Fully Efficient Direct Yb-to-Er Energy Transfer at Molecular Level in a Near-Infrared Emitting Heterometallic Trinuclear Quinolinolato Complex

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S Supporting Information

ABSTRACT: Combined chemical/photophysical studies on the mixed Yb−Er trinuclear lanthanide quinolinolato compound Yb_2ErQ_9 and on the corresponding Yb_3Q_9 analogue have been performed. In the mixed-metal molecular species, the ligands, acting as a bridge, allow the two metals to lie at optimal distance for direct Yb-to-Er resonance energy transfer, which reaches nearly unitary efficiency. The obtained results show that polynuclear lanthanide complexes provide a suitable strategy for achieving effective erbium sensitization in solution-processable molecular materials.
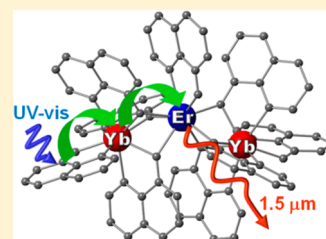
SECTION: Molecular Structure, Quantum Chemistry, and General Theory

Lanthanide ions emitting in the near-infrared (NIR) region are of considerable current interest for various applications in the telecommunication or biomedical fields.[1−3] In fact, these ions exhibit emission peaks wavelengths falling in telecom windows and suitable penetration of the radiation in biological tissue. However, the very small absorption coefficients of the lanthanide-based absorption transitions require the use of highly efficient light-harvesting "antennas" for resonance energy transfer (RET) to the higher energy levels of these emitting ions. In recent years there has been significant interest in Er^{3+} sensitization through RET from Yb^{3+} in ion-implanted/codoped glass host materials because the absorption cross section of Yb^{3+} at 1 μm is approximately 10 times higher than that of Er^{3+} and energy transfer can occur between the $^2F_{5/2}$ level of Yb^{3+} and the resonant $^4I_{11/2}$ level of Er^{3+}. Enhancement of Er^{3+} NIR emission at 1.5 μm has been achieved in glass host Yb−Er codoped optical fiber amplifiers.[4−8] For efficient Yb-to-Er RET through a Förster's mechanism, the distance between the two ions must be limited.[9] However, it is often difficult to control the Er^{3+} and Yb^{3+} doping concentration accurately and homogeneously, resulting in difficult quantitative analysis of RET from Yb^{3+} to Er^{3+}.[2] A strategy to achieve composition control can rely on the encapsulation of Er and Yb in the same molecule to afford intermetallic communication between lanthanide ions at short distance in a discrete polynuclear architecture.

So far there has been very limited work on mixed lanthanide complexes for NIR luminescence,[10−16] and, to the best of our knowledge, there are only a couple of very recent reports of mixed Yb−Er heterobimetallic molecular complexes.[10,11] Erbium emission enhancement was found in some of the very few reported cases of codoped Yb−Er compounds such as mononuclear Er and Yb complexes stoichiometrically cocrystallized[12] or equimolar mixture forming dimers in solutions of noncoordinating solvents[13] and polymeric structures.[14,15] In these compounds, however, Yb-to-Er RET can only be observed for samples in the solid state or in solution/suspension of selected solvents. This hampers the processing potential of these materials through convenient, easy-to-handle, solution methods such as the sol−gel process[17] or by techniques commonly used for the fabrication of electroluminescent devices such as vacuum deposition.[18−20]

Because of its coordinating properties and bridging ability toward lanthanide ions, the 8-quinolinolato (Q) ligand is a good candidate to prepare polynuclear discrete lanthanide complexes in which the metal centers lie at short distances (within few angstroms) from each other.[21−26] In the trinuclear Er_3Q_9[23,24] and Ho_3Q_9[25] complexes the Q ligands fully saturate the metal coordination sphere and prevent water molecules (the most important quenchers for NIR emission) from directly binding to the lanthanide ion. Moreover, it has been demonstrated that 8-quinolinolato ligands are highly efficient light-harvesting "antennas" for RET to the higher energy levels of NIR-emitting lanthanide ions (sensitized emission).[27−32]

Herein we report a novel trinuclear mixed Yb−Er quinolinolato (Q) complex, Yb_2ErQ_9, in which fully efficient direct Yb-to-Er energy transfer is demonstrated at molecular

