Supporting Information for: Empirical Parameter to Compare Molecule-electrode Interfaces in Large-area Molecular Junctions

Marco Carlotti\textsuperscript{1,3,\$}, Saurabh Soni\textsuperscript{1,4,\$}, Andrii Kovalchuk\textsuperscript{1}, Sumit Kumar\textsuperscript{5}, Stephan Hofmann\textsuperscript{5}, and Ryan C. Chiechi\textsuperscript{*1,2}

\textsuperscript{1}Stratingh Institute for Chemistry, University of Groningen, Nijenborgh 4, 9747 AG Groningen, the Netherlands
\textsuperscript{2}Present address: Department of Chemistry, North Carolina State University, Raleigh, North Carolina 27695-8204, United States
\textsuperscript{3}Present address: Italian Institute of Technology, Center for MicroBioRobotics, Viale Rinaldo Piaggio 34, 56025, Pontedera, Italy
\textsuperscript{4}Present address: Hybrid Materials for Opto-Electronics Group, Department of Molecules and Materials, Faculty of Science and Technology, University of Twente, P.O. Box 217, 7500 AE Enschede, The Netherlands
\textsuperscript{5}Electrical Engineering Division, Department of Engineering, University of Cambridge, Cambridge CB3 0FA, U.K.
\textsuperscript{\$}M.C. and S.S. contributed equally to this paper.
\textsuperscript{*}e-mail: rchiech@ncsu.edu

Contents

1 Materials and Methods \hspace{1cm} S-4

2 Synthesis \hspace{1cm} S-5

3 Self-assembled Monolayers (SAMs) \hspace{1cm} S-30

SAM Fabrication \hspace{1cm} S-30
Atomic Force Microscopy Characterization . . . . . . . . . . . . . . . . . . . . . . . . . . . S-30

X-ray Photoelectron Spectroscopy . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . S-31

Experimental . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . S-31

XPS Results & Discussion . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . S-32

4 EGaIn J-V Measurement and Data Analysis S-35

Data Acquisition . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . S-35

Normalized Differential Conductance . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . S-37

Transition Voltage . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . S-38

5 Single Level Model S-40

Formulation of SLM . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . S-40

Simplified SLM for Large-area Junctions . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . S-43

Application of SLM to OPE3 and mOPE3 series . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . S-47

Extension of SLM to other molecular series . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . S-48

S-2
OPE length-dependent series ........................................... S-48

Quantum Interference based series ................................... S-49

Carboxylic acid - terminated alkanethiols. .......................... S-50

BPT-CH₃/BPT-CF₃ Binary SAMs. ....................................... S-51

Miscellaneous Molecular Rectifiers. .................................. S-51

6 DFT Calculations .......................................................... S-56

Geometry Optimization ..................................................... S-56

Transmission Calculations ............................................... S-58

Optimized Geometry Coordinates ....................................... S-61
1 Materials and Methods

All reagents were purchased from Sigma-Aldrich, Acros, or TCI Europe and used as received unless otherwise stated. Triethylamine and CHCl$_3$ were distilled over CaH and P$_2$O$_5$ respectively, and used within 10 days. Acetonitrile, toluene, dichloromethane (DCM), and tetrahydrofuran (THF), dimethylformamide (DMF) were obtained anhydrous from a house system. For non-anhydrous reactions, THF was stirred for 1 hour with basic alumina to remove BHT. NMR spectra were recorded on a Varian AMX400 (400MHz) and referenced to the solvent peak (CDCl$_3$ : H, 7.26 ppm; C, 77 ppm) relative to tetramethylsilane. We described the preparation of OPE3, and diSAc-OPE3 is described somewhere else.$^1$ Synthesis of IBzSAc synthon is provided elsewhere too.$^2$ Template stripped metal substrates were prepared by depositing a 100 nm-thick layer of Au on a Si wafer. 1x1x0.3 cm glass slides were glued to the deposited metal using an UV-curable optical adhesive (Norland series 60). The samples were cleaved from the wafer with the help of a razor and immediately used. SAMs of the compounds in this Chapter were prepared in dry toluene solutions by \textit{in situ} deprotection using DBU according to a known procedure.$^3$
2 Synthesis

![Chemical Structures](image)

**Figure S1:** Reaction scheme for the synthesis of OPEFUp, OPEFDown, mOPEFUp, and mOPEFDown. 

- **a:** TMS-acetylene, Pd(PPh₃)₄, CuI, NEt₃, THF; 
- **b:** i) TMS-acetylene, Pd(PPh₃)₄, CuI, NEt₃, THF; ii) K₂CO₃, MeOH; 
- **c:** 1, Pd(PPh₃)₄, CuI, NEt₃, THF; 
- **d:** i) TBAF, THF (3.1); ii) IPhSAc (n=0)/IBzSAc (n=1), Pd(PPh₃)₄, CuI, NEt₃, THF; 
- **e:** i) TMS-acetylene, Pd(PPh₃)₄, CuI, NEt₃, THF; ii) K₂CO₃, EtOH; 
- **f:** 1, Pd(PPh₃)₄, CuI, NEt₃, THF; 
- **g:** i) TBAF, THF (5.1); ii) IPhSAc (n=0)/IBzSAc (n=1), Pd(PPh₃)₄, CuI, NEt₃, THF.

In an oven dry flask under N₂, 2 g of 5-bromo-1,3-difluoro-2-iodobenzene (6.3 mmol) were dissolved in 25 mL of THF and the solution degassed with N₂ for 30 min. 0.9 mL of (trimethylsilyl)acetylene (0.62 g, 6.3 mmol), 146 mg of Pd(PPh₃)₄ (0.13 mmol), 40 mg of CuI (0.19 mmol), and 5 mL of NEt₃. The solution was left under stirring over 48 hours at ambient temperature. The solvent was removed under vacuum and the product purified via column chromatography (hexane) to yield a colorless oil (1.56 g, 86% yield). ¹H NMR (CDCl₃, 400MHz): 7.06-7.00 (m, 2H), 0.25 (s, 9H).
**Figure S2:** Reaction scheme for the synthesis of OPPy, mOPPy, mOPPy-2,6, OPE-OMe, and mOPE-OMe.

- **a:** i) TMS-acetylene, Pd(PPh$_3)_4$, CuI, NEt$_3$, THF; ii) TBAF, H$_2$O, THF
- **b:** i) 1, Pd(PPh$_3)_4$, CuI, NEt$_3$, THF; ii) TBAF, H$_2$O, THF
- **c:** IPhSAc (n=0)/IBzSAc (n=1), Pd(PPh$_3)_4$, CuI, NEt$_3$, THF
- **d:** i) TMS-acetylene, Pd(PPh$_3)_4$, CuI, NEt$_3$, THF; ii) TBAF, H$_2$O, THF
- **e:** i) NEt$_3$, MeSO$_2$Cl, DCM; ii) KSac, DMF
- **f:** 1-bromo-4-(phenylethynyl)benzene, Pd(PPh$_3)_4$, CuI, NEt$_3$, THF
- **g:** i) TMS-acetylene, Pd(PPh$_3)_4$, CuI, NEt$_3$; ii) TBAF, H$_2$O, THF
- **h:** i) TIPS-1, Pd(PPh$_3)_4$, CuI, NEt$_3$; ii) TBAF, H$_2$O, THF
- **i:** IPhSAc (n=0)/IBzSAc (n=1), Pd(PPh$_3)_4$, CuI, NEt$_3$, THF

2-ethynyl-1,3-difluoro-5-(phenylethynyl)benzene, 2

In an oven dry flask under N$_2$, 600 mg of 1 (2.1 mmol) were dissolved in 25 mL of THF and the solution degassed with N$_2$ for 30 min. 240 mg of phenylacetylene (2.3 mmol), 49 mg of Pd(PPh$_3)_4$ (0.04 mmol), 12 mg of CuI (0.06 mmol), and 2 mL of NEt$_3$. The solution was heated to 80 °C and left under stirring overnight. The solvent was removed under vacuum and the TMS-protected compound purified via column chromatography (hexane, $R_f = 0.5$) to obtain a colorless oil (1.56 g, 86% yield). The oil was dissolved in degassed EtOH and 0.4 g of K$_2$CO$_3$ (2.7 mmol) were added. the reaction was left overnight. 1 M HCl was added until a precipitate formed. The mixture was extracted with DCM and the organic phase dried over Na$_2$SO$_4$. The solvent was removed under vacuum to yield a pale yellow oil which crystallized upon standing (290 mg, 79% yield over 2 steps).

$^1$H NMR (CDCl$_3$, 400MHz): 7.53 (dd, $J = 6.6, 2.9$ Hz, 2H), 7.40 – 7.35 (m, 3H), 7.10 – 7.04 (m,
Figure S3: Reaction scheme for the synthesis of mOPE3 and diSAc-OPEFOut. 

