Chiroptical properties of helical assemblies: A generalized molecular approach using phenyleneethynylenes

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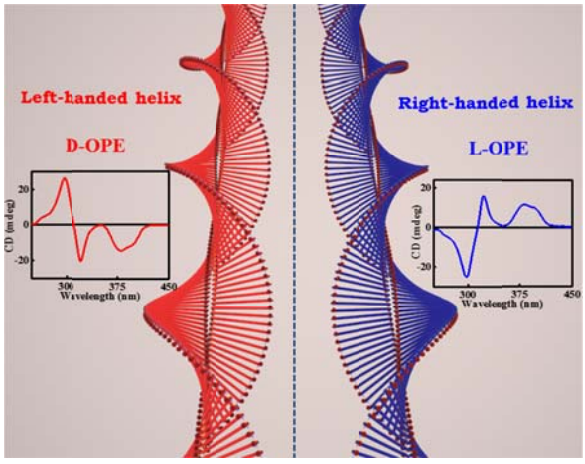
Abstract:
Evaluation of chiroptical properties of molecules and materials through their asymmetric organization has fascinated mankind in general and scientists in particular.[1] Herein we present detailed experimental investigations, which provide insight on the initial growth mechanism of chiral supramolecular assemblies. By taking oligo(p-phenyleneethynylene) (OPE) based rigid rod molecular systems as an example, we present the structural prerequisites for obtaining the left- as well as right-handed helical assemblies (M- and P-forms).[2] Various steps involved in the translation of OPE to M- and P-forms, which possess distinctly different chiroptical properties, will be discussed. Terminal carboxylic acids at the meta position of OPE assist their growth along the molecular axis whereas the amide functionality directs their assembly through the z-axis.

More importantly, the chiral groups provide the twist for OPE along z-axis yielding the corresponding M- and P-forms. Circular dichroism (CD) and NMR studies enabled the understanding of the β-sheet formation and stepwise growth of three-dimensional chiral assemblies. Bisignated CD observed in both cases can be distinguished through an inversion of their signals and explained based on asymmetric dipolar coupling mechanism. Experimental results were further supported by an analytical model using asymmetric dipolar coupling of chromophoric units in collaboration with Prof. Anna Painelli, Parma University, Italy.



References

1. Kumar, J.; Thomas, K. G.; Liz-Marzán, L. M.; *Chem. Commun.*, **2016**, *52*, 12555-12569
2. Kar, S.; Sissa, S.; Painelli, A.; Thomas, K. G.; *manuscript under preparation*