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Synthesis, Structure, and Photophysical Properties of Some Gadolinium(III) Porphyrinate Complexes

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A series of gadolinium(III) porphyrinate complexes was synthesized in moderate yield from the interaction of *meso*-substituted porphyrin free bases with $Ln[N(SiMe_3)_2]_3 \cdot x[LiCl(THF)_3]$, followed by the addition of a tripodal anion L_{OMe}^- – an effective encapsulating agent for lanthanide ions. These new complexes were fully characterized by X-ray crystallography, elemental analysis, mass spectrometry, and infrared spectroscopy. The electronic spectra show a near-infrared phosphorescence from the triplet state of the porphyrin rings and exhibit a very characteristic vibronic-structured emission.

Introduction

Lanthanide compounds have attracted attention in the field of luminescence spectroscopy. The excited-state behavior of lanthanide ions has been investigated extensively.[1–6] It is known that the narrow-band f→f emissions of the lanthanide ions are an attractive optical property. However, direct excitation of these transitions is difficult due to the low optical cross section of lanthanide ions arising from the forbidden nature of the 4f→4f transition.[7] Since the discovery that energy transfer from the triplet state of an organic ligand can efficiently sensitize the emissive states of lanthanide ions,[8] there has been considerable effort devoted to the design of ligands that can optimize this energy transfer and give rise to efficient lanthanide luminescence. We are interested in the chemistry and luminescent properties of lanthanide porphyrinate complexes. Porphyrins are promising ligands for efficient energy transfer to near-infrared (NIR) emitting lanthanide ions because their intense Soret bands lead to high-absorption cross sections, and their low-energy triplet states can efficiently sensitize the NIR-emitting states of the lanthanide ions.[9] Our previous research on the photoluminescence of lanthanide(III) monoporphyrinate complexes showed that the porphyrinate anion can sensitize NIR emission of Nd^{3+}, Yb^{3+}, and Er^{3+} ions by serving as an antenna that absorbs visible light and transfers the energy to the excited state of the lanthanide(III) ion, which then relaxes through NIR emission.[10]

However, the f→f states of gadolinium(III), Gd^{3+}, are located at exceptionally high energies owing to the extreme stability of its half-filled f-shell (f^7). The lowest-energy f→f transition appears as an emission line at 312 nm. Accordingly, Gd^{III} complexes are frequently characterized by emissive intraligand states at lower energies. Owing to the heavy-atom effect and its paramagnetism, Gd^{3+} induces strong singlet–triplet mixing in the ligand.[11] It follows that fluorescence is largely quenched, whereas phosphorescence is facilitated.[12–16] The first results on the unique luminescence properties of gadolinium–porphyrins have recently been reported.[17] Here we have extended our study to explore the chemistry of Gd^{III} porphyrinate complexes.

We have prepared a series of new Gd^{III} porphyrinate complexes where both electron-donating and electron-withdrawing groups have replaced the *meso*-phenyl rings in the porphyrin units. The tripodal anion L_{OMe}^- $[(\eta^5\text{-}C_5H_5)\text{-}Co\{P(=O)(OMe)_2\}_3^-]$ is used to stabilize labile gadolinium(III) porphyrinate complexes by effectively encapsulating the lanthanide ion, thereby shielding it from interactions with the environment.[10] The composition and identity of the new complexes were deduced by FTIR spectroscopy, mass spectrometry, elemental analysis, and absorption spectroscopy. The crystal and molecular structures of **1**, **3**, and **7** were determined by single-crystal X-ray structural analysis. The visible emissions, luminescent yields, NIR phosphorescence, and lifetimes of these complexes have been investigated in detail.