- i: phenylacetylene, Pd(PPh$_3$)$_4$, CuI, NEt$_3$, THF; 
- ii: TBAF, H$_2$O, THF; 
- b: IBzSAc, Pd(PPh$_3$)$_4$, CuI, NEt$_3$, THF; 
- c: tBuSStBu,tBu(ONO); 
- d: 13, Pd(PPh$_3$)$_4$, CuI, NEt$_3$, THF; 
- e: TiCl$_4$, AcCl, DCM.
S-(4-iodophenyl)ethanethioate, IPhSac  In a flask under inert atmosphere (N₂), 3.073 g of 4-Iodobenzenesulfonyl 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, followed by addition of the first solution. The reaction mixture was heated to 75 °C and left for 2 hours. Full conversion of the 4-Iodobenzenesulfonyl chloride was checked vial 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 reaction 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). δ 7.74 (m, 2H), 7.13 (m, 2H) 2.42 (s, 3H).

S-(4-((2,6-difluoro-4-(phenylethynyl)phenyl)ethynyl)phenyl) ethanethioate, OPEFMid-Down

In an oven dry flask under N₂, 290 mg of 2 (1.21 mmol) and 370 mg of IPhSAc (1.33 mmol) were dissolved in 25 mL of THF and the solution degassed with N₂ for 30 min. 28 mg of Pd(PPh₃)₄ (0.02 mmol), 7 mg of CuI (0.04 mmol), and 1 mL of NEt₃. The solution was heated to 80 °C and left under stirring overnight. The solvent was removed under vacuum and the residue pread-
sorbed on silica. The compound was purified via column chromatography (hexane/ethyl acetate 9:1, $R_f = 0.5$) followed by recrystallization from hexane. The product was obtained as a pale yellow solid (186 mg, 40% yield). $^1$H NMR (CDCl$_3$, 400MHz): 7.61 (d, $J = 8.3$Hz, 2H), 7.53 (dd, $J = 6.5$, 3.1Hz, 2H), 7.42 (d, $J = 8.2$Hz, 2H), 7.40-7.35 (m, 3H), 7.07-7.13 (m, 2H), 2.44 (s, 3H). $^{13}$C NMR (CDCl$_3$, 101 MHz): 195.78, 165.13 (dd, $J = 254.1$, 6.5 Hz), 136.86, 134.97, 134.44, 131.78, 131.15, 127.83 (d, $J = 11.9$ Hz), 126.20, 124.77, 117.25 – 116.82 (m), 102.34, 95.91, 89.79, 80.46, 32.96. $^{19}$F NMR (CDCl$_3$, 376 MHz): 107.49 (d, $J = 7.5$ Hz).

S-4-((2,6-difluoro-4-(phenylethynyl)phenyl)ethynyl)benzyl ethanethioate, mOPEFMid-Down

In an oven dry flask under N$_2$, 170 mg of 2 (0.71 mmol) and 230 mg of IBzSAc (0.78 mmol) were dissolved in 25 mL of THF and the solution degassed with N$_2$ for 30 min. 16 mg of Pd(PPh$_3$)$_4$ (0.01 mmol), 4 mg of CuI (0.02 mmol), and 0.5 mL of NEt$_3$. The solution was heated to 80°C and left under stirring overnight. The solvent was removed under vacuum and the residue preadsorbed on silica. The compound was purified via column chromatography (hexane/ethyl acetate 10:1, $R_f = 0.4$) followed by recrystallization from hexane. The product was obtained as a pale yellow solid (148 mg, 52% yield). $^1$H NMR (CDCl$_3$, 400MHz): 7.55 – 7.51 (m, 2H), 7.41 (d, $J = 8.4$ Hz, 2H), 7.35 - 7.39 (m, 3H), 7.16 (d, $J = 8.3$ Hz, 2H), 7.06 - 7.12 (m, 2H), 4.05 (s, 2H), 2.35 (s, 3H). $^{19}$F NMR (CDCl$_3$, 376 MHz): 107.73 (d, $J = 7.2$ Hz).
In an oven dry flask under N₂, 902 mg of 1 (3.11 mmol), 1.6 mL of (triisopropylsilyl)acetylene (1.3 g, 7.16 mmol), 180 mg of Pd(PPh₃)₄ (0.16 mmol), 59 mg of CuI (0.31 mmol), and 15 mL of NEt₃ were dissolved in 40 mL of THF. The solution was heated to 30 °C and left under stirring overnight. The solution was then extracted with NH₄Cl aq. sat. and the organic phase dried over Na₂SO₄. The product was purified via column chromatography (hexane, \( R_f = 0.9 \)) to obtain a colorless oil (878 mg, 73% yield). \(^1\)H NMR (CDCl₃, 400MHz): 7.03 – 6.93 (m, 2H), 1.13 (s, 20H), 1.17 – 1.05 (m, 8H), 0.29 (s, 9H).

In a flask, 878 mg of 3 (2.43 mmol), were dissolved in 125 mL of degassed MeOH and 672 mg of K₂CO₃ (4.86 mmol) were added. The reaction was left overnight and 1 M HCl was added until a precipitate formed. The mixture was extracted with CHCl₃ and the organic phase dried over Na₂SO₄. The solvent was removed under vacuum to yield a pale yellow oil 652 mg). In an oven dry flask under N₂, 490 mg of the latter oil (1.54 mmol), 0.35 mL of iodobenzene (638 mg, 3.13 mmol), 116 mg of Pd(PPh₃)₄ (0.10 mmol), 36 mg of CuI (0.19 mmol), and 5 mL of NEt₃ were dissolved in 50 mL of THF. The solution was left at 40 °C for 2 days. The solution was then extracted with NH₄Cl aq. sat. and the organic phase dried over Na₂SO₄. The solvent was removed and the product was purified by filtration over a short silica plug (hexane) to obtain an opalescent colorless oil (510 mg, 58% yield over 2 steps). \(^1\)H NMR (CDCl₃, 400MHz): 7.60 (dd, \( J = 6.7, 3.0 \) Hz, 2H), 7.43 – 7.32 (m, 3H), 7.05 (d, \( J = 7.1 \) Hz, 2H), 1.15 (d, \( J = 2.8 \) Hz, 21H). \(^1\)C NMR (CDCl₃, 101 MHz):
In a flask, 510 mg of 4 (1.29 mmol) were dissolved in 150 mL of degassed THF and the solution put in an ice bath. 2.58 mL of a 1 M tetrabutylammonium fluoride solution in THF containing 5% vv. H₂O (2.58 mmol) were added dropwise and the reaction allowed to rt overnight. The solutes were preadsorbed on silica and the product purified by filtration over a short silica plug (hexane) to obtain white needle crystals (274 mg, 89% yield). ¹H NMR (CDCl₃, 400MHz): 7.60 (dd, J = 6.6, 2.9 Hz, 2H), 7.38 (dd, J = 5.3, 1.9 Hz, 3H), 7.06 (d, J = 7.0 Hz, 2H), 3.25 (s, 1H). ¹³C NMR (CDCl₃, 101 MHz): 165.04 (dd, J = 253.8, 6.4 Hz), 134.51, 131.82, 131.07, 126.04 (t, J = 11.7 Hz), 118.23 – 117.06 (m), 106.38 (t, J = 19.9 Hz), 103.54 (t, J = 3.3 Hz), 83.90 (t, J = 3.8 Hz), 83.47, 78.52, 20.81, 16.09. ¹⁹F NMR (CDCl₃, 376 MHz): -107.29 (d, 6.5 Hz).

S-(4-((3,5-difluoro-4-(phenylethynyl)phenyl)ethynyl)phenyl) ethanethioate, OPEFMidUp

In an oven dry sealable Schlenk under N₂, 133 mg of 4.1 (0.56 mmol), 228 mg of IPhSAc (0.82 mmol), 32 mg of Pd(PPh₃)₄ (0.03 mmol), 10 mg of CuI (0.06 mmol), and 1 mL of NEt₃ were dissolved in 15 mL of THF. The solution was heated to 55 °C and left under stirring overnight. The solvent was removed under vacuum and the residue preadsorbed on silica. The compound was purified via
column chromatography (hexane/ethyl acetate 9:1, $R_f = 0.4$) followed by recrystallization from hexane. The product was obtained as a off-white solid (97 mg, 55% yield). $^1$H NMR (CDCl$_3$, 400MHz): 7.59 (dd, $J = 6.7$, 3.0 Hz, 2H), 7.55 (d, $J = 8.2$ Hz, 2H), 7.42 (d, $J = 8.1$ Hz, 2H), 7.38 (dd, $J = 5.3$, 1.7 Hz, 3H), 7.10 (d, $J = 7.1$ Hz, 2H), 2.45 (s, 3H).

