Supporting Information for: Length-dependent Thermopower of Self-Assembled Monolayers of Alkanethiolates Depends on Direction of Temperature Gradient

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S1 Electrode Temperatures

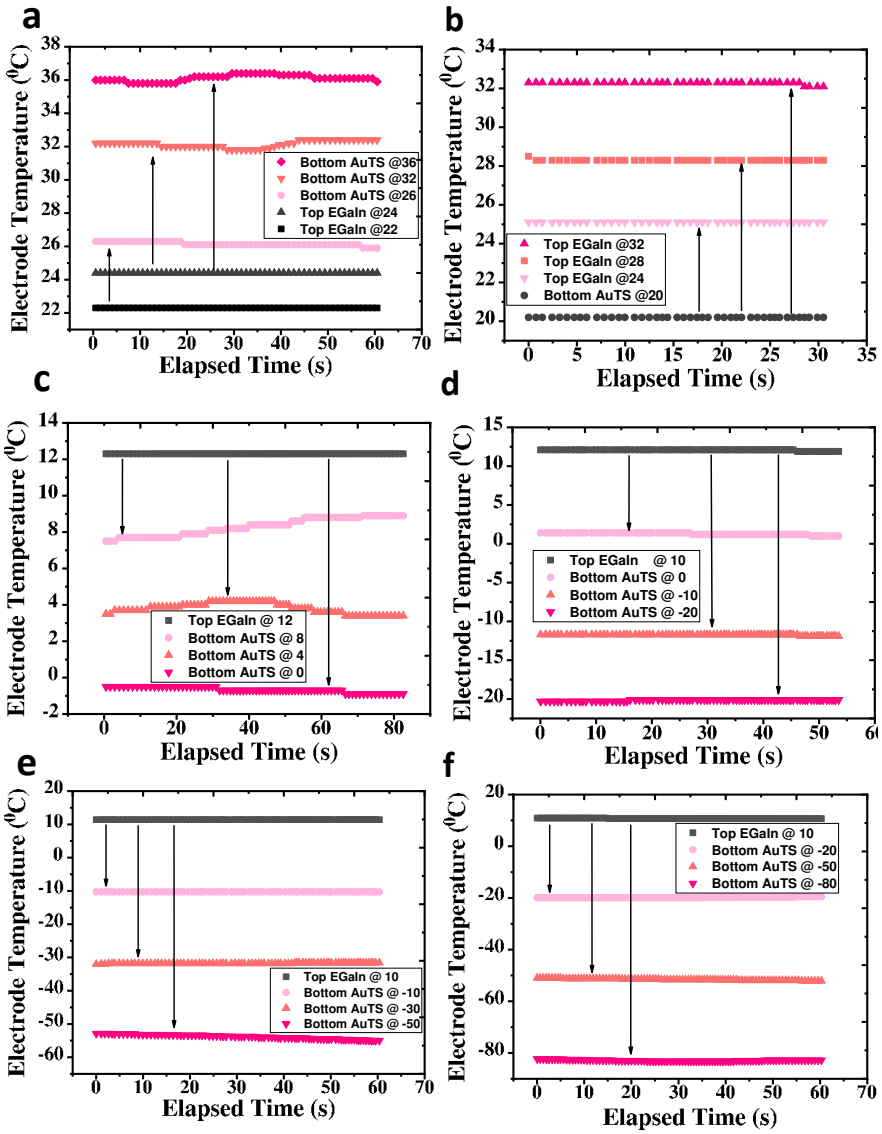

Figure S1: Electrode temperature plots against time (s) depicting the Au^{TS} and EGaIn temperature holds for a) positive ΔT at ambient temperatures, b) negative ΔT at ambient temperatures, c) negative ΔT where EGaIn is fixed at 12^0C and Au^{TS} changes 8, 4, 0^0C, d) negative ΔT where EGaIn is fixed at 10^0C and Au^{TS} changes 0, -10, -20^0C, e) negative ΔT where EGaIn is fixed at 10^0C and Au^{TS} changes -10, -30, -50^0C, and f) negative ΔT where EGaIn is fixed at 10^0C and Au^{TS} changes -20, -50, -80^0C

