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Supplementary Material

Ultrafast interface charge transfer dynamics on P3HT/MWCNT nanocomposites probed by resonant Auger spectroscopy

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Core Hole Clock Approach description

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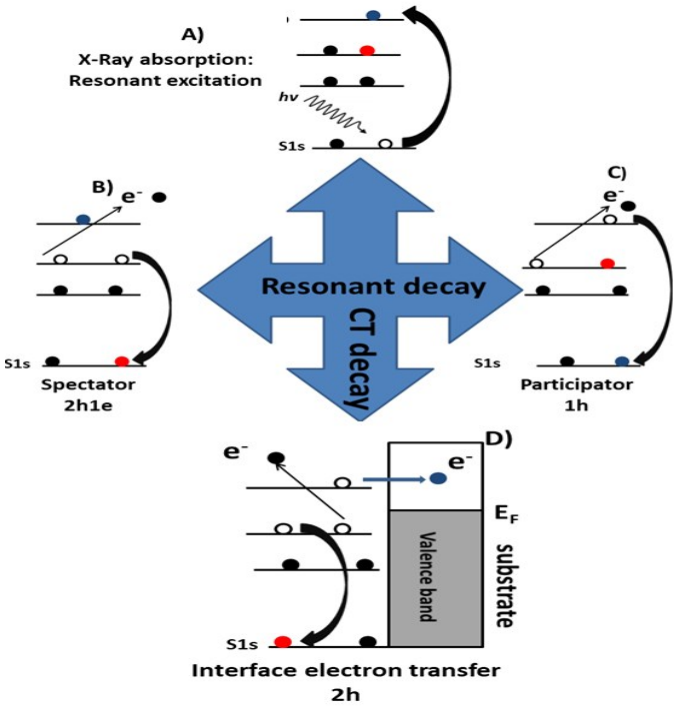
Table S1. Fitting parameters of the S-K edge NEXAFS spectrum of P3HT/Fe-MWCNT - 10 % film.

Fig. S2. S-*K* $L_{2,3}$ $L_{2,3}$ resonant Auger spectra deconvolution for: P3HT/Fe-MWCNT - 10 % film measured at three photon energies (2471.6, 2473.6 and 2474.4 eV). The spectator and normal Auger decay channels are leveled as SP1 (green), SP2 (blue) and NA (red), respectively. The Rydberg state is represented by wine color.

Core Hole Clock Approach description

Scheme 1 represents how the core-hole clock method works. Initially, the excitation of a core electron (S 1s) to unoccupied states is generated by absorption of X-ray photon leaving the system in a core hole excited state (scheme 1A). Resonant (scheme 1B and 1C) and non-resonant (scheme 1D) electron decay channels can be observed depending on whether the excited electron is still atomically localized during core hole lifetime or if it is delocalized out of the atom before core hole refilling. Two Resonant decay channels can be reached after core hole excitation: Participator decay where excited electron is involved in the core-hole decay resulting in one-hole final state (1h) and Spectator decay where the excited electron acts as spectator (does not participate in the decay process) resulting in a two hole and one electron final state (2h1e) The non-resonant decay channel consists of two holes (2h) final state reached when the electron is transferred out of the atom during core hole lifetime (Scheme 1D). The latter is energetically equivalent to normal Auger decay due to a direct core level photoionization process called charge transfer (CT-Auger) channel. The charge transfer time (τ_{CT}) is calculated from the branching ratio of the competing Resonant and non-Resonant Auger decay channels, assuming that the two processes are independent, and using the natural lifetime (τ_{CH}) of the core-excited state as an internal reference. [1] In the CHC approach depending on the data quality the accessible CT range is $0.1*\tau_{CH} \leq \tau_{CT} \leq 10*\tau_{CH}$. [2-4]

The Resonant (spectator SP) and Non-resonant (CT-Auger) decay channels are identified due to their behavior when the incident photon energy is tuned across the core excitation resonance. In spectator decay channels, the kinetic energy of the emitted electron shifts up when the photon energy is tuned across the resonance, while the CT-Auger contribution keeps a constant kinetic energy independent of the energy of the incident photon.



Scheme 1. Schematic representation of the core-hole clock method. (A) Core level resonant excitation into an unoccupied electronic state. (B) Spectator decay process with a 2h1e final state. (C) Participator decay process, 1h final state. (D) The electron is transferred to the substrate (or molecular environment), resulting in core-hole decay processes via a normal Auger decay with a 2h final state.

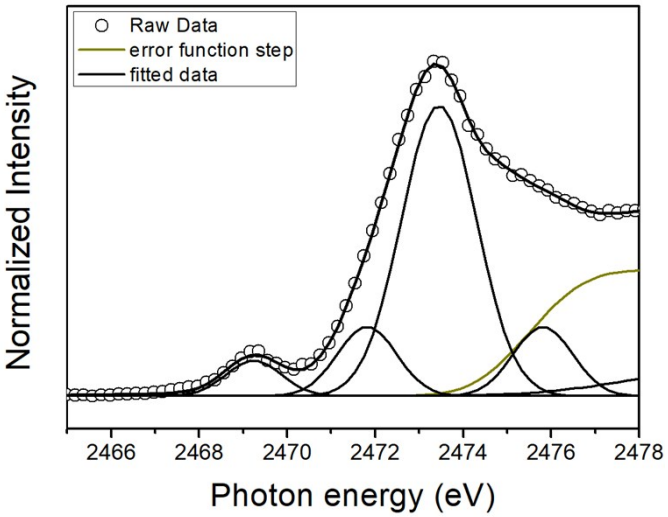


Fig. S1. Fitted NEXAFS spectrum of P3HT/Fe-MWCNT-10 %, film.

Table S1. S-K edge NEXAFS spectrum fitting parameters of P3HT/Fe-MWCNT - 10 % film.

Peak	P3HT/Fe-MWCNT -10 %		
	Photon energy (eV)	FWHM (eV)	Area (%)
1	2471.6	1.75	10
2	2473.6	1.59	51
3	2474.4	1.92	15

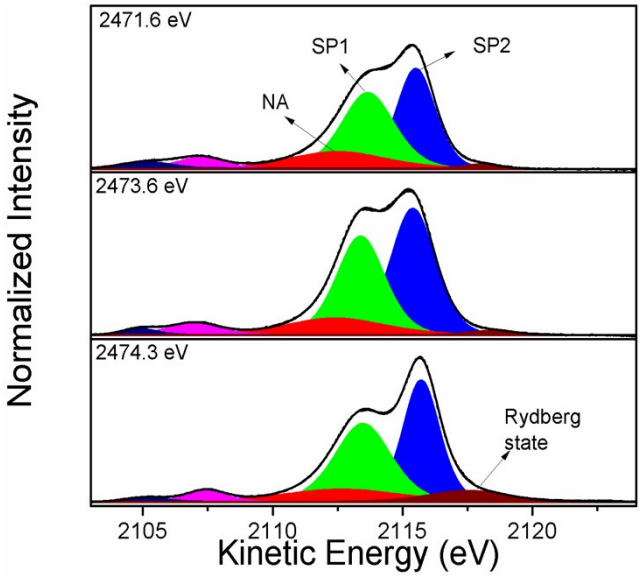


Fig. S2. S-*K* $L_{2,3}L_{2,3}$ resonant Auger spectra deconvolution for: P3HT/Fe-MWCNT - 10 % film measured at three photon energies (2471.6, 2473.6 and 2474.4 eV). The spectator and normal Auger decay channels are leveled as SP1 (green), SP2 (blue) and NA (red), respectively. The Rydberg state is represented by wine color.

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