$^{19}$F NMR (CDCl$_3$, 376 MHz): -107.52 (d, $J = 7.1$ Hz).

S-4-((3,5-difluoro-4-(phenylethynyl)phenyl)ethynyl)benzyl ethanethioate, mOPEFMidUp

In an oven dry sealsable Schlenk under N$_2$, 250 mg of 4.1 (1.05 mmol), 368 mg of IBzSAc (1.26 mmol), 60 mg of Pd(PPh$_3$)$_4$ (0.05 mmol), 20 mg of CuI (0.11 mmol), and 1 mL of NEt$_3$ were dissolved in 15 mL of THF. The solution was heated to 40°C and left under stirring overnight. The reaction was filtered, the solvent was removed under vacuum, and the residue preadsorbed on silica. The compound was purified via column chromatography (hexane/ethyl acetate 9:1) followed by recrystallization from hexane. The product was obtained as a off-white solid (177 mg, 42% yield). $^1$H NMR (CDCl$_3$, 400MHz): 7.53 (dd, $J = 5.9$, 2.2 Hz, 2H), 7.51 (d, $J = 8.1$ Hz, 2H), 7.40 – 7.35 (m, 3H), 7.29 (d, $J = 8.2$ Hz, 2H), 7.12 – 7.06 (m, 2H), 4.13 (s, 2H), 2.36 (s, 3H). $^{13}$C NMR (CDCl$_3$, 101 MHz): 197.43, 166.36 (d, $J = 6.7$ Hz), 163.84 (d, $J = 6.7$ Hz), 141.60, 134.65, 134.48, 131.73, 131.65, 131.06, 127.29 (t, $J = 11.8$ Hz), 125.05, 123.75, 117.73 – 116.39 (m), 105.52 (t, $J = 19.9$ Hz), 103.32, 95.39, 90.10, 78.83, 35.89, 32.97. $^{19}$F NMR (CDCl$_3$, 376 MHz): -107.73 (d, $J = 7.1$ Hz).
((4-bromophenyl)ethynyl)trimethylsilane, 1, and 1,4-bis((trimethylsilyl)ethynyl)benzene, 16

In a oven dry flask, 5 g of 4-bromo-iodobenzene (17.7 mmol), 32 mL of (trimethylsilyl)acetylene (22.4 g, 19.5 mmol), 150 mg of Pd(PPh₃)₄ (0.13 mmol), 50 mg of CuI (0.26 mmol), and 10 mL of NEt₃ were dissolved in 30 mL of THF. The reaction was left at rt over the weekend. It was then filtered in stirring hexane and water and 6 M HCl was added until net acidity. The organic phase was washed with water, dried over Na₂SO₄, and the solvent removed under vacuum. The residue was purified via column chromatography (hexane) to obtain pure 5 (2.61 g, 58% yield) and 21 (284 mg, 6% yield) as white solids. 5: ¹H NMR (CDCl₃, 400MHz): 7.47 – 7.37 (m, 2H), 7.38 – 7.27 (m, 2H), 0.24 (s, 9H). ¹³C NMR (CDCl₃, 101 MHz): 133.35, 131.44, 122.71, 122.07, 103.83, 95.56, -0.14. 21: ¹H NMR (CDCl₃, 400MHz): 7.39 (s, 4H), 0.24 (s, 18H).

2-ethynyl-1,3-difluorobenzene, 2

In an oven dry seleable Schlenk under N₂, 2 g of 2,6-difluoro-iodobenzene (8.33 mmol), 1.73 mL of (trimethylsilyl)acetylene (1.21 g, 12.5 mmol), 150 mg of Pd(PPh₃)₄ (0.13 mmol), 50 mg of CuI (0.26 mmol), and 10 mL of NEt₃ were dissolved in 10 mL of THF. The reaction was left at 60 °C overnight. It was then filtered in stirring hexane and water and 6 M HCl was added until net acidity. The organic phase was washed with water, dried over Na₂SO₄, and the solvent removed under vacuum. The residue was purified by filtration over a short silica plug (hexane) to obtain the TMS-protected 6 as an opalescent oil (1.50 g, 86% yield). 1.1 g of the latter (5.26 mmol), were dissolved in 70 mL of degassed MeOH and 1.09 g of K₂CO₃ (7.89 mmol) were added. The reaction was left
overnight and in a stirring mixture of DCM and water. The organic phase was washed with water, dried over Na$_2$SO$_4$, and the solvent removed under vacuum to yield a colourless volatile liquid (650 mg, 77% yield over 2 steps). $^1$H NMR (CDCl$_3$, 400MHz): 7.37 – 7.21 (m, 1H), 6.98 – 6.85 (m, 2H), 3.51 (s, 1H). $^{19}$F NMR (CDCl$_3$, 376 MHz): -107.65 (d, 6.7 Hz).

$((4-((2,6$-difluorophenyl)ethynyl)phenyl)ethynyl)trimethylsilane, 3

In an oven dry seleable Schlenk under N$_2$, 650 mg of 2 (4.71 mmol), 954 mg of 1 (3.77 mmol), 210 mg of Pd(PPh$_3$)$_4$ (0.18 mmol), 70 mg of CuI (0.37 mmol), and 10 mL of NEt$_3$ were dissolved in 5 mL of THF. The reaction was left at 60 °C over the weekend. The solvent was removed under vacuum and the residue dissolved in hexane and filtered. The product was purified via column chromatography (hexane/ethyl acetate 10:1) to obtain a pale green oil (640 mg, 56% yield). $^1$H NMR (CDCl$_3$, 400MHz): 7.53 – 7.49 (m, 2H), 7.48 – 7.44 (m, 2H), 7.34 – 7.18 (m, 1H), 7.02 – 6.86 (m, 2H), 0.26 (s, 9H). $^{19}$F NMR (CDCl$_3$, 376 MHz): -107.33 (t, J = 6.5 Hz).

2-((4-ethynylphenyl)ethynyl)-1,3-difluorobenzene, 3.1

In a flask, 640 mg of 3 (2.1 mmol) were dissolved in 100 mL of degassed THF and the solution put in an ice bath. 2.3 mL of a 1 M tetrabutylammonium fluoride solution in THF (2.3 mmol) and 0.1 mL of H$_2$O were added dropwise and the reaction allowed to rt overnight. The solutes were preadsorbed on silica and the product purified by filtration over a short silica plug (hexane) to a white needle solid (500 mg, 99% yield). $^1$H NMR (CDCl$_3$, 400MHz): 7.66 – 7.43 (m, 5H), 7.00 –
S-(4-((4-((2,6-difluorophenyl)ethynyl)phenyl)ethynyl)phenyl) ethanethioate, OPEFDown

In an oven dry seable Schlenk under N₂, 270 mg of 3.1 (1.1 mmol), 347 mg of IPhSAc (1.2 mmol), 60 mg of Pd(PPh₃)₄ (0.05 mmol), 20 mg of CuI (0.11 mmol), and 1 mL of NEt₃ were dissolved in 15 mL of THF. The solution was heated to 60 °C and left under stirring overnight. The reaction was filtered, the solvent was removed under vacuum, and the residue preadsorbed on silica. The compound was purified via column chromatography (hexane/ethyl acetate 3:1, R_f = 0.6) followed by recrystallization from DCM/hexane. The product was obtained as a off-white solid (202 mg, 52% yield). ¹H NMR (CDCl₃, 400MHz): 7.60 – 7.49 (m, 6H), 7.43 – 7.39 (m, 3H), 6.95 (dd, J = 8.4, 7.0 Hz, 2H), 2.44 (s, 3H). ¹³C NMR (CDCl₃, 101 MHz): 196.00, 165.59 (dd, J = 254.1, 5.4 Hz), 136.87, 135.07, 134.83, 134.37, 134.26, 134.02, 133.50, 132.53 (t, J = 10.1 Hz), 131.02, 126.84, 126.05, 125.26, 114.73 – 112.83 (m), 93.36, 93.26, 32.94. ¹⁹F NMR (CDCl₃, 376 MHz): -107.31 (d, J = 6.6 Hz).

