT wrapped on SWNT and corresponding absorption spectra show that there are no metallic peaks in the range of 400–600 nm (see details in Figures S2 and S3, Supporting Information). Resonant Raman spectra and electrical property measurements are also used to evaluate the purity of the s-SWNTs in the sample. For Raman spectra, we focused on the peak position of the radical breathing mode (RBM) of SWNTs. The 532 nm laser (2.33 eV) is mainly in resonance with m-SWNTs within RBM ranging from 180 to 280 cm^{-1} . Several peaks are observed in this range for raw SWNTs, indicating the existence of m-SWNTs. In comparison, the RBM peaks vanish (Figure 1d) for SWNTs dispersed by P3DDT, PCO, and P3DDT/PCO, which indicates selective enrichment of s-SWNTs by these three systems. The 633 nm laser (1.96 eV) is in resonance with m-SWNTs within the range of RBM peaks from 180 to 230 cm^{-1} and s-SWNTs from 230 to 300 cm^{-1} .^[20] Resonances for both m-SWNTs and s-SWNTs are observed for the unsorted SWNTs. For SWNTs sorted by P3DDT, PCO, and P3DDT/PCO, the absence of RBM peaks (Figure 1e) in the region of m-SWNTs is evidence for the efficient enrichment of s-SWNTs. TFT devices are fabricated to verify the purity of sorted s-SWNTs. It was reported that the probability of percolative transport through metallic networks becomes higher when the channel length decreases.^[34,35] So it is helpful to achieve on/off ratio which reflects the precise purity of s-SWNTs with smaller channel length. Based on this, five kinds of layout are designed with different channel lengths (L) and constant width ($W = 500 \mu\text{m}$) for each kind of solution, where $L = 2, 5, 10, 20,$ and $50 \mu\text{m}$ correspondingly. For each

layout, a group of ten devices is fabricated. Typical transfer curves of the SWNT TFTs with layout $L = 2 \mu\text{m}$, $W = 500 \mu\text{m}$ are shown in Figure 1f. The performance of TFTs with $L = 5, 10, 20,$ and $50 \mu\text{m}$ is similar to TFTs with $L = 2 \mu\text{m}$ (see Figures S8–S10, Supporting Information). The trend that the average on/off ratio increases as the channel length increased is not observed.^[34,35] Instead, the on/off ratio decreases only a little but still all higher than 10^5 when the channel length is reduced to 2 μm . Besides, the off-currents for each series of TFT devices do not change significantly with the change of channel length. The off-currents for PCO and PCO-P3DDT systems are 10^{-10} A and a little higher than 10^{-10} A for P3DDT system. The possible reason for this can be the very low content of m-SWNTs in all the three kinds of samples. So the purity of s-SWNTs sorted by PCO-P3DDT system is very high.

To gain better insight into the mechanism of enhancement by the mixed-extractor system, a series of experiments has been designed. The ratio of concentrations of the two molecules $C_{\text{P3DDT}}/C_{\text{PCO}}$ in the mixed-extractor system is varied to check its influence on the yield of the sorted s-SWNTs. As shown in Figure 2, When C_{P3DDT} is kept at 0.5 mg mL^{-1} , the absorption value increases along with C_{PCO} . However, the enhancement factor increases more gradually at higher PCO concentrations, which indicates the possible existence of a peak value for the enhancement factor. To explore this, the total concentration of P3DDT and PCO is kept constant at 1.0 mg mL^{-1} and the ratio of P3DDT/PCO is varied between 3:1, 1:1, and 1:3. The highest yield is attained at a P3DDT/PCO ratio of 1:1, suggesting the P3DDT/PCO mixed-extractor system has optimal performance when their concentrations are equal.

