

Electronic Supplementary Information

Titanosiloxanes Consisting of Tetrahedrally Coordinated Ti Cores and Branched Siloxane Cages

Shohei Saito,^{a‡} Kenta Kawamura,^{a‡} Naoto Sato,^a Takamichi Matsuno,^{a,b} Hiroaki Wada,^a
Kazuyuki Kuroda,^{a,b} Atsushi Shimojima^{a,b*}

^a *Department of Applied Chemistry, Faculty of Science and Engineering, Waseda University, 3-4-1 Okubo, Shinjuku-ku, Tokyo 169-8555 (Japan), Fax: (+81)-3-5286-3281, E-mail: shimojima@waseda.jp*

^b *Kagami Memorial Research Institute for Materials Science and Technology, 2-8-26 Nishiwaseda, Shinjuku-ku, Tokyo 169-0051 (Japan)*

[‡] *These authors equally contributed to this work.*

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Experimental details

1. Materials

Acetonitrile (super anhydrous, FUJIFILM Wako Pure Chemical Co., 99.8%), trichloro(cyclopentadienyl)titanium(IV) (CpTiCl_3 , Tokyo Chemical Industry Co., Ltd., >98.0%), trichlorosilane (Tokyo Chemical Industry Co., Ltd., >98.0%), *N,N*-diethylhydroxylamine (Et_2NOH , Sigma-Aldrich Co., LLC., $\geq 98\%$), toluene (super anhydrous, FUJIFILM Wako Pure Chemical Co., 99.5%), 1,3,5,7,9,11,14-heptaisobutyltricyclo[7.3.3.1^{5,11}]heptasiloxane-endo-3,7,14-triol (${}^i\text{Bu}_7(\text{HO})_3\text{Si}_7\text{O}_9$, Sigma-Aldrich Co., LLC., 97%), tetrahydrofuran (THF, FUJIFILM Wako Pure Chemical Co., 99.5%), hexane (super anhydrous, FUJIFILM Wako Pure Chemical Co., 96.0%), and titanium(IV) chloride (TiCl_4 , FUJIFILM Wako Pure Chemical Co., 99.0%) were used as received. DOWEX (TM) 50Wx8 50-100 Mesh (H) cation exchange resin (FUJIFILM Wako Pure Chemical Co.) was dried under vacuum before use. Triethylamine (Et_3N , FUJIFILM Wako Pure Chemical Co., 99.0%) was dehydrated before use. The dehydration was performed using Molecular Sieves 3A 1/8 (pore size: 3 Å, pellet diameter: 1/8 inch, FUJIFILM Wako Pure Chemical Co.), followed by distillation.

2. Synthesis

2.1 Synthesis of ${}^i\text{Bu}_7(\text{HO})\text{Si}_8\text{O}_{12}$

${}^i\text{Bu}_7(\text{HO})\text{Si}_8\text{O}_{12}$ was synthesized by reacting mono-hydride POSS (${}^i\text{Bu}_7\text{HSi}_8\text{O}_{12}$) with H_2O in the presence of Et_2NOH as a catalyst. ${}^i\text{Bu}_7\text{HSi}_8\text{O}_{12}$ was obtained by reacting incompletely condensed POSS (${}^i\text{Bu}_7(\text{HO})_3\text{Si}_7\text{O}_9$) with trichlorosilane (HSiCl_3) according to a previous procedure.^[1] To a mixture of ${}^i\text{Bu}_7\text{HSi}_8\text{O}_{12}$ and H_2O in THF, a 1 vol% solution of Et_2NOH in THF was added. The molar ratio of ${}^i\text{Bu}_7\text{HSi}_8\text{O}_{12} : \text{H}_2\text{O} : \text{Et}_2\text{NOH}$ was 1 : 40 : 0.03. The mixture was stirred at room temperature for 1 d, and then a strong-acid cation-exchange resin was added, and the mixture was stirred for further 3 h to remove Et_2NOH . The resin was removed by filtration and the solvent was removed from the filtrate under reduced pressure to give ${}^i\text{Bu}_7(\text{HO})\text{Si}_8\text{O}_{12}$ as a white solid (yield: 98%).

${}^i\text{Bu}_7(\text{HO})\text{Si}_8\text{O}_{12}$. ${}^1\text{H}$ NMR (500.16 MHz; CDCl_3 ; 25 °C; TMS) $\delta = 0.56\text{--}0.66$ ppm (14H, $\text{SiCH}_2\text{CH}(\text{CH}_3)_2$), 0.92–1.02 ppm (42H, $\text{SiCH}_2\text{CH}(\text{CH}_3)_2$), 1.80–1.92 ppm (7H, $\text{SiCH}_2\text{CH}(\text{CH}_3)_2$); ${}^{13}\text{C}$ NMR (126.77 MHz; CDCl_3 ; 25 °C; TMS) $\delta = 22.34, 22.44, 22.50$, and 22.56 ppm ($\text{SiCH}_2\text{CH}(\text{CH}_3)_2$), 23.83 and 23.88 ppm ($\text{SiCH}_2\text{CH}(\text{CH}_3)_2$), 25.70 ppm ($\text{SiCH}_2\text{CH}(\text{CH}_3)_2$); ${}^{29}\text{Si}$ NMR (99.37 MHz; CDCl_3 ; 25 °C; TMS) $\delta = -66.74$ ppm (3Si, $(\text{SiO})_3\text{SiCH}_2\text{CH}(\text{CH}_3)_2$), -67.80 ppm (4Si, $(\text{SiO})_3\text{SiCH}_2\text{CH}(\text{CH}_3)_2$), -101.04 ppm (1Si, $(\text{SiO})_3\text{Si}(\text{OH})$).

2.2 Synthesis of (*i*Bu₇Si₈O₁₃)₄Ti

(*i*Bu₇Si₈O₁₃)₄Ti was synthesized by the reaction of *i*Bu₇(HO)Si₈O₁₂ with TiCl₄ in a hexane solution containing Et₃N to trap HCl as triethylamine hydrochloride (Et₃N·HCl). *i*Bu₇(HO)Si₈O₁₂ and Et₃N were dissolved in hexane (40 mL per 1 g of *i*Bu₇(HO)Si₈O₁₂). A 5 vol% solution of TiCl₄ in hexane was slowly added to a hexane solution of *i*Bu₇(HO)Si₈O₁₂ and Et₃N. The molar ratio of *i*Bu₇(HO)Si₈O₁₂ : TiCl₄ : Et₃N was 4 : 1 : 4.8. After stirring the mixture at 0 °C for 6 h, Et₃N·HCl was removed by filtration. Note that the filtration was performed under N₂ atmosphere because (*i*Bu₇Si₈O₁₃)₄Ti is sensitive to H₂O. By removing hexane under reduced pressure, a powder containing (*i*Bu₇Si₈O₁₃)₄Ti was obtained. The powder was purified by recrystallization. After dissolution of the powder in the binary acetonitrile-toluene solvent (0.3 mL of acetonitrile and 0.5 mL of toluene per 0.1 g of the powder) at 70 °C, the mixture was cooled at room temperature for 1 d. Then, (*i*Bu₇Si₈O₁₃)₄Ti was obtained as colorless needle crystals (yield: 33%).

(*i*Bu₇Si₈O₁₃)₄Ti. ¹H NMR (500.16 MHz; CDCl₃; 25 °C; TMS) δ = 0.56–0.65 ppm (14H, SiCH₂CH(CH₃)₂), 0.91–1.03 ppm (42H, SiCH₂CH(CH₃)₂), 1.79–1.93 ppm (7H, SiCH₂CH(CH₃)₂); ¹³C NMR (126.77 MHz; CDCl₃; 25 °C; TMS) δ = 22.31 and 22.58 ppm (SiCH₂CH(CH₃)₂), 23.77, 23.85, and 23.90 ppm (SiCH₂CH(CH₃)₂), 25.75 and 25.85 ppm (SiCH₂CH(CH₃)₂); ²⁹Si NMR (99.37 MHz; CDCl₃; 25 °C; TMS) δ = –66.97 ppm (12Si, (SiO)₃SiCH₂CH(CH₃)₂), –67.89 ppm (4Si, (SiO)₃SiCH₂CH(CH₃)₂), –68.01 ppm (12Si, (SiO)₃SiCH₂CH(CH₃)₂), –115.15 ppm (4Si, (SiO)₃SiOTi); MALDI-TOF MS calcd for C₁₁₂H₂₅₂O₅₂Si₃₂TiNa⁺ [M + Na]⁺: 3400.8; found: 3401.9.

2.3 Synthesis of (*i*Bu₇Si₈O₁₃)₃TiCp

(*i*Bu₇Si₈O₁₃)₃TiCp was synthesized by the reaction of *i*Bu₇(HO)Si₈O₁₂ with CpTiCl₃ in a hexane solution containing Et₃N. After *i*Bu₇(HO)Si₈O₁₂ and Et₃N were dissolved in hexane (50 mL per 1 g of *i*Bu₇(HO)Si₈O₁₂), a 0.7 wt% solution of CpTiCl₃ in toluene was added. The molar ratio of *i*Bu₇(HO)Si₈O₁₂ : CpTiCl₃ : Et₃N was 3 : 1 : 3.2. After stirring the mixture at room temperature for 1 d, Et₃N·HCl was removed by filtration. Note that the filtration was performed under a N₂ atmosphere because (*i*Bu₇Si₈O₁₃)₃TiCp is sensitive to H₂O. By removing hexane and toluene under reduced pressure, a yellow powder containing (*i*Bu₇Si₈O₁₃)₃TiCp was obtained. After GPC separation, (*i*Bu₇Si₈O₁₃)₃TiCp was obtained (yield: 35%).

(*i*Bu₇Si₈O₁₃)₃TiCp. ¹H NMR (500.16 MHz; CDCl₃; 25 °C; TMS) δ = 0.54–0.68 ppm (SiCH₂CH(CH₃)₂), 0.91–1.03 ppm (SiCH₂CH(CH₃)₂), 1.78–1.96 ppm (SiCH₂CH(CH₃)₂), 6.53 ppm (C₅H₅); ¹³C NMR (126.77 MHz; CDCl₃; 25 °C; TMS) δ = 22.31, 22.42, and

22.55 ppm ($\text{SiCH}_2\text{CH}(\text{CH}_3)_2$), 23.81 and 23.86 ppm ($\text{SiCH}_2\text{CH}(\text{CH}_3)_2$), 25.69, 25.72, 25.73, and 25.83 ppm ($\text{SiCH}_2\text{CH}(\text{CH}_3)_2$), 116.26 ppm (C_5H_5); ^{29}Si NMR (99.37 MHz; CDCl_3 ; 25 °C; TMS) $\delta = -67.06$ ppm ($(\text{SiO})_3\text{SiCH}_2\text{CH}(\text{CH}_3)_2$), -67.78 ppm ($(\text{SiO})_3\text{SiCH}_2\text{CH}(\text{CH}_3)_2$), -67.85 ppm ($(\text{SiO})_3\text{SiCH}_2\text{CH}(\text{CH}_3)_2$), -111.54 ppm ($(\text{SiO})_3\text{SiOTiC}_5\text{H}_5$); MALDI-TOF MS calcd for $\text{C}_{89}\text{H}_{194}\text{O}_{39}\text{Si}_{24}\text{TiNa}^+ [\text{M} + \text{Na}]^+$: 2633.4; found: 2634.5.

Note that suitable intensity ratio of $(^i\text{Bu}_7\text{Si}_8\text{O}_{13})_3\text{TiCp}$ could not be obtained in the ^1H and ^{29}Si NMR spectra because the signals of impurity ($^i\text{Bu}_7(\text{HO})\text{Si}_8\text{O}_{12}$) overlapped to the signals of $(^i\text{Bu}_7\text{Si}_8\text{O}_{13})_3\text{TiCp}$.

2.4 Characterization

Solution-state ^1H , ^{13}C , and ^{29}Si NMR spectra were recorded on a JNM-ECZ 500 (JEOL) spectrometer with resonance frequencies of 500.16 MHz, 126.77 MHz, and 99.37 MHz, respectively, at ambient temperature. Sample solutions were put in 5 mm glass tubes. The chemical shifts were referenced to internal tetramethylsilane (TMS) at 0 ppm. Chloroform-*d* (CDCl_3) was used to obtain lock signals. In the case of $(^i\text{Bu}_7\text{Si}_8\text{O}_{13})_4\text{Ti}$, CDCl_3 was dehydrated before use to avoid hydrolysis of the Si–O–Ti bonds. The dehydration was performed using Molecular Sieves 3A 1/8. The ^{29}Si NMR measurement was performed with a 45° pulse and a recycle delay of 30 s for quantitative analyses. Matrix-assisted laser desorption/ionization mass (MALDI-TOF MS) spectra were recorded on a Bruker Autoflex instrument using dithranol as a matrix and sodium trifluoroacetate as a cationization agent. Single crystal X-ray structural analysis was performed on a XtaLAB PRO MM007 (Rigaku) diffractometer using a graphite monochromated Mo-K α ($\lambda = 0.71073 \text{ \AA}$) radiation. The structure was solved by direct methods using Olex². All calculations were performed using the Crystal Structure crystallographic software package. Refinement was performed using CrysAis^{Pro} Version 1.171.39.33c. Crystal structure models were created using VESTA software. Powder XRD measurements were performed on a RINT Ultima III diffractometer with a parallel beam geometry equipped with a scintillation detector and a parabolic multilayer mirror using Cu-K α radiation. Diffuse reflectance (DR) ultraviolet–visible (UV–Vis) spectra were recorded on a JASCO V-650 spectrophotometer with polytetrafluoroethylene polymer (Spectralon: 6916-H422A) as a reference. Gel permeation chromatography (GPC) was carried out by a LC-9100 Recycling Preparative HPLC system (Japan Analytical Industry Co., Ltd.) equipped with a refractive index (RI) detector. Two types of cross-linked polystyrene-divinylbenzene copolymer packed columns (YMC-GPC

T2000 and YMC-GPC T4000; exclusion limits of 2000 and 4000, respectively, and theoretical plate of > 20000) were used with chloroform as the eluent at a flow rate of 7.0 mL min⁻¹. Optical microscope images were taken on an OLYMPUS BX51 apparatus. The visualizing of molecular models was performed in CrystalMaker and VESTA (version 3).^[2]

Data

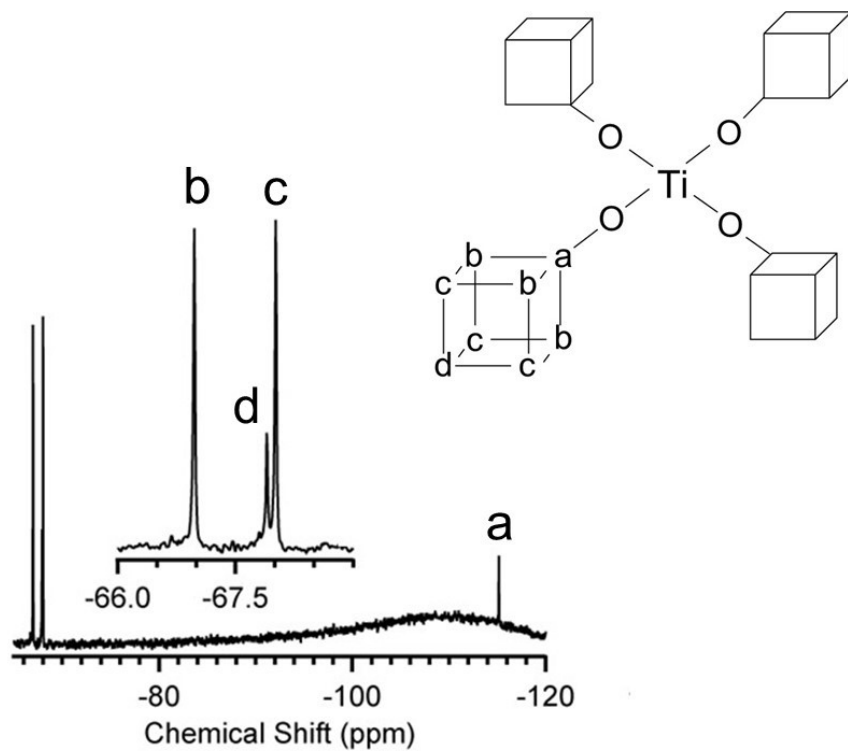


Fig. S1 ^{29}Si NMR signal assignments of $(t\text{Bu}_7\text{Si}_8\text{O}_{13})_4\text{Ti}$. Note that the assignments of the two signals at -66.97 and -68.01 ppm were speculated with reference to the ^{29}Si NMR chemical shifts of Ti-POSS complexes.^[3]

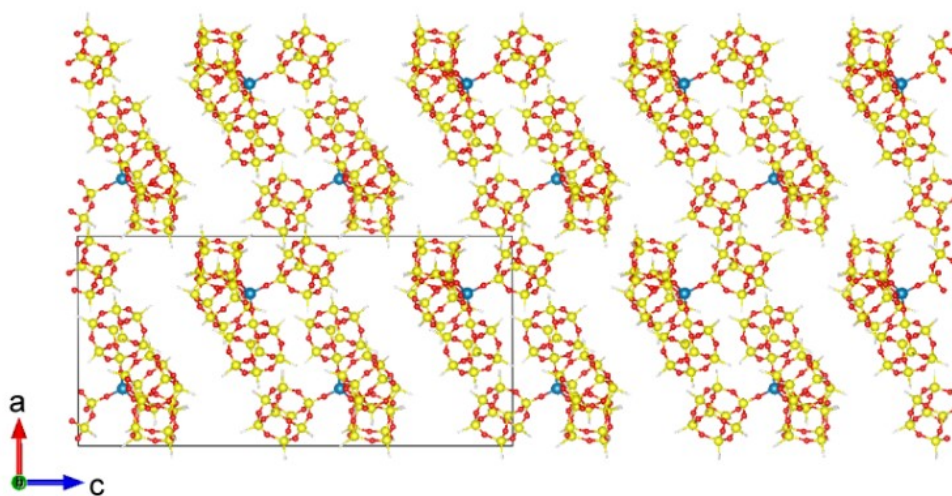


Fig. S2. Crystal structure of $(t\text{Bu}_7\text{Si}_8\text{O}_{13})_4\text{Ti}$ viewed along the b axis. Hydrogen and carbon atoms are omitted for clarity. Atom colors: Blue, Ti; Yellow, Si; Red, O. This structural model was visualized by VESTA (version 3).

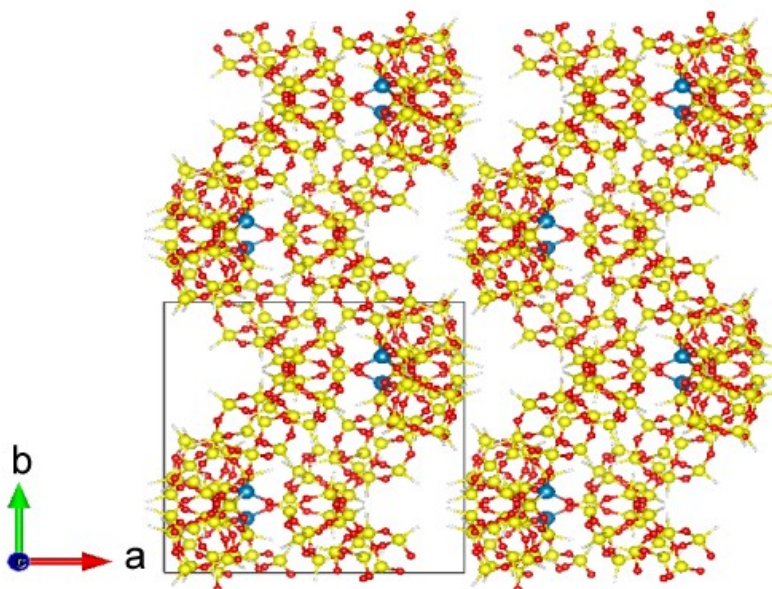


Fig. S3. Crystal structure of $(t\text{Bu}_7\text{Si}_8\text{O}_{13})_4\text{Ti}$ viewed along the c axis. Hydrogen and carbon atoms are omitted for clarity. Atom colors: Blue, Ti; Yellow, Si; Red, O. This structural model was visualized by VESTA (version 3).

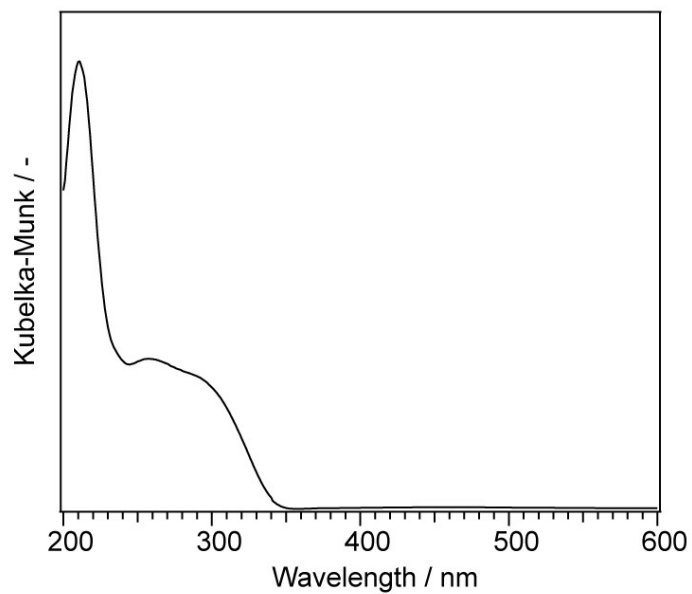


Fig. S4. UV-Vis spectrum of $(t\text{Bu}_7\text{Si}_8\text{O}_{13})_4\text{Ti}$.

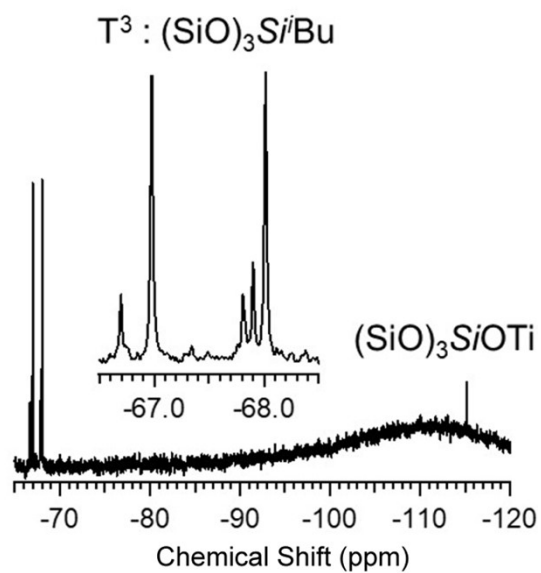


Fig. S5. ^{29}Si NMR spectrum of $(t\text{Bu}_7\text{Si}_8\text{O}_{13})_4\text{Ti}$ after leaving to stand in the air (room temperature, 40% relative humidity) for 1 d.

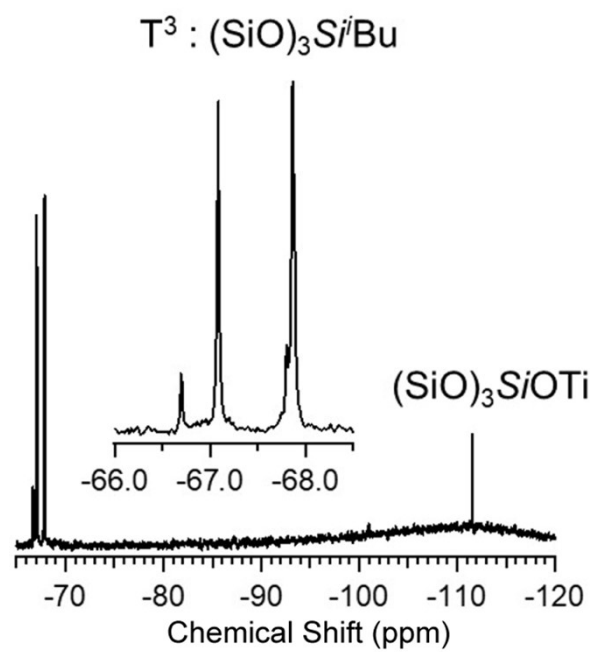


Fig. S6. ^{29}Si NMR spectrum of $(i\text{Bu}_7\text{Si}_8\text{O}_{13})_3\text{TiCp}$.

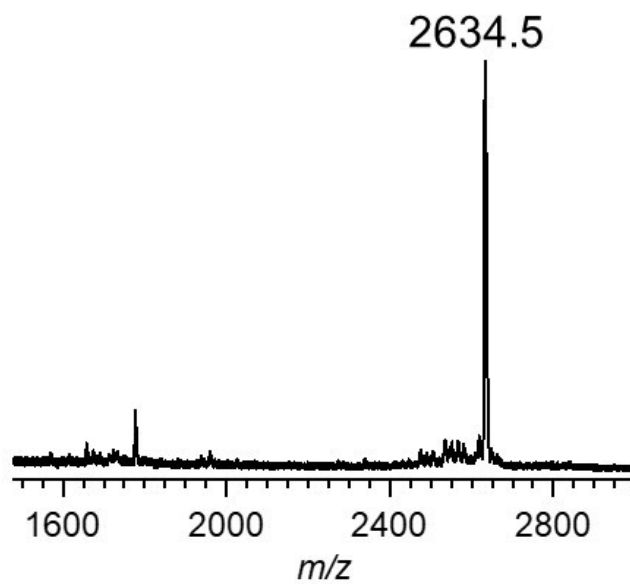


Fig. S7 MALDI-TOF MS spectrum of $(i\text{Bu}_7\text{Si}_8\text{O}_{13})_3\text{TiCp}$.

Table S1 Crystal data of (*i*Bu₇Si₈O₁₃)₄Ti

(<i>i</i> Bu ₇ Si ₈ O ₁₃) ₄ Ti	
Formula	C ₁₁₂ H ₂₅₂ O ₅₂ Si ₃₂ Ti
<i>M</i> /g· mol	3377.78
Temperature /K	93
Crystal system	monoclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> /Å	20.4538(7)
<i>b</i> /Å	21.7114(6)
<i>c</i> /Å	42.2709(12)
α /°	90
β /°	90.158(3)
γ /°	90
<i>V</i> /Å ³	18771.6(10)
<i>Z</i>	4
<i>D</i> _{calc} /g cm ⁻³	1.195
<i>F</i> (000)	5328
GoF	1.325
Total number of reflections	133642
Unique number of reflections	33639
<i>R</i> 1	0.1399
<i>wR</i> 2	0.4126

Table S2 Ti–O lengths of (*i*Bu₇Si₈O₁₃)₄Ti

	length (Å)
Ti ₁ –O ₁	1.765(8)
Ti ₁ –O ₁₄	1.735(9)
Ti ₁ –O ₂₇	1.754(7)
Ti ₁ –O ₄₀	1.766(9)

Table S3 Ti–O–Ti angles of (*t*Bu₇Si₈O₁₃)₄Ti

	angles (°)
O ₁ -Ti ₁ -O ₁₄	109.4(3)
O ₁ -Ti ₁ -O ₄₀	110.9(3)
O ₁ -Ti ₁ -O ₂₇	107.3(3)
O ₁₄ -Ti ₁ -O ₂₇	110.0(3)
O ₁₄ -Ti ₁ -O ₄₀	109.7(3)
O ₂₇ -Ti ₁ -O ₄₀	109.5(3)

Table S4 Ti–O–Si angles of (*t*Bu₇Si₈O₁₃)₄Ti

	angles (°)
Ti ₁ -O ₁ -Si ₁	176.7(4)
Ti ₁ -O ₁₄ -Si ₉	162.7(4)
Ti ₁ -O ₂₇ -Si ₁₇	172.7(4)
Ti ₁ -O ₄₀ -Si ₂₅	177.9(4)

References

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- [3] T. Hikino, Y. Kawakubo, T. Matsuno, S. Yamazoe, K. Kuroda and A. Shimojima, *Chem. Mater.*, 2024, DOI: 10.1021/acs.chemmater.4c01454.