S-4-((4-((2,6-difluorophenyl)ethynyl)phenyl)ethynyl)benzyl ethanethioate, mOPEFDown

In an oven dry seable Schlenk under N₂, 230 mg of 3.1 (1 mmol), 310 mg of IBzSAc (1.1 mmol), 60 mg of Pd(PPh₃)₄ (0.05 mmol), 20 mg of CuI (0.11 mmol), and 1 mL of NEt₃ were dissolved in 15 mL of THF. The solution was heated to 60 °C and left under stirring overnight. The reaction was filtered, the solvent was removed under vacuum, and the residue preadsorbed on silica. The
compound was purified via column chromatography (hexane/ethyl acetate 4:1, \( R_f = 0.5 \)) followed by recrystallization from DCM/hexane. The product was obtained as a off-white solid (93 mg, 23% yield). \(^1\)H NMR (CDCl\(_3\), 400MHz): 7.60 – 7.49 (m, 6H), 7.43 – 7.39 (m, 3H), 6.95 (dd, \( J = 8.4, 7.0 \) Hz, 2H), 2.44 (s, 3H). \(^{13}\)C NMR (CDCl\(_3\), 101 MHz): 197.57, 165.58 (dd, \( J = 254.0, 5.3 \) Hz), 140.90, 134.52, 134.36, 134.19, 132.53 (t, \( J = 10.0 \) Hz), 131.57, 126.39, 124.95, 124.56, 114.21 – 113.48 (m), 101.41, 93.93, 91.93, 80.67, 35.92, 33.00. \(^{13}\)C NMR (CDCl\(_3\), 101 MHz): 197.52, 165.58 (dd, \( J = 253.9, 5.3 \) Hz), 140.88, 134.51, 134.34, 134.17, 132.49 (t, \( J = 10.0 \) Hz), 131.55, 126.40, 124.96, 124.56, 114.25 – 113.09 (m), 101.40, 93.91, 91.91, 80.63, 35.92, 32.98. \(^{19}\)F NMR (CDCl\(_3\), 376 MHz): -107.28 (d, \( J = 6.6 \) Hz).

5-ethynyl-1,3-difluorobenzene, 4

In an oven dry flask under N\(_2\), 5 g of 1-bromo-3,5-difluoro-benzene (26 mmol) were dissolved in 25 mL of THF and the solution degassed with N\(_2\) for 30 min. 4.15 mL of (trimethylsilyl)acetylene (2.94 g, 29 mmol), 300 mg of Pd(PPh\(_3\))\(_4\) (0.26 mmol), 100 mg of CuI (0.53 mmol), and 10 mL of NEt\(_3\) were were added and the reaction was left at 80 \(^\circ\)C overnight. The solvent was removed under vacuum and the TMS-protected compound purified via column chromatography (hexane, \( R_f = 0.7 \)) to obtain a colorless oil (5.4 g, 99% yield). 1.2 g of the latter (5.76 mmol), were dissolved in degassed EtOH and 1.2 g of K\(_2\)CO\(_3\) (8.64 mmol) were added. 1 M HCl was added until a precipitate formed. The mixture was extracted with DCM and the organic phase dried over Na\(_2\)SO\(_4\). The solvent was removed under vacuum to yield a white solid (648 mg, 82% yield over 2 steps) \(^1\)H NMR (CDCl\(_3\), 400MHz): 7.03 – 6.97 (m, 2H), 6.82 (tt, \( J = 8.9, 2.2 \) Hz, 1H), 3.14 (s, 1H).
((4-((3,5-difluorophenyl)ethynyl)phenyl)ethynyl)trimethylsilane, 5

In an oven dry flask under N₂, 600 mg of 4 (4.34 mmol) and 1.32 g of 1 (38.5 mmol) were dissolved in 25 mL of THF and the solution degassed with N₂ for 30 min. 100 mg of Pd(PPh₃)₄ (0.09 mmol), 25 mg of CuI (0.13 mmol), and 5 mL of NEt₃ were added and the reaction was left at 80 °C overnight. The solvent was removed under vacuum and compound purified via column chromatography (hexane) to obtain a pale yellow oil which solidified upon standing (1.02 g, 76% yield). ¹H NMR (CDCl₃, 400MHz): 7.46 (s, 4H), 7.07 – 7.00 (m, 2H), 6.81 (tt, J = 9.0, 2.3 Hz, 1H), 0.26 (s, 9H).

1-((4-ethynylphenyl)ethynyl)-3,5-difluorobenzene, 5.1

In a flask, 509 mg of 5 (1.64 mmol) were dissolved in 100 mL of degassed THF. 4.1 mL of a 1 M tetrabutylammonium fluoride solution in THF (4.1 mmol) were added dropwise and the reaction left overnight. H₂O and Et₂O were added to the solution and the organic phase washed with H₂O and brine. The product purified by column chromatography (hexane) to obtain a white solid (297 mg, 76% yield). ¹H NMR (CDCl₃, 400MHz): 7.48 (s, 4H), 7.07 – 7.00 (m, 2H), 6.82 (tt, J = 8.9, 2.3 Hz, 1H), 3.19 (s, 1H).

S-(4-((4-((3,5-difluorophenyl)ethynyl)phenyl)ethynyl)phenyl) ethanethioate, OPEFUp

In an oven dry flask under N₂, 88 mg of 5.1 (0.37 mmol) and 114 mg of IPhSAc (0.41 mmol) were
dissolved in 25 mL of THF and the solution degassed with N₂ for 30 min. 8.6 mg of Pd(PPh₃)₄ (7.4 µmol), 2.1 mg of CuI (11.1 µmol), and 0.1 mL of NEt₃ were added and the reaction was left at 80 °C overnight. The solvent was removed under vacuum and compound purified via column chromatography (hexane/CHCl₃ 1:1, R_f = 0.7) followed by recrystallization from hexane to obtain a off-white solid (80 mg, 56% yield). ¹H NMR (CDCl₃, 400MHz): 7.56 (d, J = 8.3 Hz, 2H), 7.52 (s, 4H), 7.41 (d, J = 8.3 Hz, 2H), 7.08 – 7.01 (m, 2H), 6.82 (tt, J = 8.9, 2.3 Hz, 1H), 2.44 (s, 3H).

**S-(4-((4-((3,5-difluorophenyl)ethynyl)phenyl)ethynyl)benzyl) ethanethioate, mOPEFUp**

In an oven dry flask under N₂, 300 mg of 5.1 (1.26 mmol) and 400 g of IBzSAc (1.4 mmol) were dissolved in 25 mL of THF and the solution degassed with N₂ for 30 min. 29 mg of Pd(PPh₃)₄ (0.03 mmol), 7 mg of CuI (0.04 µmol), and 0.5 mL of NEt₃ were added and the reaction was left at 80 °C overnight. The precipitate was filtered off and the residue preadsorbed on silica. The compound was purified via column chromatography (hexane/ethyl acetate 10:1, R_f = 0.6) followed by recrystallization from hexane to obtain a off-white solid (201 mg, 40% yield). ¹H NMR (CDCl₃, 400MHz): 7.50 (s, 4H), 7.46 (d, J = 8.2 Hz, 2H), 7.28 (d, J = 8.2 Hz, 2H), 7.08 – 7.01 (m, 2H), 6.81 (tt, J = 8.8, 2.3 Hz, 1H), 4.12 (s, 2H), 2.36 (s, 3H).

**tert-butyl(2,6-difluoro-4-((4-(phenylethynyl)phenyl)ethynyl)phenyl)sulfane, 12**

In an oven dry selsable Schlenk under N₂, 250 mg of 11 (0.76 mmol), 100 mg of 10 (0.49 mmol), 36 mg of Pd(PPh₃)₄ (0.03 mmol), 13 mg of CuI (0.07 mmol), and 5 mL of NEt₃ were dissolved in
10 mL of THF. The reaction was left at 60 °C overnight. The reaction was filtered in a stirring mixture of hexane and water. HCl 1 M was added slowly until acidity was reached. The organic phase was washed with water until neutrality and dried over Na₂SO₄. The final compound was purified via filtration over a short plug of silica using hexane/ethyl acetate 50:1 to obtain a white solid (116 mg, 38% yield). ¹H NMR (CDCl₃, 400MHz): 7.54 (t, J = 3.7 Hz, 2H), 7.52 (d, J = 3.0 Hz, 4H), 7.39 – 7.30 (m, 3H), 7.16 – 7.09 (m, 2H), 1.35 (s, 9H). ¹³C NMR (CDCl₃, 101 MHz): 132.07, 131.64, 131.47, 128.54, 128.40, 123.78, 122.94, 121.87, 91.40, 88.85, 83.30, 78.92. ¹⁹F NMR (CDCl₃, 376 MHz): -101.67 (d, J = 6.3 Hz).

