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DOCTORAL DISSERTATION ABSTRACT

Scientific discipline: Chemistry, Physical Chemistry

Title of the doctoral dissertation: Intermolecular interactions between fluorophores carrying BF/BF$_2$ group and halogenated fluorobenzenes.

doctoral dissertation abstract:

In this thesis, the impact of halogen bonding on electronic and vibrational spectroscopic properties of organic fluoroborate compounds is explored using theoretical and computational methods. For each studied spectroscopic property, different research projects focused on the interactions between organic fluoroborate dyes and perfluorohaloarenes were carried out. In the first block of the thesis, I studied the photophysical properties associated with the electronic spectra of complexes formed through halogen bonding. In the second block of the thesis, the focus was on the distinctive signatures of halogen bonding in the infrared spectrum of molecular complexes. The design of new organic dyes and the development of strategies to obtain the desired properties is still a challenging work in synthetic chemistry. Nowadays several families of dyes are studied to provide new materials of interest for the industry. Thus, currently, this research topic is the focus of much activity and there is still plenty of room for development. The use of intermolecular interactions in such strategies to obtain dyes with desired photophysical properties has been overlooked, especially for halogen bonding. The main role of computational chemistry in this field falls to the determination of the photophysical properties of organic fluoroborates and the simulation of the effect of halogen bonding on these properties. In this thesis, two sets of dyes are studied, both formed by dyes that have been designed to be prone to interact through halogen bonds (XB) and exhibit Intramolecular Charge Transfer (ICT), with a BF/BF2 fragment as the electron-accepting group and a N,N-dimethylamino group as the electron-donating group. The first group contains the XB acceptor site outside the acceptor-donor CT pathway. The second set of dyes contains two different XB acceptor sites, one outside the CT pathway but near the BF2 group, and one between the electron acceptor and donor groups. In this way, the effect of the halogen bond in distinct positions within the molecule can be compared with the dyes of the first set. Therefore, the effect of the halogen bond in the electronic

structure of the dyes is investigated to rationalize the underlying process occurring within this intermolecular interaction. The electronic structure calculations agreed with experimental data showing a nice fit in the absorption and emission maximum wavelength changes upon complexation. The analysis of the stability of the complexes and the electron density changes during the absorption and emission processes allowed us to rationalize the effect of the halogen bonding on the photophysical properties of the organic fluoroborate dyes. The use of infrared (IR) spectroscopy for investigating intermolecular interactions, such as halogen bonding, has garnered significant attention in recent decades. While spectroscopic features have been identified to elucidate molecular complexes, understanding the physical origins of these features has remained elusive. In this thesis, a novel method has been developed to uncover the physical origins of changes in the IR spectrum of molecular complexes resulting from intermolecular interactions. This method is based on a direct connection between changes in the nuclear relaxation polarizability and changes in IR intensity due to intermolecular interactions. By linking these changes, any Energy Decomposition Analysis (EDA) can be applied, allowing for the partitioning of changes in IR intensity caused by halogen bonding into terms with different physical origins such as electrostatics, exchange, and delocalization. The application of this method to molecular complexes sharing structural similarities with the organic fluoroborate dyes studied in this thesis underscores its interpretative power, providing new insights into the effect of halogen bonding on vibrational spectroscopy and enhancing our understanding of this intermolecular interaction.

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