

H-Bonded Supramolecular Polymer for the Selective Dispersion and Subsequent Release of Large-Diameter Semiconducting Single-Walled Carbon Nanotubes

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S Supporting Information

ABSTRACT: Semiconducting, single-walled carbon nanotubes (SWNTs) are promising candidates for applications in thin-film transistors, solar cells, and biological imaging. To harness their full potential, however, it is necessary to separate the semiconducting from the metallic SWNTs present in the as-synthesized SWNT mixture. While various polymers are able to selectively disperse semiconducting SWNTs, the subsequent removal of the polymer is challenging. However, many applications require semiconducting SWNTs in their pure form. Toward this goal, we have designed a 2-ureido-6[1H]-pyrimidinone (UPy)-based H-bonded supramolecular polymer that can selectively disperse semiconducting SWNTs. The dispersion purity is inversely related to the dispersion yield. In contrast to conventional polymers, the polymer described herein was shown to disassemble into monomeric units upon addition of an H-bond-disrupting agent, enabling isolation of dispersant-free, semiconducting SWNTs.

Single-walled carbon nanotubes (SWNTs) have attracted significant interest due to their extraordinary mechanical, optical, thermal, and electronic properties.¹ As a result these properties are attractive for a wide range of emerging technologies.² However, obtaining pure semiconducting (sc) SWNTs via separation from their metallic (met) counterparts presents one of the biggest hurdles toward use of SWNTs in electronic and optoelectronic applications.³

Several methods exist for SWNT sorting according to electronic type, including DNA wrapping, density gradient ultracentrifugation, and gel chromatography.³ However, they either require special equipment or suffer from low throughput. A simpler approach involves the selective dispersion of sc-SWNTs using π -conjugated polymers.⁴ A drawback of this approach is that the polymers wrap tightly around the SWNTs and it becomes extremely difficult to remove them.⁵ However, various applications require polymer-free sc-SWNTs, which has spurred considerable effort toward the development of removable polymers.⁶ Two interesting strategies have emerged to disrupt polymer/SWNT interactions and cause SWNT release: (1) inducing a conformational change in the secondary structure of the polymer^{6b,f,g} or (2) degrading the polymer into

small units.^{6c,d} Systems under approach 1 have so far been unsuccessful in selectively dispersing sc-SWNTs, and approach 2 is destructive and precludes polymer recycling. A solution to the latter problem is to employ noncovalently linked supramolecular polymers.⁷ Indeed, the reversible dispersion of multiwalled carbon nanotubes (MWNTs)⁸ and small-diameter HiPco SWNTs⁹ was recently demonstrated with H-bonded supramolecular polymers and metal coordination-based polymers, respectively. A drawback of existing metal coordination-based polymers, however, is their low solubility in nonpolar solvents. The use of polar solvents, on the other hand, promotes poor sorting selectivity,¹⁰ requiring additional steps to remove the met-SWNTs.⁹ H-bonded supramolecular polymers that can directly disperse sc-SWNTs in nonpolar solvents therefore present a clear advantage.

Here, we present H-bonded supramolecular polymer **1** (Figure 1A), which can disperse large-diameter, arc-discharge (AD) SWNTs with very high selectivities for sc-SWNTs, and subsequently release them upon triggered polymer disassembly (Figure 1B). Compared to small-diameter SWNTs, the large-diameter SWNTs exhibit smaller Schottky barriers^{2k} in transistors and higher penetration depths in bioimaging applications.¹¹ The monomer unit **1** was designed with the following rationales: (1) Long $-C_{12}H_{25}$ side chains to enhance polymer solubility and SWNT dispersion yields;¹² (2) a fluorene moiety in the backbone to promote selectivity between sc- and met-SWNTs;^{12a,b,13} (3) terminal 2-ureido-6[1H]-pyrimidinone moieties (UPy)¹⁴ that can self-associate with very high dimerization constants (Figure 1C) to enable formation of high molecular-weight supramolecular polymers even at low monomer concentrations. This is important, as oligomers with above ca. 25 fluorene units were previously reported to be necessary to achieve stable SWNT dispersions.¹⁵ On the other hand, release of SWNTs necessitates polymer degradation into assemblies with less than 4 fluorene units,^{15a} which can be achieved in our case via addition of trifluoroacetic acid (TFA),¹⁶ an agent that is very effective in disrupting hydrogen bonds.

