Enhancement of near-IR emission by bromine substitution in lanthanide complexes with 2-carboxamide-8-hydroxyquinoline

Markus Albrecht,*[a] Olga Osetska,[a] Jürgen Klankermayer,[b] Roland Fröhlich,[c] Frédéric Gumy[d] and Jean-Claude G. Bünzli[d]

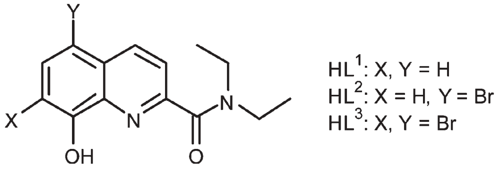
Received (in Cambridge, UK) 2nd January 2007, Accepted 24th January 2007
First published as an Advance Article on the web 9th February 2007
DOI: 10.1039/b618918k

Three novel 2-carboxamide-8-hydroxyquinoline derivatives wrap helically around trivalent lanthanide ions to form monometallic 3 : 1 complexes possessing strong NIR emission.

8-Hydroxyquinolines and derivatives thereof are important ligands for the formation of metal complexes. Initially they were mainly used for extraction purposes.[1] Recently the chemistry of 8-hydroxyquinoline experiences a renaissance due to the importance of its aluminium complex as emitter for organic light emitting devices (OLEDs).[2]

Other appropriate emitters are complexes of lanthanide(III) ions.[3] However, combination of 8-hydroxyquinolines with lanthanide(III) ions does not lead to emission in the visible. Due to the low energy LUMO of the ligand, effective energy transfer to the metal occurs mainly in case of the near-IR emitting metal ions erbium(III), neodymium(III), and ytterbium(III).[4,5] In a recent study Van Deun, Binnemans *et al* have shown that simple 8-hydroxyquinoline ligands form complexes with lanthanide(III) ions which possess either 4 : 1, 6 : 2 or 8 : 3 stoichiometry.[6] Imbert *et al* describe tetrapodal quinolines (Tox, Tsox) for the formation of NIR emitting complexes in water.[7]

Our idea is to extend the coordination site of 8-hydroxyquinoline[8] by attachment of amide substituents in the 2-position in order to obtain 3 : 1 complexes. In those complexes the metal should be shielded against intrusion of solvent molecules (*e.g.* water) into the first coordination sphere. In order to enhance the energy transfer from the ligand to the lanthanide ions, both the parent compound HL^1 and its corresponding bromide-substituted derivatives HL^2 and HL^3 were synthesized.[4]



Complexes of the ligands HL^{1-3} were prepared by reaction with appropriate hydrates of lanthanide(III) salts ($LaCl_3$, $Yb(SO_3CF_3)_3$, $EuCl_3$, $Er(SO_3CF_3)_3$, $NdCl_3$) in methanol at 55 °C using potassium carbonate as base. After evaporation of solvent, red solids were obtained which were extracted with dichloromethane. The neutral red LnL_3 complexes can be recognized by their solubility in dichloromethane as well as in methanol, while the yellow side products LnL_nX_m (X = Cl, SO_3CF_3; $n + m = 3$) are only soluble in methanol. Elemental analyses† confirm the formation of the tris complexes, except in the case of ErL^2_3 which could not be obtained in analytically pure form. Nevertheless, solubility in dichloromethane and the characteristic red colour indicate the predominant presence of the tris complexes. In all cases ESI MS shows the presence of peaks corresponding to the LnL_3 species.

An X-ray structural analysis of $ErL^1_3 \cdot K(SO_3CF_3) \cdot$ ether·chloroform has been obtained after crystallizing the crude product from THF–ether–chloroform. Fig. 1 shows the solid state structure of ErL^1_3. As predicted, $(L^1)^-$ acts as a tridentate ligand coordinating to the metal by the quinolinate oxygen (Er–O = 2.313(3), 2.329(3), 2.347(3) Å) and nitrogen atom (Er–N = 2.494(4), 2.500(4), 2.484(4) Å) as well as through the amide oxygen (Er–O = 2.415(3), 2.424(4), 2.431(4) Å). The three ligand strands coordinate to the metal ion in a helical fashion, leading to a coordination number of nine at the erbium(III) ion. In the obtained crystal only the *syn* arrangement of the ligands is observed, while in solution of the pure ErL^1_3 complex, the presence of the *syn* as well as of the *anti* isomers is expected. The *syn* arrangement in the solid state is probably due to coordination of the potassium cation of $K(SO_3CF_3)$ to the three phenolate oxygen atoms of the $(L^1)^-$ ligands in ErL^1_3. Thus, the complex acts as a tridentate ligand for potassium.

Inversion related pairs of K^+ and triflate ions link the ErL^1_3 moieties to form a large centrosymmetric dimer.

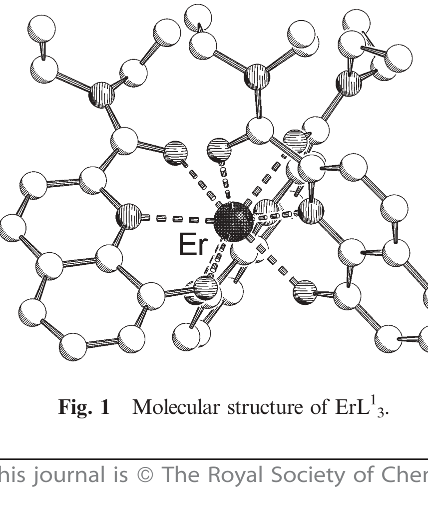


Fig. 1 Molecular structure of ErL^1_3.

---

[a] *Institut für Organische Chemie, RWTH Aachen, Landoltweg 1, D-52074, Aachen, Germany.*
E-mail: markus.albrecht@oc.rwth-aachen.de
[b] *Institut für Technische und Makromolekulare Chemie, RWTH Aachen, Worringer Weg 1, D-52074, Aachen, Germany*
[c] *Organisch-Chemisches Institut, Universität Münster, Corrensstrasse 40, D-48149, Münster, Germany*
[d] *Laboratory of Lanthanide Supramolecular Chemistry, École Polytechnique Féderale de Lausanne (EPFL), BCH 1402, CH-1015, Lausanne, Switzerland*

Crystals of YbL^3_3 have been obtained from DMF. The solid state structure as determined by X-ray crystallography is shown in Fig. 2. In contrast to ErL^1_3, which is obtained in the solid state as the *syn* isomer, YbL^3_3 crystallizes as the *anti* isomer. Bond lengths of the chelating ligands are Yb–O_{quin} = 2.344(9) and 2.284(9) Å, Yb–N = 2.484(11) and 2.455(11) Å, and Yb–O_{amide} = 2.363(9) and 2.415(10) Å for the two parallel oriented ligands and Yb–O_{quin} = 2.363(9) Å, Yb–N = 2.437(11) Å, and Yb–O_{amide} = 2.376(9) Å for the third one.

In order to probe the complex structure in solution we have performed NMR studies with diamagnetic LaL^3_3 in CD_2Cl_2. Only broad signals are observed at room temperature. However, upon cooling of the sample to 235 K a sharpening of the resonances occurs and five sets of signals are observed for the ligand $(L^3)^-$. This results in ten sets of resonances for protons of the ethyl groups. Coupling patterns can be assigned by low-temperature COSY NMR spectroscopy.

Resonances for two ethyl groups without diastereotopic protons at δ = 3.42 (CH_2), 1.18 (CH_3); 3.59 (CH_2), 1.24 (CH_3) ppm are assigned as arising from the free ligand HL^3 since they correspond to resonances occurring in the NMR spectrum of HL^3. Six of the remaining eight sets of signals (δ = 2.31 CH_2, 0.43 CH_3, and 3.83 CH_2, 1.48 CH_3; 3.22/2.82 CH_2, 0.63 CH_3; 3.83/3.49 CH_2, 1.38 CH_3; 3.74/3.59 CH_2, 1.42 CH_3; 3.01/2.83 CH_2, 0.57 CH_3; 3.38/3.21 CH_2, 0.92 CH_3; 3.83/3.42 CH_2, 1.25 CH_3 ppm) show diastereotopic methylene protons. This behaviour is caused by the chirality of the complexes and by the inequivalence of the four different types of ligands in the *syn* and *anti* isomer of LaL^3_3. The *syn* isomer possesses C_3 symmetry and generates only one set of signals, while the unsymmetrical anti isomer results in three sets. From a statistical point of view, the two isomers should be formed in a 1 : 3 *syn* : *anti* ratio, matching the observed relative intensities of the resonances from the differently coordinated ligands.

Solid phase photophysical data have been collected for the LnL_3 complexes (Ln = La, Eu, Er, Nd, Yb) at 295, 77 and 10 K.‡ All three lanthanum complexes display similar spectra with a broad emission band having a maximum at 650 nm (295 K) or 630 nm (77 K) when excited at 277, 370, or 522 nm; these wavelengths correspond to absorption bands of the coordinated ligands. The quantum yield of the ligand-centred fluorescence amounts to Q = 0.44(5)% for LaL^1_3. No triplet state emission could be evidenced. A similar situation is met for the Eu(III) complexes, no metal-centred emission being detected, while the singlet state emission is quite weak. The lack of Eu-centred emission is due to the low-lying excited states of the quinoline derivatives and their inability to transfer energy to the trivalent europium centre. On the other hand, the electronic features of the ligands L^- are better suited for populating the NIR emitting excited states of trivalent neodymium, erbium, and ytterbium. With these three metal ions, effective energy transfers take place from the ligands to the metal and NIR emission could be detected for all nine complexes, as demonstrated by the excitation spectra which match the ligand absorption spectra. High-resolution low-temperature spectra show the characteristic ligand-field splitting of the emitting and ground levels and their analysis will be reported elsewhere. We focus here on the room temperature data (Fig. 3) and on the effect of bromination on the quantum yields of the metal-centred luminescence and lifetimes of the excited states (Table 1). All of the excitation spectra are alike, with a broad band extending from 250 through 570 nm and displaying two main maxima in the ranges 370 and 520 nm.

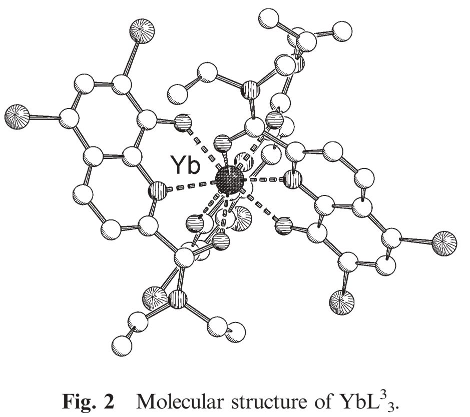


Fig. 2 Molecular structure of YbL^3_3.

All three neodymium(III) complexes show well emissive behaviour upon excitation in the UV or visible (355–488 nm). Typical emission bands for the $^2F_{3/2} \rightarrow {}^4I_{11/2}$, $^2F_{3/2} \rightarrow {}^4I_{13/2}$, and $^2F_{3/2} \rightarrow {}^4I_{9/2}$ transitions are observed. The quantum yields of the metal-centred luminescence upon ligand excitation, $Q^{Ln}{}_L$ increase in the series NdL^1_3 < NdL^2_3 < NdL^3_3. The presence of two bromine atoms results in a total improvement by a factor of approximately 2.9. This could be due to the "heavy atom effect" of the bromine substituent which seems to be additive upon successive addition of bromine atoms to the quinoline backbone (enhancement factors 1.6 and 1.7, respectively). In parallel, the Nd($^2F_{3/2}$) lifetimes increase by a slightly larger factor (4-fold), pointing to a decrease in the non-radiative de-activation processes.

Similar results are obtained for the erbium(III) complexes which display the typical $^4I_{13/2} \rightarrow {}^4I_{15/2}$ transition centred at 1.54 μm. Hereby the quantum yields $Q^{Ln}{}_L$ increase in the series ErL^1_3 < ErL^2_3 < ErL^3_3 by a similar factor when compared to the Nd(III) complexes, approximately 2.8, while the Er($^4I_{13/2}$) lifetimes increase 3.5-fold.

The ytterbium(III) complexes display the characteristic $^2F_{5/2} \rightarrow {}^7F_{7/2}$ emission around 980 nm and possess the largest quantum yields, up to $Q^{Ln}{}_L$ = 1.40% for YbL^3_3. But in this series, there is no

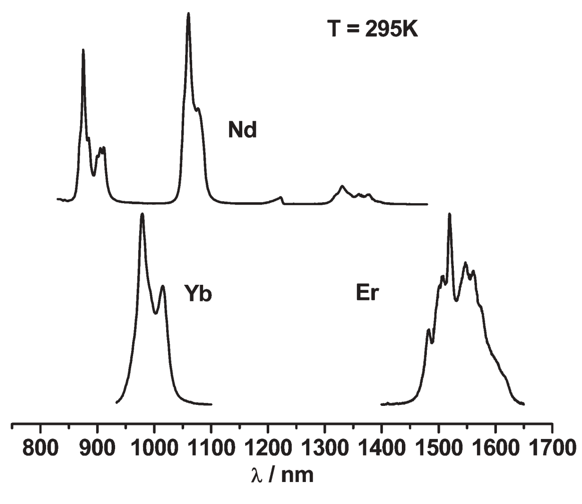


Fig. 3 High-resolution emission spectra of solid samples of LnL^3_3 under ligand excitation at 370 nm.

Table 1 Results of the solid phase photophysical measurements at 295 K for complexes LnL_3 at room temperature. Quantum yields $Q^{Ln}{}_{L}$ [%, excitation in the range 350–400 nm] as well as lifetimes τ [μs, excitation at 355 nm] of the excited states for the NIR emission are listed

L		NdL_3	ErL_3	YbL_3
L^1	Q (%)	0.14(2)	0.012(1)	0.56(5)
	τ/μs	0.39(1)	1.15(2)	11.1(1)
L^2	Q (%)	*0.23(4)*[a]	[b]	0.60(6)
	τ/μs	*0.69(2)*[a]		10.5(1)
L^3	Q (%)	0.40(2)	0.033(5)	1.40(15)
	τ/μs	1.57(1)	4.05(5)	20.6(2)

[a] Analysis shows eight water molecules per complex; [b] no correct analysis for $ErL^2{}_3$ (Q = 0.021(1)%, τ = 2.30(1) μs).

substantial improvement when a single bromine atom is introduced, the overall 2.5-fold enhancement being entirely due to the addition of the second bromine and, moreover, the $Yb(^2F_{5/2})$ lifetime is lengthened by the same factor. One of the yellow side products of reaction of L^3 with $Yb(SO_3CF_3)_3$ has a much larger quantum yield ($Q^{Ln}{}_{L}$ = 2.24%, τ = 29.0 μs). However, the nature of this complex is still under investigation (the elemental analysis appears to be consistent with $[YbL^3(SO_3CF_3)_2]$).

In conclusion, we demonstrate here that simple and easy to synthesize ligands derived from 8-hydroxyquinoline yield mono-metallic tris complexes in which the NIR-luminescence of trivalent lanthanide ions (Nd, Er, Yb) is substantially sensitised, particularly when the ligands are substituted by bromine atoms. The obtained quantum yields are sizeable and they increase by a factor 2.5–3 upon disubstitution by bromine atoms. It should be pointed out, that the complexes even can be excited in the visible (up to 550–570 nm), which is important for potential applications.

This work was supported by the Deutsche Forschungsgemeinschaft (Schwerpunktprogramm 1166).

Notes and references

† Analysis for $LaL^1{}_3 \cdot H_2O$ (calc. C: 56.89 H: 5.34 N: 9.48, found: C: 56.60 H: 4.85 N: 9.67), $EuL^1{}_3 \cdot 2.5\,H_2O$ (calc. C: 54.43 H: 5.44 N: 9.07, found: C: 54.43 H: 5.22 N: 9.31), $NdL^1{}_3$ (calc. C: 57.71 H: 5.19 N: 9.61, found: C: 58.23 H: 5.88 N: 9.60), $ErL^1{}_3 \cdot 3H_2O$ (calc. C: 53.04 H: 5.40 N: 8.84, found: C: 52.75 H: 5.17 N: 9.38), $YbL^1{}_3 \cdot 2.5H_2O$ (calc. C: 53.22 H: 5.32 N: 8.87, found: C: 53.66 H: 5.52 N: 8.38), $LaL^2{}_3 \cdot H_2O$ (calc. C: 44.90 H: 3.95 N: 7.48, found: C: 44.79 H: 4.90 N: 7.49), $EuL^2{}_3 \cdot 3H_2O$ (calc. C: 43.02 H: 4.13 N: 7.17, found: C: 43.06 H: 3.87 N: 6.99), $NdL^2{}_3 \cdot 8H_2O$ (calc. C: 40.20 H: 4.66 N: 6.70, found: C: 39.99 H: 4.21 N: 6.39), $ErL^2{}_3$ (no correct analysis), $YbL^2{}_3 \cdot H_2O$ (calc. C: 43.58 H: 3.83 N: 7.26, found: C: 43.50 H: 4.14 N: 7.17), $LaL^3{}_3 \cdot 2H_2O$ (calc. C: 36.60 H: 3.14 N: 6.10, found: C: 36.85 H: 3.53 N: 6.08), $EuL^3{}_3$ (calc. C: 37.22 H: 2.90 N: 6.20, found: C: 37.03 H: 3.40 N: 6.05), $NdL^3{}_3 \cdot CH_3OH$ (calc. C: 37.44 H: 3.14 N: 6.09, found: C: 37.69 H: 3.72 N: 6.51), $ErL^3{}_3$ (calc. C: 36.81 H: 2.87 N: 6.13, found: C: 36.54 H: 3.05 N: 6.08), $YbL^3{}_3 \cdot 3H_2O$ (calc. C: 35.27 H: 3.17 N: 5.88, found: C: 35.05 H: 3.08 N: 5.69).

Analysis for $YbL^3(O_3SCF_3)_2 \cdot 3H_2O$ (calc. C: 20.75 H: 2.07 N: 3.02, found: C: 20.54 H: 2.08 N: 2.65).

Crystal data for $ErL^1{}_3$: $(C_{14}H_{15}N_2O_2)_3Er \cdot (CF_3SO_3)K \cdot C_4H_{10}O \cdot CHCl_3$, M = 1278.76, triclinic, space group $P\bar{1}$ (No. 12), a = 13.531(1), b = 15.467(1), c = 15.721(1) Å, α = 115.44(1), β = 110.20(1), γ = 91.18(1)°, V = 2732.4(3) Å^3, D_c = 1.554 g cm^{-3}, μ = 1.866 mm^{-1}, Z = 2, λ = 0.71073 Å, T = 223(2) K, 25206 reflections collected ($\pm h$, $\pm k$, $\pm l$), $[(sin\theta)/\lambda]$ = 0.59 Å^{-1}, 9457 independent (R_{int} = 0.067) and 7647 observed reflections $[I \geqslant 2\sigma(I)]$, 666 refined parameters, R = 0.046, wR^2 = 0.115, CCDC 632286.

Crystal data for $YbL^3{}_3$: $(C_{14}H_{13}N_2O_2Br_2)_3Yb$, M = 1376.29, orthorhombic, space group $Pccn$ (No. 56), a = 27.425(1), b = 15.739(1), c = 23.156(1) Å, V = 9995.1(8) Å^3, D_c = 1.829 g cm^{-3}, μ = 6.717 mm^{-1}, Z = 8, λ = 0.71073 Å, T = 223(2) K, 55638 reflections collected ($\pm h$, $\pm k$, $\pm l$), $[(sin\theta)/\lambda]$ = 0.59 Å^{-1}, 8818 independent (R_{int} = 0.134) and 5437 observed reflections $[I \geqslant 2\sigma(I)]$, 556 refined parameters, R = 0.077, wR^2 = 0.228, CCDC 632287. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b618918k

‡ Low-resolution emission spectra were measured on a Fluorolog FL 3–22 spectrometer from Spex-Jobin-Horiba equipped for both visible and NIR measurements, as described in ref. 9. Quantum yield data were gathered on the same instrument, using a home-modified integrating sphere from Oriel and the procedure described in ref. 10 (λ_{exc} = 370 nm); spectra were corrected for the instrumental function. High-resolution spectra and lifetimes were measured with a previously described instrumental set-up.[11] All luminescence decays were single exponential functions, λ_{exc} = 355 nm, λ_{an} = 1059 (Nd), 1518 (Er), 979 and 1018 nm (Yb).

1 R. G. W. Hollingshead, *Oxine and its Derivatives*, Butterworths, London, 1954; H. Schmidbaur, J. Lettenbauer, D. L. Wilkinson, G. Müller and O. Kumberger, *Z. Naturforsch., Teil B*, 1991, **46**, 901.

2 W. E. Ohnesorge and L. B. Rogers, *Spectrochim. Acta*, 1959, **15**, 27; R. H. Friend, R. W. Gymer, A. B. Holmes, J. H. Burroughes, R. N. Marks, C. Taliani, D. A. Dos Santos, J.-L. Bredas, M. Lögdlund and W. R. Salaneck, *Nature*, 1999, **397**, 121; R. Pohl and P. Anzenbacher, Jr., *Org. Lett.*, 2003, **5**, 2769; C. Perez-Bolivar, V. A. Montes and P. Anzenbacher, Jr., *Inorg. Chem.*, 2006, **45**, 9610.

3 C. Piguet and J.-C. G. Bünzli, *Chem. Soc. Rev.*, 1999, **28**, 347; J.-C. G. Bünzli and C. Piguet, *Chem. Rev.*, 2002, **102**, 1897; J.-C. G. Bünzli and C. Piguet, *Chem. Soc. Rev.*, 2005, **34**, 1048; D. Parker, R. S. Dickins, H. Puschmann, C. Crossland and J. A. K. Howard, *Chem. Rev.*, 2002, **102**, 1977. For selected recent examples see: L. J. Charbonniere, R. Schurhammer, S. Mameri, G. Wipff and R. F. Ziessel, *Inorg. Chem.*, 2005, **44**, 7151; M. M. Castano-Briones, A. P. Bassett, L. L. Meason, P. R. Ashton and Z. Pikramenou, *Chem. Commun.*, 2004, **24**, 2832; S. Sivakumar, F. C. J. M. Van Veggel and M. Raudsepp, *J. Am. Chem. Soc.*, 2005, **127**, 12464.

4 M. Iwamuro, T. Adachi, Y. Wada, T. Kitamura, N. Nakashima and S. Yanagida, *Bull. Chem. Soc. Jpn.*, 2000, **73**, 1359; R. Van Deun, P. Fias, K. Binnemans and C. Görller-Walrand, *Phys. Chem. Chem. Phys.*, 2003, **5**, 2754.

5 For other NIR emitting coordination compounds see *e.g.*: N. M. Shavaleev, G. Accorsi, D. Virgili, Z. R. Bell, T. Lazarides, G. Calogero, N. Armaroli and M. D. Ward, *Inorg. Chem.*, 2005, **44**, 61; S. Torelli, D. Imbert, M. Cantuel, G. Bernardinelli, S. Delahaye, A. Hauser, J.-C. G. Bünzli and C. Piguet, *Chem.–Eur. J.*, 2005, **11**, 3228.

6 R. Van Deun, P. Fias, P. Nockemann, A. Schepers, T. N. Parac-Vogt, K. Van Hecke, L. Van Meervelt and K. Binnemans, *Inorg. Chem.*, 2004, **43**, 8461.

7 S. Comby, D. Imbert, A.-S. Chauvin and J.-C. G. Bünzli, *Inorg. Chem.*, 2006, **45**, 732; D. Imbert, S. Comby, A.-S. Chauvin and J.-C. G. Bünzli, *Chem. Commun.*, 2005, 1432.

8 M. Albrecht, O. Osetska and R. Fröhlich, *Dalton Trans.*, 2005, 3757.

9 S. Comby, D. Imbert, C. Vandevyver and J.-C. G. Bünzli, *Chem.–Eur. J.*, 2007, **13**, 936.

10 J. C. de Mello, H. F. Wittmann and R. H. Friend, *Adv. Mater.*, 1997, **9**, 230.

11 S. Comby, D. Imbert, A.-S. Chauvin and J.-C. G. Bünzli, *Inorg. Chem.*, 2006, **45**, 732.