

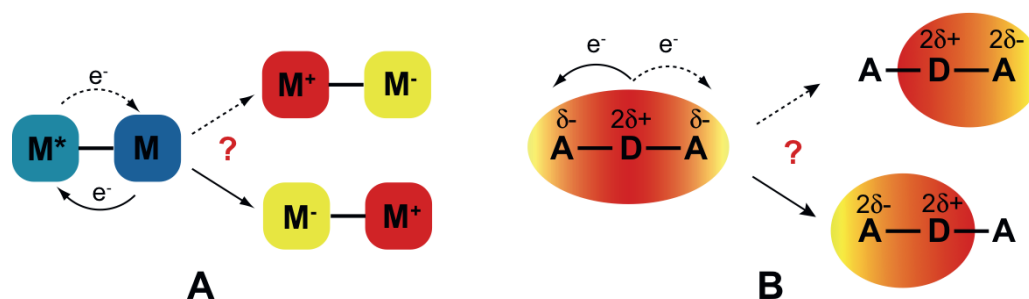
# Photoinduced symmetry-breaking charge-transfer

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A substantial number of symmetric molecular systems, including the reaction centre of photosynthetic bacteria, undergo photoinduced charge transfer along one of two, or more, energetically equivalent pathways, which results in a breaking of their symmetry.<sup>[1]</sup> Over the past years, we have been investigating two different types of such photoinduced symmetry-breaking (SB) charge-transfer (CT) processes that are schematised in Fig. 1.



*Figure 1: Two different types of SB-CT processes: A) photoinduced charge separation between two identical molecules; B) excited-state symmetry breaking in quadrupolar molecules.*

We will present several examples where photoinduced charge separation between identical molecules (Fig.1A) was observed.<sup>[1,2]</sup> In such cases, it was not clear whether symmetry is broken upon photoexcitation, i.e. whether the excited subunit acts exclusively as acceptor (A) or donor (D), or both hole and electron transfers are equally probable. From polarized transient electronic absorption measurements with a bipyrene system, we could show that symmetry is not broken by photoexcitation and that the direction of the charge separation is entirely driven by solvent fluctuations.<sup>[3]</sup>

The strong fluorescence solvatochromism observed with many quadrupolar molecules having an A- $\pi$ -D- $\pi$ -A or a D- $\pi$ -A- $\pi$ -D motif was explained in terms excited-state SB driven by structural and/or solvent fluctuations (Fig.1B).<sup>[4]</sup> However, the dynamic of this process and its exact origin were essentially unknown due to the lack of a clear spectroscopic signature of SB in the near-UV and visible regions. Direct visualization of SB was achieved by IR probing specific vibrations, i.e. -C $\equiv$ C- or -C $\equiv$ N stretching modes, localized in the middle or at the end of the two D- $\pi$ -A branches of quadrupolar molecules.<sup>[5-7]</sup> Our results reveal that, for the systems investigated, SB is driven by solvent fluctuations. In nonpolar solvents, the excited state remains symmetric during its whole lifetime. However in polar solvents, the excited state evolves from symmetric to asymmetric on a timescale similar to that of solvation. The magnitude of the

SB, i.e. excitation partially or entirely localized on one branch, was found to depend on several factors, including the solvent polarity and the size of the molecule.

SB in A- $\pi$ -D- $\pi$ -A type molecules leads to different basicities of the A ends and, thus, to different hydrogen-bond accepting strengths. As a consequence, a marked amplification of the SB in protic solvents was observed due to the formation of a tight asymmetric H-bonded complex.<sup>[6]</sup> The formation of this complex was found to strongly accelerate the decay of the excited state. The mechanism of this H-bond induced non-radiative deactivation could be elucidated by monitoring vibrational modes of the solvent molecules

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### References:

- [1] E. Vauthey, *ChemPhysChem*, **2012**, 13, 2001
- [2] O. Yushchenko, D. Villamaina, N. Sakai, S. Matile, E. Vauthey, *J. Phys. Chem. C*, **2015**, 119, 14999
- [3] V. Markovic, D. Villamaina, I. Barabanov, L.M.L. Daku, E. Vauthey, *Ang. Chem. Int. Ed.*, **2011**, 50, 7596
- [4] F. Terenziani, A. Painelli, C. Katan, M. Charlot, M. Blanchard-Desce, *J. Am. Chem. Soc.*, **2006**, 128, 15742
- [5] B. Dereka, A. Rosspeintner, Z. Li, R. Liska, E. Vauthey, *J. Am. Chem. Soc.*, **2016**, 138, 4643
- [6] B. Dereka, A. Rosspeintner, M. Krzeszewski, D.T. Gryko, E. Vauthey, *Ang. Chem. Int. Ed.*, **2016**, 55, 15624
- [7] B. Dereka, M Koch, E. Vauthey, *Acc. Chem. Res.*, **2017**, 50, 426