

Electronic Supplementary Information

Hierarchical Functionalisation of Single-Wall Carbon Nanotubes with DNA Through Positively Charged Pyrene

Chia-Ling Chung,^a Christelle Gautier,^{a#} Stéphane Campidelli^a and Arianna Filoramo^{*a}

CEA, IRAMIS, SPEC, Laboratoire d'Electronique Moléculaire, F-91191 Gif sur Yvette,
France. Fax: +33 (0)1 69 08 66 40; Tel: +33 (0)1 69 08 86 35; E-mail:
arianna.filoramo@cea.fr

Present address: Université d'Angers, CNRS UMR6200, Institut des Sciences et
Technologies Moléculaires d'Angers Moltech Anjou, 2 Boulevard Lavoisier, 49045 Angers,
France

Preparation of SWNT/pyrene⁺ solution

1mg of trimethyl-(2-oxo-2-pyrene-1-yl-ethyl)-ammonium bromide and 1 mg of purified SWNTs were first sonicated in 10 ml of MilliQ water. The sonication was performed using a power of about 48W in 40 kHz Fisherbrand US bath of 2.8 L. The so obtained suspension was centrifugated at 5 000 g for 1h to remove the biggest insoluble aggregates (sediment D1) as shown in the first centrifugation step of Fig. S1. The supernatant Su1 containing SWNT/pyrene⁺ and the excess of free pyrene was transferred into a new tube and then centrifuged at 20 000 g for 1h (second centrifugation step in Fig. S1). This time supernatant Su2 was discarded and the sediment D2 was recovered. To ensure the complete removal of unlinked pyrene, D2 was mixed with 10ml of MilliQ water and sonicated at about 48W in 40 kHz Fisherbrand US bath of 2.8 L. This solution was then centrifuged at 20 000 g and the sediment recovered. This new sediment D3 was used to prepare SWNT/pyrene⁺ solution. The concentration of such solution was tuned by choosing the appropriate quantity of MilliQ water to disperse D3 and checked by UV-Vis-NIR absorption spectra.

More in details, to perform experiments with different DNA/SWNT molar ratios, we first estimated the relative concentrations of the nanotube solutions thanks to absorption spectroscopy (by the intensity of S₂₂ band of SWNT solution at 940 nm). This absorption value is compared to the one of a nanotube solution prepared with a known weight/solvent concentration.

This protocol is necessary since by the successive suspensions and centrifugations the final quantity of suspended nanotubes is lower than the initially weighted one. Then, to calculate the molar concentration it is approximated that the nanotubes are all around 500nm in length.

Obviously, this absorption method gives only approximated relative (i.e. from sample to sample) values for the nanotube concentrations but not their absolute values. However, this approach has the merit of fixing a point of comparison for all the experiments.

Once the relative concentration of nanotube solution is estimated, to obtain the desired DNA/SWNT molar ratio simple dilutions are performed before performing the reactions.

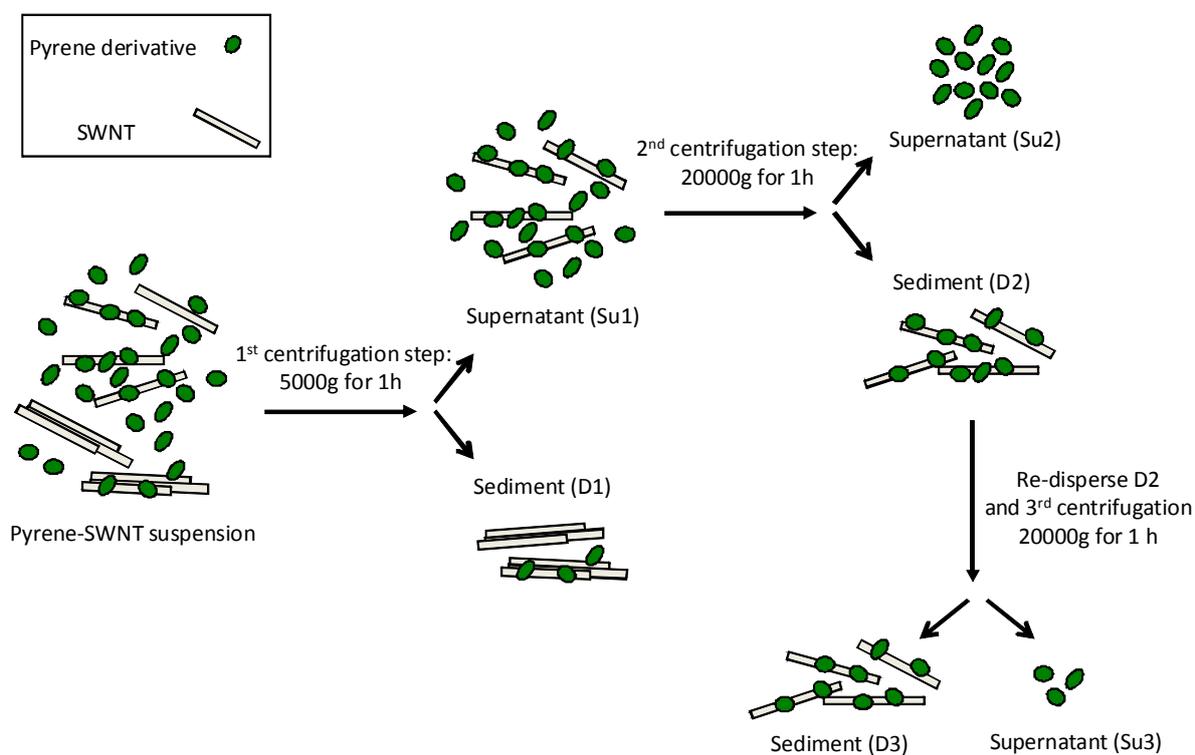


Fig. S1 Scheme of fabrication of SWNT/pyrene⁺ solution where the big aggregate of nanotubes and excess of free pyrene have been removed.

AFM, UV-Vis-NIR and Raman characterization of SWNT/pyrene⁺ hybrids

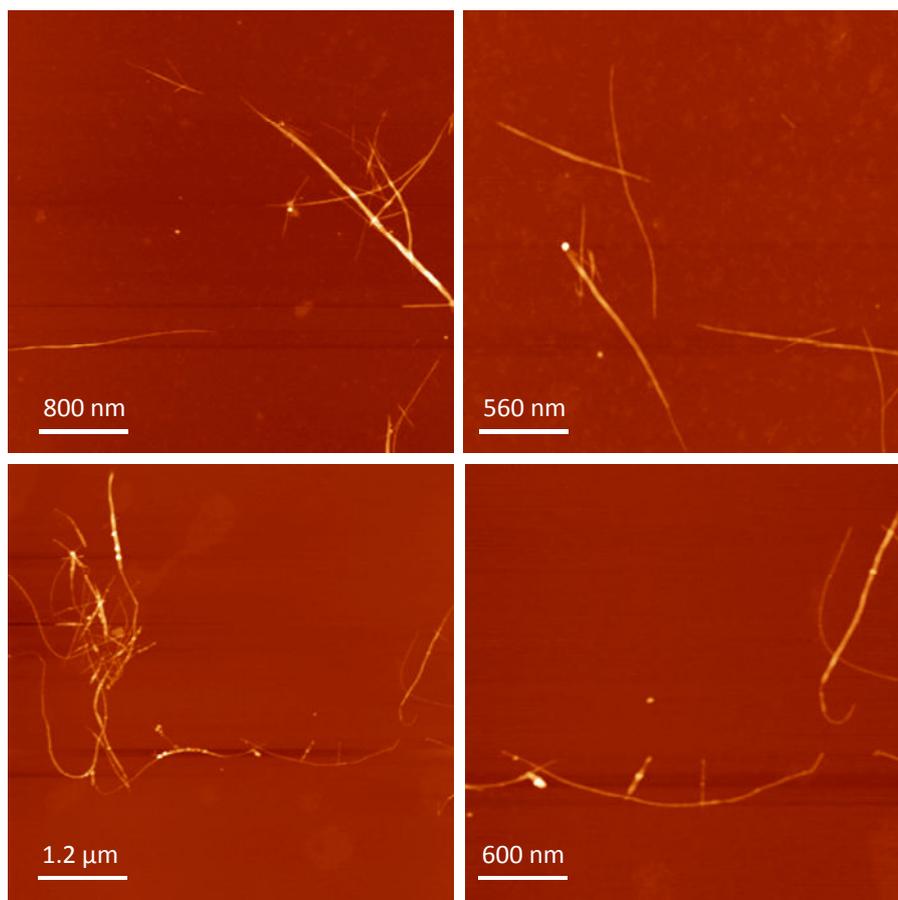


Fig. S2. AFM images of purified SWNTs (top images) SWNT/Pyrene⁺ (bottom images) deposited on mica. No significant difference can be observed with respect of bare SWNT.

