

Polyconjugation from Molecular Spectroscopy

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The discovery of the semiconducting properties of π -conjugated organic oligomers and polymers has been a turning point in the development of new electronic devices and transformed the study of these systems in an emerging research field. Since then, many efforts have been devoted to generate structural features that bring about new and outstanding properties for optoelectronics, spintronics and magnetic devices, non-linear optics, or singlet fission processes. Since the behavior of the π -electrons determines the properties of these molecules, 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 these materials and develop *ad hoc* synthesis for desired application. In this context, the co-existence of alternative π -electron delocalization frameworks with the main linearly conjugated sequence must be considered as the existence of contributing resonance structures can modify significantly the optical, electronic and molecular properties of the system under study.

In this communication, three different policonjugation patterns are addressed and their influence on the π -systems is revealed through electronic and vibrational spectroscopies. 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, policonjugation leads to exceptional thermal conductivity, intramolecular charge gradient, or non-Aufbau structures as the so-called HOMO-SOMO inversion. In most of cases, the alternative resonance structures are usually diradical forms of the molecule of interest. In consequence, also diradical properties must be taken into consideration in the study of these polyconjugated systems.