DOI: 10.1002/ange.200504286

# Organizing Supramolecular Functional Dye–Zeolite Crystals**

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Sunlight is absorbed in the antenna system of a green leaf where it is transported by supramolecularly organized chlorophyll molecules for the purpose of energy transformation. The aim of our research is to develop a similar transport of light in an artificial system in which dye-loaded zeolite L crystals adopt the antenna function and to find out if and how this can be used in photoelectronic devices. Organic dye molecules have the tendency to form aggregates even at low concentration. These aggregates are known to generally cause fast thermal relaxation of electronic excitation energy. The main role of the zeolite as a host is to prevent this aggregation and to superimpose a specific organization.[1] We have shown that zeolite L[2] is an ideal host for this purpose. Supramolecular organization of dyes inside the one-dimensional channels of this material has been realized and their communication via stopcock molecules with molecules in the environment with a polymer or a semiconductor as well as solubilization of dye-loaded zeolite L crystals has been demonstrated.[3,4]

We know that in chemical devices a high degree of supramolecular organization is important for attaining the desired macroscopic properties.[5] A possibility for achieving a high level of organization is the controlled assembly of the zeolite crystals into oriented structures and the preparation of monodirectional materials. In the case of cylindrically shaped zeolite L, this implies the alignment of many crystals on a surface, and has the consequence of the alignment of a large number of one-dimensional channels. An overview of the antenna material, of the stopcock-plugged antenna material, and of the desired organization of the zeolite L crystals resulting in monodirectional functional materials is illustrated in Figure 1.

The preparation of dense monolayers of zeolite crystals in the nanometer to micrometer size regime was first reported for zeolite A[6] and later considerably improved and also extended to other types of zeolites.[7] As a general rule, we can state that the successful assembly of small zeolite crystals largely depends on the availability of a narrow size distribution and a well-defined morphology. The successful assembly of oriented zeolite L monolayers, which can then be modified to result in organized supramolecular functional materials, offers a new challenge. Table 1 gives an overview of the different ways of preparing such monolayers on a substrate. An underlying principle that has to be respected is that the interaction between the base of the cylindrically shaped zeolite L crystals and the substrate must be stronger or preferably much stronger than that between the coat of the crystals and the substrate and, importantly, any interaction between the zeolite crystals. Working with an excess of crystals, fixing them in the right way to the substrate, and washing away the excess material has, under these conditions, a high chance of leading to the desired material. Subsequent insertion of dye molecules into the channels and the addition of stopcocks is only possible if the channels are not blocked or damaged during the preparation of the monolayer. The procedure leads to materials with exciting properties, for example, to systems where electronic excitation energy is transported in one direction only.

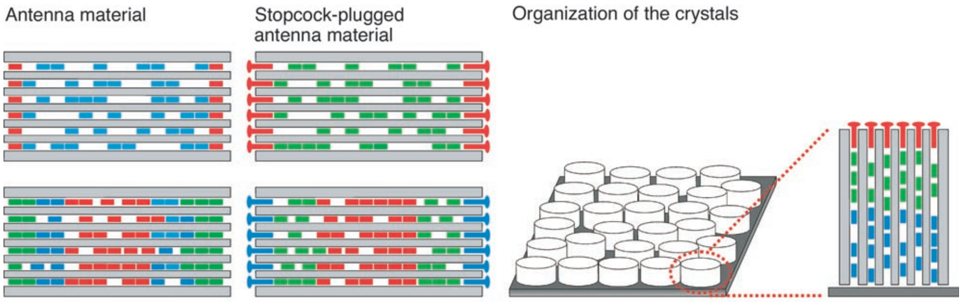

*Figure 1.* Different stages of organization. Left: Supramolecularly organized dye–zeolite crystals. Middle: Stopcock-plugged dye–zeolite crystals. Right: Organization of supramolecular functional dye–zeolite crystals in oriented monolayers.

