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Zeolite Microcrystals as Hosts for Supramolecular Organization of Dye Molecules

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Abstract. Zeolite microcrystals can act as host for supramolecular organization of molecules, complexes, clusters, and quantum-size particles. They allow the design of precise and reversible functionalities. Techniques for arranging zeolite microcrystals of good quality and narrow size distribution as dense monograin layers on different substrates can be used to realize specific properties. The chemical reactivity between the intercalated molecules offers possibilities for *in situ* synthesis of molecular chains, clusters, and quantum-size particles, which might not be accessible otherwise. In some cases, guest-host reactivity must be considered. The reactivity of intercalated compounds with (small) molecules penetrating from the outside is an option for changing the composition of a material, *i.e.*, molecules intercalated as monomers in a first step can be linked to form chains. New electronic structures are accessible either by specific geometrical arrangements made possible by the structure of the host and/or by explicitly involving its electronic properties. Some systems meet the conditions necessary for the occurrence of intrazeolite charge transport (ionic and electronic), realized by the guests in their ground state and in electronically excited states under high-vacuum conditions or in the presence of a solvent, depending on the composition and the structure of the material. In this article, we focus on organic dye molecules in the one-dimensional channels of zeolites with a hexagonal framework. This system consists of supramolecularly organized dye molecules. It is shown to provide fascinating possibilities for building an artificial antenna device which consists of highly concentrated monomeric dye molecules of up to 0.4M with a large *Förster* energy-transfer radius and a high luminescence quantum yield in an ideal geometrical arrangement of optimal size. Extremely fast electronic excitation-energy transport has been demonstrated by us in oxonine- and pyronine-dye-loaded zeolite L microcrystals. Many other highly organized dye-zeolite materials can be prepared, and they are expected to show a wide variety of challenging properties. We report on methods to distinguish between dye molecules which are inside of a microcrystal and those adsorbed on its outer surface, and we explain a demonstration experiment illustrating the intercalation of thionine into zeolite L and the thus resulting improved chemical stability of this dye.

Introduction

Zeolite microcrystals can act as hosts for supramolecular organization of molecules, ions, complexes, clusters, and quantum-size particles. They allow the design of precise and reversible functionalities. The possibility of arranging zeolite microcrystals of good quality and narrow size distribution as dense monograin layers on different substrates can be used to realize specific properties. New electronic structures are accessible either by specific geometrical arrangements made possible by the structure of the host and/or by explicitly involving their electronic properties. Some systems meet the *conditions necessary for the occurrence of intrazeolite charge transport* (ionic and electronic), realized by the guest molecules in the ground state and in electronically excited states under high-vacuum conditions or in presence of a solvent, depending on the composition and the structure of the material. A comprehensive review article on zeolite-based materials has been published recently [1].

Three functionalities are of special importance in our research: *intrazeolite ion transport, intrazeolite charge transport,* and *intrazeolite excitation-energy transport* (energy migration). The zeolite acts as a host which is not actively involved in the corresponding process, but provides the necessary geometrical and chemical environment. It can also lead to largely *improved chemical stability* of intercalated species by shielding them from chemicals with which they would otherwise react or by preventing intramolecular rearrangements due to the limited free space available. A number of methods have been developed for preparing zeolites containing the desired molecules, ions, complexes, or clusters. These are crystallization inclusion, ion exchange, incorporation from the gas phase, or *in situ* syntheses. Each of these methods has its advantages and disadvantages depending on the specific problem to be solved.

In this article, we focus on supramolecularly organized dye molecules in the channels of hexagonal zeolite microcrystals. They provide fascinating possibilities for building an artificial *antenna device* which consists of highly concentrated monomeric dye molecules with a large *Förster* energy-transfer radius, which also means a large spectral overlap, and a high luminescence quantum yield in an ideal geometrical arrangement of optimal size [2–7].

Dye Molecules in the Channels of Hexagonal Zeolite Microcrystals

Dye molecules in zeolites have been investigated for different purposes such as persistent spectral hole burning due to optical bistabilities and the generation of the second harmonics; see, *e.g.*, [8–16]. We have worked on devices for extremely fast energy migration [2–7]. A schematic view of the antenna system for light harvesting as studied by us is illustrated in *Fig. 1*. It consists of well-arranged monomeric dye molecules with high luminescence quantum yield at very high concentrations of up to 0.4M. Organic dye molecules have the tendency to form aggregates at much lower concentrations, which is known to cause fast thermal relaxation of electronic excitation energy. The role of the zeolite is to prevent this aggregation and to superimpose a specific organization which means that the system has to be well-designed, which is possible as we have shown recently [6][7]. In such an antenna, light is absorbed by one of the strongly luminescent chromophores, in-

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dicated by the bars in *Fig. 1*. Due to the short distances and the specific arrangement of the electronic transition dipole moments of the dyes, the excitation energy is transported by *Förster*-type energy migration [17] anisotropically to a specific trap, indicated as a star. The ideal dimension of a microcrystal containing several thousand chromophores is in the order of a micrometer or smaller [5–7].

To realize this antenna, we use zeolites bearing linear channels running through the whole microcrystal, as explained in *Fig. 2*, and thus allowing the formation of highly anisotropic dye assemblies consisting of monomers. The dimension of the channels and the dyes to be intercalated have to be chosen so that the dyes can enter as monomers only. Examples of zeolites with such channels, large enough to take up organic dye molecules, are reported in *Table 1* [18]. The appropriate channels are mainly found for hexagonal structures, but also some appropriate orthorhombic structures are known. Most of our studies have so far focused on zeolite L. For this reason, I will now concentrate on this zeolite type. The basic principles are, however, the same for other zeolites with a similar structure.

