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Synthesis, Crystal Structure, and Photophysical Properties of Novel (Monophthalocyaninato)lanthanide Complexes Stabilized by an Organometallic Tripodal Ligand

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An unprecedented series of (monophthalocyaninato)lanthanide(III) complexes {[PcYb(L_{OMe})] (**3**) and [(tBu)$_4$PcLn(L_{OMe})] [Ln = Yb (**4**), Er (**5**)]} {Pc = phthalocyaninate, L_{OMe}^- = [(cyclopentadienyl)tris(dimethylphosphito)cobaltate(III)]} were prepared by the reaction of Ln[N(SiMe$_3$)$_2$]$_3$·[LiCl(THF)$_3$]$_x$ (Ln = Yb or Er) with the corresponding phthalocyanine [H_2Pc and H_2(tBu)$_4$Pc] followed by Na(L_{OMe}). X-ray structural analysis of **3** reveals that the Yb^{3+} ion is seven-coordinate, surrounded by four nitrogen atoms from the phthalocyaninate dianion and three oxygen atoms from the anionic tripodal L_{OMe}^- ligand. The photophysical properties of these new mixed-metal (monophthalocyaninato)lanthanide complexes are investigated. An efficient intramolecular energy transfer from ligand-centered states to the metal ion manifold or metal-centered states takes place for the Er^{3+} complex, but there is a significant back-energy transfer for the Yb^{3+} complex. Singlet oxygen ($^1O_2$) phosphorescence was detected instead of the Yb^{3+} emission in the photoluminescence spectra of **3** and **4** in the NIR region, but only the Er^{3+} ion emission was observed for **5**.

Introduction

Phthalocyanines (Pc) and their metal complexes (PcM) have been studied for many years in great detail, mostly for their wide varieties of high-technology applications, including their use in dyes and catalysts,[1,2] semiconducting materials,[3] nonlinear optical (NLO) devices,[4] liquid crystals,[5] Langmuir–Blodgett films,[6] electrochromic and electroluminescent displays,[7] photovoltaic cells,[8] photosensitizers,[9] gas sensors,[10] and other areas.[11,12] Recently, phthalocyaninato rare-earth complexes have received considerable attention because of their appealing semiconducting, electrochemical, and photophysical properties.[13–15] However, most of these efforts have been mainly focused on the substituted bis(phthalocyaninato), heteroleptic bis(phthalocyaninato), tri(phthalocyaninato), heteroleptic tri(phthalocyaninato), and mixed porphyrinato–(na)phthalocyaninato rare-earth complexes.[15–18] Reports on the monophthalocyaninato rare-earth complexes are scarce, possibly because of their instability. Bo and coworkers[19] reported that (monophthalocyaninato)erbium complexes exhibit the characteristic Er^{3+} ion emission, but their sandwich-type phthalocyaninato counterparts do not. This indicates that the monophthalocyaninato rare-earth complexes have unique photophysical properties different from the sandwich-type phthalocyaninato rare-earth complexes. This arouses our special interest in the synthetic and spectroscopic study of (monophthalocyaninato)lanthanide complexes. Nevertheless, the synthesis of stable (monophthalocyaninato)lanthanide complexes is still a challenge. It has been reported that the tripodal anionic ligand, [(cyclopentadienyl)tris(dimethylphosphito)cobaltate(III)] (L_{OMe}^-), is capable of stabilizing labile normal porphyrinate lanthanide(III) complexes by effectively encapsulating the lanthanide ion, thereby shielding it from interactions with the environment.[20,21] We have extended this strategy to phthalocyanines and herein report the synthesis and characterization of the first examples of novel (monophthalocyaninato)-lanthanide(III) complexes stabilized by an organometallic tripodal ligand.

