Electronic Supplementary Information (ESI)

Synthesis and isolation of non-chromophore cage-rearranged silsesquioxanes from base-catalyzed reactions

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EXPERIMENTAL SECTION

Materials

Octakis(3-chloropropyl)octasilsequioxane (1) was prepared according to a literature report.\textsuperscript{5d} 2-nitrophenol (purity; 98%), 3-nitrophenol (purity; 99%), and anhydrous N, N-dimethyl formamide were purchased from Sigma Aldrich, used without additional purification, while the commercial grade of hexane, ethyl acetate, and methylene chloride was further distilled. Precoated silica gel 60 F\textsubscript{254} plates and silica gel (No. 60) used for chromatography were purchased from Merck & Co., Inc.

Instrumentation

Fourier transform nuclear magnetic resonance spectra were obtained by using a Bruker-Ascend\textsuperscript{TM} 400 high-resolution magnetic resonance spectrometer for \textsuperscript{1}H (400 MHz), \textsuperscript{13}C\{\textsuperscript{1}H\} (100 MHz) and \textsuperscript{29}Si\{\textsuperscript{1}H\} (79 MHz) nuclei. Chemical shifts were reported in $\delta$ units (parts per million) relative to tetramethylsilane (TMS) and residual solvents peaks were used as a reference. High-resolution mass spectrometry was performed with a VQ-TOF 2 Micromass spectrometer.

General procedure to prepare sodium o-nitrophenolate and m-nitrophenolate salts.

Either 2-nitrophenol or 3-nitrophenol was dissolved in a sodium hydroxide solution (1 M) at a molar ratio of 1:1. Then, the solution mixture was stirred at room temperature for 1 hour until becoming a clear solution. Evaporation of water gave derivatives of nitrophenolate sodium salts. Then, the solid salts were further dried under a vacuum for an overnight, while being heated at 70°C to complete a perfect dryness.
Synthesis of octakis(3-propyl-o-oxynitrobenzene)octasilsesquioxane (2), decakis(3-propyl-o-oxynitrobenzene)decasilsesquioxane (3), and dodecakis(3-propyl-o-oxynitrobenzene)dodecasilsesquioxane (4).

