Supplementary Information

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Generation Information

(a) Synthesis of new compounds

All air and water sensitive reactions were carried out under a nitrogen atmosphere with dry solvents under anhydrous conditions, unless otherwise noted. All the chemicals were purchased commercially and used without further purification. Anhydrous THF and toluene were distilled from sodium-benzophenone, and dichloromethane was distilled from calcium hydride. Yields refer to chromatographically, unless otherwise stated. Reactions were monitored by thin-layer chromatography (TLC) carried out on 0.25 mm silica gel plates (60F-254) that were analyzed by staining with KMnO$_4$ (200 mL H$_2$O of 1.5 g KMnO$_4$, 10 g K$_2$CO$_3$ and 1.25 mL of 10% aqueous NaOH), fluorescence upon 254 nm irradiation or by staining with anisaldehyde (450mL of 95% EtOH, 25 mL of conc.H$_2$SO$_4$, 15 mL of acetic acid, and 25 mL of anisaldehyde). Silica gel (60, particle size 0.040 – 0.063 mm) was used for flash chromatography. NMR spectra were recorded on either a 400 ($^1$H: 400 MHz, $^{13}$C: 100 MHz), or 500 ($^1$H: 500 MHz, $^{13}$C: 125 MHz). The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, b = broad. High-resolution mass spectra were obtained from a MALDI-TOF Mass Spectrometer.

(b) Photophysical measurement

UV-Visible absorption spectra in the spectral range 200 to 1100 nm were recorded by an HP UV-8453 spectrophotometer. Single-photon luminescence spectra were recorded using an Edinburgh Instrument FLS920 Combined Fluorescence Lifetime and Steady state spectrophotometer that was equipped with a red sensitive single photon counting photomultiplier by Peltier Cooled Housing. The spectra were corrected for detector response and stray background light phosphorescence. The quantum yields of the compounds were measured by Demountable 142 mm (inner) diameter barium sulfide-coated integrating sphere supplied with two access ports.

(c) Binding constant and binding ratio

For the spectrofluorometric titrations, all of the solvents that were used were of analytical grade and the water that was used was purified by double distillation. Measurements were taken after equilibrium was attained and the $^5$D$_0 \rightarrow ^7$F$_2$ emission (europium) was monitored. Luminescent responses in terms of $I_o / (I - I_o)$ were plotted as a function of analyte concentration. For the determination of binding strengths of the various analyte adducts, a series of analyte solutions, at a known concentration, were mixed with the anion solutions at various concentrations. The titration curve was then fitted either with the 1:1 or 1:2 Benesi-Hildebrand equations (below) to check whether it was a 1:1 or 1:2 donor-acceptor interactions.

The 1:1 donor-acceptor interaction was analyzed by Benesi-Hildebrand equations for spectrofluorometric titration.
The 1:2 donor-acceptor interaction was analyzed by Benesi-Hildebrand equations for spectrofluorometric titration.

\[
\frac{I_o}{I - I_o} = \left( \frac{a}{b - a} \right) \left( \frac{1}{K_B [\text{substrate}]} + 1 \right)
\]

\[
\frac{I_o}{I - I_o} = \left( \frac{a}{b - a} \right)^2 \left( \frac{1}{K_B [\text{substrate}]} \right)^2 + 1
\]

\(I_o\) and \(I\) are the luminescence intensity of the fluorogenic reagent in the absence and presence of the substrate, respectively; \(a\) and \(b\) are constants and \([\text{substrate}]\) is the concentration of target analyte. The binding constants, \(K_B\), were estimated from the ratio between the y-intercept to the slope that was obtained from the line of best fit by using Benesi-Hildebrand equations depending on 1:1 or 1:2 host-guest interactions respectively.\(^1\)

(d) HPLC analysis

The reverse-phase HPLC analysis of these five europium complexes was carried out at room temperature by using an Agilent ZORBAX SB-C18 Stable Bond Analytical 4.6 X 150mm 5-micron column. The mobile phase is 0.1% formic acid in mQ water and 0.1% formic acid in acetonitrile solvent system, and the flow rate is 1.0 mL/min. Solvent gradient program is listed in the follow Table.

