

Syntheses, Structures, and Luminescence of Novel Lanthanide Complexes of Tripyridylamine, *N,N,N',N'*-Tetra(2-pyridyl)-1,4-phenylenediamine and *N,N,N',N'*-Tetra(2-pyridyl)biphenyl-4,4'-diamine

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Two novel blue luminescent bridging ligands *N,N,N',N'*-tetra(2-pyridyl)-1,4-phenylenediamine (tpdp) and *N,N,N',N'*-tetra(2-pyridyl)-1,1-biphenyl-4,4'-diamine (tpbpd) have been synthesized. Several novel lanthanide complexes containing 2,2',2''-tripyridylamine (2,2',2''-tpa), 2,2',3''-tpa, tpdp, or tpbpd ligands have been synthesized and characterized structurally, which include Pr(hfa)₃(2,2',2''-tpa), **1**, Ln(tmhd)₃(2,2',3''-tpa), **2** (Ln = Dy, **2a**; Eu, **2b**; Tb, **2c**; Sm, **2d**), [Eu(tmhd)₃][Pr(hfa)₃](2,2',3''-tpa), **3**, [Pr(hfa)₃]₂(tpdp), **4**, and [Ln(hfa)₃]₂(tpbpd), **5**, where Ln = Pr (**5a**), Eu (**5b**), tmhd = 2,2,6,6-tetramethyl-3,5-heptanedionato, and hfa = hexafluoroacetylacetonate. The Dy(III), Eu(III), and Tb(III) complexes display a bright photoluminescence, which can be achieved by either a direct excitation process or an indirect excitation process. Compounds **2a**–**2d** can be sublimed readily.

Introduction

The chemistry of lanthanides has attracted much attention because of their unique chemical and physical properties and their applications in a variety of advanced materials.^{1,2} Recently, a number of luminescent lanthanide compounds have been demonstrated to be promising emitters in electroluminescent displays,² which prompted us to investigate and synthesize new luminescent lanthanide compounds. Luminescence of lanthanide ions usually originates from f → f electronic transitions, which are very weak in the absence of activators.³ In order for lanthanide compounds to be useful in electroluminescent displays, ligands that can activate the luminescence of lanthanide

ions must be present in the compounds. The role of the activator ligand is to transfer energy to the lanthanide ion through intersystem crossing and intersystem energy-transfer processes to enhance the emission energy of the lanthanide. Consequently, one of the requirements for the activator ligand is that it must have a band gap greater than that of the lanthanide ion in addition to being an efficient emitter itself in the UV or near-UV region.^{1d,3}

During our recent investigation of blue luminescent organic and organometallic compounds, we have observed that di(2-pyridyl)amine and its derivatives typically have a large excitation band gap and emit fairly efficiently either in the UV or near-UV region.^{4,5} Furthermore, the di(2-pyridyl)amine-based ligands are capable of chelating to a metal ion, making them ideal candidates as activators for luminescent lanthanide ions. Herein we report the results of our investigation of syntheses, structures, and luminescence of several novel lanthanide complexes using ligands that contain the di(2-pyridyl)amino functional group.

Experimental Section

All reactions were carried out under a nitrogen atmosphere. All starting materials were purchased from Aldrich Chemical Co. and used without further purification unless otherwise stated. Tetrahydrofuran, hexane, and toluene were distilled from sodium and benzophenone under a nitrogen atmosphere, and dichloromethane was distilled from P₂O₅ under a nitrogen atmosphere. ¹H NMR spectra were recorded on Bruker Avance 300 MHz spectrometer. The Canadian Microanalytical Service Ltd., Delta, British Columbia, performed the elemental analyses. TLC was carried out on SiO₂ (silica gel, F254, Whatman), and column chromatography was also carried out on silica (silica gel 60, 70–230 mesh). Melting points were determined on a Fisher-Johns melting point apparatus, and excitation and emission spectra were recorded on a Photon Technologies International QuantaMaster model C-60 spec-

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trometer at ambient temperature. The phosphorescent and fluorescent spectra and decay lifetime of phosphorescence/lanthanides were recorded on a Time Master spectrometer of Photon Technologies International under a nitrogen atmosphere. The fluorescent lifetime was obtained by the method of single-photon counting. NaX zeolite was used to record the lamp profile. The syntheses of 2,2',2''-tripyrindylamine (2,2',2''-tpa) and 2,2',3''-tripyrindylamine (2,2',3''-tpa) were carried out according to a previously reported procedure.⁵

Synthesis of *N,N,N',N'*-Tetra(2-pyridyl)-1,4-phenylenediamine (tpdp). A 3.42 g (0.020 mol) sample of 2,2'-dipyridylamine, 2.83 g (0.012 mol) of 1,4-dibromobenzene, 1.46 g (0.026 mol) of potassium hydroxide, and 0.103 g of cupric sulfate were placed in a 100 mL flask. The mixture was heated to 180 °C and stirred for 6 h. The reaction was monitored by TLC. After the reaction mixture was cooled to ambient temperature, dichloromethane and water were added to dissolve the solids. The aqueous phase was discarded, and the organic phase was washed with distilled water until the pH was 7. Na₂SO₄ was used to dry the organic phase. The product was isolated by using a chromatographic column with ethanol as the eluant. Light-yellow crystals of tpdp were obtained in 29% yield from an ethanol/hexane solution. Mp: 206–208 °C. ¹H NMR (δ, ppm; CDCl₃, 298 K): 8.36 (1 H, d, ³J = 5.1 Hz), 7.60 (1 H, dd, ³J = 8.1 Hz, ³J = 7.2 Hz), 7.20 (1 H, s), 7.09 (1 H, d, ³J = 8.1 Hz), 6.96 (1 H, dd, ³J = 7.2 Hz, ³J = 5.1 Hz). MS (CI): *m/z* = 417.5 (M⁺, 100%).

Synthesis of *N,N,N',N'*-Tetra(2-pyridyl)biphenyl-4,4'-diamine (tpbpd). Tpbpd was synthesized by the reaction of 4,4'-bromobiphenyl with dipyrindylamine using the same procedure and the same conditions as for tpdp. Light-yellow crystals of tpbpd were obtained in 33% yield from an ethanol/hexane solution. Mp: 225–227 °C. ¹H NMR (δ, ppm; CDCl₃, 298 K): 8.39 (1 H, d, ³J = 4.8 Hz), 7.61 (1 H dd, overlap with 1 H, d, ³J = 8.4 Hz), 7.26 (1 H, d, ³J = 8.4 Hz), 7.06 (1 H, d, ³J = 8.4 Hz), 6.98 (1 H, dd, ³J = 4.8 Hz, ³J = 6.3 Hz). MS (CI): *m/z* = 493.4 (M⁺, 100%).

Synthesis of Pr(hfa)₃(2,2',2''-tpa), **1.** A 218 mg (0.29 mmol) quantity of Pr(hfa)₃ and 71 mg (0.29 mmol) of 2,2',2''-tpa were dissolved in dichloromethane. The mixture was stirred for 1 h. After concentration of the solution, a small amount of hexane was added. Light-green crystals of Pr(hfa)₃(2,2',2''-tpa) were obtained in 85% yield. Mp: 195–197 °C. Anal. Calcd for Pr(hfa)₃(2,2',2''-tpa): C, 35.66; H, 1.50; N, 5.55. Found: C, 35.84; H, 1.37; N, 5.47.

Synthesis of Dy(tmhd)₃(2,2',3''-tpa), **2a.** A 71 mg (0.10 mmol) quantity of Dy(tmhd)₃ and 25 mg (0.10 mol) of 2,2',3''-tpa were dissolved in dichloromethane separately and then mixed together. The mixture was stirred for 1 h at ambient temperature. After concentration of the solution, a small amount of hexane was added. Colorless crystals of **2a** were obtained in 83% yield. Mp: 134–136 °C. Anal. Calcd for Dy(tmhd)₃(2,2',3''-tpa): C, 60.02; H, 7.24; N, 5.83. Found: C, 60.21; H, 7.17; N, 5.82.