In a 50 ml of dried round bottom flask, sodium o-nitrophenolate salt (4.23 g, 26.2 mmol) was further dried for 5 hours under vacuum while being heated at 70°C. Then, dried compound 1 (2.00 g, 1.93 mmol) was added, followed by the addition of dried DMF (15 mL) into the solid mixture. Then, the reaction solution was heated to 100°C for 1 day. The reaction was then stopped by cooling down in an ice bath. In order to remove soluble inorganic salts, 150 ml of cold CH₂Cl₂ and 50 ml of cold deionized water were added into the reaction mixture, becoming a two-phase solution between organic and aqueous layers. The aqueous layer was extracted by 50 mL of CH₂Cl₂ for three times. After that, combined organic layers were washed with 50 ml of cold deionized water and saturated NaHCO₃ solution for three times. Then, it was further washed with cold deionized water until the organic phase changed color from orange to light yellow in order to completely remove an excess of 2-nitrophenol. Anhydrous sodium sulfate was added into the organic solution resulting in a clear yellow solution, followed by a filtration. Evaporation of organic solvent gave a yellow sticky crude product (3.48 g). Finally, the crude product was purified by silica gel column chromatography (100% CH₂Cl₂ to obtain three major products at Rf at 0.38, 0.30 and 0.24, identified as T₈, T₁₀, and T₁₂ products, respectively. Compound 2 (T₈, 0.2993 g, 0.1612 mmol, 5% yield),¹H NMR (CDCl₃): δ 0.82 (m, 2H), 1.93 (m, 2H), 4.06 (t, 2H, J(H-H) = 6.28 Hz), 6.94 (m, 1H), 7.07 (d, 1H, J(H-H) = 8.04 Hz), 7.46 (m, 1H), 7.77 (dd, 1H, J(H-H) = 3.24 Hz). ¹³C{¹H} NMR (CDCl₃): δ 152.46, 139.86, 134.10, 125.46, 119.94, 114.52, 71.05, 22.61, 7.92 ppm. ²⁹Si{¹H} NMR (CDCl₃): δ -66.70 ppm. HRMS (ESI): [M+Na]⁺ calcld for [C₇₂H₈₀N₈O₃₆Si₈Na]⁺, m/z 1879.2727; found, m/z 1879.2657. Compound 3 (T₁₀, 0.6422 g, 0.2768 mmol, 18% yield),¹H NMR (CDCl₃): δ 0.82 (m, 2H), 1.93 (m, 2H), 4.06 (t, 2H, J(H₁-H₂) = 6.28 Hz), 6.94 (m, 1H), 7.07 (d, 1H, J(H₁-H₂) = 8.08 Hz), 7.46 (m, 1H), 7.77 (dd, 1H, J(H₁-H₂) = 3.24 Hz). ¹³C{¹H} NMR (CDCl₃): δ 152.83, 140.11, 134.43, 125.46, 119.84, 111.52, 71.50, 22.91, 7.92 ppm. ²⁹Si{¹H} NMR (CDCl₃): δ -68.41 ppm. HRMS (ESI): [M+Na]⁺ calcld for [C₹₀H₁₀₀N₁₀O₄₅Si₁₀Na]+, m/z 2343.3434; found, m/z 2343.3255. Compound 4 (T₁₂, 0.1285 g, 0.04616 mmol, 4% yield) ¹H NMR (CDCl₃): δ 0.84 (m, 2H), 1.93 (m, 2H), 4.06 (t, 2H, J(H₁-H₂) = 6.10 Hz), 6.99 (m, 1H), 7.08 (d, 1H, J(H₁-H₂) = 8.40 Hz), 7.45 (m, 1H), 7.74 (dd, 1H, J(H₁-H₂) = 3.11 Hz). ¹³C{¹H} NMR (CDCl₃): δ 152.90, 140.03, 134.46, 125.68, 120.09, 115.02, 71.61, 23.34, 9.52, 8.94 ppm. ²⁹Si{¹H} NMR (CDCl₃): δ
Synthesis of octakis(3-propyl-\(m\)-oxinoitrobenzene)octasilsesquioxane (5), decakis(3-propyl-\(m\)-oxinoitrobenzene)decasilsesquioxane (6), and dodecakis(3-propyl-\(m\)-oxinoitrobenzene)dodecasilsesquioxane (7).

To complete a perfect dryness of sodium salt, \(m\)-nitrophenolate sodium salt was further dried under a vacuum at 70 °C for 5 hours until the orange solids of the salt hydrate to dried red powder. Then, dried compound 1 (2.00 g; 1.93 mmol) and sodium \(m\)-nitrophenol salt (3.73 g, 23.1 mmol) were added into 50 mL of dried round bottom flask, dried under vacuum at room temperature for an additional hour. Anhydrous N,N-dimethyl formamide (DMF) (15 mL) was added into the solid mixture. After heating at 70°C for 24 hours, the reaction mixture was cooled down in an ice-bath, followed by the addition of cold CH\(_2\)Cl\(_2\) (150 mL) and deionized water (50 mL) to extract products in organic layer out from aqueous layer. The aqueous layer was further extracted by 50 mL of CH\(_2\)Cl\(_2\) (3 times). The combined organic layers were further washed with saturated NaHCO\(_3\) and washed with water in the final. The organic solution was dried by anhydrous sodium sulfate. Then, evaporation of organic layer gave the yellow sticky crude product (3.07g), and analyzed by thin-layer chromatography (TLC) with 10% of hexane in CH\(_2\)Cl\(_2\). The result showed three separate spots at \(R_f = 0.35, 0.25\) and 0.14, identified as T\(_8\), T\(_{10}\), and T\(_{12}\) products, respectively. Compound 5 (T\(_8\), 0.11 g, 0.0592 mmol, 3% yield), \(^1\)H NMR (CDCl\(_3\)): \(\delta 0.82 (t, 2H, J_{(H-H)} = 3.09 Hz), 1.92 (m, 2H), 3.96 (t, 2H, J_{(H-H)} = 6.44 Hz), 7.16 (dd, 1H, J_{(H-H)} = 3.37 Hz), 7.37 (t, 1H, J_{(H-H)} = 8.22 Hz), 7.63 (t, 1H, J_{(H-H)} = 2.14 Hz), 7.74 (dd, 1H, J_{(H-H)} = 3.09 Hz). \(^{13}\)C\{\(^1\)H\} NMR (CDCl\(_3\)): \(\delta 159.38, 149.14, 129.97, 121.61, 115.70, 108.39, 70.01, 22.54, 8.09\) ppm. \(^{29}\)Si\{\(^1\)H\} NMR (CDCl\(_3\)): \(\delta -66.70\) ppm. HRMS (ESI): [M+Na]\(^+\) calcd for [C\(_{72}\)H\(_{80}\)N\(_8\)O\(_{36}\)Si\(_8\)Na]\(^+\), \(m/z\) 1879.2727; found, \(m/z\) 1879.2875. Compound 6 (T\(_{10}\), 0.42 g, 0.1808 mmol, 12% yield), \(^1\)H NMR (CDCl\(_3\)): \(\delta 0.82 (t, 2H, J_{(H-H)} = 8.20 Hz), 1.92 (m, 2H), 3.95 (t, 2H, J_{(H-H)} = 6.42 Hz), 7.15 (dd, 1H, J_{(H-H)} = 3.39 Hz), 7.36 (t, 1H, J_{(H-H)} = 8.22 Hz), 7.62 (t, 1H, J_{(H-H)} = 2.22 Hz), 7.74 (dd, 1H, J_{(H-H)} = 3.15 Hz). \(^{13}\)C\{\(^1\)H\} NMR (CDCl\(_3\)): \(\delta 159.60, 149.32, 130.20, 121.78, 115.86, 108.68, 70.36, 22.99, 8.96\) ppm. \(^{29}\)Si\{\(^1\)H\} NMR (CDCl\(_3\)): \(\delta -68.53\) ppm. HRMS (ESI): [M+Na]\(^+\) calcd for [C\(_{90}\)H\(_{100}\)N\(_{10}\)O\(_{45}\)Si\(_{10}\)Na]\(^+\), \(m/z\) 2343.3434; found, \(m/z\) 2343.3512. Compound 9 (T\(_{12}\), 0.26 g, 0.0933 mmol, 7% yield), \(^1\)H
NMR (CDCl₃): δ 0.86 (t, 2H, J_{H-H} = 8.24 Hz), 1.95 (m, 2H), 3.95 (t, 2H, J_{H-H} = 4.18 Hz), 7.13 (dd, 1H, J_{H-H} = 8.24 Hz), 7.31 (t, 1H, J_{H-H} = 8.16 Hz), 7.58 (t, 1H, J_{H-H} = 2.06 Hz), 7.68 (dd, 1H, J_{H-H} = 3.12 Hz). ¹³C{¹H} NMR (CDCl₃): δ 159.60, 149.38, 130.29, 121.74, 116.00, 108.74, 70.47, 23.26, 9.58, 9.01 ppm. ²⁹Si{¹H} NMR (CDCl₃): δ -68.21, -70.90 ppm. HRMS (ESI): [M+Na]⁺ calcd for [C₁₀₈H₁₂₀N₁₂O₅₄Si₁₂Na]⁺, m/z 2808.4175; found, m/z 2808.4812

General procedure to prepare cage-rearranged silsesquioxanes (T₈, T₁₀, and T₁₂) under base-catalyzed reaction at different reaction times.

In each reaction cycle, compound 1, 1.00 g, 0.96 mmol) and K₂CO₃ (0.0625 g, 0.45 mmol) were added into dried two-neck round bottom flask equipped with condenser and magnetic stirring bar. The solid mixture was dried under vacuum for 1 hour. Then, anhydrous DMF (10 ml) was added to the solid mixture. Then, the reaction mixture was heated at 60°C under dried nitrogen to vary reaction times for 15 mins, 30 mins, 1 hr, 2 hrs, 4 hrs, 8 hrs, 16 hrs, and 24 hrs. Isolated yields of each product were determined using conventional liquid chromatography as shown in Figure S1. To work up, the solution mixture was then extracted using CH₂Cl₂ (3 x 50 mL). The organic phase was collected and extracted further using H₂O (3 x 100 mL). The organic layer was dried by anhydrous sodium sulfate and evaporated to obtain pale white viscous liquid. The crude product was purified by silica gel column chromatography (30% CH₂Cl₂/Hexane) to obtain three major products at R_f at 0.41, 0.35 and 0.28, identified as octakis(3-chloropropyl)octasilsesquioxane (1), decakis(3-chloropropyl)decasilsesquioxane (8) and dodecakis(3-chloropropyl)dodecasilsesquioxane (9), respectively. Compound 1, ¹H NMR (CDCl₃): δ 0.79 (m, 2H), 1.86 (m, 2H), 3.53 (t, 2H, J_{H-H} = 6.58 Hz). ¹³C{¹H} NMR (CDCl₃): δ 9.34, 26.25, 47.02 ppm. ²⁹Si{¹H} NMR (CDCl₃): δ -67.07 ppm. HRMS (ESI): [M+Na]⁺ calcd for [C₂₄H₄₈Cl₈NaO₁₂Si₈]⁺, m/z 1058.8647; found, m/z 1058.8539. Compound 8, ¹H NMR (CDCl₃): δ 0.79 (m, 2H), 1.86 (m, 2H), 3.53 (t, 2H, J_{H-H} = 6.52 Hz). ¹³C{¹H} NMR (CDCl₃): δ 9.34, 26.25, 47.02 ppm. ²⁹Si{¹H} NMR (CDCl₃): δ -68.94 ppm. HRMS (ESI): [M+Na]⁺ calcd for [C₃₁H₆₂Cl₁₀NaO₁₄Si₁₀]⁺, m/z 1316.8527; found, m/z 1316.8177. Compound 9, ¹H NMR (CDCl₃): δ 0.77 (m, 2H), 1.85 (m, 2H), 3.54 (t, 2H, J_{H-H} = 6.58 Hz). ¹³C{¹H} NMR (CDCl₃): δ 10.00, 10.49, 26.50, 26.60, 47.15, 47.21 ppm. ²⁹Si{¹H} NMR (CDCl₃): δ -68.68, -71.34 ppm. HRMS (ESI): [M+Na]⁺ calcd for [C₃₆H₇₂Cl₁₂NaO₁₈Si₁₂]⁺, m/z 1576.8021; found, m/z 1576.8498.
Figure S1: Weight percentages of compounds 1 (T₈), 8 (T₁₀), and 9 (T₁₂) with time for base-catalyzed reactions. Isolated yields determined using conventional liquid chromatography.
Figure S2: $^1$H-NMR (400 MHz) of octakis(3-chloropropyl)octasilsesquioxane (1) in CDCl$_3$

Figure S3: $^{13}$C{$^1$H} NMR (100 MHz) of octakis(3-chloropropyl)octasilsesquioxane (1) in CDCl$_3$
Figure S4: $^{29}$Si$^1$H NMR (79 MHz) of octakis(3-chloropropyl)octasilsesquioxane (1) in CDCl$_3$

Figure S5: HRMS (ESI) of octakis(3-chloropropyl)octasilsesquioxane (1)
**Figure S6:** $^1$H NMR (400 MHz) of decakis(3-chloropropyl)decasilsesquioxane (8) in CDCl$_3$

**Figure S7:** $^{13}$C{$^1$H} NMR (100 MHz) of decakis(3-chloropropyl)decasilsesquioxane (8) in CDCl$_3$
Figure S8: $^{29}$Si{$^{1}$H} NMR (79 MHz) of decakis(3-chloropropyl)decasilsesquioxane (8) in CDCl$_3$

Figure S9: HRMS (ESI) of decakis(3-chloropropyl)decasilsesquioxane (8)
Figure S10: $^1$H NMR (400 MHz) of dodecakis(3-chloropropyl)dodecasilsesquioxane ($9$) in CDCl$_3$

Figure S11: $^{13}$C{$^1$H} NMR (100 MHz) of dodecakis(3-chloropropyl)dodecasilsesquioxane ($9$) in CDCl$_3$
Figure S12: $^{29}$Si{¹H} NMR (79 MHz) of dodecakis(3-chloropropyl)dodecasilsesquioxane (9) in CDCl₃

Figure S13: HRMS (ESI) of dodecakis(3-chloropropyl)dodecasilsesquioxane (9)
Figure S14: $^1$H NMR (400 MHz) of octakis(3-propyl-o-oxynitrobenzene)octasilsesquioxane (2) in CDCl$_3$

Figure S15: $^{13}$C\{\textsuperscript{1}H\} NMR (100 MHz) of octakis(3-propyl-o-oxynitrobenzene)octasilsesquioxane (2) in CDCl$_3$
Figure S16: $^{29}$Si-$^1$H NMR (79 MHz) of octakis(3-propyl-0-oxynitrobenzene)octasilsesquioxane (2) in CDCl$_3$

Figure S17: HRMS (ESI) of octakis(3-propyl-0-oxynitrobenzene)octasilsesquioxane (2)
**Figure S18:** $^1$H NMR (400 MHz) of decakis(3-propyl-o-oxynitrobenzene)decasilsesquioxane (3) in CDCl$_3$

**Figure S19:** $^{13}$C{${^1}$H} NMR (100 MHz) of decakis(3-propyl-o-oxynitrobenzene)decasilsesquioxane (3) in CDCl$_3$
Figure S20: $^{29}$Si-{$^1$H} NMR (79 MHz) of decakis(3-propyl-o-oxynitrobenzene)decasilsesquioxane (3) in CDCl$_3$.

Figure S21: HRMS (ESI) of decakis(3-propyl-o-oxynitrobenzene)decasilsesquioxane (3)
**Figure S22:** $^1$H NMR (400 MHz) of dodecakis(3-propyl-o-oxynitrobenzene)dodecasilsesquioxane (4) in CDCl$_3$

**Figure S23:** $^{13}$C{$_1^1$H} NMR (100 MHz) of dodecakis(3-propyl-o-oxynitrobenzene)dodecasilsesquioxane (4) in CDCl$_3$
Figure S24: $^{29}$Si-{1H} NMR (79 MHz) of dodecakis(3-propyl-o-oxynitrobenzene)dodecasilsesquioxane (4) in CDCl$_3$

Figure S25: HRMS (ESI) of dodecakis(3-propyl-o-oxynitrobenzene)dodecasilsesquioxane (4)
Figure S26: $^1$H-NMR (400 MHz) of octakis(3-propyl-$m$-oxynitrobenzene)octasilsequioxane (5) in CDCl$_3$

Figure S27: $^{13}$C{^1}H NMR (100 MHz) of octakis(3-propyl-$m$-oxynitrobenzene)octasilsequioxane (5) in CDCl$_3$
**Figure S28:** $^{29}$Si{H} NMR (79 MHz) of octakis(3-propyl-m-oxynitrobenzene)octasilsesquioxane (5) in CDCl$_3$.

**Figure S29:** HRMS (ESI) of octakis(3-propyl-m-oxynitrobenzene)octasilsesquioxane (5)
Figure S30: $^1$H NMR (400 MHz) of decakis(3-propyl-$m$-oxynitrobenzene)decasilsesquioxane (6) in CDCl$_3$

![NMR spectrum of decakis(3-propyl-$m$-oxynitrobenzene)decasilsesquioxane (6) in CDCl$_3$](image)

Figure S31: $^{13}$C-{$^1$H} NMR (100 MHz) of decakis(3-propyl-$m$-oxynitrobenzene)decasilsesquioxane (6) in CDCl$_3$

![NMR spectrum of $^{13}$C-{$^1$H} of decakis(3-propyl-$m$-oxynitrobenzene)decasilsesquioxane (6) in CDCl$_3$](image)
**Figure S32:** $^{29}\text{Si}^1\text{H}$ NMR (79 MHz) of decakis(3-propyl-$m$-oxynitrobenzene)decasilsesquioxane (6) in CDCl$_3$.

**Figure S33:** HRMS (ESI) of decakis(3-propyl-$m$-oxynitrobenzene)decasilsesquioxane (6)
Figure S34: $^1$H NMR (400 MHz) of dodecakis(3-propyl-$m$-oxynitrobenzene)dodecasilsesquioxane (7) in CDCl$_3$.

Figure S35: $^{13}$C{$^1$H} NMR (100 MHz) of dodecakis(3-propyl-$m$-oxynitrobenzene)dodecasilsesquioxane (7) in CDCl$_3$. 
Figure S36: $^{29}$Si{$^1$H} NMR (79 MHz) of dodecakis(3-propyl-$m$-oxynitrobenzene)dodecasilsesquioxane (7) in CDCl$_3$

Glass wall

Figure S37: HRMS (ESI) of dodecakis(3-propyl-$m$-oxynitrobenzene)dodecasilsesquioxane (7)