Time- and Space-Resolved Luminescence of a Photonic Dye – Zeolite Antenna**

Marc Pauchard, Stefan Huber, Rachel Méallet-Renault, Huub Maas, Robert Pansu, and Gion Calzaferri*

Organic dye molecules tend to form aggregates which are known to cause fast thermal relaxation of the electronically excited states. They are often unstable on irradiation under many conditions. Encapsulation in an appropriate host not only prevents the dyes from dimerization and protects them against unwanted bimolecular reactions and isomerization, but it can also lead to supramolecular organization. We found that zeolite L is a very suitable host material for the development of organic/inorganic composites with photonic antenna properties for light harvesting and transport.[1, 2] Zeolite L is a crystalline aluminosilicate in which connected SiO_4 and AlO_4 tetrahedra give rise to one-dimensional channels arranged in a hexagonal structure.[3–5] Other host materials with linear channels, such as AlPO-5, ZSM-5, and mesostructured systems, have been studied for obtaining new optical materials.[6–11] Control of the shape and size of the crystals is a necessary prerequisite for particular applications. Large crystals of a few hundred to a few thousand nanometers are very useful for studying the optical and photophysical properties of dye – zeolite composites on single crystals by means of optical microscopy methods.[12, 13] Crystals in the range of a few tens to a few hundred nanometers are needed for high-efficiency photonic antenna materials, useful as fluorescent microprobes in cell biology and analytical chemistry,[14] for developing a new generation of dye-sensitized solid-state solar cells,[15] or for preparing a new generation of light-emitting diodes. A synthesis which allows fine tuning of zeolite L materials in the size range from 30 nm to 3000 nm is available.[16] We recently reported the preparation of sophisticated bipolar optical antennae for light harvesting and transport.[17] The principle is based on the use of a zeolite L crystal as the host for organizing several thousand dyes as monomers into well-defined zones (Figure 1 A). After selective excitation of dye1, located in the middle part, the light energy is carried spectrally from the blue to green (dye2) to red (dye3) and spatially from the crystal center to its left and right surface.

The general synthesis concept of this kind of sandwich materials is based on the specific geometrical constraints imposed by the parallel arrangement of one-dimensional channels of the host. Zeolite L crystals usually have cylinder morphology. The number of parallel channels which coincide with the *c* axis of the hexagonal framework is equal to $1.07r_{\mathrm{cyl}}^2$, where r_{cyl} is the radius of the crystal in nm. The length of a unit cell along the *c* axis is 0.75 nm. This means that a crystal of, for example, 900 nm diameter and 1500 nm length gives rise to about 217000 parallel channels, each consisting of 2000 unit cells (u.c.). Under appropriate conditions, molecules enter the channels from both sides with the same probability. For the preparation of the material depicted in Figure 1 A, we first inserted a neutral dye1 from the gas phase, filling the channels to the desired degree (see Scheme 3 in reference [17]). Although neutral dyes are usually displaced by water molecules, conditions could be found under which a cationic dye2 could be added from an aqueous suspension. The process could be sufficiently well controlled so that a specifically desired space was left for the third dye3 to be inserted. This principle can be extended to more than three different dyes.

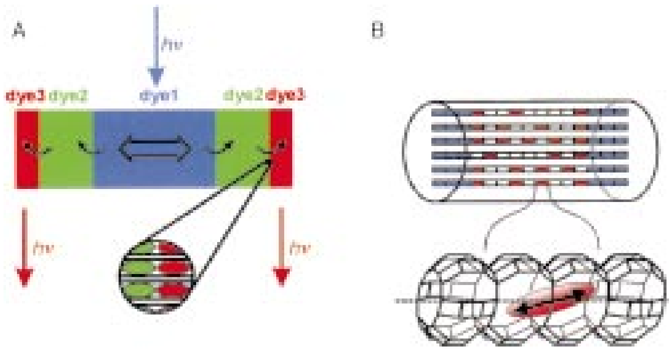

Figure 1. A) Principle of a bipolar three-dye photonic antenna. The enlarged section shows the organization of individual dye molecules at the domain boundary between dye2 and dye3. B) Schematic representation of a cylindrical zeolite L crystal consisting of organized dyes with donor molecules at both ends and acceptor molecules in the middle part. The enlargement shows a detailed view of a channel with a dye and its electronic transition moment (arrow) which is parallel for long molecules and bent for shorter ones with respect to the channel axis. The diameter of the channel windows is 0.71 nm and the largest free diameter is 1.26 nm. The center-to-center distance between two channels is 1.84 nm.

