Photoinduced symmetry-breaking charge transfer

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The reaction centre of photosynthetic bacteria consists of a pair of bacteriochlorophyll surrounded by two identical branches of protein-bound cofactors. Despite this high symmetry, charge separation from the excited bacteriochlorophyll pair occurs preferentially along one of the branches. This symmetry-breaking process was found to originate from the asymmetry of the protein environment.[1] Over the past years, similar photoinduced symmetry-breaking processes have been observed in molecular systems characterised by two or more, apparently equivalent, charge-transfer pathways.[2] Some of our efforts to understand the origin of these phenomena in liquid solutions will be presented.

Photoinduced charge separation between identical molecules, i.e. $M^{*}+M \rightarrow M^{+}+M^{-}$ or $M^{-}+M^{+}$, will first be discussed. Using polarised transient electronic absorption, we could show that both electron transfer (M^{*} is oxydized) and hole transfer (M^{*} is reduced), occur with the same probability and that the direction of the charge separation is determined by the environment.[3] We will discuss how such processes can be advantageously exploited for applications in artificial photosynthesis and photovoltaics.[4]

The second part will focus on excited-state symmetry breaking in D-π-A-π-D and A-π-D-π-A molecules. The latter are characterised by symmetric and quadrupolar electronic ground state and Franck-Condon excited state, but their fluorescence points to a highly dipolar relaxed excited state.[5] The break-up of the symmetry in the excited state could be visualised in real time using time-resolved IR spectroscopy. The extent of symmetry breaking was found to strongly depend on solvent polarity and to occur on the time scale of solvent motion, pointing to a crucial role of the environment.[6, 7] On the other hand, structural disorder in the ground state due to the quasi-free rotation around the π bridges is not sufficient to induce excited-state symmetry breaking in non-polar solvents.

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