Results and Discussion

Scheme 1 shows the chemical structures and the strategies for the synthesis of the (monophthalocyaninato)lantha-

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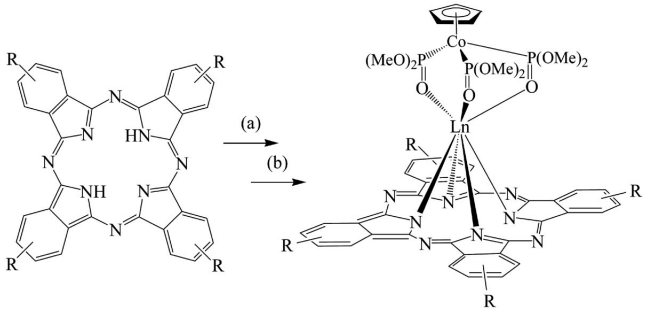
nide(III) complexes discussed in the present study. The precursor complex, $Ln[N(SiMe_3)_2]_3{\cdot}[LiCl(THF)_3]_x$ (Ln = Yb or Er), was generated in situ from the reaction of anhydrous $LnCl_3$ with three equivalents of $Li[N(SiMe_3)_2]$ in tetrahydrofuran. The phthalocyanine free-base **2** was treated with an excess amount of the precursor complex under nitrogen in toluene heated at reflux for 12 h. Excess NaL_{OMe} was then added to the reaction mixture at room temperature, which was stirred under nitrogen for 1 h. This procedure gave green crystals of $[(t\text{Bu})_4\text{PcLn}(L_{OMe})]$ [Ln = Yb (**4**), Er (**5**)] in about 65% yield. As phthalocyanine **1** is insoluble in most organic solvents, $[\text{PcYb}(L_{OMe})]$ (**3**) was obtained in less than 10% yield even when the reaction was carried out in high boiling solvents such as *o*-dichlorobenzene, dioxane, bis(2-methoxyethyl) ether, etc.



1 (R = H): H_2Pc
2 (R = *t*Bu): $H_2(t\text{Bu})_4\text{Pc}$
3 (R = H, Ln = Yb): $\text{PcYb}(L_{OMe})$
4 (R = *t*Bu, Ln = Yb): $(t\text{Bu})_4\text{PcYb}(L_{OMe})$
5 (R = *t*Bu, Ln = Er): $(t\text{Bu})_4\text{PcEr}(L_{OMe})$

Scheme 1. Synthesis of (monophthalocyaninato)lanthanide complexes **3**–**5**: (a) $Ln[N(SiMe_3)_2]_3{\cdot}[LiCl(THF)_3]_x$, reflux in dry toluene; (b) NaL_{OMe}, room temperature.

These lanthanide complexes are thermally and air stable, and can be purified by column chromatography. While bis(phthalocyaninato) lanthanide sandwich complexes of the Pc_2Ln type were formed in the actual reaction process, work up also led to the production of some Pc_2Ln complexes and the recovery of the phthalocyanine free-base when the same reaction was carried out without the subsequent addition of L_{OMe}^-. This suggests that the lanthanide(III) monophthalocyaninate intermediate was rather unstable and that the tripodal anion is capable of stabilizing labile (monophthalocyaninato)lanthanide(III) complexes by effectively encapsulating the lanthanide ion and thereby shielding it from interactions with the environment.

All of these (monophthalocyaninato)lanthanide(III) complexes were characterized by accurate mass spectrometric and spectroscopic techniques. The MALDI-TOF high-resolution mass spectra (HRMS) of complexes **3**–**5** exhibit $[M]^+$ peaks at 1137.0735, 1361.3246, and 1355.3272, respectively, which deviate by less than 4 ppm from the theoretical values of 1137.0775, 1361.3282, and 1355.3222. Their isotopic distribution patterns match the theoretical results as well. The $^{31}P\{^1H\}$ NMR spectra (vs. 85% H_3PO_4) of **3**–**5** display a singlet at δ = 64.82, 64.24, and –202.03 ppm, respectively, for the phosphito groups of the anionic L_{OMe}^- ligand. The ^1H NMR spectra (in $CDCl_3$) of **3**–**5** show a singlet at δ = –6.022, –6.090, and –50.575 ppm, respectively, for the five cyclopentadienyl protons.

