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Publisher's version / Version de l'éditeur:

<https://doi.org/10.1021/acsnano.7b08818>

ACS Nano, 12, 2, pp. 1910-1919, 2018-01-09

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Sorting of Semiconducting Single-Walled Carbon Nanotubes in Polar Solvents with an Amphiphilic Conjugated Polymer Provides General Guidelines for Enrichment

Jianying Ouyang*, Jianfu Ding, Jacques Lefebvre, Zhao Li, Chang Guo, Arnold J. Kell, and Patrick R. L. Malenfant*

Security and Disruptive Technologies Portfolio, National Research Council Canada, 1200 Montreal Road, Ottawa, Ontario K1A 0R6, Canada

S Supporting Information

ABSTRACT: Conjugated polymer extraction (CPE) has been shown to be a highly effective method to isolate high-purity semiconducting single-walled carbon nanotubes (sc-SWCNTs). In both literature reports and industrial manufacturing, this method has enabled enrichment of sc-SWCNTs with high purity ($\geq 99.9\%$). High selectivity is typically obtained in nonpolar aromatic solvents, yet polar solvents may provide process improvements in terms of yield, purity and efficiency. Using an amphiphilic fluorene-*alt*-pyridine conjugated copolymer with hydrophilic side chains, we have investigated the enrichment of sc-SWCNTs in polar solvents. Various conditions such as polymer/SWCNT ratio, solvent polarity, solvent dielectric constant as well as polymer solubility and SWCNT dispersibility were explored in order to optimize the purity and yield of the enriched product. Herein, we provide insights on CPE by demonstrating that a conjugated polymer having a hydrophobic backbone and hydrophilic oligo(ethylene oxide) side chains provides near full recovery (95%) of sc-SWCNTs using a multiextraction protocol. High purity is also obtained, and differences in chiral selectivity compared to analogous hydrophobic systems were confirmed by optical absorption and Raman spectroscopy as well as photoluminescence excitation mapping. Taking into consideration the solvent dielectric constant, polarity index as well as polymer solubility and SWCNT dispersibility provides a better understanding of structure–property effects on sc-SWCNT enrichment. The resulting hydrophilic SWCNT dispersions demonstrate long-term colloidal stability, making them suitable for ink formulation and high-performance thin-film transistors fabrication.

KEYWORDS: enrichment, high-purity semiconducting SWCNT, polar solvents, poly(fluorene-*alt*-pyridine), amphiphilic polymer, thin-film transistors, inkjet printing

High-purity semiconducting single-walled carbon nanotubes (sc-SWCNTs) will be critical to the performance of future electronic devices ranging from high-performance field-effect transistors to printed thin-film transistors (TFTs) and sensors.^{1–4} Conjugated polymer extraction (CPE) enables a simple and scalable way for the enrichment of sc-SWCNTs,^{5–7} and the polymers used are generally polyfluorene-^{8–12} and poly(3-alkylthiophene)-based.^{13–15} It has been reported that the sc-SWCNT selectivity of the extraction is highly dependent on both the polymer structure and solvent nature (polarity, viscosity, density), and to date most of the literature has focused on nonpolar aromatic solvents to maximize sc-purity,^{3–24} with only a few successful examples employing polar solvents.^{18,21–24}

Hwang *et al.* reported that the highest selectivity in terms of diameter and chiral angle was observed in toluene using

poly(9,9-dioctylfluorene) (PFO) and poly[(9,9-dioctylfluorenyl-2,7-diyl)-*alt*-(1,4-benzo-2,1'-3-thiadiazole)] (PFO-BT).¹⁶ Lower selectivity and high-metallic SWCNT content was observed in a polar solvent including tetrahydrofuran (THF) and chloroform. Qian *et al.* also reported that selectivity only existed in toluene and *m*-xylene with no selectivity in chloroform and THF using poly(9,9-dioctylfluorene-*co*-bithiophene) (F8T2).¹⁷ When a thiophene unit was introduced between the two monomer units of PFO-BT, namely poly[2,7-(9,9-dioctylfluorene)-*alt*-4,7-bis(thiophen-2-yl)benzo-2,1,3-thiadiazole] (PFO-DBT), a high selectivity was observed in THF.¹⁸ More recently, Wang *et al.* reported that a high

Received: December 13, 2017

Accepted: January 9, 2018

Published: January 9, 2018

Figure 1. Overview of sc-SWCNTs enriched in 1,4-dioxane using the amphiphilic polymer: (a) Schematic representation of the polymer P(FEt₃M-Py-2,5). (b) Optical absorption spectrum, showing no metallic SWCNT features; (right-insert) Raman spectrum (RBM region, excited with 785 nm laser), with no noticeable SWCNT metallic features for the enriched material (red curve) compared to unsorted plasma SWCNTs (black curve) having a prominent metallic SWCNT peak centered at 159 cm⁻¹; (left-insert) PLE mapping, showing distinctive (n,m) chiralities. (c) Transistor characteristics from a random network of sc-SWCNT (channel length/width is 20/2000 μm. Source-drain bias is -1 V with linear current density per width >0.1 mA/mm). See Figure S1C for transistor characteristics with shorter channel lengths, and Figures S4A and S5A for a more detailed interpretation of Raman and PLE data, respectively.

