Supporting Information for

Alkali-Metal- and Halide- Free Dinuclear Mixed- Valent Samarium and Europium Complexes

Nishya F. M. Mukthar, Nathan D. Schley, Gaël Ung*

Department of Chemistry, University of Connecticut, 55 N. Eagleville Road, U-3060, Storrs, CT, 06269- 3060, USA
E-mail: gael.ung@uconn.edu

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Experimental Section

Chemicals and reagents

Pyrrole (C_4H_5N, 98+%) and 3-pentanone ($C_5H_{10}O$, 99%) were purchased from Alfa Aesar. Mercury (Hg, 99.99%) and 12-crown-4-ether($C_8H_{16}O_4$, 98%) were purchased from sigma Aldrich. $SmCl_3$ (anhydrous, 100%) and $EuCl_3$ (anhydrous, 100%) were purchased from Strem Chemicals. Methanesulfonic acid (CH_3SO_3H, 70%) was purchased from Acros Organics. Lithium bis(trimethylsilyl)amide ($C_6H_{18}Si_2NLi$, 97%) was purchased from Aldrich. Toluene was refluxed over sodium and distilled under nitrogen before use. Any other solvents used for experiments under nitrogen were dried using a solvent purification system from Pure Process Technologies. All reactions except the ligand synthesis were performed under nitrogen.

Apparatus

All NMR spectra were obtained using a Bruker AVANCE 300 MHz or Bruker AVANCE III 400 MHz Spectrometer. Absorption and emission spectra were collected on a HORIBA Duetta Spectrophotometer using HORIBA EzSpec software. Cyclic voltammograms were collected on a CH Instruments Electrochemical Analyzer using a three-electrode system. Single-crystal X-ray diffraction studies were performed at Vanderbilt University, all measurements were made on a Rigaku Oxford Diffraction Supernova Eos CCD with filtered Cu Kα or Mo Kα radiation at a temperature of 100 K.

Synthesis of calix[4]-pyrrole: The synthesis of calix[4]pyrrole was adapted from Jacoby et al.[1] Freshly distilled pyrrole (11.6 mL, 167.2 mmol), 3-pentanone (17.7 mL, 167.2 mmol), and methanesulfonic acid (55.5 μL/ 10mmol of pyrrole) were mixed in ethanol and refluxed for 4.5 hrs. The dark brown reaction mixture was allowed to cool down to room temperature and placed in the refrigerator overnight. The white crystalline solid formed was filtered off, recrystallized from ethanol several times to remove unreacted pyrrole, washed with cold ethanol and dried under vacuum (17.4 g, 77%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 0.63 (t, *J = 9.7 Hz*, C**H$_3$**, 24H), 1.8 (br s, C**H$_2$**, 16H), 5.93 (s, C_4**H$_2$**NH, 8H), 6.98 (s, C_4H_2N**H**, 4H).

Preparation of $Sm(N(SiMe_3)_2)_3$ (μ-Cl)Li(thf)$_3$: The synthesis of $Sm(N(SiMe_3)_2)_3$ (μ-Cl)Li(thf)$_3$ was adapted from Bradley et al.[2] Lithium bis(trimethylsilyl)amide (1.163 g, 6.950 mmol) was dissolved in dry THF (15 mL) under nitrogen and cooled down to 0 °C. Samarium(iii) chloride (0.595 g, 2.317 mmol) was added portion wise over 30 minutes. Then the reaction mixture was stirred at room temperature for 24 hours. THF was removed under vacuum and the residue was extracted with n-pentane. Off white needle like crystals were obtained by slow evaporation of pentane (1.983 g, 96%). ^{1}H NMR (C_6D_6, 400 MHz): δ (ppm) -1.56 (s, SiC**H$_3$**, 54H), 1.35 (s, THF, 12H), 3.41 (s, THF, 12H).

Preparation of $Eu(N(SiMe_3)_2)_3$ (μ-Cl)Li(thf)$_3$: Prepared according to the same procedure described for $Sm(N(SiMe_3)_2)_3$ (μ-Cl)Li(thf)$_3$ (0.620 g, 90%). ^{1}H NMR (C_6D_6, 400 MHz): δ (ppm) 1.31 (s, THF, 12H), 3.61 (s, THF, 12H), 6.95 (s, SiC**H$_3$**, 54H).

Preparation of (η^5:η^1:η^5:η^1 Et$_8$-calix[4]pyrrolyl){SmN(SiMe$_3$)$_2$}$_2$: The synthesis was adapted from the procedure reported by Zhou et al.[3] A toluene solution of calix[4]pyrrole (0.124 g, 0.23 mmol in 2.0 mL of toluene) was added dropwise to a toluene solution of $Sm(N(SiMe_3)_2)_3$ (μ-

Cl) $Li(thf)_3$ (0.407 g, 0.458 mmol in 5.5 mL of toluene) under nitrogen and stirred at room temperature for six days and then at 100°C for one day. Solvent was removed under vacuum and extracted with pentane. Needle like crystals were obtained by slow evaporation of pentane (0.600 g, 23%).^{1}H NMR (C_6D_6, 400 MHz): δ (ppm) -0.91 (s, C**H$_3$**, 36H), -0.63 (t, *J = 6.7 Hz*, C**H$_3$**, 24H), 0.29 (s, C**H$_2$**, 16H), 10.14 (s, C_4**H$_2$**N, 8H). Elem. Anal. for $C_{48}H_{84}N_6Si_4Sm_2$ calcd. C, 49.77; H, 7.31; N, 7.26; found: C, 49.82; H, 7.38; N, 7.36.

Preparation of (η^5: η^1: η^5: η^1 Et$_8$ -calix[4]pyrrolyl){EuN(SiMe$_3$)$_2$}$_2$: Prepared according to the same procedure described for (**η^5: η^1: η^5: η^1** Et$_8$-calix[4]pyrrolyl){SmN(SiMe$_3$)$_2$}$_2$ (0.231 g, 59%). ^{1}H NMR (C_6D_6, 400 MHz): δ (ppm) -5.97 (s, C_4**H$_2$**N, 4H), 8.69 (s, C**H$_2$**, 16H), 10.69 (s, C**H$_3$**, 24H), 45.19 (s, C_4**H$_2$**N, 4H). Elem. Anal. for $C_{48}H_{84}N_6Si_4Eu_2$ calcd. C, 49.64; H, 7.29; N, 7.24; found: C, 49.64; H, 7.30; N, 7.24.

Preparation of (η^5: η^1: η^5: η^1 Et$_8$ -calix[4]pyrrolyl){Sm$_2$(N(SiMe$_3$)$_2$)(thf)}: To a THF solution of (***η***^{5}: ***η***^{1}: ***η***^{5}: ***η***^{1} Et$_8$ -calix[4]pyrrolyl){SmN(SiMe$_3$)$_2$}$_2$ (0.036 g, 0.031 mmol) under nitrogen was added sodium amalgam (0.007 g, 0.304 mmol Na(s) in Hg)[4] at room temperature and stirred overnight. After sodium amalgam was separated from the reaction solution solvent was removed under vacuum. Then the brown solid obtained was dissolved in pentane and treated with a drop of 12-crown-4 ether diluted in pentane. The solid that precipitated out was filtered and solvent was removed under vacuum (27 mg, 77%). 1H NMR (C_6D_6, 400 MHz): δ (ppm) -18.05 (s, THF, 4H), -7.71 (s, THF, 4H), -4.31 (s, C**H$_3$**, 12H), -2.60 (s, **CH$_3$**, 12H), 1.35 (s, C**H$_2$**, 8H), 2.55 (s, C**H$_2$**, 8H), 2.94 (s, C**H$_3$**, 18H), 12.96 (s, C4**H$_2$**N, 4H). Elem. Anal. for $C_{46}H_{74}N_5OSi_2Sm_2$ calcd. C, 51.64; H, 6.97; N, 6.55; found: C, 52.02; H, 6.88; N, 6.43.

