Chiroptical Spectroscopy of C_3 Molecules

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The relevance of molecules with C_3 symmetry comes from the fact of many of them, upon assembling as columnar helical macromolecules, are ideal platform for electro-optical devices, for example as liquid crystals. The properties of these devices are highly dependent of the structure of the bulk aggregates, and consequently they can be controlled by modifying the position and nature of the stereocenters in the molecular building blocks. In the limit, the changes at molecular level can be enhanced in the assembly and new applications may arise.

In this work we present an electronic and vibrational chiroptical study on a series of star-shaped molecules based on the octopolar C_3-symmetric 1,3,5-(phenylene-ethynylene)-benzene block (Fig. 1). Functionalization of either outer (R') or inner (R) benzenes allows us to change the position of the asymmetric carbon, which is the true origin of the enantiomeric excess at the macroscale.

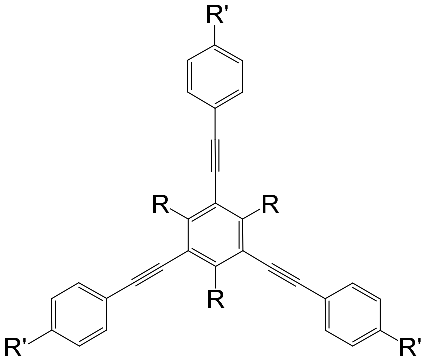

Fig. 1. The structure of the octopolar C_3-symmetric building block molecule.

As chiral substituents, R and R', we used amides, ethers and esters functionalized with aliphatic chains containing asymmetric carbon atoms. These groups allow the formation of hydrogen bonds between the monomers which reinforce the non-covalent interactions (π-stacking, electrostatic, hydrophobic). Four different molecules were thus employed as building blocks of columnar helical stacks in which the molecular chirality was enhanced. In general, homochirality in the self-assemblies (M- or P-type helix) was observed as dependent of the intrinsic chirality (R- or S-enantiomer). Chiroptical characterization was largely performed by both electronic (ECD) and vibrational (VCD) circular dichroism which, in combination with theoretical calculations, allowed us to relate the helix handedness with the molecular chirality. In addition, circularly polarized luminescence (CPL) was successfully recorded for the two enantiomers of an amide-functionalized molecule. The CPL activity in these molecules showed a strong solvent dependence (the signal was recorded in methyl-cyclohexane, but was absent in chloroform). These data provided us new insights on the transmission of the chirality to the excited states, which is essential for designing of luminescent superstructures.