selectivity for sc-SWCNTs was observed in toluene and other aromatic or cyclic-aliphatic nonpolar solvents using poly(3-dodecylthiophene), while no selectivity was observed in THF or *N*-methyl-2-pyrrolidone (NMP).¹⁹ Adronov and co-workers have demonstrated that THF can be used to provide high selectivity with a poly(2,7-carbazole) derivative having 3,4,5-tris(hexadecyloxy)phenyl side chains and an alkyl spacer.²⁰ They have also shown that a poly(fluorene-co-pyridine) derivative with dodecyl side chains are effective at sorting sc-SWCNT in THF.²¹ Recently, Toshimitsu demonstrated an elegant enrichment process using dynamic supramolecular coordination chemistry whereby the system needed a mixture of toluene and benzonitrile, in which the polar solvent, benzonitrile, was required to solubilize the self-assembled metal coordination polymer.²² In another example by the same authors, a hydrogen-bonding polymer composed of dicarboxylic- and diaminopyridyl-fluorenes provided high selectivity in a mixture of toluene/acetone.²³ In all of these examples, the conjugated polymer structures possess hydrophobic backbones and side chains, with some examples having moieties in the backbone capable of hydrogen bonding and/or strong solvent coordination. As such, polymers are needed to expand the parameter space and provide a better understanding of structure–property relationships (polymer design and solvent effects) that simultaneously optimize yield, purity, and process efficiency. To our knowledge, successful sc-SWCNT enrichment has yet to be reported with conjugated polymers having a hydrophobic backbone and hydrophilic side chains.²⁴ This advance in polymer design broadens solvent options for enrichment and has provided insight into structure–property

relationships that govern the enrichment process, enabling near full recovery of high-purity sc-SWCNT.

Polar solvent systems are of interest for ink formulation as a wider variety of solvents with ideal rheological properties for printed electronics may be used.^{25,26} In order to obtain dispersions in polar solvents, two strategies may be adopted. One is ligand exchange, which involves replacing the original wrapping polymer with a hydrophilic polymer that has a higher affinity for the SWCNT surface after enrichment.^{27,28} Although effective, partial exchange may result in a composite coating even after multiple exchange cycles. The direct enrichment approach in polar solvents assures a single wrapping polymer in the final product. Hence, we have designed and synthesized a fluorene/pyridine alternating copolymer with hydrophilic side chains for the direct enrichment of large diameter sc-SWCNT. The effects of the polymer structure and solvent properties on the enrichment were investigated in detail with a focus on optimizing yield and purity. This polymer, poly(9,9-bis(2-(2-(2-methoxyethoxy)ethoxy)ethyl)fluorene-*alt*-pyridine-2,5) [P(FEt₃M-Py-2,5)] possesses a rigid and hydrophobic backbone with highly hydrophilic side chains (see Figure 1a). Compared to 9,9-dialkylfluorene homopolymers such as poly(9,9-di-*n*-dodecylfluorene) (PFDD), the pyridine unit enhances the interaction between polymer and SWCNTs by donating the lone electron pair on the nitrogen atom to the SWCNT, resulting in a tighter wrapping configuration, leading to an increase in the selectivity and yield of enrichment.^{29–33} The use of oligo(ethylene oxide) (*n* = 3) side chains renders the polymer more soluble in polar solvents, thus expanding the diversity of solvents (and solvent mixtures) for SWCNT

Table 1. Comparison of Enrichment Performance in Various Solvents Using P(FEt₃M-Py-2,5), with $\phi > 0.33$ ^a

solvent	yield (%)	purity ϕ	extractions combined	polymer solubility (mg/mL)	SWCNT dispersibility (mg/L)	dielectric constant (25 °C)	polarity index (25 °C)	dipole moment (D, 25 °C)
toluene	30	0.37–0.40	Ex1 to 5	2.3	2.8×10^{-3}	2.4	2.4	0.31 (20 °C)
1,4-dioxane	38	0.36–0.40	Ex1 to 3	84	8.1×10^{-3}	2.3 (20 °C)	4.8	0.45
THF	22	0.33–0.36	Ex1 to 2	32	1.2×10^{-2}	7.6	4.0	1.75
MC	0	All <0.33	Ex1 to 5	4.7	18	14.8	5.5 ^b	2.04 ^b

^aThe polymer/SWCNT weight ratio was 0.5:1 for all solvents. ^b2-Methoxyethanol used as proxy for methyl carbitol (MC). Polarity index (a relative measure of the degree of interaction of the solvent with various polar test solutes), dielectric constant, and dipole moment values are taken from <http://macro.lsu.edu/howto/solvents/Polarity%20index.htm>

dispersion. This polymer constitutes an interesting addition to the conjugated polymer library applied to the enrichment of sc-SWCNTs.^{5,6,24,34,35}

Herein, we describe the use of polar solvents and solvent mixtures in sc-SWCNT enrichment. After screening a series of polar organic solvents, we found that excellent enrichment performance can be realized in 1,4-dioxane, and to a lesser extent in THF, and carbitols. It was found that polymer solubility in relation to SWCNT dispersibility should be considered for effective enrichment. If polymer solubility is too low and SWCNT dispersibility (high colloidal stability in the absence of polymer) is too high, then CPE will not be effective. Solvent composition, polarity index, and dielectric constant are relevant parameters that will determine the polymer solubility and SWCNT dispersibility as well as colloidal stability. Furthermore, the structure–property relationships uncovered during our exploration of polar solvents led us to examine solvent mixtures, whereby a significant yield improvement with good sc-purity using carbitol-toluene mixtures was observed. The resulting sc-SWCNTs provide excellent device characteristics when employed as the semiconducting channel material in TFTs and can be readily dispersed into carbitol and alkanols, favored solvents for use in commercial printing processes.

