

# Charge-Transfer States in Molecular Donor-Acceptor Dyad: Importance of State-Specific Solvation

Aaron Forde<sup>1,2</sup>, Victor M. Freixas<sup>3</sup>, Sebastian Fernandez-Alberti<sup>3</sup>, Amanda J. Neukirch<sup>1</sup>, Sergei Tretiak<sup>1,4</sup>

<sup>1</sup>*Theoretical Division, Los Alamos National Laboratory, Los Alamos, New Mexico 87545*

<sup>2</sup>*Center for Nonlinear Studies, Los Alamos National Laboratory, Los Alamos, New Mexico 87545*

<sup>3</sup>*Departamento de Ciencia y Tecnología, Universidad Nacional de Quilmes/CONICET, B1876BXD, Bernal, Argentina*

<sup>4</sup>*Center for Integrated Nanotechnologies, Los Alamos National Laboratory, Los Alamos, New Mexico 87545*

Charge-transfer states arise at interfaces which are important in a variety of scenarios, such as charge-separation in the reaction centers of photosynthetic systems and at donor-acceptor regions in opto-electronic devices. Charge-transfer excited-states are delicate to capture accurately with *ab Initio* electronic structures as they require inclusion of non-local exchange interactions along with the distinction between non-equilibrium and equilibrium solvation.

To illustrate the importance of non-equilibrium and equilibrium solvation we explore a recent class of donor-acceptor dyads based on the fluorescent BODIPY functionalized with triphenylamine (TPA) shows the peculiar property of dual fluorescence. It is hypothesized that instead of the sensitized charge-transfer state being optically dark it provides an additional bright radiative pathway. For donor-acceptor dyads we use time-dependent density functional theory to characterize the energetic alignment of excitonic and charge-transfer states in a BODIPY-TPA molecular complex. We observe that using a long-range exchange corrected functional in combination with state-specific solvation scheme, as opposed to linear-response solvation, gives a qualitatively correct alignment of the exciton and charge-transfer states with an enhancement in oscillator strength for the equilibrium solvated charge-transfer state, in agreement with experiment. This work provides rationalization of experimentally observed of charge-transfer state emission and provides a foundation to explore charge-transfer using *ab Initio* excited-state non-adiabatic dynamics.