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PAPER

Silica sol–gel glasses incorporating dual-luminescent Yb quinolinolato complex: processing, emission and photosensitising properties of the 'antenna' ligand†‡

Flavia Artizzu,*[a,b] Francesco Quochi,[b] Michele Saba,[b] Danilo Loche,[a] Maria Laura Mercuri,[a] Angela Serpe,[a] Andrea Mura,[b] Giovanni Bongiovanni[b] and Paola Deplano*[a]

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The $[Yb(5,7ClQ)_2(H5,7ClQ)_2Cl]$ (**1**) complex, that exhibits dual-luminescence in the visible (ligand-centered) and in the NIR (Yb-centered), has been incorporated into a silica sol–gel glass obtaining **1**-doped glassy material which is optically transparent and homogeneous and with good mechanical properties. The doped sol–gel glass can be considered a "solid state solution" and photophysical studies demonstrate that the emissive properties of the dopant complex are preserved in the silica matrix. Observed NIR decay times fall in the μs range and are likely limited by "second-sphere" matrix interactions. The ligand-to-metal energy transfer mechanism occurs on ultrafast timescale and involves ligand triplet states. The sensitization efficiency of the antenna quinolinolato ligand toward Yb^{3+} is estimated to be as high as ~80%. The Yb natural radiative lifetime observed for **1** in MeCN–EtOH solution (τ_{rad} = 438 μs) is the shortest reported so far for ytterbium complexes.

Introduction

Near-infrared emitting lanthanide quinolinolates are of interest in view of their possible applications as optically emitting materials at telecom wavelengths (optical fibers and amplifiers) and for medical imaging purposes.[1–9] Near-infrared (NIR) emission related to lanthanide 4f intrashell transitions is sensitized by resonance energy transfer (RET) from the quinolinolato ligand acting as efficient "antenna" chromophore after convenient photoexcitation in the near-UV-visible spectral region. Through this indirect sensitization process, the low emission quantum yield after direct excitation of lanthanide ions, due to their intrinsic weak absorptivity, can be improved.[10–22]

We are extensively investigating the structure–property relationship of this class of emitting molecules through combined chemical and photophysical studies to more deeply understand the decay processes affecting the quantum yield of NIR luminescence.[20,21,23,24] It has been found that the ligand-to-metal energy transfer process occurs through a two-step mechanism involving the triplet state of the quinolinolato ligand. This mechanism results in an exceptionally efficient process leading to lanthanide (Er^{3+}, Yb^{3+}) sensitization efficiencies up to population inversion threshold. These findings confirm that quinolinolato ligands are very appealing antennae for sensitizing lanthanide NIR emission.[11,24,25]

However, the use of lanthanide chelate complexes in optical devices may be limited by poor thermal stability and low mechanical strength. These difficulties can be overcome by incorporation of lanthanide complexes into a suitable rigid matrix such as a silica host material provided that it does not significantly affect the luminescence properties of the compounds.[26] It is known that silica glasses doped with luminescent lanthanides are suitable materials for use in the fabrication of optical devices, such as lasers and optical fibres,[27] being highly transparent and homogeneous and having good mechanical properties. Moreover, the silica matrix hardly influences the energy levels of the lanthanide ions and has also a negligible absorption coefficient at the excitation wavelengths used in photoluminescence experiments. In order to check if lanthanide quinolinolate complexes are suitable dopants into silica sol–gel glasses, we have selected $[Yb(5,7ClQ_2)(H5,7ClQ)_2Cl]$ (H5,7ClQ = 5,7-dichloroquinolinol), fully characterised chemically and photophysically in solution and the solid state,[24] to be incorporated into a silica sol–gel glass and report here a study on its properties. Our results on the photocycle of the resulting silica sol–gel glasses provide encouraging evidence for their prospects as large-cross section solid-state NIR emitters and amplifiers.

Experimental section

General

Chemicals. All the reagents and solvents were purchased from Aldrich and used without further purification.

[a]*Dipartimento di Scienze Chimiche e Geologiche, Università di Cagliari, SS 554 Bivio per Sestu, I-09042, Monserrato-Cagliari, Italy. E-mail: f.artizzu@unica.it, deplano@unica.it; Fax: (+) 39 0706754456*
[b]*Dipartimento di Fisica, Università di Cagliari, SS 554 Bivio per Sestu, I-09042, Monserrato-Cagliari, Italy*

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Spectroscopy. Absorption UV-Vis-NIR spectra of solutions and of sol–gel glass samples were collected with a Varian Cary 5 spectrophotometer. The absorption spectrum of a blank undoped sol–gel glass was taken as baseline for the **1**-doped sol–gel glass spectrum. Vibrational FT-IR spectra on KBr pellets were collected with a Bruker Equinox 55 spectrophotometer.

