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| Title            | Near-IR Luminescent Yb-III Coordination Polymers Composed of Pyrene Derivatives for Thermostable Oxygen Sensors                                                                                                                                                                                                                                                                                                                                                                    |
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# Near-IR luminescent Yb(III) coordination polymers composed of pyrene derivatives for thermo-stable oxygen sensors

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**Abstract:** This work synthesized oxygen sensitive and near infrared (NIR) luminescent Yb(III) coordination polymers incorporating ligands based on pyrene derivatives: Yb(III)-TBAPy and Yb(III)-TIAPy (TBAPy: 1,3,6,8-tetrakis(*p*-benzoate)pyrene, TIAPy: 1,3,6,8-tetrakis(3,5-isophthalic acid)pyrene). The coordination structures of these materials were characterized using electrospray ionization mass spectrometry, X-ray diffraction and thermogravimetric analysis, while the porous structure of the Yb(III)-TIAPy was evaluated based on its adsorption isotherm. The NIR luminescence properties of the Yb(III)-TBAPy and Yb(III)-TIAPy were examined by acquiring emission spectra and determining emission lifetimes under air, argon and vacuum. The Yb(III)-TIAPy exhibited high thermal stability (with a decomposition temperature of 400 °C), intense luminescence (with an emission quantum yield under argon of 6.6%) and effective oxygen-sensing characteristics. These results suggest that NIR luminescent Yb(III) coordination polymers made using pyrene derivatives could have applications in novel thermo-stable oxygen sensors.

## Introduction

Lanthanide(III) complexes with narrow emission bands and long emission lifetimes based on *4f-4f* transitions have attracted interest as luminescent materials for use in displays, optical sensors and bio-imaging applications.<sup>[1-3]</sup> The photo-excitation of organic aromatic ligands with large absorption coefficients ( $> 10,000 \text{ M}^{-1}\text{cm}^{-1}$ ) in such complexes results in intense photosensitized luminescence. This phenomenon is due to energy transfer between excited triplet states associated with  $\pi-\pi^*$  transitions in the aromatic ligands and *4f* orbitals in the lanthanide(III) ions.<sup>[4]</sup> However, these excited triplet states are quenched by the triplet state of atmospheric oxygen, such that the emission intensity for such materials is reduced in the presence of oxygen. Based on this photophysical quenching, lanthanide(III) complexes with aromatic ligands have applications in oxygen sensors. In 2000, Amao and co-workers reported the first oxygen sensor based on this process, using a luminescent Eu(III) complex with thenoyltrifluoroacetylacetonate ligands.<sup>[5]</sup> Parker

and Maury employed oxygen-sensitive mixed Eu(III)/Tb(III) complexes having conjugated alkynyl chromophore-triazacyclononane ligands.<sup>[6]</sup> Faulkner researched bimetallic Eu(III)/Tb(III) complexes that displayed luminescence proportional to the ambient oxygen concentration.<sup>[7]</sup> Various other luminescent lanthanide(III) complexes with oxygen sensing properties have also been reported.<sup>[8-14]</sup>

Here, we focus on pyrene derivatives with carboxyl groups: TBAPy (1,3,6,8-tetrakis(*p*-benzoate)pyrene) and TIAPy (1,3,6,8-tetrakis(3,5-isophthalic acid)pyrene) for oxygen-sensitive lanthanide luminophores. These moieties are well known to be useful in the construction of three-dimensional metal coordination polymers,<sup>15</sup> and such polymers incorporating In(III), Zr(II), Ce(III) or Eu(III) have been found to have characteristic nano-porous solid structures and to show gas adsorption.<sup>[15-18]</sup> These pyrene derivatives can also have applications in luminescent materials as  $\pi$ -conjugated luminescent organic dyes with high emission quantum yields.<sup>[19]</sup> The absorption wavelengths associated with the luminescence of these compounds coincides with the output wavelengths of blue LEDs, which can therefore be used as excitation sources in optical devices. To date, a number of Tb(III) and Eu(III) complexes with pyrene derivatives as ligands have been reported to be usable with blue LEDs.<sup>[20-23]</sup>

Luminescent lanthanide coordination polymers incorporating TBAPy and TIAPy are expected to allow the fabrication of novel oxygen-sensitive luminophores. However, the excited triplet state energy levels of both TBAPy and TIAPy are lower than the emission energy levels of lanthanide(III) ions that emit in the visible region of the spectrum, such as green luminescent Tb(III), red luminescent Eu(III) and deep-red luminescent Sm(III) ions. This scenario results in non-radiative quenching of the excited lanthanide ions.<sup>[15,16]</sup> Therefore, combinations of pyrene-based compounds and visible-luminescent lanthanide ions do not make effective luminescent oxygen sensors. For this reason, the work reported herein attempted to use Yb(III) ions to produce luminescent lanthanide coordination polymers composed of TBAPy and TIAPy. Yb(III) complexes show near infrared (NIR) luminescence assigned to the  $^2F_{5/2}-^2F_{7/2}$  magnetic dipole transition at 970 nm. The energy gap between the  $^2F_{7/2}$  and  $^2F_{5/2}$  levels is  $10,200 \text{ cm}^{-1}$ ,<sup>[24]</sup> and this value is less than that for the excited triplet states of TBAPy and TIAPy ( $> 15,000 \text{ cm}^{-1}$ ). In addition, diketonate Yb(III) complexes incorporating pyrene derivatives have been reported to function as photosensitized NIR luminophores, albeit with low emission quantum yields ( $< 1.0\%$ ).<sup>[25]</sup> The NIR luminescence of Yb(III) complex could also be helpful in undersea and biomedical experiments, because of the high optical transparency (800-1000 nm).

