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On-Chip Chemical Self-Assembly of Semiconducting Single-Walled Carbon Nanotubes (SWNTs): Toward Robust and Scale Invariant SWNTs Transistors

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In this paper, the fabrication of carbon nanotubes field effect transistors by chemical self-assembly of semiconducting single walled carbon nanotubes (s-SWNTs) on prepatterned substrates is demonstrated. Polyfluorenes derivatives have been demonstrated to be effective in selecting s-SWNTs from raw mixtures. In this work the authors functionalized the polymer with side chains containing thiols, to obtain chemical self-assembly of the selected s-SWNTs on substrates with prepatterned gold electrodes. The authors show that the full side functionalization of the conjugated polymer with thiol groups partially disrupts the s-SWNTs selection, with the presence of metallic tubes in the dispersion. However, the authors determine that the selectivity can be recovered either by tuning the number of thiol groups in the polymer, or by modulating the polymer/SWNTs proportions. As demonstrated by optical and electrical measurements, the polymer containing 2.5% of thiol groups gives the best s-SWNT purity. Field-effect transistors with various channel lengths, using networks of SWNTs and individual tubes, are fabricated by direct chemical self-assembly of the SWNTs/thiolated-polyfluorenes on substrates with lithographically defined electrodes. The network devices show superior performance (mobility up to $24 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$), while SWNTs devices based on individual tubes show an unprecedented (100%) yield for working devices. Importantly, the SWNTs assembled by mean of the thiol groups are stably anchored to the substrate and are resistant to external perturbation as sonication in organic solvents.

toward the application of nanotubes as active material for electronic devices started in the early 2000s, but the interest in them initially declined due to practical challenges in the separation of the semiconducting species from the metallic ones.

Recently, the selection of semiconducting SWNTs (s-SWNTs) has shown very remarkable progress with the development of several methods, which results in s-SWNT inks of high purity.^[1–3] Among these methods, especially the polymer wrapping technique, has shown great potential owing to the ability to achieve purity above 99.9% without damaging the SWNT walls.^[4,5] Polyfluorene derivatives have been the first class of conjugated polymers which have been demonstrated to select semiconducting SWNTs due to their capacity to interact preferentially with nearly armchair carbon nanotubes.^[6] Following this discovery, several approaches, such as the modification of alkyl side chains^[7] or the polymer backbones,^[8] have been used to obtain higher or better s-SWNTs selection. Nowadays, a number of different conjugated polymers are effectively used to select semiconducting SWNTs of different diameter and chiralities.^[9]

The availability of pure and concentrated solutions of s-SWNT allowed more recently the fabrication of highly performing field-effect transistors (FETs),^[10,11] light-emitting devices,^[12,13] logic gates,^[14] sensors,^[15] and photovoltaics devices.^[16,17]

The last major challenge to overcome before technological applications of s-SWNTs in electronics can be truly realized is the placement of billions of single nanotubes (with target $125 \text{ SWNT } \mu\text{m}^{-1}$) in predetermined positions on a surface with industrial precision and reproducibility.^[18,19] The simple alignment of the SWNTs has been one of the first approaches proposed toward the solution of this challenge. Aligned nanotube networks perpendicular to the source–drain electrodes in SWNT-FETs have shown superior performance compared to random networks.^[10,20–23] Several techniques such as blade coating^[10] and Langmuir–Blodgett^[20,24] have been reported

Single-walled carbon nanotubes (SWNTs) integrated in electronic devices have the potential to overcome the lithographic and economic limits of silicon based electronics. Research

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to achieve partially aligned SWNT networks. However, the precise placement of carbon nanotubes on a substrate has obtained till now little attention. Two techniques are mostly reported: the direct growth of nanotubes on a substrate,^[25] or their self-assembly from solution onto a device structure. The direct growth is obtained by chemical vapor deposition (CVD), which gives rise to a mixture of metallic and semiconducting tubes. Therefore, metallic nanotubes should be removed after deposition.^[25]

Solvent evaporation-assisted self-assembly,^[21] solution shearing,^[22] and hydrophilic/hydrophobic self-assembly^[26] have allowed to obtain dense and aligned carbon nanotube networks. However, serious challenges such as the necessity of complex pre patterning of the substrate with chemical species to attract or repel SWNTs are present.^[22,26]

