

Rare earth ions in porous matrices

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Initially motivated by the commercial need for cheaper and environmentally friendly luminescent materials for the application in fluorescent lamps and cathode ray tubes, the search for new matrices for optically active species has penetrated a scope far beyond „classical“ solid state materials. Porous matrices with voids ranging from the nano- to the microscale have become the subject of recent investigations. Crystalline, amorphous, organomorphous, nanosized matrices and matrices, which are amorphous on the atomic level but have a translational superstructure on the microscale (zeolites, sol-gel materials, polymers, nanoparticles and photonic crystals), are addressed. The optical technologies covered in this research range from mercury free discharge lamps, plasma displays, organic and polymeric light emitting diodes, novel laser materials to biophotonics and the new generation of white emitting AlGaIn solid state light emitting diodes (LEDs). Due to specific specific properties (e.g. high quantum yields, narrow line emission), rare earth ions are indispensable components these approaches, be it in the nanoscaling zeolites, sol-gel matrices, or as the active component in optically functional polymers. Optical properties of hybrid materials composed of either rare earth ions as such, their complexes or nanoparticles in these matrices, with potential applications in mentioned fields in mind, will form the scope of the present report.

1. Introduction

The major applications of luminescent materials have traditionally been in lighting, displays and fluorescent paints. In the last decades, several „high tech“ and completely new applications have added to this scope, e.g. communication technologies, organic light emitting diodes (OLEDs), biolabels, or the recent white light emitting diodes, in which rare earth ions, phosphors in particular, are an essential component. Presently applied phosphors are highly optimized materials — often at the physical boundaries. However, some visions, such as quantum yields in excess of 100% (multiphoton emitters, [1]) or appreciably cheaper material costs remain to be tackled. In many applications of phosphors, maintenance of high efficiencies on reducing the grain size to the nanoscale is desirable (e.g. in OLEDs [2], biolabels based on fluorescent nanoparticles [3] or in the production of transparent polymer hybrids for fibre communication [4] and phosphor converted white LEDs).

Considering the enormous amount of known and documented luminescent materials and phosphors, respectively, it seems worthwhile to assume a somewhat more distant look at the matter, if evaluating approaches to surpass „classical“ materials in one or the other optical property. The view taken in this report, as summarized in Fig. 1, should be considered as „a guideline to imagination“ rather than of high precision. While the rare earth ions in mentioned classical applications are guests in various (micro-) crystalline solids, the *sizes of occupied sites* enter the consideration mostly as a restricting factor. The effects imparted by the size restriction may very well be beneficial, e.g. *via* desired crystal field splitting, rigidity and others. However, the size restriction to a few hundred picometers at best excludes

a wide range of highly efficient luminescent entities from corresponding „classical“ applications. To be mentioned are dye molecules, molecular ions or nano-particles, which escape many applications due to morphological, chemical, textural, handling or stability problems.

Nano-, meso- and microporous matrices (generously including glasses and polymers in this scope) can provide a solution to the size dilemma. We believe that hybrid materials composed of the porous matrix and occluded

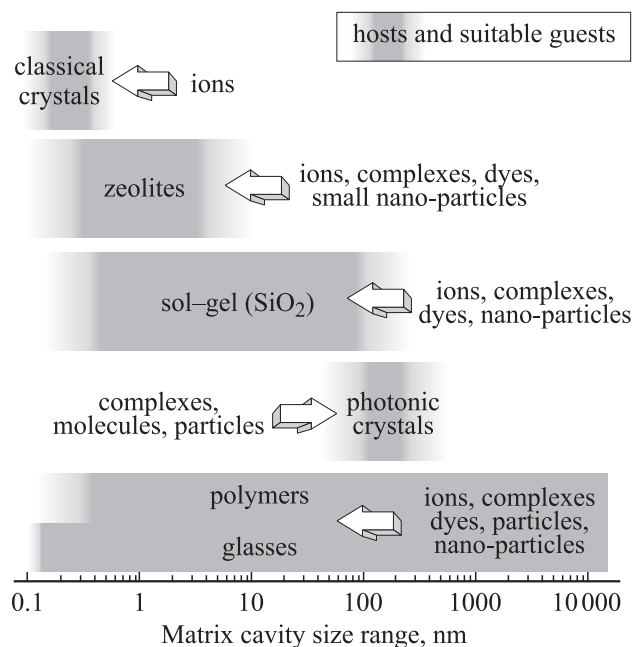


Figure 1. Range of voids provided for the accommodation of luminescent entities.