The solid-state structure of **3** was ascertained by X-ray crystallography. The compound crystallized in the $P2_1/c$ space group. A perspective view of **3** is depicted in Figure 1. The crystal structure analysis revealed that the Yb^{3+} ion is sandwiched between the phthalocyaninato ring and the anionic tripodal ligand and is seven-coordinate, surrounded by four nitrogen atoms from the phthalocyaninate dianion and three oxygen atoms from the L_{OMe}^- anion. The L_{OMe}^- anion caps on the Yb^{3+} ion. The average bond lengths between Yb^{3+} and N atoms of the phthalocyaninato ring and O atoms of L_{OMe}^- are 2.329 and 2.252 Å, respectively. The average Yb–N distance is longer than the average Yb–O distance. This reflects the higher affinity of the Yb^{3+} ions for the O atoms over the N atoms. The three mean planes (C_5 of the cyclopentadienyl ring, N_4 of the phthalocyaninate ligand, and O_3 of the phosphito groups) are almost parallel to one another. The dihedral angles formed between the C_5 and O_3 mean planes, O_3 and N_4 mean planes, and C_5 and N_4 mean planes are, respectively, 1.1, 3.2, and 2.1°. The angle formed between the Yb···Co line and the normal to the N_4 plane is 86.3°. The Yb^{3+} center is 1.219 Å above the plane formed by the four phthalocyaninato N atoms and 1.493 Å below the plane formed by the three phosphito O atoms.

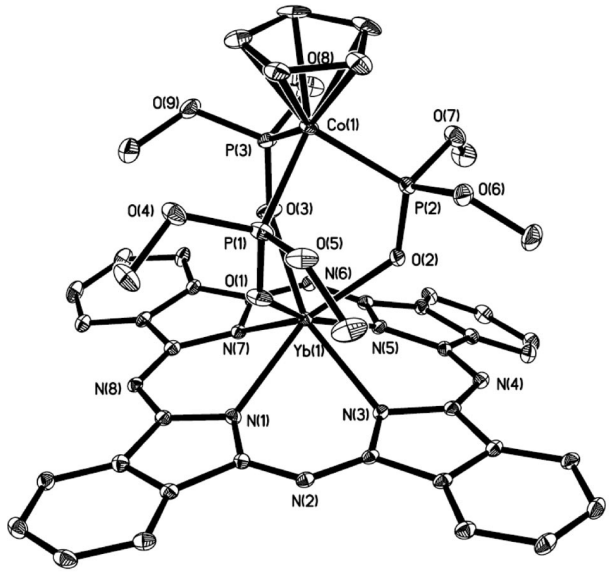


Figure 1. A perspective view of compound **3**. Hydrogen atoms were omitted for clarity. Selected bond lengths [Å] and bond angles [°]: N(1)–Yb(1) 2.331(3), N(3)–Yb(1) 2.322(3), N(5)–Yb(1) 2.332(3), N(7)–Yb(1) 2.331(3), O(1)–Yb(1) 2.245(3), O(2)–Yb(1) 2.269(2), O(3)–Yb(1) 2.241(3), O(1)–Yb(1)–O(2) 79.10(11), O(1)–Yb(1)–O(3) 82.91(11), O(2)–Yb(1)–O(3) 80.21(10), N(1)–Yb(1)–N(3) 73.69(10), N(1)–Yb(1)–N(5) 116.97(11), N(1)–Yb(1)–N(7) 73.66(10), N(3)–Yb(1)–N(5) 74.44(10), N(3)–Yb(1)–N(7) 116.88(10), N(5)–Yb(1)–N(7) 74.71(10).

The absorption, excitation, and emission spectra of compounds **3**–**5** in toluene at room temperature were measured. The photophysical properties are summarized in Table 1. In

the UV/Vis region, compounds **3**–**5** exhibit similar absorption spectra, which are typical of "normal" monomeric metallophthalocyanines having a +2 or +3 central metal ion. For instance, the UV/Vis spectrum of **3** shows a strong Q band at 671 nm and two additional weak bands at 606 and 642 nm, and a strong B band at 339 nm. The absorption can be assigned to the $\pi \rightarrow \pi^*$ transitions of the phthalocyaninate ligand. Compounds **3**, **4**, and **5** also display similar visible emission spectra with fluorescence peaks at 697, 688, and 688 nm, lifetimes (τ) of 9.76, 7.55, and 4.97 ns, and quantum yields (Φ_{em}) of 0.019, 0.017, and 0.017, respectively. The excitation spectra of complexes **3**–**5** monitored at their emission maxima matched well with their absorption spectra. Thus, the visible fluorescence of compounds **3**–**5** can be assigned to the intraligand emission. At 77 K, the emission spectrum of compounds **3**–**5** was basically the same as their room temperature spectrum (with peaks at 693, 686, and 688 nm, respectively). However, ligand-centered (LC) long-lived phosphorescence was not observed.

