

*Supporting Information*

## **Electric Field Breakdown in Single Molecule Junctions**

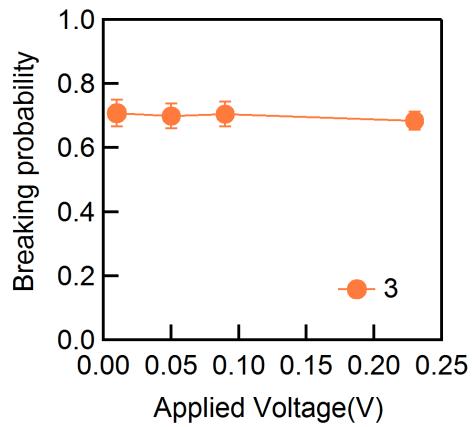
**Haixing Li,<sup>†</sup> Timothy A. Su,<sup>‡</sup> Vivian Zhang,<sup>‡</sup> Michael L. Steigerwald,<sup>\*,‡</sup> Colin Nuckolls,<sup>\*,‡</sup> and Latha Venkataraman<sup>\*,†</sup>**

<sup>†</sup>Department of Applied Physics and Applied Mathematics and <sup>‡</sup>Department of Chemistry, Columbia University, New York, New York 10027, United States

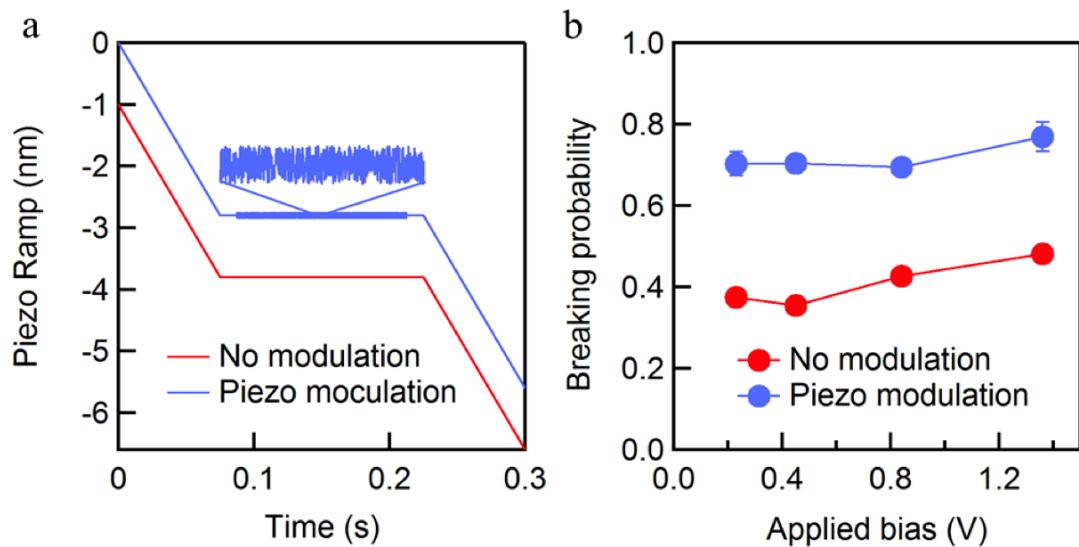
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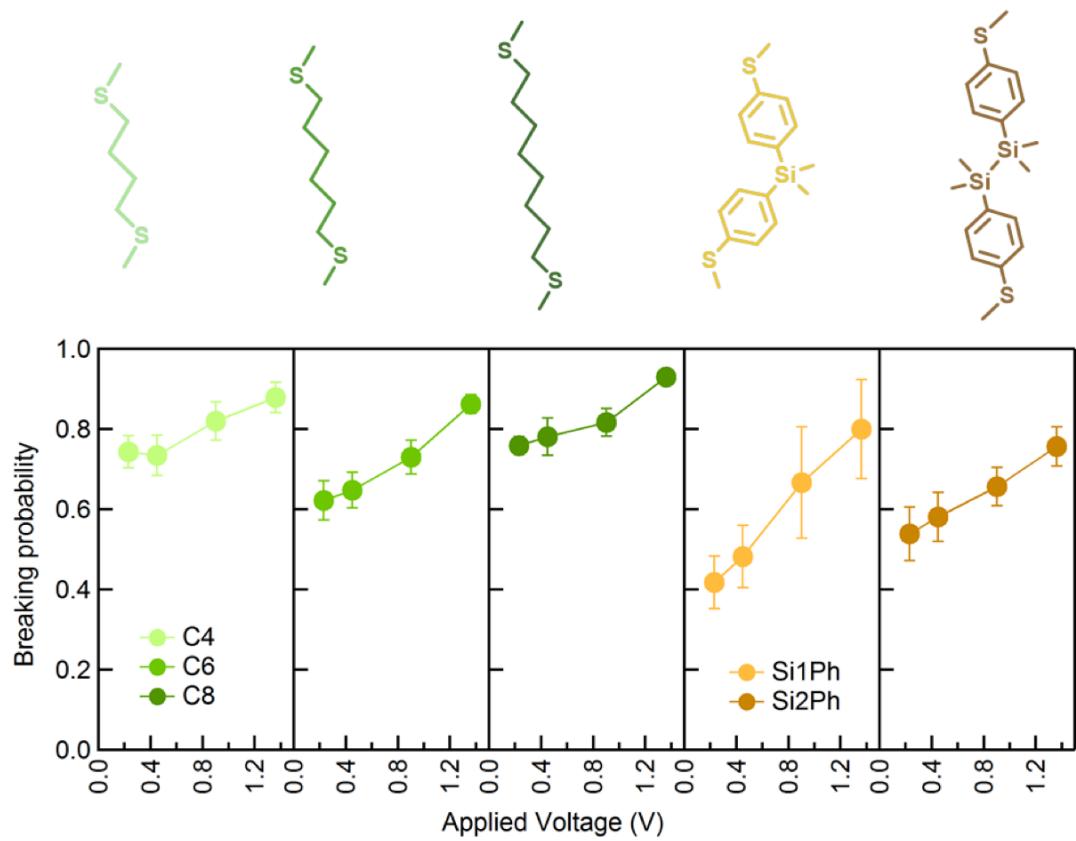
## I. Supplemental Figures from Main Text



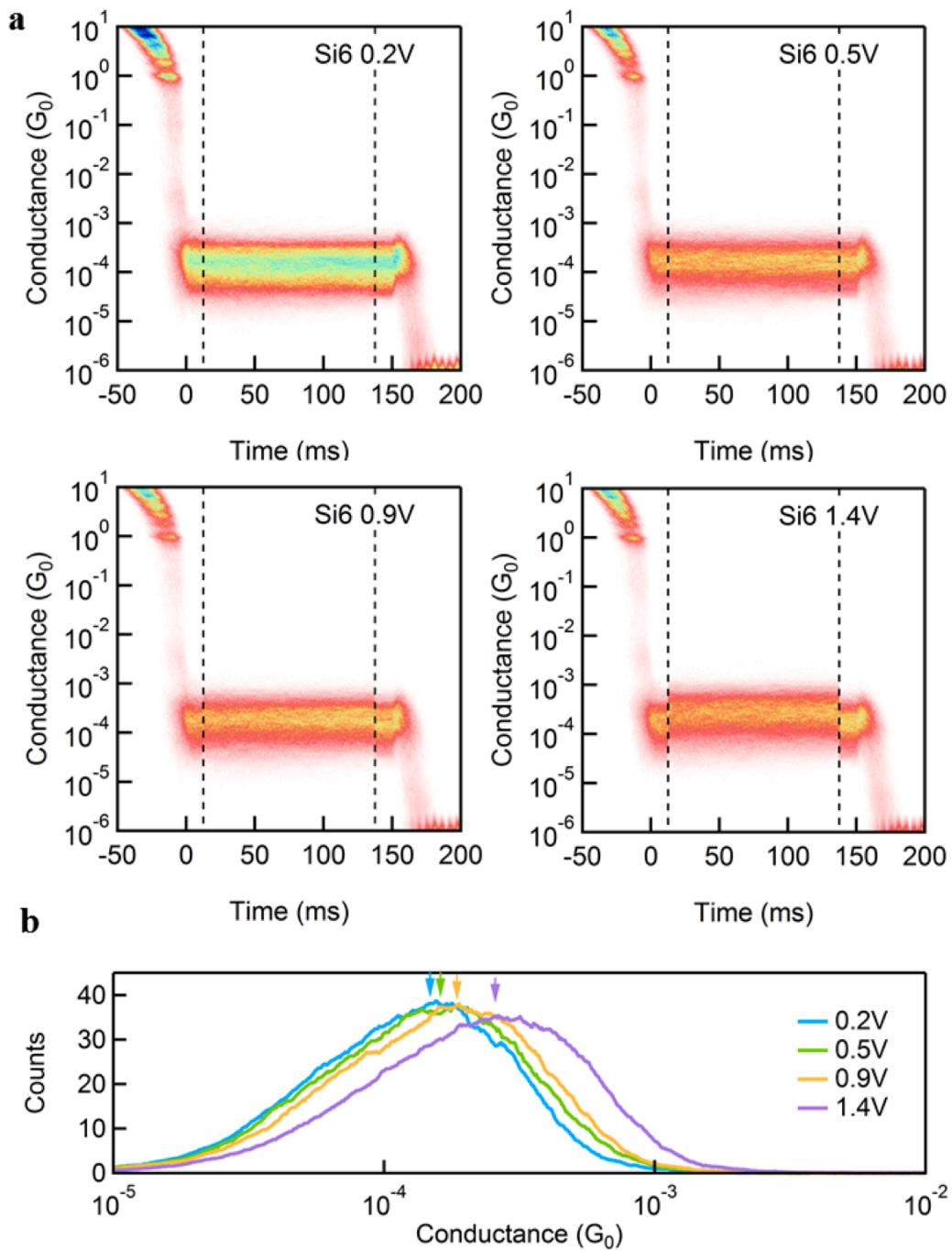
**Figure S1.** Junction breaking probability at low bias for molecule **3**.



