Supporting information for:

Pronounced Environmental Effects on Injection

Currents in EGaIn Tunneling Junctions

Comprising Self-Assembled Monolayers

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SAM formation and EGaIn J-V measurement

Care must be taken when forming SAMs from conjugated “molecular wire” compounds such as these because of the tendency for the deprotected dithiol(ates) to lie flat due to their bidentate structure and favorable π-Au interactions. Self-assembled monolayers of molecular wires on Au-on-mica were previously formed from a mixture of THF and Et₃N, but in the current work AuTS is used, which is supported by optical adhesive and is therefore incompatible with THF. Thus, the procedure was modified and SAMs were formed by incubating the thioacetate precursors with 1x1 cm template-stripped Au surfaces (100 nm-thick) overnight in 3 mL of 50 µM solution of the respective compound in freshly distilled toluene followed by addition of 0.05 mL of 17 mM diazabicycloundec-7-ene (DBU) solution in toluene 1h prior the measurement. The substrates were then rinsed with ethanol and let to dry for 15 minutes. During SAM formation, leaving the metal substrate in contact with the compound solution and the deprotecting agent for longer time increase the risk of multi-layers formation in case of di-SAco derivatives. The thicknesses of the OPE SAMs measured by ellipsometry are reported in Table S1 together with theoretical lengths obtained from the minimized geometry of the molecules (as S-terminal CH distance). These latter have been used in the calculation of the β-values. In Table S2 are reported the number of traces collected for the different compounds and the yield of working junctions obtained by the number of junctions that did not fail during the bias scanning or when initially tested with a potential of 0.5 V divided by the total number of junctions formed. The number of working junctions can be obtained dividing by 10 the number of traces.
Table S1

|                | Theoretical length (Å) | Ellipsometric thickness (Å) |
|----------------|------------------------|-----------------------------|
| OPE1           | 5.6                    | 11.4                        |
| OPE2           | 12.1                   | 23.7                        |
| OPE3           | 18.7                   | 25.1                        |
| OPE4           | 25.2                   | 26.4                        |
| OPE2-diSAc     | 12.9                   | 13.6                        |
| OPE3-diSAc     | 19.3                   | 15.0                        |
| OPE4-diSAc     | 25.9                   | 17.1                        |

Table S2

|                | Flowbox                  |                     | Ambient                  |                     |
|----------------|--------------------------|---------------------|--------------------------|---------------------|
|                | n. of traces  | Yield (%) | n. of traces | Yield (%) |
| OPE1           | 650          | 92        | 450          | 75        |
| OPE2           | 480          | 90        | 450          | 74        |
| OPE3           | 650          | 93        | 510          | 67        |
| OPE4           | 640          | 97        | 450          | 84        |
| OPE2-diSAc     | 600          | 88        | 560          | 32        |
| OPE3-diSAc     | 600          | 92        | 490          | 60        |
| OPE4-diSAc     | 450          | 88        | 570          | 40        |
| C10SH          | 270          | 70        | 120          | 60        |
| C12SH          | 270          | 75        | 390          | 50        |
| C14SH          | 190          | 79        | 140          | 93        |
| C16SH          | 100          | 90        | 170          | 74        |
Synthesis and Characterization

Synthesis of OPE4

OPE4 was prepared according to the scheme in Fig. S1. 1-ethynyl-4-((4-(phenylethynyl)phenyl)ethynyl)benzene (1) was synthesized elsewhere. Pipsyl chloride (95%), N,N-dimethylacetamide (99.8%), acetyl chloride (99%) and dichlorodimethylsilane (≥ 98.5%) were purchased from Sigma-Aldrich and used as received. Pd(PPh₃)₃ and CuI were purchased from ACROS Organics and stored under nitrogen in the dark at 4 °C. NEt₃ was distilled over CaH prior use. Tetrohydrofuran (THF) was obtained dry from a solvent purification system present in the lab. The rest of the solvents were used as received. ¹H-NMR and ¹³C-NMR spectra were recorded on a Varian AMX400 (400 MHz) and a Varian VXR-400 (400 MHz) at room temperature. All the spectra were referenced to the solvent line of CDCl₃ relative to tetramethylsilane (H, 7.26 ppm; C, 77.0 ppm). FT-IR spectra were recorded on a Nicolet Nexus spectrometer using the SMART iTR for ATR measurement (diamond).