In this study, highly luminescent Yb(III) coordination polymers made with TBAPy and TIAPy are reported. The structures of these materials are shown in Figs. 1a and 1b (Yb(III)-TBAPy and Yb(III)-TIAPy, respectively). The TBAPy and TIAPy ligands both

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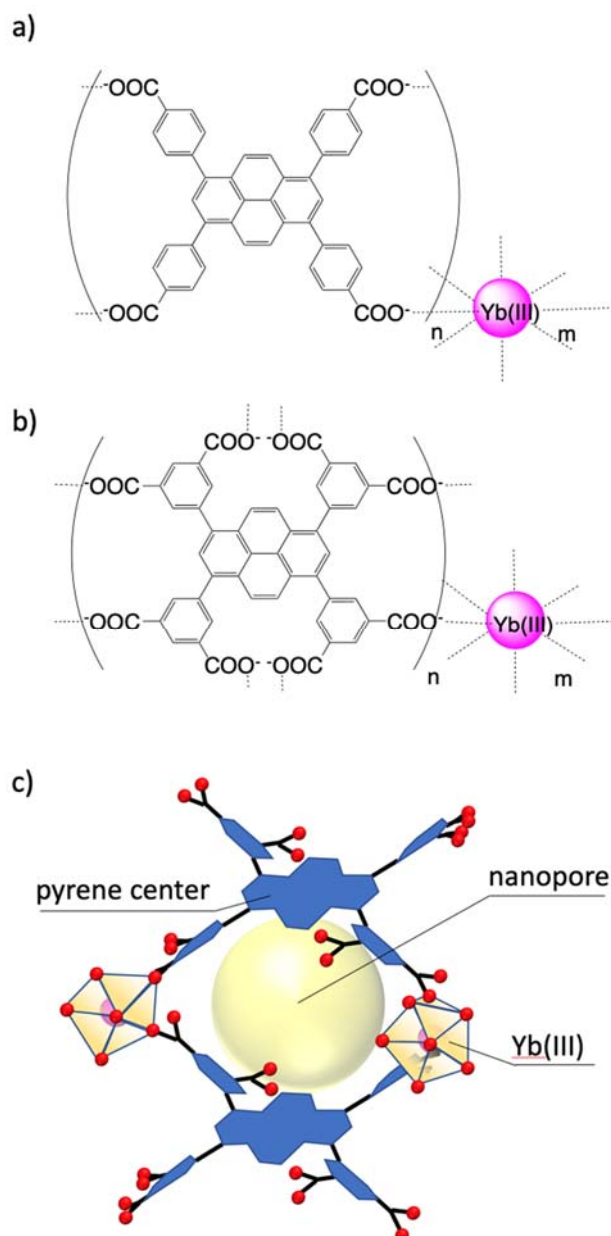
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## FULL PAPER

possess four benzene rings and have four and eight carboxyl groups, respectively. These carboxyl groups promote the formation of tightly packed, thermally stable, porous structures that enhance oxygen adsorption by the Yb(III) coordination polymers. The Yb(III)-TBAPy and Yb(III)-TIAPy were obtained by the hydrothermal reactions of YbCl<sub>3</sub> with H<sub>4</sub>-TBAPy and H<sub>8</sub>-TIAPy in a mixed solvent composed of dimethyl formamide (DMF), dioxane and water. In addition, a sample of Eu(III)-TBAPy was prepared for comparison purposes.



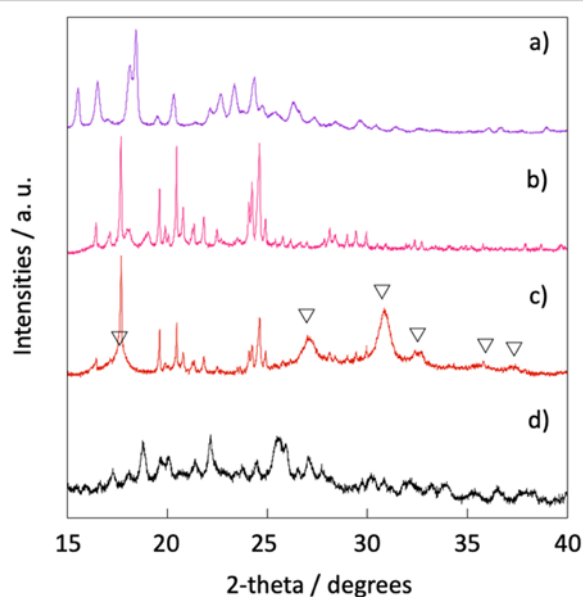
**Figure 1.** Chemical structures of a) Yb(III)-TBAPy and b) Yb(III)-TIAPy. c) illustration image of Yb(III)-TIAPy based on CCDC990747.<sup>[16]</sup>

Yb(III)-TIAPy was also synthesized via the complexation of YbCl<sub>3</sub> with H<sub>8</sub>-TIAPy in an aqueous solution of ammonia. The coordination structures of these complexes were characterized using electrospray ionization mass spectrometry (ESI-MS), X-ray diffraction (XRD) and thermogravimetric analysis (TGA). The tight porous structure of the Yb(III)-TIAPy was also examined using its adsorption isotherm (Fig. 1c) and this material was found to contain nanopores, based on Brunauer–Emmett–Teller (BET) calculations. Decomposition temperature of the Yb(III)-TIAPy was estimated to be 400 °C. The NIR luminescence properties of the Yb(III)-TBAPy and Yb(III)-TIAPy were assessed by acquiring emission spectra and determining emission lifetimes. The emission quantum yield of the Yb(III)-TIAPy was found to be 6.6% under argon, which is similar to values previously reported for highly luminescent Yb(III) complexes.<sup>[24]</sup> The oxygen-sensing abilities of these materials were evaluated based on their emission spectra and lifetimes under air, argon and vacuum. The thermo-stable and oxygen-sensitive Yb(III) luminophore is demonstrated as an effective solid-state oxygen sensor.