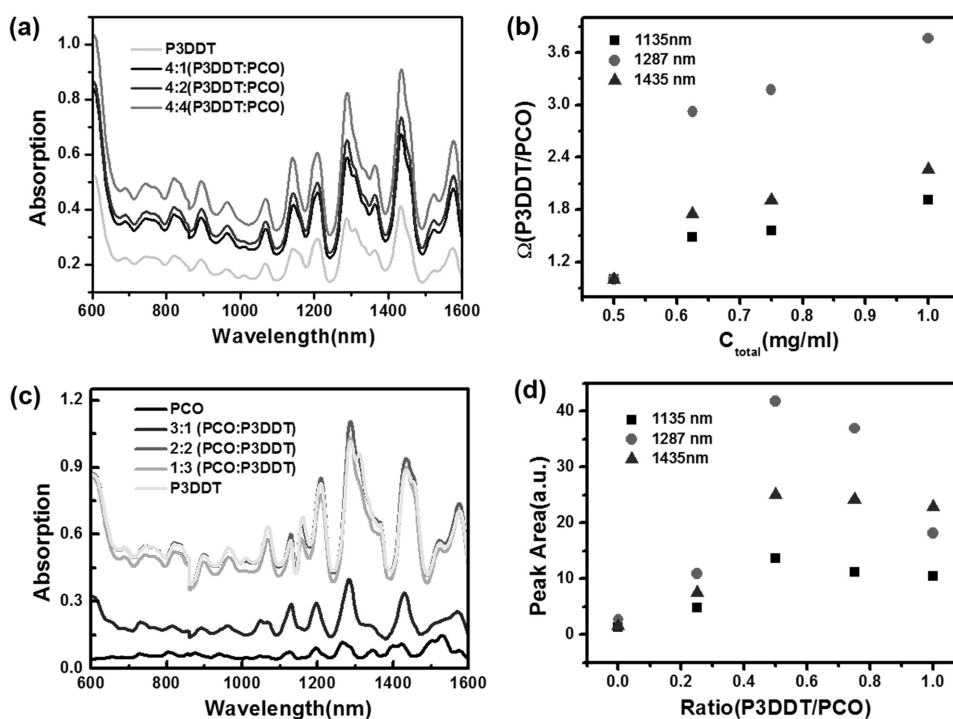


Figure 2. a) Absorption spectra of s-SWNT sorted by the P3DDT/PCO system with different concentrations of PCO. b) Peak areas of s-SWNT solution in (a) at three different wavelengths. c) Absorption spectra of s-SWNT sorted by the P3DDT/PCO system with different ratios of PCO to P3DDT. The total concentration is kept constant. d) Peak areas of s-SWNT solution in (c) at three different wavelengths.

