

## Supplementary Material

# **Evaluation of the electronic properties of perfluorophenyl functionalized quinolines and their hybrids with carbon nanostructures**

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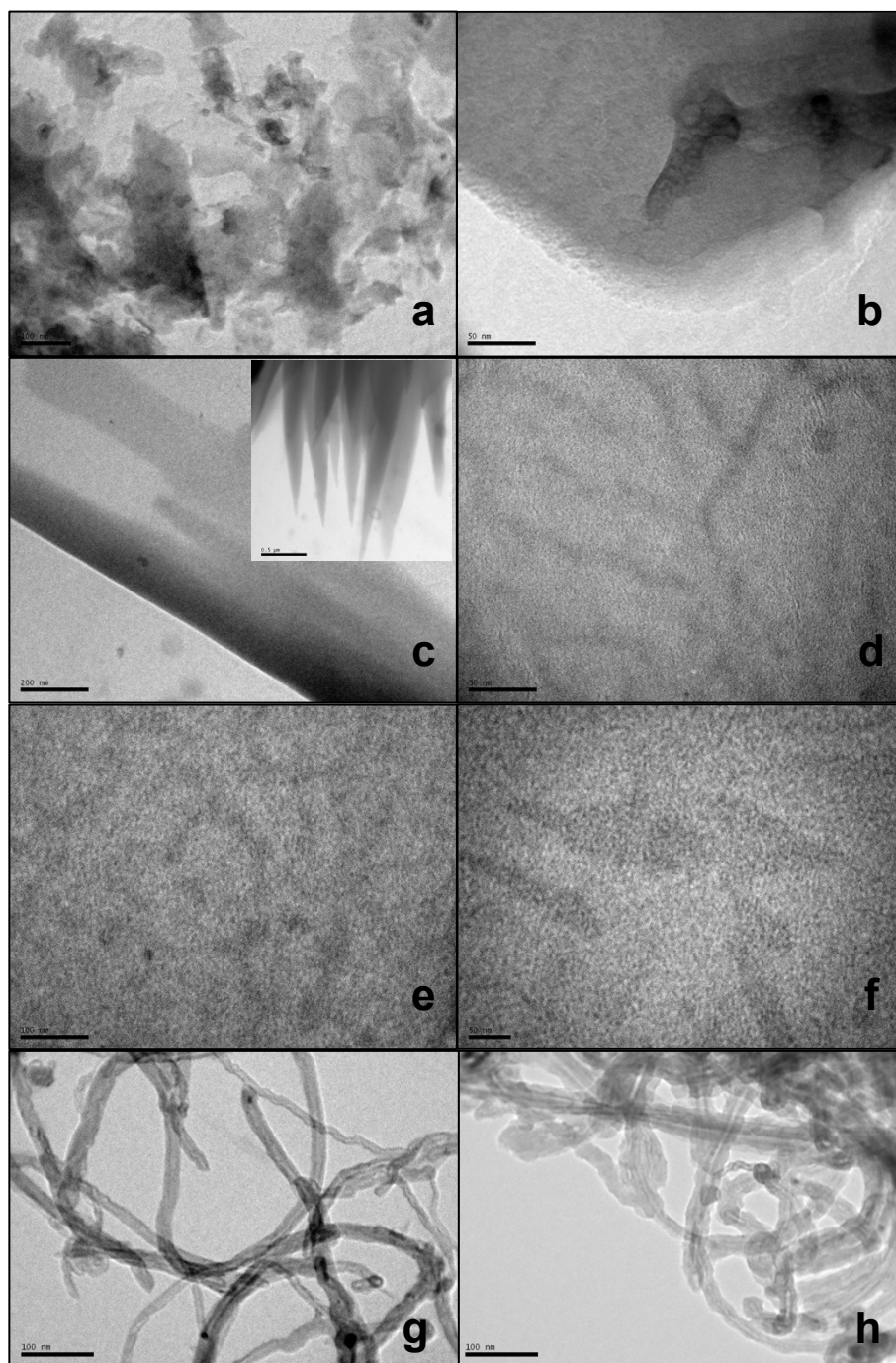
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## 1.1. Morphological Characterization

The morphology of thin films of the materials studied here was investigated by TEM microscopy (Figure SM1). The samples of the initial perfluorophenylquinolines bearing phenyl- (Ph-5FQ), dodecyloxybiphenyl- ( $C_{12}(\text{Ph})_2$ -5FQ) and phenol- (HOPh-5FQ) tails were prepared by using diluted solutions of THF while their respective hybrids with  $C_{60}$  were prepared by using toluene as solvent. The HOPh-5FQ-N-MWCNT hybrid was suspended in ethanol. The net Ph-5FQ (Figure SM1a) formed an inhomogeneous film whereas the  $C_{12}(\text{Ph})_2$ -5FQ (Figure SM1c) and the HOPh-5FQ (Figure SM1e) formed significantly more uniform films. Moreover, for the  $C_{12}(\text{Ph})_2$ -5FQ case, as can be seen in the inset of Figure SM1c needle like structures were observed at lower magnifications which are attributed to the organization ability of the dodecyloxy long alkyl tails that force the whole quinoline molecules to a better packing and dense crystallization.

