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Separation of Semiconducting Carbon Nanotubes for Flexible and Stretchable Electronics Using Polymer Removable Method

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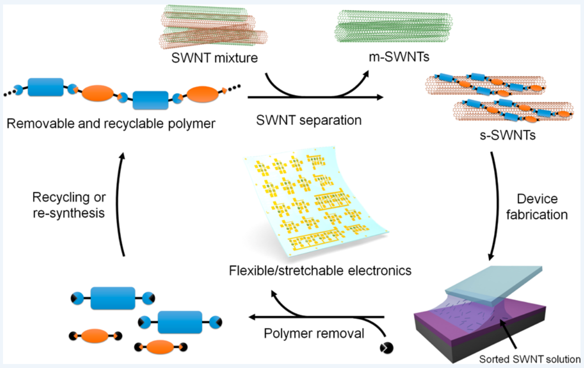

CONSPECTUS: Electronics that are soft, conformal, and stretchable are highly desirable for wearable electronics, prosthetics, and robotics. Among the various available electronic materials, single walled carbon nanotubes (SWNTs) and their network have exhibited high mechanical flexibility and stretchability, along with comparable electrical performance to traditional rigid materials, e.g. polysilicon and metal oxides. Unfortunately, SWNTs produced en masse contain a mixture of semiconducting (s-) and metallic (m-) SWNTs, rendering them unsuitable for electronic applications. Moreover, the poor solubility of SWNTs requires the introduction of insulating surfactants to properly disperse them into individual tubes for device fabrication.

Compared to other SWNT dispersion and separation methods, e.g., DNA wrapping, density gradient ultracentrifugation, and gel chromatography, polymer wrapping can selectively disperse s-SWNTs with high selectivity (>99.7%), high concentration (>0.1 mg/mL), and high yield (>20%). In addition, this method only requires simple sonication and centrifuge equipment with short processing time down to 1 h. Despite these advantages, the polymer wrapping method still faces two major issues: (i) The purified s-SWNTs usually retain a substantial amount of polymers on their surface even after thorough rinsing. The low conductivity of the residual polymers impedes the charge transport in SWNT networks. (ii) Conjugated polymers used for SWNT wrapping are expensive. Their prices ($100−1000/g) are comparable or even higher than those of SWNTs ($10−300/g). These utilized conjugated polymers represent a large portion of the overall separation cost.

In this Account, we summarize recent progresses in polymer design for selective dispersion and separation of SWNTs. We focus particularly on removable and/or recyclable polymers that enable low-cost and scalable separation methods. First, different separation methods are compared to show the advantages of the polymer wrapping methods. In specific, we compare different characterization methods used for purity evaluation. For s-SWNTs with high purity, i.e., >99%, short-channel (smaller than SWNT length) electrical measurement is more reliable than optical methods. Second, possible sorting mechanism and molecular design strategies are discussed. Polymer parameters such as backbone design and side chain engineering affect the polymer−SWNT interactions, leading to different dispersion concentration and selectivity. To address the above-mentioned limiting factors in both polymer contamination and cost issues, we describe two important polymer removal and cycling approaches: (i) changing polymer wrapping conformation to release SWNTs; (ii) depolymerization of conjugated polymer into small molecular units that have less affinity toward SWNTs. These methods allow the removal and recycling of the wrapping polymers, thus providing low-cost and clean s-SWNTs. Third, we discuss various applications of polymer-sorted s-SWNTs, including flexible/stretchable thin-film transistors, thermoelectric devices, and solar cells. In these applications, polymer-sorted s-SWNTs and their networks have exhibited good processability, attractive mechanical properties, and high electrical performance. An increasing number of studies have shown that the removable polymer approaches can completely remove polymer residues in SWNT networks and lead to enhanced charge carrier mobility, higher conductivity, and better heterojunction interface.

■ INTRODUCTION

Single-walled carbon nanotubes (SWNTs) are often considered as a viable alternate to silicon-based digital logic technology.[1] In particular, semiconducting (s-) SWNTs have high carrier mobilities over 10^5 cm^2/(V s) and have thus been exploited as building blocks for future high-performance electronics.[2] On the other hand, next-generation wearable or biointegrated electronics demand an electronic technology that matches the soft, elastic, and curved nature of human body, while possessing electrical properties comparable to conventional rigid silicon-based technology.[3] SWNT networks are extremely flexible and intrinsically stretchable without noticeable performance degradation after mechanical bending or stretching.[4,5] Although their charge transport is limited by tube−tube junctions, high carrier mobilities over 50 cm^2 V^{-1} s^{-1} and low sheet resistances < 100 Ω/□ have been realized for SWNT networks.[6,7] SWNT networks have thus become one of the most promising materials for flexible and stretchable electronics.[3−5,8,9]

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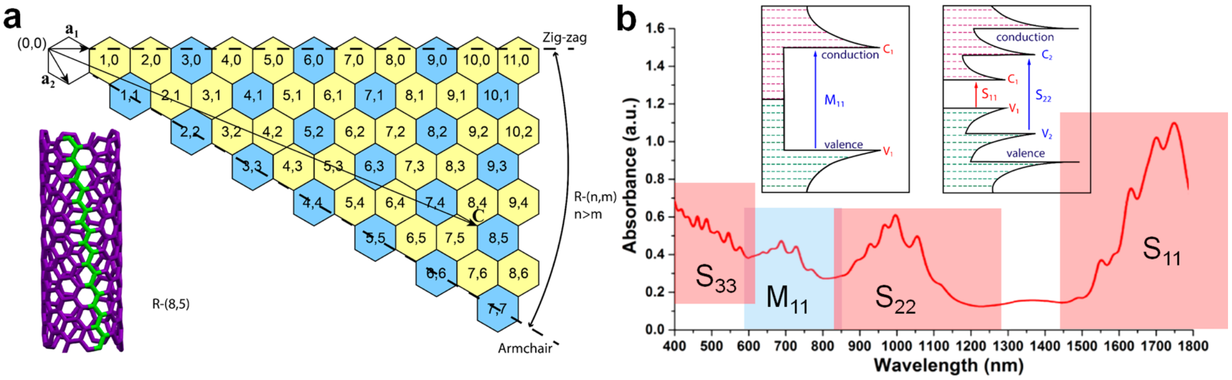

Figure 1. (a) Chirality map of SWNTs. The metallicity is governed by their chirality. If $|n - m|$ is a multiple of 3, the nanotubes are metallic (blue). All the reminders are semiconducting (yellow). Inset shows a model of *R*-(8,5) SWNT. (b) Absorption spectrum of an arc-discharge SWNT sample. Different electronic transitions are labeled. Inset shows the density of state plots and corresponding electronic transitions of m-SWNTs (left) and s-SWNTs (right).

Table 1. Properties and Potential Applications of Several Commercially Available Raw SWNTs

	CoMoCAT	HiPCO	plasma torch	arc discharge	TUBALL
diameters (nm)	0.7−0.9	0.8−1.2	1.1−1.5	1.2−1.7	1.5−2.0
band gaps (eV)	1.2−1.1	1.1−0.8	0.9−0.7	0.8−0.6	0.7−0.5
costs (USD)	\$300−700/g	\$300−600/g	\$10−40/g	\$100−300/g	\$4−20/g
TFT mobilities ($cm^2/(V\ s)$)	1−3	5−12	20−40	20−60	NA
preferred applications	solar cells and thermoelectrics	NIR-II bioimaging and TFTs	TFTs and thermoelectrics	TFTs and computing	high-performance computing

SWNTs with purity of 30−70 wt % have recently became commercially available with costs as low as \$2−10/g.[10] Unfortunately, these SWNTs always contain a mixture of semiconducting and metallic (m-) SWNTs. Moreover, the poor solubility of SWNTs requires the addition of dispersants to generate individual tubes for fabricating uniform SWNT networks. Conjugated polymer wrapping has emerged as one of the most efficient methods for SWNT purification with high separation efficiency and cost advantage. In this Account, we survey recent development of selective dispersion/separation of SWNTs using polymer wrapping, with particular emphasis on removable polymer based separation methods. Applications of polymer-sorted SWNTs in flexible and stretchable electronics and distinct advantages of removable polymer approach will also be discussed.