An alternative strategy for obtaining a controllable deposition of SWNTs is through chemical self-assembly.^[27,28] The chemical self-assembly has the advantages of being a less stringent process and the attachment to the substrate/electrode is by covalent bonding, which is therefore highly robust, thermally stable, and can be chemically resistant to a variety of reagents. However, some of the examples reported in literature use chemical functionalization of the SWNTs walls,^[29] which is well known to be detrimental toward charge transport.^[30,31]

In this work we report the chemical modification of side chains of polyfluorenes with thiol groups with the aim of obtaining chemical self-assembly of semiconducting carbon nanotubes onto lithographically defined gold electrodes. We found that the insertion of thiol groups in the polymer structure somewhat decreases the selectivity of the conjugated polymer toward s-SWNT. Polyfluorene derivatives decorated with 2.5% of thiolated side chains give the highest purity and the highest yield of s-SWNT. These high-purity s-SWNTs were further employed for the chemical self-assembly of the polymer wrapped tubes onto silicon substrates with prepatterned gold electrodes. The chemically self-assembled network transistors showed ambipolar properties with 3 orders of magnitude higher on-current compared to the reference devices fabricated with SWNTs selected with a polymer without thiol functionalization (not chemically self-assembled). The robustness of the attachment is demonstrated by the substantial amount of SWNTs resisting to sonication in organic solvents. Furthermore, single SWNTs devices were fabricated by self-assembly, showing that the process is 100% reliable, giving for all the fabricated samples working devices.

Recently, we have demonstrated that it is possible to use a block copolymer combining poly(9,9-dioctylfluorene-2,7-diyl) and single-strand DNA (PFO-*b*-ssDNA) both for selecting semiconducting nanotubes and for their self-assembly by using substrates functionalized with self-assembled monolayers containing the complementary DNA sequence to the one functionalizing the PFO side chains.^[32] Even though this approach demonstrated to be effective (97.6% working FETs), we observed some major drawbacks, such as the high cost of DNA with precise sequences and the difficulty of the selection process due to the fact that also DNA sequences interacts with the SWNT walls.^[33,34]

In order to obtain a less expensive route to perform chemical self-assembly of the nanotubes, different functional groups can

be considered, between them thiols are very interesting, as they exhibit specific interaction with several metals.^[35]

An attempt toward chemical self-assembly of SWNTs was recently reported by using SWNTs wrapped with polythiophene derivatives with side chains bearing reactive side groups for the attachment to metals or polar substituents for electrostatic interaction.^[36] The authors obtained in this way deposition of SWNTs with high surface selectivity and density. However, in this study polythiophene derivatives with hexyl alkyl chains, which display low selectivity and low yield for semiconducting carbon nanotubes were used.^[11] It is therefore not surprising that this study does not mention any data on the selectivity of the polymer, and does not report devices fabricated by chemical self-assembly of SWNTs.^[36]

Figure 1a shows the schematic of the chemically self-assembled SWNTs on gold electrodes in the case of the network devices, i.e., when the transistor channel length is longer than the average length of the individual tubes; and in the case of a single SWNT FET, i.e., when a single SWNT is able of crossing the channel. Figure 1b shows the structure of the polyfluorene derivatives functionalized with thiol groups, including an alternating copolymer with a 50%-content of thiolated side chains (PF12-F6Sac), a random copolymer with 2.5% thiolated side chains (PF12-F6Sac2.5%), and for comparison, a structurally related nonthiolated polyfluorene (PF12-F6). As mentioned previously we chose polymers with alkyl chains of 12 C atoms, which we have been reported to be very effective in the selection of s-SWNTs.^[7]