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Result and Discussion

Synthesis and Characterization of Porphyrin Ligands

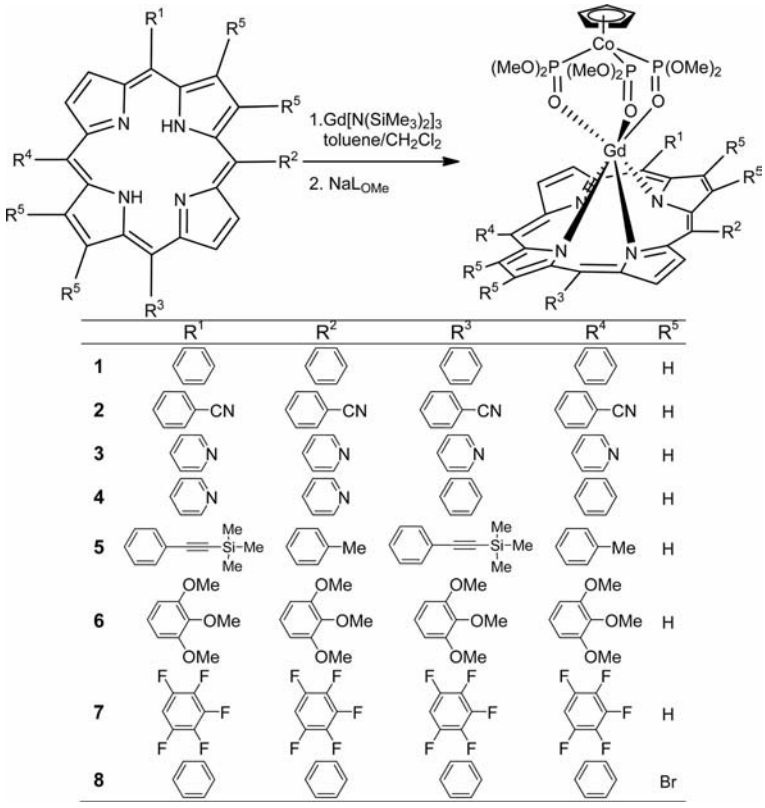
The highly symmetric porphyrin free bases 5,10,15,20-tetraphenylporphyrin, 5,10,15,20-tetrakis(4-cyanophenyl)porphyrin, 5,10,15,20-tetrakis(4-pyridyl)porphyrin, 5,10,15,20-tetrakis(pentafluorophenyl)porphyrin, and 5,10,15,20-tetrakis(3,4,5-trimethoxyphenyl)porphyrin were prepared by direct condensation of the respective benzaldehyde and pyrrole in propionic acid according to Rothemund's method and purified by column chromatography using silica gel.[18] The less symmetric porphyrin free bases 5,15-bis[4-{2-(trimethylsilyl)ethynyl}phenyl]-10,20-bis(*p*-tolyl)porphyrin, 5,15-bis(phenylethynyl)-10,20-bis(*p*-tolyl)porphyrin, and 5,15-bis(isopropylphenyl)porphyrin were prepared by condensation of the corresponding dipyrromethane and benzaldehyde in dichloromethane in the presence of acid catalysts such as trifluoroacetic acid or $BF_3{\cdot}Et_2O$.[19] The β-substituted porphyrin 2,3,12,13-tetrabromo-5,10,15,20-tetraphenylporphyrin was prepared according to a reported procedure.[20]

Synthesis and Characterization of Gadolinium(III) Porphyrinate Complexes

Our facile method has been widely used for the preparation of NIR-emissive monoporphyrinate lanthanide complexes.[10] Under nitrogen, the porphyrin free base is heated with a fivefold excess of $Gd[N(SiMe_3)_2]_3{\cdot}x[LiCl(THF)_3]$, which is generated in situ from the reaction of anhydrous $GdCl_3$ with 3 equiv. of $Li[N(SiMe_3)_2]$ in THF, in dry toluene under reflux for 48 h, followed by stirring of the resulting mixture with a slight excess of NaL_{OMe} in air at room temperature, which gives purple complexes in high yields (Scheme 1). The complexes are air-stable and soluble in chloroform, dichloromethane, and *N*,*N*-dimethylformamide. All of the complexes **1**–**8** gave satisfactory elemental analyses corresponding to the general formula [(Por)-$Ln(L_{OMe})$] (Por = porphyrinate dianion) and exhibited $[M + 1]^+$ peaks in their mass spectra. For instance, the ESI-HRMS of **1** and **2** exhibited $[M + 1]^+$ peaks at *m*/*z* = 1221.1491 and 1320.1181, respectively, which deviate less than 5 ppm from the theoretical values of 1221.1456 and 1320.1188, respectively, and their isotopic distribution patterns match the theoretical distribution. The IR spectra of **2** and **5** exhibit $\tilde{\nu}_{C\equiv N}$ and $\tilde{\nu}_{C\equiv C}$ peaks at around 2227 and 2156 cm^{-1}, respectively.

X-ray Structural Analysis

Crystals of **1**, **3**, and **7** suitable for X-ray diffraction studies were grown by slow concentration of a solution of the compound in chloroform/hexane at room temperature. Perspective views of the compounds are shown in Figures 1, 2, and 3, respectively. Selected bond lengths and angles are summarized in Table 1. Crystal structure analyses revealed



Scheme 1. Preparation of Gd^{III} porphyrinate complexes **1**–**8**.

