

Mimicking the antenna system of green plants

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Artificial photonic antenna systems have been realised by incorporating organic dyes in a microporous material.[1] We have been using zeolite L in most of our experiments as it has proven to be a very versatile host. Its crystals are cylindrically shaped porous aluminosilicates featuring a hexagonal symmetry. The size and aspect ratio of the crystallites can be tuned over a wide range. A nanometre sized crystal consists of many thousand one-dimensional channels oriented parallel to the cylinder axis. These can be filled with suitable organic guests. Geometrical constraints of the host structure lead to supramolecular organisation of the guests in the channels. Thus very high concentrations of monomeric dye molecules can be realised. A special twist is added to these systems by plugging the channel openings with a second type of fluorescent dye, which we call stopcock molecule. The two types of molecules are precisely tuned to each other; the stopcocks are able to accept excitation energy from the dyes inside the channel, but cannot pass it back.[2]

The supramolecular organisation of dyes inside the zeolite channels is what we call the first stage of organization. It allows light harvesting within the volume of a dye-loaded zeolite L crystal and also radiationless energy transport to either the cylinder ends or centre. The second stage of organisation represents the coupling to an external acceptor or donor stopcock fluorophore at the ends of the zeolite L channels, which can then trap or inject electronic excitation energy. The third stage of organization is realised by interfacing the material to an external device via a stopcock intermediate. We observed that electronic excitation energy transfer in dye-zeolite L materials occurs mainly along the channel axis. This important finding means that organised, uni-directional materials can be prepared. In order to achieve this, we prepared zeolite L monolayers, filled them with luminescent dyes, and finally added a stopcock. These procedures and their repercussions on the design of novel materials will be discussed.[3,4]

[1] *Photon-Harvesting Host-Guest Antenna Materials*. G. Calzaferri, S. Huber, H. Maas, C. Minkowski, *Angew. Chem. Int. Ed.* **42**, 2003, 3732. [2] a) *Trapping Energy from and Injecting Energy into Dye-Zeolite Nano-antennae*. H. Maas, G. Calzaferri, *Angew. Chem. Int. Ed.* **41**, 2002, 2284. b) *Sequential Functionalization of the Channel Entrances of Zeolite L Crystals*. S. Huber, G. Calzaferri, *Angew. Chem. Int. Ed.* **43**, 2004, 6738. [3] *Organizing supramolecular functional dye-zeolite crystals*. A. Zabala Ruiz, H. Li, G. Calzaferri, *Angew. Chem. Int. Ed.* **45**, 2006, 5282. [4] a) *Transparent Zeolite-Polymer Hybrid Materials with Tunable Properties*. S. Suárez, A. Devaux, J. Bañuelos, O. Bossart, A. Kunzmann, G. Calzaferri, *Adv. Func. Mater.* **17**, 2007, 2298. b) *Advanced photon harvesting concepts for low energy gap organic solar cells*. R. Köppe, O. Bossart, G. Calzaferri, N.S. Sariciftci, *Solar Energy Materials and Solar Cells*, **91**, 2007, 986. c) *Self-assembling living systems with functional nanomaterials*. Z. Popovi, M. Otter, G. Calzaferri, L. De Cola., *Angew. Chem. Int. Ed.* **46**, 2007, 6188. d) *Nanochannels for supramolecular organisation of dyes*. André Devaux, Katsiaryna Lutkouskaya, Gion Calzaferri, Le-Quyen Dieu, Dominik Brühwiler, Luisa De Cola, and Tomás Torrs. *Photochemistry in Switzerland, Special Issue CHIMIA* **61**, 2007, 626-630.