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Electronic Structure of Organic Semiconductors

Polymers and small molecules

Luís Alcácer

Chapter 1

Introduction

Organic semiconductors, both polymers and small molecules, are a class of materials, which are emerging as the basis for a new technological paradigm, aiming at ultra low-cost, lightweight and flexible electronic devices for displays, circuits, solar cells and sensors, which can be printed on anything and placed anywhere.

The first studies on the optoelectronic properties of organic materials can be traced to the beginning of the 20th century as, for example, with the report of the photoelectric effect in anthracene [1]. However, the first report on an organic material with a significant conductivity (10^{-3} to 1 $\text{ohm}^{-1}\,\text{cm}^{-1}$) was due to Akamatu, Inokuchi and Matsunaga in 1954 for a perylene–bromine complex [2].

Real interest in the electrical properties of organic materials was triggered by a seminal paper of William Little, from Stanford University in 1964, who proposed a model to synthesize a room temperature organic superconductor [3]. This led, a few years later, to the new field of research of condensed matter physics in one dimension entitled *one-dimensional conductors*, or in plain words, *organic metals and semiconductors*. In these organic materials, when crystalline, the conductivity is extremely anisotropic, being high along one direction and orders of magnitude lower in perpendicular directions. This is possible in two instances: (i) in solids in which flat organic molecules, with a high degree of conjugation, are stacked on top of each other and, through π–π intermolecular interactions, electrons can travel along the stacking axis, and (ii) in conjugated polymer chains, in which alternating double and single bonds enable the overlap of p orbitals that create a system of delocalized π-orbitals allowing electrons to travel along the polymer chain.

In the late 1960s and early 1970s, several organic semiconductors, particularly in the form of charge transfer salts, were reported and the subject became of great interest, especially among physicists, aiming at high temperature organic superconductivity. In 1979, the first organic superconductor was synthesized by Klaus Bechgaard and was found to have a transition temperature of $T_c = 1.1$ K under an external pressure of 6.5 kbar [4]. This was not a high temperature superconductor

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but still gave rise to an intense and exciting search for new organic superconductors, and, as a consequence, many new organic conductors and some superconductors were synthesized and thoroughly studied.

Little's idea was based on a conjugated polymer type chain, and such a polymer should be a metal or a semiconductor, depending on the crystal structure. Polyacetylene was the simplest conjugated polymer chain and had been under investigation for some time [5], but it only exhibited high conductivity through heavy doping[1] [6]. This serendipitous discovery led to intense research on conducting polymers, which were the subject of the 2000 Nobel Prize in Chemistry awarded to Alan Heeger, Alan MacDiarmid and Hideki Shirakawa. A new technology emerged and is now the important field of organic semiconductors and organic electronics.

The design and synthesis of novel organic semiconductors based on the chemical intuition of synthetic chemists has had significant success in the past, but it is ultimately time-consuming due to the nearly limitless number of promising candidate materials. A more rational and more efficient approach consists of the combination of chemical intuition with the application of predictive computational design based on quantum chemical calculations. The use of such methods to predict the electronic properties offers significant advantages: it is inherently more time and cost-efficient; and it can greatly reduce the number of potential targets for experimental synthesis. An important domain where theory can specifically contribute is the comprehensive prediction of how different chemical functional groups modulate the electronic and optical properties in order to ultimately guide the organic synthesis.

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[1] For a long time, polyacetylene was thought to be a metal, which led researchers to purify it as much as possible, but, contrary to what was expected, the higher the degree of purity, the more insulating it would become. In a happy chance of serendipity, a student from Professor Shirakawa's group polymerised acetylene with a thousand times more catalyst than usually and obtained a conducting and golden film on the walls of the reactor. Later on, Shirakawa collaborated with Alan J Heeger and Alan MacDiarmid, and in 1976, they discovered that the oxidation of polyacetylene with iodine increased the conductivity by a factor of 10^8.