S2 Alkanethiol Thermal Voltages

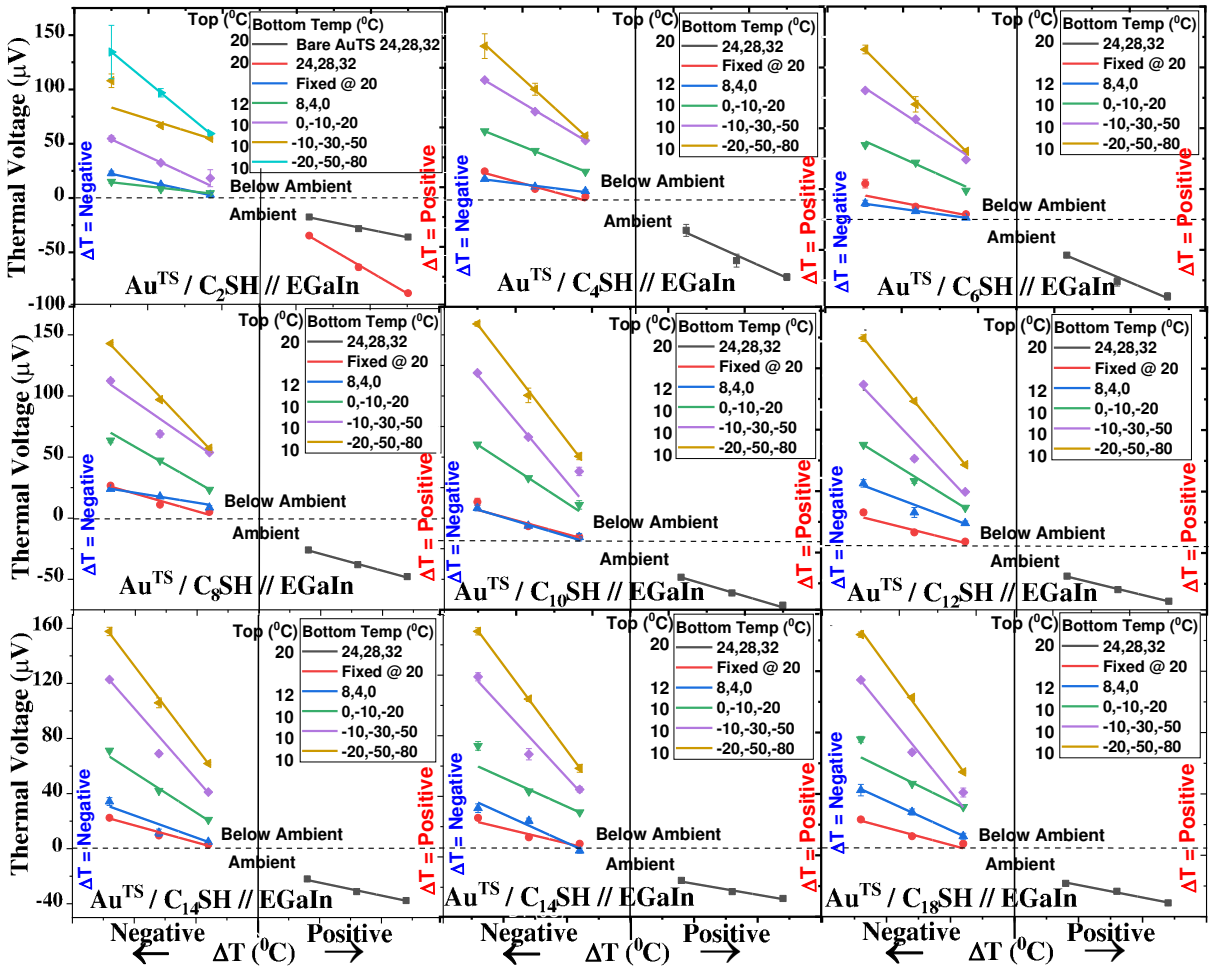

Figure S2: SCn plots of thermovoltage against different ΔTs where the Au^{TS} electrode temperature is above and below EGaIn electrode temperature as seen in Figure S1 (a - f)

Table S1: Seebeck coefficients of SCn at different ΔT.

