Supplementary Information

Ordering phthalocyanine-C_{60} fullerene conjugates on individual carbon nanotubes

Giovanni Bottari,[a] David Olea,[b] Vicente López,[c] Cristina Gomez-Navarro,[b] Felix Zamora,*[b] Julio Gómez-Herrero*[b] and Tomás Torres*[a]

[a]Departamento de Química Orgánica (C-I), Universidad Autónoma de Madrid, Campus de Cantoblanco, 28049 Madrid, Spain, [b]Departamento de Física de la Materia Condensada (C-III), Universidad Autónoma de Madrid, Campus de Cantoblanco, 28049 Madrid, Spain, [c]Departamento de Química Inorgánica (C-VIII), Universidad Autónoma de Madrid, Campus de Cantoblanco, 28049 Madrid, Spain.

*E-mail: tomas.torres@uam.es, felix.zamora@uam.es, julio.gomez@uam.es

Contents

1. General remarks and methods

Abbreviations: Pc = phthalocyanine, HOPG = highly oriented pyrolytic graphite, AFM = atomic force microscopy, CVD = chemical vapour deposition, SWCNT = single-walled carbon nanotube, SWCNT/SiO_2 substrates = SWCNTs grown by catalyst-assisted CVD on silicon oxide substrates.

The synthesis of Pc-C_{60} dyad **1** and Pc **2** have been reported elsewhere.[1]

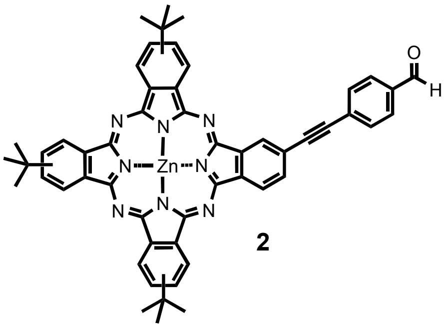
The microscopy studies were realised using an AFM from Nanotec Electrónica (www.nanotec.es) mounting an Olympus cantilever (nominal force constant of 0.75 N/m) operating in tapping mode at room temperature in ambient air conditions. The AFM topographic images obtained were processed using the WSxM program.[2]

The drop-casted SWCNT/SiO_2 substrates investigated by AFM were prepared by drop-casting onto the substrate a 20 µl-drop of a toluene solution of one of the organic compounds (*i.e.* Pc-C_{60} dyad **1**, Pc **2** or C_{60}), and then letting the drop dry at room temperature in ambient air conditions.

The dip-coated SWCNT/SiO_2 substrates investigated by AFM were prepared by dipping the substrate (dip-coating apparatus from Nanoinnova® with a constant speed of 4 cm/min) in a toluene solution of one of the organic compounds (*i.e.* Pc-C_{60} dyad **1**, Pc **2** or C_{60} fullerene), and then letting to dry at room temperature in ambient air conditions.

The SWCNT/SiO_2 substrates used in this study were prepared as follows: A silicon substrate was dipped for 10 sec in a 5,7 mM 2-propanol solution of $Fe(CO)_5$, then for 2 sec in *n*-hexane and finally dried with argon. The AFM analysis of the as-prepared substrate confirmed the formation of a homogeneous dispersion of iron particles (~4-5 nm in height). Thermal CVD synthesis of the SWCNTs onto the silica substrates was performed in a CVD system from Nanoinnova® at a constant pressure of 1.2 bar. Initially, a mixture of hydrogen (1500 cm^3/min) and argon (200 cm^3/min) was fluxed at 900 ºC for 20 min to ensure the complete reduction of the catalyst to the metallic form. Subsequently, ethylene (2 cm^3/min) was added for 5 min to the hydrogen/argon mixture which flows were maintained constant to the initial flow-rates. Finally, the flows of argon and ethylene were kept constant while reducing the hydrogen's flow (100 cm^3/min every 5 min) down to 200 cm^3/min and then the process stopped. Scanning electron microscope (JEOL JM6400) and AFM were used for the structural characterisation of the pristine SWCNT/SiO_2 substrates.

The minimized structure of Pc-C_{60} dyad **1** and ethynyl-benzaldehyde-substituted Pc **2** were obtained by using the HyperChem Professional v. 7.5 program with the MM^+ force field.



2

Fig. S1. Molecular structure of the aldehyde-substituted Pc **2**.

2. HyperChem minimized structures of Pc-C_{60} dyad 1 and ethynyl-benzaldehyde-substituted Pc 2.

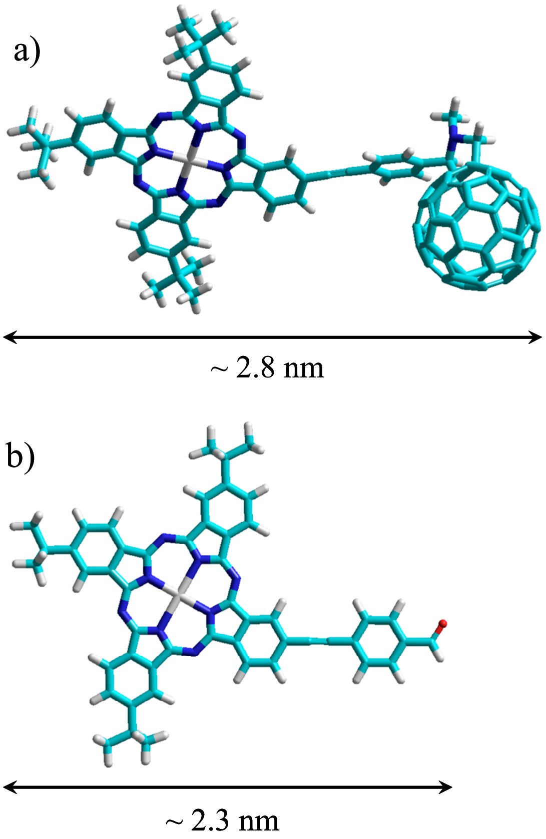


Fig. S2. Computer-simulated three-dimensional structures of a) Pc-C_{60} dyad **1** and b) ethynyl-benzaldehyde-substituted Pc **2** obtained by using the HyperChem program with the MM^+ force field. Carbon atoms are in light blue, nitrogen atoms are in dark blue, the zinc atoms are in grey and the oxygen atom is in red. The approximate length of the minimized structures of Pc-C_{60} dyad **1** and ethynyl-benzaldehyde-substituted Pc **2** is ~2.8 nm and ~2.3 nm respectively.

3. AFM studies on Pc-C_{60} dyad 1, Pc 2 and C_{60} fullerene.

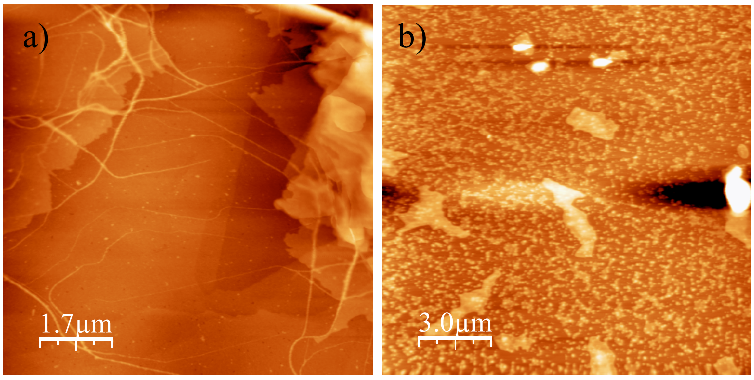


Fig. S3. AFM topographic images of a drop-casted toluene solution of Pc-C_{60} conjugate **1** ([**1**] = 10^{-5} M) on a) HOPG and b) a silicon oxide substrate.