Microscopy. Transmission electron microscopy (TEM) was done on samples drop cast from ethanolic suspension onto copper grid mounted holey carbon films, on a Hitachi H-7000 instrument running at 100 kV.

X-Ray diffraction. Wide-angle X-ray diffraction XRD patterns were recorded on a Panalytical Empyrean diffractometer equipped with a graphite monochromator on the diffracted beam and a X'Celerator linear detector. The scans were collected within the range of 10–90° (2θ) using Cu Kα radiation.

Thermal analysis. Thermal gravimetric analysis (TG) and simultaneous differential thermal analysis (DTA) were carried out on a Mettler-Toledo TGA/STDA 851. Thermal analysis data were collected in the 25–800 °C range, under oxygen flow (heating rate = 10 °C min^{-1}; flow rate = 50 mL min^{-1}).

Syntheses

Synthesis of [Yb(5,7ClQ)$_2$(H5,7ClQ)$_2$Cl] (1). Synthesis was carried out as reported in ref. 24. Electronic absorption spectroscopy, MeCN–EtOH (1 : 1) (λ_{max}/nm ($10^{-3}\varepsilon$/mol^{-1} dm^3 cm^{-1})): 340 (9.58 ± 0.03), 381 (8.00 ± 0.02).

Synthesis of 1-doped silica sol–gel glass

Preparation of the sol mixture. 8 mL of absolute ethanol, 8 mL of tetramethoxysilane (TMOS), 8 mL of glycidoxypropyltrimethoxysilane (GLYMO) and 4 mL of water were mixed in a round-bottom flask. This mixture (sol) was maintained 1 day under stirring at room temperature.

Preparation of the doped glass. 2 mL of a 1 × 10^{-3} M solution of **1** in MeCN–EtOH 1 : 1 were added to 3 mL of the sol solution and the mixture was maintained under stirring at 50 °C for 1 h. The mixture was then transferred into a cylindrical glass vial and allowed to cool down at room temperature. Afterwards, the vial was covered with Parafilm pierced with a needle to allow the solvent to evaporate slowly. After a few days, depending on the viscosity of the sol–gel, two or three more holes were made in the Parafilm and the sample was allowed to stand at RT until the glass formed. The sample thickness was about 1 mm and the estimated concentration of **1** was ~3 × 10^{-3} M. Electronic absorption spectroscopy (λ_{max}/nm): 340, 391; FT-IR (KBr pellet, cm^{-1}): 3480w, br, 2952w, 2922w, 2885vw, 1647w, 1384s, 1207s, 1098vs, 1037vs, 906m, 855m, 797m, 758m, 694mw, 568mw, 450s. Thermal gravimetric analysis (TG) and simultaneous differential thermal analysis (DTA) show a very limited weight loss (around 1%) below 80 °C, accompanied in the DTA curve by an endothermic effect, likely due to some residual/adsorbed water. In the range 200–300 °C the weight loss is about 50% and corresponds to exothermic peaks in the DTA indicating that the weight loss in this region can be attributed to the combustion of organics, *i.e.* the aliphatic chains of the ORMOSIL and the 5,7ClQ ligand.

