Functional Monolayers

DOI: 10.1002/anie.200905354

# Orienting Zeolite L Microcrystals with a Functional Linker[**]

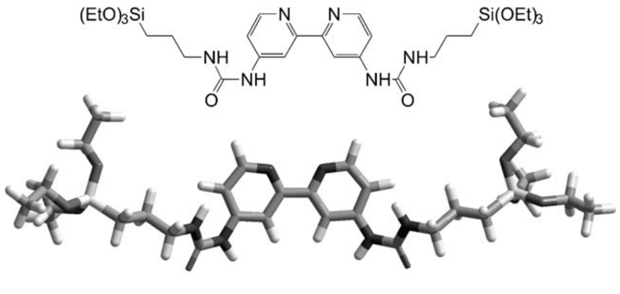
Yu Wang, Huanrong Li,* Yu Feng, Hongjie Zhang,* Gion Calzaferri,* and Tiezhen Ren

One-dimensional channel materials as formed by some zeolites and mesoporous silicas are attractive hosts for the preparation and investigation of hierarchically organized inorganic–organic hybrid materials, presenting a successive ordering from the molecular up to the macroscopic scale.[1–4] We have been using zeolite L (ZL) as a host in most of our experiments. ZL crystals feature strictly parallel channels arranged in a hexagonal symmetry. The size and aspect ratio of the colorless crystallites can be tuned over a wide range. Their one-dimensional channels can be filled with suitable guests. Geometrical constraints imposed by the host structure lead to supramolecular organization of the guests in the channels. The supramolecular organization of dyes inside the ZL channels is the first stage of organization. It allows light harvesting within the volume of a dye-loaded ZL crystal and also allows radiationless energy transport to either the cylinder ends or to the center of the channel. One-dimensional excitation-energy transport has been observed in these guest–host materials.[5] The second stage of organization is the coupling of an external acceptor or donor stopcock fluorophore to the ends of the ZL channels, which can then trap or inject electronic excitation energy. The third stage of organization is achieved by interfacing the material to an external device through a stopcock intermediate.[1,3]

In device chemistry, a high degree of supramolecular organization is important for attaining the desired macroscopic properties. A possibility for achieving such organization is the controlled assembly of the zeolite crystals into oriented structures and the preparation of monodirectional materials. The preparation of dense monolayers of zeolite crystals in the nanometer to micrometer size regime was first accomplished with zeolite A, for which the first ship-in-a-bottle synthesis on a monolayer was also reported.[6,7] An important step in the preparation of stable oriented zeolite monolayers with dense packing was introduced by covalently binding the crystals to a substrate,[8] by using ionic linkage,[9] and by hydrogen-bond fixation.[10] Microcontact transfer printing of oriented ZL monolayers has recently been reported.[11]

The successful assembly of zeolite crystals largely depends on the availability of crystals with a narrow particle size distribution and well-defined morphology. Hexagonal ZL crystals can be assembled in several ways, as we have discussed. Subsequent insertion of guests into the channels and addition of stopcocks is, however, only possible if the free channel openings are not blocked or damaged during the preparation of the monolayer. If successful, the procedure leads to materials with exciting properties, such as transfer of electronic excitation energy in one direction only. First materials with such unidirectional electronic excitation energy transport properties have been realized,[12] and improvement of the methods for preparing corresponding zeolite monolayers on a substrate, which we call c-oriented open-channel monolayers (c-ocMLs), has been demonstrated.[13]

The idea of this work is to achieve higher organization and additional functionality by using a functional linker that has the ability to coordinate and sensitize lanthanide ions $Ln^{3+}$ and that is also able to self-assemble on a surface through hydrogen bonding. To explore this concept we synthesized the triethoxysilylated molecule **1** and tested its ability to bind on a quartz substrate, to coordinate $Ln^{3+}$ ions and sensitize their luminescence, and to allow realization of c-ocMLs.



