Inorg. Chem. **2005**, *44*, 9829–9836

Synthesis, Characterization, and Luminescence Properties of a New Series of Eu^{3+}-Containing Macrocycles

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Received August 3, 2005

The synthesis and structural characterization of a series of neutral Eu^{3+}-containing macrocyclic complexes, **Eu(4)**–**Eu(7)**, are reported. The synthetic pathway herein allows for the size and functionality of the macrocycle to be tailored in one step from a common precursor (*N*,*N*′′-bis(*p*-isothiocyanatobenzylcarbamoylmethyl)diethylenetriamine-*N*,*N*′*N*′′-triacetic acid, (**3**) in high yield. The macrocyclic ligands **4**–**7** have within their structure a bis-amide derivative of diethylenetriaminepentaacetic acid (DTPA) functioning as the europium chelate that is bridged through thiourea groups by either a butyl (**4**), hexyl (**5**), octyl (**6**), or *m*-benzyl (**7**) linker. The two thiourea groups were designed into the host macrocycle to serve as hydrogen-bond donors to potential guest molecules that may alter the luminescence properties of the parent macrocycle. Characterization of the luminescence of **Eu(4)**–**Eu(7)** reveals an antenna effect from the ligand, and the luminescence lifetime data reveals the presence of one coordinated water molecule in aqueous solution.

Introduction

Anions play essential roles in biological and environmental systems. For example, DNA, amino acids, and a majority of enzyme substrates are anionic or have anionic components.[1,2] Anions are present in detergents and fertilizers and as additives in foods and drinking water. The ability to detect various quantities of specific anions in different media is important for monitoring pollutant levels and studying biological processes. For this reason, a large area of interest in the field of supramolecular chemistry has evolved to include studies of anion binding, transport, and recognition.[1] Designing molecules with the potential to selectively identify a specific anion is a current challenge within this field. In recent years, several articles have appeared in the literature, summarizing and highlighting the diverse approaches toward anion complexation and sensing.[2−6] Many groups have employed a variety of potential binding sites (metals, organic cations, hydrogen-bond donors), yielding a growing number of systems, many of which take advantage of a fluorophore as the signaling unit.[4−6] Fluorescence signaling, including lanthanide luminescence, has been widely applied to cation recognition as well, mainly due to its potential for "on/off" switching and high sensitivities.[7−9]

Numerous ion-sensing systems exploit photoinduced electron transfer (PET) to an aromatic moiety or a metal ion as a luminescence quenching mechanism.[5−10] A number of anion sensors use a thiourea group as the binding site and PET donor.[10] Thioureas are neutral hydrogen-bond donors that, based on the design of the receptor, can selectively bind anions such as acetate,[11a] fluoride,[11b] dihydrogen phosphate,[12b]

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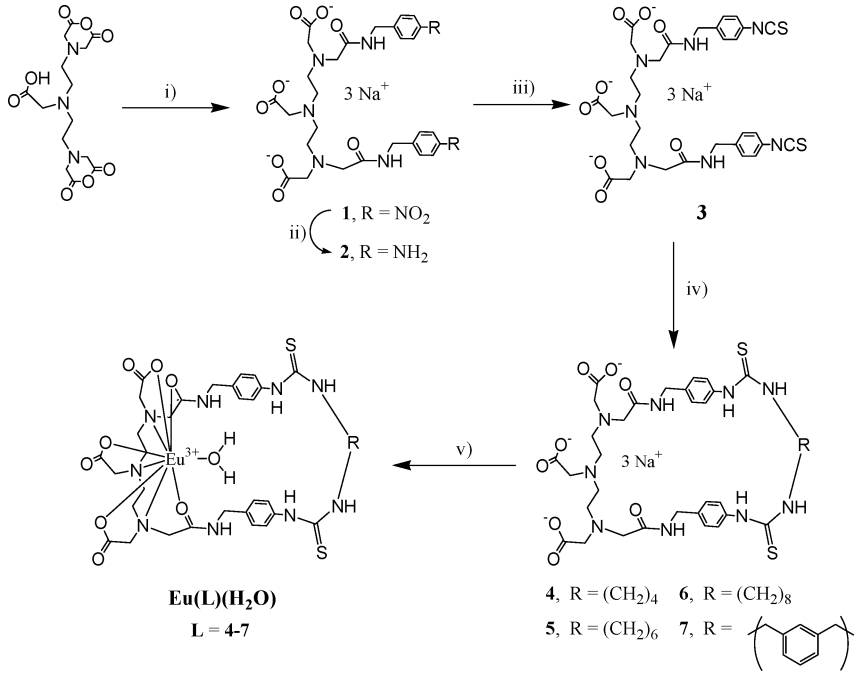
10.1021/ic051324x CCC: $30.25 © 2005 American Chemical Society
Published on Web 12/01/2005

Scheme 1. Synthesis of Macrocyclic Ligands **4**−**7** as Trisodium Salts.[a]



[a] (i) 4-nitrobenzylamine, $N(et)_3$, DMF; (ii) 10% Pd/C, H_2, MeOH; (iii) $CSCl_2$, $CHCl_3$, H_2O, $NaHCO_3$; (iv) H_2NRNH_2, Na_2CO_3, MeOH/H_2O (high dil); (v) $EuCl_3$, H_2O.

or bis-carboxylates.[10a−b] Upon anion binding, the signal is typically a change in fluorescence intensity,[10] absorption wavelength,[11] or ^{1}H NMR chemical shift of the receptor.[12] In addition, a few macrocyclic thioureas have been developed with the intention of improving selectivity through preorganization.[12]

Our design strategy is to integrate several components of successful anion sensing systems into a new series of macrocycles featuring lanthanide luminescence as the signal and thioureas as the binding sites. Previously studied thiourea-based systems have utilized simple organic fluorophores such as anthracene[10a−c] or pyrene.[10d−e] Lanthanide luminescence allows for time-resolved fluorescence measurements to be obtained, which is important to eliminate the fluorescent background possible in biological samples.[6−7,13] To the best of our knowledge, this is the first examination of a lanthanide-based macrocycle to incorporate thiourea groups for potential application in anion sensing. Also, we have chosen a chelate (*N*,*N*′′-bis-amide derivative of diethylenetriaminepentaacetic acid, DTPA) that is responsible for binding the lanthanide moiety to provide the signaling event. DTPA-based macrocycles and their lanthanide complexes have been previously studied.[14] However, as shown in Scheme 1, the synthetic pathway chosen to create our systems allows for both the size and functionality of the pocket to be tailored easily through altering the diamine used in the cyclization step. Here, we report the synthesis and characterization of a series of lanthanide-containing macrocycles, **Eu(4)**−**Eu(7)** (Scheme 1). These macrocycles will serve as models to study energy-transfer phenomena with lanthanide ions upon specific binding events and have potential to be utilized for anion recognition applications.