The preparation of zeolite L monolayers was carried out with two types of medium-sized cylindrically shaped zeolite L crystals: 1 μm average length of average aspect ratio (length to diameter ratio) 1.0, and 200 nm average length of average aspect ratio 0.3.[8] Different chemical procedures were followed depending on the reagents used. The incorporation of the dyes and the attachment of stopcock molecules at the channel ends, after calcining the monolayers of oriented zeolite L crystals, led to monodirectional materials. The molecules that have been used as covalent linkers to synthesize the zeolite L monolayers, the dyes that have been

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[**] This work was supported by the Schweizerischer Nationalfonds zur Förderung der wissenschaftlichen Forschung (NF 200020-105140) and by the European Comission through the Human Potential Programme (RTN NANOCHANNEL, grant no. HRPN-CT-2002-00323). We would like to thank Dr. D. Pflieger from Clariant for providing some chemicals, Beatrice Frey for the SEM measurements, and Dr. M. Jazdzyk for the $C_{60}$ sample.

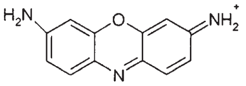
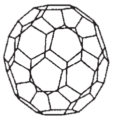
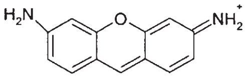
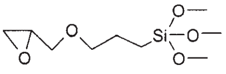
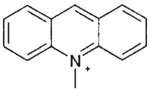
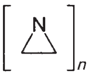
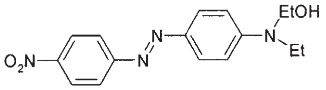
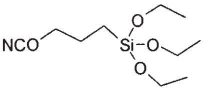
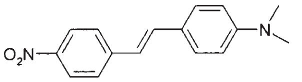
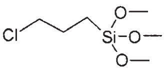
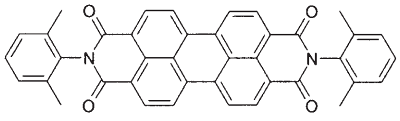
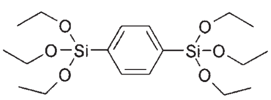
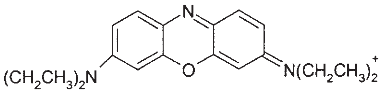
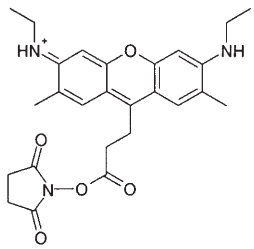
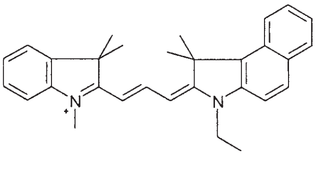
***Table 1:*** Procedures for preparing zeolite monolayers.

| A | B | C | D |
|---|---|---|---|
| cleaning the substrate | | | |
| – | specific modification of the substrate | specific modification of the zeolite | specific modification of both zeolite and substrate |
| sedimentation of a calculated amount of zeolite onto the substrate | addition of an excess of zeolite suspended in an appropriate solvent and reaction with the substrate | | |
| fixation of the zeolite crystals—monolayer assembly | migration and bond formation of the zeolite with the substrate monolayer assembly | | |
| – | washing off the excess of zeolite crystals | | |
| – | optional: calcination at 600 °C under $O_2$ flow | | |

inserted in the channels of zeolite L monolayers, and the stopcock molecules that have been attached are shown in Table 2. The stability of the monolayers was tested before calcination by sonicating the samples in toluene. This test was used because sonication is the best way to clean the monolayers from an excess of crystals. The stability was always considerably improved by the calcination process.