We were interested in reversing the scheme in Figure 1 A and in having a red dye in the center, followed by a green and then a blue one because such systems could become useful for analytical purposes or for developing a new generation of LEDs. It turned out that it is indeed possible to prepare such materials with, for example, Ox^+ (red) in the middle followed by Py^+ (green) and POPOP (blue) (Scheme 1).

The Ox^+ and Py^+ dye molecules are incorporated into the zeolite by ion exchange from an aqueous solution. After drying the loaded zeolite together with the neutral dye at 70 °C/4×10^{-3} mbar in a glass ampoule for 6 h, the ampoule is sealed and the neutral dye is incorporated into the Ox^+/Py^+-loaded zeolite in a rotating oven at 150 °C for 60 h. The ampoule is broken and the zeolite is immediately suspended in dry *n*-butanol. The final product is obtained after washing the zeolite with dry *n*-butanol.

The characterization is simplified when working with relatively large crystals. It is unambiguous when dealing with only two different dyes and we therefore report data on such a

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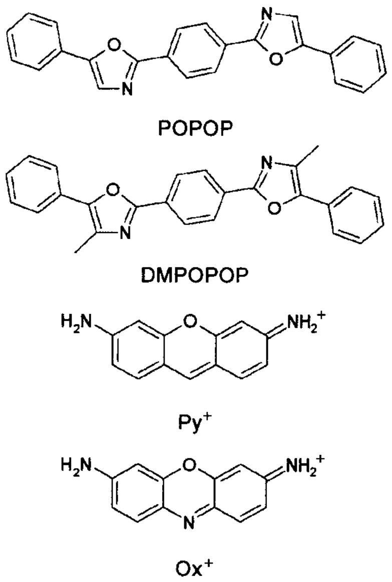

Scheme 1. Dyes used for the introduction into zeolite L.

system (Figure 1B). The rectangles symbolize adsorption sites, consisting of one, two, or more unit cells, depending on the size of the dyes. Red marked rectangles are filled with red-emitting dyes and blue marked ones with blue-emitting dyes. We have realized this by first inserting Ox$^+$ and then DMPOPOP into zeolite L. This material represents the first dye–zeolite composite with the ability to transport electronic excitation energy from the border of the cylindrical crystal to its center. The dyes were chosen because of their favorable structural and spectroscopic properties. Their absorption and fluorescence spectra (Figure 2A) are well separated in energy so that the individual components can be clearly distinguished. Nevertheless, the spectral overlap $J_{\mathrm{DMPOPOP,Ox^+}}$ between the emission of DMPOPOP and the absorption of Ox$^+$ is sufficient to allow energy transfer from DMPOPOP to Ox$^+$ ($J_{\mathrm{DMPOPOP,Ox^+}} = 6 \times 10^{-14}\ \mathrm{cm^3\,M^{-1}}$).

Stationary energy migration experiments were carried out on an ensemble, and space- and time-resolved measurements were made on single crystals containing 0.0475 Ox$^+$ per u.c. located in the middle and 0.043 DMPOPOP per u.c. at both ends. An Ox$^+$ molecule occupies two unit cells and a DMPOPOP molecule three of them, due to their size. This means that the occupation probability per site was 0.095 and 0.13, respectively. The energy transfer from excited DMPOPOP molecules to an Ox$^+$ molecule can be observed upon specific excitation of the DMPOPOP molecule at 325 nm (Figure 2B). We show, as a reference (dashed line in Figure 2B), the luminescence observed for a sample containing the same amount of Ox$^+$, but no DMPOPOP. From this it is evident that the appearance of the emission above 600 nm is due to energy transfer from excited DMPOPOP to Ox$^+$.