T_{EGaIn} (°C)	20	(24,28,32)	12	10	10	10
T_{AuTS} (°C)	(24,28,32)	20	(0,4,8)	(-10,-20,-30)	(-20,-40,-60)	(-30,-60,-90)
SCn	S ($\mu\mathrm{V\,K^{-1}}$)					
$n = 2$	6.63 ± 0.29	1.79 ± 0.36	1.45 ± 0.20	3.49 ± 0.63	6.65 ± 1.44	9.19 ± 0.01
$n = 4$	5.29 ± 0.72	1.99 ± 0.09	1.41 ± 0.24	4.57 ± 0.05	6.82 ± 0.12	10.29 ± 0.20
$n = 6$	4.29 ± 0.50	2.00 ± 0.91	2.46 ± 0.08	4.76 ± 0.91	7.17 ± 0.89	10.47 ± 0.23
$n = 8$	2.75 ± 0.20	2.88 ± 0.66	1.32 ± 0.19	4.95 ± 0.45	7.34 ± 1.22	10.69 ± 0.33
$n = 10$	2.39 ± 0.17	2.37 ± 0.71	1.33 ± 0.44	5.19 ± 0.22	8.42 ± 1.41	11.34 ± 0.24
$n = 12$	2.27 ± 0.10	2.32 ± 0.69	3.59 ± 0.66	5.75 ± 0.18	9.82 ± 1.54	11.58 ± 0.02
$n = 14$	1.99 ± 0.17	2.47 ± 0.36	1.27 ± 0.86	6.22 ± 0.63	10.28 ± 0.63	11.97 ± 0.37
$n = 16$	1.64 ± 0.26	3.02 ± 0.45	3.93 ± 0.98	6.12 ± 0.88	10.45 ± 1.57	12.54 ± 0.11
$n = 18$	1.78 ± 0.20	3.10 ± 1.37	4.19 ± 0.14	6.16 ± 0.93	10.40 ± 1.61	12.57 ± 0.14

Table S2: Length-dependence of Seebeck coefficients.

SCn	T_{AuTS} (°C)	T_{EGaIn} (°C)	β^S (μV/Kn)
$2-18$	$-20, -50, -80$	10	0.24 ± 0.00
$2-18$	$-10, -30, -50$	10	0.32 ± 0.05
$2-18$	$0, -10, -20$	10	0.14 ± 0.02
$2-18$	$8, 4, 0$	12	0.16 ± 0.01
$2-18$	20	$24, 28, 32$	0.00 ± 0.02
$12-18$	$24, 28, 32$	20	-0.10 ± 0.03
$2-10$	$24, 28, 32$	20	-0.53 ± 0.04

S2.1 Transmission and Seebeck Calculations

The conductance of $\mathrm{Au^{TS}}$/SCn//EGaIn junctions can be approximated using a single-level Lorenzian model Eq. (S1) where $\mathcal{T}(E)$ is the total transmission probability as a function of energy and Γ is the broadening, which is decreases with increasing chain-length.[1] This formulation assumes E_{HOMO} is closest to E_{F} and, therefore, is the major contributor to the transport level.

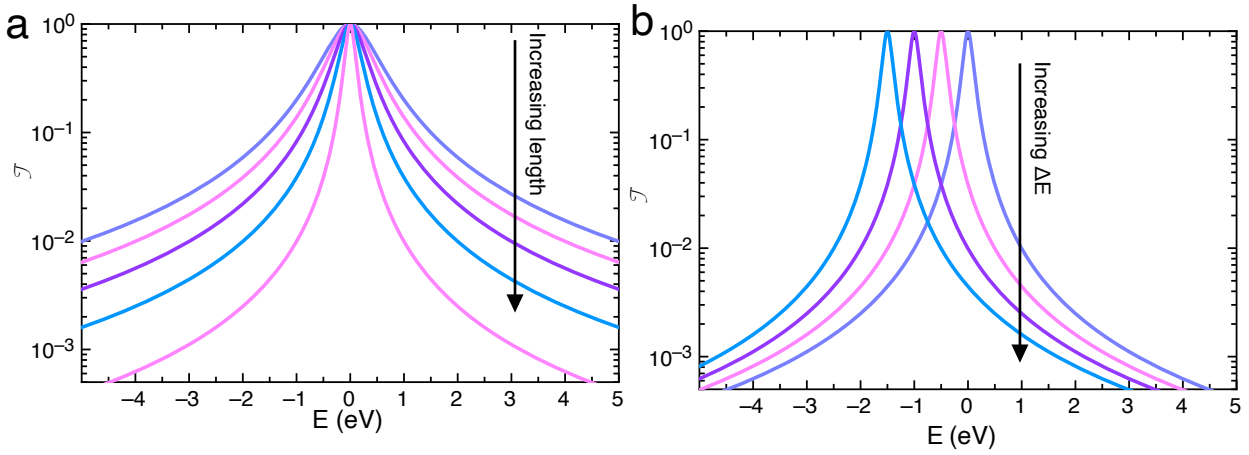

Figure S3: An idealized Lorentzian single-energy level zero-bias transmission probability ($\mathcal{T}$) versus level alignment ($E - E_{\mathrm{HOMO}}$) illustrating how conductance decreases with increasing length by changing Γ (a) and how conductance decreases with increasing E_{HOMO}, *i.e.*, increasing molecular orbital gap (b).

$$\mathcal{T}(E) = \frac{\Gamma^2}{(E_{\mathrm{HOMO}} - E)^2 - \Gamma^2} \tag{S1}$$

Figure S3a is a plot of Eq. (S1) showing how a series of SCn can produce a length-dependent conductance even though E_{HOMO} does not vary with increasing length. As the alkane backbone lengthens, Γ decreases, causing $\mathcal{T}$ to increase at a fixed $E - E_{\mathrm{HOMO}}$. Figure S3b shows the opposite case, in which Γ is held constant and E_{HOMO} changes. This situation represents a series of molecules in which Γ does not change with length, but the frontier molecular orbital gap changes, for example a series of conjugated molecules in which the conjugation length increases with length or length is held constant and functional groups change the gap.

Equation (S1) can be combined with the Mott equation to estimate the Seebeck coef-

ficient using Eq. (S2) where k_B is the Boltzmann constant and e is elementary charge.[2] In a system where Γ and E_{HOMO} both change across a series, the dependence of S becomes more complex. Figure S4 shows plots of Eq. (S2) in which Γ and E_{HOMO} change across a series, with insets showing how opposite length-dependences can result depending on whether E_{HOMO} increases or decreases with Γ. While such behavior is expected for series of molecules in which the degree of π-conjugation changes with length, only Γ should change for alkanes because the distance between the electrodes increases, but the frontier molecular orbital energies of alkanes are independent of the length of the alkane. Adding a γn term to E_{HOMO} to account for a length-dependent shift in E in Eq. (S3) mathematically yields the same behavior shown in Fig. S4 without changing E_{HOMO}. Such a shift could be induced by the voltage difference that develops in the leads when a temperature gradient is applied. Since the measured voltage of a junction is the sum of the Seebeck voltages of the leads, contacts and SAM, this voltage is subtracted from the total measured voltage to determine the Seebeck coefficient of a SAM.

$$S(E) \approx \frac{\pi^2 k_B^2 T}{3e} \frac{\partial \ln \mathcal{T}(E)}{\partial E} \tag{S2}$$

$$\mathcal{T}(E) = \frac{\Gamma^2}{(n\gamma + E_{HOMO} - E)^2 + \Gamma^2} \tag{S3}$$

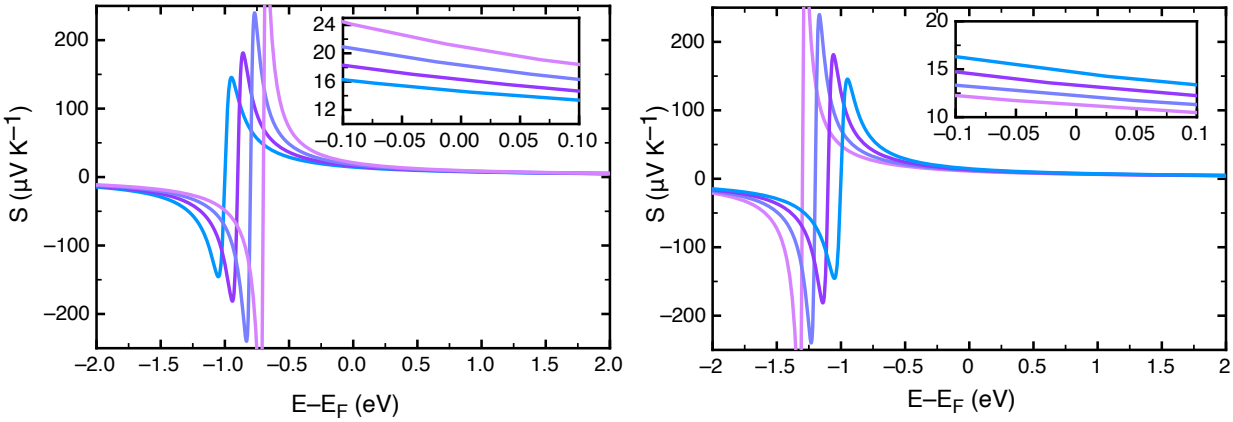

Figure S4: Plots of S with changing Γ accompanied by small shifts in E. Insets show how the direction of the length-dependence of S depends on whether $E - E_{\mathrm{F}}$ increases or decreases with Γ.

References

(1) Malen, J. A.; Yee, S. K.; Majumdar, A.; Segalman, R. A. *Chem. Phys. Lett.* **2010**, *491*, 109–122.

(2) Paulsson, M.; Datta, S. *Phys. Rev. B* **2003**, *67*, 241403.