Efficient near-infrared emission of a Ytterbium(III) compound with a green light rhodamine donor†‡

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A new approach to design and synthesize efficient near-infrared luminescent ytterbium(III) compound has been achieved through incorporating a ring-opened rhodamine unit as energy donor with the excitation wavelength in the visible range (500 nm). The tetradentate binding unit of ligand fulfills the high coordination numbers of the lanthanide cation ensuring the efficient NIR emission.

Lanthanide-based near-infrared (NIR) emitters are of particular interest for their potential applications in medical imaging and optical communication due to: (a) their sharp emission bands that can be easily discriminated from background fluorescence; (b) their long luminescent lifetimes, which allow the removal of background fluorescence and increased assay sensitivity through time-resolved measurements; (c) their use in multiphoton excitation techniques and (d) their narrow emission bandwidths of lanthanide cations allowing for the simultaneous detection of several cations during the same experiment (multiplex assay).1,2

Due to the low extinction coefficients of the Laporte forbidden f–f transitions, lanthanide ions are commonly indirectly excited by an aromatic chromophores or “antenna” possessing a reasonably large molar absorption cross section. One of the challenges in design of luminescent lanthanide tags for application in bioanalyses and bioimaging is to shift the excitation wavelength from the UV to the visible range, because that biomolecules are usually damaged by UV light and, in practice, long wavelength sensitization will allow use of the cheap and widely available semiconductor diode lasers in the red region of the spectrum. Hence, the sensitizers with the absorption maximum in the visible region (>500 nm) are desired, despite that NIR-emitting lanthanides have a comparatively small energy gap between the sensitizer triplet state and the energy accepting state, which markedly extends the available absorption envelope into the visible region and the consequent range of sensitizing chromophores that can be employed.3 Toward this end, a number of NIR emitting lanthanide complexes that have visible light absorbing antennas, such as fluorescein, lissamine, porphyrins, ferrocene, and metal complexes, were reported.

To seek new strategies for design of luminescent lanthanide tags with excitation wavelength in low energy range, herein, we design and synthesize a new sensitizing chromophore, HQR1 (Scheme 1) by combining an 8-hydroxy quinoline-2-carboxaldehyde unit with a rhodamine 6G unit via a carbohydrazone linker. The long wavelength absorption maximum (ca. 500 nm) of the ring-opened tautomer of rhodamine 6G chromophore coupled with the suitable triplet excited state of rhodamine 6G allows for the sensitization of NIR emitting lanthanide ions. Furthermore, the relative transparency of human tissue at approximately 1000 nm suggests that in vivo luminescent probes operating at this wavelength (Yb-based emission) could have diagnostic value.11

Scheme 1 Molecular structure of the ligand HQR1 and the possible energy transfer pathway of the YbIII compound.

Ligand HQR1 was easily formed by a Schiff-base reaction of rhodamine-6G hydrazone and 8-hydroxyquinoline-2-carboxaldehyde in methanol solution. The syntheses of complexes 1 and 2 were carried out in methanol solution by the reaction of 8-hydroxyquinoline-2-carboxaldehyde (HQR1) with Yb(NO3)3·5H2O and GdCl3·6H2O, respectively. Upon coordination, the rhodamine 6G group of the ligand change its forms from a closed and non-fluorescent spirolactam-ring tautomer to a ring-opened tautomer while the 8-hydroxyquinoline unit loses a proton, leading to the formation of a tetratdentate ligand and consequent lanthanide complexes.

The resulting mononuclear complexes 1 and 2 have similar coordination moiety in despite of use of different lanthanide ions and counter anions, which indicate that the nearly planar rigid ONNO tetratdentate ligand has universal coordination tendency to lanthanide ions and can prevent lanthanide ions from the coordination of counter anions or methanol, water solvents. As a representative, the structure of complex 1 will be addressed in detail here.§ The YbIII ion was chelated by two ONNO tetratdentate units from two QR1 ligands, respectively, fulfilling the coordination environment of the central lanthanide ion. Associated with the tetratdentate chelation unit, atoms O(1), O(2),
N(1), N(2), N(3) and C(1) to C(11) are co-planar with the mean deviation from plane of 0.0253 Å in complex 1 (Fig. 1). The Yb–O and Yb–N bond distances are comparable with that of other Yb(III) complexes. The two tetradentate units in complex 1 adopt the same conformation (the chelating mode) and are perpendicular to each other with a dihedral angle of 89.5°. The central lanthanide ion was largely surrounded by hydrophobic phenyl rings, which is beneficial for reduction of high-energy vibrations in close proximity to the lanthanide.

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ESI-MS of the complexes in acetonitrile solution are consistent with the formation of the desired lanthanide assemblies and reflect the high stability of these lanthanide complexes in solution phase. Fig. 2 exhibits one of ESI-MS spectra of these complexes as representative. The +1 charged peak at m/z = 1339.46 and +2 charged peak at m/z = 570.22 are assigned to the species of [Yb(HQR1)2]−2H+ and [Yb(HQR1)−H]2+, respectively. The peak at m/z = 662.19 in the ESI-MS spectrum of compound 2 also suggests the formation of [Gd(HQR1)−H]+. Furthermore, the isotopic distributions of the peaks corresponding to the parent ions unambiguously confirm the monometallic nature of the complexes.

Both compounds 1 and 2 exhibit the characteristic rhodamine absorption band at 525 nm, indicating the presence of its ring-opened tautomer (Fig. 3). The peaks at around 310 nm and 335 nm are assigned to the transitions of the 8-hydroxyquinoline unit. Upon excitation of compound 1 at 500 nm, strong characteristic rhodamine luminescence was observed at 560 nm. The luminescence spectrum of the Gd(III) analogue was also measured for reference. Although the UV-vis absorptions of Gd(III) compound 2 and Yb(III) compound 1 is almost same, the luminescence intensity of the former is obviously higher than that of the latter under the same condition. Since the Gd(III) has no energy level below 32 000 cm−1 to accept any energy from the rhodamine moiety, it is suggested that the lowering of luminescence intensity of the Yb(III) compound 1 arises from the energy transfer from the rhodamine triplet state to the excited state of Yb(III) center.

As expected, the emission spectrum (Fig. 4) of lanthanide compound 1 in acetonitrile solution (10 μM) upon ligand-mediated excitation at 500 nm clearly shows the characteristic emission bands of the Yb(III) at 980 nm, which is assigned to the 2F5/2 → 2F7/2 transition. It should be noted that the Yb(III) ion emission in this complex is not a single sharp band but an envelope of bands arising at the lower energy side (1001 and 1017 nm) of the primary 980 nm emission band. The similar splitting has been reported previously. According to the literature, these bands arise from the crystal-field splitting of the emitting and/or fundamental state as a consequence of ligand-field effects. The quantum yield (ca. 1.1 ± 0.1%) of the Yb(III) complex 1 is comparable with the value reported for other Yb(III) complexes in solution. Clearly, rhodamine 6G has a good electronic structure to act as an efficient antenna because the energy of its triplet state (~17 000 cm−1) is compatible for efficient energy transfer to the low accepting level
and counterions. No positions free for vibronically deactivating solvent molecules occupy eight coordination sites around the ytterbium ion, leaving it likely to benefit from the fact that the rigid tetradentate ligands is responsible for photosensitized NIR luminescence of Yb(III). To our surprise, an analogous Nd(III) compound does not exhibit any obvious characteristic NIR emission, though the Nd(III) has closer accepting level at 11 300 cm⁻¹ than that of Yb(III) to the rhodamine triplet state. In order to preclude the influence of C–H stretches and carbonyl stretch vibration, emission spectra of the Nd³⁺ and Yb³⁺ complexes were also checked with the polycrystalline samples. These results indicated that the Nd³⁺ complex was non-luminescent both in the solid state and in the solution (excitation at 500 nm). To get further information about the possible luminescent quenching about the vibrations, the luminescence in deuterated solvents including CD₃CN and d₆-DMSO were further measured. The Nd³⁺ complex was non-luminescent, but the Yb³⁺ complex was luminescent active in deuterated solvents when excited at 500 nm. It seemed that the ring C–H stretches and the carbonyl stretch vibration did not mode the reason why the Nd³⁺ complex was non-luminescent.

This result drives us to consider the possibility of other mechanisms operating the efficient energy transfer of Yb(III) complex rather than a Dexter mechanism of energy transfer. Some theoretic work indicated that Yb(III) is not common among near-infrared-emitting lanthanide ions in case of an excitation mechanism possibly different from the antenna effect. In 1997, Horrocks and co-workers proposed the internal redox process is responsible for photosensitized NIR luminescence of Yb(III) in proteins and complexes. Later on, Reinhard and Güdel thought the lanthanide ion with its ligands can be treated as one chromophore. The emitting level is dominated by nonradiative relaxation processes from highly excited states of the chromophore rather than energy transfer from the ligand to the excited state of the lanthanide ion.

In conclusion, we report a new approach to achieve NIR lanthanide luminescence by excitation at visible range (> 500 nm). The specific rigid tetradentate feature of the sensitizing ligand successfully eliminating the competitive coordination of solvents and other molecules, coupled with the appropriate triplet excited state of rhodamine facilitates the efficient near-infrared emission of Yb(III) complex.

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Notes and references

§ Crystallography: Yb compound 1. C₆₀H₇₀YbN₁₁O₁₃, Mᵣ = 1516.54, monoclinic space group P2₁/c, a = 24.168(2) b = 20.340(2), c = 15.204(1) Å, β = 96.30(1)°, V = 7428.7(11) Å³, µ = 1.327 mm⁻¹, Z = 4, T = 293 K. 44417 reflections were collected of which 13 063 reflections were unique (Rₛₒₐ = 0.0492). The final refinement gave R₁ = 0.0555 and wR₂ = 0.1637 for 9188 reflections with I ≥ 2σI. Gd compound 2. C₆₀H₇₀ClGdN₁₁O₁₃, Mᵣ = 1540.21, triclinic space group P1, a = 12.516(1), b = 16.174(1), c = 20.393(2) Å, α = 103.98(1), β = 98.56(1), γ = 104.84(1)°, V = 3772.2 (5) Å³, µ = 0.974 mm⁻¹, Z = 2, T = 293 K. 19 280 reflections were collected of which 13 116 reflections were unique (Rₛₒₐ = 0.0459). The final refinement gave R₁ = 0.0638 and wR₂ = 0.1547 for 7749 reflections with I ≥ 2σI.


13 Second order signals were avoided using a filter (550 nm) due to the 500 nm excitation.