**S-(2,6-difluoro-4-((4-(phenylethynyl)phenyl)ethynyl)phenyl) ethanethioate, TailDown** in an oven dry flask under N₂, 116 mg of 12 (0.29 mmol) and 4.1 mL of acetylchloride (4.53 g, 58 mmol) were dissolved in 25 mL of DCM. 0.03 mL of TiCl₄ were added. After 1 hour the content of the flask was poured in a stirring mixture of DCM and water and the Na₂CO₃ aq. sat. was added slowly until neutrality. The organic phase was then extracted with water, dried over Na₂SO₄, and preabsorbed on silica. The final compound was purified via column chromatography (hexane/ethyl acetate 100:1 increasing to 40:1) and recrystallized from DCM/hexane to obtain an off-white solid (55 mg, 49% yield). ¹H NMR (CDCl₃, 400MHz): 7.57 – 7.47 (m, 6H), 7.38 - 7.35 (m, 3H), 7.20 – 7.10 (m, 2H), 2.49 (s, 3H). ¹³C NMR (CDCl₃, 101 MHz): 192.49, 164.80 (dd, J = 251.1, 5.6 Hz), 134.40, 134.30, 134.27, 131.24, 131.05, 126.80, 125.51, 124.35, 117.68 – 117.21 (m), 95.33, 94.45, 91.49, 91.09, 32.67. ¹⁹F NMR (CDCl₃, 376 MHz): -104.10 (d, J = 7.1 Hz).
**tert-butyl(3,5-difluoro-4-iodophenyl)sulfane, 13** In a vacuum flask, 501 mg of 3,5-difluor4-iodo-aniline (1.96 mmol) were dissolved in 7 mL of degassed di-tert-butyl-disulfide and the solution placed in a bath at 65 °C. After reaching the desired temperature, 0.36 mL of tert-butyl-nitrite (0.31 g, 3 mmol) were added dropwise. As soon as gas evolution stopped, the excess the flask was placed at the rotary evaporator to remove the volatile compounds and finally the di-tert-butyl-disulfide was removed under vacuum distillation (1 mtorr, 33 °C). The dark residue was preadsorbed on silica and purified via column chromatography (hexane, Rf = 0.8) to obtain the desired product as an orange oil (203 mg, 32% yield). ¹H NMR (CDCl₃, 400MHz): 7.08 – 7.00 (m, 2H), 1.31 (s, 9H). ¹⁹F NMR (CDCl₃, 376 MHz): -92.57 (d, J = 6.0 Hz).

**tert-butyl(3,5-difluoro-4-((4-(phenylethynyl)phenyl)ethynyl)phenyl)sulfane, 14**

In an oven dry seable Schlenk under N₂, 200 mg of 13 (0.61 mmol), 100 mg of 10 (0.49 mmol), 28 mg of Pd(PPh₃)₄ (0.02 mmol), 10 mg of CuI (0.05 mmol), and 5 mL of NEt₃ were dissolved in 10 mL of THF. The reaction was left at 60 °C overnight. The reaction was filtered in a stirring mixture of hexane and water. HCl 1 M was added slowly until acidity was reached. The organic phase was washed with water until neutrality, dried over Na₂SO₄ and preadsorbed on silica. The final compound was purified via column chromatography (hexane/ethyl acetate 100:1) to obtain a white solid (104 mg, 53% yield). ¹H NMR (CDCl₃, 400MHz): 7.60 – 7.48 (m, 6H), 7.36 (dd, J = 5.1, 1.9 Hz, 3H), 7.17 – 7.06 (m, 2H), 1.34 (s, 9H). ¹⁹F NMR (CDCl₃, 376 MHz): -107.85 (d, J = 7.1 Hz)
4-ethynylpyridine, 6

In an oven dry sealeable Schlenk under N₂, 2 g of 4-iodo-pyridine (9.8 mmol), 2 mL of (trimethylsilyl)acetylene (1.42 g, 15 mmol), 150 mg of Pd(PPh₃)₄ (0.13 mmol), 50 mg of CuI (0.26 mmol) were dissolved in 10 mL of NEt₃. The reaction was left at 60 °C over the weekend. The solvent was removed under vacuum and the residue extracted with hot hexane. The TMS-protected compound was purified by filtration over a short plug of silica using hexane/ethyl acetate 5:1 and obtained as a brown oil (1.42 g, 83% yield). The latter was dissolved in 70 mL of THF and the solution placed in an ice bath. 9.6 mL of a tetrabutylammonium fluoride solution 1 M in THF (9.6 mM) and 0.48 mL of H₂O were added dropwise and the bath removed. After 25 minutes, the solution was dried with Na₂SO₄ and the product preadsorbed on silica. The final compound was purified via filtration over a short plug of silica using hexane/ethyl acetate 3:1 to obtain white flaky crystals (440 mg, 35% yield over 2 steps) which were immediately used in the next step. ¹H NMR (CDCl₃, 400MHz): 8.60 – 8.53 (m, 2H), 7.36 – 7.28 (m, 2H), 3.28 (s, 1H).

4-((4-ethynylphenyl)ethynyl)pyridine, 7

In an oven dry sealeable Schlenk under N₂, 1 g of 1 (4.1 mmol), 420 mg of 6 (4.1 mmol), 150 mg of Pd(PPh₃)₄ (0.13 mmol), 50 mg of CuI (0.26 mmol), and 4.5 mL of NEt₃ were dissolved in 10 mL of THF. The reaction was left at 60 °C overnight. The solvent was removed under vacuum and the residue extracted with hot hexane. The TMS-protected compound was purified via column chromatography (hexane/ethyl acetate 3:1) and obtained as yellow crystals (473 mg, 42% yield). These latter were dissolved in 40 mL of THF and the solution placed in an ice bath. 1.8 mL of
a tetrabutylammonium fluoride solution 1 M in THF (1.8 mM) and 0.09 mL of H$_2$O were added dropwise and the bath removed. After 25 minutes, the solution was dried with Na$_2$SO$_4$ and the product preadsorbed on silica. The final compound was purified via filtration over a short plug of silica using hexane/ethyl acetate 2:1 to obtain a white solid (231 mg, 30% yield over 2 steps) which was immediately used in the next step. $^1$H NMR (CDCl$_3$, 400MHz): 8.63 (s, 2H), 7.50 (s, 4H), 7.42 - 7.41 (m, 2H), 3.21 (s, 1H).

\[ \text{S-(4-((4-(pyridin-4-ylethynyl)phenyl)ethynyl)phenyl) ethanethioate, OPPy} \]

In an oven dry seleable Schlenk under N$_2$, 190 mg of 7 (0.93 mmol), 286 mg of IPhSAc (1.03 mmol), 54 mg of Pd(PPh$_3$)$_4$ (0.04 mmol), 24 mg of CuI (0.13 mmol), and 1 mL of NEt$_3$ were dissolved in 10 mL of THF. The reaction was left at 60 °C overnight. The solvent was removed under vacuum and the residue preadsorbed on silica. The product was purified via column chromatography (hexane/ethyl acetate 1:1) and recrystallized from hexane to obtain a off-white solid (102 mg, 31% yield). $^1$H NMR (CDCl$_3$, 400MHz): 8.62 (d, J = 5.5 Hz, 2H), 7.56 (d, J = 8.2 Hz, 2H), 7.54 (s, 4H), 7.43 – 7.33 (m, 4H), 2.44 (s, 3H). $^{13}$C NMR (CDCl$_3$, 101 MHz): 195.96, 152.47, 136.89, 134.83, 134.48, 134.36, 133.85, 131.14, 128.16, 126.72, 126.44, 124.72, 96.16, 93.64, 93.07, 91.09, 32.95.

\[ \text{S-4-((4-(pyridin-4-ylethynyl)phenyl)ethynyl)benzyl ethanethioate, mOPPy} \]

In an oven dry seable Schlenk under N$_2$, 97 mg of 7 (0.27 mmol), 87 mg of IBzSAc (0.30 mmol), 30 mg of Pd(PPh$_3$)$_4$ (0.03 mmol), 10 mg of CuI (0.05 mmol), and 0.3 mL of NEt$_3$ were dissolved
in 10 mL of THF. The reaction was left at 50 °C overnight. The solvent was removed under vacuum and the residue preadsorbed on silica. The product was purified via column chromatography (hexane/ethyl acetate 3:2) and recrystallized from hexane to obtain a off-white solid (81 mg, 81% yield). 

1H NMR (CDCl₃, 400MHz): δ 8.65 (s, br, 2H), 7.52 (s, 4H), 7.49 – 7.44 (m, 2H), 7.40 (s, br, 2H), 7.28 (d, J = 8.1 Hz, 2H), 4.11 (s, 2H), 2.35 (s, 3H). 197.51, 141.00, 134.51, 134.44, 134.27, 131.57, 126.77, 124.45, 124.44, 96.17, 94.18, 91.73, 91.01, 35.90, 32.98.