Experimental Section

General. All reagents used in the synthesis, if not specified, were obtained from Aldrich Chemical Co. (Milwaukee, WI) and were used without further purification. The mass spectra were obtained from an IonSpec HiResESI mass spectrometer in positive ion mode. NMR spectra were collected on a Bruker AC-250 MHz or a Bruker AV-400 MHz spectrometer. All NMR samples prepared in D_2O were adjusted to pD = 10 with Na_2CO_3. ^{1}H NMR samples were standardized relative to sodium 3-(trimethylsilyl)propionate (δ = 0.0 ppm). ^{13}C NMR samples in D_2O were standardized relative to DMSO, which was assigned at δ = 39.5 ppm. Elemental analysis of **3** was performed by the University of Illinois Microanalytical

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Laboratory, and elemental analyses of **4**−**7** and **Eu(4)**−**Eu(7)** were performed by Midwest Microlab, LLC. Determination of the %Eu content was performed using a Perkin-Elmer ELAN 6000 Inductively Coupled Plasma Mass Spectrometer. Ultraviolet absorption data was obtained using a Varian Cary 50 UV−visible spectrophotometer. Luminescence studies were performed using a Varian Cary Eclipse fluorescence spectrophotometer**.** Thin-layer chromatography (TLC) was performed using TLC plastic sheets (silica gel 60 F_{254}) from Merck (Darmstadt, Germany). The TLC solvent system for determination of all retention factors (R_f) was 2:1:1 (acetonitrile/methanol/water). Dialysis membranes [500 molecular weight-cutoff (MCWO)] were manufactured by Spectrum Laboratories, Inc. (Rancho Dominguez, CA).

Synthesis. Trisodium *N,N′′*-Bis(*p*-nitrobenzylcarbamoylmethyl)diethylenetriamine-*N,N′N′′*-triacetate (1). *p*-Nitrobenzylamine (1.73 g, 11.3 mmol) was generated from its hydrochloride salt in an aqueous solution of NaOH at pH = 12 and extracted using ether, which was promptly removed by evaporation. This yellow solid was dissolved in anhydrous DMF (15 mL), affording a yellow solution. Anhydrous triethylamine (5 mL) was then added to the solution of *p*-nitrobenzylamine via syringe. This solution was then added via syringe to a mixture containing diethylenetriaminepentaacetic acid bis-anhydride (DTPA-BA) (1.50 g, 4.2 mmol) and anhydrous DMF (15 mL) under N_2(g). This solution was then stirred for 30 h, and the resulting mixture turned deep yellow in color. Upon removal of solvent, a thick yellow oil remained and H_2O (35 mL) was added to give a cloudy yellow mixture. Aqueous NaOH (1M) was then added (to pH 10), and this aqueous solution was washed with ether (5 × 25 mL) to remove unreacted amine. Upon removal of water and drying under vacuum overnight, the title compound was obtained as a yellow crystalline solid. Yield: 2.63 g, 77.6%. ESI-MS: *m*/*z* 728.1895 [**1**H^+]. Anal. Calcd for $C_{28}H_{33}N_7O_{12}Na_2 \cdot 6H_2O$: C, 41.33; H, 5.57; N, 12.05. Found: C, 41.37; H, 5.42; N, 11.85. R_f = 0.39. ^{1}H NMR (400 MHz, D_2O): δ_H 8.17 (d, 4H, Ar*H*), 7.48 (d, 4H, Ar*H*), 4.51 (s, 4H), 3.32 (s, 4H), 3.21 (s, 4H), 3.15 (s, 2H), 2.74 (br s, 8H). ^{13}C NMR (100 MHz, CD_3OD): δ_C 179.1, 174.2, 148.4, 148.1, 129.6, 124.6, 61.3, 60.6, 60.0, 55.6, 55.3, 43.4.

Trisodium *N,N′′*-Bis(*p*-aminobenzylcarbamoylmethyl)diethylenetriamine-*N,N′N′′*-triacetate (2). Compound **1** (1.01 g, 1.39 mmol) and 10% Pd/C (0.807 g) were placed in a flask, and methanol was added (70 mL), dissolving **1** and forming a black, turbid solution upon stirring. This solution was degassed by bubbling N_2 through the solution for 1 h. H_2 was then bubbled into the mixture using a needle outlet. After 35 min the outlet was removed and the solution stirred under H_2. After 2 h, the reaction appeared to be complete by TLC; however, the mixture was allowed to stir for a total of 5 h to ensure complete conversion. The solution was then vacuum-filtered through Celite, the solvent removed, and vacuum-dried, yielding the desired compound as a white powder. Yield: 0.863 g, 93.0%. ESI-MS: *m*/*z* 668 [**2**H^+]. Anal. Calcd for $C_{28}H_{36}N_7O_8Na_3 \cdot 2.5H_2O$: C, 47.19; H, 5.80; N, 13.76. Found: C, 47.47; H, 5.93; N, 13.58. R_f = 0.11. ^{1}H NMR (400 MHz, D_2O): δ_H 7.11 (d, 4H, Ar*H*), 6.82 (d, 4H, Ar*H*), 4.28 (s, 4H), 3.19 (s, 4H), 3.13 (s, 4H), 2.97 (s, 2H), 2.52 (br s, 8H). ^{13}C NMR (100 MHz, CD_3OD): δ_C 179.1, 173.4, 147.9, 129.9, 129.5, 116.7, 61.1, 59.9, 55.0, 54.9, 43.8.

N,N′′*-Bis(*p*-isothiocyanatobenzylcarbamoylmethyl)-diethylenetriamine-*N,N′N′′*-triacetic Acid (3).** Compound **2** (0.500 g, 0.749 mmol) and $NaHCO_3$ (0.300 g, 3.57 mmol) were dissolved in 165 mL of H_2O. This solution was then carefully added dropwise to a solution of thiophosgene ($CSCl_2$, ***CAUTION!) (1.08 g, 9.40 mmol) in 165 mL of $CHCl_3$ over 65 min with vigorous stirring. The reaction stirred for 5 h and the layers were allowed to separate. The aqueous layer was removed and the organic layer was then washed with H_2O (2 × 100 mL). The aqueous portions were combined and then washed with $CHCl_3$ (3 × 150 mL) to remove unreacted thiophosgene. It should be noted that all steps were performed in a closed hood due to the toxic nature of this reaction. Hydrochloric acid (1 M) was then slowly added until a white precipitate formed. The solution was then filtered to isolate the precipitated product (**3**), which was then dried under vacuum. Yield: 0.350 g, 61.0%. ESI-MS: *m*/*z* 686.1727 [**3**H^+]. Anal. Calcd for $C_{30}H_{33}N_7O_8S_2Na_2 \cdot 2H_2O$ C, 47.05; H, 4.87; N, 12.80; S, 8.37. Found: C, 46.92; H, 4.97; N, 12.66; S, 8.31. R_f = 0.42. ^{1}H NMR (400 MHz, D_2O): δ_H 7.30 (d, 4H, Ar*H*), 7.28 (d, 4H, Ar*H*), 4.39 (s, 4H), 3.28 (s, 4H), 3.18 (s, 4H), 3.05 (s, 2H), 2.70 (br s, 8H). ^{13}C NMR (100 MHz, 9:1 CD_3OD:D_2O): δ_C 179.2, 174.3, 139.8, 136.3 (*SCN*), 131.0, 130.1, 126.9, 60.5, 60.3, 55.1, 54.2, 51.9, 43.4.

General Procedure for Macrocycle Synthesis. Butyl Macrocycle (4). Compound **3** (0.167 g, 0.218 mmol) and Na_2CO_3 (0.060 g, 0.566 mmol) were dissolved in 20 mL of 1:1 MeOH/H_2O. A solution of 1,4-diaminobutane (0.023 g, 0.260 mmol) was prepared in 20 mL of MeOH. The two solutions were then added dropwise to a vigorously stirred solution of MeOH (20 mL) in equal amounts by pipet to a three-neck reaction flask over 1 h. The reaction was left to stir for 20 h, after which the solvent was evaporated down to ∼5 mL. Hydrochloric acid (0.5 M) was then slowly added until pH = 3, where a white precipitate had formed. The solution was then filtered and dried under vacuum to isolate the precipitate, **4**, as a monosodium salt. Yield: 0.123 g, 72.8%. ESI-MS: *m*/*z* 796.28 [**4**Na^+]. IR (KBr): cm^{-1} 3280 (br), 3055, 2934, 1720, 1643 (s), 1539 (s), 1512, 1385, 1344, 1314, 1237, 1092 (w), 1018 (w). Anal. Calcd for $C_{34}H_{46}N_9O_8S_2Na \cdot 2H_2O$: C, 49.09; H, 6.06; N, 15.15. Found: C, 49.59; H, 6.16; N, 14.97. R_f = 0.33. ^{1}H NMR (400 MHz, D_2O): δ_H 7.39 (d, 4H, Ar*H*), 7.23 (br s, 4H, Ar*H*), 4.40 (s, 4H), 3.54 (br s, 4H), 3.25 (s, 4H), 3.16 (s, 4H), 3.02 (s, 2H), 2.63 (br s, 8H), 1.58 (br s). ^{13}C NMR (100 MHz, D_2O): δ_C 180.0, 179.8, 175.2, 162.6 (*CS*), 138.2, 136.5, 129.9, 127.3, 59.6, 59.5, 53.1, 52.3, 45.3, 43.4, 26.9.

Hexyl Macrocycle (5). Compound **3** (0.167 g, 0.218 mmol), Na_2CO_3 (0.060 g, 0.566 mmol), and 1,6-diaminohexane (0.030 g, 0.258 mmol) were reacted as described above for compound **4**. Compound **5** was isolated as a monosodium salt. Yield: 0.115 g, 65.7%. ESI-MS: *m*/*z* 824.25 [**5**Na^+]. IR (KBr): cm^{-1} 3302 (br), 3070, 2923, 1720, 1643 (s), 1539 (s), 1514, 1388, 1344, 1314, 1241, 1092 (w), 1018 (w). Anal. Calcd for $C_{36}H_{51}N_9O_8S_2Na \cdot 2H_2O$: C, 50.28; H, 6.33; N, 14.66. Found: C, 50.72; H, 6.49; N, 14.59. R_f = 0.30. ^{1}H NMR (400 MHz, D_2O): δ_H 7.39 (d, 4H, Ar*H*), 7.22 (br s, 4H, Ar*H*), 4.41 (s, 4H), 3.54 (br s, 4H), 3.25 (s, 4H), 3.18 (s, 4H), 3.04 (s, 2H), 2.62 (br s, 8H), 1.59 (br s, 4H), 1.33 (br s, 4H). ^{13}C NMR (100 MHz, D_2O): δ_C 179.8, 179.5, 175.0, 162.6 (*CS*), 137.8, 136.3, 129.5, 126.8, 59.6, 59.4, 53.0, 52.3, 45.5, 43.1, 28.8, 26.4.

Octyl Macrocycle (6). Compound **3** (0.167 g, 0.218 mmol), Na_2CO_3 (0.060 g, 0.566 mmol), and 1,8-diaminooctane (0.037 g, 0.256 mmol) were reacted as described above for **4**. Compound **6** was isolated as a monosodium salt. Yield: 0.147 g, 81.2%. ESI-MS: *m*/*z* 852.34 [**6**Na^+]. IR (KBr): cm^{-1} 3286 (br), 3059, 2929, 1722, 1640 (s), 1540 (s), 1512, 1385, 1316, 1236, 1100 (w), 1020 (w). Anal. Calcd for $C_{38}H_{55}N_9O_8S_2Na \cdot H_2O$: C, 52.46; H, 6.49; N, 14.49. Found: C, 53.02; H, 6.54; N, 14.56. R_f = 0.35. ^{1}H NMR (400 MHz, D_2O): δ_H 7.32 (d, 4H, Ar*H*), 7.16 (br s, 4H, Ar*H*), 4.39 (s, 4H), 3.53 (br s, 4H), 3.22 (s, 4H), 3.16 (s, 4H), 3.02 (s, 2H), 2.56 (br s, 8H), 1.58 (br s, 4H), 1.31 (br s, 8H). ^{13}C NMR (100 MHz,

D_2O): δ_C 179.8, 179.6, 174.8, 163.4 (*C*S), 137.4, 136.6, 129.5, 126.3, 59.6, 59.2, 53.0, 52.5, 45.6, 43.1, 28.8, 28.7, 26.5.

***m*-Benzyl Macrocycle (7).** Compound **3** (0.167 g, 0.218 mmol), Na_2CO_3 (0.060 g, 0.566 mmol), and *m*-xylylenediamine (0.035 g, 0.254 mmol) were reacted as described above for **4**. Compound **7** was isolated as a monosodium salt. Yield: 0.098 g, 85.5%. ESI-MS: *m*/*z* 843.82 [**7**Na^+]. IR (KBr): cm^{-1} 3332 (br), 3049, 2923, 1730, 1642 (s), 1540 (s), 1514, 1394, 1343, 1314, 1232, 1092 (w), 1018 (w). Anal. Calcd for $C_{38}H_{47}N_9O_8S_2Na\cdot H_2O$: C, 52.95; H, 5.61; N, 14.62. Found: C, 52.91; H, 5.51; N, 14.07. $R_f = 0.38$. ^1H NMR (400 MHz, D_2O): δ_H 7.31 (d, 4H, Ar*H*), 7.20 (m, 8H, Ar*H*), 4.8 (s, 4H, hidden under HOD resonance), 4.34 (s, 4H), 3.22 (s, 4H), 3.16 (s, 4H), 2.94 (s, 2H), 2.57 (br d, 8H). ^{13}C NMR (100 MHz, D_2O): δ_C 180.3, 179.8, 174.9, 163.2 (*C*S), 139.4, 137.6, 136.2, 129.5, 126.9, 126.5, 124.0, 59.6, 59.2, 52.9, 52.4, 48.4, 43.0.

General Procedure for Eu Complex Formation with Macrocycles. Eu(4). Macrocycle **4** (0.050 g, 0.063 mmol) was dissolved in an aqueous NaOH solution (10 mL; 2.7×10^{-2} M), and $Eu(Cl)_3$ (0.017 g, 0.066 mmol) in H_2O (10 mL) was added dropwise over 45 min. This mixture was stirred at 45 °C for 5 h. The solution was evaporated down to ~5 mL under reduced pressure and then transferred into a 500 MWCO cellulose membrane for dialysis (24 h; 3 × 4 L H_2O exchange). The water was evaporated and the remaining solid dried under vacuum to yield an off-white powder. Yield: 0.057 g, 95%. ESI-MS: *m*/*z* 924.20 [**Eu(4)**H^+]. UV−vis (DMSO) λ_{max}/nm (ϵ/M^{-1} cm^{-1}): 274 (19800). IR (KBr): cm^{-1} 3418 (br), 3264, 3088, 2929, 1621 (s), 1539, 1514, 1399, 1314, 1257, 1095 (w), 1021 (w), 927 (w). Anal. Calcd for $C_{34}H_{44}N_9O_8S_2Eu_{0.9}\cdot 5H_2O\cdot 3NaCl$: C, 34.81; H, 4.64; N, 10.75; Eu, 11.66. Found: C, 34.11; H, 4.22; N, 9.63; Eu, 10.67.

Eu(5). Macrocycle **5** (0.052 g, 0.065 mmol) and $Eu(Cl)_3$ (0.017 g, 0.066 mmol) were reacted as described above for **Eu(4)**, yielding an off-white powder. Yield: 0.058 g, 94%. ESI-MS: *m*/*z* 951.98 [**Eu(5)**H^+]. UV−vis (DMSO) λ_{max}/nm (ϵ/M^{-1} cm^{-1}): 273 (22000). IR (KBr): cm^{-1} 3434 (br), 3264, 3088, 2929, 1621 (s), 1542, 1514, 1399, 1314, 1257, 1095 (w), 1018 (w), 927 (w). Anal. Calcd for $C_{36}H_{48}N_9O_8S_2Eu\cdot 5H_2O\cdot 3NaCl$: C, 35.55; H, 4.81; N, 10.36; Eu, 12.49. Found: C, 34.28; H, 4.59; N, 9.54; Eu, 11.53.

Eu(6). Macrocycle **6** (0.054 g, 0.065 mmol) and $Eu(Cl)_3$ (0.017 g, 0.066 mmol) were reacted as described above for **Eu(4)**, yielding an off-white powder. Yield: 0.062 g, 97%. ESI-MS: *m*/*z* 980.04 [**Eu(6)**H^+]. UV−vis (DMSO) λ_{max}/nm (ϵ/M^{-1} cm^{-1}): 274 (23200). IR (KBr): cm^{-1} 3429 (br), 3088, 2929, 1616 (s), 1553, 1512, 1402, 1314, 1257, 1095 (w), 1021 (w), 927 (w). Anal. Calcd for $C_{38}H_{52}N_9O_8S_2Eu\cdot 5H_2O\cdot 2NaCl$: C, 38.49; H, 5.27; N, 10.63; Eu, 12.81. Found: C, 38.85; H, 5.15; N, 10.11; Eu, 12.08.

Eu(7). Macrocycle **7** (0.053 g, 0.065 mmol) and $Eu(Cl)_3$ (0.017 g, 0.066 mmol) were reacted as described above for **Eu(4)**, yielding an off-white powder. Yield: 0.058 g, 92%. ESI-MS: *m*/*z* 972.46 [**Eu(7)**H^+]. UV−vis (DMSO) λ_{max}/nm (ϵ/M^{-1} cm^{-1}): 275 (23000). IR (KBr): cm^{-1} 3418 (br), 3093, 2918, 1608 (s), 1539, 1512, 1399, 1317, 1257, 1095 (w), 1018 (w), 927 (w). Anal. Calcd for $C_{38}H_{44}N_9O_8S_2Eu\cdot 4H_2O\cdot 2NaCl$: C, 39.35; H, 4.52; N, 10.87; Eu, 13.10. Found: C, 39.72; H, 4.49; N, 10.34; Eu, 13.20.

Luminescence Studies. Excitation and emission spectra of **Eu(4)**−**Eu(7)** (DMSO, 2.0×10^{-5} M) were obtained in phosphorescence mode with a total decay time of 0.02 s, a delay time of 0.10 ms, and a gate time of 5.0 ms. Excitation and emission slit widths were both set at 10 nm. The excitation wavelengths (λ_{exc}) used in the emission studies were either 274 or 395 nm. The emission wavelength (λ_{em}) for the excitation studies was 615 nm. Determination of the luminescence lifetime (τ) of **Eu(4)**−**Eu(7)** was performed in both H_2O and D_2O (3.5×10^{-5} M) with a delay time of 0.05 ms, a gate time of 0.1 ms, $\lambda_{exc} = 272$ nm, and $\lambda_{em} = 615$ nm. Excitation and emission slit widths were 10 nm. Calculations of q used the equation $q = 1.11[k_{H_2O} - k_{D_2O} - 0.31 + 0.075n_{O=CNH}]$ where k is the rate of luminescence decay and $n_{O=CNH}$ is the number of amide N−H oscillators in which the amide carbonyl oxygen is coordinated to Eu^{3+}.[15]

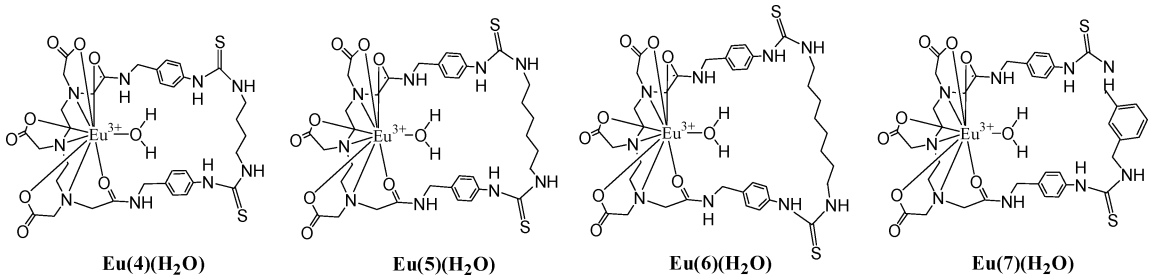
Results

Macrocycle Synthesis and Characterization. The syntheses of macrocyclic ligands **4**−**7** are shown in Scheme 1. The first step involves opening the bis-anhydride of DTPA (DTPA-BA) with 2 equiv of *p*-nitrobenzylamine to yield the bis-amide, **1**. The ^1H NMR spectrum of **1** indicates high conversion. The ESI-MS data support this conclusion with major peaks occurring at 662, 684, 706, 728, and 750 *m*/*z*. The peak at 662 is identified as **1** with each carboxylate protonated and ionized with an additional proton, denoted **1**H_4^+. Each successive peak in the series is due to replacement of one proton with a sodium ion (684 $m/z = \mathbf{1}H_3Na^+$, 706 $m/z = \mathbf{1}H_2Na_2^+$, 728 $m/z = \mathbf{1}HNa_3^+$, 750 $m/z = \mathbf{1}Na_4^+$).

Compound **2** is generated by catalytic hydrogenation of the nitro group in **1**. TLC analysis during the course of this reaction shows complete disappearance of **1** after 2 h with concurrent appearance of **2**. The ^1H NMR spectrum of **2** lacks resonances from the nitrobenzyl precursor, and a large upfield shift of the aromatic resonances occurs (consistent with formation of an electron-donating amino group as a substituent). In the ESI mass spectrum of **2**, peaks at 624, 646, 668, and 690 are obtained, where the peak at 624 is due to the monosodium species, **2**H_3Na^+, and each successive peak thereafter is the result of the replacement of a proton with a sodium ion (646 $m/z = \mathbf{2}H_2Na_2^+$, 668 $m/z = \mathbf{2}HNa_3^+$, 690 $m/z = \mathbf{2}Na_4^+$) similar to the result obtained with **1**. The next step in the synthetic route requires reaction of **2** with excess thiophosgene ($CSCl_2$) in a two-phase reaction to generate the bis-isothiocyanate **3**.[16] Full caution (closed hood, lab coat, and gloves) must be taken when working with thiophosgene due to its high toxicity and volatility. The desired product (**3**) is obtained in an efficient manner and isolated by precipitation with acid, which effectively removes trace impurities resulting from addition of only 1 equiv of *p*-nitrobenzylamine to DTPA-BA in the first step of the reaction sequence. The monosubstituted impurities are retained in the aqueous layer due to the presence of four carboxylic acid groups and only one aromatic ring. The ^1H NMR spectrum of **3** reveals two resonances in the aromatic region ($\delta = 7.28$ and 7.30 ppm) consistent with conversion to the isothiocyanate-substituted benzene rings. Elemental analysis of this compound indicates a formula of $C_{30}H_{33}N_7O_8S_2Na_2\cdot 2H_2O$, consistent with the proposed structure, where two waters of hydration persist after drying under vacuum. Two major peaks occur in the ESI mass spectrum corresponding to **3**H_4^+ and **3**H_3Na^+ at $m/z = 686$ and 708, respectively. Macrocyclic, oligomeric, and all trace solvents

(15) Supkowski, R. M.; Horrocks, W. D., Jr. *Inorg. Chim. Acta* **2002**, *340*, 44−48.
(16) Brechbiel, M. W.; Gansow, O. A.; Atcher, R. W.; Schlom, J.; Esteban, J.; Simpson, D. E.; Colcher, D. *Inorg. Chem.* **1986**, *25*, 2772−2781.

Chart 1. Macrocyclic Eu^{3+} Chelates, **Eu(4)**−**Eu(7)**



are not detected at this stage. The first three steps in this synthesis yield **3** in a highly pure form and thus, purification via chromatography is deemed unnecessary for any of these precursor molecules.

Compound **3** is the synthetic precursor to forming macrocycles **4**−**7**. The key step in the synthesis of these systems is the cyclization step, where, for example, 1,4-diaminobutane is reacted with **3** under highly diluted conditions to generate **4** in high yield. NMR data indicate the formation of a single product in this reaction, characterized by a few large changes. For example, ^{1}H NMR resonances appear in the aliphatic region of the spectrum (δ = 3.54 and 1.58 ppm), corresponding to two sets of four equivalent methylene protons, which represents linking of the aliphatic chain to form the macrocycle. In the ^{13}C NMR spectrum of **4**, the resonance near 136.3 ppm (characteristic of the isothiocyanate group) is absent; however, a new peak appears at 162.6 ppm, indicative of the newly formed thiourea functionality. In addition, new resonances appear in the aliphatic region at 45.3 and 26.9 ppm, ascribed to the carbons linking the thiourea moieties together. Similar spectral changes are also observed in the NMR spectra of **5**−**7**, indicating complete conversion of the starting material to the desired products.

The ESI-MS of **4** has a major peak at m/z = 796 which corresponds to the neutral ligand ionized with a sodium ion, $\mathbf{4}H_3Na^+$. In addition, similar to the pattern observed in compounds **1** and **2**, there are significant peaks at m/z = 774 $[\mathbf{4}H_4]^+$, 818 ($\mathbf{4}H_2Na_2^+$), 840 ($\mathbf{4}HNa_3^+$), and 862 ($\mathbf{4}Na_4^+$). These results indicate this product to be the [1:1] macrocycle, where [1:1] denotes the ratio of DTPA precursor and the diamine that form the final product, as shown in Chart 1. The ESI-MS data for **4**−**7** are similar with respect to the formation of exclusively the [1:1] product. In addition, a small peak at m/z = 708 is observed as a fragmentation product in the mass spectra for **4**−**7** and is most likely not due to the presence of unreacted **3**, which has the same m/z ratio. Small peaks are also found in the region of the MS where [2:2] macrocyclic products would appear (m/z = 1547−1701 for **4**). However, an ESI-MS-MS experiment using **6** as a model revealed that these peaks are due to proton or sodium ion-bound dimers that decompose at low energy into the monomer. The NMR and elemental analysis data support this conclusion that the [1:1] products of **4**−**7** are obtained in a pure form.

The DTPA unit of these macrocycles is an octadentate ligand for lanthanide metals. Addition of $Eu(Cl)_3$ to aqueous solutions of **4**−**7** gives the final macrocyclic products **Eu(4)**−**Eu(7)**. The products are purified by dialyzing each compound in ultrapure H_2O using a 500 MWCO membrane to remove salts and any excess reactants. The infrared spectra of **Eu(4)**−**Eu(7)** show intense bands at ~1610 cm^{-1}, which is a lower stretching frequency than expected for amide or carboxylate C═O's, and is consistent with coordination of these groups to Eu^{3+}. In addition, complexation with Eu^{3+} simplifies the ESI mass spectra of **4**−**7**, and in the spectrum of **Eu(4)**, for example, the major peaks occur at m/z = 924 and 946, corresponding to the **[Eu(4)]**H^+ and **[Eu(4)]**Na^+ ionized species, respectively. In the case of **Eu(5)**, **Eu(6)**, and **Eu(7)**, peaks for the proton-ionized species occur at m/z = 952, 980, and 972, respectively. The isotopic distribution pattern for **[Eu(7)]**H^+ is shown in Figure 1. The highest peak at 972.1992 is due to the complex with the major isotope, ^{153}Eu, whereas the peak at 970.1854 is attributed to the complex with ^{151}Eu.

Luminescence Studies. All the complexes studied have similar excitation and emission spectra, and the luminescence spectra of **Eu(4)**, shown in Figure 2, are representative of the spectra observed for products **Eu(5)**−**Eu(7)**. The excitation spectrum of **Eu(4)** (Figure 2a, emission at 615 nm) is dominated by a broad band at 250−325 nm with a maximum at 276 nm. This large band is primarily due to the absorbance of the benzene sensitizers present in the macrocycle structures. However, significant bands arising from direct excitation of Eu^{3+} are also observed in the region from 310 to 480 nm. The most intense band, at 395 nm, is characteristic of Eu^{3+} absorption. The general UV−vis absorption spectrum of **Eu(4)** shows only a broad band at 250−305 nm that is much more symmetrical in shape than the broad band in the

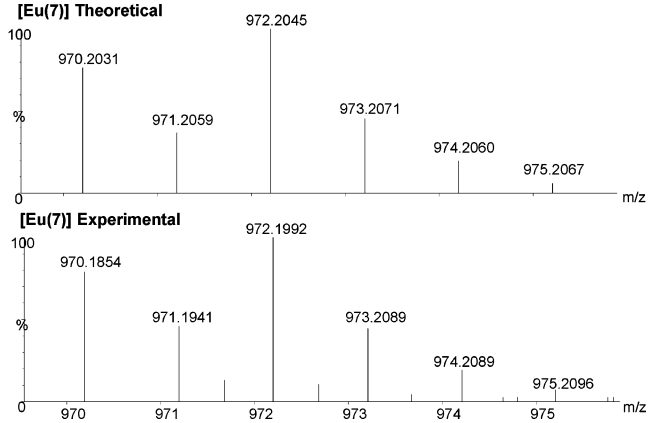


Figure 1. ESI isotopic distribution pattern for $[Eu(7)]H^+$. Top: theoretical distribution. Bottom: actual.

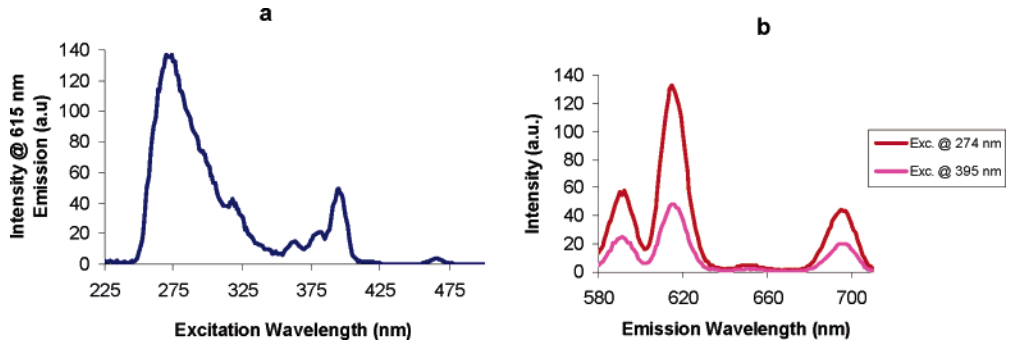


Figure 2. Excitation (a) and emission (b) spectra of **Eu(4)** in DMSO (2.0×10^{-5} M).

