Tuning the Electronic Structure of Graphene by Molecular Dopants: Impact of Substrate

A. Giannakopoulos[1‡], C. Christodoulou[2‡], G. Ligorio[2], M. Oehzelt[2,3], M. Timpel[2], J. Niederhausen[2], L. Pasquali[4,6,7], A. Giglia[4], K. Parvez[5], K. Müllen[5], D. Beljonne[1], N. Koch[2*] and M.V. Nardi[2]*

[1] Laboratory for Chemistry of Novel Materials, University of Mons, Place du Parc 20, 7000, Mons, Belgium
[1*] E-mail: david.beljonne@umons.ac.be
[2] Humboldt-Universität zu Berlin, Institut für Physik, Brook-Taylor-Straße 6, 12489 Berlin, Germany
[2*] E-mail: norbert.koch@physik.hu-berlin.de
[3] Helmholtz-Zentrum BERLIN für Materialen und Energie GmbH, Albert Einstein Strasse 16, 12489, Berlin, Germany
[4] IOM-CNR, Area Science Park, SS 14 Km, 163.5, 34149, Basovizza, Tieste, Italy
[5] Max Planck Institute für Polymerforschung, Ackermanweg 10, 55128, Mainz, Germany
[6] University of Modena e Reggio Emilia, Engineering Department. "E. Ferrari", Via Vigolese 905, 41125, Modena, Italy
[7] Department of Physics, University of Johannesburg, PO Box 524, Auckland Park, 2006, South Africa
[‡] These authors contributed equally to this work.

In 2004, K. Novoselov and A. Geim found a way to isolate a few micrometers of perfect single-atom layers from graphite using a scotch tape[1]. This new material is called *graphene*, and its discovery marks the commencement of 2D materials research. Theoretical predictions[2] and experimental measurements[3-5] indicate that *graphene* has exceptional properties. However, to turn these attractive properties into useful applications, its electronic structure needs to be properly fine-tuned[6]. This work aims at a theoretical investigation of the electronic properties of *graphene*, after interaction with organic conjugated molecules through a charge transfer mechanism.

First principle calculations were used to study the electronic structure at the interface between a strong molecular acceptor, *1,3,4,5,7,8-hexafluorotetracyano-napththoquinodimethane* (F_6TCNNQ) and a graphene layer supported on either an insulating or a metallic substrate. We find evidence for fundamentally different charge re-distribution mechanisms in the two ternary systems, as a consequence of the insulating versus metallic character of the substrates. While electron transfer occurs exclusively from graphene to F_6TCNNQ on the insulating support (p-doping of graphene), the metallic substrate electron reservoir induces an additional electron density flow to graphene decorated with the acceptor monolayer. Remarkably, graphene on the metallic substrate is n-doped, and even remains n-doped upon F_6TCNNQ deposition, in contrast to common expectations. A large increase in WF, ~1eV, was obtained in both cases and confirmed by UPS and XPS spectroscopic measurements. The effect was more pronounced on the metallic substrate because of the larger electrostatic potential drop associated with the longer-distance graphene-mediated metal-F_6TCNNQ electron transfer. We thus provide means to realize high work function surfaces for both p- and n-type doped graphene.

References

[1] K.S. Novoselov et al., Science 306, (2004) 666-669
[2] P. Wallace, Phys. Rev. 71, (1947) 622
[3] I.W. Frank et al., J. Vac. Sci. Technol. A 25, (2007) 2558
[4] H.K. Chae et al., Nature 427, (2004) 523-527
[5] M.D. Stoller et al., Nano Lett. 8, (2008) 3498-3502
[6] C. Christodoulou et al., J. Phys. Chem. C 118, (2014) 4784-4790
[7] The authors acknowledge funding from the 7th Marie Curie ITN GENIUS program. Research in Mons is also supported by the OPTI2MAT Excellence Program of Région Wallone and FNRS/FRFC. Research in Berlin was further supported by the DGF (SFB951) and the Helmholtz Energy Alliance "Hybrid Photovoltaics".

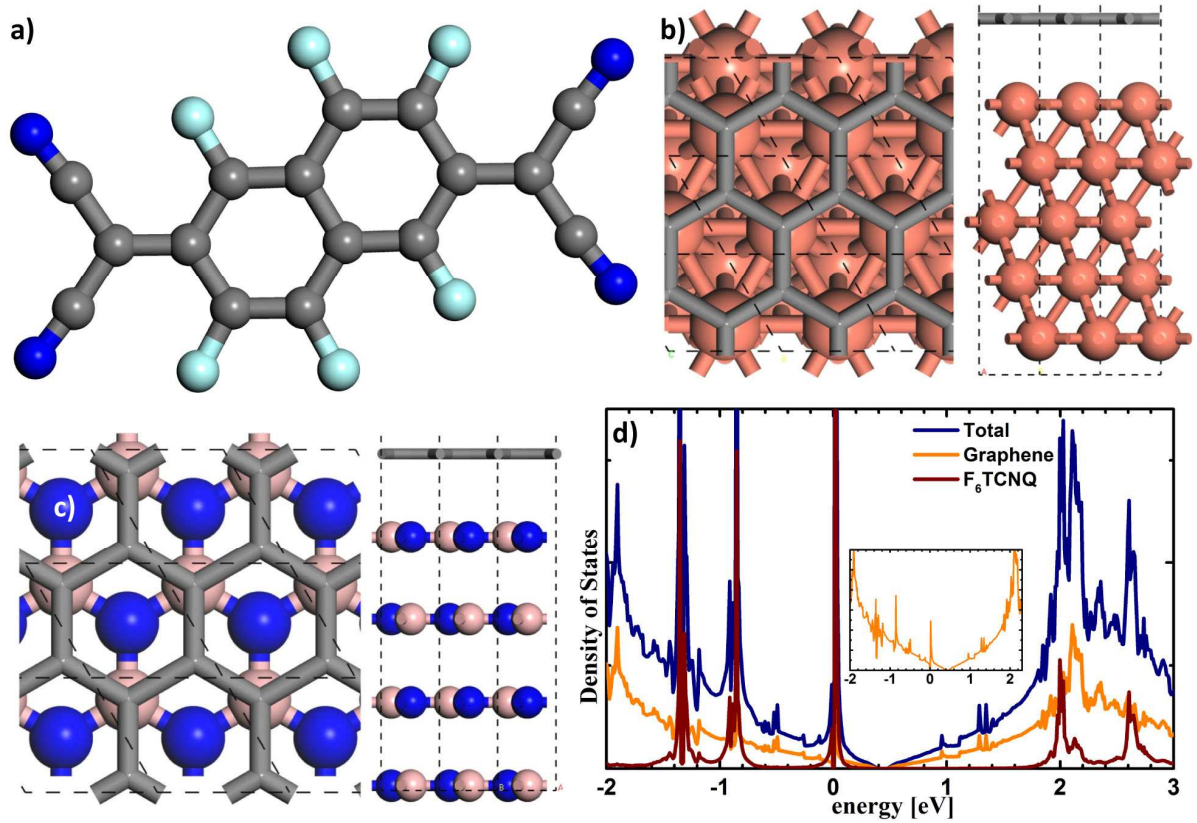

Figure 1: a) F_6TCNNQ molecule, Carbon [C] atoms in grey, Nitrogen [N] atoms in blue, Fluorine [F] atoms in cyan blue. b) Graphene-on-copper(111) unitcell (top and side views). c) Graphene-on-hexagonal Boron-Nitride unitcell (top and side views). d) Partial density of State (PDOS) plot for F_6TCNNQ on graphene-in-vacuum.