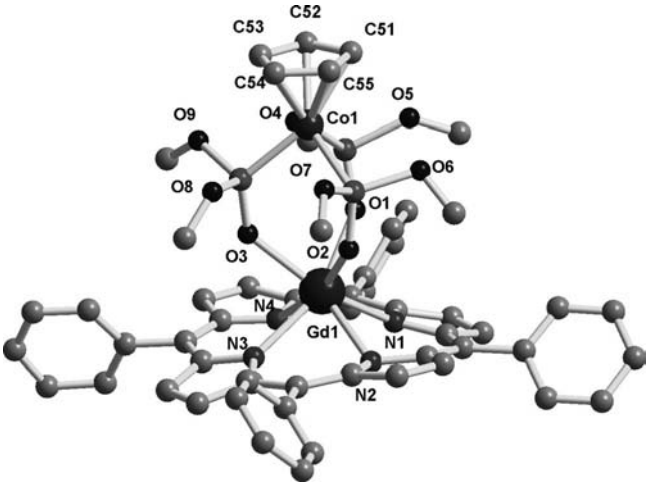


Figure 1. Perspective drawing of **1**.

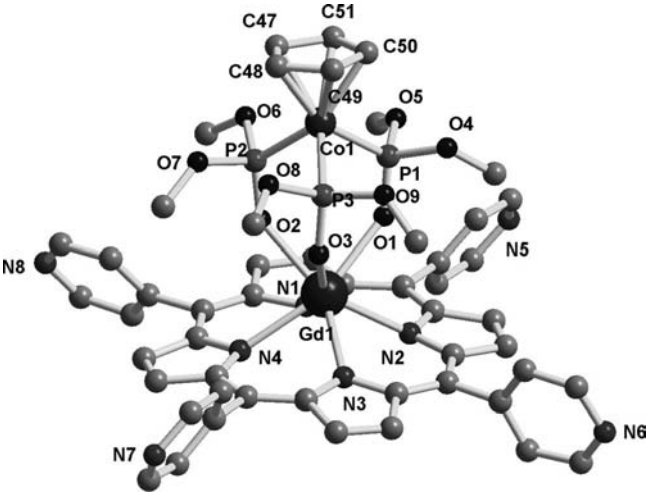


Figure 2. Perspective drawing of **3**.

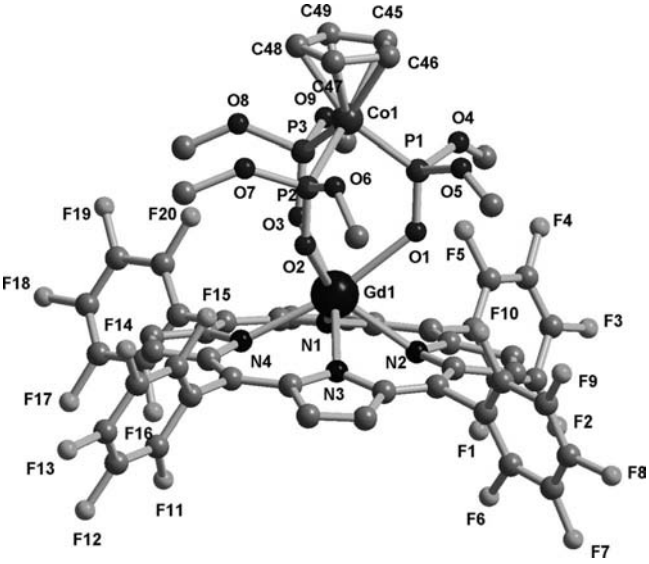


Figure 3. Perspective drawing of **7**.

that the Gd^{III} ions are seven-coordinate, surrounded by four N atoms of the porphyrinate and three O atoms of the three phosphito groups. The Gd–N and Gd–O distances are in the following ranges: 2.349(6)–2.362(6) Å (Gd–N) and 2.223(11)–2.266(10) Å (Gd–O) for **1**; 2.411(5)–2.422(5) Å (Gd–N) and 2.327(13)–2.358(16) Å (Gd–O) for **3**; 2.386(4)–2.450(4) Å (Gd–N) and 2.188(8)–2.428(7) Å (Gd–O) for **7**. The average Gd–N distances of **1** (2.401 Å), **3** (2.415 Å), and **7** (2.428 Å) are much longer than those of the Yb^{III} or Er^{III} cationic complexes of the type $[Ln(TMPP)(H_2O)_3]^+$ (Yb–N 2.301 Å; Er–N 2.329 Å). This is probably a reflection of the larger ionic radius of the gadolinium ion.[10] The three mean planes (C_5 of the cyclopentadienyl ring, N_4 of the porphyrin, and O_3 of the phosphito groups) are almost parallel. The dihedral angles formed between the four phenyl rings and the N_4 mean plane are 49.1, 49.3,

Table 1. Selected bond lengths [Å] and angles [°] for compounds **1**, **3**, and **7**.

