

Supporting Information:

Replacing $-\text{CH}_2\text{CH}_2-$ with $-\text{CONH}-$ does not significantly Change Rates of Charge

Transport through $\text{Ag}^{\text{TS}}-\text{SAM}/\text{Ga}_2\text{O}_3/\text{EGaIn}$ Junctions

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Experimental

Materials: All reagents were purchased from Sigma-Aldrich, and were used as supplied unless otherwise specified. All organic solvents were purchased from VWR or Sigma-Aldrich. Water used in the synthesis was purified using a Millipore Q-POD® water-purification system. For the top electrode, high purity eutectic gallium-indium (EGaIn) alloy was obtained from Sigma-Aldrich, and used as supplied. All thiols used to make SAMs were purified by silica-gel column chromatography (using 15% ethyl acetate in hexane, and gravity elution). All purified thiols were maintained under a N₂ atmosphere at <4 °C, and purity was checked immediately before use (These precautions were necessary because primary thiols readily oxidize at on exposure to air). To ensure purity, all compounds that had been stored were checked by ¹H NMR before use. All SAMs were prepared under ambient conditions as previously described.¹⁻³

Characterization: A Bruker DPX 400 or a Varian INOVA 500 instrument recorded ¹H and ¹³C NMR spectra using CDCl₃ as solvent and TMS as an internal standard. All ¹H NMR spectral data were compared to literature values.⁵

Preparation of Template-Stripped Silver: We prepared our surfaces as described previously.^{3,4} On clean, ultra-flat silicon 111 wafers (with the native oxide) we deposited a 450-nm-thick film of Ag using an e-beam evaporator (Temescal, base pressure 2 x 10⁻⁶ Torr). On the exposed surface of the metal film were attached plasma-cleaned glass supports using a thin film of photo-curable optical adhesive (Norland optical adhesive 81). Curing the optical adhesive under broad-band UV light for at least 2 hours attached the glass supports to the metal surface.

General procedure for the preparation of the SAM: SAMs were prepared as previously described.^{2,3} To prepare SAMs, the ultra-flat metal film templated on the silicon wafer was cleaned by soaking the chips in absolute ethanol for 5 minutes, then detached by cutting around

the support using a razor blade. The film and glued support were then lifted from the silicon wafer, rinsed with absolute ethanol, then immersed in a 3-mM thiol solution for 3 hours to form the SAM.

General procedure for the preparation of the SAM of *N*-propyl-12-mercaptododecanamide (11,3): We added *N*-propyl-12-mercaptododecanamide (3.8 mg, 0.015 mmoles) in 5 mL of anhydrous EtOH to a scintillation vial. The solution was sonicated for 5 mins, sealed, and degassed by bubbling nitrogen through the solution for *ca.* 3 min. We placed a glass-supported template-stripped silver film (Ag^{TS}) in the thiol solution with the exposed metal face up. The solution was then degassed by bubbling dry N₂ through it for 2 mins, then maintained the reaction vessel under positive N₂ pressure for 3 h. The Ag^{TS} film with the SAM on it was removed from solution and rinsed by repeatedly dipping the chip into anhydrous EtOH. Blowing a stream of nitrogen over the chip evaporated the solvent on the SAM slowly. Charge-transport measurements were taken in less than 3 h after the SAM formation.

All other SAMs were prepared in a similar manner.

Measurement of Current Density through SAMs Containing Amides. We prepared SAMs, and fabricated junctions, using procedures described previously^{2,3} by bringing cone-shaped tips of Ga₂O₃/EGaIn into contact with SAMs formed on ultra-flat, template-stripped silver (Ag^{TS}) substrates. We measured the current through the junction using a Keithley 6430 sub-femtoamp source-meter, and calculated the current density (*J*) using the area of the junction estimated by measuring the diameter, under 450x magnification, of the contact (assumed to be circular) between the cone-shaped tip and the substrate. We know this area is three-to-ten times larger than the electrically active area, from measurements to be described elsewhere, and this systematic error should be considered if measurements of absolute current density are needed.

