DOI: 10.1002/chem.200901687

Surface Modification and Functionalization of Microporous Hybrid Material for Luminescence Sensing

Huanrong Li,*[a] Wenjing Cheng,[a] Yu Wang,[a] Binyuan Liu,[a] Wenjun Zhang,[a] and Hongjie Zhang*[b]

Abstract: We report here on the preparation of novel luminescent core-shell material by initial coating with polyelectrolytes and subsequent with a silica shell on the lanthanide complexes loaded zeolite L microcrystals. Lanthanide complexes loaded zeolite L was prepared by insertion of 2-thenoyltrifluoroacetone (TTA) into the nanochannels of zeolite crystals by gas diffusion of TTA to Eu^{3+} exchanged zeolite L, coating a silica shell on the lanthanide complexes loaded zeolite L resulted to the novel luminescent core-shell material. The luminescent core-shell material was further functionalized with silylated terbium(III) complex and the obtained material was used as the luminescence sensing of dipicolinic acid (DPA), which is a major constituent of many pathogenic spore-forming bacteria.

Keywords: lanthanides · luminescence · sensors · silica shell · zeolites

Introduction

Zeolites can host a great variety of photochemically and photophysically active guests. An increased chemical or thermal stability of the inserted species can often be observed in such host–guest materials. Therefore, they have attracted considerable interest for constructing novel materials designed at nanosized level and they are of particular interest in the area of optical materials for which predefined distances or a specific spatial pattern of the guests is required to obtain a desired optical response.[1] Further functionalities can be added by assembling such host–guest systems into well-defined macroscopic structures on various supports.[2–6] The versatility of pore structure and morphologies provided by different types of zeolite offers many possibilities for the design of host–guest systems with specific properties.[7] Among them, zeolite L crystals have played a great role in the construction of host–guest systems due to their special structures.[8] Zeolite L is a crystalline aluminosilicate in which corner-sharing SiO_4 and AlO_4 tetrahedra produce one-dimensional channels arranged in a hexagonal structure.[9] The channels have a smallest free diameter of about 0.71 nm, the largest diameter inside is 1.26 nm. The distance between the centers of two neighboring channels is 1.84 nm. Many different guest species, including neutral and cationic organic dyes, have been incorporated into the one-dimensional channels of zeolite L crystals.[10] Photonic antenna materials have been obtained by inserting two or three different type of dyes in which the donors are either located in the middle of the zeolite channels and the acceptors at the end or vice versa.[8]

Complexes between lanthanides and organic ligands (especially Eu^{3+} diketonate and Tb^{3+} heterocyclic complexes) have long been known to give intense emission lines upon UV-light irradiation, because of the effective intramolecular energy transfer from the ligands to the central lanthanide ions. The importance of lanthanide ions is related to the particularities of their luminescence, that is, long decay times and narrow-band emission. The organic ligand not only protects the metal ions from vibrational coupling, but also increases the light absorption cross section by the "antenna effect".[11] A few reports concern different Ln^{3+} species, including lanthanide complexes, embedded in zeolites, mainly

---

[a] Prof. H. Li, W. Cheng,+ Y. Wang,+ Prof. B. Liu, Prof. W. Zhang
School of Chemical Engineering and Technology
Hebei University of Technology, Tianjin 300130 (P. R. China)
Fax: (+86) 225264294
E-mail: lihuanrong@hebut.edu.cn

[b] Prof. H. Zhang
State Key Laboratory of Rare Earth Resource Utilization
Changchun Institute of Applied Chemistry
Chinese Academy of Sciences, Changchun 130022 (P. R. China)
Fax: (+86) 43185698041
E-mail: hongjie@ciac.jl.cn

