

Polyfluorenes for Selective Wrapping of Single-Walled Carbon Nanotubes



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Abstract

Single-walled carbon nanotubes (SWCNTs) are one of the most promising components of the large family of carbon materials. SWCNTs are synthesized in metal-catalyzed, solidstate template processes as a mixture of metallic and semiconducting (sc.) tubes. The large-scale separation of these two tube types is one of the biggest challenge for their commercialization and application in electronics.^[1] So far, the separation can be achieved by different methods, including strategies from biochemistry (i.e. encapsulation with DNA) or by spontaneous wrapping of conjugated polymers around SWCNTs with diameters about 1 nm.^[2] Many different polymer structures have been tested with the ability to discriminate SWCNTs of different diameter and helicity on demand. PFO (poly(9,9-dioctylfluorene-2,7-diyl)) has been demonstrated to be a very efficient polymer for separation of SWCNTs with small diameters (0.8–1.2 nm). Earlier studies ascribed the discrimination mechanism to the nature of the polymer backbone. Yet recent research showed indications, that the side chain of the polymers also plays an important role in wrapping and selection mechanism.^[3]

Here we demonstrate the selection of sc. SWCNTs in a wider diameter range (0.8–1.6 nm) by using polyfluorene derivates with alkyl chains of increasing length. SWCNTs of different diameter could be selected by tuning the length of the alkyl side chains. The high amount of sc. SWCNTs in the prepared dispersions is demonstrated by optical spectroscopy and by fabrication of high performance field-effect transistors. The role of the alkyl chain length in the sorting of sc. SWCNTs is rationalized by means of molecular dynamics (MD) simulations.^[2]

Synthesis			Polymer M _n (g/mol) M _w (g/mol) PD			PD	Chirality Map of SWCNTs		
	Br Br		PF6	320 000	850 000 2.60	0,75 nm 1,51 nm			
	a)		PF8*	-	58 000	-			
H ₁₃ C ₆ C ₆ H ₁₃	¥ R, R	H ₃₇ C ₁₈ C ₁₈ H ₃₇	PF12	34 200	67 300	1.97			



Figure 1: General synthesis route for homopolymers poly(9,9-dialkylfluorene-2,7-diyl)s; **a)** NaOH 50 wt%, RBr, TBAB, DMSO, 3 h, 80 °C; **b**) Ni(COD)₂, 2,2'-bipyridine, COD, THF, 120 °C, 15 min microwave. **PF6** R = C₆H₁₃, **PF8** R = C₈H₁₇, **PF12** R = C₁₂H₂₅, **PF15** R = C₁₅H₃₁, **PF18** R = C₁₈H₃₇.



Figure 3: Absorption spectra of dispersed SWCNTs.

a) Absorption spectra of HiPco SWCNTs (average diameter 1 nm) dispersed with different derivatives of polyfluorene in toluene (continuous lines) (the color code for the different polymers is given in the panel b) and dispersed with SDBS in water (dashed line).

b) Absorption spectra of SO SWCNTs (average diameter 1.4 nm) dispersed with different polyfluorene derivatives in toluene (continuous lines, with color codes indicated in the inset) and dispersed with SDBS in water (dashed line).

(14,7) and (12,10) SWCNT species got the highest absorption in b).

FET properties



Figure 2: (a) Chirality map of SWCNTs selected by polymer wrapping. The color of the dots inside the hexagons indicates which of the polyfluorene derivatives (color code used for the chemical structures) is able to select the nanotubes. (b) Chemical structure of the polyfluorene derivatives used: PF6, PF8, PF12, PF15, and PF18. (c) Structure as obtained by molecular dynamics simulations of three PF12 chains wrapped around a (12,10) nanotube after 10 ns at constant-pressure in toluene solution.

