

# Electronic excitation energy transfer from dye-loaded zeolite L monolayers to a semiconductor

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## ABSTRACT

In device engineering, a high degree of supramolecular organisation is required to achieve certain desired macroscopic properties. Dye-loaded zeolite L host-guest materials have been successfully used in the realisation of efficient light-harvesting antenna systems. A new hierarchy of structural order is introduced by arranging the zeolite L crystals into densely packed, oriented monolayers on a substrate. We developed methods to synthesise such monolayers, to fill them with dyes and to terminate them with a luminescent stopcock. By the subsequent insertion of different types of dye molecules in a zeolite L monolayer, the first unidirectional antenna system was realised. Such antenna materials open possibilities for the design of a novel thin layer, silicon based solar cell, where the excitation energy can only migrate in one direction towards the zeolite-semiconductor interface. The electronic excitation energy is then transmitted to the semiconductor by Förster resonance energy transfer (FRET) via stopcock molecules attached to the channel ends. Direct transfer of electrons is prevented by an insulating layer. We report here on the UV-VIS absorption as well as NIR luminescence spectroscopy results obtained from such materials.

**Keywords:** Energy transfer, FRET, monolayers, zeolite L, semiconductors.

## 1. INTRODUCTION

Artificial photonic antenna systems that mimic natural photosynthesis can be realised by means of a host-guest technique. Zeolite L has proven to be an ideal host material for the supramolecular organization of molecules.<sup>1</sup> Zeolite L is a cylindrically shaped aluminosilicate featuring hexagonal symmetry.<sup>2-3</sup> A nanometre sized crystal consists of many thousand one dimensional channels oriented parallel to the cylinder axis. These can be filled with suitable organic guests, like fluorescent dye molecules, allowing the creation of strongly luminescent materials. Geometrical constraints of the host lead to supramolecular organisation of the guests in the channels. Thus very high concentrations of monomeric dye molecules can be realized and the short distances between them lead to fast radiationless Förster type energy migration.<sup>1</sup> The length of the zeolite host can be tuned between 30 to 10'000 nm.<sup>4</sup> Thus, bidirectional photonic antenna materials can be prepared in which monomeric dyes are present in a high concentration. The possibility of electronic energy transfer from an excited molecule to nearby semiconductor was already proposed by Dexter in 1979.<sup>5</sup> Different attempts have been made to realize this idea.<sup>6</sup> Recently, energy transfer from such bidirectional photonic antenna materials to bulk silicon has been demonstrated. In this system, light is absorbed by dyes located inside of the zeolite L crystals, migrates radiationlessly along the channels, and is finally transferred to the silicon substrate through an adequate stopcock molecule via Förster resonance energy transfer (FRET). Nevertheless, the system resulting from this coupling may only reach a theoretical maximum efficiency of 50% as the harvested excitation energy is transferred to acceptor dyes located at both ends of the channels.<sup>7-8</sup> Thus mono-directional antenna systems are highly desired because there the energy would be transported in one direction only. An asymmetric dye loading of zeolite L crystals is the preferred way for preparing such materials. This type of loading is possible if the channel openings are selectively closed on one side so that the dyes can only be inserted from other side in sequence. This can be realised by assembling a monolayer of zeolite crystals on a substrate.

Stimulated by the successful preparation of high quality close-packed zeolite A and ZSM-5 crystals, we have obtained perfect assembly of aligned zeolite L crystals in a monolayer.<sup>9-10</sup> By the subsequent insertion of different types of dye molecules in a zeolite L monolayer, the first unidirectional antenna system was realised. Such antenna materials open

possibilities for the design of a novel thin layer, silicon based solar cell, as illustrated in Figure 1. The small composite crystals, arranged with their *c*-axes perpendicular to the surface of a semiconductor, allow the transport of excitation energy towards the zeolite-semiconductor interface by energy migration. The stopcock molecules, which are located at only one channel end, enable FRET from the antenna to the semiconductor layer. This layer can be very thin (< 200 nm) as the electron-hole pair forms near the surface. Direct transfer of electrons from antenna to semiconductor is prevented by introducing an insulating layer. We report here on the deposition of a thin silicon layer on top of dye-loaded, stopcock modified zeolite L monolayers as well as on electronic excitation energy transfer experiments from such monolayers to the semiconductor.

