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Published on 24 July 2009 on http://pubs.rsc.org | doi:10.1039/B906494J

Perfluorinated nitrosopyrazolone-based erbium chelates: a new efficient solution processable NIR emitter†

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Received (in Cambridge, UK) 1st April 2009, Accepted 9th July 2009
First published as an Advance Article on the web 24th July 2009
DOI: 10.1039/b906494j

We show the design and synthesis of new perfluorinated nitrosopyrazolone-based ligands and the original method employed for their complexation of erbium ions in the presence of the co-ligand perfluorotriphenylphosphine oxide; the resulting chelate is non-hygroscopic, solution processable and possesses a NIR emission with lifetimes as long as 16 μs.

Interest in the development of efficient NIR emitting organic derivatives is connected with the recent development of plastic optical fibers.[1] While in fact it is accepted that silica-based optical technologies will remain unchallenged for long distance information transmission, short distance telecommunications, such as LAN, are expected to profit from alternative, low cost, plastic-based solutions. However, the more the absorption (and emission) of an organic compound is shifted towards low energies, the less the compound becomes able to stand long term exposure to ambient atmosphere, especially under the device operating conditions (illumination, temperature, moisture...). This observation indicates how challenging the task of designing efficiently NIR operating organic materials may be.

The development of lanthanide-based emitting chelates represents a valuable solution. These particular compounds profit from the favorable properties of a conjugated organic ligand (efficient absorption in the UV-Vis spectrum, stability, solubility, compatibility with plastic fibers and polymers in general) and from the peculiar emission capabilities of lanthanide ions, in this case the Er^{3+} $^4I_{13/2} \rightarrow {}^4I_{15/2}$ transition at 1550 nm, matching well the POF (plastic optical fiber) transmission–loss dispersion minima.[2]

Lanthanide ions cannot be efficiently pumped directly; their absorption transitions are in fact prohibited on symmetry grounds. The population of the rare-earth excited states is best achieved through energy transfer from suitable organic ligands.[3] This strategy has been so far successfully applied to several lanthanides, including europium, whose complexes are widely employed as emitting materials in LED technologies.[4]

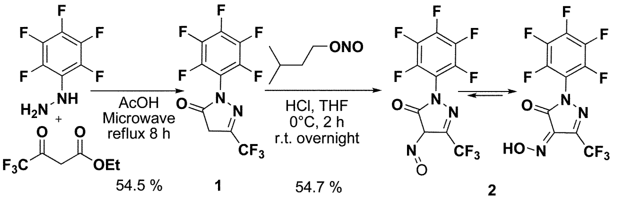
The case of erbium chelates is however more complex. Erbium emission is in fact particularly prone to non-radiative relaxation due to dipole coupling of the ion excited states with the high energy vibrational modes of the ligands and the coordinating solvent molecules. In this respect the presence of O–H, N–H and even C–H groups in close proximity to erbium is a well known and a very efficient relaxation pathway.[5] In the case of erbium tri(hydroxyquinolinate) (ErQ_3), the most studied erbium chelate, the excited state lifetime drops from the milliseconds commonly observed in erbium doped glass-based devices to a mere 0.2–2 μs depending on the environment.[6]

Recently, the use of fluorinated ligands afforded a viable solution to the vibrational quenching issue.[7] The most notable drawback of this approach is the relatively high absorption energy of the ligands employed so far, whose absorption cut-off scarcely reaches the 400 nm wavelength.[8] In view of practical applications it would be highly profitable to employ ligands having absorption spectra compatible with broad-band, low cost light sources such as high-power LED now available in the near UV region, *i.e.* 407 nm GaN laser diodes. Moreover most of the known perfluorinated chelates have been processed by high temperature vacuum evaporation, a relatively high cost process especially when compared with spin or blade coating.

We here propose a new class of perfluorinated ligands, pertaining to the class of nitrosopyrazolone derivatives, possessing efficient erbium chelating capabilities, relatively low band gaps and facile preparation procedures. Moreover, the compounds we obtained are highly soluble in common organic solvents, thus enabling the preparation of films by spin coating, and they are completely hydrophobic.

The new ligand **2** was prepared according to the classic pyrazolone synthetic scheme. Pentafluorophenyl hydrazine was thus reacted with ethyl 4,4,4-trifluoroacetoacetate in refluxing acetic acid and under microwave irradiation to give the pyrazolone derivative **1**, nitrosation of which with isoamylnitrite in THF afforded the pure ligand **2** in an overall yield of 30%. See Scheme 1.

A slight modification of the same procedure afforded ligand **3**, the hydrogenated analog of ligand **2** which was made for comparison (see the ESI†).



