LETTERS

Transfer of Electronic Excitation Energy between Dye Molecules in the Channels of Zeolite L

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We show that the intercalation of dye molecules, which penetrate the cylinders from the bottom and the top surface, into the linear channels of zeolite L can be observed with the help of a fluorescence microscope. By means of a polarizer, we have proved the alignment of the dye molecules in the channels, because maximum luminescence appears parallel to the longitudinal axis of the microcrystals and extinction perpendicular to it. A simple and elegant experiment for the visual proof of the energy transfer from pyronine to oxonine in zeolite is based on the observation that both dyes are intercalated from an aqueous solution within about the same time. This leads to high dye concentrations in the zeolite and therefore to short distances between the molecules, which enables energy transfer between them. This experiment also allows a simple determination of the shortest distances between neighboring dye molecules along linear channels.

Introduction

The intercalation of appropriate dyes into zeolites leads to highly anisotropic arrangements in which the dye molecules are present as monomers up to very high concentrations.[1] Fluorescent dyes thus help to create organized systems that absorb light within the volume of microcrystals and are able to transport excitation energy to a defined site on their surfaces.[2] We describe the intercalation of the two cationic dyes pyronine (X = O, Y = C−H) and oxonine (X = O, Y = N) into the channels of zeolite L shown in Figure 1. For lack of space, these dyes and therefore also their electronic transition dipole moment $\mu_{S_1 \leftarrow S_0}$ are arranged lengthwise in the channels. Such systems allow a very fast energy migration, preferably along the channels,[2] as a sequence of Förster processes.[3] The calculated number of energy-transfer steps per time unit k^E depending on the dye loading p was reported in Figure 4 of ref 2; p adopts values between 0 for an unloaded zeolite to 1 for a zeolite loaded to its maximum. The energy migration constants k^E of oxonine and pyronine differ at the same p to a factor of 4, which is due to the different spectral overlap between the absorption and emission spectrum of these dyes. Owing to their favorable orientation and spectral properties, the calculated k^E of the dyes are, even at low loadings, higher than those of a natural antenna system, for which 0.2 ps^{-1} has been measured.[4] The supramolecularly organized dye molecules therefore meet an important condition for an artificial antenna system.[5] Organic dyes in the cavities of zeolites are examined in view of nonlinear optical properties of these materials and possible applications as data storage devices.[6] In contrast to such applications, antenna systems need microcrystals of not more than a few micrometers in length because, otherwise, radiative and nonradiative relaxation processes dominate.[2]

In this work we show how the intercalation of pyronine and oxonine into the cylindrical zeolite L microcrystals can be made visible. Moreover, a simple and elegant experiment for the visual proof of the energy transfer from pyronine to oxonine in zeolite is described. This experiment furnishes information about the distance between dye molecules in zeolites. Since the material's morphology is essential,[7] we have refined the synthesis procedure[8] for the production of cylindrical zeolite L.

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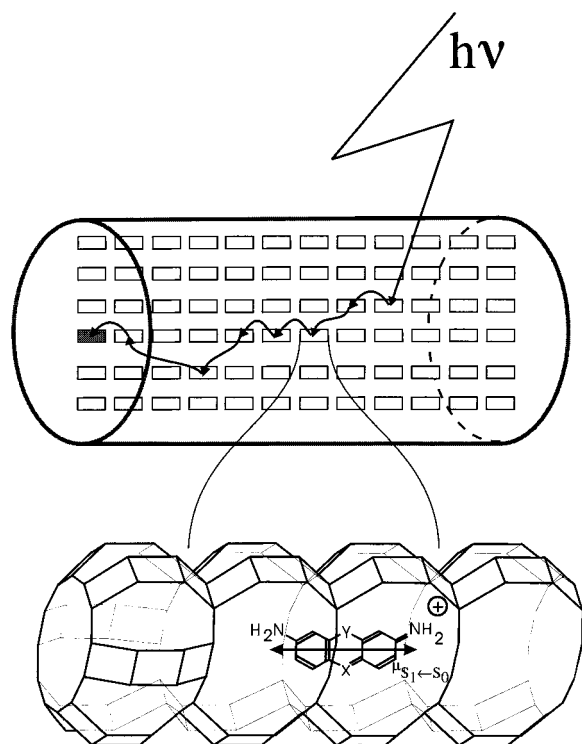
Figure 1. Schematic representation of an artificial antenna system based on organic dyes as chromophores. The rectangles symbolize sites for the dye molecules. The enlargement shows a detail of the zeolite L channels, with a dye molecule (pyronine, X = O, Y = C−H; oxonine, X = O, Y = N) and its electronic transition dipole moment, which is aligned along the channels.[2]