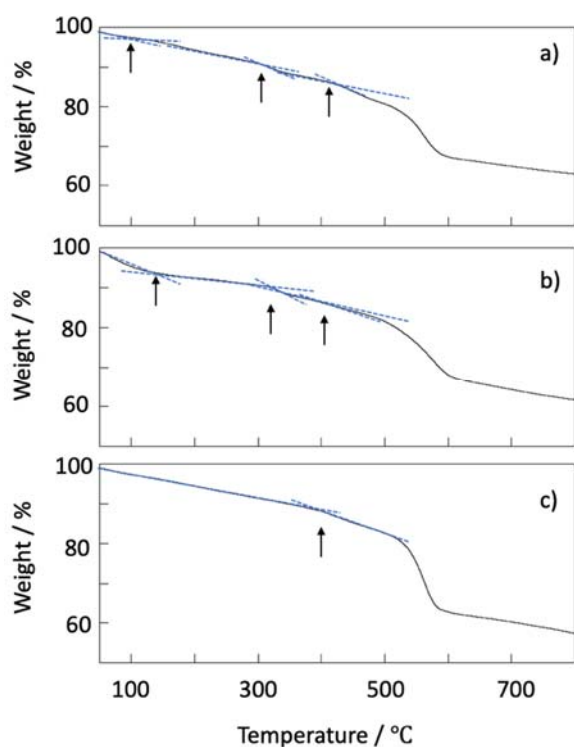
## Results and Discussion

### Structures of Yb(III)-TBAPy and Yb(III)-TIAPy in solid state:

Yb(III)-TBAPy and Yb(III)-TIAPy were synthesized based on the hydrothermal reactions of YbCl<sub>3</sub> with H<sub>4</sub>-TBAPy and H<sub>8</sub>-TIAPy, respectively, at 85 °C for 48 h. Eu(III)-TBAPy was also prepared as a standard lanthanide coordination polymer. The formation of coordination networks in the Yb(III)-TBAPy, Yb(III)-TIAPy and Eu(III)-TBAPy was confirmed using IR spectroscopy and ESI-MS. The XRD patterns obtained from the TBAPy, Yb(III)-TBAPy, Yb(III)-TIAPy and Eu(III)-TBAPy are provided in Fig. 2. The powder TBAPy pattern (Fig. 2a) is seen to be different from that for the Eu(III)-TBAPy (Fig. 2b), while the Yb(III)-TBAPy pattern (Fig. 2c) agrees with the pattern produced by Eu(III)-TBAPy. The similar XRD patterns produced by the Yb(III)-TBAPy and Eu(III)-TBAPy indicate the formation of a three-dimensional network structure with porous cavities in Yb(III)-TBAPy. The crystal grain sizes in Yb(III)-TBAPy and Eu(III)-TBAPy as calculated using the Scherrer equation were 102 and 104 nm, respectively. We also observed broad peaks at 17.50°, 27.07° and 30.87°, which were assigned to Yb<sub>3</sub>O<sub>4</sub>, as indicated by triangles in Fig. 2c. These Yb<sub>3</sub>O<sub>4</sub> nanoparticles may have been attached to the Yb(III)-TBAPy crystal surfaces. The XRD pattern produced by the Yb(III)-TIAPy is significantly different to those for both Yb(III)-TBAPy (Fig. 2d) and the powder TIAPy (Fig. S1), possibly due to variations in the packing structures in the crystals of these materials. The coordination of Yb(III) ions with the TIAPy ligands was confirmed based on shifts in the IR peaks due to C=O groups (TIAPy: 1685 cm<sup>-1</sup>, Yb(III)-TIAPy: 1538 cm<sup>-1</sup>) as well as the ESI-MS data. The main small angle peaks for Yb(III)-TIAPy at 8.40°, 9.22°, 12.73° and 14.38°, are very similar to those reported for three-dimensional Eu<sub>2</sub>(H<sub>2</sub>TIAPy)(H<sub>2</sub>O)<sub>4</sub> with porous cavities (Fig. S1).<sup>[16]</sup> The IR results obtained from the Yb-TIAPy prepared by a hydrothermal reaction are also similar to those for Yb(III)-TIAPy prepared by complexation (Figs. S2). It is therefore evident that the network porous structure formed by the Yb ions and TIAPy ligands is not affected by the preparation method.



**Figure 2.** XRD patterns of a) TBAPy molecule, b) Eu(III)-TBAPy, c) Yb(III)-TBAPy, and d) Yb(III)-TIAPy.

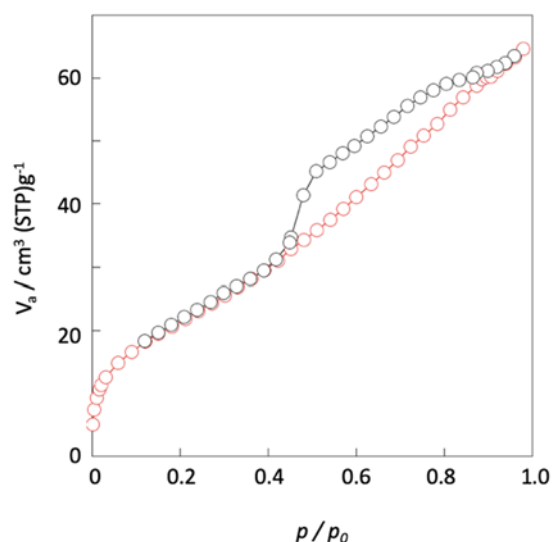


**Figure 3.** TGA curves of a) Yb(III)-TBAPy, b) Yb(III)-TIAPy prepared by hydrothermal reactions of YbCl<sub>3</sub> with H<sub>4</sub>-TBAPy and H<sub>8</sub>-TIAPy in DMF/dioxane/water mixed solution and c) Yb(III)-TIAPy prepared by the complexation of YbCl<sub>3</sub> with H<sub>8</sub>-TIAPy in aqueous solution with ammonia.

The TGA data for Yb(III)-TBAPy and Yb(III)-TIAPy are shown in Fig. 3. Inflection points at approximately 100 and 300 °C in the Yb(III)-TBAPy plot can possibly be ascribed to the elimination of

argon gas, DMF and 1,4-dioxane from porous cavities (Fig. 3a). Inflection points are also evident in the data for the Yb(III)-TIAPy prepared by a hydrothermal reaction, at the same temperatures (Fig. 3b). In contrast, Yb(III)-TIAPy prepared by complexation (Fig. 3c) undergoes a monotonic mass decrease from 20 to 300 °C, due to the loss of adsorbed argon gas. The mass loss for this specimen at 400 °C was found to be 11.4%. The sudden change in the inclinations of the TGA data at approximately 500 °C in the Yb(III)-TBAPy and Yb(III)-TIAPy plots is attributed to decomposition of the network structure and the partial volatilization of TBAPy and TIAPy. The decomposition temperatures (dp) for these materials are much higher than those previously reported for one- and two-dimensional Eu(III) coordination polymers (dp for [Eu(hfa)<sub>3</sub>(dppb)]<sub>n</sub> (hfa: hexafluoroacetylacetonate, dppb: 1,1'-biphenyl-4,4'-diylbis(diphenylphosphine oxide) = 306 °C, dp for [Eu<sub>3</sub>(hfa)<sub>9</sub>(tppb)]<sub>n</sub> (tppb: tris(4-diphenylphosphorylphenyl)benzene) = 354 °C).<sup>[26–28]</sup> The Yb-TBAPy and Yb-TIAPy frameworks are therefore evidently thermally stable at high temperatures.

