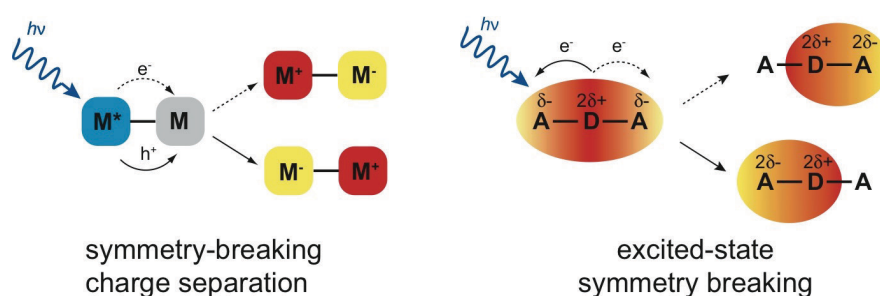


## PHOTOINDUCED SYMMETRY-BREAKING CHARGE-TRANSFER

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A substantial number of symmetric molecular systems, including the reaction centre of photosynthetic bacteria, undergo photoinduced charge transfer along one among several energetically equivalent pathways, resulting in a breaking of their symmetry.<sup>[1]</sup> Some of our efforts toward a better understanding of the origin and dynamics of these processes will be presented.



Photoinduced charge separation between two identical sub-units will be illustrated by studies on bichromophoric molecules. They reveal the importance of the environment for the direction of the charge separation and of the distance between the sub-units for the extent of asymmetry in charge distribution.

Most symmetric quadrupolar and octupolar  $D-(\pi-A)_{2,3}$  or  $A-(\pi-D)_{2,3}$  molecules behave like their dipolar  $D-\pi-A$  analogue once in the electronic excited state. This was ascribed to excited-state symmetry breaking, where electronic excitation, originally distributed evenly over the molecule, localises on a single  $D-\pi-A$  branch.<sup>[2]</sup> We will show how this process can be directly visualised using time-resolved IR spectroscopy.<sup>[3]</sup> The influence of various parameters, such as solute-solvent interactions and structural disorder on the symmetry breaking will be discussed.<sup>[3,4]</sup>

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