Important results were obtained in single-crystal experiments. We know that the $S_1 \leftrightarrow S_0$ π,π* electronic transition moment of Ox$^+$ shows a cone-shaped distribution with a half-cone angle of 72° with respect to the channel axis, while it is parallel for DMPOPOP.[12] Observing crystals in a microscope equipped with polarizers, an appropriate set of filters, and using an immersion lens, one can see the pictures shown in Figure 3B. The blue emission on the left is observed through a polarizer parallel to the cylinder axis when specifically exciting DMPOPOP at $\lambda = 330–385$ nm, while the red emission in the middle is seen when the polarizer is turned into the vertical position. The picture on the right-hand side is observed without polarizer upon excitation of Ox$^+$ at $\lambda = 545–580$ nm. The shape of the crystal as determined by electron microscopy is shown in Figure 3C.

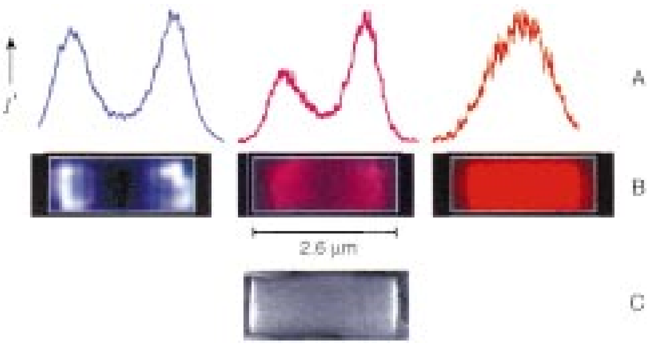

Figure 3. A) Scanning confocal optical microscopy results of a DMPOPOP,Ox$^+$–zeolite L crystal. B) Immersion microscopy images. C) Side view of a zeolite crystal observed by means of electron microscopy. For details see text.

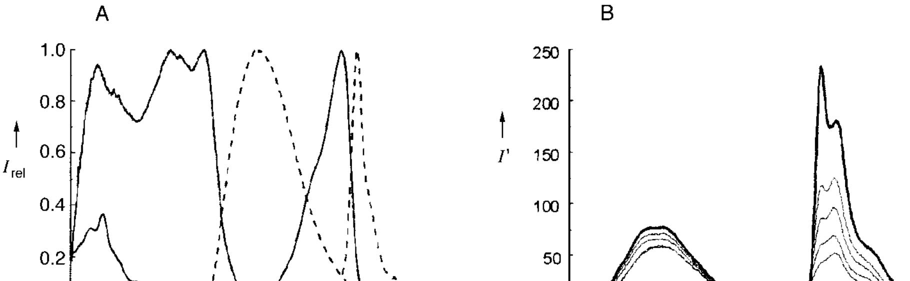

Figure 2. A) Excitation (solid) and emission (dashed) spectra of DMPOPOP–zeolite L in 1-butanol (388 nm, 464 nm) and of Ox$^+$–zeolite L in water (595 nm, 605 nm); ($\varepsilon_{\mathrm{DMPOPOP}}$ (λ_{max}) ~ 50000 L mol^{-1} cm^{-1}, $\varepsilon_{\mathrm{Ox^+}}$ (λ_{max}) ~ 84000 L mol^{-1} cm^{-1}). The spectra are scaled to the same height (I_{rel}). In the confocal microscopy experiments DMPOPOP was excited at 320 nm and the emission detected at 470 nm, whereas Ox$^+$ was excited at 490 nm and the emission detected at 660 nm. B) Temperature dependence of the luminescence of DMPOPOP,Ox$^+$–zeolite L samples upon excitation at 325 nm (bold spectrum is at 80 K, the others at higher temperatures up to room temperature). The dashed line is the luminescence of Ox$^+$–zeolite L upon excitation at 330 nm at 80 K (as a reference). I' = photon count in Hz.