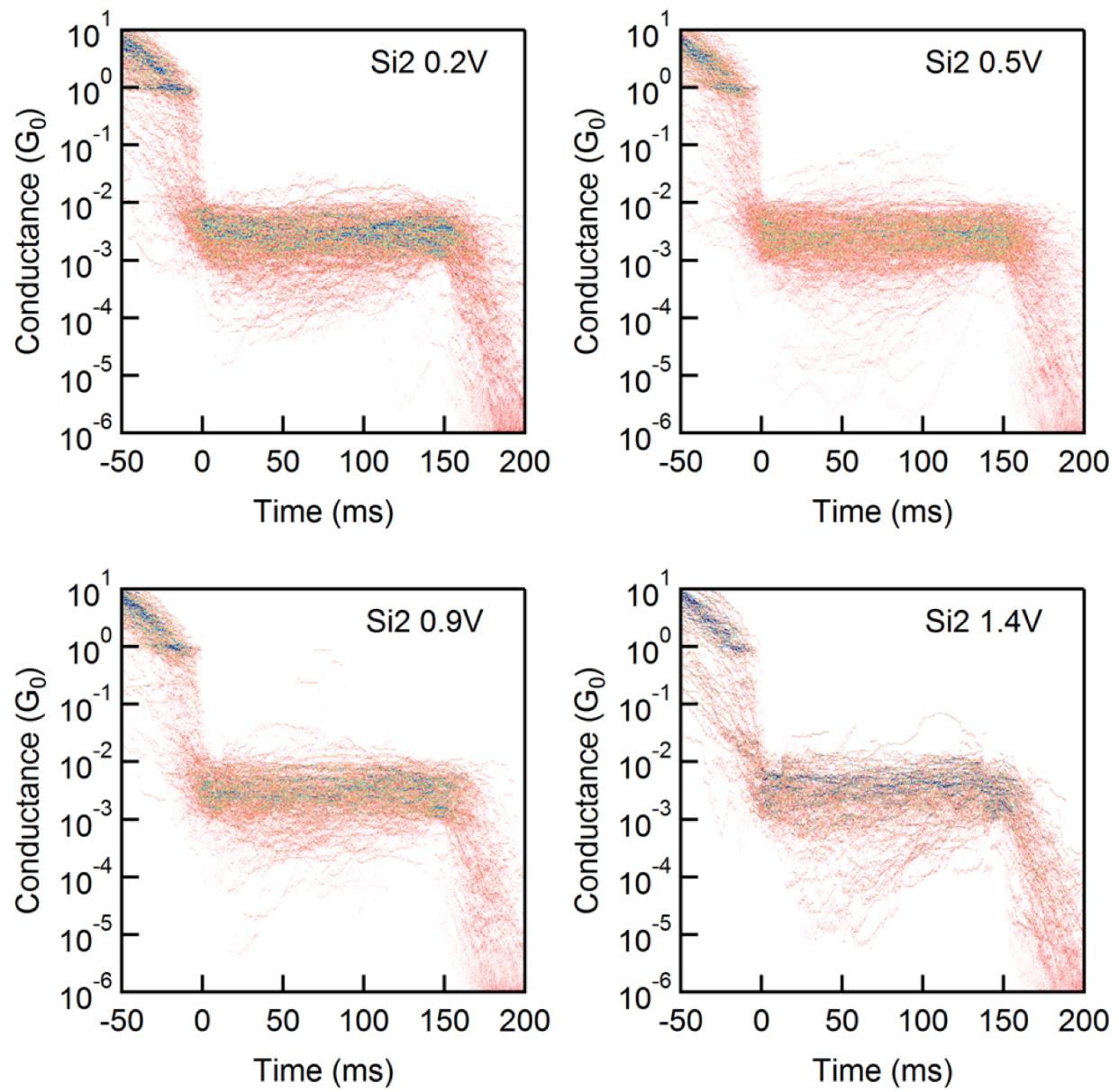
**Figure S2.** Control experiment with piezo modulation. (a) Two piezo ramps with (blue) and without (red) an additional mechanical modulation. The modulation is added by applying white noise within 1 Å to the piezo. (b) Junction breaking probability plotted against the applied bias voltage with (blue) and without (red) piezo modulation for molecule **Si4** (structure in Figure 4 in manuscript).



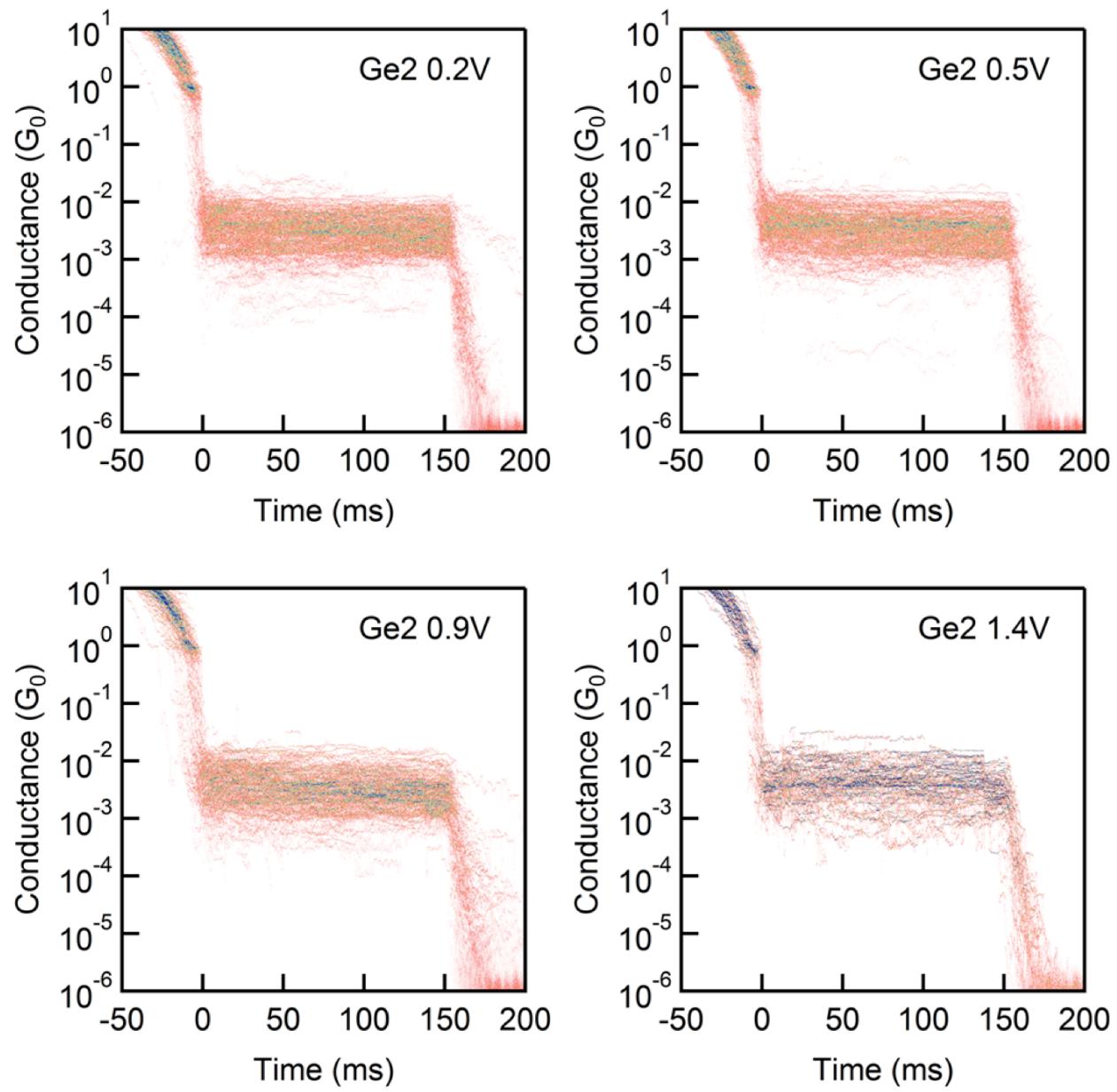
**Figure S3.** Junction breaking probability plotted against the applied voltage for molecules **C4**, **C6**, **C8**, **Si1Ph**, **Si2Ph** terminated with methylsulfide ( $\text{SMe}$ ) linker group; structures are shown above. Error bars show the standard deviation determined from variations in sets of thousand measurements.



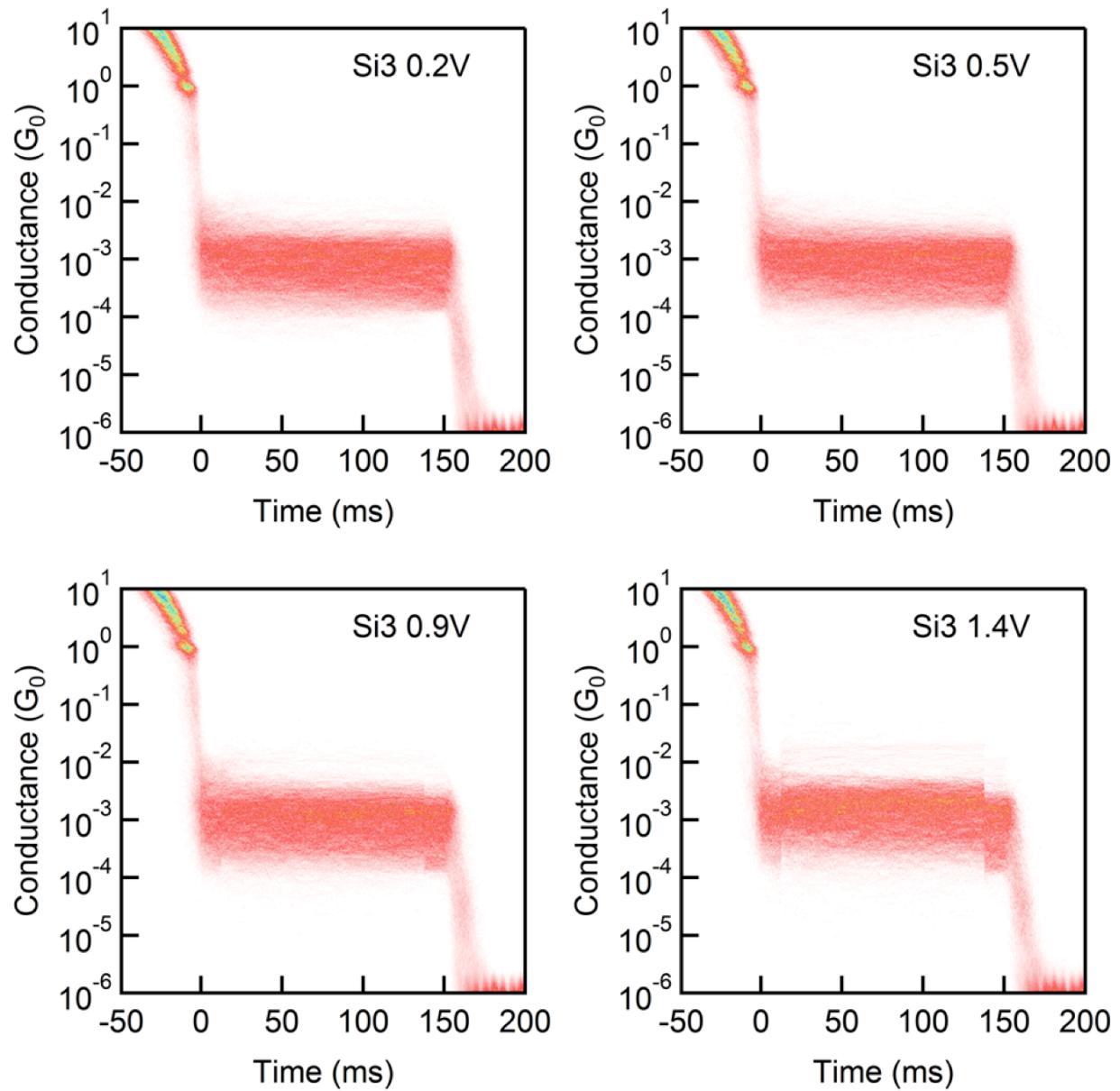
**Figure S4.** Determination of the conductance of molecule **Si6** with  $\text{CH}_2\text{-SH}$  linkers (structure shown in Figure 4 in manuscript) at different voltages. (a) Two-dimensional conductance histograms of sustaining traces under an applied voltage of 0.2V, 0.5V, 0.9V and 1.4V. (b) Respective conductance profiles generated from the 125 ms windows delineated by the black dashed lines in Figure S4(a) where a voltage pulse is applied. Arrows indicate the conductance peak values at different applied bias voltages.



