

Sensitized NIR Erbium(III) Emission in Confined Geometries: A New Strategy for Light Emitters in Telecom Applications

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Infrared light sources, especially those falling into the silica transparency windows, play an essential role in telecom technologies where signal transmission is based on silica optical fibers. In long haul transmission, silica remains unchallenged; however, local area networks, data links, and computer networks consisting of complex high density circuitry require low cost alternative solutions for signal generation and distribution. Erbium-doped materials have attracted considerable attention in the past few years because of their potential applications in optoelectronics and telecommunications. The intraconfigurational $4f-4f$ transitions between the first excited level ($^4I_{13/2}$) and the ground state ($^4I_{15/2}$) occurring at ca. $1.54 \mu\text{m}$ corresponds in fact to the window of minimum attenuation in the silica-based optical fibers currently used in optical communications.

Although erbium ions exhibit very favorable luminescent properties, their absorption cross sections are very small, leading to inefficient emission from the $4f$ levels under direct excitation. This limitation can be circumvented by using NIR luminescent lanthanide complexes with organic ligands that sensitize the emission of the lanthanide ion by intramolecular energy transfer from the organic component.² On the other hand it is well established that NIR-emitting Ln^{3+} ions are particularly susceptible to vibrational deactivation. Species containing high-energy oscillators, such as C–H and O–H bonds (typically found in the ligand, coordinated solvent, and moisture), can quench the metal excited states nonradiatively, leading to decreased luminescence intensities and shorter excited-state lifetimes.^{3,4}

It is well established that use of halogenated organic components significantly increases the quantum yield of the NIR emission of the complex.^{5–7} Mancino et al.⁶ described an erbium complex with a tetrapentafluorophenylimidodiphosphinate ligand, where the observed NIR emission lifetime of $200 \mu\text{s}$ is the longest ever reported for an erbium(III) organic complex under excitation through an organic chromophore. Song et al.⁸ obtained an erbium complex with perfluorodiphenylphosphinic acid with an NIR PL lifetime, measured under direct excitation (978 nm) of Er^{3+} ions, of 0.336 ms. Unfortunately, the presence of halogenated groups in the organic part, because of their electron-withdrawing properties, strongly hinders the formation of complexes with lanthanide ions, and even if such compounds can be obtained they are more sensitive and unstable compared to its nonhalogenated counterparts. As a result of these synthetic difficulties, only a few examples of $\text{Ln}(\text{III})$ complexes with fully fluorinated ligands have been reported.^{6,7,9}

To overcome the limitations of the perfluorinated ligand chemistry, incorporation of lanthanides into a zeolite matrix provides a promising alternative.^{10–12} In such systems emission from the metal ion is efficiently sensitized by the organic molecule loaded into a zeolite nanochannel, bypassing the formation of a real chemical bond between them. Organic molecules, where the formation of the stable complex fails, can then be used as sensitizers. This

procedure is particularly advantageous for fluorinated molecules where the high electronic affinity of the fluorine atoms reduces the electronic density on the coordination sites, hence decreasing the ability of complex formation. Moreover, it has been recently reported that zeolite surfaces can be chemically modified, leading to the fabrication of transparent zeolite-polymer hybrid materials, that can open a way to manufacture zeolite based plastic-compatible telecom light sources.^{13,14} To the best of our knowledge the efficient NIR emission of such systems has not been reported until now.

In this communication we demonstrate for the first time the possibility to obtain sensitized, highly efficient NIR emission of Er^{3+} ions exchanged within a zeolite matrix. The $1.5 \mu\text{m}$ emission is excited via energy transfer from decafluorobenzophenone (DFB) molecules that upon filling the zeolite nanochannels act as light harvesting antenna (Figure 1). Removal of water molecules from zeolite L structure and the use of perfluorinated organic molecules result in a strongly enhanced NIR emission with a longer lifetime (>2 orders of magnitude longer) than in erbium complexes with organic, nonfluorinated ligands.

In our experiment we used zeolite L, which has been proven to be a very versatile host material,^{15,16} exchanged with erbium(III) ions, and loaded with DFB molecules. The details of the synthesis are shown below under Sample Preparation.