Different experimental conditions and reagents have been tested for obtaining oriented zeolite L monolayers. Details of the different procedures are reported in the Experimental Section. Based on a previous report,[9] $C_{60}$ was tested as a functional interconnecting covalent linker between the amino-modified zeolite L and the amino-tethered glass plate. The degree of coverage and the homogeneity of the monolayers is acceptable for some applications and the stability is high. It was possible to sonicate the sample for more than ten minutes without damaging the layers. The degree of coverage and close packing as well as the stability obtained with a GOP-TMS linker is unsatisfactory. After a few minutes of sonication all the crystals fell off. The use of PEI as a molecular linker[10]

***Table 2:*** Molecules used in this study.[a]

| Abbreviation | Structural formula | Abbreviation | Structural formula |
|---|---|---|---|
| $Ox^+$ |  | $C_{60}$ |  |
| $Py^+$ |  | GOP-TMS |  |
| $MeAcr^+$ |  | PEI |  |
| DR1 |  | TES-PCN |  |
| DANS |  | CP-TMS |  |
| DXP |  | BTESB |  |
| Ox1 |  | | |
| ATTO520 |  | Cy02702 |  |

[a] Left: Dyes inserted in the channels of zeolite L crystals on the monolayer. Right: Covalent linkers that have been used to synthesize the monolayers. Bottom: ATTO520 and Cy02702 are the stopcock molecules that have been attached to the channel ends of the zeolites.

yielded monolayers of acceptable coverage and homogeneity for some applications. Crystals are bound to each other in some areas, which hinders the formation of a clean monolayer. The monolayer is, however, strongly bound to the glass surface and it was possible to sonicate the sample for more than ten minutes without damaging the layer. The degree of coverage and of close packing is high with TES-PCN. The binding of the crystals to the glass surface is not very strong and sonicating the sample for more than five minutes resulted in a severe loss of crystals. The reaction with CP-TMS consists of two steps:[7b,11] the tethering of CP-TMS to the glass surface and reaction of bare zeolite L with the CP-TMS-tethered glass plates. Both types of zeolite L yielded high quality monolayers. We tested two different ways of promoting the reaction between the zeolite L crystals and the functional groups tethered to the glass surface: reflux and sonication. Figure 2 a shows the SEM images of samples prepared under reflux. The degree of packing and of coverage is good. However, binding the zeolite crystals under sonication results in both the degree of coverage and the packing being significantly higher (Figure 2b). Carrying out the reaction under sonication turned out to be more convenient and also more successful; it involves considerable less reaction time. This way of treating zeolite L with a surface-modified glass plate was then applied in all other comparable procedures, for example, when using GOP-TMS, TES-PCN, and BTESB. The binding of the zeolite L monolayer and the glass surface through a CP-TMS linker seemed to be strong, and the sample could be sonicated for more than five minutes without any noticeable changes. In the case of a BTESB linker, a procedure that resulted in very good quality monolayers involved first tethering BTESB to the glass surface followed by treating the bare zeolite L crystals with the BTESB-tethered glass plates under sonication. Figure 2c shows the SEM images of samples prepared by this method. The degree of coverage is high and the degree of close packing is very high. However, the stability of the so-obtained zeolite L monolayers is less good than that obtained following the procedure used for CP-TMS. Sonication of the sample for more than three minutes can cause a great loss of crystals.

The procedures involving TES-PCN, CP-TMS, and BTESB as covalent linkers thus led to closely packed zeolite L monolayers with a very high degree of coverage over the whole plate. The binding of zeolite L crystals onto the TES-PCN/CP-TMS/BTESB-coated glass plate probably proceeds by nucleophilic substitution of the terminal cyanate/chloro/triethoxy groups, respectively, by the surface hydroxy groups on the channel openings of the zeolite L crystals. The strength of the binding between the zeolite monolayer and the glass surface is weak when using TES-PCN and BTESB, whereas it is strong when using CP-TMS. It seems that the nucleophilic substitution of a terminal halide[7c] induces much stronger binding between the zeolite L crystals and the glass surface than the nucleophilic substitution of a terminal cyanate or triethoxy group. The procedures involving $C_{60}$ and PEI as covalent linkers led to zeolite L monolayers with the strongest binding to the glass surface. The binding of amino-modified zeolite L crystals onto the $C_{60}$-coated glass plate proceeds by amine addition to $C_{60}$.[9] The binding of GOP-TMS zeolite L crystals onto the GOP-TMS-coated glass plate through PEI proceeds through a nucleophilic ring opening of the epoxy groups tethered on the glass and on the zeolite L surfaces by the amino groups of PEI.[10]