Photoluminescence spectra of HiPco SWCNTs





Absorption spectra of dispersed SWCNTs

Molecular models of (14,7) SO SWCNT



	PF12-HiPco	PF12-SO
Hole mobility (cm²/Vs)	5.7	14.3
Electron mobility (cm²/Vs)	3.6	16.4
On/off ratio	> 10 ⁵	> 10 ⁴

Table 2: Field-effect transistors properties madefrom PF12-HiPco and PF12-SO SWCNTs hybrids. SiO_2 as dielectric, ionic gel = [EMIM][TFSI] forcreating a EDL gated FET. Drain voltage for on/offratio measurement $V_D = 0.2$ V.

Figure 5: a) Molecular models of the optimized structures of (14,7) nanotube covered by three polymer chains in the T (left) and P (right) configurations. From top to bottom: **PF12**, **PF15**, and **PF18**. The red circles indicate: (1) uncovered nanotube surface; (2) alkyl tails oriented outward the nanotube surface; (3) detaching of polymer backbone from nanotube wall.

(b) Binding energy divided by the length of the nanotube covered by the polymers. On the right side of the figure are shown the configurations with the polymer backbone perpendicular (T) and parallel (P) to the tube surface.



Figure 6: (a) AFM images of a randomly distributed SO SWCNT network on a mica substrate. (b) Height profile of three different SWCNTs from the AFM image showing an average diameter of about 3 nm.



Figure 4: Photoluminescence of HiPco SWCNTs. **(a)** Photoluminescence intensity of HiPco SWCNTs wrapped with different polyfluorene derivatives. **(b)** Photoluminescence yield of different SWCNTs wrapped by polyfluorene derivatives. **(c)** Decay of the photoluminescence of (7,5) tubes wrapped by different polyfluorene derivatives. **(d)** Decay of the photoluminescence of (7,6) tubes wrapped by different polyfluorene derivatives.

Conclusion

- Sc. SWCNTs could be efficiently separated and individualized using long alkyl chain polyfluorene derivatives.
- Our polyfluorenes exhibit affinity for a number of sc. SWCNT chiralities containing small diameter nanotubes (Ø = 0.8–1.2 nm) as well as in large diameter tubes (Ø ≈ 1.4 nm) (Fig. 2 and 3).
- Long photoluminescence lifetimes and the elevated photoluminescence yield (Fig. 4) measured especially for PF12-wrapped SWCNTs verify high sample qualities.
- Dispersions containing SWCNT species (ø > 1.2 nm) that could not be selected previously.
- Polyfluorenes with long side chains yield dispersions of highly individualized sc. SWCNTs with very high concentrations (Fig. 6).
- The understanding of the wrapping process is provided by molecular dynamics simulations (long alkyl tails on polyfluorenes provide stronger binding to the nanotube wall) → variety of wrapping geometries allow more nanotube species to be suspended. (Fig. 5).
- MD-simulations (Fig. 5) show average diameter around 2.8 nm for tubes (12,10) with a single polymer layer of PF12 chains in the T-configuration (Fig. 6, AFM height profile is 3 nm).
- Exceptional quality of the samples demonstrated by high mobility and on/off ratio of network FETs fabricated with the PF12-wrapped SWCNTs hybrids.
- On/off ratio of 10⁵ and mobilities μ > 14 cm²V⁻¹s⁻¹ for holes μ > 16 cm²V⁻¹s⁻¹ for electrons (Tab. 2, SO SWCNTs network FETs with ion-gel gating).

Atomic force microscopy (AFM) images of SO SWCNTs

[3] J. Gao, M. A. Loi, E. J. F. de Carvalho, M. C. dos Santos, ACS Nano 2011, 5, 3993.

P. Gordiichuk, A. Herrmann, S. J. Marrink, M. C. dos Santos, U. Scherf, M. A. Loi, Adv. Mat. 2013, 25, 2948.

[2] W. Gomulya, G. D. Constanzo, E. J. Figueiredo de Carvalho, S. Z. Bisri, V. Derenskyi, M. Fritsch, N. Fröhlich, S. Allard,

[1] M. C. Herasm, *Nat. Nanotech.* **2008**, 3, 387.

References: