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# Effect of temperature on the selection of semiconducting single walled carbon nanotubes using Poly(3-dodecylthiophene-2,5-diyl)

Widianta Gomulya [a], Jorge Mario Salazar Rios [a], Vladimir Derenskyi [a], Satria Zulkarnaen Bisri [a], Stefan Jung [b], Martin Fritsch [b], Sybille Allard [b], Ullrich Scherf [b], Maria Cristina dos Santos [c,*], Maria Antonietta Loi [a,*]

[a] Zernike Institute for Advanced Materials, University of Groningen, Nijenborgh 4, Groningen 9747 AG, The Netherlands
[b] Chemistry Department and Institute for Polymer Technology, Wuppertal University, Gauss-Str. 20, D-42119 Wuppertal, Germany
[c] Instituto de Física, Universidade de São Paulo, 05508-090 São Paulo, SP, Brazil

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ABSTRACT

We report on the investigation of the temperature effect on the selective dispersion of single-walled carbon nanotubes (SWNTs) by Poly(3-dodecylthiophene-2,5-diyl) wrapping. The interaction mechanism between polymer chains and SWNTs is studied by controlling the polymer aggregation via variation of the processing temperature. Optical absorption and photoluminescence measurements including time resolved photoluminescence spectroscopy are employed to study the degree of interaction between the polymer in different aggregation states and the carbon nanotubes. At low processing temperatures, results are consistent with the planarization of the polymer chains and with SWNTs working as seeds for polymer aggregation. The formation of small clusters due to the inter-digitation of alkyl tails between neighboring polymer-wrapped SWNTs allows the formation of the SWNT bundles, as experimentally evidenced and investigated by molecular dynamics simulations. The interaction between the tubes within the bundles, which is reflected in the variation of the photoluminescence dynamics of the polymer, can be suppressed by warming up the sample.

## 1. Introduction

Single walled carbon nanotubes have become one of the most attractive nano-materials since their discovery more than 2 decades ago [1,2]. They are quasi-one-dimensional objects which exhibit outstanding properties such as high thermal conductivity, outstanding mechanical strength, high charge mobility along their axis, and strong exciton confinement [3,4]. All these unique properties give expectation for their use in a wide range of applications, from improved mechanical properties of materials to electronic devices [5,6]. Numerous methods have been developed to mass-produce carbon nanotubes. However, all of these methods generate mixtures of semiconducting and metallic species, which limit their use in electronic devices. Many techniques have been developed to separate semiconducting SWNTs (s-SWNTs) from metallic species, which can be roughly subdivided into two big families depending on the use of covalent or non-covalent

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* Corresponding authors.
E-mail addresses: mcsantos@if.usp.br (M.C. dos Santos), m.a.loi@rug.nl (M.A. Loi).

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functionalization [7]. The non-covalent functionalization is advantageous with respect to the covalent method because it does not affect the electronic properties of the SWNTs. These non-covalent functionalization methods rely on the wrapping of nanotubes with different molecules such as surfactants [8], DNA [9], and conjugated polymers [10].

Polymer wrapping of SWNTs is preferable to the other techniques due to the high selectivity, easy availability of the conjugated polymers and simplicity of processing [10]. The selectivity has been explained by the $\pi$–$\pi$ interaction between s-SWNTs and the conjugated polymer chains, where the polymer backbone follows the helical structure of the nanotube, while the alkyl side chains help to increase the surface coverage and the binding energy, thus lowering their total potential energy [10–12]. Among the many available conjugated polymers, most research has focused on the use of polyfluorene and its derivatives [10,13,14]. Other polymers however, such as polycarbazole [15] and polythiophene [16] derivatives have also demonstrated good selectivity. It is important to note that the effectiveness of the selectivity strongly depends not only on the structure of the conjugated polymer, but also on many other parameters such as solvent [13]; polymer molecular weight [17]; polymer concentration as well as the duration of sonication and centrifugation [18]. All these parameters have been found to have significant influence on the effectiveness of the s-SWNT selection, and their effects could be detected in the optical properties of the sample (absorption and photoluminescence) and transport properties (i.e. charge carrier mobility). Knowledge of how the different preparation parameters influence the selection mechanism is fundamental for understanding the polymer-wrapping mechanism and also to improve it.

To date, the most unexplored parameter with respect to its effect on the selectivity for semiconducting SWNT species is the temperature. Lee et al. reported carbon nanotube selection using P3DDT, where the best P3DDT-SWNT dispersion was achieved by sonication of the mixture at 50 °C, which corresponds to the melting temperature of the polymer side-chains [16]. In contrast, in some other reported protocols it is stated that the sonication process should be done at low temperature [10]. These inconsistencies point to the necessity to systematically investigate the influence of temperature in the nanotube selection process.

In this article, we report a systematic investigation on the effect of temperature during different steps of the s-SWNT selection process using P3DDT. The interaction between polymer chains and SWNTs is investigated by optical absorption, steady-state and time resolved photoluminescence measurements. First, we study the effect of the polymer aggregation during the s-SWNTs purification process, which is indicated by the appearance of a new feature in the absorption spectrum of the polymer at 600 nm. We found the polymer aggregation to be stabilized by the interaction with the carbon nanotubes. The shorter lifetime of the polymer PL evidences the formation of small SWNT bundles in samples which originate from aggregated P3DDT solutions. These bundles can be destroyed with a mild temperature treatment. The formation of SWNT bundles by interdigitation of alkyl chains is supported by molecular dynamics simulations.

In addition, we performed experiments varying the sonication temperature to understand the effect on the nanotube individualization. Optimal dispersions are found for temperatures ranging from 10 °C to 20 °C. Optical investigations provide evidence of the formation of small bundles for sonication performed at 0 °C, which also in this case, can be destroyed by heating the sample to 50 °C.

## 2. Experimental section

### 2.1. *Preparation of the semiconducting SWNT dispersion*

Poly(3-dodecylthiophene-2,5-diyl) was synthesized via GRIM method [19]. The molecular weight ($M_n = 26.800$ g/mol, $M_W = 29.000$ g/mol) was determined by gel permeation chromatography (GPC) (using polystyrene standards, and THF as eluent, see Fig. S1 Supplementary data). HiPCO SWNT were purchased from Unidym Inc. and used as received. To investigate the effect of polymer aggregation, dispersions with 1 mg SWNT, 3 mg polymer in 10 mL toluene were prepared. First, the polymer was dissolved in toluene and then the solution was sonicated with cup horn bath (Misonix 3000) at 15 W, 50 °C to fully dissolve the polymer. This gives rise to a non-aggregated polymer solution of orange color. A second type of sample is obtained by sonication of the polymer solution at 10 °C, resulting in a red colored solution that shows the signature of polymer aggregation in the absorption spectrum. After preparation of the two types of polymer solutions, SWNT was added, then the samples were sonicated with cup horn bath ultrasonicator for 2 h at 65 W, 10 °C, followed by ultracentrifugation (Beckman Coulter Optima XE-90, rotor: SW55Ti) at 40,000 rpm (196,000*g*) for 1 h to remove all the remaining bundles and impurities. The ultracentrifugation is performed always at 10 °C to reduce solvent evaporation. To investigate the effect of the sonication temperature on the selectivity of the nanotubes, the SWNT-P3DDT solution was prepared from non-aggregated (orange) polymer solutions. The temperature of the bath used during sonication was varied between 0 °C and 80 °C with a close circuit chiller. The supernatant was carefully separated from the pellet for further measurement.

Free polymer removal is obtained using a previously described procedure, in which the precipitation of the polymer-wrapped SWNTs is provoked by a sequence of ultracentrifugation steps [20]. The obtained pellet is subsequently washed and re-dispersed in toluene. The procedure is repeated several times until no changes in the absorption spectra are observed.

### 2.2. *Optical characterization of the semiconducting SWNT dispersion*

Optical measurements were performed to check the concentration of the carbon nanotubes selected by the polymers. Absorption spectra were recorded by a UV–Vis–NIR spectrophotometer (Shimadzu UV-3600). Photoluminescence (PL) measurements were conducted by exciting the polymer solutions at 380 nm by the second harmonic of a Kerr mode-locked Ti-sapphire laser, delivering 150 fs pulses with repetition frequency of ~76 MHz. SWNTs were excited at a wavelength of 760 nm. Steady state photoluminescence spectra were recorded in transmission mode by a Si-CCD from Hamamatsu and InGaAs photodetector array from Andor, while the time-resolved PL measurements were recorded by a streak camera with a visible- and a NIR-sensitive photocathode (Hamamatsu Photonics) working in synchroscan mode (time resolution around 2 ps). All measurements were carried out at room temperature and the spectra were corrected for instrumental response.

### 2.3. *Molecular dynamics simulation*

The binding of P3DDT polymer chains to SWNTs was studied through a molecular modeling technique involving alternate steps of energy minimizations and molecular dynamics. Nanotubes of diameters close to 1 nm and near-armchair chiral indices were chosen, as they are the ones evidenced by the experiments. The classical CVFF950 force field was used [21]. Forces include bond stretching, bond angle and torsion angle potentials, van der Waals interactions and Coulomb interactions between atomic charges internally stored in this force field, as implemented in the package Cerius 2 [22]. Polymer chains contain 20 repeat units and the nanotube lengths are 100 to 200 Å, with open ends. Simulations were run in the microcanonical NVE ensemble at $T = 300$ K. The initial atom velocities were set according to Maxwell–Boltzmann distribution plus an impulse at a given direction to mimic the effect of an ultrasound wave. The integration time step was 1 fs and the dynamics cycles lasted 50 ps. Energy minimizations and 50 ps dynamic cycles were repeated to a total of 1 ns simulation time. A toluene layer was included to cover the superstructures following a procedure previously described [11,12].

## 3. Results and discussion

In the last years, the polymer-wrapping method has proven to be very effective in dispersing and selecting s-SWNTs [10]. One important aspect in the sample preparation procedure is the solubility of the polymer. When polymers such as polyfluorene are solubilized in very “good” solvents such as chloroform or Tetrahydrofuran, no s-SWNT selectivity is observed [10,13]. The best selectivity for s-SWNT has been observed only when the dispersion is carried out using “poor” solvents, such as toluene or xylene [13]. Nevertheless, if the polymer cannot be well dissolved, its interaction with the nanotubes will be obstructed, thus it is important to control the polymer solubility to obtain a good SWNT dispersion.

Polyfluorene, which is one of the most selective conjugated polymers for s-SWNTs, is known to display a small feature in the absorption spectrum at 437 nm. This is the fingerprint of the so-called beta phase, which is due to the interaction between the alkyl side chains when the polymer is in a poor solvent. The formation of the beta phase is typically observed in Poly(9,9-di-n-dodecylfluorenyl-2,7-diyl) (PFO), but not in polyfluorenes with longer alkyl side chains [23].

Polythiophenes are known to exhibit high crystallinity (polymer aggregates) because of the planarization of the thiophene rings. This kind of polymer aggregation can be destroyed either by applying thermal energy to the solution [24], or by dissolving the polymer in a superior solvent [25]. The importance of the polymer solubilization in the selection of s-SWNTs is investigated. Fig. 1a shows the absorption of pristine P3DDT in two forms, with- (red curve) and without-aggregation (orange curve). The aggregation level is controlled by varying the thermal energy used in the solubilization of the polymer chains. Solutions prepared at 50 °C have an orange color, while those prepared at 10 °C are red, indicating the presence of polymer aggregates [26–28]. The color change derives from the red shift of the main absorption peak from 450 nm to 470 nm (corresponding to the $\pi$–$\pi^*$ transition of the thiophene ring) and by the increased prominence of the feature appearing between 580 nm and 600 nm (corresponding to the vibronic side-band transition and 0–0 transition) (see Fig. 1a) [29], which indicates polymer planarization. Importantly, by increasing the temperature, the aggregation of the polymer can be totally suppressed.

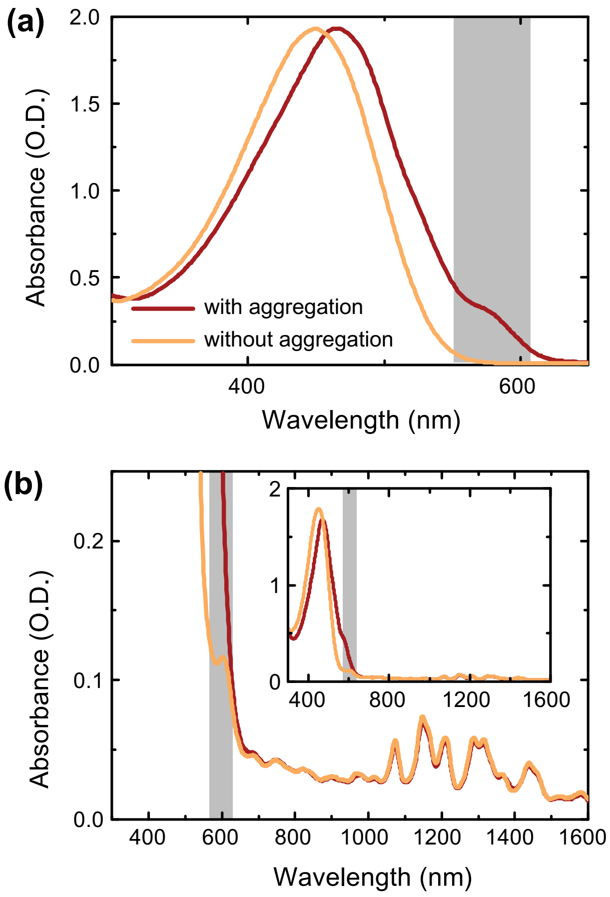

**Fig. 1 – (a) Absorption spectra of pristine P3DDT solution prepared at 10 °C (with aggregation) (red) and (without aggregation) 50 °C (orange). (b) Absorption spectra of the P3DDT-wrapped SWNT prepared with polymer solutions as in (a) (colors are corresponding). The gray area indicates the spectral region between 580 nm and 600 nm, where the peak related to the formation of the aggregate is located the. Inset: Full spectra of measurements displayed in (b). (A color version of this figure can be viewed online.)**

Both forms of the polymer show similar ability to select single walled carbon nanotubes as displayed in Fig. 1b. The absorption features in the spectra ranging from 700 to 900 nm and 1000 to 1600 nm correspond to $E_{22}$ and $E_{11}$ transitions of semiconducting tubes, respectively. While the metallic nanotubes have absorption in the range 500–600 nm, which cannot be observed because overlap with the polymer absorption. Small differences in the absorption of these two samples can be observed: first, the polymer peak in the sample produced with polymer without aggregation (orange solution) is blue shifted, similarly to the pristine polymer solution (without SWNTs), as can be seen in Fig. 1a. Second, the dispersion prepared with the orange solution shows an enhanced absorption peak at 600 nm (gray area in Fig. 1b).

Interestingly, the aggregation signature, i.e. the 600 nm peak, cannot be avoided even when using the non-aggregated polymer form for the dispersion (Fig. 1b). This observation is in contrast with the findings obtained with the pristine P3DDT polymer solution, in which the 580–600 nm peak can be completely removed by heating the solution to 50 °C [30]. In the case of the sample prepared with the non-aggregated form, this peak indicates the planarization of the polymer chains due to the adsorption on the nanotube wall. For samples prepared with the aggregated polymer, the high intensity of the absorption feature indicating the aggregation originates from two contributions: the aggregation already present in the pristine polymer, and the planarization of the polymer due to the interaction with the SWNT walls (vide supra).

As a further check of this interpretation, steady state and time resolved photoluminescence were performed on the samples with- and without-polymer aggregates. The photoluminescence of the solution shows two peaks, corresponding to the vibronic transitions of the polymer (Fig. S2). However, due to the strong luminescence from the free polymer chains that are still present in the solution, and the strong self-absorption of the polymer, it is difficult to extract useful information from these measurements. Therefore, it is important to completely remove the free polymer chains that still present in the solution to understand the difference between the samples with- and without-aggregation. The removal process is equally effective for both samples as shown in Fig. 2. Here, the $\pi$–$\pi^*$ transition peak completely disappears and as replacements, the two peaks at 580 and 600 nm become prominent, indicating a higher planarization of the polymer chains interacting with the SWNT walls. The intensity of the polymer peaks in both samples is similar, proving that the higher intensity peak at 600 nm in the samples with aggregation (before free polymer removal, red spectra in Fig. 1b) originated mainly from aggregates of the free polymer in solution.

The PL spectra of these super-clean samples are identical as shown in Fig. 3a. Fig. 3b shows the PL decays (measured at 580 nm) of the P3DDT-SWNT hybrids, prepared from polymer solutions with- and without-aggregation. The P3DDT-SWNT dispersion prepared with the orange solution shows similar behavior as the free polymer chains and is well fitted with a mono-exponential function with lifetime $\tau = 481 \pm 10$ ps, while the P3DDT-SWNT hybrid prepared with

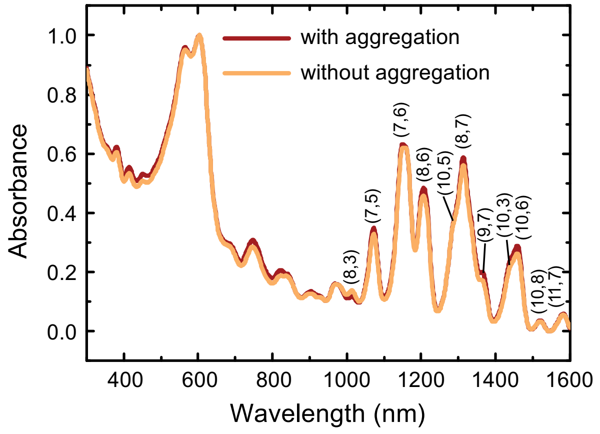

**Fig. 2 – Normalized absorption spectra of polymer-wrapped SWNT dispersions after complete free polymer removal prepared with P3DDT with- and without-aggregation. The assignment of the chiralities follow previously reported literature data [16]. (A color version of this figure can be viewed online.)**

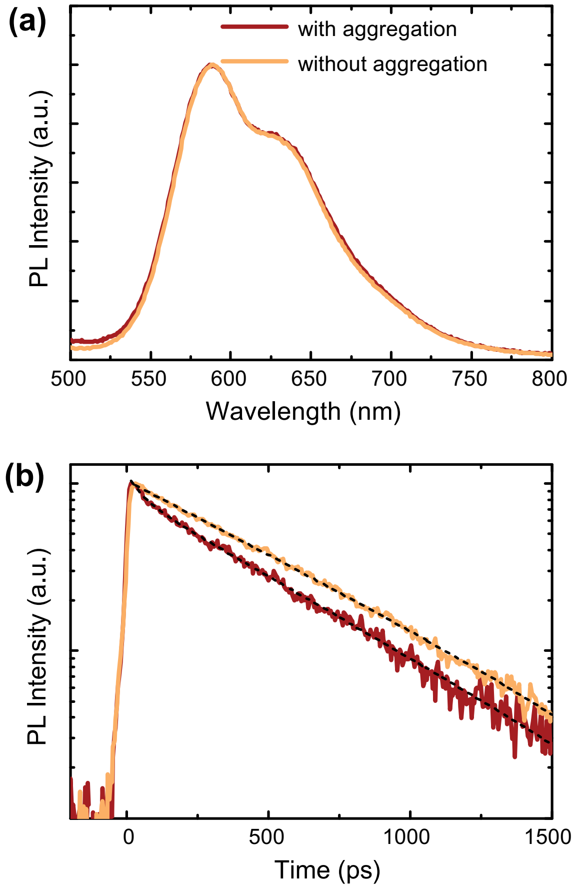

**Fig. 3 – (a) Photoluminescence spectra (polymer component) of P3DDT-wrapped SWNT dispersions after complete free polymer removal, obtained from polymer solutions with- and without-aggregation. (b) Time resolved photoluminescence of the samples as in (a) measured at 580 nm. The dashed black lines are the fittings of the experimental data. (A color version of this figure can be viewed online.)**

the red solution containing aggregated polymer, shows a bi-exponential behavior with time decays $\tau_1 = 53 \pm 5$ ps and $\tau_2 = 436 \pm 10$ ps. A similar behavior has been observed by Gao et al., in PFO/SWNT hybrids [11]. However, what appears peculiar in the P3DDT-SWNT case is that only the lifetime of the two samples differs while both the absorption and the steady state PL are identical.

It is important to note that the lifetime of the pristine polymer with-aggregation is also shorter (520 ps) than the non-aggregated one (400 ps; averaged from tri-exponential), and this is due to the opening of non-radiative channels provided by the inter-chain interactions [27]. Since in our samples the free polymer has been fully removed, as proven by the absorption and PL spectra, it is unlikely that inter-chain interactions between free polymer chains could occur. We propose therefore, that in the SWNTs wrapped with the aggregated polymer, the polymer conformation around the SWNT wall is different from that in the samples fabricated with the non-aggregated solution. This different conformation could favor the formation of small carbon nanotube bundles, which could also be induced by interdigitation of the P3DDT alkyl side chains. Once formed, these bundles increase the probability of excitation transfer from the polymer to the SWNTs and inter-nanotube transfers.

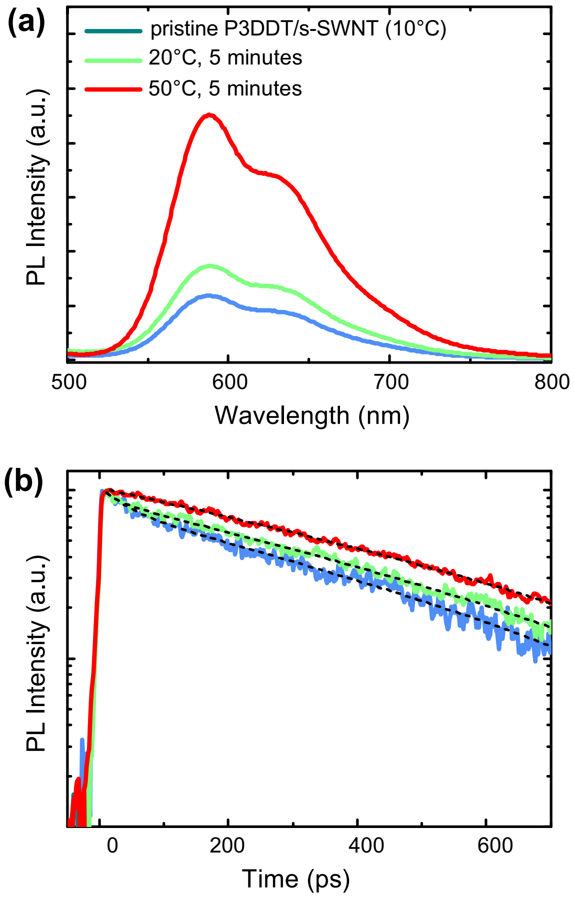

**Fig. 4 – Comparison of the polymer photoluminescence spectra (a) and decays (b) in s-SWNTs wrapped with P3DDT after complete free polymer removal, obtained from solution with-aggregation at 10 °C (blue curve); after sample treatment at 20 °C for 5 min (green curves); after thermal treatment at 50 °C for 5 min (red curve). The black dashed lines are the fittings to the experimental curves. (A color version of this figure can be viewed online.)**

To verify the plausibility of the depicted mechanism we have performed a control experiment. The sample obtained with the red-form of the polymer (at 10 °C) was measured just after centrifugation, while a second fraction of the sample was heated with a hot plate at 20 °C (about room temperature) and a third fraction at 50 °C. After heating the PL intensity increases and the lifetime becomes longer and mono-exponential as shown in Fig. 4a and b, respectively. The fitting to the PL decay gives for the 10 °C sample lifetimes $\tau_1 = 34$ ps and $\tau_2 = 406$ ps; for the 20 °C sample $\tau_1 = 33$ ps and $\tau_2 = 436$ ps; and for the 50 °C sample $\tau = 498$ ps. It is important to notice that the phenomena is not reversible by cooling the solutions which have been treated at higher temperature. This finding provides very strong evidence for the formation of small clusters of nanotubes by interdigitation of the alkyl side chains of P3DDT.

Molecular dynamics simulations are a powerful tool to investigate the precise microscopic mechanism leading to these surprising experimental observations. P3DDT polymer chains possess characteristics leading to an efficient wrapping on nanotubes: a relatively flexible backbone, aromatic rings in the main chain, and long lateral alkyl tails. The last feature also facilitates the wrapping around larger diameter nanotubes [12]. As we show below, the P3DDT-SWNT suspensions present more absorption peaks than the suspensions prepared with PFO [10,11], and a similar selectivity as that obtained with dodecyl-polyfluorenes [12], including species

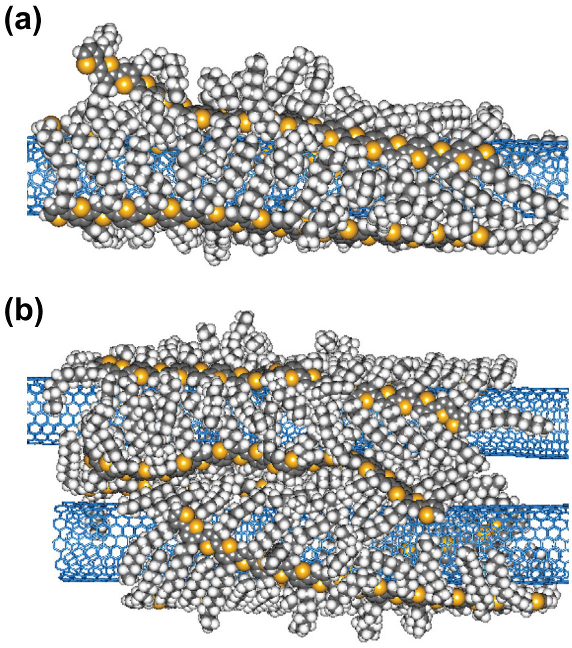

**Fig. 5 – Assembly of P3DDT polymers on nanotubes in toluene solutions (toluene not shown for clarity). Carbon nanotubes are represented by the blue structures, and the polymers by overlapping spheres: yellow = S, gray = C, white = H. (a) (12,7) nanotube wrapped by 3 polymer chains; (b) A dyad of (12,10) and (10,9) SWNTs wrapped by 7 polymer chains.**

from the large diameter side of the typical HiPCO diameter distribution. For this reason we chose, for the simulations, nanotubes having diameters ~1.3 nm, which are also more difficult cases for polymer wrapping.

The assembly of polymer chains around a single nanotube was carried out by allowing the chains to approach the nanotube, through impulse dynamics, until the total coverage of the nanotube surface was reached. The calculations showed that up to three chains can attach to nanotubes having diameters close to 1 nm, as shown in Fig. 5a. This figure also evidences the tendency of P3DDT to adopt a helical conformation, the interdigitation of alkyl tails and the crowding of alkyl groups on the nanotube surface (at the left end) prevents the thiophene rings from fully adhering to the surface. These segments of chains not attached to the nanotube and the long alkyl tails that point outwards can easily bind to other polymer chains, provoking the growth of polymer aggregates around the nanotube, or they can bind to another nanotube.

Fig. 5b shows a pair of nanotubes wrapped by seven polymer chains in which more than one chain binds to the two tubes at the same time. This is made possible by the alkyl tail length being long enough so as to hold small diameter nanotubes efficiently and at the same time to provide some degree of conformational disorder, offering another example of the efficiency of long saturated carbon chains in dispersing carbon nanotubes [31]. Interestingly, in these dyads the nanotubes are not coaxially aligned and there is at least one polymer layer between them, which can explain the variation in the dynamics of PL reported in Fig. 3b.

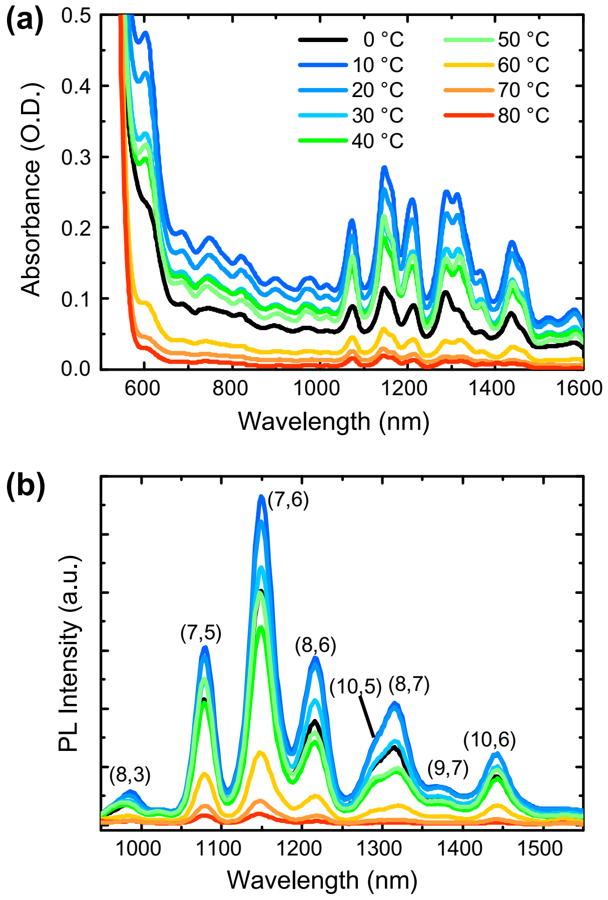

**Fig. 6 – Absorption (a) and Photoluminescence spectra (b) of P3DDT-wrapped SWNTs in toluene, the samples are obtained with sonication at different temperatures starting from a polymer solution without-aggregation.**

In addition to the investigation of the temperature effects on the polymer aggregation and the resulting selectivity, we performed further experiments to investigate the effect of the temperature during the sonication process, which can play an important role in the final SWNT dispersion quality. In particular, when we aim at obtaining a dense network of s-SWNTs for fabrication of electronic devices, it is important to increase the SWNT concentration in the final solution without damaging the purity of the sample [20,32]. Fig. 6a depicts absorption spectra of P3DDT-dispersed carbon nanotubes at various sonication temperatures, ranging from 0 °C to 80 °C, from which the s-SWNT concentration can be determined (Table S2, Supplementary data). It is important to note that these are not super-clean samples (obtained with extensive removal of the excess polymer) but are samples as reported in Fig. 1. Here, the highest SWNTs concentration are obtained by sonicating the P3DDT–SWNT solutions between 10 °C and 20 °C. Furthermore, the concentration of selected SWNT drastically drops when the sonication is performed at temperatures higher than 50 °C. This behavior, which is highly reproducible by careful control of the sonication bath temperature, is in marked contrast to what was previously reported [16]. This result is in agreement with a previous report showing that by long sonication a lower SWNTs concentration is obtained, due to the temperature increase [33].

The important feature evidenced by these measurements is that the peak at 600 nm, attributed to polymer aggregation, is proportional to the concentration of carbon nanotubes and is independent of the sonication temperature. To quantify it, we calculated the relative intensity of the polymer aggregation absorption peak and the strongest SWNT absorption at 1147 nm, which corresponds to the (7,6) nanotube. The relative intensity is ~1.6 (Table S1, Supplementary data), except for samples sonicated at 0 °C where relative intensity is doubled, showing that at this temperature there is more polymer aggregation in the solution. Fig. S3, shows the absorption spectra of Fig. 6a normalized to the (7,6) tubes intensity. The increasing of the sonication temperature results in higher selectivity toward small diameter SWNT, while the selectivity to the large diameter ones is decreasing. A deep microscopic understanding of this temperature dependent population variation would require a separate study.

The photoluminescence spectra of the nanotube samples are shown in Fig 6b and the normalized PL yield (Integrated PL/Absorption) of several tube chiralities are shown in the Fig. S4 of the Supplementary data. Individualized SWNTs are expected to have higher PL yields than bundles. The PL yield shows that the P3DDT individualize smaller diameter nanotubes better than larger ones. However, if the temperature changes there is no big variation of the Quantum Yield. Only the sample prepared at 0 °C is an exception, showing higher PL yield for small diameter tubes. With the exception of 0 °C, we conclude that the variation of temperature affects final concentration and higher selectivity of smaller diameter SWNTs, with similar quality of individualization.

To explain this variation at 0 °C, we propose that the polymer aggregation leads to inter-chain interaction between neighboring polymer-wrapped SWNTs, that could induce them to precipitate during the centrifugation due to their larger mass. This gives rise to a lower nanotube concentration in solution, but with a higher quality of individualization (higher PL yield). Also in this case, the formation of small wrapped-SWNT bundles can be clarified by performing a heating treatment (50 °C, 5 min) right after the sonication of the solution at 0 °C and before the ultracentrifugation process. Through this thermal treatment, we obtain 50% higher carbon nanotube content than the solutions that did not undergo any treatment, as shown in Fig. S5. This indicates that the post-preparation thermal treatment effectively destroys the polymer–polymer interaction in the small bundles, leaving high quality individually dispersed carbon nanotubes in the supernatant.

## 4. Conclusion

In conclusion, we have systematically investigated the effect of temperature toward s-SWNTs selectivity by P3DDT polymer wrapping. The interaction of the polymer chains with the SWNT wall stabilizes planarization of the polymer chains, which becomes very evident in super-clean samples where the excess polymer has been fully removed. These samples display different PL features depending on the state of aggregation of the polymer, despite of their identical absorption spectra. The shorter lifetime measured in super-clean samples prepared from the aggregated polymer solution, results from the formation of small bundles and opening of new non-radiative channels. The formation of these small bundles is confirmed by molecular dynamics simulations and by the fact that the interaction between tubes is suppressed when thermally treating the solution at 50 °C. Furthermore we demonstrate that increasing the temperature during sonication results in higher level of bundling and precipitation of SWNTs thus lowering the final concentration, and at the same time select better smaller diameter tubes. The optimal sonication temperature for obtaining dispersion of high concentration containing individualize s-SWNT is between 10 to 20 °C. Sonication at lower temperature (0 °C), gives rise to small bundles of polymer-wrapped SWNTs which can be destroyed upon annealing.

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## Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.carbon.2014.11.037.

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