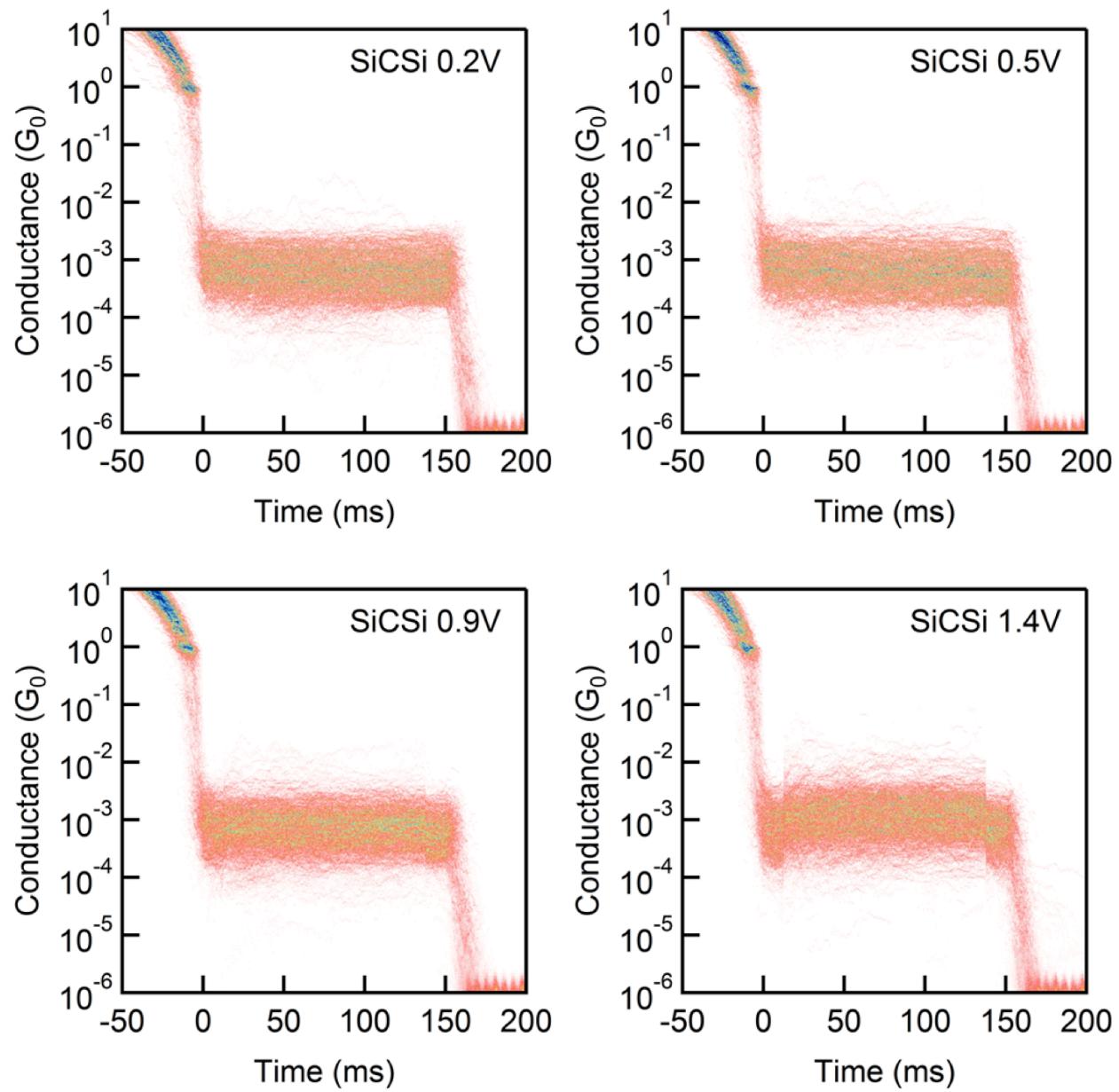
**Figure S5.** 2D conductance histograms of sustaining **Si2** with  $\text{CH}_2\text{-SH}$  linker.



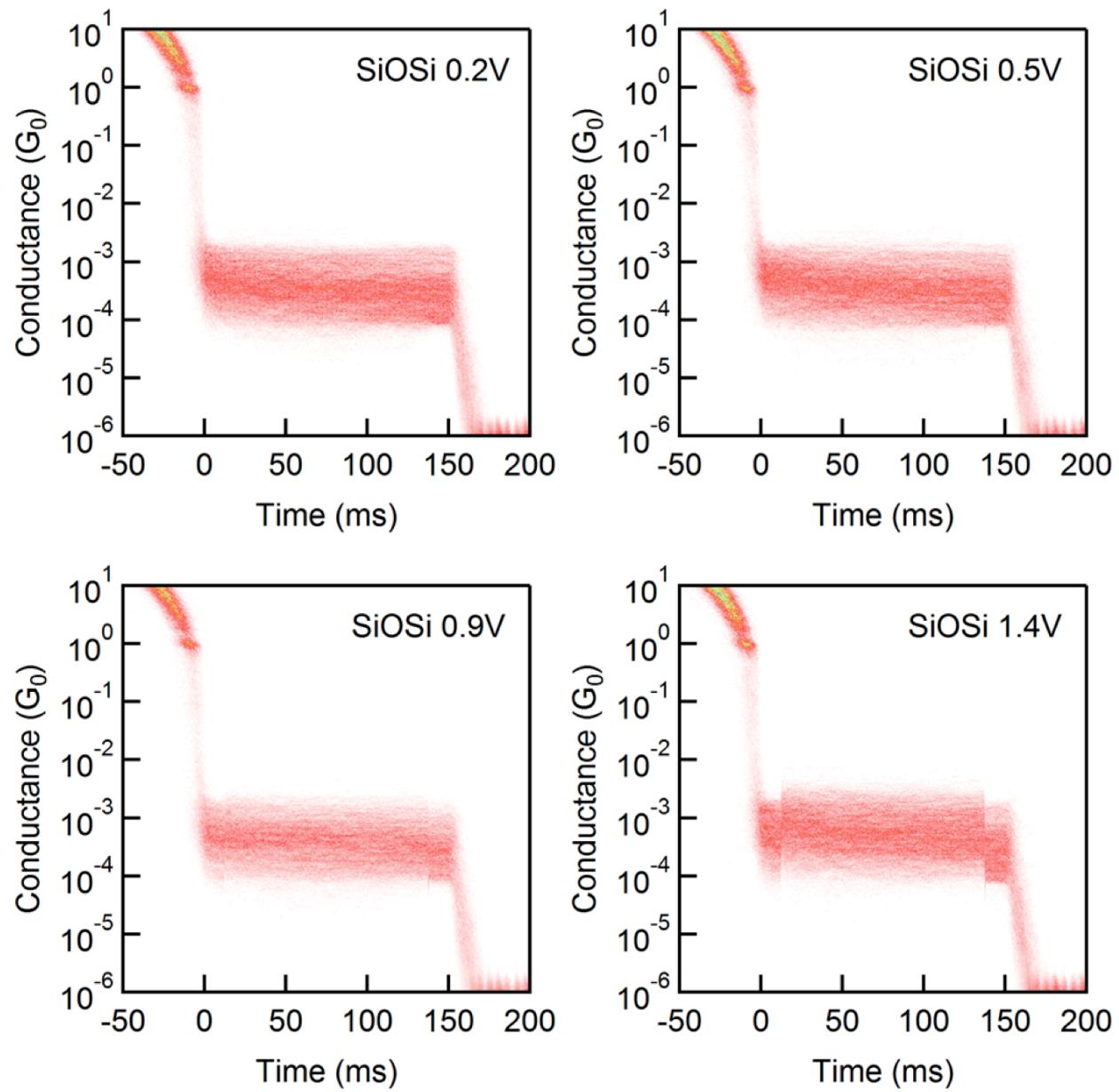
**Figure S6.** 2D conductance histograms of sustaining **Ge2** with  $\text{CH}_2\text{-SH}$  linker.



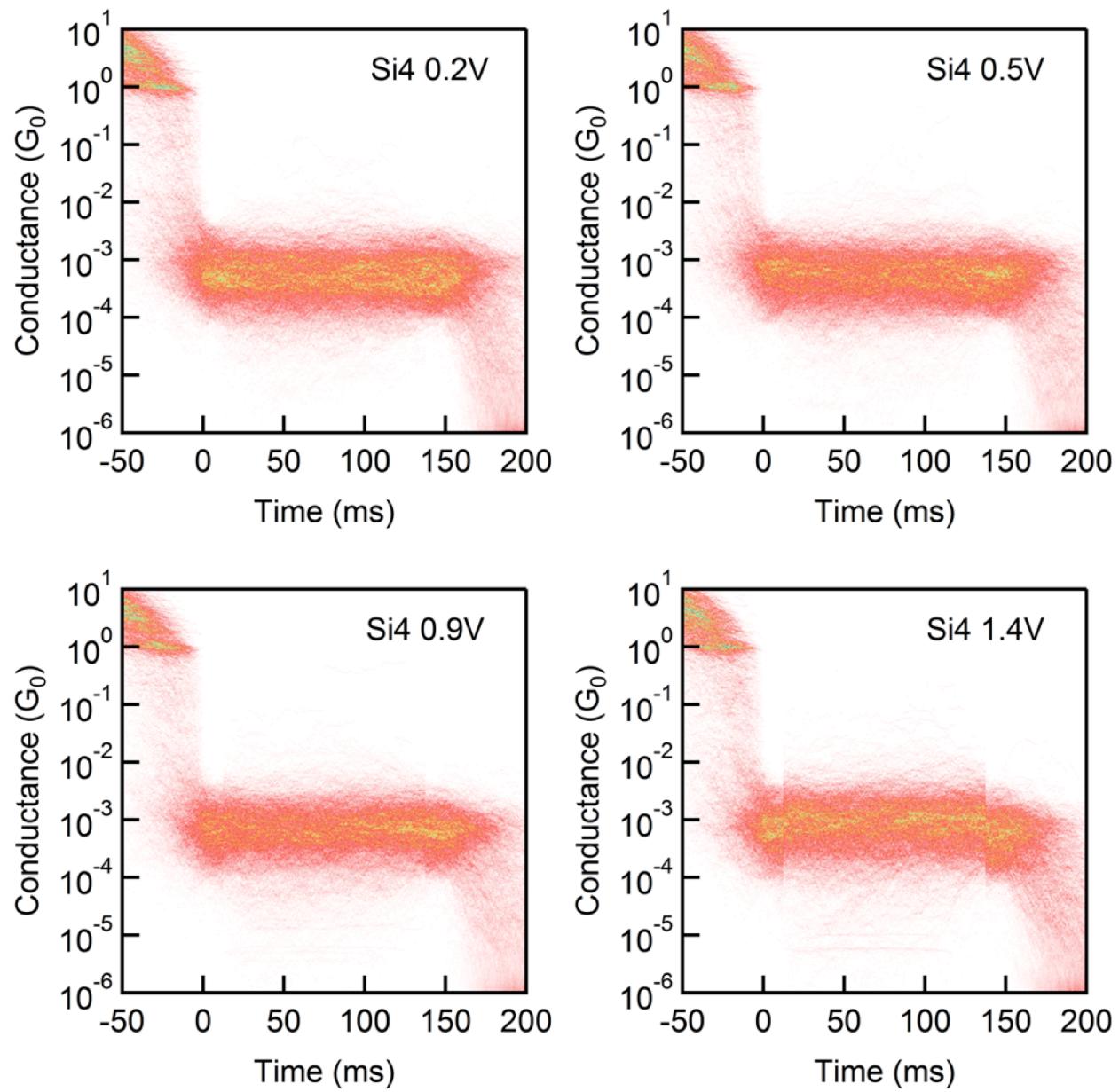
**Figure S7.** 2D conductance histograms of sustaining Si3 with  $\text{CH}_2\text{-SH}$  linker.