Figure 2a shows the absorption spectra of high pressure carbon monoxide disproportionation (HiPCO) SWNTs selected by these polyfluorene derivatives (Figure 1b) containing different percentage of thiol groups. The reference polymer containing no thiol group, poly{(9,9-didodecylfluorene-2,7-diyl)-*alt*-(9,9-dihexylfluorene-2,7-diyl)} (PF12-F6), shows the highest concentration of s-SWNTs (see the Experimental Section). The introduction of the thiol functional groups disrupts the SWNT/polymer interaction, resulting in a lower absorbance of the s-SWNTs dispersion. Moreover, when a high concentration of thiol groups (50%) is attached to the polymer side chains (PF12-F6Sac), the lower selectivity for s-SWNTs is accompanied by an increase of the background absorption, which is due to the metallic SWNTs plasmon resonances.^[37] The presence of some metallic SWNTs is also indicated by the presence of several peaks in the range between 500 and 650 nm.^[6] The electron density of the thiol groups can explain the presence of metallic tubes in solutions obtained with polymers bearing high thiol concentration. Recently, we have shown that metallic SWNTs are selected by polymers containing high concentration of nitrogen atoms, due to the electron rich nature (lone pair) of the nitrogen.^[38] Similarly, electron lone pairs on the sulfur atom in the thiol group can interact with the highly polarizable walls of the metallic SWNT species.

To reduce the metallic SWNT content in the dispersions, several different approaches can be utilized. Considering the above-mentioned reason for the presence of metallic tubes, the first strategy is to reduce the number of thiol groups in the polyfluorene side chains. As it is shown in Figure 2a, the reduction of the number of thiol groups to 2.5% (PF12-F6Sac2.5%) reestablishes the selectivity for s-SWNTs.

Figure 1. a) Schematic of the attachment of the SWNTs wrapped by the thiol side-functionalized polymer chains to the gold electrodes. In the left side, network SWNT FET; in the right-side, single s-SWNT FET. b) Chemical structures of the thiol-functionalized conjugated polymers investigated in this work.

Another potential pathway to reduce the metallic content is through fine tuning of the polymer:SWNT ratio. It has been reported that by increasing the SWNT to polymer ratio, a lower concentration but higher purity s-SWNT dispersion can be obtained.^[39] The absorption spectra of the SWNT dispersions obtained with the three polymers under study, after optimization (see the Experimental Section) and removal of the free polymer chains by performing double step ultracentrifugation^[40] are displayed in Figure 2b. The assignment of the s-SWNT chiralities, according to a modified Kataura equation,^[7] is displayed in Figure 2b. All side chain functionalized polymers select the same species of SWNTs, however, while PF12-F6SAc select a very similar population (also as proportions) of SWNTs than the reference polymer, the PF12-F6SAc2.5% modifies the distribution of selected s-SWNTs, by favoring the selection of smaller diameter tubes. We notice that the polydispersity index of the PF12-F6SAc2.5% (see Table S1 in the Supporting Information) is more than two times larger than one of the other two polymers.

To verify the quality of our s-SWNT dispersions, photoluminescence measurements were performed on the enriched samples where the final concentration was adjusted to be similar in value. The steady state PL measurements are reported in Figure S1a in the Supporting Information, showing that the reference sample has the highest PL intensity, while with the increasing of the number of thiol groups in the polymer chains the PL intensity decreases. The lowering of the steady state PL intensity can be attributed to the presence of small bundles, which may also contain metallic nanotubes.^[41] Time-resolved

spectroscopy measurements can be used to further elucidate the origin of this phenomenon. The exciton decay dynamics of (7,5) tubes are shown in Figure S1b in the Supporting Information. The long decay component of the exciton lifetime of the individualized s-SWNTs is in the range between 20 and 30 ps, which is comparable to the lifetimes previously reported for highly individualized polyfluorene-wrapped s-SWNTs.^[7,42,43]

This demonstrates the individualization of the tubes and especially in small bundles the absence of metallic carbon nanotubes. It has been reported that when metallic SWNTs are present in bundles, the exciton lifetime of the nanotube reduces by one order of magnitude.^[44] The nanotubes selected by PF12-F6SAc show the shortest lifetime, in agreement with the lowest steady state PL, confirming the highest number of pathways for exciton relaxation due to the probable formation of small bundles also with metallic species.