<table>
<thead>
<tr>
<th>Time /min</th>
<th>0.1% CHOOH in mQ water /%</th>
<th>0.1% CHOOH in CH(_3)CN /%</th>
</tr>
</thead>
<tbody>
<tr>
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<td>5</td>
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</tr>
<tr>
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</tbody>
</table>
Experimental Details

a) Synthesis of new compounds

**Compound 3.** To a solution of 1\(^2\) (1.0 g, 3.77 mmol) in THF (30 mL) and 1-ethyl-4-propoxybenzene (2) (723 mg, 4.52 mmol) in Et\(_3\)N (10 mL) was added CuI (72 mg, 0.377 mmol) and Pd(PPh\(_3\))\(_2\)Cl\(_2\) (79 mg, 0.113 mmol). The dark-brown mixture was heated in the dark at 40 °C for 3 h. After cooling to room temperature, the reaction was quenched by the addition of a saturated NH\(_4\)Cl aqueous solution. The aqueous phase was extracted with EtOAc (3 × 50 mL) and then the combined organic layers were dried over MgSO\(_4\), filtered, and concentrated. Silica gel flash column chromatography (hexane/ethyl acetate = 10/1 to 2/1) of the residue gave a white solid (852 mg, 78%) as the product. 3: \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 7.47 (\(d, J = 9\) Hz, 2H), 7.35 (s, 2H), 6.91 (d, \(J = 9\) Hz, 2H), 4.83 (s, 4H), 3.95 (t, \(J = 7\) Hz, 2H), 1.88-1.80 (m, 2H), 1.05 (t, \(J = 7\) Hz, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 160.3, 158.0, 133.7, 124.5, 124.3, 113.3, 96.6, 85.6, 69.7, 63.6, 22.8, 10.5; HRMS (ESI) m/z calcd. for C\(_{12}\)H\(_{21}\)NO\(_3\) (M+H)+ 298.1443, found 298.1438.

**Compound 4.** To a stirred solution of 3 (560 mg, 1.89 mmol) and Et\(_3\)N (573 mg, 5.67 mmol) in CH\(_2\)Cl\(_2\) (25 mL) was added methanesulfonyl chloride (326 mg, 2.84 mmol) dropwise. After 20 min, the reaction was quenched by the addition of a saturated NaHCO\(_3\) aqueous solution (30 mL). The organic phase was dried over MgSO\(_4\), filtered, and concentrated. To a stirred solution of the residue in acetone (20 mL) at room temperature was added LiBr (12 mmol). The resulting mixture was stirred at 60 °C for 2 hours and then concentrated. The residue was dissolved in water (30 mL) and extracted with CH\(_2\)Cl\(_2\) (3 × 30 mL). The combined organic layers were dried over MgSO\(_4\), filtered, and concentrated. Silica gel flash column chromatography (hexane/ethyl acetate = 15/1 to 8/1) of the residue gave a white solid (672 mg, 84%) as the product. 4: \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 7.49 (\(d, J = 9\) Hz, 2H), 7.44 (s, 2H), 6.91 (d, \(J = 9\) Hz, 2H), 4.52 (s, 4H), 3.95 (t, \(J = 7\) Hz, 2H), 1.88-1.79 (m, 2H), 1.054 (t, \(J = 7\) Hz, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 160.2, 156.8, 133.6, 124.5, 114.7, 95.5, 85.1, 69.6, 33.2, 22.5, 10.5; HRMS (ESI) m/z calcd. for C\(_{18}\)H\(_{17}\)Br\(_2\)NO (M+H)+ 421.9755, found 421.9749.

**Compound 5.** To a stirred solution of 4 (300 mg, 0.71 mmol) and NaHCO\(_3\) (270 mg, 3.55 mmol) in acetonitrile (15 mL) was added dropwise 1-aza-18-crown ether (184 mg, 0.70 mmol) at 80 °C for 1 hour. The resulting mixture was heated under reflux for 2 hours. After cooling to room temperature, the reaction was quenched by the addition of water. The aqueous phase was extracted with CH\(_2\)Cl\(_2\) (3 × 25 mL) and the combined organic layers were dried over MgSO\(_4\), filtered, and concentrated. Silica gel flash column chromatography (dichloromethane /methanol = 25/1 to 10/1) of the residue gave a white solid (175 mg, 42%) as the product. 5: \(^1\)H NMR (400 MHz, CD\(_2\)OD): \(\delta\) 7.55 (s, 1H), 7.52 (d, \(J = 9\) Hz, 2H), 7.42 (s, 1H), 6.97 (d, \(J = 9\) Hz, 2H), 4.82 (s, 2H), 3.98 (t, \(J = 7\) Hz, 2H), 3.79 (s, 2H), 3.73-3.53 (m, 2OH), 2.76 (s, 4H), 1.88-1.80 (m, 2H), 1.05 (t, \(J = 7\) Hz, 3H); \(^{13}\)C NMR (100 MHz, CD\(_2\)OD): \(\delta\) 160.4, 158.0, 134.0, 133.3, 124.5, 124.1, 114.5, 113.3, 95.1, 84.6, 69.2-66.9 (10C, crown ether), 69.3, 58.5, 54.2 (2C, crown ether), 53.4, 32.7, 22.2, 9.4; HRMS (ESI) m/z calcd. for C\(_{30}\)H\(_{42}\)BrN\(_2\)O\(_6\) (M+H)+ 605.2226, found 605.2221.
**Compound L1.** To a solution of 5 (100 mg, 0.16 mmol) in acetonitrile at room temperature was added NaHCO₃ (61 mg, 0.80 mmol) and tri-t-butyl 2,2',2''-(1,4,7,10-tetraazaacyclododecane-1,4,7-triyl)triacetate (82 mg, 0.16 mmol). After stirring at 80 °C for 6 hours, the reaction was quenched with water. The aqueous phase was extracted with CH₂Cl₂ (3×25 mL) and the combined organic layers were dried over MgSO₄, filtered, and concentrated. Silica gel flash column chromatography (dichloromethane/methanol = 25/1 to 10/1) gave a white oil (108 mg, 60%) as the product. ¹H NMR (400 MHz, CD₂OD): δ 7.85 (s, 1H), 7.52 (s, 1H), 7.46 (d, J = 9 Hz, 2H), 6.96 (d, J = 9 Hz, 2H), 3.98 (t, J = 6 Hz, 2H), 3.88 (s, 4H), 3.73-3.53 (m, 20H), 3.50 (s, 6H), 2.83 (s, 4H), 3.20-2.30 (m, 16H), 1.88-1.80 (t, J = 6 Hz, 2H), 1.52-1.49 (m, 27H), 1.06 (t, J = 7 Hz, 3H); ¹³C NMR (100MHz, CD₂OD): δ 173.3, 173.2, 160.3, 158.17, 133.69, 133.13, 129.00, 124.44, 123.91, 119.05, 114.80, 114.58, 114.46, 113.49, 94.60, 85.2, 82.3, 82.0, 69.4-67.5 (10C, crown ether), 69.3, 59.9, 59.3, 55.9-55.5 (8C, DO3A), 54.2 (2C, crown ether), 53.5, 27.1, 27.1, 22.2, 9.4; HRMS (ESI) m/z calcd. for C₅₆H₉₁N₄O₁₂ (M+H)+ 1039.6695, found 1039.6689.

**Compound EuL1.** L1 (30 mg, 0.029 mmol) was dissolved in TFA (2 mL) and the mixture was stirred at room temperature under argon for 12 hours. After removal of the volatiles, the light-yellow residue was dissolved in CH₂Cl₂ and concentrated to ensure the removal of TFA. Hydrolysis of the t-butyl ester groups was confirmed by ¹H NMR of the crude product. To a stirred solution of the residue in methanol (2 mL) was added EuCl₃·6H₂O (0.032 mmol) followed by adjustment of the pH to 5.8. The mixture was stirred at room temperature for 30 h and then concentrated. Recrystallization of the residue from CH₂CN gave an off-white solid (17.4 mg, 60%) as the product. EuL1: HRMS (ESI) m/z calcd. for C₄₄H₆₃EuN₆NaO₁₂ (M+Na)+ 1043.3614, found 1043.3680.

**Compound LaL1.** L1 (30 mg, 0.029 mmol) was dissolved in TFA (2 mL) and the mixture was stirred at room temperature under argon for 12 hours. After removal of the volatiles, the light-yellow residue was dissolved in CH₂Cl₂ and concentrated to ensure the removal of TFA. Hydrolysis of the t-butyl ester groups was confirmed by ¹H NMR of the crude product. To a stirred solution of the residue in methanol (2 mL) was added La(OTf)₃ (0.030 mmol) followed by adjustment of the pH to 5.8. The mixture was stirred at room temperature for 30 h and then concentrated. Recrystallization of the residue from CH₂CN gave an off-white solid (18.7 mg, 65%) as the product. LaL1: HRMS (ESI) m/z calcd. for C₄₄H₆₃LaN₆NaO₁₂ (M+Na)+ 1029.3465, found 1029.3413.
**Scheme S1** The synthesis of negative control compound EuL2

**Compound 7.** To a solution of 6 (2.0 g, 6.82 mmol) in THF (30 mL) at room temperature was added a solution of 1-ethynyl-4-propoxybenzene (2) (1.20 g, 7.50 mmol) in Et$_3$N (10 mL) and then CuI (0.130 g, 0.682 mmol) and Pd(PPh$_3$)$_2$Cl$_2$ (0.143 g, 0.205 mmol). The resulting dark-brown mixture was heated in the dark at 40 ºC for 4 hours. After cooling to room temperature, the reaction was quenched by the addition of a saturated NH$_4$Cl aqueous solution. The aqueous phase was extracted with EtOAc (3 × 50 mL) and the combined organic layers were dried over MgSO$_4$, filtered, and concentrated. Silica gel flash chromatography (hexane/ethyl acetate = 10/1 to 2/1) of the residue gave a white solid (1.80 g, 81%) as the product. 7: $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.08 (s, 1H), 7.58 (s, 1H), 7.48 (d, $J = 9$ Hz, 2H), 6.90 (d, $J = 9$ Hz, 2H), 4.86 (s, 2H), 4.01 (s, 3H), 3.95 (t, $J = 7$ Hz, 2H), 1.85-1.78 (m, 2H), 1.05 (t, $J = 7$ Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 165.3, 160.3, 147.2, 134.0, 133.7, 125.7, 125.3, 114.8, 113.5, 96.1, 85.1, 69.7, 64.6, 53.0, 22.5, 10.5; HRMS (ESI) m/z calcd. for C$_{19}$H$_{20}$NO$_4$ (M+H)$^+$ 326.1392, found 326.1382.

**Compound 8.** To a stirred solution of 7 (1.0 g, 3.10 mmol) in CH$_2$Cl$_2$ (15 mL) at room temperature was added imidazole (253 mg, 3.73 mmol) and TBSCI (560 mg, 3.73 mmol). After stirring at room temperature for 2 hours, the reaction was quenched by addition of
water (20 mL). The aqueous phase was extracted with CH₂Cl₂ (3 × 20 mL) and the combined organic layers were dried over MgSO₄, filtered, and concentrated. Silica gel flash column chromatography (hexane/ethyl acetate = 15/1 to 10/1) of the residue afforded a pale yellow oil (1.25 g, 92%) as the product. 8: ¹H NMR (400 MHz, CDCl₃): δ 8.06 (s, 1H), 7.75 (s, 1H), 7.51 (d, J = 9 Hz, 2H), 6.90 (d, J = 9 Hz, 2H), 4.93 (s, 2H), 4.01 (s, 3H), 3.96 (t, J = 7 Hz, 2H), 1.84-1.80 (m, 2H), 1.05 (t, J = 7 Hz, 3H), 0.98 (s, 9H), 0.15 (s, 6H); ¹³C NMR (400 MHz, CDCl₃): δ 165.5, 162.3, 160.2, 147.1, 133.8, 133.7, 125.3, 124.7, 113.7, 95.4, 85.6, 69.7, 65.9, 53.1, 30.6, 25.7, 22.5, 10.5, -3.6; HRMS (ESI) m/z calcd. for C₂₅H₃₆NO₅Si (M+H)+ 440.2257, found 440.2284.

**Compound 9.** To a stirred solution of 8 (500 mg, 1.14 mmol) in toluene (10 mL) at room temperature was added 1-aza-18-crown ether (358 mg, 1.37 mmol) and Et₃N (23 mg, 0.23 mmol). The resulting mixture was heated under reflux for 6 hours and then concentrated. Silica gel flash column chromatography (dichloromethane/methanol = 40/1 to 20/1) of the residue gave a pale yellow oil (688 mg, 90%) as the product. 9: ¹H NMR (400 MHz, CDCl₃): δ 7.57 (s, 1H), 7.53 (s, 1H), 7.48 (d, J = 9 Hz, 2H), 6.89 (d, J = 9 Hz, 2H), 4.82 (s, 2H), 3.95 (t, J = 7 Hz, 2H), 3.82 (m, 4H), 3.75-3.55 (m, 20H), 1.82 (m, 2H), 1.067, 1.04 (t, J = 7 Hz, 3H), 0.977 (s, 9H), 0.145 (s, 6H); ¹³C NMR (100 MHz, CDCl₃): δ 168.7, 160.3, 160.1, 133.9, 133.6, 129.5, 123.5, 122.5, 115.4, 114.7, 113.7, 95.3, 85.8, 70.7-69.5 (10 C, crown ether), 69.3, 65.6, 52.16, 49.8, 47.2, 29.7, 29.4, 26.0, 25.1, 22.5, 10.5, -5.3; HRMS (ESI) m/z calcd. for C₃₆H₅₅N₂O₆Si (M+H)+ 671.3728, found 671.3785.

**Compound 10.** To a stirred solution of 9 (688 mg, 1.03 mmol) in THF (10 mL) at room temperature was added TBAF (2 ml, 1.0 M THF solution). The resulting mixture was stirred at room temperature for 1 hour and then concentrated. Silica gel flash column chromatography (dichloromethane/methanol = 30/1 to 15/1) of the residue gave a white solid (515 mg, 90%) as the product. 10: ¹H NMR (400 MHz, CDCl₃): δ 7.53 (s, 1H), 7.41 (d, J = 9 Hz, 2H), 7.35 (s, 1H), 6.83 (d, J = 9 Hz, 2H), 4.67 (s, 2H), 4.07 (s, 1H), 3.89 (t, J = 7 Hz, 2H), 3.78-3.54 (m, 24H), 1.80-1.73 (m, 2H), 1.00 (t, J = 7 Hz, 3H); ¹³CNMR (100 MHz, CDCl₃): δ 168.8, 160.1, 159.2, 153.6, 133.6, 123.8, 122.5, 114.7, 113.7, 95.4, 85.5, 70.7-69.5 (10 C, crown ether), 69.3, 64.4, 49.9, 47.2, 22.5, 10.5; HRMS (ESI) m/z calcd. for C₁₈H₂₆NO₃ (M+H)+ 557.2863, found 557.2862.

**Compound 11.** To a stirred solution of 10 (500 mg, 0.90 mmol) and Et₃N (273 mg, 2.70 mmol) in CH₂Cl₂ (25 mL) at room temperature was added methanesulfonyl chloride (155 mg, 1.35 mmol) dropwise. After stirring at room temperature for 20 min, the reaction was quenched by the addition of a saturated NaHCO₃ aqueous solution (30 mL). The organic phase was separated, dried over MgSO₄, filtered and concentrated. To a stirred solution of the crude product in acetone (20 mL) at room temperature was added LiBr (1.8 mmol). The resulting mixture was stirred at 60 °C for 2 hours and then concentrated. The residue was dissolved in water (30 mL) and extracted with CH₂Cl₂ (3 × 30 mL). The combined organic layers were dried over MgSO₄, filtered, and concentrated. Silica gel flash column chromatography (dichloromethane/methanol = 30/1 to 15/1) of the residue gave a white solid (415 mg, 75%) as the product. 11: ¹H NMR (400 MHz, CD₂OD): δ 7.63 (s, 1H), 7.60 (s, 1H), 7.52 (d,
\( J = 9 \text{ Hz}, 2H \), 6.96 (d, \( J = 9 \text{ Hz}, 2H \), 4.72, 4.61 (s, 2H), 3.98 (t, \( J = 7 \text{ Hz}, 2H \), 3.88-3.55 (m, 24H), 1.88-1.78 (m, 2H), 1.05 (t, \( J = 7 \text{ Hz}, 3H \)); \(^{13}\text{C NMR (100 MHz, CD}_{3}\text{OD):} \delta 169.2, 160.5, 156.7, 154.4, 134.2, 133.4, 125.2, 124.8, 123.9, 123.8, 114.5, 113.2, 95.7, 95.7, 84.3, 70.2-68.7 (10 C, crown ether), 69.3, 49.7, 47.15, 32.0, 22.2, 9.4; HRMS (ESI) m/z calcd. for \( \text{C}_{30}\text{H}_{40}\text{BrN}_{2}\text{O}_{7} (\text{M}+\text{H})^{+} \) 619.2019, found 619.2017.

**Compound L2.** To a solution of 11 (150 mg, 0.24 mmol) in acetonitrile (30 mL) at room temperature was added \( \text{NaHCO}_{3} \) (92 mg, 1.21 mmol) and DO3A(O^t\text{Bu})\text{3} (123 mg, 0.24 mmol). After stirring at 80 °C for 6 hours, the reaction was quenched by addition of water (30 mL). The aqueous phase was extracted with \( \text{CH}_{2}\text{Cl}_{2} \) (3 × 25 mL). The combined organic layers were dried over \( \text{MgSO}_{4} \), filtered, and concentrated. Silica gel flash chromatography (dichloromethane/methanol = 25/1 to 10/1) of the residue gave a white oil (164 mg, 65%) as the product. 12: \(^{1}\text{H NMR (400 MHz, CDCl}_{3}: \delta 7.91 (s, 1H), 7.57 (s, 1H), 7.36 (d, \( J = 9 \text{ Hz}, 2H \), 6.84 (d, \( J = 9 \text{ Hz}, 2H \), 3.95 (t, \( J = 7 \text{ Hz}, 2H \), 3.88 (s, 2H), 3.81-3.61 (m, 24H), 3.12 (s, 6H), 3.05-2.40 (m, 16H, cyclen), 1.88-1.80 (m, 2H), 1.44 (s, 27H), 1.06 (t, \( J = 7 \text{ Hz}, 3H \)); \(^{13}\text{C NMR (100 MHz, CDCl}_{3}: \delta 173.5, 172.7, 168.6, 160.1, 157.0, 154.1, 133.9, 133.6, 133.4, 126.1, 123.9, 114.6, 113.6, 95.3, 85.3, 82.8, 82.3, 70.3 (10 C, crown ether), 69.7, 60.2, 56.2, 55.8, 53.5, 51.1, 50.2, 49.86, 46.8, 28.0, 27.8, 22.5, 10.5; HRMS (ESI) m/z calcd. for \( \text{C}_{56}\text{H}_{89}\text{N}_{6}\text{O}_{13} (\text{M}+\text{H})^{+} \) 1053.6488, found 1053.6480.

**Compound EuL2.** L2 (30 mg, 0.028 mmol) was dissolved in TFA (2 mL) and the resulting mixture was stirred at room temperature under argon for 12 hours. After removal of TFA, the pale yellow residue was dissolved in \( \text{CH}_{2}\text{Cl}_{2} \) and concentrated to ensure the removal of TFA. Hydrolysis of the \( t \)-butyl ester groups was confirmed by \(^{1}\text{H NMR of the crude product.} \) The residue was then dissolved in water/methanol (2:1 v/v, 3 mL) and treated with EuCl\text{3}•6\text{H}_{2}\text{O (0.028 mmol). After adjustment of the pH to 7.0 with sodium hydroxide, the mixture was stirred at room temperature for 30 hours and then concentrated. Recrystallization of the residue from \( \text{CH}_{3}\text{CN} \) gave a pale white solid (20 mg, 68%) as the product. EuL2: HRMS (ESI) m/z calcd. for \( \text{C}_{46}\text{H}_{60}\text{EuN}_{6}\text{NaO}_{13} (\text{M}+\text{Na})^{+} \) 1057.3407, found 1057.3483.
Scheme S2  The synthesis of negative control compounds EuL3, L4 and L5

**Compound L3.** To a solution of 12 (80 mg, 0.24 mmol) in acetonitrile (15 mL) at room temperature, was added K$_2$CO$_3$ (92 mg, 1.21 mmol) and DO3A(OtBu)$_3$ (123 mg, 0.24 mmol). After stirring at 80 ºC for 6 hours, the reaction was quenched by addition of water (15 mL). The aqueous phase was extracted with CH$_2$Cl$_2$ (3×15 mL). The combined organic layers were dried over MgSO$_4$, filtered, and concentrated. Silica gel flash column chromatography (dichloromethane/methanol = 30/1 to 20/1) of the residue gave an off-white oil (124 mg, 68%) as the product. $^1$H NMR (500 MHz, CDCl$_3$) δ 8.20 (d, J = 7 Hz, 1H), 7.44 (d, J = 7 Hz, 2H), 7.24 (s, 1H), 7.17 (d, J = 7 Hz, 1H), 6.86 (d, J = 7 Hz, 2H), 3.93 (t, J = 7 Hz, 2H), 3.57 (s, 2H), 3.21-2.30 (m, 22H), 1.80-1.76 (m, 2H), 1.46 (s, 18H), 1.38 (s, 9H), 1.05 (t, J = 7 Hz, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$) δ 172.7, 172.4, 160.1, 158.8, 148.6, 133.4, 132.8, 124.9, 123.6, 114.7, 113.5, 95.1, 85.2, 81.9, 81.8, 69.6, 58.7, 56.3, 55.5, 53.3, 50.3, 27.9, 22.4, 10.3; HRMS (ESI) m/z calcd. for C$_{43}$H$_{66}$N$_5$O$_7$ (M+H)$^+$ 764.4962, found 764.4961.