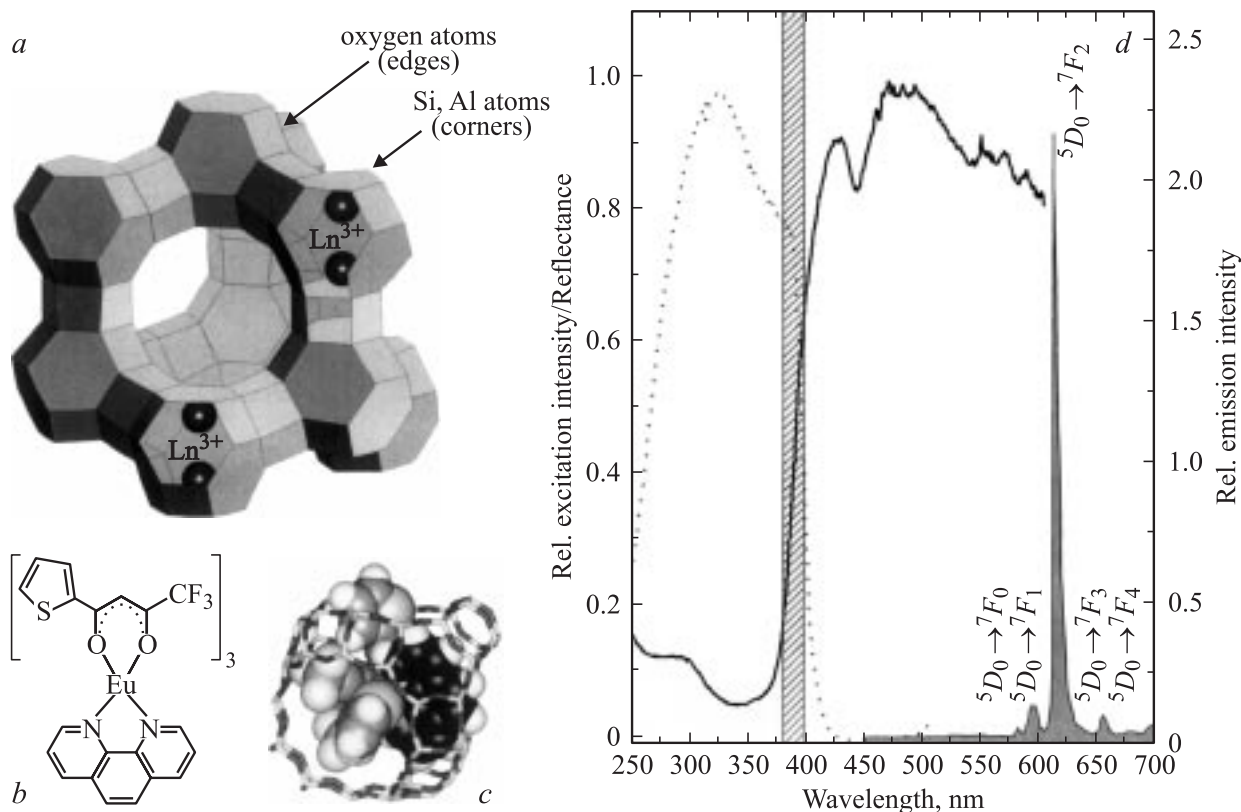


Figure 2. Intrazoeolite luminescence: *a*) Tb^{3+} , Ce^{3+} doped and calcined zeolite X (up to 16 Ln^{3+}/UC [6]); *b*) $\text{Eu}(\text{tffa})_3\text{phen}$; *c*) model of $\text{Eu}(\text{tffa})_3\text{phen}$ occluded in the zeolite X supercage, $[\text{Eu}(\text{tffa})_3\text{phen-X}]$; *d*) optical properties of $[\text{Eu}(\text{tffa})_3\text{phen-X}]$; the hatched area corresponds to the emission of a commercial UV-LED (Nichia).

guests as listed above will open a range of applications in which materials with typical solid state properties are desired on one hand, but the molecular or nanoscale properties of the guests need to be retained on the other hand. In summary the goals in investigating luminescence in microporous hosts are as follows:

- (i) to make chemically „impossible“ luminescent species possible (isolated ions, complex ions, imbedded and stable nano-particles);
- (ii) a description of confinement behaviour (cavity and size dependence, influence of matrix);
- (iii) a search for exploitation possibilities, i.e., potential applicatory fields: new (VUV) phosphors (for plasma display panels, quantum cutters downconverters for lighting), transparent luminescent polymerrare earth composites from dissolution/dispersion of complexes and nanophosphors (for OLEDs, signalling, marking, safety, fiber amplifiers, LEDs), near infrared (NIR) and upconverted emission (for lasers, bio-labeling).