RESULTS AND DISCUSSION

Single Solvent Effects on Enrichment Yield and Purity. Intuitively, a high selectivity for sc-SWCNT enrichment should entail the use of a solvent that provides suitable polymer solubility in conjunction with adequate SWCNTs dispersibility as to yield individualized SWCNTs, yet neither of these parameters have ever been quantified or considered in the context of sc-SWCNT enrichment.^{5–7,19} It is important to note that the raw SWCNT material typically used in CPE may contain as much as 50% by weight amorphous carbon/catalyst impurities (see Figure S1A in Supporting Information for TGA results), hence the ability to disperse SWCNTs into individualized SWCNTs and separate them from amorphous carbon while maintaining good conditions for selective dispersion of sc-SWCNT is paramount. We examined a series of polar solvents (see Table S1 and Scheme S1) in order to correlate their intrinsic properties (polarity, dielectric constant) with their ability to solubilize the polymer and disperse SWCNTs in the absence of polymer. Based on these observations, we focused on three polar solvents (1,4-dioxane, tetrahydrofuran (THF), and methyl carbitol (MC)) for the enrichment and one nonpolar solvent (toluene) for comparison, with the data summarized in Table 1. The polymer solubility was determined using Beer's law. Solvent dielectric constant, polarity index, dipole, and viscosity values were taken from the literature. SWCNT dispersibility in the absence of

polymer was determined based on the S₂₂ absorbance peak maxima at ~950 nm and calculated by $A = \epsilon CL$ ($\epsilon = 48.3$ mL/mg·cm).¹⁰ Yield (%) is calculated based on literature methods,^{12,24,30} which is the mass percentage of enriched sc-SWCNTs relative to the sc-SWCNT in feed raw, that is, $\text{mass}(\text{enriched}) / [\text{mass}(\text{feed raw}) \times 0.4 \times 0.67]$ (40% SWCNT content determined by TGA and 2:1 ratio of sc:m in the raw SWCNT soot; 10% catalyst and 50% amorphous carbon make up the remaining content of the raw soot). The cumulative yield is based on the sum of all extractions collected having $\phi > 0.33$. In our previous work, we proposed to use the ϕ value to estimate the sc-purity of the enriched large diameter sc-SWCNTs.¹⁰ This value is calculated from the absorbance *vs* wavelength and is defined as the ratio of the integrated area without the trapezoid background over the whole integrated area under the S₂₂ and M₁₁ bands. ϕ values over 0.41 correspond to >99.9% sc-purity or more based on Raman mapping.³⁶ Typically, the M₁₁ band in the absorption spectrum is absent when the sc-purity is higher than 99% with ϕ values over 0.33.^{10,36}

It is clear that the SWCNT dispersibility increases from toluene to 1,4-dioxane and THF (Figure S1B), which is consistent with previous reports that THF has a higher dispersing power than toluene toward small-diameter (*ca.* 0.7 nm) SWCNTs.³⁷ In methyl carbitol, the SWCNT sample was dispersed at a much higher concentration with the presence of dispersed amorphous carbon (which constitutes 50% of the raw material) convoluting the interpretation due to a featureless absorption spectrum (Figure S1B). The polymer solubility is over an order of magnitude higher upon going from toluene to 1,4-dioxane. Though they have similar dielectric constants, 1,4-dioxane may solvate the ethylene oxide side chains more effectively due to a higher polarity index and dipole as well as structural similarity. A decrease in polymer solubility in going to higher polarity THF and MC is consistent with the solvent favoring the side chains over the backbone. Increased SWCNT dispersibility as a function of higher polarity, dielectric constant, and solvent dipole among the polar solvents is also expected.

As can be seen in Table 1, 1,4-dioxane outperforms THF and MC with respect to purity and enables a more efficient extraction process (fewer extractions) compared to toluene. Figure 1 summarizes the detailed characterization for a typical extraction obtained using P(FEt₃M-Py-2,5) in 1,4-dioxane, including absorption spectroscopy, Raman scattering (radial breathing mode, RBM), and PLE mapping (Figure 1b), details of which are provided in Figures S4A and S5A. In many respects, the spectral quality of the enriched fraction is very similar to dispersions obtained from PFDD/toluene reported previously.^{10,11} The quality of enriched product was further confirmed with random network transistors having mobility approaching 10 cm²/(V s) and current on/off ratio of 10⁴–10⁵

Figure 2. Absorption spectra of supernatants obtained from multiple extractions (pre, first, second, and third) using P(FEt₃M-Py-2,5) in 1,4-dioxane with 0.5:1 polymer/SWCNT weight ratio (a). The inserts show the enriched sc-SWCNT calculated yield (%) / purity (ϕ) for each extraction. The enrichment performance as a function of extraction number with varied polymer/SWCNT ratios is shown in (b), with a break at 0.33 for the y axis (ϕ).

Figure 3. (a) Absorption spectra of supernatants obtained from typical extractions using P(FEt₃M-Py-2,5) with polymer/SWCNT weight ratios of 0.5:1 in 1,4-dioxane (black), THF (red), methyl carbitol (blue), and toluene (green). (b) The enrichment performance as a function of extraction number in the four solvents, with a break at 0.33 for the y axis (ϕ). See Figure S2A for all absorption spectra.

(Figure 1c). Table 1 summarizes both yield and sc-purity values for all solvents, with details described further below.

Though most reports on CPE involve a single extraction,^{9,12,13,16,18,19,30} we observed that a multiple-extraction process using a low polymer/SWCNT ratio can maintain a high purity while effectively promoting the yield.¹⁰ Figure 2 compares the performance of multiple extractions in 1,4-dioxane with polymer/SWCNT weight ratio varying from 1:1, 0.5:1 to 0.25:1. In our previous work using a multiple-extraction process in nonpolar solvents,^{10,11} the initial extraction yielded no sc-SWCNTs in the nearly clear supernatant and thus was referred to as a pre-extraction or conditioning step. When that is the case, the precipitate from the pre-extraction is then subjected to CPE, subsequently enabling the first, second, and third extractions. When a 1:1 polymer/SWCNT ratio was applied here (Figure 2b red), the pre-extraction provided nanotubes in the supernatant with a yield of 5.2% and ϕ value of 0.35.¹⁰ The subsequent extractions resulted in a yield and ϕ value of 17.0% and 0.39 for the first extraction, 18.1% and 0.35 for the second extraction, and 16.3% and 0.30 for the third extraction. It is obvious that the yield for each extraction remained in the range of ~15–20%, but the purity decreased dramatically when the extraction cycles were increased with

