

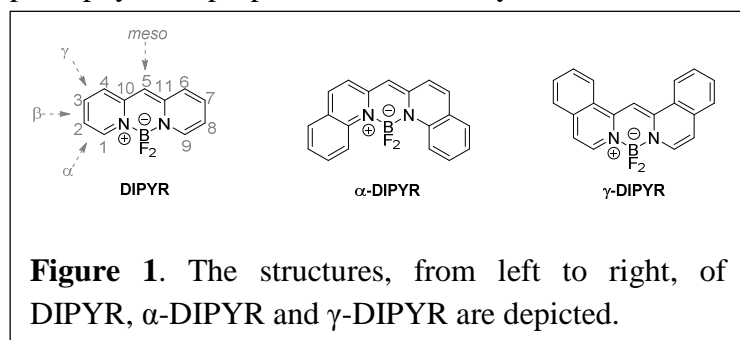
Novel BODIPY and DIPYR Chromophores for Optoelectronic Applications

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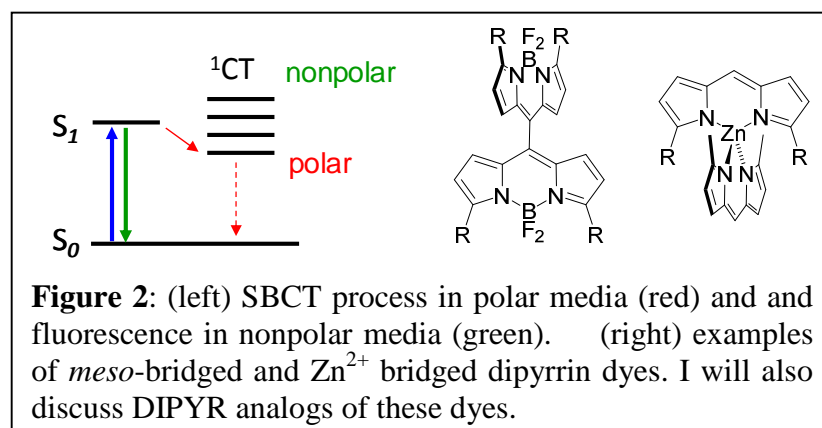
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Boron dipyrromethenes (BODIPY) derivatives have found widespread utility as chromophores in fluorescent applications, but little is known about the photophysical properties of pyridine-based BODIPY analogues, dipyridylmethene dyes. Indeed, it has been reported that boron difluoride dipyridylmethene (DIPYR) is non-emissive, and that derivatives of DIPYR have modest, if any, luminescence. We have studied a range of dipyridyl, diquinolyl and diisoquinolyl methene based dyes (Figure 1). These dyes absorb strongly in the blue-green part of the spectrum ($\lambda_{em} = 450\text{--}520\text{ nm}$, $\epsilon = 2.9\text{--}11 \times 10^4\text{ M}^{-1}\text{cm}^{-1}$) and display green fluorescence with high quantum yields ($\Phi_{PL} = \text{up to } 0.8$). Key photophysical properties in these systems were evaluated using TD-DFT methods and compared to experiment. It was revealed though theoretical analysis and comparison with experiment that high quantum yields of the quinoline and isoquinoline derivatives are a result of the relative reordering of S_1 and T_2 state energies upon benzannulation of the parent structure. The intense absorption



and high emission efficiency of the benzannulated derivatives make these compounds an intriguing class of dyes for further derivatization. I will discuss the dyes depicted in Figure 1 as well as range of other materials based on the dipyridyl-methene motif.

A key limitation of Organic photovoltaic devices (OPVs) are their low open circuit voltages (V_{oc}), which are typically well below the energy of the light absorbed. We achieve V_{oc} values closer to the theoretical limits, using materials that involve symmetry breaking charge transfer (SBCT).¹ These materials are symmetric molecules that spontaneously form an intramolecular charge transfer complex, with nearly complete one electron transfer from one part of the molecule to another. The charge transfer state (CT) is lower in energy than the singlet excited state (S_1) in polar media and higher than S_1 in nonpolar media (Figure 2), allowing us to use



solvent choice to tune the nature of the excited state. This minimizes the energy offset needed at the donor/acceptor interface to drive charge transfer and charge separation. Incorporating the SBCT process into an OPV pushes the V_{OC} close to the theoretical limits. We have characterized the SBCT process in a family of BODIPY and DIPYR materials, with high potential in OPVs. We have investigated both meso bridged dyes² and dyes coupled through Zn^{2+} ³ (Figure 2). The kinetics of formation of the SBCT process have been characterized by ultrafast spectroscopic techniques. We have explored these materials as both donors and acceptors in OPVs and found that they give good performance and high V_{OC} . I will discuss the syntheses and photophysical properties of these materials as well as their application to OPVs.

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References:

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