

cysteamine ethanolic solution for 2 h. The Au samples were then removed from the adsorption solution and thoroughly washed in distilled water. The poly(allylamine) osmium derivative was adsorbed on the modified gold electrode from 0.4% w/v aqueous solutions for 10 min. GOx was adsorbed from a 1  $\mu$ M aqueous solution. After adsorption the modified electrodes were thoroughly rinsed with distilled water.

The redox polymer Os(bpy)<sub>2</sub>ClPyNHpoly(allylamine) (PAH-Os) was synthesized as previously reported.<sup>[10]</sup>

Glucose solutions were prepared from a stock solution equilibrated in the anomers, and kinetics herein refer to the total glucose concentration. All solutions were prepared in Milli-Q (Millipore®)-water and stored at 4 °C. Enzyme catalysis experiments were carried out under N<sub>2</sub> atmosphere.

A standard three-electrode electrochemical cell was employed with a home-built operational amplifier potentiostat. The reference electrode was a saturated calomel electrode, and all potentials herein are quoted with respect to this reference; a platinum auxiliary electrode was employed.

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**Keywords:** electrochemistry · enzyme catalysis · monolayers · nanostructures · sensors

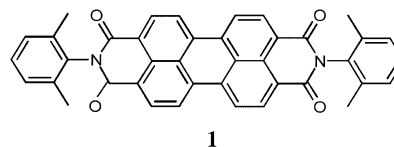
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## Energy Transfer from Dye–Zeolite L Antenna Crystals to Bulk Silicon

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The possibility of radiationless electronic excitation energy transfer due to a dipole–dipole interaction from an excited molecule to a nearby semiconductor was first proposed by Dexter.<sup>[1]</sup> Different attempts followed to observe this experimentally by measuring the photophysical properties of monolayers or sub-monolayers of fluorescing dyes on semiconductor surfaces separated by a spacer layer thus preventing direct electronic contact.<sup>[2–6]</sup> However, to obtain appreciable electronic excitation energy transfer to the semiconductor, the dyes on it should absorb most of the light, which is not achievable by a monolayer. Multilayers cannot be used because of the very efficient quenching of the electronic excitation. We have therefore devised a new type of host–guest material that enables us to circumvent this problem. The material consists of zeolite L crystals containing organized dye molecules that behave as monomers. As a host we used zeolite L, a crystalline aluminosilicate with hexagonal symmetry, which consists of one-dimensional channels running through the whole crystal. The latter are ideal for incorporating organic dye molecules. Details of these host–guest materials, which allow light harvesting within the volume of the crystals and fast excitation energy transport to stopcock molecules—acceptor dyes located at the external zeolite L surface—have recently been reported. We also showed that these stopcock molecules attached selectively to the base of the zeolite L crystals because of their shape, and due to the fact that the base and coat of the crystals have distinctly different chemical properties.<sup>[7–9]</sup> Here, we report the first successful experiments on excitation energy transfer from dyes inside the zeolite L channels to dyes covalently bound on its external surface and further through a thin layer of silicon dioxide, preventing electron transfer, to a silicon semiconductor. The system is explained in Figure 1 where we show a single channel of such an acceptor,donor-zeolite L composite placed on a semiconductor. We used *N,N'*-bis(2,6-dimethylphenyl) perylene-3,4,9,10-tetracarboxylic diimide (DXP, **1**)

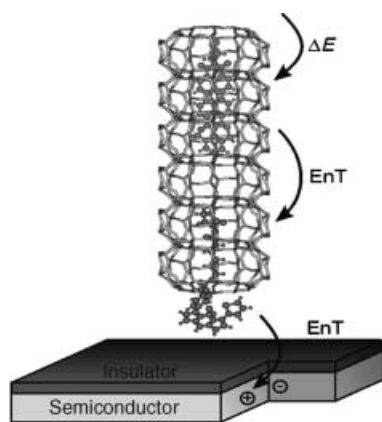


as the donor encapsulated in zeolite L, and ATTO680 as the acceptor bound to the surface of the crystals because both are strongly luminescent, stable dyes with matching absorption and fluorescence spectra. ATTO680 is an aminoreactive dye whose structure has not yet been published by the supplier (Fluka). The

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principle of the reaction used to covalently bind the dye to the channel openings of the zeolite L crystal is shown in Figure 2.