Eu(tmhd)₃(2,2',3''-tpa), **2b** (mp, 134–136 °C), Tb(tmhd)₃(2,2',3''-tpa), **2c** (mp, 135–136 °C), and Sm(tmhd)₃(2,2',3''-tpa), **2d** (mp, 125–126 °C) were obtained in >80% yield by the same procedure as for **2a**. Anal. Calcd for Eu(tmhd)₃(2,2',3''-tpa), **2b**: C, 60.62; H, 7.32; N, 5.90. Found: C, 60.08; H, 7.35; N, 5.78. Anal. Calcd for Tb(tmhd)₃(2,2',3''-tpa), **2c**: C, 60.25; H, 7.22; N, 5.86. Found: C, 60.03; H, 7.21; N, 5.63. Anal. Calcd for Sm(tmhd)₃(2,2',3''-tpa), **2d**: C, 60.80; H, 7.28; N, 5.91. Found: C, 60.63; H, 7.22; N, 5.83.

Synthesis of [Eu(tmhd)₃][Pr(hfa)₃](2,2',3''-tpa), **3.** A 70 mg (0.10 mmol) quantity of Eu(tmhd)₃ and 25 mg (0.10 mmol) of 2,2',3''-tpa were dissolved in dichloromethane, and the mixture was stirred for 2 h at ambient temperature. A total of 76.2 mg (0.10 mmol) of Pr(hfa)₃ was added to the mixture, and the mixture was then stirred for 2 h at ambient temperature. After concentration of the solution, a small amount of hexane was added. Light-green crystals of [Eu(tmhd)₃](2,2',3''-tpa)[Pr(hfa)₃] were obtained in 35% yield. Mp: 124–125 °C. Anal. Calcd for [Eu(tmhd)₃][Pr(hfa)₃](2,2',3''-tpa): C, 44.20; H, 4.24; N, 3.27. Found: C, 43.97; H, 4.14; N, 3.99.

Synthesis of [Pr(hfa)₃]₂(tpbd), **4.** A 76 mg (0.10 mmol) quantity of Pr(hfa)₃ and 21 mg (0.050 mmol) of tpbd were dissolved in dichloromethane. The mixture was stirred for 2 h and then was filtered. After concentration of the solution, a small amount of hexane was added. Light-green crystals were obtained in 70% yield. Mp: 266–

270 °C. Anal. Calcd. for [Pr(hfa)₃]₂(tpbd): C, 34.67; H, 1.35; N, 4.33. Found: C, 34.21; H, 1.59; N, 4.37.

Synthesis of [Pr(hfa)₃]₂(tpbpd), **5a.** Compound **5a** was obtained by the reaction of Pr(hfa)₃ with tpbpd in a 2:1 ratio using the same procedure as for compound **4**. Light-green crystals of [Pr(hfa)₃]₂(tpbpd) were obtained in 88% yield. Mp: 236–239 °C. Anal. Calcd for [Pr(hfa)₃]₂(tpbpd): C, 36.91; H, 1.50; N, 4.17. Found: C, 36.49; H, 1.55; N, 4.14. [Eu(hfa)₃]₂(tpbpd), **5b**, was obtained by the same procedure as for **5a** in 73% yield. Mp: 220–223 °C. Anal. Calcd for [Eu(hfa)₃]₂(tpbpd): C, 36.55; H, 1.49; N, 4.13. Found: C, 37.35; H, 1.93; N, 4.23.

X-ray Diffraction Analyses. All crystals were obtained either from CH₂Cl₂/hexane solutions or from THF/hexane solutions. All crystals were mounted on glass fibers. Data for the free ligand tpbpd and compound **5b** were collected on a Smart CCD 1000 X-ray diffractometer, while data for compounds **1**, **2b**, and **4** were collected on a Siemens P4 single-crystal diffractometer with graphite-monochromated Mo Kα radiation, operating at 50 kV and 35 mA at 23 °C. The data for tpbpd, **2b**, **4**, and **5b** were collected over 2θ 3–47°, while the data for **1** were collected over 2θ 3–50°. Three standard reflections were measured every 197 reflections. No significant decay was observed for all samples. Data were processed on a Pentium PC using the Bruker AXS SHELXTL NT software package⁶ (version 5.10) and corrected for absorption, Lorentz, and polarization effects. Neutral atom scattering factors were taken from Cromer and Waber.⁷ The crystals of **2b** and **5b** belong to the triclinic space group *P* $\bar{1}$, while the crystals of tpbpd, **1**, and **4** were determined to be of the monoclinic space groups *P*2₁/*c*, *P*2₁, and *P*2₁/*n*, respectively, on the basis of systematic absences and successful structural solution and refinement. All structures were solved by direct methods. Some of the CF₃ groups in compounds **4** display a typical 2-fold rotational disorder, which has been modeled and refined successfully. Some of the *tert*-butyl groups of the tmhd ligands in compounds **2b** and **5b** also display a rotational disorder and were modeled and refined successfully. Two of the hfa ligands in compound **1** display an unusual disorder (see discussion section), and as a consequence, all fluorine atoms on these two hfa ligands are disordered and could not be completely modeled. Two of the pyridyl rings of the 2,2',2''-tpa ligand in **1** are also disordered but refined and modeled successfully. The poor quality of crystal data for compound **1** is due to the incomplete modeling of the disordered fluorine atoms. All non-hydrogen atoms were refined anisotropically except the disordered atoms. The positions for all hydrogen atoms in all compounds except those on disordered atoms were calculated, and their contributions in structural factor calculations were included. The crystals of **2a**, **2c**, **2d**, and **5a** have unit cell parameters similar to those of **2b** and **5b** (e.g., **2a**, *a* = 12.679(7) Å, *b* = 14.000(3) Å, *c* = 14.665(3) Å, α = 78.463(8)°, β = 89.06(3)°, γ = 83.46(2)°, *V* = 2532.9(18) Å³; **5a**, *a* = 12.013(3) Å, *b* = 17.105(2) Å, *c* = 20.320(3) Å, α = 83.55(1)°, β = 83.11(2)°, γ = 74.44(2)°, *V* = 3979(1) Å³). Therefore, we did not perform the structural solution and refinements on **2a**, **2c**, **2d**, and **5a**. The crystallographic data for compounds **1**, **2b**, **4**, and **5b** and the free tpbpd ligand are given in Table 1.

Results and Discussions

Syntheses and Structures of Ligands. The syntheses of 2,2',2''-tripyrindylamine (2,2',2''-tpa) and 2,2',3''-tripyrindylamine (2,2',3''-tpa) were described in a previous report.⁵ The attempted synthesis of 2,2',4''-tpa was unsuccessful. The syntheses of *N,N,N',N'*-tetra(2-pyridyl)-1,4-phenylenediamine (tpdp) and *N,N,N',N'*-tetra(2-pyridyl)biphenyl-4,4'-diamine (tpbpd) were carried out by the reaction of di(2-pyridyl)amine with 1,4-dibromobenzene or 4,4'-dibromobiphenyl using Ullmann condensation methods⁸ where copper(II) and KOH were used as catalysts (Scheme 1). The ligands have been fully characterized by spectroscopic analyses.

(6) SHELXTL NT: Crystal Structure Analysis Package, version 5.10; Bruker AXS Inc.: Madison, WI, 1999.