1-ethynyl-3,5-dimethoxybenzene, 10

In an oven dry sealeable Schlenk under N₂, 5 g of 1-bromo-3,5-dimethoxybenzene (23 mmol), 4.88 mL of (trimethylsilyl)acetylene (3.39 g, 35 mmol), 1.33 g of Pd(PPh₃)₄ (1.15 mmol), 307 mg of CuI (1.61 mmol) were dissolved in 50 mL of NEt₃. The reaction was left at 75 °C overnight. The reaction mixture was poured in a stirring mixture of water and DCM and the water phase acidified by adding slowly 70 mL of HCl 6 M. The TMS-protected product was purified by filtration over two short silica plugs using DCM and hexane as eluents for the first and the latter respectively and was recovered and a pale yellow solid (1.92 g, 37% yield). 0.5 g of the latter (2.13 mmol) were dissolved in 10 mL of THF and the solution placed in an ice bath. 3.2 mL of a tetrabutylammonium fluoride solution 1 M in THF (3.2 mmol) and 0.15 mL of H₂O were added dropwise and the reaction allowed to rt overnight. The final compound was purified via filtration over a short plug of silica using DCM to obtain an off-white solid (301 mg, 32% yield over 2 steps). 1H NMR (CDCl₃, 400MHz): 6.58 (t, J = 2.4, 2H), 6.40 (t, J = 2.3 Hz, 1H), 3.70 (s, 6H), 3.03 (s, 1H).
In a oven dry flask, 10 g of 4-bromo-iodobenzene (35 mmol), 8.6 mL of (triisopropylsilyl)acetylene (6.99 g, 38.5 mmol), 150 mg of Pd(PPh₃)₄ (0.13 mmol), 50 mg of CuI (0.26 mmol), and 10 mL of NEt₃ were dissolved in 15 mL of THF. The reaction was left at 30 °C over the weekend. The solvent was removed and the product purified via column chromatography (hexane) to obtain a colourless oil (9.26 g, 81% yield). ¹H NMR (CDCl₃, 400MHz): 7.43 (d, J = 8.7 Hz, 2H), 7.33 (d, J = 8.7 Hz, 2H), 1.12 (s, 21H).

1-(((4-ethynylphenyl)ethynyl)-3,5-dimethoxybenzene, 11

In an oven dry seable Schlenk under N₂, 550 mg of 10 (3.39 mmol), 1.35 g of TIPS-1 (4.01 mmol), 198 mg of Pd(PPh₃)₄ (0.17 mmol), 65 mg of CuI (0.34 mmol) were dissolved in 15 mL of NEt₃. The reaction was left at 80 °C overnight. The solvent was removed under vacuum and the residue preadsorbed on silica. The latter was washed with hexane and the TIPS-protected compound collected using chloroform as a white solid (701 mg, 49% yield). 650 mg of these latter 1.64 mmol were dissolved in THF and the solution placed in an ice bath. 3.3 mL of a tetrabutylammonium fluoride solution 1 M in THF (3.3 mmol) were added dropwise and rea left overnight. water and Et₂O were added to the mixture and the organich phase washed with water and dried over Na₂SO₄. The product was purified via column chromatography (hexane) to yield a white solid (615 mg, 48% yield over 2 steps). ¹H NMR (CDCl₃, 400MHz): 7.47 (s, 4H), 6.68 (d, J = 2.3 Hz, 2H), 6.47 (t, J = 2.3 Hz, 1H), 3.81 (s, 6H), 3.17 (s, 1H).
**S-(4-((3,5-dimethoxyphenyl)ethynyl)phenyl)ethynyl)phenyl) ethanethioate, OPE-OMe**

In a dry flask equipped with a condenser, 470 mg of 20 (1.8 mmol), 560 mg IPhSAc (2 mmol), 42 mg of Pd(PPh₃)₄ (0.04 mmol), 10 mg of CuI (0.5 mmol), and 1 mL of NEt₃ were dissolved in 25 mL of THF. The reaction was kept at 80 °C for 2 days. The solvent was removed under vacuum and the product purified via column chromatography (hexane/ethyl acetate 4:1, $R_f = 0.4$) followed by recrystallization from hexane to yield 460 mg of an off-white solid (62% yield). ¹H-NMR (CDCl₃, 400 MHz) 7.55 (d, $J = 8.3$ Hz, 2H), 7.51 (s, 4H), 7.40 (d, $J = 8.2$ Hz, 2H), 6.69 (d, $J = 2.3$ Hz, 2H), 6.48 (t, $J = 2.3$ Hz, 1H), 3.81 (s, 6H), 2.44 (s, 3H). ¹³C NMR (CDCl₃, 101 MHz): 196.02, 163.22, 136.87, 134.81, 134.25, 130.95, 126.91, 126.89, 125.89, 125.43, 112.03, 104.71, 94.05, 93.36, 93.13, 91.23, 58.10, 32.94.

**S-4-((3,5-dimethoxyphenyl)ethynyl)phenyl)ethynyl)benzyl ethanethioate, mOPE-OMe**

In a dry flask equipped with a condenser, 470 mg of 20 (1.8 mmol), 584 mg IBzSAc (2 mmol), 42 mg of Pd(PPh₃)₄ (0.04 mmol), 10 mg of CuI (0.5 mmol), and 1 mL of NEt₃ were dissolved in 25 mL of THF. The reaction was kept at 80 °C for 2 days. The solvent was removed under vacuum and the product purified via column chromatography (hexane/ethyl acetate 4:1, $R_f = 0.4$) followed by recrystallization from hexane to yield 436 mg of an off-white solid (57% yield). ¹H-NMR (CDCl₃, 400 MHz) 7.55 (d, $J = 8.3$ Hz, 2H), 7.51 (s, 4H), 7.40 (d, $J = 8.2$ Hz, 2H), 6.69 (d, $J = 2.3$ Hz, 2H), 6.48 (t, $J = 2.3$ Hz, 1H), 3.81 (s, 6H), 2.44 (s, 3H). ¹³C NMR (CDCl₃, 101 MHz): 197.52, 163.21, 140.81, 134.48, 134.21, 134.16, 131.54, 126.93, 125.77, 125.58, 124.63, 112.02, 104.68, 93.89, 93.64, 91.98, 91.29, 58.10, 35.92, 32.98.
1-ethynyl-4-(phenylethynyl)benzene, 12

In an oven dry seleable Schlenk under N$_2$, 980 mg of 1 (3.87 mmol), 0.65 mL of phenylacetylene (0.65 g, 6.37 mmol), 150 mg of Pd(PPh$_3$)$_4$ (0.96 mmol), 50 mg of CuI (0.26 mmol), and 5 mL of NEt$_3$ were dissolved in 15 mL of THF. The reaction was left at 50 °C overnight. The reaction was filtered in a stirring mixture of hexane and water. 50 mL of HCl 1 M were added. The organic phase was washed with water until neutrality and dried over Na$_2$SO$_4$. The TMS-protected compound was purified via column chromatography (hexane/ethyl acetate 40:1) to obtain flaky white crystals (725 mg, 68% yield). These latter were dissolved in 125 mL of MeOH and 570 mg of K$_2$CO$_3$ (4.2 mmol) were added and the solution left overnight under stirring. The content of the flask was then poured in a stirring mixture of water and DCM. 50 mL of 6 M HCl were added and the organic phase extracted with water. It was then dried over Na$_2$SO$_4$ and the solid preadsorbed on silica. The desired compound was purified via column chromatography (hexane) to obtained a white solid (407 mg, 52% yield over 2 steps). $^1$H NMR (CDCl$_3$, 400MHz): 7.57 – 7.53 (m, 2H), 7.49 (s, 4H), 7.37 (dd, J = 5.0, 1.8 Hz, 3H), 3.19 (s, 1H). $^{13}$C NMR (CDCl$_3$, 101 MHz): 132.07, 131.64, 131.47, 128.54, 128.40, 123.78, 122.94, 121.87, 91.40, 88.85, 83.30, 78.92.

S-4-((4-(phenylethynyl)phenyl)ethynyl)benzyl ethanethioate, mOPE3 In an oven dry flask under N$_2$, 100 mg of 10 (0.49 mmol) and 158 mg of IBzSAc (0.54 mmol) were dissolved in 15 mL of NEt$_3$ and the solution degassed with N$_2$ for 30 min. 15 mg of Pd(PPh$_3$)$_4$ (0.01 mmol) and 3 mg
of CuI (0.02 mmol) were added and the reaction was left at 80 °C overnight. The precipitate was filtered off and the residue preadsorbed on silica and the solvent removed under vacuum. The compound was purified via column chromatography (hexane/CHCl₃ 1:1, \( R_f = 0.7 \)) followed by recrystallization from hexane to obtain a off-white solid (50 mg, 30% yield). \( ^1H \) NMR (CDCl₃, 400MHz): 7.55 – 7.51 (m, 2H), 7.50 (s, 4H), 7.46 (d, \( J = 8.1 \) Hz, 2H), 7.35 (dd, \( J = 5.1, 2.0 \) Hz, 3H), 7.29 (s, 2H), 4.12 (s, 2H), 2.36 (s, 3H).