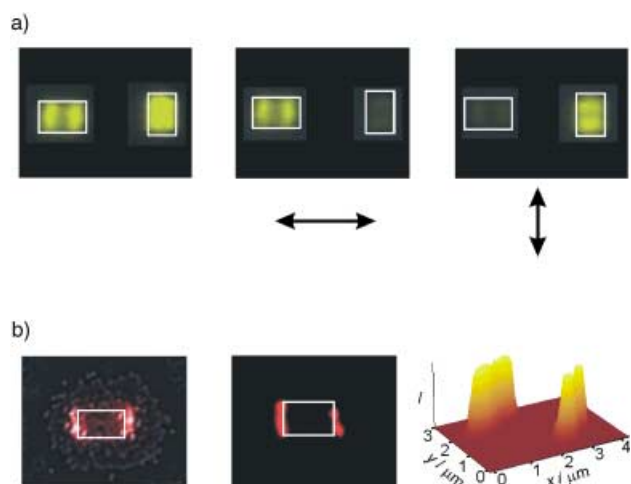
Figure 3 shows fluorescence microscopy images of two perpendicularly oriented DXP-zeolite L crystals, about 2  $\mu\text{m}$  in length, and one ATTO680-zeolite L of the same size, modified



**Figure 1.** Scheme which explains the organization of the dye-zeolite L semiconductor system. We show the structure of a single channel of an ATTO680,DXP-zeolite L on a silicon surface with an insulating layer. The arrows indicate light absorption ( $\Delta E$ ) and radiationless excitation energy transfer (EnT).

only at the base, as well as the confocal microscopy image of the latter. DXP-zeolite L crystals showed a strong fluorescence anisotropy: The fluorescence was only visible when the polarization of the transmitted light was parallel to the crystal axis. The conventional and confocal microscope images of the ATTO680-zeolite L crystal clearly show that the molecules are only present at the base of the cylinder, as has been found in other cases.<sup>[8, 9]</sup> The corresponding excitation and fluorescence spectra of DXP-zeolite L and ATTO680-zeolite L are shown in Figure 4a.

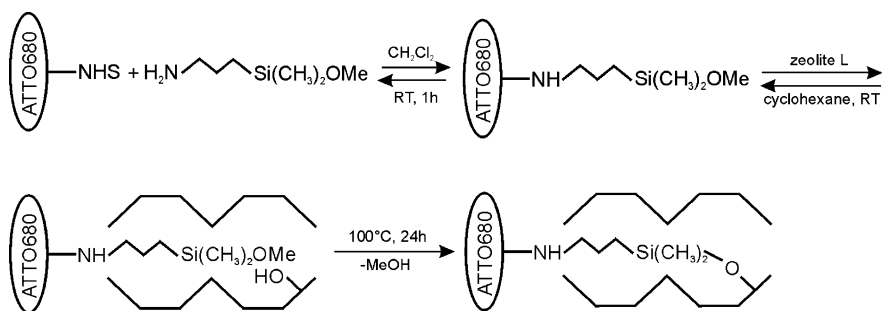
To prepare antenna systems, DXP-zeolite L crystals were modified on the external surface with covalently bound ATTO680. For these experiments, small zeolite L crystals with sizes in the range of 30 nm were used. When DXP was excited selectively, the fluorescence of the ATTO680 even exceeded the emission of the donor dye, as shown in Figure 4b. The excitation spectrum shows that the emission of the acceptor ATTO680 was also intense when directly excited at the absorption maximum of the dye. The fluorescence spectra of ATTO680,DXP-zeolite L monolayers on quartz, Si-therm (SiO<sub>2</sub> layer > 100 nm) and Si-nat