Preparation of (η^5: η^1: η^5: η^1 Et$_8$ -calix[4]pyrrolyl){Eu$_2$(N(SiMe$_3$)$_2$)(thf)}: To a THF solution of (η^5: η^1: η^5: η^1 Et$_8$ -calix[4]pyrrolyl){EuN(SiMe$_3$)$_2$}$_2$ (0.035 g, 0.029 mmol) under nitrogen was added sodium amalgam (0.007 g, 0.304 mmol $Na_{(s)}$ in Hg)[4] at room temperature and stirred overnight. After sodium amalgam was separated from the reaction solution solvent was removed under vacuum. Then the dark brown solid obtained was dissolved in pentane and treated with a drop of 12-crown-4 ether diluted in pentane. The solid that precipitated out was filtered and the filtrate was concentrated by slow evaporation to get needle like crystals (29 mg, 90%). NMR signals for this are extremely broad due to high paramagnetic nature of the complex. Elem. Anal. for $C_{46}H_{74}N_5OSi_2Eu_2$ calcd. C, 51.48; H, 6.95; N, 6.53; found: C, 51.28; H, 6.90; N, 6.42.

Preparation of (η^5: η^1: η^5: η^1 Et$_8$ -calix[4]pyrrolyl)Sm$_4$(μ-O)$_2$(thf)$_2$ with silanol: To a THF solution of (η^5: η^1: η^5: η^1 Et$_8$ -calix[4]pyrrolyl){Sm$_2$(N(SiMe$_3$)$_2$)(thf)} (0.036 g, 0.034 mmol) under nitrogen was added a THF solution of silanol (0.003 g, 0.034 mmol) dropwise at room temperature. The reaction mixture was stirred for eight days at room temperature and the solvent was removed under vacuum. Then the greenish brown crude obtained was dissolved in pentane and concentrated by slow evaporation to get needle like crystals (18 mg, 58%). ^{1}H NMR (C_6D_6, 400 MHz): δ (ppm) -20.70 (s, THF, 8H), -11.76 (s, THF, 8H), -9.52 (s, C**H$_3$**, 24H), -5.71 (s, C**H$_2$**, 16H), -5.09 (s, C**H$_2$**, 16H), 0.22 (s, C**H$_3$**, 24H), 4.28 (s, C4**H$_2$**N, 8H), 10.79 (s, C4**H$_2$**N, 8H). NMR signals for this are broad due to paramagnetic nature of the compound. Elem. Anal. for $C_{80}H_{112}N_8O_4Sm_4$ calcd. C, 51.90; H, 6.10; N, 6.05; found: C, 51.92; H, 6.15; N, 5.95.

Preparation of (η^5: η^1: η^5: η^1 Et$_8$ -calix[4]pyrrolyl)Sm$_4$(μ-O)$_2$(thf)$_2$ with water: Nitrogen was bubbled through a few mL of DI water and a dilute solution of water in THF was prepared. One

equivalent of the above solution was added dropwise to a THF solution of (η^5: η^1: η^5: η^1 Et_8-calix[4]pyrrolyl){$Sm_2(N(SiMe_3)_2)(thf)$} (0.036 g, 0.034 mmol) under nitrogen at 0 °C. The reaction mixture was stirred for an hour at 0 °C and the solvent was removed under vacuum. Then the greenish brown crude obtained was dissolved in pentane and concentrated by slow evaporation to get crystals (10 mg, 33%). ^{1}H NMR (C_6D_6, 400 MHz): δ (ppm) -20.78 (s, THF, 8H), -11.52 (s, THF, 8H), -10.13 (s, C**H$_3$**, 24H), -5.76 (s, C**H$_2$**, 16H), -5.08 (s, C**H$_2$**, 16H), 0.22 (s, C**H$_3$**, 24H), 4.13 (s, C4**H$_2$**N, 8H), 10.82 (s, C4**H$_2$**N, 8H). NMR signals for this are broad due to paramagnetic nature of the compound. Elem. Anal. for $C_{80}H_{112}N_8O_4Sm_4$ calcd. C, 51.90; H, 6.10; N, 6.05; found: C, 51.97; H, 6.14; N, 6.00.

NMR

Calix[4]pyrrole:
^{1}H (400.144 MHz, $CDCl_3$)

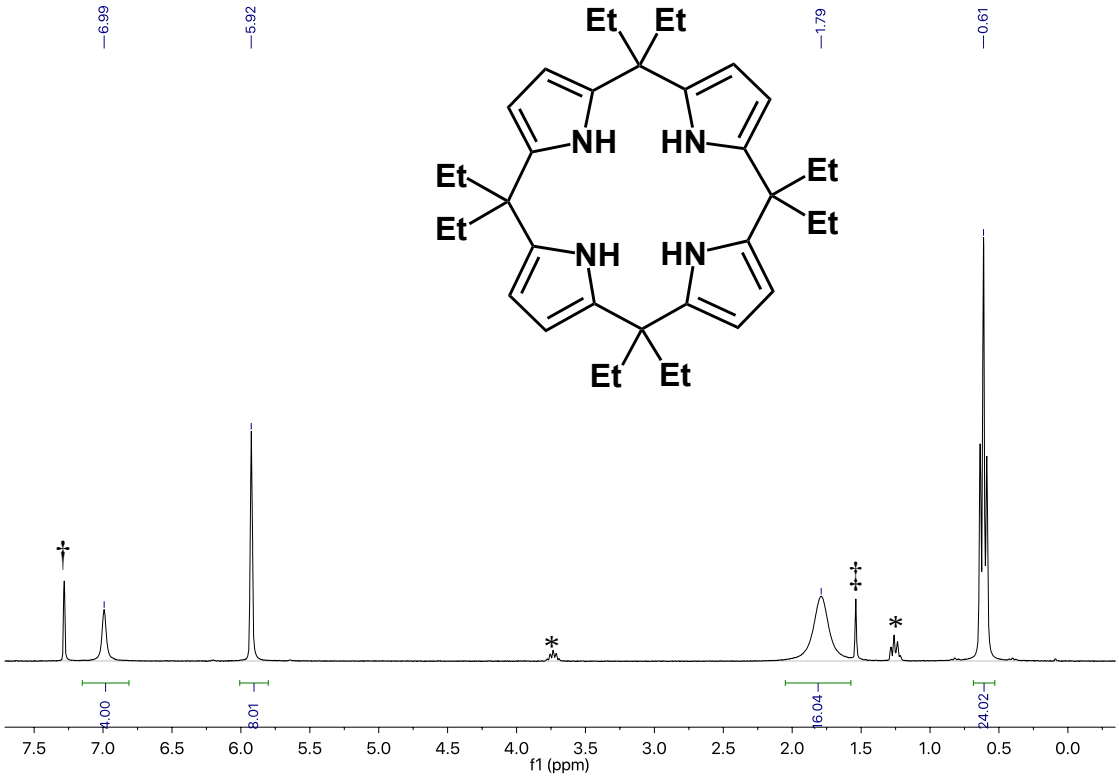

Figure S1: Proton NMR spectrum of Calix[4]pyrrole in $CDCl_3$. †residual $CHCl_3$, ‡H_2O, *iPrOH

$Sm(N(SiMe_3)_2)_3$ (μ-Cl)$Li(thf)_3$:
^1H (400.144 MHz, C_6D_6)

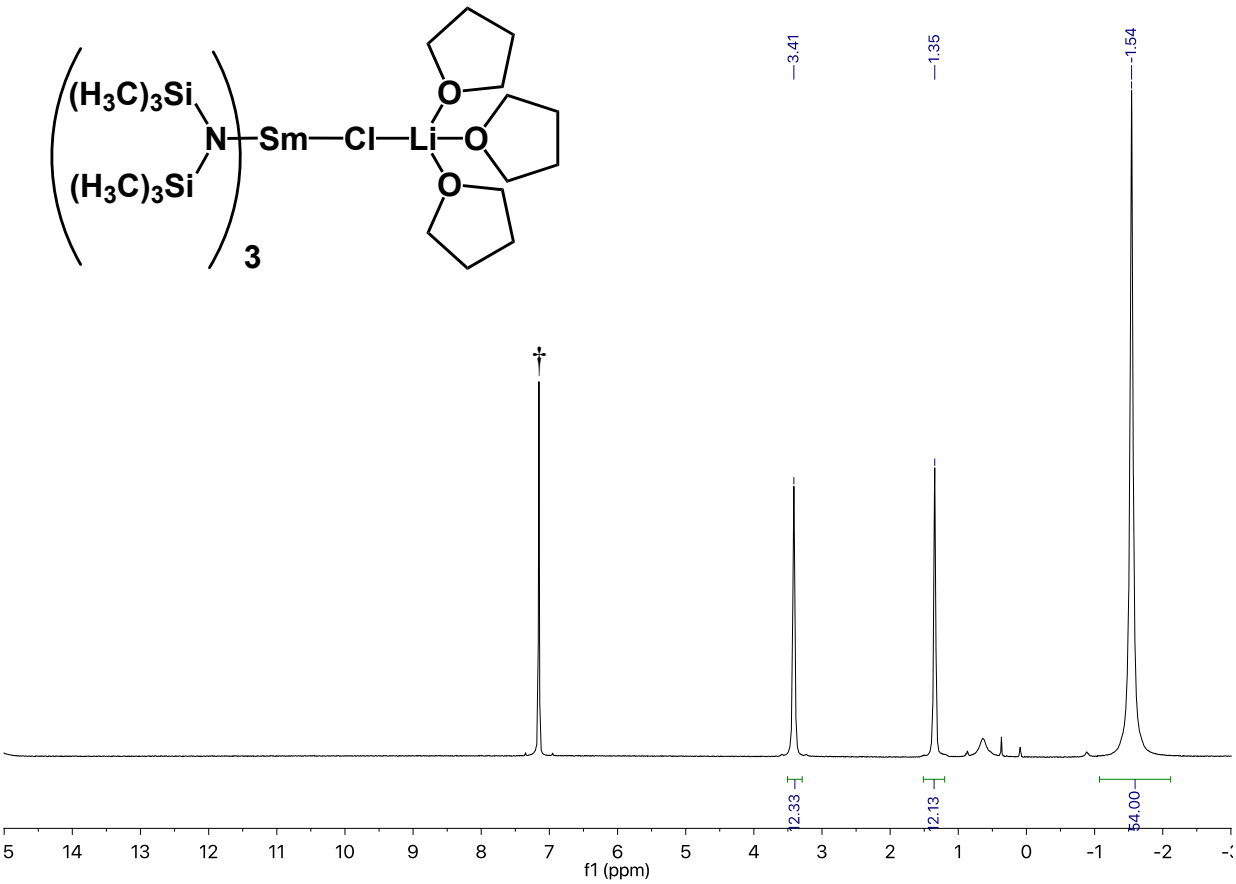

Figure S2: Proton NMR spectrum of $Sm(N(SiMe_3)_2)_3$ (μ-Cl)$Li(thf)_3$ in C_6D_6. †residual C_6H_6

$Eu(N(SiMe_3)_2)_3$ (μ-Cl)$Li(thf)_3$:
^1H (400.144 MHz, C_6D_6)

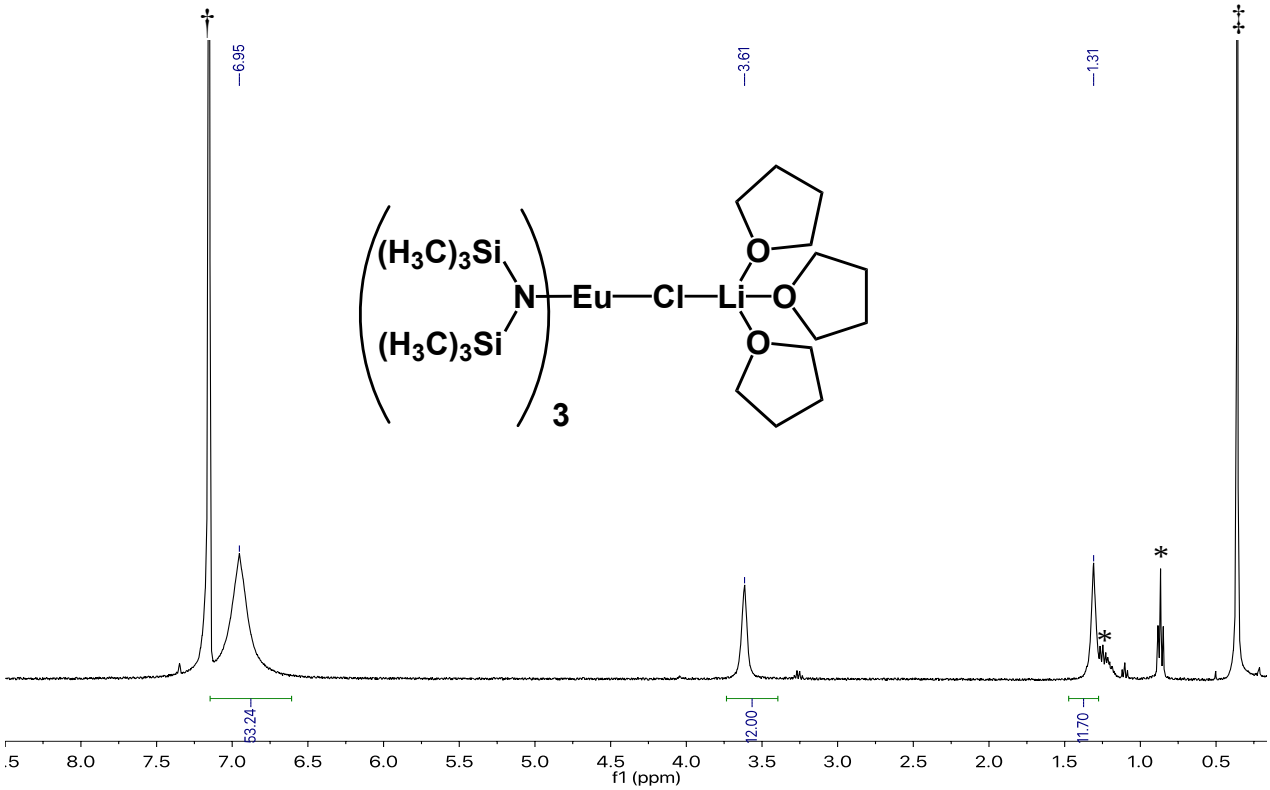

Figure S3: Proton NMR spectrum of $Eu(N(SiMe_3)_2)_3$ (μ-Cl)$Li(thf)_3$ in C_6D_6 †residual C_6H_6, ‡grease, *pentane.

(η^5: η^1: η^5: η^1 Et_8 -calix[4]pyrrolyl){$SmN(SiMe_3)_2$}$_2$:
^{1}H (400.144 MHz, C_6D_6)

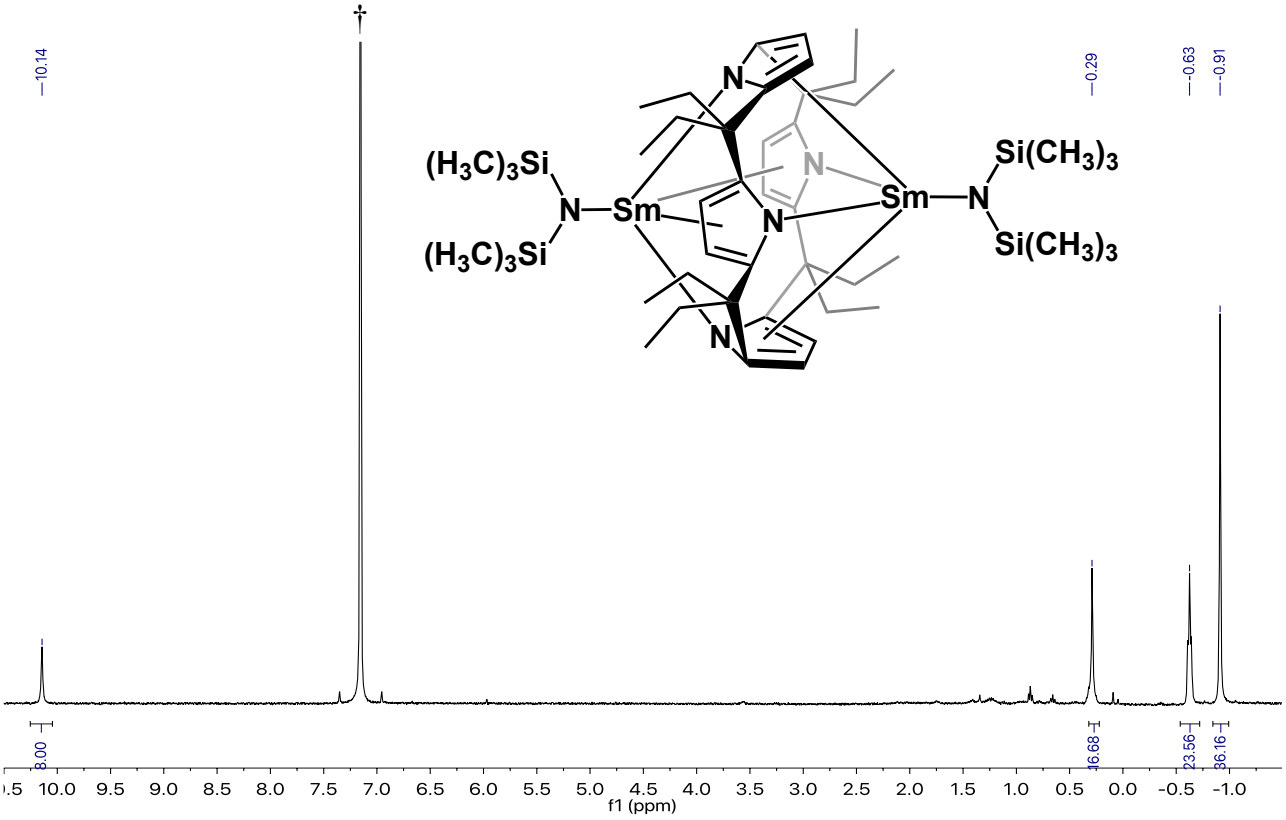

Figure S4: Proton NMR spectrum of (η^5: η^1: η^5: η^1 Et_8 -calix[4]pyrrolyl){$SmN(SiMe_3)_2$}$_2$ in C_6D_6, †residual C_6H_6

(η^5: η^1: η^5: η^1 Et_8 -calix[4]pyrrolyl){EuN($SiMe_3$)$_2$}$_2$:
^{1}H (400.144 MHz, C_6D_6)

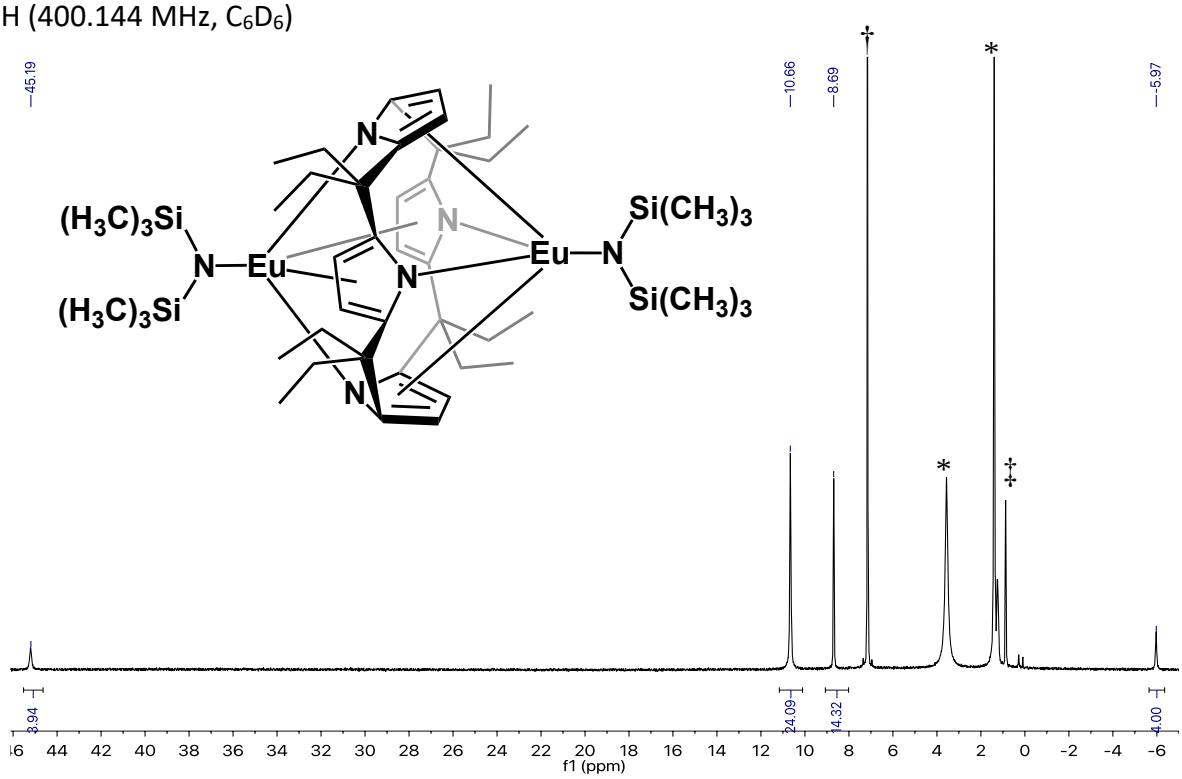

Figure S5: Proton NMR spectrum of (η^5: η^1: η^5: η^1 Et_8 -calix[4]pyrrolyl){EuN($SiMe_3$)$_2$}$_2$ in C_6D_6, †residual C_6H_6, ‡grease, *thf.

(η^5: η^1: η^5: η^1 Et_8 -calix[4]pyrrolyl){$Sm_2(N(SiMe_3)_2)(thf)$}:
^1H (400.144 MHz, C_6D_6)

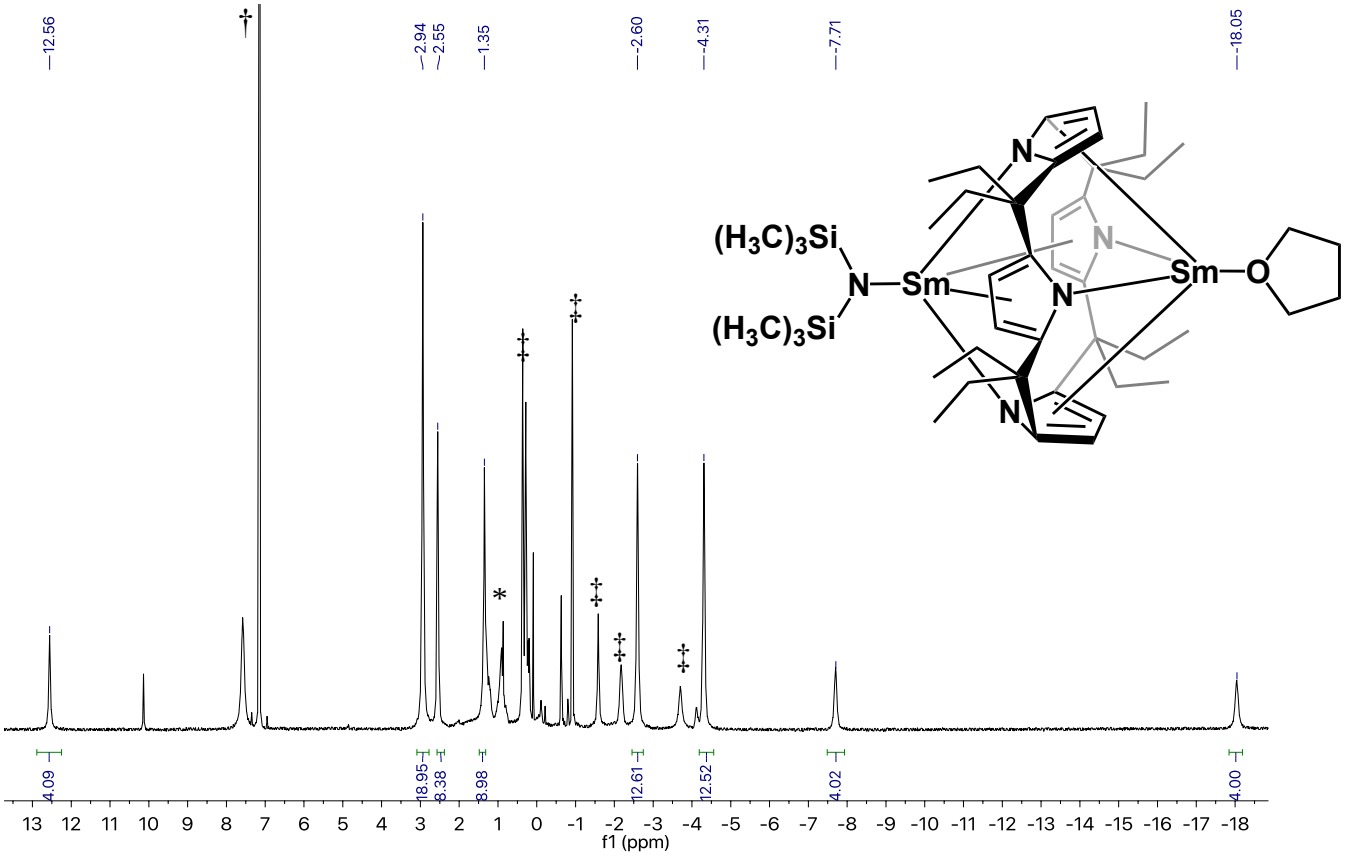

Figure S6: Proton NMR spectrum of (η^5: η^1: η^5: η^1 Et_8 -calix[4]pyrrolyl){$Sm_2(N(SiMe_3)_2)(thf)$} in C_6D_6, †residual C_6H_6, ‡unidentified impurity, *pentane.

(η^5: η^1: η^5: η^1 Et_8 -calix[4]pyrrolyl)$Sm_4(\mu\text{-}O)_2(thf)_2$
^1H (400.144 MHz, C_6D_6)

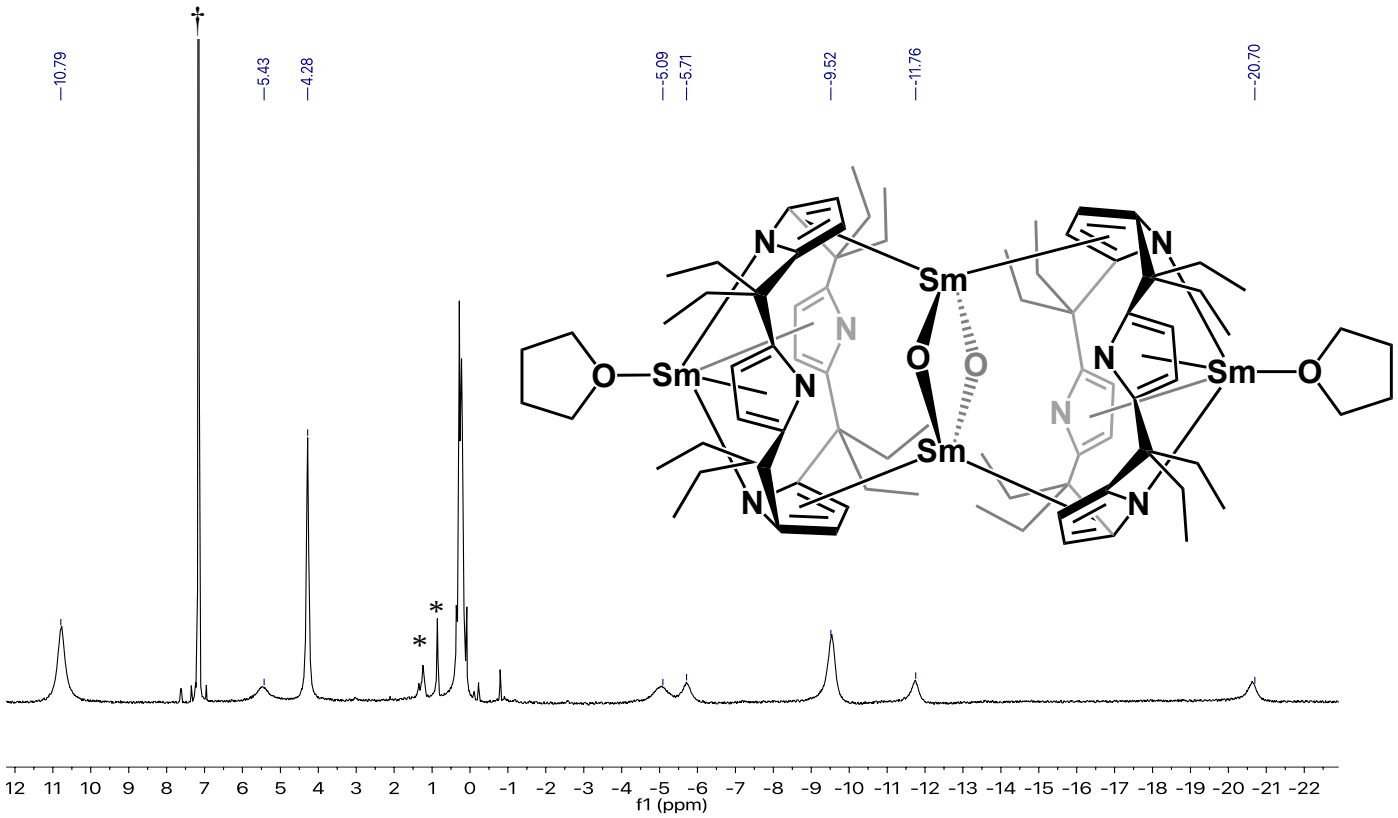

Figure S7: Proton NMR spectrum of (η^5: η^1: η^5: η^1 Et_8 -calix[4]pyrrolyl)$Sm_4(\mu\text{-}O)_2(thf)_2$ in C_6D_6, †residual C_6H_6, *pentane.

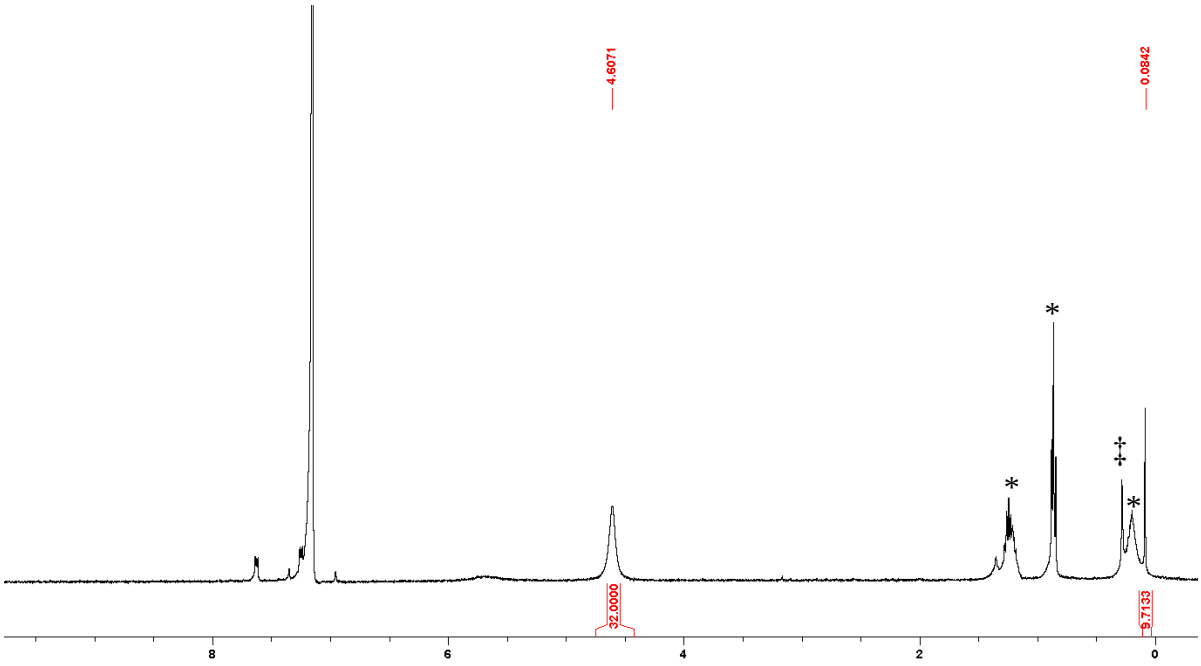

Figure S8: Proton NMR spectrum of the precipitate generated after addition of 12-crown-4, * pentane, ‡ grease

Photophysical Data

Absorption and emission of Sm complexes

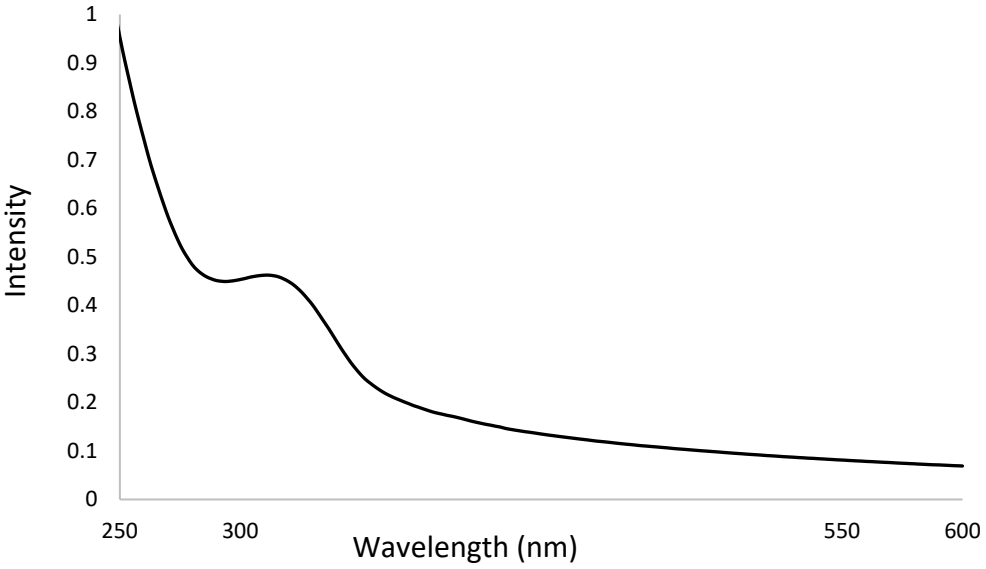

Figure S9: Absorption spectrum of (η^5: η^1: η^5: η^1 Et_8 -calix[4]pyrrolyl){$SmN(SiMe_3)_2$}$_2$ in pentane

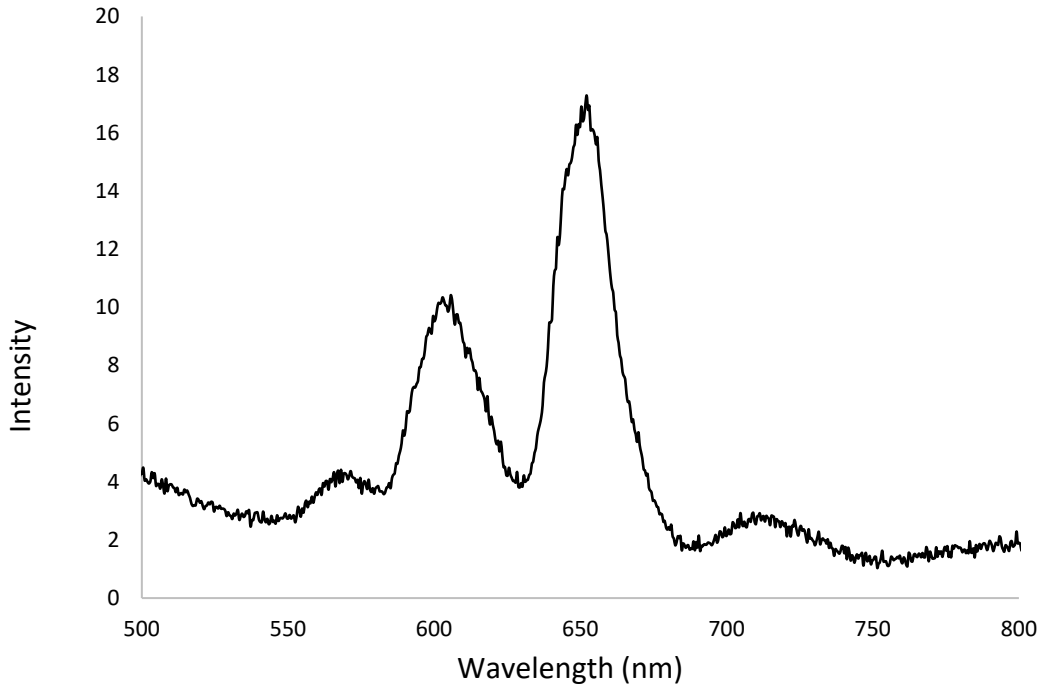

Figure S10: Emission spectrum of (η^5: η^1: η^5: η^1 Et_8 -calix[4]pyrrolyl){$SmN(SiMe_3)_2$}$_2$ in pentane. Excitation at 320 nm

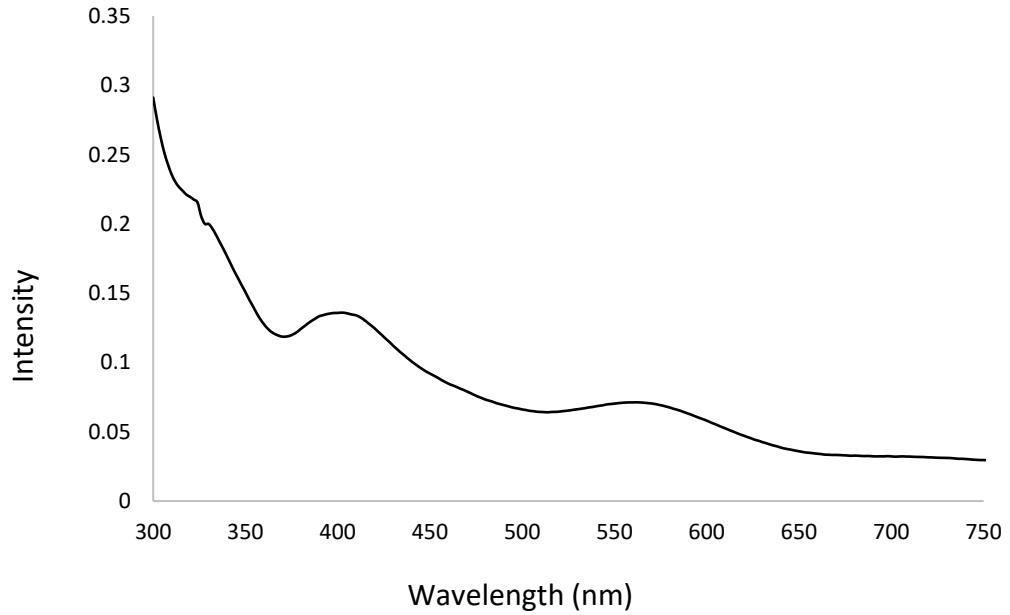

Figure S11: Absorption spectrum of (η^5: η^1: η^5: η^1 Et_8 -calix[4]pyrrolyl){$Sm_2(N(SiMe_3)_2)(thf)$} in pentane

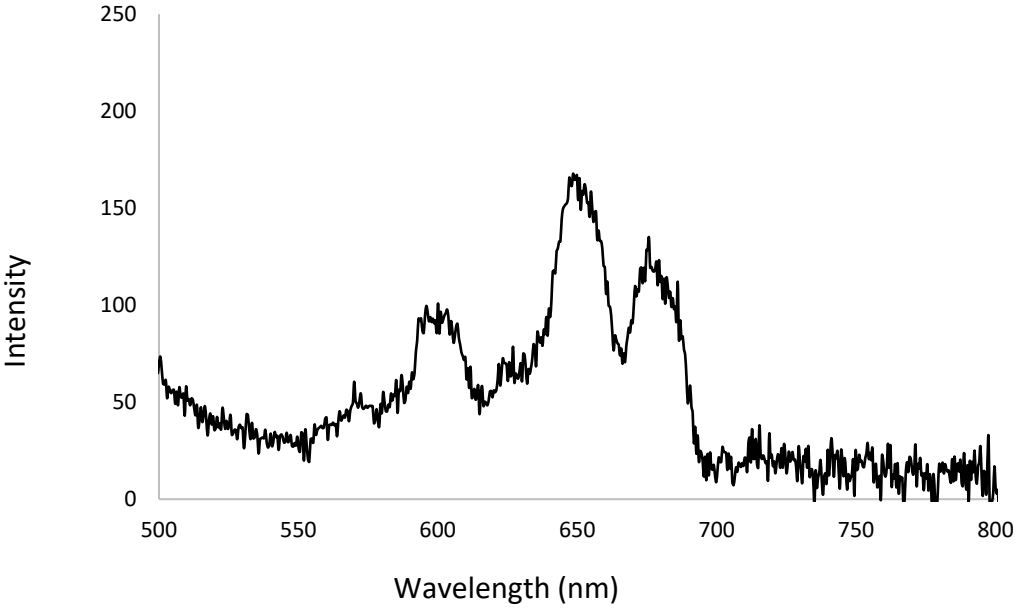

Figure S12: Emission spectrum of (η^5: η^1: η^5: η^1 Et_8 -calix[4]pyrrolyl){$Sm_2(N(SiMe_3)_2)(thf)$} in pentane. Excitation at 327 nm

Electrochemical Data

Cyclic voltammogram of (η^5: η^1: η^5: η^1 **Et$_8$** -calix[4]pyrrolyl){SmN(SiMe$_3$)$_2$}$_2$

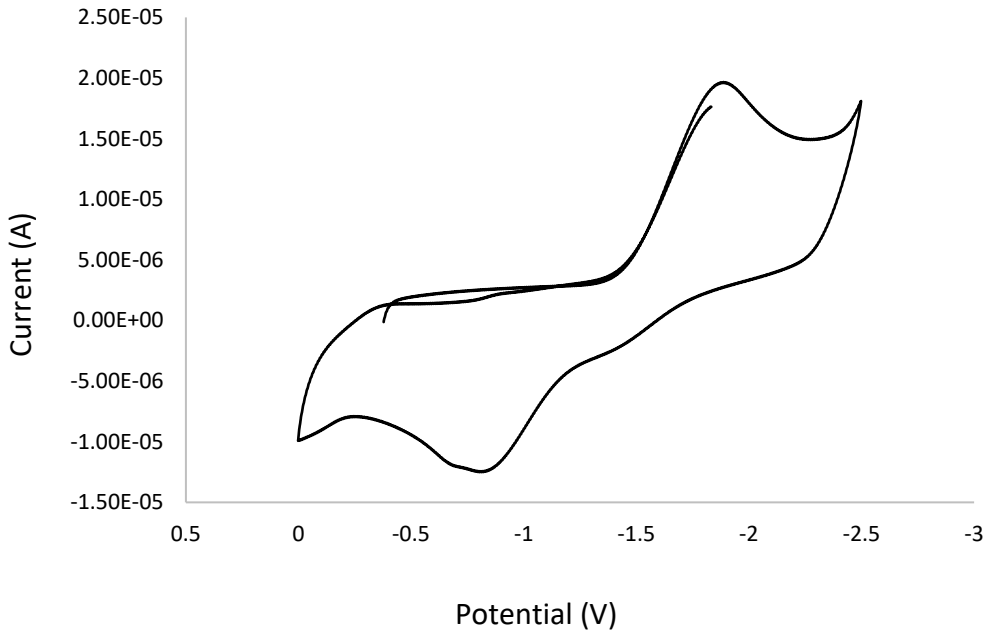

Figure S13: One electron reduction of (η^5: η^1: η^5: η^1 Et$_8$ -calix[4]pyrrolyl){SmN(SiMe$_3$)$_2$}$_2$

Cyclic voltammogram of (η^5: η^1: η^5: η^1 Et$_8$ -calix[4]pyrrolyl){EuN(SiMe$_3$)$_2$}$_2$

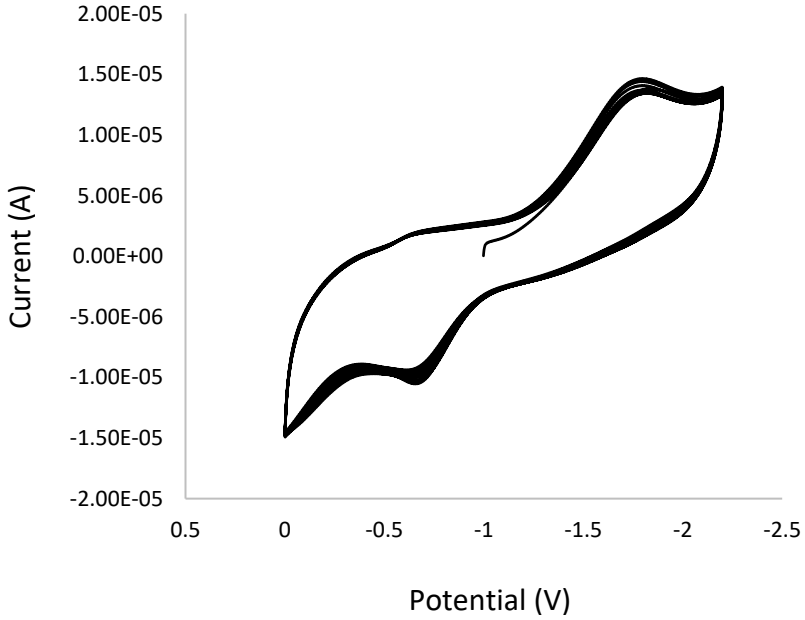

Figure S14: One electron reduction of (η^5: η^1: η^5: η^1 Et$_8$ -calix[4]pyrrolyl){EuN(SiMe$_3$)$_2$}$_2$

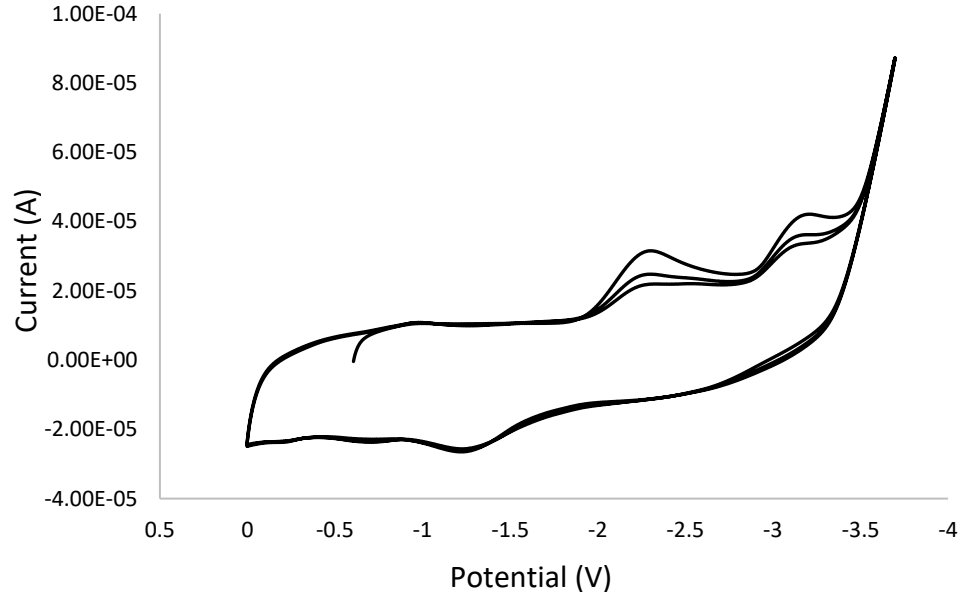

Figure S15: Extended voltammogram of (η^5: η^1: η^5: η^1 Et_8 -calix[4]pyrrolyl){$SmN(SiMe_3)_2$}$_2$

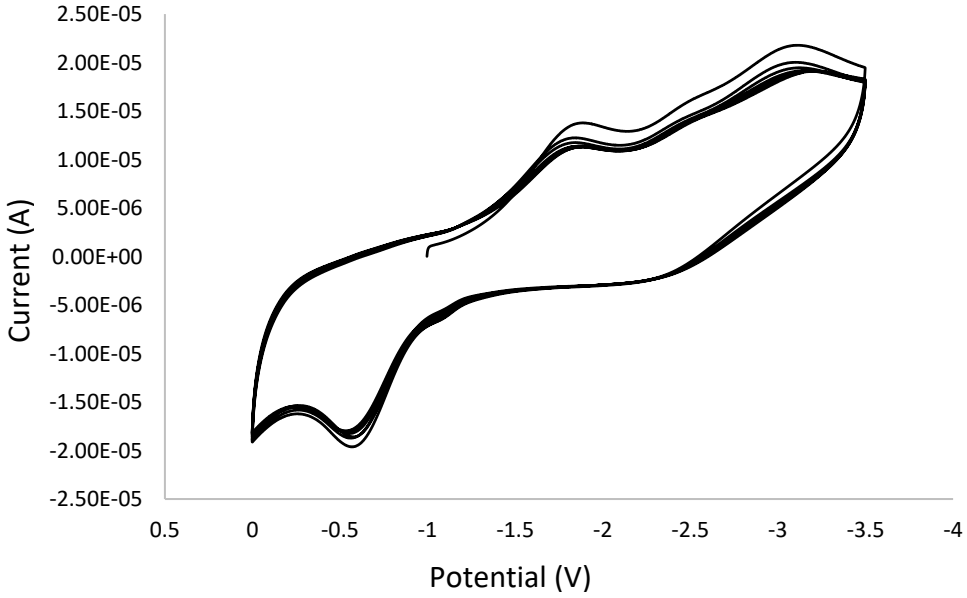

Figure S16: Extended voltammogram of (η^5: η^1: η^5: η^1 Et_8 -calix[4]pyrrolyl){$EuN(SiMe_3)_2$}$_2$

Mass Spectrometry

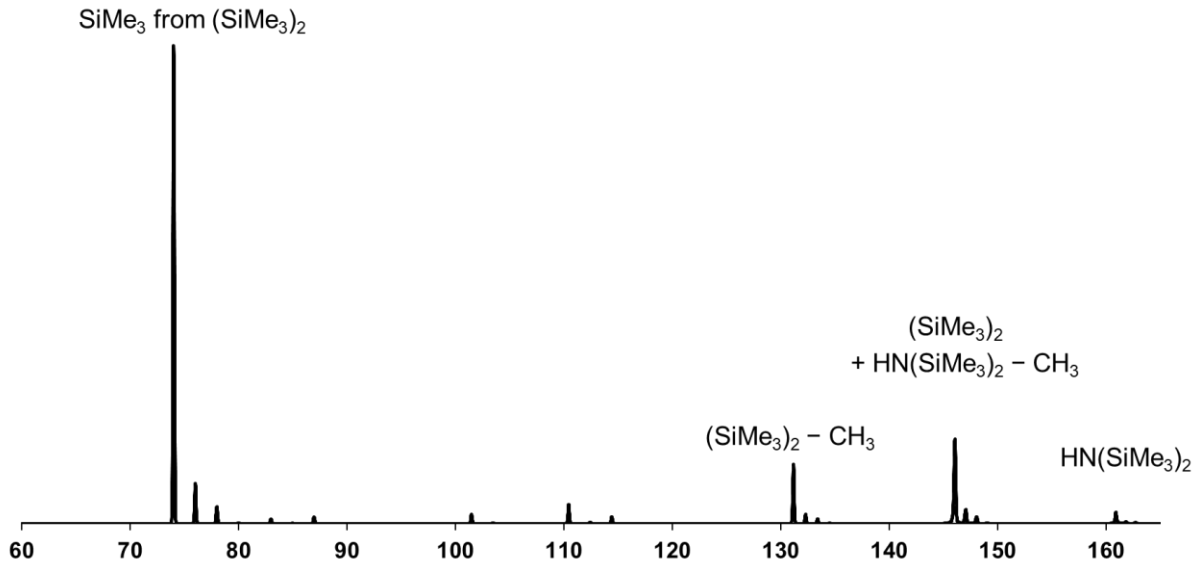

Figure S17: Electronic ionization high resolution mass spectrum of the volatiles obtained from the reaction with silanol.

X-Ray Crystallography

(η^5: η^1: η^5: η^1 Et_8 -calix[4]pyrrolyl){$SmN(SiMe_3)_2$}$_2$ Complex.

Crystal data and structure refinement for NM132 (1).

Identification code	NM132 (1)
Empirical formula	$C_{48}H_{84}N_6Si_4Sm_2$
Formula weight	1158.27
Temperature/K	100.01(10)
Crystal system	triclinic
Space group	P-1
a/Å	11.4659(3)
b/Å	11.7021(3)
c/Å	21.3015(6)
α/°	79.168(2)
β/°	79.681(2)
γ/°	76.855(2)
Volume/Å^3	2705.71(13)
Z	2
ρ_{calc}g/cm^3	1.422
μ/mm^{-1}	2.274
F(000)	1188.0
Crystal size/mm^3	0.399 × 0.386 × 0.275
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.576 to 60.552
Index ranges	-16 ≤ h ≤ 16, -16 ≤ k ≤ 15, -29 ≤ l ≤ 30
Reflections collected	65776
Independent reflections	14653 [R_{int} = 0.0552, R_{sigma} = 0.0440]
Data/restraints/parameters	14653/0/561
Goodness-of-fit on F^2	1.116
Final R indexes [I>=2σ (I)]	R_1 = 0.0395, wR_2 = 0.0823
Final R indexes [all data]	R_1 = 0.0460, wR_2 = 0.0850
Largest diff. peak/hole / e Å^{-3}	2.71/-1.25

(η^5: η^1: η^5: η^1 Et_8 -calix[4]pyrrolyl){$EuN(SiMe_3)_2$}$_2$ Complex.

Crystal data and structure refinement for NM210b (1).

Identification code	NM210b (1)
Empirical formula	$C_{48}H_{84}Eu_2N_6Si_4$
Formula weight	1161.49
Temperature/K	100.01(10)
Crystal system	triclinic
Space group	P-1
a/Å	11.4426(5)
b/Å	11.6392(5)
c/Å	21.2371(9)
α/°	79.337(4)
β/°	79.682(4)
γ/°	77.099(4)
Volume/Å^3	2681.2(2)
Z	2
ρ_{calc}g/cm^3	1.439
μ/mm^{-1}	2.444
F(000)	1192.0
Crystal size/mm^3	0.154 × 0.046 × 0.038
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.942 to 60.59
Index ranges	-14 ≤ h ≤ 16, -15 ≤ k ≤ 16, -29 ≤ l ≤ 29
Reflections collected	14131
Independent reflections	14131 [R_{int} = ?, R_{sigma} = 0.1208]
Data/restraints/parameters	14131/0/562
Goodness-of-fit on F^2	1.029
Final R indexes [I>=2σ (I)]	R_1 = 0.0585, wR_2 = 0.1056
Final R indexes [all data]	R_1 = 0.1028, wR_2 = 0.1237
Largest diff. peak/hole / e Å^{-3}	2.88/-2.00

(η^5: η^1: η^5: η^1 Et_8 -calix[4]pyrrolyl){$Eu_2(N(SiMe_3)_2)(thf)$}

Crystal data and structure refinement for NM100_2.

Identification code	NM100_2
Empirical formula	$C_{46}H_{74}Eu_2N_5OSi_2$
Formula weight	1073.20
Temperature/K	100.00(10)
Crystal system	monoclinic
Space group	C2/c
a/Å	13.7438(4)
b/Å	20.1221(6)
c/Å	17.6945(4)
α/°	90
β/°	90.855(2)
γ/°	90
Volume/Å^3	4892.9(2)
Z	4
ρ_{calc}g/cm^3	1.457
μ/mm^{-1}	2.626
F(000)	2188.0
Crystal size/mm^3	0.306 × 0.249 × 0.045
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.658 to 60.48
Index ranges	-18 ≤ h ≤ 18, -27 ≤ k ≤ 28, -23 ≤ l ≤ 24
Reflections collected	30304
Independent reflections	6620 [R_{int} = 0.0589, R_{sigma} = 0.0486]
Data/restraints/parameters	6620/0/262
Goodness-of-fit on F^2	1.097
Final R indexes [I>=2σ (I)]	R_1 = 0.0407, wR_2 = 0.0939
Final R indexes [all data]	R_1 = 0.0515, wR_2 = 0.0998
Largest diff. peak/hole / e Å^{-3}	3.20/-1.20

(η^5: η^1: η^5: η^1 Et_8 -calix[4]pyrrolyl)$Sm_4(\mu\text{-}O)_2(thf)_2$

Crystal data and structure refinement for NM229_twin1_hklf4.

Identification code	NM229_twin1_hklf4
Empirical formula	$C_{47}H_{64}N_4O_2Sm_2$
Formula weight	1017.72
Temperature/K	100.01(10)
Crystal system	monoclinic
Space group	C2/c
a/Å	17.9470(8)
b/Å	21.5868(6)
c/Å	23.2649(9)
α/°	90
β/°	108.706(4)
γ/°	90
Volume/Å^3	8537.1(6)
Z	8
ρ_{calc}g/cm^3	1.584
μ/mm^{-1}	20.763
F(000)	4112.0
Crystal size/mm^3	0.159 × 0.122 × 0.08
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	6.618 to 146.804
Index ranges	-22 ≤ h ≤ 21, -26 ≤ k ≤ 26, -28 ≤ l ≤ 28
Reflections collected	9870
Independent reflections	9870 [R_{int} = ?, R_{sigma} = 0.0443]
Data/restraints/parameters	9870/102/546
Goodness-of-fit on F^2	1.116
Final R indexes [I>=2σ (I)]	R_1 = 0.0659, wR_2 = 0.1888
Final R indexes [all data]	R_1 = 0.0831, wR_2 = 0.2030
Largest diff. peak/hole / e Å^{-3}	1.58/-2.33

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