![Reaction scheme for OPE4 synthesis.](image)

(4-iodophenyl)ethanethioate (2). The procedure for the synthesis of this compound was taken from the literature. In a flask under inert atmosphere (N₂), 3.073 g of pipsyl chloride (10.2 mmol) and 2.8 mL of N,N-dimethylacetamide (2.63 g, 30.2 mmol) were dissolved in 80 mL of degassed 1,2-dichloroethane. In a different flask under inert atmosphere (N₂), 2.36
g of Zn (36.3 mmol) and 4.3 mL of Cl₂SiMe₂ (4.58 g, 53.3 mmol) were stirred in 80 mL of degassed 1,2-dichloroethane at 60 °C for 30 minutes, then the first solution was added. The reaction mixture was heated to 75 °C and left for 2 h. Absence of pipsyl chloride was checked via TLC (Rf ~ 0.4 in hexane). The solution was then cooled to 45 °C and 0.94 mL of acetyl chloride (1.038 g, 13.2 mmol) were added. The reactor was left at 50 °C for 30 minutes. The reaction mixture was filtered still hot and the filtrate poured in 300 mL of water. The aqueous phase was extracted with dichloromethane (3x150 mL). The organic solvent was evaporated in vacuo and the product purified by sublimation (70 °C, 5 · 10⁻⁴ mbar) to obtain 2.420 g of white crystals (83% yield). ¹H-NMR (400 MHz, CDCl₃) δ 7.74(m, 2H), 7.13(m, 2H), 2.42(s, 3H). IR (ATR, cm⁻¹): 1691, 1464, 1381, 1353, 1119, 1087, 1004.

S-(4-((4-((4-(phenylethynyl)phenyl)ethynyl)phenyl)ethynyl)phenyl) ethanethioate, OPE4. In a dry flask under nitrogen atmosphere 26.1 mg of 1 (86 µmol), 26.6 mg of 2 (96 µmol), 3.0 mg of Pd(PPh₃)₄ (2.6 µmol), and 1.4 mg of CuI (7.3 µmol) were dissolved in 3.5 mL of dry THF and 35 µL of NEt₃. The system was heated to 50 °C for 1 hour and then slowly allowed to room temperature over 16 hours. The reaction mixture was poured in 200 mL of water which was carefully acidified with few drops of HCl 6 M until slight acidity was reached. The water phase was extracted with DCM (3x30 mL), the organic phase was dried over Na₂SO₄, and the solvent removed under vacuum. The product was preabsorbed on silica and purified by column chromatography (SiO₂, hexane:DCM 1:1) and recrystallized from chloroform. 17 mg of product as yellow powder were collected (35% yield). ¹H-NMR (400 MHz, CDCl₃) δ 7.55 (m, 4H), 7.52 (s, 8H), 7.38 (m, 5H), 2.44 (s, 3H).

Variable temperature J-V measurements

Using a mask and metal deposition we prepared arrays of 3 Au electrodes (300 µm wide, 1.5 cm long, and 100 nm thick; larger round pads at the end of the electrode were used to easily
contact the lines) on Si/SiO\(_2\) wafers. The arrays were then transfer on glass slides (1.5x2x0.2 cm) using template stripping techniques. Since the optical adhesive (OA, Norland, No. 61) adheres strongly to Si/SiO\(_2\) and prevents the lift off of the electrodes, we functionalized the wafer with 1H,1H,2H,2H-perfluorooctyltrichlorosilane by gas phase deposition of the FOTS for 1.5 hours.

SAMs of OPE\textsubscript{3} and OPE\textsubscript{4} were grown in the flowbox controlled environment (1-3% oxygen, humidity <10%) by immersion of the electrodes in 10 mL of a 50 \(\mu\)M solution of the desired OPE compound in distilled toluene overnight, followed by addition of 0.1 mL of a 17 mM DBU solution in distilled toluene 1 hour before the measurement. The samples were then rinsed with EtOH and let dry for 10 minutes. PDMS channels (15 \(\mu\)m and 30 \(\mu\)m wide, 50 \(\mu\)m deep, 1 cm long) were obtained by polymerizing the PDMS over a master that was prepared using standard photolithography techniques. The channels were oxidized in oxygen plasma (500 mbar, 300 s) and moved in the flowbox where they were placed over the samples (perpendicular to the electrodes) and carefully filled with EGaIn applying one drop of alloy on one inlet and reduced pressure on the other.

The samples were placed in a cryogenic chamber filled with nitrogen. We biased the EGaIn top-electrode and grounded the Au bottom-electrode, and acquired \(J\) at different potentials to obtain \(J(V)\) curves. We performed scans in the +0.5 V/-0.5 V range (5 scans per junction from 0 V → 0.5 V → −0.5 V → 0 V, steps of 0.05 V) initially at room temperature and then slowly step-wise lowering the temperature with liquid nitrogen to 188 K for OPE\textsubscript{3} and 153 K for OPE\textsubscript{4} (these temperatures were dictated by short circuits). The results proposed in Figure S2 and Figure S3 are averages of 2 samples (6 junctions) per compound. As it possible to observe, \(J\) only varies slightly with the temperature as it is expected for tunneling junctions (Fig.
Figure S2: Variable temperature $I$-$V$ plots for OPE3 (left) and OPE4 (right) at different temperature. Error bars are confidence intervals calculated with $\alpha = 0.05$.

Figure S3: Arrhenius plots of $\ln|I|$ vs. $1/T$ for OPE3 (blue up-triangles) and OPE4 (dark cyan down-triangles). Error bars are confidence intervals calculated with $\alpha = 0.05$. 
Effect of the environment on EGaIn measurements of conjugated molecules

To investigate the reasons behind the differences in conductivity of Au\textsuperscript{TS}/SAM//Ga\textsubscript{2}O\textsubscript{3}/EGaIn junctions upon environment, SAMs of OPE3 SAM were prepared and measured subsequently in both a EGaIn setup in the flowbox and a EGaIn setup outside. A sample of OPE3 on gold was prepared as described in the section 'SAM formation and EGaIn J-V measurement' and initially measured inside the flowbox (20 junctions, 1\textsuperscript{st} run); then the same sample was transferred outside and measured with the EGaIn setup in the open environment (20 junctions, 2\textsuperscript{nd} run); finally it was transferred back in the flowbox where it was measured again (20 junctions, 3\textsuperscript{rd} run). This experiment was repeated two times and the data merged together. In Figure S4 are reported the current density histograms with Gaussian fits. The yield of working junctions was 91%, 73% and 91% for the 1\textsuperscript{st} run (flowbox), 2\textsuperscript{nd} run (ambient), and the 3\textsuperscript{rd} run (flowbox) respectively. Compared to the data obtained outside, those inside the flowbox present a much narrower distribution and higher yield of working junctions, as already pointed out in the main text. Surprisingly, when the sample was brought back in the flowbox for the second time, the data spreading and the yield resembled those of the 1\textsuperscript{st} run, thus indicating that the different environmental conditions in the flowbox play the major role in affecting the current density in the case of OPEs. Only the current density is affected slightly and could be the effect of partial oxidation of the sample. It is worth mentioning that the two EGaIn setup are completely identical and give identical results when placed in the same environment.
Figure S4: Histograms for Log $|J|$ at −0.5 V for Au$^{TS}$/OPE3//Ga$_2$O$_3$/EGaIn junctions measured: in the flowbox, first run (top, blue); and then in ambient, second run (middle, black); and finally again in the flowbox, third run (bottom, red). The solid black lines are Gaussian fits for the measurements, which were only possible for data acquired in the flowbox.
Figure S5: Images of drops of glycerin on SAMs of OPE3/AuTS showing no qualitative difference in the wetting properties in ambient (left) and flowbox (right) conditions.
References

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