Assembling p-type molecules on single wall carbon nanotubes for photovoltaic devices[†][‡]

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We report the design and synthesis of an oligothiophene molecule that noncovalently functionalizes carbon nanotubes to create a hybrid material for photovoltaic devices.

The design of hybrid materials for electronic properties offers many opportunities for the integration of functions.^{1–3} In this context, the incorporation of single wall carbon nanotubes (SWNTs) into polymeric solar cells is appealing because of their excellent electron transfer abilities,⁴ and because they are flexible and optically transparent.⁵ They may therefore play a key role in creating flexible organic solar cells. Current bulk heterojunction solar cells composed of poly-3-hexylthiophene (P3HT) and [6,6]-Phenyl C61 butyric acid methyl ester (PCBM) have been successful in achieving efficiencies of 5%.⁶ SWNTs have been introduced into solar cells as both a flexible replacement for ITO^{7,8} and for photoinduced charge transfer and collection from the polythiophene layer.⁹⁻¹¹ Specifically for P3HT/fullerene hybrid devices, it has been shown that integrated SWNTs in the active layers improve performance by increasing charge collection and fill factors, resulting in a significant increase in efficiencies.^{11,12} Hybrid SWNT-thiophene materials are generally made by either physical methods such as milling¹³ or sonication,^{11,14} layerby-layer techniques with charged polymers,¹⁵ or by covalent functionalization¹⁶ which degrades the electronic properties of the nanotubes. A preferable method is to promote self-assembly of a p-type molecular coating around the nanotube¹⁷ in a manner that preserves the electronic properties of the tubes without adding charges that might complicate its use as a photovoltaic material. Self-assembly of designed conjugated molecules to enhance conductivity has been previously studied by us and others.^{18,19} The self-assembly approach would provide a pathway for efficient charge transport within the p-type semiconducting regions and also ensure excellent charge collection by the nanotube.

In this work, rational molecular design was used to construct a molecule that assembles on carbon nanotubes, **5TPY**, and we report the synthesis and characterization of the oligothiophene-coated SWNTs and the measurement of films of the hybrid material in photovoltaic devices. In order to promote assembly, the molecular design consists of three segments (Fig. 1a): a binding group, a flexible alkyl linker, and an electronically active molecular segment. To ensure strong noncovalent nanotube binding of the molecule to the nanotube sidewall, pyrene is used as the CNT-binding group. Pyrene is known to adsorb to carbon nanotubes through π - π stacking interactions.^{20,21} A short flexible linker between the pyrene and the rigid oligothiophene allows for some conformational freedom and also aids in solubility. The additional conformational freedom may enable ordering of the electronically active segment. A quinquethiophene segment serves as the electronically active segment and is terminated with a short, branched alkyl group which provides additional solubility.

We synthesized **5TPY** as detailed in Scheme 1 in a convergent fashion, building outward from the thiophene core. Commercially available 2-thiophenecarbonitrile was reduced and immediately protected in a single step. Selective bromination at the 2-position with NBS could then be accomplished on 1. Deprotection of 1 with TFA and DCM enabled amidation with 1-pyrenebutyric acid using DPTS²² and EDCI. A Stille coupling with 5-(tributyltin)-2,2'-bithiophene resulted in terthiophene intermediate **5**. Monobromination of **5** was achieved with NBS to enable the final Stille coupling with **7**. Compound **7** was made by the etherification of



Fig. 1 (a) Structure of **5TPY**. (b) Illustration of a molecule designed to noncovalently functionalize carbon nanotubes by assembling around the nanotube (c).

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Scheme 1 Reagents and conditions: (i) LiAlH₄, Et₂O, 0 °C, 1 h, then Boc₂O, rt, 1 h; (ii) NBS, DMF, 0 °C, 4 h; (iii) TFA, CH₂Cl₂, rt, 1 h; (iv) 1-pyrenebutyric acid, EDCI, DPTS, CH₂Cl₂, rt, 1 h; (v) 5-(tributyltin)-2,2'-bithiophene, Pd(PPh₃)₄, DMF, 80 °C, 18 h; (vi) Pd(PPh₃)₄, DMF, toluene, 80 °C, 18 h; (vii) NaH, DMF, 2-ethylhexyl bromide; (viii) THF, *n*BuLi, -78 °C, 2 h, Bu₃SnCl.