■ ADVANTAGES OF THE POLYMER WRAPPING METHOD

SWNTs can be viewed as rolled-up sheets of graphene along a vector **C** defined by two indices (*n*, *m*) and a pair of basis vectors ($\mathbf{a}_1$, $\mathbf{a}_2$) (Figure 1a). Depending on the indices (*n*, *m*), SWNTs may be either metallic or semiconducting even if they have nearly identical diameters. In addition, SWNTs with identical chiral vectors can take different handedness, e.g. right handedness *R*-(8,5) and left handedness *L*-(5,8). Electronic properties of SWNTs depend on their diameters and chiralities. To date, SWNTs with different diameters are commercially available in large quantity, thus enabling broad electronic and optical applications (Table 1).

To realize optimal electronic property, purification methods that can achieve low polydispersity of SWNTs in terms of their metallicity, diameter, chirality, handedness, and length have been developed. The purification methods can be categorized into two types: covalent and noncovalent. The covalent method uses selective chemical reactions to functionalize or eliminate SWNTs, which are irreversible and typically result in structural defects in SWNTs.[11] Noncovalent method, which should not significantly alter SWNT electronic properties, is more suitable for electronic applications. Several types of noncovalent separation technologies have been reported, including DNA wrapping, density gradient ultracentrifugation (DGU), gel chromatography, and polymer wrapping.[11−14] DNA wrapping requires specifically designed DNA, which is difficult to scale up.[12] DGU and gel chromatography methods require long purification time (18−24 h) and multiple tedious iterations to produce high purity s-SWNT. These methods also suffer from low yields (typically <5%).[13,14] Among these methods, polymer wrapping allows extraction of s-SWNT with high selectivity (>99%), high concentration (0.01−0.1 mg/mL), and high yield (>20%), but only uses simple sonication and centrifuge equipment with processing times as short as 1 h.[15−19] In addition, through rational molecular design, polymer can selectively extract a specific chirality (*n*, *m*) of s-SWNTs.[20,21]

The raw SWNTs generally exhibit four absorption bands corresponding to different interband transitions of s-SWNTs (S_{11}, S_{22}, and S_{33}) and m-SWNTs (M_{11}) (Figure 1b). The absorption ratios between the first interband transition of m-SWNTs (M_{11}) and the second interband transition of s-SWNTs (S_{22}) can be used to estimate the sorting purity.[17] Raman spectroscopy is also used for qualitative purity estimation by comparing the radial breathing mode (RBM) peaks of different types of SWNTs or calculating the intensity ratio of the metallic G^-_m band and the G^+ band. The decrease or disappearance of the characteristic metallic tube peaks indicate the removal of the corresponding m-SWNTs. Absorption spectroscopy is fast and efficient, suitable for initial screening of different sorting conditions. However, when the SWNT purity is high (>98%), this method may overestimate

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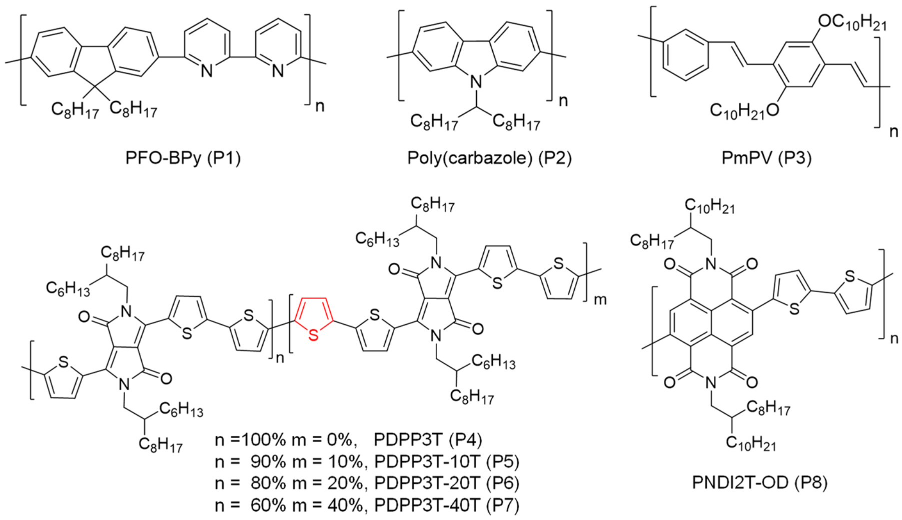

Figure 2. Different polymer backbones used for selective dispersion of s-SWNTs.

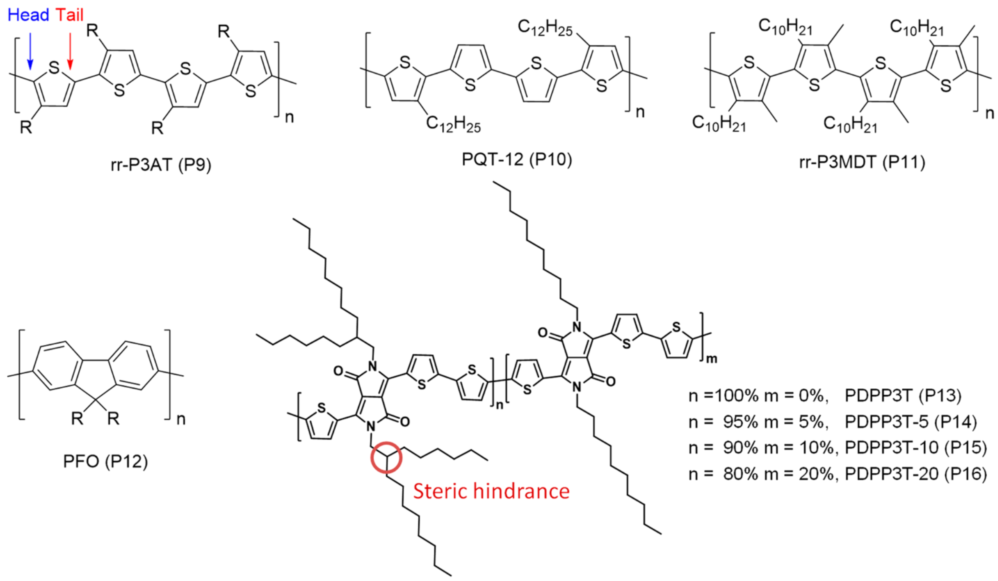

Figure 3. Side chain effects in the selective dispersion of s-SWNTs.

the purity due to the complicated nature of SWNT absorption spectrum.[14,22] Direct electrical measurement of single tubes using short channels (channel length smaller than tube length) provides direct information about electronic purity.[22,23] m-SWNTs can be easily identified using electrical measurement because of their low on/off ratios ($<10^2$). If a large amount of devices are randomly tested, purity can be accurately calculated based on the numbers of shorted devices and the total devices measured.

