Supporting Information for:
Response vs. Chain Length of Alkanethiol-Capped Au Nanoparticle Chemiresistive Chemical Vapor Sensors

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Appendix A.

The concentration of analyte sorbed into the sensing material at equilibrium can be calculated by using the $K$ value of the analyte/material, given by:

$$K = \frac{C_{A,\text{film}}}{C_V}$$

(1)

where $C_{A,\text{film}}$ (mol L$^{-1}$) is the concentration of analyte in the film and $C_{A,V}$ (mol L$^{-1}$) is the concentration of analyte in the vapor phase. $C_{A,\text{film}}$ is obtained with the value of $K$ in conjunction with the use of $P/P^\circ$ to calculate $C_V$ through the ideal gas equation ($P/RT = C_V$). Because it is assumed that sorption can only take place at the organic layer, the ligand concentration, $C_{\text{ligand}}$, in the film can obtained from the density of the condensed ligand (~0.84 g/ml). The sorbed analyte mole ratio is then:

$$X_n = \frac{C_{A,\text{film}}}{C_{\text{ligand}} + C_{A,\text{film}}}$$

(2)

Figure S3 shows the value of $X_n$ for Hex, Tol, EtOAc and BuOH. As $P/P^\circ$ increased, higher values of $X_n$ were obtained, as expected.

The dielectric constant of a mixture of two components depends on the volume fraction of both components, $\gamma_1$ and $\gamma_2$. For a given mixture of two substances having dielectric constants $\varepsilon_1$ and $\varepsilon_2$, respectively:

$$\gamma_1 + \gamma_2 = 1$$

(3)

For independent substances, having $D_1$ and $D_2$, the 2-component value of the electric displacement is given by $D = \gamma_1 D_1 + \gamma_2 D_2$. The electric field, $E$, throughout the mixture is given by $E = \gamma_1 E_1 + \gamma_2 E_2$. Hence, the resulting dielectric constant of the mixture is given by:

$$\varepsilon_s = D / E$$

(4)

where for each component, $D_1 = \varepsilon_1 E_1$ and $D_2 = \varepsilon_2 E_2$. Reynolds et al. demonstrated that an expression describing $\varepsilon_s$ for a mixture of two components can be derived:

$$\varepsilon_s = \varepsilon_2 + (\varepsilon_1 - \varepsilon_2) \gamma_1 F_1$$

(5)
where $F_1 = E_1/E$, which is assumed to approach unity. $X_n$ can be used to estimate the value of $\gamma_1$ (i.e. vapor sorbed) and $X_{\text{ligand}} = 1 - X_n$. 
Table S1. Partial pressure values as a function of temperature for \textit{n}-hexane and ethanol.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Hex (P/P° x 10^3)</th>
<th>EtOH (P/P° x 10^3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>2.7</td>
<td>3.8</td>
</tr>
<tr>
<td>11</td>
<td>1.9</td>
<td>2.4</td>
</tr>
<tr>
<td>18</td>
<td>1.4</td>
<td>1.5</td>
</tr>
<tr>
<td>25</td>
<td>1.0</td>
<td>1.0</td>
</tr>
<tr>
<td>32</td>
<td>0.74</td>
<td>0.67</td>
</tr>
<tr>
<td>39</td>
<td>0.56</td>
<td>0.46</td>
</tr>
</tbody>
</table>
**Figure S1.** Thermogravimmetric analysis of alkanethiol capped Au-NP films.
Figure S2. Baseline corrected single responses for a resistance change response (black) and the baseline-corrected response (red) for a Au-C8 sensor due to sorption of hexane ($P/P^\circ = 0.0010$).
Figure S3. Relative differential resistance response as a function of $P/P^o$ for a Au-C8 sensor.
Figure S4. Optical spectra for a Au-C8 film during exposure to air (5 L min$^{-1}$) and ethanol at $P^o$. No change in the plasmon resonance is observed. A red-shift in the plasmon resonance would have indicated an increase of the dielectric constant of the film.
Figure S5. Mole ratio, $X_n$, between the moles of sorbed analyte sorbed and the moles of ligands in the film, as a function of $P/P^0$, for Hex, Tol, EtOAc and BuOH; a) Au-C4, b) Au-C5, c) Au-C6, d) Au-C7, e) Au-C8, f) Au-C9, g) Au-C10, h) Au-C11.
**Figure S6.** Static dielectric constant, $\varepsilon_s$, of the ligand/analyte organic interface as a function of $P/P^0$ for Hex, Tol, EtOAc and BuOH; a) Au-C4, b) Au-C5, c) Au-C6, d) Au-C7, e) Au-C8, f) Au-C9, g) Au-C10, h) Au-C11.
The diagrams show the relationship between $\text{P/P}_0 \times 10^3$ and $\omega_\infty$, $\varepsilon_\infty$, $\omega_s$, and $\varepsilon_s$. The graphs illustrate how the properties change with varying $\text{P/P}_0$ for different solvents: Hex, Tol, EtOAc, and BuOH.
**Figure S7.** Scanning electron micrographs of a Au-C8 film that was treated under different vapors. Micrograph a) shows the as prepared Au-C8 film, micrograph b) shows a film that was presented to a saturated Hex vapor stream for 12 h, micrograph c) shows a film that was presented to a saturated EtOH vapor stream for 12 h.