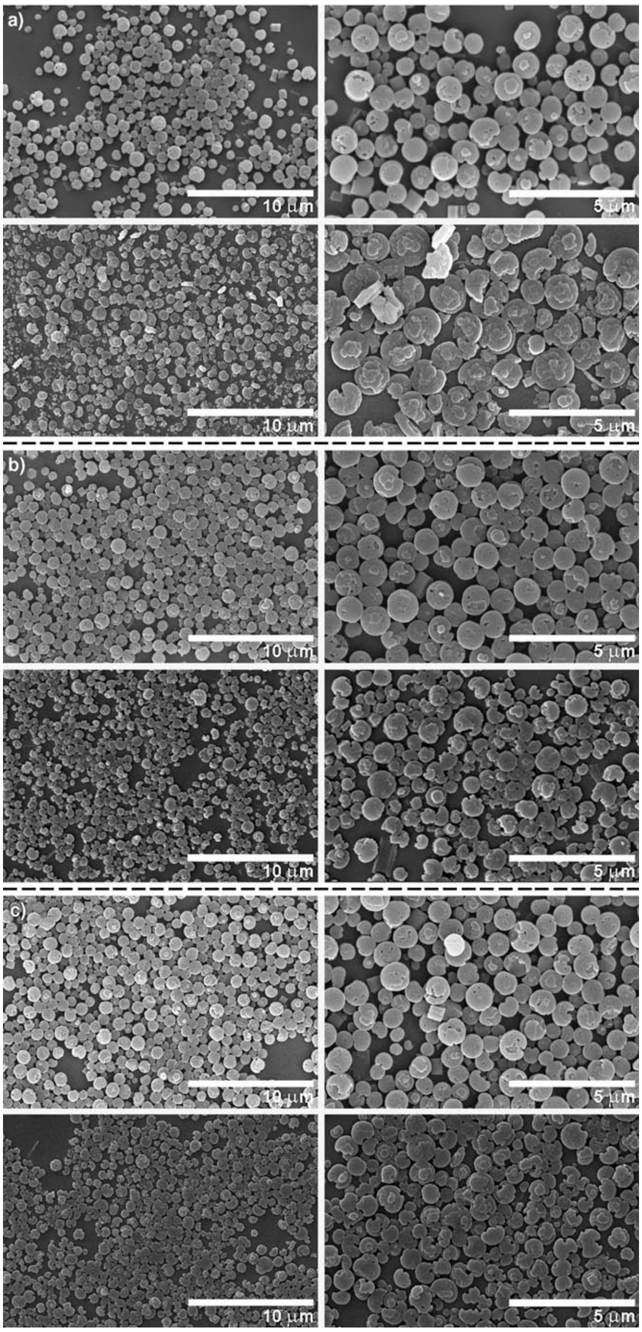


***Figure 2.*** SEM images of zeolite L monolayers after cacination, prepared by using: a) CP-TMS as a covalent linker under reflux, b) CP-TMS under sonication, c) BTESB. Each example contains four images: Upper: 1 μm crystals at two different magnifications. Lower: disc-shaped crystals at two different magnifications.

An important prerequisite for obtaining a high degree of coverage and of close packing is to use a considerable excess of zeolite L crystals when treating them with the modified glass surface. Hence, an underlying principle that has to be respected is that the interaction between the base of the crystals and the substrate must be stronger than any other interaction. A process to account for the close-packing phenomenon is surface migration. It can take place if the interaction of zeolite L crystals with the modified glass plate is sufficiently weak at the initial state of the reaction so that migration can take place to form a dense package. In the next step, stronger binding is achieved. On the basis of this, we can understand why sonication is so successful in promoting the reaction during the monolayer assembly process: It helps the zeolite L crystals to rapidly find available sites on the surface by rapid surface migration.