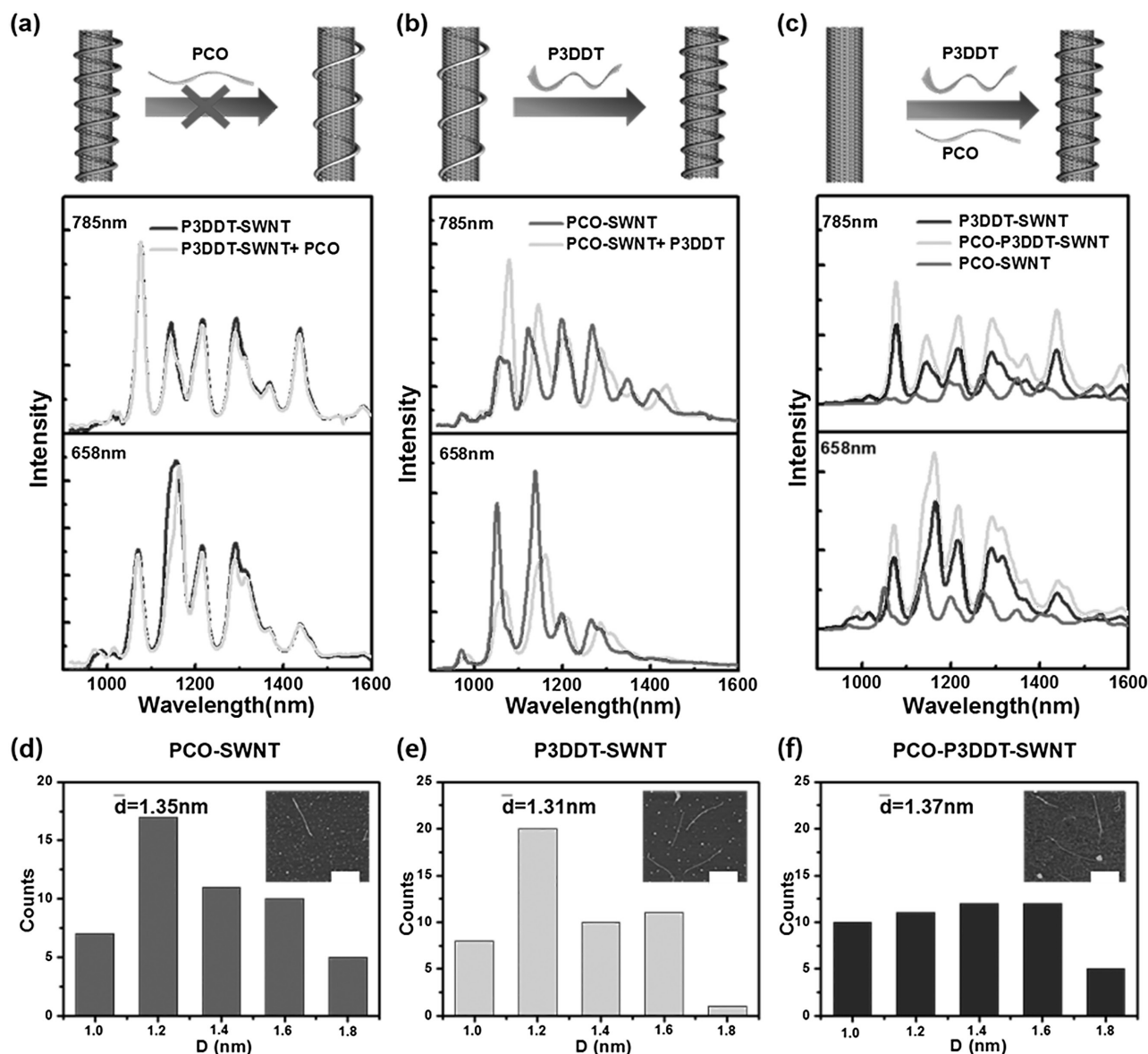


Figure 3. a–c) Difference of the binding ability between PCO and P3DDT is evaluated by comparing the fluorescence emission spectra when changing the addition sequence of the sorting molecules. The spectra are excited at 785 and 658 nm, respectively. a) s-SWNTs are first sorted by P3DDT and then sonicated with PCO added. The peak pattern and position of the fluorescence spectra show almost no change. b) s-SWNTs are first sorted by PCO and then sonicated with P3DDT added. The peak pattern and position of the fluorescence spectra changed dramatically, and the peak positions are more similar to those of P3DDT sorted s-SWNTs. c) The fluorescence spectra of s-SWNTs which are sorted by P3DDT, PCO, and mixed-extractor. The peak pattern and position of s-SWNTs sorted by mixed-extractor system is similar to that of P3DDT sorted SWNTs. d–f) AFM images and diameter distribution of s-SWNT sorted by PCO, P3DDT, and mixed-extractor, respectively. The similar and small diameters of the s-SWNT complex in the three sorting systems indicate that individual s-SWNTs are wrapped by a single molecular layer each case.

To distinguish the binding characteristics of the two molecules, we examine the influence of addition sequence of the two molecules on the dispersion of the SWNTs. As seen from the fluorescence spectra, after PCO is added to the s-SWNTs solution dispersed by P3DDT, peak positions of the sorted s-SWNTs do not obviously change (Figure 3a). However, when the adding sequence is reversed, a shift of peak positions is observed (Figure 3b). The fluorescence spectra in Figure 3c show that P3DDT/PCO-SWNTs have peak positions nearly identical with

P3DDT-SWNTs, but have higher intensities for these peaks. It is known that the fluorescence peak position of s-SWNT shift as the local environment (such as solvent, or wrapped molecule) changes. The solvent used in all the sorting systems is toluene, so a change of molecule wrapped on the s-SWNT is presumed to account for the shift of fluorescence peak positions. One possible wrapping change is that P3DDT molecules replace the PCO molecules initially wrapped on s-SWNTs. This would imply that P3DDT has stronger binding ability to

s-SWNTs than PCO. Another possibility is that bilayer molecular structures form and cause the shift in fluorescence peak positions. The Nicholas group has reported several examples of bilayer coating of SWNTs with different molecules in a desired order.^[2,7,33] Although these nanostructures are fabricated in a mild way, rather than the violent sonication used in our system, it is still possible that the s-SWNTs are coated by two layers of molecules. To investigate this, we use an atomic force microscope (AFM) to measure the height of the wrapped s-SWNTs lying on a substrate, which can reflect the wrapping structure of the SWNT. The s-SWNTs sorted by P3DDT, PCO, and mixed-extractor are measured, and the statistics on their heights are shown in Figure 3d–f. Almost all the diameters of wrapped SWNTs are smaller than 2 nm, which means that the SWNTs are all individual and covered by only one molecular layer, because the height of an SWNT wrapped by two molecular layers would be more than 4 nm.^[7]