■ POLYMER SORTING MECHANISM AND MOLECULAR DESIGN

Possible Sorting Mechanism

Compared to s-SWNTs, m-SWNTs exhibit over 10^3 larger polarizability due to their high carrier concentration.[24] Because of the strong polarizability of m-SWNT, theoretical studies indicate that m-SWNT/polymer complexes possess stronger charge transfer interactions than s-SWNT/polymer complexes.[25] The more polar m-SWNT/polymer complexes tend to aggregate or bundle in nonpolar solvents, forming a sediment after centrifugation while s-SWNT/polymer complexes remained in the supernatant. This mechanism has been supported by several experimental results including solvent,[26] polymer backbone,[27] and side chain effects.[28] For example, only nonpolar solvents (e.g., toluene, *m*-xylene) usually have shown good selectivity for s-SWNTs, whereas polar solvents (e.g., tetrahydrofuran) provided much lower selectivity for s-SWNTs.[26,28] Sorting temperature and polymer/SWNT ratios also affect the dispersion concentration and selectivity. Usually, there is an optimal temperature for polymer wrapping on SWNT,[19] and higher SWNT/polymer ratios lead to higher selectivity.[17,28] To realize single-chirality sorting, chiral groups on either polymer side chain or backbone have been incorporated. Molecular modeling indicates that the single-chirality selectivity might be due to a cooperative effect between the chiral groups and polymer wrapping conformations.[20,21]

Polymer Backbone Design

Since the first discovery of fluorene-based polymers that can selective disperse s-SWNTs (P12, R = C_8H_{17}),[16] a significant number of polymers have been investigated (Figure 2), including poly(fluorenes) (P1 and P12),[16,18] poly(carbozoles) (P2),[29] poly(phenylenevinylenes) (P3),[30] regioregular polythiophenes (P9),[19,24,31] and diketopyrrolopyrrole (DPP) (P4−P7 and P13−P16)[27,28]/naphthalene diimide (NDI) (P8) based donor−acceptor (D-A) polymers.[32] Mistry et al. studied the capability of nine fluorene-based polymers to disperse large-diameter (∼1.3 nm) s-SWNTs. They found different polymer backbones have largely different dispersion abilities, in which PFO-BPy (P1) showed the best dispersion yield of 33% and high selectivity of 99%. Low band gap D−A polymers usually have large planar conjugated backbones and strong $\pi-\pi$ interactions with SWNTs. Our group have developed DPP based D−A polymers to selectively disperse s-SWNTs.[27,28] Compared to our reported regioregular (rr-) P3DDT (P9, R = $C_{12}H_{25}$) that mainly disperse SWNTs with diameters in the range of 1.3−1.4 nm, DPP polymers showed strong dispersion ability for even larger diameter SWNTs (with diameters of ∼1.5 nm and some dispersed tubes are even >1.6 nm). Our group also investigated the molecular design strategy for DPP polymers by introducing more thiophene units into DPP polymer backbones (P4−P7). We observed that introducing electron-rich thiophene units can considerably increase the dispersion ability and selectivity of DPP polymers. After polymer backbone engineering, the selectivity for large diameter (1.4−1.6 nm) s-SWNTs increased from 96.7% to 99.6% as estimated by electrical measurements.[27] The improved selectivity for s-SWNTs is due to the stronger polymer backbone and SWNT interaction after introducing thiophene units. The stronger interaction enhances the charge transfer interactions of polymer/m-SWNTs complex. This complex tends to aggregate or bundle in nonpolar solvents typically used for sorting and form sediment after centrifugation, leaving s-SWNTs behind in the supernatant.

Side Chain Engineering

Polymer side chains are more than just groups to enhance the polymer's solubility. They are also able to affect polymer-SWNT supramolecular structures and polymer−SWNT interactions (Figure 3). Poly(3-alkyl thiophenes) (P3ATs, P9) have three possible couplings: head-to-head (HH), tail-to-tail (TT) and head-to-tail (HT). HH connection produces large dihedral angles in backbone and weak $\pi-\pi$ stacking interactions. Our group have previously demonstrated that rr-P3ATs (HT coupling) can selectively disperse semiconducting HiPCO and CoMoCAT SWNTs with high yield and high selectivity.[19,31] We observed that the dispersion concentration was directly related to parameters such as side chain length, configuration, and density. Among all the polythiophenes including rr-P3ATs (R = C_6H_{13}, C_8H_{17}, $C_{10}H_{21}$, $C_{12}H_{25}$), PQT-12, rr-P3MDT, and regiorandom P3ATs, poly(3-dodecylthiophene-2,5-diyl) (rr-P3DDT, R = $C_{12}H_{25}$) showed the strong dispersion ability toward s-SWNTs, whereas PQT-12, rr-P3MDT, and regiorandom P3ATs did not noticeably disperse any SWNTs. This result reveals, for the first time, the importance of the side chains for polymer wrapping. Similar side-chain effects were also observed in fluorene-based polymers (P12).[17] Although branched alkyl chains provide polymers with better solubility, they are also observed to invariably hinder close intermolecular $\pi-\pi$ stacking in polymer transistors.[33] We found that the polymer−SWNT interactions can be modulated (P13−P16) by systematically varying the ratios of branched to linear alkyl chains.[28] In specific, polymer PDPP3T-10 (P15) with 10% linear alkyl side chains showed the highest dispersion yield and best selectivity. In this case, branched alkyl chains provide better solubility for the rigid DPP polymers, while linear alkyl side chains provide better $\pi-\pi$ stacking interactions with SWNTs.

■ REMOVABLE POLYMERS FOR SCALABLE AND "CLEAN" SORTING

Polymer sorting is fast, low-cost and scalable. However, it has two major drawbacks: (i) Due to the strong polymer-SWNT interactions and tight polymer wrapping, the purified s-SWNTs retain a substantial amount of residual polymers on their surface even after thorough rinsing.[34] The residual polymers are detrimental as they lower the electrical performance of SWNT networks due to the low conductivity of the polymers. (ii) Conjugated polymers are expensive as their prices ($100−1000/g) are comparable or even higher than those of SWNTs ($10−300/g).[10] In polymer sorting, the amount of polymers used is similar to that of the unpurified SWNTs. Therefore, the used conjugated polymers account for a large portion of the total cost.

To remove polymers from closely wrapped SWNTs, two strategies have been employed: (i) changing polymer wrapping conformations (Figure 4); (ii) depolymerize polymers into small units which have less interactions with SWNTs (Figure 5). Zang et al. demonstrated the use of a conformational

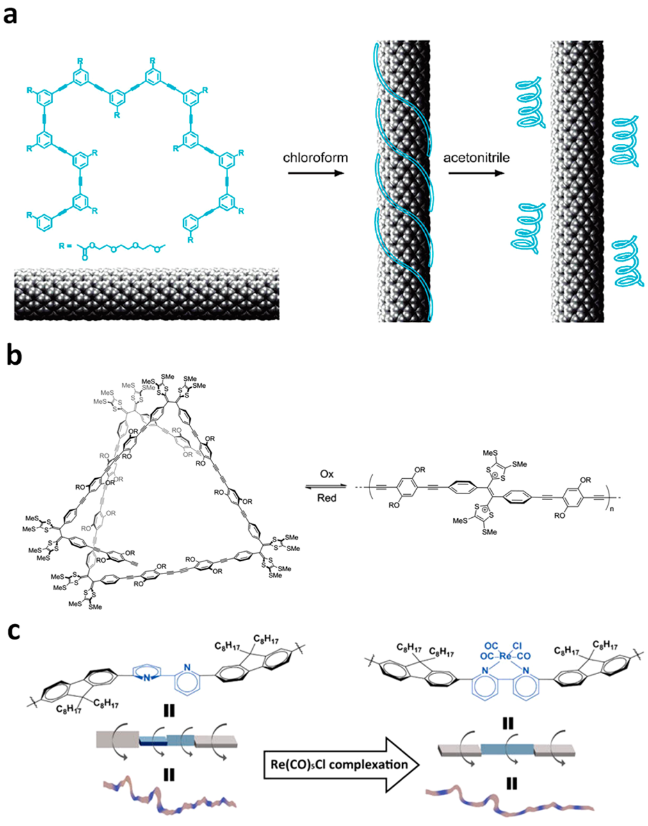

Figure 4. Removal of wrapped polymers by changing the polymer conformations. Polymer conformation change (a) using different solvents,[35] (b) using redox reaction or protonation,[34,36] and (c) through metal chelation.[37] Panel (a) reproduced from ref 35. Copyright 2010 American Chemical Society. Panel (b) reprinted with permission from ref 36. Copyright 2013 Royal Society of Chemistry. Panel (c) reproduced from ref 37. Copyright 2015 American Chemical Society.