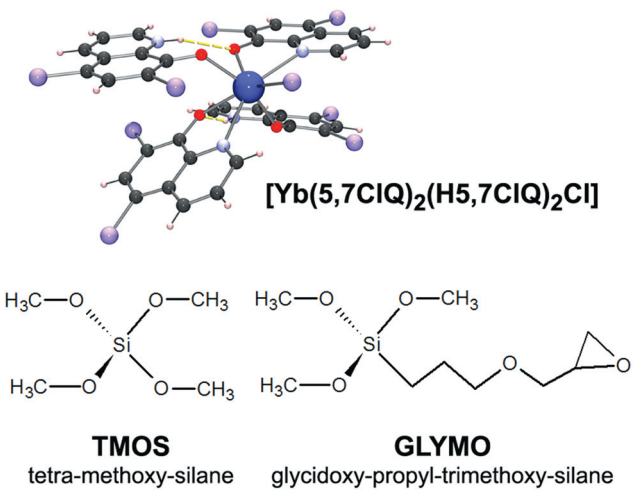
Transient optical spectroscopy

Photoluminescence (PL) and photoinduced absorption were excited at 392 nm wavelength by the frequency-doubled output pulses of a regenerative Ti:sapphire amplifier (Quantronix INTEGRA C) running at a repetition frequency of 1 kHz. The PL transient was spectrally dispersed in a 0.3 m imaging spectrograph (Acton SpectraPro 2300i) and captured by a streak camera (Hamamatsu C5680) operating in single-shot mode. Experimental data show that effective temporal resolution is ~30 ps in the operating conditions (with 70–100 s accumulation time). Photoinduced absorption was probed by broadband synchronous pulses obtained by supercontinuum generation in a sapphire plate. The optical probe beam transmitted through the sample was spectrally dispersed using a SpectraPro 2300i spectrograph and detected by a charge-coupled device (Andor NEWTON). The pump–probe time delay was varied using a motorized optical delay stage. Photoinduced absorption was measured as the differential transmission signal $\Delta T/T = (T - T_0)/T_0$, where T (T_0) is the transmitted probe pulse energy in presence (absence) of the pump pulse. Near-infrared emission transients were measured using a DC-125MHz NIR photoreceiver (NewFocus 1811) and a 1 GHz digitizing oscilloscope (Tektronik TDS 5104). Photoexcitation fluences were kept below the level of one excitation per complex per laser pulse in all experiments.

Results and discussion

Preparation of Yb-doped sol–gel glasses

The tetrakis-complex [Yb(5,7ClQ$_2$)(H5,7ClQ)$_2$Cl] (**1**), which has been fully characterised through solid-state and solution studies was selected as dopant to prepare Yb-doped sol–gel glasses.[24] In this complex the ytterbium ion is hepta-coordinated to four ligands, two anionic N,O chelated and two in the zwitterionic form acting as monodentate oxygen donors with a chloride completing the lanthanide coordination sphere, as shown in Scheme 1.



Scheme 1 Structures of [Yb(5,7ClQ$_2$)(H5,7ClQ)$_2$Cl] dopant complex and the silica precursors.

The silica matrix was prepared from a mixture of the two precursors shown in Scheme 1: tetramethoxysilane (TMOS) and the organically-modified silicon alkoxide (ORMOSIL), glycidoxypropyltrimethoxysilane (GLYMO). ORMOSILs are formed by a silicate backbone in which alkoxidic –OR groups are replaced by organic –R groups.[28] These precursors have been selected in view of the following more appealing features over the commonly used tetraalkoxysilanes such as TMOS and TEOS (tetraethoxysilane): (i) improved mechanical properties of the glass (lower shrinkage) due to the filling of the pores by bulky organic groups, (ii) high thermal stability and damage threshold upon lasing in photoluminescence experiments,[29] and (iii) decrease of the polarity of the material due to the formation of hydrophobic domains. As a consequence, water molecules potentially entrapped in the matrix are expected to be expelled and, at the same time, diffusion of water molecules from the environment into the porous glass should be hampered. Moreover the number of residual Si–OH groups in the silica host is reduced.[26,30] In particular, GLYMO has been selected in view of the fact that the epoxy group is expected to react readily with water molecules, lowering the water content in the sol–gel material, and thus reducing quenching phenomena affecting NIR luminescence.[26,30d] In addition, **1** itself being highly hydrophobic, its solubility into the organically modified sol–gel matrix is improved, leading to a homogeneous final material. This should also help in avoiding the presence of molecular aggregates and clusters, which may diminish the luminescence quantum yield through self-extinction processes (concentration effect).[31]

The preparation of the doped sol–gel glass was performed through a one-step process in which a solution of the lanthanide complex in MeCN–EtOH (1 : 1 v/v) solvent mixture was mixed with the liquid sol matrix (ethanolic mixture of TMOS and GLYMO precursors where the hydrolysis reaction was already started) at 50 °C and at neutral pH. Hydrolysis and condensation reactions in the sol–gel process were carried out without acidic or basic catalysis in order to avoid possible degradation of **1** in view of the acid–base properties of the Q ligand.[32] For this reason, TMOS, which hydrolyses easily under neutral conditions, was preferred to the more commonly used TEOS (tetraethoxysilane). These optimized conditions led to the best results in terms of transparency, homogeneity and mechanical resistance of the doped glass.

The resulting doped sol solution was then added into a Teflon vial and allowed to age at room temperature. Slow solvent evaporation led to the formation of a homogeneous and transparent yellow glass as shown in Fig. 1. Sample homogeneity at nanometric level was also confirmed by TEM (Fig. 1b), and further evidence of the amorphous character of the doped glass was provided by XRD analysis, showing only the typical amorphous silica haloes (Fig. SI1, ESI†).