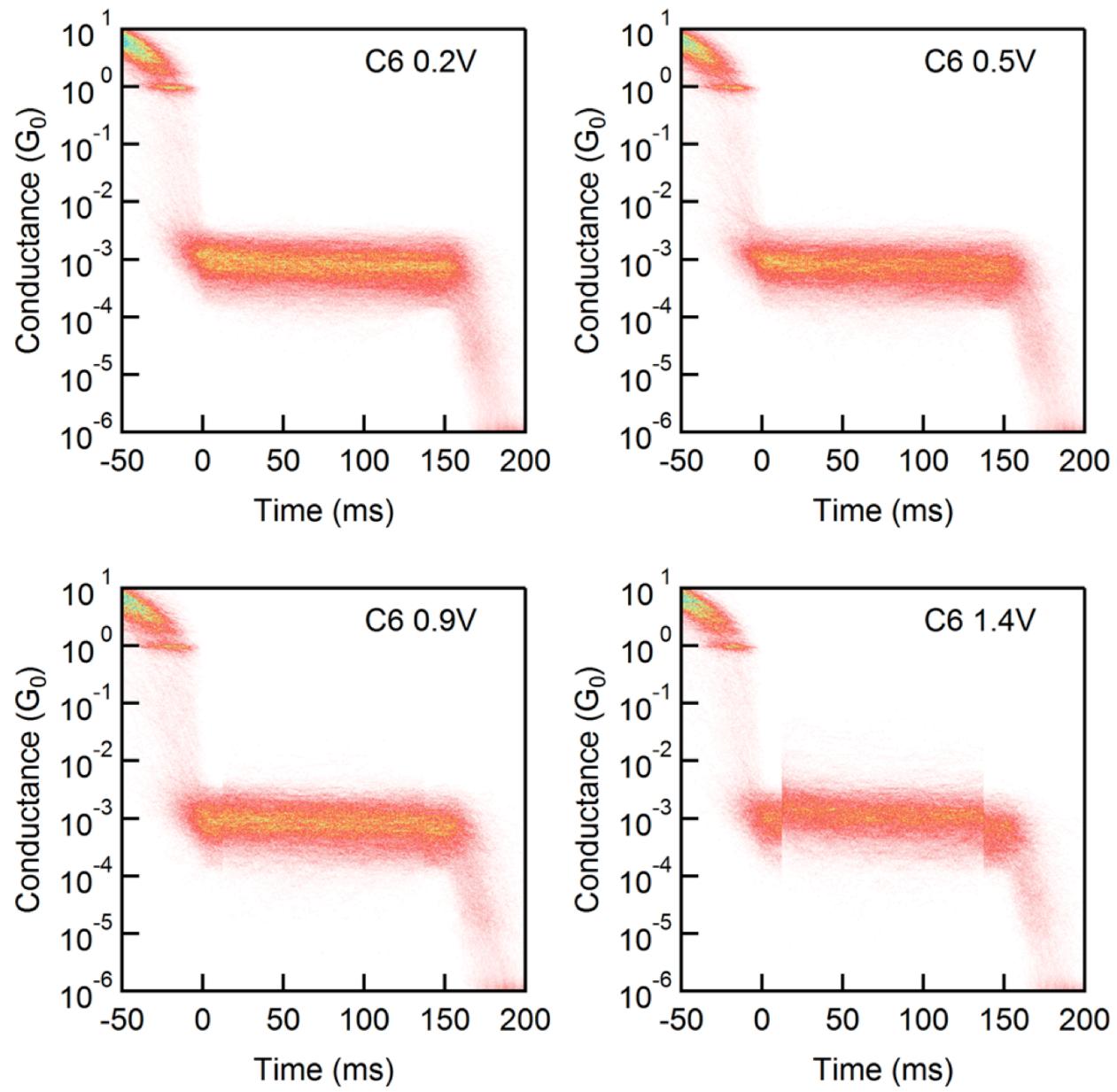
**Figure S8.** 2D conductance histograms of sustaining **SiCSi** with  $\text{CH}_2\text{-SH}$  linker.



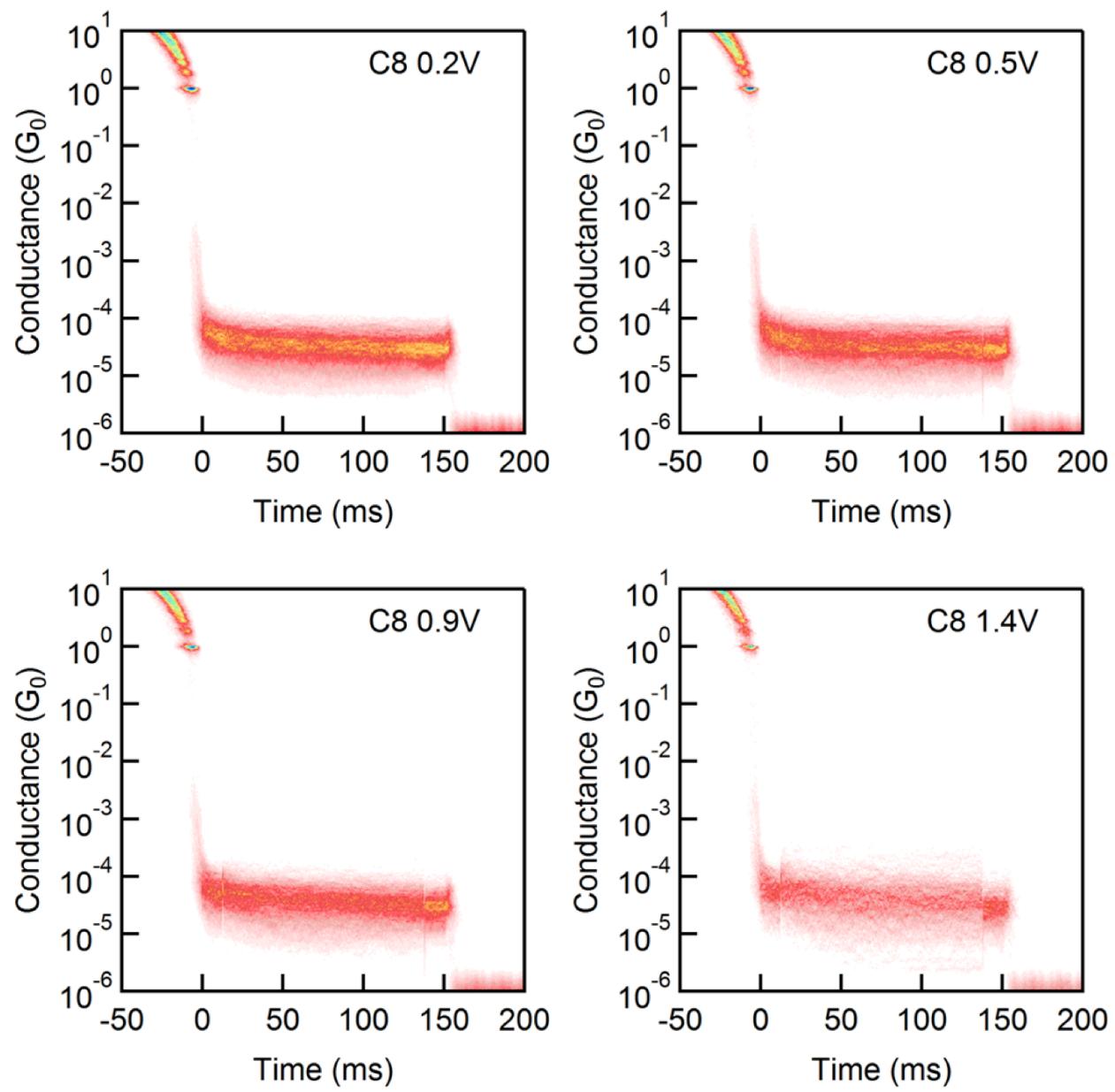
**Figure S9.** 2D conductance histograms of sustaining **SiOSi** with  $\text{CH}_2\text{-SH}$  linker.



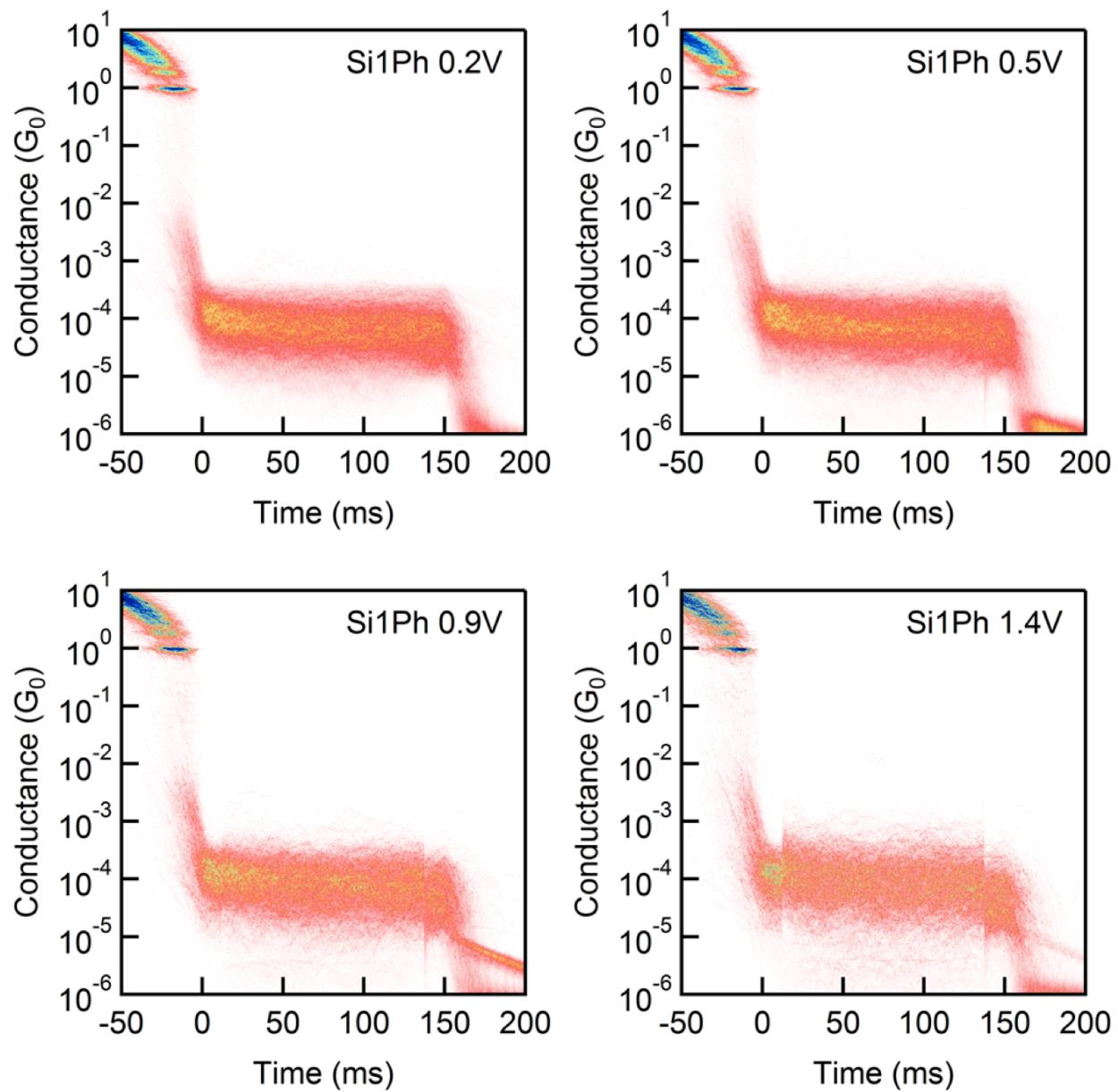
**Figure S10.** 2D conductance histograms of sustaining **Si4** with  $\text{CH}_2\text{-SH}$  linker.



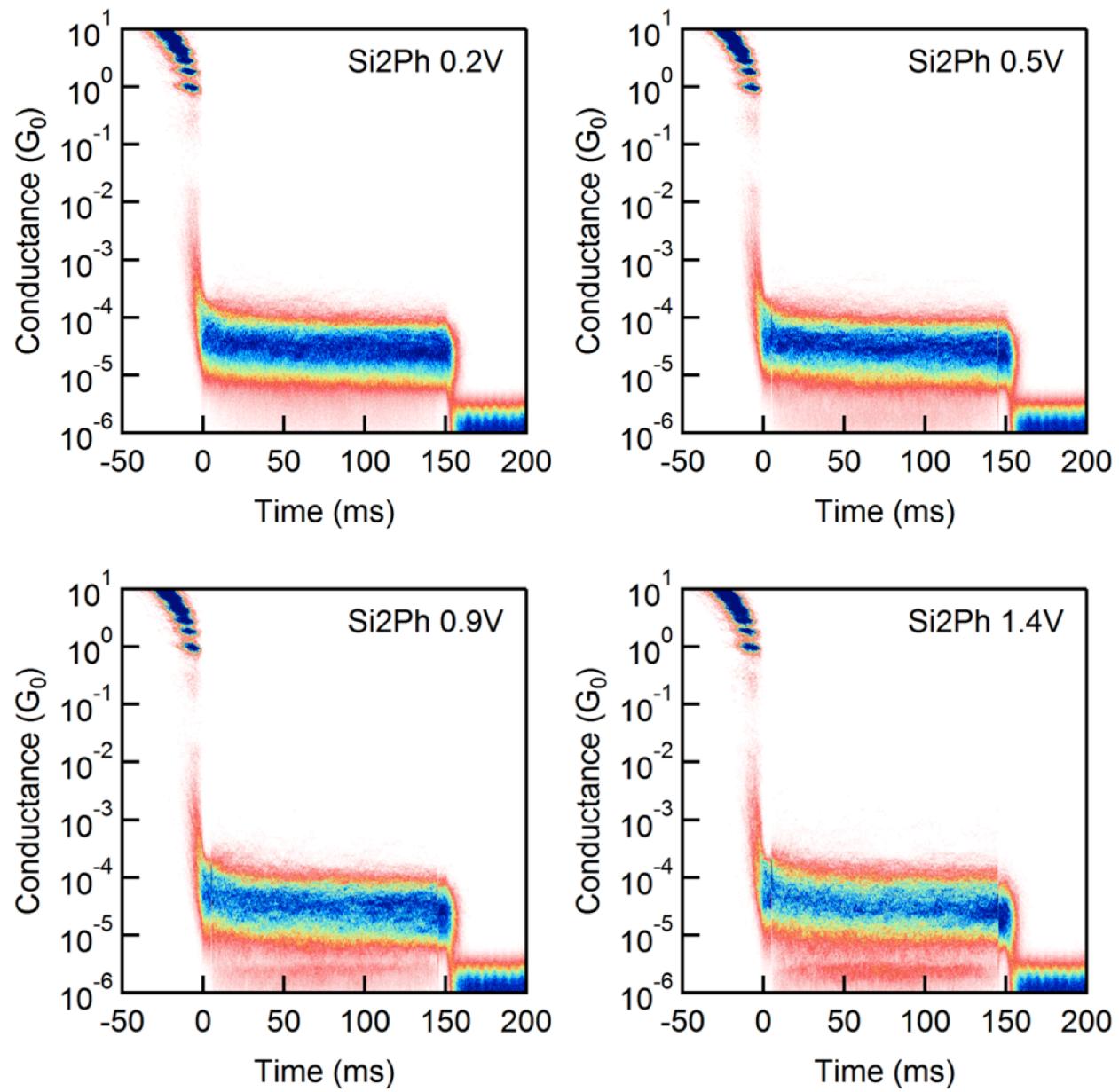
**Figure S11.** 2D conductance histograms of sustaining **C6** with SH linker.



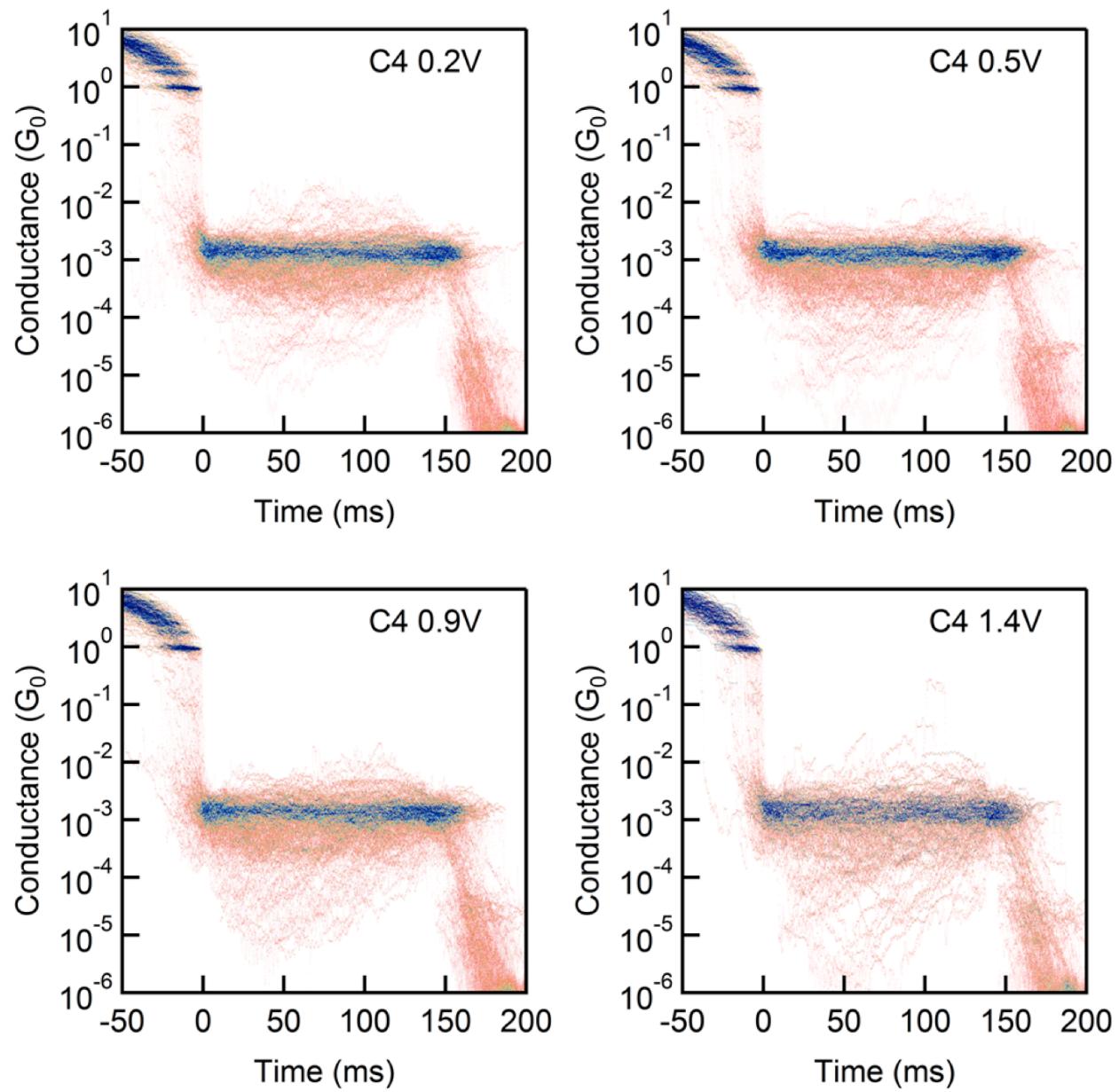
**Figure S12.** 2D conductance histograms of sustaining **C8** with SH linker.



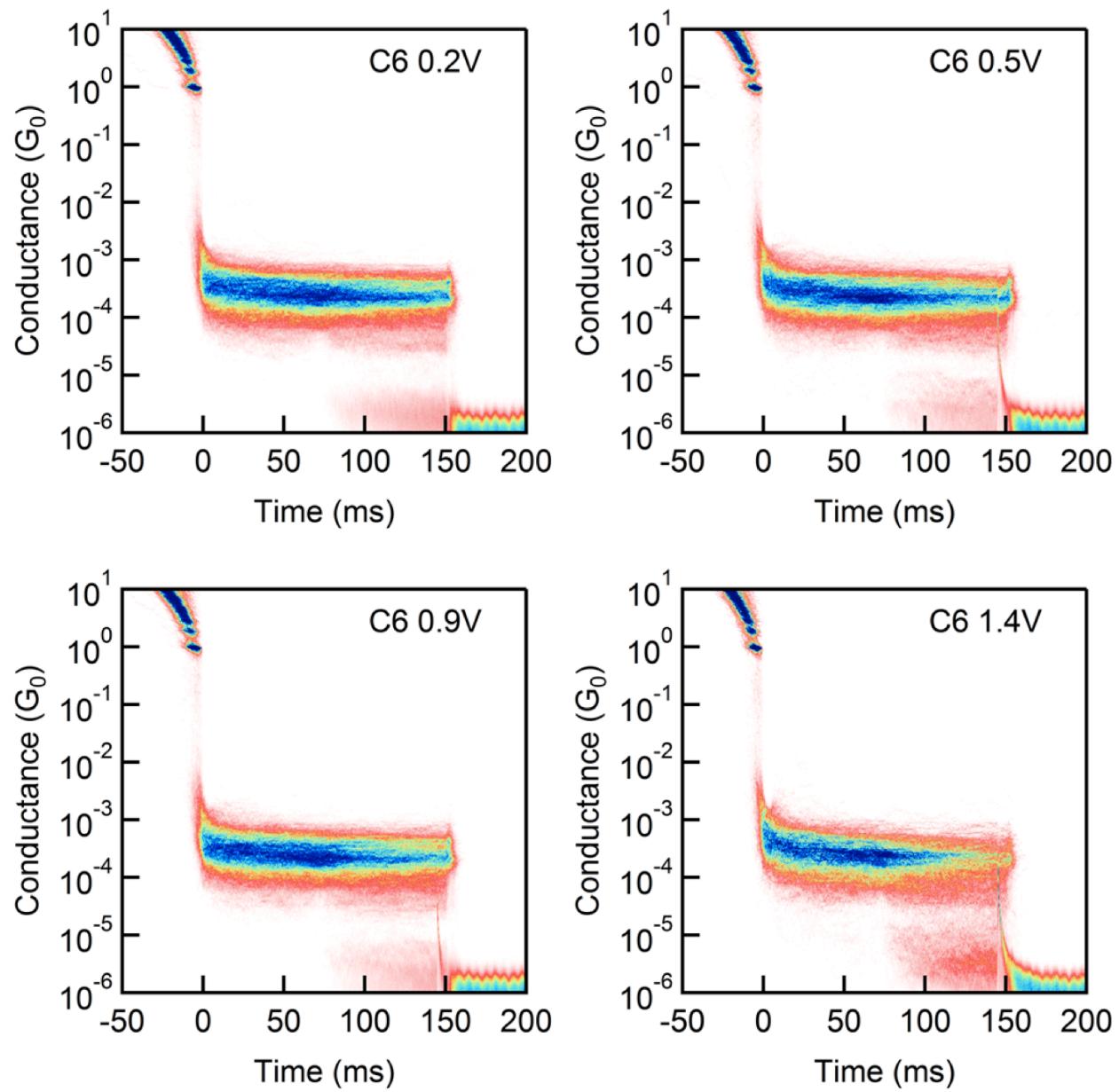
**Figure S13.** 2D conductance histograms of sustaining **Si1Ph** with SMe linker.



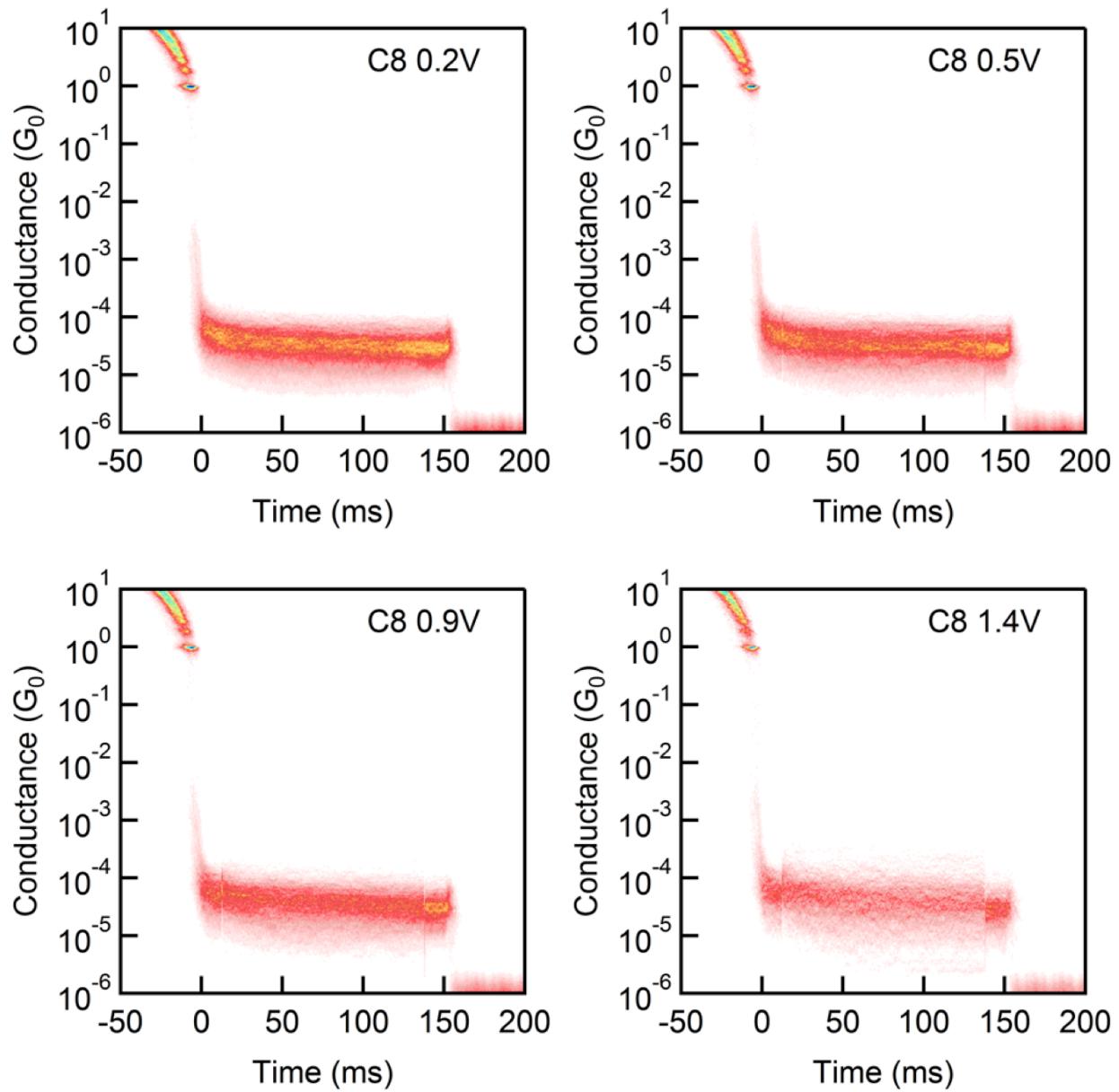
**Figure S14.** 2D conductance histograms of sustaining **Si2Ph** with SMe linker.



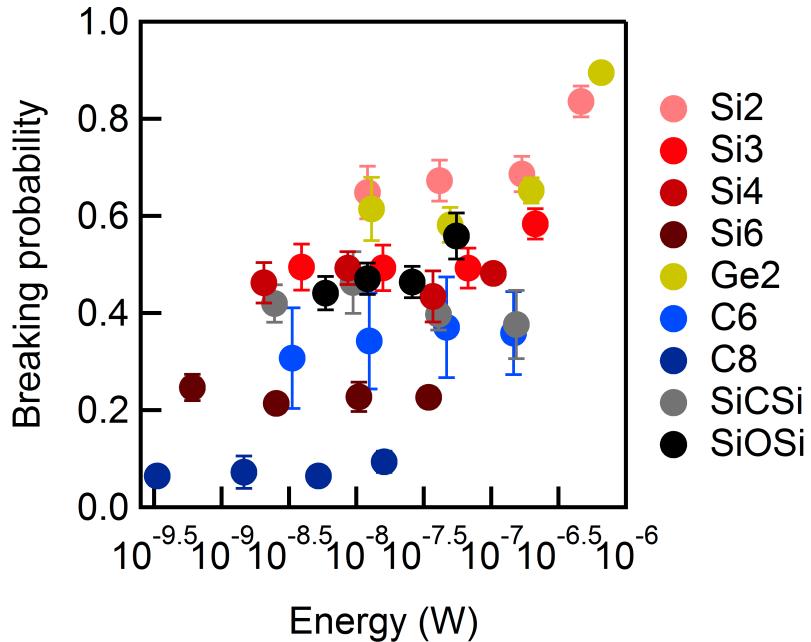
**Figure S15.** 2D conductance histograms of sustaining **C4** with SMe linker.



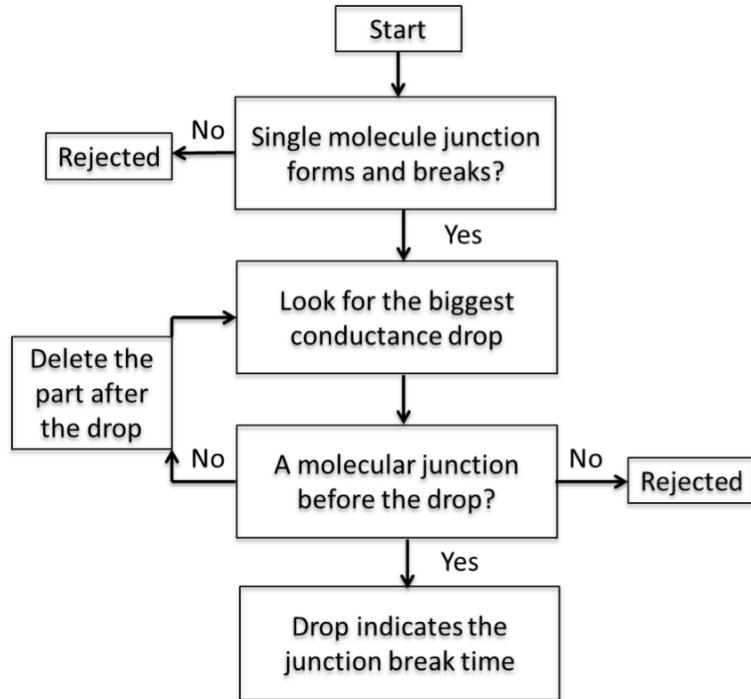
**Figure S16.** 2D conductance histograms of sustaining **C6** with SMe linker.



**Figure S17.** 2D conductance histograms of sustaining **C8** with SMe linker.



**Figure S18.** Junction rupture probability plotted against the heat produced (calculated as (current)  $\times$  (voltage)) for each junction on a semi-logarithm scale. Plot is generated from the same dataset as **Figure 5a** in the manuscript. Error bars show the standard deviation determined from variations in sets of thousand measurements.



**Scheme S1.** Time dependence analysis algorithm flow chart.

We apply an automated algorithm that looks for the first large conductance drop during the hold using a previously detailed method.<sup>1</sup>

## II. Synthetic Procedures and Characterization of Compounds

All reactions were performed in oven-dried or flame-dried round bottom flasks, unless otherwise noted.

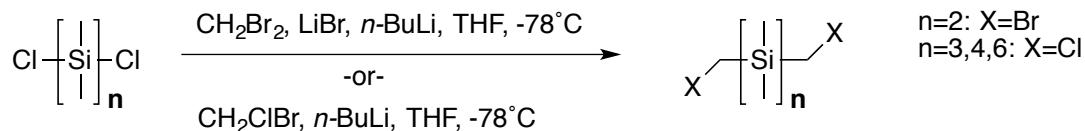
The flasks were fitted with rubber septa and reactions were conducted under a positive pressure of nitrogen or argon unless otherwise noted. Anhydrous and anaerobic solvents were obtained from a Schlenk manifold with purification columns packed with activated alumina and supported copper catalyst (Glass Contour, Irvine, CA). Automated flash chromatography was performed using a Teledyne Isco Combiflash R<sub>f</sub>200 and Redisep R<sub>f</sub> Gold Silica columns.

*Materials.* Commercial reagents were used without further purification unless otherwise noted. The  $\alpha,\omega$ -dichlorooligosilanes, **Si1Ph**, **Si2Ph** and **C8** with SMe linkers were synthesized according to literature procedures.<sup>1,2</sup>

*Instrumentation.* <sup>1</sup>H, <sup>13</sup>C, and <sup>29</sup>Si NMR spectra were recorded on a Bruker DRX300 (300 MHz), Bruker DRX400 (400 MHz) or a Bruker DMX500 (500 MHz) spectrometer. Chemical shifts for protons are reported in parts per million downfield from tetramethylsilane and are referenced to residual protium in the NMR solvent (CHCl<sub>3</sub>:  $\delta$  7.26). Chemical shifts for carbon are reported in parts per million downfield from tetramethylsilane and are referenced to the carbon resonances of the solvent (CDCl<sub>3</sub>  $\delta$  77.16). Chemical shifts for silicon are reported in parts per million downfield from tetramethylsilane and referenced to the silicon resonance of tetramethylsilane (TMS  $\delta$  0.0). The silicon NMR resonances were determined with a DEPT pulse sequence. Data are represented as follows: chemical shift, multiplicity (s = singlet, d = doublet, dd = doublet of doublets, t = triplet, m = multiplet), coupling constants in Hertz, and integration. The mass spectroscopic data were obtained at the Columbia University mass spectrometry facility using a JEOL JMSHX110A/110A tandem mass spectrometer. We note that our mass spectrometry facility was unable to ionize the  $\alpha,\omega$ -bis(halomethyl)permethyloligosilanes so mass spectrometry analysis for these compounds is not provided.

## Synthetic Details

### I. $\alpha,\omega$ -bis(halomethyl)permethyloligosilanes



We synthesized the bis(bromomethyl)tetramethyldisilane from a method adapted from Block *et al.*<sup>3</sup> Anhydrous lithium bromide (0.87 g, 10.00 mmol, 2.00 equiv.) was added to an oven-dried 100 mL round bottom flask equipped with a stir bar and septum. 35 mL THF was added to the flask, followed by the dichlorotetramethyldisilane (0.99 g, 5.00 mmol, 1.00 equiv.) and dibromomethane (3.48 g, 20.00 mmol, 4.00 equiv.). A slight yellow coloration was observed upon mixing these constituents. The reaction flask was cooled to -78°C and submerged deeply into the dry ice-acetone bath to ensure the sides of the glass were cold as well. A 1.64 M solution of *n*-butyllithium in hexanes (9.14 mL, 15.00 mmol, 3.00 equiv.) was added to the reaction flask very slowly down the side of the flask using a syringe pump. Slow generation of the bromomethyl lithiate is desirable. The butyllithium was added in this fashion over an hour. The reaction mixture was warmed slowly to room temperature overnight. The THF was evaporated and the remaining residue was stirred with hexanes for 5 minutes. After this period, the hexanes solution was filtered over Celite and evaporated to yield a crude oil product. This material was then chromatographed over silica in 100% hexanes and visualized with Hanessian's Stain to achieve the desired product. Clear, colorless oil (1.04 g, 69% yield). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 2.63 (s, 4H), 0.25 (s, 12H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 17.65, -3.71. <sup>29</sup>Si NMR (60 MHz, CDCl<sub>3</sub>) δ -14.07.

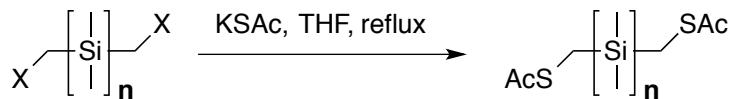
The  $n=3,4,6$   $\alpha,\omega$ -bis(halomethyl)permethyloligosilanes were synthesized from a method adapted from Kobayashi and Pannell.<sup>4</sup> The following is a representative procedure. A flame-dried round bottom flask equipped with a stir bar and septum was charged with the bis(chloromethyl)hexamethyltrisilane

(1.35 g, 5.51 mmol, 1.00 equiv.) followed by the bromochloromethane (2.14 g, 16.54 mmol, 3.00 equiv.) and THF (31 mL) as solvent. The reaction flask was cooled to -78°C and submerged deeply into the dry ice-acetone bath to ensure the sides of the glass were cold as well. A 1.654 M solution of *n*-butyllithium in hexanes (7.00 mL, 11.58 mmol, 2.10 equiv.) was added to the reaction flask very slowly down the side of the flask using a syringe pump. The butyllithium was added in this fashion over an hour. The reaction mixture was warmed slowly to room temperature overnight. The THF was evaporated and the remaining residue was stirred with hexanes for 5 minutes. After this period, the hexanes solution was filtered over an alumina plug and evaporated to yield pure product. Colorless oil (1.40 g, 93% yield). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 2.92 (s, 4H), 0.22 (s, 12H), 0.20 (s, 6H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 31.47, -4.19, -6.27. <sup>29</sup>Si NMR (60 MHz, CDCl<sub>3</sub>) δ -11.07, -48.86.

n=4: The bis(chloromethyl)octamethyltetrasilane was synthesized with the same general procedure with the following exceptions: dichlorooctamethyltetrasilane was used instead of dichlorohexamethyltrisilane. Colorless oil (1.56 g, 91% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 2.91 (s, 4H), 0.21 (s, 12H), 0.20 (s, 12H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 31.66, -3.99, -5.41. <sup>29</sup>Si NMR (60 MHz, CDCl<sub>3</sub>) δ -10.60, -44.77.

n=6: The bis(chloromethyl)dodecamethylhexasilane was synthesized with the same general procedure with the following exceptions: dichlorododecamethylmethylhexasilane was used instead of dichlorohexamethyltrisilane. Clear, colorless oil (0.37 g, 83% yield). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 2.92 (s, 4H), 0.22 - 0.20 (three overlapping singlets, 36H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 31.82, -3.98, -4.19, -5.11. <sup>29</sup>Si NMR (60 MHz, CDCl<sub>3</sub>) δ -10.67, -39.36, -43.30.

## II. $\alpha,\omega$ -bis(acetylthiomethyl)permethyloligosilanes



We synthesized the  $\alpha,\omega$ -bis(acetylthiomethyl)permethyloligosilanes with a general procedure adapted from literature methods.<sup>3,5</sup> Potassium thioacetate (0.83 g, 6.11 mmol, 2.40 equiv.) was added to a 50 mL round bottom flask equipped with a stir bar and condenser followed by 13 mL THF. Bis(bromomethyl)tetramethyldisilane (0.77 g, 2.55 mmol, 1.00 equiv.) was dissolved in 3 mL THF and added to the flask at room temperature. The reaction mixture was refluxed overnight. The solvent was removed *in vacuo* and the crude material was passed through a silica plug with dichloromethane. The resulting product was an orange oil with a dank odor (766 mg, quantitative yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 2.34 (s, 6H), 2.20 (s, 4H), 0.16 (s, 12H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 196.72, 30.32, 12.97, -3.76. <sup>29</sup>Si NMR (60 MHz, CDCl<sub>3</sub>) δ -16.56. HRMS predicted for C<sub>10</sub>H<sub>22</sub>O<sub>2</sub>S<sub>2</sub>Si<sub>2</sub> 294.06, observed 295.0666 (FAB+).

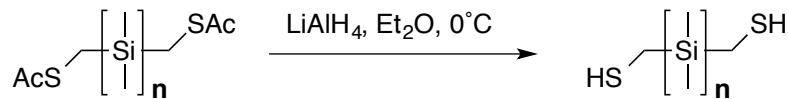
n=3: The bis(acetylthiomethyl)hexamethyltrisilane was synthesized with the same general procedure with the following exceptions: bis(chloromethyl)hexamethyltrisilane was used instead of bis(bromomethyl)tetramethyldisilane and the crude material was purified by silica gel chromatography with a gradient from 100% hexanes to 1:3 hexanes:dichloromethane. Orange oil (720 mg, 75% yield). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 2.34 (s, 6H), 2.21 (s, 4H), 0.17 (s, 6H), 0.16 (s, 12H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 196.87, 30.32, 13.52, -3.15, -6.33. <sup>29</sup>Si NMR (60 MHz, CDCl<sub>3</sub>) δ -13.33, -48.12. HRMS predicted for C<sub>12</sub>H<sub>28</sub>O<sub>2</sub>S<sub>2</sub>Si<sub>3</sub> 352.08, observed 351.0749 (FAB+).

n=4: The bis(acetylthiomethyl)octamethyltetrasilane was synthesized with the same general procedure with the following exceptions: bis(chloromethyl)octamethyltetrasilane was used instead of

bis(bromomethyl)tetramethyldisilane Orange oil (1.00 g, quantitative yield).  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  2.34 (s, 6H), 2.20 (s, 4H), 0.19 (s, 12H), 0.15 (s, 12H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  196.92, 30.32, 13.66, -2.98, -5.41.  $^{29}\text{Si}$  NMR (60 MHz,  $\text{CDCl}_3$ )  $\delta$  -12.67, -44.49. HRMS predicted for  $\text{C}_{14}\text{H}_{34}\text{O}_2\text{S}_2\text{Si}_4$  410.11 observed 409.1011 (FAB+).

n=6: The bis(acetylthiomethyl)dodecamethylhexasilane was synthesized with the same general procedure with the following exceptions: bis(chloromethyl) dodecamethylhexasilane was used instead of bis(bromomethyl)tetramethyldisilane and the crude material was purified by silica gel chromatography with a gradient from 100% hexanes to 1:3 hexanes:dichloromethane. Orange oil (82 mg, 37% yield).  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  2.34 (s, 6H), 2.20 (s, 4H), 0.21 (s, 12H), 0.19 (s, 12H), 0.15 (s, 12H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  197.05, 30.34, 13.71, -2.95, -4.16, -5.15.  $^{29}\text{Si}$  NMR (99 MHz,  $\text{CDCl}_3$ )  $\delta$  -12.71, -39.37, -43.01. HRMS predicted for  $\text{C}_{18}\text{H}_{46}\text{O}_2\text{S}_2\text{Si}_6$  526.16, observed 525.1490 (FAB+).

### III. $\alpha,\omega$ -bis(methylthiol)permethyloligosilanes (**Si2**, **Si3**, **Si4**, **Si6**)



We synthesized the  $\alpha,\omega$ -bis(methylthiol)permethyloligosilanes with a general procedure adapted from literature methods.<sup>3,5</sup> Lithium aluminum hydride (0.50 g, 13.16 mmol, 5.06 equiv.) was added to a flame-dried 100 mL round bottom flask equipped with a stir bar and rubber septum. 15 mL  $\text{Et}_2\text{O}$  was added to the flask and the flask was cooled to 0°C. bis(acetylthiomethyl)tetramethyldisilane (0.76 g, 2.60 mmol, 1.00 equiv.) was dissolved in 10 mL  $\text{Et}_2\text{O}$  and added dropwise by syringe pump over 30 minutes. The reaction mixture was stirred overnight to room temperature. The reaction mixture was then cooled to 0°C

and quenched by a dropwise addition of 2 M HCl solution (5.1 mL), after which the reaction mixture was stirred at room temperature for 10 minutes. The reaction mixture was filtered over an alumina plug and the solids were washed with Et<sub>2</sub>O. Solvent was removed *in vacuo* to yield a colorless oil (279 mg, 51% yield). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 1.80 (d, *J* = 6.9 Hz, 4H), 1.21 (t, *J* = 7.0 Hz, 2H), 0.20 (s, 12H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 7.28, -4.08. <sup>29</sup>Si NMR (60 MHz, CDCl<sub>3</sub>) δ -14.34. HRMS predicted for C<sub>6</sub>H<sub>18</sub>S<sub>2</sub>Si<sub>2</sub> 210.04, observed 209.0311 (FAB+).

n=3: The bis(methylthiol)hexamethyltrisilane was synthesized with the same general procedure with the following exception: bis(acetylthiomethyl)hexamethyltrisilane was used instead of bis(acetylthiomethyl)tetramethyldisilane. Colorless oil (152 mg, 57%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 1.79 (d, *J* = 6.9 Hz, 4H), 1.19 (t, *J* = 6.9 Hz, 2H), 0.19 (two overlapping singlets, 18H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 7.71, -3.72, -5.99. <sup>29</sup>Si NMR (60 MHz, CDCl<sub>3</sub>) δ -11.03, -48.59. 03079. HRMS predicted for C<sub>8</sub>H<sub>24</sub>S<sub>2</sub>Si<sub>3</sub> 268.06, observed 267.0544 (FAB+).

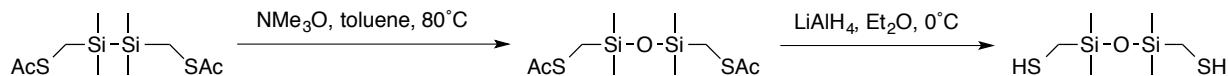
n=4: The bis(methylthiol)octamethyltetrasilane was synthesized with the same general procedure with the following exception: bis(acetylthiomethyl)octamethyltetrasilane was used instead of bis(acetylthiomethyl)tetramethyldisilane. Colorless oil (307 mg, 66% yield). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 1.78 (d, *J* = 6.9 Hz, 4H), 1.18 (t, *J* = 6.9 Hz, 2H), 0.19 (s, 12H), 0.18 (s, 12H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 7.81, -3.59, -5.22. <sup>29</sup>Si NMR (60 MHz, CDCl<sub>3</sub>) δ -10.47, -44.67. HRMS predicted for C<sub>10</sub>H<sub>30</sub>S<sub>2</sub>Si<sub>4</sub> 326.09, observed 325.0784 (FAB+).

n=6: The bis(methylthiol)dodecamethylhexasilane was synthesized with the same procedure with the following exception: bis(acetylthiomethyl)dodecamethylhexasilane was used instead of

bis(acetylthiomethyl)tetramethyldisilane. Clear, colorless oil (55 mg, 84% yield).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  1.78 (d,  $J$  = 6.9 Hz, 4H), 1.18 (t,  $J$  = 6.9 Hz, 2H), 0.20 (s, 12H), 0.20 (s, 12H), 0.18 (s, 12H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  7.85, -3.59, -4.11, -4.98.  $^{29}\text{Si}$  NMR (99 MHz,  $\text{CDCl}_3$ )  $\delta$  -10.51, -39.37, -43.19. HRMS predicted for  $\text{C}_{14}\text{H}_{42}\text{S}_2\text{Si}_6$  442.13, observed 441.1276 (FAB+).

#### IV. SiOSi, SiCSi, Ge2 with methylthiol linkers

##### Bis(methylthiol)tetramethyldisiloxane (**SiOSi**)

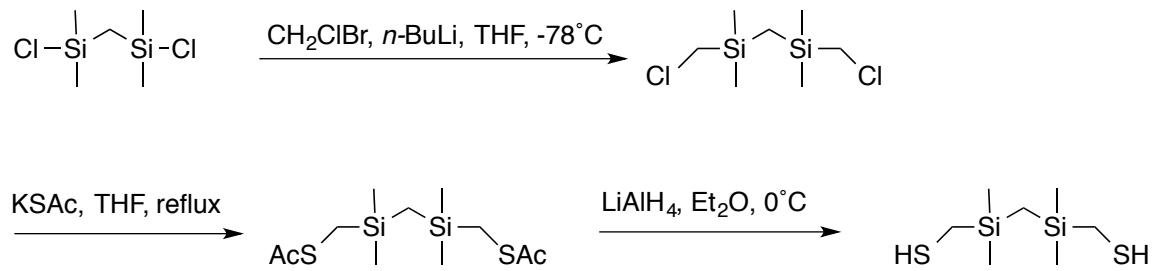


Bis(acetylthiomethyl)tetramethyldisilane (0.84 g, 2.84 mmol, 1.00 equiv.) was added to a 50 mL round bottom flask followed by trimethylamine N-oxide (0.43 g, 5.68 mmol, 2.00 equiv.) and 16 mL toluene. The reaction mixture was heated for two hours at 80°C. The reaction mixture was concentrated *in vacuo* and purified by silica gel chromatography with a gradient from 100% hexanes to 1:3 hexanes:dichloromethane to yield a orange oil (669 mg, 76% yield).  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  2.34 (s, 6H), 2.11 (s, 4H), 0.15 (s, 12H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  196.67, 30.31, 15.26, 0.19.  $^{29}\text{Si}$  NMR (60 MHz,  $\text{CDCl}_3$ )  $\delta$  5.03. HRMS predicted for  $\text{C}_{10}\text{H}_{22}\text{O}_3\text{S}_2\text{Si}_2$  310.05, observed 295.0673 [M-CH<sub>3</sub>]<sup>+</sup> (FAB+).

The bis(acetylthiomethyl)tetramethyldisiloxane was converted to the bis(methylthiol)tetramethyldisiloxane with the same general method described in part III for the  $\alpha,\omega$ -bis(methylthiol)oligosilanes with the following exception: bis(acetylthiomethyl)dodecamethylhexasilane was used instead of bis(acetylthiomethyl)tetramethyldisilane Colorless oil (85 mg, 34% yield).  $^1\text{H}$  NMR

(300 MHz,  $\text{CDCl}_3$ )  $\delta$  1.66 (d,  $J = 7.1$  Hz, 4H), 1.22  $\delta$  1.14 (m, 2H), 0.20 (s, 12H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  9.19, -0.52.  $^{29}\text{Si}$  NMR (60 MHz,  $\text{CDCl}_3$ )  $\delta$  7.62. HRMS predicted for  $\text{C}_6\text{H}_{18}\text{OS}_2\text{Si}_2$  226.03, observed 227.0404.

**Bis((methylthiol)dimethylsilyl)methane (**CSiC**)**



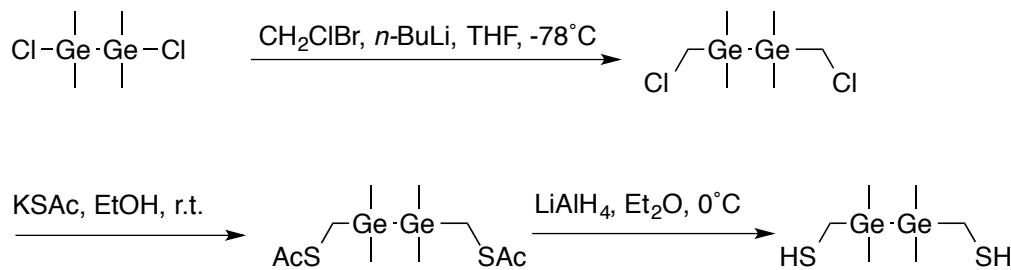
The bis((chloromethyl)dimethylsilyl)methane was synthesized with the same general method described in Part I for the bis(chloromethyl)hexamethyltrisilane with the following exceptions: bis(chlorodimethylsilyl)methane<sup>6</sup> was used instead of dichlorohexamethyltrisilane and a mixture of products was obtained—this mixture was carried forward to the next step without purification.

The bis((acetylthiomethyl)dimethylsilyl)methane was synthesized with the same general method described in Part II with the following exceptions: the reaction mixture from the previous step was used instead of bis(chloromethyl)tetramethyldisilane and the crude material was purified by silica gel chromatography with a gradient from 100% hexanes to 1:3 hexanes:dichloromethane to yield an orange oil (244 mg, 28% yield over two steps).  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  2.34 (s, 6H), 2.09 (s, 4H), 0.11 (s, 12H), -0.10 (s, 2H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  196.81, 30.33, 15.31, 0.83, -0.65.  $^{29}\text{Si}$  NMR (60 MHz,  $\text{CDCl}_3$ )  $\delta$  2.21. HRMS predicted for  $\text{C}_{11}\text{H}_{24}\text{O}_2\text{S}_2\text{Si}_2$  308.08, observed 309.0832 (FAB+).

The bis((methylthiol)dimethylsilyl)methane was synthesized with the same general method described in Part III with the following exceptions: bis((acetylthiomethyl)dimethylsilyl)methane was used instead of bis(acetylthiomethyl)tetramethyldisilane. Colorless oil (118 mg, 66% yield).  $^1\text{H}$  NMR (500

MHz,  $\text{CDCl}_3$ )  $\delta$  1.67 (d,  $J$  = 7.0 Hz, 4H), 1.13 (t,  $J$  = 7.0 Hz, 2H), 0.14 (s, 12H), -0.05 (s, 2H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  9.51, -0.59, -1.26.  $^{29}\text{Si}$  NMR (99 MHz,  $\text{CDCl}_3$ )  $\delta$  3.42. HRMS predicted for  $\text{C}_{7}\text{H}_{20}\text{S}_2\text{Si}_2$  224.05, observed 225.0594 (FAB+).

## Ge2



The bis(chloromethyl)tetramethyldigermane was synthesized with the same general method described in Part I for the bis(chloromethyl)hexamethyltrisilane with the following exceptions: dichlorotetramethyldigermane<sup>7</sup> was used instead of dichlorohexamethyltrisilane and a mixture of products was obtained—this mixture was carried forward to the next step without purification.

The bis(acetylthiomethyl)tetramethyldigermane was synthesized with the same general method described in Part II with the following exceptions: the reaction was conducted in ethanol (0.2 M with respect to the digermane) rather than THF and stirred at room temperature instead of at reflux, the reaction mixture from the previous step was used instead of bis(chloromethyl)tetramethyldisilane, and the crude material was purified by silica gel chromatography with a gradient from 100% hexanes to 7:3 hexanes:ethyl acetate to yield an orange oil (200 mg, 30% yield over two steps).  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  2.33 (overlapping singlets, 10H), 0.34 (s, 12H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  197.11, 30.29, 13.01, -3.25. LRMS predicted for  $\text{C}_{10}\text{H}_{22}\text{Ge}_2\text{O}_2\text{S}_2$  383.95, observed 382.99 (FAB+).

The bis(methylthiol)tetramethyldigermane was synthesized with the same general method described in Part III with the following exceptions: bis(acetylthiomethyl)tetramethyldigermane was used

instead of bis(acetylthiomethyl)tetramethyldisilane. Colorless oil (81 mg, 54% yield).  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  1.98 (d,  $J = 6.9$  Hz, 4H), 1.34 (t,  $J = 6.9$  Hz, 2H), 0.37 (s, 12H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  7.50, -3.77. HRMS predicted for  $\text{C}_6\text{H}_{18}\text{Ge}_2\text{S}_2$  301.93, observed 302.9350 (FAB+).

## References

- (1) Aradhya, S. V.; Frei, M.; Hybertsen, M. S.; Venkataraman, L. *Nature materials* **2012**, *11*, 872.