Light-Harvesting Antenna Materials

Host–Guest Antenna Materials

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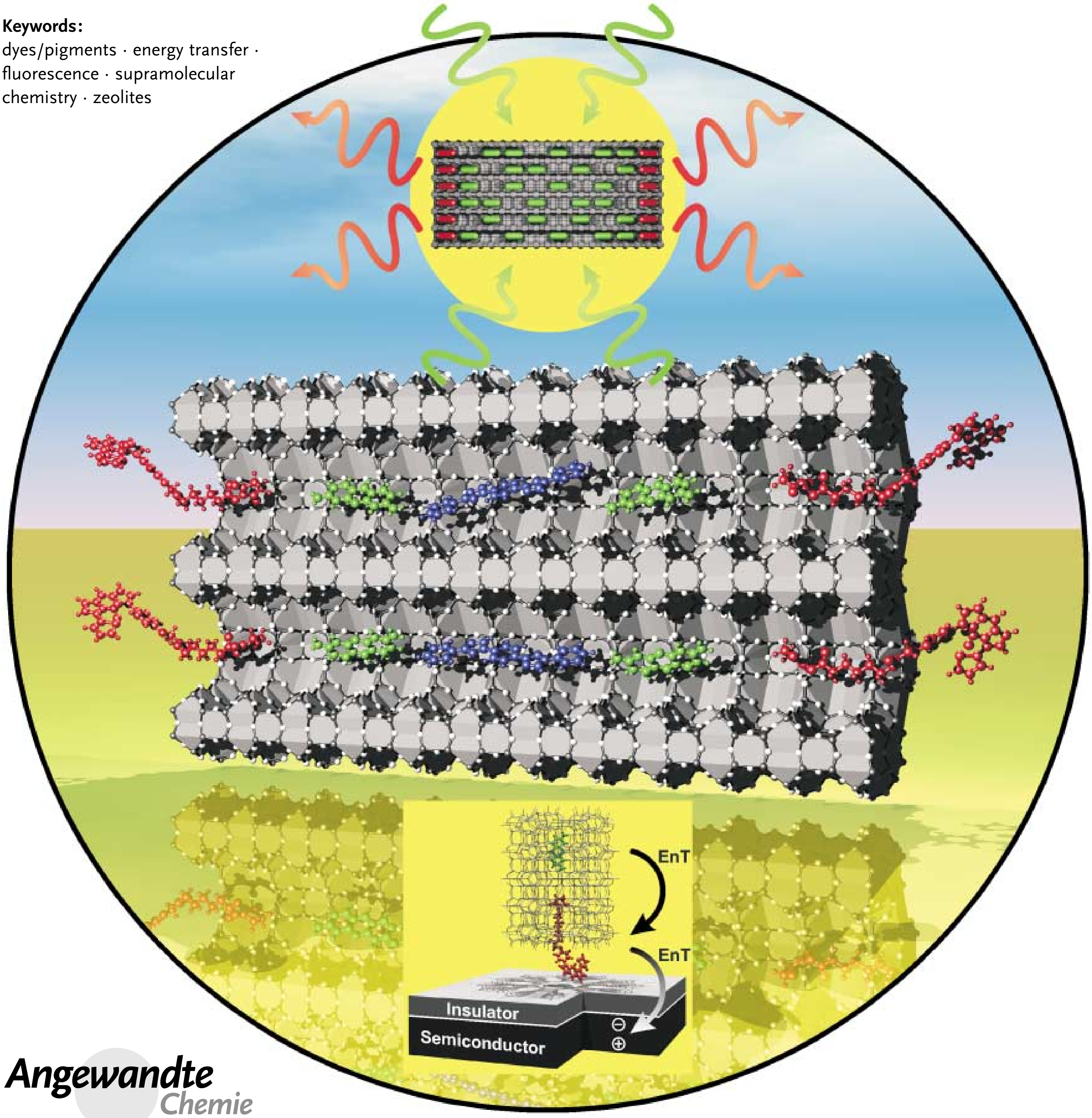

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The focus of this review is on host–guest composites with photonic antenna properties. The material generally consists of cylindrical zeolite L crystals the channels of which are filled with dye molecules. The synthesis is based on the fact that molecules can diffuse into individual channels. This means that, under the appropriate conditions, they can also leave the zeolite by the same way. In some cases, however, it is desirable to block their way out by adding a closure molecule. Functionalization of the closure molecules allows tuning of, for example, wettability, refractive index, and chemical reactivity. The supramolecular organization of the dyes inside the channels is a first stage of organization. It allows light harvesting within a certain volume of a dye-loaded nanocrystalline zeolite and radiationless transport to both ends of the cylinder or from the ends to the center. The second stage of organization is the coupling to an external acceptor or donor stopcock fluorophore at the ends of the channels, which can trap or inject electronic excitation energy. The third stage of organization is the coupling to an external device through a stopcock molecule. 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.