Confocal microscopy data were measured by means of instrumentation which has been reported in reference [18]. The intensity profile on the left of Figure 3A was observed when scanning the emission at 470 nm along the crystal axis, upon excitation at 320 nm. The profile in the middle was observed when monitoring the emission at $\lambda >$ 610 nm after excitation at

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320 nm, while the profile on the right was seen when the sample was excited at 490 nm. These data show that the organization of the dyes inside the crystal corresponds to the scheme in Figure 1 B. They also beautifully illustrate the energy transfer from the DMPOPOP to the Ox^+ and that the energy migration length of excited Ox^+ is not sufficient to fill such large crystals homogeneously, as expected from theoretical considerations.[1] Energy transfer and migration in this system is governed by the dipole – dipole mechanism, which is also known as Förster energy transfer.[19–21]

The fluorescence decay of DMPOPOP observed on a single DMPOPOP – zeolite L crystal excited at 320 nm can be roughly described by a biexponential (31 %, 3.35 ns; 69 %, 1.0 ns) with an average fluorescence lifetime of 1.78 ns (Figure 4 A, blue). The decay of Ox^+ observed on a single DMPOPOP,Ox^+ – zeolite L crystal excited at 495 nm is also biexponential (57 %, 2.6 ns; 43 %, 0.5 ns) with an average fluorescence lifetime of 1.71 ns (Figure 4 A, green). The decay of DMPOPOP in such a crystal excited at 320 nm and observed at 470 nm is more complex and has an average fluorescence lifetime of 300 ps (Figure 4 A, red). The reason for this is that energy transfer takes place from excited DMPOPOP to Ox^+. The reduction of the excited donor lifetime expectancy by a factor of 6 means that 83 % of the absorbed photons are transferred from excited DMPOPOP to Ox^+ by Förster energy transfer.

After excitation of a DMPOPOP,Ox^+ – zeolite L crystal at 320 nm, the Ox^+ emission was measured at different positions in the crystal. The emission wavelength was chosen above 660 nm to make sure that no DMPOPOP emission was mixed in. Four regions indicated by the colors yellow, red, green, and blue can be distinguished (Figure 4 B and C). The yellow signal outside the crystal is due to noise and scattered photons. The red signal, observed at the border of the crystal, originates from excited Ox^+ molecules that are very close to the DMPOPOP molecules. They have a fast rise time and decay. The rise time is somewhat slower if we move further into the crystal (green) and it is substantially delayed in the middle part of the crystal (blue). The presence of a slow rise time and of a delayed decay shows that Ox^+ fluorescence is excited indirectly through DMPOPOP. The spatial dependence of this effect beautifully demonstrates the dynamics of the energy transfer and energy migration from the border of the crystal to the center, which means that our dream of an "inverted photonic antenna" as illustrated in Figure 1 B has become reality. This is a sound basis for detailed experimental and theoretical studies of the challenging opportunities of supramolecularly organized dyes in the channels of appropriate microporous host materials for light harvesting, transport, and trapping.