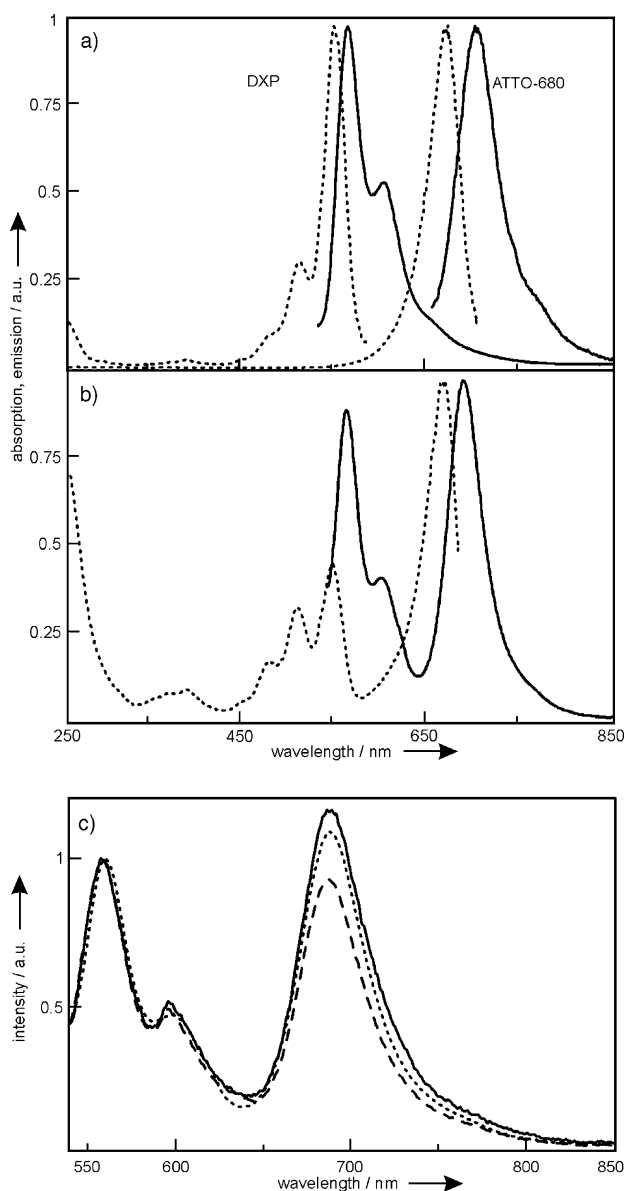
**Figure 3.** Optical fluorescence microscopy images of dye-zeolite L crystals. The white rectangles indicate the single zeolite L crystals. a) Two perpendicularly oriented DXP-zeolite L crystals. The fluorescence is shown without polarizer (left) and with a polarizer (middle and right, the arrows indicating the direction of the transmitted light). b) Conventional (left) and confocal (middle, right) fluorescence microscopy images of an ATTO680-zeolite L crystal modified only at the base of the cylinder.

(SiO<sub>2</sub> layer  $\sim$  3 nm) after selectively exciting the DXP molecules and scaling the DXP fluorescence band to same height are shown in Figure 4c. The ATTO680 fluorescence of the monolayer on Si-nat shows a decrease whereas it stayed about the same on quartz and on Si-therm. Time-resolved fluorescence decay measurements of the DXP and the ATTO680 fluorescence from ATTO680,DXP-zeolite L crystals as monolayers on Si-therm and Si-nat were performed. The fluorescence decays after selectively exciting the DXP molecules are shown in Figure 5. Whereas the decay remained the same for the DXP emission on Si-nat and Si-therm, it decreased for the ATTO680 emission measured on Si-nat.

The ATTO680,DXP-zeolite L antenna crystals showed impressive energy transfer from DXP to ATTO680 upon selective excitation of DXP. This observation confirms the results which have been reported for BTRX,Py<sup>+</sup> and B493/503,Ox<sup>+</sup>-zeolite L.<sup>[7]</sup> Due to geometrical restrictions of the one-dimensional channels of the host, the encapsulated DXP molecules are present as monomers aligned with their transition dipole moments parallel to the channel axis. This leads to very fast energy migration parallel to the channel axes of the zeolite L, until the excitation reaches an ATTO680 acceptor molecule at the end of a channel where it is emitted as deep red fluorescence. Since an excess of 3-aminopropyltrimethylethoxysilane (APES) was used for the surface modification of the small crystals, acceptors may also sit on the coat, and not only on the base of the crystals. Because the ATTO680 molecules at the base can be excited by energy transfer from DXP, the resulting



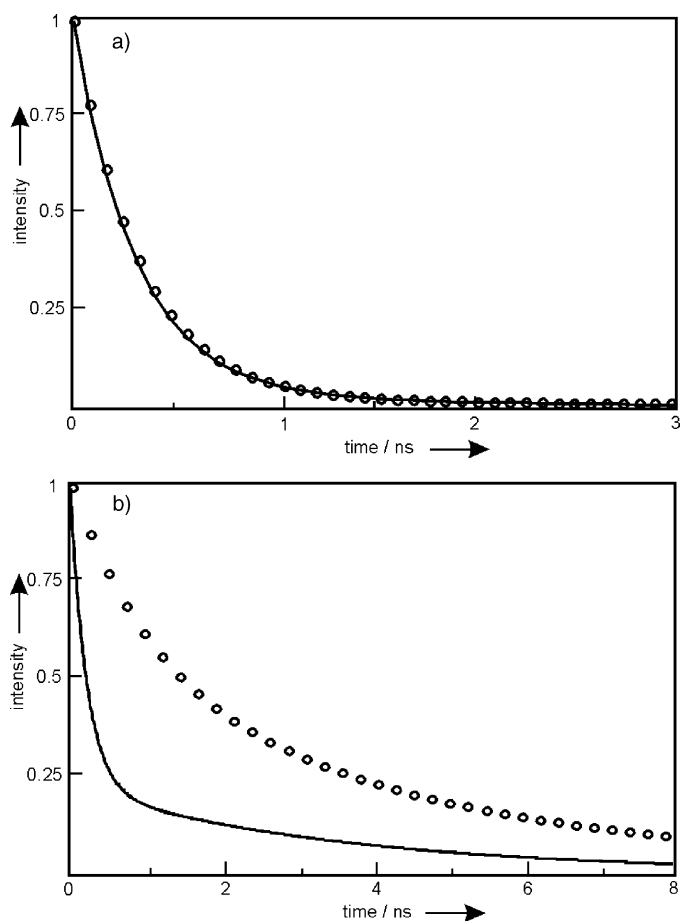
**Figure 2.** Reaction principle used to covalently bind the ATTO680 aminoreactive dye to the end of one channel.