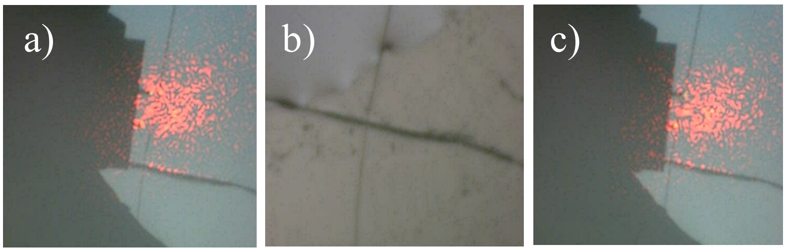


Fig. S4. Optical micrographs describing the three-step process used in order to re-encounter in the AFM experiments a particular SWCNT on a SWCNT/SiO_2 substrate after the drop-casting of a toluene solution of Pc-C_{60} dyad **1**. Two perpendicular lines were gently carved in the middle of a pristine SWCNT/SiO_2 substrate using a metal cutter. The pristine substrate was then scanned with a AFM tip in dynamic mode until a particular SWCNT ("reference" SWCNT) possessing an easy-to-distinguish shape was found. a) A video-connected optical microscope (Navitar tenX) placed vertically over the SWCNT/SiO_2 substrate was then used to optically record the position of the AFM cantilever when the "reference" SWCNT was scanned. b) The AFM cantilever was then removed from above the SWCNT/SiO_2 substrate and a toluene solution of dyad **1** drop-casted onto the SWCNT/SiO_2 substrate and let to evaporate (*N.B.* in the picture is possible to see the front of the evaporating droplet). Once the drop was completely evaporated, c) the AFM cantilever was re-positioned above the drop-casted SWCNT/SiO_2 substrate roughly at the same position where the "reference" SWCNT was scanned with the help of the video-connected optical microscope by using the two perpendicular lines carved onto the SWCNT/SiO_2 substrate as reference axes. Micrometer-square areas of the drop-casted SWCNT/SiO_2 substrate were then scanned using the AFM tip in dynamic mode until the "reference" SWCNT was re-encountered.

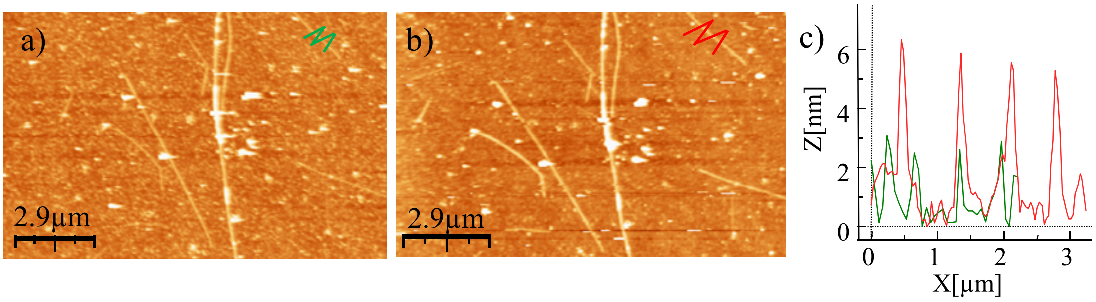


Fig. S5. AFM topographic images of the same SWCNT before a) and after b) drop-casting of Pc-C_{60} **1** on a SWCNT/SiO_2 substrate ([**1**] = 10^{-9} M). c) AFM topographic profiles of the zig-zag lines in a) (green) and b) (red).

