Linear Correlation between 1H NMR Chemical Shift and Absorption Maximum in Quadrupolar Centrosymmetric Dyes

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We compared the experimental chemical shift in 1H NMR spectroscopy with the absorption and emission maxima in a series of pyrrolo[3,2-b]pyrroles. Upon identifying, for the first time, a linear correlation between the absorption maximum and the 1H NMR chemical shift, we extended our investigation toward diketopyrrolopyrroles, other pyrrolo[3,2-b]pyrroles, and thieno[3,2-b]thiophenes, using density functional theory (DFT) computations. This correlation is nearly linear across all the studied families of compounds. However, two key criteria must be fulfilled to ensure the linearity: the compared compounds must exhibit steric similarity and the entire system must be conjugated. The paramagnetic contribution to the chemical shift was approximately four times greater than the diamagnetic contribution among the examined compounds. Additionally, we observed a linear relationship between the HOMO-LUMO energy gap and the chemical shift. Notably, the prediction of the absorption and emission maxima based on the chemical shifts proved to be more accurate than the excitation energy calculations when using long-range corrected functionals, such as CAM-B3LYP. These findings contribute to a deeper understanding of the electronic structure of quadrupolar dyes and provide a framework for a more efficient and rapid design of novel optoelectronic materials.

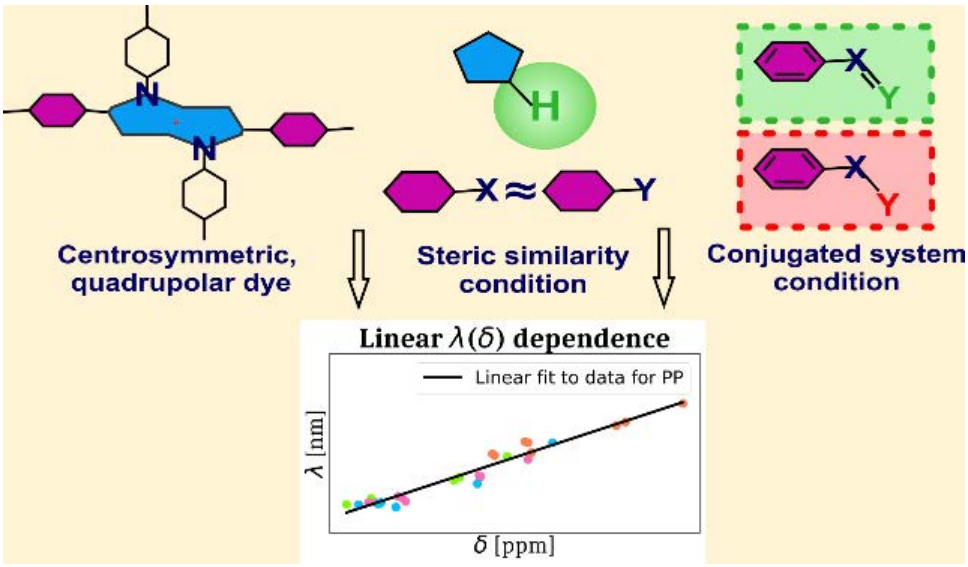

Figure 1. The conditions that enable linear correlation between absorption maximum and 1H NMR chemical shift..

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