**tert-butyl(2,6-difluoro-4-iodophenyl)sulfane, 13**

In a rotavapor flask, 495 mg of 2,6-difluoro-4-iodo-aniline (1.94 mmol) were dissolved in 8 mL of degassed di-tert-butyl-disulfide and the solution placed in a bath a 65 °C. After reaching the desired temperature, 0.36 mL of tert-butyl-nitrite 0.31 g, 3 mmol) were added dropwise. As soon as gas evolution stopped, the excess the flask was placed at the rotary evaporator to remove the volatile compounds and finally the di-tert-butyl-disulfide was removed under vacuum distillation (1 mtorr, 33 °C). The dark residue was preadsorbed on silica and purified via column chromatography (hexane, \( R_f = 0.6 \)) to obtain the desired product as a colorless oil (250 mg, 39% yield). \( ^1H \) NMR (CDCl₃, 400MHz): 7.36 – 7.31 (m, 2H), 1.30 (s, 9H). \( ^13C \) NMR (CDCl₃, 101 MHz): 166.81 (dd, \( J = 252.7, 4.3 \) Hz), 124.01 (dd, \( J = 28.9, 2.6 \) Hz), 112.33 (t, \( J = 23.2 \) Hz), 96.46 (t, \( J = 10.6 \) Hz), 51.60, 33.64. \( ^19F \) NMR (CDCl₃, 376 MHz): -100.55 (d, \( J = 5.6 \) Hz).

**1,4-diethynylbenzene, 14**
1.91 g of **TMS-21** (7.06 mmol) and 1.50 g of K₂CO₃ (10.6 mmol) were dissolved in 20 mL of MeOH and 5 mL of EtOH. After 2 hours of vigorous stirring, the solution was diluted using 50 mL of water and extracted with Et₂O. The organic phase was washed with brine and dried over MgSO₄. The solvent was removed in vacuum to obtain 0.88 g of **21** (99% yield) as a brownish solid sufficiently pure for further elaborations. ¹H-NMR (CDCl₃, 400MHz) 7.44 (s, 4H), 3.17 (s, 2H).

**1,4-bis((4-(tert-butylthio)-3,5-difluorophenyl)ethynyl)benzene, 15**

In an oven dry sealable Schlenk under N₂, 102 mg of **11** (0.31 mmol), 20 g of **21** (0.16 mmol), 30 mg of Pd(PPh₃)₄ (0.03 mmol), 10 mg of CuI (0.05 mmol) were dissolved in 6 mL of THF and 2 mL of NEt₃. The reaction was left at 60 °C overnight. The solvent was removed under vacuum and the residue preadsorbed on silica. The product was purified via column chromatography (hexane:ethylacetate 5:1) to yield a white solid (35 mg, 67% yield). ¹H-NMR (CDCl₃, 400MHz) 7.53 (s, 2H), 7.13 (d, J = 6.2 Hz, 2H), 1.34 (s, 9H). ¹⁹F NMR (CDCl₃, 376 MHz): -102.52 (d, J= 6.2 Hz).

**S,S’-((1,4-phenylenebis(ethyne-2,1-diyl))bis(2,6-difluoro-4,1-phenylene)) diethanethioate, diSAc-OPEFOut**

In an oven dry flask under N₂, 133 mg of **22** (0.25 mmol) and 3.6 mL of acetylchloride (3.96 g, 50 mmol) were dissolved in 25 mL of DCM. 0.06 mL of TiCl₄ (0.09 g, 0.51 mmol) were added. After 1 hour the content of the flask was poured in a stirring mixture of DCM and water and the Na₂CO₃ aq. sat. was added slowly until neutrality. The organic phase was then extracted with water, dried over Na₂SO₄, and preabsorbed on silica. The final compound was purified via column...
chromatography (hexane/ethyl acetate 5:1, $R_f = 0.6$) and recrystallized from DCM/hexane to obtain an off-white solid (21 mg, 17% yield). $^1$H-NMR (CDCl$_3$, 400MHz) 7.53 (s, 4H), 7.16 (d, J = 7.0 Hz, 4H), 2.49 (s, 6H). $^{13}$C NMR (CDCl$_3$, 101 MHz): $\delta$ 192.43, 164.81 (dd, J = 251.1, 5.8 Hz), 134.51, 129.94 (t, J = 10.1 Hz), 125.40, 117.51 (dd, J = 26.1, 2.7 Hz), 94.97, 91.58, 32.68. $^{19}$F NMR (CDCl$_3$, 376 MHz): -103.97 (d, J = 7.1 Hz).
3 Self-assembled Monolayers (SAMs)

SAM Fabrication

SAM preparation procedure was adapted from our previous study. Briefly, we incubated the thioacetate precursors of all the measured compounds with 1x1 cm² 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 90 min prior to the measurement. The substrates were then rinsed with absolute ethanol inside a flowbox (O₂ = 1 – 3% and relative humidity < 10%) and left to dry for 15 min.

Atomic Force Microscopy Characterization

AuTS surfaces were prepared using the procedure as described by Weiss et al. To check for surface roughness we used atomic force microscopy (AFM) to image the surface topology and extract the root mean square roughness of the prepared substrate. The peak force tapping AFM measurements were performed using the same procedure as described before. Briefly, Bruker AFM multimode MMAFM-2 was used with a ScanAsyst-Air probe of resonance frequency 70 Hz and spring constant of 0.4 N m⁻¹, purchased from Bruker. The surface was scanned at a rate of 0.7 Hz and 512 samples per line were recorded. The scans were analysed with Nanoscope Analysis 1.5 software from Bruker to extract the surface roughness. One such 1 μm × 1 μm surface scan of bare AuTS sur-
face is provided in Figure S4 which shows atomically flat islands of gold atoms with a root mean square roughness values of 0.35 nm.

![Atomic force microscopy image](image)

**Figure S4:** Atomic force microscopy 1 µm × 1 µm height image of a bare AuTS substrate that yields RMS roughness of 0.35 nm.

---

**X-ray Photoelectron Spectroscopy**

**Experimental**

X-ray Photoelectron Spectroscopy (XPS) was performed using an Escalab 250XI spectrometer from Thermo Fisher Scientific (West Sussex, UK). The instrument was operating in constant analyser energy (CAE) mode. A monochromatic Al-Kα source (hv = 1486.74 eV) with the spot size of 900 micron. The survey scans and narrow scan were acquired by using pass energy of 100 eV.
and 50 eV, respectively. The data acquisition and fitting parameter are same as mentioned above. The pressure in the measurement chamber was below $1 \times 10^{-9}$ mbar during data acquisition. XPS spectra were analysed by using the least-squares curve fitting program Winspec.\textsuperscript{6} Deconvolution of the spectra included a Shirley\textsuperscript{7} baseline subtraction and fitting with a minimum number of peaks consistent with the structure of the molecules on a surface, taking into account the experimental resolution. The profile of the peaks was taken as a convolution of Gaussian and Lorentzian functions. Binding energies are reported $\pm$ 0.1 eV and referenced to the Au 4f7/2 photoemission peak originating from the substrate, centered at a binding energy of 84 eV.\textsuperscript{8} All measurements were carried out on freshly prepared samples; on each surface 5 points were measured to check for reproducibility.