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1. Introduction

Plants are masters of efficiently transforming sunlight into chemical energy. In this process, every plant leaf acts as a photonic antenna in which photonic energy in the form of sunlight is absorbed and transported by chlorophyll molecules. In natural photosynthesis, light is absorbed by a photonic antenna system of a few-hundred chlorophyll molecules arranged in a protein environment. These devices allow fast energy transfer from an electronically excited molecule to an unexcited neighboring molecule in such a way that the probability that the excitation energy reaches the reaction center is very high. Trapping occurs there. It has been reported that the anisotropic arrangement of chlorophyll molecules is important for efficient energy migration.[1]

Several attempts to build an artificial antenna are presented in the literature. Multinuclear luminescent metal complexes,[2,3] multichromophore cyclodextrins,[4] Langmuir–Blodgett films,[5–7] dyes in polymer matrices,[8–10] and dendrimers[11] have been investigated. In some cases aspects of artificial antenna systems are also found in sensitization processes in silver halide photographic materials[12] and the spectral sensitization of polycrystalline titanium dioxide films.[13,14] In natural antennae the formation of quenching aggregates is prevented by fencing the chlorophyll molecules in polypeptide cages.[15] A similar approach consists of enclosing dyes inside a nanoporous material and by choosing conditions such that the cavities are only able to uptake monomers but not aggregates.[16]

Our approach is based on using zeolites bearing a channel structure as a host. The light transport is made possible by specifically organized dye molecules which mimic the function of chlorophyll in the natural antennae. In most of our experiments we use zeolite L as a host because of its versatility. Zeolite L crystals consist of an extended one-dimensional tube system.[17,18] We have filled each individual tube with successive chains of various electronically non-interacting joined dye molecules. Light shining on the cylinder is first absorbed, and the energy is then transported by the dye molecules inside the tubes to the desired place. We have shown that photonic antenna materials can be prepared, not only for light harvesting within the volume of a dye loaded nanocrystalline zeolite L,[19,20] but also for radiationless transport of the electronic excitation energy to a target molecule fixed at the ends of the nanochannels or from an injector molecule fixed at the “entrances”.[21] A schematic view of the photonic antenna invented by us[22,23] is illustrated in Figure 1. The monomeric dye molecules are represented by rectangles. The dye molecule which has been excited by absorbing an incident photon transfers its electronic excitation to a neighboring molecule. After a series of such steps the electronic excitation reaches a luminescent trap (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. This means that a detailed understanding of the photochemical and photophysical processes

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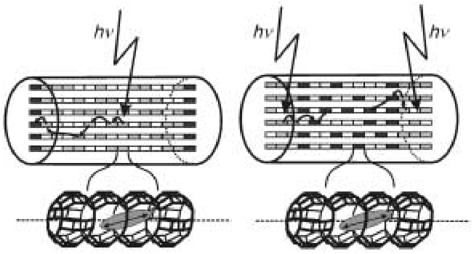

Figure 1. Representation of a cylindrical nanocrystal consisting of organized dye molecules acting as donors (gray rectangles) and acceptors (black rectangles). Left: The donors are in the middle part of the crystal and the acceptors at the ends of each channel. Right: The donors are at the ends of each channel and the acceptors are in the middle part. The enlargements show details of a channel with a dye and its electronic transition moment (double-headed arrow) which is parallel to the channel axis for long molecules and twisted for shorter ones. The diameter of the channel windows of zeolite L is 0.71 nm and the largest free diameter is 1.26 nm. The center-to-center distance between two channels is 1.84 nm.

taking place is important. Studies can be carried out on single crystals, or on crystals dispersed in a solvent, in a polymer matrix, but also on thin layers, for example, coated on a support.

We consider the supramolecular organization of the dyes inside the channels as a first stage of organization (Figure 1 and 2a). 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 center. This first stage is well mastered as we will show below. A second stage of organization is the coupling to an external acceptor or donor stopcock fluorophore at the ends of the zeolite L channels (Figure 2b) which can trap electronic excitation energy from donor molecules inside the crystal or inject electronic excitation energy to acceptors inside the channels.[24] We have so far demonstrated that this works for three different stopcock fluorophores;[21,25] additional stopcock molecules are currently being explored. A third stage of organization is the coupling to an external device through a stopcock unit. We distinguish between the coupling to an artificial reaction center of 1) molecular dimensions, 2) macromolecular dimensions (photoconducting or conducting polymer, quantum dots), and 3) macroscopic dimensions (semiconductor, conductor, quantum wells). Figure 2c shows as an example the coupling to a semiconductor device, by which energy transfer from the photonic antenna through an insulating layer creates an electron-hole pair in the semiconductor.

Favorable conditions for realizing such a device are a high concentration of monomeric dye molecules with high luminescence quantum yield, an ideal geometrical arrangement of the chromophores, and an optimal size of the device. The type of host materials we are interested in are shown in Figure 3. Organic dyes have the tendency to form aggregates even at low concentration. Aggregates are known to cause fast thermal relaxation of electronic excitation energy. The role of the host is to prevent this aggregation and to superimpose a specific organization. The idea is to choose the diameter of the channels and the dyes such that the dyes cannot glide past each other. This arrangement allows the formation of highly anisotropic dye assemblies. Large amplitude motions of the dye molecules but also the diffusion of reactive molecules can be reduced or even completely suppressed because of the restricted space available and hence very stable materials can result. Host materials which meet the desired geometrical properties can be found among the zeolites.[18]

2. Hexagonal Zeolite Crystals as Hosts for Dyes

Examples of hexagonal zeolites with channels large enough to accommodate organic dye molecules (see Figure 3), are reported in Table 1. Our investigations have concentrated on zeolite L as a host. The reason for this is that neutral as well as cationic dyes can be inserted into the channels of zeolite L and that synthesis procedures for controlling the morphology of zeolite L crystals in the size regime of 30 nm to about 3000 nm are available.[19,26–30] Many results obtained with zeolite L are valid for other nanoporous materials as well.

Zeolite L is a crystalline aluminosilicate with hexagonal symmetry. Its anionic framework with the positions of the charge-compensating cations is illustrated in Figure 4. The crystals consist of so-called cancrinite cages (ε cages) linked

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