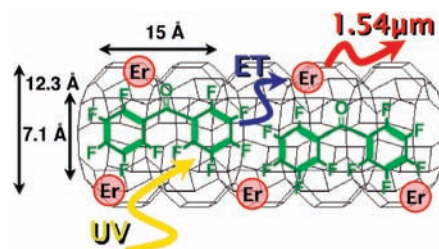


Figure 1. Sketch showing the dimension of the Zeolite L pore, and schematic illustration of the energy transfer between the dye and the erbium(III) ions inside the zeolite nanochannel.

The UV-vis absorption spectrum of Er^{3+} exchanged zeolite loaded with DFB (ErZEO-DFB) is shown in Figure 2, together with the absorption spectrum of pure DFB in dichloromethane (CH_2Cl_2) solution. The spectrum of the dye loaded ion exchanged zeolite sample exhibits a strong peak at $\sim 280 \text{ nm}$ ascribed to the DFB absorption.

This absorption band is broader and shifted to longer wavelengths than the corresponding band observed for pure DFB, which could be related to the possible creation of different types of dimers or oligomers of DFB.^{17,18} Calzaferri et al.^{19,20} suggested that this behavior is strictly related to the specific organization of the dye inside the zeolite L nanochannels, which is different when compared to a solution or a single crystal, as well as with interaction of the

dye with Al^{3+} centers present in zeolite. It is important to notice that the intensities of the native erbium(III) absorption lines are barely detectable (inset Figure 2).

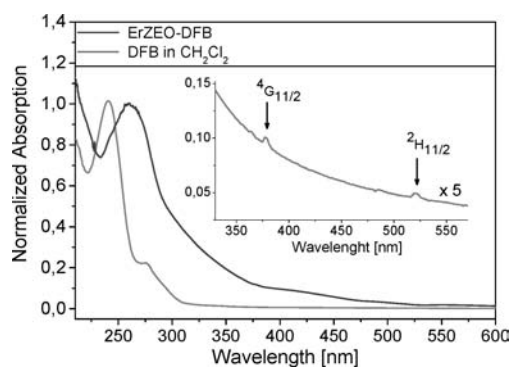


Figure 2. Normalized absorption spectra of ErZEO-DFB dispersed in fluorolube oil, and pure DFB in CH_2Cl_2 solution. The inset is the enlarged part of the ErZEO-DFB spectrum corresponding to the main Er^{3+} absorption bands.

Figure 3 shows the NIR PL spectrum obtained for the dye-loaded sample under excitation at the dye absorption band maximum of 280 nm. The PL spectrum of the Zeolite: Er^{3+} sample without the dye under direct excitation of native erbium(III) energy levels is also included for comparison. The strong PL peak with a maximum at $1.54 \mu\text{m}$, observed for the dye-loaded material, corresponds to the typical intraconfiguration $4f-4f$ transitions from the $^4\text{I}_{13/2}$ to the $^4\text{I}_{15/2}$ states of Er^{3+} . Remarkably, the full width at half-maximum (fwhm) of the $1.54 \mu\text{m}$ PL band ($\sim 86 \text{ nm}$) is substantially broader than those observed for the Er^{3+} doped into inorganic hosts like SiO_2 ($\sim 11 \text{ nm}$)²¹ or Al_2O_3 ($\sim 55 \text{ nm}$),²² and it is also broader than PL bands observed in most of the erbium(III) organic complexes.²³ The broader fwhm is beneficial for wave division multiplexed signal amplifications.²¹ The PL spectrum recorded under the same conditions on an exchanged zeolite L not filled with the dye does not show any detectable emission. At this wavelength there are no Er^{3+} levels enabling the direct excitation of erbium emission. Therefore, we conclude that the luminescence observed under 280 nm excitation results from the photosensitization of Er^{3+} ions incorporated into the zeolite structure by DFB molecules loaded into zeolite nanochannels (see Figure 1).

