Chiroptical Properties of Supramolecular Assemblies: a Combined Experimental and Theoretical Study

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The translation of chirality from the molecular level to supramolecular assemblies and materials is a key phenomenon in chemistry, biology and material science, and the mechanism that governs the trasmission of chirality across different length-scales deserves attention. Here we present a combined experimental and theoretical work, with the aim to investigate the formation of chiral assemblies.

Two phenyleneethynylene-based molecules, modified with D-and Lisomers, have been synthesized and their photophysical properties have been investigated. The two molecules show identical linear absorption spectrain the UV-Vis region: in methanol two well-separated bands are observed, with maxima at 305nm and 365nm. The formation of chiral supramolecular assemblies in methanol/water mixtures is demonstrated by extensive experimental characterization, including UV-Vis spectroscopy, circular dichroism, NMR spectroscopy and AFM. Electronic circular dichroism spectra of aggregates show unusual bandshapes in the UV-Vis region: the high-energy transition show the typical bisignated structure of exciton coupled systems, while a non-bisignated signal is registered for the low energy transition. The exciton model is adopted to investigate the optical behaviour of aggregates in the UV-Vis region, modeling intermolecular interactions in the dipolar approximation. This simple model allows to investigate the origin of the complex chiroptical properties: we demonstrate that the interactions between non-degenerate excitons play a crucial role in determining the non-bisignated signal of the low-energy band. The model is applied to different helicoidal gometries, and satisfactorily rationalize experimental results.