As it would go beyond the scope of this report to cover all aspects indicated in Fig. 1 and the goals of the previous list, we will exemplarily focus on the accommodation of metalloorganic complexes and fluoride nanoparticles in zeolites, sol-gel (SG) matrix and polymers.

2. Metallo-organic zeolite hybrids

Zeolites are microcrystalline solids mainly composed of Si, Al and O, which are forming typical cavities and channels of molecular dimensions within the crystals. Certainly the most striking feature of zeolite structures is their unique topology with well-ordered, hospitable cages and channels with diameters in the nanometer regime, in addition to the structural features they exhibit useful intrinsic chemical and physical properties (e.g. easy accessibility, relative „good“ stability and large band gap). In the area of optical materials, zeolites will be of particular interest when specific distances or a spatial pattern of atomic, ionic, molecular or nanoscaled guest species are required in order to obtain the desired physical effects.

„Free“ ions can readily be accommodated in the cavities of zeolite X and Y (Fig. 2, *a*, [5]). To this end, very efficient UV emitters based on Ce^{3+} incorporation and green emitters using the couple Ce^{3+} , Tb^{3+} with quantum efficiencies near 100% in the UV and 80% in visible have been realised [5,6]. However, these investigations also reveal the need for alternative sensitisation schemes for e.g. lamp applications.

Rare earth complexes with ligands rather than Ce^{3+} as sensitizers can be used to improve the absorptivity. As

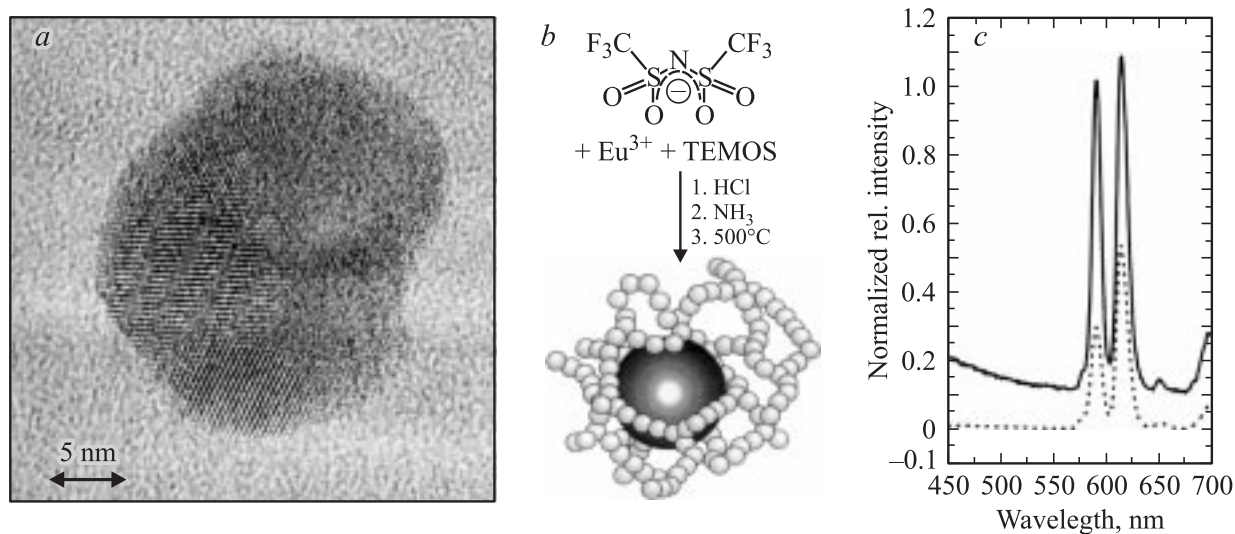


Figure 3. Fluoride nanoparticles in SG matrix: *a* — HRTEM of oxfluoride particle in SG matrix obtained from thermolysis of $\text{Eu}(\text{O}_2\text{C}-\text{CF}_3)_3$ precursor. *b* — preparation of SG hosted fluorides; details see text; *c* — emission spectra of fluorides; dashed line — $\text{Eu}(\text{pms})_3$ precursor; solid line — occluded fluoride particles.