Scheme 1

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† Electronic supplementary information (ESI) available: Synthetic procedures, IR-spectra and DSC traces for ligands and complexes. Details on the photophysical characterization. See DOI: 10.1039/b906494j

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The structure of the nitrosopyrazolone ligands resembles that of a β-diketone, whose efficient chelating and excitation transfer capabilities towards lanthanides are well known.[9] Also, in a recent paper Zhang and co-workers demonstrated the favorable chelating capabilities of acylated pyrazolone derivatives towards erbium ions in the framework of NIR electroluminescent organic devices.[10] When compared to either standard or perfluorinated β-diketonates, ligand **2** shows a more extended conjugated structure, a design feature intended to enhance the ligand visible region absorption capabilities.

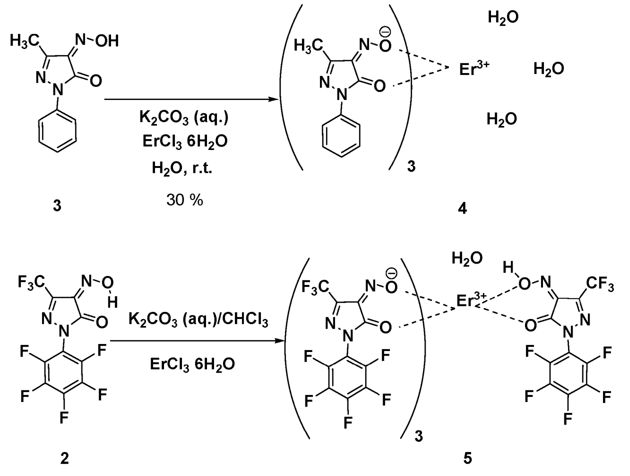
Hydrogenated and fluorinated ligands were converted to the corresponding potassium salt and reacted with a stoichiometric amount of $ErCl_3$, in water in the case of **3** and in a water–chloroform biphasic mixture in the case of ligand **2**. To the best of our knowledge the latter is an original, and resourceful, synthetic procedure.[11] In all of the attempts we made to react ligand **2** under homogeneous conditions we recovered a light pink, very insoluble precipitate that was identified as $Er(OH)_3$.

Interestingly, while in the case of **3** we obtained the trihydrated chelate **4**, ligand **2** gave, under the described biphasic conditions, the tetrakis compound **5**. In both cases the Er coordination number is 9, a common value observed in the lanthanide series. We speculate that the strong hydrophobic character imparted to the chelate by the presence of the fluorinated ligand **2** prevents more than one molecule of water from entering the coordination sphere. See Scheme 2.

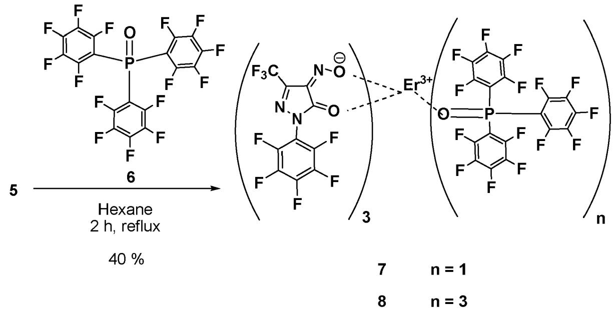
The residual water molecule was successfully removed from the coordination sphere of complex **5** by reaction with an excess of perfluorotriphenylphosphine oxide **6** in refluxing hexane. The hydrated complex, insoluble in hot hexane, gradually dissolves upon the addition of the phosphine oxide. See Scheme 3.

The complex **7** separated, after a few minutes of reflux, as a light orange solid and was immediately hot filtered. Cooling of the filtrate afforded a second light yellow precipitate that was identified as derivative **8**.

Both chelates are soluble in common organic solvents, derivative **8** in particular is highly soluble in hexane and CCl_4. All chelates were characterized by FT-IR (ATR mode) and elemental analysis (C, H, N).[12]



Scheme 2



Scheme 3

As shown in Fig. S1 of the ESI†, the final complex was isolated in a completely anhydrous form. In particular the IR spectrum of **8** shows the complete disappearance of any band in the 4000–2000 cm^{-1} region, in contrast to the spectrum of **5** where the O–H stretching mode of both the coordinating H_2O molecules and of the ligand **2** are clearly visible. We stored **7** and **8** under ambient atmosphere without taking any particular precautions and did not observe any water uptake even 6 months after the original preparation.

Fig. 1 shows the UV-Vis absorption spectrum of chelate **8** in a 1.2×10^{-5} M $CDCl_3$ solution. The inset shows a snapshot of the 500–700 nm region absorption spectrum of a 10^{-4} M chelate solution. The $^2H_{11/2}$ and $^4F_{9/2}$ Er^{3+} absorption lines, although overlapping with the ligand onset absorption, are clearly distinguishable.[13]

The relatively low energy gap of the chelates enabled us to carry out time resolved luminescence measurements at the 355 nm excitation wavelength. Then, we characterized chelates **4**, **5**, **7** and **8** in solution as well as in powder form and as cast films. The characterization of hydrogenated complex **4** is reported in the ESI†. For each sample we observed the expected characteristic emission around 1530 nm, due to the Er^{3+} $^4I_{13/2} \rightarrow {}^4I_{15/2}$ transition. We did not observe any direct emission from the ligand. This feature suggests a complete energy transfer to the erbium ion and enables the evaluation of the emission efficiency on the basis of the measured lifetime.[7] Fig. 2 shows a representative PL (photoluminescence) spectrum and decay profile of a powder sample.

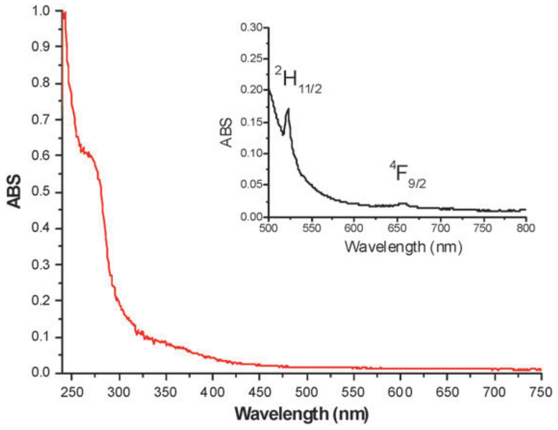


Fig. 1 UV-Vis absorption ($CDCl_3$ solution, 1.2×10^{-5} M, 1 cm optical path) of derivative **8**. Inset: snapshot of a 10^{-4} M solution absorption.

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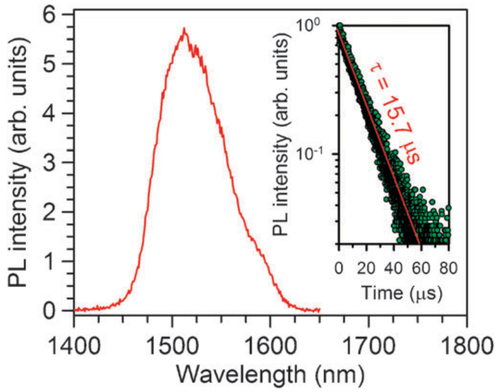

Fig. 2 PL spectrum (red line) and decay profile (inset, green dots) of a powder sample of chelate **7** excited at 355 nm. The red straight line is the fit of the luminescence decay with a single exponential function.

Table 1 PL lifetime data for **4**, **5**, **7** and **8** for various sample types

Sample type and complex	PL lifetime $\tau_1/\mu s$	Sample type and complex	PL lifetime $\tau_1/\mu s$
4		**7**	—
Solution (CCl_4)	5.4	Solution (CCl_4)	16.0
		Solution ($CDCl_3$)	14.4
5		Solid	15.7
Solution (CCl_4)	5.4	Film	15.2
Powder	5.1	**8**	—
		Solution (CCl_4)	14.7
		Powder	14.5

The luminescence decay of the emission signal at 1530 nm was shown to be best described by a single exponential process (powder samples). This demonstrates that even in the solid state erbium ions do not interact strongly, thus avoiding additional deactivation channels for the excitation energy. Table 1 summarizes the results obtained with the various samples we measured. The results clearly indicate that the lifetimes are significantly enhanced by ligand fluorination and complete removal of any hydrogen containing molecule. Chelate **7** in particular shows a solid powder emission lifetime of 15.7 μs which is substantially preserved upon deposition as a spin coated film.

As we mentioned above, the PL natural lifetimes for erbium ions are of the order of milliseconds. We speculate that the still somewhat short lifetime of the anhydrous complexes **7** and **8** could be due to the presence of trace amounts of hydrogen containing impurities coming from the employed starting materials.

Structural studies are currently being performed in order to resolve the complex crystal structure and the possible occurrence of polymorphism. Moreover, studies will be directed at the complete characterization of the specific energy transfer processes taking place between ligand and ion, with particular focus on the role of perfluorination in the overall process efficiency.

In conclusion, we believe that the exploitation of both the ligand **2**, providing an efficient antenna effect, and the co-ligand **6**, having a crucial role in the complete removal of water from the erbium coordination sphere in both **7** and **8**, represents an important entry in the growing field of NIR emitting organic materials. This is in accordance with the three most favorable features they possess: ease of preparation, high solubility providing processability, low optical gap enabling visible region pumping by commercially available LEDs. We expect to be able to further increase the performance of the complexes through the development of different functionalization patterns around the nitrosopyrazolone structure.

This work has been supported by the INSTM Consortium (PRISMA 2007), Ministero Istruzione, Università e Ricerca (PNR-FIRB RBNE033KMA) and by the Fondazione Cariplo (2005, research title: Compositi polimerici a base di innovativi complessi organolantanidi per amplificatori ottici usati nelle telecomunicazioni).

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