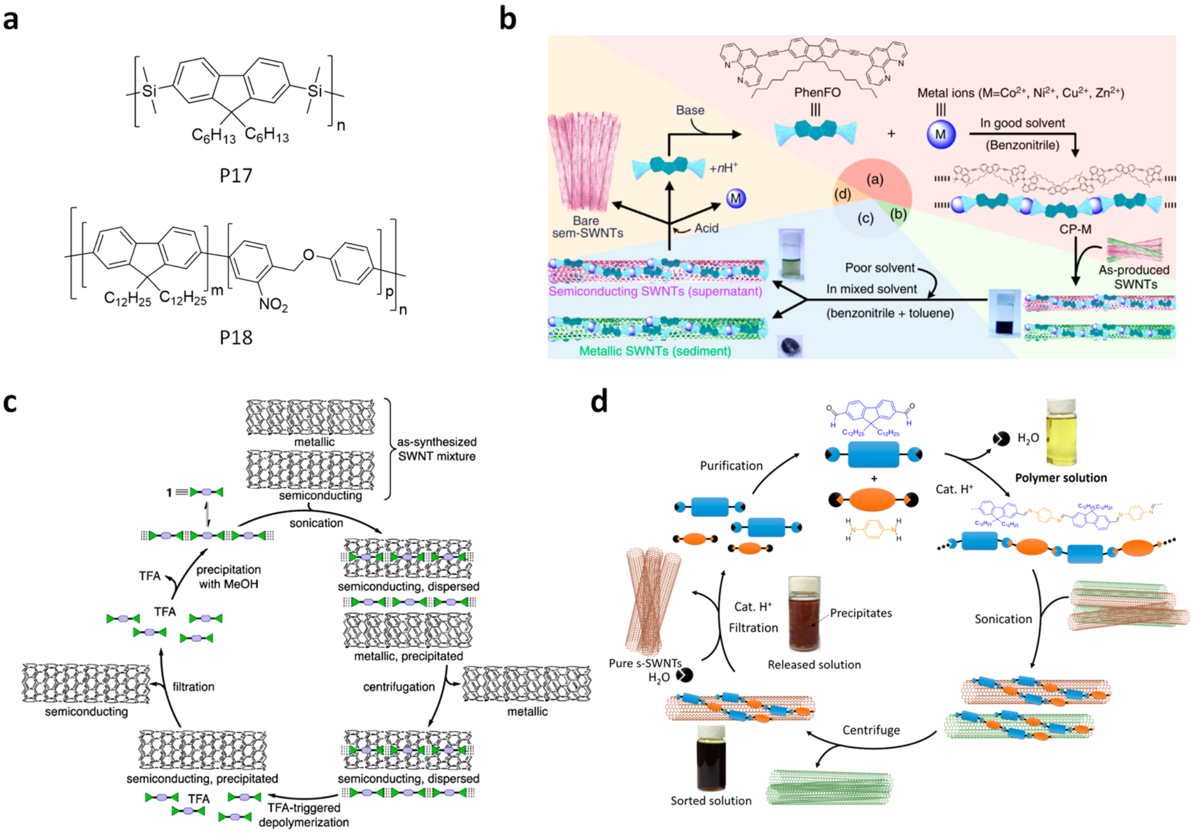

Figure 5. Removal of wrapped polymers by depolymerization into smaller units. (a) Releasing SWNTs through irreversible depolymerization.[38,39] (b) Coordination polymers for SWNT releasing and polymer cycling.[40] Reprinted with permission from ref 40. Copyright 2014 Nature Publishing Group. (c) H-bonding polymers for large-diameter SWNT sorting. Reproduced from ref 41. Copyright 2015 American Chemical Society. (d) Removable and recyclable imine-based polymer for scalable SWNT sorting. Reproduced from ref 10. Copyright 2016 American Chemical Society.

foldable oligomer (foldamer) to disperse and release CoMoCAT SWNTs in different solvents (Figure 4a).[35] The foldamer can fold into a helical conformation in polar solvents (e.g., acetonitrile) through intramolecular $\pi-\pi$ interaction and solvophobic interaction between its hydrophobic backbone and the polar solvent. In chlorinated solvents, e.g. chloroform, the foldamer is in unfolded conformation and can wrap around SWNTs; whereas in polar solvents, the foldamer changes to its folded conformation and releases bare SWNTs, resulting in SWNT precipitates. Besides solvents, polymer conformation can also be changed by redox reactions, selective protonation, or metal ligand chelation. Polymers containing tetrathiafulvalene vinylogue (TTFV) units adopt folding conformations in the neutral state and can effectively disperse and individualize SWNTs (Figure 4b). Upon oxidation or protonation, these polymers change their conformation to linear due to the formation of TTFV cations. The polymers with linear conformations have much less interactions with SWNTs and result in the dissociation of the polymer/SWNT complexes.[34,36] PFO-BPy (P1) have shown high selectivity > 99% for s-SWNTs. Using this polymer, Gopalan et al. used metal ligand $Re(CO)_5Cl$ to selectively chelate the bipyridine unit, change the polymer rigidity, and release the wrapped s-SWNTs (Figure 4c).[37] They found that metal ligand binding triggered 85% removal of the polymer from arc-discharge s-SWNTs and 72% from CoMoCAT s-SWNTs.

Depolymerizing wrapped polymers into small molecules can be achieved by introducing reactive building blocks on the polymer backbones (Figure 5a). Chan-Park et al. reported a series of removable alternating copolymers containing disilane bonds on polymer backbone (Figure 5a, P17).[38] The polymer showed high selectivity for larger-chiral-angle (25°−28°) HiPCO s-SWNTs. After sorting, the polymer wrapped on SWNTs can be easily washed off after dissociating the disilane bonds using hydrofluoric acid. Using photocleavable *o*-nitrobenzylether group (Figure 5a, P18), Mayor et al. reported fluorene-based photocleavable polymers for sorting and releasing of HiPCO tubes.[39] They found that several adjacent fluorene moieties are required in order to selectively disperse particular (*n*, *m*) species. Photoirradiation of the polymer induces the cleavage of the polymer backbone and releases sorted SWNTs.

Although these irreversible depolymerization methods provide "clean" SWNTs without polymer contaminations, the degraded polymers unfortunately cannot be recycled, yielding high material cost for large-scale separation. Supramolecular polymers with noncovalently linked backbone are excellent candidates for reversible sorting and releasing of SWNTs. Nakashima and Toshimitsu reported efficient separation of s-SWNTs using metal-coordination polymers.[40] After sorting, the coordination polymers can be removed by adding acids and depolymerize to monomers (Figure 5b). They achieved highly selective dispersion of semiconducting HiPCO tubes and the wrapping polymers can be completely removed. In addition, the depolymerized monomers can be reused in the subsequent sorting experiment. To obtain large-diameter s-SWNTs, our group have developed a H-bonded supramolecular polymer for dispersing large-diameter, arc-discharge SWNTs (Figure 5c).

