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Ln(III) complexes as potential phosphors for white LEDs

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7 Summary, general discussion and outlook

7.1 Summary

7.1.1 Introduction

In the Chapter 1 of this thesis, a general introduction into energy requirements of artificial light sources, light source principles and color vision is given. It is shown that a substantial amount of energy can be saved when current lamps are replaced by more efficient light sources. A discussion of several approaches towards highly efficient solid state light sources (SSLs) based on light emitting diodes (LEDs) is given. Although white light emitting SSLs already exist, their properties such as efficiency and emission spectrum can be improved significantly. The approach of using an LED emitting in the near-UV region combined with a layer of down-conversion phosphors shows potential. However, the required phosphor materials that can be efficiently excited in the near-UV are lacking. In this respect, complexes of the trivalent lanthanoid ions are promising. In such compounds, the line-like emission of the lanthanoid ion can be efficiently excited via the ligand centered absorption bands. The ligands in turn can be tuned to match the excitation source, for instance by introduction of substituents. Details on the energy transfer mechanisms in these complexes and the photophysics of the trivalent lanthanoid ions are given, as well as some basic lanthanoid coordination chemistry. The final section of the chapter deals with various approaches towards highly efficient photoluminescent complexes described in this thesis.

7.1.2 Substituted phenanthrolines as antennae

1,10-Phenanthroline is known to be an efficient sensitizer of Eu(III)-centered luminescence. Unfortunately, the maximum excitation wavelength of this compound occurs at 355 nm. For this reason, the ligand 1,10-phenanthroline cannot be used to excite Eu(III) emission with a In:GaN based LED emitting in the near-UV. To investigate whether it is possible to shift this excitation maximum to longer wavelengths, a series of eight new Eu(III)-based coordination compounds with 1,10-phenanthroline bearing a chloro-, methoxy-, ethoxy-, cyano-, carboxylic acid, methyl carboxylate-, ethyl carboxylate, and amino-substituent on the 2-position have been prepared. This work is described in Chapter 2. It was found that all compounds except for $[\text{Eu}(\text{2-amino-1,10-phenanthroline})_2(\text{NO}_3)_3]$ show photoluminescence characteristic of the Eu(III) ion upon excitation with nUV radiation. It was established that in $[\text{Eu}(\text{2-chloro-1,10-phenanthroline})_2(\text{NO}_3)_3]$, the luminescence apparently is quenched by a low-lying LMCT-band. A high quantum yield of 78% is found for $[\text{Eu}(\text{2-chloro-1,10-phenanthroline})_2(\text{NO}_3)_3]$, but its excitation maximum is incompatible with the emission of a near UV LED. The excitation maximum of the compounds $[\text{Eu}(\text{2-(ethylcarboxylate)-1,10-phenanthroline})_2(\text{NO}_3)_3]$ and $[\text{Eu}(\text{2-methoxy-1,10-phenanthroline})_2(\text{NO}_3)_3]$ is at 370 nm, but the low quantum efficiency limits their application as a phosphor. In all cases, the overall quantum yield of the compounds is limited by the low intrinsic quantum yield of the Eu(III) ion (17-52%). Also in Chapter 2, the first-time use of 1-methyl-1,10-phenanthroline-

2(*1H*)-one, a synthetic intermediate, as a ligand is reported, using Eu(III) as central ion. Using X-ray crystallography, the ligand is found to bind to the metal *via* its carbonyl oxygen, resulting in a compound that shows moderately efficient luminescence with a quantum yield of 22% at 355 nm excitation.