ligands we have investigated aromatic carboxylates and β -diketonates; for completeness, the work on inorganic anions (vanadates, molybdates, tungstates) should also be mentioned, in which the transition metalates possess the $\text{O} \rightarrow \text{M}^{+\text{VI}}$ charge transfer states in the UV, which can be exploited for sensitisation [7–9]. The organic ligands studied provide high absorptivities due to allowed $\pi-\pi^*$ transitions, the corresponding molecular singlet states after spin-orbit-coupling-mediated intersystem crossing into a molecular triplet state can very efficiently transfer their energy to the rare-earth in [10] and yield very high quantum efficiencies. Such complexes cover a wide range of excitation wavelengths, both by appropriate choice of the „parent“ ligand itself or appropriate substitution. Metallo-organic inclusion complexes have recently been reviewed [11]. Figs. 2, *b* and *c* depict the illustrative example of inclusion of $\text{Eu}(\text{tfa})_2\text{phen}$, which exhibits a quantum yield of approximately 80% [12]. Of interest is the overlap of the hatched area, which represents the emission spectrum of a commercial UV-LED with the excitation band: obviously, this rare earth complex-zeolite hybrid can be an interesting component in UV-LED driven optical devices, e.g. phosphor converted white LEDs, if imbedded in the polymer dome in front of the LED chip.

3. Fluoride nanoparticles in SG matrix

As opposed to zeolites, SG materials are amorphous hosts with additional degrees of freedom in guest size. While nearly all of the inclusion candidates depicted in Fig. 1 are the subject of ongoing research, we will here present a recent example of fluoride nanoparticle synthesis in sol-gel matrix. Our studies have thus far been restricted to SiO_2 -based matrices.

The use of rare earth fluorides in optical applications is often hampered by hydrolytic and photochemical instability, but due to intrinsic properties (low phonon frequencies, wide band gap), the fluoride lattice is often the most efficient or even indispensable, as it is the case as for rare-earth based multiphoton emission (MPE), which addresses the desire for quantum yields in excess of 100% [1,13,14]. As high energy excitation sources are required for MPE, from an applicational point of view, only the Xe_2 -excimer emission with a maximum at 172 nm seems feasible. At this wavelength the absorptivity of most fluorides is unsatisfying. One approach to the problem is a coating of the fluoride particles to protect and at the same time sensitize the emission. In order to accomplish energy transfer from the coating to the interior, the coating has to be very thin, which would in turn again go to the cost of absorptivity. To enable short transfer distances, but high coating to core ratios, the particles have to be very small. Thus, core-shell nanoparticles may offer a conceivable solution. The generation of rare earth fluoride particles in SG matrix is particularly promising, because the matrix can be made transparent to the Xe_2 -excimer discharge on one hand, and secondary chemical manipulation of the particles in this open pore structure should be possible without risk of uncontrolled particle growth on the other hand.

The synthesis of the $(\text{Cd}, \text{Eu})\text{F}_3$ -nanoparticles, one promising MPE candidate, was performed altering a literature method describing the preparation of nano- LaF_3 in SiO_2 -based SG matrix [15]. As the aim was not the manufacture of glassy monoliths, the use of the inhibiting DMF was refrained from, additionally, trifluoroacetic acid ($\text{H}(\text{tfa})$) only yielded oxfluorides after thermal decomposition of the $\text{Ln}(\text{tfa})_3$ -SG precursor in our experiments. The particles formed are in the range of 20 nm as revealed