Fig. S3 shows the absorption UV-Vis-NIR absorption spectra both of the pyrene⁺, SWNT/pyrene⁺ and SWNT solutions. The presence of the pyrene⁺ is clearly observable on the UV-Vis-NIR spectrum of the SWNT/pyrene⁺ between *ca.* 300 and 450 nm.

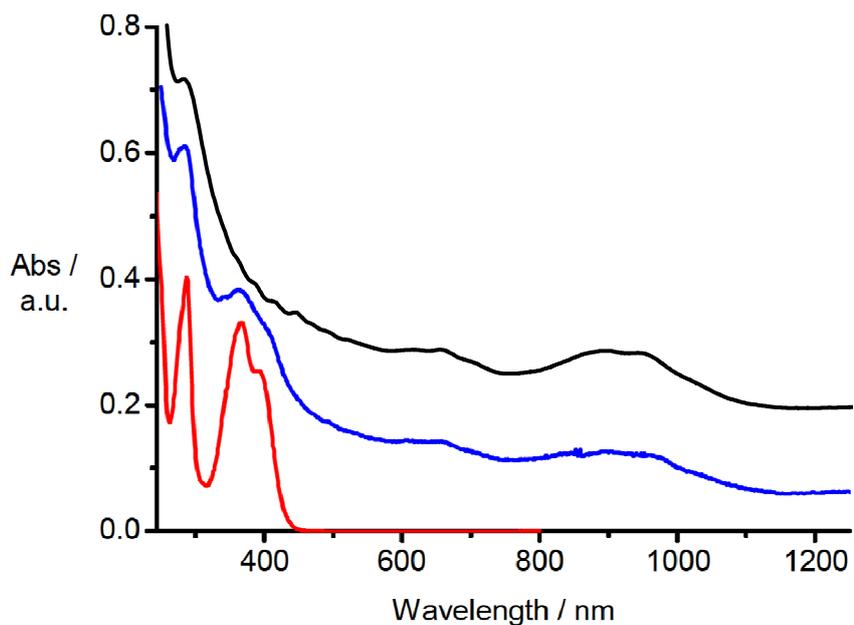


Fig. S3. UV-Vis-NIR spectra of pyrene⁺ (red line), SWNT/pyrene⁺ (blue line) and purified SWNTs (black line).

In Fig. S4 we report the Raman spectra of purified SWNTs and SWNT/pyrene⁺ using the 457.9 nm line of Argon-Krypton laser as excitation wavelength, blue and red curves respectively.

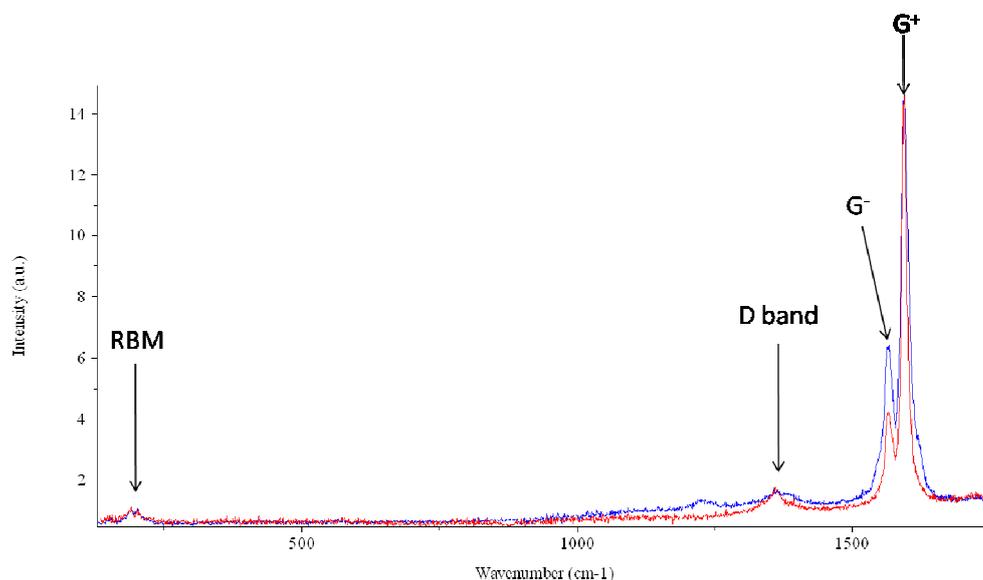


Fig. S4. Raman spectra of purified SWNTs (red curves) and SWNT/pyrene⁺ (blue curves) recorded with 457.9nm Ar-Kr line as excitation wavelength (2.7eV). The spectra have been normalized with respect to G⁺ value.