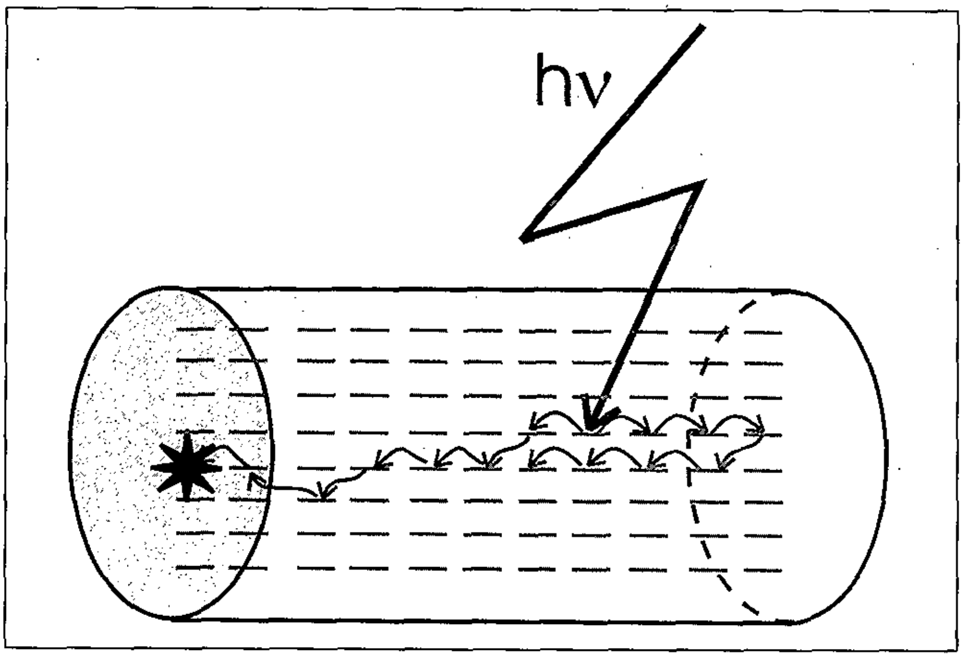


Fig. 1. *Schematic view of an artificial antenna for light harvesting.* Light is absorbed by a chromophore (strongly luminescent organic dye), indicated by the bars, and transported by energy migration to a specific trap, indicated as a star.

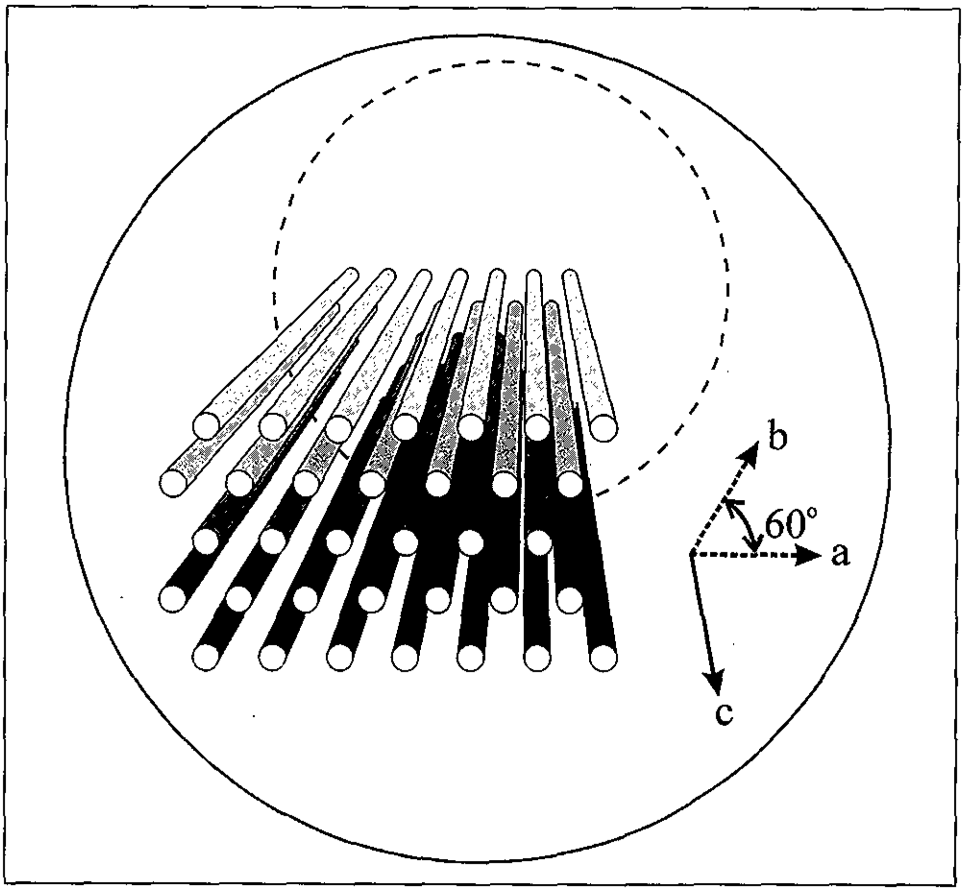


Fig. 2. *Schematic view of some channels in a hexagonal zeolite*

Table 1. *Lattice Constants* a, b, *and* c *and Free Opening Diameters Ø of Hexagonal Zeolites with Linear Channels* (in Å) [18]

	a=b	*c*	Ø
Mazzite	18,4	7,6	7,4
$AlPO_4$-5	13,4	8,4	7,3
Zeolite L	18,4	7,5	7,1
Gmelinite	13,8	10	7
Offretite	13,3	7,6	6,8
CoAPO-50	12,8	9	6,1
Cancrinite	12,8	5,1	5,9
VPI-5	19,0	8.4	12,1

To gain a better understanding of the geometrical situation, we show in *Fig. 3* a side view and a space-filling top view of the zeolite L together with a type of dye which has already been successfully used by us [2–7]. From this we see that while the dye molecules can penetrate the channel, formation of dimers inside the channels is not possible.