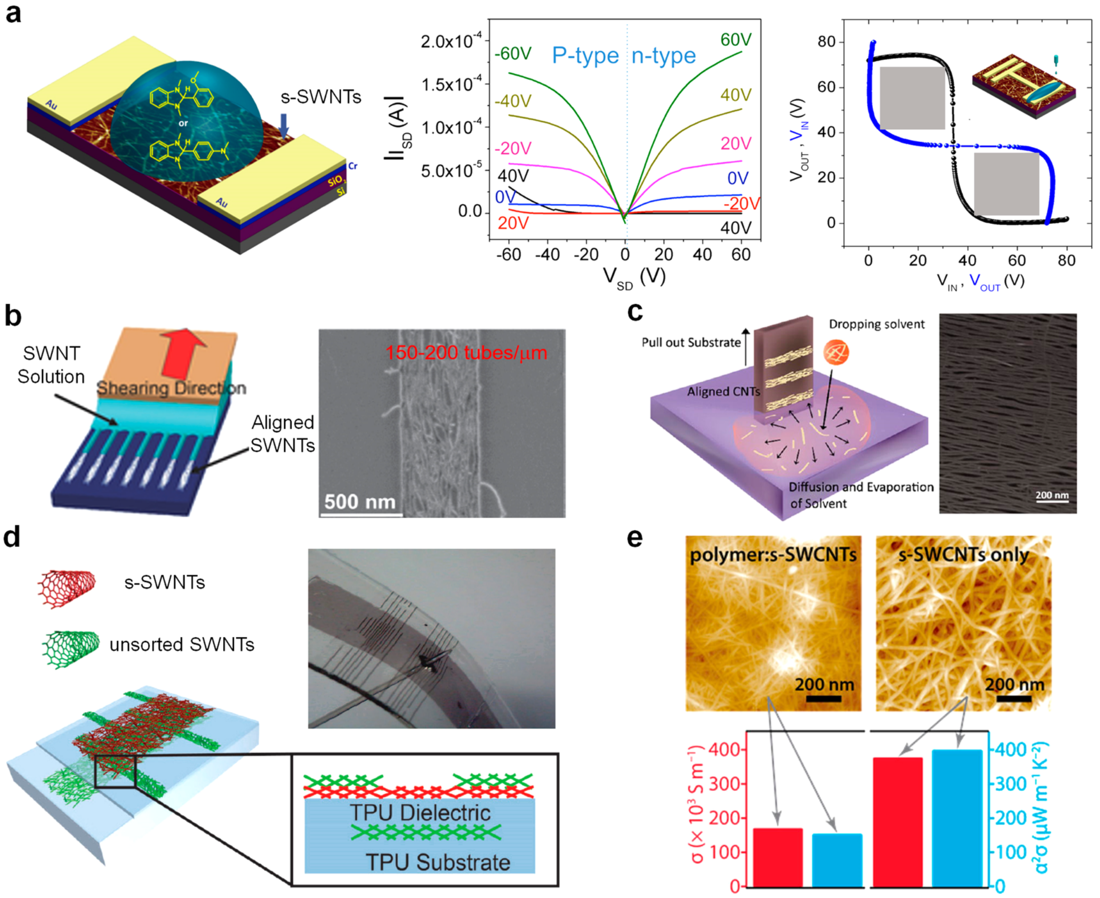

Figure 6. Polymer-sorted SWNTs for flexible and stretchable electronics. (a) N-type molecular doping of SWNT networks to realize complementary CNT logics.[45] Reprinted with permission from ref 45. Copyright 2014 National Academy of Sciences. (b) Large-area assembly of densely aligned SWNTs using solution shearing method.[46] Reprinted with permission from ref 46. Copyright 2015 John Wiley and Sons. (c) FESA method for depositing polymer sorted SWNTs. SEM image shows a packing density over 40 tubes/μm.[6] (d) Durable and highly stretchable SWNT transistors. Inset: photo of the punctured stretchable device.[9] Reprinted with permission from ref 9. Copyright 2016 John Wiley and Sons. (e) Comparison of the AFM image, conductivity, and thermoelectric power factors of polymer-containing s-SWNT and polymer-removed s-SWNT networks. Reproduced from ref 48. Copyright 2016 American Chemical Society.

Using strong hydrogen-bonding 2-ureido-6[1*H*]-pyrimidinone (UPy) moieties, the monomer can self-associate into high molecular weight polymers even at low monomer concentrations. The H-bonded supramolecular polymer exhibited highly selective (>99%) dispersion of large-diameter (1.25–1.52 nm) s-SWNTs. Benefiting from the reversible nature of H-bonding, the polymer can thus be depolymerized, removed and recycled after adding an acid to disrupt the H-bonds.

The above-described polymer removing methods are either not recyclable or requiring multistep synthesis of noncovalent bonding moieties. In addition, all the reports typically employ prepurified raw SWNTs with 50–70% SWNT content as starting materials. Our group recently developed a removable and recyclable imine conjugated polymer for s-SWNTs separation (Figure 5d). The imine bonds (C═N) in backbone break easily with exposure to catalytic amount of acid. This polymer exhibited strong dispersion ability for large-diameter s-SWNTs with high concentration (optical density up to 2.498), high yield (23.7%, vs theoretical s-SWNTs in the mixture), and high selectivity (99.7%, estimated by electrical measurement). In addition, as-produced raw SWNTs (30% purity) can be used directly as the starting materials without affecting the sorting yield and selectivity. After s-SWNT separation, the polymer can be depolymerized, removed, and recycled, yielding polymer-free s-SWNTs. The recycled monomers can then be directly used for repolymerization after removing the SWNT/amorphous carbon residues. This purification can be easily performed using a short column chromatography. The imine polymer only employ dialdehyde and diamine functionalized building blocks without complicated synthesis, e.g., cleavable groups and noncovalent groups. This approach can be readily used for other π-conjugated structures to further optimize the sorting yield and selectivity for different types of SWNTs, thus providing a simple yet general strategy for removable polymer sorting.

■ APPLICATIONS OF POLYMER-SORTED SWNTs

Compared to CVD-growth tubes, solution-sorted SWNTs and their networks have relatively low electrical performance. However, several key advantages such as low cost, low temperature processability, and outstanding mechanical properties, have rendered sorted SWNTs very suitable for flexible and stretchable electronics. Polymer wrapping has been successfully used for dispersion of s-SWNT with diameters of 0.7–1.7 nm, covering bandgaps of 1.2–0.5 eV (Table 1). s-SWNTs with diameters around 1.4 nm are preferred for flexible thin-film transistors (TFTs) due to their smaller Schottky barrier, higher drive current, and good on–off ratios over 10^5.[1] Compared to surfactant/water dispersed SWNTs that usually require surface modification, e.g., poly-L-lysine, for high-density SWNT networks,[8,42] polymer-wrapped SWNTs typically do not need any surface modification to enable dense SWNT networks on oxide substrates.[17] SWNT TFTs fabricated by solution shearing method have exhibited high mobilities > 50 $cm^2/(V\ s)$ and on/off ratios > 10^5.[27] The good solution processability of SWNT TFTs allows large-area inkjet or screen printing.[43] Zhou et al. demonstrated fully screen-printed and flexible active-matrix electrochromic displays using silver nanoparticles as the conductor, sorted s-SWNTs as the semiconductor, and barium titanate as the insulator.[44] This work suggests that solution-processed SWNT TFTs are promising for large-area mass production of low-cost electronics. By combining p-type SWNTs with n-type metal oxide, Zhou et al. reported large-scale complementary logic circuits containing >500 SWNT transistors on flexible substrate, indicating good uniformity and high device yield of SWNT TFTs.[8] To realize n-type transistors, our group used two 1*H*-benzoimidazole derivatives to n-dope the SWNT TFTs (Figure 6a).[45] After doping, we observed that the charge carrier density and threshold voltage of the SWNT transistors can both be tuned, and hence, unipolar n-type SWNT transistors were obtained. Combining both p-and n-type SWNT transistors, highly noise-resistant and low-power consumption logic gates were realized on a flexible substrate.