The gas adsorption capacity of Yb(III)-TIAPy was estimated using the nitrogen adsorption isotherm shown in Fig. 4. The difference between the adsorption and desorption rate constants for this material produced hysteresis in the isotherm. The effective increase in the plot at approximately  $p/p_0=0$  corresponds to the adsorption of gas in nanopores. Using the ideal gas law, we calculated the nitrogen adsorption amount at a pressure ( $P$ ) of 101.33 kPa and a temperature ( $T$ ) of 273 K (that is, STP conditions), using an ideal gas constant ( $R$ ) of 8.31 J K<sup>−1</sup> mol<sup>−1</sup> and a volume ( $V$ ) of 64.69 cm<sup>3</sup> ( $p/p_0=1.0$ ). The adsorption amount was found to be  $8.01 \times 10^{-2}$  g/g, which is equivalent to 8 wt% for Yb(III)-TIAPy.



**Figure 4.** Nitrogen-adsorption isotherm of Yb(III)-TIAPy measured at 77 K.

This increases to 12% using argon instead of nitrogen, which is close to the 11.4% mass loss exhibited by Yb(III)-TIAPy during TGA, and is attributed to argon desorption. This result provides further evidence that the framework decomposition temperature

## FULL PAPER

for Yb(III)-TIAPy is 400 °C. The specific surface area of Yb(III)-TIAPy was estimated from BET calculations to be 52.9 m<sup>2</sup>/g (Fig. S3). Overall, these results establish that Yb(III)-TIAPy has a three-dimensional network structure and nano-sized porous cavities suitable for gas adsorption.

**Emission properties:** The excitation and emission spectra of Yb(III)-TBAPy and Yb(III)-TIAPy in the solid state are presented in Figs. 5a and 5b, respectively. The band at approximately 970 nm in response to excitation at 350 nm is assigned to <sup>2</sup>F<sub>7/2</sub>-<sup>2</sup>F<sub>5/2</sub> transitions of Yb(III) ions. We also observed green emission bands produced by both materials, at 547 and 560 nm, respectively. These emission bands were red-shifted from the fluorescence peaks of the original TBAPy and TIAPy ligands (Figs. S4a and S4b). Chelation of the Yb(III) ions with the carboxyl groups of the ligands could possibly stabilize the LUMOs of the TBAPy and TIAPy, resulting in red-shifts of the fluorescence bands produced by the pyrene centers. The excitation bands for Yb(III)-TBAPy and Yb(III)-TIAPy monitored by tracking emission at 970 nm (associated with the 4f-4f transitions of Yb(III) ions) were similar to their absorption bands. These excitation spectra indicate that Yb(III)-TBAPy and Yb(III)-TIAPy are excited by blue light irradiation (465 nm). From these results, it is evident that excitation of the pyrene-based ligands of the Yb(III)-TBAPy and Yb(III)-TIAPy effectively generated photosensitized luminescence (see supporting information, NIR luminescence).

The time-resolved emission profiles produced by Yb(III)-TBAPy and Yb(III)-TIAPy at 970 nm upon excitation in air both exhibit double exponential decay, with sub-microsecond and microsecond scale lifetimes, as shown in Figs. 5c and 5d. These decay curves are attributed to the presence of two types of luminescent Yb(III) ions in the samples. The emission lifetimes were determined from the slopes of logarithmic plots of the decay profiles. The two components of emission lifetimes for Yb(III)-TBAPy were estimated to be 31.2 ns and 509 ns. The two-emission center might be originated from the surface and internal luminescence, respectively. The two emission lifetimes for Yb(III)-TIAPy (10.3 μs and 27.8 μs) are much longer than those for Yb(III)-TBAPy. The elimination of coordinated water and DMF molecules from cavities in the Yb(III)-TIAPy could potentially reduce the non-radiative constant,  $k_{nr}$ , resulting in an increase in lifetime. Prior work with NIR luminescent lanthanide coordination compounds such as Yb(III), Nd(III) and Er(III) complexes has shown that coordinated water and solvent molecules promote effective non-radiative transition via vibrational relaxation.<sup>[25,29,30]</sup> Thus, the present time-resolved emission measurements indicate that Yb(III)-TIAPy did not have coordinated water or solvent molecules in its pores or on its surface.

The emission quantum yields and the radiative and non-radiative constants for Yb(III)-TBAPy and Yb(III)-TIAPy were determined using the Strickler-Berg equation. The radiative and observed lifetimes can be expressed as

$$\tau_{rad} = \frac{1}{k_r} \quad (1)$$

$$\tau_{obs} = \frac{1}{k_r + k_{nr}} \quad (2)$$

The radiative rate constant ( $k_r$ ), non-radiative rate constant ( $k_{nr}$ ) and 4f-4f emission quantum yield ( $\Phi_{EM}$ ) for the Yb(III) compounds are given by the equations,

$$k_r = \frac{1}{\tau_{rad}} = 2300 \times \frac{8\pi c n^2 \tilde{\nu}_A^2 g_l}{N_A g_u} \int \epsilon(\tilde{\nu}) d\tilde{\nu} \quad (3)$$

