Communication

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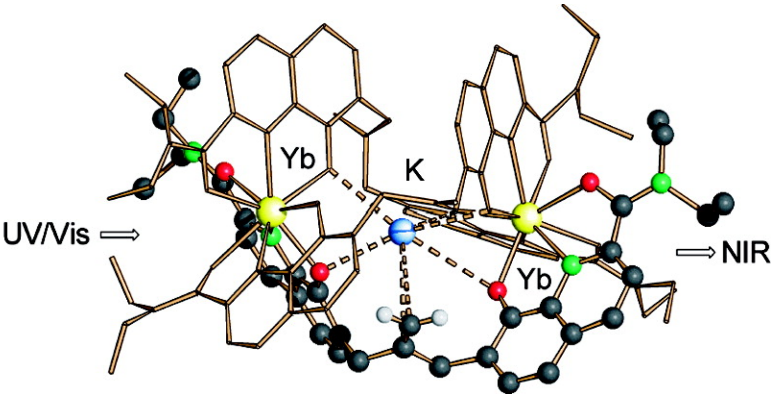

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Highly Efficient Near-IR Emitting Yb/Yb and Yb/Al Helicates

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The molecular (bottom up) approach to nanotechnology depends on the preparation or self-assembly of functional entities. Those have to possess specific and encoded properties to be used as, for example, switches, light-converting devices, molecular conductors, or for information storage.

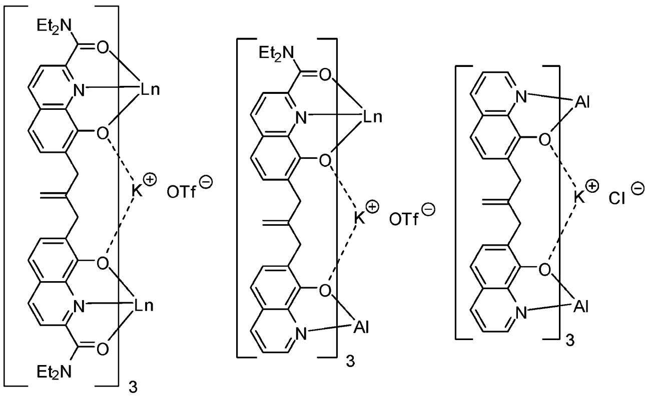
Lanthanide (Ln)-based near-infrared (NIR) emitters are of particular interest due to their potential in medical imaging and optical communication.[1] For the sensitization of Ln luminescence (either in the visible (vis) or NIR region), an adjacent strongly absorbing light harvester is required to overcome the low absorption coefficients of the trivalent lanthanides. The emitting states of the metals are populated by energy transfer (ET) from the ligand to the metal. As an alternative, directional energy transfer can occur from a closely attached metal complex to the lanthanide.[2] This was first achieved by Piguet and Bünzli for helicates with metal separations in the range of 8.8−9.0 Å.[3,4]

Here we present the design, characterization, and optical spectroscopy of new luminescent Ln/Ln, Ln/Al, and Al/Al (Ln = Eu, Gd, Yb) helicates based on 8-hydroxyquinolines (Chart 1). Particularly, the structure and NIR emission[5] properties of the homodinuclear Yb/Yb and the first p−f heterodinuclear Al/Yb helicates are addressed. Ln coordination is achieved by the recently introduced tridentate 2-amidoquinolinate binding unit, while aluminum(III) binds to bidentate hydroxyquinolinate.[6] The latter unit was chosen because of its unique emitting properties and its use as an active component in OLEDs.[7]

The complexes **1a,b** are prepared from ligand and metal triflates in a 2:3 ratio, while the heterodinuclear compounds **2a,b** are obtained from Ln triflates, $AlCl_3 \cdot xH_2O$, and the sequential ligand (1:1:3). K_2CO_3 was always added as base and as template. The synthesis of **3** was described earlier.[8]

Single crystals of **1a** were obtained from methanol/THF/chloroform/ether.[9] The structure of the cation (Figure 1) reveals the helical twist of the ligands around the Yb···K···Yb axis (162.7°). The Yb(III) ions are separated by 7.77 Å, while the templating potassium ion shows distances of 3.91 and 3.95 Å to the f metals. Each Yb ion is coordinated by three tridentate syn-arranged 2-amidoquinolinates.[6] Potassium is incorporated in an unusual matter in the cavity of the complex. It coordinates to three internal oxygen atoms with relatively short contacts of 2.7−2.8 Å. Two longer K···O bonds (3.44 and 3.57 Å) are also observed. However, one "open" front of the cation is directed toward the vinylic unit of a spacer. K−C distances of 3.22 and 3.48 Å are observed. Apparently, encapsulation enforces at least weak η^2-interaction of K^+ to the C═C bond in the crystal.

Chart 1. Homo- and Heterodinuclear Complexes ($OTf^- = [F_3CSO_3]^-$) (Eu(III) Helicates were Observed Spectrophotometrically but were Not Isolated)



Ln = Yb (**1a**)
Ln = Gd (**1b**)

Ln = Yb (**2a**)
Ln = Gd (**2b**)

3

The interaction between Yb(III) (or Eu(III)) triflate and the deprotonated symmetrical ligand has been quantified in acetonitrile in the absence of templating potassium ion by UV−vis titration. The obtained cumulative stability constants are listed in Table 1 and are very similar for Yb(III) or Eu(III); Ln_2L_3 proved to be the most stable species in solution (see Supporting Information).

NIR/vis emission spectra of **1a**, **2a**, and **3** upon ligand excitation are depicted in Figure 2, while relevant parameters for **1a** and **2a** are listed in Table 2.

The Yb(III) complexes **1a** and **2a** display efficient NIR emission upon excitation at 350 nm, arising from the $Yb(^2F_{5/2} \rightarrow {}^2F_{7/2})$ transition. The integrated NIR/vis photon ratios are 90 and 30 for **1a** and **2a**, respectively. The vis luminescence of **1a** and **2a** is centered around 630 nm, similar to that of the corresponding Gd(III) complexes **1b** and **2b** (Figure S3) with a nonemissive f metal center and is attributed to transitions within the electronic states of the ligands. Although the ligands in **1a** and **2a** are different, the $Yb(^2F_{5/2} \rightarrow {}^2F_{7/2})$ emission spectra are very similar at both 298 (Figure 2a,b) and 10 K (Figure S4), indicating a similar structural environment for the Yb(III) ions in both helicates.

The NIR quantum yield of **2a** is about 12% higher than that of **1a**. As for the quantum yields, the lifetime of the heterodinuclear complex **2a** is higher by about 16% with respect to the homodinuclear helicate **1a**. The longer luminescence lifetime and larger quantum yield of **2a** indicate less competitive nonradiative decay of the Yb(III) ions. This can possibly be traced back to an interaction between the two metal ions in **1a** leading to self-quenching.

The dinuclear Al(III) complex **3** exhibits bright green luminescence with a maximum around 535 nm (Figure 2c), similar to aluminum trisquinolinate.[7] Surprisingly, this green emission is not

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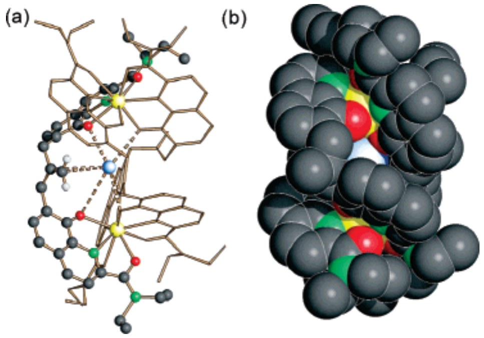

Figure 1. Molecular structure of the cation of **1a**. H-atoms (except the two vinylic H in a) as well as triflate and water are omitted for clarity. Color code: Yb, yellow; K, blue; N, green; O, red, C, black. (a) The ligand exhibiting an unusual alkene−potassium coordination is shown as ball-and-stick model. (b) Space-filling model showing the helical arrangement of the ligands around the Yb···K···Yb axis.

Table 1. Cumulative Stability Constants (log $\beta_{mn}(\sigma)$) for the Complexes $[Ln_mL_n]^{3m-2n}$ (acetonitrile, 298 K, M = Eu, Yb)

species	Eu	Yb
$[LnL_2]^-$	13.9(2)	13.3(2)
$[LnL_3]^{3-}$	18.5(3)	18.1(3)
$[Ln_2L_3]$	**26.1(3)**	**25.7(3)**
$[Ln_2L_2]^{2+}$	19.3(2)	19.0(2)

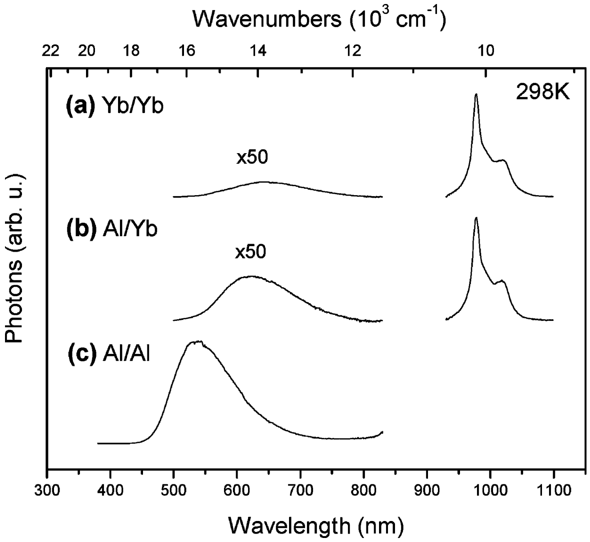

Figure 2. Normalized room temperature emission spectra upon excitation at 350 nm of powders of (a) **1a**, (b) **2a**, and (c) **3**. The vis emission spectra of a and b are multiplied by a factor of 50.

Table 2. Room Temperature Luminescence Lifetimes of Yb^{3+} ($^2F_{5/2}$) Monitored at 980 nm upon Excitation at 355 nm and Quantum Yields Measured in an Integration Sphere upon Excitation at 392 nm of Powders of **1a** and **2a**

	1a	**2a**
$\tau \pm 2\sigma$ (298 K)	18.8 ± 0.1 μs	22.6 ± 0.2 μs
$\Phi \pm 2\sigma$ (298 K)	1.04 ± 0.07%	1.17 ± 0.03%

observed in the emission spectrum of **2a**, which indicates energy transfer from the aluminum quinolinate to the electron-poor amidoquinolinate moiety of the ligand.

In summary, we have shown that self-assembly of the homobimetallic helicates is templated by a potassium cation through a rare $K^+-\pi$ interaction of C═C η^2-bond type. However, in acetonitrile solution, absence of the templating cation is not detrimental to the formation of very stable Ln_2L_3 helicates.

The compounds **1a/2a** incorporating Yb(III) ions display efficient NIR emission, demonstrating that the choice of the sensitizing units is adequate. The ligand design is versatile enough to plan the isolation of other homo- and heterometallic NIR-emitting helicates, as well as of enantiomerically pure assemblies. Further investigations on the self-assembly of homo- and heteronuclear lanthanide(III) complexes are in progress.

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Supporting Information Available: Experimental data, details of the stability constant determination, the photophysical studies, and X-ray structure analysis. This material is available free of charge via the Internet at http://pubs.acs.org.

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(9) X-ray data for $[K(C_{32}H_{34}N_4O_4)_3Yb_2]*CF_3SO_3*H_2O*1/2CH_3CN$, M = 2188.69, monoclinic, space group $P2_1/c$ (No. 14), $a = 15.831(1)$, $b = 24.262(1)$, $c = 26.818(2)$ Å, $\beta = 91.52(1)°$, $V = 10296.9(11)$ Å^3, $D_c = 1.412$ g cm^{-3}, $\mu = 1.938$ mm^{-1}, $Z = 4$, $\lambda = 0.71073$ Å, $T = 198(2)$ K, 35448 reflections collected ($\pm h$, $\pm k$, $\pm l$), $[(\sin\theta)/\lambda] = 0.54$ Å^{-1}, 13431 independent ($R_{int} = 0.180$) and 5398 observed reflections $[I \geq 2\sigma(I)]$, 557 refined parameters, $R = 0.140$, $wR^2 = 0.387$.

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