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Table 1. Crystallographic Data

	tpbpd	1	2b	4	5b
formula	C ₃₂ H ₂₄ N ₆	C ₃₀ H ₁₂ N ₄ O ₆ F ₁₈ Pr	C ₄₈ H ₇₅ N ₄ O ₆ Eu	C ₅₆ H ₂₆ N ₆ O ₁₂ F ₃₆ Pr ₂	C ₆₂ H ₃₀ N ₆ O ₁₂ F ₃₆ Eu ₂
fw	492.57	1007.34	956.07	1940.64	2038.85
space group	P2 ₁ /c	P2 ₁	P $\bar{1}$	P2 ₁ /n	P $\bar{1}$
a, Å	11.6017(2)	10.239(2)	12.858(3)	9.062(3)	11.9628(7)
b, Å	10.5589(11)	15.980(4)	14.030(6)	20.236(4)	17.0621(10)
c, Å	10.3432(11)	12.5409(17)	14.686(4)	19.239(5)	20.1673(12)
α , deg	90	90	78.40(3)	90	83.6470(10)
β , deg	100.194(3)	113.465(11)	88.759(17)	92.48(3)	83.4090(10)
γ , deg	90	90	83.54(3)	90	75.145(2)
V, Å ³	1247.1(2)	1882.3(7)	2578.7(14)	3524.9(18)	3938.3(4)
Z	2	2	2	2	2
D _{calc} , g cm ⁻³	1.312	1.777	1.231	1.828	1.719
temp, °C	23	23	23	23	23
μ , cm ⁻¹	0.80	14.29	12.62	15.22	17.21
2 θ , max, deg	47	50	47	47	47
reflms measd	6247	3583	7999	5610	20 272
reflms used	1795	3384	7604	5216	11 355
params	172	507	613	581	1027
final R ^a (I > 2 σ (I))	R1 = 0.0501, wR2 = 0.1196	R1 = 0.0548, wR2 = 0.1436	R1 = 0.0454, wR2 = 0.1203	R1 = 0.0677, wR2 = 0.1209	R1 = 0.0523, wR2 = 0.1148
R ^a (all data)	R1 = 0.1118, wR2 = 0.1410	R1 = 0.0646, wR2 = 0.1585	R1 = 0.0549, wR2 = 0.1291	R1 = 0.1622, wR2 = 0.1554	R1 = 0.0963, wR2 = 0.1278
goodness of fit on F ²	0.852	1.185	1.126	0.988	0.872

^a R1 = $\sum|F_o| - |F_c|/\sum|F_o|$. wR2 = $[\sum w(F_o^2 - F_c^2)^2]/[\sum w(F_o^2)^2]^{1/2}$. w = $1/[\sigma^2(F_o^2) + (0.075P)^2]$, where P = $[\max(F_o^2, 0) + 2F_c^2]/3$.

Our previous study showed that 2,2',2''-tpa and 2,2',3''-tpa ligands are nonplanar with a propeller shape.⁵ The tppd and tpbpd ligands are novel organic molecules. Biphenyl-4,4'-diamine-based organic molecules such as N,N'-di-1-naphthyl-N,N'-diphenylbenzidine (NPB) and N,N'-diphenyl-N,N'-bis(3-methylphenyl)biphenyl-4,4'-diamine (TPD) are well-known hole-transporting materials in organic light-emitting devices (OLEDs).⁹ We therefore decided to examine the crystal structure of tpbpd by a single-crystal X-ray diffraction analysis. As shown by Figure 1, the tpbpd ligand has an inversion center of symmetry and the biphenyl portion of the ligand is planar. However, the pyridyl groups are not coplanar with the biphenyl portion, as indicated by the dihedral angles of 116.3° between the N(1) ring and the biphenyl and 91.7° between the N(2) ring and the biphenyl. The dihedral angle between N(1) and N(2) rings is 62.5°. The nonplanarity of the tpbpd molecule is clearly caused by the steric interactions between C-H groups.

Syntheses and Structures of Lanthanide Complexes of Tripyridylamines. The lanthanide compounds used in our study all contain ligands that are derivatives of acetylacetonate because these ligands are well-known to provide high volatility and solubility to the metal complexes,¹⁰ thus facilitating vacuum deposition of the metal complex, a process commonly used for fabrications of OLEDs. We have found that the 2,2',2''-tripyridylamine ligand readily forms new complexes Ln(hfa)₃-(2,2',2''-tpa) with Ln(hfa)₃, hfa = hexafluoroacetylacetonato, but does not react with Ln(tmhd)₃, tmhd = 2,2,6,6-tetramethyl-3,5-heptanedionato, or 2,4-tert-butylacetylacetonato. An example

of the new Ln(hfa)₃(2,2',2''-tpa) complexes is Pr(hfa)₂(2,2',2''-tpa), **1**, which is fully characterized by elemental and single-crystal X-ray diffraction analyses.

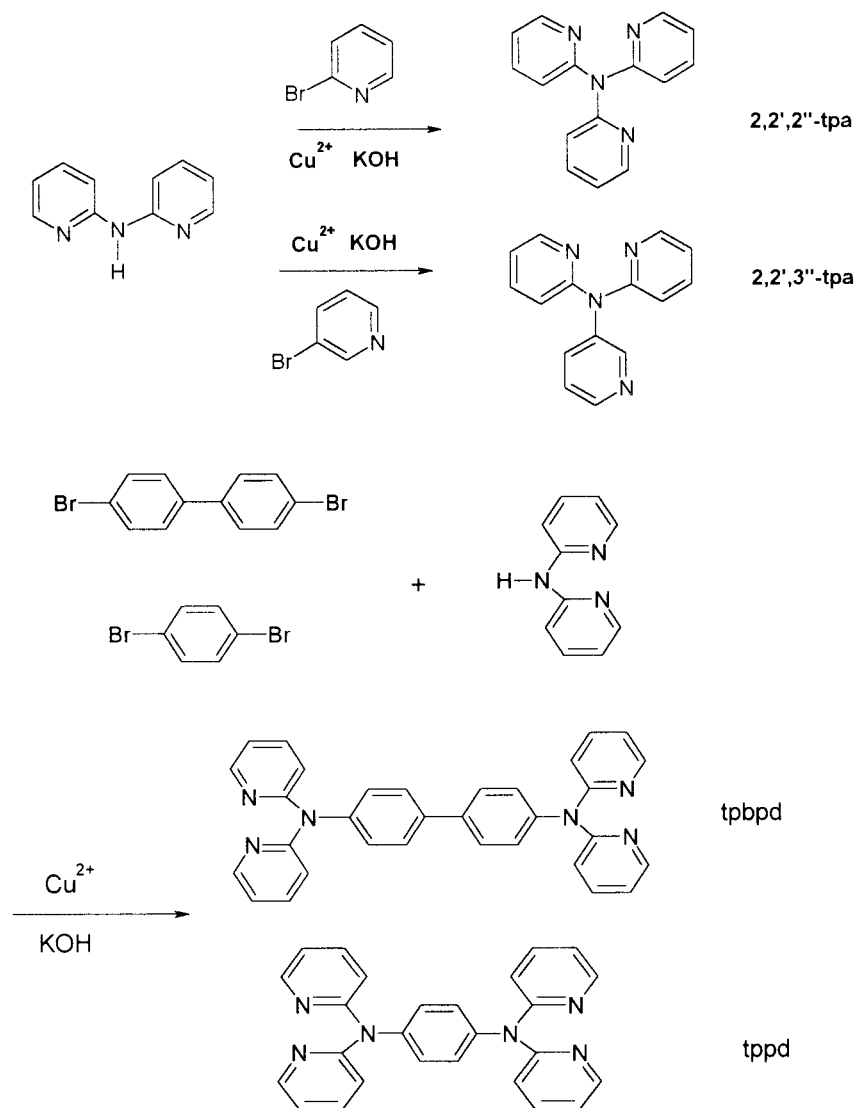
The structure of **1** is shown in Figure 2. The carbon atoms on two of the hfa ligands in **1** are disordered over two sites with a 50% occupancy for each site. The third hfa ligand does not show any disorder. Two of the pyridyl rings (N(1) and N(2)) of the 2,2',2''-tpa ligand also display some degree of disordering. As a result of the disordering, the quality of the structure of **1** is not very good. Nonetheless, the crystal structure established unequivocally that the 2,2',2''-tpa ligand is chelated to the Pr(III) center through two of the 2-pyridyl groups and that the third 2-pyridyl group is not coordinated (N(4) is 4.615 Å away from Pr(1)). A similar bonding mode displayed by 2,2',2''-tpa has been observed recently in a Zn(II) complex⁵ and a Ru(II) complex.¹¹ The amino nitrogen atom N(3) is 3.06(1) Å away from Pr(1). If N(3) can be considered as a weakly bound donor atom, the coordination number of Pr(III) in **1** is 9, quite common for lanthanide compounds.¹² The Pr(1)-N(1), Pr(1)-N(2), and Pr(1)-O bond lengths in **1** are typical.¹² The fact that the third pyridyl ring is not coordinated can be attributed to the steric hindrance exposed by the hfa ligands. It is, however, puzzling that the 2,2',2''-tpa ligand does not form a complex with Ln(tmhd)₃, since one would anticipate that at least one of the 2-pyridyl groups can bind to the Ln(III) center in Ln(tmhd)₃, despite the increased steric interactions in Ln(tmhd)₃, compared to that of Ln(hfa)₃. We obtained some clues for this puzzle by examining the complex Ln(tmhd)₃(2,2',3''-tpa), **2**, obtained from the reaction of Ln(tmhd)₃ with 2,2',3''-tpa in a 1:1 ratio.

