

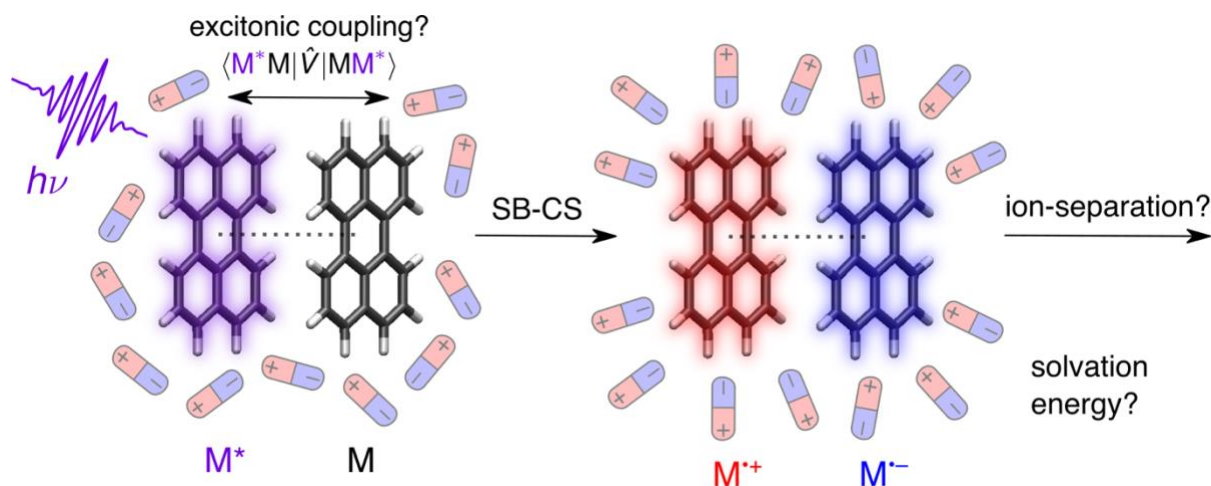
Understanding Photoinduced Symmetry-Breaking Charge Separation

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Symmetry-breaking charge separation^[1-2] (SB-CS) is a photoinduced electron-transfer reaction in which the chromophore (M) acts as both donor and acceptor, i.e. $M^* + M \rightarrow M^{*\cdot} + M^{\cdot-}$. Compared to conventional photoinduced electron-transfer with distinct donor and acceptor moieties, most of the light energy is converted into charges with low thermal losses due to the intrinsically low driving force of the reaction. Furthermore, the resulting ion pair may exhibit a long lifetime, as back electron transfer becomes highly exergonic and occurs in the Marcus inverted region. This extended lifetime may facilitate separation of the ion pair into free charge carriers which are sought after in applications such as organic photovoltaics or photoredox catalysis.

Although SB-CS is interesting from an applications point-of-view, the molecular requirements enabling this process remain poorly understood. Using stationary as well as time-resolved laser spectroscopic techniques, we investigate how chromophore geometry and excitonic coupling can be fine-tuned to favor SB-CS over competing pathways such as excimer formation.^[3,4] We further examine the role of the environment which determines the solvation energy required to stabilize the ionic species and drive the reaction.^[3]



References:

- [1] E. Vauthey, *ChemPhysChem* **2012**, 8, 2001–2011.
- [2] J. Wega, *Chimia* **2025**, 79, 263–266.
- [3] J. Wega, E. Vauthey, *Photochem. Photobiol. Sci.* **2024**, 23, 93–105.
- [4] J. Wega, Z. Ke-Feng, J. Lacour, E. Vauthey, *J. Phys. Chem. Lett.* **2024**, 15, 2834–2840.