PhD thesis available on:

Fullerene-based molecular materials for (opto)electronic devices & lithium batteries

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Discovered only two decades ago, fullerene molecules, and in particular C_{60}, have become a standard system to explore molecular matter thanks to their extremely rich behaviour which includes order-disorder transitions, molecular magnetism, and superconductivity.
Fullerene-based materials have interesting charge conduction properties that are very promising for opto-electronic applications,[1] as well as ionic mobility higher than standard ionic conductors,[2,3] suggesting a possible application as electrode materials in alkali-ion batteries.[4,5] The mechanism beyond transport phenomena is still debated, and in particular the observation of metallic-like behaviour and superconductivity is surprising, since most other organic materials behave as semiconductors.

Goals Investigate electron and lithium transport in different fullerene systems and correlate it with the material's structure and the molecular dynamics and degrees of freedom.[6]

Materials

1) Fullerene derivatives (fullerenes functionalized with molecular groups covalently attached to it) such as hydrogenated fullerenes H_xC_{60}, that allow higher Li-ion storage density than C_{60};
2) Binary compounds of fullerenes with electron-donor or electron-acceptor molecules which may act as spacer or induce a particular crystal structure;[7,8,9]
3) Endohedral fullerides, where an atom or molecular group is trapped inside the hollow fullerene cage, that possess interesting dielectric/metallic properties intertwined with the motion of the encapsulated species,[10,11] and in some cases much higher mobility than C_{60} (4 orders of magnitude[12] in $Li@C_{60}$).

Methods Thermodynamic, structural and electric characterizations will be carried out. Lithium mobility studies will be performed to identify the most suited materials for Li-ion batteries and develop experimental recipes to improve the lithium storage efficiency. Mobility and molecular dynamics measurements, as well as monitoring of order-disorder transitions, will be carried out using *broadband dielectric spectroscopy* as a function of temperature, pressure and frequency. This characterization will enable to design strategies to increase the material's performance in devices and for lithium storage. Thin films of the materials will be studied optically and by AFM microscopy and X-ray diffraction. *Thin-film transistors* (TFT)[13] and photovoltaic or light-emitting devices will be fabricated and characterized. In transistors, evidence for ambipolar (electron- and hole-) transport will be sought, and information on both the ionic (Li^+) and charge mobility, and on the density of states[14] in the gap, will be extracted.

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[6] Electronic conduction is strongly dependent on molecular arrangement and dynamics, besides on the filling of molecular orbitals: in solid C_{60} the molecules rotate very rapidly at room temperature, while upon cooling a phase transition to an orientationally ordered phase takes place across which the conductivity raises by more than one order of magnitude [E. A. Katz *et al*., **J. Appl. Phys.** 93, 3401 (2003)]. In alkali-intercalated A_nC_{60}, where charge-transfer from the alkali species occurs, the conductivity strongly depends on the stoichiometry: stable compounds form for n=1,3,4 and 6; while the first two display metallic behaviour, the latter are insulating.
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