NIR luminescence of gadolinium porphyrin complexes

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Dedicated to the memory of the late professor Alan Adler of Western Connecticut State University

Abstract

Most lanthanide porphyrin derivatives exhibit 'normal' absorption spectra with Q and B bands. The rare earth ions have little effect on the absorption spectra, which are much like those of other closed-shell metalloporphyrins. However, their emission spectra vary according to which lanthanide ion is present. We observe two types of emissions: (i) a line emission arising from the lanthanide ion f–f transitions and (ii) π-π* emission from the triplet state of porphyrin. In this Letter, we focus on the emission from gadolinium porphyrin complexes. The oxygen sensitivity was measured in solution and polymeric film. Both intensity and lifetime Stern–Volmer plots were measured.
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1. Introduction

Since the classic research of Weissman [1], Abramson [2] and of Crosby [3], lanthanide complexes have attracted many researchers. They have been investigated as laser materials, electroluminescent devices, biological indicators [4] and immunoassay sensors [5]. In general, the organic ligands of the complex absorb light and transfer the energy to the lanthanide ion through the triplet state of the ligand. Emission then occurs from the metal ion as an f–f transition. Crosby elegantly reviewed the process of energy transfer from the triplet manifold of the complex to the lanthanide ion levels in 1966, and the weight of the literature to date accepts this plausible mechanism. For example, all europium ion emission originates from the $^5D_0$ energy level with the strongest emission being the $^5D_0 \rightarrow {}^7F_2$ transition at approximately 615 nm. Complexes of ytterbium, neodymium, and erbium produce near-IR (NIR) lumines-cence at 980 nm, 1065 nm and 1520 nm, respectively from the f-shell.

Lanthanide porphyrin complexes were first synthesized by Horrocks [6] as potential nuclear magnetic resonance probes and shift reagents. Adler [7] investigated lanthanide-binding mechanisms by porphyrins. Buchler [8] synthesized a series of lanthanide porphyrins that have double-decker structures. These species produce near-infra-red charge transfer absorption bands whose frequencies are inversely proportional to the lanthanide ion radius. A great majority of publications on lanthanide porphyrins are focused on their medical applications as magnetic resonance imaging contrast agents [9]. Gadolinium texaphyrin, an expanded porphyrin ring species, is being investigated for cancer therapy as an efficient radiation sensitizer in addition to its role as a contrast agent [10]. The coordination of lanthanide porphyrins with chiral amino acids was detected using circular dichroism spectroscopy [11].

The groups at Minsk [12,13] and Seattle [14] were the first to evaluate the luminescence spectral properties of lanthanide porphyrins. Both groups found that the lanthanide porphyrins have similar absorption spectra with only

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minor changes for different complexed metal ions. However, the emission behavior varied greatly depending on the lanthanide ion. In summary: open shell lanthanides showed only very weak fluorescence (Eu, Ho, Er, Tm), complete shell Lu porphyrin (f^{14}) and empty shell La porphyrin (f^0) showed a moderate fluorescence, and half-filled shell Gd porphyrin (f^7) produced a moderate triplet phosphorescence around 700 nm. Measurement at 7.2 K produces no change in the spectrum or the lifetime from that observed at 77 K [15]. Yb porphyrin (f^{13}) has two types of emission: moderate phosphorescence and a weak 970 nm f–f band.

This Letter reports the luminescence of the series of lanthanide porphyrins in the near-infrared region. The visible emissions are reported elsewhere [12–14]. Luminescence yields, lifetimes and oxygen sensitivity of these complexes will be discussed in detail. Results presented here have the potential to be the first steps toward the creation of a biological sensor utilizing the special properties of Gd porphyrins in the near-infrared region.

2. Experimental

PtTFPL [(platinum tetra(pentafluorophenyl)porpholactone], lanthanide TFPP [Gd, Yb, Ho, Er, Tb tetra(pentafluorophenyl)porphine], GdTPP [Gd tetraphenylporphine], and GdOEP [Gd octaethylporphine] were purchased from Frontier Scientific in Logan, UT. All of the porphyrins were exposed to pyridine and sodium acetate at pH 9 to establish acetylacetonate as counter ion. Lanthanide TPyP [Gd, Yb, Ho, Er, Tb, Nd tetra(p-pyridyl)porphines] were made by the group of the late Alan Adler [16,17]. All lanthanides exhibited +3 charge and we believe the counter ion is acetylacetonate.