So far, it is established that the sorted s-SWNT is wrapped in a single layer of P3DDT or PCO, and P3DDT can replace the PCO wrapped on s-SWNTs because P3DDT has strong binding to s-SWNTs. As has been mentioned, in both fluorescence and absorption spectra, P3DDT/PCO-SWNTs have similar peak positions but higher peak intensities compared with the P3DDT-SWNTs. The most reasonable explanation for this observation is that most of the s-SWNTs are actually wrapped by P3DDT in the mixed-extractor system, and the higher intensity is due to the enhanced wrapping efficiency of P3DDT. During the sonication process in the P3DDT/PCO-SWNT system, there are two ways to form SWNT/P3DDT composites. One way is that P3DDT wraps the SWNTs directly, and the other way is that P3DDT exchanges PCO, which wraps the SWNTs first. If the first way dominates, no enhancement effect would be found by introducing the PCO. Therefore, it must be the replacement of PCO by P3DDT that results in the enhanced efficiency of P3DDT in this mixed-extractor system. Since the total amount of P3DDT is not changed by mixing with PCO, to disperse more s-SWNTs, the average number of P3DDT molecules consumed for stabilizing single s-SWNTs should be reduced. In other words, the utilization efficiency of P3DDT should be increased to realize the enhancement. Based on the above analysis, we propose a model describing how the replacement process enhances the utilization efficiency of P3DDT. As illustrated schematically in **Figure 4**, SWNTs are first partially disassembled from bundles in the powder by ultrasonication, assisted by the conjugated-molecule wrapping by P3DDT or by PCO. The SWNTs then either reassemble or disperse as individual SWNTs stabilized in toluene by the conjugated molecules. Then P3DDT molecules either replace the PCO molecule wrapping on the s-SWNTs in solution or extract s-SWNTs from bundles in the powder. It is supposed that there is a lower barrier for P3DDT capturing SWNT from PCO-SWNT composite than for directly extracting SWNT from powder sample in

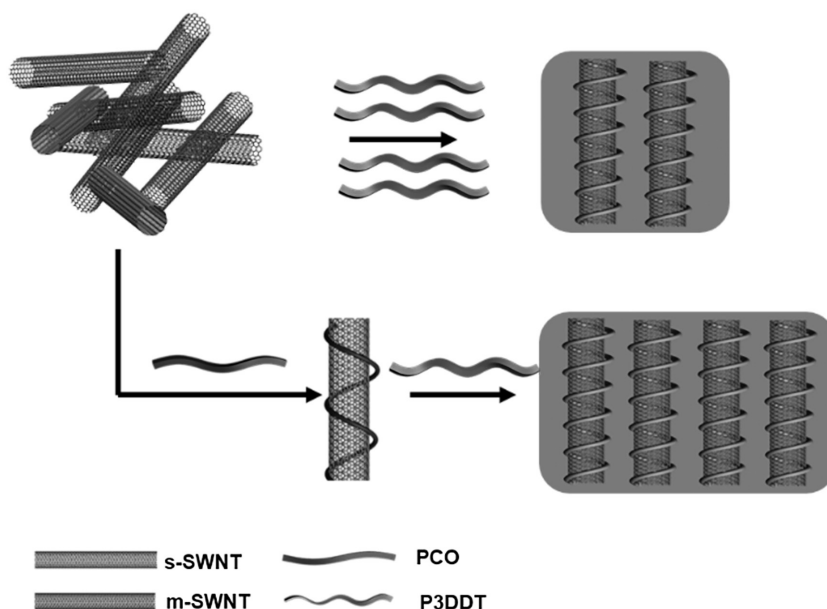


Figure 4. Schematic of sorting mechanism of s-SWNTs with enhanced yield by the mixed-extractor system consisting of P3DDT and PCO molecules.