Cationic dyes of the type shown in *Fig. 3* can be intercalated by ion exchange. Neutral dyes can be intercalated from the gas phase. But how can we distinguish between dye molecules which are inside the channels of a microcrystal and those adsorbed on its surface? This is a very important question which we have studied in detail. It is obvious that otherwise very powerful techniques such as X-ray diffraction, different kinds of NMR, or SEM (SEM = Scanning Electron Microscopy) are by far not sensitive enough to detect a few molecules which might sit on the outer surface of a microcrystal instead of being inside a channel. There is no single method available which could be applied in general. However, we found a number of sensitive experiments which, when ap-

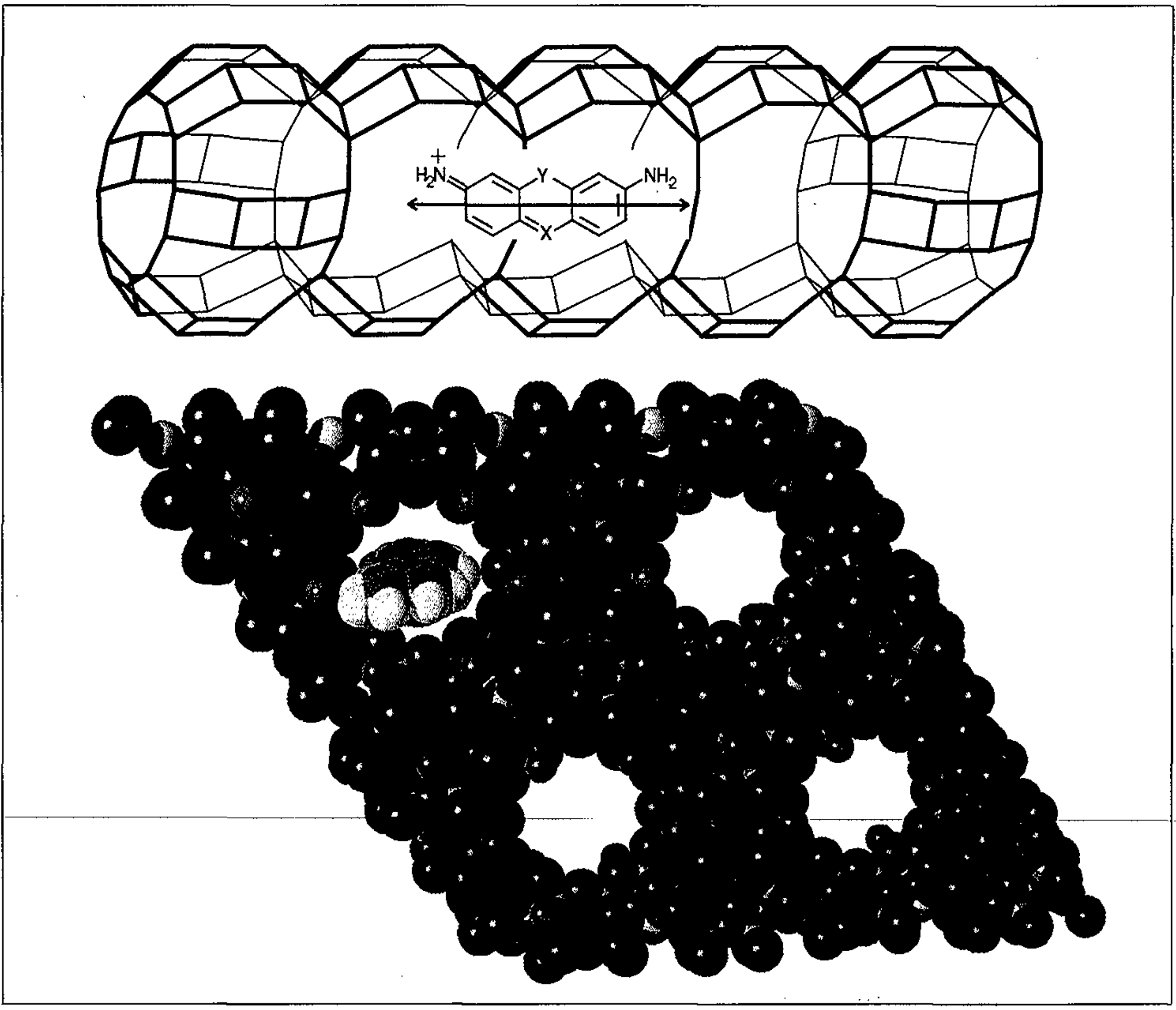


Fig. 3. *Structure of zeolite L and of dye molecules inside a channel and a space-filling model.* Thionine: X = N, Y = S; Oxonine: X = N, Y = O; Pyronine: X = CH, Y = O. The arrow illustrates the electronic transition dipole moment for the first allowed electronic transition.

propriately used, allow to characterize samples with respect to this question very well. In some cases, the difference of the absorption and emission spectra between the acidic and the basic form of a dye can be used [2] or, alternatively, the sometimes very different luminescence behavior of a monomeric dye inside and outside of a channel [19]. The difference in the absorption spectra of the monomers and the aggregates and especially the luminescence quenching of the aggregates (very efficiently formed at the outer surface of the microcrystals) can often be used as a sensitive probe [4][20]. Solvatochromism with a solvent which can not enter the cavities of the zeolite and thus only shows effects with molecules at the outer surface can be very useful [4]. Two methods which can also be used as a tool for preparing dye-loaded zeolite microcrystals which are very pure in the sense of not containing any dye molecules at their outer surface are based on specific transport properties observed when the zeolite microcrystals are suspended in a pure solvent or a solvent containing a specific reagent. To explain the principle of these two methods we first refer to a study entitled ‘Resorufin in the Channels of Zeolite L’ recently published by us [19].