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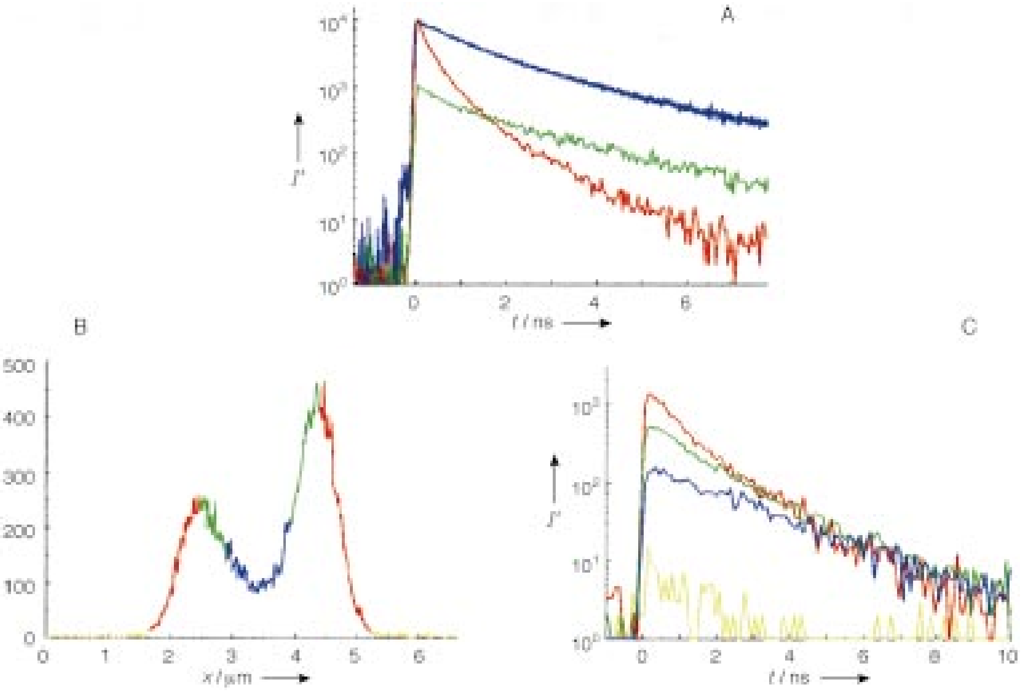

Figure 4. Luminescence decay on single dye-loaded zeolite L crystals in a confocal microscope. A) Decay observed as an average over the whole crystal. Blue: Decay of DMPOPOP fluorescence at 470 nm when a DMPOPOP-zeolite L crystal is excited at 320 nm with 1.2-ps pulses. Green: Decay of Ox^+ luninescence at (600 ± 4) nm when a DMPOPOP,Ox^+ – zeolite L crystal is excited at 495 nm. Red: Decay of DMPOPOP luminescence at 470 nm when a DMPOPOP,Ox^+ – zeolite L crystal is excited at 320 nm. B and C) Time- and space-resolved confocal microscopy results for a DMPOPOP,Ox^+ – zeolite L crystal. B) Decay of the Ox^+ emission similar to that in Figure 3 A (middle) but with the different regions indicated by different colors (yellow, red, green, and blue). C) Decay of the luminescence of Ox^+ above 660 nm when a DMPOPOP,Ox^+ – zeolite L crystal is excited at 320 nm at the different positions indicated in B).

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A Fully Characterized Complex Ion with Unreduced TCNQ as Fourfold Bridging Ligand: $[(\mu_4\text{-TCNQ})\{fac\text{-Re(CO)}_3\text{(bpy)}\}_4]^{4+}$[**]

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Coordination compounds of 7,7,8,8-tetracyano-*p*-quinodimethane (TCNQ) and of the related tetracyanoethene (TCNE)[1] have found wide interest in materials science as potential organic conductors[2] and molecular magnets.[3] As universal π-acceptor components and archetypical "non-innocent" ligands, these TCNX molecules can exist in several readily accessible oxidation states (TCNX^0, paramagnetic $\text{TCNX}^{\bullet-}$ or TCNX^{2-}), they may form stacks with mixed valency, they can be coordinated through the carbon π system, or act as σ donors through the nitrile-N atoms and thus bind (bridge) up to four metal centers. All these features have led to a wide variety of unusual geometrical and electronic structures.[1] Although discrete complexes with tetranucleating TCNQ or TCNE ligands have been reported with manganese,[4] ruthenium,[5] osmium,[6] iron,[7] rhenium,[8] and copper,[9] no structural information has been obtained yet for such species. Based on spectroscopic data, some of these systems were described as tetrametalla π systems with extensive metal/ligand electron delocalization.[4–6] On the other hand, there has been a number of structurally characterized coordination polymers involving silver,[10, 11] dimolybdenum,[12] diruthenium,[13] and dirhodium units;[13] however, these extended systems could not be studied as individual entities in solution, for example, by electrochemical methods.