**Figure 4.** Excitation and fluorescence spectra, scaled to be the same height at the absorption and emission maxima. a) Excitation (••••) and fluorescence (—) spectra of DXP-zeolite L and ATTO680-zeolite L crystals. b) Excitation (••••) (emission at 720 nm) and fluorescence (—) (excitation at 515 nm) spectra of ATTO680,DXP-zeolite L crystals. c) Fluorescence spectra (excitation at 515 nm) of ATTO680,DXP-zeolite L monolayers on quartz (—), on Si-therm (••••) and on Si-nat (---).

transfer efficiency is smaller than we would expect for a perfect material. Hence, it should be possible to improve the material by modifying the DXP-Zeolite L crystals exclusively at the base, as shown for a 2  $\mu\text{m}$  ATTO680-zeolite L crystal in Figure 3 b.

Energy transfer is known to be strongly dependent on the donor–acceptor distance.<sup>[8]</sup> Radiationless excitation energy transfer can only be expected from the antenna composite to silicon through the thin silicon dioxide layer of the Si-nat sample in ATTO680,DXP-zeolite L monolayers on Si-therm and Si-nat. Moreover, the distance between the DXP encapsulated in the zeolite L and the silicon is larger than that between the ATTO680 on the external surface and the silicon. Therefore, energy transfer



**Figure 5.** Time-resolved fluorescence decays of ATTO680,DXP-zeolite L crystals as monolayers on Si-therm (○) and Si-nat (—) when DXP is selectively excited at 496 nm. a) Fluorescence decay of the encapsulated DXP measured at 560 nm. b) Fluorescence decay of the ATTO680 measured at 710 nm.

is only expected to be observable in the latter case. The fluorescence intensity of ATTO680 relative to the DXP emission indeed showed a decrease on Si-nat compared to monolayers on quartz and Si-therm. It is difficult to prove energy transfer from a dye to a semiconductor on the basis of stationary fluorescence data. It has been reported that fluorescence intensity changes of Langmuir–Blodgett films on insulating spacer layers can also be interpreted by interference phenomena.<sup>[6]</sup> However, to have interference phenomena, the thickness of the spacer layer has to be of the order of a quarter of the wavelength of the emitted light, which is approximately the case for the thick (Si-therm) but definitely not for the 3 nm (Si-nat) SiO<sub>2</sub> layer.

Since energy transfer is also accompanied by a corresponding decrease in the donor fluorescence lifetime, time-resolved measurements give additional important information. The fluorescence decay of DXP from ATTO680,DXP-zeolite L monolayers is the same on Si-therm and Si-nat, showing that no energy transfer from encapsulated DXP to silicon was observed. But the fluorescence decay of ATTO680 on Si-nat is much faster than on Si-therm. This is a clear proof that radiationless electronic excitation energy transfer from the encapsulated DXP via the

externally attached ATTO680 through the insulating thin SiO<sub>2</sub> layer to the silicon semiconductor has taken place. Radiationless energy transfer from ATTO680 to silicon over a thin silicon dioxide layer can take place, since the ATTO680 molecules located on the SiO<sub>2</sub>/zeolite L interface are much closer to the semiconductor than the encapsulated DXP molecules.

In conclusion, we have shown for the first time that radiationless excitation energy transfer from a dye inside the channels of a zeolite L to a dye covalently bound on the external surface and further through a thin insulating layer to a semiconductor takes place. Since the dyes are encapsulated in a high concentration, a monolayer of the crystals shows strong absorption. Radiationless energy transfer from zeolite L antenna systems to a semiconductor could be much improved by learning how to align the individual crystals on the surface of the semiconductor, and how to prepare monodirectional materials, as discussed in ref. [8].

## Experimental Section

Pure zeolite L materials were synthesized and characterized as described in ref. [10]. The potassium exchanged form of zeolite L was used. For fluorescence and confocal microscopy images, zeolite L crystals 2 μm long and with a diameter of 1 μm were used, whereas for the energy transfer experiments much smaller crystals, with a length and diameter of about 30 nm, were used. The neutral DXP was obtained from Fluka and was purified by vacuum sublimation. DXP has high fluorescence quantum yield ( $\varphi_f = 0.96$  in ethanol), high extinction coefficient ( $\epsilon_{\text{max}} = 89000 \text{ M}^{-1} \text{ cm}^{-1}$  in ethanol), and a fluorescence lifetime of  $\tau_0 = 3.45 \text{ ns}$  in degassed ethanol.<sup>[11]</sup> The aminoreactive dye ATTO-TEC 680 *N*-hydroxysuccinimidyl ester (ATTO680) was obtained from Fluka and used as received. The fluorescence lifetime published by the manufacturer is  $\tau_0 = 3.4 \text{ ns}$  in ethanol with a quantum yield of  $\varphi_f = 0.4$  in ethanol. Insertion of the DXP into the zeolite L crystals was achieved by the single ampoule gas phase method.<sup>[8]</sup> The amount of DXP was calculated to achieve a loading of  $p = 0.2$  which corresponds to a concentration of 0.05 M. The DXP-zeolite L crystals were washed with dichloromethane and methanol to get rid of the molecules adsorbed on the external surface. The washed crystals were dried overnight at 100 °C. The DXP-zeolite L (10 mg) was suspended in 5 mL of dry toluene containing 5 μL of APES and refluxed for 2 h at 120 °C, yielding DXP-zeolite L crystals having amino groups covalently attached to the external surface. After washing the crystals twice with toluene, they were again dried at 100 °C for 3 h and suspended in 5 mL of dry dichloromethane. The aminoreactive dye ATTO680 was added and the suspension was stirred at room temperature for 3 h. The amount added was calculated such that every ATTO680 molecule could occupy an area of  $50 \times 50 \text{ \AA}$ , preventing the formation of dimers. The ATTO680,DXP-zeolite L crystals were washed with dichloromethane and methanol. This resulted in ATTO680,DXP-zeolite L crystals where the ATTO680 was spread homogeneously over the whole external surface of the zeolite L crystals (base and coat). Such antenna systems were used for the energy transfer experiments. Monolayers were prepared from a suspension of the crystals in acetone. About 20 μg of crystals were used for a monolayer on a 1.5 cm<sup>2</sup> surface. The layer substrates were cleaned in a solution of 70% H<sub>2</sub>SO<sub>4</sub> and 30% H<sub>2</sub>O<sub>2</sub> and rinsed with an excess of doubly distilled water. Thick (> 100 nm) SiO<sub>2</sub> layers (*Si-therm*) on a silicon wafer were thermally

grown at 1100 °C, whereas a silicon wafer with naturally grown SiO<sub>2</sub> (~3 nm) was used in the other case (*Si-nat*).

Alternatively, the aminoreactive dye was first reacted with an excess of APES in dichloromethane. The dichloromethane was evaporated and the resulting solid was washed with cyclohexane to take away the excess of APES, yielding APES-ATTO680. Zeolite L crystals (10 mg) were suspended in cyclohexane and a calculated amount of the APES-ATTO680 dye, dissolved in dichloromethane, was added such that it could occupy every channel end. The suspension was put in an ultrasonic bath for 30 min. The crystals were centrifuged and the colored crystals were put in an oven at 100 °C for 24 h to let the APES-ATTO680 bind covalently to the zeolite L, leading to crystals only modified with ATTO680 at the base of the cylinders. Fluorescence spectra were recorded on a LS 50 B Perkin–Elmer luminescence spectrophotometer and fluorescence microscopic images were taken with an Olympus BX 60 microscope equipped with a Kappa CF 20 DCX air-cooled CCD camera. By inserting a polarizer in front of the camera, the fluorescence images could be examined at different polarizations. Confocal fluorescence microscopy was done with a flouview FV300, Olympus, accessory equipped with an argon ion laser operating at 488 nm. Time-resolved measurements were recorded with the multiple-frequency phase fluorimetry setup described in ref. [12] and analyzed accordingly.

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