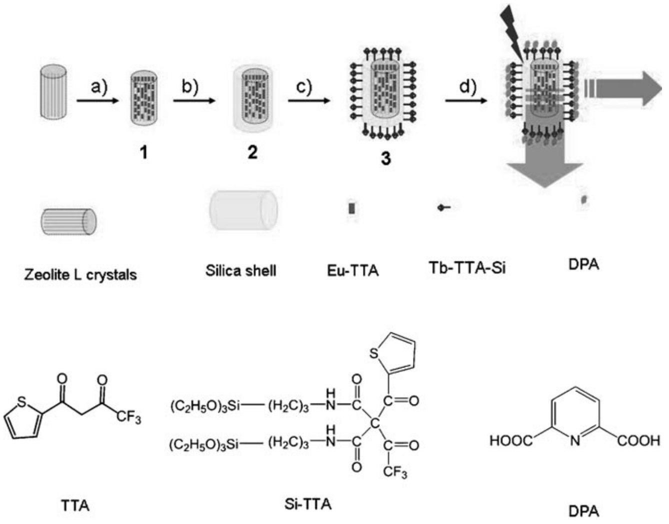
[+] These authors equally contributed to this work

© 2010 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

Faujasites.[12] Little attention has been paid to the insertion of organolanthanide complexes into the channels of zeolite L, despite of the fact that zeolite L seems currently to be the only nanochannel material that can be synthesized in a size range starting from about 30 nm up to several thousand nm and with crystals of different morphology ranging from discs to elongated cylinders.[13] Recently we and others have focused on the insertion of lanthanide complexes into the nanochannels of zeolite L crystals.[14]

Unfortunately, leakage of the guest species from the nanochannels of the host–guest materials is often observed when used in solution because the inclusion of the guest species is a thermodynamically reversible process. It has been reported recently that coating the dye-loaded zeolite L initial with polyelectrolyte (e.g., poly(allylamine hydrochloride) (PAH) and and poly(vinylpyrrolidone) (PVP)) and subsequently with a silica shell by means of sol–gel processes can block the entrances of nanochannels of the zeolite and thus can prevent the leakage of the dyes from the nanochannels.[15] Furthermore, there are some other advantages of the silica shells, including stability of aqueous dispersions, biocompatibility, and easy modification through the co-condensation of siloxy-derived molecules.[16]

We report herein the preparation of luminescent lanthanide complexes loaded zeolite L/silica core-shell composite following the procedure reported in reference [15]. We also demonstrate the ability to further functionalize the core-shell composite for the luminescence sensing of dipicolinic acid (DPA), which is a major constituent of many pathogenic spore-forming bacteria. To the best of our knowledge, this is the first report of luminescent lanthanide-loaded zeolite L/silica core-shell composite and their use in the detection of DPA. The synthesis principle is summarized in Scheme 1.



Scheme 1. Illustration for the preparation of **1**, **2** and **3** and the principle for DPA detection.

Results and Discussion

Insertion of europium(III) complex into the nanochannels of zeolite L crystals by gas diffusion of 2-thenoyltrifluoroacetone (TTA) to europium(III)-exchanged zeolite L leads to luminescent microporous hybrid materials **1**. TTA was chosen, since β-diketone ligands are known to be very efficient sensitizer for europium(III) ions.[17] Figure 1 shows the excitation and emission spectra of **1**. The excitation spectrum, obtained by monitoring the $^5D_0\rightarrow{}^7F_2$ transition at 612 nm, displays a broad excitation band ranging from 250 to 400 nm, which may result from the $\pi\rightarrow\pi^*$ transitions of the organic ligands. The absence of intra-4f^6 transitions in the excitation spectrum indicates that an energy transfer occurs from the ligands to the central Eu^{3+} ions. Excitation of the ligands (337 nm) leads to sharp emission peaks arising from transitions between $^5D_0\rightarrow{}^7F_J$ crystal-field components ($J=0, 1, 2, 3, 4$) with the hypersensitive transition $^5D_0\rightarrow{}^7F_2$ as the most prominent line, suggesting that the europium(III) ion sites are indeed without a center of inversion. The typical red color of europium emission is mostly attributed to the strongest transition $^5D_0\rightarrow{}^7F_2$ centered at 612 nm. The intensity ratio (R) of $^5D_0\rightarrow{}^7F_2$ line with respect to that of $^5D_0\rightarrow{}^7F_1$ line for **1** is 9.9. It is known that the R value can be considered as a parameter to probe the "asymmetry" of the europium(III) sites.[18] It has been generally accepted that the asymmetry parameter becomes larger as the interaction of europium(III) with its neighbors becomes stronger and the europium(III) site symmetry becomes lower.[19]Here the R value is about 9.9, indicating that the local surrounding observed in our sample is highly asymmetric if taking into account that R value reported for europium(III) ions in aqueous solution, in which they are directly coordinated to 8–9 water molecules, is 0.43.[20]