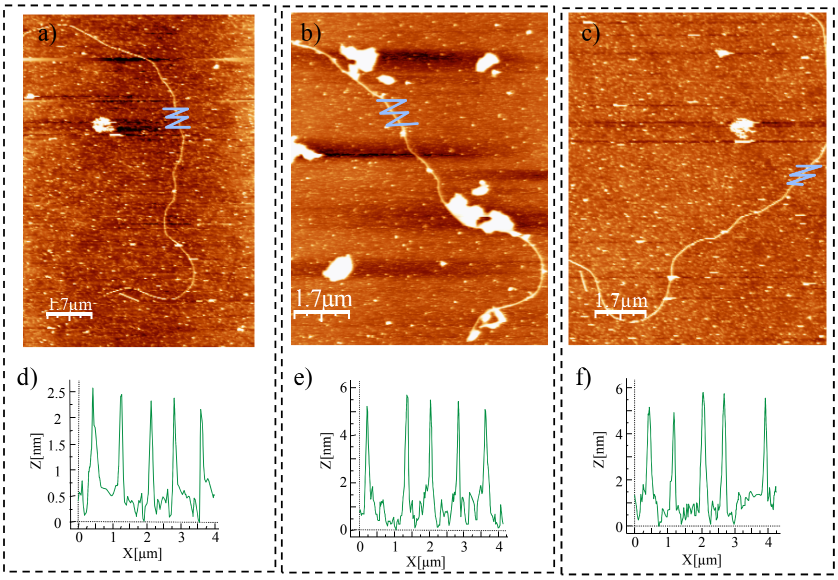


Fig. S6. AFM topographic images of the same micrometer-scale region of the SWCNT/SiO_2 substrate: a) Pristine substrate, b) after drop casting of a solution of Pc-C_{60} conjugate **1** ([**1**] = 10^{-7} M), c) after gently rinsing the drop-casted substrate with toluene. d) AFM topographic profiles of the zig-zag lines in a). e) AFM topographic profiles of the zig-zag lines in b). f) AFM topographic profiles of the zig-zag lines in c).

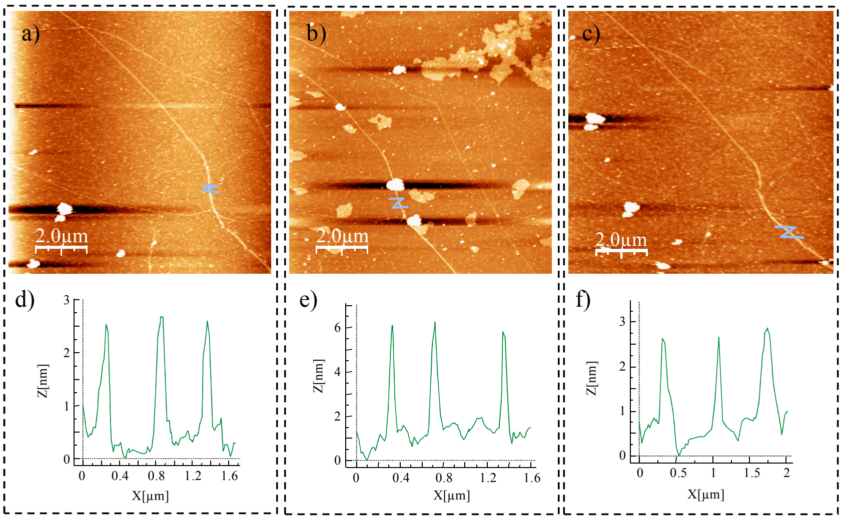


Fig. S7. AFM topographic images of the same micrometer-scale region of the SWCNT/SiO_2 substrate: a) Pristine substrate, b) after drop casting of a solution of Pc-C_{60} conjugate **1** ([**1**] = 10^{-7} M), c) after leaving the drop-casted substrate overnight in toluene. d) AFM topographic profiles of the zig-zag lines in a). e) AFM topographic profiles of the zig-zag lines in b). f) AFM topographic profiles of the zig-zag lines in c).

