Electronic Supplementary Information Section

Here we provide a concise description of the experimental setup used for time resolved NEXAFS measurements on free clusters. A more extensive description can be found in P. Piseri et. al, *J. El. Spectr. Rel. Phen.*, 2008, **166-167**, 28 (ref. [22] in the paper).

Experimental setup

To characterize clusters in the gas phase by X-ray absorption we developed a dedicated apparatus that was directly interfaced to the Gas Phase beamline of the Elettra synchrotron radiation facility in Trieste (Italy). The apparatus, consists of three differentially evacuated UHV chambers. The first chamber hosts the free jet expansion from the PMCS. The cluster source is equipped with an aerodynamic lens system focusing the clusters into a highly collimated molecular beam [K. Wegner et al., *J. Phys. D: Appl. Phys.*, 2006, **39**, R439]. Since the conductance of the focusing nozzle is low, at every working cycle of the pulsed source a time in the order of 100 ms is required for emptying completely the cluster source cavity. During the time the clusters spend in the cavity they can undergo cluster-cluster interactions leading to their further aggregation and rearrangement: thus the cluster size and structure evolve with increasing residence time in the source. As the clusters exit from the source cavity and get into the supersonic beam, their further evolution is quenched owing to the collision-less environment of the supersonic beam and to the further cooling occurring in the free jet expansion.

The central part of the cluster beam enters the second chamber of the apparatus through a skimmer. Here the ionic component of the cluster beam is deflected by an electrostatic field, while neutral clusters reach the interaction chamber through a small diaphragm, where they cross the soft x-ray photon beam coming from the GasPhase beamline. Differential pumping of the three chambers and the high collimation of the cluster beam ensure a pressure in the interaction chamber in the range of 10^{-9} mbar during source operation. Photo-emitted electrons from the clusters are collected by a channel electron multiplier connected to counting/timing electronics.

The detector signal is fed to a time to digital converter (TDC) triggered by the PMCS discharge, so that electron counts can be resolved by detection time within each cluster source pulse.

Time resolved measurements

To catch the full timing information relative to each event, without reduction in counting efficiency, a large dynamic range TDC system with multiple channels and multi-hit capability has been set up.

The system is based on a TDC chip from Acam GmbH (8 channels, resolution better than 100ps, <5 ns dead time) and implemented using the ATMD-GPX PCI board test system from the same manufacturer (see http://www.acam.de/fileadmin/Download/pdf/English/DB_AMGPX_e.pdf for details). The board is installed in a dedicated computer running on Linux OS and managed by an *ad hoc* developed server application that can be controlled via the PC's Ethernet interface in a client/server architecture. The TDC is set in a self-retriggering mode and coupled to a software counter indexing retriggering cycles; the server application stores the timing information relative to any possibly occurred stop event. This system allows high-resolution acquisition of a very large number of stop hits, in an indefinite time range after a single start. System testing proved its effectiveness for average counting rates up to 300 KHz, well above the regime encountered in present experiment.

The signals from the channel electron multiplier is fed to the one ot the TDC stop channels after discrimination (Ortec® CF8000, pulse rise time 1 ns, pulse width 10 ns). As previously said, the TDC start is triggered by a logic signal synchronous to the cluster source pulsed-valve opening. Thanks to this every count is recorded together with the delay time lapsed between the starting of the cluster source and the detection of the electron. This delay time correspons, once subtracted the short delay between the pulsed-valve opening and the source disccharge (~300 μs) and the small time of flight of the cluster from the source to the interaction region (~1 ms), to the residence time of the cluster inside of the source.

A second identical TDC system is synchronously triggered and used to measure complementary information with pulse-to-pulse resolution; these are namely: the ion count signals from the beam diagnostics detectors in the third chamber; photon and cluster beam fluxes, after

conversion of the photodiode and microbalance signals with volt-to-frequency converters (VFC); Ar ion counts from a gas-cell in the diagnostics chamber of the GasPhase beamline, for absolute photon flux determination. Separate files are recorded containing the full information relative to 30 s accumulation time; each file corresponds to one row in a log file where information read from the beamline control system is stored (storage ring parameters, photon energy, undulator's gaps, etc.).

Time resolved NEXAFS spectra are obtained by *a posteriori* analysis of the data recorded in the mass storage device of the PC. For each photon energy used, the electron counts collected by the TDC stop channel are selected within the desired intervals of residence time (in the present case 11 delay time intervals were chosen: 7 ms long, ranging from 15 to 82 ms). The resulting electron yields are then normalized to the measured x-ray photon flux and cluster flux.

Evaluation of the fraction of NEXAFS signal related to sp-bonds (X_{sp})

In order to study the evolution of the *sp*-bonds contents in the carbon NP as a function of delay time, we calculated, for each time resolved NEXAFS spectra in Figure 1B (see the paper), the fraction of NEXAFS signal related to *sp*-bonds: X_{sp}.
X_{sp} is defined as

$$X_{sp} = 100 \cdot \frac{A[\pi^*_{C \equiv C}]}{A[\pi^*_{C = C}] + A[\pi^*_{C \equiv C}]}$$

where $A[\pi^*_{C=C}]$ and $A[\pi^*_{C\equiv C}]$ are integral intensities from the spectra in Fig. 1B in two 0.6 eV wide energy windows centred at 284.7 eV and 285.9 eV, respectively (shaded regions in Fig. 1B). Thanks to this definition X_{sp} is the percentage of the integrated intensity of the NEXAFS spectra in the energy region relative to the π^* resonance for *sp* hybridization, in respect to the integrated intensity in the regions relative to both sp^2 and *sp* hybridizations.

In order to estimate the influence of the choice of the width of the energy windows used for evaluating $A[\pi^*_{C\equiv C}]$ and $A[\pi^*_{C=C}]$ on the obtained value of X_{sp}, we calculated X_{sp} also when using widths ranging from 0.1 to 1 eV. The small variations in the obtained values of X_{sp} account for the ordinate error bars in Figure 1C. Although the used definition of X_{sp} is only qualitative, it avoids the high arbitrariness involved in spectra fitting, especially concerning the choice of the fitting curve for the post edge region.

NEXAFS measurements on cluster assembled films

In order o measure the NEXAFS spectra of thin films obtained by depositing the carbon nanoparticles, a copper substrate holder can be inserted by a vacuum translator at the crossing point between the cluster and the photon beam. The substrate holder temperature can be varied during the deposition in the range 270 - 350 K. Furthermore, the substrate holder is connected to ground through a pico-amperometer, so that NEXAFS measurements on clusters assembled films can be easily performed also during cluster deposition and thus at conditions where the sample is continuously refreshed.