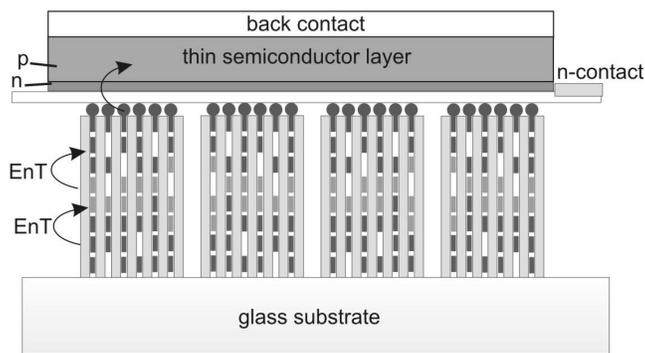


Figure 1. Schematic representation of a novel concept for the preparation of thin layer, silicon based solar cells that will be discussed in this work.

## 2. RESULTS AND DISCUSSION

We start this section by introducing the concept of occupation probability. Dye molecules are positioned at sites along the large, one-dimensional channels of zeolite L. The length of such a site corresponds to a number  $s$  multiplied by the unit cell length, so that one molecule fits exactly into one site. The value of  $s$  depends on the size of the molecule and the length of the primitive unit cell (0.75 nm in the case of zeolite L). A site can either be occupied by a molecule or be empty. Under equilibrium conditions, all sites have the same probability of being occupied by a molecule. The occupation probability  $p$  is equal to the ratio of the occupied to the total number of equivalent sites. For example, a zeolite L channel with a length of 700 nm contains 932 unit cells. A molecule like Ox has a length of around 1.5 nm, so  $s$  is equal to 2 and the number of sites in such a channel will correspond to 466. If we now fill half of these sites with an Ox molecule, the occupation probability  $p$  will be 0.5 Ox molecules per site ( $p = 0.5$ ).

We are currently in the process of separately investigating the different reaction steps necessary to realise a device as depicted in Figure 1. The six-step strategy we devised for realising it is outlined in ref. 11. The system we will report on consists of zeolite L crystals arranged in a densely packed, oriented monolayer on a glass substrate. The monolayers were prepared according to a recently developed procedure.<sup>10,12</sup> After monolayer preparation, the zeolite channels can be sequentially filled with different dyes.

Abbreviation	Structural Formula	Abbreviation	Structural Formula
Ox		PC25	
Qu			

Table 1. Dye molecules used in this study

All dyes that were used in this study are summarised in Table 1. These three dyes were chosen not only for their optical properties, but also for their ability to be readily included into zeolite monolayers. In order to prepare our device, we will start by inserting PC25 and subsequently Ox in the zeolite channels. The dye Qu is then attached to the open channel entrances to act as a stopcock. The system is finalised by vapour depositing a silicon layer ( $> 75$  nm) on top of the monolayer. This device has not yet been fully realised. We will report here on the results obtained on four partial systems: an empty zeolite L monolayer covered with a 75 nm thick silicon layer, two similar ones loaded with Ox and PC25 respectively, and one with zeolite channel openings terminated by Qu.

These prepared materials were investigated by means of UV-VIS absorption as well as NIR luminescence spectroscopy. The latter plays an important role in these studies, as the stopcock molecule should have its emission maximum in this range for optimum energy transfer to the silicon. Another use for this technique will be to monitor the charge recombination processes in the semiconductor layer in air and at room temperature.

Luminescence spectra of zeolite L monolayers loaded with either Ox or PC25 are given in Figure 2 (both with an estimated occupation probability  $p$  of 0.004 dye molecules per site). The PC25 loaded zeolite L monolayer exhibits an excitation band around 470 nm and an emission peak at 485 nm. The luminescence spectra of the Ox containing layer feature a narrow emission peak at 610 nm, while the excitation maximum lies at 605 nm. The emission and absorption spectra of Qu in a 1-butanol solution ( $c = 7.4 \times 10^{-6}$  M) are depicted in Figure 3 C) and will be discussed a bit later. From the spectral properties of the dyes, we expect an efficient resonance energy transfer from Ox to PC25 and finally to the stopcock molecule Qu. Once the electronic excitation energy reaches Qu, it will be transferred radiationlessly to the silicon layer coated on top of it. In the resulting system, the FRET process can only occur in one direction: from the zeolite antenna material to the semiconductor. Thus, the new hierarchy of structural order attained by organising supramolecular functional dye-zeolite crystals into oriented monolayers leads to the successful realisation of a unidirectional antenna system.

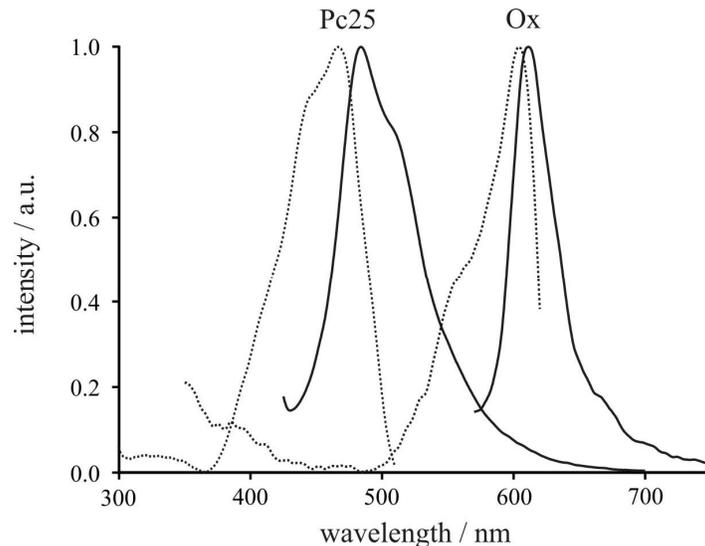


Figure 2. Luminescence spectra of dye-loaded zeolite L monolayers. Absorption (dashed) and emission (solid) spectra of a zeolite L monolayer loaded with either PC25 or Ox, respectively. In both cases, the occupation probability  $p$  was estimated to be equal to 0.004 dyes per site. The emission spectrum of PC25 was excited at 400 nm, while its excitation was detected around 540 nm. Ox excitation was detected at 650 nm and its emission spectrum was excited at 650 nm.

Some recently recorded NIR spectra are summarised in Figure 3. All spectra were excited around 460 nm with an argon ion laser. The partial systems investigated thus far include a silicon covered zeolite L monolayer and a similar monolayer with crystals terminated by a quinolinium derivative (Qu) as a stopcock molecule. In Figure 3 A), we show the NIR luminescence spectrum of a thin layer of silicon (75 nm thick) deposited on zeolite L monolayer. The clearly resolved band around 1062 nm can be attributed to the silicon, proving that we are able to directly excite the silicon layer at 540 nm and to detect its luminescence in air at room temperature. The emission spectrum of a monolayer of zeolite L crystals terminated with Qu, given in Figure 3 B), features a broad band at 960 nm. For comparison, we show in Figure 3 C) the

absorption and emission spectra of Qu solution in 1-butanol ( $7.4 \times 10^{-6}$  M). The absorption spectrum shows three peaks: a very intense one at 521 nm and two weaker luminescence bands at 780 nm and 860 nm. These bands correspond to those of the monomeric form of Qu.<sup>13</sup> The luminescence spectrum of this solution, excited at 540 nm, exhibits also a very broad band around 930 nm. These spectral characteristics make Qu a candidate for the stopcock molecule in our intended application.

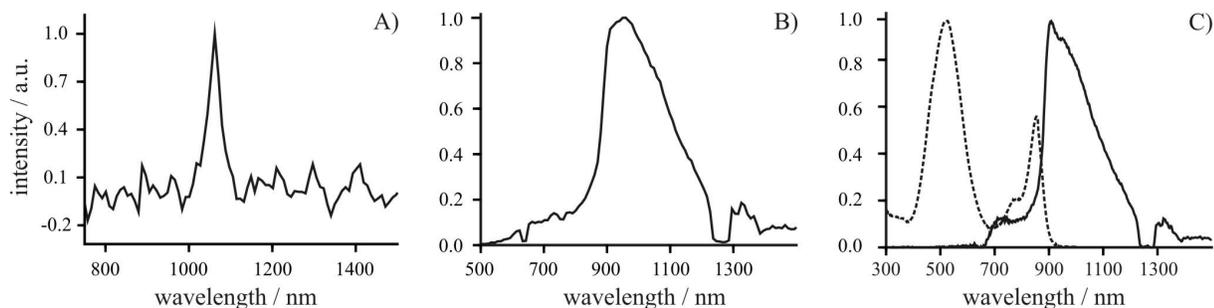


Figure 3. A) NIR emission spectrum of a 75 nm thick silicon layer deposited on a zeolite L monolayer. B) Luminescence spectrum of zeolite L monolayer, where the channels are terminated with the dye Qu. C) Absorption (dashed) and emission (solid) spectra of a Qu solution in 1-butanol ( $7.4 \times 10^{-6}$  M). All luminescence spectra were excited with an argon ion laser around 460 nm.

### 3. CONCLUSIONS

The results reported here prove that the prepared zeolite L monolayers can be successfully loaded with different types of dyes. It is possible to obtain high quality luminescence and absorption spectra from these types of materials. The spectral and insertion properties of the dyes PC25, Ox, and Qu make them prime candidates for our experiments. We expect that the realisation of a system to demonstrate FRET from the zeolite L antenna material to silicon will be soon possible.

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