**Compound EuL3.** L3 (0.020 mmol) was dissolved in TFA (1 mL) and the mixture was stirred at room temperature under argon for 12 hours. After removal of TFA under reduced pressure, the pale yellow residue was dissolved in CH$_2$Cl$_2$, and concentrated to ensure the removal of TFA. Hydrolysis of the t-butyl ester groups was confirmed by $^1$H NMR of the crude product. The residue was then dissolved in water/methanol (2:1 v/v, 3 mL) and treated with EuCl$_3$·(H$_2$O)$_6$ (0.020 mmol). After adjustment of the pH to 7.0 with a 1 N aqueous sodium hydroxide solution, the mixture was stirred at 70 ºC for 24 hours and then concentrated.
Recrystallization of the residue from CH₂CN gave an off-white solid (75%) as the product.

**EuL₃:** HRMS (ESI) m/z calcd. for C₃₁H₄₁Eu₃N₅O₈ (M+H₂O+H⁺) 764.2167, found 764.2221, (M+H)⁺ 746.2062, found 746.2051;

**Compound L₄.** To a stirred solution of 1₂ (235 mg, 0.71 mmol) and NaHCO₃ (270 mg, 3.55 mmol) in acetonitrile (15 mL) was added 1-aza-18-crown ether (184 mg, 0.71 mmol) at 80 °C for 1 hour. The resulting mixture was heated under reflux for 2 hours, and the reaction was quenched by the addition of water. The aqueous solution was extracted with CH₂Cl₂ (3 × 25 mL) and then the combined organic layer was dried over MgSO₄, filtered, and concentrated. Silica gel flash column chromatography (dichloromethane/methanol = 40/1 to 30/1) gave a white solid (299 mg, 82%).

**L₄:** ¹H NMR (400 MHz, CDCl₃): δ 8.54 (d, J = 5 Hz, 1H), 7.46 (d, J = 9 Hz, 2H), 7.28 (d, J = 4 Hz, 2H), 6.88 (d, J = 9 Hz, 2H), 3.92 (t, J = 7 Hz, 2H), 3.78-3.59 (m, 22H), 1.84-1.75 (m, 2H), 1.01 (t, J = 7 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 160.2, 149.9, 133.6, 133.3, 125.6, 124.5, 114.7, 113.5, 85.3, 69.6, 69.2, 69.0, 68.9, 68.8, 68.8, 66.7, 59.1, 53.8, 29.7, 22.5, 10.5, 1.0; HRMS (ESI) m/z calcd. for C₂₉H₄₆N₂O₆ (M+H)⁺ 513.2966, found 513.2956.

**Compound L₅.** To a stirred solution of 1₃ (133 mg, 0.45 mmol) in acetonitrile (5 mL) was added NaHCO₃ (76 mg, 95 mmol) and 1-aza-18-crown-6 ether (120 mg, 0.45 mmol). The resulting mixture was stirred under refluxing condition for 12 hour. The mixture was then cooled to room temperature and washed with water (5 mL). The aqueous phase was extracted with EtOAc (3 × 25 mL) and the combined organic layers were dried over MgSO₄, filtered, and concentrated. To a solution of crude L₄ in THF (20 mL) and 1-ethynyl-4-propoxybenzene (72.3 mg, 0.45 mmol) in Et₃N (1 mL) was added CuI (7.2 mg, 0.038 mmol) and Pd(PPh₃)₂Cl₂ (7.9 mg, 0.01 mmol). The dark-brown mixture was heated in the dark at 40 °C for 3 hour. After cooling to room temperature, the reaction was quenched by the addition of saturated NH₄Cl aqueous solution. The aqueous phase was extracted with EtOAc (3 × 25 mL) and then the combined organic layers were dried over MgSO₄, filtered, and concentrated. Silica gel flash column chromatography (dichloromethane/methanol = 40/1 to 30/1) of the residue gave a white solid (170 mg, 74% from 1₃) as the product.