The synthesis of compound **1** was achieved via Heck coupling between vinyl-UPy **2** and diiodo-fluorene **3** in good yield on a 2 g scale (Figure 1A).¹⁷ Its ability to form a

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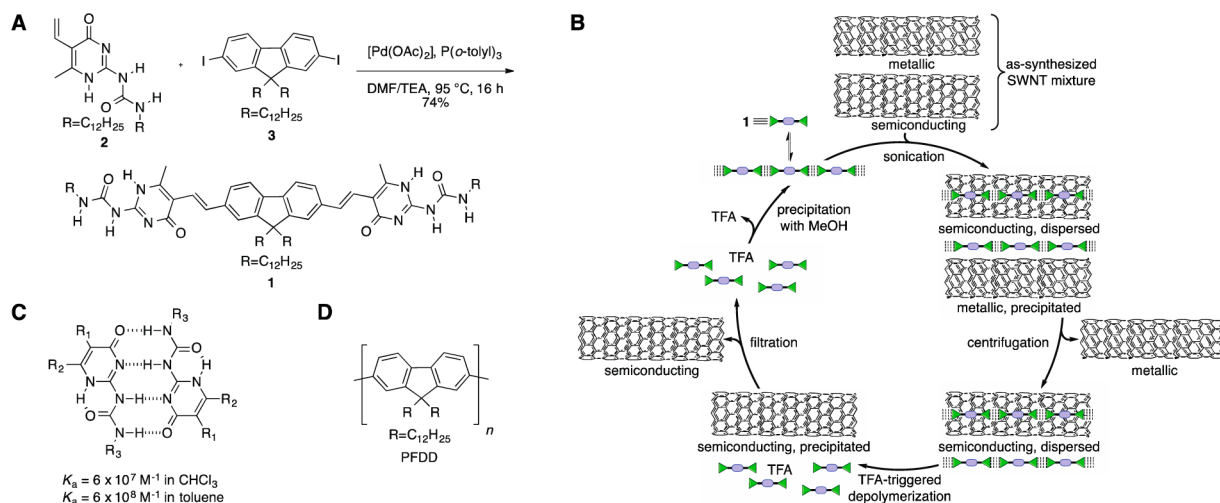


Figure 1. (A) Structure and synthesis of monomer unit **1**. (B) Envisioned sc-/met-SWNT separation cycle using supramolecular polymer **1**. (C) Self-association scheme of the 2-ureido-6[1H]-pyrimidinone moiety (UPy)¹⁴ that is employed as a terminal unit in monomer **1**. (D) Structure of poly(9,9-di-*n*-dodecylfluorene) (PFDD) used as a conventional fluorene-based reference polymer.

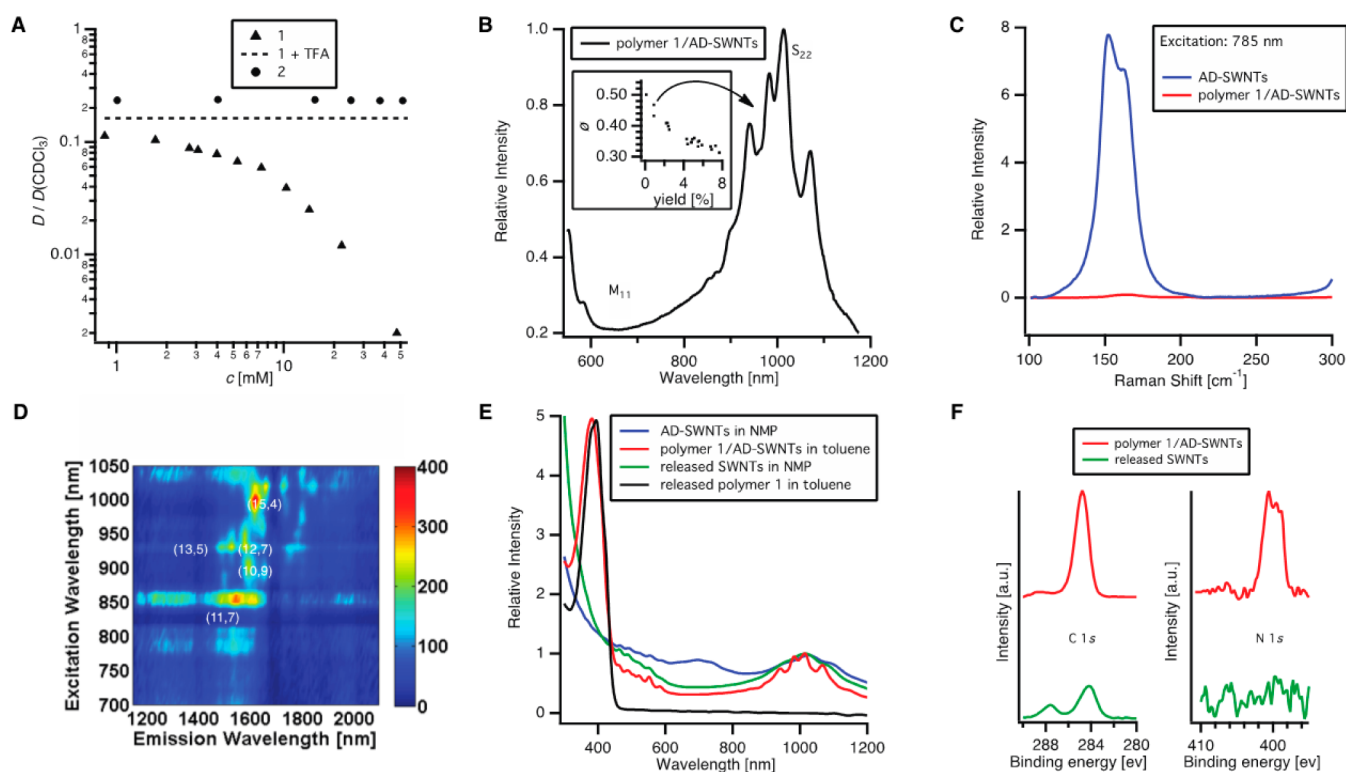


Figure 2. (A) Relative diffusion coefficients of compound **1** and monofunctional reference compound **2** in CDCl_3 as a function of their concentrations. (B) Absorption spectrum of a polymer **1**/arc-discharge (AD)-SWNT dispersion with $\phi = 0.47$ in toluene. Inset shows the plot of all ϕ /yield-pairs for polymer **1**/AD-SWNT dispersions obtained for various dispersion conditions. (C) Raman spectrum of the radial breathing mode (RBM) region of as-received and polymer **1**-dispersed AD-SWNTs (excitation wavelength: 785 nm). (D) Photoluminescence vs excitation (PLE) map of a polymer **1**/AD-SWNT dispersion in toluene. (E) Absorption spectra demonstrating sc-SWNT enrichment upon dispersion with polymer **1**, and quantitative separation of sc-enriched SWNTs after disassembly of polymer **1** with TFA. (F) X-ray photoelectron spectroscopy (XPS) on the polymer **1**-dispersed and released SWNT samples.

supramolecular polymer in solution was assessed by diffusion-ordered NMR spectroscopy (DOSY) in CDCl_3 . The DOSY technique enables determination of diffusion coefficients, which are inversely related to the molecular weights of the investigated entities.¹⁸ While the relative diffusion coefficient $D/D(\text{CDCl}_3)$ of reference compound **2**, which is present as a hydrogen-bonded dimer, is constant over the investigated

concentration range, the $D/D(\text{CDCl}_3)$ of bifunctional compound **1** significantly decreases with increasing concentration, indicating polymeric behavior (Figure 2A). A titration study of supramolecular polymer **1** with compound **2** as a monofunctional chain stopper allowed us to relate the $D/D(\text{CDCl}_3)$ of polymer **1** to its molar mass.¹⁹ Thus, at $c = 50$ mM, at which compound **1** produces a highly viscous solution, the molar mass

is $M = 2\,600\,000\text{ g mol}^{-1}$, which corresponds to an association of $N = 2200$ monomeric units. As the release of dispersed SWNTs from polymer **1** necessitates its disassembly into short oligomeric units,^{15a} we also tested whether addition of TFA would cause depolymerization of **1**. Indeed, addition of small quantities of TFA led to an increase of $D/D(\text{CDCl}_3)$ to a value corresponding to a molar mass of $M = 1308\text{ g mol}^{-1}$, which is in good agreement with the molar mass $M = 1224\text{ g mol}^{-1}$ of monomeric **1**.

Having prepared and characterized supramolecular polymer **1**, we tested its ability to disperse arc-discharge SWNTs (P2-SWNTs, purchased from Carbon Solutions, Inc.). The dispersion experiments were performed in toluene due to its low intrinsic ability to disperse SWNTs.^{10b} In a typical experiment, the polymer **1**/SWNT mixture was tip-sonicated for a given amount of time at a given sonication power and then centrifuged for 30 min at 17 000 rpm. The supernatant was removed and analyzed by absorption spectroscopy, which provided information about the yield and purity of the obtained SWNT dispersion. Because polymer **1** can be removed from the dispersed SWNTs (*vide infra*), we were able, for the first time, to directly quantify the SWNT dispersion yield by measuring the mass of released SWNTs without contamination from the polymer.²⁰ A precise determination of the sc-SWNT purity above 99% is not possible via absorption spectroscopy.^{2k} The ϕ value, which is defined as the ratio of peak/background area in the range containing S_{22} and M_{11} absorptions,^{12a} has recently been proposed as a relative measure of sc-SWNT purity. Higher ϕ values correlate with higher sc-SWNT purities, and ϕ values of 0.40 have been attributed to sc-SWNT purities of over 99%.^{12a}

Modification of dispersion parameters, including the polymer **1**/SWNT ratio, SWNT concentration, sonication power, and sonication time, strongly affects the yield and purity of the obtained SWNT dispersions.²¹ Notably, plotting ϕ vs yield shows an inverse relationship between those quantities (Figure 2B, inset). Figure 2B shows the absorption spectrum obtained with dispersion parameters optimized toward high purity (5 mg AD SWNTs, 5 mg polymer **1**, 20 min sonication at 30% power), with $\phi = 0.47$ and a 0.9% yield. The peaks in the range of 800–1200 nm correspond to the S_{22} transitions of sc-SWNTs. The absence of peaks in the range of 600–800 nm attributed to M_{11} transitions of metallic SWNTs reflects the high sc-SWNT purity of the sample. In fact, the ϕ value of 0.47 is significantly higher than that of commercially available 99.9% sc-SWNTs (Figure S14).^{12a,22} The high sc-SWNT enrichment for higher ϕ values was confirmed by Raman spectroscopy: the met-SWNTs radial breathing mode (RBM) peaks in the 100–200 cm^{-1} region of as-received AD-SWNTs probed with a 785 nm laser are barely detectable in the SWNT sample dispersed by polymer **1** (Figure 1C). A photoluminescence vs excitation (PLE) map was recorded in order to assign the individual chiral indices of the dispersed SWNTs (Figure 2D). At least 12 different chiralities contribute to the overall spectrum. The two strongest signals are tentatively assigned to the (15,4) and (11,7) SWNTs. The diameters of the 5 most abundant SWNTs are in the range of 1.28–1.39 nm, while the diameter range of all 12 identified SWNTs is 1.25–1.52 nm.

Monofunctional UPy compound **2** (Figure S13), similar to short, oligomeric fluorene derivatives,^{15a} is not able to disperse SWNTs. We therefore attribute the ability of compound **1** to disperse SWNTs to its supramolecular polymerization. Importantly, compared to the corresponding conventional

polymer, poly(9,9-di-*n*-dodecylfluorene) (PFDD, Figure 1D), polymer **1** achieves a nearly 7-fold higher SWNT dispersion yield and a higher sc-SWNT purity under identical dispersion conditions (5 mg SWNT, 5 mg polymer, sonication for 30 min at 70% power; for polymer **1**: $\phi = 0.31$, yield = 7.5%; for PFDD: $\phi = 0.27$, yield = 1.1%, Figure S13).

Release of the enriched sc-SWNTs was achieved via addition of 1% TFA to the polymer **1**/SWNT dispersion, resulting in SWNT precipitation. In contrast, SWNT precipitation from the PFDD/SWNT dispersion did not occur even upon addition of 3% TFA. Thus, we attribute the TFA-assisted SWNT release from polymer **1** to its disassembly into monomeric units. The precipitated SWNTs were filtered over a 0.2 μm PTFE membrane, washed with toluene, and dried in air. The absorption spectrum of the filtrate showed only signals attributed to compound **1** and no SWNT signals, indicating that SWNT release from polymer **1** is quantitative (Figure 2E). Compound **1** was reisolated by simple precipitation with MeOH, allowing its reuse in future SWNT dispersions. The filtered SWNTs were redispersed in NMP, a solvent that disperses SWNTs without surfactants.²³ Compared to the as-received AD-SWNT sample in NMP, the released SWNT sample shows no metallic SWNT absorptions in the 600–800 nm region (Figure 2E). Importantly, the spectrum of the released sample also exhibits no signals in the polymer **1** region at 320–450 nm, demonstrating that the polymer removal is quantitative. Quantitative removal of polymer **1** was also demonstrated by X-ray photoelectron spectroscopy (XPS): the N 1s peak attributed to the N atoms in compound **1** was not present in the released SWNT sample (Figure 2F).

In summary, we have developed H-bonded supramolecular polymer **1**, which can selectively disperse and then release sc-SWNTs, presenting significant advantages over covalent polymers. The ability to obtain polymer-free sc-SWNTs allows them to be redispersed in other solvents using other dispersing agents, which makes them more versatile. At the same time, we have developed a UPy precursor that can be conveniently attached to a halogenated π -conjugated system via cross-coupling chemistry. Thus, our approach can be extended to other π -conjugated systems typically employed in the framework of organic electronics.

■ ASSOCIATED CONTENT

📄 Supporting Information

Synthesis and characterization data, dispersion study data, details on DOSY, UV/vis, Raman, PLE, and XPS data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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