Experimental Section

Pyronine and oxonine were synthesized and purified according to the procedure in literature.[9] Synthesis of zeolite L: The molar composition of the initial solution was 2.6 K_2O, 1.0 Al_2O_3, 9.7 SiO_2, 161.3 H_2O. $Al(OH)_3$ was dissolved in boiling heat in a solution consisting of KOH and water and, with strong stirring, added to a mixture of colloidal silica and water. After a few minutes this mixture had turned into a thick gel, which was then transferred into a pressure-tight PTFE reaction vessel. Crystallization followed without stirring at 160 °C within 6 days. After cooling, the upper part of the strongly alkaline solution was decanted. The white residue was washed with boiling water until the latter reacted neutrally and then air-dried for 14 h at 100 °C. With this procedure, cylindrical microcrystals of 1.5 μm in length and a diameter of 950 nm were obtained. If the molar composition of the initial solution is 3.3 K_2O, 1.0 Al_2O_3, 9.7 SiO_2, 162.0 H_2O, the same procedure leads to zeolite L microcrystals of 300 nm in length and 750 nm in diameter. The zeolite L microcrystals were characterized by X-ray powder diffraction, thermogravimetry, and electron microscope. For the production of dye zeolites of different loadings, zeolite L (**1**, 10 mg; **2**, 4 mg; **3**, 2 mg; **4**, 1 mg; **5**, 0.5 mg) was added to 2.5 mL of an aqueous dye solution consisting of 1×10^{-6} M pyronine and 6.6×10^{-7} M oxonine, treated in an ultrasonic bath for 10 min, and boiled at reflux for 2 h. The conditions guaranteed a quantitative transfer of the dye molecules from the solution into the channels of the zeolite in all dye−zeolite experiments.[1] Hence, the dye concentration in the zeolite microcrystals can be directly determined from the amount and the concentration of the applied dye solution. In the energy-transfer experiments, the concentration of each dye with respect
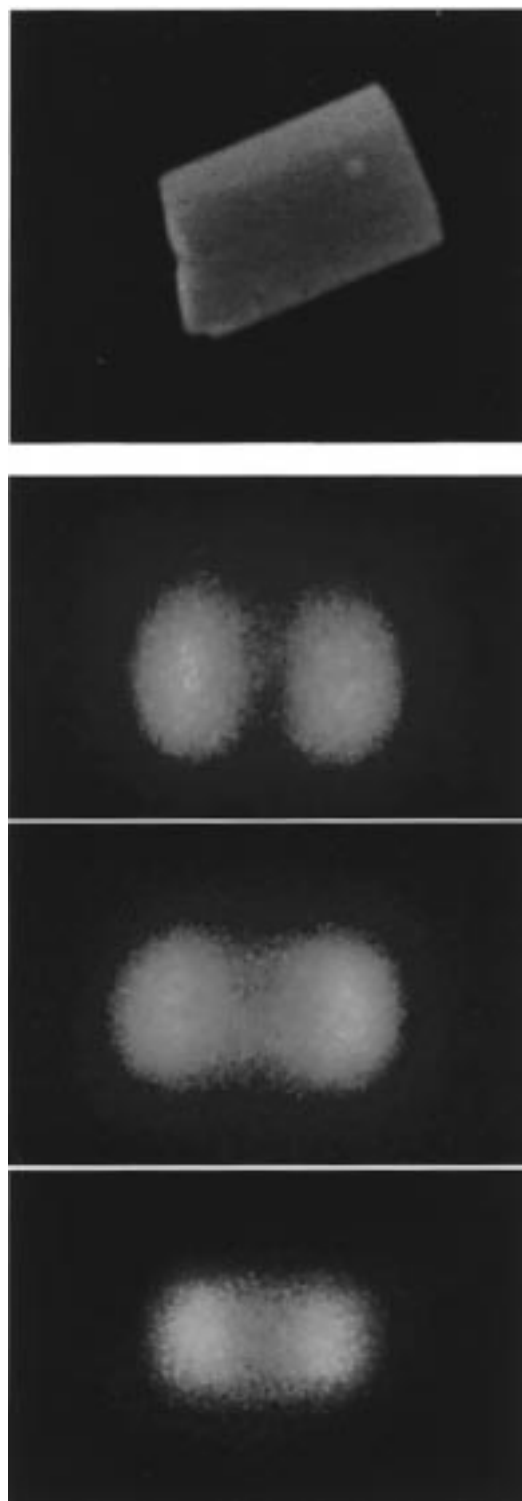
Figure 2. (a, upper) Electronic microscope picture of a zeolite L microcrystal with a length of 1.5 μm. (b, lower) Fluorescence microscope pictures of single zeolite L microcrystals having a length of about 1.5 μm. Top: 5 min exchange with pyronine. Middle: 2 h exchange with pyronine. Bottom: 2 h exchange with pyronine and afterward 2 h exchange with oxonine.

