

Supporting Information

Cage-Rearranged and Cage-Intact Syntheses of Azido-Functionalized Larger T₁₀ and T₁₂ POSS

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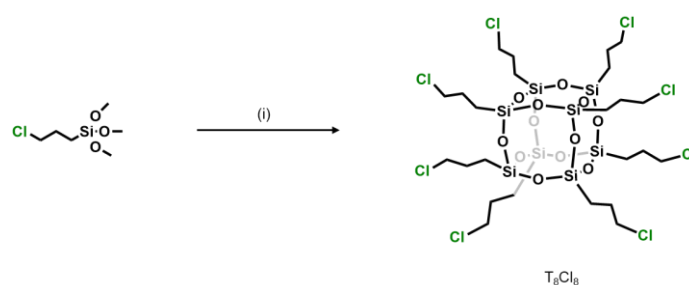
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Experimental Section

Scheme S1. Synthetic route of T₈Cl₈.^a

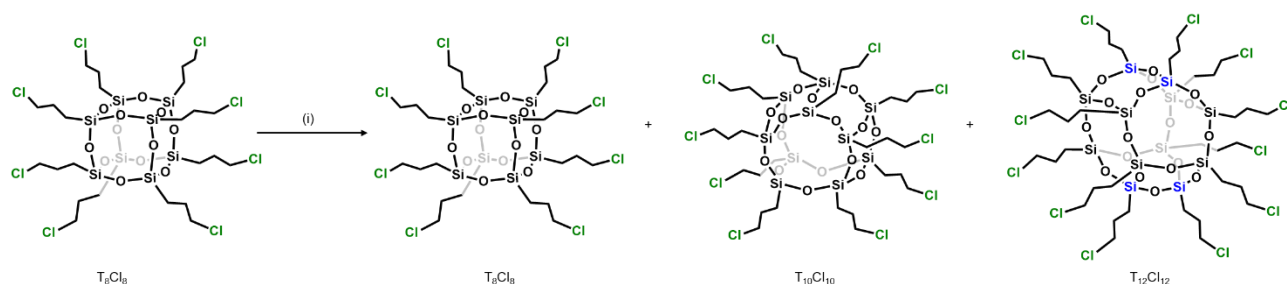


^a Reagent and conditions: (i) HCl/Methanol, 60 °C, 72 h, yield: ~32%.

Synthesis of octa (3-chloropropyl) POSS (T₈Cl₈). The title compound was synthesized via the hydrolytic condensation of 3-chloropropyltrimethoxysilane as reported by Dittmar et al.¹ To a round-bottomed flask equipped with a magnetic stirrer, a condenser, and an addition funnel, methanol

(400 mL) and concentrated hydrochloric acid (22.5 mL) were mixed. Then, 19.87 g of 3-chloropropyltrimethoxysilane was dropwise added. After that, the mixture was heated to 60 °C and the white crystalline precipitate began to form after 20 h. 72 h later, the reaction was finished and the precipitated products were collected, washed with methanol, and dried in a vacuum to give a white powder. Yield: 32%. ¹H NMR (400 MHz, CDCl₃, δ, ppm): 3.54 (16 H, t, -CH₂Cl), 1.88 (16 H, m, -CH₂-), 0.80 (16 H, m, -SiCH₂-). ¹³C NMR (100 MHz, CDCl₃, δ, ppm): 46.98, 26.21, 9.30. ²⁹Si NMR (79 MHz, CDCl₃, δ, ppm): -67.08. MALDI TOF (MS): Calcd. For (C₁₆H₂₄O₁₂Si₈Cl₈Na): 1058.87 Da, Found: 1059.03 Da.

Scheme S2. Synthetic route of T₁₀Cl₁₀, and T₁₂Cl₁₂ from cage-rearranged T₈Cl₈.^a



^a Reagent and conditions: (i) K₂CO₃, DMF, 60 °C, 1 h, yield: ~56% for T₈Cl₈, ~24% for T₁₀Cl₁₀, and ~20% for T₁₂Cl₁₂.

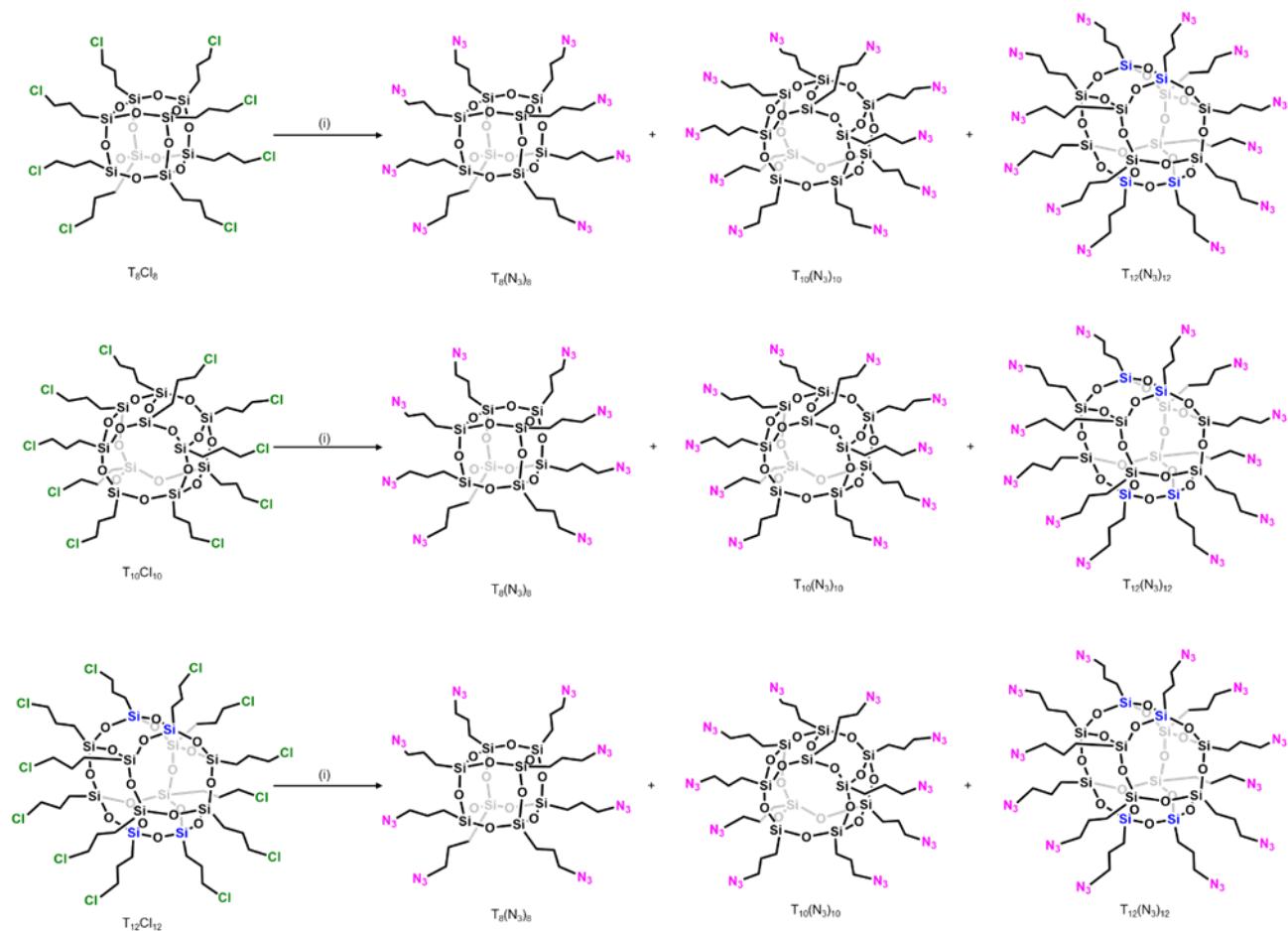
Syntheses of T₁₀Cl₁₀ and T₁₂Cl₁₂. The title compounds were synthesized following the literature procedure.² T₈Cl₈ (2 g, 1.938 mmol), K₂CO₃ (0.125 g, 0.904 mmol), and anhydrous DMF (20 mL) were mixed in a round bottom flask equipped with a magnetic stirring bar under nitrogen atmosphere. The mixture was then heated to 60 °C and reacted for 1 h. Afterward, the mixture was extracted using DCM (150 mL) and the organic phase was concentrated. The resulting viscous liquid was transferred onto a silica gel column using PE/DCM (v/v = 2/1) as eluent to obtain the desired products (*R_f* = 0.5 for T₈Cl₈, *R_f* = 0.35 for T₁₀Cl₁₀, and *R_f* = 0.25 for T₁₂Cl₁₂).

T₁₀Cl₁₀. White powder, isolated yield: 24%. ¹H NMR (400 MHz, CDCl₃, δ, ppm): 3.54 (20 H, t, -CH₂Cl), 1.86 (20 H, m, -CH₂-), 0.80 (20 H, m, -SiCH₂-). ¹³C NMR (100 MHz, CDCl₃, δ, ppm): 47.25, 26.56, 10.05. ²⁹Si NMR (79 MHz, CDCl₃, δ, ppm): -68.95. MALDI TOF (MS): Calcd. For

(C₂₀H₃₀O₁₅Si₁₀Cl₁₀Na): 1316.84 Da, Found: 1317.05 Da.