To evaluate the efficiency of the Er^{3+} sensitized emission, its NIR luminescence decay profiles (Figure 4) were measured upon excitation of the ErZEO-DFB absorption band at 280 nm, or under direct excitation of Er^{3+} level $^4\text{G}_{11/2}$ at 378 nm for the Er(III)-exchanged sample without the dye. The NIR PL decay profile measured for the Zeolite: Er^{3+} is well fitted by a single-exponential function with a lifetime of 0.38 ms. The lifetime observed in the pure erbium-exchanged zeolite matrix is relatively short when compared to other inorganic matrices,²⁴ most likely because of the presence of silanol ($\text{Si}-\text{O}-\text{H}$) groups in the zeolite framework.²⁵ These groups could be partially removed by applying a more intense annealing process at high temperature under vacuum. This process would lead, however, to the creation of oxygen vacancies.²⁶ Moreover, the presence of silanol groups is necessary for further modification of the zeolite surface to obtain materials fully dispersible in organic solvents and polymers, enabling the production of plastic-compatible devices.

The $1.54 \mu\text{m}$ Er^{3+} emission decay for the dye-loaded sample is biexponential with lifetime of 23 and 210 μs . The overall contribution of the longer lifetime component is $\sim 88\%$. The occurrence of the short component in the decay transient is most likely the result

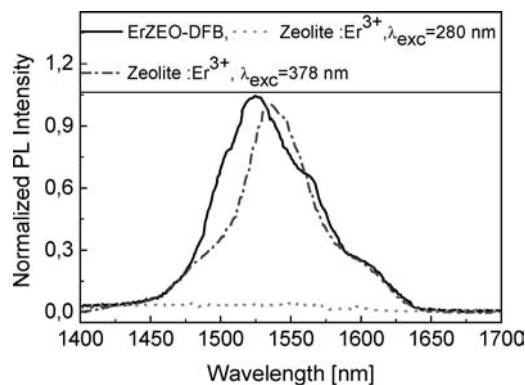


Figure 3. Normalized NIR photoluminescence spectra of ErZEO-DFB in powder and Zeolite: Er^{3+} without the dye, recorded under 280 nm diode excitation (dye-loaded and pure Zeolite: Er^{3+}) or 378 nm Ti:Sapphire laser excitation (Zeolite: Er^{3+}).

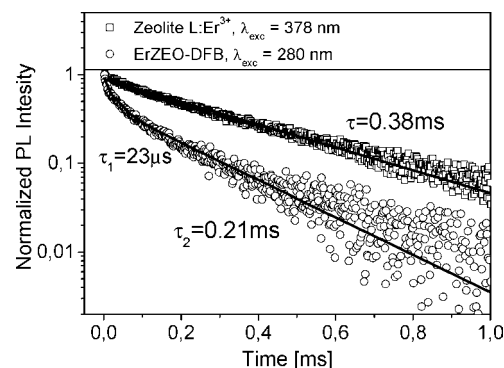


Figure 4. Normalized photoluminescence decay traces recorded under 280 nm diode excitation (ErZEO-DFB) or 378 nm Ti:Sapphire laser excitation (Zeolite: Er^{3+}), while monitoring the 1535 nm erbium(III) emission.

of some nonfully fluorinated molecules of benzophenone present as an impurity in commercial DFB, rather than the presence of water molecules. The decay of the sample containing only the erbium exchanged sample (without the DFB) is in fact a single-exponential. Moreover, the short component of $\sim 23 \mu\text{s}$ has a lifetime comparable with the one observed in our studies of a $1.54 \mu\text{m}$ emission of Er^{3+} ions sensitized by partially fluorinated benzophenones. When considering these hydrogen containing ligands, the presence of C-H overtones, which are resonant with the NIR emission of the Er^{3+} ions, enhances the nonradiative decay of the $^4\text{I}_{13/2}$ electronic level. In the zeolite channels the close proximity between the sensitizer and the emitting ion can lead to the enhancement of both the emission process, when the appropriate ligand is used, and the quenching process because of vibrational coupling. The observed NIR emission lifetime of Er^{3+} in dry erbium-exchanged zeolite (without organic dye) of 0.38 ms suggests that the NIR emission of the dye-loaded sample (0.21 ms) is not significantly quenched in the presence of organic species.