All fullerene hybridized perfluorophenylquinoline molecules with  $C_{60}$  (Figures SM1b, d, f) produced uniform films in the nanometer scale. No formation of aggregates or  $C_{60}$  clusters was detected. In particular, the Ph-5FQ-N- $C_{60}$  and the  $C_{12}(\text{Ph})_2$ -5FQ-N- $C_{60}$  showed very finely dispersed nanophase separated domains in the order of few nanometers, whereas the HOPh-5FQ-N- $C_{60}$  showed slightly bigger domains. The TEM images Figure SM1g, SM1h present the pristine and the functionalized MWCNTs with the phenol perfluorophenylquinoline molecule, respectively. As can be seen from both images, the CNTs form bundles due to the drop-casting deposition of the samples on the TEM grid. In some distinct positions along the HOPh-5FQ-N-MWCNT film a very thin surrounding layer could be detected around the MWCNTs. However, no significant differentiations on CNTs outer wall were observed after functionalization, as expected, due to the small size of the HOPh-5FQ molecule compared to the dimensions of the MWCNTs, and the relevantly small functionalization degree.



**Figure SM1:** TEM images of (a) Ph-5FQ (scale bar 100nm), (b) Ph-5FQ-N-C<sub>60</sub> (scale bar 50nm), (c) C<sub>12</sub>(Ph)<sub>2</sub>-5FQ (scale bar 200nm), (d) C<sub>12</sub>(Ph)<sub>2</sub>-5FQ-N-C<sub>60</sub> (scale bar 50nm), (e) HOPh-5FQ (scale bar 100nm), (f) HOPh-5FQ-N-C<sub>60</sub> (scale bar 50nm), (g) pristine MWCNT (image from Nanothinx S.A., scale bar 100nm), (h) HOPh-5FQ-N-MWCNT (scale bar 100nm). The inset in (c), present lower magnifications of the sample with the scale bar corresponding to 0.5μm.

## 1.2. Effect of substrate preparation method on XPS results

The effect of oxygen plasma substrate treatment on the quality of the organic layer was investigated by XPS using the Ph-5FQ molecule as a case study. Plasma treated and a non-treated Si wafers were coated and analysed for comparison. The results from the XPS analysis are shown in table SM1.

The surface atomic ratios presented here have been corrected using a correction factor  $f$  to account for the fact that the signal originates from a thin layer.

An example of this calculation is shown here for the case of Ph-5FQ on plasma treated Si substrate:

$$\text{Correction factor} \quad f = [1 - \exp(-d/\lambda_1)] / [1 - \exp(-d/\lambda_2)] \quad (1)$$

$$\text{Corrected surface atomic ratio} \quad F:C = f \times (F:C)_m \quad (2)$$

Where  $d$  is the thickness of the film,  $\lambda_1$  and  $\lambda_2$  the inelastic mean free paths of F1s and C1s electrons through the polymer and their values are 2.4 nm and 3.3 nm respectively [SM1].

From the C1s/Si2p intensity ratio the film thickness for this sample is calculated to be  $d = 4 \pm 0.5$  nm and the measured and RSF weighted  $(F:C)_m = 1.115$ .

Using these values the correction factor is calculated to be  $f = 1.1$  and  $F:C = 0.125$

**Table SM1:** Surface atomic ratios\* measured by XPS on Ph-5FQ samples deposited on plasma treated and untreated Si wafers.

<b>Substrate Treatment of Si wafer</b>	<b>% At. F:C (nominal 0.185)</b>	<b>% At. N:F (nominal 0.2)</b>	<b>% At. N:C (nominal 0.037)</b>	<b>% At. F/Si</b>
<b>Non-treated</b>	0.004	0.15	0.006	0.06
<b>O- plasma treated</b>	0.125	0.25	0.031	0.19