All absorbance measurements were taken on a Hewlett–Packard 8453 Diode array UV/vis spectrophotometer. A small amount of the solid samples were dissolved in the appropriate solvent and scanned from 300 to 800 nm.

NIR emission spectra were recorded on a modified SPEX Fluorolog 2 (J.Y. Horiba, Edison, NJ) equipped with a liquid nitrogen cooled Ge diode detector (EO817L; North Coast Scientific Corp.). As an excitation source, a 450 W Xe-lamp (Osram) in conjunction with a double-grating monochromator was used. Emission spectra were recorded at 77 K employing a liquid nitrogen filled dewar and pyrex NMR tubes (4 mm diameter). The emission spectra were corrected for the wavelength sensitivity of the detector.

Phosphorescence lifetimes were measured at 77 K exciting with pulses from a Lambda Physik dye laser (FL3002; Laser dye: Stilbene 3) which was pumped with a Lambda Physik Excimer laser (Lextra 50). The phosphorescence was collected and isolated using lenses and monochromators (H10 for Vis spectral range and 1681B for NIR spectral range; Jobin-Yvon Inc.) and focused onto Hamamatzu photomultiplier tubes (PMT) (R928 for the visible spectral range and H9170–45 for NIR spectral range). The photocurrent from the PMT was amplified (SR 560, Stanford

Research Systems) and stored on a digital oscilloscope (TDS 360, Tektronix). We estimate the lifetime measurement error to be $\approx 5\%$.

A Stern–Volmer plot, which is inverse luminescence intensity versus pressure, characterizes oxygen sensitivity [18]. These plots are generated in our laboratory using a home-built instrument that can measure intensity as a function of pressure and temperature that is referred to as the PMT Survey Apparatus [19]. It measures a single point that is spatially averaged over ~ 1 cm^2 at constant temperature. This instrument has a sample chamber which is temperature and pressure controlled. It uses filtered light from a tungsten lamp to excite the molecule, and detects the filtered emission using a photomultiplier tube. The excitation light is filtered using a 400 nm band pass filter with a 20 nm width at half height. The emitted light is filtered using long-wavelength pass filters. The pressure is set to vacuum then to atmospheric pressure for initial calibration. The computer controlled valve mechanism sets the desired pressure.

3. Results and discussion

The absorption spectra of all measured lanthanide complexes have clear Q and strong Soret bands. We confirmed the observation of Shinoki [20] that absorption peaks shift with the choice of solvent but preserve the vibronic spacing. Using hydrocarbon, oxygen, and nitrogen containing solvent types, the GdTFPP Soret band shifts. Ethanol solvent produces a Soret band at 418 nm, methylcyclohexane (MCH) moves this band to 420 nm, and triethylamine redshifts this band even further to 424 nm. Similarly, the Q absorption bands red-shift from 550 nm when using ethanol and MCH as solvents to 554 nm for triethylamine solvent. Their relative extinction coefficients also change as a function of the solvent. These spectral shifts are attributed to complexing of the solvent and the axial coordination sites of Gd porphyins [21].

3.1. Luminescence properties

Three types of luminescence measurements were carried out: (i) emission and excitation spectra (ii) lifetime and (iii)
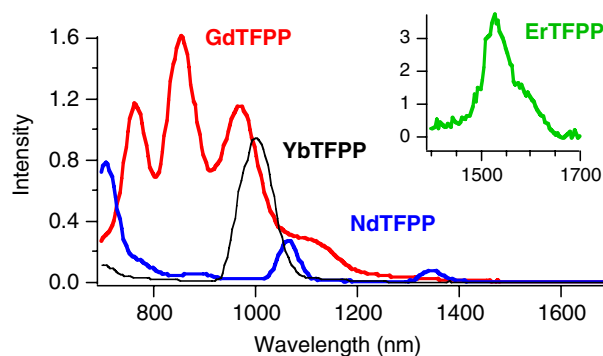

