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Can Magnetic Circular Dichroism Spectroscopy provide a new perspective towards CISS effect understanding?

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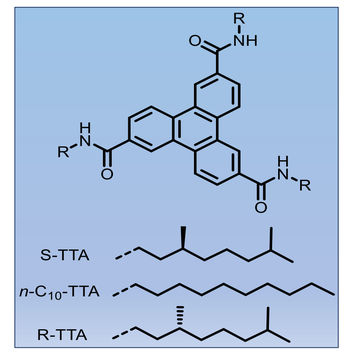
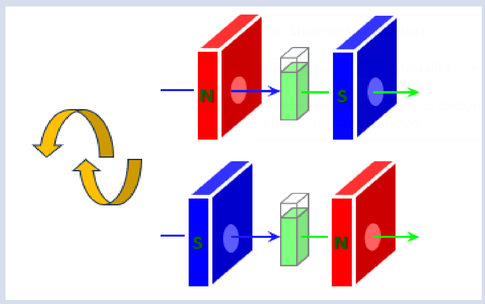
Introduction: Spin selective transport was prior observed in polymers and supramolecular structures that are based on homochiral building blocks possessing stereocenters as well as in achiral polymers where supramolecular chirality was induced by chiral solvent that was removed from the fibers before measurements. In the latter case, it was shown that the spin polarization correlates with the CD intensity of the CD spectra of the supramolecular polymers, indicating that the effect is nonlocal. In this work, we extend the degree of spectroscopic investigation, by applying Magnetic Circular Dichroism technique to study the properties of triphenylene-2,6,10-tricarboxamide (TTA) based supramolecular polymers. These polymers form helical aggregates in non-polar solvents such as Decalin and Methylcyclohexane while they remain in their monomeric state in polar solvents such as Chloroform. However, also at higher concentrations in polar solvents, they tend to form aggregates.

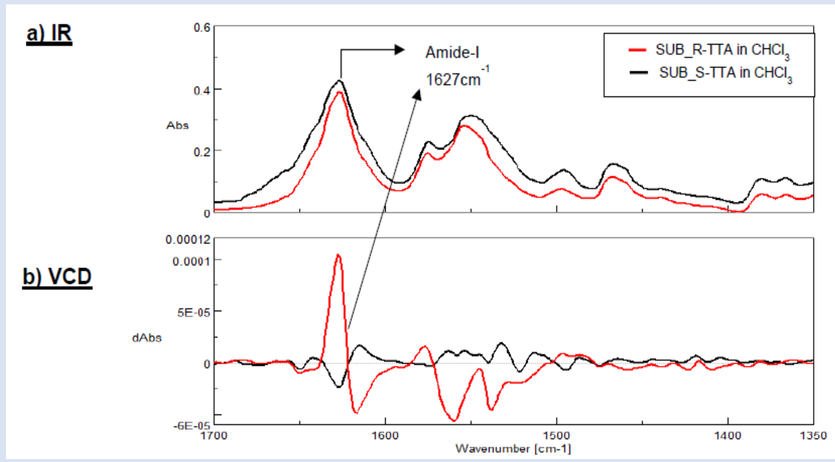


Magnetic Circular Dichroism is a Chiroptical Spectroscopy Technique based on the Faraday effect where optical activity is induced in matter by means of a longitudinal magnetic field.



Our aim here is to investigate the complementarity of MCD with CD for a better comprehension of the mechanism underlying the CISS effect in supramolecular systems.

At first step, the structural pattern of the system is analyzed by means of VCD and IR spectroscopy. Infrared analysis confirms the presence of an amide-I band at around 1627cm^{-1} from the IR spectrum and a corresponding doublet present in the VCD spectrum. The unbalanced ratio between the two enantiomers is probably due to not fully resolved enantiomeric purification process.



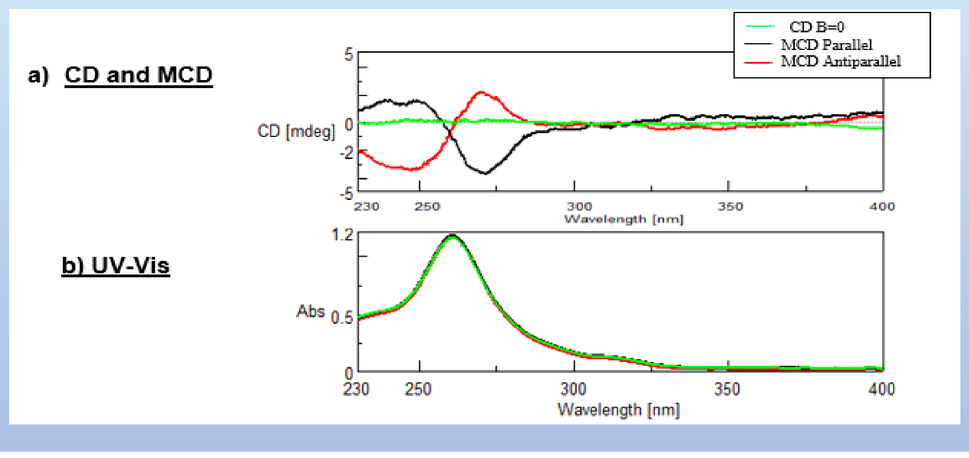
a)IR and b)VCD spectra of chiral S-TTA and R-TTA in $CHCl_3$

CD and MCD Investigation:

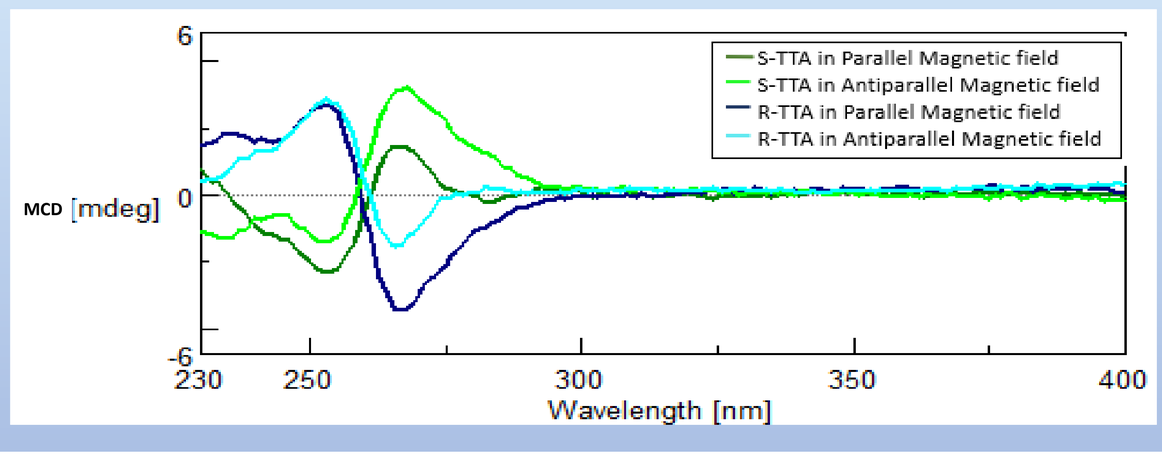
As reported previously [1], achiral TTA-based supramolecular polymers show a flat CD spectrum indicating a net racemic mixture of P and M helices. On the other side, application of a magnetic field results in a positive or negative Cotton effect with a maximum centered at 266nm.

The helical arrangement induced by magnetic field application is similar to the one obtained when monomers are dissolved in a chiral solvent (such as (S)- and (R)-1-chloro-3,7-dimethyloctane), as though as when supramolecular assemblies are generated by the arrangement of chiral monomers. [1]

MCD spectra Achiral-TTA in decalin

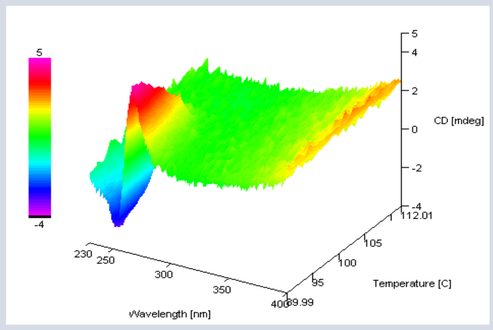


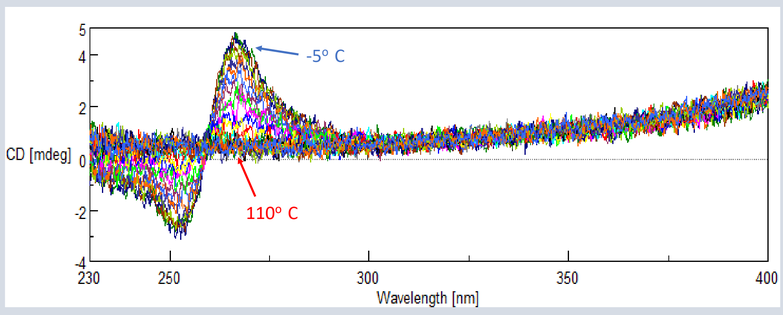
MCD spectra chiral-TTAs in Methylcyclohexane



Temperature Dependent Behaviour Investigation:

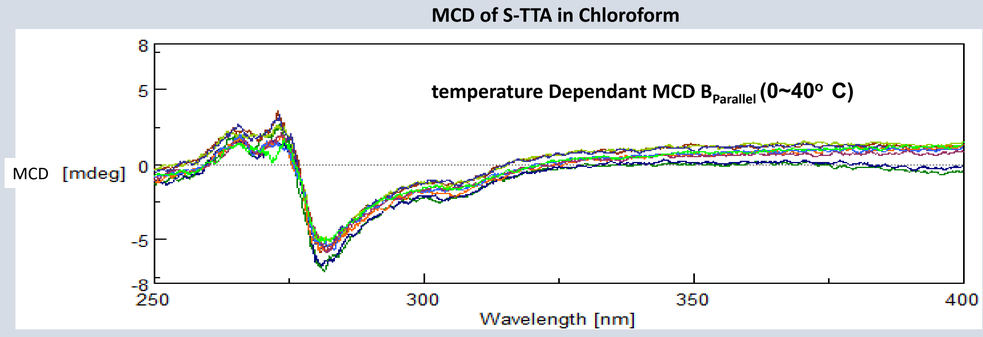
As a next step, we proceeded studying CD and MCD sample responses under variable temperature conditions.





S-TTA in Methylcyclohexane: temperature dependant CD (-5° C ~110° C)

MCD of S-TTA in Chloroform



Conclusions and Outlook:

- Being the supramolecular arrangement process strongly depending on the sample temperature, extension of the capability of measuring MCD in a wider temperature range is planned.
- Extension of the investigation to other classes of compounds (e.g. metal porphyrins) will be exploited.
- Combination of Chiral Spectroscopic Investigation with Quantification of CISS effect by various complementary methods is a mandatory step.

References:

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