Spectroscopic and Computational Studies of Benzo[c][1,2,5]thiadiazole Donor-Acceptor Dyes
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Organic donor-acceptor (D-A) dyes have been of significant interest in recent years as a result of potential applications in organic photovoltaics, dye-sensitized solar cells and non-linear optics. Specifically, D-A dyes incorporating benzo[c][1,2,5]thiadiazole (BTD) have shown promise in these fields due to a low band gap and highly tunable optical properties.

These tunable optical properties stem from charge-transfer (CT) transitions, which are typical for D-A dyes. CT transitions result in a shift of electron density from the donor to the acceptor moiety and modulation of the coupling between the donor and acceptor allows fine control of photophysical properties. Such systems result in partially zwitterionic excited states which can undergo solvent stabilization. Thus, variation of the solvent environment can also be utilized as a tuning mechanism.

In the pursuit of specialized photophysical properties, intense electronic absorption in the visible region for example, many predictive tools have been developed to identify promising synthetic targets. One powerful and widely used approach is density functional theory (DFT). DFT provides a computationally efficient and reasonably accurate method to model chemical systems. Despite its wide use, which DFT methods are most effective is subject to debate and varies significantly depending on the chemical system investigated or the target information. In the case of this study, particular attention is paid to the influence of HF and functionals are specifically picked based on their common/wide use in donor-acceptor studies. The inclusion of experimental and calculated Raman crosssections provides additional testing of the calculations via experimental data, a technique not widely utilized in the literature.

We report a series of seven D-A BTD dyes with varying degrees of sterically bulk so as to conformationally control the D-A torsion angle. Also included are several permutations of the D-A framework to investigate linker and donor effects. The dependence of optical properties on solvent is investigated both experimentally (with optical/vibrational spectroscopies) and theoretically (with a DFT calculation library, using six different functionals with different levels of HF exchange, M06L - 0%, B3LYP - 20%, PBE0 - 25%, M06 - 27%, CAM-B3LYP - 19-65% and ωB97XD - 22-100%, with five different solvents). In order to identify possible correlation these data are subjected to principal component analysis (PCA).
Figure 1 The BTD-TPA framework which was modulated to form six structurally varied compounds; and PCA scores plot indicating a successful separation of non-Hartree Fock functionals (M06L) range separated functionals (CAM-B3LYP and ωB97XD), for all compounds across solvent.

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REFERENCES