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When is a polymer conjugated?

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When considering the nanoscale structure of an electronic material, one typically focuses on the arrangement in space and the interactions between different molecules. The molecule itself is thought of more in terms of a black box. Yet extrapolating from the chemical structure of a macromolecule, such as a conjugated polymer, to its physical function is by no means trivial. How can one be sure that all pi-bonds really are of the type insinuated by quantum chemistry? Time and frequency-domain spectroscopy - most notably pump-probe, upconversion and photon-echo techniques; and the single-molecule approach - have uncovered surprising heterogeneity in intramolecular couplings within nominally homogeneous pi-conjugated systems. The problem with any spectroscopic approach, however, lies in the fact that one and the same experiment is employed to extract both electronic and conformational information, which are intrinsically interrelated. We reverse this conventional approach of adopting the spectroscopy to a particular material and instead focus on a unique set of model systems with predefined physical shape in order to reveal the intricacies of electronic structure. Shape-persistent conjugated macrocycles can be synthesized with molecular weights comparable to those of short polymers, yet with unparalleled physical control over the actual pi-electron system. Such rings reveal, using single-molecule techniques, the effect of dynamic conjugation: spontaneous symmetry breaking of the pi-system due to interactions with the environment. Chromophores, the electronically-active subunits of pi-conjugated macromolecules, are found to form dynamically, leading to rapid jumps in the polarization of light emitted from such symmetric molecules. This insight reveals that nanoscale structure fundamentally begins at the level of individual carbon bonds, which can exhibit pronounced fluctuations.