to the zeolite volume was within the range of 5×10^{-4} and 1×10^{-2} mol/L. This means that the dye loading p, as defined in ref 2, was in the range of 1×10^{-3} to 2×10^{-2}. Fluorescence spectra were recorded on a Perkin-Elmer Luminescence Spectrometer LS50B and fluorescence microscopic pictures with an Olympus BX60 (filter block U-MNB).
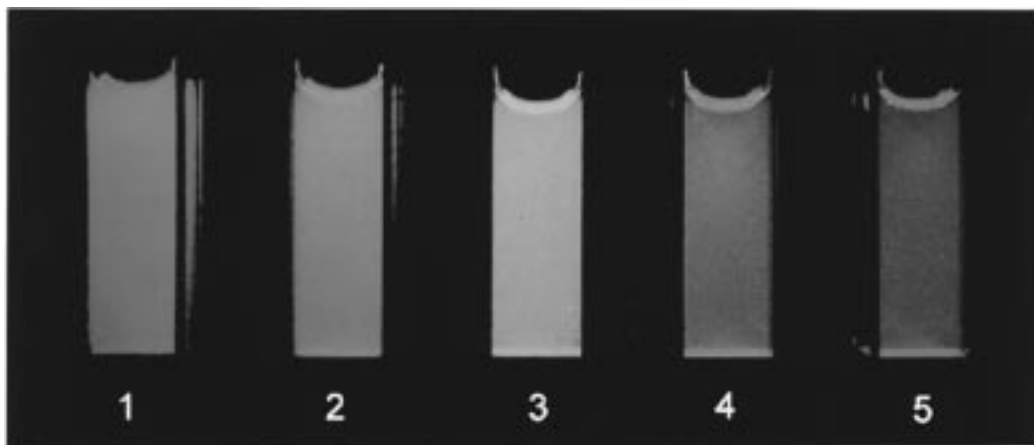
Figure 3. Photographic picture of the fluorescence of suspensions **1**−**5** after specific excitation of pyronine at 254 nm. The dye concentration inside the zeolite microcrystals decreases from **1** to **5** at a factor of 20.

Results and Discussion

We were able to show that the intercalation of dye molecules, which penetrate the cylinders from the bottom and the top surface, into the linear channels of zeolite L can be observed with the help of a fluorescence microscope. For this purpose, microcrystals of 0.95 μm in diameter and 1.5 μm in length were used, which corresponds to the EM picture in Figure 2a. Fluorescence microscope pictures of such samples after different exchange times are shown in Figure 2b. After an exchange time of 5 min with pyronine, its characteristic green fluorescence can be observed at both ends of the cylinder, while the section in the middle remains dark (Figure 2b, top). During this short exchange time, the dye molecules, coming from both sides, only penetrate a small part of the inside. After an exchange time of 2 h, the fluorescent areas have become larger because the dyes on both sides have moved toward the inside (Figure 2b, middle). If this sample is then exchanged with an oxonine solution for 2 h, a stacking of the molecules inside the microcrystal is achieved. This can be made visible by the green emission of pyronine in the inside and the yellow emission of oxonine near the bottom and the top surface (Figure 2b, bottom). The emission of oxonine here appears yellow instead of red because, for technical reasons, the picture has been taken through a filter that only lets the energy-rich part through. The stacking of the dyes shows very nicely that during the oxonine exchange, the intercalated pyronine does not leave the zeolite any more. Otherwise, a blending of the dyes in the solution and therefore also inside the zeolite could be observed. The stacking also shows that, inside the channels, the dyes cannot glide past each other because the channels are too narrow. With the help of a polarizer, we have proved the alignment of the dye molecules in the channels, because maximum luminescence appears parallel to the longitudinal axis of the microcrystals and extinction appears perpendicular to it.

The idea for the visual proof of energy transfer from pyronine to oxonine in zeolite L is based on the observation that both dyes are absorbed from an aqueous solution within about the same time. This leads to high dye concentrations in zeolite and therefore to short distances between the molecules, which allows energy transfer between them. To carry out the experiments, five suspensions with zeolite loaded to different degrees were produced by exchanging different amounts of zeolite L in the same volumes of a dissolved pyronine−oxonine mixture. The amount of zeolite decreases in the suspensions from **1** to **5** by a factor of 20 in the total. The dye concentrations inside the zeolite microcrystals, as well as the loadings p_{Py} and
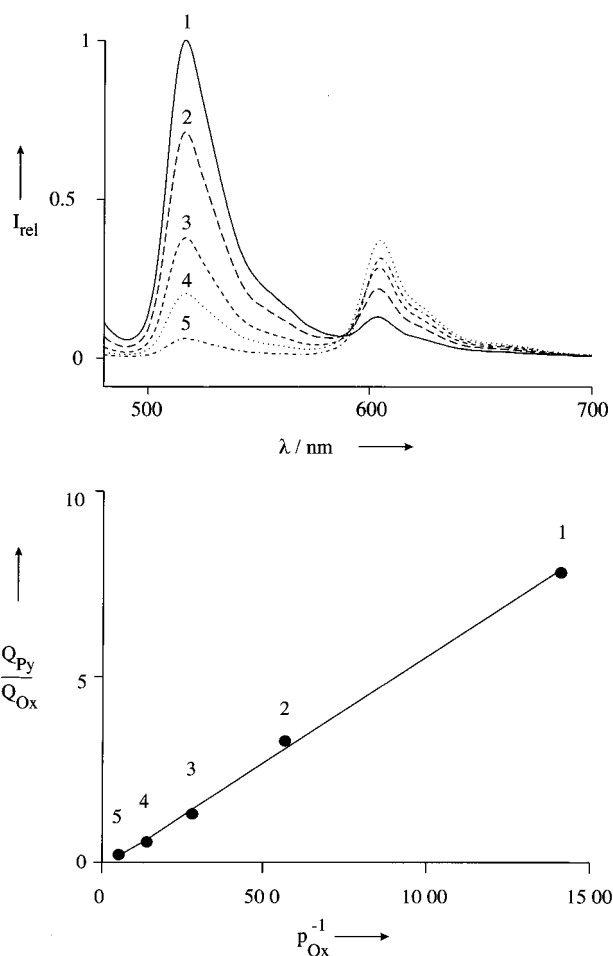
Figure 4. Fluorescence spectroscopic examinations of suspensions **1**−**5** after specific excitation of pyronine at 470 nm. (a, top) Fluorescence spectra. (b, bottom) Relation Q_{Py}/Q_{Ox} of the emission intensities of pyronine and oxonine as a function of the oxonine loading p_{Ox} of the zeolite.

p_{Ox}, (correspondingly) increase by the same factor because the chosen amounts allow a quantitative transfer of dyes from the solution to zeolite.[1] The experiments were carried out with zeolite L microcrystals of a diameter of 760 nm and a length of 300 nm, which shortens the exchange time. The fact that the energy transfer of excited pyronine to oxonine depends on the zeolite loading can be observed very nicely if radiation is used at 254 nm where only pyronine absorbs, as illustrated in Figure 3. The increase in loading leads to a gradual replacement of

the green emission of pyronine, which is predominant in sample **1**, by the red emission of oxonine, which has replaced almost all of it in sample **5**. Corresponding quantitative experiments are shown in Figure 4, again after specific excitation of pyronine, which here occurs at 470 nm. At the lowest loading, the green emission of pyronine predominants with a maximum at 523 nm. An increase in loading causes this emission to decrease and the emission of oxonine to increase with a maximum at 609 nm. At the highest loading, there is almost only oxonine luminescence left, which corresponds to the emission of sample **5** in Figure 4. The proportion of the integrated emission intensities Q_{Py}/Q_{Ox} of pyronine and oxonine versus p_{Ox} is shown in Figure 4b. Q_{Py}/Q_{Ox} is a measure of the energy-transfer rate from pyronine to oxonine. If the rate increases, the emission intensity of pyronine decreases and the one of oxonine increases, which leads to a decrease of Q_{Py}/Q_{Ox}. The distance R between the centers of donor and acceptor molecule is decisive for the occurrence of energy transfer. For this reason, the energy-transfer rate is determined by the probability that an oxonine molecule is present at a distance between R_0 and $2R_0$ of an excited pyronine, whereby R_0 corresponds to the shortest distance between the centers of two dyes along a channel. This probability is given at a regular molecule distribution by the oxonine loading p_{Ox} of zeolite. This means that the energy-transfer rate is in proportion to p_{Ox}. Correspondingly, Q_{Py}/Q_{Ox} is in proportion to p_{Ox}^{-1}, which can be seen in Figure 4b. R_0 can be calculated from the increase of Q_{Py}/Q_{Ox} with p_{Ox}^{-1}. Energy-transfer experiments therefore allow a simple determination of the shortest distances between neighboring dye molecules along linear channels. With the present data, this results in 21 Å. A dye therefore occupies about three unit cells along a channel because the length of the zeolite L unit cell is 7.5 Å.[2] In an analogous experiment with ZSM-12, 19 Å was found for R_0, which in this material corresponds to about four unit cells of 5 Å each.

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