Polyconjugation for Organic Electronics

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Since the discovery of the semiconducting properties of π-conjugated organic oligomers and polymers, many efforts have been devoted to generating structural features that bring about new and outstanding properties for optoelectronics, spintronics and magnetic devices, non-linear optics, or singlet fission processes. In this sense, the play between the resonance and π-electron delocalization phenomena in π-conjugated organic materials is the origin of their semiconducting behavior. For this reason, establishing not only the electron delocalization mechanism and its extension, but also which factors disturb the π-electron density is of utmost importance to enhance the proper performance of the electronic devices and develop *ad hoc* synthesis for desired application.

In this context, the search for novel features has brought to light the capabilities of polyconjugated organic molecules, in which alternative π-electron delocalization frameworks can co-exist with the main linearly conjugated sequence. Despite the resonance structures corresponding to the electron delocalization through these pathways may not be the largest contributing forms, their existence can modify significantly the optical, electronic and molecular properties of the system under study.

In this communication, different polyconjugation patterns are addressed and their influence on the π-systems is revealed through electronic and vibrational spectroscopies as well as quantum chemistry calculations. Through-bond π-electron delocalization is exemplified by molecules with cross-conjugated and parallelly-conjugated frameworks. For the former, the two π-conjugated pathways compete for the π-electron density in the common sections of the molecule. Conversely, parallel π-conjugated sequences do not share any fragment. On the other hand, through-space π-conjugation is demonstrated in spiro molecules, in which a proper spatial configuration allows the interaction between π-conjugated moieties disconnected by an insulating atom. In these systems, polyconjugation leads to exceptional thermal conductivity, intramolecular charge gradient, or non-Aufbau structures as the so-called HOMO-SOMO inversion.