**1**

The flexible linker **1** has two urea groups, which can form hydrogen bridges. Self-assembly of molecules on a surface through urea hydrogen bonding has been observed.[14] The 2,2′-bipyridine (bpy) group of **1** is known to be a good coordination site for $Ln^{3+}$. The intense luminescence of the corresponding complexes is sensitized by energy transfer from the coordinating bpy unit to the rare-earth ion by the so-

---

[*] Y. Wang, Prof. Dr. H. Li, Y. Feng, T. Ren
School of Chemical Engineering and Technology
Hebei University of Technology, Tianjin 300130 (China)
Fax: (+86) 22-2656-4294
E-mail: lihuanrong@hebut.edu.cn
Prof. Dr. H. Zhang
State Key Laboratory of Rare Earth Resource Utilization
Changchun Institute of Applied Chemistry
Chinese Academy of Sciences, Changchun, 130022 (China)
E-mail: hongjie@ciac.jl.cn
Prof. Dr. G. Calzaferri
Department of Chemistry and Biochemistry, University of Bern
Freiestrasse 3, CH-3012 Bern (Switzerland)
E-mail: gion.calzaferri@iac.unibe.ch

[**] This work is financially supported by the National Natural Science Foundation of China (No. 20871040, No. 20901022), Program for New Century Excellent Talents in University (NCET), the Key Project of Chinese Ministry of Education (208016), the Scientific Program launched in 2008 by Hebei province (08965110D) and Tianjin Natural Science Foundation (09JCYBJC05700).

called antenna effect.[15–18] Substrate functionalized by **1** should then be able to form monolayers of oriented ZL microcrystals. In Figure 1 we illustrate 1) the binding of **1** to the OH groups present on the quartz plate and 2) the binding of **1** with simultaneous coordination of $Ln^{3+}$ to the bpy coordination site. These procedures lead to the functionalized quartz plates **1**-quartz and **1**($Ln^{3+}$)-quartz, respectively. The functionalized plates can then be immersed in a suspension of ZL crystals in toluene to realize step (3), the formation of the c-ocMLs ZL-**1**-quartz and ZL-**1**($Ln^{3+}$)-quartz, respectively.

A simple and direct method for testing reaction 1 in Figure 1 consists of exposing **1**-quartz to a solution of $EuCl_3$ in ethanol. Coordination of $Eu^{3+}$ to the bpy group of **1** should lead to characteristic excitation and emission spectra similar to those of $[Eu^{3+}(bpy)_n]$. In fact, we observed that the **1**-quartz plates display bright red emission after immersion for about 30 min. The excitation spectrum shown in Figure 2 was obtained by monitoring the $^5D_0\rightarrow{}^7F_2$ transition of $Eu^{3+}$ at 612 nm. The broad band can be attributed to the absorption of **1**. The five prominent lines at 578, 593, 612, 652, and 701 nm in the emission spectrum can be assigned to the $^5D_0\rightarrow{}^7F_J$ ($J=0$–4) transition with the red $J=2$ line as the dominant feature. This result confirms that the bpy moiety of **1** tethered on the substrate absorbs the excitation energy and transfers it to the $Eu^{3+}$ ion. Vigorous stirring of the functionalized substrate in ethanol did not cause any decrease in the emission intensity of $Eu^{3+}$.

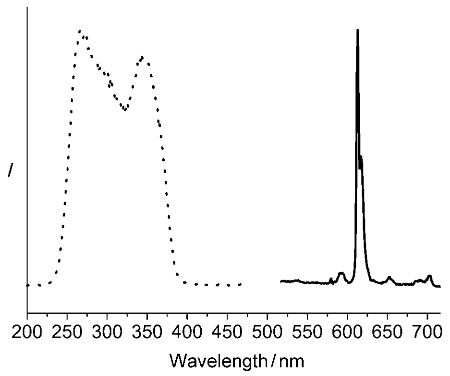


***Figure 2.*** Luminescence of **1**-quartz after immersion in an ethanol solution of $EuCl_3$ for 30 min. The excitation spectrum (-----) was obtained by monitoring the $^5D_0\rightarrow{}^7F_2$ emission at 612 nm, and the emission spectrum (——) was obtained upon excitation at 336 nm. Both spectra were measured at room temperature in air.

The monolayers were prepared on quartz plates of 10 × 10 or 10 × 20 mm size using medium-sized cylindrical ZL crystals of 1 μm average length and diameter.[19] The initially transparent **1**-quartz plates turn opaque upon contact with the suspension of ZL in dry toluene under vigorous sonication. The opaque samples become semitransparent after sonication for 5 s in pure toluene, which was used for removing physisorbed excess ZL. The scanning electron microscopy