Zeolite L containing the resorufin anion (Res^-) in its anionic framework can be prepared by incorporating the neutral resorufin molecule (ResH) from the gas phase and then exchanging the protons with potassium ions, which leads to dark violet-colored microcrystals. The reversibility of the deprotonation/protonation reaction of resorufin can be monitored by measuring the UV/VIS absorption spectrum of the samples. While Res^- is strongly fluorescent in solution, the fluorescence is completely quenched when Res^- is located inside the channels of potassium zeolite L. This allows the investigation of the exit kinetics as a function of the size of the solvent molecules which enter the zeolite channels and displace the incorporated resorufin irreversibly. Three cases can be distinguished concerning the mechanism of the displacement process: In case 1, the solvent molecules can pass a dye molecule inside the channel easily. In case 2, the solvent molecules are considerably hindered when passing a dye molecule inside the channel, and in case 3, the solvent molecules are too large to pass a dye molecule and hence the exit rate of dye molecules is zero.

Fig. 4, bottom, illustrates the solvent dependence of the displacement of incorporated resorufin molecules. It is fastest in water and decreases with increasing size of the solvent molecules. There is virtually no displacement in propan-1-ol, although a slight increase of fluorescence intensity can be observed compared to the measurement in butan-1-ol, which provides the baseline for the experiment. It thereby has to be considered that the solubility of Res$^-$ is similar in the investigated solvents. Since the fluorescence quantum yield increases from water (0.6) to methanol (0.9), the investigated effect is even more distinct than the experiment might suggest. The series

water >> methanol > ethanol > propan-1-ol $\gtrsim$ butan-1-ol

which outlines the ability of solvent molecules to displace intercalated resorufin molecules is independent of the initial loading of the zeolite samples. However, the total displacement after a certain period of time depends on the loading and on the quality of the loading of the zeolite samples. The following values for the total displacement after 100 min have been obtained by the procedure described in the experimental section of [19]: 43% for water, 6% for methanol, 2% for ethanol, and 0% for propan-1-ol and butan-1-ol. In the case of the alcohols, the zeolite samples retained their dark violet color, but a pale orange-colored zeolite was obtained after the experiment in water.

The displacement process in water, although starting very fast, levels off after a certain period of time. Centrifuging the suspension, removing the supernatant solution, and adding fresh water does not accelerate the process, thus confirming its irreversibility. This fact resulted in the