**L₅:** ¹H NMR (400 MHz, CDCl₃): δ 7.52 (s, 1H), 7.46-7.27 (m, 5H), 6.88 (d, J = 9 Hz, 2H), 3.94 (t, J = 7 Hz, 4H), 3.69-3.62 (m, 20H), 2.94 (s, 4H), 1.86-1.78 (m, 2H), 1.04 (t, J = 7 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃): δ 159.3, 133.0, 132.4, 130.6, 129.4, 128.5, 123.7, 115.0, 114.5, 87.9, 70.5, 70.1, 69.6, 53.8, 29.70, 22.5, 10.5; HRMS (ESI) m/z calcd. for C₃₀H₄₁NO₆ (M+H)⁺ 512.3014, found 512.3006.
$^1$H NMR and $^{13}$C NMR spectra of 3
$^1$H NMR and $^{13}$C NMR of spectra of 4
$^1$H NMR and $^{13}$C NMR spectra of 5
$^1$H NMR and $^{13}$C NMR spectra of L1
$^1$H NMR and $^{13}$C NMR spectra of 7
$^1$H NMR and $^{13}$C NMR spectra of 8
$^1$H NMR and $^{13}$C NMR spectra of 9
$^1$H NMR and $^{13}$C NMR spectra of 10
1H NMR and 13C NMR spectra of 11
$^1$H NMR and $^{13}$C NMR spectra of L2
$^1$H NMR and $^{13}$C NMR spectra of L3
$^1$H NMR and $^{13}$C NMR spectra of L4
$^1$H NMR and $^{13}$C NMR spectra of L5
HRMS of L1

HRMS of EuL1

S24
Table S1. Solvent gradient for HPLC

<table>
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<tr>
<th>Time /min</th>
<th>0.1% CHO0H in mQ water /%</th>
<th>0.1% CHOOH in CH₃CN /%</th>
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<tr>
<td>0.0</td>
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<tr>
<td>20.0</td>
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</table>

Figure S1  HPLC trace of Eu complexes. Experimental conditions: Agilent ZORBAX SB-C18 Stable Bond Analytical 4.6 X 150 mm 5-micron, 1.0mL/min flow rate, Retention Time: EuL1 in 9.67 min, con.Eu-1 in 10.60 min.
**Figure S2**  Left: UV-vis absorption spectrum of L1 (top) and EuL1 (bottom) in methanol. Right: Excitation spectra of EuL1. (H2O, λ_em = 615 nm, 10 μM).

**Figure S3**  Job’s plot of EuL1 towards Cu²⁺ ions.
Figure S4  Fluorescence response of EuL1 at various pH values (2-12) in the absence (black) or presence (red) of Cu$^{2+}$ (10 μM). All spectra were acquired in water with $\lambda_{ex}$ at 325 nm.

Figure S5  The emission intensity at 615 nm upon addition of H$_2$S from 0 to 10 min.
Table S2  Luminescence lifetimes (τ/ms), number of inner sphere water molecules (q), quantum yield (φ) of **EuL1** (50 µM in water) alone, with Cu$^{2+}$ ion, and with Cu$^{2+}$ ion and H$_2$S.

<table>
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<tr>
<th>Complex</th>
<th>$\tau_{H2O}$</th>
<th>$\tau_{D2O}$</th>
<th>q$^a$</th>
<th>φ (H$_2$O)$^b$</th>
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<tr>
<td>EuL1</td>
<td>0.61</td>
<td>1.20</td>
<td>0.66</td>
<td>0.5%</td>
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<td>EuL1+Cu$^{2+}$</td>
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<td>_$^c$</td>
<td>_$^d$</td>
<td>_$^d$</td>
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<tr>
<td>EuL1+Cu$^{2+}$+H$_2$S</td>
<td>0.34</td>
<td>0.47</td>
<td>0.68</td>
<td>1.1%</td>
</tr>
</tbody>
</table>

$^a$ Values of the number of coordinated water molecules, q, (±20%), were determined according to the literature procedures.$^5$ $^b$ The quantum yields were measured by integrated sphere in aqueous solution.$^7$ $^c$ The fluorescence signal is too weak to be detected. $^d$ Not determined.

Figure S6 Temperature dependent luminescence study of the **EuL1-Na$_2$S** complex
**Figure S7**  HMRS spectrum of EuL1 with Cu$^{2+}$ and Na$_2$S.

**Figure S8**  $^1$H NMR spectrum of LaL1
Figure S9 $^1$H NMR spectrum of LaL1+Cu$^{2+}$

Figure S10 $^1$H NMR spectrum of LaL1+Cu$^{2+}$+H$_2$S
References