Self-assembled monolayers of molecules bearing thiol functional groups onto metal surfaces have been studied for many years because of the high reactivity and strengths of the bond.^[35,45,46] Metals that show specific bonding with thiols are gold, silver, copper, and palladium. For real-world applications of self-assembly, palladium and gold are the most attractive metal electrodes due to their high chemical stability and low toxicity.^[35] We have therefore tested the capacity of our SWNTs wrapped with thiol-functionalized polymers to assemble on gold surfaces by immersing the substrates in the SWNT solution for about 1 h. For this purpose, we used s-SWNTs selected with PF12-F6SAc2.5%, as the solutions are highly dense of semiconducting SWNTs (0.18 mg mL⁻¹).

Figure 2. a) Absorbance of s-SWNT dispersion with polyfluorene derivatives containing 0% (black), 2.5% (red), and 50% (green) of thiol groups at their side chains. Dispersions are prepared with the same initial polymer/SWNT ratio. b) Absorbance of the same samples as in (a) after optimization of the processing parameters to remove the metallic SWNTs, and after enrichment. The chiralities are assigned following the method proposed in ref. [7].

Atomic force microscopy (AFM) based analysis of the SWNT networks, obtained with PF12-F6SAc2.5%-SWNTs and PF12-F6-SWNTs dispersions, on gold and silicon substrates is reported in Figure S2 in the Supporting Information. On the gold substrate we clearly observe a homogenous network of highly individualized carbon nanotubes when they are wrapped with PF12-F6SAc2.5%, several nanotubes are resisting to the sonication of the substrate for 30 min (Figure S2b, Supporting Information), while the reference sample on gold shows a higher density of SWNTs (Figure S2c, Supporting Information) and the complete removal of the nanotubes after sonication (see Figure S2d, Supporting Information). On the SiO₂ substrate little amount of SWNTs wrapped by PF12-F6SAc2.5% is found after immersion of the substrate for 1 h (Figure S2e, Supporting Information) and no trace of SWNTs is found after 30 min sonication (Figure S2f, Supporting Information). These measurements confirm that thiol functionalization is a valid strategy for the fabrication of homogeneous SWNT networks and can also aid in efficient contact formation with the gold electrodes.

To further demonstrate that thiol-functionalized conjugated polymers are an industrial compatible answer to the long-standing problem of the placeability of s-SWNTs, we fabricated SWNT field-effect transistors by chemical self-assembly. The sorted s-SWNTs were deposited by soaking the silicon substrate with the prepatterned gold electrodes in the enriched dispersion for 1 h. Electrodes defining a channel length of 20 μm and channel width of 1 mm were used. As the average length of the SWNTs is around 1 μm , we aim at the self-assembly of a network of SWNTs crossing the FET channel.

Figure 3a shows the comparison of the output curves of the SWNT-FETs fabricated by SWNTs selected by the reference polymer (PF12-F6) and by the thiol functionalized polymer PF12-F6SAc2.5%. Both devices show ambipolar transport with almost symmetric electron and hole current, but devices fabricated from SWNTs wrapped by thiolated polymer show 3 orders of magnitude higher on-current compared to that of the reference devices, demonstrating a better SWNT attachment to the electrode/substrate during the immersion time. Compared to the reference devices, these devices also show better carrier injection as evidenced by the shape of the output characteristics at low source-drain voltage. The better injection could be ascribed to the effect of the thiol dipole at the gold interface but also to the proximity of the SWNT with the electrode due to the chemical attachment. A noticeable reduction of currents at high gate and source-drain voltages is observed from the output curves of the SWNT-PF12-F6SAc2.5% sample, a similar effect has been reported for many ambipolar devices.^[47] In such devices, the holes and electrons can be injected simultaneously from both electrodes. At low source-drain voltage, only one type of charge carrier is present in the active layers, for example, holes (electrons) for negative (positive) gate bias. The carriers with opposite sign are blocked due to the Schottky barrier at the source/drain electrodes. When the source-drain voltage is further increased, the opposite carrier starts to be injected into the active layer due to the lowering of the barrier. At this high voltage, both carriers exist in the active layer, and can therefore recombine, resulting in the reduction of the current. Since carbon nanotubes are 1D direct band gap materials with relatively strong exciton binding energy, the electron and hole recombination might result in light emission as has been demonstrated by different authors.^[12,13,21]

