Supporting Information

Ultrafast Hole Transfer from (6,5) SWCNT to P3HT:PCBM Blend by Resonant Excitation

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In **Figure S1** we present the transient absorption spectra for the P3HT:PCBM and the P3HT:PCBM:SWCNT samples pump in the NIR region and probe in the visible spectral region. As showed in Figure S1 there is not spectral response of the P3HT:PCBM blend when pumped in the NIR region if not in presence of the (6,5) SWCNTs. Confirming that the possible occurrence of a two photon process is not influencing the observed behavior of the P3HT:PCBM:SWCNT sample.



Figure S1. Transient absorption spectra at 1ps of P3HT:PCBM:SWCNT (red line) and P3HT:PCBM (magenta line) pump at 870 nm and probe in the VIS region. Differential transmission dynamics at 600 nm for both samples.

In **Figure S2** we present the transient absorption spectra for the P3HT:PCBM and the P3HT:PCBM:SWCNT samples pump in the VIS region and for the P3HT:PCBM:SWCNT sample pump also in the NIR region and all probe in the visible spectral region. As we expected, when pump at 400 nm we observe the appearance of the P3HT main excitonic (around 600 nm) and vibronic peaks (around 520 nm and 560 nm respectively). As well as an intense PA signal usually ascribed to the P3HT polaron around 650 nm – 750 nm. Once we pump the P3HT:PCBM:SWCNT sample in the NIR region (selectively into the SWCNTs) we observed the typical spectrum from the P3HT, which is only possible due to a photoinduced charge transfer from the SWCNTs to the P3HT, leading to the appearance of the P3HT main excitonic and vibronic peaks. However, it is interesting to note that while the main excitonic peak remains in the same wavelength range, the vibronic peaks suffer from a small energy shift towards lower energies and some differences in their spectral shapes.



Figure S2. Transient absorption spectra of Structure 3 (red line), P3HT:PCBM blend (magenta line) pump at 400 nm and transient absorption spectra of Structure 3 (blue line) pump at 870 nm at 1 ps time delay.

In **Figure S3** the transient absorption spectra (a) and the kinetics (b) for P3HT (pink), P3HT:SWCNT (dark yellow) and SWCNT:P3HT (dark cyan) samples are presented. The samples were prepared following a bilayer configuration, with similar parameters to the ones used for structures 1 and 2. As we can observed from the transient absorption spectra, the spectral shape and the relative intensities of the vibronic and main peaks, for the tree different samples, differ as a consequence of the degree of interaction achieved by the materials despite the P3HT layer has the same characteristics for all of them.



Figure S3. Transient absorption spectra and dynamics for P3HT (pink line), P3HT:SWCNT (dark yellow) and SWCNT:P3HT (dark cyan) samples, pump at 400 nm.

In **Figure S4** we show the normalized transient absorption spectra of Structure 1 (green line) and Structure 2 (blue line) at 1 ps, pumping at 870 nm and probing in the visible. This measurement, with a clear PB related to P3HT in Structure 1, and less intense and evident peaks in Structure 2 indicates the occurrence of a charge transfer from (6,5) SWCNTs to P3HT in both structures but a smaller probability and intensity in the case of the Structure 2.



Figure S4. Normalized transient absorption spectra of Structure 1 (green line) and Structure 2 (blue line) at 1 ps, pumping at 870 nm and probe in the visible.

In **Figure S5** we show the intensity dependent kinetics for five chosen intensities representative of the behavior of the different samples studied. As observable the kinetics intensity varies linearly with the power values, showing that the processes observed in the (6,5) SWCNTs are not related to nonlinear effects and the conclusions reach for the high intensities measurements performed could be also inferred to lower pump intensities.



Figure S5. Intensity dependent kinetics of (6,5) SWCNTs present in the different blends studied.

As a counter experiment to better understand the different photophysical behaviour of the Structure 1 and 2, we measured one of the samples (P3HT:PCBM/SWCNT, Structure 2) changing the direction of the incident beam from the front to the forward of the sample. In

Figure S6 we show the normalized absorption spectrum, the kinetics and the normalized absorption spectra of the P3HT:PCBM/SWCNT (Structure 2) sample measured from front and back.

As we can observed from the measurements there is not difference in the transient absorption spectra when we measured the same sample from the front and from the opposite side. We believe that the differences in signal we observed in the transient absorption spectra are due to the fact that the two structures (SWCNT/P3HT:PCBM, Structure 1 and P3HT:PCBM/SWCNT, Structure 2), achieved a different degree of interpenetration of the SWCNTs into the P3HT:PCBM domain giving place to a larger intermixing for the Structure 1.



Figure S6. (a) Steady State Absorption Spectra of the P3HT:PCBM/SWCNT, Structure 2 (blue line) and the same Structure 2 but measured from the opposite side (bordeaux line).(b) Kinetics probed at 1025 nm upon selective excitation of the S_1 transition for the SWCNTs, at 870 nm of Structure 2 measured from the front (blue line) and the opposite side (bordeaux line). (c, d) Normalized transient absorption spectra of Structure 2 measured from the front (blue line) and the opposite side (bordeaux line) and the opposite side (bordeaux line).