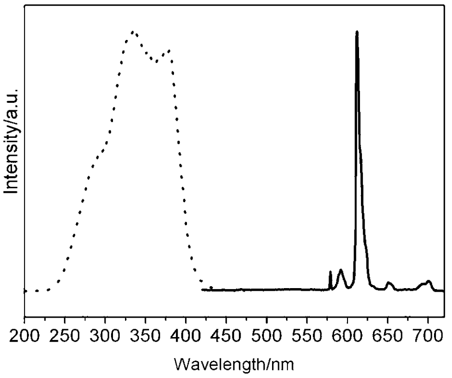


Figure 1. Excitation (dotted line) and emission (solid line) spectra of hybrid material **1**. The excitation spectrum was obtained by monitoring at 612 nm, the emission spectrum was obtained by excitation at 337 nm. Both spectra were obtained at room temperature.

Coating the silica shell on microporous hybrid material **1** following the procedure reported in reference [6] produces the core-shell hybrid material **2**. The formation of the silica shell was obsereved by SEM (Figure 2). After the growth of

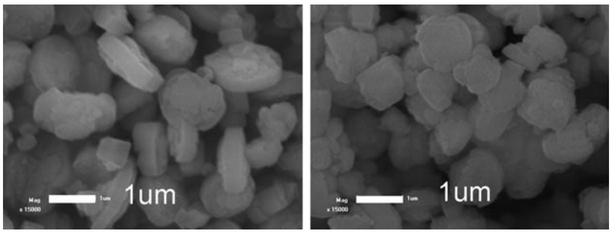


Figure 2. SEM images of hybrid material **1**(left) and **2**(right).

silica coating, the bases of the disc-shape zeolite L crystals become much smoother compared to those of the bare zeolite L crystals as revealed in Figure 2. The formation of core-shell structure can also be proved by the XPS analysis of the silica-coated sample **2**. The measured molar ratio of Al/Si for hybrid material **1** is very close to the calculated value (1:3, $(M)_9[Al_9Si_{27}O_{72}]\cdot n H_2O$), whereas this value for hybrid material **2** is 0, implying the existence of an SiO_2 shell on the surface of zeolite L crystals. More evidence comes from the fact that the peak corresponding to aluminum oxide has disappears (Figure 3), which indicates that the silica-shell-coat on the zeolite L crystals might be thicker than 4–5 nm.[15,21]

Figure 4 presents the excitation and emission spectra of hybrid material **2**. No significant changes were observed in the emission and excitation spectra between microporous hybrid materials **1** and **2** as shown in Figures 4 and 3. To investigate the protection of the guest species in the nanochannels of zeolite L crystals, UV/Vis measurements of supernatant solutions from hybrid materials **1** and **2** in ethanol after 20 h of stirring were performed and the absorption spectra are presented in Figure 5. As revealed in Figure 5 a, the strong and broad band in the absorption spectrum of supernatant solutions from **1** can be ascribed the absorption of TTA released from the nanochannels of zeolite L, in which the end entrances of the channels are open and allowed for the outlet of guest species; on the other hand only very weak and neglectable absorption band can be observed for

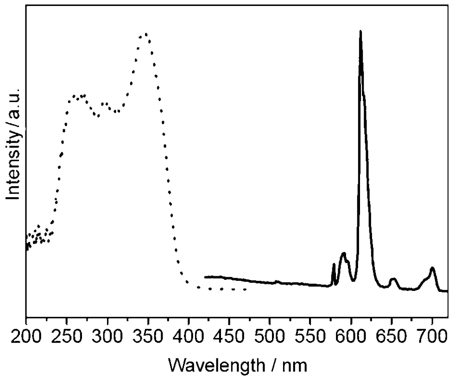


Figure 4. Excitation (dotted line) and emission (solid line) spectra of hybrid material **2**. The excitation spectrum was obtained by monitoring at 612 nm, the emission spectrum was obtained by excitation at 337 nm. Both spectra were obtained at room temperature.

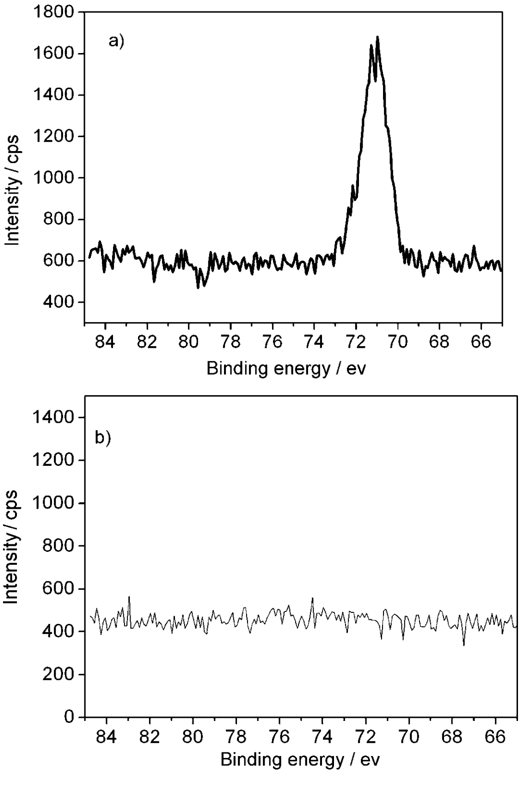


Figure 3. XPS spectra of a) hybrid material **1** and b) hybrid material **2**.

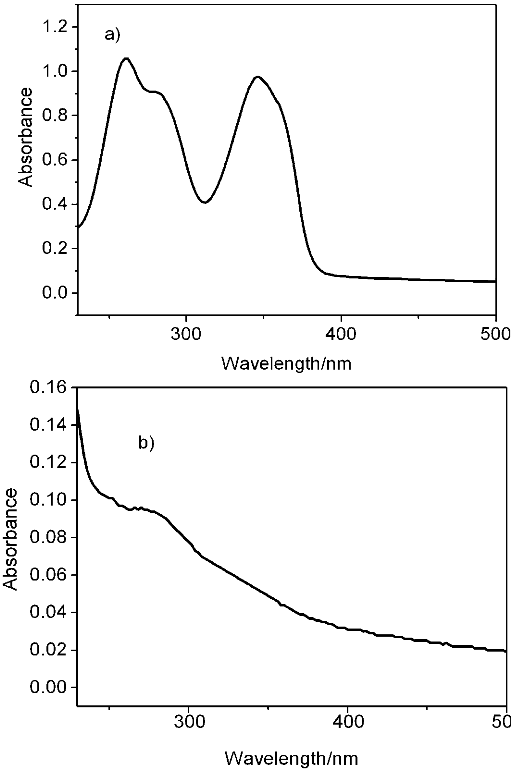


Figure 5. Absorption spectra of the filtered supernatant solutions after 24 h of stirring of a) hybrid material **1** and b) hybrid material **2**.

hybrid material **2**. However, the emission intensity of **2** is almost as the same as that of **1**, despite the complicated treatment during the preparation procedure, while the emission intensity of **1** was significantly decreased when treated according to the procedure used in the preparation of **2** but without addition of PAH, PVP, and TEOS (Figure 6). This could be ascribed to isolation of the zeolite system from the external environment through an impermeable silica coating in which the polyelectrolyte layers act as steric and electrostatic barriers.[15,22]

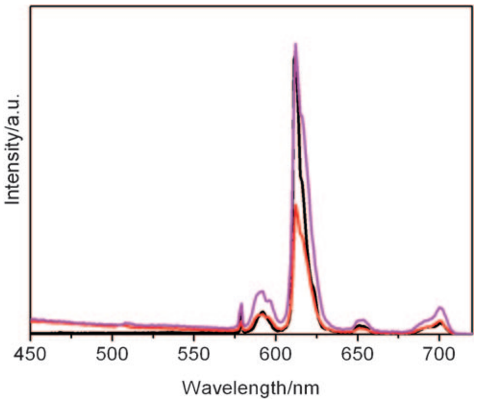


Figure 6. Emission spectra of hybrid materials **1** (magenta), **2** (black) and **1** (red) upon treatment according to the procedure used in the preparation of **2**, but without addition of PAH, PVP and TEOS.

Further function of the new luminescent microporous hybrid materials with a silylated TTA-Tb led to **3**, which can be used as luminescence probes for anthrax and other bacterial spores by complexing to DPA, which is a major constituent of many spore-forming bacteria.[16,23] Hybrid material **3** only shows europium(III) luminescence and no emission from terbium(III) is found when excited at 278 nm, because TTA could not sensitize the luminescence of terbium(III). The europium(III) complex from inside the nanochannel of zeolite L crystals encapsulated in the silica, as an internal calibration, is protected from the external influences such as solvents, providing a stable reference signals. Terbium(III) luminescence became clearly visible upon the addition of DPA to an ethanolic dispersion of **3** due to the formation of the Tb–TTA–DPA complex. The intensity of terbium(III) luminescence is increased upon addition of the increasing concentration of the DPA, whereas no significant changes were observed for the intensity of europium(III) emissions as revealed in Figure 7. It is worth noting that the terbium(III) can still be detected even at the relatively low concentration of DPA (0.05 μm).

Conclusion

In summary, a novel core-shell organic–inorganic hybrid material displaying characteristic features of europium(III) was obtained by coating europium(III)-loaded zeolite L crystals with silica; these shells prevent the leakage of TTA from the channel. The core-shell material was further functionalized with terbium(III) complexes for the detection of DPA, an important molecular marker in spore-producing bacteria. This study also extends the application of zeolite L based hybrid materials to the field of biosensors. Owing to the versatility of zeolite crystals and the luminescent dyes, the present approach should allow for the synthesis of novel core-shell hybrid materials for future sensing. For instance, Lu and co-workers[24] have developed a highly sensitive of the europium-based sensor for CaDPA. In all probability, novel systems in which luminescent dyes (e.g., pyronine (Py+)[25]) for the calibration loaded inside the nanochannel of zeolite L and [Eu(EDTA)(H_2O)$_3$] anchored onto the silica shell may be developed as a luminescent probe for DPA detection. The advantage of zeolite L compared to silica is that it can prevent the self-aggregation of dyes and superimpose a specific organization (e.g., the anisotropic intense luminescence[15]) with a high concentration of monomers.[26] These studies are in progress in our lab.

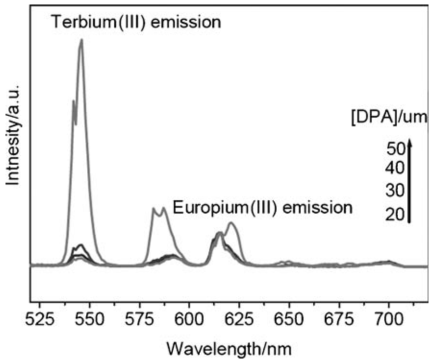


Figure 7. Fluorescence response of **3** upon addition of different concentration of DPA. ($\lambda_{ex}=278$ nm).

Experimental Section

Materials: Pure zeolite L crystals were synthesized and characterized as described previously.[13] Disc-shaped crystals (1 μm × 0.2 μm) and nanosized crystals (100 nm) were used in this study. The potassium exchanged form was used. 2-Thenoyltrifluoroacetone (TTA) was purchased from Aldrich and used as received. Si–TTA was synthesized according to the reported procedure.[27] $TbCl_3 \cdot 6H_2O$ and $EuCl_3 \cdot 6H_2O$ were obtained by dissolving Tb_4O_7 and Eu_2O_3 in concentrated hydrochloric acid. Europium(III)-exchanged zeolite L(Eu^{3+}-ZeoL) crystals were prepared as described in reference [14].

Preparation of 1: The Eu^{3+}–ZeoL was degassed and dried for 2 h at 423 K and then kept in contact with the TTA vapor at 393 K for 24 h. The resulting material (**1**) was washed with CH_2Cl_2 for three times in order to remove only physically adsorbed TTA, and dried at 40°C in vacuum for 12 h.

Preparation of 2: Material **2** was prepared according to the procedure described in reference [6] as follows. Material **1** (10 mg) was dispersed in deionized water (10 mL) and added dropwise under vigorous stirring to aqueous PAH previously sonicated for 20 min (2 g L^{-1}, 10 mL). Stirring was continued for 3 h and the resulting mixture was centrifuged at 4000 rpm for 20 min to remove excess PAH and redispersed in deionized water (10 mL). The suspension was mixed with aqueous PVP (4 gL^{-1}, 20 mL) and stirred overnight. The mixture was centrifuged and the precipitate was redispersed in ethanol (15 mL). Ammonia (1 mL, 25% in water) was then added under vigorous stirring, and finally TEOS (0.01 mL) was added under stirring. The mixture was allowed to react for 3 h and was then centrifuged. The resulting material (**2**) was dried overnight.

Preparation of 3: Si-TTA (30 mg) dissolved in THF (1 mL) was added dropwise to an aliquot of suspension of **2** (60 mg) in ethanol (26 mL) under stirring. The resulting mixture was stirred at room temperature for 16 h, and the material was recovered by centrifugation, was washed three times with THF, and was redispersed in ethanol (5 mL). The pH of the suspension was adjusted to approximately 8 by addition of an appropriate amount of aqueous ammonia. Then $TbCl_3$ in ethanol (2.5 mL, 0.12 M) was added and the reaction was continued for 5 h to yield **3**, which was isolated by centrifugation and washed for three times with ethanol and dried at 60 °C overnight.

Luminescent detection of dipicolinic acid: An aqueous solution of dipicolinic acid (DPA) sodium salt was added to the suspension of **3** in ethanol (1 mgmL^{-1}), the concentration of DPA was incrementally increased from 0.05 μm to 150 μm. After each addition, the sample was excited at 278 nm and the emission spectrum was recorded.

Characterization: SEM images were obtained from a FE-SEM (Hitachi S-4300) at an acceleration voltage of 10 kV. TEM was carried out with a JEOL 2000-FX transmission electron microscope. The XPS measurement was performed on a Perkin–Elmer PHI-1600 spectrometer with $Mg_{K\alpha}$ (1253.6 eV) radiation.UV/Vis spectra were recorded on a VARIAN CARY 50 UV/Vis spectrophotometer. The steady-state luminescence spectra 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 per mm), an emission monochromator (600 lines per mm), and a semiconductor cooled Hamamatsu RMP928 photomultiplier tube.

Acknowledgements

This work is financially supported by National Natural Science Foundation of China (No. 20871040, No. 20901022), the Key Project of Chinese Ministry of Education (208016), Ministry of Personal, People's Republic of China and Department of Personal Hebei Province (2006332), the Scientific Program launched in 2008 by Hebei province (08965110D) and Tianjin Natural Science Foundation (09JCYBJC05700)

---

[1] a) A. D. Schlüter, *Functional Molecular Nanostructures*, Springer, Berlin, **2005**; b) *Host–Guest Systems Based on Nanoporous Crystals* (Eds.: F. Laeri, F. Schueth, U. Simon, M. Wark), Wiley-VCH, Weinheim, **2003**; c) M. B. J. Roeffaers, R. Ameloot, M. Baruah, H. Uji-i, M. Bulut, G. De Cremer, U. Müller, P. A. Jacobs, J. Hofkens, B. F. Sels, D. E. De Vos, *J. Am. Chem. Soc.* **2008**, *130*, 5763; d) M. Busby, C. Blum, M. Tibben, S. Fibikar, G. Calzaferri, V. Subramania, L. De Cola, *J. Am. Chem. Soc.* **2008**, *130*, 10970; e) R. Xu, G. Zhu, X. Yin, X. Wan, S. Qiu, *J. Mater. Chem.* **2006**, *16*, 2200; f) Y. Wada, M. Sato, Y. Tsukahara, *Angew. Chem.* **2006**, *118*, 1959; *Angew. Chem. Int. Ed.* **2006**, *45*, 1925; g) M. Busby, H. Kerschbaumer, G. Calzaferri, L. De Cola, *Adv. Mater.* **2008**, *20*, 1614.