Thermal gravimetric analysis (TG) and simultaneous differential thermal analysis (DTA) showed the presence of a very limited water content (around 1%) in the final material (Fig. SI2, ESI†).

Spectroscopic studies and photophysical properties

Recent chemical and photophysical studies of **1** in DMSO solution and in the solid state have established that **1** shows

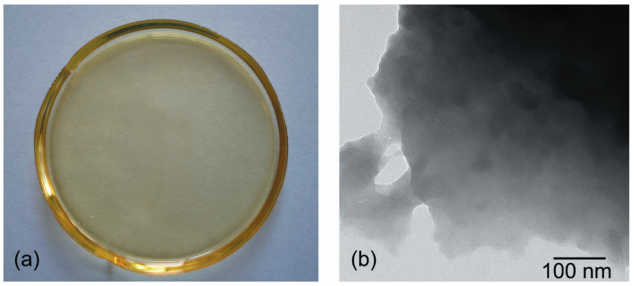


Fig. 1 (a) Sol–gel glass sample doped with **1** under white light illumination; (b) TEM image of **1**-doped sol–gel glass.

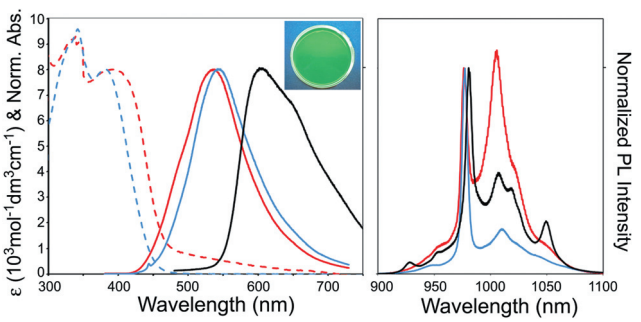


Fig. 2 UV-visible absorption spectra of **1** in MeCN–EtOH solution (dashed blue line) and in doped sol–gel glass sample (dashed red line) and normalised photoluminescence (PL) spectra in the visible and near-infrared spectral regions acquired after photo-excitation at 392 nm (MeCN–EtOH solution, blue line; sol–gel glass sample, red line; crystals, black line). Inset: **1**-doped sol–gel glass under UV light.

dual-luminescence in the visible (ligand-centered emission) and in the NIR (metal-centered luminescence) upon ligand photoexcitation in the near-UV.[24] Similar studies on **1**-doped sol–gel glass show that these features are preserved in the silica host material as reported below. The obtained glass sample is optically homogeneous throughout the bulk/surface.

Absorption and photoluminescence (PL) spectra in the visible and in the near-infrared regions of the **1**-doped sol–gel glass are shown in Fig. 2. Absorption and PL spectra of **1** in the MeCN–EtOH solution used for the preparation of the glass sample and PL spectra of crystals of **1** are also reported for comparison.

A summary of spectroscopic data (absorption and PL) for **1** in different matrices is reported in Table 1.

As shown in Fig. 2, the absorption spectra of the solution and of the **1**-doped sol–gel glass are both dominated by two intense ligand bands and display very similar spectral features despite a small band broadening in the glass absorption spectrum. The more intense peak near 340 nm in both spectra arises from the contribution of both the anionic and the zwitterionic forms of the quinolinolato ligand. The low-energy peak, centered at about 391 and 381 nm in the glass and solution spectrum, respectively, is attributable to a $^1(\pi$–$\pi)^*$ ligand-centered transition with ILCT character and closely reflects that of the deprotonated form of the ligand, as expected for closed-shell metal complexes with a high ionic character of the metal–ligand bonding.[33]

Photoexcitation in the lowest ligand absorption band yields ligand-centered fluorescence $^1(\pi$–$\pi)^*$ in the green (λ_{max} ~

Table 1 Absorption and PL peak positions of **1** in different matrices

Matrix	Absorption λ_{max}/nm	Vis PL λ_{max}/nm
MeCN–EtOH solution	340, 381	541
DMSO solution[24]	343, 396	545
Doped sol–gel glass	338, 391	537
Solid state (crystals)[24]	351, 410, 494	603

540 nm) for both solution and doped sol–gel glass, whereas a remarkable red-shift is instead observed in the case of crystalline sample (λ_{max} = 603 nm), that has been attributed to "excimer-like" emission due to the extensive π-stacking of **1** observed in the crystal structure.[24]

Peak positions related to ligand-centered transitions in both absorbance and photoluminescence spectra are slightly affected by the nature of the matrix (Table 1). A weak blue shift is observed in MeCN–EtOH solution compared to solutions in more polar solvents.[24] Similarly, the observed hypsochromic shift of sol–gel glass fluorescence with respect to solution may be related either to a change in the complex environment in the organosilica matrix, due to the filling of the pores by organic hydrophobic chains, or to a weak rigidochromic effect.[34]

The Yb^{3+} emission band at 1 μm due to the intrashell $^2F_{5/2} \rightarrow {}^2F_{7/2}$ transition, is moderately broadened and partially resolved into multiplets (Stark lines) due to the partial removal of the degeneracy of 4f ground ($^2F_{7/2}$) and excited ($^2F_{5/2}$) levels into $2J + 1$ terms by crystal field effects, which makes f–f transitions allowed to some extent. The observed fine structure arising from this Stark splitting is in accordance with the low-symmetry of the metal environment.[35] The spectral profile of **1**-doped sol–gel glass is slightly modified with respect to solution and solid state, showing an increase of the relative intensity of the peak at 1005 nm compared to the $^2F_{5/2}(0') \leftrightarrow {}^2F_{7/2}(0)$ transition at 977 nm. This sequence of peaks has been observed in eight-coordinated ytterbium complexes.[36] An increase of the coordination number of Yb in the sol–gel glass cannot be ruled out by taking into account that several potential oxygen donors are available in the organically-modified silica matrix.

Time-resolved measurements in the near-infrared under femtosecond laser pulse excitation yield bi-exponential decays for both solution and **1**-doped sol–gel glass samples with similar ytterbium emission lifetimes, τ_{obs1} = 0.85 μs, τ_{obs2} = 2.51 μs and τ_{obs1} = 0.63 μs, τ_{obs2} = 3.69 μs, respectively (Fig. 3). Each constant has approximately 50% weight in both cases.

In order to compare these absolute values to those found for analogous ytterbium compounds or for **1** in other matrices,[24] the ytterbium intrinsic quantum yield, Φ_{Yb}, is required. Φ_{Yb} represents the ratio between the rate constants of radiative ($\kappa_{rad} = 1/\tau_{rad}$) and nonradiative excited state deactivation ($\kappa_{obs} = 1/\tau_{obs}$) processes of Yb^{3+} in a specific environment.[37–41] The ytterbium "natural" radiative lifetime, τ_{rad}, is the intrinsic radiative strength of the emitting oscillator in the absence of nonradiative deactivation. Usually this value is taken from literature data and is assumed to be constant in different solvents.[42] However, since it depends on several parameters, including the refractive index of the medium and the coordination environment, it seemed to us important to experimentally determine τ_{rad} for **1** in MeCN–EtOH solution from spectroscopic data (absorption cross-section, σ_{Yb})

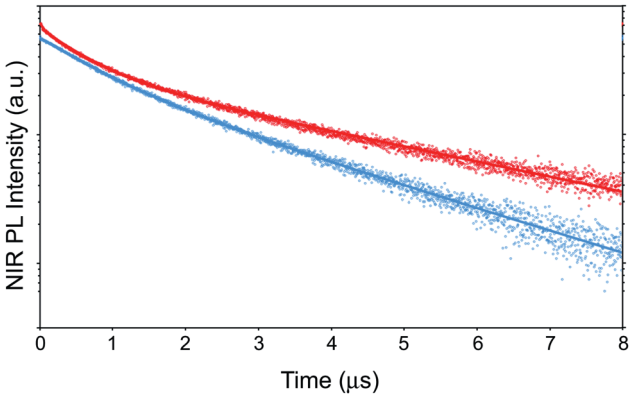


Fig. 3 Normalised NIR experimental decay of **1** as doped sol–gel glass (red dots) and in MeCN–EtOH solution (blue dots). Solid curves represent best fitting to experimental data. The emission signal is reported on a logarithmic scale.

through the Strickler–Berg equation.[43] The obtained value, τ_{rad} = 440 μs, is the smallest ever reported for ytterbium complexes, indicating an extremely high radiative strength of Yb^{3+} in such an environment. It should also be pointed out that the shortening of τ_{rad} with respect to radiative lifetime found for **1** in anhydrous DMSO solution (τ_{rad} = 690 μs) exceeds that expected on the basis of the difference in refractive indexes of the solvents and may therefore be related to a second-sphere solvent interaction.[44] The obtained results and the apparent discrepancy with literature data point out that the use of intrinsic quantum yields evaluated through 'literature' data should be discouraged, while the availability of experimental data is crucial to assess reliable photophysical parameters in luminescent lanthanide complexes. Experimental data and equations used for evaluating the radiative lifetime of **1** in MeCN–EtOH solution are given in ESI†.

The obtained ytterbium intrinsic quantum yield in MeCN–EtOH solution, $\Phi_{YbMeCN/EtOH}$ = 0.43%, is quite low and appreciably lower than the value found for complex **1** in anhydrous DMSO solution (Φ_{YbDMSO} = 1.1%, τ_{obs} = 7.85 μs),[24] indicating the occurrence of significant nonradiative processes affecting the NIR emission. These low quantum yields can be, in most part, explained by taking into account quenching phenomena due to Förster resonance energy transfer (FRET)[45] from the emitting lanthanide ion to the strongly resonant oscillating C–H and/or O–H groups present in the surroundings (deactivation *via* vibrational excitation). In the case of the MeCN–EtOH solution the additional presence, with respect to anhydrous DMSO, of ethanolic OH groups and/or water molecules in the solvent mixture, will lead to increased nonradiative processes. In fact the third harmonic of stretching vibration of these groups is extremely resonant (~980 nm) with Yb^{3+} 1 μm luminescence and provides an important supplementary non-radiative deactivation channel (likely due to a second-sphere solvent interaction) accounting for the further shortening of τ_{obs} (Fig. 4). Similar considerations can be extended to the organically-modified sol–gel glass, where "second-sphere" quenching effects can be ascribed to the presence of aliphatic chains and hydrolysed epoxy groups of the GLYMO precursor and/or to solvent molecules potentially entrapped into the pores. Moreover a self-quenching effect may be operational, due to the high

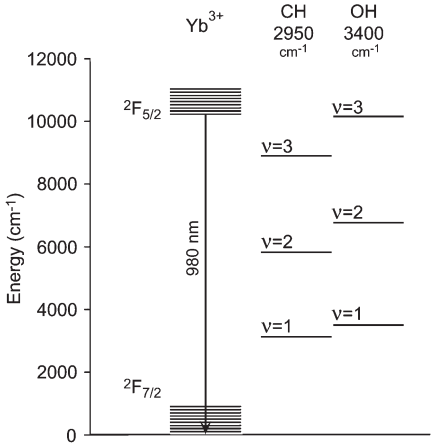


Fig. 4 Energy gaps of emitting levels of Yb^{3+} compared to the energy of vibrational modes of C–H and O–H groups and their harmonics.

concentration of the doped material in the sol–gel glass, but the observed NIR-dynamics (see Fig. 3) show only minor differences between the two curves of **1** in doped sol–gel glass and solution. Future work is addressed to overcome the quenching processes by suitably changing the starting material in order to take advantage of the promising properties of the glasses for future applications in optical devices, in terms of preparative procedures (low-cost and energy saving), and quality of the glass for optical transparency, homogeneity, mechanical strength and thermal stability.

Direct measurement of total quantum yield for NIR emission after ligand excitation in MeCN–EtOH solution yields $\Phi_{tot} = 0.30 \times 10^{-2}$.[46] The ligand-to-metal sensitization efficiency, η_{sens}, is therefore calculated through the equation:

$$\Phi_{tot} = \eta_{sens}\Phi_{Yb} \quad (1)$$

a value close to 80% is determined confirming that the upper emitting $^2F_{5/2}$ level of the ytterbium ion is efficiently populated by RET from the quinolinolato ligand.

Photophysical properties of **1** in different matrices are summarized in Table 2.

To go deeper into the ligand-to-metal energy transfer mechanism and clarify if its efficiency is maintained when incorporating **1** into the silica matrix, combined transient PL and excited state absorption (ESA) experiments with subpicosecond photoexcitation in the fundamental absorption band of the ligand have been performed. The obtained results are summarized in Fig. 5 and time constants of ligand emission dynamics and excited state kinetics are reported in Table 3.

Transient PL data are spectrally integrated over the excited singlet fluorescence emission spectrum (470–570 nm spectral window). As shown in Fig. 5a, singlet excited state decay is bi (tri)-exponential in the doped sol–gel glass (MeCN–EtOH solution) sample and is dominated by ultrafast components yielding time constants of the order of tens of ps (Table 3). These findings are in agreement with values previously found for **1** in DMSO solution and as a crystalline sample[24] as well as for analogous erbium quinolinolates,[11] suggesting that ligand singlet states are strongly deactivated by intersystem-crossing (ISC) to ligand excited triplet states favoured by the presence of the heavy lanthanide ion (heavy-atom effect). A 10% signal fraction

