

Constructing Dye-Zeolite Photonic Nanodevices

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In natural photosynthesis, light is absorbed by photonic antenna systems consisting of a few hundred chlorophyll molecules. These devices allow fast energy transfer from an electronically excited molecule to an unexcited neighbour molecule in such a way that the excitation energy reaches the reaction centre with high probability. Trapping occurs there. The anisotropic arrangement of the chlorophyll molecules is important for efficient energy migration. In natural antennae the formation of aggregates is prevented by fencing the chlorophyll molecules in polypeptide cages. A similar approach is possible by enclosing dyes inside a microporous material and by choosing conditions such that the cavities are able to uptake only monomers but not aggregates. In most of our experiments we have been using zeolite L as a host because it was found to be very versatile. Its crystals consist of an extended one-dimensional tube system and can be prepared in the size range from 30 nm up to 6000 nm. We have filled the individual tubes with successive chains of different dye molecules and we have shown that photonic antenna materials can be prepared, not only for light harvesting within the volume, but also for radiationless transport of electronic excitation energy to a target molecule fixed at the ends of the nanochannels as well as with an injector molecule fixed at their „entrances”. The dye molecules in the figure below are represented by rectangles. The molecule which has been excited by absorbing an incident photon transfers its electronic excitation to another one. After a series of such steps the electronic excitation reaches a luminescent trap, pictured as dark rectangles. The energy migration is in competition with spontaneous emission, radiationless decay, quenching, and photochemically induced degradation. Fast energy migration is therefore crucial if a trap should be reached before other processes can take place.

We consider the supramolecular organization of the dyes inside the channels as a *first stage of organization*. It allows light harvesting within a certain volume of a dye loaded zeolite and radiationless energy transport to both ends of the cylinder or from the ends to the centre. A *second stage of organization* is the coupling to an external acceptor or donor stopcock fluorophore. A *third stage of organization* is the coupling to an external device via a stopcock intermediate. We distinguish between the coupling to artificial reaction centres of molecular

dimension, macromolecular dimension, and macroscopic dimension. The wide-ranging tunability of these highly organized materials offers fascinating new possibilities for exploring excitation energy transfer phenomena, and challenges for developing new photonic devices.[1-4]

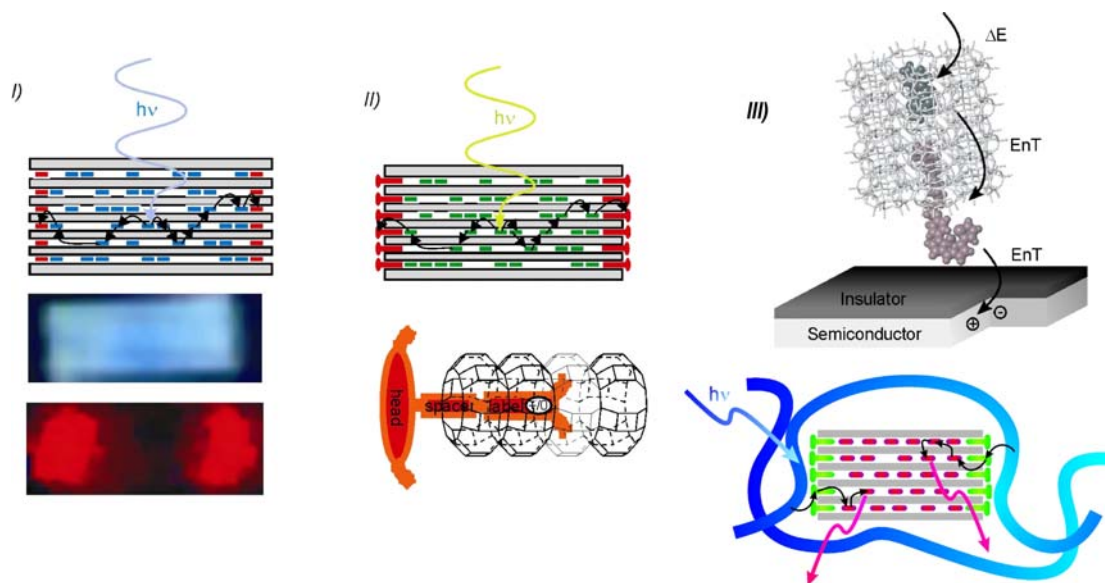


Figure: I) dye-loaded zeolite L antenna; blue emitting donors inside the zeolite L transfer electronic excitation energy to red emitting acceptors at the left and right of the crystal. A crystal containing a donor in the middle part and an acceptor at both ends as seen in an optical microscope is shown. II) antenna system with stopcock molecules as external traps and picture of a stopcock at the end of a channel. The stopcock consists of a head, a spacer, and a label. III) Top: EnT from a photonic antenna to a semiconductor, creating an electron hole pair in the semiconductor (radiationless near field process). Bottom: EnT from a luminescent polymer into a stopcock modified system. The luminescent polymer is drawn as a blue ribbon.

[1] G. Calzaferri, S. Huber, H. Maas, C. Minkowski, *Angew. Chem. Int. Ed. Engl.* **2003**, *42*, 3732-3758.

[2] M. Yatskou, M. Meyer, S. Huber, M. Pfenniger, G. Calzaferri, *Chem. Phys Chem* **2003**, *4*, 567-587.

[3] a) S. Huber, G. Calzaferri, *Chem. Phys Chem* **2004**, Volume 5, Issue 2 (February).

b) H. Maas, G. Calzaferri, *The Spectrum* **2003**, Volume 16, Issue 3, 18-24.

[4] A. Devaux, C. Minkowski, G. Calzaferri, *Chem. Eur. J.* **2004**, in press.