The intrinsic quantum yield of the sensitized NIR luminescence of Ln(III) ion can be estimated using the following relationship between the experimentally determined lifetime of Ln(III) (τ_{obs}) and its radiative lifetime (τ_{rad}):

$$\Phi = \tau_{\text{obs}} / \tau_{\text{rad}}$$

Using a typical τ_{rad} value of 8.00 ms for Er(III) in inorganic hosts,²⁴ we estimate the intrinsic quantum yield of the sensitized luminescence to be 2.5%. To the best of our knowledge, it is one of the highest values reported for the $1.54 \mu\text{m}$ emission of

erbium(III) ions sensitized by organic dyes. Since the emission of the dye is completely suppressed in the presence of Er^{3+} ions (see Supporting Information) the transfer efficiency from the DFB molecules to the lanthanide ions should be close to one and the total emission quantum yield must approach the intrinsic one in this materials. It must also be noted that all the optical properties of these materials are preserved after 6 months of storage under proper conditions, thus demonstrating the stability of the material.

In conclusion, we showed a novel approach to obtain NIR emitters for the third telecommunication window. The highly efficient $1.54 \mu\text{m}$ emission was obtained from erbium(III) ions incorporated into a dye-loaded zeolite structure. This structure acts as a light harvesting antenna, circumventing the need of organic complex formation. The lifetime of the obtained NIR emission is >2 orders of magnitude longer than that for erbium complexes with nonfluorinated organic ligands, and the NIR quantum efficiency is as high as 2.5%.

This approach allows a broad modification of the optical properties of the material by using both an abundance of perfluorinated molecules that in most cases do not create complexes with Ln(III) ions and zeolite hosts with different frameworks. This approach may open a new way of manufacturing efficient NIR emitting plastic-compatible devices useful in a broad spectrum of communication applications, because functionalized zeolites can be successfully incorporated into polymer matrices.

Sample Preparation. The sodium form of zeolite L ($\text{Si}/\text{Al} = 3.0$, $\text{Na}/\text{Al} = 1.0$, $21\text{-H}_2\text{O}$; ZeoChem. Co. Switzerland) was stirred in an 0.05 M aqueous solution of $\text{ErCl}_3 \cdot 6\text{H}_2\text{O}$ (99.999% ChemPur) for 16 h at 353 K to exchange the potassium ions with Er(III) ions. The product was separated by centrifugation, then washed with deionized water and ethanol, and dried in air at room temperature. The obtained powder was dehydrated by annealing in three steps of 12 h each, at 470 K in air, then at 650 K under mild vacuum, and finally at 850 K under flowing dry O_2 to prevent oxygen vacancies formation. The resulted white powder of completely dry erbium exchanged zeolite was then exposed to DFB (98%, Fluka) vapor at 383 K for 12 h. The reaction sequence was carried out in a sealed, specially designed two-chamber ampule to avoid exposure of the zeolites to the air atmosphere. The amount of exchanged Ln^{3+} ions per unit cell is estimated to be 1, which is the maximum loading that can be expected, since 3.6 monovalent ions per unit cell can be exchanged. This gives 5% of Er^{3+} concentration.²⁷

Spectroscopy. For NIR PL measurements the sample, sealed in the quartz ampule for water protection, was illuminated with a nonfocused beam of a 280 nm LED (Seul Optodevices) with excitation power of $10 \mu\text{W}$, and a pulse repetition rate of 200 Hz. A 378 nm Ti:Sapphire laser with the power of $200 \mu\text{W}$ was also used. The NIR luminescence spectra have been detected by a nitrogen cooled PMT (Hamamatsu R5509-73) with a high speed amplifier (Hamamatsu C5594), and a 74100 Cornestone 2601/4 (ORIEL) monochromator (band-pass 15 nm). For time-resolved measurements, a PCI plug-in multichannel scaler ORTEC 9353 100-ps Time Digitizer/MCS has been used in a photon counting acquisition mode, with a time resolution better than 100 ns. The

absorption spectra were recorded on a Cary Varian 50 SCA N spectrophotometer on homogeneous suspensions of the obtained material in a fluorolube oil.

Acknowledgment. This work was supported by the European Commission through the Human Potential Program RTN “Nanomatch”, Contract No. MRTN-CT-2006-035884.

Supporting Information Available: PL spectra in visible range, XRD spectra, absorption spectra of pure zeolite and loaded with DFB, PL decay traces after 6 months of sample storage. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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JA907927S