New materials for solving old problems

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Luminescent solar concentrators were suggested by R. L. Garwin as early as 1960 for the collection of light from scintillation counters.^[1] Interest for using them for collecting and concentrating solar radiation came more than ten years later.^[2] A luminescent solar concentrator LSC utilizes a luminescent medium to absorb radiation and total internal reflection to collect it. Theory of operation and techniques for performance evaluation has been reported.^[3] The medium strongly absorbs light in a portion of the solar spectrum and then emits it at longer wavelengths where it should not be reabsorbed. Collection is achieved since most of the light is emitted at angles more grazing than the critical angle for total internal reflection. This light is thus trapped in the collector and will propagate by successive reflections to the edges, where it can be coupled out. No device useful for solar energy applications has been realized so far, despite of the very appealing concept and some industrial efforts. The most pressing problems that have been understood since almost 30 years are the self-absorption of the fluorescence, always present if strongly fluorescent dyes are used, and to some extent also the photo-stability of the materials, especially the chromophores.

Recently, ways for overcoming the most severe problems of LSC devices have been proposed and this has created new interest.^[4-7] The problem of self-absorption is illustrated in Figure 1 for the commercially available dye PR149. We observe that for conditions that allow nearly quantitative absorption of the incoming light, about 43 % of the fluorescent light is reabsorbed. This is not acceptable in a device.



Figure 1. Absorption and fluorescence spectrum of PR149 in diluted solution $c \cdot d = 10^{-7} \text{ M} \cdot \text{cm}$ (solid) and for a more concentrated situation $c \cdot d = 10^{-4} \text{ M} \cdot \text{cm}$ (dashed).

This problem can be solved by using the possibility to build very efficient antenna systems. We have shown that one-dimensional channel materials, such as zeolites and mesoporous silicas, are very attractive hosts for the preparation and investigation of hierarchically organized structures, presenting a successive ordering from the molecular up to macroscopic scale. We have built and investigated artificial photonic antenna systems that have been synthesized by incorporating organic

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dyes into one-dimensional nanochannel materials.[8] We have been using zeolite L as a host in most of our experiments since it has proven to be an excellent choice. Zeolite L crystals feature strictly parallel channels arranged in a hexagonal symmetry. The size and aspect ratio of the colorless crystallites can be tuned over a wide range. Its one-dimensional channels can be filled with suitable organic guests. Geometrical constraints imposed by the host structure lead to supramolecular organization of the guests in the channels. Thus high concentration of very weakly or non-interacting dye molecules can be realized. The supramolecular organization 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 to the centre. One-dimensional excitation energy transport was observed in these guest-host materials; see Figure 2.

The combination of a tuneable host morphology and the possibility of obtaining highly organized molecular patterns of guests leads to a variety of potential optical and photoelectronic applications of dye-zeolite L materials. Strongly absorbing systems exhibiting efficient FRET along the c-axis of the zeolite crystals are accessible by inclusion of multiple types of dyes, forming the basis for novel light-harvesting devices. The FRET processes can be fine-tuned by an appropriate choice of dye molecules, whereas the ordering of the dyes can be extended to the macroscopic level by an oriented arrangement of the dye-loaded zeolite crystals. The robust zeolite framework can further be selectively functionalized at the external crystal surfaces and/or the pore entrances. The embedding of dye-loaded zeolite crystals into organic matrices is used for the development of novel luminescent solar concentrators, where self-absorption and stability problems are solved.^[9]



Figure 2: From organisation to application. *Left:* Fluorescence behavior of a donor,acceptor-zeolite L antenna. Top: Scheme of an antenna crystal and processes taking place upon excitation of a donor molecule (green): absorption of incident light, energy migration from an excited donor molecule to a neighboring unexcited one and trapping by an acceptor (red), fluorescence of both donor and acceptor. Lower: Confocal microscopy images of an antenna crystal upon selective excitation of the donor and observation through an appropriate filter (left) and confocal microscopy images upon selective excitation of the acceptor (right).[8] *Right:* The alignment of dye molecules in the channels of zeolite L can be extended to the macroscopic scale by preparing monolayers of crystals with defined morphology. Systems including multiple types of dye monomers form the basis for the design of novel device architectures for LSC. ^[7]

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