Table 1. Photophysical data of compounds **3**–**5**.[a]

	Absorption λ_{max} [nm] ($\log \varepsilon$ [$dm^3 mol^{-1} cm^{-1}$])	Excitation λ_{ex} [nm]	Emission at 298 K λ_{em} [nm] (τ, $\Phi_{em} \times 10^2$)[b]
3	339 (4.83), 606 (4.56) 642 (4.53), 671 (5.39)	339	697 (9.76 ns, 1.9)
4	349 (4.90), 611 (4.57) 649 (4.57), 678 (5.38)	349	688 (7.55 ns, 1.7)
5	349 (4.93), 611 (4.60) 649 (4.58), 678 (5.41)	349	688 (4.97 ns, 1.7) 1537[c]

[a] Measurements were performed in 1×10^{-6} M solutions in toluene. [b] Quantum yields were measured relative to $H_2(t\text{Bu})_4\text{Pc}$ in toluene (Φ_{em} = 0.67). [c] Because of the limitation of the instrument, we were unable to determine the lifetime of the NIR emission.

In addition to the visible emission, the Er complex **5** also exhibits Er^{3+} ion emission in the near-infrared (NIR) region. Figure 2 shows the room-temperature NIR emission and excitation spectra of **5** in toluene. The emission peak at 1537 nm can be assigned to the $^4I_{13/2} \rightarrow {}^4I_{15/2}$ transition of Er^{3+}. The excitation spectrum of **5** monitored at 1537 nm shows its excitation bands at 356, 614, and 680 nm, which almost coincide with its visible absorption bands at 349, 611, and 677 nm, respectively. This clearly indicates that the NIR emission originates from the $\pi \rightarrow \pi^*$ transitions of the phthalocyaninate antenna, and excitation of phthalocyanine is the photophysical pathway leading to the observable NIR luminescence. On the contrary, we were unable to observe the characteristic Yb^{3+} ion emission in **3** or **4** upon optical excitation in the absorption bands of the ligand. This is probably due to back-energy transfer from the metal excited state ($^*Ln^{3+}$) to the ligand-centered triplet state (^{3}LC). It has been shown that efficient back-energy transfer takes place in Ln^{3+} complexes when ΔE ($^3\text{LC} - {}^*Ln^{3+}$) $< 1850\ cm^{-1}$.[22] The energy level of the ^{3}LC state of the phthalocyaninate ligand of the complexes, though we were unable to detect it spectroscopically, can be estimated to be around 9300 cm^{-1} from metallophthalocyaninate spectra of 5500 cm^{-1}. It is about 2794 cm^{-1} higher than the energy of the $^4I_{13/2}$ Er^{3+} luminescent level (6506 cm^{-1}) and lies close to the energy of the $^2F_{5/2}$ Yb^{3+} luminescent level (10200 cm^{-1}).[23] Thus, an efficient intramolecular energy transfer from ligand-centered states to the metal ion manifold or metal-centered states is observed for the Er^{3+} complex, and significant back-energy transfer is observed for the Yb^{3+} complex. It is well documented that the ^{3}LC phosphorescence of phthalocyaninate ligands can be quenched effectively by molecular oxygen with the production of singlet oxygen ($^1O_2$). It should be noted that for compounds **3** and **4**, NIR emission corresponding to Yb^{3+} phosphorescence was not observed even in the absence of molecular oxygen. The presence of the ^{3}LC state can be inferred by the photogeneration of $^1O_2$. Figure 3 shows the phosphorescence spectra of $^1O_2$ generated upon photoirradiation of an aerated solution of **3**, **4**, and $H_2(t\text{Bu})_4\text{Pc}$ in toluene (1.0×10^{-5} M) at 671, 678, and 699 nm, respectively. The results reveal that $^1O_2$ was produced upon photoexcitation of **3** or **4**. A comparison of $^1O_2$ phosphorescence intensity at 1270 nm shows that **3** and **4** are much better $^1O_2$ generators than $H_2(t\text{Bu})_4\text{Pc}$. This is due to the heavy-atom effect of the Yb^{3+} ion which, upon coordination with the phthalocyaninate ligand, enhances the intersystem crossing from the ^{1}LC to the ^{3}LC state. However, $^1O_2$ phosphorescence was not observed upon photoirradiation of an aerated solution of **5**. This suggests that the rate of energy transfer from the ^{3}LC state to the metal excited state ($^*Ln^{3+}$) is faster than the rate of reaction between the ^{3}LC state and molecular oxygen ($^3O_2$). The photophysical and photochemical processes of compounds **3**–**5** are shown in Figure 4. Upon photoirradiation, the phthalocyaninate ligand is excited to its singlet state (S_1), which then undergoes either fluorescence or energy transfer to its triplet state (T_1). In its triplet state, the phthalocyaninate ligand can either interact with molecular oxygen ($^3O_2$) to generate $^1O_2$ or transfer its energy to the excited state of the lanthanide ion ($^*Ln^{3+}$), with rate constants of $k(O_2)$ and k(et), respectively. In the case of the Er^{3+} complex (**5**), where the energy of the emissive $^4I_{13/2}$ state of Er^{3+} is much lower than that of the T_1 state and back-energy transfer is insignificant, efficient energy transfer takes place [$k(\text{et}) >> k(O_2)$]. This results in the sensitization of the Er^{3+} ion without the observation of the $^1O_2$ phosphorescence in the NIR region. However, in the case of the Yb^{3+} complexes (**3** and **4**), where the energy of the emissive $^2F_{5/2}$ state of Yb^{3+} is about the same energy as that of the T_1 state and back-energy transfer becomes significant, energy transfer to the emissive state is very inefficient [$k(O_2) >> k(\text{et})$]. Consequently, only $^1O_2$ phosphorescence and not Yb^{3+} ion emission is observed in the NIR region. In the absence of molecular oxygen, the T_1 or $^*Yb^{3+}$ state undergoes a nonradiative decay.