The transfer characteristics of the corresponding SWNT-FETs fabricated by SWNTs selected by PF12-F6SAc2.5% and by the reference polymer PF12-F6 are presented in Figure 3b. Both devices show on/off ratio of about 10^4 and 10^5 at $V_{\text{DS}} = \pm 5$ V for electrons and holes, respectively (a full device characterization with the gate current is reported in Figure S3, Supporting Information). The increase of the off-current by increasing source-drain voltage is a typical characteristic of ambipolar transistors.^[12] Since both carriers can be injected into the channel simultaneously, the devices cannot be completely turned off at high drain voltages. For these transistors the charge carrier mobilities are extracted from the $I_{\text{D}}-V_{\text{G}}$ characteristics in the linear region at $V_{\text{DS}} = \pm 5$ V. For the devices fabricated with PF12-F6SAc2.5%-SWNTs, we obtained effective mobilities of 9.2 and 16 $\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$ for holes and electrons, respectively. While reference devices show mobilities of 0.05 and 0.07 $\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$ for holes and electrons, respectively. The

Figure 3. a) Output and b) transfer characteristic of SWNT-FETs dispersed by PF12-F6 (top) and PF12-F6SAc2.5% (bottom). The channel length is 20 μm and channel width 1 mm.

mobility values obtained with the self-assembled SWNTs are extremely high especially considering their ambipolarity, the small diameter carbon nanotubes, the very simple device structure (SiO_2 dielectric), and the fact that no correction for contact resistance and effective coverage of the SWNTs was used. For comparison, these mobilities are close to those obtained by our group (14 and 16 $\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$) using large diameter nanotubes (1.5 nm diameter) and ion gel as gate dielectric.^[7]

To prove that SWNTs wrapped by PF12-F6SAc2.5% are chemically attached to the substrate, we performed a mild bath sonication as the one generally used to clean substrates, of the devices in toluene after electrical characterization. Interestingly, after sonication and reannealing to remove the solvent, the electrical properties of the samples fabricated by thiol self-assembly show only a decrease of the on-current of 1 order of magnitude (see Figure S4a, Supporting Information), while the reference sample shows a reduction of the on-current by more than 2 orders of magnitude from the already much lower starting value (Figure S4b, Supporting Information). The transistors reported in Figure 3 have a channel of 20 μm , which is about 10 times longer than the average length of the SWNTs. In this case, as a single SWNT cannot cross the channel it is necessary to have a percolation pathway from nanotube to nanotube through the channel. The reduction of the current after sonication for the sample fabricated with SWNTs wrapped by the thiol-functionalized polymers therefore appears as mostly due to the loss of some of the tubes in the middle of the channel, not directly attached to one of the electrodes. We therefore fabricated field effect transistors with smaller channels (2.5 μm), to better exploit the chemical self-assembly possibilities of our thiol-functionalized conjugated polymers.

Figure 4a shows a three-dimensionally represented AFM topographic image of the channel of the transistor (2.5 μm)

with the SWNTs forming a network between the electrodes, here as expected less tubes are necessary to cross the channel. Figure 4b is an AFM image of similar SWNTs as depicted in Figure 4a but with higher magnification showing the pronounced surface features and interconnected tubes.

Similarly to the longer channel FETs described previously, the output curve (Figure 4c) shows ambipolar transport with comparable currents (3 and 1 mA at $V_{GS} = \pm 50$ V) for hole and electron accumulation regimes, respectively. The on/off ratio obtained from the I_D - V_G transfer characteristic is only 10^3 (Figure 4d), which is substantially lower than the 10^5 obtained with the 20 μm channel transistors. The high off-current is the factor limiting the on/off ratio in these devices, which can be either due to the presence of the small amount of metallic species in the solution^[38] or to the simultaneous injection of both type of carriers into the channel.^[12] The effective charge carrier mobilities extracted from the linear regime of I_D - V_G characteristics at $V_{DS} = \pm 5$ V are 24.2 and 17.7 $\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$ for holes and electrons, respectively. It is important to underline that these mobilities are not corrected for contact resistance and are not scaled with the effective size of the SWNTs, therefore are underestimated. The summary of the statistics of the figures of merit (mobility and on/off ratio) of the network SWNT devices fabricated with the different polymers is reported in Figure S5 (Supporting Information). For the 2.5 μm channel devices only the results obtained with PF12-F6SAc2.5% are reported as the FETs fabricated with PF12-F6SAc wrapped SWNTs were affected by excess of metallic species.