5-hydroxymethyl-2,2'-bithiophene with 2-ethylhexyl bromide followed by selective deprotonation and quenching with tributyltin chloride.

Purified HiPCO SWNTs were noncovalently functionalized by ultrasonicating in a 0.15 mM solution of **5TPY** in chlorobenzene at 0 °C for one hour. A film of **5TPY–SWNT** hybrid material was prepared by collecting the functionalized nanotubes by vacuum filtration onto a cellulose ester filter. The film was used directly for optical spectroscopic analysis or it was transferred to other substrates by dissolving the filter with acetone.

The absorption and emission spectra of 5TPY in dichloromethane and in films with and without SWNTs are shown in Fig. 2. In solution, the characteristic pyrene absorbance is observed at 343 nm with a large absorbance peak from the quinquethiophene appearing at 422 nm. The emission spectrum of **5TPY** shows the vibrational structure²³ of the oligothiophene segment with peaks at 490 nm and 522 nm. The 5TPY solid-state spectra show broadening in both the absorption and the emission spectra and the loss of the vibrational fine structure in the emission. The 5TPY-CNT hybrid film shows absorption due to the SWNTs with some additional features from the 5TPY visible, but with significant broadening. Upon assembly on the SWNTs, the emission of the 5TPY film is significantly quenched. While some loss of **5TPY** emission signal could be due to absorption (40%) by the SWNTs, light filtering cannot fully account for the 90% loss of



Fig. 2 Top: Absorption (left) and emission (right) of $1.5 \,\mu$ M 5TPY in DCM. Bottom: Absorption (left) and emission (right) of films of 5TPY without (blue) and with (black) SWNTs.

signal at the emission peak at 523 nm. The significant loss of signal is attributed to fluorescence quenching by either energy^{24,25} or charge²⁶ transfer from the chromophore to the carbon nanotube.

Evidence of the assembly of **5TPY** on SWNTs is observed in TEM images of nanotubes collected on a carbon grid. Both single tubes (Fig. 3a) and bundles of tubes (Fig. 3b) appear



Fig. 3 TEM images of (a) single tubes and (b) bundles of tubes functionalized with **5TPY**. (c) SEM cross-sectional image of a device and (d) plot of the measured IV.

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to be coated with **5TPY**. The organic layer is approximately 1–2 nm thick, suggesting monolayer or near-monolayer coverage. The theoretical molecular length calculated using a MM2 force field (HyperChem) is 2.3 nm. It is possible that the angle of the molecular backbone is tilted towards the tube, nearly prone to the surface of the tube.

Photovoltaic devices were fabricated by depositing a thin (25-50 nm) 5TPY-CNT film onto an ITO coated glass substrate via the filter dissolution process described above. This film was then covered with 150-200 nm of an n-type acceptor layer of PCBM that was spin cast at 1000 rpm from a 25 mg mL⁻¹ solution in an equal mixture of chloroform and chlorobenzene. The top contacts were formed by thermal evaporation of 250 nm of aluminium using a shadow mask and the devices (4 mm²) were tested in air immediately after fabrication under standard AM1.5 illumination. Fig. 3d shows a representative I-V curve of a device with a power conversion efficiency of 0.02%. Six devices were fabricated with shortcircuit currents varying from -3.1 to -2.3 mA cm⁻² and open circuit voltages from 12.5 to 27.5 mV. Dark curves for these devices all pass through zero and controls without 5TPY showed no photovoltaic effect. The very low open circuit voltages and linear I-V characteristics of these devices are likely the result of significant shorting between the CNTs and the Al top contact. This shorting is difficult to entirely eliminate when using a solution processed acceptor layer. To avoid shorting it is also helpful to use very thin 5TPY-CNT films, but this results in limited light absorption and subsequent low short circuit currents. Future device optimization may avoid this problem by either using only semiconducting nanotubes²⁷ or converting the mixture *via* chemical methods.²⁸

In conclusion, we have developed a strategy to assemble electronically active coatings on carbon nanotubes that creates a hybrid material for photovoltaic devices. This method uses rational molecular design to assemble quinquethiophene segments around the nanotube without changing the covalent structure of CNTs. Molecular design for self-assembly of p-type overcoats on carbon nanotubes may be a useful chemistry to create flexible organic solar cells.

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