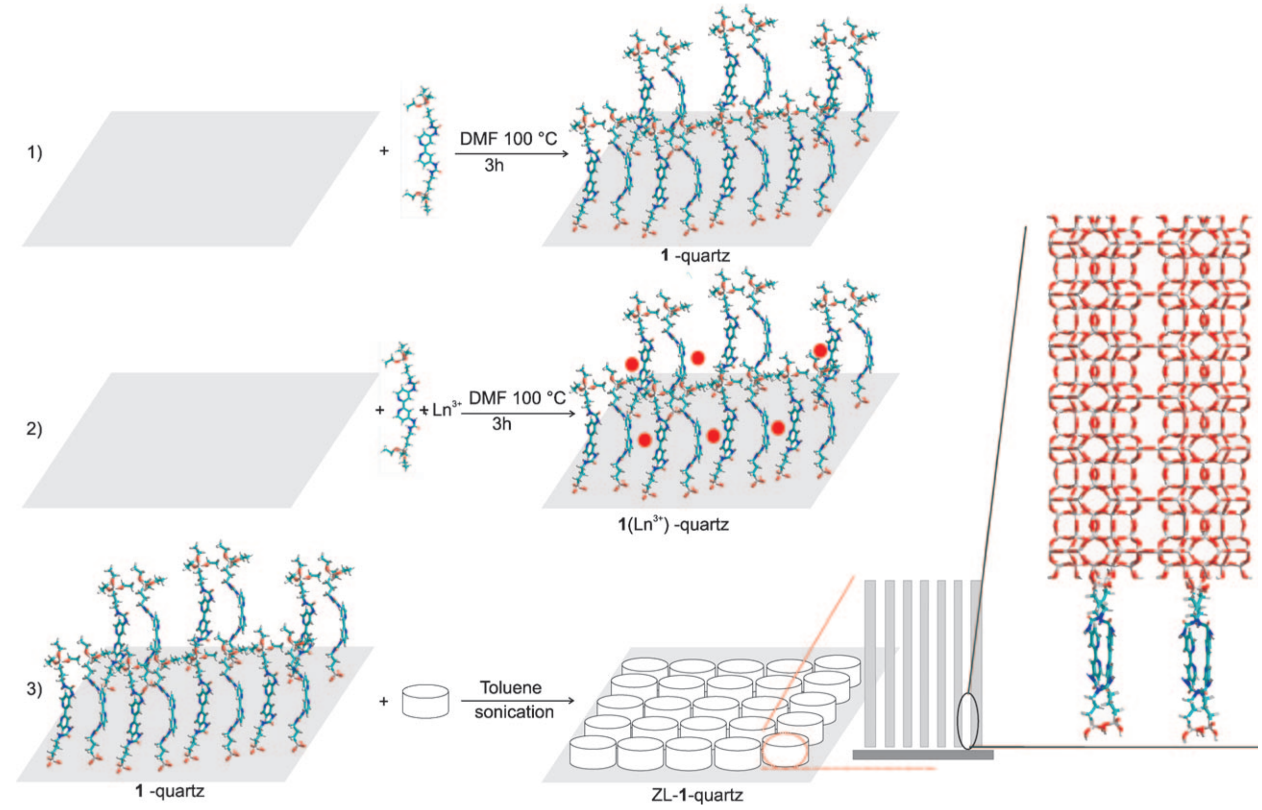


***Figure 1.*** Binding of **1** to the OH groups of a quartz substrate and subsequent formation of a c-ocML. 1) The arrangement **1**-quartz is stabilized by urea hydrogen bonding. 2) Additional stabilization and functionalization through coordination to a rare-earth ion $Ln^{3+}$ (red circles) results in **1**($Ln^{3+}$)-quartz. 3) Sonicating **1**-quartz in a dispersion of ZL crystals in dry toluene leads to the ZL-**1**-quartz c-ocML. The same procedure with **1**($Ln^{3+}$)-quartz results in ZL-**1**($Ln^{3+}$)-quartz.

(SEM) images of the ZL-**1**-quartz samples shown in Figure 3 reveal the presence of densely packed ZL monolayers. Nearly all ZL crystals stand on the substrate with their *c* axis perpendicular to the surface. This orientation and the high degree of coverage imply that the interaction between the crystal base and the substrate is much stronger than any other interactions.[12] The dense packing is homogeneous over the entire plate, as illustrated in Figure 3 with different magnifications of the SEM images. This dense packing indicates that a large number of strong covalent linkages between the crystals and the substrate are formed. These linkages derive from the nucleophilic substitution of the terminal triethoxy groups of the attached linker **1** by the surface hydroxy groups on the base of the ZL crystals. It makes sense to assume that a considerable amount of **1** is oriented perpendicular to the substrate, as suggested by Figure 1, possibly favored by the urea groups, which can self-assemble on the surface through hydrogen bonding. It has been documented that bis(trialkoxysilylated) organic molecules bearing bis(urea) groups tend to self-assemble through hydrogen-bonding interactions involving the urea units.[14]

