Sensitization of the NIR emission of Nd(III) by the α 4 atropoisomer of a meso-tetraphenyl porphyrin bearing four 8-hydroxyquinolinylamide chelates[†]‡

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The α4 atropoisomer of the meso tetrakis 8-hydroxyquinolinylamide porphyrin and its Pd complex binds Nd(III) and sensitizes efficiently its near infrared (NIR) emission when excited in the visible domain.

For many optical devices such as for example amplifiers¹ and lasers,² the luminescence properties³ of lanthanide ions are of particular interest. Indeed, lanthanide ions emit narrow bands ranging from visible to near-infrared.⁴ However, owing to the low absorption coefficients of Laporte-forbidden-f-f transitions, the emission must be sensitized by an energy transfer from chromophoric ligands⁵⁻⁹ located in the proximity of the lanthanide ion (antenna effect). Furthermore, in order to avoid quenching of the emission by non-radiative deactivation, the lanthanide cations must be protected by the presence of multidentate ligands.¹⁰

Here we report on the a4 atropoisomer of a mesotetraphenylporphyrin-based ligand bearing four 8-hydroxyquinolinyl amide chelates 2 (Scheme 1, Fig. 1) as an efficient sensitizer for the NIR emission of Nd(III).

Our design principle was based on the use of the porphyrin backbone as an antenna. The latter is perfectly suited for the sensitization of NIR emission of lanthanide cations, since it offers a triplet excited state^{4,11} typically in the range of $12\,000-17\,000$ cm⁻¹ which is higher, but still close in energy to the emitting levels of Er(III) (6500 cm⁻¹), Yb(III) (10 200 cm⁻¹)



Fig. 1 Schematic representations of the α 4 atropoisomer of the porphyrin 2 (a), [2-Nd]⁻ (b), 2-Pd (c) and [(2-Pd)–Nd]⁻ (d).

and Nd(III) (11 360 cm^{-1}). Moreover, by exploiting the binding ability of the tetraaza core of the porphyrin, it should be possible to tune the nature and the energy of the excited state by the introduction of various transition metals (Fig. 1(c)). Using the peripheral positions on the porphyrin backbone such as the β -pyrrolic positions one may further adjust the electronic levels of the antenna. Finally, by using aryl groups bearing a bulky substituent at the ortho position connected to the meso positions, one may take advantage of the formation of atropoisomers¹² and thus, in the case of the $\alpha 4$ isomer, preorganise four chelates for binding the lanthanide ion which usually adopts a coordination number in the range of 8-12 (Fig. 1(a)). We have previously achieved this by synthesising atropoisomers of a meso-(tetra-phenylcatecholamide) porphyrin.¹³

As a chelating moiety, 8-hydroxyquinoline, a monoanionic ligand when deprotonated, appeared to us as the candidate of choice. For orientation and distance reasons, the connection of the chelate was achieved using the position 7 of 8-hydroxyquinolinyl. Finally, the rather rigid amide group was used for joining the chelate and the *meso*-arylporphyrin moiety. It is worth noting that, based on CPK models, a distance of ca. 5 Å between the centroid of the four pyrrole moieties of the porphyrin and the Ln cation may be expected (Fig. 1(b)). Furthermore, the localisation of four chelates in close proximity for binding of the lanthanide ion should protect the latter from direct interactions with solvent molecules. Both the short distance mentioned above and the protection of the emitting centre should lead to efficient NIR luminescence.

For exploring the role played by transition metals complexed by the porphyrin core (Fig. 1(d)), Pd(II) appeared as an interesting candidate since Pd-porphyrin complexes possess a very efficient intersystem crossing due to the heavy metal effect and therefore the lowest excited state is a long lived triplet state as can be easily demonstrated by its efficient quenching by oxygen.^{11a}

The synthesis of compound 2 (Scheme 1) was based on the use of the a4 atropoisomer of meso-tetrakis(o-aminophenyl)porphyrin 1. The latter was prepared following the described procedure by Lindsey et al.¹⁴ The condensation of 1 with 8-hydroxy-7-quinolinecarboxylic acid, prepared according to a published procedure,¹⁵ in the presence of HBTU as a coupling reagent¹⁶ afforded the compound **2** in *ca.* 80%yield (see ESI[‡] for detailed synthesis). It is worth noting that the reaction must be performed at room temperature in order to avoid atropoisomerisation. The synthesis of the Nd(III)

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complex [2-Nd]⁻ was achieved in 82% yield in CH_2Cl_2 upon treatment of 2 by Nd(acac)₃(H₂O)₂ in the presence of one equivalent of tetrabutylammonium hydroxide (TBAOH). The [2-Nd]TBA complex is soluble in most halogenated solvents and in THF (see ESI[‡]).

For the synthesis of the heterobimetallic species [(2-Pd)Nd]TBA, in order to avoid the binding of Pd(II) by the hydroxyquinolinyl chelates, a strategy based on a threestep procedure was developed. Starting with a mixture of atropoisomers of the porphyrin 1, the reaction, under Ar, with Pd(OAc)₂ in a refluxing mixture of CHCl₃ and MeOH afforded all the metallated atropoisomers of 1-Pd. The mixture was first enriched in the $\alpha 4$ atropoisomer upon heating in toluene in the presence of silica¹⁴ and subsequently purified by column chromatography on alumina affording 1-Pd in 24% yield. The complex 2-Pd was obtained in 67% yield upon coupling of 1-Pd with 8-hydroxy-7-quinolinecarboxylic acid in the presence of HBTU in CH₂Cl₂. Finally, the formation of [(2-Pd)Nd]TBA was achieved in 55% yield as described above for [2-Nd]TBA. However, owing to the low solubility of 2-Pd complex, a mixture of CH₃CN-CH₂Cl₂ was used.

As a reference for the photophysical studies, the chelate 3 was synthesised and its Nd(III) complex [(3)₄Nd]TBA prepared



Fig. 2 Absorption spectra of **2**, [**2**-Nd]⁻, **2**-Pd, [(**2**-Pd)–Nd]⁻ in THF at room temperature.

in 73% yield upon addition of 1 eq. Nd(acac)₃ and 1 eq. TBAOH to a solution of **3** (4 eq.) in CH_2Cl_2 - CH_3CN (see ESI^{\ddagger}).

For the reference chelate **3**, the electronic absorption spectrum in THF shows an absorption maximum at 255 nm assigned to a π - π * transition¹⁷ and a shoulder at 277 nm which can be attributed to partial deprotonation of the ligand (Table 1). When compared to 8-hydroxyquinoline,¹⁸ the observed blue-shift of *ca*. 50 nm of the most intense band is due to the presence of the electron withdrawing amide group in position 7. For [(3)₄Nd]TBA, a shift of *ca*. 20 nm in the absorption maxima and the appearance of a new band at 350 nm attributed to an ILCT transition are observed (Table 1, Fig. 2).

In THF, for all four porphyrin complexes **2**, $[2-Nd]^-$, **2**-Pd and $[(2-Pd)-Nd]^-$, the UV part of the electronic spectra (Table 1) presents a relatively intense absorption band centred around 250–280 nm (Fig. 2) which can be assigned to π - π * transitions of the quinolinyl moiety as discussed previously.

The visible part of the electronic spectra of **2** and $[2-Nd]^-$ is characteristic of a free-base porphyrin with an intense Soret band around 423 and 431 nm, respectively, together with four Q bands between 510 and 650 nm (Table 1, Fig. 2).

Upon binding of Nd(III) ion, the Soret band is shifted by 8 nm and the relative intensity of the two Q bands Q(1,0) and Q(0,0) changes (Q(0,0) less intense than Q(1,0)). This might be due to a deformation of the porphyrin core induced by the presence of Nd(III). The absorption spectra of the two palladium complexes 2-Pd, and $[(2-Pd)-Nd]^-$ also display an intense Soret band at 421 and 424 nm, respectively, and only

Table 1	Spectral	data a	at RT	in	THF
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	Absorption λ/nm (ϵ/M^{-1} cm ⁻¹)	Emission λ/nm		
2	284 (8.65 × 10 ⁴), 423 (2.43 × 10 ⁵), 517 (1.67 × 10 ⁴), 549 (0.44 × 10 ⁴), 501 (0.56 × 10 ⁴), 647 (0.15 × 10 ⁴),	659; 723 ^{<i>a</i>}		
[2 -Nd] ⁻	$548 (0.44 \times 10^{\circ}), 591 (0.56 \times 10^{\circ}), 646 (0.15 \times 10^{\circ})$ $280 (6.16 \times 10^{4}), 431 (1.26 \times 10^{5}), 522 (1.10 \times 10^{4}),$	665, 720, 1070, 1340 ^a		
2 -Pd	$560 (0.85 \times 10^{\circ}), 591 (0.68 \times 10^{\circ}), 654 (0.30 \times 10^{\circ})$ $254 (9.62 \times 10^{4}), 421 (2.03 \times 10^{5}), 527 (1.99 \times 10^{4}),$	570, 620, 705, 776 ^a		
[(2- Pd)–Nd] ⁻	$558(0.40 \times 10^4)$ 277 (4.97 × 10 ⁴), 424 (0.92 × 10 ⁵), 532 (1.12 × 10 ⁴),	570, 620, 700, 773, 1069, 1343 ^a		
3	560 (0.26 \times 10 ⁴) 255 (3.20 \times 10 ⁴), 277 (1.90 \times 10 ⁴)	494		
$[(3)_4 \text{Nd}]^-$	$275(11.5 \times 10^4), 350(3.1 \times 10^4)$	498, 1065, 1338		
^a Degassed solution RT.				



Fig. 3 Excitation spectrum of [2-Nd]⁻ and [(2-Pd)–Nd]⁻ by monitoring the emission at 1070 nm, and emission spectra (dotted line) of Nd(III) porphyrin complexes while exciting at 429 nm in degassed THF at RT.

two Q bands around 530 and 560 nm are observed as expected (Table 1, Fig. 2).¹⁹ The less pronounced shift of *ca*. 3 nm in the Soret band for $[(2-Pd)-Nd]^-$ with respect to 2-Pd is probably due to the rigidification of the porphyrin ring upon binding of Pd(II). No change is observed for the relative intensity of the Q bands upon binding of Nd(III).

In THF, upon excitation at around 425 nm, both [2-Nd]⁻ and [(2-Pd)–Nd]⁻ complexes display Nd-centred NIR luminescence, in addition to the porphyrin centred emissions in the visible region (Fig. 3). However, the presence of Nd(III) causes partial quenching of the porphyrin centred luminescence. At RT, in degassed and aerated solution as well as at 77 K, the luminescence spectrum (Fig. 3) in the 1000–1500 nm range consists of two bands at 1065 and 1340 nm corresponding to the expected f–f transitions (${}^{4}F_{3/2} \rightarrow {}^{4}I_{11/2}$ and ${}^{4}F_{3/2} \rightarrow {}^{4}I_{13/2}$, respectively). The excitation spectra of [2-Nd]⁻ and [(2-Pd)–Nd]⁻ species while monitoring the emission from Nd at 1070 nm (Fig. 3) are identical to the porphyrin absorption spectra (Fig. 2) demonstrating thus the antenna effect of the porphyrin moiety in both complexes.

The total emission spectra in the NIR region (1000-1500 nm) for $[(3)_4\text{Nd}]^-$, $[2\text{-Nd}]^-$ and $[(2\text{-Pd})-\text{Nd}]^-$ were recorded under the exact same conditions in the presence and in the absence of O₂ while exciting at 350 nm. In all cases, enhanced emission from the Nd(III) ion was observed in anaerobic conditions. Under aerobic conditions, *ca.* 12–25% quenching of the Nd emission could be estimated. These observations imply that: (i) a triplet excited state is involved in the energy transfer processes, (ii) in the presence of O₂, two competitive processes, *i.e.* energy transfer and quenching by oxygen of a triplet state, are taking place and (iii) the intramolecular energy transfer is relatively fast.

In conclusion, ligand **2**, a preorganised porphyrin-based ligand bearing four monoanionic chelates on the same face of the backbone, offers two distinct coordinating poles consisting of the porphyrin macrocyclic core and four 8-hydroxyquinolines organised in a convergent manner. The difference in binding propensity of the two coordinating poles was exploited for the formation of mononuclear ([**2**-Nd]⁻) and heterobinuclear ([**(2**-Pd)–Nd]⁻) Neodymium complexes. In both types of complexes, the porphyrin backbone plays the role of sensitizer. Indeed, excitation in the visible region (Soret band of the porphyrin) leads to an efficient NIR emission of Nd(III). A detailed study of the photophysics of the system as well as the use of ligand 2 in conjunction with other d and f metals are currently under investigation.

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