1			
Bond lengths			
Gd(1)–N(1)	2.396(6)	Gd(1)–N(2)	2.413(6)
Gd(1)–N(3)	2.397(6)	Gd(1)–N(4)	2.399(6)
Gd(1)–O(1)	2.279(11)	Gd(1)–O(2)	2.326(10)
Gd(1)–O(3)	2.307(11)	P(1)–O(1)	1.503(11)
P(2)–O(2)	1.481(10)	P(3)–O(3)	1.490(11)
Bond angles			
N(1)–Gd(1)–N(2)	74.2(2)	N(1)–Gd(1)–N(3)	117.81(19)
N(4)–Gd(1)–N(1)	76.83(11)	N(2)–Gd(1)–N(3)	74.0(2)
N(4)–Gd(1)–N(2)	116.8(2)	N(4)–Gd(1)–N(3)	74.6(2)
O(1)–Gd(1)–O(2)	79.3(4)	O(2)–Gd(1)–O(3)	78.9(4)
O(1)–Gd(1)–O(3)	78.9(4)		
3			
Bond lengths			
Gd(1)–N(1)	2.411(5)	Gd(1)–N(2)	2.417(5)
Gd(1)–N(3)	2.422(5)	Gd(1)–N(4)	2.413(5)
Gd(1)–O(1)	2.332(15)	Gd(1)–O(2)	2.327(13)
Gd(1)–O(3)	2.358(16)	P(1)–O(1)	1.508(16)
P(2)–O(2)	1.498(14)	P(3)–O(3)	1.509(16)
Bond angles			
N(1)–Gd(1)–N(2)	74.25(16)	N(1)–Gd(1)–N(3)	117.79(17)
N(4)–Gd(1)–N(1)	75.22(16)	N(2)–Gd(1)–N(3)	74.36(16)
N(4)–Gd(1)–N(2)	117.49(16)	N(4)–Gd(1)–N(3)	73.98(16)
O(1)–Gd(1)–O(2)	77.8(5)	O(2)–Gd(1)–O(3)	76.4(5)
O(1)–Gd(1)–O(3)	79.8(5)		
7			
Bond lengths			
Gd(1)–N(1)	2.438(2)	Gd(1)–N(2)	2.386(4)
Gd(1)–N(3)	2.440(2)	Gd(1)–N(4)	2.450(4)
Gd(1)–O(1)	2.428(7)	Gd(1)–O(2)	2.283(6)
Gd(1)–O(3)	2.188(8)	P(1)–O(1)	1.462(8)
P(2)–O(2)	1.442(6)	P(3)–O(3)	1.518(8)
Bond angles			
N(1)–Gd(1)–N(2)	73.5(2)	N(1)–Gd(1)–N(3)	117.11(8)
N(4)–Gd(1)–N(1)	74.9(2)	N(2)–Gd(1)–N(3)	74.36(16)
N(4)–Gd(1)–N(2)	116.64(10)	N(4)–Gd(1)–N(3)	75.36(19)
O(1)–Gd(1)–O(2)	78.7(3)	O(2)–Gd(1)–O(3)	77.4(3)
O(1)–Gd(1)–O(3)	81.4(3)		

68.8, and 61.6° for **1**, 58.4, 78.2, 61.0, and 58.3° for **3**, and 69.9, 70.4, 71.7, and 72.3° for **7**. The Gd(1) atom lies 1.2496, 1.2506, and 1.2709 Å above the porphyrin ring [N(1)–N(4)] for **1**, **3**, and **7**, respectively.

Photophysical Properties of Gadolinium(III) Porphyrinate Complexes

It is known that the Gd^{3+} ion generally does not accept energy from organic ligands, because the energies of the intraligand states of these donor species are below that of the first excited $^6P_{7/2}$ state of the Gd^{3+} ion. Since there is a large energy gap (ca. 32000 cm^{-1}) between the $^8S_{7/2}$ ground state and the first $^6P_{7/2}$ excited state of the Gd^{3+} ion,[21,22] it cannot be reached by energy from the lower-lying first excited T_1 state of the porphyrin ligands by energy transfer. However, the paramagnetic Ln^{3+} ions, and in particular the Gd^{3+} ion with a $4f^7$ configuration, can induce an increase in the intersystem crossing from the singlet state to the triplet state of organic ligands, owing to the increase in the mixing of singlet and triplet states (heavy-ion effect).[23] Although metal-centered luminescence cannot be observed, the emission spectra and decay-time measurements for Gd^{III} complexes allow the identification of the lowest triplet state of the ligand in the complex.

The photophysical properties of **1**–**8** are summarized in Table 2. The electronic absorption spectra of complexes **1**–**8** are characteristic of normal metalloporphyrins.[24] The Soret band for complexes **1**–**7** was observed at about 425–432 nm and that of complex **8** at 444 nm. The Q-bands for these Gd^{III} porphyrinate complexes were observed at 558–562 and 590 nm. Steady-state fluorescence measurements at room temperature reveal a large $Q_x(0,0)$ emission band for Gd^{III} porphyrinate complexes **1**–**7** (in toluene) at 640–656 nm, and a small low-energy $Q_x(0,1)$ shoulder at 710–720 nm (Figure 4). Excitation spectra of the vibronic bands of the complexes in CH_3CN solution at 298 K (monitored at 650 nm) were observed at 560 and 596 nm, which almost coincide with the visible absorption bands at 550 and 588 nm. This shows that the excitation of the complexes originates from π→π* transitions of the porphyrinate.[10a] The visible emissions in the range of 600–727 nm of all the complexes show quite a fast decay time (ca. 6–8 ns). In addition, under ambient conditions, complexes **1** and **3** display evident phosphorescence at 781 and 791 nm, respectively, in analogy to the phosphorescence of many other complexes of heavy metals (Figure 4).[25]

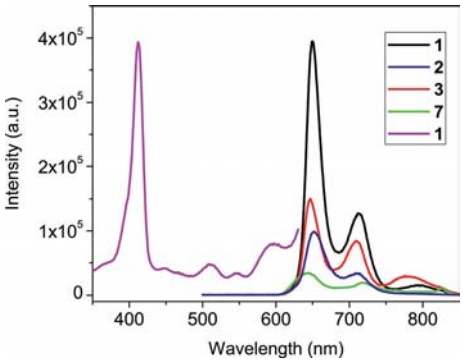


Figure 4. Steady-state fluorescence measurements of **1**, **2**, **6**, and **7** in CH_3CN (1×10^{-7} M) at room temperature.

Emission spectra were also recorded in CH_3CN at 77 K. In the visible range at low temperature, when excited at 430 nm, only complexes **5** and **7** display two apparent peaks at about 665 and 729 nm, which are assigned similarly to the visible fluorescence partly due to the short lifetime (ca. 15–17 ns) of both bands. The emission spectra extend towards the longer wavelengths with a series of additional bands in the range of 800–1400 nm, which represent the phosphorescence from the triplet state of the porphyrin rings and exhibit a very characteristic vibronic-structured emission. The lifetimes have typical values for Gd^{III} porphyrinate complexes that vary from 129 to 190 μs. As expected, all the vibronic bands of each Gd complex in the NIR range show similar emission lifetimes. These measured lifetimes are in agreement with some known triplet-state values of metal porphyrinates.[25] Figure 5 shows a progression of structured bands that occur between 600 nm and 1400 nm. The emission band maxima are presented in Table 2. It should be noted that the phosphorescent state of Gd–porphyrins is rather unusual. Normal phosphorescence occurs from the lowest triplet state. However, the Gd ion has a 7/2 state where there are seven unpaired electrons in the f-shell of the metal atom. Thus, the three states of the triplet become 24 states: a sextet, an octet, and a decet.[17]

Table 2. Absorption and photoluminescence data for **1**–**8**.

	Absorption λ_{max} [nm] ($\log \varepsilon$ [$dm^3\,mol^{-1}\,cm^{-1}$])[a]	Luminescence at 298 K λ_{em} [nm] ($\Phi_{em} \times 10^3$)[b,c]	Luminescence at 77 K λ_{em} [nm][b]
1	428 (5.86), 559 (4.35)	656, 720 (0.21)	927, 1004, 1060
2	432 (5.63), 561 (4.16)	654, 720 (1.5)	928, 1004, 1060
3	428 (5.67), 558 (4.15)	652, 716 (0.25), 777	925, 1004, 1060
4	425 (5.56), 557 (4.51)	660, 720	925, 1004, 1060
5	432 (5.68), 562 (4.20)	656, 720 (1.1)	664, 732, 926, 1001, 1042
6	431 (5.76), 560 (4.26)	656, 722 (0.36)	665, 729, 924, 999, 1041
7	425 (5.66), 556 (4.24)	652, 727 (0.18)	927, 1004, 1060
8	444 (5.64), 559 (4.28)	652, 720	923, 1003, 1042