With methods for preparing oriented zeolite L monolayers in hand, it is now possible to modify them by inserting dye molecules. For this purpose materials with CP-TMS and BTESB linkers were calcined to burn away the organic part and to better close the channel openings on the side in contact with the glass plate. Consecutive insertion of dyes was realized by similar procedures as described in references [3a] and [12]. Table 2 shows a representative list of dyes we have inserted to date into the channels of zeolite L crystals organized as monolayers. Figure 3 shows fluorescence microscopy images of two zeolite L monolayers loaded with $Py^+$ and $Ox^+$. Strong luminescence of the samples can be observed. This observation also proves that the pores in the zeolite L crystals are still open after the calcination process.

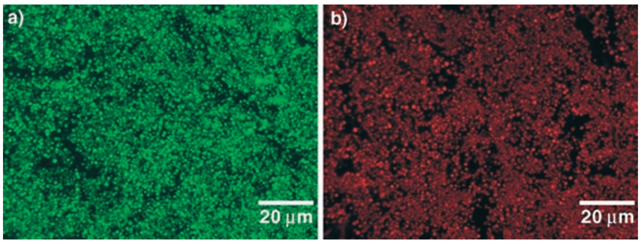


*Figure 3.* Fluorescence microscopy images of monolayers loaded with one dye: a) $Py^+$/zeolite L, b) $Ox^+$/zeolite L.

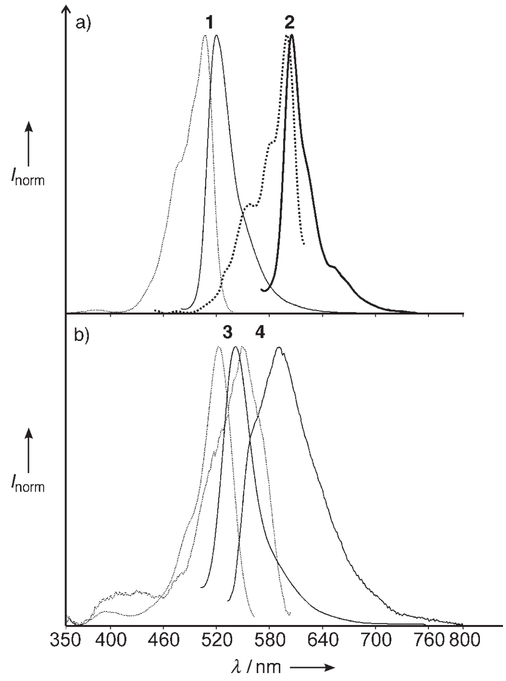


*Figure 4.* Excitation (dotted) and emission (solid) spectra of the dyes used in this study measured on oriented dye/zeolite L layers on quartz. Spectra have been scaled to the same height at the maxima. a) $Py^+$/zeolite L (**1**) and $Ox^+$/zeolite L (**2**). The emission and the excitation spectra of **1** were recorded upon excitation at 460 nm and detection at 560 nm, respectively. Those of **2** were recorded upon excitation at 560 nm and detection at 640 nm, respectively. b) Excitation and emission spectra of ATTO520 (**3**) and Cy02702 (**4**) attached to the zeolite L channel entrances. The emission and the excitation spectra of (**3**) were recorded upon excitation at 460 nm and detection at 600 nm, respectively. Those of **4** were recorded upon excitation at 470 nm and detection at 630 nm.

The consecutive insertion of two different dyes which cannot glide past each other as a result of spatial restrictions is the basis for the preparation of an antenna system capable of efficiently transporting electronic excitation energy. The $Py^+$/$Ox^+$ pair is ideal for testing this. The high fluorescence quantum yield and the favorable spectral properties (Figure 4a) of these dyes allow the system to have very efficient Förster-type electronic excitation energy transfer.[13] An oriented $Ox^+$/$Py^+$/zeolite L monolayer was prepared by first inserting $Py^+$ (donors) followed by insertion of $Ox^+$ (acceptors). The spectra shown in Figure 5a illustrate that considerable energy transfer from the electronically excited $Py^+$ unit to the $Ox^+$ moiety occurs after selective excitation of the donor.

Extension beyond the interior of the zeolite crystals is achieved by selectively positioning molecules at the entrances of the zeolite channels.[14] Table 2 shows the two types of stopcock dyes that have been used. The location of the stopcocks allows their use as traps or injectors of electronic excitation energy. We used ATTO520 to act as a donor in a $Ox^+$/zeolite L monolayer and Cy02702 to act as an acceptor in a $Py^+$/zeolite L monolayer. In both cases the spectral overlap between the donor emission and the acceptor excitation is considerable (Figure 4), so that energy transfer can occur upon selective excitation of the donor molecule (Figure 5b,c). Figure 5b shows the spectra of an oriented ATTO520/$Ox^+$/zeolite L monolayer. Figure 5c shows the spectra of an oriented Cy02702/$Py^+$/zeolite L monolayer.

In conclusion, a new hierarchy of structural order has been reached by organizing supramolecular functional dye–zeolite crystals as oriented monolayers. Different procedures to generate robust monolayers of zeolite L crystals, which have their channels perpendicular to the surface of the substrate, have been described. Subsequent insertion of dyes into the open channel ends was performed and energy transfer was tested. Coupling dye-loaded zeolite monolayers to an external acceptor or donor stopcock dye at the channel ends which trap electronic excitation energy from donor molecules inside the crystal or inject it to an acceptor inside the channels has been demonstrated. These materials are the basis for systems where excitation energy is transported in one direction only, thus largely extending the possibilities to

