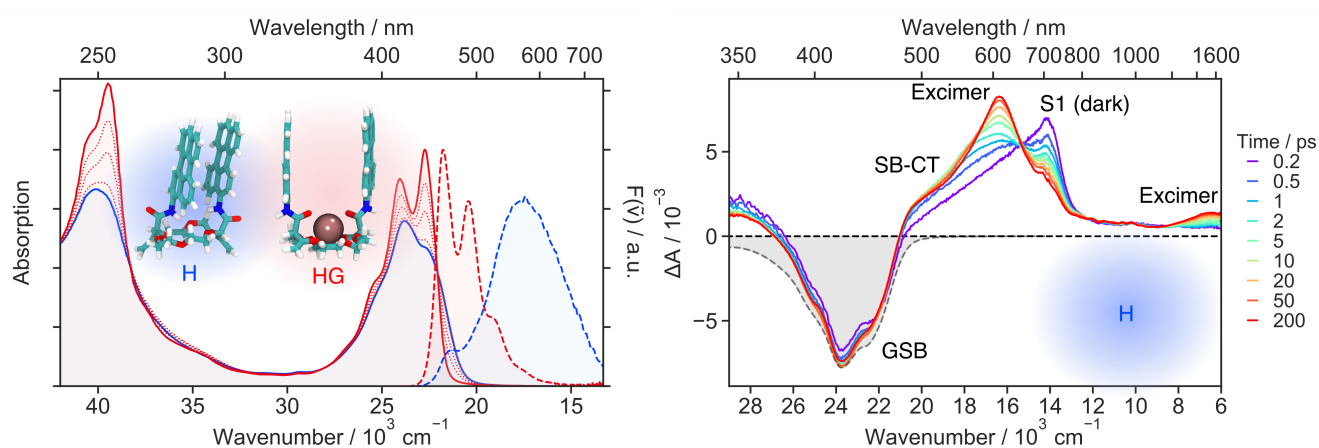


Tuning symmetry breaking charge separation of perylene bichromophores by conformational control

Alexander Aster,^a Giuseppe Licari,^c Francesco Zinna^b, Elodie Brun^b, Tatu Kumpulainen^a, Emad Tajkhorshid,^c Jerome Lacour^b, and Eric Vauthey^{a*}

^a Department of Physical Chemistry, ^b Department of Organic Chemistry, University of Geneva, CH-1211 Geneva, Switzerland. ^c Department of Biochemistry, Center for Biophysics and Quantitative Biology, Urbana, Illinois, USA. alexander.aster@unige.ch

The structure-property relationship in multichromophoric systems is crucial to establish design principles in organic electronics as well as fully comprehend how nature converts sunlight to energy. Bichromophores, consisting of two identical chromophores linked in a controlled geometry, are the model of choice to study how inter-chromophore conformation, can be used to tune the photophysical properties of a material.



In this communication, we will present a series of bichromophores consisting of two perylene heads, linked to different crownether backbones, which upon complexation of a cation change geometry and thereby the inter-chromophore conformation.

Transient absorption from femtosecond to microsecond and from UV to NIR as well as broadband fluorescence upconversion are paired with molecular dynamics simulation. This allows to link the intermolecular geometry with the adiabatic dimer states formed in close proximity and the dynamics in which they are populated.

We will show that controlling the conformational restrictions can turn on and off symmetry breaking charge transfer (SB-CT), allow for excimer formation, and even tune the SB-CT rate over 2 orders of magnitude.