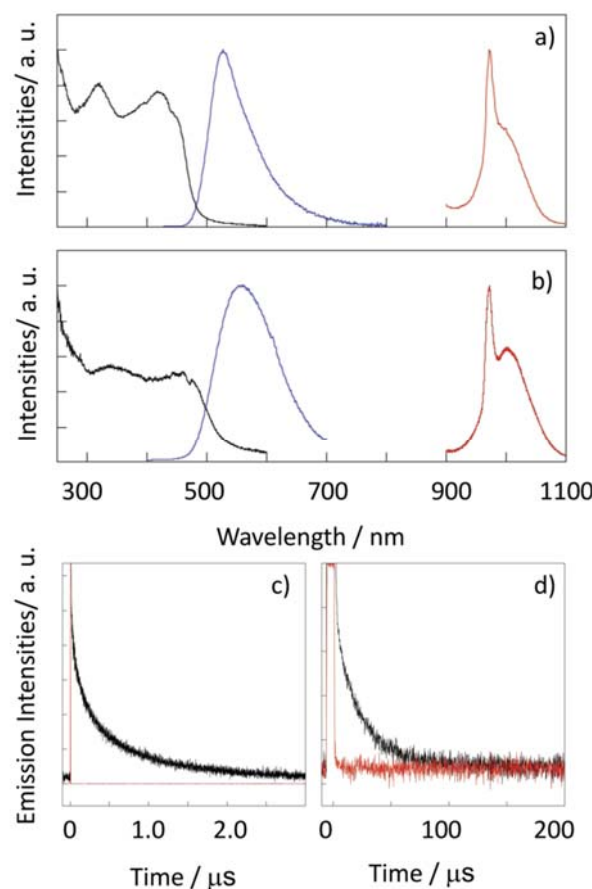
$$\tilde{\nu}_A = \frac{\int \tilde{\nu} \cdot \epsilon(\tilde{\nu}) d\tilde{\nu}}{\int \epsilon(\tilde{\nu}) d\tilde{\nu}} \quad (4)$$

$$k_{nr} = \frac{1}{\tau_{obs}} - \frac{1}{\tau_{rad}} \quad (5)$$

and

$$\Phi_{Em} = \frac{k_r}{k_r + k_{nr}} = \frac{\tau_{obs}}{\tau_{rad}} \quad (6)$$

where  $c$ ,  $\tilde{\nu}$ ,  $N_A$ ,  $\epsilon(\tilde{\nu})$ , and  $g_l$  and  $g_u$  are the speed of light in a vacuum, the frequency of the transition, the refractive index of the medium, Avogadro's constant, the absorption coefficient, and the degeneracies of the ground and excited states, respectively.



**Figure 5.** Excitation (black), phosphorescence (blue) and 4f-4f emission (red) spectra for a) Yb(III)-TBAPy and b) Yb(III)-TIAPy (red) in solid. Excitation wavelength for phosphorescence and emission spectra are at 350 nm. Monitor wavelength for excitation spectra are at 972 nm. Emission lifetime profiles of c) Yb(III)-TBAPy and d) Yb(III)-TIAPy in solid. Red lines in c and d are reference without samples. Excitation wavelength are at 355 nm (single photon counting method).

The  $\tilde{\nu}_A$  value in Equation 3 represents the barycenter of the 4f-4f absorption transition. Using these equations, the  $k_r$  constants for Yb(hfa)<sub>3</sub>(tppo)<sub>2</sub> (hfa: hexafluoroacetylacetonate, tppo: triphenylphosphineoxide), Yb(hfa)<sub>3</sub>(biphepo) (biphepo: 2,2'-bis(diphenylphosphoryl)biphenyl) and Yb(bta)<sub>3</sub>(biphepo) (bta: 1-benzoyl-3,3,3-trifluoroacetate) were estimated to be  $1.7 \times 10^3$ ,  $1.7 \times 10^3$  and  $2.1 \times 10^3$  s<sup>-1</sup>, respectively (Table 1). Based on our

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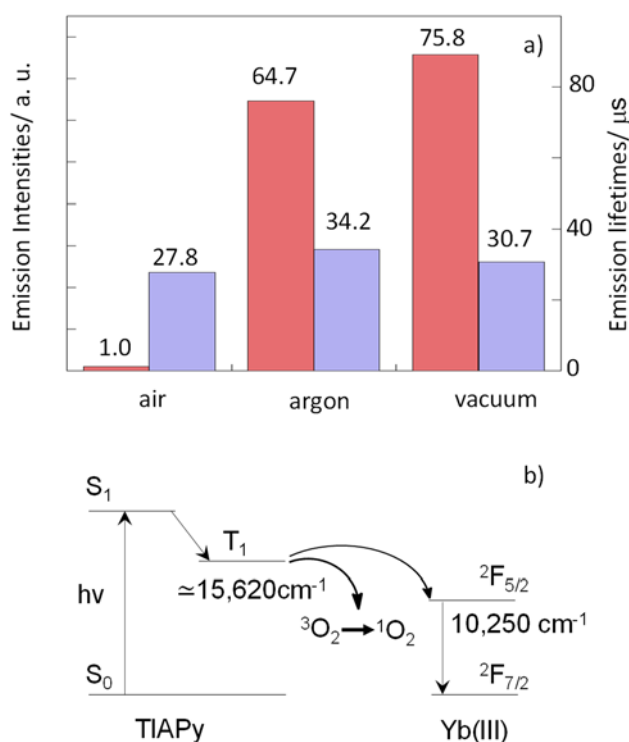
calculations for the Yb(III) complexes, we determined that the  $k_r$  value for Yb(III)-TIAPy is  $1.9(\pm 0.2) \times 10^3$ , because the  $\varepsilon(\tilde{\nu})$  associated with the 4f-4f forbidden transition in solid Yb(III)-TIAPy powder is similar to those previously reported for other Yb(III) complexes.<sup>[25, 31]</sup> The emission quantum yields for Yb(III)-TIAPy were calculated using observed longer emission lifetimes (Table 1). The yield for Yb(III)-TIAPy in air ( $5.3 (\pm 0.5\%)$ ) is much larger than those of Yb(III) complexes with  $\beta$ -diketonate ligands containing pyrene framework ( $< 1.0\%$ ).<sup>[32]</sup> The yield was also found to be less than values previously reported for our Yb(III) complexes because of the larger  $k_{nr}$ . This larger  $k_{nr}$  value is ascribed to the vibrational characteristics of the TIAPy ligands, which contain aromatic groups and C-H bonds with high vibrational frequencies. Previously, we reported that aromatic moieties and C-H bonds in Eu(III) and Yb(III) complexes tend to increase  $k_{nr}$  and so decrease the emission quantum yield.<sup>[33]</sup> We also found that the  $k_{nr}$  value for Yb(III)-TIAPy is on the same order of magnitude (that is, approximately  $10^3 \text{ s}^{-1}$ ) as those for the corresponding Yb(III) complexes shown in Table 1. The estimated  $k_{nr}$  for Yb(III)-TIAPy indicates the formation of direct bonds between Yb(III) ions and TIAPy ligands together with the presence of C-H bonds having high vibrational frequencies.