As their strong absorption in the red (Q band) overlaps the region of maximum light penetration in tissues, we forecast that these kinds of (monophthalocyaninato)ytterbium complexes will be promising candidates for photodynamic therapy. Work along this direction will be pursued.

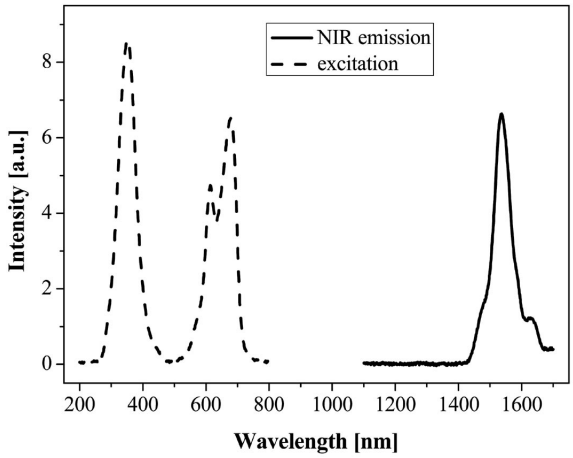


Figure 2. Room-temperature NIR emission (excited at 677 nm) and excitation (monitored at 1537 nm) spectra of [(tBu)$_4$PcEr(L$_{OMe}$)] (**5**) in toluene.

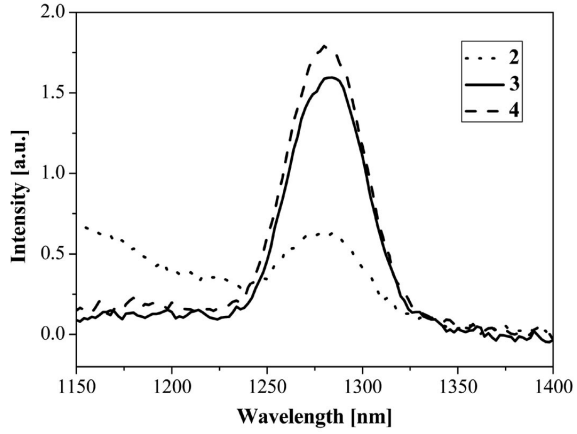


Figure 3. Phosphorescence spectra of $^1O_2$ generated from photoirradiation of [H$_2$(tBu)$_4$Pc] (**2**), [PcYb(L$_{OMe}$)] (**3**), and [H$_2$(tBu)$_4$-PcYb(L$_{OMe}$)] (**4**) solutions in toluene (1.0×10^{-5} M) excited at 699, 671, and 678 nm, respectively.