To achieve higher mobility, aligned and densely packed SWNT arrays are desired. Using solution shearing method, our group realized large-scale alignment of polymer-sorted SWNTs on a patterned silicon wafer (Figure 6b).[46] The wafer was patterned with alternating regions of solvent wetting and dewetting regions. Polymer-sorted SWNT solutions were applied on the wafer by a shearing blade. Densely aligned SWNTs (150−200 tubes/μm) were deposited on the solvent wetting regions as the solution meniscus separating and drying. Arnold et al. reported a dose-controlled floating evaporative self-assembly (FESA) method to deposit polymer-sorted SWNTs with high alignment. The FESA method provided a packing density of 28−49 tubes/μm. Devices based on this method showed on-conductance of up to 261 μS/μm and on−off ratios of $>10^5$ for a channel length of 240 nm.[6] To achieve high mobility, removal of the polymer residues on SWNTs is necessary. They used extensive solvent rinsing and thermal annealing (>300 °C) to remove polymers and improve the device performance.[6] However, extensive solvent rinsing led to the decrease of the tube density. High temperature annealing also introduces defects on carbon nanotubes (CNTs) and is not compatible with flexible substrates. Therefore, removable polymer sorting provides a simple and effective approach to obtain "clean" SWNT networks.

Various materials have been explored for stretchable electronics, including liquid metals, polymers, metal nanostructures and SWNTs.[3] Among these materials, SWNT networks are intrinsically stretchable with comparable performance as traditional electronic materials, e.g., polysilicon and metal oxides. With ion gel gate dielectrics and buckled metal conductors, Arnold et al. demonstrated SWNT transistors that are stretchable up to 50%.[47] Our group recently demonstrated a highly stretchable, transparent, and conductive SWNT electrodes that can accommodate strains of up to 150% and conductivities as high as 2200 S/cm.[5] Coupled with polymer-sorted s-SWNTs and a tough thermoplastic polyurethane (TPU), our group proceed to fabricate a highly stretchable and durable SWNT TFT.[9] After an initial conditioning strain cycle, the TFT device is stretchable to 100% strain with little degradation of the device performance even after 1000 stretching cycles. The device is also mechanically durable and works well after sudden impacts, tear, or puncture with a needle (Figure 6d). Using Ag nanowire as the conductive electrodes and polyurethane-*co*-polyethylene glycol as the dielectric layer, Pei et al. also developed a solution-processed fully stretchable SWNT transistor.[4] The stretchable TFT exhibited high optical transmittance of >90% and can be stretched up to 50% while retaining a high mobility.

Thermoelectric (TE) devices are promising for recovering waste heat by converting it to electricity, especially useful for harvesting power needed for wearable electronics. Large-scale implementation of TE device requires low-cost and high-efficiency materials that can be large-scale coated on heat exchanger surfaces. The TE efficiency is given by the figure of merit $zT = \alpha^2\sigma T/k$, where α is the Seebeck coefficient, σ is the electrical, and k is the thermal conductivity. s-SWNTs are promising materials for thermoelectric applications because they have theoretically high α up to 2000 μV/K at room temperature, which is about 6−10 times larger than that of commonly used thermoelectric materials.[49] Using polymer-sorted SWNTs, Blackburn and co-workers demonstrated that high-purity and chirality-controlled s-SWNT networks exhibited a high thermoelectric power factor of 340 $\mu W/mK^2$.[50] To further improve the power factor, they used the H-bonded supramolecular polymer (previously developed by our group, Figure 5c) to selectively disperse s-SWNTs.[48] After complete removal of the H-bonded supramolecular polymer, the resulting SWNT film exhibited higher charge carrier mobility and enhanced carrier doping, leading to a factor of ∼2.5 increase in the thermoelectric power factor (Figure 6e). As discussed above, the removability and recyclability of the removable polymers can lower the cost of the separation process and improve the TE performance, and therefore may further advance the applications of SWNT in large-scale and low-cost TE devices.

s-SWNTs were also incorporated as the near-infrared optical absorber in heterojunction photovoltaic and photodetector devices. Arnold et al. demonstrated that electronic-type-sorted, chirality-controlled s-SWNTs/C_{60} devices exhibited a 10-fold gain in zero-bias quantum efficiency and higher power conversion efficiency.[51] Our group used smaller-diameter CoMoCAT tubes with wider bandgaps to improve the device performance of type-II heterojunction solar cells formed with SWNTs and C_{60}. We indeed observed that by minimizing the presence of polymer residues in s-SWNT films and improving the interfacial heterojunction, a 10-fold improvement in performance was realized in s-SWNT/C_{60} based solar cells.[52] This result further validates the importance of the removable polymer sorting strategy for electronic applications.

■ SUMMARY AND OUTLOOK

In this Account, we have summarized recent advances on polymer sorting mechanism, molecular design strategies, as well as SWNT purity evaluation methods. Removable polymer approaches are particularly attractive because they enable lower cost, less polymer residuals, and higher performance. Despite these advantages, other important aspects of polymer sorting methods still need to be investigated or improved, such as polymer sorting for m-SWNTs (since there is still no known polymer that can sort m-SWNTs with high selectivity), polymer structure/sorting property relationship, selectivity improvement toward narrow diameter or chirality distribution, easier and faster polymer removal design, and high-uniformity high-density SWNT network deposition methods. We believe that the designability and structure diversity of polymers will allow further optimization of the overall sorting yield, selectivity, and processability of SWNTs to enable better performance and broader electronic applications.

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Igor Pochorovski obtained his Bachelor's degree in chemistry and biochemistry from the LMU Munich, then spent a summer as a visiting researcher at UC Berkeley working in the group of Prof. F. D. Toste. After completing his Master's studies at ETH Zurich, Igor joined Prof. F. Diederich for his Ph.D. (2010–2013), where he was working on molecular basket systems. He was a postdoctoral scholar with Prof. Z. Bao at Stanford University (2014–2016), working on the development of supramolecular polymers for SWNT sorting.

Zhenan Bao received her Ph.D. from University of Chicago. After spending 8 years in Bell Laboratories as a Distinguished Member of Technical Staff, she joined Stanford as an Associate Professor in 2004. She is a member of the National Academy of Engineering. Selected recent awards include ACS Polymer Science Award in 2017, L'Oréal-UNESCO Women in Science Prize in 2017, ACS Arthur Cope Scholar Award in 2011, RSC Beilby Medal and Prize in 2009, and IUPAC Creativity in Applied Polymer Science Prize in 2008.

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■ REFERENCES

(1) Tulevski, G. S.; Franklin, A. D.; Frank, D.; Lobez, J. M.; Cao, Q.; Park, H.; Afzali, A.; Han, S.-J.; Hannon, J. B.; Haensch, W. Toward High-Performance Digital Logic Technology with Carbon Nanotubes. *ACS Nano* **2014**, *8*, 8730–8745.

(2) Franklin, A. D. Nanomaterials in transistors: From high-performance to thin-film applications. *Science* **2015**, *349*, aab2750.

(3) Rogers, J. A.; Someya, T.; Huang, Y. Materials and Mechanics for Stretchable Electronics. *Science* **2010**, *327*, 1603–1607.

(4) Liang, J.; Li, L.; Chen, D.; Hajagos, T.; Ren, Z.; Chou, S.-Y.; Hu, W.; Pei, Q. Intrinsically stretchable and transparent thin-film transistors based on printable silver nanowires, carbon nanotubes and an elastomeric dielectric. *Nat. Commun.* **2015**, *6*, 7647.

(5) Lipomi, D. J.; Vosgueritchian, M.; Tee, B. C. K.; Hellstrom, S. L.; Lee, J. A.; Fox, C. H.; Bao, Z. Skin-like pressure and strain sensors based on transparent elastic films of carbon nanotubes. *Nat. Nanotechnol.* **2011**, *6*, 788–792.

(6) Brady, G. J.; Joo, Y.; Wu, M.-Y.; Shea, M. J.; Gopalan, P.; Arnold, M. S. Polyfluorene-Sorted, Carbon Nanotube Array Field-Effect Transistors with Increased Current Density and High On/Off Ratio. *ACS Nano* **2014**, *8*, 11614–11621.

(7) Green, A. A.; Hersam, M. C. Colored Semitransparent Conductive Coatings Consisting of Monodisperse Metallic Single-Walled Carbon Nanotubes. *Nano Lett.* **2008**, *8*, 1417–1422.