Scheme 1. Synthesis of 1 and 2

$2Yb^{3+} + Ln^{3+} + 3$ [quinolinol ligand] $\xrightarrow[NH_3]{H_2O}$ [structure]

Ln = Yb (1), Er (2)
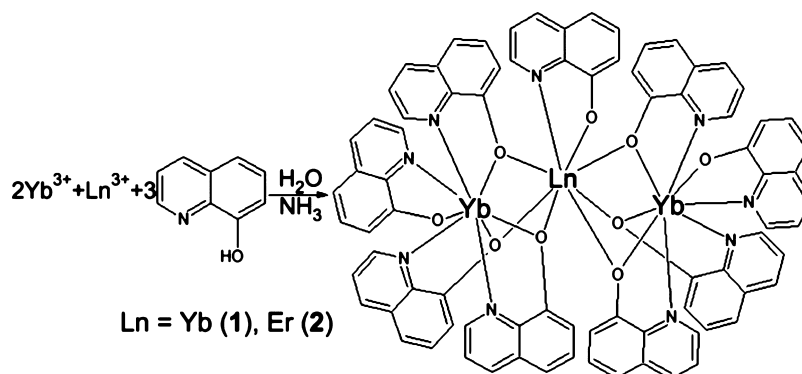
level in a solution-processable emissive material. To add further support to our findings, results are compared with those found for the complex Yb_3Q_9 whose trinuclear structural arrangement is newly demonstrated here.

The syntheses of Yb_3Q_9 (1) and Yb_2ErQ_9 (2) were carried out following the synthetic procedure already optimized for the preparation of Er_3Q_9.[23,24] 1 was synthesized using $YbCl_3$ as starting material through a one-pot reaction, whereas the mixed complex 2 was similarly prepared by adding Yb and Er salts in 2:1 molar ratio to the ligand solution. Microcrystalline pure products were obtained after recrystallization from CH_3CN. See Scheme 1.

Analytical data for these compounds (elemental analysis, vibrational spectroscopy in the mid- and far-infrared) compare well with those of the analogous Er_3Q_9 complex, suggesting the same stoichiometry and trinuclear structural arrangement for 1 and 2, which also have similar powder X-ray diffraction patterns (Supporting Information).

EDX analysis on crystalline samples confirms the purity and homogeneity of the compounds and provides evidence of Yb:Er molar ratio close to 2:1 in 2 (Supporting Information). The ESI-mass spectra of 1 and 2 (Figure 1) show the presence of
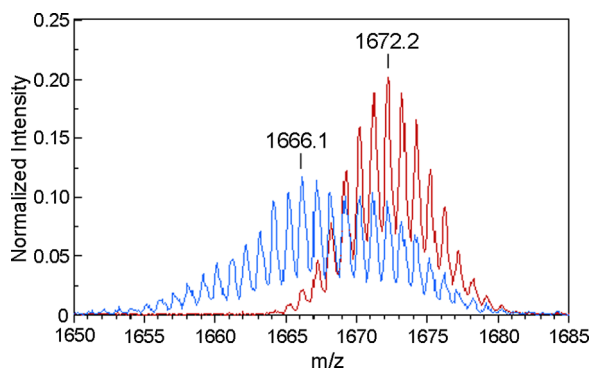

Figure 1. Expanded region of the ES(+) mass spectrum of 1 (red) and 2 (blue) in $CH_3CN/MeOH$ 3/1.

peaks related to $[Ln_3Q_8]^+$ fragments similarly to results found for Er_3Q_9,[23] clearly demonstrating that both compounds possess a trinuclear structure that is also preserved in solution. The most intense peak in the spectrum of 2 is related to the mixed species $[Yb_2ErQ_8]^+$ ($m/z=1666.54$), confirming the coexistence of Yb and Er in the same discrete molecular architecture. The asymmetric shape of this peak hints at a statistical mixture of Yb/Er trinuclear species in the sample. (See the Supporting Information.)

Taking the molecular structure of Er_3Q_9 as model,[23] it is then possible to reasonably assume an intermetallic $Yb^{3+}\cdots Er^{3+}$ distance of ~3.5 Å. Such short distance will prove crucial to allow for efficient intermetallic communication through RET between the two metals.