[2] a) Y. Yan, T. Bein, *J. Phys. Chem.* **1992**, *96*, 9387; b) T. Bein, *Chem. Mater.* **1996**, *8*, 1636; c) A. R. Pradhan, M. A. Macnaughtan, D. Raftery, *J. Am. Chem. Soc.* **2000**, *122*, 404.

[3] K. B. Yoon, *Acc. Chem. Res.* **2007**, *40*, 29.

[4] J. Choi, S. Ghosh, Z. Lai, M. Tsapatsis, *Angew. Chem.* **2006**, *118*, 1172; *Angew. Chem. Int. Ed.* **2006**, *45*, 1154.

[5] a) C. Leiggener, G. Calzaferri, *ChemPhysChem* **2004**, *5*, 1593–1596; b) A. Zabala Ruiz, H. Li, G. Calzaferri, *Angew. Chem.* **2006**, *118*, 5408–5413; *Angew. Chem. Int. Ed.* **2006**, *45*, 5282–5287; c) S. Huber, A. Z. Ruiz, H. R. Li, G. Patrinoin, C. Botta, G. Calzaferri, *Inorg. Chim. Acta* **2007**, *360*, 869–875; d) P. Laine, M. R. Seifert, R. Giovanoli, G. Calzaferri, *New J. Chem.* **1997**, *21*, 453–460; e) C. Leiggener, G. Calzaferri, *Chem. Phys. Chem.* **2004**, *5*, 1593–1596; f) J.-W. Li, K. Pfanner, G. Calzaferri, *J. Phys. Chem.* **1995**, *99*, 2119–2126; g) G. Calzaferri, A. Z. Ruiz, H. R. Li, S. Huber, WO 012216, **2007**; G. Calzaferri, H. R. Li, D. Bruehwiler, *Chem. Eur. J.* **2008**, *14*, 7442–7449.

[6] 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.

[7] C. Baerlocher, W. M. Meier, D. H. Olson, *Atlas of Zeolite Framework Types*, 5th ed., Elsevier, Amsterdam, **2001**.

[8] a) S. Hashimoto, K. Samata, T. Shoji, N. Taira, T. Tomita, S. Matsuo, *Microporous Mesoporous Mater.* **2009**, *117*, 220; b) S. Hashimoto, H. R. Moon, K. B. Yoon, *Microporous Mesoporous Mater.* **2007**, *101*, 10; c) H. R. Li, A. Devaux, Z. Popovic, L. De Cola, G. Calzaferri, *Microporous Mesoporous Mater.* **2006**, *95*, 112; d) G. Calzaferri, S. Huber, H. Maas, C. Minkowski, *Angew. Chem.* **2003**, *115*, 3860; *Angew. Chem. Int. Ed.* **2003**, *42*, 3732; e) G. Calzaferri, M. Pauchard, H. Mass, S. Huber, A. Khatyr, T. Schaafsma, *J. Mater. Chem.* **2002**, *12*, 1; f) G. Calzaferri, K. Lutkouskaya, *Photochem. Photobiol. Sci.* **2008**, *7*, 879.

[9] a) P. A. Anderson, R. Armstrong, P. P. Edwards, *Angew. Chem.* **1994**, *106*, 669; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 641; b) T. Ohsuna, Y. Horikawa, K. Hiraga, O. Terasaki, *Chem. Mater.* **1998**, *10*, 688.

[10] S. Megelski, A. Lieb, M. Pauchard, A. Drechsler, S. Glaus, C. Debus, A. J. Meixner, G. Calzaferri, *J. Phys. Chem. B* **2001**, *105*, 25.

[11] a) S. I. Weissman, *J. Chem. Phys.* **1942**, *10*, 214; b) N. Sabbatini, M. Guardingli, J. M. Lehn, *Coord. Chem. Rev.* **1993**, *123*, 201.

[12] a) M. Lezhnina, F. Laeri, L. Benmouhadi, U. Kynast, *Adv. Mater.* **2006**, *18*, 280; b) D. Sendor, U. Kynast, *Adv. Mater.* **2002**, *14*, 1570; c) M. Alvaro, V. Fornés, S. Garcia, H. Garcia, J. C. Scaiano, *J. Phys. Chem. B* **1998**, *102*, 8744; d) Y. Wada, T. Okubo, M. Ryo, T. Nakazawa, H. Hasegawa, S. Yanagida, *J. Am. Chem. Soc.* **2000**, *122*, 8583; e) Y. Wada, M. Sato, Y. Tsukahara, *Angew. Chem.* **2006**, *118*, 1959; *Angew. Chem. Int. Ed.* **2006**, *45*, 1925; f) I. L. V. Rosa, O. A. Serra, J. E. Nassar, *J. Lumin.* **1997**, *72*, 532.