The structure of Eu(tmhd)₃(2,2',3''-tpa), **2b**, was determined by a single-crystal X-ray diffraction analysis. As shown in Figure 3, the Eu(III) center in **2b** is coordinated by three tmhd

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Scheme 1



ligands and the 2,2',3''-tpa ligand. However, unlike 2,2',2''-tpa that chelates to the Pr(III) center in **1** by two 2-pyridyl groups, the 2,2',3''-tpa ligand is bound to the Eu(III) in **2b** as a terminal ligand through the 3-pyridyl nitrogen atom only. Clearly the tmhd ligand is sterically more demanding than the hfa ligand, thus preventing the chelating mode of 2,2',3''-tpa in **2b**. In fact the terminal binding mode through the 3-pyridyl group displayed by the 2,2',3''-tpa ligand has been observed previously⁵ in a very crowded Zn(II) complex, $Zn(O_2CCF_3)_2(2,2',3''\text{-tpa})_4$. The amino nitrogen atom N(4) and the two 2-pyridyl nitrogen atoms N(2) and N(3) are 5.76(1), 6.32(1), and 7.77(1) Å, respectively, away from the Eu(1) atom, thus precluding any bonding interactions with the europium center. The coordination number of the Eu(III) center in **2b** is therefore 7. The Eu–O bond lengths in **2b** is slightly shorter than Pr–O bond lengths in **1**, while the Eu(1)–N(1) bond length in **2b** is similar to those of Pr(1)–N(1) and Pr(1)–N(2) in **1**. The structure of **2b** demonstrates that the coordination sphere around the Eu(III) center in $Eu(tmhd)_3$ is indeed very crowded such that the chelating mode by two 2-pyridyl groups is not favorable. The binding of the 2-pyridyl group to the Eu(III) center in **2b**, even as a terminal ligand, would bring the entire 2,2',3''-tpa ligand close to the tmhd ligands, resulting in considerable steric interactions. Perhaps, as a consequence, instead of the 2-pyridyl group, the

3-pyridyl group is bound to the Eu(III) center in **2b**. We believe that it is for the same reason that 2,2',2''-tpa does not react with $Ln(tmhd)_3$.

Although the two 2-pyridyl groups in the 2,2',3''-tpa ligand cannot bind to $Ln(tmhd)_3$, it is possible for them to chelate to a $Ln(hfa)_3$ complex, as demonstrated by the structure of **1**. Attempts to isolate and characterize the mononuclear $Ln(hfa)_3(2,2',3''\text{-tpa})$ from the reaction of $Ln(hfa)_3$ with 2,2',3''-tpa were unsuccessful. We have, however, succeeded in attaching a Pr(hfa)₃ unit to the vacant chelate binding site of the 2,2',3''-tpa ligand in **2b** and isolated a novel dinuclear mixed-metal compound $[Eu(tmhd)_3][Pr(hfa)_3](2,2',3''\text{-tpa})$, **3**, from either the reaction of **2b** with $Pr(hfa)_3$ or the reaction of $Eu(tmhd)_3$ and $Pr(hfa)_3$ with 2,2',3''-tpa in a 1:1:1 ratio. The composition of **3** was confirmed by elemental analysis. The crystals of **3** are, however, not suitable for single-crystal X-ray diffraction analyses. Nonetheless, on the basis of the structures of **1** and **2b**, we believe that the 2,2',3''-tpa ligand in compound **3** functions as a bridging ligand by binding to the Eu(III) center via the 3-pyridyl group and chelating to the Pr(III) center via two 2-pyridyl groups. The proposed structure for compound **3** is shown in Chart 1. Compound **3** demonstrates that the 2,2',3''-

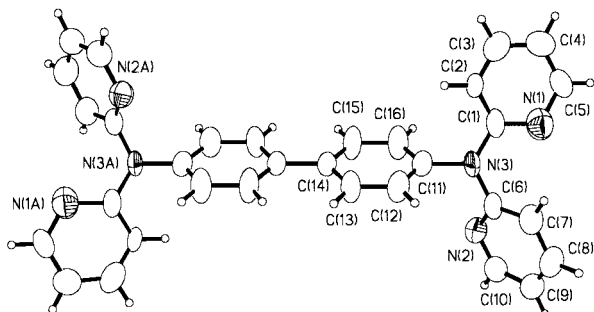


Figure 1. Structure of the tpbpd ligand with 50% thermal ellipsoids and labeling schemes.

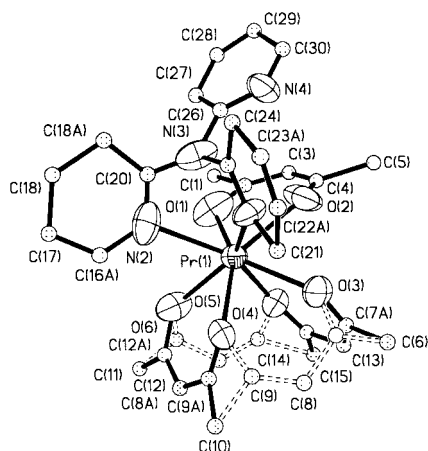


Figure 2. Structure of compound **1** with 50% thermal ellipsoids and labeling schemes. The second set of the disordered hfa ligands is shown by dashed lines. For clarity, fluorine atoms are omitted and all carbon atoms are shown as isotropic spheres. Only one set of atoms is shown for the disordered pyridyl rings.

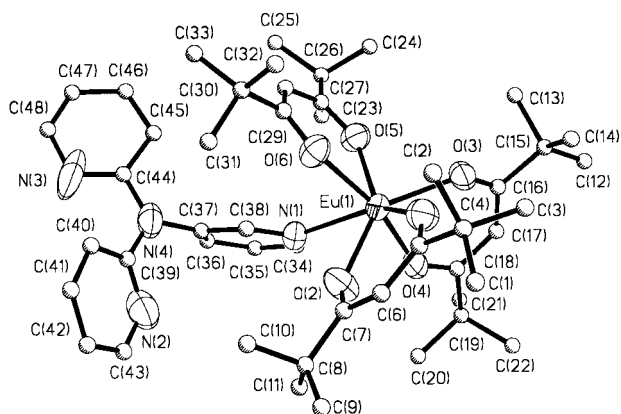


Figure 3. Structure of compound **2b** with 50% thermal ellipsoids and labeling schemes. For clarity, all carbon atoms are shown as isotropic spheres and only one set of atoms for each of the disordered *tert*-butyl groups is shown.

tpa ligand is a good bridging ligand for selectively binding to two different metal ions to form dinuclear mixed-metal compounds.

Compounds **1**–**3** are all air-stable and highly soluble in common organic solvents such as diethyl ether, toluene, and THF. Compounds **2a**–**2d** can be sublimed readily at 145 °C and 0.08 mmHg pressure to form a clear and transparent film. The volatility of **1** and **3** was not investigated because of the compounds' lack of luminescence.

Syntheses and Structures of Lanthanide Complexes of *N,N,N',N'*-Tetra(2-pyridyl)-1,4-phenylenediamine and

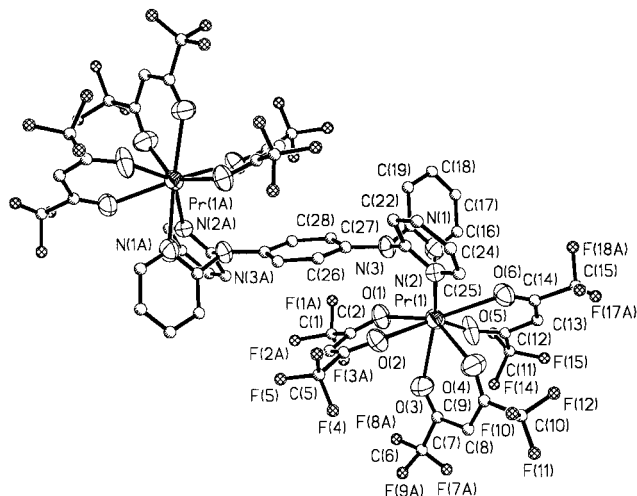
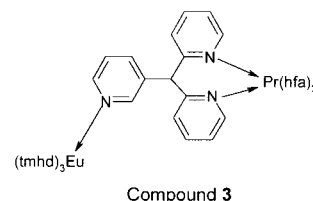


Figure 4. Structure of compound **4** with labeling schemes and 50% thermal ellipsoids. For clarity, all carbon atoms and fluorine atoms are shown as isotropic spheres. Only one set of atoms for each of the disordered CF₃ groups is shown.