P3DDT/PCO mixed-extractor system. The replacement of PCO by P3DDT reduces the number of molecules needed to provide colloidal stability to the SWNT dispersion. Thus, more SWNTs are extracted via the pathway with P3DDT replacing PCO in the PCO-SWNT composite. Moreover, the released PCO molecules from the exchange process are available to solubilize more s-SWNTs. This also contributes to the remarkable increase in concentration of isolated s-SWNTs. We call this process “pre-extraction and replacement.” Correspondingly, P3DDT is defined as the extractor, and PCO is defined as an enhancer.

The replacement process results from the difference in binding ability to SWNT between the two species of molecules. The wrapping efficiency of SWNTs by a molecule is known to be directly related to the rigidity of its structure. Proper rigidity is necessary for forming an ordered supramolecular structure around an SWNT, which is considered key for selectivity toward the s-SWNT and even toward certain chirality.^[21,26,32] However, if the backbone of the molecule is too stiff, folding of the molecules around the nanotube is inhibited. The more flexible backbone and longer alkyl side chain of P3DDT molecule lead to better binding ability compared with PCO, and the better wrapping ability of P3DDT enables the replacement of PCO molecules around the SWNTs.

It is desirable that other molecule combinations could be found that behave according to our scheme and that better enhancement effects could be obtained through an optimized combination of molecules. Therefore, principles are developed for how to choose candidate molecules for effective mixed-extractor system offering enhanced yield of s-SWNTs. Both enhancer and extractor molecules should be able to extract s-SWNTs from bundles in the powder sample. The extractor molecule should have structures that render proper flexibility for more efficient coating of SWNTs to replace the enhancer molecule. To test this principle, another conjugated molecule 1,2,5,6-tetra(5-hexylthiophene-2-yl)-hexaazapentacene (4HP)^[35]

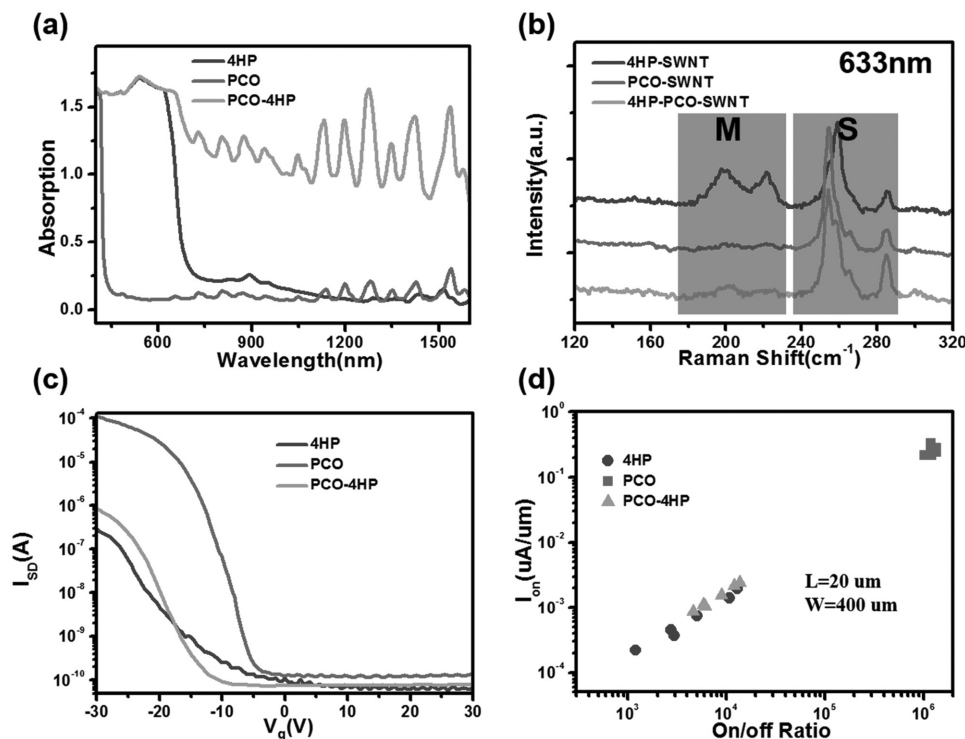


Figure 5. Characterization of s-SWNT sorting efficiency for 4HP, PCO, and the combination of the two molecules. a, b) Absorption spectra of s-SWNT solution sorted by 4HP, PCO, and mixed-extractor system, respectively. c, d) Typical transfer characteristic and corresponding I_{on} versus on/off ratio (I_{on}/I_{off}) plot for TFTs fabricated with s-SWNT sorted by 4HP, PCO, and mixed-extractor system, respectively.