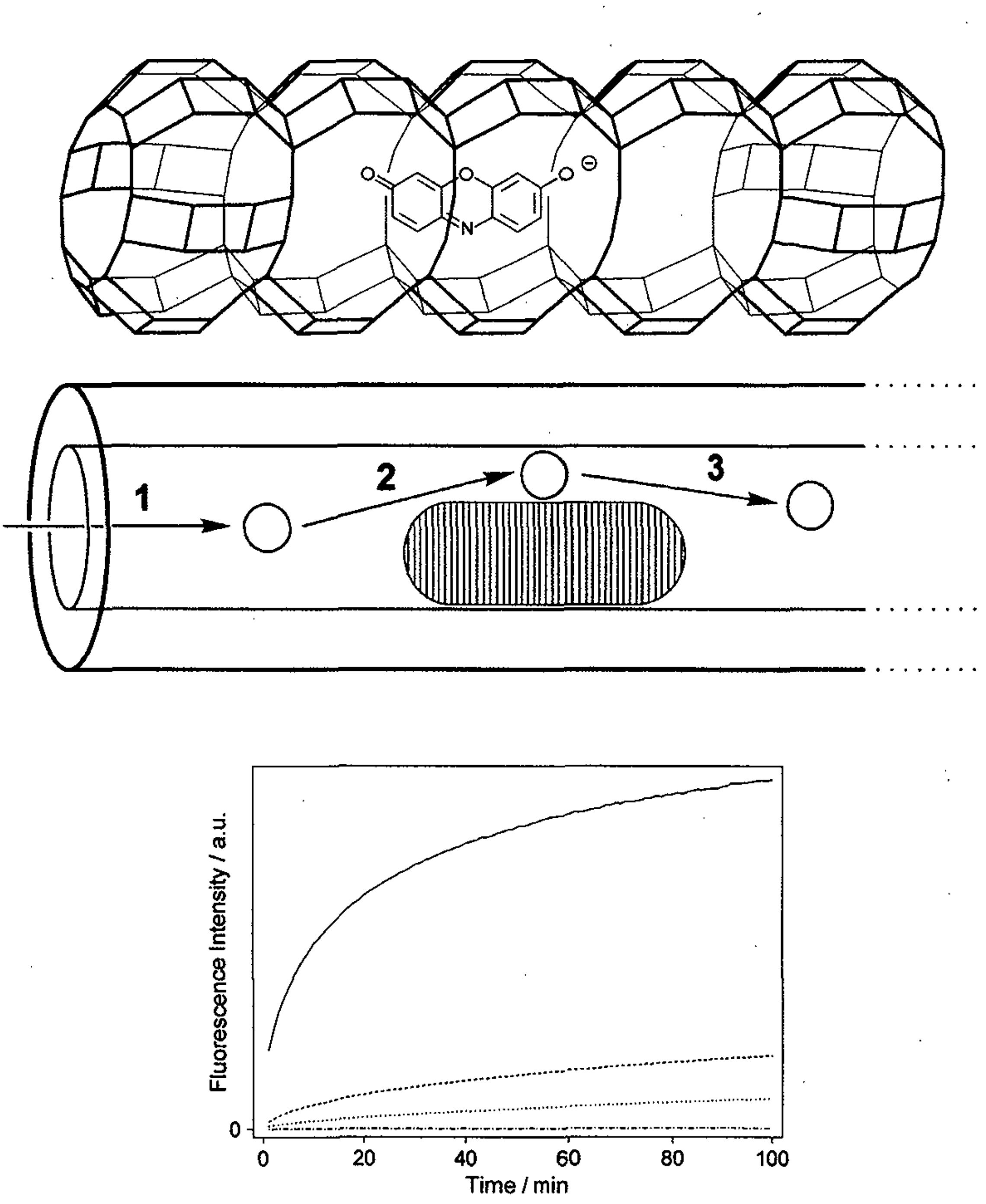


Fig. 4. Top: *The resorufin anion in a channel of zeolite L, occupying approximately two unit cells, is illustrated.* Middle: *Mechanism of the displacement of the dye molecule by solvent molecules.* Bottom: *Experimental exit kinetics monitored by the fluorescence intensities of suspension of Res$^-$-loaded zeolite samples in different solvents: water (—); methanol (---); ethanol (· · ·); propan-1-ol* (-·-) [19].

observation that not only the quantity but also the quality of the loading changed during the displacement. Based on these observations and the consideration of space-filling *van der Waals* models, we deduced a mechanism for the displacement process (*Fig. 4*, middle). The main channels of zeolite L consist of sections with a length of 7.5 Å in the *c*-direction. The sections are joined by twelve-membered ring windows having a free diameter of *ca.* 7.1 Å. These rings make up the narrowest parts of the main channel. The largest free diameter is *ca.* 13 Å and lies midway between the twelve-membered rings. These structural properties are simplified in *Fig. 4* by drawing two cylindrical channels. The displacement process can be outlined as follows: In a first step, the solvent molecules penetrate into the channel until they find an intercalated resorufin. This process is probably very fast, since the diffusion of the penetrating solvent through the channel is only hindered by other solvent molecules already present. It thereby has to be pointed out that in zeolite L, the solvent can only enter the main channels through the windows at both ends and that the investigated solvent molecules are small enough to easily enter through these windows. To further penetrate into the channel, the solvent must now pass the resorufin. This second step is decisive for the rate of displacement, and its speed will depend on the size of the solvent molecules. After passing the resorufin, the solvent moves on until it encounters the next resorufin. All of the above-mentioned processes of solvent diffusion are reversible, and solvent molecules may also pass a resorufin molecule in the opposite direction and subsequently leave the channel. Most importantly, the second step results in an accumulation of diffusing solvent molecules in the void volume around the resorufin, which leads to the mobilization of the latter. The thereby initiated diffusion of the resorufin will, after a certain period of time, result in its release into the solution surrounding the zeolite. The resorufin molecules in solution are deprotonated and will therefore not be able to reenter the zeolite channel. It follows that the rate of the increase of the concentration of Res^- in the solution is a measure for the ability of the solvent to pass the resorufin molecules inside the zeolite main channel. Understanding the exit kinetics of a molecule intercalated in the one-dimensional channels of zeolite L and of similar materials, it follows that dye molecules remaining at the outer surface of the zeolite microcrystals can easily be washed away by means of an appropri-