When compared with the spectrum of SWNT the Raman spectrum of SWNT/pyrene⁺ present some features related to the presence of pyrene. An additional band is recorded at about 1220-1248 cm⁻¹. We can also note a modification of nanotube D band profile with a contribution at about 1386 cm⁻¹. Moreover, shoulders around the G bands are present both on low and high energy sides (respectively around 1545 cm⁻¹ and 1625 cm⁻¹). These features can be attributed to the presence of adsorbed pyrene onto the SWNTs. In the literature, Raman signal of pyrene have been reported in these ranges.^{1,2} However, in the reported studies the measured or calculated spectra are generally richer in spectral features, the energy frequencies are slightly shifted and the observed peaks have smaller bandwidths. We attribute these changes to the fact that (i) our pyrene carries an ammonium ion that can shift or modify the vibrational properties of the molecule,² (ii) the interaction with the SWNTs surface can induce some broadening³ and (iii) the used resonance condition are different.^{1a}

Preparation of dsDNA

896 base pairs (bp) double stranded DNA (dsDNA) was utilized for DNA-SWNT hybrids. dsDNA fragments were synthesized from pBluescript SK⁺ utilizing Polymerase Chain Reaction (PCR). The PCR reaction was carried out in a 50 μ L reaction mixture with the following final composition: 1 \times PCR buffer (50 mM KCl and 20 mM Tris/HCl pH 8.4); 2.0 mM MgCl₂; 200 μ M dNTPs; 200 nM of each primer; 0.1 units of Taq polymerase; 0.2 ng pBSK⁺ template; and sterile water. The primers were purchased from Eurogentec S.A. and their sequences are presented in table S1. The PCR amplification reaction was performed in a Mastercycler gradient PCR system (Eppendorf) under the following conditions: denaturation at 94 °C for 3 min; followed by 30 cycles of: 94 °C for 30 s, 64.4 °C for 30 s, 72 °C for 1 min, concluding with a 5 min 72 °C extension step and hold at 16 °C. The synthesis scheme is shown in figure 12. After PCR was completed, the generation of the correct product was

confirmed through gel electrophoresis. The PCR fragments and Quick-Load 1kb DNA ladder (BioLabs) were run in a 1% agarose gel, with ethidium bromide (Sigma) staining, to ensure the correct length fragments were generated. The concentration of PCR fragments were evaluated by the absorption of UV-visible spectroscopy (PERKIN ELMER Lambda 900) at 260 nm wavelength.

Table S1: PCR primer sequences.

Size	Oligo	Sequence (5' – 3')
896 bp	896rv	GCA TTG GTA ACT GTC AGA CC
	896fw	CGG TAT CAG CTC ACT CAA AG

Deposition of SWNT/DNA hybrids for AFM imaging

Mica surface was pre-treated with poly-L-lysine as follows: a droplet of 0.0001% of poly-L-Lysine freshly diluted in milliQ water is deposited on freshly cleaved mica for 5min., and extensively rinsed with water and dried with a soft nitrogen flow. Then 10 μ l droplet of reaction solution was deposited onto this pre-treated mica surface and incubated at 35°C under wet atmosphere for 30 min. Finally the surface is rinsed with milliQ water and gently dried under nitrogen flow before performing AFM imaging.

References

- 1 (a) C. M. Jones and S. A. Asher, *J. Chem Phys.* 1988, **89**, 2649. (b) H. Shinohara, Y. Yamakita, K. Ohno, *J. Mol. Struct.* 1998, **442**, 221.
- 2 J. Neugebauer and E. J. Baerends, *J. Phys. Chem. A* 2005, **109**, 2100.
- 3 P. Leyton, J. S. Gomez-Jeria, S. Sanchez-Cortes, C. Domingo, and M. Campos-Vallette, *J. Phys. Chem. B* 2006, **110**, 6470.