Molecular Biradicals: Towards Functional Nano-Scale Biradicals

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Molecular radicals and biradicals have been largely understood in chemistry as reactive intermediates in chemical reactions (i.e., organic and electrochemical processes, polymerization initiators, etc.). Many examples however exist in the recent literature concerning molecular stable radical units used as the basic components of organic-based magnetic materials. A requirement for these substrates to be active as magnets is ferromagnetic coupling between the basic molecules bearing the unpaired electrons: through space magnetic exchange is the most common mechanism of spin alignment giving rise to the ferromagnetic materials. These exchange interactions are usually small and a strong temperature dependence of the macroscopic magnetic property is observed. Often low temperature magnets are obtained and only a few of these are still active at room temperature. Another exigent quest for magnetic molecules is the ability to combine electron conduction and spin transport, two requirements needed for spintronics. For the advance of this field, it would be necessary to conceive relative large conjugated radicals capable of stabilizing the injected charge and facilitate electron transport. At this point molecularly stable biradicals with aligned spins, or triplets, might offer reliable alternatives for spintronic substrates, since the net spin of the triplet resides in large conjugated units very favourable for electron migration.

Figure 1. Triplet species residing either in the ground (blue) or in very low lying energy excited states (red).

Figure 2. Closed and open shell forms of the singlet ground state in equilibrium with the triplet of the viologens.

In this keynote, a few concepts and examples of large-size conjugated molecules having an active triplet species either as the ground electronic state or as the lowest lying energy excited state are described together with their thermal interconversion. In Figure 1, the molecular structures of these examples are depicted. In the first two cases, based on quinoidal viologens and oligothiophenes, the triplet states are the first lowest lying excited states and are in thermal equilibrium with the singlet biradical ground electronic states. The thermal
modulation between the low and high spin states allows the thermal switching between an “on” and an “off” magnetic state. The concepts exploited in these two cases are the pro-aromatic character of the quinoidal platforms for which, given a certain number of pro-aromatic units, the system “prefers” to break a double bond generating two unpaired electrons being the promoters of the magnetically active triplets such as depicted in Figure 2. The third example represents the opposite situation.

![Figure 2. Bipolaron to polaron-pair balance in long oligothiophene dications.](image)

In the last example of this keynote, our interest turns to the charge carrier determination in heavily doped (i.e., oxidized) polythiophene. Here it will present new Raman spectroscopic data in a twelve-thiophene model dication and that are in line with the existence of well separated two polarons instead of a confined bipolaron, or polaron-pair. In addition, it is proved that these are not two independent polarons or radical cations but their spins are coupled giving rise to a singlet biradical and, much more interesting, to a triplet biradical with exploitable magnetic properties. These Raman data are extended to the case of the conducting polythiophene where the possible presence of thermal magnetism would confer to the polymer an additional property complementing its electrical conductivity.

In summary, four examples of long conjugated molecules having a biradical structure acting on it have been described based on their spectroscopic properties, mainly Raman vibrational spectroscopy. The search of these species supposes the description of nano-sized spin bearing molecules which can act as building blocks for nano-structures with potential applications in a variety of multifunctional devices, single molecules devices among many others.

References:


