Effects of Progressive Halogen Substitution on the Photoluminescence Properties of an Erbium−Porphyrin Complex

Roberto Pizzoferrato,*,† Roberto Francini,‡ Serena Pietrantoni,‡ Roberto Paolesse,§ Federica Mandoj,§ Angelo Monguzzi,⊥ and Francesco Meinardi⊥

Dipartimento di Ingegneria Meccanica - CNSIM, Università di Roma Tor Vergata, Via del Politecnico, 1-00133 Roma, Italy, Dipartimento di Fisica - CNSIM, Università di Roma Tor Vergata, Via della Ricerca Scientifica, 1-00133 Roma, Italy, Dipartimento di Scienze e Tecnologie Chimiche, Università di Roma Tor Vergata, Via della Ricerca, Scientifica 1-00133 Roma, Italy, and Dipartimento di Scienza dei Materiali, Università di Milano−Bicocca, Via Cozzi, 53-20125 Milano, Italy

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We have investigated the photoluminescence properties of porphyrin-based erbium and gadolinium complexes at different levels of halogen substitution. Both the intensity and the decay time of the erbium near-infrared emission correlate with the degree of the halogenation. Conversely, no clear correlation is found with the triplet-state energy levels nor with the intensity of the residual visible emission. Such findings confirm that the key role in the low efficiency of the near-infrared emission is played by the nonradiative quenching of the erbium emitting level due to the vibrational modes of the surrounding C−H bonds.

1. Introduction

The introduction of erbium-doped fiber amplifiers (EDFAs)[1,2] for optical telecomm has given a great thrust to the research for the exploitation of the 1.54 μm emission of Er(III). More recently, the development of organic-based electrooptics has pointed out the need to bind the erbium ion to organic ligands in order to avoid clustering at high concentrations. Such lanthanide coordination compounds present the further advantage of combining the high spectral purity of the lanthanide photoluminescence with the strong molar absorptivity and tuneability of organic chromophores, thus compensating for the small absorption cross section of the forbidden intra-4f transitions of erbium. It is generally accepted that these features are based on the efficient optical excitation of the “antenna” organic ligand into its singlet state, followed by intersystem crossing (ISC) to the lower-lying triplet state. ISC is greatly enhanced by the presence of heavy atoms, such as the lanthanide itself, in the organic molecule. Energy transfer from the ligand triplet state to the upper levels of the erbium ion may then occur with an efficiency depending the coordination geometry and the matching between the energy levels.

On such a basis, several erbium-containing compounds have been synthesized and characterized over the past decade,[3–25] with the aim of enhancing the near-infrared (NIR) emission and improving the physical processability and compatibility of the materials. Specifically, great attention has been paid to the investigation and engineering of the intramolecular energy transfer through the choice of specific organic ligands, as well as to reducing the quenching of the radiative emission. For examples, Werts et al.[3,4] synthesized luminescent erbium complexes based on fluorescein antenna chromophores and first pointed out the importance of effective intersystem crossing for obtaining strong emission bands. Reinhoudt et al. carried out systematic studies using triphenylene[5,6] or lissamine ligand groups[7,8] in polydentate hemispherand complexes. They concluded that energy-transfer rates should be improved by direct coordination of the antenna ligand to the lanthanide ion. On the other hand, Hwan Kyu Kim et al.[9,10] investigated intramolecular processes in erbium-cored supramolecular complexes based on platinumporphyrin ligands with no direct coordination to the erbium ion. The authors’ calculations suggest that the excitation is conveyed to the erbium ion through Förster resonant transfer from the ligand first triplet excited state to the lanthanide $^4F_{9/2}$ and $^4I_{9/2}$ states.

Förster resonant transfer has also been investigated as the main mechanism responsible for the low efficiency of the NIR emission.[11–15] In fact, coupling to the overtones of high-energy oscillators, notably the O−H and C−H bonds of the ligands and solvents, causes rapid vibrational quenching of the luminescence in the infrared region.[16] This shows up in the reduction of the emission decay time from the value $\tau \approx 8$ ms, in the isolated ion to values in the range of 1−2 μs in typical lanthanide complexes. Consequently, the overall radiative efficiency is generally as low as $\phi \approx 10^{-4}$. Halogenation of the hydrogen-containing ligands has been suggested[16] as a way to overcome such effects and has been carried out in few cases[17–20] with different results. For example, a moderate increase of about 30% in the emission efficiency has been found in erbium quinolinates with a measured lifetime of $\tau = 1.9$ μs.[17] Quite differently, a much more noticeable growth to $\tau = 741$ μs has been achieved in an imidodiphosphinate complex.[19] The authors also found evidence of a new low-lying ligand triplet state due to fluorination which seems to quench the luminescence of visible emitting lanthanides through intramolecular nonradiative processes. A stretched exponential decay function with an average lifetime of $\tau = 300$ μs was found in a similar erbium compound.[20] This latter result, however, was obtained upon direct optical excitation into the $^2H_{11/2}$ level of the Er(III) ion,

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* To whom correspondence should be addressed. E-mail: Pizzoferrato@uniroma2.it.

† Dipartimento di Ingegneria Meccanica - CNSIM, Università di Roma Tor Vergata.

‡ Dipartimento di Fisica - CNSIM, Università di Roma Tor Vergata.

§ Dipartimento di Scienze e Tecnologie Chimiche, Università di Roma Tor Vergata.

⊥ Università di Milano−Bicocca.

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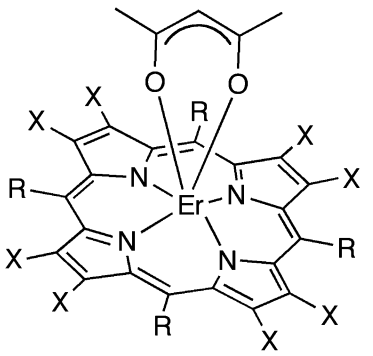

Er(acac)TPP: $R = C_6H_5$ $X = H$

Er(acac)FTPP: $R = C_6F_5$ $X = H$

Er(acac)BrFTPP: $R = C_6F_5$ $X = Br$

Figure 1. Molecular structures of the erbium complexes (a) Er(acac)TPP), (b) Er(acac)FTPP, and (c) Er(acac)BrFTPP.

which does not involve the typical antenna sensitizing mechanism. Moreover, in both of the cases with increased lifetime,[19,20] no direct measurement of the NIR efficiency has been carried out. Such promising, even though scattered, results demand further investigations on the effects of halogen substitution on the overall photophysics of the complex, with specific regard to the intramolecular energy-transfer processes.

Within the framework outlined above, we have investigated the effects on the photoluminescence properties of a two-step progressive halogen substitution of porphyrin-based erbium and gadolinium complexes. In detail, the following complexes have been synthesized and characterized: unsubstituted (acetylacetonate)Er(III)-5,10,15,20-tetraphenylporphyrin (hereafter referred to as **Er(acac)TPP**); the partially fluorinated derivative (acetylacetonate)Er(III)-5,10,15,20-tetrakis(pentafluorophenyl)porphyrin **Er(acac)FTPP** with the substitution of only the aromatic hydrogens of the external four phenyl rings; the completely brominated on the beta pyrrolic positions (acetylacetonate)Er(III)-2,3,7,8,12,13,17,18-octabromo-5,10,15,20-tetrakis(pentafluorophenyl)porphyrin **Er(acac)BrFTPP** (see Figure 1).

Moreover, Gd(acac)TPP and the respective halogenated derivatives have also been synthesized in order to investigate the characteristics of the ligand triplet levels through phosphorescence measurements.

2. Experimental Methods

2.1. Synthesis. 5,10,15,20-Tetraphenylporphyrin (TPP), 5,10,15,20-tetrakis(pentafluorophenyl)porphyrin (FTPP), and the corresponding erbium and gadolinium metal complexes have been prepared following the common synthetic procedures reported in the literature.[26]

Er(acac)BrFTPP and Gd(acac)BrFTPP were obtained using a slightly modified version of the Bhyrappa and Krishnan approach.[27]

To a stirred solution of Ln(acac)FTPP (0.04 mmol) in 50 mL of $CHC1_3$ was added a solution of liquid bromine (48 μL; 1.0 mmol) in 15 mL of $CHC1_3$ over a period of 15 min at room temperature. The stirring was continued for a further period of 1 h. Pyridine (80 μL, 1.0 mmol) in 15 mL of $CHC1_3$ was added dropwise over a period of 15 min, and the solution was stirred for another 1 h. Then, the reaction mixture was treated with 100 mL of 20% (v/v) aqueous sodium metabisulfite solution to destroy the excess of bromine. The organic layer was separated and dried over anhydrous sodium sulfate, and the solvent was evaporated under reduced pressure. The product was directly crystallized from CH_2Cl_2/hexane to obtain a green compound.

Spectroscopic data for Er(acac)BrFTPP. Yield: 27%. Found: C, 31.5; H, 0.4; N, 3.0. $ErC_{49}H_7O_2N_4F_{20}Br_8$ requires C, 32.3; H, 0.9; N, 2.4%. UV–vis: $\lambda_{max}(CH_2Cl_2)$, 433, 566, and 599 nm. MS (MALDI): m/z 1870 (M^+), isotope pattern in accord with Br_8 substitution.

Spectroscopic data for Gd(acac)BrFTPP. Yield: 32%. Found: C, 31.6; H, 0.4; N, 3.0. $GdC_{49}H_7O_2N_4F_{20}Br_8$ requires C, 30.8; H, 0.8; N, 3.5%. UV–vis: $\lambda_{max}(CH_2Cl_2)$, 431, 565, and 601 nm. MS (MALDI): m/z 1860 (M^+), isotope pattern in accord with Br_8 substitution.

2.2. Photophysical Measurements. For the optical measurements in liquid solution, spectroscopic-grade deuterated tetrahydrofuran (THF) and chloroform were used as purchased from Aldrich, either stabilized with amylene or ethanol. Thin films for phosphorescence measurements were prepared by spin coating chloroform solutions of PMMA/complex mixtures on glass substrates with speed values in the range of 300–800 rpm for 1 min. Vacuum annealing at 90 °C for 20 min was carried out to remove residual solvent. Absorption spectra of the liquid solutions were measured with a Perkin–Elmer Lambda 19 spectrophotometer by using quartz cells with a length of either 0.1 or 1 cm. Steady-state photoluminescence (PL) emission spectra were recorded on a standard setup with a photomultiplier for the visible range (Hamamatsu R3896) and a liquid-nitrogen cooled Ge detector for the NIR spectra (EO817L, North Coast Scientific Corp.) after passing the same dual-port 25 cm monochromator (Oriel Cornerstone 260). Different light sources were used for excitation, that is, the 458, 488, and 514 nm lines of an Ar ion laser (with a power density of less than 50 mW/cm^2), the 410 nm line of a InGaN laser, and the monochromatized output of a Hg–Xe cw discharge lamp. Phosphorescence measurements were carried out by using a slightly different setup equipped with a 30 cm monochromator (Acton Standard, Princeton Instruments) and a Hamamatsu CCD for steady-state spectra recording. The CCD was substituted with a Hamamatsu R2949 photomultiplier and a gated photon counter/multiscaler board (B&H PMS-300 time resolution of 200 ns) for phosphorescence lifetime measurements. In both PL and phosphorescence setups, the emission spectra were corrected for the wavelength sensitivity of the systems.

A third setup was used for decay time measurements of the NIR emission by exciting the sample at 335 nm with a pulsed Nd:YAG laser (Laser export mod. LCS-DTL-374QT) and collecting the PL signal with a nitrogen-cooled PMT (Hamamatsu R5509-73) coupled to a monochromator (Cornestone 2601/4, ORIEL). The overall time resolution, operating in photon counting mode by means of a multichannel scaler (ORTEC 9553), was better then 50 ns.

3. Results and Discussion

3.1. Absorption Spectra. The erbium complexes have first been characterized as regards their optical properties in the visible range. Figure 2 shows the absorption spectra of the **Er(acac)TPP** complex (black line) and its fluorinated **Er(acac)FTPP** (red line) and bromofluorinated **Er(acac)BrFTPP** (blue line) derivatives in deuterated THF 10^{-5} M solutions. For comparison, the absorption spectrum of the free base porphyrin molecule H_2TPP in THF is also reported (dashed green line). Considering that the peak intensity values in the measured data do not vary significantly over the different species, the reported curves are normalized to the maximum intensity for an easier comparison. The spectra of all of the complexes exhibit the

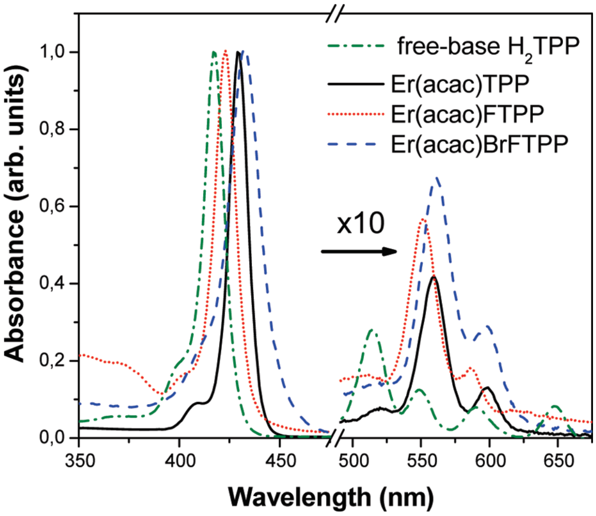

Figure 2. Absorption spectra of the erbium complex and halogen derivatives along with the porphyrin free base H_2TPP at 10^{-5} M in liquid THF.

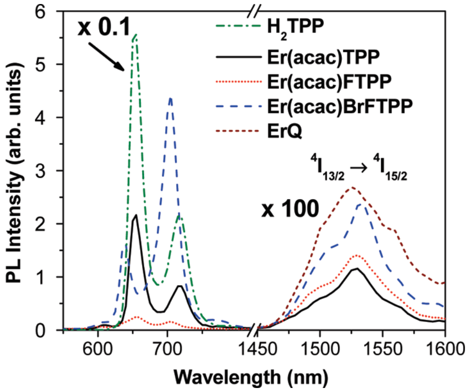

Figure 3. Photoluminescence spectra of the erbium complex and halogenated derivatives along with the porphyrin free base H_2TPP at 10^{-5} M in liquid THF. The spectrum of erbium quinoline ErQ_3 is also reported for comparison. All of the spectra are excited at $\lambda_{exc} = 410$ nm.

typical features of porphyrins, including the Soret band in the range of 420−440 nm, representing the transition from the ground state to the second excited singlet state (S_2), and the correspondingly weaker Q-bands (500−650 nm) corresponding to the transitions to the first excited singlet state (S_1). Comparing **Er(acac)TPP** with the free base, we note that the coordination to erbium affects two regions of the spectrum of the ligand in different ways. Specifically, a moderate red shift (11 nm) is observed in the peak position of the Soret band without any appreciable change of the curve shape. More significantly, a general reorganization of the relative intensities is observed in the Q-bands. In particular, the first and fourth bands almost disappear, while the Q(1,0) band at 552 nm grows by four times. All of these effects are consistent with the pseudonormal nature of the lanthanide monoporphyrinates.[28] In such complexes, the positions of absorption structures are mainly determined by the $\pi \rightarrow \pi^*$ transitions of the porphyrin ring, while the lanthanide substituent only increases the macrocycle symmetry. As a consequence, the splitting in four Q-bands due to the lower symmetry of free base porphyrin is removed by the erbium coordination, and only two Q-bands remain. From this point on, we note that the substitution of the halogens for the peripheral hydrogens does not promote further relevant changes in the halogenated derivatives **Er(acac)FTPP** and **Er(acac)BrFTPP** (red and blue lines), apart from minor shifts and intensity variations in both the Soret and Q-structures.