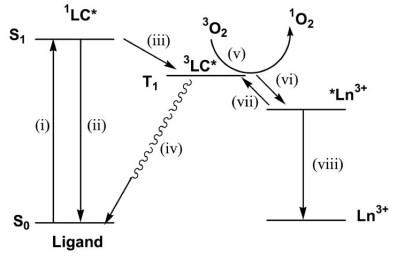


Figure 4. Photophysical and photochemical processes of lanthanide(III) phthalocyaninate complexes. (i) Photoexcitation, (ii) fluorescence, (iii) intersystem crossing, (iv) nonradiative decay, (v) generation of $^1O_2$ with a rate constant of $k(O_2)$, (vi) energy transfer with a rate constant of k(et), (vii) back-energy transfer, and (viii) near-infrared emission.

Concluding Remarks

In summary, the first examples of (monophthalocyaninato)lanthanide(III) complexes (**3**–**5**) have been synthesized and characterized. The photophysical properties of these complexes and the crystal structure of **3** have been examined. From spectroscopic analyses, a difference in the emission pathways for the Yb^{3+} and Er^{3+} complexes was observed: an efficient ligand-to-metal energy transfer takes place for **5**, but the Yb^{3+} complexes **3** and **4** are associated with a significant back-energy transfer. Singlet oxygen ($^1O_2$) phosphorescence was detected instead of Yb^{3+} emission in the photoluminescence spectra of **3** and **4** in the NIR region, but only the Er^{3+} ion emission was observed for **5**.

Experimental Section

General: All reactions were carried out in a dry nitrogen atmosphere. Solvents were dried by standard procedures, distilled, and deaerated prior to use. All chemicals were obtained from Aldrich Chemical Company and, where appropriate, degassed before use. Yb[N(SiMe$_3$)$_2$]$_3$·[LiCl(THF)$_3$]$_x$ and Er[N(SiMe$_3$)$_2$]$_3$·[LiCl(THF)$_3$] were prepared according to the literature methods.[24] Electronic absorption spectra in the UV/Vis region were recorded with a Varian Cary 100 UV/Vis spectrophotometer, steady-state visible fluorescence and photoluminescence excitation spectra were recorded with a Photon Technology International (PTI) Alphascan spectrofluorimeter, and quantum yields were measured relative to H$_2$(tBu)$_4$-Pc in toluene (Φ_{em} = 0.67).[25] NMR spectra were recorded with a Varian Unity Inova 400 MHz spectrometer. ^{1}H NMR chemical shifts were referenced to internal $CDCl_3$ and then re-referenced to TMS (δ = 0.00 ppm), and shifts from the $^{31}P\{^1H\}$ NMR spectra were referenced to external 85% H_3PO_4. High- and low-resolution mass spectra, reported as m/z, were obtained with an Autoflex Bruker MALDI-TOF system and a Finnigan MAT SSQ710 mass spectrometer, respectively. The NIR emission spectra were recorded with a PTI QM4 luminescence spectrometer. Singlet oxygen was detected directly by its phosphorescence emission at 1270 nm using an InGaAs detector on the PTI QM4 luminescence spectrometer.