Using the nitrile-binding and potentially π back-donating organometallic complex fragment $[\text{Re(CO)}_3\text{(bpy)}]^+$ (bpy = 2,2′-bipyridine),[14] we have now obtained the tetranuclear complex cation $[(\mu_4\text{-TCNQ})\{fac\text{-Re(CO)}_3\text{(bpy)}\}_4]^{4+}$ (**1**),[15] which has unprecedented electronic characteristics and which could be structurally studied as the tetrakis(hexafluorophosphate) salt.[16]

There are no unusual interionic contacts in the crystal, especially no indications for coordination polymer formation. Figure 1 illustrates that the TCNQ molecule acts as an esentially planar $\mu_4,\eta^1{:}\eta^1{:}\eta^1{:}\eta^1$-bridging ligand towards four cations $[fac\text{-Re(CO)}_3\text{(bpy)}]^+$. In comparison to TCNQ, $\text{TCNQ}^{\bullet-}$ and the coordination polymers referred to above,[13] the bond parameters of the bridging molecule in the cation **1** point to relatively little metal-to-ligand π-electron delocalization, as illustrated by the bond length of 1.377(14) Å for the exocyclic bond (C9–C10). This bond should lengthen towards a C–C single bond value on significant electron acquisition by TCNQ.[1] The binding of $[fac\text{-Re(CO)}_3\text{(bpy)}]^+$ by the nitrile groups of TCNQ occurs in two different conformations, either

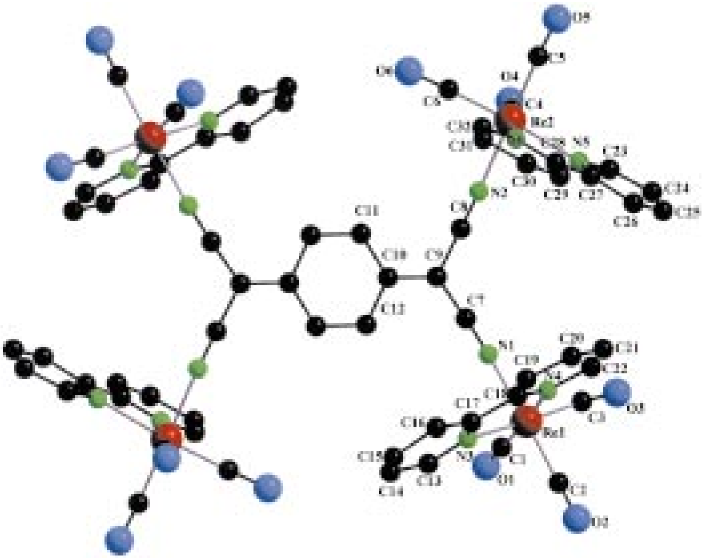

Figure 1. Molecular structure of the tetracation **1** in the crystal of $[(\mu_4\text{-TCNQ})\{fac\text{-Re(CO)}_3\text{(bpy)}\}_4](\text{PF}_6)_4$ (**1**-$(\text{PF}_6)_4$). Selected bond lengths [Å] and angles [°]: Re1-N1 2.098(7), Re1-N3 2.175(8), Re1-N4 2.137(10), Re2-N2 2.121(8), Re2-N5 2.216(10), Re2-N6 2.161(10), C7-C9 1.390(14), C8-C9 1.487(13), C9-C10 1.377(14), C10-C11 1.423(14), C11-C12 1.372(16), C10-C12 1.453(15), Re1-Re2 8.18, Re1-Re2A 10.02, Re1-Re1A 12.97, Re2-Re2A 12.89; C9-C7-N1 176.0(10), C9-C8-N2 178.2(11), C7-N1-Re1 170.9(8), C8-N2-Re2 174.2(9).

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