Table 2 Photophysical parameters of **1** in different matrices

Matrix	τ_{obs}/μs	τ_{rad}/μs	Φ_{tot} (%)	η_{sens} (%)
MeCN–EtOH solution	0.85(1) (~50%), 2.51(1) (~50%); av. 1.9(1)	440(20)	0.30(6)	70(20)
DMSO solution[24]	7.85(1)	690(35)	1.40(30)	95(5)[a]
Doped sol–gel glass	0.63(1) (~50%), 3.69(1) (~50%); av. 2.4(1)	—	—	—
Solid state (crystals)[24]	7.10(1)	—	—	—

[a] Lies within the error bar of the calculated value: 120(30)%.

of excited singlets in **1**-doped sol–gel decays with a time constant τ_2 = ~2 ns. This value is consistent to that observed (8.5 ns) for tris(8-quinolinolato)aluminium(III) (AlQ_3), where the heavy-atom effect is negligible, suggesting that this slower singlet decay component may originate from a small fraction of dissociated ligands dispersed in the silica matrix.[11] This fraction appears to be negligible in MeCN–EtOH solution, where the long-lived signal amplitude is as small as 0.3%.

Singlet and triplet dynamics have then been determined from transient absorption signals probed by differential transmission ($-\Delta T/T$) in the 600–620 nm spectral range (Fig. 5b). Curve fitting of the measured excited state kinetics confirms that singlet deactivation (SD, dashed curves in Fig. 5b) occurs on an ultrafast timescale, with decay time as fast as 5 ps in MeCN–EtOH solution (Table 3).

For both samples, triplet population shows ultrafast activation (TA) with time constants (τ_{TA}) that are inferred to be equal to singlet decay times. Curve fitting yields triplet lifetimes (τ_{TD}, Table 3) of the order of hundreds of ps that are in agreement with previous reports for erbium quinolinolates (80–100 ps), and much shorter than the value found for a gadolinium quinolinolate analogue (~1.4 ns),[11] where no ligand-to-metal energy transfer can occur due to the high energy of the Gd^{3+} first excited state.[47] These findings clearly point out that ligand excited triplets are effectively deactivated through resonant energy transfer to ytterbium upper levels. Other mechanisms, such as photosensitization through internal redox processes[48] or phonon-assisted energy transfer,[49] that are often invoked to account for ytterbium sensitization, seem to be less likely.

Deconvolution of the excited state absorption (ESA) experimental curve for the doped glass gives an estimated ~85% of excited triplets that are likely to efficiently feed ytterbium upper levels (long-dashed black curve in Fig. 5b, left panel). Bearing in mind that 90% of excited singlets decay to triplet states, these outcomes suggest that the ligand-to-metal energy transfer efficiency (η_{sens}) in **1**-doped sol–gel glass can be estimated to be as high as 70–80%, in close agreement with value calculated through eqn (1) for MeCN–EtOH solution.

We can definitely conclude that the emissive properties of **1** are preserved in the doped sol–gel glass that shows dual emission in the visible (ligand-centered) and in the NIR (metal-centered) upon antenna sensitization in the near-UV. The close similarity of spectroscopic profiles and photophysical properties of the **1**-doped sol–gel glass compared to a solution of **1** in the same solvent mixture used for the preparation of the glass