by XRD and TEM analysis (Fig. 3, obtained on „Holey–Carbon“–copper net, JEM 3010 at 300 kV). Fluorides could only be obtained replacing acetic acid by HCl and using bis(perfluoromethanesulfonimide) $\text{H}[(\text{F}_3\text{C}-\text{SO}_2)_2\text{N}]$ (H(pms)) instead of H(tfa). Coincidentally, $\text{Ln}(\text{pms})_3$ converts into LnF_3 at almost the same 400°C as $\text{Ln}(\text{tfa})_3$. Typically, the rare earth content was adjusted to 5% of the tetraethyorthosilicate used. The chemical identity of the sample (oxifluoride vs fluoride) was determined by the analytical $\text{Ln}:\text{F}$ ratio, but more readily by the emission spectra, which in case of the Eu-oxifluorides yields the characteristic emission pattern of oxygen coordinated Eu^{3+} in glassy matrix, dominated by $\text{Eu}^{3+} \ ^5D_0 \rightarrow \ ^7F_2$ with a weaker and broad $\ ^5D_0 \rightarrow \ ^7F_2$ emission (compare e.g. to [16]). As opposed to that, pure fluoride particles are characterized by a $\ ^5D_0 \rightarrow \ ^7F_1/\ ^5D_0 \rightarrow \ ^7F_2$ emission ratio near 1 or even larger [17], see Fig. 3.

Calcined $(\text{Gd},\text{Eu})\text{F}_3$ nanoparticle embeddings in amorphous, porous SiO_2 -matrix were consecutively treated for the generation of a shell in an aqueous suspension. We found the following scheme to yield first acceptable results (S.G. = sol-gel matrix):

1. $(\text{Eu}_{0.1}\text{Gd}_{0.9}\text{F}_3)_{\text{nano}}\text{-S.G.} + \text{Gd}^{3+}$

$$\xrightarrow[\text{(N}_4\text{CH}_2)_6]{\Delta, 80-90^\circ\text{C}} \{[(\text{Eu}_{0.1}\text{Gd}_{0.9}\text{F}_3)_{\text{nano}}]\text{Gd}(\text{OH})_3\}\text{-S.G.}$$
2. $(\text{Eu}_{0.1}\text{Gd}_{0.9}\text{F}_3)_{\text{nano}}\text{-S.G.} + \text{Gd}^{3+}$

$$\xrightarrow{\Delta, 500^\circ\text{C}} \{[(\text{Eu}_{0.1}\text{Gd}_{0.9}\text{F}_3)_{\text{nano}}]\text{GdO}_3\}\text{-S.G.}$$

The calcined gels containing the fluoride particle described in the previous paragraph (300 mg) were suspended in 40 ml of a dilute aqueous solutions of Gd^{3+} (10–3 mol/l) and 7-fold excess of urotropine or urea respectively. On heating such suspensions (2 h, 80°C), homogeneous precipitation of $\text{Gd}(\text{OH})_3$ with urotropine occurs, which is preferably formed on surfaces that can serve as nuclei. In the present case, the nanoparticles adopt the role of the nucleating surface and at least an appreciable amount of the $\text{Gd}(\text{OH})_3$ precipitates on the particles. After calcination at 500°C the resulting product shows a small amount of penetration of oxygen into the core, leading to a slight decrease in the Eu^{3+} ($\ ^5D_0 \rightarrow \ ^7F_1/\ ^5D_0 \rightarrow \ ^7F_2$) emission ratio on *core* excitation at 392 nm, whereas on Gd^{3+} excitation (274 nm, $\ ^8S_{7/2} \rightarrow \ ^6I_J$) the ratio is reversed (Fig. 4). These results show that it is possible to build up shells around the occluded particles on one hand, and furthermore, that energy transfer is observed from the shell to the core on the other hand. The particle efficiency increases by some 30% on deposition of the coating, but we expect that optimally adjusted preparative parameters will allow yet further improvements. We would like to mention briefly, that after having taken advantage of the unique possibility of study these coating effects in the porous matrix under stable conditions, we were also able to