noticeable metallic features at ~700 nm in their absorption spectrum for the third extraction. Figure 2a (and Figure 2b black) shows that at a reduced polymer/SWCNT ratio of 0.5:1, the enrichment yielded no nanotubes in the pre-extraction and a slightly reduced yield of 9.3%, 14.4%, and 14.1%, but with much higher ϕ values of 0.40, 0.38, and 0.36 from first, second, and third extractions, with an overall yield of 37.8%. At a 0.25:1 ratio (Figure 2b green), the enrichment progressed slower, with no sc-SWCNTs enriched in the pre-extraction and first extraction, very little in second extraction, and a total yield of 14.5% was obtained in the third and fourth extractions with ϕ 0.38 and 0.37, respectively. It is clear that a polymer/SWCNTs ratio of 0.5:1 is a good compromise to achieve high purity and high yield of sc-SWCNTs, consistent with previous observations with PFDD extraction in toluene.^{10,11} The reproducibility of enrichment is excellent as demonstrated in 1,4-dioxane with 0.5:1 polymer/SWCNT ratio (Figure S2A-e).

In comparison, tetrahydrofuran provides a good solubility (32 mg/mL) for P(FEt₃M-Py-2,5) while a higher SWCNT dispersibility (1.2×10^{-2} mg/L) compared to 1,4-dioxane (Table 1). The enrichment was examined in THF with varied polymer/SWCNT ratios (1:1, 0.5:1, and 0.25:1), and 0.5:1 was also the optimum ratio to achieve the best compromise

Table 2. Comparison of Enrichment Performance in 1:1 Mixed Solvents Systems with P(FEt₃M-Py-2,5), with Exclusion of the Extractions Having $\phi < 0.33^a$

solvent mixture (1:1)	yield (%)	purity, Φ	extractions combined	dielectric constant (ϵ at 25 °C) ^b	viscosity (cP at 25 °C) ^c
THF:MC	0	all <0.33	Ex1 to 3	11.2	1.47
toluene:MC	95	0.33–0.39 ^d	Ex1 to 5	8.6	1.52
dioxane:MC	58	0.33–0.38 ^d	Ex1 to 4	8.5	1.97
toluene:THF	19	0.36	Ex2 to 4	5.0	0.51
dioxane:THF	20	0.35	Ex1	4.9	0.76
toluene:dioxane	29	0.35–0.38	Ex1 to 3	2.3	0.81

^aThe polymer/SWCNT weight ratio was 0.5:1 for all solvent mixtures. ^bDielectric constant of mixed solvents is calculated.⁴² ^cViscosity of mixed solvents (the three from the top) was measured; the rest are calculated assuming a linear relationship with composition. ^d ϕ values are determined by redispersion of the final products in 1,4-dioxane due to bundling.

between high purity and yield (see Figure S2B and Table S2). Figure 3 compares the enrichment results in various solvents with a fixed 0.5:1 polymer/SWCNT ratio. The enrichment in THF yielded no sc-SWCNTs in the pre-extraction, the value decreased from ϕ 0.36, 0.33, to 0.20 for the first, second, and third extractions, respectively, with a cumulative yield of 22.2% with first and second extraction combined, providing inferior performance compared to 1,4-dioxane despite the fact that both are cyclic ethers (Figure 3b red). This result can be rationalized based on SWCNT dispersibility, which is 1.5 $\times$ higher in THF compared to 1,4-dioxane, while the polymer solubility is less than half. THF has a higher dielectric constant (7.58) than that of 1,4-dioxane (2.21); the higher dielectric constant and higher dipole may impede the reaggregation of m-SWCNTs under these conditions, which we believe is largely driven by the polarizability of m-SWCNTs and their propensity to rebundle with doped sc-SWCNTs.^{19,38} Effective screening of charged species and dipolar interactions by more dipolar THF molecules will mitigate the effects of atmospheric doping, affecting the rebundling process, thus reducing selectivity and the sc-purity.

Methyl carbitol is an interesting polar solvent with low toxicity (acute toxicity: rat oral LD₅₀ > 7000 mg/kg) thus making it more widely accepted in the printing industry. Carbitols have high viscosities and boiling points as well as low evaporation rates, important properties to obtain suitable inks to achieve high printing uniformity.³⁹ Methyl carbitol provides a lower solubility (4.7 mg/mL) for P(FEt₃M-Py-2,5) compared to THF and 1,4-dioxane, which in and of itself is not an issue when you consider that polymer solubility in toluene is half that obtained in methyl carbitol. However, the significantly higher dispersibility toward SWCNT in methyl carbitol is not conducive to providing high sc-purity (Table 1). Interestingly, when methyl carbitol was used (Figure 3b blue), the pre-extraction yielded no SWCNTs, the first extraction resulted in little SWCNTs, and the subsequent three extractions provided sc-SWCNTs with ϕ 0.23–0.28. Further extraction (fifth) led to a very low purity (ϕ 0.21). So the cumulative yield is zero because all extractions have $\phi < 0.33$ (Table 1). The lower ϕ values in MC might be attributed to both higher amorphous carbon content and m-SWCNT content. In separate experiments, it was found that methyl carbitol is very effective at dispersing amorphous carbon, a behavior that seems to peak at dielectric constants of $\sim$ 13. It is remarkable in fact that methyl carbitol leads to any enrichment at all, having a dielectric constant of 14.8, which would mitigate selective m-SWCNTs bundling and reaggregation.¹⁹ Various solvent parameters interplay to affect the enrichment performance. A suitable polar solvent should have high polymer solubility in

conjunction with adequate dispersibility toward individualized SWCNTs, the ratio of which becoming relevant at the extreme end of the range where high polymer solubility and SWCNT dispersibility seem to necessitate a larger polymer solubility/SWCNT dispersibility ratio such as in the case of 1,4-dioxane in order to provide high sc-yield and purity (ϕ 0.36–0.40). Improved process efficiency (fewer extraction cycles) requires low-medium range dielectric constants (i.e., dielectric constants <10) and adequate solvent polarity to maximize the dispersion yield (individualized SWCNTs yet low colloidal stability for amorphous carbon), while keeping in mind that maintaining a dielectric environment that is conducive to enabling a doping mediated enrichment mechanism.³⁸