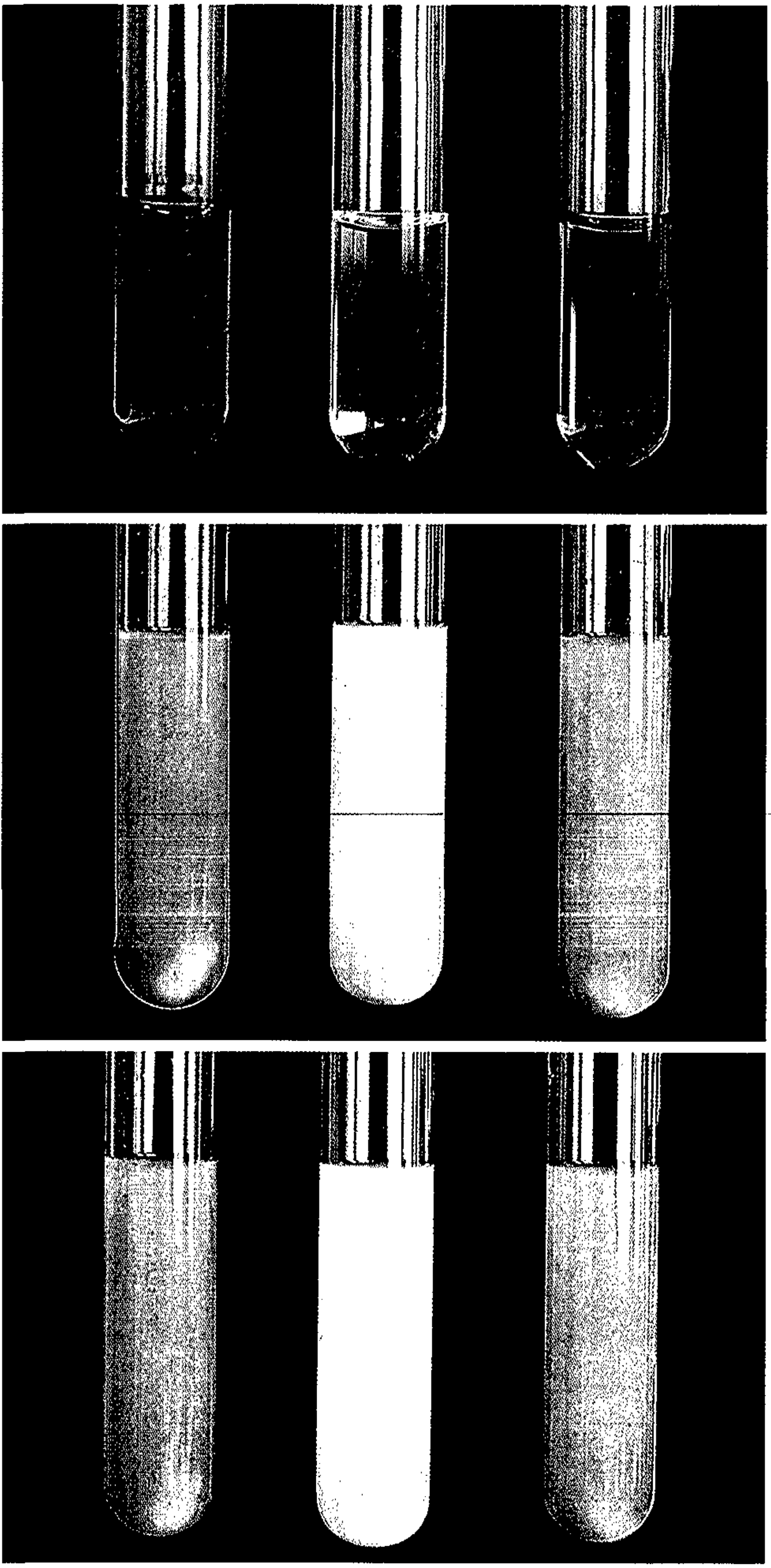
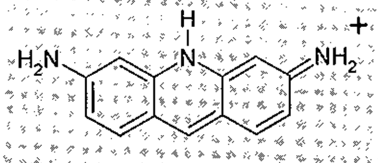
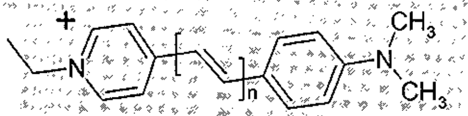
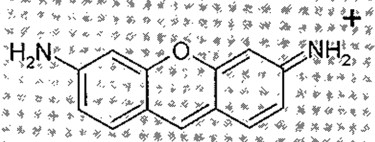
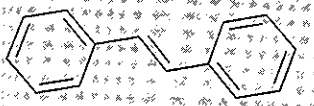
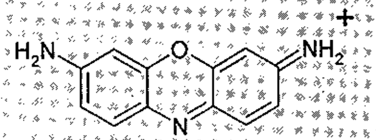
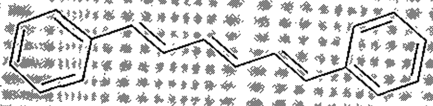
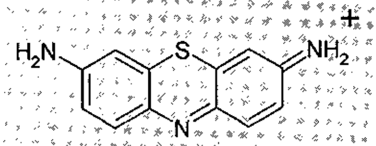
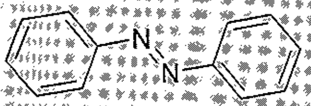
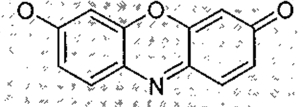
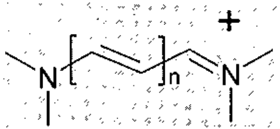
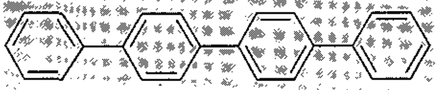
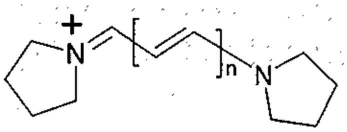
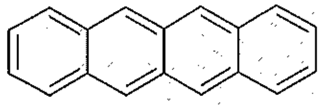
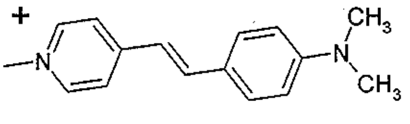
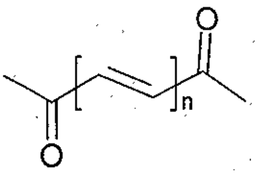


Fig. 5. *Demonstration experiment, illustrating the formation of aggregates when zeolite L is added to a solution of thionine in water and intercalation of the thionine upon heating (details see text)*

Table 2. *Examples of Dye Molecules which have an Appropriate Structure for Being Intercalated into the Channels of a Hexagonal Zeolite.* Most of them have already been intercalated into zeolite L; abs = absorption; em = emission.

	Structure of the ionic molecules	abs/em		Structure of the ionic and neutral molecules, respectively	abs/em
Proflavine		480 nm/ 500 nm	Pyridine dyes		
Pyronine		510 nm/ 517 nm	Stilbene		280 nm/ 315 nm
Oxonine		600 nm/ 609 nm	Diphenyl- hexatrien		380 nm/ 425 nm
Thionine		620 nm/ 634 nm	Azobenzene		350 nm/ 370 nm
Methyl- viologen		257 nm	Biphenyl		247 nm/ 315 nm
Resorufin		560 nm/ 600 nm	*p*-Terphenyl		275 nm/ 339 nm
Cyanine dyes		Depending on *n*, UV to IR	*p*-Quater- phenyl		294 nm/ 374 nm
Cyanine dyes		Depending on n, UV to IR	Tetracene		476 nm
Pyridine dyes		500 nm/ 740 nm	Carotenoides, Carotenes, Xanthenophylle (simplified scheme) [22]		Depending on *n*, UV to IR

ate pure solvent. This is now regularly used in our laboratory.

One can, however, also deduce other consequences from this understanding. The molecules inside of the channels are not accessible to anionic chemicals unless drastic conditions are applied, because, being negatively charged, they have difficulties to enter the negatively charged zeolite channels. This can be used to destroy specifically molecules on the outer surface of the microcrystal by means of an anionic reagent without affecting molecules which are inside. This is best explained by means of a demonstration experiment with thionine and zeolite L. Part of it is illustrated in *Fig. 5*, where at the top, two test tubes containing 4 ml of a $2 \cdot 10^{-5}$M aqueous solution of thionine are shown. The test tube in the middle contains pure water and serves as a reference. Adding to each of these test tubes 2 ml of a zeolite L suspension (2 g zeolite L in 100 ml of water) results in the situation shown in the middle. From spectroscopic studies we know that the color corresponds to thionine aggregates immediately formed at the outer surface of the microcrystals [2]. When heating a test tube containing thionine and zeolite L and keeping its content at near boiling for *ca.* 1 min, a sudden color change is observed (*Fig. 5*, bottom, right). The color remains when the test tube is cooled to r.t. It is caused by the molecules which have entered the channels of the zeolite, where they can only exist as monomers. In a next step, not illustrated in *Fig. 5*, we add to the three test tubes a few drops of a 13% hypochlorite solution. The effect is striking: while the color of the top and middle samples bleaches rapidly, nothing happens to the bottom one. This illustrates nicely how intercalating a dye in an appropriate host can change properties; in this case the stability. This experiment is used in our laboratory as a very fast and convenient probe to check the success of a zeolite L syntheses; it works also for other zeolites with large enough pores. If this test is negative, we can skip the more involved powder X-ray and SEM characterizations, because the test surely indicates that a material without or with too small pores was obtained and that a new synthesis is necessary.

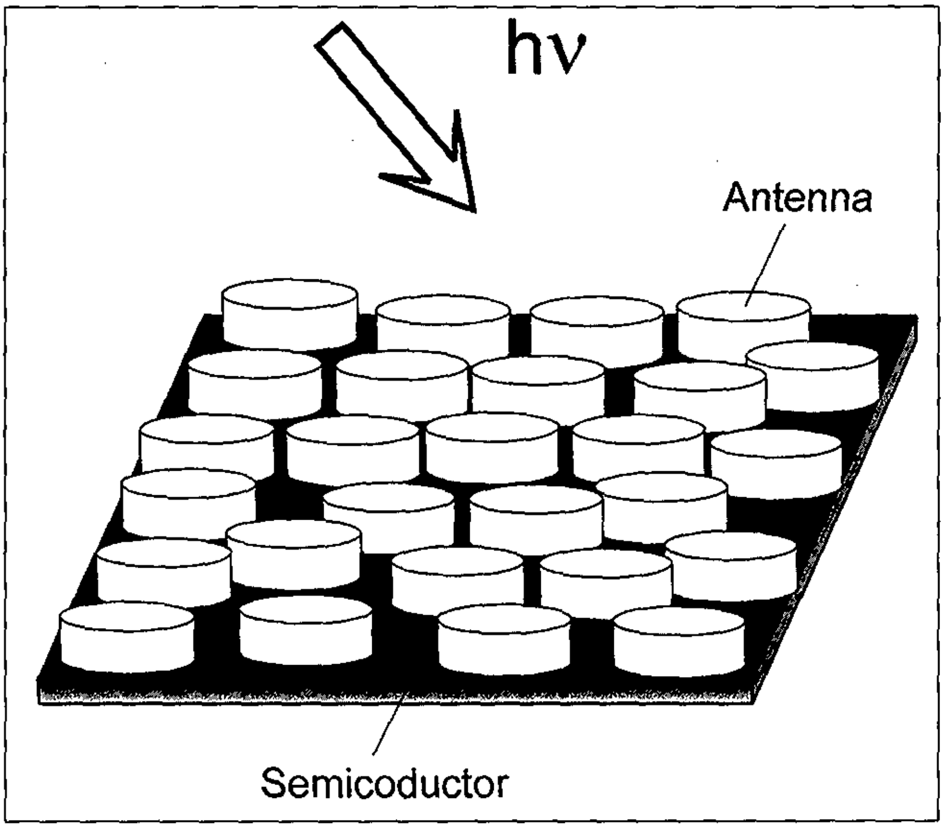


Fig. 6. *Speculation on a new type of dye-sensitized solar cell.* The cylinders represent dye-loaded zeolite L microcrystals of about 1 µm length (details see text).