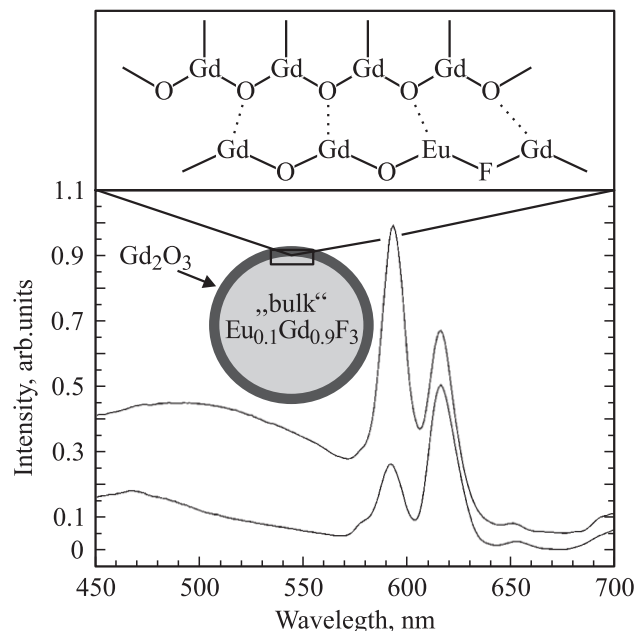


Figure 4. Core modifications on SG-embedded fluoride particles: $\text{Gd}(\text{OH})_3$ -coated particles after calcination; Eu^{3+} emission at $\lambda_{\text{exc}} = 395$ nm (top) and 274 nm (bottom).

transfer some of the results to free standing *nanoparticles*, whose efficiency now very closely approaches that of their *microsized* counterparts.

4. Metallo-organic complexes in polymers

Polymers are probably the most flexible host matrix with regard to guest size. To this end we have investigated the insertion of complexes and small phosphor nanoparticles in polyurethanes and silicones. While the nanoparticles typically require surface modifications to render them compatible with the hydrophobic polymers, complexes with organic ligands can be readily dissolved in the prepolymers. We can distinguish between solid solutions and backbone anchored complexes. Dissolved complexes will preferentially be formed with such systems, which are coordinatively saturated, such as the complex $\text{Eu}(\text{tfa})_3\text{phen}$, (see also above, metallo-organic zeolite hybrids), which we could successfully incorporate into silicones and polyurethanes. Backbone support may be realized by letting reactive substituents on the ligands react with the prepolymers. Also conceivable would be „donor-acceptor“ interactions by allowing polymer donor atoms to fill the coordination sphere of coordinatively saturated complexes. Examples for backbone support are the reactions of terbium salicylate $\text{Ta}(\text{O}_2\text{C}-\text{C}_6\text{H}_4-\text{OH})_3$ ($\text{Tb}(\text{sal})_3$) and terbium *p*-amino-benzoate $\text{Tb}(\text{O}_2\text{C}-\text{C}_6\text{H}_4-\text{NH}_2)_3$ ($\text{Tb}(\text{paba})_3$), e.g. with

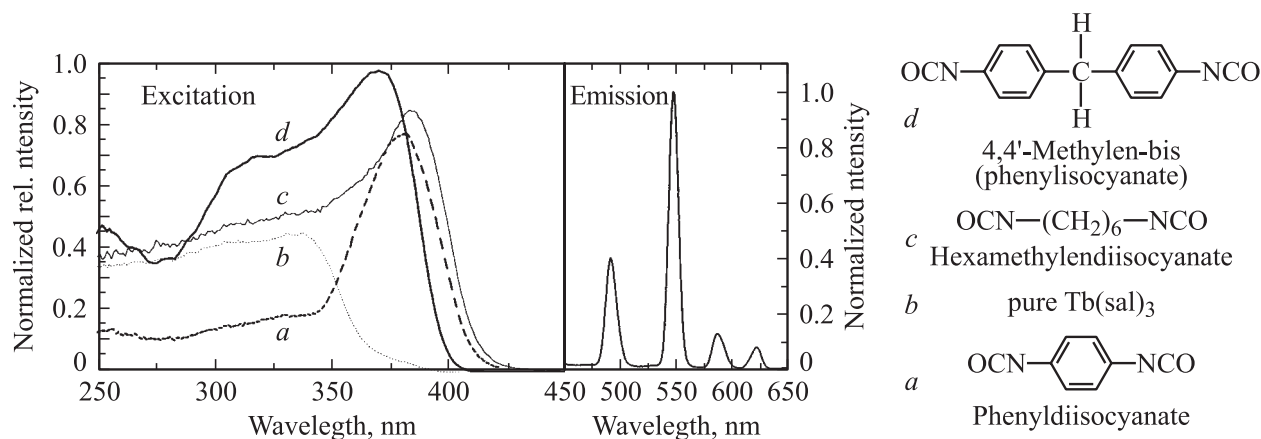
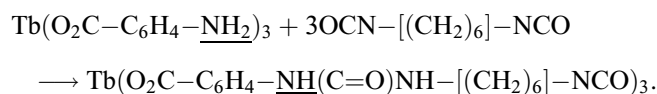
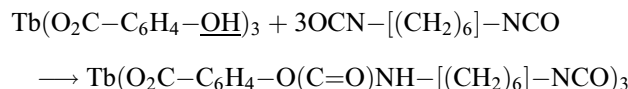