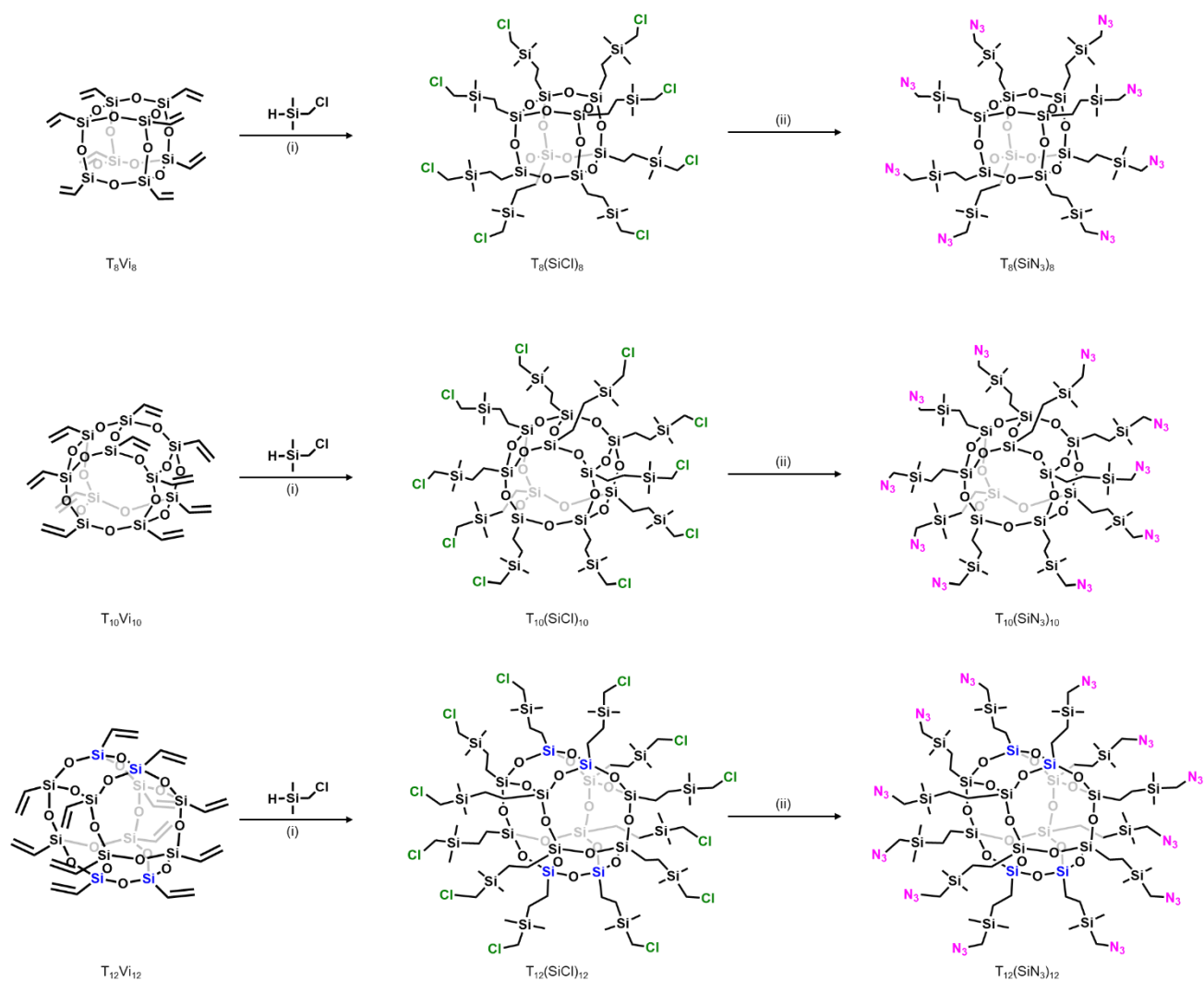
T₁₂Cl₁₂. White powder, yield: 20%. ¹H NMR (400 MHz, CDCl₃, δ, ppm): 3.54 (24 H, t, -CH₂Cl), 1.85 (24 H, m, -CH₂-), 0.79 (24 H, m, -SiCH₂-). ¹³C NMR (100 MHz, CDCl₃, δ, ppm): 47.20, 26.56, 10.60. ²⁹Si NMR (79 MHz, CDCl₃, δ, ppm): -68.71, -71.37. MALDI TOF (MS): Calcd. For (C₂₄H₃₆O₁₈Si₁₂Cl₁₂Na): 1576.80 Da, Found: 1577.11 Da.

Scheme S3. Reaction route for rearrangement of T₈Cl₈, T₁₀Cl₁₀, and T₁₂Cl₁₂ to T_n(N₃)_n mixtures (n = 8, 10, 12).^a



^a Reagent and conditions: (i) NaN₃, DMF, 60 °C, 16 h.

Scheme S4. Synthetic route of $T_8(\text{SiN}_3)_8$, $T_{10}(\text{SiN}_3)_{10}$, and $T_{12}(\text{SiN}_3)_{12}$.^a



^a Reagent and conditions: (i) Karstedt's, toluene, 70 °C, 72 h, yield: ~93% for $T_8(\text{SiCl})_8$, ~87% for $T_{10}(\text{SiCl})_{10}$, and ~85% for $T_{12}(\text{SiCl})_{12}$; (ii) NaN_3 , NaI, DMF, THF, 60 °C, 24 h, yield: ~90% for $T_8(\text{SiN}_3)_8$, ~87% for $T_{10}(\text{SiN}_3)_{10}$, and ~83% for $T_{12}(\text{SiN}_3)_{12}$.

Instrumentation and Characterizations. The ^1H , ^{13}C , and ^{29}Si NMR spectra were acquired in CDCl_3 using a Bruker 400 MHz NMR spectrometer at ambient temperature. Matrix-assisted laser desorption ionization time of flight mass spectroscopy (MALDI-TOF MS) was performed on an ultraflextreme MALDI TOF/TOF Mass Spectrometer (Bruker Daltonics) in positive reflection mode. Size exclusion chromatography (SEC) results were obtained on an HLC-8320GPC instrument (Tosoh Corp., Japan) using THF as the eluent with a sample concentration of 3 mg mL^{-1} and a flow rate of 0.6 mL min^{-1} . Fourier transform infrared (FT-IR) spectra were recorded on a Nicolet 6700

spectrometer after mixing the samples with KBr and pressing them into pellets for further measurement. The energy dispersive X-ray spectroscopy (EDS) of C, N, O, and Si elements were captured using a Nova NanoSEM450 SEM (FEI, America) equipped with an X-MaxN EDS (Oxford Instruments, England) at a 20 kV accelerating voltage, and a thin layer of gold was sputtered onto the sample's surface prior to measurement. High performance liquid chromatography (HPLC) analyses were performed using a chromatographic system comprising an LC-100 pump (Wufeng Instrument, China) and an E800 evaporative light scattering detector (SANAER Instrument, China), with THF/H₂O (3/1, v/v) employed as the mobile phase.

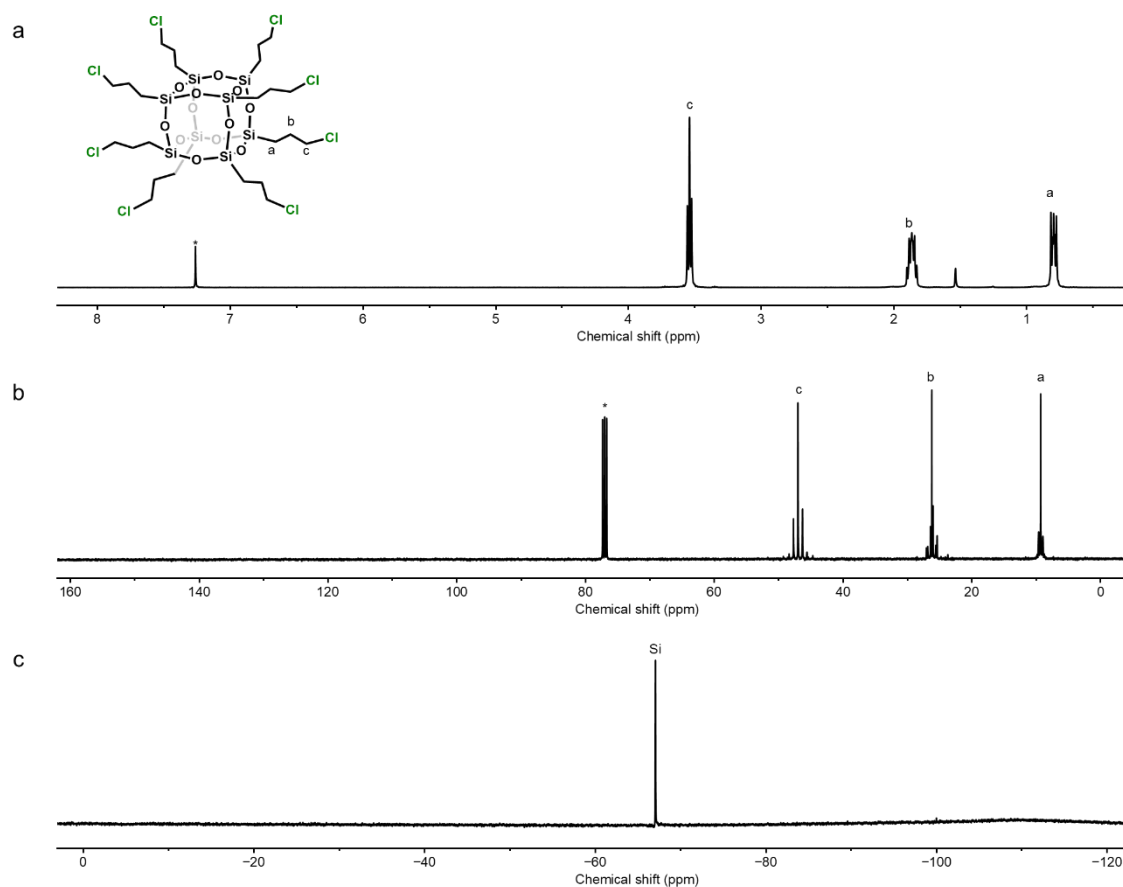


Fig. S1. (a) ¹H NMR, (b) ¹³C NMR, and (c) ²⁹Si NMR of T₈Cl₈. Asterisk represents signal from CDCl₃.