7.1.3 Ln(III) complexes with small aromatic ligands

As described in Chapter 1 of this thesis, small aromatic molecules can be used as efficient antennae for sensitizing emission of the lanthanoid ions. Both mononuclear complexes and metal organic frameworks can be formed with these ligands and the lanthanoid ions. In Chapter 3, the synthesis of compounds of Eu(III) and Tb(III) with furan-2,5-dicarboxylic acid (H_2fda) and a compounds of Tb(III) with 2-hydroxytrimesic acid (H_4tma) are described. It is found that refluxing the ligand H_2fda with lanthanoid salts in N,N-dimethylformamide (dmf) gives rise to coordination compounds that analyze as $(H_2NMe_2)_6Ln_4(fda)_7Cl_4$. Recrystallisation of these compounds from water results in the formation of a one-dimensional coordination polymer. Both the dmf compounds and the coordination polymer of Eu(III) and Tb(III) show photoluminescence characteristic of the lanthanoid ion. In general, the emission intensity of the compounds is weak. The emission intensity of the recrystallized compounds is even lower. This is readily understood, as the *Ln*(III) ion is surrounded by five molecules of water that can quench luminescence by vibronic coupling. The ligand H_4tma is found to give rise to a rigid three-dimensional metal-organic framework with a high density when reacted with $TbCl_3$ in water under hydrothermal conditions. Moreover, this compound shows bright luminescence with a photoluminescence quantum yield of 67%. This high efficiency, combined with an excitation maximum of 378 nm, make this compound an ideal candidate green phosphor material for application in LEDs.

7.1.4 Phenol-type ligands as sensitizers

In Chapter 4, the synthesis of ten novel Eu(III) and Tb(III) complexes with 2-(4,5-dihydro-1,3-oxazol-2-yl)phenol (**L1**) and its thiazolyl analog (**L2**) as ligands is described. It is found that these phenol-type ligands are suitable for sensitization of luminescence of both Eu(III) and Tb(III) ions. The luminescence intensity of in particular the Eu(III) complexes is found to be highly sensitive to the metal-to-ligand (M:L) ratio; Eu(III) complexes with a M:L ratio of 1:3 practically do not exhibit photoluminescence, while those with a 1:4 ratio show fairly bright photoluminescence with quantum yields of 20% (Eu**L2**_4) and 43% (Eu**L1**_4). The antenna efficiency is found to be around 90% in both complexes but the overall quantum yield appears to be limited by the low intrinsic quantum yields of the Eu(III) ion. The 1:3 complexes are not luminescent, which is readily explained by the presence of a low-lying LMCT state. The presence of such state is evidenced from an additional band in the absorption spectra of the Eu(III) compounds when compared to their Tb(III) analogs. In general, the Tb(III) complexes show

photoluminescence regardless of the M:L ratio, and the luminescence efficiencies of the Tb(III) complexes with **L2** as a ligand are comparatively low. The compound Tb**L1_4** shows very intense photoluminescence with a quantum efficiency as high as 79% upon excitation at 360 nm while Tb**L2_4** on the contrary shows faint luminescence. This is explained by a poor spectral match between the **L2** T* state and the Tb(III) 5D_4 state. Overall, **L1** appears to be a better antenna than **L2** for both Eu(III) and Tb(III) ions. An attempt at recrystallisation of Eu**L1_3** and Tb**L1_3** from DMSO gave rise to the formation of an octanuclear complex in which the metal centers are tightly linked together by carbonate ions that have formed from CO₂ captured from the atmosphere. The Eu(III) complex shows very faint luminescence upon excitation with nUV radiation, while the Tb(III) complex has a fairly high quantum efficiency of 51%.

7.1.5 Tuning Eu(III) complexes with dibenzoyl methanates

Dibenzoylmethane (Hdbm) is a molecule that can highly efficiently sensitize luminescence of the Eu(III) ion. Presently, studies on the effect of the introduction of substituents on dbm⁻ on its ability to sensitize Eu(III) luminescence are scarce. Also, the influence of the cations on the luminescence of anionic complexes of formula [Eu(dbm)₄]⁻ is poorly investigated. In Chapter 5, the synthesis of seven complexes of Eu(III) with halogen-substituted dbm ligands is described. Based on the position of the substituents on the phenyl groups with respect to the chelating 1,3-diketo moiety (ortho, meta or para), the compounds are classified into three groups. The emission spectra of the complexes are analyzed using JO theory, and differences between the ligand substitution patterns are apparent from the intensity parameters $\Omega_{2,4,6}$. The ligands with a 4-Br and a 4-F substituent are found to have high antenna efficiencies of around 90%, but the intrinsic quantum yield of the Eu(III) ion is very low in these compounds. The compounds with a 3-F, 3-Cl, 3-Br and 3-I substituent show lower antenna efficiencies (54 to 62%). The intrinsic quantum yield of the Eu(III) ion is increased in these compounds, resulting in overall photoluminescence quantum yields of 22-35%. The compound with the 2-Cl substituent on the ligand shows by far the longest experimental lifetime (0.89 ms) and the lowest Ω_2 parameter of the series. In Chapter 5, it is shown that these properties can be at least qualitatively understood by considering the electron-withdrawing properties of the substituents. The strong influence of the counter ion on the luminescent properties of [Eu(dbm)₄]⁻ is demonstrated by the comparison of the luminescent properties of the compounds with HNEt₃⁺, Li⁺, and NBu₄⁺ counter ions. Moreover, the crystal structures of the two latter compounds have been determined and are reported.

7.1.6 Triboluminescence

Some complexes of the trivalent lanthanoid ions are found to exhibit luminescence upon fracture of the crystallites in a phenomenon known as triboluminescence (TrL). Although not yet fully resolved, it appears that the TrL mechanism involves energy transfer from the

ligand-centered excited state to the lanthanoid excited state, similar to the mechanism for photoluminescence of such compounds. In addition, there is still disagreement on whether only compounds with structures with a non-centrosymmetric space group can exhibit TrL [1]. One of the compounds that shows the brightest TrL is the Eu(III) coordination compound $\text{HNEt}_3[\text{Eu}(\text{dibenzoylmethanate})_4]$, which is closely related to the compounds discussed in Chapter 5. For these reasons series of lanthanoid coordination compounds with the general formula $\text{HNEt}_3[\text{Ln}(\text{dibenzoylmethanate})_4]$ ($\text{Ln} = \text{La}, \text{Nd}, \text{Sm}, \text{Eu}, \text{Tb}, \text{Dy}, \text{Ho}, \text{Er}, \text{Tm}, \text{Yb}$) has been synthesized. Crystal structures of the compounds with $\text{Ln} = \text{La}, \text{Nd}$ and Sm are described, and photo- and triboluminescence studies indicate that the only compounds to exhibit visible photoluminescence, those with $\text{Ln} = \text{Sm}, \text{Eu}$, are also the only ones to exhibit detectable TrL. This is in agreement with the mechanism of ligand mediated excitation of the $\text{Ln}(\text{III})$ ion. The Sm -compound is identified as a novel triboluminescent compound; because it crystallizes in a non-centrosymmetric space group the compound does not disprove the relation between TrL and a non-centrosymmetric space group.

7.2 General discussion and outlook

The aim of the research described in this thesis was to investigate the potential of photoluminescent $\text{Ln}(\text{III})$ complexes as future phosphor materials for In:GaN light emitting diode based solid state light sources. Many requirements have to be met before such application can be considered, i.e. a high lumen-equivalent emission spectrum, a high absorption coefficient at the LED emission maximum, high quantum efficiency, a high stability and low thermal quenching. In this work, focus was put on shifting the wavelength of most efficient excitation towards 400 nm, whilst maintaining a high photoluminescence quantum yield. Many different kinds of ligands were investigated for their ability to sensitize luminescence of the $\text{Eu}(\text{III})$ and $\text{Tb}(\text{III})$ ions.

It is shown that indeed $\text{Eu}(\text{III})$ complexes with high photoluminescence quantum yields and long-wavelength excitation maxima can be obtained. It is shown that derivatives of dibenzoylmethane give rise to $\text{Eu}(\text{III})$ complexes with those desirable photophysical properties. In addition, it is demonstrated that substituting the dibenzoylmethane ligands has a profound impact on the quantum efficiency, and in addition that the counter ions provide valuable handlebars for further improving the emission quantum yield. However, $\text{Eu}(\text{III})$ complexes with closely related ligands have been demonstrated to exhibit poor photostability [2]. It would be valuable to investigate the influence the substituents on the dbm-ligands have on the photostability of their $\text{Eu}(\text{III})$ complexes. Elucidation of the decomposition products could give useful information on the mechanism of the decomposition pathway. For example, from research on the photostability of Hdbm-type molecules for application in sunscreen agents, these molecules are found to show higher photostability when in their 'keto-enol'-form compared to their 'diketo'-form [3, 4]. When

coordinated to Eu(III) in complexes, the tautomeric form of the ligands resembles that of the keto-enol form more closely than that of the diketo-form.

The Eu(III) complexes with derivatives of 1,10-phenanthroline are promising in terms of their efficiency, but the excitation maximum needs to be shifted further towards the visible part of the electromagnetic spectrum. It is shown that indeed substitution on the 2-position can establish a slight shift of the excitation maximum. In this research, only substitution on the 2-position of the aromatic system of the phenanthroline molecule was investigated. It would be of great interest to see the influence of substitution on other positions on the antenna properties. Extension of the aromatic system of 1,10-phenanthroline has been demonstrated to not give the desired shift [5]. The excitation maximum should be shifted at least 10 more nanometers before excitation with In:GaN based LEDs becomes possible, and photoluminescence quantum yields should be increased. It was shown that for the Eu(III) complexes with phenanthroline-based ligands, the low intrinsic quantum yield (Φ_{Ln}) of the Eu(III) ion was severely limiting the overall quantum yield. As the intrinsic quantum yield is often lowered by coupling of the $Ln(III)$ excited state to vibrational modes of the ligand, it is quite possible that a different ligand substitution pattern will influence Φ_{Ln} . It would be interesting to find if there is a relation between the substitution pattern of the ligand and Φ_{Ln} . In the present study, only complexes with nitrate ligands besides the substituted phenanthrolines were studied. It would be interesting to study the influence of other anionic ligands on the luminescent properties of the Eu(III) complexes.

As shown in Chapter 3, an interesting class of coordination compounds is formed by the metal organic frameworks. Although the compounds with furan-2,5-dicarboxylic acid have photophysical properties that make them unsuitable for application as a phosphor, the metal organic framework of Tb(III) with 2-hydroxytrimesic acid has potential. Its high quantum efficiency of 67% combined with an excitation maximum at 378 nm make this compound a good candidate material for a new phosphor. The use of ligands with slightly different arrangements of functional groups around the benzene ring would be highly interesting, as this will most likely give rise to compounds with a very different structure. If a ligand can be found that is able to efficiently sensitize luminescence by both Eu(III) and Tb(III) ions, it would be possible to make a metal organic framework of which the emission spectrum can be tuned during synthesis by varying the Eu:Tb ratio.

In this work, it is shown that Tb(III) based coordination compounds with high photoluminescence quantum efficiency and long wavelength excitation maxima can be obtained. Most notably, the complex with the phenol-oxazoline ligand in Chapter 4 stands out, with a quantum yield of 79% and an excitation maximum of 370 nm. In case of the latter compound, it would be worthwhile to investigate the photoluminescence properties of neutral heteroleptic coordination compounds, e.g. those described by the general formula $[Ln(III)(L1^-)_3(L2)]$, HL1 being the phenol-oxazoline ligand and L2 a neutral ligand such as

1,10-phenanthroline or 2,2'-bipyridine. Because it is shown that not only the ligand, but also the M:L ratio is an important parameter determining the photophysical properties of the complex, this offers an interesting way for tuning the properties. In addition, it would be fascinating to see what luminescent behavior such Eu(III) complexes would exhibit.

In this thesis, it is shown that *Ln*(III) coordination compounds with their excitation maximum and a strong absorption in the nUV region ($\lambda_{\text{exc}} > 360$ nm) and a high photoluminescence quantum yield ($\Phi > 70\%$) can be synthesized. In addition, the luminescence of these compounds is purely due to the 4f-4f transitions of the *Ln*(III) ion and therefore is well suitable for application as a phosphor for lighting technology. With these highly desirable photophysical properties in mind, it can be concluded that further investigations on the potential of this class of compounds as a phosphor material is at least as useful as the work that is currently being widely performed on the improvement of oxide-type phosphors.

7.3 References

- [1] F.A. Cotton, L.M. Daniels, and P. Huang, *Inorg. Chem. Commun.*, 4 (2001) 319-321.
- [2] L.D. Carlos, C.D.M. Donegá, R.Q. Albuquerque, S. Alves, J.F.S. Menezes, and O.L. Malta, *Mol. Phys.*, 101 (2003) 1037 - 1045.
- [3] W. Schwack and T. Rudolph, *J. Photochem. Photobiol., B*, 28 (1995) 229-234.
- [4] I. Karlsson, L. Hillerstrom, A.L. Stenfeldt, J. Martensson, and A. Borje, *Chem. Res. Toxicol.*, 22 (2009) 1881-1892.
- [5] J.W. Verhoeven, E.B. Van Der Tol, F.J. Steemers, W. Verboom, D. Reinhoudt, Nicolaas, and J.W. Hofstraat, Complex comprising a rare-earth metal ion and a complexing moiety, Pat.no WO 1998/049163k 1998.