Chart 1



***N,N,N',N'*-Tetra(2-pyridyl)biphenyl-4,4'-diamine.** The tpbd ligand and the tpbpd ligand have two symmetric chelating sites. One can therefore anticipate that these ligands can be used as bridging ligands to form dinuclear metal complexes. Indeed, the reaction of Ln(hfa)₃ with tpbd or tpbpd in a 2:1 ratio yielded readily novel dinuclear lanthanide complexes, of which [Pr(hfa)₃]₂(tpba), **4**, and [Eu(hfa)₃]₂(tpbpd), **5b**, were characterized by single-crystal X-ray diffraction analyses.

The structures of **4** and **5b** are shown in Figures 4 and 5, respectively. As observed in compound **1**, the 2-pyridyl groups in **4** and **5b** are chelated to the Ln(hfa)₃ unit. Compound **4** has an inversion center of symmetry. The amino nitrogen atom N(3) in **4** is 3.039(9) Å from Pr(1) and again can be considered as a weakly bound donor. Similarly, the amino nitrogen atoms N(2) and N(5) in **5b** are 3.043(5) and 3.035(5) Å from Eu(1) and Eu(2), respectively. The lanthanide ions in **4** and **5b** can therefore be considered as 9-coordinate. The most striking difference between the structures of **4** and **5b** is the orientation of the two Ln(III) units; the two Pr(III) units in **4** have a trans geometry with respect to the benzene ring, while the two Eu(III) units in **5b** have a cis geometry with respect to the biphenyl portion. Clearly steric interactions between the two Pr(III) units prevent the cis geometry in **4**. The relatively long biphenyl linkage in **5b**, on the other hand, allows sufficient space so that the two Eu(III) units can be cis to each other. In solution, the most favorable geometry for **5b** is most likely the trans one. The observed cis geometry in the crystal structure of **5b** is likely favored by the packing of molecules in the solid state. The Pr(1)–Pr(1A) separation distance in **4** is 10.090(3) Å, while the Eu(1)–Eu(2) separation distance in **5b** is 12.714(2) Å. Unlike the free tpbpd ligand where the biphenyl portion is planar, the biphenyl unit in **5b** is not planar with a dihedral angle of 37.7° between the two phenyl rings. The structures of

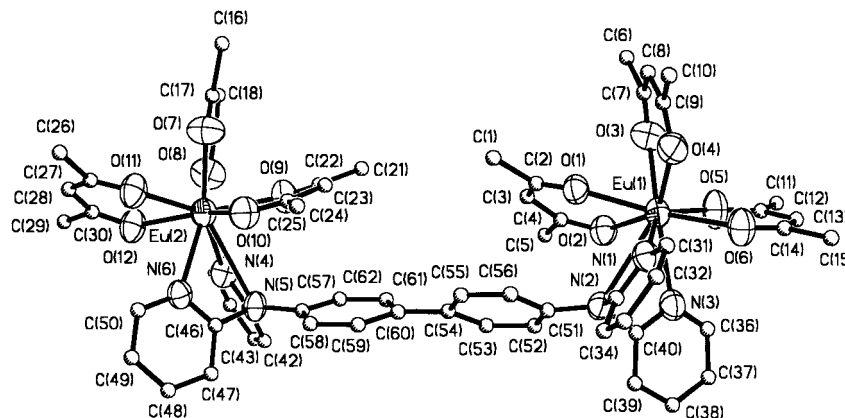


Figure 5. Structure of compound **5b** with labeling schemes and 50% thermal ellipsoids. For clarity, all carbon atoms and fluorine atoms are shown as isotropic spheres and all methyl groups on the tmhd ligands are omitted.

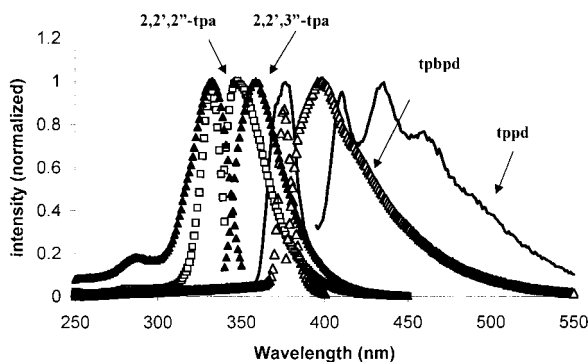


Figure 6. Excitation and emission spectra of 2,2',2''-tpa (empty square), 2,2',3''-tpa (solid triangle), tppd (solid line), and tpbpd (empty triangle) ligands in THF solution.

4 and **5b** demonstrate that tppd and tpbpd ligands are useful bridging ligands for linking two identical metal ions.

Compounds **4** and **5** are air-stable and very soluble in diethyl ether, THF, or toluene but cannot be sublimed under our laboratory conditions (0.1–0.01 mmHg).

Luminescent Properties of Ligands and the Lanthanide Complexes. Ligands 2,2',2''-tpa, 2,2',3''-tpa, tppd, and tpbpd are all luminescent in solution and the solid state. However, the excitation and emission energy for each ligand varies considerably, as shown by Figure 6 and Table 3. The emission bands of 2,2',2''-tpa and 2,2',3''-tpa are relatively narrow and are in the UV region. In contrast, tppd and tpbpd have a broad emission band in the blue region. The emission band of the tppd ligand is so broad that it covers the entire 400–550 nm region. The emission maximum for tppd and tpbpd in the solid state is at 415 nm. The blue luminescence of tppd and tpbpd makes them possible candidates as blue emitters in OLEDs. In addition, because several biphenyl-4,4'-diamine-based molecules have been shown to be excellent hole-transporting materials, tpbpd may also be able to function as a hole-transporting material in OLEDs. The potential applications of tppd and tpbpd in OLEDs are currently being investigated in our laboratory, and the results will be reported in due course.

In addition to being fluorescent in the UV and near-UV regions, the ligands can be excited from 334 to 378 nm, making them possible candidates as activators for lanthanide luminescence. We have observed that none of the tpa, tppd, and tpbpd ligands is capable of activating the luminescence of Pr(III). However, these new ligands can promote luminescence from Eu(III), Tb(III), and Dy(III) ions, as demonstrated by the bright luminescence observed in compounds **2a**, **2b**, **2c**, and **5b**.

The excitation and emission spectra of **2a**, **2b**, **2c**, and **5b** are shown in Figures 7, 8, 9, and 11, respectively. Dy(tmhd)₃ has no detectable emission in the visible range. In contrast, the complex Dy(tmhd)₃(2,2',3''-tpa), **2a**, emits a bright-yellow color. As shown in Figure 7, when the compound is excited at $\lambda = 350$ nm, there are two narrow emission bands, one at $\lambda = 573$ nm corresponding to the ${}^4F_{9/2} \rightarrow {}^6H_{13/2}$ transition and one at $\lambda = 483$ nm corresponding to the ${}^4F_{9/2} \rightarrow {}^6H_{15/2}$ transition,³ that are characteristic of Dy(III). A broad band from 260 to 410 nm dominates the excitation spectrum of **2a** and is believed to be mostly ligand excitation bands. In addition, several weak and sharp bands are also present in the excitation spectrum of **2a**, which can be attributed to the transitions ${}^4G_{11/2} \rightarrow {}^6H_{15/2}$ ($\lambda = 427$ nm), ${}^4I_{15/2} \rightarrow {}^6H_{15/2}$ ($\lambda = 455$ nm), and ${}^4F_{9/2} \rightarrow {}^6H_{15/2}$ ($\lambda = 474$ nm). The 573 nm emission band can be obtained either by using an excitation wavelength that is within the broad excitation band or by using the Dy(III) excitation energy at 455 nm. However, using an excitation energy of 350 nm yielded the most intense Dy(III) yellow emission band, indicating that the emission of the Dy(III) ion is favored by an indirect excitation or energy-transfer process.³ The fact that the Dy(tmhd)₃ compound has no detectable emission while **2a** is a bright-yellow emitter further supports the idea that the 2,2',3''-tpa ligand is an effective activator for Dy(III) in **2a**.