3.2. Visible Emission. Figure 3 compares the emission spectrum of the free base H_2TPP to the data of the **Er(acac)TPP** complex and related halogenated derivatives in THF solutions. All of the spectra are excited at $\lambda_{exc} = 410$ nm. The free base molecule shows the well-known visible fluorescence with two peaks at 653 and 720 nm originating from the porphyrin singlet states.[28,29] This emission is strongly reduced in all of the erbium-coordinating complexes due to ISC, which conveys the singlet excitation into the ligand triplet state.[28] Similarly to this quenching and as a result of the energy transfer from the triplet states to the lanthanide energy levels, the characteristic NIR emission of the $^4I_{13/2} \rightarrow {}^4I_{15/2}$ transition of Er^{3+} appears at 1540 nm, as will be discussed later. Interestingly, the ratio of the visible emission of the free base to that of the erbium complexes, hereafter referred to as the quenching factor, varies in the range from 10 to 100 over the different complexes, even without a clear correlation with the degree of halogenation. Moreover, with respect to **Er(acac)TPP**, the halogen substitution performed in **Er(acac)FTPP** and **Er(acac)BrFTPP** produces noticeable changes in the relative intensities of the two visible bands and, to a lesser extent, in the positions of their peaks.

In any case, it should be pointed out that the visible emissions in the range of 600−720 nm of all of the complexes exhibit quite fast decay times (i.e., shorter than 1 μs), as is demonstrated by time-resolved measurements reported below. This is particularly relevant in comparison with the visible phosphorescence (with lifetimes as long as 40 μs) found at 665 and 730 nm in erbium complexe which include three platinum-coordinated porphyrins as ligand groups.[9,10] In the present case, instead, the short decay times and the presence of other emissions at lower energies (see next paragraph) strongly suggest that the visible emissions of all of the complexes still represent fluorescence from the ligand singlet states, as is the case of the free base emission. Such a different behavior in the emission properties of similar lanthanide coordination compounds can be explained as follows. In platinum-coordinated ligands, ISC is more efficiently induced by the heavier platinum central substituent, independently from the presence of the lanthanide, which is coordinated to another site of the complex. This configuration enhances the transfer of the singlet excitation to the triplet state, thus the growth of triplet population, while the energy transfer to the erbium ion stands as a separate process in competition with the triplet radiative decay (phosphorescence). As a result, fluorescence from the ligand singlet states is not observed, and the phosphorescent emission is reduced by only 13% upon erbium coordination to the platinum-containing ligand.[10] In the present complexes, instead, both ISC and triplet depletion through energy transfer are caused by the same central erbium substituent. Therefore, the optical excitation in the Soret band is rapidly transferred to the lanthanide levels without emission of phosphorescence, and the visible fluorescence is quenched by more than 90% in comparison to that of the free base.

3.3. Phosphorescent Emission in Gd Complexes. In order to investigate the role of the triplet state in the physical picture outlined above, photoluminescence time decay measurements have been carried out on the erbium complexes and on specifically synthesized gadolinium−porphyrin complexes. Gd(III) complexes are commonly used as model systems, owing to their lack of energy transfer as a result of the lanthanide ion emitting levels having higher energies compared to the ligand singlet and triplet states. This prevents the depletion of the ligand

