Luminescence quenching measurements on zeolite L monolayers

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ABSTRACT

The luminescence quenching of the oxygen sensitive Ru^{2+} complex (Ru-ph4-TMS) used as a stopcock and attached to a zeolite L monolayer has been investigated. The luminescence lifetime of the attached Ru-ph4-TMS was the same under N_2 and under O_2 atmosphere. This remarkable result is attributed to the shielding provided by the channels of the zeolite L crystals arranged as a monolayer. The emitting ^{3}MLCT state of the Ru-ph4-TMS stopcock is localized on the ligand bearing the phenyl groups forming the tail of this complex, which deeply penetrates into the zeolite L channel.

Keywords: luminescence, ruthenium, supramolecular assembly, host-guest, oxygen, zeolite, monolayer

1. INTRODUCTION

Well working photonic antenna systems have been made, in which electronic excitation energy migrates within the dye-loaded zeolite L channels.[1] Zeolite L is an aluminosilicate with one-dimensional channels running along the c-axis of the hexagonal crystals.[2] The channels have an opening diameter of 7.1 Å and reach 12.6 Å at the widest place. The one-dimensional channel system of the zeolite L makes it a versatile host material. Fluorescent dyes of appropriate size can easily enter the channels. Once they are inside, they cannot pass each other or form dimers due to spatial restrictions. Excitation energy can then either travel from the channel ends to the inside of the crystals or vice versa, depending on the sequence of the inserted donor and acceptor dyes. Interesting attempts of panchromatic chromophore mixtures in $AlPO_4$-5 molecular sieves and in faujasites have been reported.[3]

An advanced stage of organisation is obtained by the addition of fluorescent stopcock molecules. Stopcock molecules have a tail that can enter into the channels and a head that is too large to enter (see Fig. 1). They connect the inside of the crystals with their environment via energy transfer.

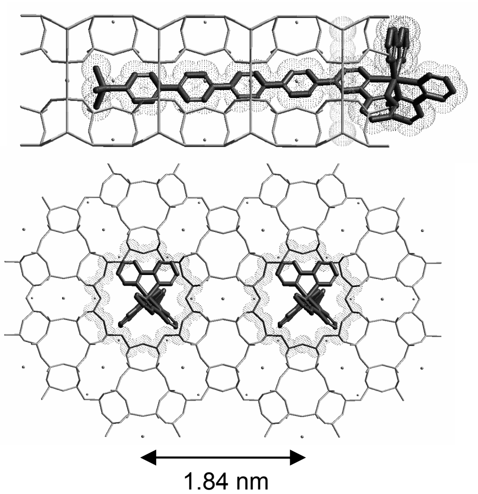

Figure 1: Structure of the (Ru-ph4-TMS)-zeolite L assembly. Only part of the zeolite channel framework is shown in order to better visualize the arrangement. Upper: Side view showing how the tail is protected by the zeolite channel. Lower: top view illustrating the space needed for the stopcocks to arrange properly.

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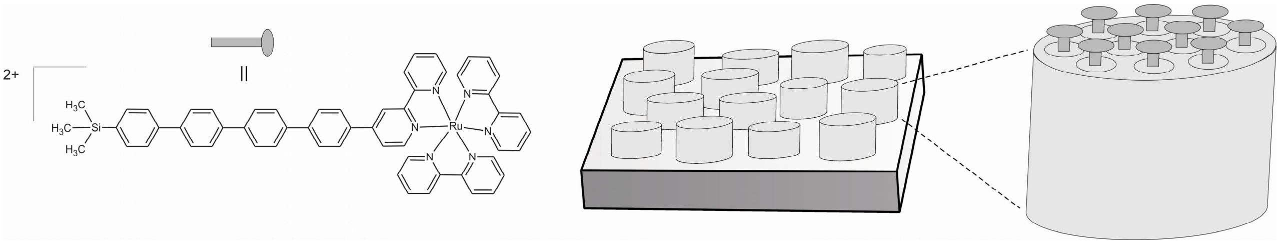
The stopcocks enable injection of excitation energy from the outside environment into the crystals, as well as absorption of light and transport of the excitation energy by encapsulated dyes and further donation to the outside.[4] It has been shown that the energy transfer from the $[Ru(bpy)_2bpy\text{-}ph_4\text{-}Si(CH_3)_3]^{2+}$ stopcock, abbreviated as Ru-ph4-TMS, to encapsulated oxazine dyes (Ox1) is very efficient.[5] We show in Figure 1 that the tail of this stopcock fits nicely into the zeolite L channel, whereas its head is too large to enter. This arrangement is stabilized by electrostatic forces because the zeolite framework is negatively charged. The lower view illustrates that the distance between two channels allows enough space for the complexes to arrange properly. The Ru-ph4-TMS stopcock (Fig. 1) is a triplet emitter, and, as many other long lived species, is quenched by dioxygen[6] via a diffusion controlled collision.[7] We have observed that the luminescence quenching of the Ru-ph4-TMS stopcock by O_2 is much weaker when the former is bound to the zeolite L, and we found that this is due to the delocalization of the emitting ^{3}MLCT state over the bpy-ph4 ligand shielded by the zeolite L, which hinders the O_2 in making successful collisions.[8]