Compound **2b** has an intense and narrow emission band at $\lambda = 613$ nm because of the ${}^5D_0 \rightarrow {}^7F_2$ transition, as shown in Figure 8. Weak emission bands of the ${}^5D_0 \rightarrow {}^7F_1$ and ${}^5D_0 \rightarrow {}^7F_0$ transitions were also observed. Unlike compound **2a** where the excitation bands are dominated by contributions from the ligand, the excitation spectrum of **2b** has negligible contributions from the ligand. The sharp excitation band at $\lambda = 465$ nm can be attributed to the ${}^5D_2 \rightarrow {}^7F_{0,1}$ transitions, while the two excitation bands at $\lambda = 532$ and 539 nm are due to the ${}^5D_1 \rightarrow {}^7F_{0,1}$ transitions. Although Eu(III) emission bands were observed when using an excitation wavelength less than 400 nm, they are very weak. To achieve intense emission from **2b**, it is necessary to excite the molecule at $\lambda = 465$ nm. Therefore, we believe that the excitation of Eu(III) in **2b** is favored by a direct excitation process.

Compound **2c** emits an intense yellow-green color when irradiated by UV light. The emission spectrum of **2c** has an intense and narrow emission band at $\lambda = 550$ nm due to the ${}^5D_4 \rightarrow {}^7F_5$ transition, as shown in Figure 9. A moderate emission band at $\lambda = 492$ nm due to the ${}^5D_4 \rightarrow {}^7F_6$ transition and weak emission bands of ${}^5D_4 \rightarrow {}^7F_4$ and ${}^5D_4 \rightarrow {}^7F_3$ transitions were also observed. Similar to that of **2a**, compound **2c** has a broad ligand excitation band. The characteristic narrow excitation

Table 2. Selected Bond Lengths [Å] and Angles [deg]

		Tpbbpd					
N(1)–C(5)	1.381(4)	C(5)–N(1)–C(1)	116.4(3)	C(7)–C(6)–N(3)	121.3(3)		
N(1)–C(1)	1.399(4)	C(2)–C(1)–N(3)	119.3(3)	C(9)–C(10)–N(2)	124.7(4)		
C(1)–N(3)	1.393(4)	C(2)–C(1)–N(1)	122.3(3)	C(16)–C(11)–N(3)	122.8(4)		
N(2)–C(6)	1.321(4)	N(3)–C(1)–N(1)	118.4(3)	C(12)–C(11)–N(3)	119.1(4)		
N(2)–C(10)	1.344(4)	C(6)–N(2)–C(10)	116.9(3)	C(15)–C(14)–C(14A)	121.7(5)		
N(3)–C(6)	1.403(4)	C(1)–N(3)–C(6)	123.3(3)	C(13)–C(14)–C(14A)	122.0(5)		
N(3)–C(11)	1.450(4)	C(1)–N(3)–C(11)	119.1(3)				
C(13)–C(14)	1.372(5)	C(6)–N(3)–C(11)	116.7(3)				
C(14)–C(15)	1.368(5)	C(4)–C(5)–N(1)	122.0(4)				
C(14)–C(14A)	1.496(6)	N(2)–C(6)–C(7)	122.7(3)				
C(15)–C(16)	1.389(5)	N(2)–C(6)–N(3)	115.9(3)				
Compound 1							
Pr(1)–O(1)	2.364(18)	O(1)–Pr(1)–O(4)	83.1(5)	O(1)–Pr(1)–O(3)	135.3(6)	O(2)–Pr(1)–N(2)	120.4(8)
Pr(1)–O(4)	2.407(7)	O(1)–Pr(1)–O(6)	78.8(7)	O(4)–Pr(1)–O(3)	70.1(6)	O(3)–Pr(1)–N(2)	136.4(5)
Pr(1)–O(6)	2.411(18)	O(4)–Pr(1)–O(6)	73.0(6)	O(6)–Pr(1)–O(3)	123.1(2)	O(1)–Pr(1)–N(1)	119.8(6)
Pr(1)–O(5)	2.437(8)	O(1)–Pr(1)–O(5)	149.8(8)	O(5)–Pr(1)–O(3)	67.2(6)	O(4)–Pr(1)–N(1)	141.5(7)
Pr(1)–O(2)	2.505(17)	O(4)–Pr(1)–O(5)	89.7(3)	O(2)–Pr(1)–O(3)	70.9(6)	O(6)–Pr(1)–N(1)	137.7(5)
Pr(1)–O(3)	2.526(15)	O(6)–Pr(1)–O(5)	71.0(6)	O(1)–Pr(1)–N(2)	83.4(6)	O(5)–Pr(1)–N(1)	83.2(5)
Pr(1)–N(2)	2.62(2)	O(1)–Pr(1)–O(2)	70.2(5)	O(4)–Pr(1)–N(2)	148.0(7)	O(2)–Pr(1)–N(1)	78.8(7)
Pr(1)–N(1)	2.640(16)	O(4)–Pr(1)–O(2)	81.4(6)	O(6)–Pr(1)–N(2)	76.0(7)	O(3)–Pr(1)–N(1)	72.3(5)
		O(6)–Pr(1)–O(2)	141.8(6)	O(5)–Pr(1)–N(2)	87.6(6)	N(2)–Pr(1)–N(1)	69.8(4)
		O(5)–Pr(1)–O(2)	137.7(7)				
Compound 2b							
Eu(1)–O(3)	2.307(3)	O(3)–Eu(1)–O(2)	136.21(15)	O(2)–Eu(1)–O(4)	87.35(15)	O(4)–Eu(1)–O(6)	163.99(13)
Eu(1)–O(2)	2.314(4)	O(3)–Eu(1)–O(1)	79.48(14)	O(1)–Eu(1)–O(4)	110.46(14)	O(3)–Eu(1)–N(1)	135.26(14)
Eu(1)–O(1)	2.316(4)	O(2)–Eu(1)–O(1)	71.95(14)	O(5)–Eu(1)–O(4)	101.67(14)	O(2)–Eu(1)–N(1)	73.81(14)
Eu(1)–O(5)	2.318(4)	O(3)–Eu(1)–O(5)	79.81(14)	O(3)–Eu(1)–O(6)	119.82(13)	O(1)–Eu(1)–N(1)	143.82(14)
Eu(1)–O(4)	2.320(4)	O(2)–Eu(1)–O(5)	143.34(15)	O(2)–Eu(1)–O(6)	89.39(15)	O(5)–Eu(1)–N(1)	73.24(14)
Eu(1)–O(6)	2.328(4)	O(3)–Eu(1)–O(2)	136.21(15)	O(1)–Eu(1)–O(6)	83.30(14)	O(4)–Eu(1)–N(1)	79.02(13)
Eu(1)–N(1)	2.624(4)	O(3)–Eu(1)–O(4)	72.22(12)	O(5)–Eu(1)–O(6)	72.20(12)	O(6)–Eu(1)–N(1)	85.01(14)
Compound 4							
Pr(1)–O(4)	2.377(9)	O(4)–Pr(1)–O(5)	94.7(3)	O(4)–Pr(1)–O(6)	70.7(3)	O(3)–Pr(1)–N(1)	142.6(3)
Pr(1)–O(5)	2.377(9)	O(4)–Pr(1)–O(1)	141.0(3)	O(5)–Pr(1)–O(6)	69.1(3)	O(6)–Pr(1)–N(1)	73.6(3)
Pr(1)–O(1)	2.380(8)	O(5)–Pr(1)–O(1)	85.7(3)	O(1)–Pr(1)–O(6)	142.7(3)	O(4)–Pr(1)–N(2)	85.6(3)
Pr(1)–O(2)	2.415(8)	O(4)–Pr(1)–O(2)	86.1(3)	O(2)–Pr(1)–O(6)	142.8(3)	O(5)–Pr(1)–N(2)	140.5(3)
Pr(1)–O(3)	2.466(9)	O(5)–Pr(1)–O(2)	143.8(3)	O(3)–Pr(1)–O(6)	120.8(3)	O(1)–Pr(1)–N(2)	117.9(3)
Pr(1)–O(6)	2.471(8)	O(1)–Pr(1)–O(2)	71.9(3)	O(4)–Pr(1)–N(1)	142.2(3)	O(2)–Pr(1)–N(2)	75.7(3)
Pr(1)–N(1)	2.604(10)	O(4)–Pr(1)–O(3)	69.7(3)	O(5)–Pr(1)–N(1)	83.6(3)	O(3)–Pr(1)–N(2)	141.9(3)
Pr(1)–N(2)	2.610(9)	O(5)–Pr(1)–O(3)	72.4(3)	O(1)–Pr(1)–N(1)	76.7(3)	O(6)–Pr(1)–N(2)	73.9(3)
		O(1)–Pr(1)–O(3)	73.4(3)	O(2)–Pr(1)–N(1)	116.8(3)	N(1)–Pr(1)–N(2)	73.0(3)
		O(2)–Pr(1)–O(3)	74.1(3)				
Compound 5b							
Eu(1)–O(1)	2.338(6)	O(1)–Eu(1)–O(3)	77.9(2)	O(1)–Eu(1)–N(3)	116.8(2)	O(9)–Eu(2)–O(11)	143.5(2)
Eu(1)–O(3)	2.367(6)	O(1)–Eu(1)–O(2)	72.18(19)	O(3)–Eu(1)–N(3)	144.7(2)	O(10)–Eu(2)–O(11)	82.5(2)
Eu(1)–O(2)	2.371(6)	O(3)–Eu(1)–O(2)	78.5(2)	O(2)–Eu(1)–N(3)	76.6(2)	O(8)–Eu(2)–O(11)	114.5(2)
Eu(1)–O(4)	2.373(6)	O(1)–Eu(1)–O(4)	76.35(19)	O(4)–Eu(1)–N(3)	141.1(2)	O(12)–Eu(2)–O(11)	70.1(2)
Eu(1)–O(5)	2.377(6)	O(3)–Eu(1)–O(4)	71.3(2)	O(5)–Eu(1)–N(3)	79.2(2)	O(7)–Eu(2)–N(4)	142.2(2)
Eu(1)–O(6)	2.396(6)	O(2)–Eu(1)–O(4)	140.0(2)	O(6)–Eu(1)–N(3)	76.4(2)	O(9)–Eu(2)–N(4)	78.8(2)
Eu(1)–N(1)	2.538(6)	O(1)–Eu(1)–O(5)	145.2(2)	N(1)–Eu(1)–N(3)	74.4(2)	O(10)–Eu(2)–N(4)	120.1(2)
Eu(1)–N(3)	2.589(7)	O(3)–Eu(1)–O(5)	73.3(2)	O(1)–Eu(1)–N(2)	71.40(17)	O(8)–Eu(2)–N(4)	73.4(2)
Eu(1)–N(2)	3.041(6)	O(2)–Eu(1)–O(5)	83.0(2)	O(3)–Eu(1)–N(2)	143.5(2)	O(12)–Eu(2)–N(4)	74.3(2)
Eu(2)–O(7)	2.334(6)	O(4)–Eu(1)–O(5)	111.6(2)	O(2)–Eu(1)–N(2)	73.77(18)	O(11)–Eu(2)–N(4)	137.5(2)
Eu(2)–O(9)	2.367(6)	O(1)–Eu(1)–O(6)	140.97(19)	O(7)–Eu(2)–O(9)	78.8(2)	O(7)–Eu(2)–N(6)	143.6(2)
Eu(2)–O(10)	2.384(6)	O(3)–Eu(1)–O(6)	113.3(2)	O(7)–Eu(2)–O(10)	80.6(2)	O(9)–Eu(2)–N(6)	118.8(2)
Eu(2)–O(8)	2.391(6)	O(2)–Eu(1)–O(6)	145.1(2)	O(9)–Eu(2)–O(10)	72.0(2)	O(10)–Eu(2)–N(6)	76.1(2)
Eu(2)–O(12)	2.393(6)	O(4)–Eu(1)–O(6)	73.0(2)	O(7)–Eu(2)–O(8)	71.3(2)	O(8)–Eu(2)–N(6)	141.7(2)
Eu(2)–O(11)	2.401(6)	O(5)–Eu(1)–O(6)	70.4(2)	O(9)–Eu(2)–O(8)	73.6(2)	O(12)–Eu(2)–N(6)	81.2(2)
Eu(2)–N(4)	2.557(6)	O(1)–Eu(1)–N(1)	76.0(2)	O(10)–Eu(2)–O(8)	139.0(2)	O(11)–Eu(2)–N(6)	78.0(2)
Eu(2)–N(6)	2.587(7)	O(3)–Eu(1)–N(1)	140.5(2)	O(7)–Eu(2)–O(12)	105.9(2)	N(4)–Eu(2)–N(6)	74.2(2)
Eu(2)–N(5)	3.035(6)	O(2)–Eu(1)–N(1)	119.9(2)	O(9)–Eu(2)–O(12)	140.3(2)	O(4)–Eu(1)–N(2)	118.30(19)
		O(4)–Eu(1)–N(1)	74.1(2)	O(10)–Eu(2)–O(12)	147.4(2)	O(5)–Eu(1)–N(2)	124.98(19)
		O(5)–Eu(1)–N(1)	138.6(2)	O(8)–Eu(2)–O(12)	71.0(2)	O(6)–Eu(1)–N(2)	102.94(19)
		O(6)–Eu(1)–N(1)	72.8(2)	O(7)–Eu(2)–O(11)	71.5(2)		