[a] Absorption measurements were carried out in toluene. [b] Emission measurements were carried out at a concentration of 1×10^{-7} M in CH_3CN at room temperature and 77 K. [c] The quantum yield standard used in this study was the Zn^{II} complex of tetraphenylporphyrin in degassed, anhydrous benzene (Φ_{em} = 0.04 at 298 K).[26]

The 24 states interconvert quickly compared to the lifetime of the triplet. The substituents on the *meso* positions on the porphyrin core have little effect on the fluorescence position. However, the substitution of electron-donating groups typically changes the fluorescence intensity and lifetime. Compared with **1**, **2**, **3**, and **7**, which have electron-withdrawing groups substituted at *meso* positions on the porphyrin core, **5** exhibits a much weaker luminescence in the NIR range because of the electron-donating group on the porphyrin core. Excitation spectra of the vibronic bands of the complexes were determined in CH_3CN solution at 77 K (monitored at 1002 nm). All the complexes show one broad excitation peak at around 430 nm, which suggests that there is the possibility of a more complex structure involved in the emission process. Generally, one could expect that these systems are merely phosphorescent at room or low temperature due to the open-shell f^7 Gd center. However, the complexes here display mixed singlet and triplet luminescence, from which we cannot exclude the possibility of the presence of traces of free porphyrins formed by demetallation.

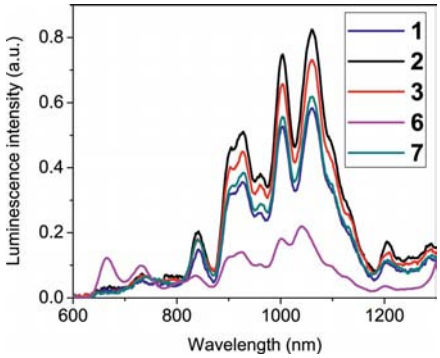


Figure 5. Photoluminescence spectra of **1**, **2**, **3**, **6**, **7**, and **8** excited at 430 nm in CH_3CN (1×10^{-7} M) at 77 K.

Concluding Remarks

A new series of gadolinium(III) porphrinate complexes stabilized by the tripodal anion L_{OMe}^- have been prepared. Characterization of these rare-earth complexes was accomplished by spectroscopic, X-ray crystallographic, and photophysical methods. The visible emissions, luminescence yields, NIR phosphorescence, and lifetimes of these complexes have been examined. The electronic spectra reveal the NIR phosphorescence from the triplet state of the porphyrinato ligand and show a very characteristic vibronic-structured emission, as previously reported for other Gd–porphyrin complexes.[17]

Experimental Section

General: All reagents and solvents were of commercial reagent grade and used without further purification except where noted. Dichloromethane was distilled from calcium hydride. Toluene and THF were distilled under nitrogen in the presence of sodium chips by using benzophenone ketyl as an indicator. The freshly distilled solvents for use in reactions were bubbled with nitrogen for at least 10 min to remove residual oxygen. Pyrrole was freshly distilled from calcium hydride before use. Elemental analyses (C, H, N) were performed at the Shanxi University, P. R. China. NMR spectra were recorded with a JEOL EX270 spectrometer. ESI-HR mass spectra were recorded with a QSTAR mass spectrometer. The electronic-absorption spectra in the UV/Vis region were recorded with a Hewlett Packard 8453 UV/Vis spectrophotometer. Steady-state visible-fluorescence and PL-excitation spectra were measured with a Photon Technology International (PTI) Alphascan spectrofluorimeter. Visible-decay spectra were recorded with a pico-N_2 laser system (PTI Time Master) with λ_{exc} = 337 nm. The quantum yields of visible emissions were computed based on the Zn^{II} complex of tetraphenylporphyrin in degassed, anhydrous benzene (Φ_F = 0.04 at 298 K).[26] NIR emission at low temperature was carried out with a PTI QM4 spectrofluorometer with a PTI QM4 near-infrared InGaAs detector, and the solution samples were prepared with freeze-pump-thaw cycles (three times) before emission detection.