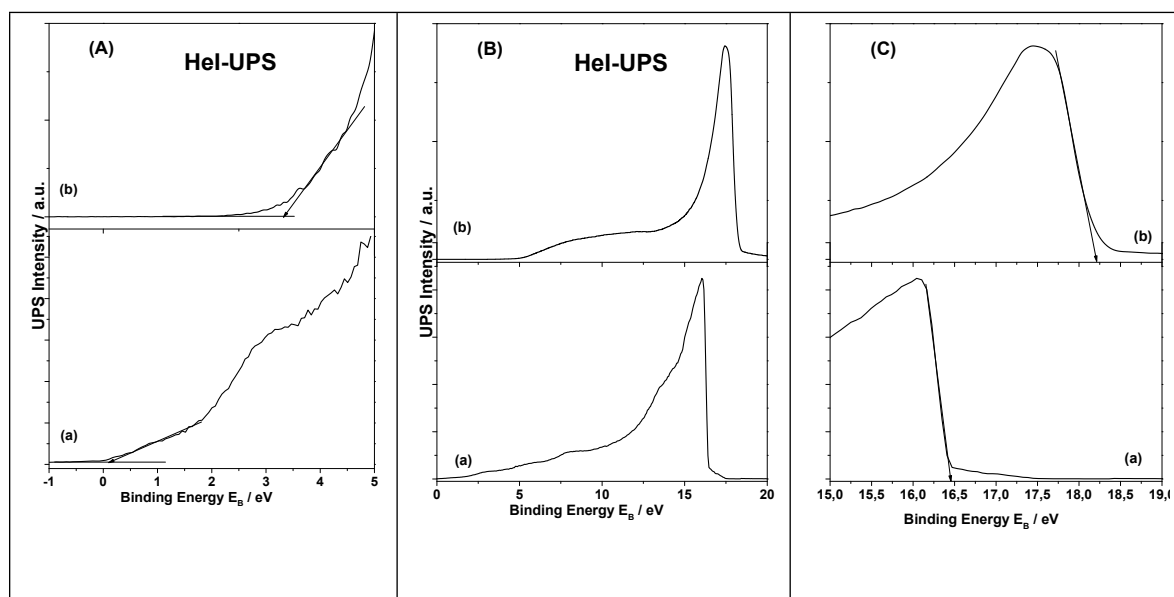
\*the ratios are corrected for thickness

Bare Si wafer after oxygen plasma treatment was measured with XPS and only traces of carbon were detected on the surface.

It can be seen that the F:Si surface atomic ratio is considerably lower on the untreated sample. This is due to the high intensity of the Si2p photo-peak (not shown) and indicates that the organic layer is not homogeneously distributed on the Si wafer. Furthermore, the F:C and N:C surface atomic ratios measured on the sample deposited on non-treated Si wafer are lower than the nominal values while the ratios on the treated sample are close to nominal. The reason for all the above observations is the considerable amount of surface carbon contamination on the untreated Si surface.

### 1.3. UPS spectra of C<sub>60</sub> and SWCNTs and cut off assignment on UPS spectra

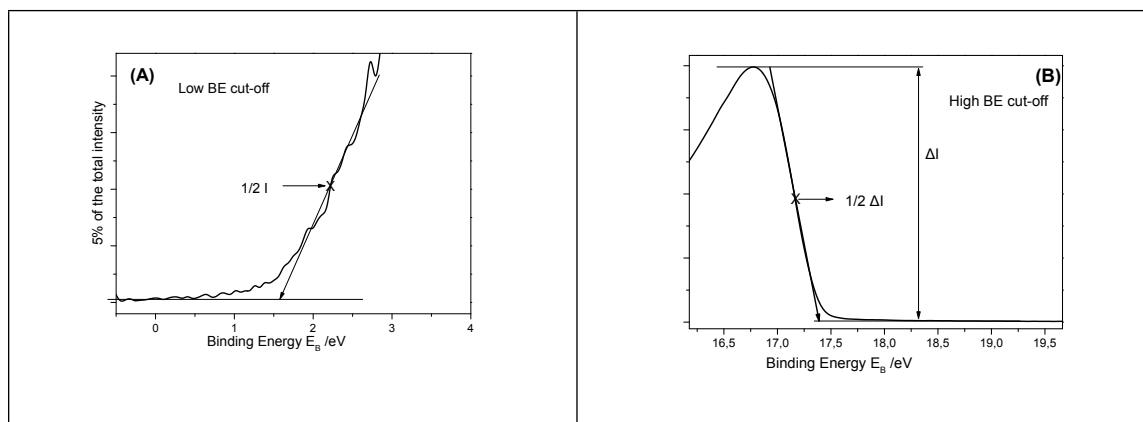
UPS spectra of C<sub>60</sub> and MW-CNTs deposited on ITO are shown below.



**Figure SM2:** UPS HeI spectra of (a) MWCNT (b) C<sub>60</sub> on ITO substrate. (A) the HOMO cut off, (B) the full spectrum and (C) the High BE cut off

The HOMO level (IP) for C<sub>60</sub> has been determined to be 6.1eV and for the CNTs 4.9 eV

The absolute energy value of the HOMO level (or Ionisation Potential, IP) is calculated by adding the energy values of the Work function and the HOMO cut off ( $E_v$ ) and is presented in Table 3 of the main article.



**Figure SM3:** A magnified area of UPS HeI low binding energy and (B) high binding energy cut off.

In order to measure the HOMO cut-off, the low binding energy region is magnified (zoomed in to 5% of the total intensity). The HOMO cut off is determined to be the intersection between the line drawn at the edge and the horizontal axis (Figure SM3A).

In the high binding energy region, the Work Function is determined in the same way without enlargement of the area (Figure SM3B).

The instrumental resolution (analyser broadening) has been determined to be 0.1 eV. Therefore, the high BE cut off positions are corrected by subtracting 0.1 eV from the values determined from the spectra while the true HOMO cut off positions are determined by adding 0.1 eV.

## 2. References

[SM1] S. Tanuma, C. J. Powell, D. R. Penn, Surf. Interface Anal. 21, (1993) 165