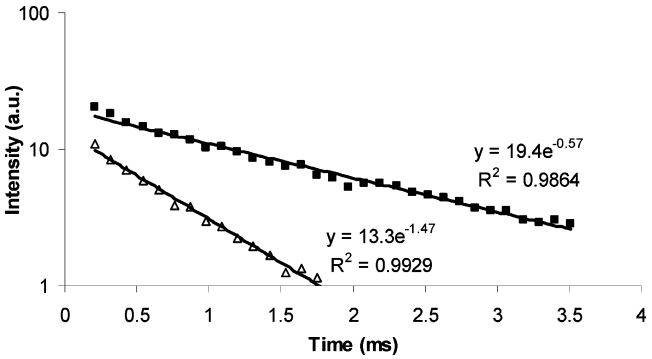


Figure 3. Decay of the luminescence emission (λ_{exc} = 272 nm; λ_{em} = 615 nm) of a 3.5×10^{-5} M solution of **Eu(4)** in H_2O (open triangle) and D_2O (closed square).

Table 1. Summarized Luminescence Lifetime Data of **Eu(4)**−**Eu(7)**

compound	τ_{H_2O} (ms)	τ_{D_2O} (ms)	q^a
Eu(4)	0.68	1.74	0.82
Eu(5)	0.71	1.63	0.69
Eu(6)	0.79	2.04	0.68
Eu(7)	0.75	2.08	0.78

[a] Values for q were calculated using the method from Horrocks et al.[15]

excitation spectrum (λ_{em} = 615 nm) and is attributed to absorption from the aryl portion of the ligand.

The emission spectra taken at excitation wavelengths of 274 and 395 nm of complex **Eu(4)** are shown in Figure 2b. Again, similar emission spectra to that shown in Figure 2b are observed for all products **Eu(4)**−**Eu(7)**. At a 274 nm excitation wavelength, the emission intensity for the three main emission bands [$^5D_0 \rightarrow {}^7F_1$ (λ_{max} = 592 nm), $^5D_0 \rightarrow {}^7F_2$ (λ_{max} = 615 nm), and $^5D_0 \rightarrow {}^7F_4$ (λ_{max} = 695 nm)] is approximately 2.5 times more intense than when excited at 395 nm (the wavelength used for direct excitation of Eu^{3+}). The degree of luminescence enhancement via energy transfer from the ligand for complexes **Eu(4)**−**Eu(7)** is very similar, even though **Eu(7)** contains a *m*-xylene linker.

Luminescence lifetime data also have been obtained for the complexes **Eu(4)**−**Eu(7)** to determine q, the number of coordinated water molecules in aqueous solution. Experimental lifetime data from the study of **Eu(4)** are shown in Figure 3, and the summarized results from studies of all the complexes are shown in Table 1. The luminescence lifetime, τ, has been determined in both H_2O and D_2O.[15] Calculations of q were performed using the equation $q = 1.11[k_{H_2O} - k_{D_2O} - 0.31 + 0.075n_{O=CNH}]$ where k is the rate of luminescence decay ($k = 1/\tau$) and $n_{O=CNH}$ is the number of amide N−H oscillators in which the amide carbonyl oxygen is coordinated to Eu^{3+}.[15] For the Eu^{3+} complexes studied, $n_{O=CNH} = 2$ and $q \approx 1$ in all cases. The octadentate macrocyclic ligand in **Eu(4**−**7)** allows for one vacant coordination site on the metal to be filled by solvent, resulting in the preferred nine-coordinate complex.[14a]

Discussion

The design principles behind this new series of macrocycles, **Eu(4)**−**Eu(7)**, require three components: (i) a lanthanide chelate complex that serves as the signaling unit, (ii) an aromatic moiety that functions both as a spacer and a light harvesting unit (antenna), and (iii) thiourea groups that function as the anion binding pocket. This pocket can be tailored by substitution of the functional group between the two opposing thioureas, which may potentially allow for increased selectivity based on anion shape recognition through incorporation of additional binding sites.[17] Applying these systems for anion sensing depends on excitation of the organic chromophore on the macrocyclic ligand, which transfers energy to the Eu^{3+} center, resulting in luminescence.[6,7] Our working hypothesis is that hydrogen-bonding interactions between the thiourea hydrogens and bound anionic acceptors could affect the energy transfer between chromophore and Eu^{3+}, therefore resulting in a detectable change in luminescence intensity. Gaining an understanding of this process and mechanism is the goal of this research and has driven the design of these new macrocycles. These first models were created to study the efficiency of the synthetic pathway, which incorporates simple substituted benzene groups as the antenna with differing hydrocarbons linking the functional thiourea groups together. Here, we have developed a versatile route that allows for a systematic variation in the final structure through choice of an appropriate diamine moiety to form a variety of macrocycles. The cyclization step, which results in formation of two thiourea functionalities in the cyclic binding pocket, proceeds in high yield and with minimal byproducts for a number of diamines of different lengths. This result demonstrates the versatility and promise for future models to study anion sensing and energy transfer mechanisms involving lanthanide metals.

The first three synthetic steps en route to macrocycles **4**−**7** (Scheme 1) are high yielding with minimal purification

(17) Hay, B. P.; Firman, T. K.; Moyer, B. A. *J. Am. Chem. Soc.* **2005**, *127*, 1810−1819.

required, resulting in an overall yield of 44.0% for **3** from DTPA-BA. In particular, column chromatography is not needed to isolate **3** in high purity. The synthesis of macrocycles **4**−**7** from **3** can be compared to previous one-step syntheses, where reaction of the bis-anhydride of DTPA with various diamines resulted in a vast array of macrocyclic ligands for lanthanide ions.[14] Dilute conditions (20−40 mM) with either DMF,[14b−c] DMSO,[14e−f] or MeOH[14d] are used to avoid formation of oligomers, and post-purification yields ranged from 10 to 45%.[14] In the synthesis of **4**−**7**, a bicarbonate-buffered H_2O/MeOH solvent system is used at high dilution (2 mM), with yields between 70% and 80%. The bis-isothiocyanate **3** is stable in the presence of H_2O under these conditions, and the reaction proceeds in good yield. Previous syntheses of macrocyclic thioureas (that lack a metal chelating group) through the reaction of bis-isothiocyanates with diamines under high dilution (2 mM in $CHCl_3$) have resulted in similar yields, 70−79%.[12b] In the current work, the synthetic scheme producing **4**−**7** maintains the higher yields particular to the isothiocyanate reaction, while also producing a DTPA-containing macrocycle.