Synthesis of Gd[N(SiMe$_3$)$_2$]$_3$·*x*[LiCl(THF)$_3$] (A): Gd[N(SiMe$_3$)$_2$]$_3$·*x*[Li(THF)$_3$Cl] (*x* = 3–5) was prepared as described previously for Yb[N(SiMe$_3$)$_2$]$_3$·*x*[LiCl(THF)$_3$].[9]

General Procedure for the Preparation of [(Por)Gd(L_{OMe})]: All of the [(Por)Gd(L_{OMe})] complexes were prepared according to the same procedure. Typically, a solution of **A** (2.5 mL, 0.52 mmol of Gd) was transferred to a Schlenk flask, and the solvent was removed under vacuum. CH_2Cl_2 (10 mL) was added, the mixture was centrifuged, and the clear layer transferred to a Schlenk flask with dry porphyrin free base (0.1 g, 0.16 mmol) dissolved in toluene (15 mL). The resulting solution was heated to reflux until most of the free base had coordinated to the metal ion. NaL_{OMe} (0.1 g, 0.22 mmol) was then added, and the mixture was heated with stirring for another 12 h before the reaction solution was cooled to room temperature. Upon completion of the reaction, the solvent was removed under vacuum, and the residue was dissolved in chloroform, filtered, and purified by chromatography on silica gel using $CHCl_3$/petroleum ether (1:1, v/v) as eluent. The product was dissolved in CH_2Cl_2 (5 mL), and the solution was filtered. Diffusion of methanol into the CH_2Cl_2 solution gave purple crystals of the desired complexes.

1: Yield: 86%. M.p. > 300 °C. IR (in KBr): $\tilde{\nu}$ = 2939, 2833, 1596, 1514, 1475, 1439, 1327, 1128, 1089, 1037, 1009, 985, 796, 725, 701, 591 cm^{-1}. $C_{55}H_{51}CoGdN_4O_9P_3$ (1221.13): calcd. C 54.10, H 4.21, N 4.59; found C 54.15, H 4.32, N 4.48. ESI-HRMS (positive mode in methanol): calcd. for $[C_{55}H_{51}CoGdN_4O_9P_3]^+$ 1221.1456; found 1221.1491 $[M]^+$.

2: Yield: 79%. M.p. > 300 °C. IR (in KBr): $\tilde{\nu}$ = 2939, 2826, 2227, 1603, 1517, 1497, 1439, 1329, 1133, 1035, 1007, 986, 807, 794, 726, 582 cm^{-1}. $C_{59}H_{47}CoGdN_8O_9P_3$ (1321.17): calcd. C 53.64, H 3.59, N 8.48; found C 53.75, H 4.01, N 8.27. ESI-HRMS (positive mode in methanol): calcd. for $[C_{59}H_{48}CoGdN_8O_9P_3]^+$ 1320.1188; found 1320.1181 $[M + 1]^+$.

3: Yield: 80%. M.p. > 300 °C. IR (in KBr): $\tilde{\nu}$ = 2940, 2833, 1591, 1538, 1474, 1406, 1332, 1134, 1069, 1038, 1009, 985, 801, 774, 725, 660, 582 cm^{-1}. $C_{51}H_{47}CoGdN_8O_9P_3$ (1225.09): calcd. C 50.00, H 3.87, N 9.15; found C 51.02, H 3.95, N 9.11. ESI-HRMS (positive mode in methanol): calcd. for $[C_{51}H_{48}CoGdN_8O_9P_3]^+$ 1232.1486; found 1232.1490 $[M + 1]^+$.

4: Yield: 70%. M.p. > 300 °C. IR (in KBr): $\tilde{\nu}$ = 2940, 2826, 1591, 1524, 1482, 1438, 1379, 1331, 1203, 1131, 1039, 1009, 986, 796, 774, 727, 701, 579 cm^{-1}. $C_{53}H_{49}CoGdN_6O_9P_3$ (1223.11): calcd. C 52.05, H 4.04, N 6.87; found C 53.15, H 4.12, N 6.78. ESI-HRMS

Table 3. Crystallographic data for compounds **1**, **3**, and **7**.

	1·3CHCl$_3$	**3**	**7**
Empirical formula	$C_{58}H_{54}Cl_9CoGdN_4O_9P_3$	$C_{51}H_{47}CoGdN_8O_9P_3$	$C_{55}H_{31}CoF_{20}GdN_4O_9P_3$
Molecular mass	1579.19	1225.06	1580.93
Crystal size [mm]	0.40 × 0.40 × 0.30	0.32 × 0.26 × 0.20	0.32 × 0.25 × 0.20
Crystal system	monoclinic	triclinic	monoclinic
Space group	$P2_1/n$	$P\bar{1}$	$P2_1$
a [Å]	12.978(4)	12.4628(7)	10.358(2)
b [Å]	33.289(10)	14.0765(8)	16.603(4)
c [Å]	15.345(5)	15.1569(8)	23.708(5)
α [°]	90	76.7590(10)	90
β [°]	95.029	78.3280(10)	90.051(4)
γ [°]	90	81.0750(10)	90
V [Å^3]	6604(3)	2518.2(2)	4077.0(15)
Z	4	2	2
$D_{calcd.}$ [g cm^3]	1.588	1.795	1.288
T [K]	293(2)	293(2)	293(2)
μ(Mo-K_α) [mm^{-1}]	1.739	1.795	1.157
F(000)	3164	1234	1554
θ range [°]	1.69–25.01	1.68–25.00	2.11–25.00
Reflections collected	30719	12681	20271
Independent reflections	11548	8747	13982
R_{int}	0.1063	0.0239	0.0231
GOF on F^2	0.939	1.050	1.080
$R1$, $wR2$ [$I > \sigma(I)$][a]	0.0598, 0.1443	0.0485, 0.1325	0.0439, 0.1098
$R1$, $wR2$ (all data)	0.1120, 0.1596	0.0578, 0.1402	0.0606, 0.1198