The relative photosensitized luminescence intensities and lifetimes of the Yb(III)-TIAPy under air, argon and vacuum in response to excitation at 350 nm, normalized with regard to the values in air, are plotted in Fig. 6. Drastic changes in the NIR luminescence intensity depending on the ambient atmosphere are evident, although the relative luminescence lifetimes are essentially unchanged. These results indicate that the photosensitized luminescence of Yb(III)-TIAPy is effectively quenched by the triplet state of oxygen in air, and that this quenching is independent of the process by which radiation is emitted from excited Yb(III) ions. The difference of the luminescence intensity between the Yb(III)-TIAPy under argon and vacuum might be originated from heavy atom effect in external gas.<sup>[34]</sup> The energy level of the excited triplet state in Yb(III)-TIAPy was estimated using time-dependent density functional theory (TD-DFT) calculations based on the TIAPy ligand, at the B3LYP level with the 6-31G(d) basis set. These calculations were performed because the emission spectrum produced by Yb(III)-TIAPy was similar to that for the TIAPy ligands. The triplet energy value was calculated to be  $15,620 \text{ cm}^{-1}$  while the Yb(III) ion  $^2F_{5/2}$  emission energy level was found to be  $10,250 \text{ cm}^{-1}$  using the Yb(III)-TIAPy emission spectrum. The associated energy transfer mechanism is illustrated in Fig. 6b.<sup>[35]</sup> In this process, the excited triplet state for the TIAPy ligands is readily quenched by triplet state oxygen molecules in the ambient air, resulting in the formation of singlet oxygen and a decrease in the NIR luminescence of the Yb(III) ions. The photophysical process in the porous Yb(III)-TIAPy is therefore affected by the surrounding atmosphere. Based on the emission lifetime in argon ( $34.2 \text{ } \mu\text{s}$ ), the emission quantum yield of Yb(III)-TIAPy under argon was determined to be  $6.6 (\pm 0.7)\%$  (Table 1), which is similar to the values reported for other highly luminescent Yb(III) complexes.

**Table 1.** Photophysical properties of Yb coordination polymers and complexes.

| compounds                                                 | $\tau_{\text{obs}}^{[a]} / \mu\text{s}$ | $\Phi_{4f-4f}^{[b]} / \%$ | $k_r / \text{s}^{-1}$      | $k_{nr} / \text{s}^{-1}$ |
|-----------------------------------------------------------|-----------------------------------------|---------------------------|----------------------------|--------------------------|
| Yb(III)-TBAPy                                             | 0.031, 0.51                             | $< 0.01$                  | -                          | -                        |
| Yb(III)-TIAPy in air                                      | 10, 28                                  | $5.3 \pm 0.5^{[c]}$       | $1.9(\pm 0.2) \times 10^3$ | $3.4 \times 10^4$        |
| Yb(III)-TIAPy in Ar                                       | 35                                      | $6.6 \pm 0.7$             | $1.9(\pm 0.2) \times 10^3$ | $2.7 \times 10^4$        |
| [Yb(hfa) <sub>3</sub> (biphepo)] <sup>[d]</sup>           | 49                                      | 8.5                       | $1.7 \times 10^3$          | $1.9 \times 10^4$        |
| [Yb(bta) <sub>3</sub> (biphepo)] <sup>[d]</sup>           | 39                                      | 8.0                       | $2.1 \times 10^3$          | $2.4 \times 10^4$        |
| [Yb(hfa) <sub>3</sub> (tpo) <sub>2</sub> ] <sup>[d]</sup> | 55                                      | 9.2                       | $1.7 \times 10^3$          | $1.7 \times 10^4$        |

[a] Emission lifetime ( $\tau_{\text{obs}}$ ) of the Yb(III)-TBAPy and Yb(III)-TIAPy were measured by excitation at 355 nm (Nd:YAG 3 $\omega$ ). [b] The emission quantum yields and the radiative and non-radiative constants for Yb(III)-TBAPy and Yb(III)-TIAPy were determined using the Strickler-Berg equation (eq. 1-6). [c] Calculation data using slow emission lifetime component ( $27.8 \text{ } \mu\text{s}$ ). [d] From ref 25. hfa: hexafluoroacetylacetonate, bta: 1-benzoyl-3,3,3-trifluoroacetate, biphepo: 2,2-bis(diphenylphosphoryl)biphenyl, tpo: triphenylphosphineoxide.



**Figure 6.** a) Emission intensities (red bars) and emission lifetimes (blue bars) of solid state Yb(III)-TIAPy at 972 nm under air, argon and vacuum. b) Illustration of 4f-4f emission ( $^2F_{5/2}$ - $^2F_{7/2}$ ) and oxygen quenching processes of Yb(III)-TIAPy. The energy level of excited triplet state of Yb(III)-TIAPy was estimated using TD-DFT calculation (B3LYP level with the basis set 6-31G(d)).

This increase in the emission quantum yield for Yb(III)-TIAPy might be due to the absence of trace levels of water in the extremely dry argon gas used in the experimental trials. In

## FULL PAPER

contrast, NIR luminescence was not exhibited by Yb(III)-TIAPy under pure oxygen. The emission signal intensity under air is also small for detection. From these reasons, it is difficult to measure the high concentration of oxygen gas (> 20%). Thus, we conclude that Yb(III)-TIAPy could function as an effective oxygen-sensitive Yb(III) coordination polymer with a high emission quantum yield.

## Conclusions

Luminescent Yb(III) coordination polymers incorporating pyrene derivatives were found to have three-dimensional porous structures and to exhibit significant luminescence in the NIR region. In particular, TIAPy units composed of pyrene centers with four benzene rings and eight carboxyl groups formed a new type of Yb(III) coordination polymer that showed high thermal stability (with a decomposition temperature of 400 °C) in conjunction with significant NIR luminescence (giving an emission quantum yield under argon of 6.6%). This material was also able to respond to the presence of oxygen. Solid-state lanthanide luminophores made with thermally stable pyrene dyes are expected to open up new frontiers in the fields of physical chemistry, coordination chemistry and materials science.