All of the spectroscopic and photophysical studies on the investigated compounds were performed on diluted (10^{-3} M) solutions of the strongly coordinating dimethyl sulfoxide (DMSO) solvent to ensure that the observed properties are related to isolated molecules rather than to aggregates or clusters.[13] The NIR absorption and photoluminescence (PL) spectra of 1 and 2 are reported in Figure 2 and compared with
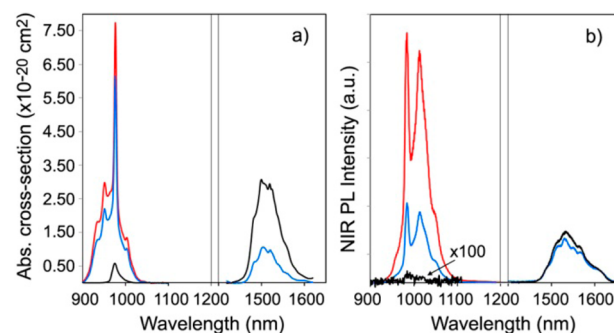

Figure 2. NIR absorption (a) and PL (b) spectra of 1 (red) and 2 (blue) compared with Er_3Q_9 (black) in DMSO solution. Er absorption cross sections at 1.5 μm are corrected for solvent effects (Supporting Information). PL spectra, obtained after ligand excitation at 392 nm, are normalized to the same complex concentration (10^{-3} M) and laser fluences.

the analogous Er_3Q_9 complex. Absorption and emission bands are related to intrashell f–f transitions of Yb^{3+} and Er^{3+}, which are slightly broadened due to small crystal field effects that partially remove the degeneracy of lanthanide f levels. 1 shows one absorption peak whose most intense line is centered at 977 nm and corresponds to the fundamental $^2F_{5/2} \leftarrow {}^2F_{7/2}$ transition of Yb^{3+} ($\sigma_{Yb}[^2F_{5/2} \leftarrow {}^2F_{7/2}] = 2.6 \times 10^{-20}$ cm^2). Two absorption bands are instead recognized for 2, which are attributed to the $^2F_{5/2} \leftarrow {}^2F_{7/2}$ transition of Yb^{3+} (1 μm, $\sigma_{Yb}[^2F_{5/2} \leftarrow {}^2F_{7/2}] = 2.8 \times 10^{-20}$ cm^2) and to the $^4I_{13/2} \leftarrow {}^4I_{15/2}$ transition of Er^{3+} at ~1.5 μm ($\sigma_{Er}[^4I_{13/2} \leftarrow {}^4I_{15/2}] = 1.0 \times 10^{-20}$ cm^2). The $Er^{3+} {}^4I_{11/2} \leftarrow {}^4I_{15/2}$ transition at 980 nm is hidden by Yb absorption in 2 but is clearly visible in the spectrum of Er_3Q_9 ($\sigma_{Er}[^4I_{11/2} \leftarrow {}^4I_{15/2}] = 0.2 \times 10^{-20}$ cm^2). See the Supporting Information. The Yb radiative lifetimes, representing the oscillator strength of the emitter in the absence of deactivating

processes, are retrieved from absorption cross sections through the Strickler–Berg equation.[33] The obtained values τ_{rad} = 620 μs for **1** and τ_{rad} = 550 μs for **2** are in accordance with those determined for similar ytterbium quinolinolato complexes[29,30,34] although significantly lower than "literature values" commonly accepted.[35]

Upon excitation in the ligand lowest absorption band at 392 nm (see the Supporting Information), **1** shows NIR PL at ~1 μm related to the $Yb^{3+2}F_{5/2} \rightarrow {}^2F_{7/2}$ transition, while **2** displays dual NIR luminescence due to the coexistence of Yb^{3+} (977 nm, ${}^2F_{5/2} \rightarrow {}^2F_{7/2}$) and Er^{3+} (1530 nm, ${}^4I_{13/2} \rightarrow {}^4I_{15/2}$). The very weak erbium emission at 980 nm (${}^4I_{11/2} \rightarrow {}^4I_{15/2}$), recognizable in the spectrum of Er_3Q_9, is probably covered by the Yb^{3+} band. Noticeably, in **2** the intensity of ytterbium luminescence is ~30% that observed for an equimolar solution of **1**, whereas erbium emission is almost as intense as in Er_3Q_9, where the erbium atomic ratio 1:3 between the two compounds. These findings hint at effective energy transfer taking place in **2** between Yb and Er, which can be better quantified through time-resolved spectroscopic studies. The NIR emission dynamics at 1 and 1.5 μm of **1** and **2** excited at 392 nm are reported in Figure 3 and compared with Er_3Q_9 as reference.

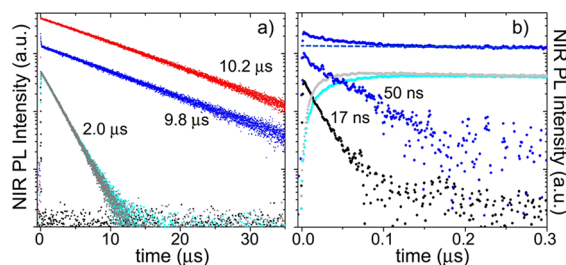**Figure 3.** (a) NIR decay dynamics of **1** (red), **2** (blue), and Er_3Q_9 (black) at 1 μm and of **2** (cyan) and Er_3Q_9 (gray) at 1.5 μm. (b) NIR dynamics on a short time scale of **2** (blue) and Er_3Q_9 (black) at 1 μm and of **2** (cyan) and Er_3Q_9 (gray) at 1.5 μm. The short-lived component of the signal of **2** is retrieved by subtracting the long-lived component attributed to Yb_3Q_9 (dashed line). Single-exponential decay time constants are also displayed. Excitation wavelength was 392 nm. Intensities are normalized to the same complex concentration (10^{-3} M) and laser fluences.

Erbium emission is detected for **2** at 1.5 μm with the same dynamics as Er_3Q_9 (τ = 2.0 μs). The $Er^{3+4}I_{13/2}$ level in Er_3Q_9 is fed through relaxation from the higher ${}^4I_{11/2}$ level, which gives a ultrafast decay at 980 nm (τ = 17 ns), shown in Figure 3b. A monoexponential decay of Yb emission is observed for **1** at 980 nm yielding a time constant of τ_{Yb} = 10.2 μs, so that the intrinsic quantum yield of Yb can be calculated as $\Phi_{Yb} = \tau_{Yb}/\tau_{rad}$ = 1.6 × 10^{-2}, in agreement with values already observed for analogous Yb quinolinolates.[29–32] For **2**, two signal components are clearly distinguishable at 1 μm with associated time constants differing by almost three orders of magnitude. The longer decay signal yields approximately the same time constant as **1** (τ_{Yb} = 9.8 μs) and can therefore be attributed to the presence of Yb_3Q_9 species in the sample. These results show that PL measurements provide useful information, not easily retrievable from conventional analytical characterization methods, of the statistical composition of **2**, which, for a nominal Yb:Er 2:1 atomic ratio, should consists of a mixture of mixed Yb–Er species, which are predominant (~44% Yb_2ErQ_9 and 22% $YbEr_2Q_9$), and homometallic ones (ca. 30% Yb_3Q_9 and a negligible amount of Er_3Q_9). In fact, the intensity of the

longer decay component in **2** is ~30% of the signal of **1**, in agreement with the Yb_3Q_9 fraction in the sample. The shorter decay component of **2** can therefore be easily extrapolated by subtracting the long-lived component to the observed decay curve, as shown in Figure 3b, and a time constant of τ_{YbEr} = 50 ns can be retrieved through monoexponential fitting. This lifetime is longer than that related to the ${}^4I_{11/2}$ level of Er^{3+}, and its intensity is about one order of magnitude higher. Therefore this ultrafast decay signal can be reliably entirely attributed to the ytterbium ${}^2F_{7/2}$ decay strongly quenched (Φ_{Yb} = 9.1 × 10^{-5}) by efficient direct energy transfer to the resonant ${}^4I_{11/2}$ level of Er^{3+}, as schematically depicted in Figure 4. These
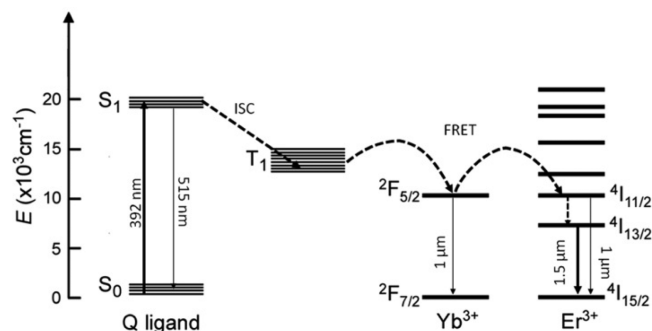

Figure 4. Jablonski diagram depicting the energy levels of the Q ligand, Yb^{3+}, and Er^{3+} and the full photocycle in trinuclear quinolinolato complexes. Dashed arrows represent nonradiative processes. Thick arrows indicate the mechanism of Yb-sensitized Er emission in mixed Yb–Er Q-complex.

considerations find further support in the analysis of the Er 1.5 μm signal rise times in Er_3Q_9 and **2**, which are compatible with the ultrafast decay time constants detected at 1 μm in the two cases (Figure 3b).

Taking into account the fact that erbium emission intensities are practically equal for equimolar solutions of **2** and Er_3Q_9, in both emission spectra (Figure 2b) and transient PL experiments (Figure 3) in a low-excitation regime of 0.1 excitations per complex (per pulse), it can be reasonably inferred that Yb-to-Er RET in the mixed molecular system is nearly quantitative. This also sounds more realistic when considering that the ultralow lifetime of the Er ${}^4I_{11/2}$ level prevents energy back transfer to Yb. The emission spectral feature observed at 1 μm for **2** (Figure 2b) can consequently be attributed solely to the Yb_3Q_9 species. The quantum efficiency of RET can be easily quantified through the formula:

$$\eta_{RET} = \frac{1}{1 + \dfrac{\tau_{RET}}{\tau_{Yb}}}$$

where τ_{RET} (= 50 ns) represents the Yb-to-Er RET time constant and τ_{Yb} is the lifetime of Yb emission in the absence of erbium energy acceptors. This calculation yields 99.5% efficiency of Yb-to-Er energy transfer in the mixed species. Even taking into account the inhomogeneous composition of **2**, which retains dual luminescence at 1 and 1.5 μm due to the coexistence of Yb_3Q_9, an overall statistical average $\eta_{RET} \approx 70\%$ is predictable, which is still higher than estimations made for Yb^{3+}-Er^{3+} codoped Al_2O_3 waveguides.[4,5] By modeling this process as a dipole–dipole Förster's resonance energy transfer (FRET)[9] and taking a reliable estimation of Yb···Er distance as r = 3.5 Å, it is then possible to calculate the Förster's radius of

$R_0 \approx 10$ Å, and the time constant of donor(Yb)−acceptor(Er) FRET, $\tau_{RET} \approx 20$ ns, which is consistent with the value observed experimentally (Supporting Information).

The validity of the Förster's model for explaining Yb-to-Er energy transfer in molecular systems is further supported by results reported by Zhong et al.[12] for cocrystallized Er and Yb mononuclear complexes. In that case, taking an average Yb···Er distance of $r = 11.75$ Å in the crystal packing, $\tau_{RET} = 1.4$ ms and $\eta_{RET} = 6.1\%$ are calculated for the solid state, in accordance with experimental data. Concerning the other example of mixed Yb−Er heteropolynuclear complexes studied by Xu et al.,[10] where $r = 3.5$ Å (av.), Yb-to-Er FRET time constants of $\tau_{RET} = 3.5$ and 3.7 μs were found in Er_2Yb_2 and Yb_2Er_2 isomers, respectively. These times are rather slow and comparable to the lifetime of Yb $^2F_{5/2} \rightarrow {}^2F_{7/2}$ emission, likely robustly quenched by the presence of OH bridging groups in the Gd_2Yb_2 (1.94 μs) and Yb_2Gd_2 (2.55 μs) reference analogs, where no intermetallic FRET is possible. This leads to an estimation of $\eta_{RET} = 35-41\%$. These efficiencies are quite low if compared with our findings, hinting at indirect energy-transfer process between Yb and Er.

In conclusion, we have prepared and studied two trimetallic lanthanide (Ln = Yb, Er) quinolinolato complexes possessing the general stoichiometry Ln_3Q_9, the ytterbium complex (**1**), and the mixed Yb−Er analogue (**2**). ESI-mass spectrometry confirms that Yb and Er coexist in the same molecular structure in **2**, and 2:1 Yb:Er ratio was further established by EDX analysis. The results of spectroscopic and time-resolved studies clearly provide evidence of direct Yb-to-Er energy transfer with nearly unity efficiency at molecular level in the mixed species. Because Yb emission is so efficiently quenched by FRET to Er, this process would likely not suffer from other competitive deactivating channels such as vibrational quenching by CH groups and even water molecules.[31] These studies will therefore provide a relevant strategy for achieving effective erbium sensitization in polynuclear complexes, where the two metals lie at short distance in the same molecular structure. It must be remarked that the encapsulation of Yb and Er in the same molecule affords a suitable precursor that can be easily processed in solution to obtain doped optical waveguides and amplifiers with controlled composition and donor−acceptor distances within the Förster's radius. Further studies are in progress in our laboratory to optimize synthetic methods to obtain pure mixed Yb−Er complexes suitable to be processed for achieving these goals.

ASSOCIATED CONTENT

ⓢ Supporting Information

Experimental section, FT-IR spectra, powder XRD patterns, EDX analysis, visible spectroscopy and PL transients, ESI-mass analysis, and Förster's model. This material is available free of charge via the Internet at http://pubs.acs.org.

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Author Contributions

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Notes

The authors declare no competing financial interest.

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REFERENCES

(1) Bünzli, J.-C. G.; Piguet, C. Taking Advantage of Luminescent Lanthanide Ions. *Chem. Soc. Rev.* **2005**, *34*, 1048−1077.

(2) Bünzli, J.-C. G.; Eliseeva, S. V. Lanthanide NIR Luminescence for Telecommunications, Bioanalyses and Solar Energy Conversion. *J. Rare Earths* **2010**, *28*, 824−842.

(3) Eliseeva, S. V.; Bünzli, J.-C. G. Lanthanide Luminescence for Functional Materials and Bio-Sciences. *Chem. Soc. Rev.* **2010**, *39*, 189−227.

(4) Strohhöfer, C.; Polman, A. Absorption and Emission Spectroscopy in $Er^{3+}-Yb^{3+}$ Doped Aluminum Oxide Waveguides. *Opt. Mater.* **2003**, *21*, 705−712.

(5) Dong, B.; Feng, Z. Q.; Cao, B. S.; Zheng, J. Z. $Yb^{3+} \rightarrow Er^{3+}$ Energy Transfer in Al_2O_3 and Temperature Characteristic of Near-Infrared Photoluminescence. *J. Sol-Gel Sci. Technol.* **2009**, *50*, 383−386.

(6) Wong, W. H.; Pun, E. Y. B.; Chan, K. S. $Er^{3+}-Yb^{3+}$ Codoped Polymeric Optical Waveguide Amplifiers. *Appl. Phys. Lett.* **2004**, *84*, 176−178.

(7) Chryssou, C. E.; Di Pasquale, F.; Pitt, C. W. Improved Gain Performance in Yb^{3+}-Sensitized Er^{3+}-Doped Alumina (Al_2O_3) Channel Optical Waveguide Amplifiers. *J. Lightwave Technol.* **2001**, *19*, 345−349.

(8) Chiasera, A.; Tosello, C.; Moser, E.; Montagna, M.; Belli, R.; Goncalves, R. R.; Righini, G. C.; Pelli, S.; Chiappini, A.; Zampedri, L.; Ferrari, M. Er^{3+}/Yb^{3+}-Activated Silica−Titania Planar Waveguides for EDPWAs Fabricated by RF-Sputtering. *J. Non-Cryst. Solids* **2003**, *322*, 289−294.

(9) Förster, T. Transfer Mechanism of Electronic Excitation. *Discuss. Faraday Soc.* **1959**, *27*, 7−17.

(10) Xu, H. B.; Deng, J. G.; Zhang, L. Y.; Chen, Z. N. Structural and Photophysical Studies on Geometric (Er_2Yb_2/Yb_2Er_2) and Configurational ($EuTb_3/Eu_3Tb$) Isomers of Heterotetranuclear Lanthanide(III) Complexes. *Cryst. Growth Des.* **2013**, *13*, 849−857.

(11) Gao, T.; Yang, Y.; Sun, W. B.; Li, G. M.; Hou, G. F.; Yan, P. F.; Lia, J. T.; Din, D. D. Syntheses, Structure and Near-Infrared (NIR) Luminescence of Er_2, Yb_2, ErYb of Homodinuclear and Heterodinuclear Lanthanide(III) Complexes Based on Salen Ligand. *CrystEngComm* **2013**, *15*, 6213−6220.

(12) Zhong, Q.; Wang, H.; Qian, G.; Wang, Z.; Zhang, J.; Qiu, J.; Wang, M. Novel Stoichiometrically Erbium-Ytterbium Cocrystalline Complex Exhibiting Enhanced Near-Infrared Luminescence. *Inorg. Chem.* **2006**, *45*, 4537−4543.

(13) Tanaka, F.; Ishibashi, T. Energy Transfer between Lanthanide Ions in Dinuclear Complexes. *J. Chem. Soc., Faraday Trans.* **1996**, *92*, 1105−1110.

(14) White, K. A.; Chengelis, D. A.; Gogick, K. A.; Stehman, J.; Rosi, N. L.; Petoud, S. Near-Infrared Luminescent Lanthanide MOF Barcodes. *J. Am. Chem. Soc.* **2009**, *131*, 18069−18071.

(15) Song, L.; Hu, J.; Wang, J.; Liu, X.; Zhen, Z. Novel Perfluorodiphenylphosphinic Acid Lanthanide (Er or Er−Yb) Complex with High NIR Photoluminescence Quantum Yield. *Photochem. Photobiol. Sci.* **2008**, *7*, 689−693.

(16) Faulkner, S.; Pope, S. J. A. Lanthanide-Sensitized Lanthanide Luminescence: Terbium-Sensitized Ytterbium Luminescence in a Trinuclear Complex. *J. Am. Chem. Soc.* **2003**, *125*, 10526−105267.

(17) Artizzu, F.; Quochi, F.; Saba, M.; Loche, D.; Serpe, A.; Mercuri, M. L.; Mura, A.; Bongiovanni, G.; Deplano, P. Silica Sol-Gel Glasses Incorporating Dual-Luminescent Yb Quinolinolato Complex: Processing, Emission and Photosensitising Properties of the 'Antenna' Ligand. *Dalton Trans.* **2012**, *41*, 13147−13153.

(18) Curry, R. J.; Gillin, W. P. 1.54 μm Electroluminescence from Erbium(III) Tris(8-hydroxyquinoline) (ErQ)-Based Organic Light-Emitting Diodes. *Appl. Phys. Lett.* **1999**, *75*, 1380−1382.

(19) Gillin, W. P.; Curry, R. J. 1.54 μm Erbium (III) Tris(8-Hydroxyquinoline) (ErQ): A Potential Material for Silicon Compatible 1.5 μm Emitters. *Appl. Phys. Lett.* **1999**, *74*, 798−800.

(20) Khreis, O. M.; Gillin, W. P.; Somerton, M.; Curry, R. J. 980 nm Electroluminescence from Ytterbium Tris(8-Hydroxyquinoline). *Org. Electron.* **2001**, *2*, 45−51.

(21) Artizzu, F.; Mercuri, M. L.; Serpe, A.; Deplano, P. NIR-Emissive Erbium−Quinolinolate Complexes. *Coord. Chem. Rev.* **2011**, *255*, 2514−2529.

(22) Van Deun, R.; Fias, P.; Nockemann, P.; Schepers, A.; Parac-Vogt, T. N.; Van Hecke, K.; Van Meervelt, L.; Binnemans, K. Rare-Earth Quinolinates: Infrared-Emitting Molecular Materials with a Rich Structural Chemistry. *Inorg. Chem.* **2004**, *43*, 8461−8469.

(23) Artizzu, F.; Deplano, P.; Marchiò, L.; Mercuri, M. L.; Pilia, L.; Serpe, A.; Quochi, F.; Orrù, R.; Cordella, F.; Meinardi, F.; et al. Structure and Emission Properties of Er₃Q₉ (Q = 8-Quinolinolate). *Inorg. Chem.* **2005**, *44*, 840−842.

(24) Artizzu, F.; Deplano, P.; Marchiò, L.; Mercuri, M. L.; Pilia, L.; Serpe, A.; Quochi, F.; Orrù, R.; Cordella, F.; Saba, M.; et al. New Insights on Near-Infrared Emitters Based on Er-Quinolinolate Complexes: Synthesis, Characterisation, Structural and Photophysical Properties. *Adv. Funct. Mater.* **2007**, *17*, 2365−2376.

(25) Leary, S. G.; Deacon, G. B.; Junk, P. C. The Synthesis of a Homoleptic Lanthanoid Complex of the 8-Quinolinolate Ion Directly from the Metal. *Z. Anorg. Allg. Chem.* **2005**, *631*, 2647−2650.

(26) Bozoklu, G.; Marchal, C.; Pecaut, J.; Imbert, D.; Mazzanti, M. Structural and Photophysical Properties of Trianionic Nine-Coordinated Near-IR Emitting 8-Hydroxyquinoline-Based Complexes. *Dalton Trans.* **2010**, *39*, 9112−9123.

(27) Quochi, F.; Saba, M.; Artizzu, F.; Mercuri, M. L.; Deplano, P.; Mura, A.; Bongiovanni, G. Ultrafast Dynamics of Intersystem Crossing and Resonance Energy Transfer in Er(III)-Quinolinolate Complexes. *J. Phys. Chem. Lett.* **2010**, *1*, 2733−2737.

(28) Quochi, F.; Artizzu, F.; Saba, M.; Cordella, F.; Mercuri, M. L.; Deplano, P.; Loi, M. A.; Mura, A.; Bongiovanni, G. Population Saturation in Trivalent Erbium Sensitized by Organic Molecular Antennae. *J. Phys. Chem. Lett.* **2010**, *1*, 141−144.

(29) Artizzu, F.; Quochi, F.; Saba, M.; Marchiò, L.; Espa, D.; Serpe, A.; Mura, A.; Mercuri, M. L.; Bongiovanni, G.; Deplano, P. Dual Emitting [Yb(5,7ClQ)₂(H5,7ClQ)₂Cl]: Chemical and Photophysical Properties. *ChemPlusChem* **2012**, *77*, 240−248.

(30) Shavaleev, N. M.; Scopelliti, R.; Gumy, F.; Bünzli, J.-C. G. Surprisingly Bright Near-Infrared Luminescence and Short Radiative Lifetimes of Ytterbium in Hetero-Binuclear Yb-Na Chelates. *Inorg. Chem.* **2009**, *48*, 7937−7946.

(31) Shavaleev, N. M.; Scopelliti, R.; Gumy, F.; Bünzli, J.-C. G. Modulating the Near-Infrared Luminescence of Neodymium and Ytterbium Complexes with Tridentate Ligands Based on Benzoxazole-Substituted 8-Hydroxyquinolines. *Inorg. Chem.* **2009**, *48*, 2908−2918.

(32) Albrecht, M.; Osetska, O.; Klankermayer, J.; Frohlich, R.; Gumy, F.; Bünzli, J.-C. G. Enhancement of Near-IR Emission by Bromine Substitution in Lanthanide Complexes with 2-Carboxamide-8-Hydroxyquinoline. *Chem. Commun.* **2007**, 1834−1836.

(33) Strickler, S. J.; Berg, R. A. Relationship between Absorption Intensity and Fluorescence Lifetime of Molecules. *J. Chem. Phys.* **1962**, *37*, 814−822.

(34) Bünzli, J.-C. G.; Chauvin, A.-S.; Kim, H. K.; Deiters, E.; Eliseeva, S. V. Lanthanide Luminescence Efficiency in Eight- and Nine-Coordinate Complexes: Role of the Radiative Lifetime. *Coord. Chem. Rev.* **2010**, *254*, 2623−2633.

(35) Werts, M. H. V.; Jukes, R. T. F.; Verhoeven, J. W. The Emission Spectrum and the Radiative Lifetime of Eu³⁺ in Luminescent Lanthanide Complexes. *Phys. Chem. Chem. Phys.* **2002**, *4*, 1542−1548.