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Cite this: DOI: 10.1039/c0xx00000x

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COMMUNICATION

Dithiafulvenyl-grafted phenylene ethynylene polymers as selective and reversible dispersants for single-walled carbon nanotubes

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Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX

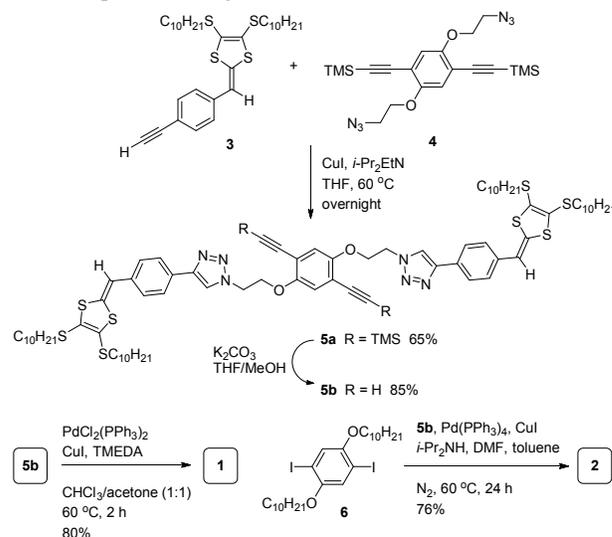
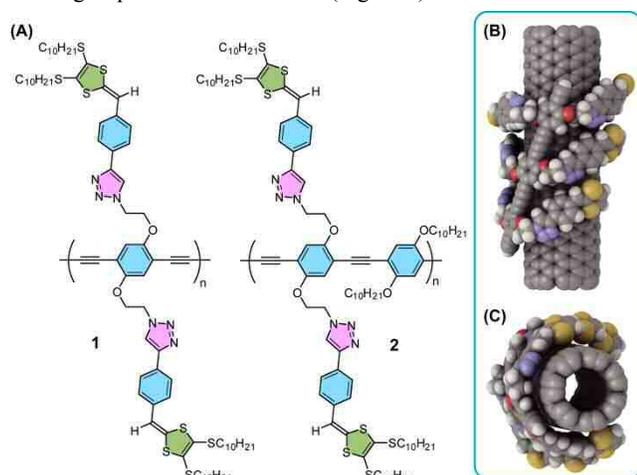
DOI: 10.1039/b000000x

Phenylene ethynylene-based π -conjugated polymers grafted with dithiafulvenyl groups on their side chains were found efficient in dispersing single-walled carbon nanotubes in a selective and controllable way.

The widespread application of single-walled carbon nanotubes (SWNTs) in materials science and biological technology^{1,2} has greatly promoted the research on new methods to produce structurally homogenous SWNTs.³ Noncovalent functionalization of SWNTs⁴ has been recognized as one of the most promising approaches, with the current state-of-the-art in the field allowing specific types of SWNTs to be sorted out of as-produced mixtures according to electronic nature,⁵ diameter,⁶ and chiral index.⁷ Generally speaking, to effectively disperse SWNTs in solvent, dispersing agents (dispersants) are required to have sufficient binding forces toward SWNTs so as to break apart their heavily entangled bundles. We recently discovered that relatively short phenylene ethynylene and phenylene vinylene oligomers when endcapped with dithiafulvenyl (DTF) groups exhibited strong supramolecular interactions with SWNTs.⁸ The performance of these relatively short DTF-functionalized oligomers in enhancing the binding strength toward SWNTs was remarkable, which in turn promoted us to conceive that polymer systems carrying DTF groups would serve as more effective SWNT dispersants. In this vein, we have subsequently investigated two phenylene ethynylene-based polymers **1** and **2** which are grafted with DTF endgroups in their side chains (Figure 1).

Fig. 1 (A) Structures of DTF-grafted phenylene ethynylene polymers **1** and **2**. (B) Front view, and (C) side view of the trimer of **1** wrapped around a (7,7) nanotube optimized by the *MMFF* force field. Note that the SC₁₀H₂₁ groups were replaced by hydrogen atoms to reduce computational cost.

The supramolecular interactions between the designed polymers and SWNTs were first surveyed by molecular modeling.⁹ Fig. 1B and C depict the minimum energy conformation of the trimer of **1** in interaction with a (7,7) SWNT, showing that the trimer adopts a folded conformation to tightly wrap itself around the nanotube sidewall. The phenylene ethynylene backbone of the trimer adheres to the SWNT at an angle of *ca.* 19° with respect to the longitudinal axis of the tube, while the DTF-appended side chains embrace the tube circumferentially at an angle of *ca.* 90°. A previous molecular dynamics (MD) study by Savens and co-workers has demonstrated that poly(phenylene ethynylene)s could adhere to the surface of SWNTs forming a robust helical superstructure.¹⁰ Polymers **1** and **2** were thus envisioned to take a unique “centipede-like” wrapping mode to result in highly efficient SWNT dispersion in organic solvents.



Scheme 1 Synthesis of DTF-grafted phenylene ethynylene polymers **1** and **2**.

The synthesis of polymers **1** and **2** was undertaken through a modular synthetic route^{11,12} as outlined in Scheme 1. Acetylenic

phenyl-DTF **3** was first reacted with diazido-phenylacetylene **4**¹² via the Cu-catalyzed alkyne-azide coupling (click reaction^{11c}) to afford precursor **5a**. Compound **5a** was then desilylated with K_2CO_3 to give free terminal dialkyne **5b**, which then underwent a Pd/Cu catalyzed homocoupling polymerization to afford polymer **1** in a good yield of 80%. Alternatively, precursor **5b** was subjected to a Sonogashira coupling polymerization with diiodoarene **6** in the presence of Pd/Cu catalyst and diisopropylamine as base to yield polymer **2** in 76% yield. The two polymers are brown coloured solids with good solubility in chlorinated and aromatic organic solvents, such as $CHCl_3$, CH_2Cl_2 , chlorobenzene, and toluene. In aliphatic hydrocarbon or polar organic solvents, however, their solubility diminished substantially. The molecular structures of **1** and **2** have been characterized by IR and NMR analysis (see the ESI). Gel permeation chromatographic (GPC) analysis shows that polymer **1** has a number-average molar mass (M_n) of 6223 g/mol relative to polystyrene standards and a polydispersity index (PDI) of 1.7, while for polymer **2** the M_n is measured to be 7275 g/mol with a PDI of 1.7.

Two types of commercially available SWNTs (HiPCO and CoMoCAT) were subjected to dispersion experiments in various organic solvents using polymers **1** and **2** as dispersants. Both polymers were found capable of effectively dispersing SWNTs in organic solvents, including $CHCl_3$, CH_2Cl_2 , chlorobenzene, toluene, and THF, wherein the polymers themselves also showed very good solubility. Fig. 2 illustrates the UV-Vis-NIR spectra of the SWNT-polymer suspensions in toluene. As a general trend, polymer **1** imparts a much better solubility to SWNTs than polymer **2**, as a result of the relatively more DTF-functionalities per repeat unit in **1**. The nanotubes dispersed by polymer **1** in solution are of much better quality than those dispersed by **2**, which is evidenced by the less significant amorphous carbon baseline in the Vis-NIR absorption spectrum. The well-resolved peaks in the Vis-NIR region are due to the inter-band electronic transitions between the van Hove singularities in the valence and conduction bands of SWNTs.^{1,13} Assignments of these peaks to specific chiral indices are made according to literature data^{1,14,15} and photoluminescence-excitation (PLE) mapping results.

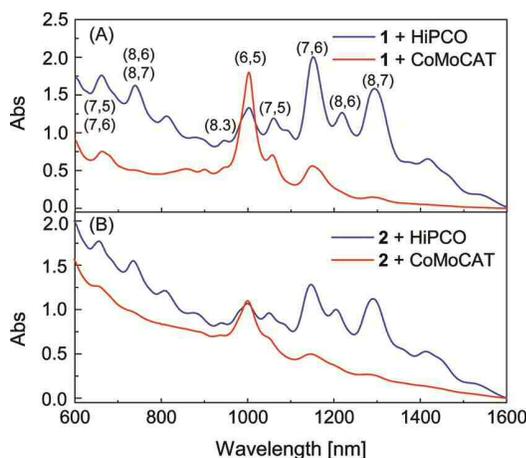


Fig. 2 Vis-NIR absorption spectra of CoMoCAT and HiPCO nanotubes dispersed in toluene with (A) polymer **1** and (B) polymer **2**.

The selectivity of polymer **1** toward SWNT dispersion was

manifested by the PLE maps shown in Fig. 3. For the dispersion of the CoMoCAT sample, (6,5) and (7,5) tubes are favoured with a small amount of (8,3) tubes co-existing in the suspension. For HiPCO nanotubes, the dispersion selectivity mainly goes to (6,5), (7,5), and (7,6) chiral indices, while some nanotubes with other chirality are also present in the suspension, including (8,3), (8,4), (8,6), (8,7), (9,4), (9,5), (10,2) and (10,3). In comparison with the types of SWNTs dispersed by a typical surfactant, sodium dodecylbenzenesulfonate (SDBS), in water (see Fig. S-21 in the ESI), polymer **1** affords a very high selectivity for (6,5), (7,5) and (7,6) tubes which are of relatively small diameter (*ca.* 0.75-0.90 nm). Such selectivity likely arises from the theoretically predicted “centipede like” binding mode, wherein the electron-rich DTF endgroups act as a major driving force for effective SWNT binding. PLE mapping studies of the suspensions of SWNTs and polymer **2**, however, did not yield meaningful results due to their poor fluorescence intensity.

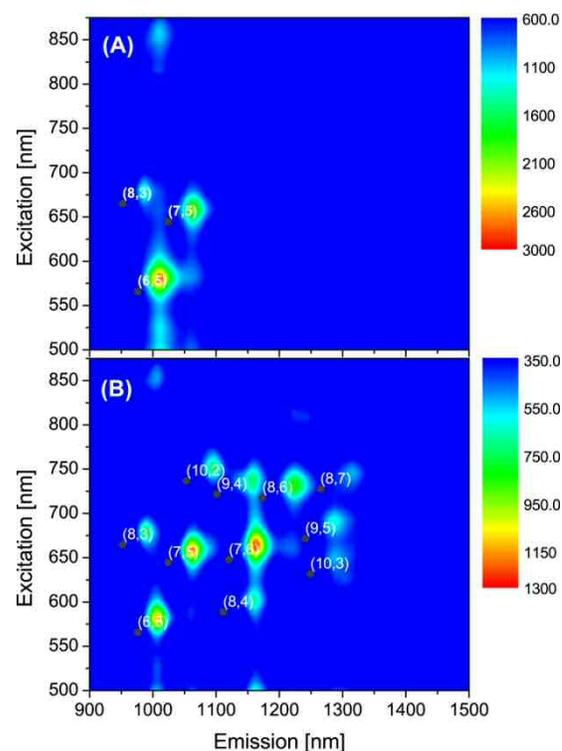


Fig. 3 PLE maps of (A) CoMoCAT and (B) HiPCO nanotubes dispersed in toluene with polymer **1**.

SWNTs dispersed with polymer **1** and **2** in chlorinated or aromatic organic solvents formed stable homogenous suspensions. There was no precipitation of SWNTs observable even after long-term (several months) storage. Addition of aliphatic hydrocarbon solvents to these suspensions, however, was found to quickly induce precipitation of SWNTs out of the polymer solution. This observation is consistent with the results of DTF-encapped π -oligomers in our previous study,⁸ offering a facile means to release pristine SWNTs from their polymer suspensions using solvent control. Controllable release of SWNTs from rationally designed supramolecular hosts has become a topic of growing interest over the past few years,^{15,16} driven by the critical demand for “additive-free” SWNTs in the fabrication of advanced

electronic and optoelectronic devices. To further explore this solvent-controlled behaviour, experiments on hexanes-induced release of SWNTs were undertaken. Fig. 4 demonstrates a reversible process of dispersing and releasing HiPCO SWNTs in different solvent systems, which could be potentially developed into a useful technique for applications where “dispersant-free” SWNTs¹⁷ are desired after solution-phase processing in order to maximize electronic and/or optoelectronic performance.

To further evaluate the efficiency of the solvent-controlled release of SWNTs, comparative Raman spectroscopic analyses were performed. As shown in Fig. 4C, the Raman spectrum of HiPCO SWNTs complexed with polymer **1** exhibits the characteristic G^+/G^- and D bands of SWNTs in the region of ca. 1200 to 2000 cm^{-1} , which are convoluted with some broad Raman peaks attributable to polymer **1**. The G^- band typical of pristine SWNTs, however, disappears in the spectrum of HiPCO/polymer **1**, which is indicative of strong electronic interactions¹⁸ between polymer **1** and SWNTs. The Raman spectrum of HiPCO SWNTs released from the polymer solution after addition of hexanes does not show any broad Raman bands due to the polymer. Instead, it shows a spectral pattern that closely resembles that of the raw pristine HiPCO sample. The comparative Raman study confirms that the DTF-grafted polymers are able to effectively release SWNTs out of the polymer dispersant, which in turn presents a significant advantage over other ways of releasing SWNTs (e.g., redox, pH, light)^{15,16} in terms of efficiency, ease of operation, and cost-effectiveness. Thermogravimetric analysis (TGA) shows that only a small amount of polymer dispersant (ca. 7.7 wt%) remains within the released SWNTs (see Fig. S-16 in the ESI for details). Nevertheless, with the redox activity of the DTF groups in the polymer side chains, it is possible that the trace amount of polymer dispersants can be further removed by using the redox or acidity-controlled methods similar to what we devised in our recent papers on a class of tetrathiafulvalene-based polymers.¹⁵

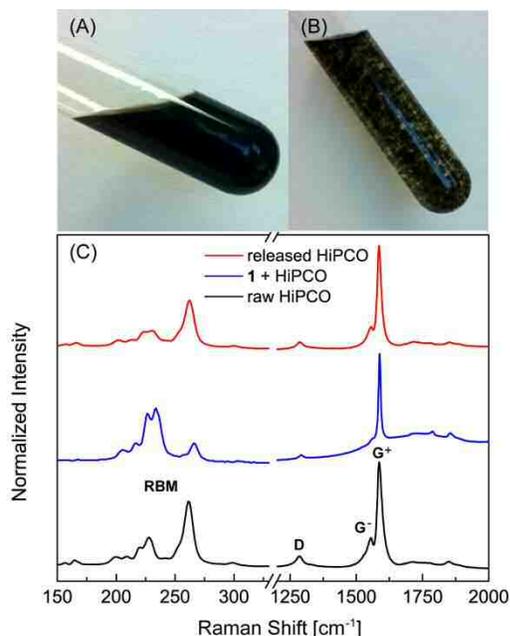


Fig. 4 (A) Photographic image of HiPCO SWNTs dispersed in a CHCl_3 solution of polymer **1** (1.5 mg/mL). (B) Photographic image showing HiPCO SWNTs precipitate out of the solution of **1** after addition of an

equal volume of hexanes. (C) Raman spectra ($\lambda_{\text{exc}} = 785 \text{ nm}$) of raw HiPCO SWNTs, HiPCO SWNTs dispersed with polymer **1**, and HiPCO SWNTs released from polymer **1** after addition of hexanes to the solution.

Preliminary investigations of electrochemically controlled SWNT release were conducted on the complexes of HiPCO SWNTs and polymer **2** dispersed in CHCl_3 (Bu_4NBF_4 was present as electrolyte). It was found that at a certain applied voltage, usually greater than +0.8 V (vs Ag/AgCl), pristine SWNTs began to precipitate out of the suspension. The remaining SWNT-polymer suspension was monitored by UV-Vis-NIR absorption analysis, and the results clearly indicate a depletion of the SWNT absorption bands in the NIR region (see Fig. S-23 in the ESI), attesting to the feasibility of separating SWNTs from the polymers by electrolysis.

The exact mechanisms for the interactions of SWNTs with DTF-grafted conjugated polymers as well as the physical origin for solvent-controlled releasing behaviour, at this juncture, have not yet been fully unravelled. However, the presence of DTF endgroups is known to be a key factor accounting for effective SWNT dispersion. Evidence for this point comes from a comparative study where a “click-generated” phenylene ethynylene polymer,¹⁹ analogous to polymer **2** but carrying *N,N*-dimethylaniline instead of phenyl-DTF endgroups in the side chains, was observed to be completely ineffective at dispersing SWNTs in common organic solvents. Given the rich π -electron properties of DTF, it is proposed that two noncovalent forces, π -stacking and charge-transfer (CT) interaction, drive the polymers to wrap SWNTs.²⁰ Our cyclic voltammetric studies show that the oxidation potential of the DTF unit in polymer **1** is shifted from +0.86 V to +1.04 V upon complexation with HiPCO SWNTs (see Fig. S-10 in the ESI), confirming the occurrence of significant CT interactions. Compared with nonpolar aliphatic hydrocarbon solvents, chlorinated solvents and aromatic solvents in theory should engender much better solvation effects on SWNT/polymer complexes assembled via π -stacking and CT interaction. To test this hypothesis, a mixed-solvent experiment was next conducted as follows. To a suspension of HiPCO SWNTs dispersed with polymer **1** in toluene were gradually added hexanes to induce partial precipitation of SWNTs. The mixtures were subjected to filtration, and the filtrate was then examined by Vis-NIR absorption analysis to monitor the compositional changes of SWNTs remaining in the solution.

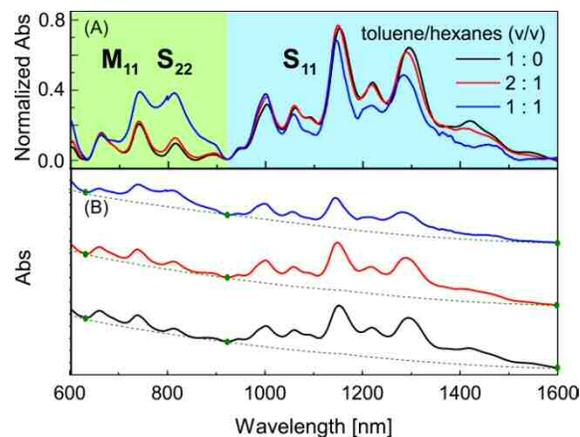


Fig. 5 (A) Vis-NIR spectra (with baseline correction) of HiPCO SWNTs dispersed with polymer **1** in toluene and hexanes mixed at various ratios

(spectra were normalized by the area underneath the peaks from 600 to 1600 nm). (B) Experimentally determined Vis-NIR spectra with baselines (dashed curves) indicated.

Fig. 5 compares the normalized absorption spectra of HiPCO SWNTs suspended in toluene and/or hexanes at various ratios. The results show that more metallic tubes remained in the solution phase than semiconducting tubes with increasing addition of hexanes. It has been known that semiconducting tubes favour to interact with electron-donating molecules via CT interaction.¹⁸ In principle, CT interaction is more sensitive to solvent effects than other noncovalent forces (e.g., van der Waals, π -stacking, and dipole-dipole interaction).²¹ Therefore, the observation that semiconducting tubes are more readily released than metallic tubes upon addition of hexanes corroborates that CT interaction plays an important role in the solvent-controlled dispersion/release behaviour.

In conclusion, we have demonstrated a “centipede wrapping” strategy for effective dispersion of SWNTs in various organic solvents using DTF-grafted π -conjugated polymers as dispersants. The dispersion appeared to be selective for small-diameter semiconducting (6,5), (5,6), and (7,6) tubes, and almost dispersant-free SWNTs could be readily released from the SWNT/polymer suspensions under easy solvent control. Moreover, the redox activity of DTF allows the polymers to be detached from SWNTs by electrolysis. Since both the solvent mixing and electrolysis methods are simple and easy to scale up in practice, it is envisaged that our DTF-grafted polymers may find potential use in developing cost-effective and large-scale methods for preparation of high-quality SWNTs.

Notes and references

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† Electronic Supplementary Information (ESI) available: The full synthetic procedures of polymer **1** and **2** as well as relevant precursors, along with their detailed spectroscopic characterization data. See DOI: 10.1039/b000000x/

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