Ligands **4**−**7** were dissolved using aqueous NaOH solution and subsequently reacted with $EuCl_3$ to yield **Eu(4)**−**Eu(7)**, respectively. Yields ranged from 92% to 97%. ESI-MS data indicate the formation of **Eu(4)**−**Eu(7)**, and intense peaks are observed for both the H^+ and Na^+ ionized species. The IR spectra of the four complexes are similar, with the most intense band occurring between 1608 and 1621 cm^{-1}. This relatively low-frequency reflects the weakening of the C═O of amide and carboxylate functionalities upon Eu^{3+} coordination. Elemental analyses of **Eu(4)**−**Eu(7)** reveals the presence of NaCl in the bulk sample, despite dialysis of the complexes. In addition, the %Eu found in the **Eu(4)** sample is slightly low, possibly due to the more tightly restricted macrocyclic ligand.

Due to the weak absorption capabilities of Eu^{3+}, organic chromophores are often used to increase ion emission through energy transfer processes.[3,4] A relatively intense emission is important for practical applications involving induced changes in the luminescent signal. Also, enhancing the emission allows low concentrations to be used. In the case of ligands **4**−**7**, only the disubstituted benzenes are possible sensitizers for the Eu^{3+} emission, and insight into the efficiency of the sensitization can be gained through analysis of the absorption, excitation, and emission spectra of these complexes. The excitation and emission spectra of **Eu(4)**−**Eu(7)** (Figure 2) are typical in that a large ligand-based excitation band (λ_{max} = 274 nm) and a Eu^{3+}-based band (λ_{max} = 395 nm) are present, with both excitations giving rise to Eu^{3+} emissions at 592, 615, and 700 nm.

The mass spectra of **Eu(4)**−**Eu(7)** indicate that a coordinated solvent molecule is not present in the isolated and dried product. However, it is important to determine if a solvent molecule is coordinated to the Eu^{3+} center in solution because the availability of an open coordination site on the metal could disrupt potential interaction of an anion with the hydrogen-bond-donating thioureas of the macrocycle, complicating future studies. In H_2O and D_2O, luminescence lifetime measurements indicate that one water molecule is coordinated in **Eu(4)**−**Eu(7)**. Previous crystal structure determinations of DTPA bis-amide macrocyclic Ln^{3+} complexes have shown that a water molecule occupies a capping position in a distorted tricapped trigonal prism (TTP) geometry.[14a−c] This capping position is not oriented toward the cavity of the macrocycle. Currently, it is unknown as to whether this ninth site is accessible in DMSO solution, but this possibility would allow Eu^{3+} to act as an additional anion binding site in macrocycles of this series.

Our hypothesis of the possible anion sensing capabilities in macrocycles such as **Eu(4)**−**Eu(7)** depends on changing the intensity of the lanthanide emission upon anion binding to the thiourea groups via hydrogen bonding. It has been reported that anion binding to thiourea lowers the oxidation potential of the sulfur atom, in effect, making it a better donor to suitable acceptors nearby.[10a−c] In PET mechanisms, the fluorescence of an aromatic group can be quenched by such a process, where typically there is a methylene spacer between the fluorophore and the thiourea group.[10a−c] In **Eu(4)**−**Eu(7)**, the thiourea moiety is directly attached to the benzene chromophore and anion binding may alter the chromophore's photophysical properties, potentially resulting in a change in Eu^{3+} luminescence. For example, significant changes in absorption spectra have occurred with simple thioureas directly covalently attached to aromatic units.[11] However, without suitable models for comparison, potential changes in the luminescence upon anion binding to **Eu(4)**−**Eu(7)** are difficult to predict. Preliminary studies in DMSO have shown that the luminescence of **Eu(4)**−**Eu(7)** increases up to ∼100% in the presence of up to 8 equiv of the tetrabutylammonium salts of dihydrogen phosphate and benzoate, but no change is observed in the presence of tetrabutylammonium iodide. These results show that a response to anions is achieved by our current system, but it is not by a PET quenching mechanism. Further studies of anion recognition with these macrocycles are currently being pursued.

Studying the effects of anion binding requires that the antenna is excited and then proceeds to transfer energy to the Eu^{3+} center. As shown in Figure 2b, the benzene spacer in **Eu(4)**−**Eu(7)** appears to function as a weak antenna, evidenced by the enhancement of Eu^{3+} luminescence when the complex is excited at 274 nm compared to 395 nm, where Eu^{3+} is excited directly. This feature is also reflected in the excitation spectra of **Eu(4)**−**Eu(7)**, which show significant bands assigned as direct excitations of Eu^{3+} (λ_{max} = 319 and 395 nm, for example), roughly one-third the intensity of the band from 250 to 305 nm where the ligand absorbs. In designing future systems analogous to **Eu(4)**−**Eu(7)**, incorporation of more efficient antenna moieties will be necessary. The *m*-xylylene linker in **Eu(7)** did not appear to have any effect on enhancing the luminescence of the complex, as compared with **Eu(4)**−**Eu(6)**. This is most likely due to a larger distance between this group and the Eu^{3+} center.

Conclusion

The synthesis, characterization, excitation−emission spectra, and luminescence lifetime data for a new series of lanthanide and thiourea-containing macrocycles **[Eu(4)−Eu(7)]** are presented. These systems represent a new series of complexes synthesized by a clean, versatile process that potentially allows for functional variability for future macrocycles. Excitation−emission spectra reveal that these complexes luminesce, and luminescence lifetime studies reveal that one water molecule is coordinated to the Eu^{3+} center in aqueous solution. Current studies are focused on designing similar macrocycles with improved sensitizers that will further enhance the antenna effect to create highly luminescent complexes. Also, studies on the anion-binding ability and response of **Eu(4)−Eu(7)** are underway to study the inclusion chemistry of this new macrocyclic system. A solid understanding of the structure of the complex, energy transfer properties of the ligand, and its interaction with various anions is necessary for developing more responsive and selective macrocyclic systems for specific anion recognition.

Acknowledgment. We would like to thank Dr. Joseph Caruso, Mr. Doug Richardson, and Mr. Kevin Kubachka for use of the ICP-MS for determinations of Eu^{3+} abundance. We also thank the University of Cincinnati and the Chemical Sensors Group for funding this project.

Supporting Information Available: Mass spectra of **3**−**7** and **Eu(4)**−**Eu(7)**, ESI-MS-MS data for **7**, ^{1}H NMR spectra of **4**−**7**, and absorption, excitation and emission spectra of **Eu(4)**−**Eu(7)**. This material is available free of charge via the Internet at http://pubs.acs.org.

IC051324X