Supporting Information

Construction of Polymeric and Oligomeric Lanthanide(III) Thiolates from Preformed Complexes $[(TMS)_2N]_3Ln(\mu\text{-}Cl)Li(THF)_3$ (Ln = Pr, Nd, Sm; $(TMS)_2N$ = bis(trimethylsilyl)amide)

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Experimental Section

Preparation of $[\{(Me_3Si)_2N\}_2(\mu\text{-}SPh)Pr(\mu\text{-}SPh)Li(THF)_2]_\infty$ (4)

Preparation of $Li[\{(Me_3Si)_2N\}_4Nd_4(\mu\text{-}SPh)_8]\cdot C_6H_6$ ($5\cdot C_6H_6$)

Preparation of $[(Me_3Si)_2N]_4(\mu_4\text{-}Cl)Sm_4(\mu\text{-}SPh)_4(\mu_3\text{-}Cl)_4Li(THF)$ (6)

Typical procedure for the ROP of ϵ-caprolactone

X-ray diffraction crystallography

References

Scheme S1

Table S1. Polymerization of ϵ-caprolactone catalysized by complexes **1**~**6**.

Table S2. Summary of crystallographic data for **4**~**8**.

Table S3. Experimental details of X-ray analysis of **4**.

Figure 1. Perspective view of a section of the polymeric chain of **4**. All hydrogen atoms are omitted for clarity.

Table S4. Experimental details of X-ray analysis of **5**.

Figure 2. Perspective view of the anion of **5**. All hydrogen atoms are omitted for clarity.

Table S5. Experimental details of X-ray analysis of **6**.

Figure 3. Molecular structure of **6**, with labeling scheme and 50% probability. The TMS, Ph groups and all hydrogen atoms are omitted for clarity.

Table S6. Experimental details of X-ray analysis of **7**.

Figure 4. Molecular structure of **7**, with labeling scheme and 50% probability. All hydrogen atoms are omitted for clarity.

Table S7. Experimental details of X-ray analysis of **8**.

Figure 5. Molecular structure of **8**, with labeling scheme and 50% probability. All hydrogen atoms are omitted for clarity.

Experimental Section

General: All manipulations were carried out under argon using standard Schlenk-techniques. Solvents (THF, toluene and n-hexane) were refluxed and distilled over sodium benzophenone ketyl under argon prior to use. $LnCl_3$[1] and $LiN(SiMe_3)_2$[2], $[(Me_3Si)_2N]_3Ln(\mu\text{-}Cl)Li(THF)_3$ (Ln = Pr (**1**), Nd (**2**), Sm (**3**))[3] were prepared according to published procedures. ϵ-Caprolactone purchased from ACROS Com., was dried by stirring with CaH_2 for 10 days, and then distilled under reduced pressure. Elemental analyses data were obtained on a Carlo-Erbo CHNO-S Elemental Analyzer. The IR spectra (KBr, disc) were recorded on a Nicolet MagNa-IR550 FT-IR spectrometer (4000-400 cm^{-1}). The uncorrected melting points were determined in argon-sealed capillary tubes on a Mel-Temo II apparatus. Molecular weight and molecular weight distributions were determined against polystyrene standard by gel permeation chromatography (GPC) on a Waters 1515 apparatus with three HR columns (HR-1, HR-2 and HR-4); THF was used as an eluent.

Preparation of $[\{(Me_3Si)_2N\}_2(\mu\text{-}SPh)Pr(\mu\text{-}SPh)Li(THF)_2]_\infty$ (4)

To a THF (30 mL) solution of **1** (1.45 g, 1.65 mmol) was slowly added a hexane (10 mL) solution of HSPh (1.27 mmol). The mixture was stirred at room temperature for overnight. The volatile species evaporate under vacuum, leaving an oily residue. Hexane (10 mL) was added to the residue, which was then stirred for a period of 15 min. After removal of the hexane by vacuum evaporation left a dry free-flowing power. The solid was washed thoroughly with hexane (20 mL) and then extracted with toluene (8 mL × 2) and the solution was combined and concentrated to about 10 mL. Colorless crystals of **4** was formed by cooling the solution to –18 °C for several days. Yield: 0.34 g (23 %). Anal. Calcd for $C_{32}H_{62}LiN_2O_2PrS_2Si_4$: C, 46.24; H, 7.52; N, 3.37 %. Found: C, 46.17; H, 7.81; N, 3.35 %. M.p.: 141-143 °C. IR (KBr, disk): 3060 (w), 2956 (m), 2878 (w), 1578 (m), 1473 (s), 1433 (m), 1251 (m), 1182 (m), 1086 (s), 1046 (m), 1024 (s), 934 (m), 885 (w), 738 (s), 694 (m), 660 (w), 477 (m), 417 (w) cm^{-1}.

The hexane solution was concentrated to about 10 mL. $[\{((Me_3Si)_2N)_2Pr(\mu'\text{-}Cl)Li(THF)_3\}(\mu\text{-}Cl)]_2$ (**7**) was formed by cooling the solution to 2 °C for several days. Yield: 0.14 g (11 %). M.p.: 101-103°C, Calc. for $C_{48}H_{120}Cl_4Li_2N_4Pr_2O_6Si_8$: C, 38.14; H, 8.00; N, 3.71 %. Found: C, 38.45; H, 8.12; N, 3.56 %. IR (KBr, disk): 2882 (s),

1627 (m), 1409 (m), 1255 (s), 1047 (s), 846 (s), 615 (w) cm^{-1}.

Preparation of Li·[{$(Me_3Si)_2N$}$_4$(μ_4-Cl)Nd_4(μ-SPh)$_8$]·C_6H_6 (5·C_6H_6)

Compound **5** was prepared as yellow crystals Li·[{$(Me_3Si)_2N$}$_4$(μ_4-Cl)Nd_4(μ-SPh)$_8$]·C_6H_6 and the unreacted precursor **2** from the reaction of anhydrous **2** (0.991 g, 1.12 mmol) with 10 mL hexane solution of HSPh (1.3 mmol) followed by procedures similar to those used in the preparation of **1** and **4**.

For **5**: Yield: 0.23 g (39 %). Anal. Calcd for $C_{72}H_{112}ClLiN_4Nd_4S_8Si_8$: C, 40.52; H, 5.29; N, 2.63 %. Found: C, 40.65; H, 5.43; N, 2.93 %. The solid does not melt, but turns opaque at about 90°C. IR (KBr, disk): 3011 (w), 2955 (w), 1578 (m), 1478 (s), 1411 (m), 1250 (s), 1180 (w), 1118 (w), 1085 (s), 1024 (m), 843 (s), 736 (s), 630 (w), 464 (w) cm^{-1}.

Preparation of [$(Me_3Si)_2N$]$_4$(μ_4-Cl)Sm_4(μ-SPh)$_4$(μ_3-Cl)$_4$Li(THF) (6)

Compound **6** was prepared as yellow crystals [{$(Me_3Si)_2N$}$_4$(μ_4-Cl)Sm_4(μ-SPh)$_4$(μ_3-Cl)$_4$Li(THF)] and pale yellow [{{$(Me_3Si)_2N$)$_2$Sm(μ'-Cl)Li(THF)$_2$}(μ_3-Cl)]$_2$ (**5**) from the reaction of anhydrous [$(Me_3Si)_2N$]$_3$Sm(μ-Cl)Li(THF)$_3$ (1.17 g, 1.31 mmol) with 10 mL hexane solution of HSPh (1.31 mmol) followed by procedures similar to those used in the preparation of **1** and **4**.

For **6**: Yield: 0.19 g (30 %). Anal. Calcd for $C_{52}H_{100}Cl_5LiN_4OS_4Si_8Sm_4$: C, 32.26; H, 5.21; N, 2.89 %. Found: C, 32.32; H, 5.33; N, 2.71 %. The solid appears to decompose above 90°C but melts around 213-217°C. IR (KBr, disk): 3047 (w), 2955 (s), 2895 (m), 1618 (w), 1598 (w), 1455 (s), 1418 (m), 1247 (s), 1092 (s), 1016 (m), 952 (s), 845 (s), 745 (s), 615 (m), 428 (m), 418 (m) cm^{-1}.

For **8**: Yield: 0.08 g (9 %). M.p. 105-107 °C. Anal. Calc for $C_{40}H_{104}Cl_4Li_2N_4O_4Si_8Sm_2$: C, 34.65; H, 7.56; N, 4.04 %. Found C, 34.73; H, 7.61; N, 4.13 %. IR (KBr, disk): 2881 (s), 1627 (m), 1404 (m), 1249 (s), 1047 (s), 841(m), 621 (w) cm^{-1}.

Typical procedure for the ring-opening polymerization of ϵ-caprolactone

An initiator, [{$(TMS)_2N$}$_2$(μ-SPh)Pr(μ-SPh)Li(THF)$_2$]$_\infty$ (0.0264g) was dissolved in 1.4 mL toluene and 0.34 mL THF. To the solution 0.34 mL of ϵ-caprolactone using a syringe at room temperature with vigorous magnetic stirring. The stirring was ceased in a few minutes due to the viscosity. The reaction mixture was quenched by the addition of 1 M HCl in EtOH after a fixed interval. The solution was then poured into 20 mL of petroleum ether to precipitate the

white oligomer. After being washed with methanol for three times, the resulting oligomer was collected and dried in vacuo.

X-ray diffraction crystallography

All measurements were made on a Rigaku Mercury CCD X-ray diffractometer (3 kV, sealed tube) by using graphite monochromated Mo-Kα (λ = 0.71070 Å). X-ray quality crystals of **4** ~ **8** were obtained directly from the above preparations. A colorless platelet of **4** with dimensions 0.14 × 0.50 × 0.45 mm, a blue chip of **5** with dimensions 0.18 × 0.36 × 0.40 mm, a yellow block of **6** with 0.19 × 0.45 × 0.40 mm, a colorless block of **7** with 0.40 × 0.30 × 0.45 mm, a colorless block of **8** with 0.44 × 0.44 × 0.50 mm were mounted in a sealed capillary. The collected data were reduced by using the program CrystalClear (Rigaku and MSC, Ver.1.3, 2001), and an empirical absorption correction was applied which resulted in transmission factors ranging from 0.520 to 0.830 for **4**, from 0.428 to 0.671 for **5**, from 0.267 to 0.563 for **6**, from 0.508 to 0.633 for **7**, from 0.386 to 0.418 for **8**. The reflection data were also corrected for Lorentz and polarization effects.

The structures of **4** ~ **8** were solved by direct methods[4] (**7**, and **8**) or heavy-atom Patterson methods[5] (**4**, **5** and **6**) and refined by full matrix least-squares on *F*.[6] Except O2, O3, C29 ~ C36 in **1**; C37 ~ C39 in **2**; O1, C49 ~ C52 in **3**; C23 in **4**; C16, C19, C20 in **5**, all the non-hydrogen atoms were refined anisotropically. All hydrogen atoms were introduced at the calculated positions and included in the structure-factor calculations. All the calculations were performed on a Dell workstation using the CrystalStructure crystallographic software package (Rigaku and MSC, Ver.3.60, 2004). Crystal and data collection parameters for **4** ~ **8** are summarized in **Table S1**.

References

(1) Taylor, M. D.; Carter, C. P. *J. Inorg. Nucl. Chem.* **1962**, *24*, 387.

(2) Ghotra, J. S.; Hursthouse, M. B.; Welch, A. J. *J. Chem. Soc., Chem. Commun.* **1973**, 669-670.

(3) Zhou, S. L.; Wang, S. W.; Yang, G. S.; Liu, X. Y.; Sheng, E. H.; Zhang, K. H.; Cheng, L.; Huang, Z. X. *Polyhedron* **2003**, *22*, 1019-1024.

(4) Sheldrick, G. M. *SHELXS-97:* Program for the Solution of Crystal Structure, University of Göttingen, Germany, 1997.

(5) Beurskens, P. T.; Admiral, G.; Beurskens, G.; Bosman, W. P.; Garcia-Granda, S.; Gould, R. O.; Smits, J. M. M.; Smykalla, C. *PATTY: The DIRDIF program system*, Technical, Report of the Crystallography Laboratory, University of Nijmegen, The Netherlands, 1992.

(6) Beurskens, P. T.; Admiral, G.; Beurskens, G.; Bosman, W. P.; Gelder, R. de., Israel, R., Smits, J. M. M., *DIRDIF-94: The DIRDIF-94 program system*, Technical, Report of the Crystallography Laboratory, University of Nijmegen, The Netherlands, 1992.

Scheme 1

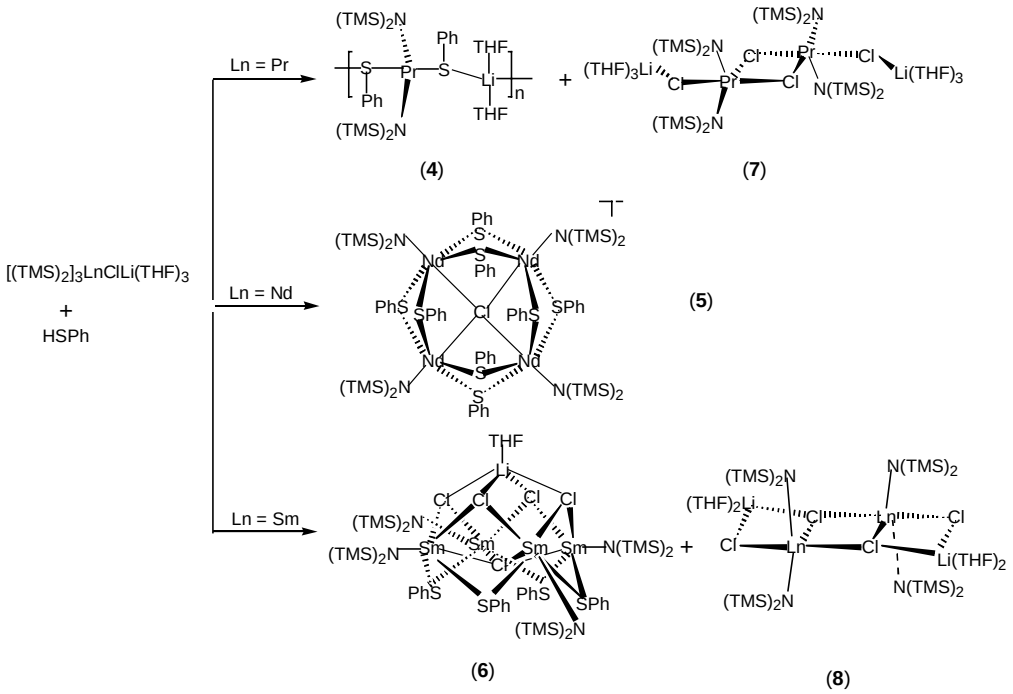

Table S1. Polymerization of ϵ-caprolactone catalysized by complexes **1**~**6**.[a]

entry[a]	cat.	time(min)	[monomer]/[cat.]	yield[b]	M_n($\times10^4$ g/mol)	M_w($\times10^4$ g/mol)	M_w/M_n[c]
1	**4**	20	400	75	3.33	5.09	1.53
2	**5**	8	400	99	2.27	3.04	1.34
3	**5**	15	600	99	2.87	4.01	1.40
5	**6**	8	400	99	2.61	3.70	1.42
6	**6**	15	600	99	3.41	4.94	1.45
7	**1**	20	400	59	2.71	5.55	2.05
8	**2**	20	400	53	2.88	5.61	1.95
9	**3**	20	400	46	2.93	5.83	1.99

(a) temperature: 298 K; solvent: THF/toluene (1:4); Vϵ-caprolactone : Vsolvent = 1:5; (b) yield: weight of polymer obtained/weight of monomer used; (c) Determined by GPC analysis in THF, calibrated to a polystyrene standard.

Table S2. Summary of crystallographic data for **4**~**8**.

Compound	**4**	**5·C_6H_6**	**6**
Empirical Formula	$C_{32}H_{62}LiN_2O_2PrS_2Si_4$	$C_{78}H_{118}ClLiN_4Nd_4S_8Si_8$	$C_{52}H_{100}Cl_5LiN_4S_4Si_8Sm_4$
Formula Weight	831.16	2212.34	1936.12
Crystal System	triclinic	monoclinic	triclinic
Space Group	*P*ī	*C2/c*	*P*ī
a (Å)	8.693(2)	18.305(2)	13.7062(11)
b (Å)	11.595(3)	24.227(2)	17.0964(13)
c (Å)	22.719(6)	24.326(3)	19.882(2)
α (°)	103.694(6)	90	75.817(4)
β (°)	95.940(6)	98.520(3)	83.698(5)
γ (°)	90.653(5)	90	77.496(4)
V (Å^3)	2211.4(10)	10669.3(19)	4401.8(6)
Z	2	4	2
ρ_{calc} (g/cm^3)	1.248	1.337	1.461
F(000)	852.00	4456.00	1920.00
μ (MoKa,cm^{-1})	1.331	2.221	3.016
R	0.0650	0.0520	0.0500
R_w	0.0780	0.0560	0.0650
GOF	1.007	1.003	1.055

To be continue **Table S2**.

Compound	**7**	**8**
Empirical Formula	$C_{48}H_{120}Cl_4Li_2N_4O_6Pr_2Si_8$	$C_{40}H_{104}Cl_4Sm_2Li_2N_4O_4Si_8$
Formula Weight	1511.70	1386.46
Crystal System	triclinic	monoclinic
Space group	*P*ī	*P*21/n
a (Å)	12.201(3)	13.1658(5)
b (Å)	13.088(3)	19.8100(7)
c (Å)	15.082(3)	13.5111(5)
α (°)	101.450(3)	90
β (°)	106.858(2)	94.190(2)
γ (°)	114.631(2)	90
V (Å^3)	1948.8(8)	3514.5(2)
Z	1	2
ρ_{calc} (g/cm^3)	1.288	1.310
F(000)	788.00	1428.00
μ (MoKa,cm^{-1})	1.534	1.976
R	0.0390	0.0390
Rw	0.0470	0.0510
GOF	1.015	1.069

Table S3. Experimental details of X-ray analysis of **4**

A. Crystal Data

Empirical Formula	$C_{32}H_{62}LiN_2O_2PrS_2Si_4$
Formula Weight	831.16
Crystal Color, Habit	colorless, platelet
Crystal Dimensions	0.14 X 0.50 X 0.45 mm
Crystal System	triclinic
Lattice Type	Primitive
Indexing Images	6 images @ 60.0 seconds
Detector Position	34.48 mm
Pixel Size	0.137 mm
Lattice Parameters	a = 8.693(2) Å
	b = 11.595(3) Å
	c = 22.719(6) Å
	α = 103.694(6)°
	β = 95.940(6)°
	γ = 90.653(5)°
	V = 2211.4(10) $Å^3$
Space Group	P-1 (#2)
Z value	2
D_{calc}	1.248 g/cm^3
F_{000}	852.00
μ(MoKα)	1.331 cm^{-1}

B. Intensity Measurements

Detector	Rigaku Mercury
Goniometer	Rigaku AFC8
Radiation	MoKα (λ = 0.71070 Å)
	graphite monochromated
Detector Aperture	70 mm x 70 mm
Data Images	720 exposures
ω oscillation Range (χ = 45.0, ϕ = 0.0)	-80.0 - 100.0°

Exposure Rate	10.0 sec./°
Detector Swing Angle	9.96°
ω oscillation Range (χ = 45.0, ϕ = 90.0)	-80.0 - 100.0°
Exposure Rate	10.0 sec./°
Detector Swing Angle	9.96°
Detector Position	34.48 mm
Pixel Size	0.137 mm
$2\theta_{max}$	55.0°
No. of Reflections Measured	Total: 25036
	Unique: 9942 (R_{int} = 0.058)
Corrections	Lorentz-polarization
	Absorption
	(trans. factors: 0.520-0.830)

C. Structure Solution and Refinement

Structure Solution	Patterson Methods (DIRDIF99 PATTY)
Refinement	Full-matrix least-squares on F
Function Minimized	Σ w (|Fo| - |Fc|)^2
Least Squares Weights	$1/[0.0008Fo^2+3.0000\sigma(Fo^2)+0.5000]$
$2\theta_{max}$ cutoff	55.0°
Anomalous Dispersion	All non-hydrogen atoms
No. Observations (I>3.00σ(I))	7167
No. Variables	446
Reflection/Parameter Ratio	16.07
Residuals: R (I>3.00σ(I))	0.0650
Residuals: R_w (I>3.00σ(I))	0.0780
Goodness of Fit Indicator	1.007
Max Shift/Error in Final Cycle	0.000
Maximum peak in Final Diff. Map	1.13 $e^-/Å^3$
Minimum peak in Final Diff. Map	-0.68 $e^-/Å^3$

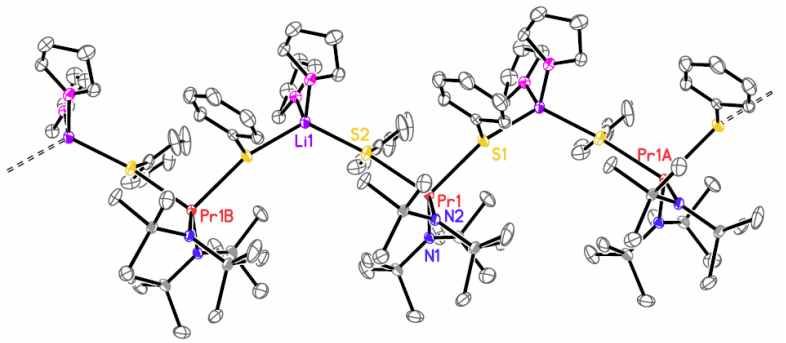

Figure 1. Perspective view of a section of the polymeric chain of **4**. All hydrogen atoms are omitted for clarity.

Table S4. Experimental details of X-ray analysis of **5**

A. Crystal Data	
Empirical Formula	$C_{78}H_{118}ClLiN_4Nd_4S_8Si_8$
Formula Weight	2212.34
Crystal Color, Habit	blue, chip
Crystal Dimensions	0.18 X 0.36 X 0.40 mm
Crystal System	monoclinic
Lattice Type	C-centered
Indexing Images	6 images @ 120.0 seconds
Detector Position	34.49 mm
Pixel Size	0.137 mm
Lattice Parameters	a = 18.305(2) Å
	b = 24.227(2) Å
	c = 24.326(3) Å
	β = 98.520(3) °
	V = 10669.3(19) $Å^3$
Space Group	C2/c (#15)
Z value	4
D_{calc}	1.377 g/cm^3
F_{000}	4456.00
μ(MoKα)	22.21 cm^{-1}

B. Intensity Measurements	
Detector	Rigaku Mercury
Goniometer	Rigaku AFC8
Radiation	MoKα (λ = 0.71070 Å)
	graphite monochromated
Detector Aperture	70 mm x 70 mm
Data Images	720 exposures
ω oscillation Range (χ = 45.0, ϕ = 0.0)	-80.0 - 100.0°
Exposure Rate	20.0 sec./°
Detector Swing Angle	9.93°

ω oscillation Range (χ = 45.0, ϕ = 90.0)	-80.0 - 100.0°
Exposure Rate	20.0 sec./°
Detector Swing Angle	9.93°
Detector Position	34.49 mm
Pixel Size	0.137 mm
$2\theta_{max}$	50.7°
No. of Reflections Measured	Total: 53499
	Unique: 9750 (R_{int} = 0.072)
Corrections	Lorentz-polarization
	Absorption
	(trans. factors: 0.428 – 0.671)

C. Structure Solution and Refinement

Structure Solution	Patterson Methods (DIRDIF99 PATTY)
Refinement	Full-matrix least-squares on F
Function Minimized	Σ w $(\|Fo\| - \|Fc\|)^2$
Least Squares Weights	$1/[0.0001Fo^2+2.0000\sigma(Fo^2)+0.5000]$
$2\theta_{max}$ cutoff	0.0°
Anomalous Dispersion	All non-hydrogen atoms
No. Observations (I>3.00σ(I))	4064
No. Variables	508
Reflection/Parameter Ratio	8.00
Residuals: R (I>3.00σ(I))	0.052
Residuals: Rw (I>3.00σ(I))	0.055
Goodness of Fit Indicator	1.003
Max Shift/Error in Final Cycle	0.000
Maximum peak in Final Diff. Map	1.07 $e^-/Å^3$
Minimum peak in Final Diff. Map	-0.69 $e^-/Å^3$

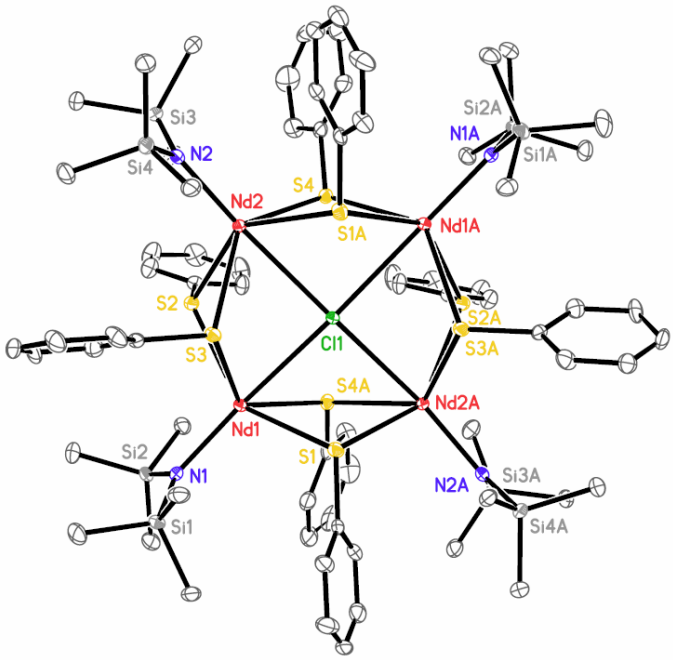

Figure 2. Perspective view of the anion of **5**. All hydrogen atoms are omitted for clarity.

Table S5. Experimental details of X-ray analysis of **6**

A. Crystal Data	
Empirical Formula	$C_{52}H_{100}Cl_5LiN_4OS_4Si_8Sm_4$
Formula Weight	1936.12
Crystal Color, Habit	yellow, block
Crystal Dimensions	0.19 X 0.45 X 0.40 mm
Crystal System	triclinic
Lattice Type	Primitive
Indexing Images	6 images @ 72.0 seconds
Detector Position	34.54 mm
Pixel Size	0.137 mm
Lattice Parameters	a = 13.7062(11) Å
	b = 17.0964(13) Å
	c = 19.882(2) Å
	α = 75.817(4) °
	β = 83.698(5) °
	γ = 77.496(4) °
	V = 4401.8(6) $Å^3$
Space Group	P-1 (#2)
Z value	2
D_{calc}	1.461 g/cm^3
F_{000}	1920.00
μ(MoKα)	3.016 cm^{-1}
B. Intensity Measurements	
Detector	Rigaku Mercury
Goniometer	Rigaku AFC8
Radiation	MoKα (λ = 0.71070 Å)
	graphite monochromated
Detector Aperture	70 mm x 70 mm
Data Images	720 exposures
ω oscillation Range (χ = 45.0, ϕ = 0.0)	-80.0 - 100.0°
Exposure Rate	12.0 sec./°
Detector Swing Angle	9.97°

ω oscillation Range (χ = 45.0, ϕ = 90.0)	-80.0 - 100.0°
Exposure Rate	12.0 sec./°
Detector Swing Angle	9.97°
Detector Position	34.54 mm
Pixel Size	0.137 mm
$2\theta_{max}$	55.0°
No. of Reflections Measured	Total: 49569
	Unique: 19710 (R_{int} = 0.036)
Corrections	Lorentz-polarization
	Absorption
	(trans. factors: 0.267 – 0.563)

C. Structure Solution and Refinement

Structure Solution	Patterson Methods (DIRDIF99 PATTY)
Refinement	Full-matrix least-squares on F
Function Minimized	Σ w (|Fo| - |Fc|)^2
Least Squares Weights	$1/[0.0010Fo^2+3.0000\sigma(Fo^2)+0.5000]$
$2\theta_{max}$ cutoff	0.0°
Anomalous Dispersion	All non-hydrogen atoms
No. Observations (I>3.00σ(I))	15339
No. Variables	777
Reflection/Parameter Ratio	19.74
Residuals: R (I>3.00σ(I))	0.050
Residuals: R_w (I>3.00σ(I))	0.065
Goodness of Fit Indicator	1.055
Max Shift/Error in Final Cycle	0.000
Maximum peak in Final Diff. Map	2.32 $e^-/Å^3$
Minimum peak in Final Diff. Map	-0.97 $e^-/Å^3$

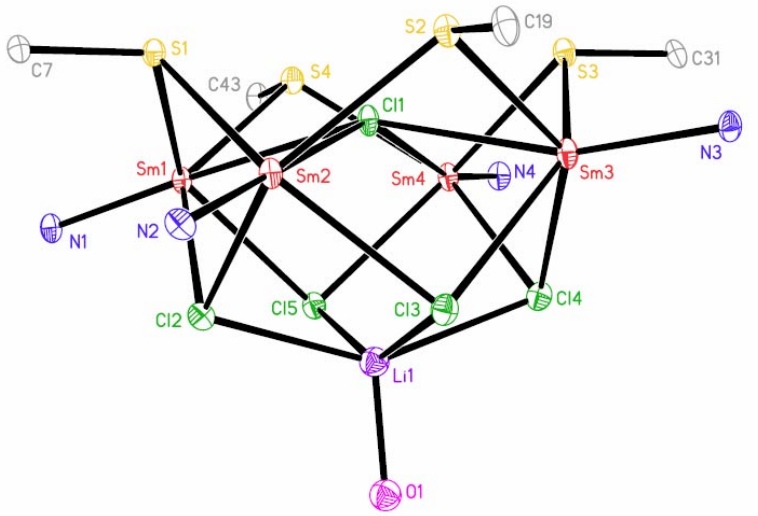

Figure 3. Molecular structure of **6**, with labeling scheme and 50% probability. The TMS, Ph and all hydrogen atoms are omitted for clarity..

Table S6. Experimental details of X-ray analysis of **7**.

A. Crystal Data

Empirical Formula	$C_{48}H_{120}Cl_4Li_2N_4O_6Pr_2Si_8$
Formula Weight	1511.70
Crystal Color, Habit	colorless, block
Crystal Dimensions	0.40 X 0.30 X 0.45 mm
Crystal System	triclinic
Lattice Type	Primitive
Detector Position	34.50 mm
Pixel Size	0.137 mm
Lattice Parameters	a = 12.201(3) Å
	b = 13.088(3) Å
	c = 15.082(3) Å
	α = 101.450(3) °
	β = 106.858(2) °
	γ = 114.631(2) °
	V = 1948.8(8) $Å^3$
Space Group	P-1 (#2)
Z value	1
D_{calc}	1.288 g/cm^3
F_{000}	788.00
μ(MoKa)	1.534 cm^{-1}

B. Intensity Measurements

Detector	Rigaku Mercury
Goniometer	Rigaku AFC8
Radiation	MoKa (l = 0.71070 Å)
	graphite monochromated
Detector Aperture	70 mm x 70 mm
Data Images	720 exposures
ω oscillation Range (χ = 45.0, ϕ = 0.0)	-80.0 - 100.0°
Exposure Rate	8.0 sec./°
Detector Swing Angle	9.94°
ω oscillation Range (χ = 45.0, ϕ = 90.0)	-80.0 - 100.0°

Exposure Rate	8.0 sec./°
Detector Swing Angle	9.94°
Detector Position	34.50 mm
Pixel Size	0.137 mm
$2\theta_{max}$	55.0°
No. of Reflections Measured	Total: 21818
	Unique: 8711 (R_{int} = 0.027)
Corrections	Lorentz-polarization
	Absorption
	(trans. factors: 0.508 – 0.633)

C. Structure Solution and Refinement

Structure Solution	Direct Methods (SHELX97)
Refinement	Full-matrix least-squares on F
Function Minimized	$\Sigma\ \omega\ (\|Fo\| - \|Fc\|)^2$
Least Squares Weights	$1/[0.0006Fo^2+3.0000\sigma(Fo^2)+0.5000]$
$2\theta_{max}$ cutoff	0.0°
Anomalous Dispersion	All non-hydrogen atoms
No. Observations (I>3.00σ(I))	7545
No. Variables	389
Reflection/Parameter Ratio	19.40
Residuals: R (I>3.00σ(I))	0.039
Residuals: R_w (I>3.00σ(I))	0.047
Goodness of Fit Indicator	1.015
Max Shift/Error in Final Cycle	0.000
Maximum peak in Final Diff. Map	1.55 $e^-/Å^3$
Minimum peak in Final Diff. Map	-0.88 $e^-/Å^3$

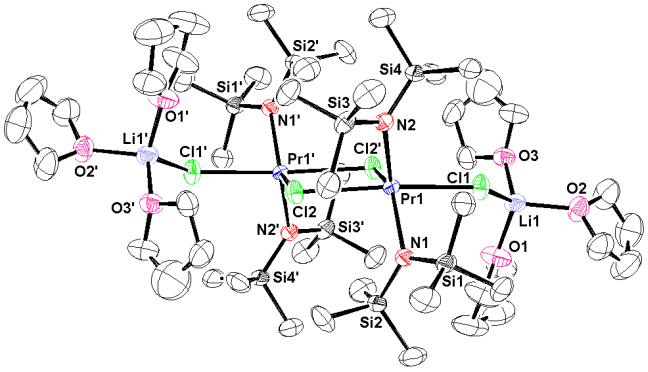

Figure 4. Molecular structure of **7**, with labeling scheme and 50% probability. All hydrogen atoms are omitted for clarity.

Table S7. Experimental details of X-ray analysis of **8**.

A. Crystal Data

Empirical Formula	$C_{40}H_{104}Cl_4Li_2N_4O_4Si_8Sm_2$
Formula Weight	1386.46
Crystal Color, Habit	colorless, block
Crystal Dimensions	0.44 X 0.44 X 0.50 mm
Crystal System	monoclinic
Lattice Type	Primitive
Detector Position	44.62 mm
Pixel Size	0.137 mm
Lattice Parameters	a = 13.1658(5) Å
	b = 19.8100(7) Å
	c = 13.5111(5) Å
	β = 94.190(2) °
	V = 3514.5(2) $Å^3$
Space Group	$P2_1/n$ (#14)
Z value	2
D_{calc}	1.310 g/cm^3
F_{000}	1428.00
μ(MoKα)	1.976 cm^{-1}

B. Intensity Measurements

Detector	Rigaku Mercury
Goniometer	Rigaku AFC8
Radiation	MoKα (λ = 0.71070 Å)
	graphite monochromated
Detector Aperture	70 mm x 70 mm
Data Images	720 exposures
ω oscillation Range (χ = 45.0, ϕ = 0.0)	-70.0 - 110.0°
Exposure Rate	12.0 sec./°

Detector Swing Angle	19.94°
ω oscillation Range (χ = 45.0, ϕ = 90.0)	-70.0 - 110.0°
Exposure Rate	12.0 sec./°
Detector Swing Angle	19.94°
Detector Position	44.62 mm
Pixel Size	0.137 mm
$2\theta_{max}$	55.0°
No. of Reflections Measured	Total: 27906
	Unique: 7996 (R_{int} = 0.025)
Corrections	Lorentz-polarization
	Absorption
	(trans. factors: 0.386 – 0.418)

C. Structure Solution and Refinement

Structure Solution	Patterson Methods (SHELX97)
Refinement	Full-matrix least-squares on F
Function Minimized	$\Sigma\ \omega\ (\|Fo\| - \|Fc\|)^2$
Least Squares Weights	$1/[0.0005Fo^2+2.0000\sigma(Fo^2)+0.5000]$
$2\theta_{max}$ cutoff	0.0°
Anomalous Dispersion	All non-hydrogen atoms
No. Observations (I>3.00σ(I))	6201
No. Variables	326
Reflection/Parameter Ratio	19.02
Residuals: R (I>3.00σ(I))	0.039
Residuals: R_w (I>3.00σ(I))	0.051
Goodness of Fit Indicator	1.069
Max Shift/Error in Final Cycle	0.000
Maximum peak in Final Diff. Map	1.58 $e^-/Å^3$
Minimum peak in Final Diff. Map	-0.70 $e^-/Å^3$

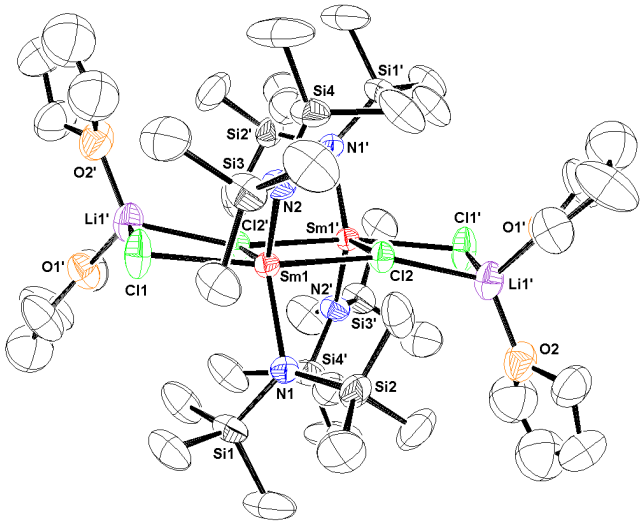

Figure 5. Molecular structure of **8**, with labeling scheme and 50% probability. All hydrogen atoms are omitted for clarity.