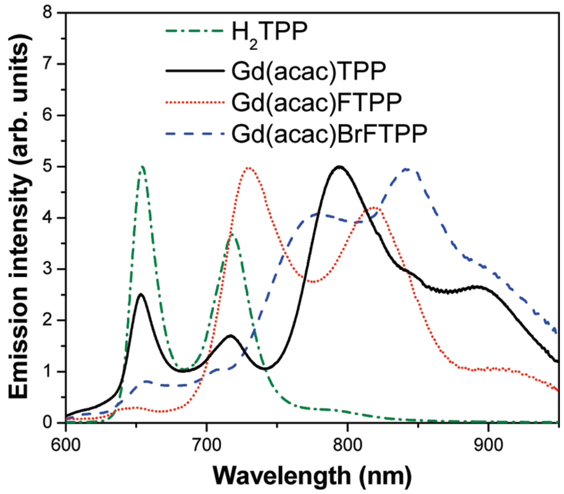

Figure 4. Photoluminescence spectra of the gadolinium complex and halogenated derivatives along with free base H_2TPP in solid solutions in PMMA films. All of the spectra are excited at $\lambda_{exc} = 410$ nm.

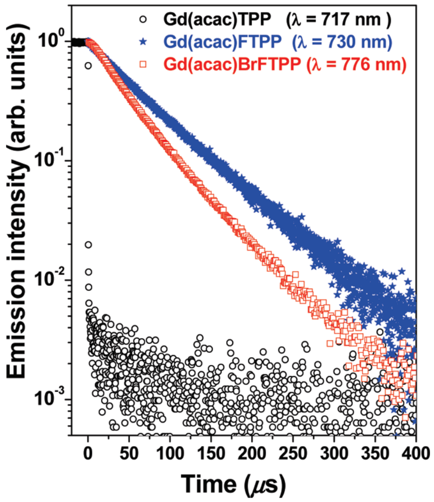

Figure 5. Decay of the photoluminescence signal in PMMA solid solutions of some of the gadolinium complexes excited at $\lambda_{exc} = 410$ nm.

triplet state and allows the emission of phosphorescence. Therefore, on the basis of the fact that the substitution with gadolinium does not alter the triplet state energies of the ligand,[30] an estimate of the erbium complex energy levels can be achieved. The Gd(III) complexes have been inserted into a rigid polymer matrix of polymethylmethacrylate (PMMA) films in order to restrict collisional deactivation. Figure 4 reports the 410 nm excited emission from samples of **Gd(acac)TPP**, gadolinium halogenated derivatives **Gd(acac)FTPP** and **Gd(acac)BrFTPP**, along with the freebase porphyrin in PMMA films. While the spectra of the free base and erbium complexes (see Supporting Information) are substantially similar to those in liquid solutions, the spectra of the gadolinium ones extend more toward the longer wavelengths with a series of additional bands in the range of 730−1000 nm. Similarly structured emissions have been reported[31] for the gadolinium complexes GdTPP and GdFTPP (without the acetylacetonate [acac] capping ligand) and attributed to the vibronic replica of the ligand triplet state. Such an attribution can also apply in the present case since time-resolved measurements (Figure 5) report decay times ranging from 50 to 70 μs for the bands in the range of 730−900 nm (see a summary in Table 1). In the present complexes, therefore, the triplet states seem to be located at energies well below the 653 and 720 nm singlet levels. This confirms the difference with respect to platinum-coordinated porphyrins[10] where the phosphorescent bands at 665 and 730 nm situate the triplet states very close to the singlet ones.

The band spectra of Figure 4 also show that the energy levels of the triplet states in the present complexes are much more sensitive to halogenation than the singlet ones, and such effects should be considered with respect to the probability of resonant transfer to the $^4F_{9/2}$ level of Er(III). However, the position of the triplet states does not show a clear correlation with the degree of halogen substitution. In fact, the partially substituted **Gd(acac)FTPP** seems to have the highest-energy onset of the triplet emission, with the band peaked at 730 nm, which is blue-shifted by as much as 64 nm with respect to the unsubstituted **Gd(acac)TPP** and by 46 nm compared to **Gd(acac)BrFTPP**. The particular behavior of **Gd(acac)FTPP** is also reflected in its triplet experimental decay time (about 70 μs), which is appreciably longer than those in the other two derivatives (50 μs). On the other hand, it is not easy to explain the relatively strong bands with singlet emissions at 653 and 717 nm of **GdTPP**. This could be due to the lower efficiency of ISC in comparison with that of the halogen-substituted derivatives as well as to the presence of impurities of the free base molecule, which exhibits a much more efficient fluorescence. Further investigations are in progress to make this point clear.

3.4. 1.5 μm Emission in Er Complexes. All of the emission spectra (see Figure 3) exhibit the typical 1540 nm emission of the $^4I_{13/2} \rightarrow {}^4I_{15/2}$ erbium transition with a line shape and fwhm very similar to those observed in other erbium complexes.[8,10,21,24,25,32] The emission of ErQ, considered as the standard model for erbium complexes,[33] is also reported for comparison. The overall NIR efficiency of the **Er(acac)TPP** complex was estimated to approximately $\phi_{IR} = 4 \times 10^{-4}$ through absolute measurements of the emitted intensity in a calibrated setup[22] and is in the range of the values reported in the literature, as discussed below. A slight increase is observed in the partially halogen-substituted **Er(acac)FTPP**, while the fully bromofluorinated **Er(acac)BrFTPP** approximately doubles the value measured in the unsubstituted complex. Such very low figures of efficiency cannot be attributed to the incomplete ISC of the singlet excitation or to the inefficient energy transfer to the erbium ion for a number of reasons. First, the intensity of the 1540 nm band among the different erbium derivatives does not correlate with the quenching factor of the visible emission (Figure 3) that varies in a range from 10 to 100. Second, even the lowest quenching factor, that is, 10 in **Er(acac)BrFTPP**, corresponds to 10% only of the absorbed energy emitted as visible radiation and thus lost for transfer to the erbium ion. This could not account by itself for the 0.04% efficiency of the NIR emission. Third, the present value of ϕ_{IR} is not far from the value of 2×10^{-4} measured in fluorescein-sensitized erbium complexes,[4] 7×10^{-5} of $Er(DBM)_3$[34] and 1×10^{-3} of similar erbium porphyrinates.[21] The same order of magnitude was also estimated from the ratio between the total and the radiative PL lifetime in terphenyl-based[6] and in pyridyltetrazine-based complexes.[24] It is quite unlikely that all of these different compounds have similarly inefficient mechanisms of ISC and energy transfer to the erbium ion. On the other hand, a recent study[35] suggests that the efficiency of the energy transfer to erbium is close to 100%. To this regard, it should also be noted that the NIR emission intensity in the present complexes seems to be independent of the large variation of the triplet energy levels observed in the different derivatives (see the band peak locations in Figure 4) but increases with the degree of halogen substitution. All of

TABLE 1: Luminescence Parameters of the Free Base and the Lanthanide Porphyrin Complexes

	emission band peaks (nm) and lifetimes				
complex	singlet		triplet		
H_2TPP	654 (<1 μs)	718 (<1 μs)			
Er(acac)TPP	655 (<1 μs)	717 (<1 μs)			
GdTPP	653 (<1 μs)	717 (<1 μs)	794 (51 μs)[a]	895 (50 μs)[a]	
Gd(acac)FTPP	649 (<1 μs)		730 (69 μs)[a]	818 (68 μs)[a]	910 (68 μs)[a]
Gd(acac)BrFTPP	656 (<1 μs)	708 (<1 μs)	776 (50 μs)[a]	845 (50 μs)[a]	900 (50 μs)[a]

[a] Uncertainties in the estimation of decay time are within ±2 μs.

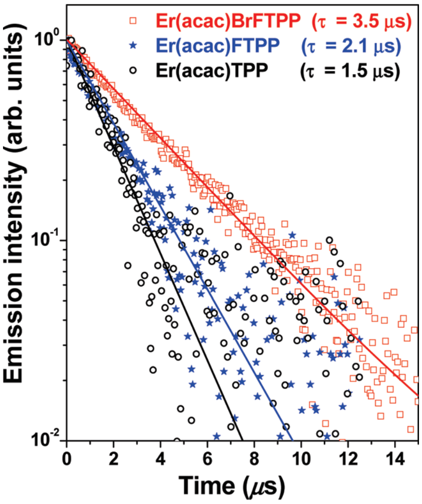

Figure 6. Decay of the NIR photoluminescence in the erbium complex and halogen derivatives excited at $\lambda_{\text{exc}} = 355$ nm.

these findings suggest that the effective bottleneck of the overall efficiency does not lie in the intramolecular energy-transfer processes. More reasonably, as underlined by several authors,[4,6,8,11−20] a strong quenching of the NIR emission may occur through Förster resonant transfer to the second overtone of the C−H vibration in the respective chemical groups of the porphyrinic ligand.

Within this framework, the strategy of substituting all of the aromatic hydrogens with halogens, presently achieved in **Er(acac)BrFTPP**, seems to be a step in the right direction since it doubles the intensity of the NIR emission regardless of the fact that it gives the lowest quenching factor of the visible emission. The improvement in efficiency is also reflected in the lifetime of the 1540 nm emission, as reported in Figure 6. The decay time progressively increases with the level of substitution from the value $\tau = 1.5$ μs in **Er(acac)TPP**, to $\tau = 2.1$ μs in **Er(acac)FTPP**, and up to $\tau = 3.5$ μs in **Er(acac)BrFTPP**. Significantly, the measured lifetimes are in good linear correlation with the intensities of the respective NIR emissions, in agreement with the linear dependence predicted for the quantum efficiency ϕ_{obs} of a quenched emission

$$\varphi_{\text{obs}} = \frac{\tau_{\text{obs}}}{\tau_{\text{rad}}} \tag{1}$$

We think such an agreement strongly supports the hypothesis that the low efficiency is definitely determined by the quenching of the erbium ion emission.

However, despite the increase due to halogenation, the observed lifetimes are still far from the typical value of the isolated erbium ion ($\tau_{\text{rad}} \approx 8$ ms) and even farther from the 200-fold increase obtained in the imidodiphosphinate complex.[19] This could be due to the incomplete halogen substitution of the present compounds since the acetylacetone capping ligand still contains both C−H and O−H groups, even though at a larger distance from the erbium ion than the aromatic groups.

4. Conclusions

We have investigated the effects produced on the optical properties of an erbium−porphyrin complex by the progressive substitution of the ligand hydrogens with halogens. While achieving an exhaustive physical knowledge of the intramolecular processes requires further quantitative analyses of the energy-transfer mechanisms, some conclusions can still be made. The efficiency of the NIR emission exhibits a clearly positive correlation with the degree of halogen substitution, while seems independent of the visible emission quenching factor and the triplet level energies. Such a behavior can interestingly be compared to the results reported in similar erbium complexes with a different ligand configuration, that is, based on platinum porphyrins. While the characteristic and nature of the visible emission is quite different due to the different dynamics of intramolecular energy transfer, the efficiency of the NIR emission is comparably low. Moreover, a significant correlation between the NIR intensity and lifetime has been found in the present complexes at different levels of halogenation. All of these findings confirm that the effective bottleneck of the sensitized NIR emission lies in the quenching of the erbium emitting level through Förster energy transfer to the second overtone of the C−H vibration. From this point of view, the substitution of the aromatic C−H bonds of the erbium-coordinating porphyrin macrocycle apears to be the right strategy. On the other hand, the relatively long distance characteristic of Förster interaction requires that all of the quenchers, that is, even the farther C−H and O−H groups of the acac capping ligand, be substituted in order to achieve an effective improvement of the quantum efficiency of the complex.

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Supporting Information Available: Figure S1 shows the 410 nm excited emission from samples of **Er(acac)TPP**, **Er(acac)FTPP**, and **Er(acac)BrFTPP** in PMMA films. The respective spectra are very similar to those in liquid solutions (Figure 3) if the broadening and spectral shift due to the solid-state environment are taken into account. As in the case of the residual visible fluorescence in liquid solutions, the intensity of the emission does not correlate with the degree of halogenation. This material is available free of charge via the Internet at http://pubs.acs.org.

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