General Procedure for the Preparation of Mercaptoalkylamides; *N*-propyl-12-

mercaptododecanamide (11,3): To a flame-dried flask maintained under an inert atmosphere (e.g., a dry stream of N₂) was added 12-bromododecanoic acid (2 g, 7.16 mmoles). The flask was then charged with 40 mL of anhydrous methylene chloride, followed by dropwise addition of oxalyl chloride (1.87 mL, 21.5 mmoles) while cooling in an ice-water bath. The mixture was allowed to warm to ambient temperature while stirring, and the reaction was allowed to continue for a further 2 h while under an inert atmosphere. The solvent and all volatile by-products were removed *in vacuo* and the resulting oily residue re-dissolved in anhydrous THF (40 mL). To the flask was then added triethyl amine (1.08 mL, 7.16 mmoles) followed by propyl amine (0.7 mL, 8.6 mmoles). The reaction mixture was allowed to continue stirring under an inert atmosphere at room temperature for at least 5 h, solvent was removed *in vacuo*, and the resulting residue purified by column chromatography (15 % EtOAc in hexane eluant) to give the 12-bromo-*N*-propyldodecanamide.

To a flask containing 50 mL of EtOH was added this 12-bromo-*N*-propyl-dodecanamide, followed by thiourea (0.65 g, 8.6 mmoles) dissolved in 50 mL of EtOH. The reaction mixture was maintained under reflux for 12 h, after which the solvent was removed *in vacuo* to give an oily residue. This oil was added to NaOH (0.9 g, 21.48 mmoles) dissolved in 50 mL of water, and the mixture was maintained under reflux for 1 h. The reaction mixture was then cooled to room temperature, and extracted with 3 x 40 mL Et₂O. The ethereal extracts were dried over anhydrous MgSO₄, solvent was removed *in vacuo*, and the product was purified by column chromatography (with 20% EtOAc in hexanes as mobile phase) to give the product in 78 % overall yield. After purification, the product was stored under argon at <4 °C and periodically checked for purity before use. The ¹H NMR data matched literature values.⁵ ¹H NMR (CDCl₃): δ

0.93 (t, 3H, $J = 7.2$ Hz), 1.28 - 1.38 (m, 14H), 1.51-1.64 (m, 7H), 2.16 (dt, 2H, $J = 4.6, 7.8$ Hz), 2.53 (dt, 2H, $J = 3.6, 7.2$ Hz), 3.32 (m, 2H), 5.40 (br, s, 1H).

All other amides were synthesized following a similar procedure, Sample ^1H NMR spectra are provided in Figure S2.

General structure of the Junction: With the structure of the molecules changed, from the previously reported (n-alkanethiols,³ we believe that the introduction of an amide moiety in the molecules making up the SAM would slightly alter the wave-function of these junctions. We provide a schematic illustration of how the more polar amide might perturb the structure of the barrier in Figure S1. The small perturbation due to the amide was, however, not sufficient to significantly change the charge transport characteristics of the amide-bearing junctions.

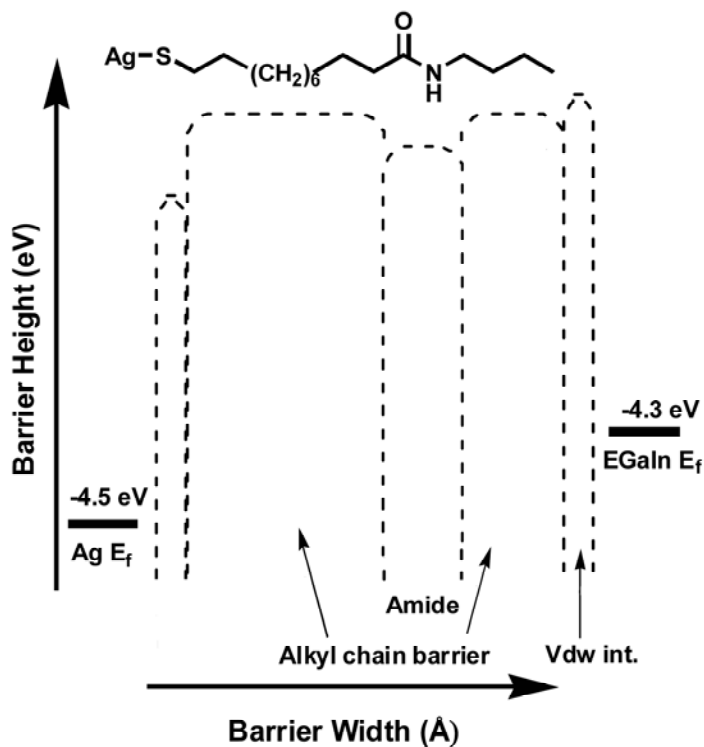
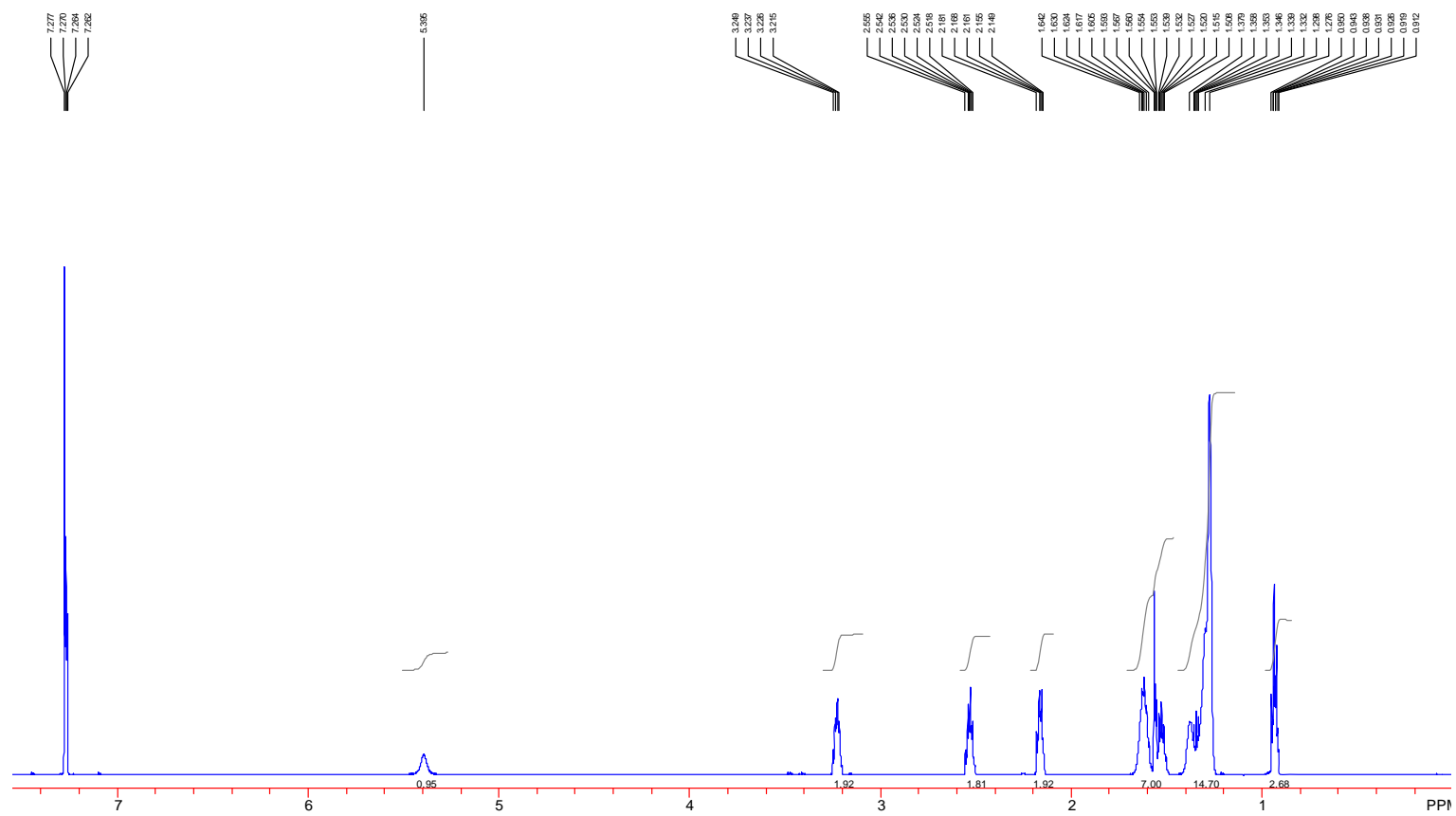


Figure S1: Schematic illustration on the effect of the amide on structure of the junction. The polar amide only slightly perturbs the wave-function of the organic part of the junction.

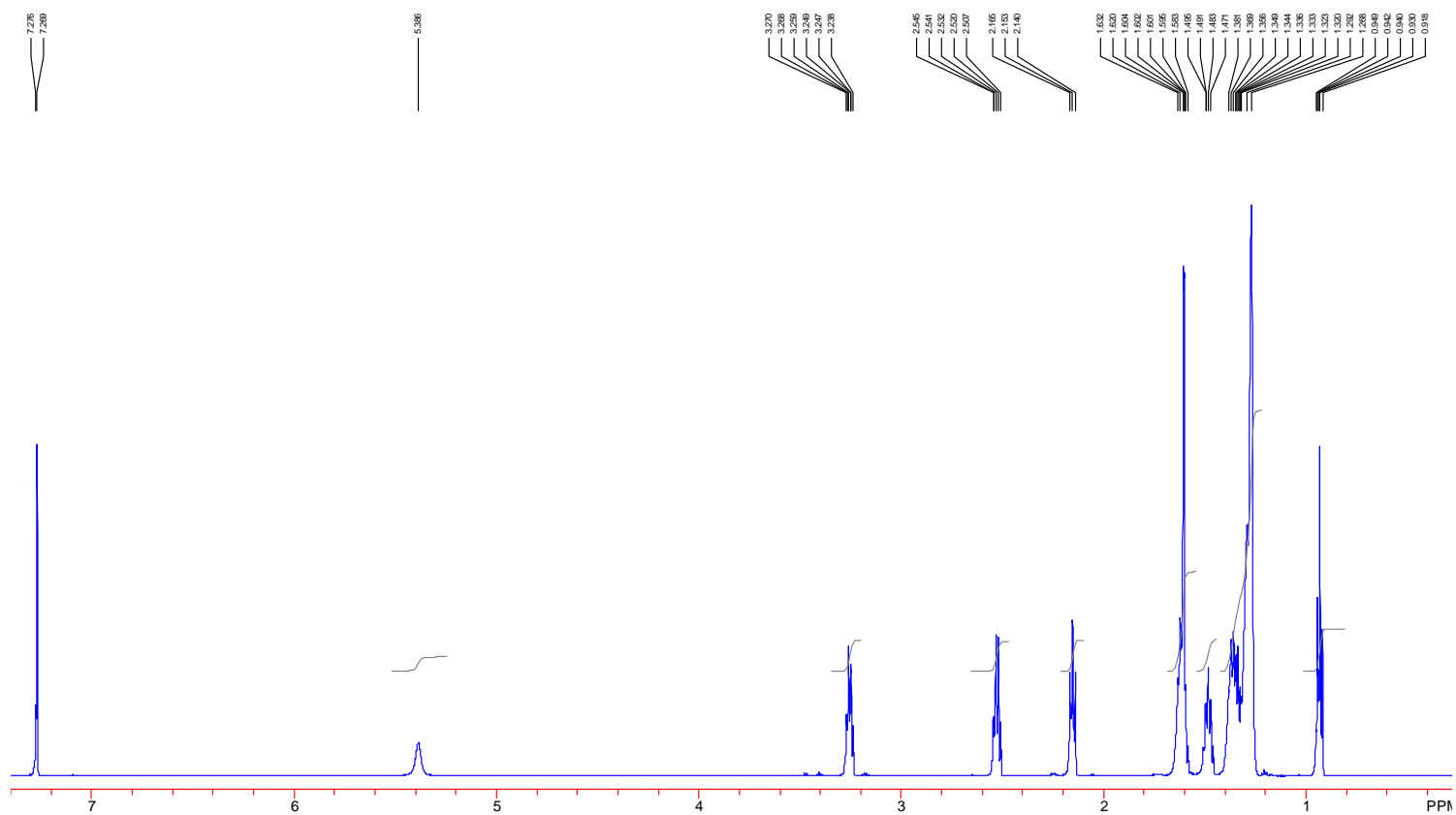
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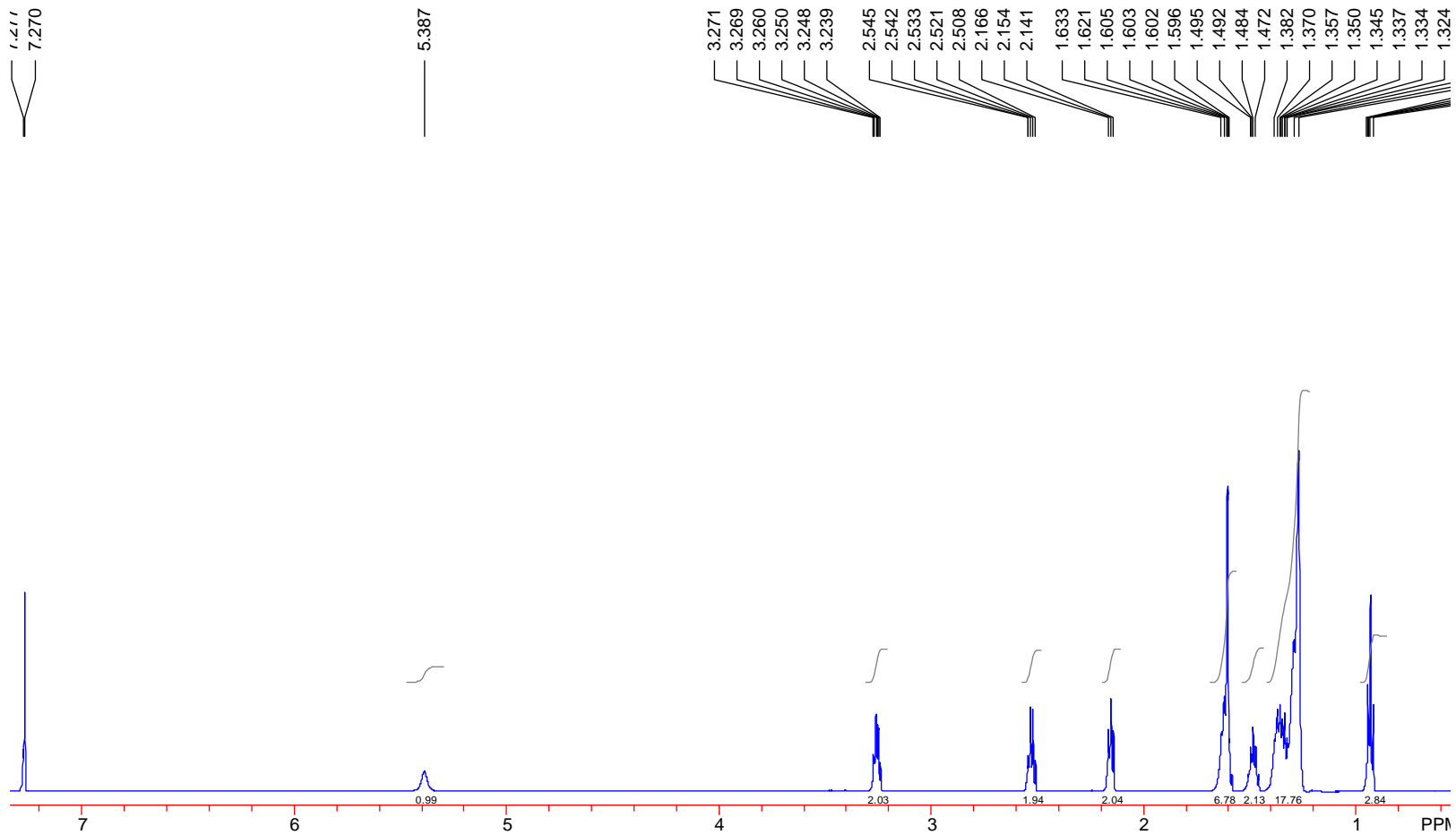
Figure S2: a) $\text{HS}(\text{CH}_2)_{11}\text{CONH}(\text{CH}_2)_3\text{H}$



b) HS(CH₂)₁₁CONH(CH₂)₄H



c) $C_{11}CONH(CH_2)_5CH_3$



d) $\text{HS}(\text{CH}_2)_{10}\text{CONH}(\text{CH}_2)_4\text{H}$