For comparison, enrichment was also examined in toluene, the most common solvent used for sc-SWCNT enrichment (Figure 3b green). The enrichment produced no sc-SWCNTs in the pre-extraction, and a cumulative yield of 30% was obtained with five extractions providing ϕ 0.37–0.40. Twice as many extractions were required to obtain a yield of $\sim$ 1/3 in toluene compared to 1,4-dioxane with similar purity. These results are also consistent with the polarity index of dioxane (4.8) being 2 $\times$ that of toluene, which would serve to enhance the polymer solubility and SWCNT dispersibility which improve the efficiency of CPE. It is interesting to note that the dielectric constants are essentially the same for these two solvents, which may explain the reason for similar purities. We believe that under these conditions, the dielectric constant is what governs the selectivity; hence toluene and dioxane provide similar purities due to having similar dielectric constants, albeit with fewer extractions for dioxane. It is also interesting to consider the case of PFDD in toluene, whereby the PFDD solubility is high (>100 mg/mL) and the SWCNT dispersibility is 2.8×10^{-3} mg/L. Under these nonpolar conditions, high purities with ϕ values >0.40 are typically obtained, but the efficiency of the extraction process is similar to what is observed with P(FEt₃M-Py-2,5) in toluene ($\sim$ 7% yield per extraction),^{10,11} consistent with purity being largely governed by the dielectric constant, but the efficiency of extraction seems to correlate more with polarity index; the latter being a better indicator of tube dispersibility. It is also worth noting that higher polymer/SWCNT weight ratios are required in the PFDD/toluene extraction (8:1) in order to obtain a similar yield of $\sim$ 1/3 (ϕ 0.36),¹¹ whereas in the case of P(FEt₃M-Py-2,5) in dioxane, a 0.5:1 ratio provides 38% yield (ϕ 0.36–0.40) in three extractions, significantly improving the economics of the process by utilizing less polymer in fewer steps.

Additionally, amphiphilic P(FEt₃M-Py-2,5) may adopt different conformations in different solvents, which may impact the stability of the SWCNT/polymer complex. In toluene, the

polymer is mainly solvated by interactions with the backbone. In 1,4-dioxane and THF, the polymer is solvated by interactions with the backbone as well as the side chains. While in carbitols, the polymer is mainly solvated by interactions with the side chains.⁴⁰ Hence, lower polymer solubility in carbitols can be rationalized. In our current work, the bundling in carbitols is evident as longer centrifugation time in carbitols decreases both purity and yield compared to shorter centrifuge time (see Figure S2C); in contrast, longer centrifuge time in 1,4-dioxane, THF, or toluene increases the purity at the expense of the yield compared to shorter centrifuge time (Figure S2D). In addition, the enriched sc-SWCNTs exhibited good long-term (up to 2 months) colloidal stability in 1,4-dioxane, THF, and toluene, while about half was precipitated in MC after 1.5 months of storage (Figure S2E). Furthermore, the ϕ value of the enriched sc-SWCNTs was increased ($\sim 11\%$) after methyl carbitol was replaced by 1,4-dioxane, indicating less bundling in 1,4-dioxane compared to methyl carbitol (Figure S2C-f).

Mixed Solvents Effects on Enrichment Yield and Purity. Given the amphiphilic nature of the polymer, we thought it interesting to investigate the enrichment in 1:1 solvent mixtures as to further explore the effects of polarity, in the hopes that synergistic effects would arise, perhaps enabling improvements in yield while maintaining high purities. Table 2 summarizes enrichment results in various 1:1 solvent mixtures and is tabulated from highest to lowest dielectric constant. For THF:MC, having a high dielectric constant, it is not surprising that there is little selectivity. Toluene and 1,4-dioxane both provided high purity when used individually, with dioxane being more efficient, yet when adding MC to either solvents, an increase in yield (3.2-fold and 1.5-fold, respectively) is observed, with a slight decrease in purity providing ϕ 0.33–0.39 and ϕ 0.33–0.38, respectively. In these experiments, the dielectric constants are essentially the same at approximately 8.5, which is consistent with having obtained similar purities. Ratios of 1:3 and 3:1 dioxane:MC provided lower yields and purities (see Figure S3B). When toluene:THF and dioxane:THF (1:1) were examined, the dielectric constant further decreased to approximately 5 in both cases. In the case of toluene:THF, the ϕ value decreased slightly to 0.36 compared to pure toluene, yet the yield decreased substantially, which is unexpected. One might expect the presence of THF to improve the yield, at the expense of purity given the higher dielectric constant of the mixture. It is also instructive to keep in mind the mixed solvent results with toluene:MC, suggesting that a dielectric constant as high as 8–9 can provide good yields and purities. In the case of the THF:dioxane, a decrease in yield is observed compared to either solvents, and purity decreases compared to dioxane and increases compared to THF. Lastly, the toluene:dioxane mixture provided a decrease both in yield and purity compared to the parent solvents. Solvent viscosity does not appear to have any impact on yield or sc-purity.^{19,41}