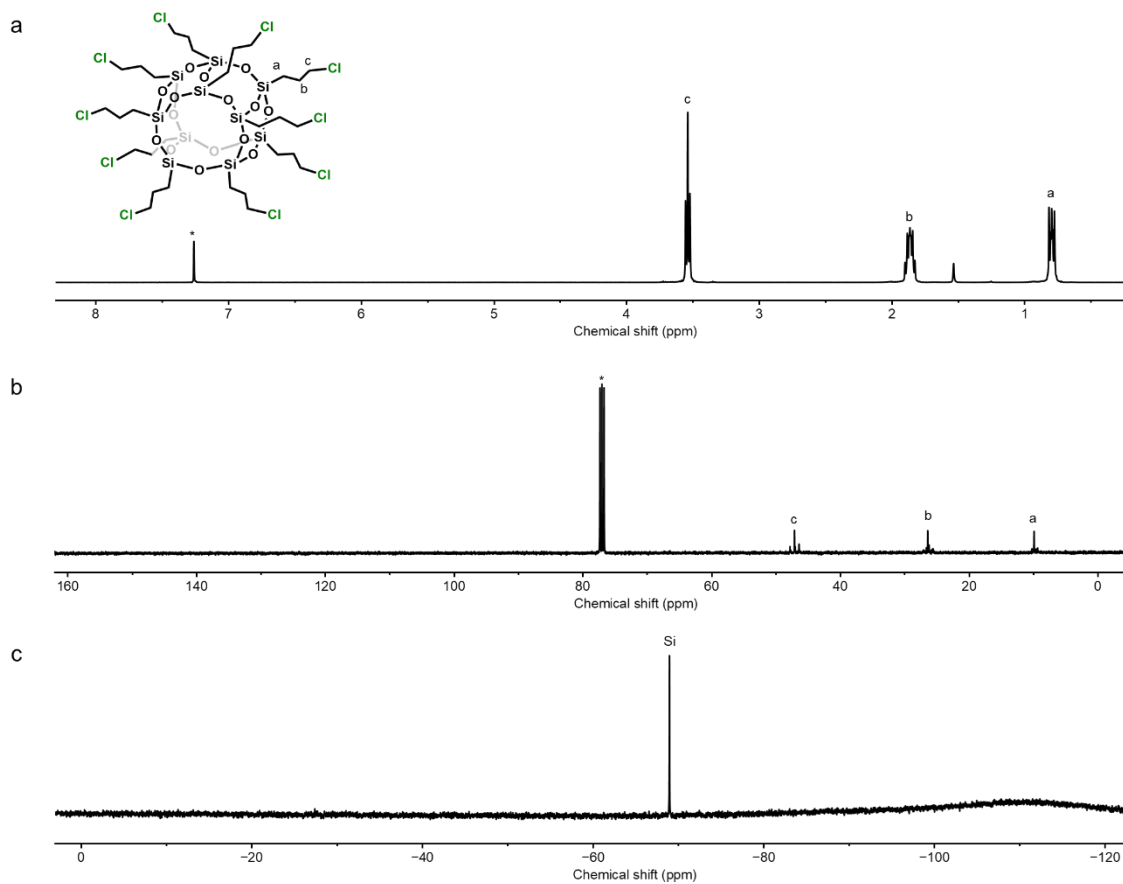


Fig. S2. (a) 1H NMR, (b) ^{13}C NMR, and (c) ^{29}Si NMR of $T_{10}Cl_{10}$. Asterisk represents signal from $CDCl_3$.

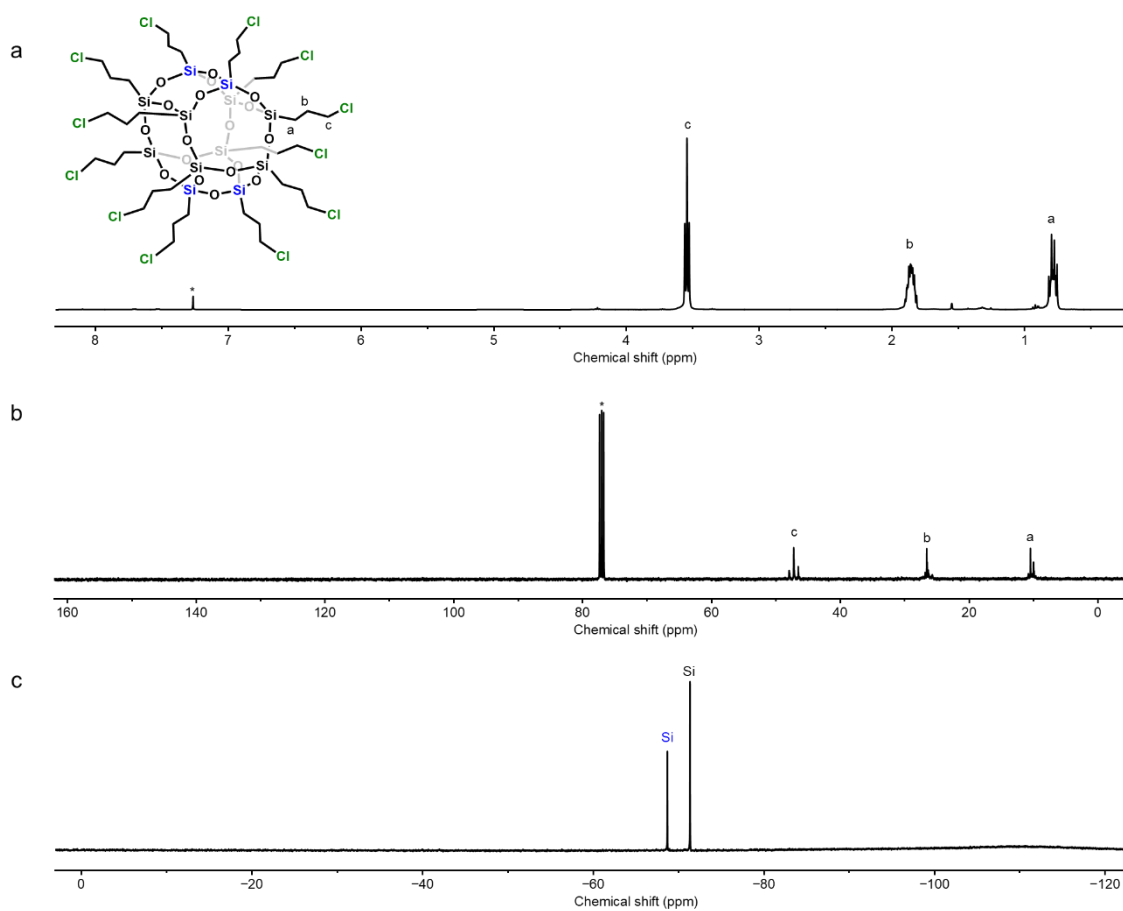


Fig. S3. (a) 1H NMR, (b) ^{13}C NMR, and (c) ^{29}Si NMR of $T_{12}Cl_{12}$. Asterisk represents signal from $CDCl_3$.

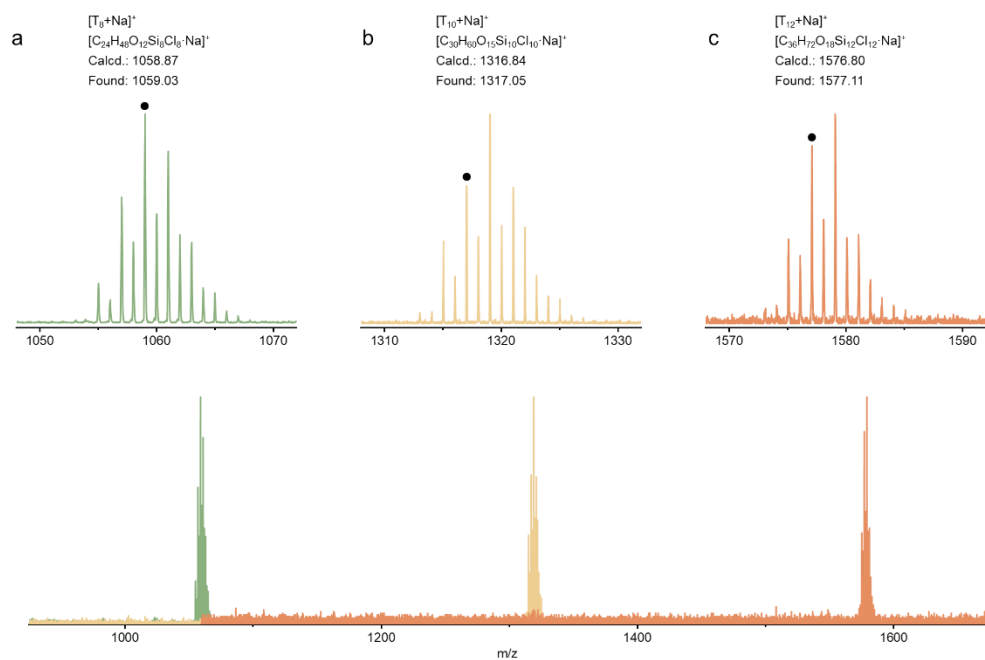


Fig. S4. MALDI-TOF MS of (a) T_8Cl_8 , (b) $T_{10}Cl_{10}$, and (c) $T_{12}Cl_{12}$.

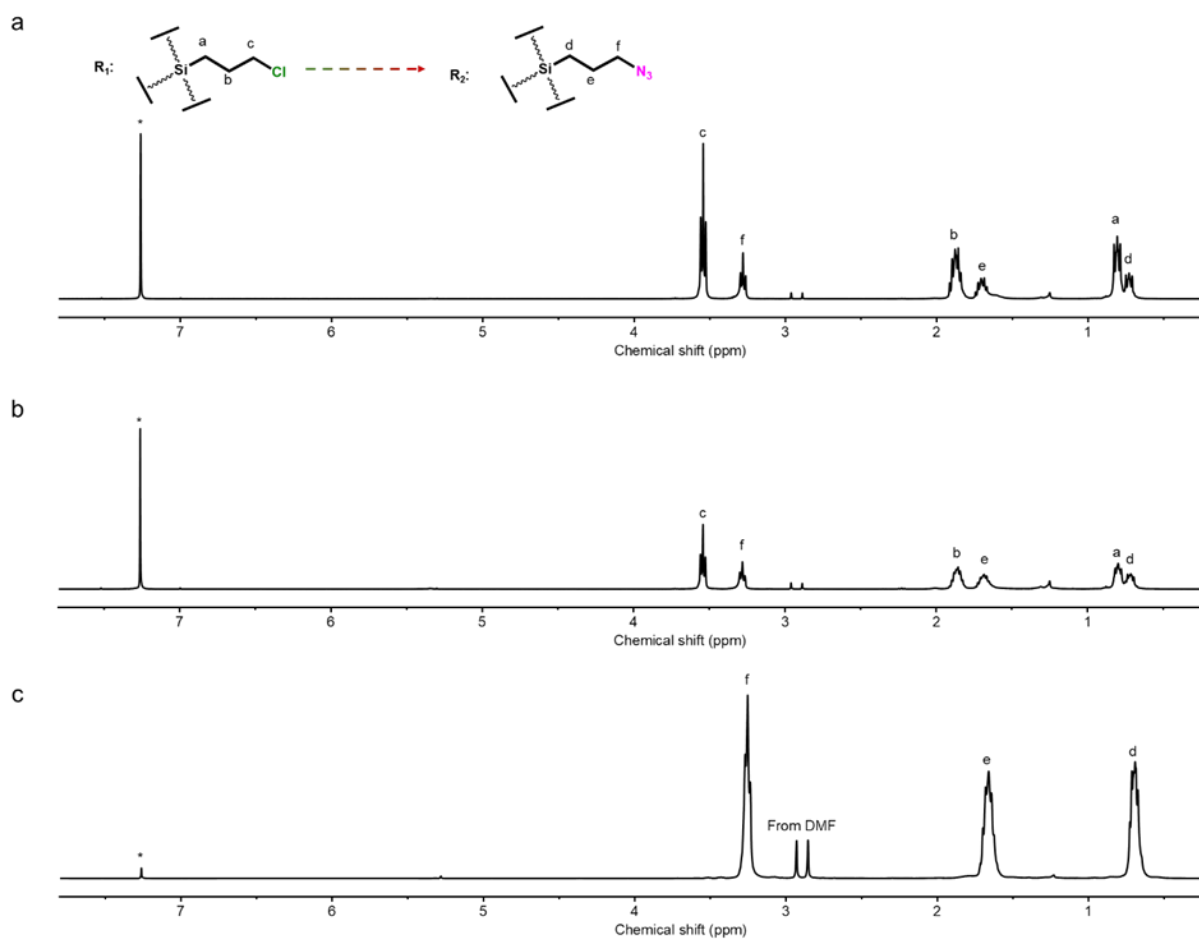


Fig. S5. 1H NMR spectra of T_8Cl_8 after reaction with NaN_3 for (a) 2 h, (b) 8 h, and (c) 16 h. Asterisk represents signal from $CDCl_3$.

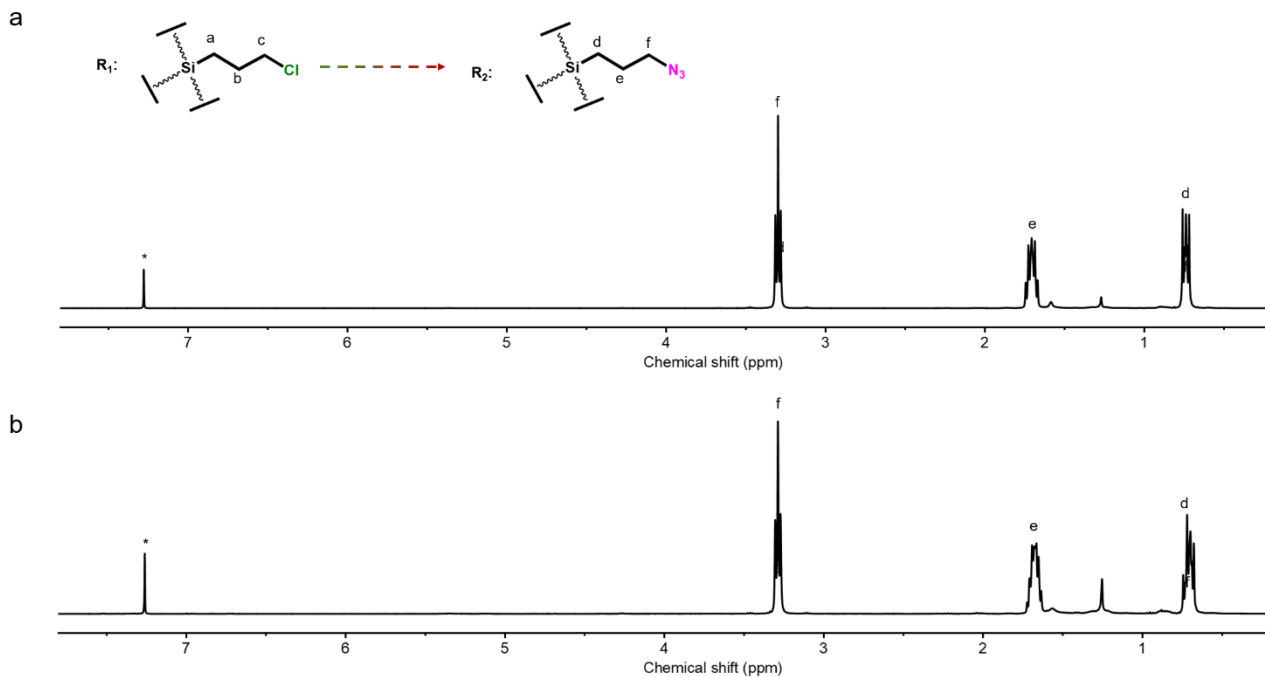


Fig. S6. ^1H NMR of $\text{T}_n(\text{N}_3)_n$ mixtures prepared from (a) $\text{T}_{10}\text{Cl}_{10}$ and (b) $\text{T}_{12}\text{Cl}_{12}$, respectively. The reaction time is 16 h. Asterisk represents signal from CDCl_3 .

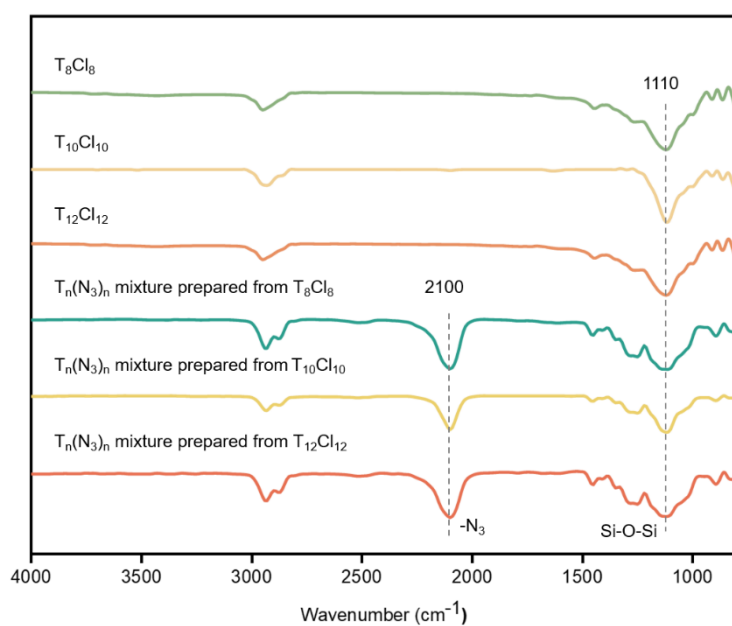


Fig. S7. FT-IR spectra of T_8Cl_8 , $\text{T}_{10}\text{Cl}_{10}$, $\text{T}_{12}\text{Cl}_{12}$, and $\text{T}_n(\text{N}_3)_n$ mixtures prepared from T_8Cl_8 , $\text{T}_{10}\text{Cl}_{10}$, $\text{T}_{12}\text{Cl}_{12}$, respectively. The reaction time is 16 h.

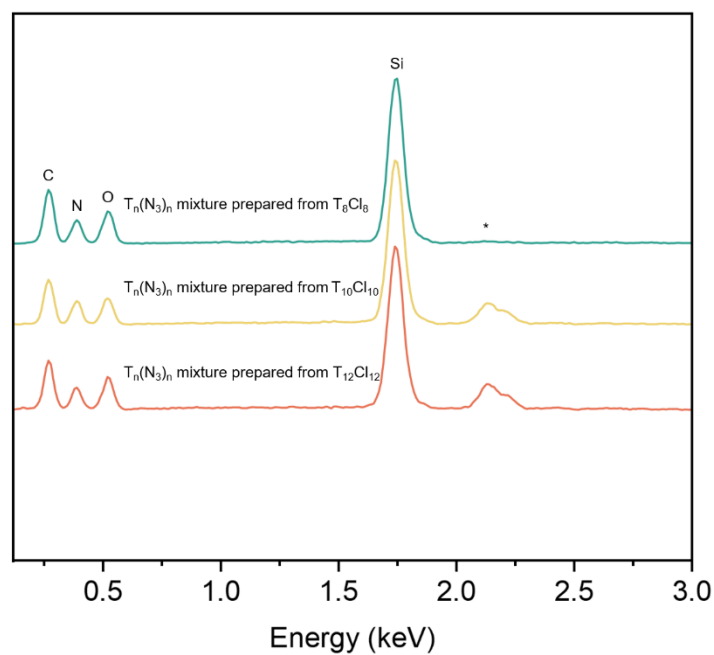


Fig. S8. EDS spectra of $T_n(N_3)_n$ mixtures prepared from T_8Cl_8 , $T_{10}Cl_{10}$, $T_{12}Cl_{12}$, respectively. Asterisk represents signal from Au.

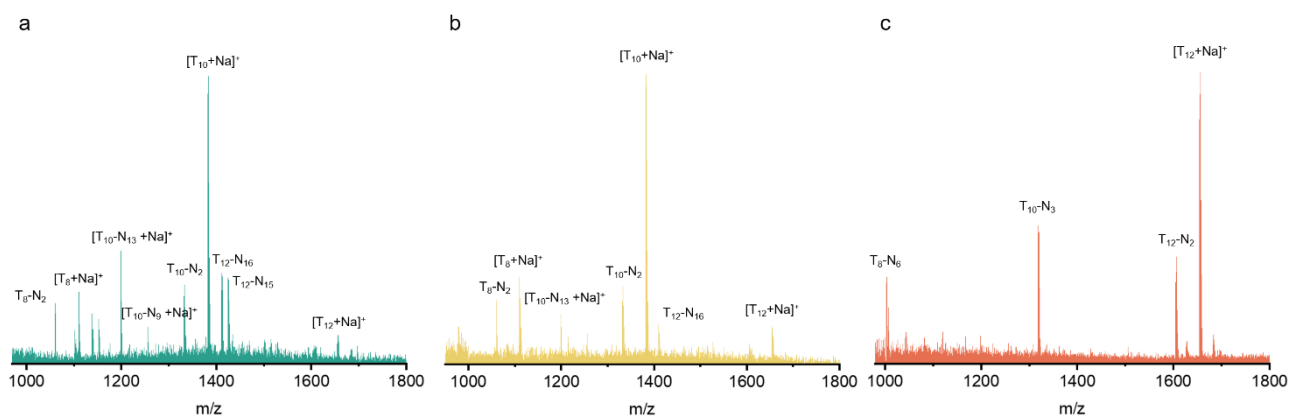


Fig. S9. MALDI-TOF MS of $T_n(N_3)_n$ mixtures prepared from (a) T_8Cl_8 , (b) $T_{10}Cl_{10}$, (c) $T_{12}Cl_{12}$, respectively. The reaction time is 16 h.

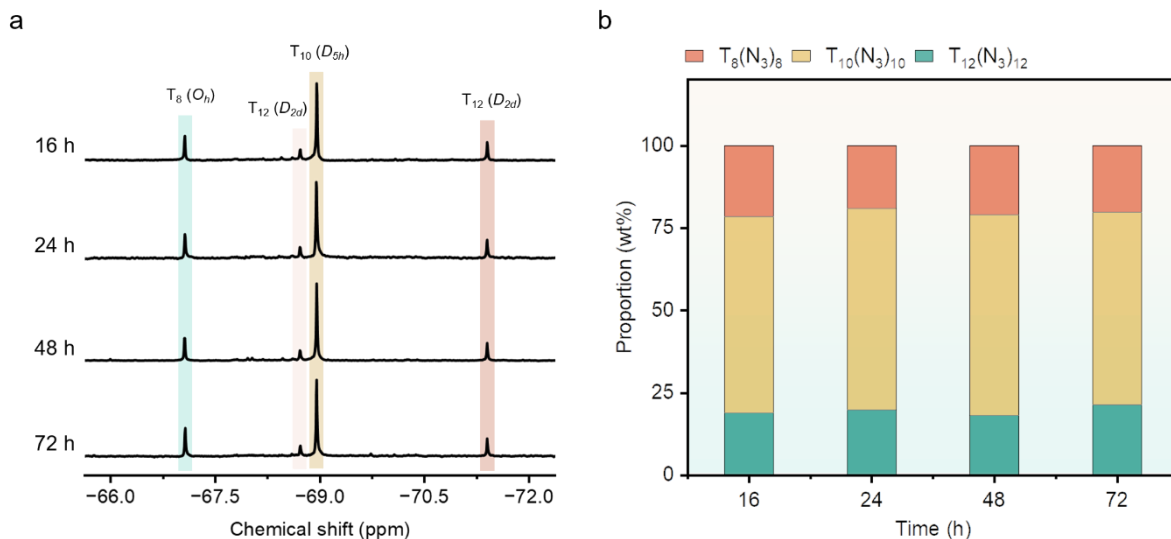


Fig. S10. (a) ^{29}Si NMR spectra of T_8Cl_8 after reaction with NaN_3 for 16, 24, 48, and 72 h; (b) their corresponding mass proportion distribution calculated based on ^{29}Si NMR spectra. It should be noted that the product yields, which were approximately 80%, remained consistent regardless of reaction time.

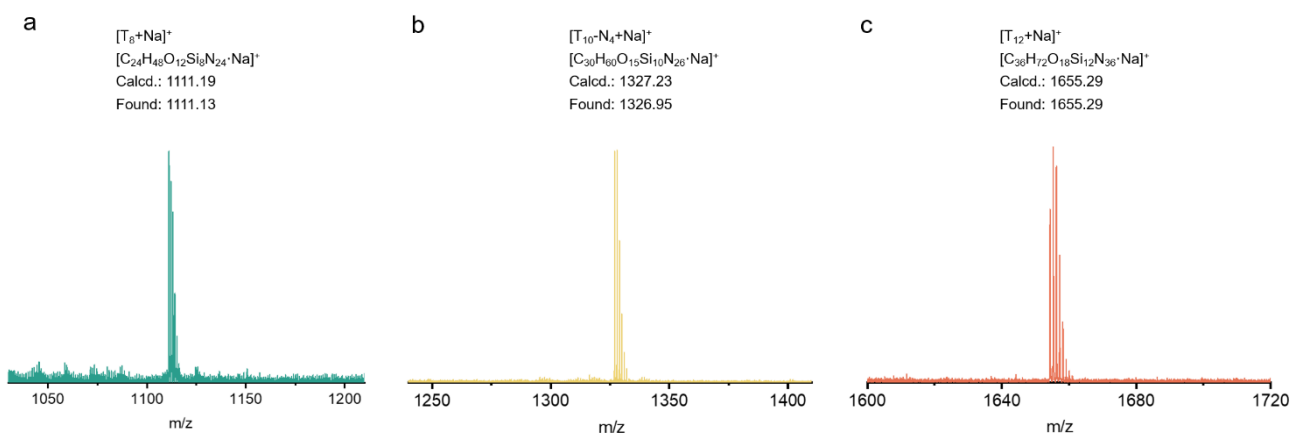


Fig. S11. MALDI-TOF MS of highly pure (a) $\text{T}_8(\text{N}_3)_8$, (b) $\text{T}_{10}(\text{N}_3)_{10}$, and (c) $\text{T}_{12}(\text{N}_3)_{12}$.

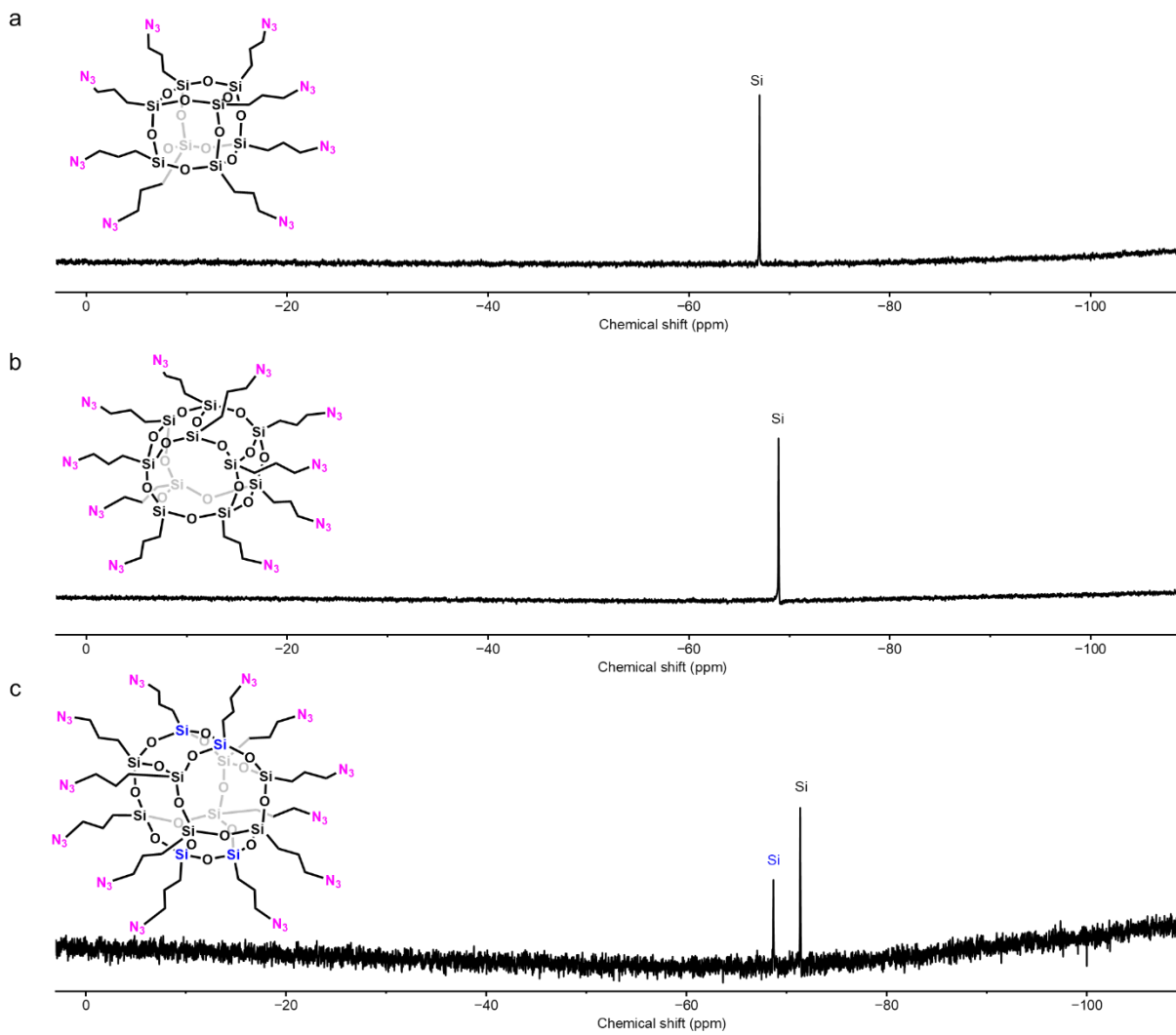


Fig. S12. ^{29}Si NMR of highly pure (a) $\text{T}_8(\text{N}_3)_8$, (b) $\text{T}_{10}(\text{N}_3)_{10}$, and (c) $\text{T}_{12}(\text{N}_3)_{12}$. Asterisk represents signal from CDCl_3 .

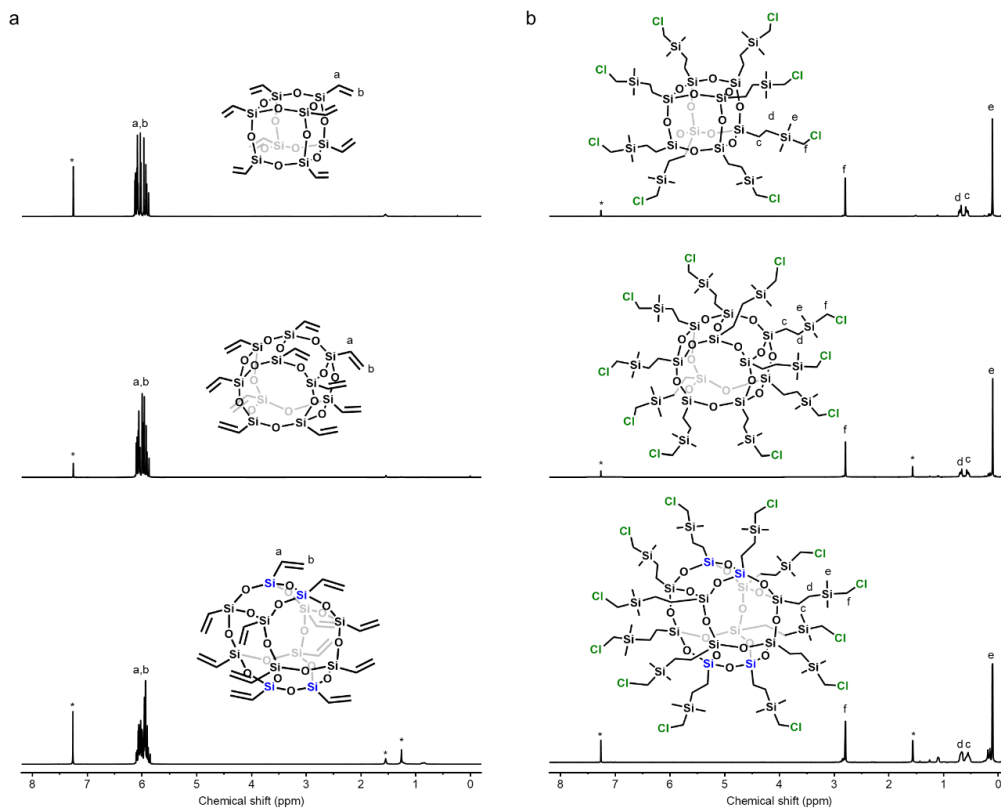


Fig. S13. ^1H NMR of (a) T_nV_n , and (b) $\text{T}_n(\text{SiCl})_n$. Asterisk represents signal from CDCl_3 .

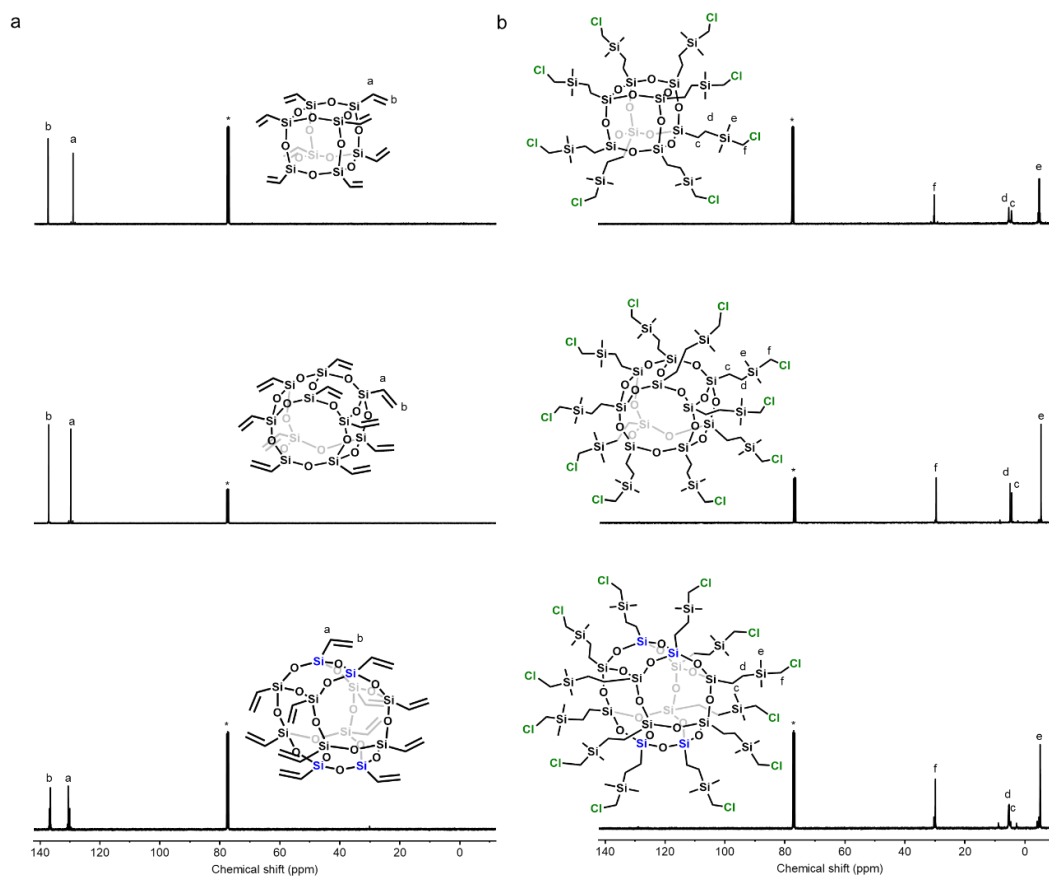


Fig. S14. ^{13}C NMR of (a) T_nV_n , and (b) $\text{T}_n(\text{SiCl})_n$. Asterisk represents signal from CDCl_3 .

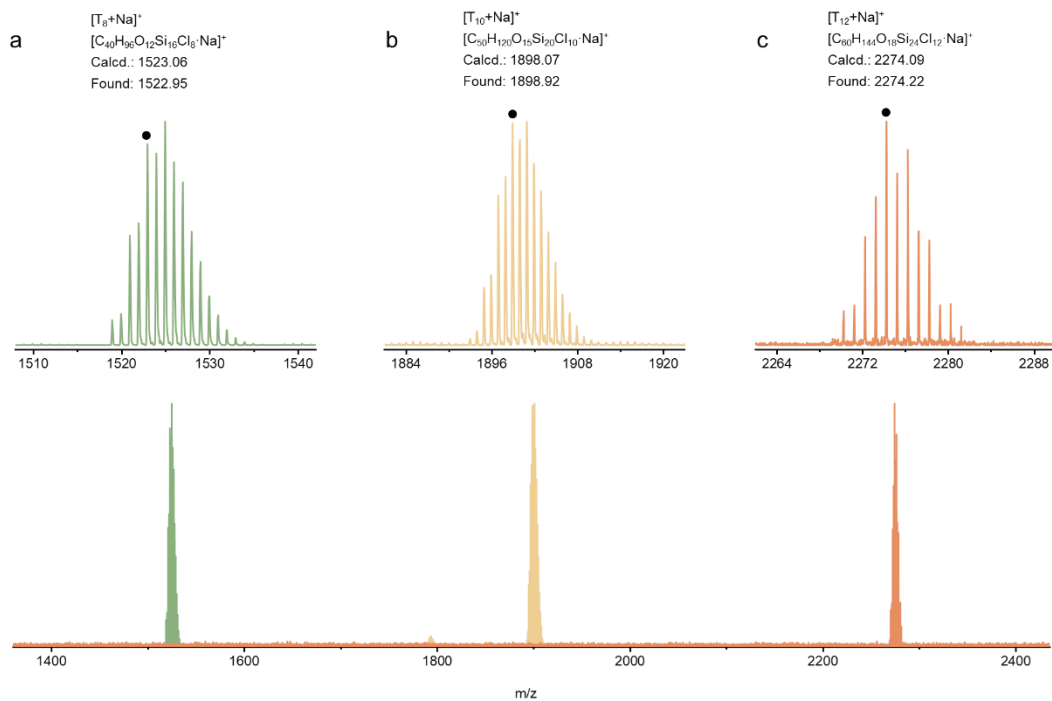


Fig. S15. MALDI-TOF mass spectra of (a) $T_8(\text{SiCl})_8$, (b) $T_{10}(\text{SiCl})_{10}$, and (c) $T_{12}(\text{SiCl})_{12}$.

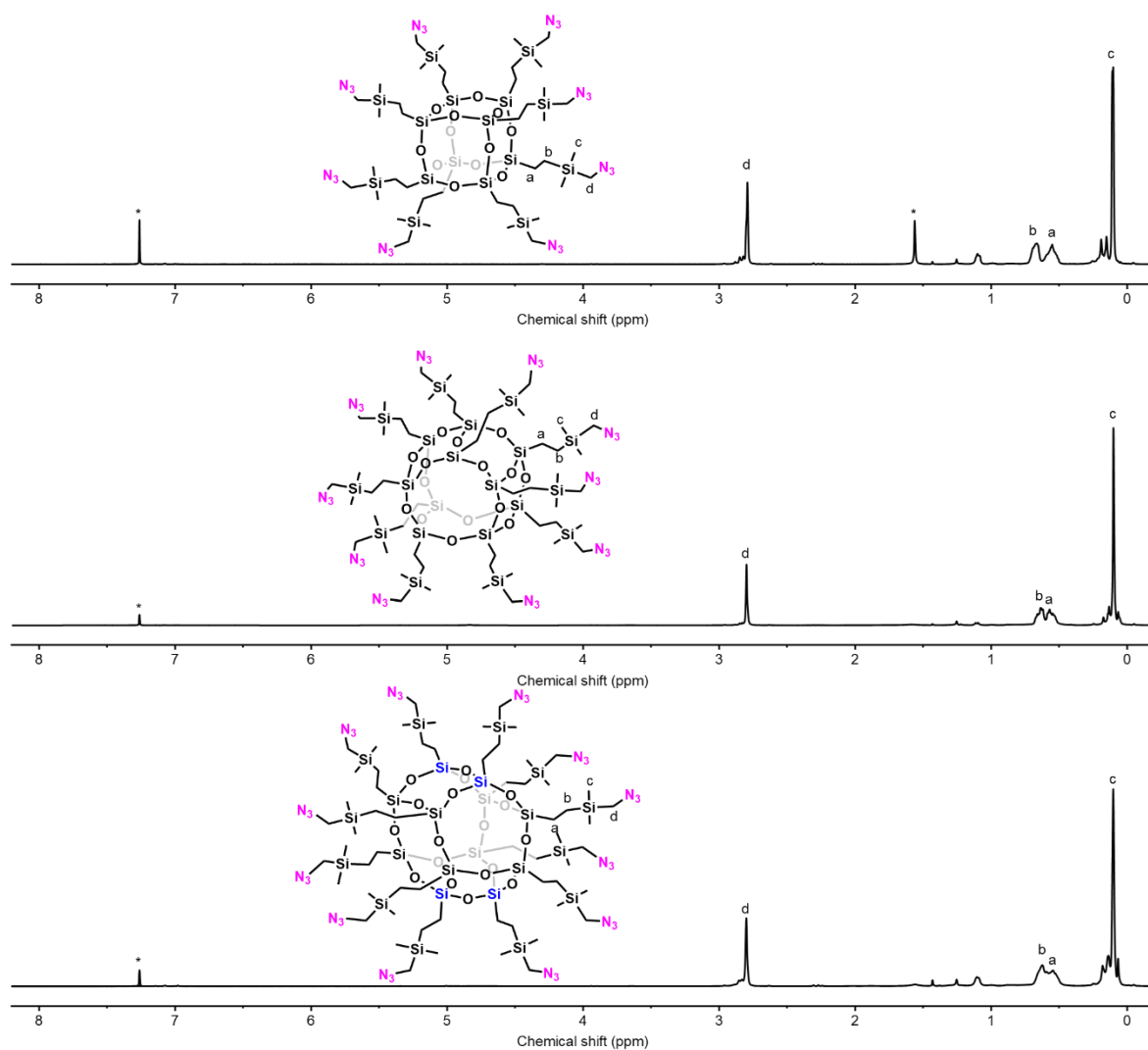


Fig. S16. ^1H NMR of $T_n(\text{SiN}_3)_n$. Asterisk represents signal from CDCl_3 .

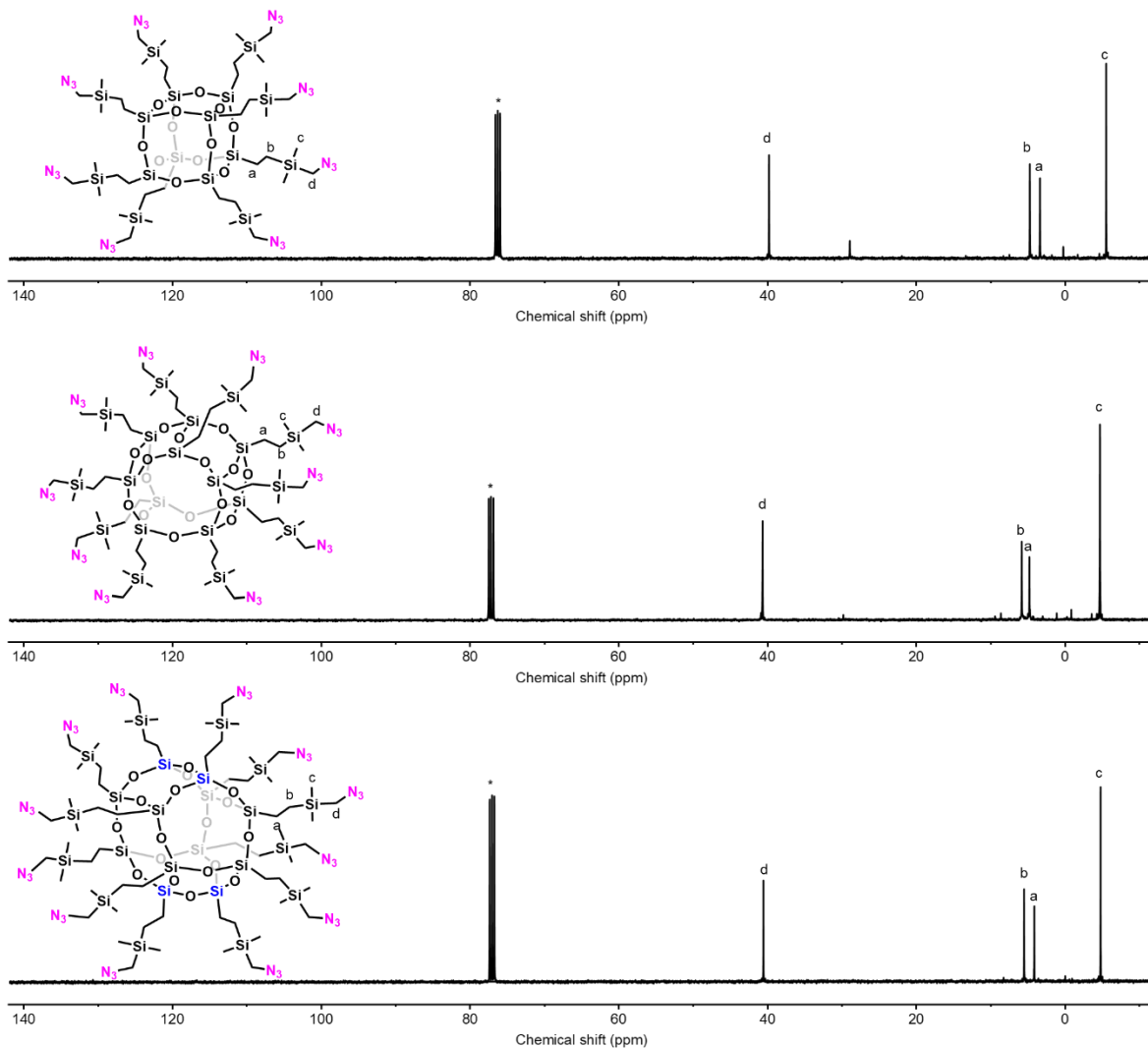


Fig. S17. ^{13}C NMR of $\text{T}_n(\text{SiN}_3)_n$. Asterisk represents signal from CDCl_3 .

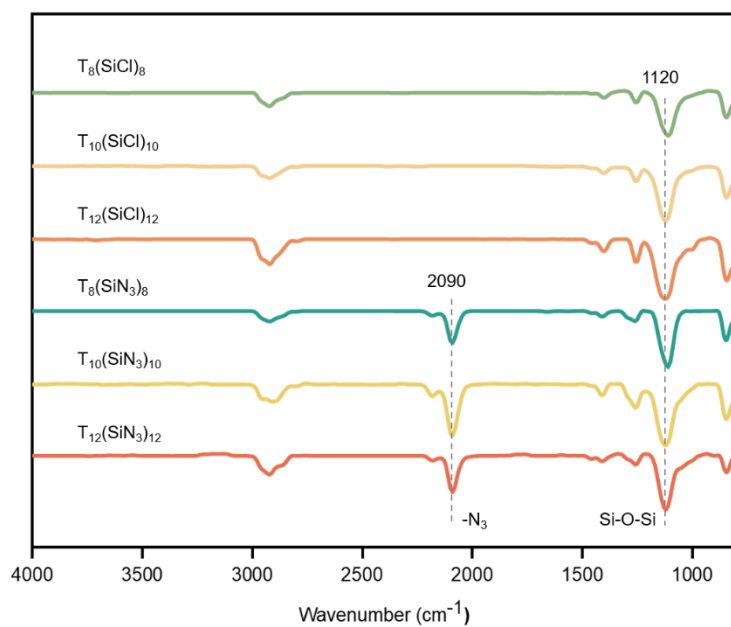


Fig. S18. FT-IR spectra of $\text{T}_8(\text{SiCl})_8$, $\text{T}_{10}(\text{SiCl})_{10}$, $\text{T}_{12}(\text{SiCl})_{12}$, $\text{T}_8(\text{SiN}_3)_8$, $\text{T}_{10}(\text{SiN}_3)_{10}$, and $\text{T}_{12}(\text{SiN}_3)_{12}$.

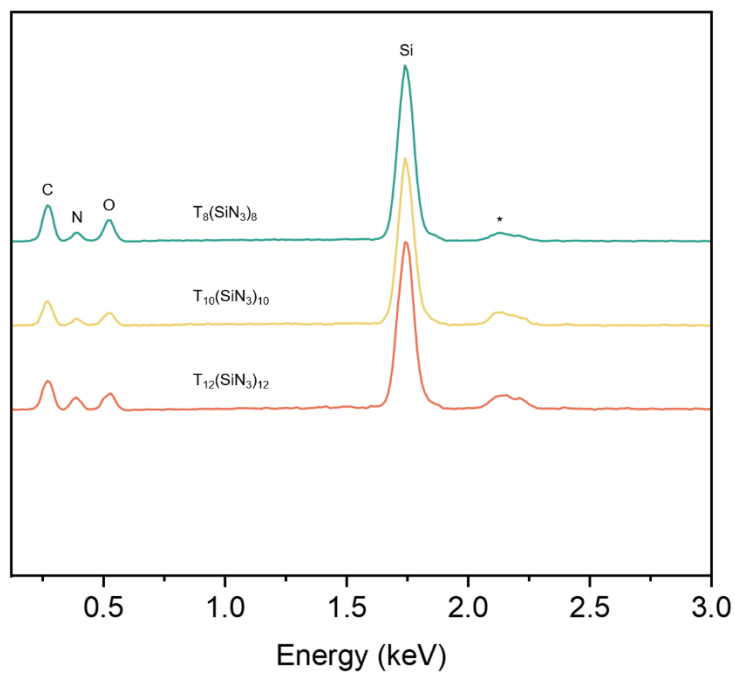


Fig. S19. EDS spectra of $T_8(\text{SiN}_3)_8$, $T_{10}(\text{SiN}_3)_{10}$, and $T_{12}(\text{SiN}_3)_{12}$. Asterisk represents signal from Au.

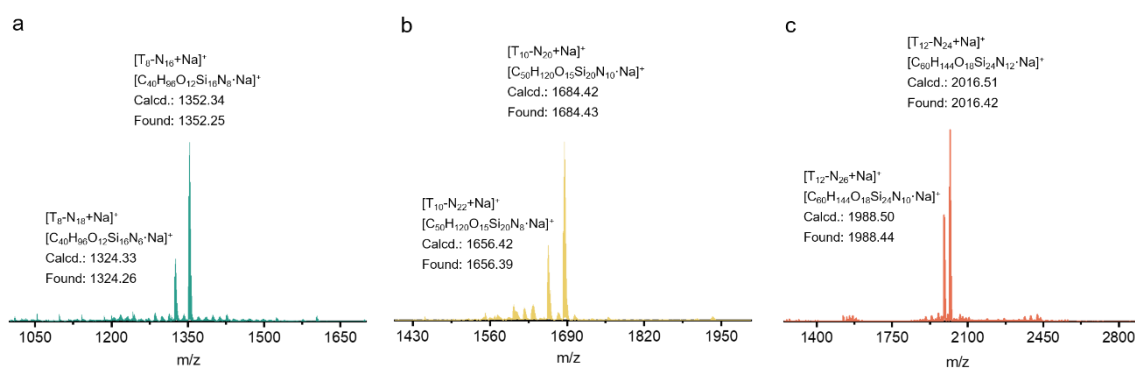


Fig. S20. MALDI-TOF MS of (a) $T_8(\text{SiN}_3)_8$, (b) $T_{10}(\text{SiN}_3)_{10}$, and (c) $T_{12}(\text{SiN}_3)_{12}$. It should be emphasized that the fragmentation of the azide functionality via expulsion of N_2 gives rise to ions 28 mass units less than the mass of the compound, as reported by Grayson et al.³

Table S1. The experimental and theoretical relative element content (mass fraction) of $T_n(N_3)_n$ mixtures prepared from T_8Cl_8 , $T_{10}Cl_{10}$, $T_{12}Cl_{12}$. ^a

Starting Material	C	N	O	Si
T_8Cl_8	34.85	28.86	19.35	16.93
$T_{10}Cl_{10}$	33.23	30.76	17.63	18.37
$T_{12}Cl_{12}$	34.40	27.76	20.04	17.80
Theoretical Value (wt%)	27.70	32.26	18.45	21.59

^a Calculated from EDS spectra.

Table S2. Product type and mass proportion distribution of $T_n(N_3)_n$ mixtures prepared from cage-rearranged T_8Cl_8 , $T_{10}Cl_{10}$, and $T_{12}Cl_{12}$. The relative mass proportions of $T_8(N_3)_8$, $T_{10}(N_3)_{10}$, and $T_{12}(N_3)_{12}$ were calculated based on the peak areas of ^{29}Si NMR spectra.

Starting Material	Characterization	$T_8(N_3)_8$	$T_{10}(N_3)_{10}$	$T_{12}(N_3)_{12}$
T_8Cl_8		19	60	21
$T_{10}Cl_{10}$	^{29}Si NMR (wt%)	18	70	12
$T_{12}Cl_{12}$		2	9	89

Table S3. The experimental and theoretical relative element content (mass fraction) of $T_8(SiN_3)_8$, $T_{10}(SiN_3)_{10}$, and $T_{12}(SiN_3)_{12}$.

Sample	C	N	O	Si
$T_8(SiN_3)_8$	39.06	16.03	13.93	30.98
$T_{10}(SiN_3)_{10}$	40.65	17.48	13.07	28.80
$T_{12}(SiN_3)_{12}$	35.87	25.05	14.67	24.41
Theoretical Value (wt%)	32.95	23.05	13.17	30.83

^a Calculated from EDS spectra.

References

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2. S. Hanprasit, N. Tungkijanansin, A. Prompawilai, S. Eangpayung and V. Ervithayasuporn, *Dalton T.*, 2016, **45**, 16117.
3. Y. Li, J. N. Hoskins, S. G. Sreerama and S. M. Grayson, *Macromolecules*, 2010, **43**, 6225.