While the AFM of the 2.5 μm channel length device shows that the SWNTs are able to cross the channel, they still form a complex network because of the large channel width. A further reduction of both channel length and width allows for better understanding the applicability and the quality of the chemical

Figure 4. a) High-resolution 3D represented topographic AFM image of SWNTs dispersed by PF12-F6SAc2.5% the scan area is $2.4 \mu\text{m} \times 1.9 \mu\text{m}$. b) Histogram based on statistical analysis of diameter distribution of polymer wrapped individual and bundles of nanotubes composing a network. The diameter is measured through section analysis across the tubes from AFM images as shown in panel (b), which is a spatially magnified AFM image over the black box region shown in panel (a). The Z scale for the inset 3D depicted AFM image is 0.1–5 nm. The Au metal electrodes (protrusions in the side of both the topographic images) are seen in the sides of AFM image in panel (a). c) Output and d) transfer characteristic (for negative V_G $V_D = -2, -5, -10$ V, and for positive V_G $V_D = +2, +5, +10$ V) of SWNT-FETs dispersed by PF12-F6SAc2.5%. The channel length is $2.5 \mu\text{m}$ and channel width 1 mm .

self-assembly of the SWNTs/thiolated-polyfluorenes on gold patterned substrates. Electrodes defining a channel length of 300 nm and channel width of 300 nm were fabricated by electron beam lithography. The thickness of the electrode was kept as low as 15 nm to facilitate the self-assembly of the SWNTs and improve the contact with the gate dielectric. In **Figure 5a** the atomic force microscopy image of one of the FETs with 300 nm source–drain distance is reported, where a single SWNT attached to the gold electrodes can be clearly observed.

Figure 5b displays the line section analysis of the height profile perpendicular to the length of the carbon nanotube, proving that an individual polymer-wrapped SWNT is crossing the transistor channel. The difference between sections taken at different points of the SWNT indicates the presence of the polymer chain around the tube (thicker profile $\approx 0.6 \text{ nm}$; size of atomic van der Waals radius).^[7] Here it is important to underline that the polymer around the SWNTs has been demonstrated to have a clear effect in the performance of the network field effect transistors as it is acting in the worst cases as a trap for charge carriers and in the best cases as a barrier.^[10,48] In the case of short channel devices Arnold et al. have recently demonstrated that the conductance increases after removal of the polymer and also the quality of the contact with the electrode increases.^[5]

The electrical characterization of a typical single SWNT transistor is shown in **Figure 5c,d**. At the opposite of the network devices, these devices exhibit p-type behavior. This could be due to the difficulty to fully remove adsorbed water from the

electrodes after fabrication.^[40] Due to short-channel effects, the output currents increase linearly with gate voltage and do not show saturation.^[49] From the transfer characteristics the on/off ratio is 10^4 at $V_{DS} = \pm 0.4 \text{ V}$, with the off-current value of about 100 pA limited by the leakage through the dielectric and the edges of the substrate. Here, we do not want to underline the transistor performance, as they were fabricated with a rather thick oxide dielectric for their short channel length, but the reliability of the chemical self-assembly process. More than 50 of this 300 nm channel length devices were tested and all of them display transistor behavior and a relatively limited spread of their behavior. The overview of the on current and on/off ratio of all the fabricated devices is reported in **Figure S6** (Supporting Information). From the data it is evident that the chemical self-assembly is highly reliable and is able to guarantee the high reproducibility in the fabrication of nanodevices based on SWNTs, which is the fundamental prerequisite for a future industrialization of carbon nanotubes based electronics.

