

# Molecular modelling and time resolved spectroscopy of electron transfer events in mid-sized molecular donor-acceptor-systems

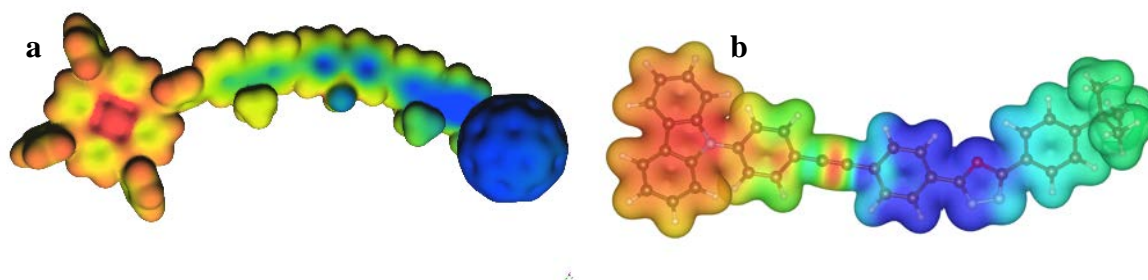
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As electron transfer is one of the key steps in various fields, such as molecular electronics or solar energy conversion, a detailed understanding of electron-transfer mechanisms is one of the main aims in modern chemistry. Especially detailed structure-property-relations are barely understood yet, leading to many trial and error attempts in this field instead of distinct designs towards the desired properties. Therefore, one research field in our groups deals with the most simplified model system for intramolecular electron transfer – the donor-bridge-acceptor system.

In this talk, I will present two recent projects in which donor and acceptor units were kept unchanged, while the bridge properties were altered. In the first project (**a**) the influence of placing an electron-accepting dibenzothiophene-S,S-dioxide bridge-unit (**S**) at different positions within a fluorene bridge (**Fl**) was studied and compared to previous studies on pure fluorene linked zinc porphyrine-fullerene dyads.[1,2] Interestingly, the inclusion of the **S**-unit allows the mechanism to be tuned for charge separation by allowing either hole- or electron-transfer. This charge-gating behavior leads to unidirectional electron transfer, enabling the charge separation to be switched on and off by controlling the excitation wavelength.



In the second project (**b**) the simplest bridge geometry, a linear carbon polyene-chain was altered by increasing the length from one to four bridge units, terminated by carbazole-donor and oxadiazole-acceptor moieties. Normally, increasing the distance between donor and acceptor leads to longer and therefore less efficient charge separation and recombination kinetics. In our model system, however, this trend is inverted, leading to faster charge separation and recombination kinetics for the longest dyad. Since this surprising finding, TD-DFT studies were performed to model the electronic properties of the excited states involved in order to elucidate the thermodynamic driving forces and reorganization energies.

[1] G. Yzambart, A. Zieleniewska, S. Bauroth, T. Clark, M. Bryce, D. M. Guldi, *J. Am. Chem. Soc.*, **2017**, submitted

[2] M. Wielopolski, G. Miguel, C. van der Pol, T. Clark, M. Bryce, D. M. Guldi, *ACS Nano*, **2010**, *4*, 6449-6492