Figure 5. Polymer (polyurethane) embedded complexes: Tb(sal)₃ coupled to various back-bones, only the emission in HDI polyurethane is given, other emission spectra are practically identical.

hexamethylenediisocyanate (HDI)



Both of the intermediates can react with polyols or amines to form the eventual polymer [18]. The silicone (not plotted) as well as the polyurethane composites show very efficient luminescence (Fig. 5). The spectral features of Eu(tffa)₃ are practically identical to the zeolitic complexes above. Worth pointing out in Fig. 5 is the tunable excitation obtained through the reaction with different diisocyanates, which again extends into the spectral range accessible with the recent UV-LEDs.

5. Summary and conclusion

Generally, classical phosphors or luminescent crystals are not yet „outperformed“ by host-guest systems, nanoparticles etc. Exceptions are fields, where conventional phosphors are not applicable and thus a comparison does not apply, (e.g. rare earth based biolabels, thin film electroluminescence, (metallo-) organic LEDs). However, as we tried to show by the few examples selected, inorganic or polymer host guest chemistry can give access to luminescent hybrid materials, which are impossible or difficult to employ in conventional applications: the very efficient diketonates or aromatic carboxylates may in inorganic porous matrices or polymers become applicable to, e.g., optical sensors, luminescent paint dispersions, luminescent markers and other fields, while matrix stabilized fluoride particles may eventually be developed into VUV excitable phosphors and applications based on NIR-excitation. The evolvement of an increasing demand for rare earth activated

nano-phosphors for, e.g., biolabels or transparent, optically functional polymers currently promotes studies on improved surface control and core-shell particles.

References

- [1] R.T. Wegh, H. Donker, K.D. Oskam, A. Meijerink. *Science* **283**, 663 (1999).
- [2] J. Nanda, S. Sapra, D. Sarma. *Chem. Mater.* **12**, 1018 (2000).
- [3] S. Coe, W.-K. Woo, M. Bawendi, V. Bulović. *Nature* **420**, 800 (2002).
- [4] N.N. Tessler, V. Medvedev, M. Kazes, S.H. Kan, U. Banin. *Science* **295**, 1506 (2002).
- [5] U. Kynast, V. Weiler. *Adv. Mater.* **6**, 937 (1994).
- [6] T. Jüstel, D.U. Wiechert, C. Lau, D. Sendor, U. Kynast. *Adv. Funct. Mater.* **11**, 105 (2001).
- [7] C. Borgmann, J. Sauer, T. Jüstel, U. Kynast, F. Schüth. *Adv. Mater.* **11**, 45 (1999).
- [8] C. Lau, H.-J. Mai, U. Kynast. *Micropor. Mesopor. Mater.* **47**, 339 (2001).
- [9] M. Lezhnina, U. Kynast. *J. Alloys Comp.* **380**, 55 (2004).
- [10] V.L. Ermolaev. *Soviet Physics Uspekhi* **80**, 333 (1963).
- [11] D. Sendor, U. Kynast. In: *Host-Guest Systems Based on Nanoporous Crystals* / Eds F. Laeri, F. Schüth, U. Simon, M. Wark. Part 4. Ch. 5. Wiley-VCH, Weinheim (2003). P. 558.
- [12] D. Sendor, U. Kynast. *Adv. Mater.* **14**, 1570 (2002).
- [13] J.L. Sommerdijk, A. Bril, A.W. de Jager. *J. Lumin.* **8**, 341 (1974).
- [14] R. Pappalardo. *Lumin.* **14**, 159 (1974).
- [15] S. Fujihara, C. Mochizuki, T. Kimura. *J. Non-crystalline Solids* **244**, 267 (1999).
- [16] R. Van Deun, K. Binnemans, C. Görller-Wallrand, J.L. Adam. *J. Phys.: Condens. Matter* **10**, 7231 (1998).
- [17] J.-L. Adam. In: *Advanced Inorganic Fluorides* / Eds T. Nakajima, B. Zemva, A. Tressaud. Elsevier, Amsterdam (2000). P. 235.
- [18] U. Kynast. Paso GmbH. „Synthesis of polymers for luminescence effects (Darstellung von Polymeren zur Erzeugung von Lumineszenzeffekten)“. EP Appl. 02025915.6 (2002).