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Sum-frequency generation from chiral bisoxazoline metal complexes: Experiments and DFT calculations

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Today, metallopolymeric entities consisting of chains of metal ions interlinked with ambidentate ligands provide an attractive route towards so called smart materials capable of adjusting their physical properties in response to changes in environmental factors and/or to external stimuli. The dynamic nature of the metal ligand bond in solution may readily be assessed through titration experiments based on linear optical properties and through vibrational spectroscopy. However, it is much more difficult to study the molecular motions persisting in the condensed phase although these are essential to the properties and performance of this class of emergent materials. C₂-symmetric bisoxazoline units have attracted much attention because they have been successfully used in enantioselective catalysis when suitably substituted at the 4-position of the oxazoline heterocyclic rings to make it a chiral centre. When two isopropyl substituted oxazoline units are attached to a vinyl group, a bidentate monotopic ligand is achieved which shows a strong absorption band near 300 nm but no circular dichroism in methanol. Optical activity is detected however as soon as transition metal ions are added to the solutions. It attests to the formation of complexes expressing their axial chirality in their electronic transitions. Moreover, after the slow evaporation of the solvent, liquid casted homonuclear homoleptic complexes are capable of generating detectable levels of sum-frequency (SFG) signals which are specific to isotropic chiral media, i.e. which lack inversion symmetry only at the molecular level. In order to interpret these results, density functional theory (DFT) based electronic structure calculations is performed on individual metal complexes to determine the possible arrangements of the ligands around the metal ions and evaluate their relative energies. Time dependent (TD-DFT) calculations are used to establish the relationships between conformational structure and optical properties. Our results carry over to the related ditopic monomers containing bisoxazoline ligand units. But now, the formation of homoleptic homochiral species generates a chiral metallopolymer and lead to the formation of films of improved quality. The possibilities of optically active SFG based microscopy to study the formation of the metallopolymeric material obtained from chiral enantiopure components holds the promise of a sensitive technique where the optical expression of chirality can be used to probe self-assembling processes which may be relevant to other types of metallopolymer.

Biography

Alex Boeglin obtained his PhD in condensed matter Physics from the University of Strasbourg (France) in 1987 on the theoretical modeling of laser induced processes in molecular systems. After Post-Doctoral work with Prof. S. H. Lin at the Department of Chemistry of the Arizona State University in Tempe (AZ), he joined the Department of Nonlinear Optics of the then newly formed Institute of Physics and Chemistry of Materials of Strasbourg as a research specialist of the CNRS. In addition to modeling the effects of relaxation and dissipation phenomena on various nonlinear optical processes in molecules and aggregates, he became gradually more involved in the evaluation of molecular hyperpolarizabilities combining semi-empirical and DFT methods. Recently, he has also been carrying out DFT calculations aimed at understanding the vibronic features observed in low temperature single molecule STM induced luminescence experiments conducted at IPCMS.

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