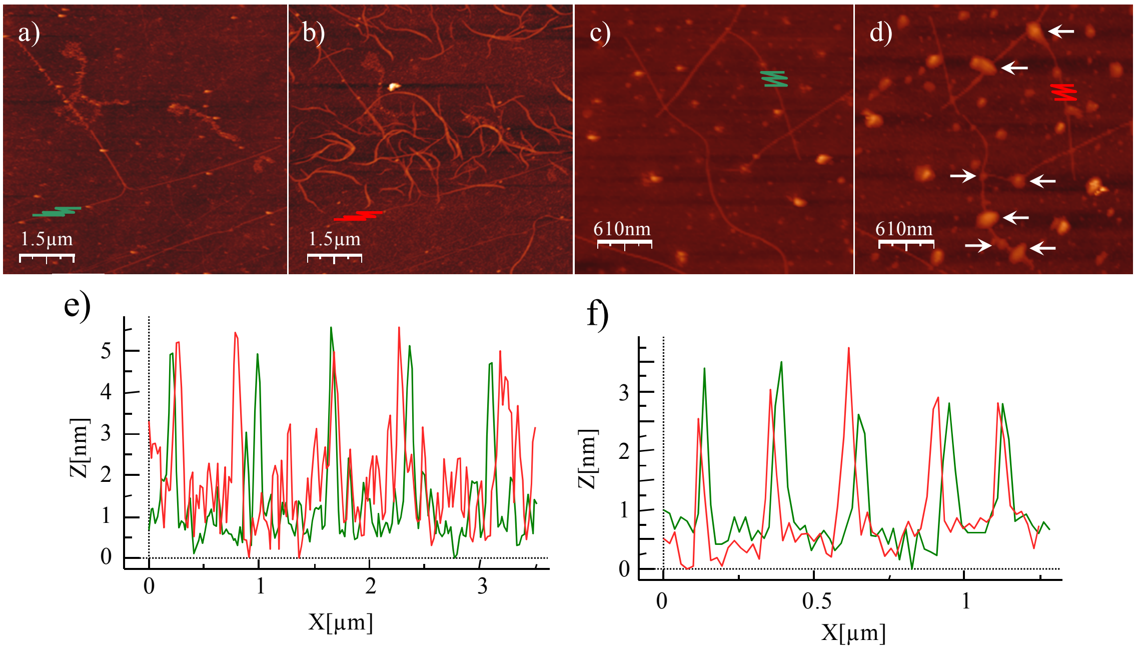


Fig. S8. AFM topographic images of a micrometer-scale region of a SWNT/SiO_2 substrate a,c) before and after the drop-casting of b) the aldehyde-substituted Pc **2** and d) C_{60}. e) AFM topographic profiles of the lines in a) (green) and b) (red). f) AFM topographic profiles of the lines in c) (green) and d) (red).

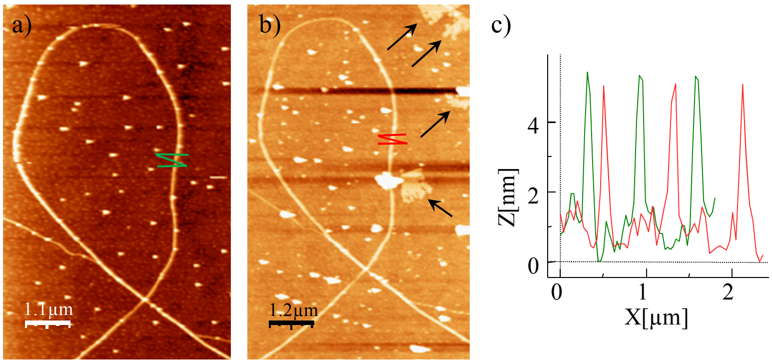


Fig. S9. AFM topographic images of the same SWCNT a) before and b) after drop-casting of a toluene solution of Pc-C_{60} conjugate **1** ([**1**] = 10^{-9} M) containing 10% of pyridine (w/w) on a SWCNT/SiO_2 substrate. c) AFM topographic profiles of the zig-zag lines in a) (green) and b) (red). The black arrows in Fig. S9b indicate the presence of some unstructured material.

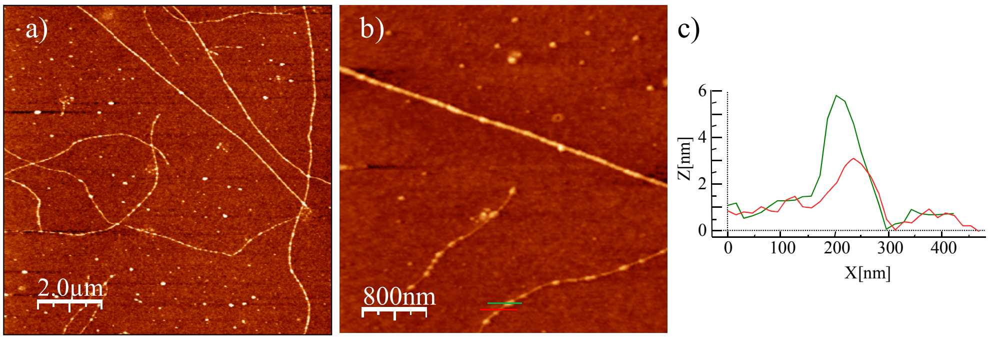
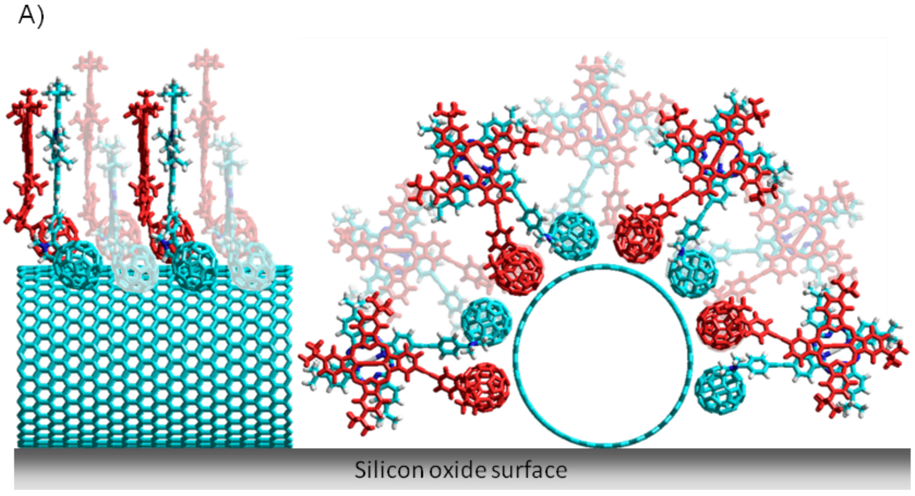


