

Acetylene-bridged Organic and Organometallic Donor-Bridge-Acceptor Systems for IR-Induced Electron Transfer Modulation

Jesús Valdiviezo¹, Xiao Li⁴, Susannah D. Bazinger⁵, Peng Zhang¹, Igor V. Rubtsov⁴, Tong Ren⁵, David N. Beratan^{1,2,3}

1. Department of Chemistry, Duke University, Durham, NC, United States.
2. Department of Physics, Duke University, Durham, NC, United States.
3. Department of Biochemistry, Duke University, Durham, NC, United States.
4. Department of Chemistry, Tulane University, New Orleans, LA, United States.
5. Department of Chemistry, Purdue University, West Lafayette, IN, United States.

The efficiency of opto-electronic devices strongly depends on the photoinduced charge separation and charge recombination rates. Current strategies to control electron transfer kinetics have reported to be chemically invasive or irreversible. In recent years, UV-IR-Vis-3-pulse experiments have indicated that IR perturbations of a specific molecular vibrational mode can influence photoinduced electron transfer rates in donor-bridge-acceptor (D-B-A) assemblies. The possibility to use infrared excitations to control electron transfer is of substantial interest, since it is a nondestructive method (the energy absorbed ranges between 2.5-8.5 kcal/mol), spatially selective (specific bonds can be excited) and infrared active functional groups can be easily incorporated into molecular architectures. Through a collaborative effort between experiment and theory, we combined synthesis, computational methods and ultrafast spectroscopy techniques to investigate the evolution of excited states in organic and organometallic D-B-A complexes (Fig 1). Under the presence of strong donors, the optical excitation of the acceptor leads to ultrafast formation of charge separated states (CSS) These fast dynamics makes them excellent candidates for electron transfer rate modulation by infra-red excitation. Moreover, it is found that the excitation of the C≡C stretching mode of the bridge slows the rate of CSS formation, providing evidence of the possibility to use IR pulses to modulate the electron transfer rate in compounds without rare-earth metals.

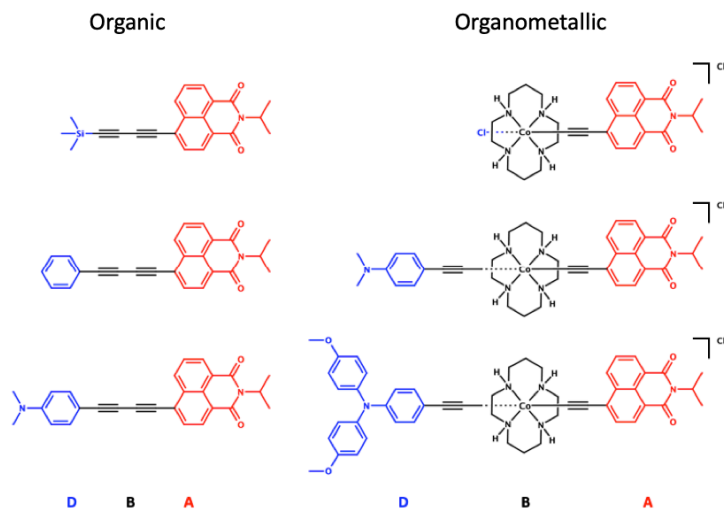


Figure 1. Structures of the organic and organometallic D-B-A compounds studied.