## Experimental Section

**Materials:** Ytterbium(III) chloride hexahydrate (99.9%) was purchased from Wako Pure Chemical Industries Ltd. 1,3,6,8-Tetrabromopyrene, 4-(methoxycarbonyl)benzeneboronic acid, dimethyl-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)isophthalate and tetrakis(triphenylphosphine)palladium(0) were obtained from Tokyo Kasei Organic Chemicals and Aldrich Chemical Company Inc. All other chemicals and solvents were reagent grade and were used without further purification.

**Apparatus:** Infrared spectra were recorded on a JASCO FT/IR-420 spectrometer. <sup>1</sup>H NMR (400 MHz) spectra were recorded on a JEOL ECS 400. Chemical shifts are reported in δ ppm, referenced to an internal tetramethylsilane standard for <sup>1</sup>H NMR. Elemental analyses were performed on a J-Science Lab JM 10 Micro Corder and an Exeter Analytical CE440. ESI-MS spectra were measured using a JEOL JMS-T100LP and a Thermo Scientific Exactive. Thermogravimetric analysis (TGA) was performed on an EXSTAR-6000 TG/DTA6300 instrument (Seiko Instruments Inc.) analyzer. XRD patterns were characterized by a RIGAKU SmartLab X-ray diffractometer with Cu Kα radiation, a D/teX Ultra detector, and a temperature control unit (Anton Paar, TCU-110).

**Preparation of 1,3,6,8-tetrakis(4-(methoxycarbonyl)phenyl)pyrene:** 4-(Methoxycarbonyl)benzeneboronic acid (2.5g, 5 mmol), tetrakis(triphenylphosphine)palladium(0) (0.1g, 0.09 mmol), and K<sub>2</sub>CO<sub>3</sub> (3g) were added to a solution of 1,3,6,8-tetrabromopyrene (1.425 g, 2.75 mmol) in 1,4-dioxane (50 ml). The solution was stirred at 85 °C for 72 hours under Ar atmosphere. The 1,4-dioxane was removed using evaporation, and, the product was extracted with chloroform. the extracts were washed with brine

three times and dried over anhydrous MgSO<sub>4</sub>. The solvent was removed, and pale-yellow solid was obtained. Yield 78%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 298K): δ 8.23 (d, 8H, -Ar), δ 8.15 (s, 4H, -Ar), δ 8.01 (s, 2H, -Ar), δ 7.75 (d, 8H, -Ar), δ 3.99 (s, 12H, -CH<sub>3</sub>) ppm. IR (ATR): 2850, 2917, 2956, 1685, 1595, 1440, 1400, 1250 cm<sup>-1</sup>. ESI-Mass (m/z): [M+H]<sup>+</sup> calcd for C<sub>48</sub>H<sub>35</sub>O<sub>8</sub> 739.23; found, 739.23.

**Preparation of H<sub>4</sub>-TBAPy (1,3,6,8-tetrakis(p-benzoic acid)pyrene):** Obtained 1,3,6,8-tetrakis(4-(methoxycarbonyl)phenyl)pyrene (1.0 g) and NaOH (2.6 g) were added in THF(85 ml)/H<sub>2</sub>O(85 ml) mixed solution. The solution was stirred at 85 °C for 12 hours. THF was removed using evaporation, additional water (20 ml) as added to the solution. The filtrate was acidified with a 50% H<sub>2</sub>SO<sub>4</sub> solution in water to obtain a yellow precipitate (pH=1). The product, which precipitated as a yellow solid, was dried in vacuum. Yield 90%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 298K): δ 13.00 (s, 4H, -COOH), δ 8.03-8.21 (m, 14H, -Ar), 7.86 (d, 8H, -Ar) ppm. IR (ATR): 2950, 1722, 1688, 1430, 1412, 1271, 1180, 1111 cm<sup>-1</sup>. ESI-Mass (m/z): [M+H]<sup>+</sup> calcd for C<sub>44</sub>H<sub>27</sub>O<sub>8</sub>, 683.17; found, 683.20.

**Preparation of octamethyl-5,5',5'',5'''-(pyrene-1,3,6,8-tetrayl)terephthalate:** Dimethyl-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)isophthalate (1.6g, 5 mmol), tetrakis(triphenylphosphine)palladium(0) (50 mg, 0.043 mmol), and K<sub>2</sub>CO<sub>3</sub> (9.92g, 6.67 mmol) were added to a solution of 1,3,6,8-tetrabromopyrene (0.43 g, 0.83 mmol) in 1,4-dioxane (120 ml). The solution was stirred at 85 °C for 48 hours under Ar atmosphere. The 1,4-dioxane was removed using evaporation, and, the product was extracted with chloroform. The extracts were washed with brine three times and dried over anhydrous MgSO<sub>4</sub>. The solvent was removed, and pale-yellow solid was obtained. Yield 78%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 298K): δ 8.82-8.72 (m, 4H, -CH), δ 8.52 (s, 8H, -CH), δ 8.26-8.02 (m, 4H, -CH), δ 7.70 (s, 2H, -CH), δ 4.00 (s, 24H, -CH) ppm. ESI-Mass (m/z): [M+Na]<sup>+</sup> calcd for C<sub>56</sub>H<sub>42</sub>O<sub>16</sub>Na 993.24; found, 993.24.