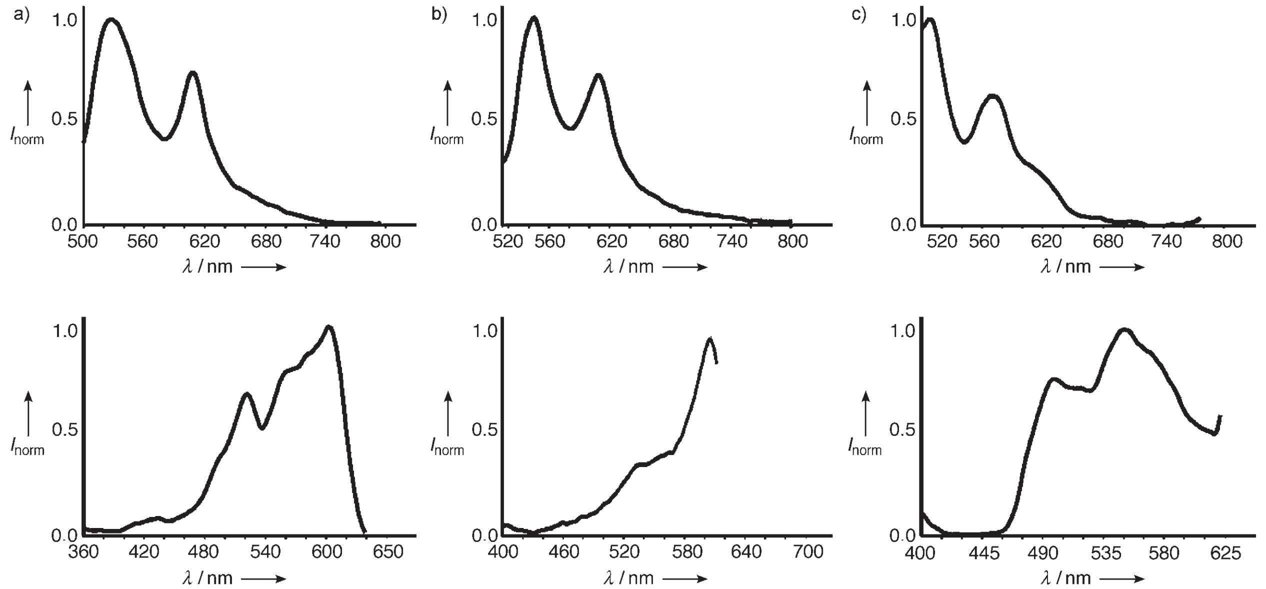


***Figure 5.*** Emission (upper) and excitation spectra (lower) of donor- and acceptor-loaded zeolite L crystals arranged as oriented monolayers on a glass plate. Spectra have been scaled to the same height at the maxima. a) Spectra of a $Ox^+/Py^+$/zeolite L monolayer. The emission spectrum was recorded after selective excitation of $Py^+$ at 460 nm and the excitation spectrum was detected at 680 nm, the wavelength at which $Ox^+$ emits. b) Spectra of an ATTO520/$Ox^+$/zeolite L monolayer. The emission spectrum was recorded after selective excitation of ATTO520 at 460 nm and the excitation spectrum was detected at 680 nm, the wavelength at which $Ox^+$ emits. c) Spectra of a Cy02702/$Py^+$/zeolite L monolayer. The emission spectrum was recorded after selective excitation of $Py^+$ at 460 nm and the excitation spectrum was detected at 680 nm, the wavelength at which Cy02702 emits.

make use of the quasi 1D electronic excitation energy transport in dye-loaded zeolite L that has recently been observed.[15] The new highly organized robust material offers unique possibilities for developing photonic devices also comprising dye-sensitized solar cells and luminescent solar concentrators.[16,17]

## Experimental Section

Materials: Zeolite L crystals of two different sizes (ca. $1 \times 1$ μm and $0.3 \times 1$ μm) were synthesized and characterized as described previously.[8] $Py^+$ acetate and $Ox^+$ perchlorate were synthesized and purified according to Ref. [18]. ATTO520 was purchased from ATTO-TECH GmbH. Cy02702 iodine was obtained from Clariant.[19] APS (purum $\geq 98\%$), GOP-TMS (purum $\geq 97\%$), toluene (puriss, absolute, over molecular sieve), ethanol (absolute, 99.8%), methanol (purum), acetonitrile (puriss., 99.5%, over molecular sieve) were obtained from Fluka; PEI (high-molecular weight, water-free), TES-PCN (95%), CP-TMS ($\geq 97\%$), and BTESB (96%) were obtained from Aldrich; the water used was doubly distilled. The substrates were round glass plates (∅ = 10 mm, thickness = 1 mm, TRABOLD, Switzerland).

Preparation of the zeolite L monolayers: $C_{60}$ as a covalent linker: Functionalization of the channel entrances of zeolite L with amino groups was done as described in an earlier report.[20] Typically, two pieces of glass plates supported on a teflon mount were immersed in a solution of APS (50 μL) in toluene (30 mL) in a round-bottomed Schlenk flask and heated at reflux for 1 h under $N_2$, cooled to RT, and washed with toluene and with copious amounts of ethanol. The APS-tethered glass plates were finally dried for approximately 2 h at 80 °C in air. $C_{60}$ (1 mg) was added to a solution of toluene (15 mL) in a round-bottomed Schlenk flask; a glass plate was then introduced and the mixture was heated at reflux for 24 h under $N_2$, cooled to RT, and washed with copious amounts of cholorobenzene. An excess of amino-modified zeolite L (between 10 and 11 mg) was added to a solution of toluene (15 mL) in a round-bottomed Schlenk flask and sonicated for 15 min, after which a $C_{60}$-coated glass substrate was introduced. The mixture was heated at reflux for 5 h under $N_2$, cooled to RT, and sonicated in fresh toluene for 3 min to remove the physisorbed zeolites. PEI as molecular linker: Zeolite L (50 mg) was suspended in a solution of GOP-TMS (0.1 M) in toluene (20 mL) in a round-bottomed Schlenk flask and heated at reflux for 3 h, cooled to RT, and the GOP-TMS-tethered zeolite crystals were washed with ethanol. Two glass plates supported on a teflon mount were then immersed into a solution of GOP-TMS (0.1 M) in toluene (20 mL) in a round-bottomed Schlenk flask and the toluene solution was heated at reflux for 3 h, cooled to RT, and then the GOP-TMS-tethered glass plates were washed with toluene. Two GOP-TMS-tethered glass plates were immersed in a solution of PEI (700 mg) in toluene (20 mL) and refluxed for 2 h. The physisorbed PEI was removed by repeatedly washing the plates with hot ethanol and doubly distilled water. An excess of amino-modified zeolite L (15 mg) was added to toluene (15 mL) in a round-bottomed Schlenk flask and sonicated for 15 min after which a GOP-TMS-PEI-coated glass plate was introduced. The mixture was heated at reflux for 3 h under $N_2$. After cooling the mixture to RT, the opaque glass plates coated with zeolite L were sonicated in fresh toluene for 3 min to remove the physisorbed zeolites. GOP-TMS, TES-PCN, CP-TMS, and BTESB as covalent linkers: Typically, two glass plates supported on a teflon mount were immersed in a solution (20 mL) of ethoxymethoxysilane (0.1 M) in toluene in a round-bottomed Schlenk flask and the mixture heated at reflux for 3 h. The ethoxymethoxysilane-tethered glass plates were washed with toluene. An excess of zeolite L (10–13 mg) was added to toluene (10 mL) in a round-bottomed Schlenk flask and sonicated for approximately 40 min. An ethoxymethoxysilane-tethered glass plate was introduced and the mixture heated at reflux for 3 h. The opaque glass plates coated with zeolite L were sonicated in fresh toluene for a maximum of 1 min to remove the physisorbed zeolites. Alternatively, an excess of zeolite L (10–13 mg) was added to toluene (10 mL) in a round-bottomed Schlenk flask and sonicated for approximately 40 min. An ethoxymethoxysilane-tethered glass plate was then introduced and sonicated for 15 to 17 min.