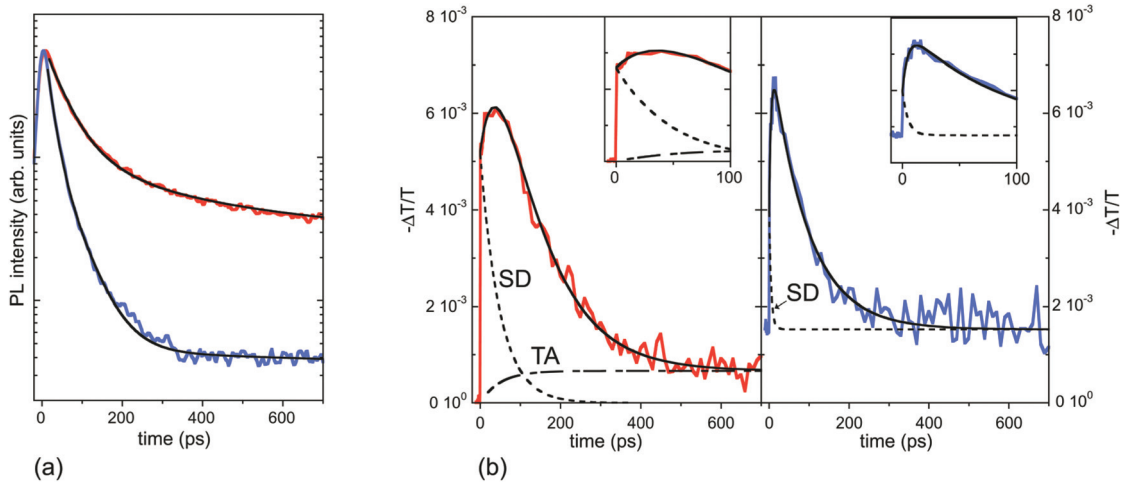


Fig. 5 (a) Transient photoluminescence of **1** in sol–gel glass (red line) and in MeCN–EtOH solution (blue line). The signal is reported on a logarithmic scale. Black solid curves are the best fit based on a bi-exponential (sol–gel glass) and tri-exponential (MeCN–EtOH solution) decay curve. (b) Transient photoinduced absorption of **1**-doped sol–gel glass (red, left) and of **1** in MeCN–EtOH solution (blue, right). Black short-dashed lines represent singlet decay components. Black long-dashed curve in the left panel represents a population of long-lived triplets not involved in Yb^{3+} sensitisation. In MeCN–EtOH solution, a steady-state ESA signal is found, which we trace back to triplet accumulation in dissociated ligands. This signal is also represented by the short-dashed line after singlet decay. In the insets signals are reported on the 0–100 ps timescale.

Table 3 Time constants of ligand dynamics for **1** in different matrices

Matrix	Transient PL τ/ps	ESA τ_{SD} (= τ_{TA})/ps	ESA τ_{TD}/ps
MeCN–EtOH solution	$\tau_1 < 30^a$ (85%), $\tau_2 = 52$ (15%), $\tau_3 = 5000$ (0.3%)	5	90
Doped sol–gel glass	$\tau_1 = 49$ (90%), $\tau_2 = 2100$ (10%)	49	108

[a] Constant determination is resolution limited.

sample suggests that the silica matrix does not significantly affect the optical properties of the complex. The glass material, that is optically transparent, can then be considered a "solid-state solution" in which the dopant lanthanide complex is homogeneously dispersed and clustering effects that can be detrimental for the optical properties are avoided.

Conclusions

$[Yb(5,7ClQ_2)(H5,7ClQ)_2Cl]$ has been selected as a prototype complex to be used as dopant in sol–gel glasses in view of the extensive knowledge available on its structure–properties relationship. Our efforts are aimed at obtaining a suitable optical material for future practical applications and for a full study of its photophysical properties in comparison with those observed for the same complex in solution or in the solid state.

It has been confirmed that the selected processing of doped glasses, based on the convenient sol–gel method, offers several advantages over the traditional melt preparation. Given that this method is a solution process, formation of the matrix can lead to a high concentration of dopant without loss of amorphous character, as demonstrated by XRD/TEM characterization. Moreover, the preparation of the sol–gel glass can be carried out under mild conditions (temperature, pH) avoiding decomposition/degradation of the dopant complex. The obtained doped material is optically transparent and homogeneous and exhibits good mechanical strength. Optical properties achievable in sol–gel materials include graded refractive indexes, waveguiding, chemical sensing, optical amplification, frequency doubling, and lasing.[50]

The obtained doped sol–gel glass can be considered a "solid state solution" whose spectroscopic and photophysical properties are very close to those observed in the precursor MeCN–EtOH solution. NIR decay times are in the μs range and are likely limited by the presence of some residual OH quencher groups in both (silica glass and solvent) the host matrices. The ligand-to-metal sensitization efficiency has been determined to be as high as 80% in MeCN–EtOH solution and combined transient PL and ESA experiments allow estimating that the effectiveness of this mechanism is maintained in the doped sol–gel glass. It has been confirmed that ligand-to-metal energy transfer involves the triplet states of the ligand and that ISC and RET from ligand triplet states to metal occur on an ultrafast timescale.

It is worth remarking that the ytterbium radiative lifetime observed in MeCN–EtOH solution is the shortest ever reported so far and is significantly shorter (37%) than the value found for **1** in other solvents such as DMSO, indicating a strong solvent effect. This outcome dramatically points out that the correct assessment of the photophysical properties of luminescent lanthanide complexes with antenna ligands is crucially dependent on the experimental determination of photophysical parameters case by case.

These results seem encouraging since they demonstrate that photophysical properties of NIR emitting lanthanide compounds are entirely maintained when they are incorporated into silica sol–gel glasses. This study opens new perspectives into the development of optical materials based on luminescent lanthanide complexes and further work will be addressed to the design and selection of suitable precursors for the preparation and processing of these materials to improve their properties.

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