## Supplementary Materials to the manuscript

The Reaction of the $\mathrm{Si}_{8} \mathrm{O}_{20}\left(\mathrm{SnMe}_{3}\right)_{8}$ Building Block with Silyl Chlorides: A New Synthetic Methodology for Preparing Nanostructured Building Block Solids

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${ }^{29} \mathrm{Si}$ Solid state NMR (SSNMR) spectra (MAS) of the product from the reaction of $\mathrm{HSiCl}_{3}$ with $\mathrm{Si}_{8} \mathrm{O}_{20}\left(\mathrm{SnMe}_{3}\right)_{8}$ in hexane with varying initial stoichiometries of $\mathrm{HSiCl}_{3}: \mathrm{Si}_{8} \mathrm{O}_{20}\left(\mathrm{SnMe}_{3}\right)_{8}$

Figure S2
${ }^{29} \mathrm{Si}$ Solid state NMR (SSNMR) spectra (MAS) of the product from the reaction of $\mathrm{Me}_{2} \mathrm{SiCl}_{2}$ with $\mathrm{Si}_{8} \mathrm{O}_{20}\left(\mathrm{SnMe}_{3}\right)_{8}$ in toluene with varying initial stoichiometries of $\mathrm{Me}_{2} \mathrm{SiCl}_{2}: \mathrm{Si}_{8} \mathrm{O}_{20}\left(\mathrm{SnMe}_{3}\right)_{8}$

Figure S3
${ }^{29} \mathrm{Si}$ Solid state NMR (SSNMR) spectra (MAS) of the product from the reaction of $\mathrm{Me}_{2} \mathrm{SiCl}_{2}$ with $\mathrm{Si}_{8} \mathrm{O}_{20}\left(\mathrm{SnMe}_{3}\right)_{8}$ in hexane with varying initial stoichiometries of $\mathrm{Me}_{2} \mathrm{SiCl}_{2}: \mathrm{Si}_{8} \mathrm{O}_{20}\left(\mathrm{SnMe}_{3}\right)_{8}$

Figure S4
BJH pore volume distribution for the reaction of $\mathrm{HSiCl}_{3}$ and $\mathrm{Si}_{8} \mathrm{O}_{20}\left(\mathrm{SnMe}_{3}\right)_{8}$ in toluene This pore size distribution is typical of all the high surface area solids investigated in these studies.

Figure S5
${ }^{29}$ Si SSNMR (MAS and CPMAS) of a nanostructure solid containing only "embedded" $\mathrm{Me}_{2} \mathrm{Si}(\mathrm{OSi} \equiv)_{2}$ groups linking $\mathrm{Si}_{8} \mathrm{O}_{20}$ building blocks. $\mathrm{SiCl}_{4}$-derived linking groups are also present in the matrix.

Figure S6
${ }^{29}$ Si SSNMR (MAS and CPMAS) of a nanostructure solid containing only "surface" $\mathrm{Me}_{2} \mathrm{SiCl}(\mathrm{OSi} \equiv)$ groups linking $\mathrm{Si}_{8} \mathrm{O}_{20}$ building blocks. $\mathrm{SiCl}_{4}$-derived linking groups are also present in the matrix.

Table S1
BET Surface area analysis of the solids resulting from the reaction of $\mathrm{Me}_{2} \mathrm{SiCl}_{2}$ with $\mathrm{Si}_{8} \mathrm{O}_{20}\left(\mathrm{SnMe}_{3}\right)_{8}$ under the conditions given. Absorption gas: nitrogen. Pore size distributions calculated using standard BJH equations.

Table S2
BET Surface area analysis of the solids resulting from the reaction of $\mathrm{HSiCl}_{3}$ with $\mathrm{Si}_{8} \mathrm{O}_{20}\left(\mathrm{SnMe}_{3}\right)_{8}$ under the conditions given. Absorption gas: nitrogen. Pore size distributions calculated using standard BJH equations.