Fig. 1. Luminescence spectra of GdTFPP, YbTFPP, NdTFPP and ErTFPP in a MCH matrix at 77 K after excitation at 420 nm.
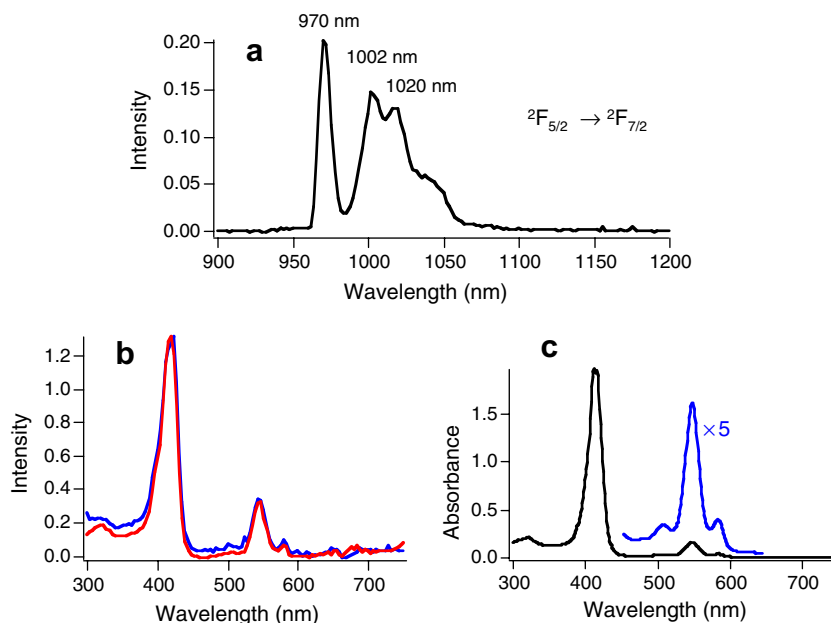
Fig. 2. (a) YbTFPP f–f emission spectrum excited at 420 nm in MCH at 77 K, (b) the excitation spectra detected at 970 nm (blue) and 1000 nm (red), (c) absorption spectrum in MCH solution at 22 °C.

relative quantum yield. The emission spectra of lanthanide porphyrins were measured at 77 K in three solvent systems: MCH, *n*-octane and ethanol. Fig. 1 compares the emission spectra of four lanthanide porphyrins excited in the Soret band. The complexes of Yb, Nd and Er porphyrins each produce known near infrared f–f rare earth emission at 970 nm, 1002 nm, 1020 nm (Yb), 890 nm, 1068 nm, 1348 nm (Nd) and 1530 nm (Er), respectively. The Gd complex on other hand appears to show a molecular porphyrin triplet emission at 726 nm, 810 nm, 922 nm, 1056 nm (GdTFPP). We observed no detectable emissions from Dy, Eu, Tb and Ho porphyrins in the spectral region of 700 nm to 1700 nm. The lack of emission from these complexes can be attributed to radiationless decay due to the presence of a low energy charge transfer state and/or to non-emitting f-shell levels below the porphyrin triplet state [12,14].

Fig. 2a shows the high resolution emission spectrum of YbTFPP at 77 K in MCH. The emission band is assigned to the Yb(III) transition $^2F_{5/2} \rightarrow {}^2F_{7/2}$, and the spectrum shows a sharp peak at 970 nm and a broad band at 1000 nm with a shoulder at 1020 nm. The excitation spectra for YbTFPP at 77 K detected at 970 nm and 1000 nm are displayed in Fig. 2b. Both excitation spectra are similar to the absorption spectrum (Fig. 2c) and validate the metal f–f emission observed.

Fig. 3 shows the emissions of four different Gd porphyrins. The spectra show a progression of structured bands that occur between 600 nm to 1200 nm that have not been previously reported. The spectra represent the phosphorescence from the triplet state porphyrins' rings and exhibit a very characteristic vibronic-structured emission. The emission band maxima are presented in Table 1, and it should be noted that for GdTFPP and GdOEP the triplet 0,0 band
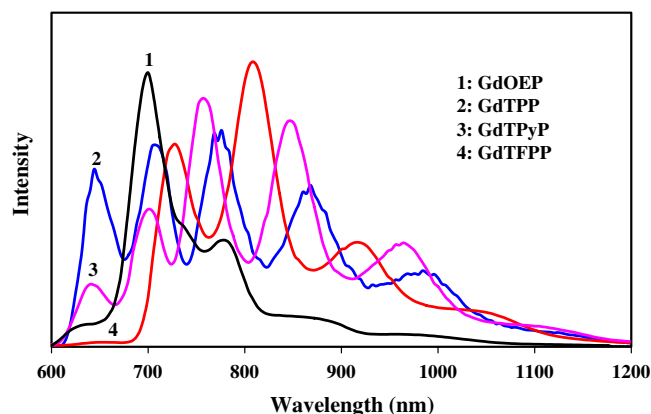

Fig. 3. Phosphorescence emission spectra of gadolinium porphyrins in MCH at 77 K.

is weak. However GdTPP and GdTPyP have strong 0,0 bands at 644 nm and 640 nm, respectively. The band spacing varies with the complex and is typical of porphyrin ring IR frequency. Excitation spectra of the vibronic bands of the measured Gd porphyrins are consistent with the absorption spectra. A detectable spectral sharpening was detected only for GdOEP in *n*-octane, as in a Shopl'skii type matrix.

The lifetimes shown in Table 1 have values for the Gd porphyrins that vary from 85 to 142 μs. As expected, all the vibronic bands of each Gd complex show the same emission lifetime. These measured lifetimes are in agreement with known triplet state values of metal porphyrins [22]. The phosphorescent state of Gd porphyrins is rather unusual.

Normal phosphorescence is from the lowest triplet. However, the Gd ion has a 7/2 state. There are 7 unpaired electrons in the f-shell of the metal. Thus the 3 states of the

Table 1
Luminescence parameters of lanthanide porphyrins

Compound	Porphyrin phosphorescence nm	Vibronic spacing cm^{-1}	Relative yield[a] %	Lifetime[b] μs
Gd(TFPP)	726, 810, 922, 1056	1430, 1500,	20	142@1050 nm
GdTPP	644, 712, 770, 870, 988, 1132	1480, 1060, 1490, 1370	24	94@990 nm
GdOEP	686, 700, 740, 786, 836, 902	290, 770, 790	54	85@1000 nm
GdTPyP	640, 704, 760, 848, 964, 1108	1420, 1050, 1365, 1420	25	134@970 nm
	Rare earth f–f transitions nm			
YbTFPP	$^2F_{5/2} \rightarrow {}^2F_{7/2}$ 970, 1002, 1020	NA	3	4@1002 nm
NdTPyP	$^4F_{3/2} \rightarrow {}^4I_{9/2}$ 890, 1068, 1348	NA	<1	0.37@1070 nm
ErTPyP	$^4I_{13/2} \rightarrow {}^4I_{15/2}$ 1530	NA	–	–

[a] Uncertainty 15%.
[b] Uncertainty 5%.

triplet become 24 states: a sextet, an octet and a decket. Apparently, the 24 states interconvert quickly as compared to the lifetime of the triplet. The lifetimes for Yb and Nd complexes are 4 and 0.37 μs, respectively, and both are representative of the f–f type transitions exhibited by other organic complexes of these metals.

A relative quantum yield of lanthanide porphyrins in MCH at 77 K was estimated using PtTFPL as a reference emitter which has emission bands in the NIR region [23]. All the samples were excited at 410 nm with an absorbance of $A = 0.3$. The recorded emission spectra were integrated and baseline subtracted. The ratio of the lanthanide porphyrins and PtTFPL integrals were used to estimate quantum yields by comparison to PtTFPL whose quantum yield is known (60%). The luminescence quantum yields in MCH are summarized in Table 1. Our uncertainties in these measurements are approximately 15%. Relatively high yields were observed for Gd porphyrins ranging from 20% to 50%. The yield for the Yb porphyrin was estimated to be ∼3% . The relatively high yield of the Gd porphyrins' phosphorescence make them a potential choice as oxygen sensor dyes.