In conclusion, we demonstrated the selection of semiconducting SWNTs by polyfluorene derivatives decorated with thiol functional groups, either at the alkyl side chains or at the chain ends. Due to their electron lone pairs, the thiol group impairs the selection of semiconducting tubes. However, the metallic content can be minimized by adjusting the concentration of the thiol functional groups, or by adjusting the process parameters. The polymer with 2.5% thiol groups in their side chains and the one with end functionalization are found to be the most effective in selecting semiconducting SWNTs. The high purity

Figure 5. a) 3D representation of a single carbon nanotube connecting a source and drain electrode (color coded in blue) on a silicon dioxide surface. The carbon nanotube is well adhered between the electrodes. The residue encompassing the carbon nanotube stems from the lithographic polymer processing and ambient contaminants. The AFM measurements were performed under standard laboratory conditions at room-temperature under tapping mode operation (scan area $1.45 \mu\text{m} \times 1.53 \mu\text{m}$). b) Line section analysis highlighting the local differences in the height profiles along the length of the carbon nanotube. Inset in panel (b) is an AFM image with line section profiles and their corresponding color-coded profiles. The height of the nanotube is measured between the cursor point arrow indicated in each section profile, one on top the nanotube and the other on the cleaner region of the underlying surface. The higher height profiles (green line section, panel (b)) reflect the presence of adsorbed contaminants on the carbon nanotube sidewall. The sample was rinsed in acetone and isopropyl alcohol to remove excessive polymer residue contamination. c) Output and d) transfer characteristic of SWNT-FETs dispersed by PF12-F6SAc2.5%. V_g varying between 0 and 40 V (−40 V) with steps of 10 V (−10 V). The black curve on the transfer plot shows the gate current.

of the individualized s-SWNTs is confirmed by optical measurements and by the fabrication of highly performing field effect transistors. Field effect transistors with different channel lengths, from 300 nm till 20 μm were fabricated by immersion of the substrates in the solution of the semiconducting SWNT wrapped with the thiolated polyfluorene. The chemical self-assembly of SWNTs shows easy fabrication, high reliability (100% working 300 nm channel length transistors), and resistance to mechanical solicitations.

Experimental Section

Polymer Synthesis: Poly{(9,9-didodecylfluorene-2,7-diyl)-alt-[9,9-bis[6-(S,S'-thioacetate)hexyl]fluorene-2,7-diyl]} (PF12-F6SAc) was prepared by reacting 503 mg potassium thioacetate with a diluted solution of 450 mg of poly{(9,9-didodecylfluorene-2,7-diyl)-alt-[9,9-bis(6-bromohexyl)fluorene-2,7-diyl]} in 40 mL of dry tetrahydrofuran (THF) by stirring the polymer solution at 70 °C for 12 h. Afterward, the solvent was

removed, and the polymer dissolved in chloroform was precipitated into cold methanol. The procedure was repeated one time. The yellowish polymer was dried under high vacuum, yield 77% (333 mg, 0.34 mmol).

Poly{(9,9-didodecylfluorene-2,7-diyl)-stat-[9,9-bis[6-(S,S'-thioacetate)hexyl]fluorene-2,7-diyl]} (PF12-F6SAc2.5%) was prepared in the following way: 1.0 g (1.51 mmol) 2,7-dibromo-9,9-didodecylfluorene and 68 mg (0.11 mmol) 2,7-dibromo-9,9-bis(6-(S,S'-thioacetate)hexyl)fluorene were placed in a Schlenk tube. Under inert atmosphere, 615 mg (3.94 mmol) 2,2'-bipyridyl and 1166 mg (4.24 mmol) bis(1,5-cyclooctadiene)-nickel(0) were added and diluted with 15 mL of anhydrous THF. Next, 0.45 mL (3.94 mmol) 1,5-cyclooctadiene were added and the resulting mixture was heated in a microwave reactor at 120 °C for 10 min. Afterward, 0.1 mL bromobenzene (0.95 mmol) was added and the reaction mixture reacted for five more minutes at 120 °C. The workup procedure follows the scheme described for PF12-F6SAc, yielding 705 mg (1.07 mmol, 87%) of a pale-yellow polymer. The molecular weights of the polymers are summarized in Table S1 (Supporting Information).