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR2 = [\Sigma w(|F_o^2| - |F_c^2|)^2/\Sigma w|F_o^2|^2]^{1/2}$.

(positive mode in methanol): calcd. for $[C_{53}H_{50}CoGdN_6O_9P_3]^+$ 1224.1432; found 1224.1466 $[M + 1]^+$.

5: Yield: 74%. M.p. > 300 °C. IR (in KBr): $\tilde{\nu}$ = 2941, 2832, 2156, 1649, 1525, 1517, 1497, 1439, 1329, 1137, 1036, 1006, 987, 863, 843, 795, 726, 587 cm^{-1}. $C_{67}H_{71}CoGdN_4O_9P_3Si_2$ (1441.60): calcd. C 55.82, H 4.96, N 3.89; found C 55.89, H 5.02, N 3.86. ESI-HRMS (positive mode in methanol): calcd. for $[C_{67}H_{71}CoGdN_4O_9P_3Si_2]^+$ 1441.2559; found 1441.2457 $[M]^+$.

6: Yield: 78%. M.p. > 300 °C. IR (in KBr): $\tilde{\nu}$ = 2938, 2832, 1578, 1502, 1463, 1407, 1345, 1233, 1132, 1007, 939, 797, 772, 724, 587 cm^{-1}. $C_{67}H_{75}CoGdN_4O_{21}P_3$ (1581.45): calcd. C 50.89, H 4.78, N 3.54; found C 50.85, H 4.62, N 3.76. ESI-HRMS (positive mode in methanol): calcd. for $[C_{67}H_{75}CoGdN_4O_{21}P_3]^+$ 1581.2727; found 1581.2774 $[M]^+$.

7: Yield: 79%. M.p. > 300 °C. IR (in KBr): $\tilde{\nu}$ = 2947, 2841, 1649, 1525, 1518, 1497, 1439, 1329, 1127, 1073, 1047, 1012, 988, 931, 758, 730, 587 cm^{-1}. $C_{55}H_{31}CoF_{20}GdN_4O_9P_3$ (1580.94): calcd. C 41.76, H 2.04, N 3.5; found C 41.39, H 2.09, N 3.44. ESI-HRMS (positive mode in methanol): calcd. for $[C_{55}H_{31}CoF_{20}GdN_4O_9P_3]^+$ 1580.9571; found 1580.9538 $[M]^+$.

8: Yield: 69%. M.p. > 300 °C. IR (in KBr): $\tilde{\nu}$ = 3055, 2941, 2835, 1596, 1472, 1441, 1304, 1175, 1131, 1086, 1025, 1005, 905, 881, 838, 794, 775, 727, 699, 587 cm^{-1}. $C_{55}H_{47}Br_4CoGdN_4O_9P_3$ (1536.72): calcd. C 42.99, H 3.08, N 3.65; found C 42.39, H 3.19, N 3.44. ESI-HRMS (positive mode in methanol): calcd. for $[C_{55}H_{48}Br_4CoGdN_4O_9P_3]^+$ 1537.7915; found 1537.7904 $[M + 1]^+$.

X-ray Crystallography: Single crystals of the Gd porphyrinate complexes suitable for structural determination were grown by slow concentration of a chloroform/hexane solution of the complexes in air. X-ray intensity data were collected at 293 K with a Bruker Axs SMART 1000 CCD area-detector diffractometer by using graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å). The collected frames were processed with the software SAINT,[27] and an absorption correction was applied (SADABS[28]) to the collected reflections. The structures of these molecules were solved by direct methods and expanded by standard difference Fourier syntheses using SHELXTL.[29] Structure refinements were made on F^2 by 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. Pertinent crystallographic data and other experimental details are summarized in Table 3. CCDC-806354 (for **1**), -806355 (for **3**), and -806356 (for **7**) contain the supplementary crystallographic data for this paper. 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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