**Preparation of H<sub>8</sub>-TIAPy (1,3,6,8-tetrakis(3,5-isophthalic acid)pyrene):** Obtained octamethyl-5,5',5'',5'''-(pyrene-1,3,6,8-tetrayl)terephthalate 8200 mg) and NaOH (1.05 g) were added in THF(20 ml)/H<sub>2</sub>O(20 ml) mixed solution. The solution was stirred at 90 °C for 12 hours. THF was removed using evaporation, additional water (20 ml) as added to the solution. The filtrate was acidified with a 50% H<sub>2</sub>SO<sub>4</sub> solution in water to obtain a yellow precipitate, which was dissolved in a minimal amount of 2M NaOH. The solution was extracted with THF and EtOAc, and the aqueous phase was acidified with 50% H<sub>2</sub>SO<sub>4</sub>. The product, which precipitated as a yellow solid, was dried in vacuum. Yield 90%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 298K): δ 8.56-8.14 (m, 18H, -CH), δ 14.00-13.00 (s, 8H, -COOH) ppm. IR (ATR): 2850, 2917, 2956, 1685, 1595, 1440, 1400, 1250 cm<sup>-1</sup>. ESI-Mass (m/z): [M+Na]<sup>+</sup> calcd for C<sub>48</sub>H<sub>26</sub>O<sub>16</sub>Na, 881.11; found, 881.11.

**Preparation of Yb(III)-TBAPy and Eu(III)-TBAPy:** Prepared H<sub>4</sub>-TBAPy (100 mg, 0.14 mmol) and ytterbium(III) nitrate hexahydrate (135 mg, 0.38 mmol) was dissolved in DMF(20 mL)/H<sub>2</sub>O(10 mL)/1,4-dioxane(10 mL) mixed solution under Ar atmosphere. A solution was stirred at 85 °C for 48 hours, the reaction mixture was filtered, and the resulting yellow solid was

washed using methanol. Obtained yellow solid was dried in vacuum. Eu(III)-TBAPy was also prepared by the same method. Yb(III)-TBAPy: IR (ATR): 3004, 2947, 1725, 1712, 1606 1429, 1406, 1317, 1308, 1267, 1188, 1176, 1103 cm<sup>-1</sup>. Eu(III)-TBAPy: IR (ATR): 3005, 2950, 1725, 1713, 1608, 1430, 1409, 1318, 1309, 1266, 1189, 1176, 1104 cm<sup>-1</sup>.

**Preparation of Yb(III)-TIAPy: Hydrothermal reaction:** Prepared H<sub>8</sub>-TIAPy (40 mg, 0.05 mmol) and ytterbium(III) nitrate hexahydrate (56 mg, 0.15 mmol) was dissolved in DMF(20 mL)/H<sub>2</sub>O(10 mL)/1,4-dioxane(10 mL) mixed solution under Ar atmosphere. A solution was stirred at 85 °C for 48 hours, the reaction mixture was filtered, and the resulting yellow solid was washed using methanol. Obtained yellow solid was dried in vacuum.

**Complexation:** Prepared H<sub>8</sub>-TIAPy (60 mg, 0.07 mmol) was dissolved in water (50 mL) with ammonia. Aqua solution with ytterbium(III) chloride hexahydrate (116 g, 0.3 mmol) was added in ammonia solution with H<sub>8</sub>-TIAPy. A solution was stirred at 85 °C for 24 hours, the reaction mixture was filtered, and the resulting yellow solid was washed using methanol and water. Obtained yellow solid was dried in vacuum. Anal. Dinuclear and trinuclear Yb(III) structures were confirmed by ESI-Mass (Fig. S4). Calcd for ESI-Mass (m/z): [C<sub>48</sub>H<sub>18</sub>O<sub>16</sub>+2H<sup>+</sup>+2Yb<sup>3+</sup>+Na<sup>+</sup>]<sup>+</sup> 1222.9; found, 1223.7, [C<sub>48</sub>H<sub>20</sub>O<sub>16</sub>+3Yb<sup>3+</sup>+CH<sub>3</sub>OH+3Cl<sup>-</sup>+2H<sub>2</sub>O]<sup>+</sup> 1579.86; found, 1579.39. IR (ATR): 1610, 1538, 1420, 1360 cm<sup>-1</sup>.

**Optical Measurements:** Emission spectra were measured using a Horiba/Jobin-Yvon FluoroLog-3 (Model: FL-1057) spectrofluorometer. The spectrofluorometer was equipped with a Hamamatsu R5509-43 photomultiplier for detecting NIR emission. The wavelength dependence of the detector response and the beam intensity of the Xe light source for each spectrum were calibrated using a standard light source. Emission lifetimes were determined from the slope of logarithmic plots of the decay profiles. Oxygen-sensitive luminescence is measured using FluoroLog-3 spectrofluorometer attached with Cryo-stat (Thermal Block Company, SA-SB245T) under vacuum, argon and air conditions.

**Estimation of porosity:** Prepared Yb(III)-TIAPy was calcined overnight under vacuum condition at 300 K using a MicrotracBEL BELPREP-vacII. After the calcination, nitrogen adsorption isotherm of Yb(III)-TIAPy was measured at 77 K using a MicrotracBEL BELsorp-mini.

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**Keywords:** ytterbium, coordination polymer, near-IR, luminescence, oxygen sensor

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FULL PAPER

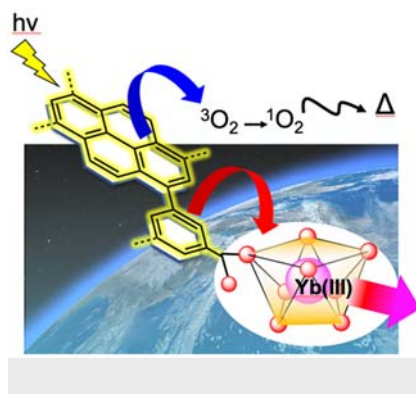
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- [35] In general, the photosensitization process of lanthanide complexes is occurred from  $T_1$  state because of fast ISC process induced by heavy atom effect. In particular, the energy gap between  $S_1$  state and emitting level of Yb(III) ion is very large ( $\Delta E = 7000 \text{ cm}^{-1}$ ), indicating the ineffective energy transfer from  $S_1$  state.
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## Entry for the Table of Contents

## FULL PAPER

Luminescent Yb(III) coordination polymers incorporating pyrene derivatives successfully showed high thermal stability (with a decomposition temperature of 400 °C) in conjunction with significant NIR luminescence (giving an emission quantum yield under argon of 6.6%). This material was also able to respond to the presence of oxygen. This thermally stable lanthanide luminophore could be used in applications involving high temperatures.



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**Page No. – Page No.**

**Yb(III) coordination polymers composed of pyrene derivatives exhibiting intense near-infrared luminescence with applications in solid-state oxygen sensors**