Dispersion of Semiconducting SWNT: HiPCO SWNTs of diameter ranging between 0.8 and 1.2 nm were purchased from Unidym Inc. and used as received. The SWNT dispersions were prepared following the previously reported methods.^[40] Specifically, a mixture of SWNT:polymer with 3:12 weight ratio in 10 mL of toluene was sonicated in a cup horn bath sonicator (Misonix 3000, output power 65 W) and then ultracentrifuged at 30 000 rpm/110 000 g (Beckman Coulter Optima XE-90; rotor: SW55Ti). The supernatant was taken and used for absorption measurement. Different SWNTs to polymer ratios were adopted to obtain the highest s-SWNTs purity for the 50% thiolated polyfluorene, with the optimal ratio being the 6:6 weight ratio. A second step ultracentrifugation was performed at 55 000 rpm/367 000 g to remove the excess (free) polymer chains, and to increase the s-SWNT concentration. The concentration of the solutions used for the experiments varied from 0.22 mg mL^{−1} for SWNTs wrapped with the

reference polymer to 0.12 mg mL^{−1} for the SWNTs wrapped by PF12-F6SAc and 0.18 mg mL^{−1} for the nanotubes wrapped by PF12-F6SAc2.5%.

Optical Absorption Spectroscopy: Absorption spectra were recorded in a wavelength range from 300 to 1800 nm in 2 mm path length quartz cuvette using an UV–Vis–NIR spectrophotometer (Shimadzu UV-3600).

Photoluminescence Measurements: Steady state and time resolved photoluminescence spectroscopy was performed by exciting the s-SWNT solutions with a mode-lock Ti:Sapphire laser at wavelength of 800 nm. The duration of the pulses was 150 fs and the repetition frequency ≈76 MHz. Steady state photoluminescence spectra were recorded with an InGaAs photodetector array from Andor while the time resolved measurements were recorded with a streak camera with an NIR-sensitive photocathode from Hamamatsu Photonics working in synchroscan mode. All measurements were performed in transmission mode with the sample at room temperature.

Device Fabrication and Characterization: Highly doped silicon substrates with 230 and 300 nm thermally grown SiO₂ dielectric were used for network and single SWNT FETs fabrication, respectively. The network devices were fabricated on lithographically defined gold electrodes of channel width equal to 1 mm and different channel lengths (20 and 2.5 μm). For the single SWNT FETs electrodes were

formed by electron beam lithography using positive polymer resist (polymethylmethacrylate [PMMA], $M_w = 950k$), followed by a developing step in methyl isobutyl ketone:isopropanol = 1:3 for 45 s. Later 3 nm Ti adhesion layer and 15 nm Au source and drain electrodes were evaporated using an electron beam evaporator (Temescal FC 2000). Finally, a lift-off procedure was performed in an ultrasonic acetone bath. Transistors formed in this way have 300 nm channel width and 300 nm channel length. After cleaning the substrates, a solution of polymer-wrapped carbon nanotubes was deposited by dip coating. Dip-coating parameters (speed and duration) were chosen in such a way to allow self-assembly of the SWNT on the gold electrodes. The substrate was subsequently baked in a nitrogen atmosphere at 120 °C for 1 h to remove the residual organic solvent.

Characterization of the SWNT Transistors: Electrical measurements were performed using a probe station placed in a nitrogen-filled glovebox at room temperature under dark conditions. The probe station was connected to Agilent E5262A Semiconductor Parameter Analyzer with a resolution of 5 pA. Because part of the fabrication process was performed in ambient conditions, the devices were annealed for 2 h at 200 °C inside the glovebox to remove adsorbed water and oxygen molecules prior to measurements.

AFM Microscopy: All AFM measurements were performed under ambient temperature and standard laboratory conditions. The AFM measurements in the main text were taken using Dimension V Bruker AFM System operated under tapping mode and using "Supersharp" tips with <5 nm tip radius, purchased from Nanosensors. The AFM images in the Supporting Information were taken with a Bruker microscope (MultiMode 8 with ScanAsyst) in ScanAsyst Peak Force Tapping mode with SCANASYST-AIR probes having elastic constant $k = 0.4 \text{ N m}^{-1}$, resonance frequency of 70 kHz, and tip radius less than 12 nm (nominal 2 nm). The images were taken with a scan rate of 1 Hz and the resolution of 512 lines/sample.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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