is chosen to compose a mixed-extractor system with PCO. The conjugated structure of 4HP provides s-SWNT selectivity by facilitating the formation of an ordered supra molecular structure, and the small molecular unit benefits the folding and rotation needed for highly effective coating on the tube wall of SWNTs. The concentration of both 4HP and PCO is 0.5 mg mL^{-1} , and HiPco SWNTs is used with initial concentration of 0.25 mg mL^{-1} in all solutions. As calculated from absorption spectra in **Figure 5**, the Ω (4HP/PCO) is 4.38. The Raman spectra confirm the high purity of s-SWNTs sorted by the 4HP/PCO mixed-extractor system. TFTs ($L = 20 \text{ }\mu\text{m}$, $W = 400 \text{ }\mu\text{m}$) fabricated with s-SWNTs sorted by 4HP/PCO mixed-extractor system have on/off ratios higher than 10^4 , which further verifies the high purity of s-SWNTs. Six other mixed-extractor systems have also been selected according to our proposed principles and all show enhanced sorting efficiency (see **Figure S6** for details, Supporting Information). The results are summarized in **Table 1**, and the relevant molecule structures are displayed in **Figure S1** (Supporting Information). To extend the application of our sorting system, mixed-extractor strategy is applied to separate Arc-SWNT, which is supposed to more suitable for fabricating high-performance TFTs because its diameter (1.3–1.8 nm) is larger than HiPco-SWNT. Significant enhancement of the sorting yield is also observed (see **Figure S11** in the Supporting Information for the results of the two representative systems, PFO-PCO system and PFO-P3DDT system). This means that our strategy is not very sensitive to nanotube diameters, and therefore promising to be applied to sort nanotubes interesting for more device applications.

In summary, we have designed a rational and convenient mixed-extractor system for highly efficient sorting of s-SWNTs. The sorting system is composed of two kinds of conjugated molecules having different binding ability for s-SWNTs, correlated with their molecular rigidity. The dispersion yield of s-SWNTs can be greatly enhanced by mixing the two molecules together, without sacrificing the high purity of sorted s-SWNTs or increasing the overall concentration of the extractors. The relationship between specific function and molecular structure during the sorting of s-SWNTs has been determined by comprehensive experiments. The enhancer molecule increases the utilization efficiency of the extractor molecule by a “pre-extraction and replacement” process. The proposed mechanism is proven to be useful for designing other efficient mixed-extractor systems such as the 4HP/PCO system and hopefully for more

Table 1. The enhancement factor of different mixed-extractor systems.

Extractor	Enhancer	Enhancement factor
P3DDT	PCO	1.92
P3DDT	PFO	1.58
P3DDT	PFP	2.27
P3DDT	4HP	2.02
PFO	4HP	1.38
PFP	4HP	10.5
PCO	4HP	4.38
PFBP	4HP	4.32

efficient sorting system with more rational combination of extractors. The mixed-extractor strategy is believed to provide a new route toward high yield separation of s-SWNTs with minor purity variation and to facilitate the fabrication of high-performance electronic devices.

Experimental Section

SWNTs separation: HiPco SWNTs were purchased from Carbon Solution. P3DDT, PCO, PFO, PFP, and PFBP were purchased from Derthon Optoelectronics Materials Science Technology Co. The 1,2,5,6-tetra(5-hexylthiophene-2-yl)-hexaazapentacene (4HP) and PCO were prepared by our group. Dispersion experiments were performed using an ultrasonicator (Sonics VC500) with a 0.7 cm diameter sonication tip. For single-extractor system P3DDT(or PCO), 4 mg P3DDT(or PCO) dissolved in 8 mL toluene and then mixed with 2 mg HiPco SWNTs. The mixture was then sonicated for 30 min at 18 W with the temperature maintained at 20 °C. The sonicated samples were then centrifuged for 30 min at 20000 g (Allegra X-22R centrifuge), and the upper 80% supernatants were carefully collected with a syringe. For the mixed-extractor system, 4 mg P3DDT and 4 mg PCO were used simultaneously and other procedures were the same as the single extractor system. The experimental procedure and the concentration of extractor molecules and SWNTs of other mixed-extractor systems were the same as the P3DDT/PCO system.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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