bands due to Tb(III) were not observed. The maximum emission intensity of the complex was achieved by excitation at $\lambda = 350$ nm, indicating that indirect excitation is operative in **2c**. In all three compounds **2a–2c**, the emission band from the ligand was either not observed or observed with a negligible intensity, in comparison to those of Ln(III) ions, an indication that the

energy transfer process in **2a–2c** is fairly efficient. But unfortunately we have not been able to evaluate quantitatively the efficiency of energy transfer involved in these complexes.

In contrast to **2a–2c**, the emission spectrum of compound **2d** is dominated by the fluorescent emission band of the 2,2',3''-tpa ligand. The characteristic narrow emission bands at 602 and

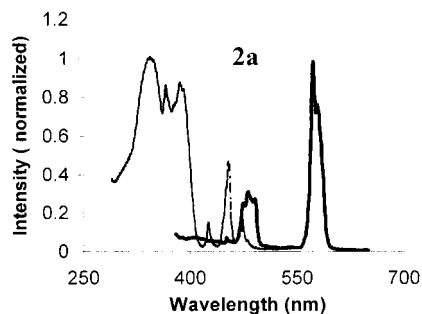


Figure 7. Excitation (dashed line) and emission (solid line) spectra of compound **2a** in the solid state at ambient temperature.

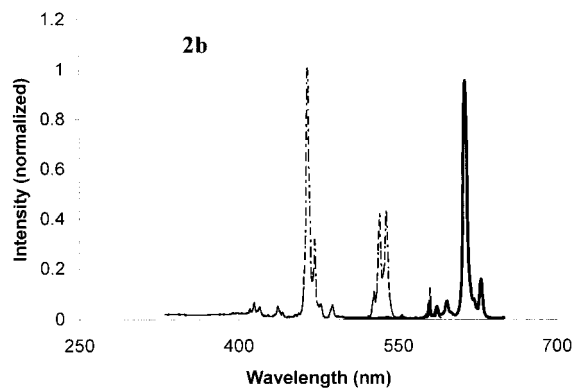


Figure 8. Excitation (dashed line) and emission (solid line) spectra of compound **2b** in the solid state at ambient temperature.