(8) Chen, H.; Cao, Y.; Zhang, J.; Zhou, C. Large-scale complementary macroelectronics using hybrid integration of carbon nanotubes and IGZO thin-film transistors. *Nat. Commun.* **2014**, *5*, 4097.

(9) Chortos, A.; Koleilat, G. I.; Pfattner, R.; Kong, D.; Lin, P.; Nur, R.; Lei, T.; Wang, H.; Liu, N.; Lai, Y.-C.; Kim, M.-G.; Chung, J. W.; Lee, S.; Bao, Z. Mechanically Durable and Highly Stretchable Transistors Employing Carbon Nanotube Semiconductor and Electrodes. *Adv. Mater.* **2016**, *28*, 4441–4448.

(10) Lei, T.; Chen, X.; Pitner, G.; Wong, H. S. P.; Bao, Z. Removable and Recyclable Conjugated Polymers for Highly Selective and High-Yield Dispersion and Release of Low-Cost Carbon Nanotubes. *J. Am. Chem. Soc.* **2016**, *138*, 802–805.

(11) Hersam, M. C. Progress towards monodisperse single-walled carbon nanotubes. *Nat. Nanotechnol.* **2008**, *3*, 387–394.

(12) Tu, X.; Manohar, S.; Jagota, A.; Zheng, M. DNA sequence motifs for structure-specific recognition and separation of carbon nanotubes. *Nature* **2009**, *460*, 250–253.

(13) Arnold, M. S.; Green, A. A.; Hulvat, J. F.; Stupp, S. I.; Hersam, M. C. Sorting carbon nanotubes by electronic structure using density differentiation. *Nat. Nanotechnol.* **2006**, *1*, 60–65.

(14) Tulevski, G. S.; Franklin, A. D.; Afzali, A. High Purity Isolation and Quantification of Semiconducting Carbon Nanotubes via Column Chromatography. *ACS Nano* **2013**, *7*, 2971–2976.

(15) Samanta, S. K.; Fritsch, M.; Scherf, U.; Gomulya, W.; Bisri, S. Z.; Loi, M. A. Conjugated Polymer-Assisted Dispersion of Single-Wall Carbon Nanotubes: The Power of Polymer Wrapping. *Acc. Chem. Res.* **2014**, *47*, 2446–2456.

(16) Nish, A.; Hwang, J.-Y.; Doig, J.; Nicholas, R. J. Highly selective dispersion of single-walled carbon nanotubes using aromatic polymers. *Nat. Nanotechnol.* **2007**, *2*, 640–646.

(17) Ding, J.; Li, Z.; Lefebvre, J.; Cheng, F.; Dubey, G.; Zou, S.; Finnie, P.; Hrdina, A.; Scoles, L.; Lopinski, G. P.; Kingston, C. T.; Simard, B.; Malenfant, P. R. L. Enrichment of large-diameter semiconducting SWCNTs by polyfluorene extraction for high network density thin film transistors. *Nanoscale* **2014**, *6*, 2328–2339.

(18) Mistry, K. S.; Larsen, B. A.; Blackburn, J. L. High-Yield Dispersions of Large-Diameter Semiconducting Single-Walled Carbon Nanotubes with Tunable Narrow Chirality Distributions. *ACS Nano* **2013**, *7*, 2231–2239.

(19) Lee, H. W.; Yoon, Y.; Park, S.; Oh, J. H.; Hong, S.; Liyanage, L. S.; Wang, H.; Morishita, S.; Patil, N.; Park, Y. J.; Park, J. J.; Spakowitz, A.; Galli, G.; Gygi, F.; Wong, P. H. S.; Tok, J. B. H.; Kim, J. M.; Bao, Z. Selective dispersion of high purity semiconducting single-walled carbon nanotubes with regioregular poly(3-alkylthiophene)s. *Nat. Commun.* **2011**, *2*, 541.

(20) Akazaki, K.; Toshimitsu, F.; Ozawa, H.; Fujigaya, T.; Nakashima, N. Recognition and One-Pot Extraction of Right- and Left-Handed Semiconducting Single-Walled Carbon Nanotube Enantiomers Using Fluorene-Binaphthol Chiral Copolymers. *J. Am. Chem. Soc.* **2012**, *134*, 12700–12707.

(21) Ozawa, H.; Fujigaya, T.; Niidome, Y.; Hotta, N.; Fujiki, M.; Nakashima, N. Rational Concept To Recognize/Extract Single-Walled Carbon Nanotubes with a Specific Chirality. *J. Am. Chem. Soc.* **2011**, *133*, 2651–2657.

(22) Kim, W.-J.; Lee, C. Y.; O'brien, K. P.; Plombon, J. J.; Blackwell, J. M.; Strano, M. S. Connecting Single Molecule Electrical Measurements to Ensemble Spectroscopic Properties for Quantification of Single-Walled Carbon Nanotube Separation. *J. Am. Chem. Soc.* **2009**, *131*, 3128–3129.

DOI: 10.1021/acs.accounts.7b00062

(23) Park, S.; Lee, H. W.; Wang, H.; Selvarasah, S.; Dokmeci, M. R.; Park, Y. J.; Cha, S. N.; Kim, J. M.; Bao, Z. Highly Effective Separation of Semiconducting Carbon Nanotubes verified via Short-Channel Devices Fabricated Using Dip-Pen Nanolithography. *ACS Nano* **2012**, *6*, 2487−2496.

(24) Wang, H.; Hsieh, B.; Jiménez-Osés, G.; Liu, P.; Tassone, C. J.; Diao, Y.; Lei, T.; Houk, K. N.; Bao, Z. Solvent Effects on Polymer Sorting of Carbon Nanotubes with Applications in Printed Electronics. *Small* **2015**, *11*, 126−133.

(25) Kanai, Y.; Grossman, J. C. Role of Semiconducting and Metallic Tubes in P3HT/Carbon-Nanotube Photovoltaic Heterojunctions: Density Functional Theory Calculations. *Nano Lett.* **2008**, *8*, 908−912.

(26) Wang, H.; Hsieh, B.; Jiménez-Osés, G.; Liu, P.; Tassone, C. J.; Diao, Y.; Lei, T.; Houk, K. N.; Bao, Z. Solvent Effects on Polymer Sorting of Carbon Nanotubes with Applications in Printed Electronics. *Small* **2015**, *11*, 126−133.

(27) Lei, T.; Pitner, G.; Chen, X.; Hong, G.; Park, S.; Hayoz, P.; Weitz, R. T.; Wong, H.-S. P.; Bao, Z. Dispersion of High-Purity Semiconducting Arc-Discharged Carbon Nanotubes Using Backbone Engineered Diketopyrrolopyrrole (DPP)-Based Polymers. *Adv. Electron. Mater.* **2016**, *2*, 1500299.

(28) Lei, T.; Lai, Y.-C.; Hong, G.; Wang, H.; Hayoz, P.; Weitz, R. T.; Chen, C.; Dai, H.; Bao, Z. Diketopyrrolopyrrole (DPP)-Based Donor−Acceptor Polymers for Selective Dispersion of Large-Diameter Semiconducting Carbon Nanotubes. *Small* **2015**, *11*, 2946−2954.

(29) Gu, J.; Han, J.; Liu, D.; Yu, X.; Kang, L.; Qiu, S.; Jin, H.; Li, H.; Li, Q.; Zhang, J. Solution-Processable High-Purity Semiconducting SWCNTs for Large-Area Fabrication of High-Performance Thin-Film Transistors. *Small* **2016**, *12*, 4993−4999.

(30) Yi, W.; Malkovskiy, A.; Chu, Q.; Sokolov, A. P.; Colon, M. L.; Meador, M.; Pang, Y. Wrapping of Single-Walled Carbon Nanotubes by a π-Conjugated Polymer: The Role of Polymer Conformation-Controlled Size Selectivity. *J. Phys. Chem. B* **2008**, *112*, 12263−12269.