Based on the results obtained with 1:1 solvent mixtures and the synergistic results observed for the toluene:MC mixture, we examined the enrichment performance in toluene (backbone solvation) with an increasing amount of methyl carbitol (side-chain solvation). The change of yield and sc-purity of enriched product as a function of MC composition (wt %) is illustrated in Figure 4 and also tabulated in Table 3 along with dielectric constant and viscosity data. Compared to pure toluene, the addition of a small amount of methyl carbitol (toluene/methyl carbitol 27:1, w/w) increased the yield dramatically from 30%

Figure 4. Change of yield (%; blue square) and sc-purity (ϕ ; red circle) of enriched products using P(FEt₃M-Py-2,5) as a function of the methyl carbitol composition (weight %) in toluene. The bar over the red circles indicates the range of ϕ values. The extractions combined are those with $\phi \geq 0.33$, hence no data point is included for pure carbitol. The blue star represents the cumulative yield, and red star represents the purity obtained for Ex1 to Ex5 at the 1:1 toluene:MC mixture. It should be noted that redispersion of the final products in 1,4-dioxane increases the ϕ ratio by 0.02 due to reduced bundling (thus ϕ values here have been corrected for batches with MC wt % $\geq 50\%$) and the use of silica gel during the enrichment as a polishing step¹¹ can improve the purity further.

to 69%, with the sc-purity (ϕ) largely maintained. At a toluene:MC ratio of 9:1, the yield increased as well to 53%, with the ϕ slightly decreased. For toluene:MC ratios of 3:1, 1:1, and 1:3, the yield and purity are very good, but it is clear that for the 3:1 and 1:3 ratios, the yield is limited when fractions with ϕ ratios < 0.33 are excluded. Interestingly, both purity and yield peaked at the 1:1 ratio, whereby up to 5 extractions could be isolated in 95% cumulative yield, where ϕ values ranging between 0.33 and 0.39 were obtained. This result is repeatable, and this trend has been observed with other sources of raw SWCNTs such as arc-tubes. Compared to pure toluene, it is interesting to note that a trace amount of MC (3.6%) can significantly increase the yield with the same purity maintained. As the ratio of toluene to MC decreases (9:1, 3:1), the dielectric constant and polymer solubility increases, the latter reaching a maximum at 1:1 solvent ratio. Compared to pure MC, the 1:1 solvent ratio has 3.5-fold improvement in yield with ϕ significantly improved. It is also interesting to note that a dielectric constant of 9 at the 1:1 solvent ratio still enables high selectivity. These results illustrate that synergistic effects may be obtained with solvent mixtures and that further improvements may be attained with the right combination of polymer composition and solvent systems.

Figure 5 provides a characterization summary for 1:1 toluene:MC including direct comparison of the absorption spectra sum-up from Ex1 to Ex5 (divided by 12) with the raw SWCNT feed fully dispersed in *N*-methyl-2-pyrrolidone (NMP, 1/12 dilution) (a); Raman spectra (b); PLE mapping (c); the enrichment performance as a function of extraction number (d), and the inset shows the cumulative yield as a function of extraction number; and (e) the transfer curve of a fully inkjet-printed top gate transistor with channel material based on sc-SWCNTs enriched in mixed toluene:MC. A yield of 100% was obtained by comparing the ratio of area integrated in the range of 450–1350 nm in Figure 5a, which is in good agreement to

Table 3. Comparison of Enrichment Performance in Mixtures of Toluene and Methyl Carbitol Using P(FET₃M-Py-2,5), with Exclusion of the extractions having $\phi < 0.33^a$

toluene: MC (w/w)	yield (%)	purity (ϕ)	extractions combined	polymer solubility (mg/mL)	SWCNT dispersibility (mg/L)	dielectric constant (25 °C) ^b	viscosity (cP, 25 °C) ^c
1:0	30	0.37–0.40	Ex1 to 5	2.3	2.8×10^{-3}	2.4	0.56
27:1	69	0.34–0.40	Ex2 to 6	23		2.8	0.66
9:1	53	0.33–0.39	Ex1 to 4	40		3.6	0.96
3:1	56	0.33–0.34	Ex2 to 3	44		5.5	1.26
1:1	95	0.33–0.39 ^d	Ex1 to 5	63	0.7	8.6	1.52
1:3	64	0.34–0.35 ^d	Ex1 to 3	44		11.7	2.54
0:1	0	All <0.33	Ex1 to 5	4.7	18	14.8	3.27

^aThe polymer/SWCNT weight ratio was 0.5:1 for all solvent mixtures. ^bDielectric constant of mixed solvents is calculated.⁴² ^cViscosities of methyl carbitol and mixed solvents were measured in our laboratories, except for 27:1 toluene/MC, which is calculated assuming a linear relationship with composition. ^dThe ϕ values are determined by redispersion of the final products in 1,4-dioxane due to significant bundling exists when MC wt % $\geq$ 50% is used.

Figure 5. Overview of sc-SWCNTs enriched in toluene/methyl carbitol (1:1, w/w) using P(FET₃M-Py-2,5): (a) Optical absorption spectrum of extractions combined from first to fifth (divided by 12) compared to that of initial raw SWCNT feed fully dispersed in NMP (1/12 dilution); (b) Raman spectra of RBM region (excited with 785 nm laser) and G and D bands (excited with 633 nm laser); (c) Photoluminescence excitation map with three assigned (n,m) species; (d) the enrichment performance as a function of extraction number, with a break at 0.33 for the y axis (ϕ). The inset shows the cumulative yield as a function of extractions number, with the gray line as a guide to the eye using an S-function as indicated on the graph. (e) The transfer curve of a fully inkjet-printed top gate transistor with the channel material based on sc-SWCNTs enriched with P(FET₃M-Py-2,5) in toluene:MC. Channel length/width is 50/1100 μm . The ink was formulated with triethylene glycol monomethyl ether as the base solvent to meet the printer-head (KM-512) requirements. The inset shows three droplets at the same speed. See Figure S4B for a more detailed interpretation of Raman data.

the total yield of 95% (Figure 5e), that is, nearly all sc-SWCNTs were extracted with five extraction cycles. Raman spectroscopy is widely used for purity assessment and chirality assignment for sc-SWCNTs. We used three fixed laser wavelengths (514, 633, and 785 nm) to analyze the samples (see Figure S4B for Raman spectra excited with the three lasers). According to the Kataura plot,^{43–48} and the diameter range of SWCNTs synthesized from a plasma torch process,⁴⁷ we are able to compare the metallic SWCNT residues in the enriched samples. When the samples were excited with 514 nm laser, no significant differences were detected because the sc-SWCNTs are dominant. The Raman spectra, RBM region

excited by 785 nm laser and G and D bands excited by 633 nm laser, show highly suppressed metallic SWCNT features. PLE mapping shows distinctive (n,m) chiralities, and the chirality selectivity is in between that of their parent solvents. The most abundant are (13,5), (10,9), (12,7), with relative intensity 100, 87, and 82, respectively, in a narrow diameter range of 1.28–1.32 nm (1.30 ± 0.02 nm). Fully printed TFTs based on sc-SWCNTs isolated using the toluene:MC mixture were similar to those isolated in 1,4-dioxane in terms of mobility and current on/off ratio (mobility $9.3 \text{ cm}^2/(\text{V s})$ and on/off $\sim 10^5$). For inkjet printing, the viscosity of the ink must meet the requirement of the printer head, which is usually much higher

than that of toluene (0.56 cP at 25 °C).²⁶ The amphiphilic polymer has good solubility in polar solvent triethylene glycol monomethyl ether (TEGM). With TEGM as the base (7.3 cP at 25 °C), the resulting polymer/SWCNTs ink provided a stable dispersion and suitable viscosity, to jet effectively using a Konica Minolta (KM-512) print head (see Figure 5e inset).

CONCLUSIONS

sc-SWCNTs can be enriched in polar solvents such as 1,4-dioxane, THF, and methyl carbitol using an amphiphilic copolymer with a hydrophobic fluorene-*alt*-pyridine backbone and hydrophilic oligo(ethylene oxide) side chains. The sc-SWCNTs enriched in 1,4-dioxane show similar sc-purity with improved extraction rate compared to toluene. The (10,9) chirality dominates in 1,4-dioxane, which is similar to that obtained for PFDD in toluene, whereas for P(FET₃M-Py-2,5) in toluene, the (13,5) chirality dominates with a narrower distribution of chiralities compared to 1,4-dioxane (see Figures S5A and S5B for details). The addition of a < 5% methyl carbitol into toluene increases the enrichment yield significantly while maintaining high purity. Furthermore, essentially all of the recoverable sc-SWCNTs contained in the raw soot were isolated (95%) with excellent purity (>99%) when a mixed methyl toluene:carbitol (1:1 w/w) solvent system was used. High purity was confirmed by spectroscopic methods and excellent TFT performance in terms of mobility and current on/off ratio.

Our detailed enrichment experiments provide some guiding principles for solvent selection to enable efficient enrichment by CPE. Suitable polymer solubility (1–100 mg/mL) and tube dispersibility ($>1 \times 10^{-3} < 1$ mg/L) can be over a fairly broad range. The ratio of these two provides some guidance: A ratio of 10^3 – 10^4 enables high sc-purity, but the ratio is not universal on its own. Viscosity does not appear to be a significant factor in sc-SWCNT enrichment. Dielectric constant and polarity can be used to boost dispersion yield, effectively enabling individualized SWCNTs, but must remain low enough as to not preclude selectivity by preventing amorphous carbon precipitation and m-SWCNT bundling. In the case of the later, the solvent must not screen charges/dipoles on p-doped sc-SWCNT or interfere with oxygen/water redox doping as to negate m-SWCNT bundling, a requirement for high-purity sc-SWCNT enrichment.³⁸ Hence, a dielectric constant between 2 and 9 and polarity index below 5 seems optimum to maximize process efficiency, yield, and purity. Intrinsic and extrinsic properties of additives/co-solvents (polarity index, dielectric constant, polymer solubility, tube dispersibility) will have different effects on enrichment depending on polymer composition/architecture and how they are used. These guidelines provide insight toward a universal understanding of CPE that may be used to simultaneously maximize yield and purity while improving process efficiency.

METHODS

Materials. All solvents (A. R. grade) were purchased from Sigma-Aldrich and used as received, except for 1,4-dioxane (certified ACS), which was from Fisher Scientific. Poly(9,9-bis(2-(2-(2-methoxyethoxy)ethoxy)ethyl)fluorene-*alt*-pyridine-2,5) (P(FET₃M-Py-2,5)) was prepared by Suzuki coupling (see Scheme S2), with M_n 10.7 kDa, PDI 4.9 as determined by gel permeation chromatography (THF as eluent). The silver molecular ink is a technology licensed by the National Research Council of Canada and GGI Solutions to Sun Chemical and marketed as Ionic Printed Solutions (IPS). SWCNT

soot (RN000 with the catalog number of RNL12-000-110) was manufactured by Raymor Inc. using a plasma torch technique.⁴⁷

SWCNT Enrichment by Polymer Extraction. A typical enrichment was conducted by dispersing 6.4 mg of raw SWCNT feed sample into 8 mL of solvent with 3.2 mg of polymer. The mixture was homogenized for 30 min at ~30 °C using horn sonication (Branson Sonifier 250, maximum power, 200 W) with a 3/16 in. mini-tip operated at a duty cycle of 60% and output of 30%. The dispersion was then centrifuged at a relative centrifuge force (RCF) of 18,700g (12500 rpm on an SS-34 rotor) for 30 min. In order to recover more SWCNT material and monitor the entire enrichment process, multiple extractions were employed by repeating the above process on the residual material from the previous centrifugation. sc-Purity is estimated using the ϕ ratio as defined previously,¹⁰ and yield (%) is calculated based on literature methods,^{12,24,30} which is the mass percentage of enriched sc-SWCNTs relative to the sc-SWCNT in feed raw, that is, $\text{mass}_{(\text{enriched})} / [\text{mass}_{(\text{feed raw})} \times 0.4 \times 0.67]$ (40% SWCNT content determined by TGA and 2:1 ratio of sc:m in plasma SWCNT raw soot).