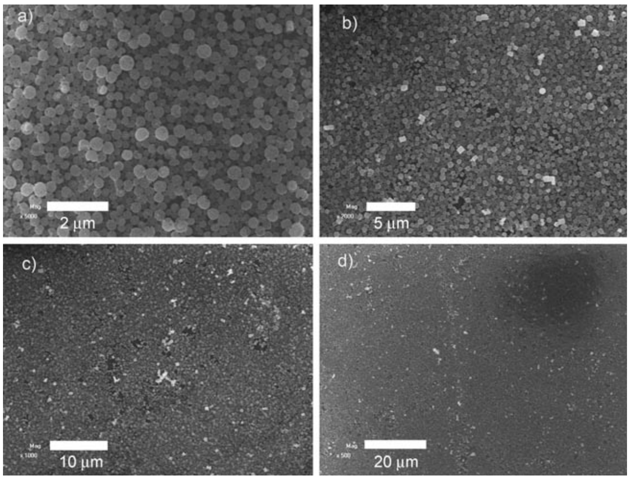


***Figure 3.*** SEM images of a ZL-**1**-quartz c-ocML at different magnifications.

The hypothesis regarding the role of the alkoxysilane groups of **1** in the assembly of the ZL microrystals into such perfect monolayers was supported experimentally. Samples of **1**-quartz were hydrolyzed and condensed by contacting with HCl (0.2 M) under heating for 3 h. The treated samples were then used to assemble ZL crystals by the procedure described above. We found that this approach leads to very poor monolayers with random orientation of the crystals, low coverage, and poor binding; most of the crystals on the samples prepared in this way are easily removed from the substrate by sonication in fresh solvent for three to five seconds. Further investigations are, however, desirable to gain a more detailed understanding of the structure of the nearly perfect layers.

Additional functionality can be added by using **1**($Ln^{3+}$)-quartz as the starting substrate for c-ocML formation according to reaction 3 in Figure 1. We have tested this method for $Eu^{3+}$ and $Tb^{3+}$ and found that the reaction works as well as reported above for **1**-quartz. Luminescence data of the **1**($Ln^{3+}$)-quartz substrate and of the ZL-**1**($Ln^{3+}$)-quartz c-ocML is reported in Figure 4. Both excitation spectra show essentially the same broad band ranging from 220–350 nm, which is also seen in Figure 2 and which can be assigned to the absorption of the bpy moiety of **1**. Excitation into this broad band leads to sharp emission lines attributed to the $^5D_0\rightarrow{}^7F_{0-4}$ transitions for ZL-**1**($Eu^{3+}$)-quartz and $^5D_4\rightarrow{}^7F_{3-6}$ for ZL-**1**($Tb^{3+}$)-quartz, respectively. The dominant emission line for ZL-**1**($Eu^{3+}$)-quartz corresponds to the $^5D_0\rightarrow{}^7F_2$ transition at 612 nm, whereas the emission $^5D_4\rightarrow{}^7F_5$ at 544 nm is the dominated feature for ZL-**1**($Tb^{3+}$)-quartz. The former is responsible for the bright red color of $Eu^{3+}$ and the latter for the characteristic green color of $Tb^{3+}$, observed upon irradiation at 254 nm (Figure 4 a1, a2, b1, b2).

So far we have reported experiments carried out with potassium ZL crystals that were not functionalized. The flexibility and robustness of the preparation of ZL-**1**-quartz c-ocMLs was further tested using ZL crystals containing guests. The successful synthesis of remarkably stable organolanthanide complexes inside the nanochannels of ZL crystals was recently reported. A ship-in-a-bottle procedure was used, which consisted of inserting bpy or 2-thenoyltrifluoroacetone (tta) from the gas phase into the nanochannels of $Ln^{3+}$-ZL crystals (Ln = Tb or Eu).[17] We therefore used the new $Ln^{3+}(bpy)_n$-ZL and $Ln^{3+}(tta)_n$-ZL hybrid materials for testing the preparation of ($Ln^{3+}(bpy)_n$-ZL)-**1**($Ln^{3+}$)-quartz and ($Ln^{3+}(tta)_n$-ZL)-**1**($Ln^{3+}$)-quartz c-ocMLs. We found that the same quality of layers as described for the ZL-**1**-quartz c-ocMLs can be achieved. Figure 4 c shows the emission spectra of a ($Eu^{3+}(tta)_n$-ZL)-**1**($Tb^{3+}$)-quartz c-ocML observed after excitation at different wavelengths and photographic images of such a layer upon UV excitation. The characteristic sharp bands at 488, 543, and 582 nm are attributed to the f–f transitions of $Tb^{3+}$ ($^5D_4\rightarrow{}^7F_J$, $J = 6,5,4$) with $^5D_4\rightarrow{}^7F_5$ transition (green emission) as the dominant feature. The bands at 588, 618, 652, and 700 nm are attributed to $Eu^{3+}$, namely the ($^5D_0\rightarrow{}^7F_J$, $J = 1,2,3,4$) transitions with the $^5D_0\rightarrow{}^7F_2$ line as the most intense feature (red line). When changing the excitation wavelength, we observe that the relative intensities of most bands also change, resulting in different colors of the plates. The green component of the emission decreases drastically upon increasing the excitation wavelength from 300 to 365 nm. The emission color of the monolayer can thus be tuned by varying the kind and ratio of lanthanide ions coordinated to the linker or inserted as guest in the channels of the zeolite and by changing the excitation wavelength.