The experiments reported in ref 8 were carried out in a (Ru-ph4-TMS)-zeolite L suspension in CH_2Cl_2. Under such conditions zeolite crystals can collide with each other, which has to be taken into account in the quantitative analysis of the data. We have recently been able to prepare dense monolayers of oriented zeolite L on a substrate.[9] This gives us a new tool for studying the important oxygen quenching reactions. The principle is explained in Scheme 1. It shows that in this arrangement only one side of the channels is accessible. This means that the diffusion of O_2 into the zeolite L from the other side of an eventually open channel, which could result in quenching of the shielded excited state of the stopcock, can no longer occur.

The aim of this paper is to study the influence of O_2 on the assembly constituted by the Ru-ph4-TMS stopcock attached to the channel entrances of a zeolite L monolayer by means of time-resolved luminescence measurements.



Scheme 1: Structure of the Ru-ph4-TMS stopcock (left) and a pictorial view of a zeolite L monolayer on a glass substrate (right) with an enlarged view of the (Ru-ph4-TMS)-zeolite L assembly. The zeolite L channels are oriented perpendicular to the substrate plane.

2. METHODOLOGY

2.1 Material

Disc-shaped crystals with an average length of 250 nm and an aspect ratio, length to diameter, of 0.3 have been used for the preparation of the oriented monolayers. The zeolite L crystals have been synthesized and characterized as previously described.[10] The oriented zeolite L monolayers have been prepared according to the procedure described in ref 9, using CP-TMS (3-chloropropyl-trimethoxysilane) as covalent linker. The Ru-ph4-TMS was synthesized according to ref 5 and was electrostatically attached to the monolayer after reflux in toluene for 12 hours at 80 ˚C. The (Ru-ph4-TMS)-zeolite L monolayer was finally washed with ethanol to remove non-attached stopcocks from the zeolite surface. The 1 cm diameter glass substrate containing the prepared monolayer was attached to a Teflon film, which in turn was inserted in a quartz cuvette and oriented 45 degrees with respect to the cuvette walls. This cuvette was then filled with toluene.

2.2 Time-resolved luminescence measurements

Time-resolved luminescence spectra have been measured for the (Ru-ph4-TMS)-zeolite L monolayer in toluene at room temperature. The measurements were made under N_2 and under O_2 atmosphere. Bubbling the samples with the corresponding gases for 10 min prior to the acquisition of the spectra was found to be sufficient. The gases were also bubbled during the measurements in order to ensure constant atmosphere. The samples were excited at 460 nm, which corresponds to the direct excitation of the ^{1}MLCT state of Ru-ph4-TMS.[5]

2.3 Equipment

The spectra were recorded on a system consisting of a Nd:YAG pulsed laser (Quantel Brilliant) and an OPO (Opotek MagicPrism Vibrant Vis) which is pumped by the third harmonic. The pulse length was 5 ns. Acquisition of the spectra was made using a time window of 900 ns, delay increments of 200 ns, and a cut off filter of 470 nm. Further details concerning this set up are reported in ref 11.

2.4 Theory

The geometry of the Ru-ph4-TMS complex has been optimized at the semiempirical PM3 level[12] and the molecular orbitals (HOMO and LUMO) calculated using the Extended-Hückel method implemented in the ICON-Edit program.[13] The latter semiempirical method was used because the emitting ^{3}MCLT state of Ru-ph4-TMS can be described mostly by single excitations between the HOMO and the LUMO.[8]

3. RESULTS

The emission spectra of the (Ru-ph4-TMS)-zeolite L monolayer in N_2 and in O_2 atmosphere are shown in Figure 2. The time delay between the curves shown is 200 ns. The great similarity between both emission spectra is remarkable. They show bi-exponential decay. The respective lifetimes (τ) and weight coefficients (c) are given in Table 1. The values of c are practically the same for the N_2 and for the O_2 atmosphere. Small changes have been observed for the lifetimes. These small changes are, however, within the experimental error. We assume that the short lifetime component under oxygen atmosphere is an indication of the existence of some stopcocks remaining in solution, since the lifetime (see Table 1) is similar to that previously obtained for this stopcock free in solution under O_2 atmosphere (τ = 167 ns)[8]. Toluene, which has been used as a solvent, can solubilize the stopcocks to a small extent. This does not explain the short lifetime component we have observed under N_2 atmosphere, however. It could be due to O_2 still remaining inside some channels.

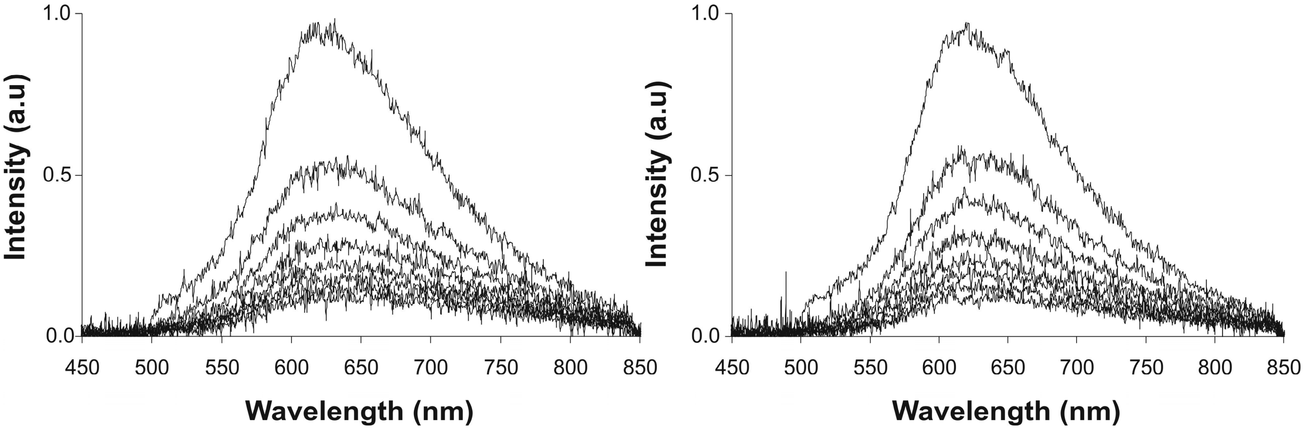


Figure 2: Time-resolved emission spectra of the (Ru-ph4-TMS)-zeolite L monolayer in toluene under O_2 (left) and under N_2 (right) atmosphere. The spectra were recorded at room temperature under excitation at 460 nm. The delay increment between consecutive spectra is 200 ns.

The bigger component of the lifetime corresponds to the supramolecular assembly of interest, i.e., the (Ru-ph4-TMS)-zeolite L monolayer. The lifetime in O_2 and in N_2 atmosphere is in the same order of magnitude as that of the free complex in solution under N_2 atmosphere (τ = 1207 ns)[8]. This means that the zeolite host provides an excellent shielding of the emitting ^{3}MLCT state of Ru-ph4-TMS, preventing the collisions between the O_2 quencher and the stopcock. The use of monolayers is the main reason for the constant values of the lifetime. Similar measurements with a (Ru-ph4-TMS)-zeolite L *suspension* result in lifetimes that vary to a greater extent upon varying the N_2/O_2 atmosphere.[8] In suspension oxygen can also quench an attached stopcock after diffusion from the other side of the channels, some of which may remain open because of the equilibrium between host-(guest)$_n$ and host-(guest)$_{n-x}$ + x·guest. The great stability of the monolayer-based assemblies also indicates that O_2 cannot enter an open channel and internally diffuse to another parallel channel.

Table 1: Lifetimes (τ, in ns) and weight coefficients (c) of the exponential luminescence decay of the (Ru-ph4-TMS)-zeolite L monolayer.

Atmosphere	τ_1	c_1	τ_2	c_2
N_2	178	0.37	1016	0.63
O_2	156	0.41	1090	0.59

The lowest occupied molecular orbital (LUMO) of Ru-ph4-TMS, calculated using the Extended-Hückel method, is shown in Figure 3. One can see that the electron density is mostly localized on the bpy-ph4 ligand, which is deep inside the zeolite L channel in the supramolecular assembly, as illustrated in Fig. 1. Upon excitation of the stopcock, electron density is transferred from the Ru^{2+} ion to the phenyl groups located on the tail, i.e. the electron density is transferred in the direction of the glass substrate.

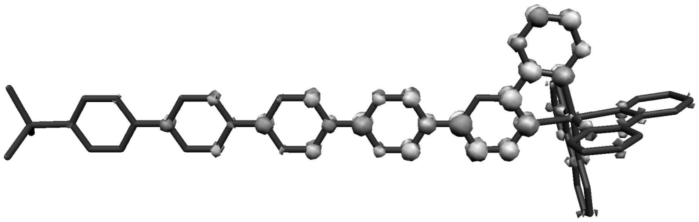


Figure 3: Electron density distribution of the LUMO of the Ru-ph4-TMS stopcock.

4. CONCLUSIONS

We have investigated the influence of O_2 on the luminescence quenching of the Ru-ph4-TMS stopcock attached to a zeolite L monolayer. The luminescence lifetime of the attached Ru-ph4-TMS stopcock is nearly the same under O_2 and under N_2 atmosphere. The zeolite L monolayers have shown to provide an excellent host for the Ru-ph4-TMS stopcock, efficiently shielding its emitting ^{3}MLCT state from direct contact with the O_2 quencher. Encapsulation of dyes with appropriate spectroscopic properties into the monolayer materials we have discussed do lead to mono-directional photonic antenna systems.

Acknowledgements

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