Characterization. Absorption spectra were collected on a UV–vis–NIR spectrophotometer (Cary 5000, Agilent) over a wavelength range from 300 to 2100 nm with an optical path of 10 mm. A double beam mode was used with a pure solvent quartz cuvette placed in the reference channel. The yield of the enrichment and the purity of the SWCNT materials obtained were evaluated from the absorption spectra based on the method described previously.^{10,11}

Raman spectra were acquired with an InVia Raman microscope (Renishaw), using 514 nm (2.41 eV), 633 nm (1.96 eV), and 785 nm (1.58 eV) laser excitation sources and 50× magnification objective lens. Full spectra were recorded from 100–3200 cm^{-1} . RBM region was averaged from 10 scans, and G band was averaged from 3 scans with a resolution of 1 cm^{-1} . The extracted supernatants were filtered through a Teflon membrane with 0.2 μm pore size to collect the extracted SWCNTs. The collected SWCNTs were then rinsed thoroughly with THF to remove unbound polymer. The Raman samples used were films after removal of unbound polymer.

Photoluminescence excitation maps (PLE) were acquired using a custom-built system with a Ti:sapphire laser as the excitation source and InGaAs photodiode array for detection (extended sensitivity between 900 and 2100 nm). Spectra were obtained from solutions drawn into capillaries with a rectangular cross-section and 100 μm path lengths.

Viscosities of mixed solvents were measured using a parallel plate rheometer (Stresstech HR from ATS Rheosystems) with a 40 mm diameter plate and a gap of 0.25 mm. All measurements were done at 25 °C. After sample loading and temperature equilibrium, a preshear of 1 s^{-1} was applied for 30 s. A linear shear rate sweep was then applied from 1×10^{-2} to $1 \times 10^2 \text{ s}^{-1}$, with measurements taken every 2 s. This sweep repeated automatically three times, with no delay between sweeps. Samples displayed a Newtonian behavior. Average viscosity values were taken from measurements at shear rates above 70 s^{-1} .

Carbon nanotube random network transistors were fabricated on commercially available Fraunhofer chips (Gen 5:230 nm SiO₂ thickness, 2000 μm channel width, 2.5, 5, 10, and 20 μm channel lengths). Prior to carbon nanotube deposition, chips were bath sonicated for 5 min each in acetone and isopropanol followed by 30 min in UV-Ozone. We found that a simple soaking process did not provide sufficient carbon nanotube adhesion. Adhesion can however be significantly improved upon applying an electrostatic field during the soaking process. Specifically for data presented in Figure 1c, a 0.2 mg/L carbon nanotube solution with 7:1 polymer:tube ratio was used in a 10 min soaking process where a 75 V bias was applied between a top electrode and the substrate (1 mm gap, approximately). After soaking, chips were rinsed in 1,4-dioxane and isopropanol. Transfer curves were obtained in air ambient using a two channel source-measure instrument to control both source-drain and gate bias as well as monitor drain and gate leakage currents. Mobility was calculated using the plate capacitor model with several transistors yielding

mobility in the 6–10 cm²/(V s) range and current on/off ratio ~10⁴–10⁵.

The fully printed top-gate TFT was fabricated on Kapton substrate using a PixDro. The substrate was cleaned with acetone and isopropanol followed by 10 min in UV-Ozone. SX-3 print-head was used to print source, drain, and gate electrodes. KM-512 print-head was used to print the semiconducting layer, while the SE-3 print-head was used to print the dielectric layer having a thickness around 235 nm. Source/drain electrodes were printed with silver molecular ink²⁶ and then thermally sintered at 250 °C for 30 min (channel length/width: 50/1100 μm). The carbon nanotube ink (43 mg/L with 2.5:1 polymer/tube ratio, formulated in triethylene glycol monomethyl ether as the base solvent) was printed over the channel. The dielectric (xdi-dcs) was subsequently printed (thickness 235 nm; dielectric constant is 3.9 and C_i = 1.47 × 10⁻⁸ F/cm²). Lastly, the gate was printed with the molecular silver ink on the top of the channel and then thermal sintered at 140 °C for 30 min.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsnano.7b08818.

Supporting Figures S1–S5, Tables S1–S2, and Schemes S1–S2 as described in the text (PDF)

AUTHOR INFORMATION

Corresponding Authors

*E-mail: jianying.ouyang@nrc-cnrc.gc.ca.

*E-mail: patrick.malenfant@nrc-cnrc.gc.ca.

ORCID

Patrick R. L. Malenfant: 0000-0001-5391-2300

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

The authors would like to thank Dr. N. Graddage for viscosity measurements and analyses, Mr. Y. Cheng for TGA measurements, Ms. O. Mozenon for ink formulation, and Dr. P. Finnie for useful discussions regarding Raman data. We also thank Dr. C. Kingston for support and maintenance of the Renishaw instrument. This work was supported by the Printable Electronics (PE) flagship program in National Research Council Canada.

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