3.2. Oxygen dependency

The phosphorescence lifetime of GdTFPP was measured as a function of oxygen concentration. The lifetimes of a 10^{-5} M ethanol solution measured at 1040 nm were taken under known pre-mixed gas mixtures of 0%, 5%, 21%, 50% and 100% oxygen with a balance of nitrogen. The sample was allowed to equilibrate for 5 min for each gas mix. Fig. 4 shows the lifetime rate constant as function of oxygen. The plot produces a linear response with an intercept of 61 μs and the slope of $(6.0 \pm 0.2) \times 10^8$ M^{-1} s^{-1}. The latter represents the GdTFPP triplet state quenching rate constant by oxygen. In a separate experiment, GdTFPP films were tested for oxygen sensitivity. Using a gas permeable polymer matrix film, the three porphyrin complexes were prepared by dissolving 5 mg of the metal complex and 500 mg of silicon polycarbonate co-polymer (General Electric, Fairfield, CT, LR 3320) in 20 ml of dichloromethane. The dried sensor film on an aluminum
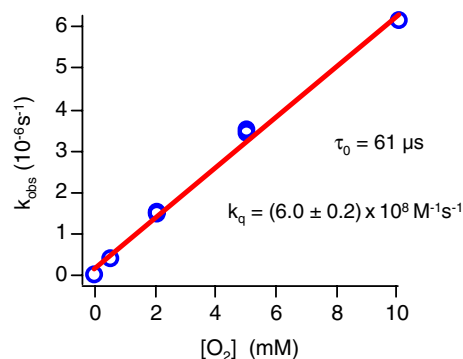

Fig. 4. Phosphorescence decay constant of GdTFPP in ethanol solution as a function of oxygen concentrations; excited at 420 nm and detected at 1044 nm at room temperature.

plate was tested by monitoring the phosphorescence intensity as a function of pressure/oxygen following standard procedure. Results of the GdTFPP film response are shown in Fig. 5 plotted as I_0/I versus oxygen in the Stern–Volmer format. Note that here I_0 is the intensity at 21% oxygen. We observed ∼70% intensity change over 0–21% oxygen range equivalent to ∼3.5% intensity per % oxygen for GdTFPP. The GdTFPP film Stern–Volmer result shows a high degree of non-linearity especially when compared with
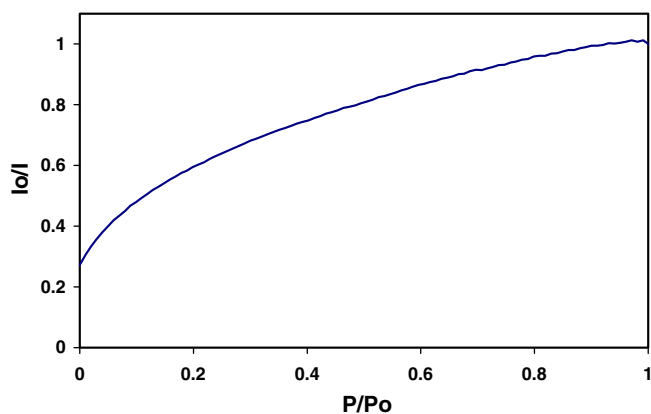

Fig. 5. Intensity Stern–Volmer plot of GdTFPP in a polymer film as a function of pressure excited at 410 nm and detected at 740 nm at room temperature.

the PtTFPP response [24]. This behavior can be attributed to the out of plane structure of the Gd porphyrin [25] while Pt porphyrin has a square planar structure with the platinum in the middle of the ring. For a YbTFPP film we measured the 970 nm line intensity decay curves and observed no response to oxygen concentrations. The lack of oxygen dependency in the YbTFPP can be attributed to the short lifetime of the f–f transition and to the reduced accessibilities of the buried f-orbital [4].

Our studies provide results on a series of stable NIR porphyrin based emitters. The complete emission spectra of four Gd porphyrins are reported for the first time and characterized. Some of the Gd porphyrin complexes are shown to be potentially useful as materials for NIR oxygen sensing.

Acknowledgements

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