[13] a) S. Megelski, G. Calzaferri, *Adv. Funct. Mater.* **2001**, *11*, 277; b) A. Zabala Ruiz, D. Bruehwiler, T. Ban, G. Calzaferri, *Monatsh. Chem.* **2005**, *136*, 77; c) A. Zabala Ruiz, D. Brühwiler, L. Q. Dieu, G. Calzaferri in *Materials Syntheses, A Practical Guide* (Eds.: U. Schubert, N. Hüsing, R. Laine), Springer, Wien, **2008**, pp. 9–19.

[14] a) Y. G. Wang, H. R. Li, L. J. Gu, Q. Y. Gan, Y. N. Li, G. Calzaferri, *Microporous Mesoporous Mater.* **2009**, *121*, 1; b) A. Monguzzi, G. Macchi, F. Meinardi, R. Tubino, M. Burger, G. Calzaferri, *Appl. Phys. Lett.* **2008**, *92*, 123301.

[15] A. Guerrero-Martinez, S. Fibikar, I. Pastoriza-Santos, L. M. Liz-Marzán, L. De Cola, *Angew. Chem.* **2009**, *121*, 1292; *Angew. Chem. Int. Ed.* **2009**, *48*, 1266.

[16] W. J. Rieter, K. M. L. Taylor, W. B. Lin, *J. Am. Chem. Soc.* **2007**, *129*, 9852.

[17] J.-C. G. Bünzli, C. Piguet, *Chem. Soc. Rev.* **2005**, *34*, 1048.

[18] R. Reisfeld, *Struct. Bonding (Berlin)* **1973**, *13*, 53.

[19] S. F. Tang, A. Bahai, A.-V. Mudring, *Angew. Chem.* **2008**, *120*, 7743; *Angew. Chem. Int. Ed.* **2008**, *47*, 7631.

[20] a) R. Reisfeld, R. A. Velapoldi, L. Boehm, M. I. Shalom, *J. Phys. Chem.* **1971**, *75*, 3980; b) B. Julián, R. Corberán, E. Cordoncillo, P. Escribano, B. Viana, C. Sanchez, *J. Mater. Chem.* **2004**, *14*, 3337.

[21] A. Madani, A. Aznar, J. Sanz, J. M. Serratosa, *J. Phys. Chem.* **1990**, *94*, 760.

[22] L. Krasemann, B. Tieke, *Langmuir* **2000**, *16*, 287.

[23] a) D. L. Rosen, C. Sharpless, L. B. McGown, *Anal. Chem.* **1997**, *69*, 1082; b) P. M. Pellegrino, N. F. Fell, D. L. Rosen, J. B. Gillespie, *Anal. Chem.* **1998**, *70*, 1755; c) A. A. Hindle, E. A. H. Hall, *Analyst* **1999**, *124*, 1599; d) M. L. Cable, J. P. Kirby, K. Sorasaenee, H. B. Gray, A. Ponce, *J. Am. Chem. Soc.* **2007**, *129*, 1474.

[24] K. L. Ai, B. H. Zhang, L. H. Lu, *Angew. Chem.* **2009**, *121*, 310; *Angew. Chem. Int. Ed.* **2009**, *48*, 304.
[25] C. Minkowski, G. Calzaferri, *Angew. Chem.* **2005**, *117*, 5495; *Angew. Chem. Int. Ed.* **2005**, *44*, 5325.
[26] R. Q. Albuquerque, G. Calzaferri, *Chem. Eur. J.* **2007**, *13*, 8939.
[27] B. Yan, Y. Li, B. Zhou, *Microporous Mesoporous Mater.* **2009**, *120*, 317.

Received: June 19, 2009
Revised: September 14, 2009
Published online: January 11, 2010

© 2010 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim