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RESEARCH REPORT

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Homodinuclear f-f and Heterodinuclear f-p Lanthanide Helicates

Markus Albrecht*^[a]

Keywords: β -diketonates; 8-hydroxyquinolines; helicate; luminescence; energy transfer

Lanthanide helicates are of interest due to their ability to emit either in the visible or in the NIR region. In this context it is important to prepare heterodinuclear helicates and to use them for the investigation of intramolecular communication processes between different complex units. In here we describe the ligand synthesis and self-assembly of homo- and heterodinuclear helicates based on β -diketonate, catechol-acyl hydrazone and 2-amido-8-hydroxyquinoline ligands.

Strongly emitting homodinuclear europium(III) complexes are obtained in addition to heterodinuclear coordination compounds. Some of the latter exhibit intramolecular energy transfer behaviour with internal quenching of an aluminum trisquinolate and enhancement of the NIR emission at an ytterbium(III), neodymium(III) or erbium(III) complex unit.

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unsymmetric ligands with a tri- and a bidentate unit or with two different tridentate ligand moieties were prepared. With those ligands homo- as well as heterodinuclear complexes can be obtained.² Lessman and Horrocks described the formation of triple stranded helicates of NIR emitting lanthanide ions with ligand units like **B**³ and the bis- β -diketonate **C** was used by Pikramenou to obtain quadruple-stranded helicates with europium(III) ions.⁴

Introduction

Helicates are coordination compounds in which linear ligand strands with several metal binding sites wrap around two or more metal ions. Depending on the number of ligands involved, double or triple stranded helicates are obtained. This kind of chemistry has been investigated for nearly 25 years using mainly p- and d-metal ions as the central metals. Only a few specific complexes with lanthanide ions were described.¹ Piguet and Bünzli developed and thoroughly investigated a new system in the early 1990s. The representative ligand **A** of their research study revealing the characteristic bis(benzimidazolyl) pyridine metal binding motif is shown in Figure 1. This system allows the preparation of symmetric ligands possessing two identical coordination sites. In addition,

Figure 1. Ligands for dinuclear triple-stranded lanthanide helicates described in the literature.

Despite these significant developments, there was still a need to develop new lanthanide helicates based on other ligand systems in order to widen the possibilities of this chemistry. Thus, dinuclear homo- and heterodinuclear lanthanide(III) helicates were made by different approaches and the emissive properties of selected complexes were studied. The results are summarized in this article.



Markus Albrecht studied Chemistry in Würzburg and Münster. He obtained his Dr. rer. nat. in 1992 and immediately became a postdoctoral fellow in the laboratories of Prof. Kenneth N. Raymond in Berkeley. In 1997 he received his habilitation at the University of Karlsruhe. His work on the metal-directed self-assembly of metallo-supramolecular aggregates was honoured with the „ADUC-Jahrespreis für Habilitanden“ and between 1998 and 2001 he was a Heisenberg-fellow of the DFG. Since spring 2002 he is Professor of Organic Chemistry at the RWTH Aachen.

Ligand synthesis

The preparation of metallosupramolecular aggregates begins with the design and the synthesis of appropriate ligands.⁵ An early consideration, which follows the concept by Piguet and Bünzli, was that tridentate ligand units should be appropriate to form tris-chelates with lanthanide(III) ions.² In this context the acylhydrazone of salicylic aldehyde

D as well as 2-amido-8-hydroxyquinoline **E** were recognized as suitable chelates. In addition we investigated the β -diketonate unit **F** which is well known to be a potent chelator for lanthanide(III) ions.

Figure 2. Ligand units for lanthanide(III) ions which are used in this study.

Synthetic strategies have to be developed to connect the ligand units in order to get homodinuclear complexes or to attach another different moiety to obtain heterotopic ligands

Ligands based on the β -diketonate unit

Bis- β -diketonate-type ligands can be easily prepared starting from dicarboxylic esters and reacting them in a double-Claisen-condensation with α -acidic ketones. In our case we started from tartaric acid esters bearing different cyclic protecting groups for the central hydroxyl groups.

Scheme 1. Claisen condensation as a keystone to obtain enantiomerically pure β -diketonate ligands.

The reaction to obtain the β -diketonate ligands is shown in Scheme 1. It proceeds easily, but leads to relatively low yield of the ligands. However, due to the facile procedure they can be obtained in gram quantities.⁶ Ligands **3** and **4** were used in coordination studies, but due to their superior sensitizing properties we only investigated ligands **3d** and **4d** most thoroughly.

Catechol-acylhydrazone ligands

Catechol-acylhydrazone ligands are also obtained in a simple approach. In a one step procedure, 2,3-dihydroxybenzaldehyde is condensed with acyl- or tosylhydrazines and the desired product is isolated in high yields.⁷

Scheme 2. Preparation of acyl- or tosylhydrazone-catechol ligands.

The ligands **7-H₂** and **9-H₂** possess two different binding sites for metal ions: the tridentate salicylic acyl- or tosylhydrazone and the bidentate catechol. Therefore they should be appropriate for the formation of heterodinuclear triple-stranded helicates with one nine- and one six-coordinate metal ion. In contrast to the tosyl substituent, the acyl group result in very different structures of the ligands. The acyl derivative with its sp^2 -carbonyl carbon atom is planar, while the tetrahedral sulfonate unit induces a kink.⁸

Ligands based on 8-hydroxyquinoline

Bis-8-hydroxyquinoline ligands can be easily prepared by Hiratani tandem-Claisen rearrangement.⁹ Therefore, in a Williamson-ether synthesis 8-hydroxyquinoline derivatives (like **10a-c**) are reacted with 3-chloro-2-chloromethyl butane to afford isobutenylidene bridged compounds **11**. Stepwise reaction enables the formation of heterotopic ethers **12**. In the key step, heating of the diethers to

approximately 160 °C results in the rearrangement reaction which liberates the OH-functionalities and simultaneously installs two new CC bonds. This reaction proceeds in high yields.¹⁰

Thus we can easily prepare homo and hetero-ditopic ligands which bear either two tridentate or one tri- and one bidentate ligand units. They are appropriate to obtain either dinuclear lanthanide(III) or heterodinuclear lanthanide(III) – p/d-metal ion helicates.

Scheme 3. Preparation of homo- and heteroditopic bis-8-hydroxyquinoline ligands.

Homodinuclear lanthanide helicates

The ligands **3**, **4** and **13** are able to form homodinuclear helicates with appropriate metal ions (e. g. lanthanide(III) ions). Therefore, corresponding coordination studies were performed.

Enantiomerically pure homodinuclear lanthanide(III) helicates with bis- β -diketonate ligands

The β -diketonate ligands **3d-H₂** and **4d-H₂** are first reacted with gallium(III) ions. The outcome of the coordination studies with the two ligands is very different. Ligand **3d** behaves as expected and forms the triple-stranded dinuclear helicate.¹¹ Ligand **4d** on the other hand possesses a conformation which is not appropriate for the formation of the helicate. Therefore, not three but only two ligands bridge two gallium ions and the vacant coordination sites at the metal ions are filled by hydroxide anions. Upon crystallization four of the dinuclear units cluster around one additional gallium(III) ion and form the nonanuclear complex cation $[(\mathbf{4d})_8\text{Ga}_9(\text{OH})_{10}]^+$.¹²

Figure 3. A triple-stranded dinuclear gallium(III) helicate (left) and a nonanuclear hydroxide bridged gallium(III) cluster (right).

Reacting the ligands **3d** and **4d** with europium(III) salts in different ratios affords dinuclear europium compounds with the composition depending on the ligand to metal ratio.

Figure 4. Triple-stranded and quadruple stranded europium(III) helicates based on bis- β -diketonate ligands **3d** and **4d**. Triple-stranded complexes are also prepared with ligands **3a** and **3b**.

The complexes show strong lanthanide emission upon excitation with UV light revealing the typical red color of europium(III) complexes. The ligands prove to be effective sensitizers for the lanthanide ion and in case of $(\mathbf{3d})_3\text{Eu}_2$ very effective energy transfer is observed. The sensitizing

ability of the ligands improves in the series **3a**<**3b**<<**3d**. The corresponding terbium(III) (**3d**)₃Tb₂ and holmium(III) complexes (**3d**)₃Ho₂ also show characteristic spectra for the respective lanthanide(III) metal ions.¹³

The observation of quadruple stranded helicates seems to be surprising but has been reported earlier by Pikramenou for related achiral systems.⁴

It is worth mentioning that all complexes of the enantiomerically pure bis-β-diketonate ligands with lanthanide(III) as well as gallium(III) or other metal ions, are obtained in enantiomerically pure form.

Homodinuclear lanthanide(III) helicates based on 2-amido-8-hydroxyquinoline ligands

8-Hydroxyquinoline derivatives had been already used in order to form lanthanide(III) complexes.¹⁴ However, most studies were based on the parent ligand which forms coordination compounds of relatively undefined stoichiometry. With respect to the photophysical behaviour of the complexes, the quinoline should be able to sensitize lanthanide ions which, due to the low lying excited state of this aromatic system, is only effective in case of NIR emitting metal ions like neodymium(III), erbium(III) and ytterbium(III).¹⁵

The present idea is to extend the coordination site of 8-hydroxyquinoline by attachment of an amide to the 2-position of the quinoline and thus to install a tridentate ligand unit which is supposed form trisligand complexes with lanthanide ions. In order to test this, the simple ligand **10a-c-H** has been made and was submitted to coordination studies with lanthanide ions.

Figure 5. Ligands (**10a-c-H**) for the formation of 3:1 lanthanide(III) complexes. Parts of the crystal structures of syn-(**10a**)₃Er (left) and anti-(**10c**)₃Yb (right) are shown.

Tris ligand lanthanide(III) complexes (**10**)₃Ln are easily obtained in this way. NMR investigations with the corresponding lanthanum(III) complexes show that the compounds are present in solution as a statistical mixture of the syn and anti isomer. However, upon crystallisation, isomerically pure complexes are obtained.

The neodymium(III), erbium(III) and ytterbium(III) complexes show good NIR-emissive properties with the quantum yields and life times being higher for complexes of the highly brominated ligand **10c** in comparison to the less brominated **10b** or unbrominated **10a**.¹⁶

The ligand unit **10a** can be triply attached to a chiral platform. The resulting tripodal ligand **15-H₃** is highly specific for the complexation of lanthanide(III) ions and forms enantiomerically pure 1:1 complexes. Thorough CD-

spectroscopic and theoretical investigations reveal that the complex unit adopts the M-configuration ("Λ").¹⁷

Figure 6. A tripodal ligand **15-H₃**, which specifically forms 1:1 lanthanide complexes.

Based on the preliminary studies with mononuclear complexes, the ditopic ligands **13-H₂** have been used in order to obtain triple stranded dinuclear helicates. Reaction of the respective ligand with lanthanide(III) salts in the presence of alkali metal carbonate as base affords the expected coordination compounds which bear an encapsulated alkali metal cation, acting as a template for the assembly of the compounds. The formation of the helicates in case of (**13b**)₃La₂, can be nicely followed by proton NMR spectroscopy. Expected shifts of the ligand are observed and the methylene units show diastereotopic behaviour only in the coordination compounds. This is due to the chirality at the complex units. In addition to the spectroscopic studies, a series of X-ray structures of lanthanide complexes of **13c** were obtained revealing the helical structure of the coordination compounds with the ligands wrapping around the metal ions. The lanthanide ions possess a coordination number of nine. In addition, the central alkali metal cation coordinates to internal oxygen atoms and is located close to the π-system of one of the isobutenylidene spacers.¹⁸

Figure 7. The solid state structure of the cation [(**13c**)₃Yb₂Rb]⁺ as a representative example for the obtained helicates (left) and a representation of the interaction of the central alkali metal cation with the six quinolinolate oxygen atoms and the vinyl group of one of the ligand strands (right).

All homodinuclear lanthanide complexes have been investigated for emitting properties and show the NIR emission spectra which are expected for ytterbium(III), erbium(III) and neodymium(III) ions. The obtained photophysical results will be briefly discussed below together with those observed for the corresponding heterodinuclear coordination compounds.

Heterodinuclear lanthanide helicates

In order to obtain heterodinuclear helicates we need ligands with two different binding units for metal ions. The different metal ions can be distinguished either by electronic or by geometric discrimination. In here the geometrical approach is described in which two binding sites of different denticity are connected to each other: one that is able to bind metals that are six coordinated, and another for metals with higher coordination numbers. If the binding sites are well chosen, coordination is very specific and the heterodinuclear complexes are formed in high yield or exclusively.

Heterodinuclear helicates with catechol acyl- and tosylhydrazones

Ligands **7-H₂** and **9-H₂** fulfil the requirements to form heterodinuclear coordination compounds. The ligands possess a bidentate catechol unit, which is directly attached to a tridentate acyl- or tosyl hydrazone of a salicylic aldehyde unit. Mixing the ligands with appropriate metal salts, heterodinuclear complexes are formed. However, this only works with high specificity if the overall charge of the coordination compound is neutral. A major driving force for the complex assembly seems to be the formation of an uncharged species. This is observed by combining gallium(III) and lanthanum(III) or titanium(IV) and calcium(II). Combinations of metals which result in charged species (e.g. Ti(IV) and La(III) or Ga(III) and Ca(II)) do not proceed quantitatively. In any case, the heterodinuclear complexes can be found as dominant species, but side products are also present.⁷

Figure 8. The structure of **(7a)₃AlLa**·DMF (a: side view, b: top view) and of **[(9)₃TiK]⁻** (c: side view, d: top view).

Figure 8 (a, b) shows as a representative example of complexes of ligands **7**, the structure of **(7a)₃AlLa**·DMF. The solvent molecule is coordinated to the lanthanum(III) ion and extends its coordination number to 10. Coordination of solvent to the lanthanide metal ion is observed in all related structures.

The corresponding complex anion **[(9)₃TiK]⁻** shows a remarkably different structure (Figure 8 c, d). Due to the tetrahedral geometry at sulfur, the terminal aromatic units are folded back and a more “compact” complex is formed. With ligand **9**, heterodinuclear lanthanide(III) complexes are also obtained but have not been structurally characterized.⁸

The formation of heterodinuclear complexes from catechol acyl- and tosyl-hydrazones opens a way to a new class of heterodinuclear helicates involving lanthanide(III) ions. The facile synthesis allows the preparation of functionalized ligands while the close proximity of the metal ions makes them potential candidates for the study of e.g. magnetic interactions between the different metal ions.

Heterodinuclear helicates with 8-hydroxyquinoline ligands: Observation of energy transfer processes

In the ligands **14** the two bidentate and the tridentate ligand units are more separated than in ligands **7** or **9**. Therefore the complex units cannot communicate (electronically or magnetically) through bonds, but can only interact through space.

Heterodinuclear coordination compounds of the ligands **14** are easily obtained by mixing three equivalents of the ligands with lanthanide(III) and aluminium(III) salts. Alkali metal carbonate has to be added in order to deprotonate the ligand units and to provide a cation which acts as a template in the formation of the heterodinuclear complex.

It was not possible to obtain a crystal structure of the heterodinuclear complexes, but they could be well

characterized by standard analytical techniques. Proton NMR spectroscopy of diamagnetic complexes shows expected shifting and diastereotopic splitting of the ligand signals upon complexation and ESI MS reveals the signals of the heterodinuclear complexes as dominant peaks. As representative example the ESI MS of **[(14c)₃AlYbK]⁺** is depicted in Figure 9.

Figure 9. ESI MS showing the dominating peak of **[(14c)₃AlYbK]⁺**.

In order to study the photophysical properties of the helicate type complexes, we prepared the homodinuclear compounds **[(13c)₃Yb₂K]OTf** and **16**, and the heterodinuclear **[(14c)₃AlYbK]OTf**.

[(13c)₃Yb₂K]OTf shows the expected near infrared emission and additionally a very weak red emission which is based on ligand luminescence due to an incomplete energy transfer from the ligand to the metal. The dinuclear aluminium complex shows green emission, which is typical for aluminium quinolates. This emission is also expected for the heterodinuclear complex **[(14c)₃AlYbK]OTf**, but here it cannot be observed. Instead, an enhancement of lifetime and quantum yield of the NIR emission is found. This is due to an internal quenching process as depicted in Figure 10 (bottom). The aluminium quinolate is internally quenched by the ytterbium quinolate unit. The acceptor substituted ligand unit bound to ytterbium has a lower lying excited state compared to the quinolate at aluminium and thus this energy transfer is possible. The energy is further transferred to the lanthanide metal ion leading to the enhanced emission.¹⁸

Figure 10. Light emitting triple stranded helicate type complexes and proposed energy transfer in a heterodinuclear ytterbium(III)-aluminum(III) complex.

The process described for **[(14c)₃AlYbK]OTf** is also found for the corresponding erbium(III) and neodymium(III) complexes. Interestingly the observation of the red ligand emission is strongly dependent on the templating cation and can be dramatically reduced by use of larger cations like rubidium or cesium.¹⁹

Conclusions

In this paper, strategies were described to obtain homo- or heterodinuclear helicate type coordination compounds involving lanthanide(III) ions at least as one of the two metal centers. It has been shown that tridentate binding sites in the ligand strands are appropriate for the coordination of lanthanide(III) ions. In order to obtain heteronuclear complexes, bi- and tridentate units must be combined.

The ligand units in this studies are based on β -diketonates, salicylic acylhydrazones and 8-hydroxyquinoline, which are all good ligands for lanthanide(III) coordination.

In case of the quinoline derivatives, heterodinuclear helicates ytterbium(III), neodymium(III) and erbium(III) as lanthanide and aluminium as the second metal are prepared. Those compounds show energy transfer from the aluminium quinolate moiety to the lanthanide complex and thus lead to an enhancement of the NIR emission.

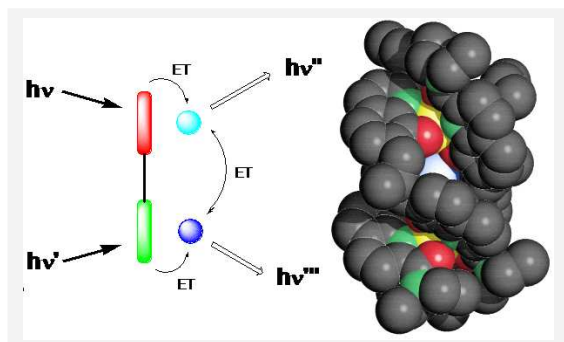
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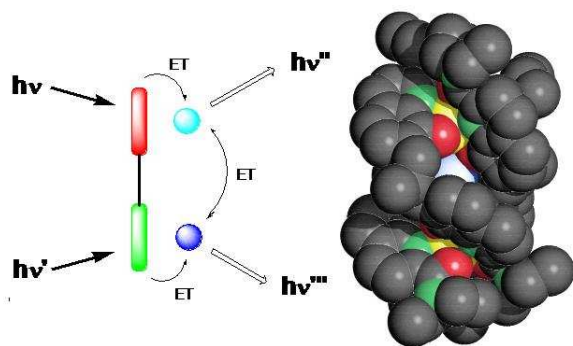
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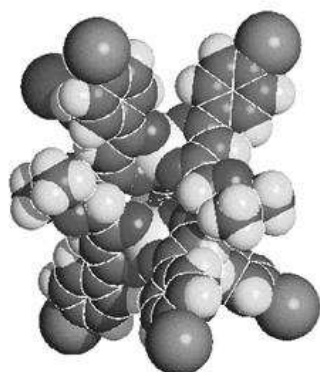
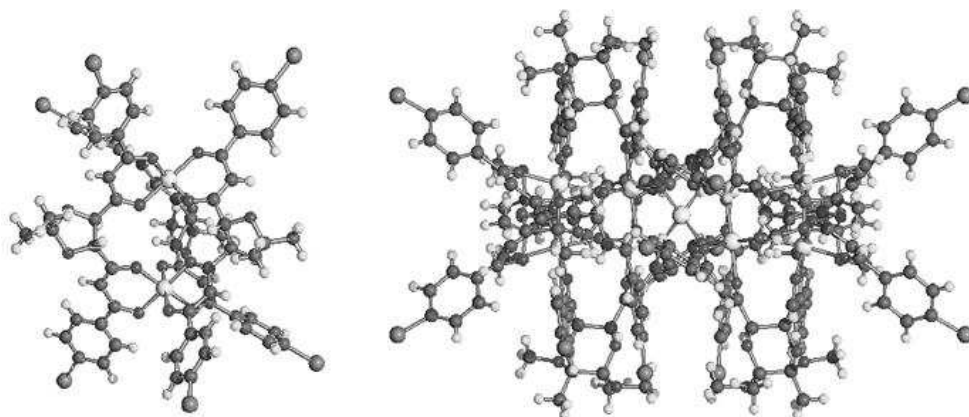
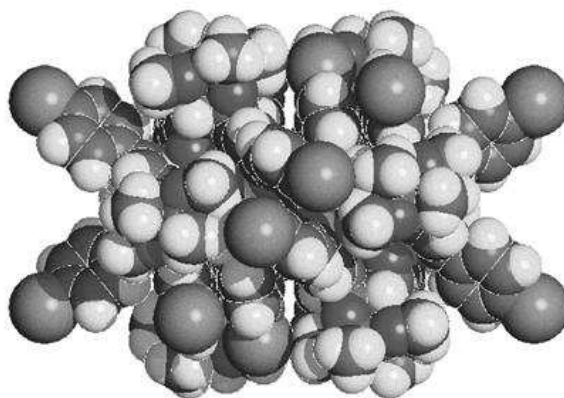
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Homo- and Heterodinuclear Lanthanide Helicates as Visible- and NIR-Emitters 

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 $[(3d)_3Ga_2]$  $[(4d)_8Ga_9(OH)_{10}]^+$

184x223mm (96 x 96 DPI)

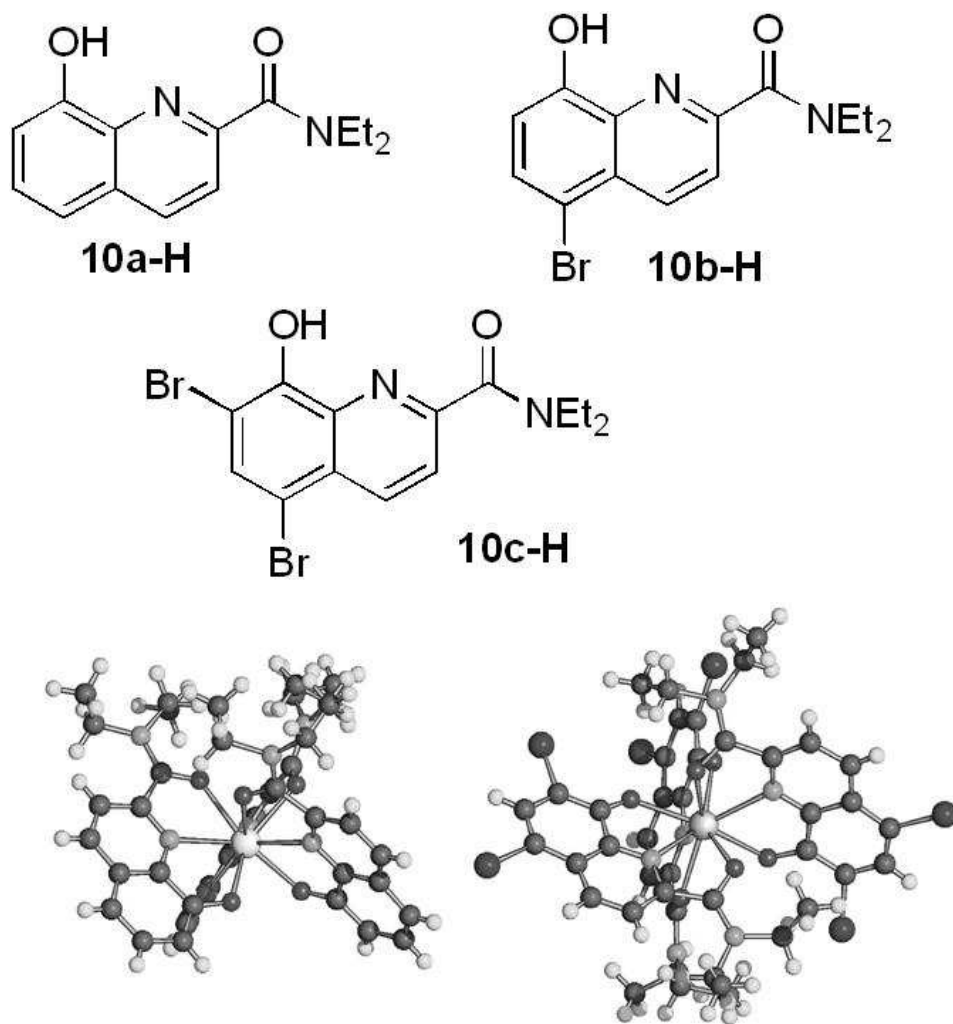


Figure 5. Ligands (10a-c)-H for the formation of 3:1 lanthanide(III) complexes. Parts of the crystal structures of syn-(10a)₃Er (left) and anti-(10c)₃Yb (right) are shown.
184x223mm (96 x 96 DPI)

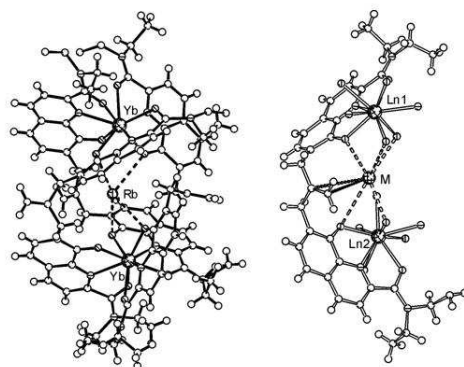


Figure 7. The solid state structure of the cation $[(13c)3Yb2Rb]^+$ as a representative example for the obtained helicates (left) and a representation of the interaction of the central alkali metal cation with the six quinolate oxygen atoms and the vinyl group of one of the ligand strands (right).
283x223mm (96 x 96 DPI)

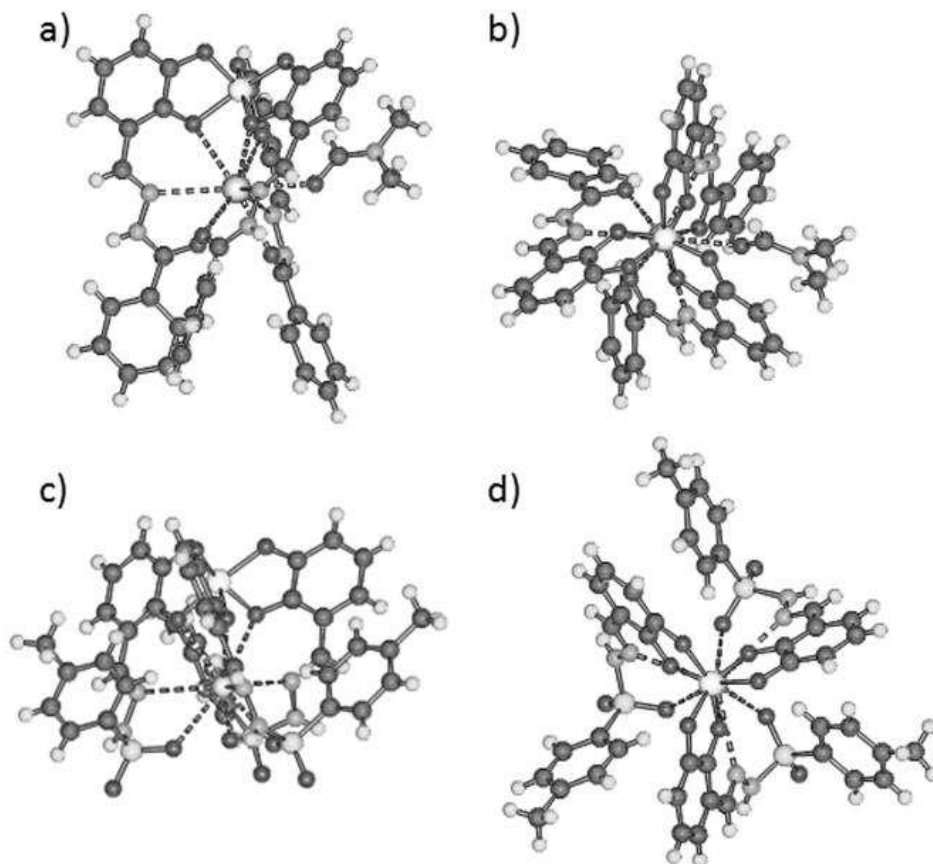


Figure 8. The structure of $(7a)_3AlLa \cdot DMF$ (a: side view, b: top view) and of $[(9)_3TiK]^-$ (c: side view, d: top view).
184x223mm (96 x 96 DPI)

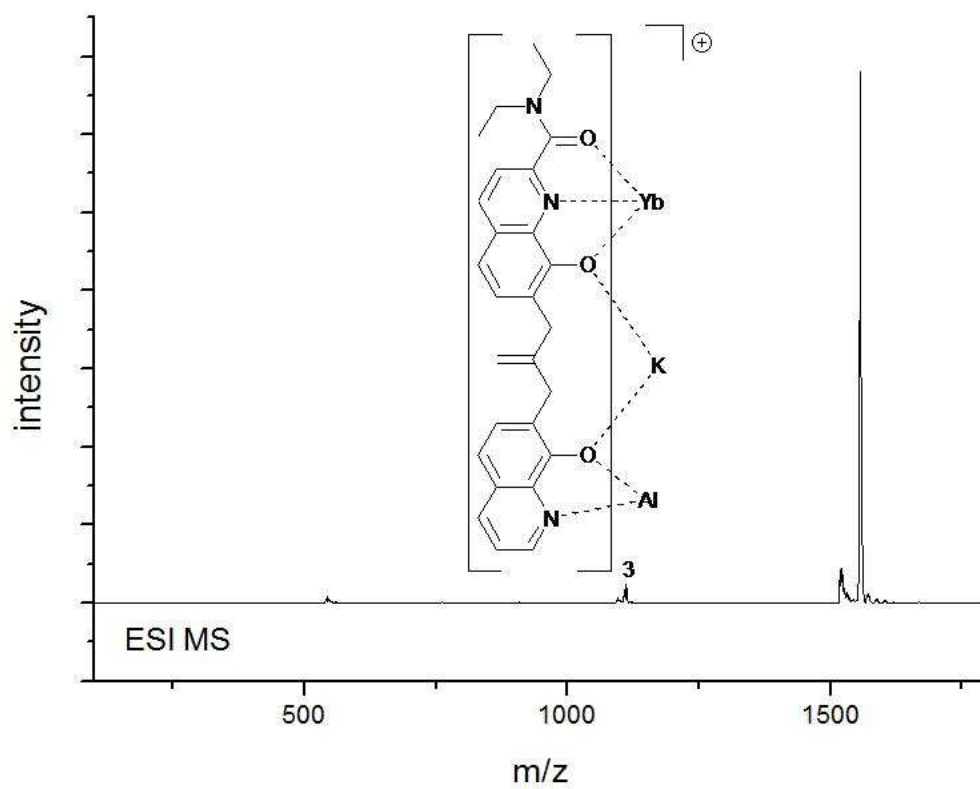


Figure 9. ESI MS showing the dominating peak of [(14c)3AlYbK]⁺.
198x223mm (96 x 96 DPI)

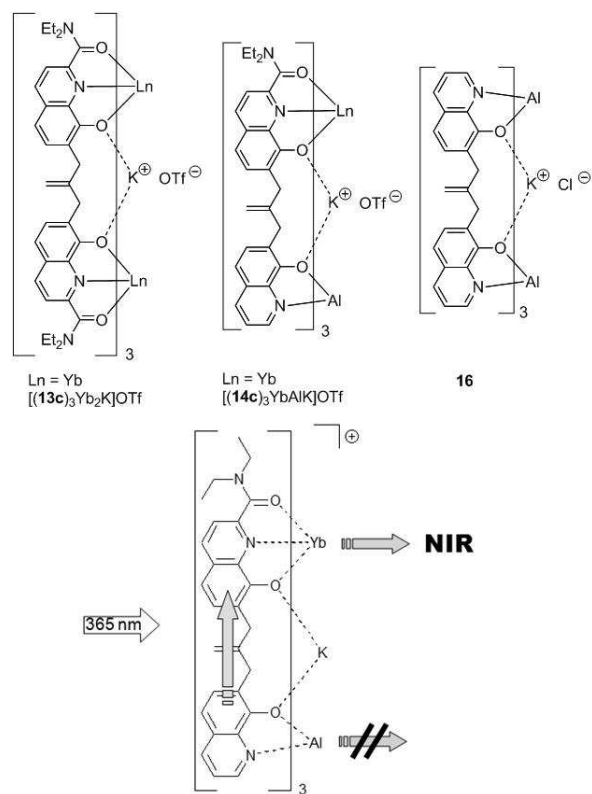


Figure 10. Light emitting triple stranded helicate type complexes and proposed energy transfer in a heterodinuclear ytterbium(III)-aluminum(III) complex.
283x223mm (96 x 96 DPI)



167x223mm (96 x 96 DPI)