Supporting Information

π -Orbital Mediated Charge Transfer Channels in a Monolayer Gr-NiPc Heterointerface Unveiled by Soft X-Ray Electron Spectroscopies and DFT calculations

Andrea Casotto,^{ab} Giovanni Drera,^a Daniele Perilli,^c Sonia Freddi,^{ad} Stefania Pagliara,^a Michele Zanotti,^a Luca Schio,^e Alberto Verdini,^e Luca Floreano,^e Cristiana Di Valentin^c and Luigi Sangaletti^{*a}

^a I-LAMP and Dipartimento di Matematica e Fisica, Università Cattolica del Sacro Cuore, via della Garzetta 48, 25133 Brescia, Italy.

*Email: <u>luigi.sangaletti@unicatt.it</u>

^b Department of Chemistry and Biochemistry, University of Notre Dame, Notre Dame, IN 46556, USA.

c Dipartimento di Scienza dei Materiali, Università degli Studi di Milano-Bicocca, via R. Cozzi 55, 20125 Milano, Italy.

d Department of Chemistry, Division of Molecular Imaging and Photonics, KU Leuven, Celestijnenlaan 200F, 3001 Leuven, Belgium.

e CNR-IOM, Lab. TASC, s.s. 14 km 163.5, 34149 Trieste, Italy.

For resistance measurements upon gas exposure, the samples (along with commercial humidity and temperature sensors) were placed on a specifically designed circuit board, connected to a computer through a National Instrument shielded I/O connector block for 68-pin and a data acquisition board. The data acquisition script has been developed in the LabVIEW environment. The basic electronic circuit for chemiresistor gas sensing measurements consists of a load resistor (R_L) in series with the sample resistance (R_S), to which a constant voltage ($V_c = 5 V$) is applied. By monitoring the voltage V_{OUT} across the sample, the R_S is measured. Ammonia exposures have been carried out in laboratory air, at room temperature, and with a relative humidity RH = (50 ± 5)%. The recovery has been always achieved in air. Figure S1 shows the resistance change upon three exposures to ammonia for both the pristine sample and the Gr-NiPc interface.



Figure S1. Resistance variation to NH_3 exposure of pristine Gr (upper panel) and NiPc – functionalized Gr (lower panel), respectively. The NH_3 concentrations used during the exposure time (yellow shadowed bars) were 5.00, 11.15 and 1.21 ppm (left to right). The resistance increases after the interaction with a reducing gas, indicating the p-type nature of both the samples.

Figure S2 shows a schematics of elementary excitations following the absorption of an X-ray from a solid. Adding up to the direct core level photoemission (i), direct valence band photoemission (ii) and Auger emission (iii) channels, the resonant photoemission (ResPES) is a relaxation channel involved in a corevalence-valence excitation process. In order, a core electron is excited to an empty state after the interaction with a photon (iv) that is resonant with the transition (ensuring that this technique is element-specific); then the relaxation pathways could result in two distinct autoionization processes, with cross sections that are greater than the one related to direct photoemission (ii). If the photoexcited electron takes part in the relaxation (participator decay, (v)), thus leading to its emission and to the filling of the core-hole by a valence electron, the system is left in a +1 charged state. This state is degenerate with the final state of a direct valence band photoemission, but with a larger yield due to the higher ionization cross section at resonance with respect to the direct valence photoemission. On the other hand, in the spectator decay relaxation (vi), the excited electron does not take part in the relaxation, while two holes are formed in the valence state. One electron relaxes to the core-hole, the other one is emitted in an Auger-like process. This is known as resonant Auger emission, and leaves again a +1 charge in the system, this time due to a two-hole one-electron final state. As compared to the normal Auger decay, the resonant one yields a shift to higher kinetic energies of the corresponding spectator states due to the screening of the core-hole by the electron photoexcited to the empty (yet bound) state.

When charge transfer processes between coupled systems occur, the electron photoexcited to an empty state is allowed to be removed before the core-hole relaxation, leading to Auger decays with a +2 local charge in the final state. As a result of competition between core-hole decay and charge transfer, the intensity of the participator states decreases, as well as the energy shift between the spectator states and normal Auger. In a first approximation, the transfer rate can be established referring to the typical lifetime of core-holes (in the range of 4-6 fs for C 1s and N 1s) from a quantitative comparison of the quenching of the participator states in a coupled system with respect to an isolated one, e.g. a molecule in the gas phase or, eventually, in a weakly bound multilayer.¹



Figure S2. Scheme of the elementary excitation and decay processes related to ResPES. (i) direct core level photoemission, (ii) direct valence band photoemission, (iii) Auger emission following the creation of a core hole, (iv) excitation from a core level to an empty state above the Fermi level following an X-ray absorption (v) Resonant photoemission with participator decay (vi) Resonant Auger emission with spectator decay.

nr. of electrons removed (e)	Dirac Cone Shift (eV)
0	0
-0.25	+0.31
-0.5	+0.43
-1	+0.61

Table S1. Dirac Cone Shift (DCS) for the different p-type doped graphene systems. In the first column is shown the number of electrons removed from a cell containing 384 *e*. The DCS is calculated as the difference between the Dirac point (evaluated from the PDOS of Figure S1) and the Fermi level.



Figure S3. Total (TDOS) density of states for pristine (in black) and p-type doped (in blue, red, and green) Gr. The number of removed electrons is indicated in the legend (top left inset). The Fermi level is scaled to zero and is indicated by a dashed line.



Figure S4. Contour plots for the frontier molecular orbitals (FMOs) of NiPc in the gas-phase (the corresponding molecular orbital diagram is shown in Figure 2 of the main text). The symmetry along with the Ni d character is shown above each panel. The occupied orbitals are shown in the first row, empty orbitals are shown in the second row. The iso-surface value is set to $4 \times 10^{-3} e^{-} Å^{-3}$.



Figure S5: Total (TDOS) and Projected (PDOS) density of states for a-b) gas-phase and c-d) Gr supported NiPc (-0.25 *e*). In panel b) and d) is shown the PDOS on the Ni d states for the gas-phase and Gr supported case, respectively. The Fermi level is scaled to zero and is indicated by a dashed line.



Figure S6: Total (TDOS) and Projected (PDOS) density of states for Gr-NiPc at different p-doping. The Fermi level is scaled to zero and is indicated by a dashed line.

REFERENCES

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