Efficient long-range ultrafast energy transfer in a novel family of multichromophoric antenna complexes investigated by ultrafast UV to Vis electronic spectroscopy

[1] M. Nazari, [2] C. D. Bösch, [1] M. Gazzetto, [1] A. Rondi, [2] S. M. Langenegger, [3]A. Monari [2]R. Häner, [1] T. Feurer, [1]A. Cannizzo

[1] Institute of Applied Physics, University of Bern, Switzerland
[2] Department of Chemistry and Biochemistry, University of Bern, Switzerland
[3]Université de Lorraine & CNRS, France

E-mail: maryam.nazari@iap.unibe.ch

We present a study on a novel family of DNA-hosted multichromophoric light-harvesting systems (MC-LHS) for supramolecular photo-catalysers. These assemblies are incorporated Phenanthrenes which are arranged in a defined and π-stacked configuration in a DNA-helix like structure with robust and strong mutual coupling (Fig. 1.a). This gives origin to an energy transfer (EnT) over nanometres with unitary quantum yield and a very high absorption cross-section. An energy acceptor (a Pyrene) can be placed in a defined place of the MC-LHS to make the EnT site-specific and unidirectional (Fig. 1.b).

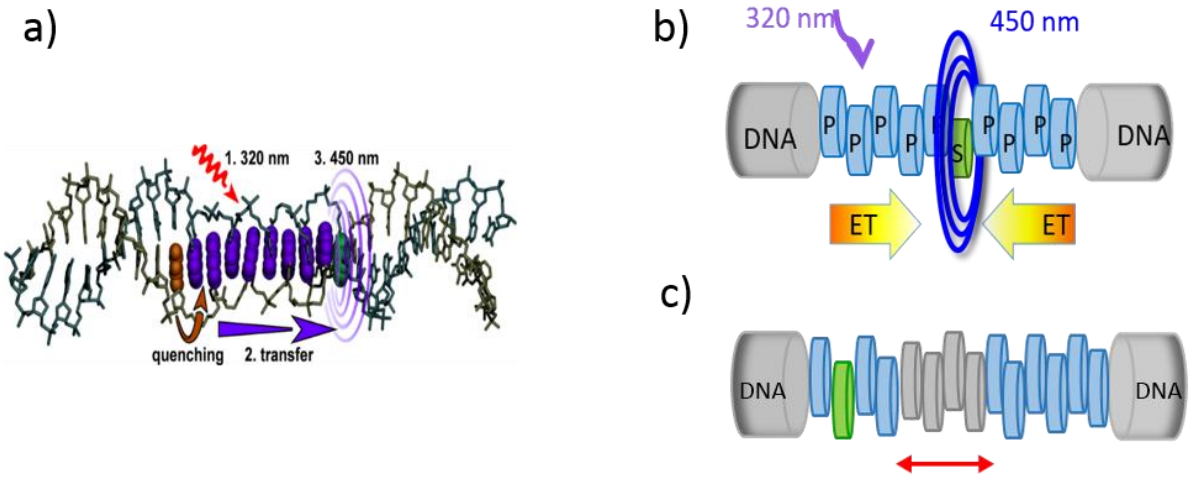

Figure 1. MC-LHS herein investigated. a) An example of molecular structure.[1,2] b) Scheme of photo-induced EnT process: upon excitation of Phenanthrenes (P) at 320nm, energy is transferred to Pyrene (S) unit, which emist at 450nm. c) Another example of investigated MC-LHS with different length and intercalated DNA nucleotides. Blue, green and gray discs represent Phenanthrene, Pyrene and DNA base pairs, respectively.

To identify the origin of such an efficient EnT we carried out an extensive study by means of UV-to-Vis transient absorption spectroscopy and TDDFT calculations on MC-LHS with different spatial arrangements and different chromophores (Fig. 1.c). The possibility to link time-resolved results, with calculations and different MC-LHS structures allowed us to clarify the origin of the t EnT mechanism, relations among structures and coupling distances.
We found that EnT occurs in few tens of fs (within our time resolution) over a typical distance of 1 nm. We observed the formation of transient delocalized states upon excitation,

which we believe to be responsible of such an efficient EnT. Transient delocalized states last for few 100s of fs before to collapse into a localized excited state centered on one of the chromophores (Fig. 2).

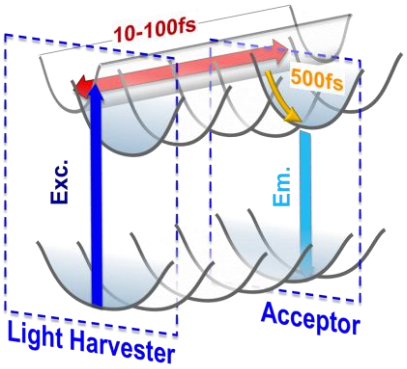

Figure 2. Proposed photocycle based on experimental evidences and calculations.

This mechanism, which at our knowledge has been never observed and proposed so far, suggests new strategies to improve the efficiency of transfer phenomena in multichromophoric systems and violates the common opinion that efficient energy and charge transfers need long-lived states.

Funding: European Research Council (ERC Starting Grant 279599-FunctionalDyna), the Swiss State Secretariat for Education, Research and Innovation (SERI). Swiss NSF through the NCCR MUST

References:

[1] F. Garo, R. Häner, Angew. Chem. Int. Ed. 2012, 51, 916-919

[2] F. Garo, R. Häner,Bioconjugate Chem., 2012, 23 (10), pp 2105–2113