A computational study of the vibrationally-resolved electronic circular dichroism spectra of single-chain transoid and cisoid oligothiophenes in chiral conformations

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Chiral polythiophenes (PTs) are interesting as organic electronics materials because of their optoelectronic properties, which may arise from ordered supramolecular packings. Chiroptical techniques like ECD can detect these packings, however, their interpretation is often based on qualitative arguments, and a detailed study from the computational point of view is necessary. PTs aggregates were previously studied using a simple dimeric model achieving a very good agreement with experiments,[1] but the possible contribution of single-chains was still unexplored.

We studied the vibronic features of single-chain polythiophenes spectra using transoid ribbons and cisoid helices ideal structures with variable number of units and inter-ring torsion angle.[2] In order to account for the flexibility introduced by this angle, a new protocol to define reduced-dimensionally spaces was developed, removing the off-equilibrium modes. Our results show that transoid ribbons ECD is monosignated, while cisoid helices can be bi- or tri-signated. These results are compared and discussed with several experimental data, allowing us to distinguish the source of the ECD spectrum: transoid ribbon, cisoid helix or aggregates.

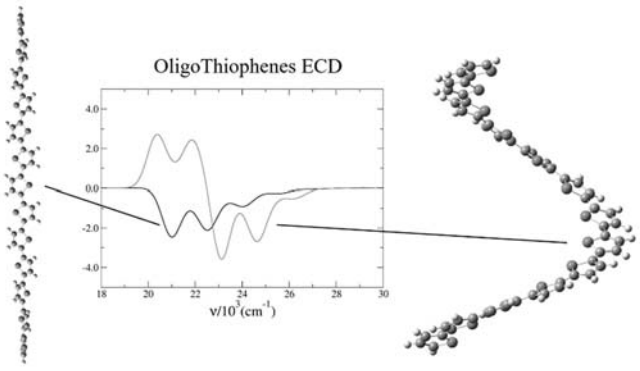

Figure 1. ECD of transoid ribbon and cisoid helix single-chain oligothiophenes.

(1) Padula, D.; Santoro, F.; Pescitelli, G. *RSC Adv.* **2016**, *6*, 37938.
(2) Aranda, D.; Cerezo, J.; Pescitelli, G; Avila Ferrer, F. J; Soto, J; Santoro, F. *Phys. Chem. Chem. Phys.* **2018**, *20*, 21864.