Calcination of zeolite L monolayers: The zeolite L monolayer was placed in a closed oven and the temperature was steadily increased up to 600 °C under oxygen where it was kept for 3 h. After calcination, the zeolite L monolayer was dipped in a 0.1 M $KNO_3$ solution for 30 min.

Functionalization of the zeolite L monolayers: The cationic dyes were inserted into the zeolite L channels by ion exchange from aqueous solutions. A calcined zeolite L monolayer was introduced in an aqueous solution of $Py^+$ or $Ox^+$ ions and heated up to 70 °C for 15 h. The zeolite L monolayer was then washed several times with doubly distilled water and with ethanol. Neutral dyes such as DR1 and DANS were inserted from the gas phase by using the single ampoule method.[3,12] The reaction time and temperature were 48 h at 170 °C for DR1 and 24 h at 270 °C for DANS. Attachement of ATTO520 to the channel ends was achieved by treatment of a zeolite L monolayer with a solution of ATTO520 in acetonitrile for 24 h at RT as described in Ref. [14]. For the electrostatic binding of the cationic dye Cy02702, a zeolite L monolayer was treated with a solution of Cy02702 in ethanol for 24 at RT.

Physical measurements: SEM measurements were carried out by means of scanning electron microscopy (Hitachi S-3000N) at an acceleration voltage of 20 kV. A 3-nm gold layer was deposited on top of the samples. Luminescence and excitation spectra were measured at RT in air with a Perkin–Elmer LS 50B instrument with a resolution of 15 nm. For the luminescence microscopy images, an Olympus BX60 microscope equipped with a Kappa CF20DCX air-cooled CCD camera was used. The $Py^+$/zeolite L monolayer sample was excited from 470 to 490 nm and the fluorescence was detected by using a 520 nm cut-off filter. The $Ox^+$/zeolite L monolayer sample was excited from 545 to 580 nm and the fluorescence was detected by using a 610 nm cut-off filter. The quality of the zeolite L monolayers was examined by dipping the glass plates coated with zeolite L in fresh toluene and immersing them in an ultrasonic bath (Branson DTH-2510, 130 W, 42 kHz) for several minutes. The glass plates were then investigated using an optical microscope and by SEM.

Received: December 2, 2005
Revised: May 4, 2006

**Keywords:** energy transfer · FRET (fluorescence resonance energy transfer) · monolayers · supramolecular chemistry · zeolites

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