To test if subsequent insertion of guests into the channels and addition of stopcocks is possible, that is, to test if the channels are not blocked or damaged during the preparation of the monolayer, we inserted luminescent dyes into the channels of ZL-**1**-quartz c-ocMLs in a similar way as described in reference [13]. Coumarin 1 was inserted into the nanochannels of ZL-**1**-quartz c-ocMLs by gas diffusion. The obtained material shows intense blue emission upon irradiation with a broad band UV lamp.

The novel strategy for arranging ZL crystals into luminescent macroscopic structures explained in Figure 1 has been

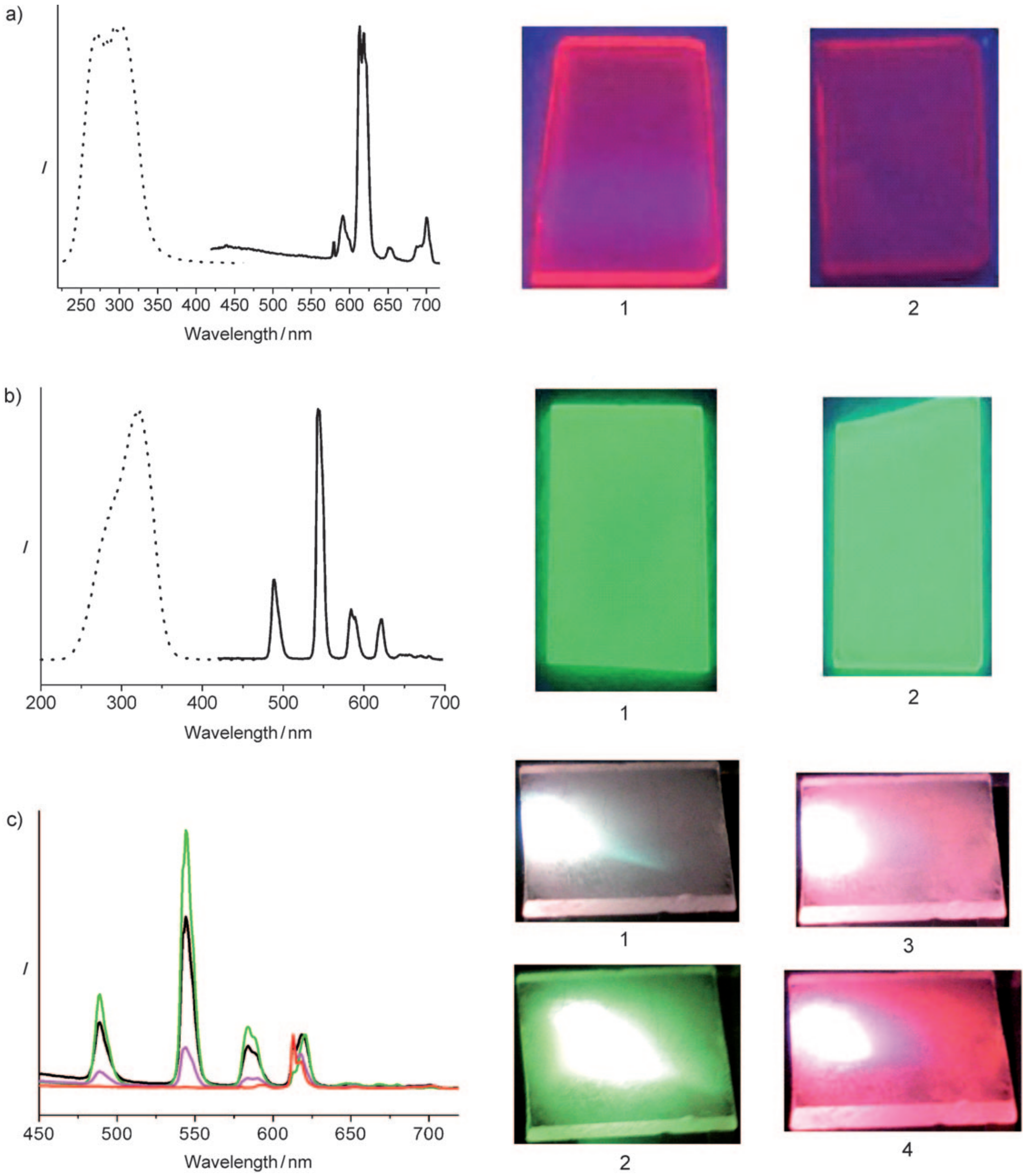


***Figure 4.*** Luminescence of **1**($Ln^{3+}$)-quartz, ZL-**1**($Ln^{3+}$)-quartz, and ($Eu^{3+}$(tta)$_n$-ZL)-**1**($Tb^{3+}$)-quartz layers observed at room temperature in air. a) Excitation spectrum of a ZL-**1**($Eu^{3+}$)-quartz sample (-----) observed at 612 nm and emission spectrum (——) upon excitation at 336 nm. b) Excitation spectrum of a ZL-**1**($Tb^{3+}$)-quartz sample (-----) observed at 544 nm and emission spectrum (——) upon excitation at 300 nm. a1, b1) Photographs of **1**($Eu^{3+}$)-quartz (a1) and **1**($Tb^{3+}$)-quartz plates (b1) upon irradiation at 254 nm. a2, b2) Photographs of ZL-**1**($Eu^{3+}$)-quartz (a2) and ZL-**1**($Tb^{3+}$)-quartz (b2) plates upon irradiation at 254 nm. c) Luminescence spectra of a ($Eu^{3+}$(tta)$_n$-ZL)-**1**($Tb^{3+}$)-quartz sample after excitation at different wavelengths: 270 (black), 300 (green), 340 (magenta), and 365 nm (red). c1–c4) Photographs of such a layer upon UV excitation at 270 (c1), 300 (c2), 340 (c3), and 365 nm (c4). The white spots are reflections from the light source.