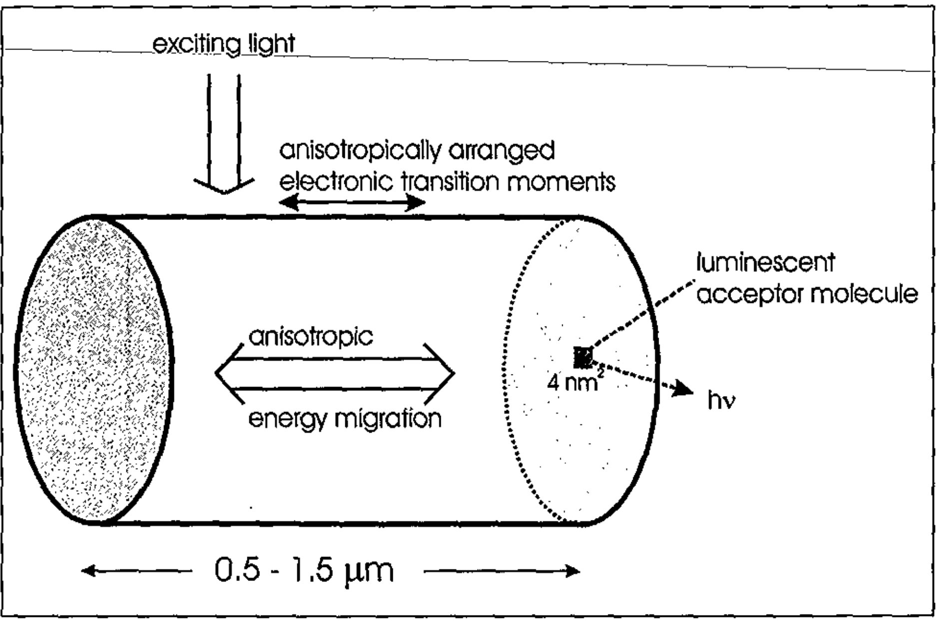


Fig. 7. *Illustration of the anisotropic properties of a dye-loaded zeolite L microcrystal*

Other experiments show how the intercalation of pyronine and oxonine into the cylindrical zeolite L microcrystals can be made visible. They have been illustrated in a report, where we also describe a simple and elegant experiment for the visual proof of the energy transfer from pyronine to oxonine [6]. We recently reported experimental results for the front-trapping efficiency of cylindrical pyronine-loaded zeolite L microcrystals of 700 nm, 1100 nm, and 1500 nm length, and of different pyronine occupation probabilities ranging from 0.03 to 0.48, modified with one oxonine molecule at the front and one at the back of each channel. Extremely fast electronic excitation-energy transport, by *Förster*-type energy migration supported by self-absorption and reemission, along the axis of the cylindrical microcrystals was observed, and we found effective energy migration length of a pyronine excitation of up to 166 nm, thus leading to fascinating properties of this material [7].

The dyes illustrated in *Fig. 3* are by far not the only ones which fit into channels of zeolite L. We have investigated a couple of other dyes, a selection of which is illustrated in *Table 2*. The cationic dyes can be intercalated by ion exchange into zeolite L and the neutral ones from the gas phase. Combining the many dyes with the different zeolites of appropriate structure, given in *Table 1*, shows that there is a large field to be explored for realizing artificial antenna systems or materials with other desired properties.

For some applications, it is desirable or even necessary to arrange the microcrystals as monomicrocrystal layers on a substrate such as a semiconductor, a conducting glass or a metal. This is explained in *Fig. 6*, where, as an example, a speculation on a new type of a dye-sensitized solar cell is illustrated. In such a device, all incoming light is absorbed within the volume of the cylindrical microcrystals of less than 1 μm length containing appropriate dye molecules for light harvesting. The excitation energy is then transported *via* energy migration to the contact surface with the semiconductor, where, by a very efficient energy transfer from an excited dye to the semiconductor, it creates an electron hole pair in the semiconductor. The semiconductor could for instance consist of a very thin silicon layer which by itself would be much to thin to absorb a significant amount of light. The electron hole pair can then be separated as in an ordinary silicon-based solar cell. This would result in a very thin solar cell only about 2 μm thick. We have shown that monomicrocrystal layers, of the type needed for realizing such a device, can be formed with zeolite A [21], and we are confident that the same will be possible with zeolite L and other zeolite microcrystals bearing the appropriate morphology.

Conclusions

Zeolite microcrystals can act as host for supramolecular organization of molecules, complexes, clusters, and quantum-size particles. They offer options for designing precise and reversible functionalities. The possibility of arranging zeolite microcrystals of good quality and narrow size distribution as dense monograin layers on different substrates can be used to achieve specific properties. This article focuses on organic dye molecules in the channels of hexagonal zeolite microcrystals bearing one-dimensional channels. Main characteristics of this material are explained in *Fig. 7* which places emphasis on the pronounced anisotropic properties for light absorption/emission and energy migration. As we explained, extremely fast electronic excitation-energy migration, supported by self-absorption and re-emission, along the axis of cylindrical microcrystals has been demonstrated by us in pyronine-dye-loaded zeolite L microcrystals modified with oxinine [7]. Many other highly organized dye-zeolite materials can be prepared and are expected to show a wide variety of challenging properties. We focus on intrazeolite electronic excitation-energy transport and on intrazeolite charge transport. The largely improved chemical stability and photochemical stability of dye molecules intercalated in an appropriate zeolite framework allows us to work with dyes which otherwise would be considered uninteresting because of lack of stability.

Also included in the actual research interests of our group are some additional properties and functionalities. The vibrational properties of the intercalated compounds can serve for structural identification, as an analytical tool to quantify the loading, to monitor the encapsulation process by *in situ* experiments, and to follow the kinetics of intrazeolite reactions. But it can also be used for studying the interactions between the intercalated molecules, *i.e.*, as a function of the loading and for studying guest-host interactions. The chemical reactivity between the intercalated molecules offers the possibility for *in situ* synthesis of chains of molecules or of clusters which might not be accessible otherwise. In some cases, guest-host reactivity must be considered. The reactivity of intercalated compounds with (small) molecules penetrating from the outside is an option for changing the composition of a material, *e.g.*, large molecules intercalated in a first step can be linked to form chains. New electronic structures are accessible either by specific geometrical arrangements made possible by the structure of the host or/and by explicitly involving its electronic properties [23]. Some systems meet the necessary conditions for the occurrence of intrazeolite charge transport (ionic and electronic) [24]. This transport is realized by the guest molecules in the ground state and in electronically excited states under high-vacuum conditions or in the presence of a solvent, depending on the composition and the structure of the material. We wonder if and under what conditions LED (LED = light-emitting diode) properties can be observed in these systems.

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