Preparations of [PcYb(L$_{OMe}$)] (3), [(tBu)$_4$PcYb(L$_{OMe}$)] (4), and [(tBu)$_4$PcEr(L$_{OMe}$)] (5)

[PcYb(L$_{OMe}$)] (3): A solution of Yb[N(SiMe$_3$)$_2$]$_3$·[LiCl(THF)$_3$]$_x$ (10 mL, 1.6 mmol) was transferred to a Schlenk flask, and the solvent was removed under vacuum. The residue was redissolved in dichloromethane (10 mL) to give a suspension, which was centrifuged. The clear layer was then transferred to another Schlenk flask with dry H$_2$Pc (0.051 g, 0.10 mmol) dissolved in toluene (60 mL). The resulting solution was heated at reflux for 3 h. Upon cooling the reaction mixture to 70 °C, anhydrous NaL$_{OMe}$ (0.080 g, 0.17 mmol) was added, and the solution was magnetically stirred for 1 h. After the reaction was complete, the solvent was removed under vacuum, and the residue was redissolved in chloroform, filtered, and chromatographed on silica gel using chloroform/hexane (v/v, 3:2) as the eluent. The second band gave [(Pc)Yb(L$_{OMe}$)] in 9% yield (10 mg). MALDI-TOF HRMS: calcd. for $[M]^+$ 1137.0775; found 1137.0735. ^{1}H NMR ($CDCl_3$): δ = –6.02 (s, 5 H), 7.58 (s, 18 H), 10.72 (s, 8 H), 14.68 (s, 8 H) ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 64.82 ppm.

[(tBu)$_4$PcYb(L$_{OMe}$)] (4): The synthesis of **4** followed the same procedures as for **3**. Yb[N(SiMe$_3$)$_2$]$_3$·[LiCl(THF)$_3$]$_x$ (10 mL, 1.6 mmol), H$_2$(tBu)$_4$Pc (0.073 g, 0.10 mmol), toluene (20 mL), and NaL$_{OMe}$ (0.080 g, 0.17 mmol) were used; yield 0.090 g (66%). MALDI-TOF HRMS: calcd. for $[M]^+$ 1361.3282; found 1361.3246. ^{1}H NMR ($CDCl_3$): δ = –6.09 (s, 5 H), 3.20–3.50 (m, 36H), 7.63 (s, 18H), 10.60–11.00 (m, 4H), 14.40–15.00 (m, 8H) ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 64.24 ppm.

[(tBu)$_4$PcEr(L_{OMe})] (5): The procedure for the preparation of **5** was the same as for **4**. Er[N(SiMe$_3$)$_2$]$_3$·[LiCl(THF)$_3$]$_x$ (10 mL, 1.6 mmol), H$_2$(tBu)$_4$Pc (0.073 g, 0.10 mmol), and NaL_{OMe} (0.080 g, 0.17 mmol) were used; yield 0.085 g (63%). MALDI-TOF HRMS: calcd. for $[M]^+$ 1355.3222; found 1355.3272. ^{1}H NMR ($CDCl_3$): δ = –50.58 (s, 5 H), 9.80–11.00 (m, 36 H), 21.20–22.50 (m, 4 H), 30.19 (s, 18 H), 34.50–38.00 (m, 8 H) ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = –202.03 ppm.

X-ray Crystallography: Single crystals of **3** suitable for X-ray diffraction study were grown by slow evaporation of solutions of the compound in chloroform/methanol at room temperature. X-ray intensity data were collected with a Bruker Axs SMART 1000 CCD area-detector diffractometer using graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å). The collected frames were processed with the SAINT software,[26] and an absorption correction was applied (SADABS[27]) to the collected reflections. The structures of these molecules were solved by direct methods and expanded by standard difference Fourier syntheses using the SHELXTL software.[28] Structure refinements were made on F^2 using the full-matrix least-squares technique. All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were placed in their idealized positions and allowed to ride on the respective carbon atoms. Crystal data: $C_{43}H_{39}CoN_8O_9P_3Yb$, MW = 1136.70, monoclinic, space group = $P2_1/c$, a = 11.559(1), b = 27.335(3), c = 14.582(2) Å, β = 110.453(2)°, V = 4316.9(8) Å^3, Z = 4, $\rho_{calcd.}$ = 1.749 Mg m^{-3}, μ(Mo-K_α) = 2.716 mm^{-1}, F(000) = 2286, T = 173 K. 24287 reflections were measured, of which 10156 were unique (R_{int} = 0.0368). Final R_1 = 0.0355 and wR_2 = 0.0884 values were obtained for 8843 observed reflections with $I > 2\sigma(I)$, 586 parameters, and GOF = 1.026.

CCDC-710061 contains the supplementary crystallographic data for compound **3**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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