found to be successful. We can conclude that dense, homogeneous, well-oriented, stable, and highly organized functional monolayers can be synthesized by this procedure. The color of the luminescence of the resulting layers can be fine tuned by changing the amount and type of lanthanide ions coordinated to the linker, by changing the guest inside the channels of the zeolite host, and by changing the excitation wavelength. These results are of great interest for applications in different fields of optoelectronics and sensing. The reaction principle is not limited to rare-earth ions but can be extended to any cations which form stable complexes with the bpy moiety of **1**.

## Experimental Section

Materials: Medium-sized cylindrically shaped ZL crystals of 1 μm average length and diameter were synthesized and characterized as described in reference [19]. $Tb^{3+}$(bpy)$_n$-ZL and $Eu^{3+}$(tta)$_n$-ZL were prepared according to reference [17]. Compound **1** was synthesized and characterized according to the procedure reported in reference [16a]. Quartz plates (10 × 10 and 20 × 10 mm) were dipped into an acid bath consisting of potassium dichromate and sulfuric acid for 12 h to remove possible organic residues on the surface. The plates were then washed with copious amounts of deionized water and dried at 80 °C in clean air for 3 h. Solutions of $EuCl_3$ and $TbCl_3$ in ethanol were prepared by first dissolving $Eu_2O_3$ and $Tb_4O_7$, respectively, in concentrated hydrochloride acid.

**1**-quartz: Typically, the quartz plates were immersed in a solution of **1** (0.5 mmol) in dry DMF (10 mL) and heated at reflux for 3 h under $N_2$, cooled to room temperature, and washed with copious amounts of DMF.

ZL-**1**-quartz c-ocML: An excess of ZL (10 mg) was added to toluene (10 mL) and sonicated for approximately 30 min, the pretreated quartz plates were introduced, and the mixture was then sonicated for 15 min. The opaque quartz plates coated with ZL were sonicated in toluene for 5 s to remove the physisorbed crystals.

ZL-**1**($Ln^{3+}$)-quartz c-ocML: $EuCl_3$ or $TbCl_3$ in ethanol (0.1 M, 2 mL) was added to **1** in DMF (5 mL, 0.1 M), and the mixture was stirred at 100 °C for 3 h. Then, two quartz plates were added and heated at 100 °C for 3 h. After cooling to room temperature, the functionalized **1**($Ln^{3+}$)-quartz samples were removed from the flask and washed with copious amounts of ethanol. An excess of ZL (10 mg) was added to dry toluene (10 mL) and sonicated for approximately 30 min, the **1**($Ln^{3+}$)-quartz samples were added, and the mixture sonicated for 15 min. The opaque quartz plates coated with ZL were sonicated in toluene for 5 s to remove the physisorbed zeolite crystals. ($Ln^{3+}(bpy)_n$-ZL)-**1**($Ln^{3+}$)-quartz and the ($Ln^{3+}(tta)_n$-ZL)-**1**($Ln^{3+}$)-quartz c-ocML were prepared the same way, but $Ln^{3+}(bpy)_n$-ZL and $Ln^{3+}(tta)_n$-ZL, respectively, were used instead of ZL. Coumarin 1 was inserted into the nanochannels of ZL-**1**-quartz c-ocML from the gas phase at 100 °C for 3 h in vacuum, and the resulting samples were washed with ethanol three times.

Physical measurements: Infrared spectra were obtained on a Bruker Vector 22 spectrometer (KBr pellets) from 400–4000 $cm^{-1}$ at a resolution of 4 $cm^{-1}$ (16 scans). $^1H$ NMR spectra were obtained on a Bruker ARX 300 apparatus. SEM images were obtained from an FE-SEM instrument (Hitachi S-4300) at an acceleration voltage of 10 kV. The steady-state luminescence spectra and the lifetime measurements were measured on an Edinburgh Instruments FS920P spectrometer, with a 450 W xenon lamp as the steady-state excitation source, a double excitation monochromator (1800 lines $mm^{-1}$), an emission monochromator (600 lines $mm^{-1}$), and a semiconductor cooled Hamamatsu RMP928 photomultiplier tube.

Received: September 24, 2009

**Keywords:** luminescence · monolayers · self-assembly · supramolecular chemistry · zeolites

---

[1] a) G. Calzaferri, K. Lutkouskaya, *Photochem. Photobiol. Sci.* **2008**, *7*, 879–910; b) G. Calzaferri, S. Huber, H. Maas, C. Minkowski, *Angew. Chem.* **2003**, *115*, 3860–3888; *Angew. Chem. Int. Ed.* **2003**, *42*, 3732–3758.

[2] a) S. Hashimoto, K. Samata, T. Shoji, N. Taira, T. Tomita, S. Matsuo, *Microporous Mesoporous Mater.* **2009**, *117*, 220–227; b) J. S. Lee, K. Ha, Y.-J. Lee, K. B. Yoon, *Top. Catal.* **2009**, *52*, 119–139; c) K. B. Yoon, *Acc. Chem. Res.* **2007**, *40*, 29–40; d) V. Ramamurthy, *Photochemistry in Organized and Constrained Media*, VCH publishers, New York, **1991**.

[3] D. Brühwiler, G. Calzaferri, T. Torres, J. Ramm, N. Gartmann, L. Q. Dieu, I. López, M. Martínez, *J. Mater. Chem.* **2009**, *19*, 8040–8067.

[4] a) S. Inagaki, O. Othani, Y. Goto, K. Okamoto, M. Ikai, K. Yamanaka, T. Tani, T. Okada, *Angew. Chem.* **2009**, *121*, 4102–4106; *Angew. Chem. Int. Ed.* **2009**, *48*, 4042–4046; b) I. B. Martini, I. M. Craig, W. C. Molenkamp, H. Miyata, S. H. Tolbert, B. J. Schwartz, *Nat. Nanotechnol.* **2007**, *2*, 647; c) E. Johansson, E. Choi, S. Angelos, M. Liong, J. I. Zink, *J. Sol-Gel Sci. Technol.* **2008**, *46*, 313.

[5] C. Minkowski, G. Calzaferri, *Angew. Chem.* **2005**, *117*, 5459–5463; *Angew. Chem. Int. Ed.* **2005**, *44*, 5325–5329.

[6] a) P. Lainé, R. Seifert, R. Giovanoli, G. Calzaferri, *New J. Chem.* **1997**, *21*, 453–460; b) J.-W. Li, K. Pfanner, G. Calzaferri, *J. Phys. Chem.* **1995**, *99*, 2119–2126; c) Y. Yan, T. Bein, *J. Am. Chem. Soc.* **1995**, *117*, 9990–9994; d) J. Li, G. Calzaferri, *J. Chem. Soc. Chem. Commun.* **1993**, 1430–1431.

[7] C. Leiggener, G. Calzaferri, *ChemPhysChem* **2004**, *5*, 1593–1596.

[8] a) A. Kulak, Y. J. Lee, Y. S. Park, K. B. Yoon, *Angew. Chem.* **2000**, *112*, 980–983; *Angew. Chem. Int. Ed.* **2000**, *39*, 950–953; b) Y. S. Choi, Y. J. Lee, Y. S. Park, K. Ha, K. B. Yoon, *J. Am. Chem. Soc.* **2000**, *122*, 5201–5209; c) J. S. Lee, H. Lim, K. Ha, H. Cheong, K. B. Yoon, *Angew. Chem.* **2006**, *118*, 5414–5418; *Angew. Chem. Int. Ed.* **2006**, *45*, 5288–5292.

[9] G. S. Lee, Y. J. Lee, K. B. Yoon, *J. Am. Chem. Soc.* **2001**, *123*, 9769–9779.

[10] G. S. Lee, Y. J. Lee, S. Y. Choi, Y. S. Park, K. B. Yoon, *J. Am. Chem. Soc.* **2000**, *122*, 12151–12157.

[11] F. Cucinotta, Z. Popović, E. A. Weiss, G. M. Whitesides, L. De Cola, *Adv. Mater.* **2009**, *21*, 1142–1145.

[12] a) A. Zabala Ruiz, H. Li, G. Calzaferri, *Angew. Chem.* **2006**, *118*, 5408–5413; *Angew. Chem. Int. Ed.* **2006**, *45*, 5282–5287; b) G. Calzaferri, A. Zabala Ruiz, H. Li, S. Huber, WO 2007/012216, **2005**.

[13] a) H. R. Li, Y. G. Wang, W. J. Zhang, B. Y. Liu, G. Calzaferri, *Chem. Commun.* **2007**, 2853–2854; b) Y. G. Wang, H. R. Li, B. Y. Liu, Q. Y. Gan, Q. L. Dong, G. Calzaferri, Z. Sun, *J. Solid State Chem.* **2008**, *181*, 2469–2472.

[14] a) N. Liu, K. Yu, B. Smarsly, D. R. Dunphy, Y. B. Jiang, C. J. Brinker, *J. Am. Chem. Soc.* **2002**, *124*, 14540–14541; b) O. J. Dautel, J. P. Lere-porte, J. J. E. Moreau, M. Wong Chi Man, *Chem. Commun.* **2003**, 2662–2663.

[15] R. G. Charles, E. P. Riedel, P. G. Haverlack, *J. Chem. Phys.* **1966**, *44*, 1356–1361.

[16] a) H. R. Li, N. Lin, Y. Wang, Y. Feng, Q. Gan, H. Zhang, Q. Dong, Y. Chen, *Eur. J. Inorg. Chem.* **2009**, 519–523; b) H. R. Li, J. Lin, H. J. Zhang, L. S. Fu, Q. G. Meng, *Chem. Commun.* **2001**, 1212–1213; c) V. Bekiari, P. Lianos, *Adv. Mater.* **1998**, *10*, 1455–1458.

[17] a) Y. G. Wang, L. J. Gu, H. R. Li, Q. Y. Gan, Y. N. Li, G. Calzaferri, *Microporous Mesoporous Mater.* **2009**, *121*, 1–6; b) H. R. Li, W. J. Cheng, Y. Wang, B. Y. Liu, W. J. Zhang, H. J. Zhang, *Chem. Eur. J.*, DOI: 10.1002/Chem.200901687.

[18] a) S. I. Weissman, *J. Chem. Phys.* **1942**, *10*, 214–217; b) N. Sabbatini, M. Guardingli, J. M. Lehn, *Coord. Chem. Rev.* **1993**, *123*, 201–228; c) H. Maas, A. Currao, G. Calzaferri, *Angew. Chem.* **2002**, *114*, 2607–2608; *Angew. Chem. Int. Ed.* **2002**, *41*, 2495–2497.

[19] a) S. Megelski, G. Calzaferri, *Adv. Funct. Mater.* **2001**, *11*, 277–286; b) A. Zabala Ruiz, D. Brühwiler, T. Ban, G. Calzaferri, *Monatsh. Chem.* **2005**, *136*, 77–89.