Fig. S10. a,b) AFM topographic images of SWCNT/SiO_2 substrates dip-coated one (a) and three (b) times in a toluene solution of the Pc-C_{60} dyad **1** ([**1**] = 10^{-5} M). c) AFM topographic profiles of the green and red lines in b).

The difference in the SWCNTs morphology observed between the drop-casted and the dip-coated samples can be probably due to the deposition technique employed. In the former case, the dyad solution is directly deposited on the SWCNT/SiO_2 substrate and the solvent allowed to evaporate slowly. This slow evaporation probably permits the dyad to uniformly organize around the carbon nanotube, if the adequate dyad concentration is used (*vide supra*), leading to the SWCNTs homogeneous supramolecular coating. On the contrary, when the sample is vertically immersed in the dyad solution, and subsequently retracted, the solvent is constantly mediating/disrupting the supramolecular interactions between the dyad and the SWCNT itself, leading to an equilibrium between dyads adsorbed on the SWCNT and dyads dissolved in solution, which ultimately lead to the formation of small supramolecular oligomers organized around the SWCNT.

4. Possible organization models for Pc-C_{60} dyad 1 around a SWCNT

When we had to propose a possible organization model for Pc-C_{60} dyad **1** around the SWCNT that could justify the observed increase in the SWCNTs' height upon the dyad casting, we mainly considered three possible supramolecular organization structures (see Fig. S11). The one that we have proposed in this communication in which the dyads are standing "upright" around the SWCNT, having the fullerene units pointing downwards towards the nanotube surface and the Pc macrocycles, which are π-π stacking between them, upwards (*i.e.* Fig. S11A), another one having the dyads standing "upright" around the SWCNT but having this time the fullerene units pointing upwards and the Pc macrocycles, also π-π stacking between them, downwards towards the nanotube surface (*i.e.* Fig. S11B), and a third one in which the dyads are lying flat around the SWCNT in a layered configuration (*i.e.* Fig. S11C).



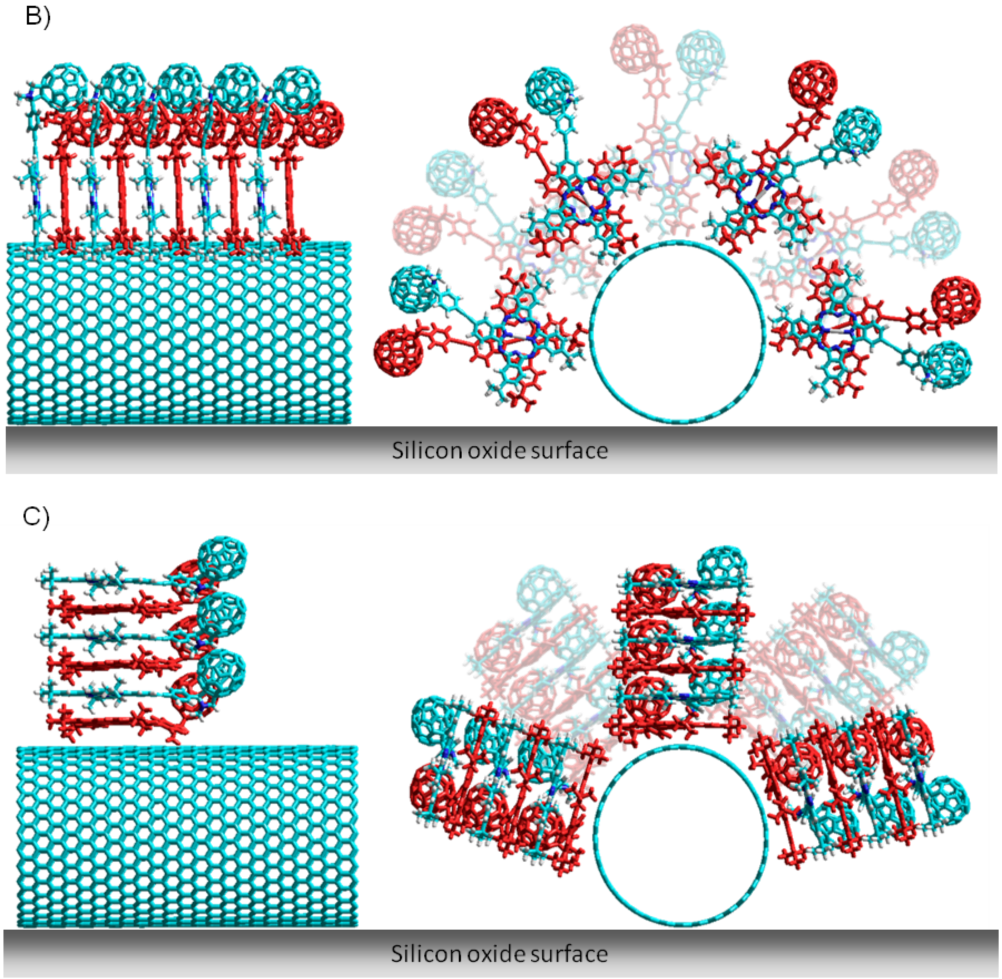


Fig. S11. The three possible organization models that we have considered for the Pc-C_{60}/SWCNT hydrid.

Among these three possible organization models proposed, we discarted the one of Fig. S11C since although few reports on the immobilization of Pcs onto the carbon nanotube sidewalls as a result of the π-π interaction between the conjugated surface of the nanotube and the aromatic Pc macrocycles have been reported (*J. Mater. Chem.,* 2002, **12**, 1636; *Langmuir,* 2007, **23**, 6424), in all these cases the formation of non-uniform nanoaggregates with diameters on the order of tens of nm has been observed on top of the carbon nanotubes as demonstrated by microscopy studies.

On the contrary, our experimental findings show that the increase in the SWCNTs' height upon the dyad casting is impressively uniform across the SWCNT and always ranging from 2.6 to 3.1 nm. The "layered" configuration of Figure 1C would not explain why the stacking of the Pc-C_{60} dyads on top of the SWCNT should terminate once the height of 2.6 - 3.1 nm has been reached, so that we have discarded this possible organization model.

We reckon that the SWCNTs' increase in height ranging from 2.6 to 3.1 nm, values extremely close to the length of the dyad from the Pc extremity to the C_{60} fullerene one (*i.e.* ~2.8 nm), is instead probably due to an "upright" arrangement of the dyad around the nanotube, thus leaving us with the two possible organization models depicted in Fig. S11A and B. As we mentioned in the text, among these two possibilities, the one of Fig. S11A appears to us to be the most probable one in light of the results obtained by the control experiments carried out (see main text).

5. Supplementary Information References

---

1 G. Bottari, D. Olea, C. Gómez-Navarro, F. Zamora, J. Gómez-Herrero and T. Torres, *Angew. Chem. Int. Ed.*, 2008, **47**, 2026.

2 I. Horcas, R. Fernanzed, J. M. Gomez-Rodriguez, J. Colchero, J. Gomez-Herrero and A. M. Baro, *Rev. Sci. Instrum.*, 2007, **78**, 013705/013701.