Figure S1


Figure S2


Figure S3


Figure S4
BJH pore volume distribution for the reaction of $\mathrm{HSiCl}_{3}$ Supp Mat Figure S4 and $\mathrm{Si}_{8} \mathrm{O}_{20}\left(\mathrm{SnMe}_{3}\right)_{8}$ in toluene
Total surface area: $672 \mathrm{~m}^{2} / \mathrm{g}$


Figure S5
${ }^{29}$ Si MAS-CPMAS NMR
Supp Mat Figure S5


Figure S6


## Supp Mat Table S1

Table S1 BET Surface area analysis of the solids resulting from the reaction of $\mathrm{Me}_{2} \mathrm{SiCl}_{2}+\mathrm{Si}_{8} \mathrm{O}_{20}\left(\mathrm{SnMe}_{3}\right)_{8}$ under the conditions given. Absorption gas: nitrogen. Pore size distributions calculated using standard BJH equations.

| Conditions | $\mathrm{Cl}: \mathrm{Sn}$ | Surface <br> Area $\left(\mathrm{m}^{2} / \mathrm{g}\right)$ | Total Pore <br> Volume $(\mathrm{cc} / \mathrm{g})$ | Average Pore <br> Radius $(\AA)$ |
| :---: | :---: | :---: | :---: | :---: |
| Toluene, $80-90^{\circ} \mathrm{C}, 2$ days | $4: 1$ | low | low | low |
| Toluene, $80-90^{\circ} \mathrm{C}, 2$ days | $3: 1$ | low | low | low |
| Toluene, $80-90^{\circ} \mathrm{C}, 2$ days | $2: 1$ | 172 | 0.150 | 17 |
| Toluene, $80-90^{\circ} \mathrm{C}, 2$ days | $1: 1$ | 669 | 0.496 | 15 |
| Hexanes, $50^{\circ} \mathrm{C}$, overnight | $4: 1$ | 13 | 0.015 | 24 |
| Hexanes, $50^{\circ} \mathrm{C}$, overnight | $3: 1$ | 29 | 0.171 | 13 |
| Hexanes, $50^{\circ} \mathrm{C}$, overnight | $2: 1$ | 12 | 0.010 | 19 |
| Hexanes, $50^{\circ} \mathrm{C}$, overnight | $1: 1$ | 14 | 0.021 | 30 |

## Table S2

## Supp Mat Table S2

Table S2 BET Surface Area Analysis of the solids resulting from the reaction of $\mathrm{HSiCl}_{3}+\mathrm{Si}_{8} \mathrm{O}_{20}\left(\mathrm{SnMe}_{3}\right)_{8}$ under the conditions given.
Absorption gas: nitrogen. Pore size distributions calculated using standard BJH equations.

| Conditions | Cl:Sn | Surface <br> Area $\left(\mathbf{m}^{2} / \mathbf{g}\right)$ | Total Pore <br> Volume $(\mathbf{c c} / \mathbf{g})$ | Average Pore <br> Radius $(\mathbf{A})$ |
| :---: | :---: | :---: | :---: | :---: |
| Toluene, $80-90^{\circ} \mathrm{C}, 2$ days | $4: 1$ | low | low | low |
| Toluene, $80-90^{\circ} \mathrm{C}$, 2 days | $3: 1$ | 558 | 0.400 | 14 |
| Toluene, $80-90^{\circ} \mathrm{C}, 2$ days | $2: 1$ | 660 | 0.513 | 16 |
| Toluene, $80-90^{\circ} \mathrm{C}, 2$ days | $1: 1$ | 672 | 0.539 | 16 |
| Hexanes, $50^{\circ} \mathrm{C}$, overnight | $4: 1$ | 336 | 0.243 | 14 |
| Hexanes, $50^{\circ} \mathrm{C}$, overnight | $3: 1$ | 324 | 0.254 | 16 |
| Hexanes, $50^{\circ} \mathrm{C}$, overnight | $2: 1$ | 401 | 0.295 | 15 |
| Hexanes, $50^{\circ} \mathrm{C}$, overnight | $1: 1$ | 58 | 0.046 | 16 |