(31) Wang, H.; Koleilat, G. I.; Liu, P.; Jiménez-Osés, G.; Lai, Y.-C.; Vosgueritchian, M.; Fang, Y.; Park, S.; Houk, K. N.; Bao, Z. High-Yield Sorting of Small-Diameter Carbon Nanotubes for Solar Cells and Transistors. *ACS Nano* **2014**, *8*, 2609−2617.

(32) Wang, H.; Li, Y.; Jiménez-Osés, G.; Liu, P.; Fang, Y.; Zhang, J.; Lai, Y.-C.; Park, S.; Chen, L.; Houk, K. N.; Bao, Z. N-Type Conjugated Polymer-Enabled Selective Dispersion of Semiconducting Carbon Nanotubes for Flexible CMOS-Like Circuits. *Adv. Funct. Mater.* **2015**, *25*, 1837−1844.

(33) Lei, T.; Wang, J.-Y.; Pei, J. Roles of Flexible Chains in Organic Semiconducting Materials. *Chem. Mater.* **2014**, *26*, 594−603.

(34) Liang, S.; Zhao, Y.; Adronov, A. Selective and Reversible Noncovalent Functionalization of Single-Walled Carbon Nanotubes by a pH-Responsive Vinylogous Tetrathiafulvalene−Fluorene Copolymer. *J. Am. Chem. Soc.* **2014**, *136*, 970−977.

(35) Zhang, Z.; Che, Y.; Smaldone, R. A.; Xu, M.; Bunes, B. R.; Moore, J. S.; Zang, L. Reversible Dispersion and Release of Carbon Nanotubes Using Foldable Oligomers. *J. Am. Chem. Soc.* **2010**, *132*, 14113−14117.

(36) Liang, S.; Chen, G.; Zhao, Y. Conformationally switchable TTFV-phenylacetylene polymers: synthesis, properties, and supramolecular interactions with single-walled carbon nanotubes. *J. Mater. Chem. C* **2013**, *1*, 5477−5490.

(37) Joo, Y.; Brady, G. J.; Shea, M. J.; Oviedo, M. B.; Kanimozhi, C.; Schmitt, S. K.; Wong, B. M.; Arnold, M. S.; Gopalan, P. Isolation of Pristine Electronics Grade Semiconducting Carbon Nanotubes by Switching the Rigidity of the Wrapping Polymer Backbone on Demand. *ACS Nano* **2015**, *9*, 10203−10213.

(38) Wang, W. Z.; Li, W. F.; Pan, X. Y.; Li, C. M.; Li, L.-J.; Mu, Y. G.; Rogers, J. A.; Chan-Park, M. B. Degradable Conjugated Polymers: Synthesis and Applications in Enrichment of Semiconducting Single-Walled Carbon Nanotubes. *Adv. Funct. Mater.* **2011**, *21*, 1643−1651.

(39) Lemasson, F.; Tittmann, J.; Hennrich, F.; Sturzl, N.; Malik, S.; Kappes, M. M.; Mayor, M. Debundling, selection and release of SWNTs using fluorene-based photocleavable polymers. *Chem. Commun.* **2011**, *47*, 7428−7430.

(40) Toshimitsu, F.; Nakashima, N. Semiconducting single-walled carbon nanotubes sorting with a removable solubilizer based on dynamic supramolecular coordination chemistry. *Nat. Commun.* **2014**, *5*, 5041.

(41) Pochorovski, I.; Wang, H.; Feldblyum, J. I.; Zhang, X.; Antaris, A. L.; Bao, Z. H-Bonded Supramolecular Polymer for the Selective Dispersion and Subsequent Release of Large-Diameter Semiconducting Single-Walled Carbon Nanotubes. *J. Am. Chem. Soc.* **2015**, *137*, 4328−4331.

(42) Wang, C.; Hwang, D.; Yu, Z.; Takei, K.; Park, J.; Chen, T.; Ma, B.; Javey, A. User-interactive electronic skin for instantaneous pressure visualization. *Nat. Mater.* **2013**, *12*, 899−904.

(43) Lau, P. H.; Takei, K.; Wang, C.; Ju, Y.; Kim, J.; Yu, Z.; Takahashi, T.; Cho, G.; Javey, A. Fully Printed, High Performance Carbon Nanotube Thin-Film Transistors on Flexible Substrates. *Nano Lett.* **2013**, *13*, 3864−3869.

(44) Cao, X.; Lau, C.; Liu, Y.; Wu, F.; Gui, H.; Liu, Q.; Ma, Y.; Wan, H.; Amer, M. R.; Zhou, C. Fully Screen-Printed, Large-Area, and Flexible Active-Matrix Electrochromic Displays Using Carbon Nanotube Thin-Film Transistors. *ACS Nano* **2016**, *10*, 9816−9822.

(45) Wang, H.; Wei, P.; Li, Y.; Han, J.; Lee, H. R.; Naab, B. D.; Liu, N.; Wang, C.; Adijanto, E.; Tee, B. C.-K.; Morishita, S.; Li, Q.; Gao, Y.; Cui, Y.; Bao, Z. Tuning the threshold voltage of carbon nanotube transistors by n-type molecular doping for robust and flexible complementary circuits. *Proc. Natl. Acad. Sci. U. S. A.* **2014**, *111*, 4776−4781.

(46) Park, S.; Pitner, G.; Giri, G.; Koo, J. H.; Park, J.; Kim, K.; Wang, H.; Sinclair, R.; Wong, H. S. P.; Bao, Z. Large-Area Assembly of Densely Aligned Single-Walled Carbon Nanotubes Using Solution Shearing and Their Application to Field-Effect Transistors. *Adv. Mater.* **2015**, *27*, 2656−2662.

(47) Xu, F.; Wu, M.-Y.; Safron, N. S.; Roy, S. S.; Jacobberger, R. M.; Bindl, D. J.; Seo, J.-H.; Chang, T.-H.; Ma, Z.; Arnold, M. S. Highly Stretchable Carbon Nanotube Transistors with Ion Gel Gate Dielectrics. *Nano Lett.* **2014**, *14*, 682−686.

(48) Norton-Baker, B.; Ihly, R.; Gould, I. E.; Avery, A. D.; Owczarczyk, Z. R.; Ferguson, A. J.; Blackburn, J. L. Polymer-Free Carbon Nanotube Thermoelectrics with Improved Charge Carrier Transport and Power Factor. *ACS Energy Lett.* **2016**, *1*, 1212−1220.

(49) Hung, N. T.; Nugraha, A. R. T.; Hasdeo, E. H.; Dresselhaus, M. S.; Saito, R. Diameter dependence of thermoelectric power of semiconducting carbon nanotubes. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2015**, *92*, 165426.

(50) Avery, A. D.; Zhou, B. H.; Lee, J.; Lee, E.-S.; Miller, E. M.; Ihly, R.; Wesenberg, D.; Mistry, K. S.; Guillot, S. L.; Zink, B. L.; Kim, Y.-H.; Blackburn, J. L.; Ferguson, A. J. Tailored semiconducting carbon nanotube networks with enhanced thermoelectric properties. *Nat. Energy* **2016**, *1*, 16033.

(51) Bindl, D. J.; Wu, M.-Y.; Prehn, F. C.; Arnold, M. S. Efficiently Harvesting Excitons from Electronic Type-Controlled Semiconducting Carbon Nanotube Films. *Nano Lett.* **2011**, *11*, 455−460.

(52) Koleilat, G. I.; Vosgueritchian, M.; Lei, T.; Zhou, Y.; Lin, D. W.; Lissel, F.; Lin, P.; To, J. W. F.; Xie, T.; England, K.; Zhang, Y.; Bao, Z. Surpassing the Exciton Diffusion Limit in Single-Walled Carbon Nanotube Sensitized Solar Cells. *ACS Nano* **2016**, *10*, 11258−11265.

DOI: 10.1021/acs.accounts.7b00062