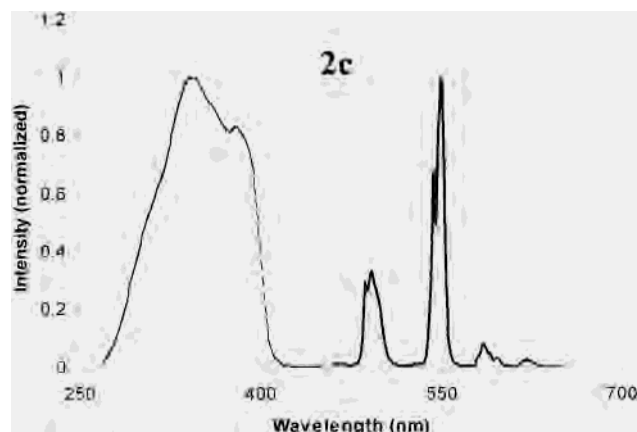


Figure 9. Excitation (dashed line) and emission (solid line) spectra of compound **2c** in the solid state at ambient temperature.

650 nm due to Sm(III) appear with a very weak intensity, barely above the noise level. The 2,2',3''-tpa ligand is therefore not capable of activating the Sm(III) ion.

To understand the role of the 2,2',3''-tpa ligand in the luminescence of **2a**–**2d**, we measured the fluorescent and phosphorescent spectra of the free ligand in the solid state at ambient temperature (Figure 10). The fluorescent band of 2,2',3''-tpa is centered at 418 nm with a decay lifetime of 8.21(3) ns. A very weak and broad phosphorescent band ranging from 460 to 600 nm was observed. (This band stretches into 600–700 nm region, but the cutoff is not clearly defined because of the scattering contribution.) The decay lifetime of the phosphorescent band is ~ 4.3 μ s. (The lifetime of the phosphorescent band could not be determined accurately because of the low emission intensity.) The fact that the phosphorescent band of the 2,2',3''-tpa ligand is overlapping with the emission bands of Dy(III) and Tb(III) may explain the effective activation of luminescence in **2a** and **2c**. The inability of 2,2',3''-tpa to

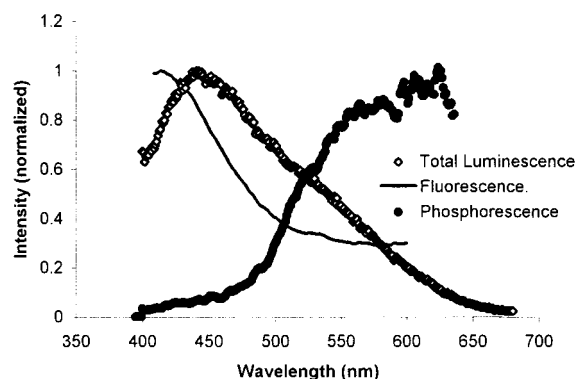


Figure 10. Emission spectra of 2,2',3''-tpa in the solid state ($\lambda_{\text{ex}} = 375$ nm) at ambient temperature: triangles, the unresolved emission spectrum; dashed line, the fluorescent spectrum; solid line, the phosphorescent spectrum.

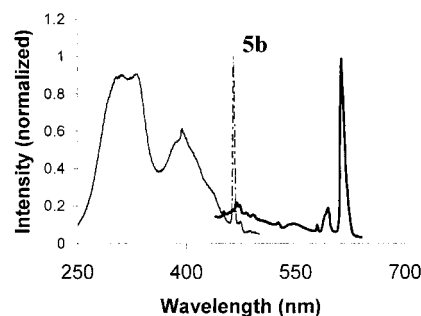


Figure 11. Excitation (dashed line) and emission (solid line) spectra of compound **5b** in the solid state at ambient temperature.

Table 3. Luminescent Data for the Ligands In THF Solution

	2,2',2''-tpa	2,2',3''-tpa	tppd	tpbpd
excitation, λ_{max} , nm	333	333	378	376
emission, λ_{max} , nm	348	361	436	401
In the Solid State				
	2,2',2''-tpa	2,2',3''-tpa	tppd	tpbpd
excitation, λ_{max} , nm	330	375	355	360
emission, λ_{max} , nm	400	435	415	415

facilitate indirect excitation of Eu(III) in **2b** or to activate Sm(III) in **2d** has not been understood. The lifetime of the emission band at 577 nm of **2a**, 615 nm of **2b**, and 550 nm of **2c** was determined to be 30.3(2), 420(10), and 552(18) μ s, respectively, which are within the general range of lifetimes for Dy(III), Eu(III), and Tb(III) ions.^{1,13} The relatively short emission lifetime for Eu(III) and Tb(III) in **2b** and **2c** may be attributed to the presence of nonradiative decay precesses.

Compound **5b** has a sharp emission band at $\lambda = 613$ nm similar to that of **2b**, as shown in Figure 11. A weak and broad emission band at $\lambda \approx 420$ – 500 nm is from the tpbpd ligand. The excitation bands of **5b** have contributions from both the ligand and the Eu(III) ion. The sharp band at $\lambda = 465$ nm due to the $^5\text{D}_2 \rightarrow ^7\text{F}_{0,1}$ transitions is again present in the excitation spectrum. There is essentially no difference in the emission

(13) (a) Dong, D.; Jiang, S.; Men, Y.; Ji, X.; Jiang, B. *Adv. Mater.* **2000**, *12*, 646. (b) Winston, H.; Marsh, O. J.; Suzuki, C. K.; Telk, C. L. *J. Chem. Phys.* **1963**, *39*, 267. (c) Sabbatini, N.; Guardigli, M.; Manet, I.; Ungaro, R.; Casnati, A.; Ziesse, R.; Ulrich, G.; Asfari, Z.; Lehn, J. M. *Pure Appl. Chem.* **1995**, *67*, 135. (d) de Mello Donegá, C.; Junior, S. A.; de Sá, G. F. *Chem. Commun.* **1996**, 1199. (e) Carnall, W. T. In *Handbook on the Physics and Chemistry of Rare Earths*; Gschneidner, K. A., Jr., Eyring, L. R., Eds.; North-Holland Publishing Company: Amsterdam, 1979; Vol. 3, Chapter 24.

spectra in terms of appearance and intensity when an excitation energy either at $\lambda = 330$ nm or at $\lambda = 465$ nm was used, indicating that both direct and indirect excitation processes are operating effectively in compound **5b**.

The mixed-metal complex $[\text{Eu}(\text{tmhd})_3][\text{Pr}(\text{hfa})_3](2,2',3''\text{-tpa})$, **3**, has no detectable emission from either the ligand or the metal ion. The fact that no detectable emission was observed in compounds **1**, **4**, and **5a** leads us to believe that instead of being activated by the ligand, the Pr(III) ion in these compounds effectively quenches emission from the ligand. We believe that the absence of emission from the Eu(III) ion and the 2,2',3''-tpa ligand in **3** can also be attributed to quenching by the Pr(III) ion. Other factors such as the presence of an LMCT state may also be responsible for the absence of emission from Eu(III) in **3**.

The luminescent spectra of the new lanthanide compounds in solution (THF or CH_2Cl_2) are dominated by excitation and emission bands that match those of the free tpa, tppd, or tpbpd ligands. We therefore believe that the tpa ligands and the tppd and tpbpd ligands in the lanthanide compounds likely undergo a dissociation/association equilibrium process in solution, precluding any meaningful study on the luminescent properties of the complexes in solution.

Conclusions

The syntheses and structures of several novel lanthanide compounds demonstrate that (a) the 2,2',2''-tpa ligand can chelate to an Ln(III) ion that is not sterically crowded, (b) the 2,2',3''-tpa ligand can function as a terminal ligand via the

3-pyridyl nitrogen donor when the Ln(III) complex is very crowded, (c) the 2,2',3''-tpa ligand can also function as a bridging ligand to form mixed-metal complexes, (d) the tppd and tpbpd ligands are effective bridging ligands for the formation of dinuclear lanthanide complexes where two identical Ln(III) centers are involved. Our study further demonstrates that the 2,2',3''-tpa ligand can activate Dy(III) and Tb(III) by an indirect excitation process and that the tpbpd ligand is capable of activating the luminescence of Eu(III) ion. A detailed kinetic study of energy transfer will certainly enable us to have a better understanding of the role of the ligands, but unfortunately such a study cannot be accomplished at this time in our laboratory because of the lack of adequate instruments. The high volatility and bright luminescence make compounds **2a–2c** potential candidates as emitters in electroluminescent devices, which is being investigated in our laboratory.

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Supporting Information Available: Listings of X-ray experimental details, atomic coordinates, thermal parameters, and bond distances and angles. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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