Exciton-coupled CD spectroscopy in the study of supramolecular systems: functional polymers, organogels, retinylidene proteins.

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Electronic circular dichroism (CD) spectroscopy is well recognized as one of the most efficient techniques for assigning absolute configuration of organic molecules and to study the secondary structure of biopolymers. However, it is in the field of supramolecular chemistry that CD shows its full potential and versatility. Chiral supramolecular systems attract a very large interest because many supramolecular architectures have been inspired by Nature. In this context, the possible applications of CD are several: a selective analytical tool to define stoichiometric ratios and derive thermodynamic parameters; a unique method to assess the handedness of supramolecular helices; a means to refine or validate supramolecular structures. Exciton-coupled CD (ECCD) is a well-known chirality mechanism leading to intense CD spectra which arises when a molecule contains two or more dissimetrically arranged chromophores which interact with each other through space. Exciton chirality rule is a very popular approach to assign absolute configurations, because the sign of ECCD spectra may be immediately correlated with the absolute molecular geometry. When a chiral aggregate of a chromophoric monomer is formed, ECCD also responds in a very sensitive way, often producing CD signals which are more complex and much more intense than those of the isolated chromophores. We may say in such a case that CD looks at the aggregate structure from the viewpoint of the chromophores. Not surprisingly then, the CD spectra of many chiral aggregates are interpretable in terms of exciton coupling. In the lecture a few examples of application of ECCD to very different supramolecular systems will be presented, ranging from chiral organogels, to conjugated polymers, to rhodopsin-like proteins (see Figure), focusing in each case on the type of structural information which can be extracted from CD spectra.