**XPS Results & Discussion**

![Figure S5: (a) XPS spectra of carbon 1s and sulphur 2p2/3 core level for OPE-OMe/Au/mica SAMs deprotected via DBU. (a) C1s spectra: shows blue curve for C≡C/C-cyclic (285.0 eV) and red curve for the C-S/C-O-C peak (285.5 eV 286.0 eV). (b) Sulfur spectra: indicating a doublet at 162.0 eV for gold-sulfur bonds along with an additional intense and broad peak at 164.0 eV representiative of more than one component like disulfide, unbounded thioacetate or physisorbed thioacetate on the surface.](image-url)

Figure S5 and Figure S6 shows the XPS spectra of OPE-OMe and diSAc-OPE4F SAMs, re-
Figure S6: (a) XPS spectra of carbon 1s and sulphur 2p2/3 core level for diSAc-OPE4F/Au/mica SAMs deprotected by DBU. (a) C1s spectra: show blue curve for C≡C/C-cyclic (285.0 eV),9 black curve indicating the C-S/C-C-F peak (285.9 eV),13 red curve is representative of the thioacetate component C-C=O(287.0 eV)14 and the green curve indicating the C-F bond (288.3 eV).15 (b) Sulphur spectra: indicating a doublet 162.0 eV11 for gold-sulfur bonds along with an additional intense and broad peak at 164.0 eV12 representative of more than one component like disulfide, unbounded thioacetate or physisorbed thioacetate on the surface.

respectively, grown on atomically-flat gold surfaces. The S 2P core level spectra of OPE-OMe SAMs confirms that 90% S-species are chemically bounded (blue curve) to the gold surface (chemisorbed), and only 10% were unprotected or physisorbed thioacetate (red curve) on the surface. The ratio of chemisorbed sulphur (black) and thioacetate (red) is ≈1:1 for the diSAc-OPE4F SAMs (Figure S6), which agrees with the presence of an extra thioacetate terminal group on the top of the diSAc-OPE4F SAM. The absence of 167.0 eV and higher (oxidized forms of sulphur) peak confirms that sulphur species of both the SAMs were chemically preserved on the surface. The C 1s core level spectra of both the SAMs have C-cyclic/C≡C peak (285.0 eV) which confirms that the core structure of these OPE3 derivatives is preserved. The presence of C-O-C (red curve) and C-S species (blue curve) in Figure S5 confirms the core modification in the geometry of these OPE-OMe molecules compared to the reference OPE3 molecule. Similarly, the presence of C-F, C-C=O, and C-S species (in Figure S6) confirms the presence of diSAc-OPE4F molecules on the surface in the
expected geometry. Similarly, the N 1s, C 1s, and S 2p XPS spectra of OPPy and mOPPy are shown in Figure S7, while OPE3 and diSAc-OPE3 molecules have been reported earlier in Ref. 3 and 16, respectively.

Figure S7: XPS spectra of SAMs of mOPPy (a–c) and OPPy (d–f): (a, d) N 1s core-level region of both the SAMs indicating two distinct peaks. The first peak corresponds to the pyridyl nitrogen within the range of 399.0 eV–399.4 eV\textsuperscript{17} and the high binding energy component in the range of 401.5 eV–401.1 eV\textsuperscript{18} is attributed to pyridine moieties engaged in hydrogen bonding (H-bonds) with adsorbed water molecules. (b, e) C 1s core-level region of a mOPPy & OPPy SAMs shows the three main singlet peaks at 284.5 eV\textsuperscript{19} (black), 285.6 eV\textsuperscript{20,21} (red) and 288.0 eV\textsuperscript{22–24} (blue), corresponding to the C=C/C=C, C=S/C=N=C, and C=O, respectively.\textsuperscript{11} (c, f) S 2P core-level region of a SAMs with the binding energy range of 161.9 eV–162.0 eV\textsuperscript{9,25,26} and 163.8 eV–163.6 eV\textsuperscript{9,11,26–29} indicative of chemisorbed and physisorbed sulfur species on gold surface, respectively.
4 EGaIn J-V Measurement and Data Analysis

Data Acquisition

The details of the EGaIn setup are described elsewhere. All the measurements were performed inside a \( \text{N}_2 \) flowbox (\( \text{O}_2 = 1-3\% \) and relative humidity < 10\%). For each compound, 3-4 substrates were prepared and at least 12 \( \text{Au}^{TS} / \text{SAM} / \text{Ga}_2\text{O}_3 / \text{EGaIn} \) junctions per sample were measured (5 scans from 0 V \( \rightarrow \) 1 V \( \rightarrow \) –1 V \( \rightarrow \) 0 V, steps of 0.05 V) for a total of at least 180 traces per SAM. A new EGaIn tip was prepared every 6 junctions and flattened by gently pushing it on a Si wafer few times according to the procedure reported by Simeone et al. In Table S1 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:** Number of working EGaIn junctions and total yield for the compounds studied in this manuscript but not shown in ?? of the main text.

|            | no. of junctions | Yield (%) |
|------------|------------------|-----------|
| mOPE3      | 29               | 52        |
| OPEFTopDown| 48               | 73        |
| OPEFTopUp  | 44               | 96        |
| mOPEFTopDown| 36              | 72        |
| mOPEFTopUp | 31               | 31        |
| OPE-OMe    | 29               | 83        |
| mOPE-OMe   | 41               | 96        |
| OPPy       | 35               | 88        |
| mOPPy      | 36               | 88        |
| diSAC-OPEFOut | 36          | 82        |

S-35
The data were acquired as described and then parsed in a “hands-off” manner using Scientific Python to produce histograms of $J$ for each value of $V$ and the associated Gaussian fits (using a least-squares fitting routine). The data for OPE3 and diSac-OPE3 were already presented elsewhere\textsuperscript{3} and their values adjusted for the new series resistance of the setup.

**Figure S8:** (a) Plot of $\log|J|$ vs. $V$ for Au\textsuperscript{TS}/SAM//Ga\textsubscript{2}O\textsubscript{3}/EGaIn junctions comprising OPE3, mOPE3, and diSac-OPE3 (see legend). (b) Plot of $\log \chi$ vs. $V$ for the same junctions. Error bars represent 95% confidence intervals. (c) NDC plot for the same junctions.

We also plotted the asymmetry in $J - V$ curves plotted in Figure S9. While differences in $J$ were dubious, there were observable effects in asymmetry: we found a maximum of $\log \chi = 0.34$ for OPE3 but only 0.16 for mOPE3 at 1 V (Figure S9). We ascribe this decrease to the smaller degree of interaction between the molecule and the bottom electrode for mOPE3\textsuperscript{31} As can be seen from ?? in the main text, when compared to OPE3, mOPE3 had a similar $V_{\text{trans}}^-$ but a larger $V_{\text{trans}}^+$. This correlates to the fact that these two molecules have similar LUMO while the HOMO of mOPE3 is lower in energy (by 0.1 eV).
Figure S9: Asymmetry ratio $\chi = J(V_+)/J(V_-)$ plotted against the bias voltage for the derivatives of OPE3 and mOPE3 molecular wires shown in the ?? in the main text.

Normalized Differential Conductance

The Normalized Differential Conductance (NDC) is calculated from the $J - V$ data as $(dJ/dV) \cdot (V/J)$ and it can be used to extract information about the transport between the electrodes: off-resonant tunneling should describe a bowl-shaped curve with a minimum of 1 at 0 V, while deviation from this mechanism can affect the line shape.\textsuperscript{32,33} Indeed, an NDC plot resembling a bowl is found for all the wires, indicating that off-resonant tunneling is the principal tunneling mechanism.
Figure S10: NDC plot for the Au$^{TS}$/SAM//Ga$_2$O$_3$/EGaIn junctions for the molecules from OPE and mOPE series reported in the main text.

Transition Voltage

Another feature of the NDC plots is that we can use them to estimate the value of the transition voltage ($V_{\text{trans}}$). This parameter is calculated as the minimum in Fowler-Nordheim plot ($\ln(J/V^2)$ vs. $1/V$) or as the maximum in the $|V^2/J|$ vs. $V$ plot, but this analysis can be misleading when $V_{\text{trans}}$ falls outside or very close to the extremes of the experimental bias window as it is the case for most of the compounds analyzed in this study. All these methods are mathematically equivalent and consist only in a re-plot of the data to highlight features of the $J(V)$ curve which are not easy to find in $J(V)$ or Log$(J(V))$ plots commonly used in the field. The use of NDC plots can help in
these cases as $V_{\text{trans}}$ appears as the $V$ value at which NDC equals 2, but can also be extracted by mathematical means from any point in the measured bias.$^{32}$
5 Single Level Model

Single level model (SLM) is an analytical tool developed\textsuperscript{34–36} from the Landauer model which considers charge transport being dominated by a single molecular level, usually the occupied level (HOMO). SLM also considers lorentzian broadening of the coupling parameter between the molecule and the two electrodes ($\Gamma$). It can further be used to extract the energy offset between the frontier levels of the molecule in the gap and the metal electrodes ($\epsilon_h$) from the transition voltage ($V_{\text{trans}}$) spectroscopy. We use a modified version of the SLM to understand the coupling of SAMs with the top electrode in the form of the parameter $\alpha$ as described in this section.

Formulation of SLM

Following from previous work,\textsuperscript{34–36} it has been shown that the $V_{\text{trans}}$ obtained from $J - V$ measurements can be converted to the tunneling barrier energy offset ($\epsilon_h$) using:

$$eV_{\text{trans}} = \frac{2\epsilon_h}{\sqrt{3}} \quad \text{(S1)}$$

where $e$ is the charge of an electron. In this work, we extract the transition voltages ($V_{\text{trans}}$) from the Gaussian-averaged NDC plots with $V_{\text{trans}}$ being the voltage value corresponding to NDC $= 2$, as described in section 4 and in accordance with Vilan.\textsuperscript{32} The current-voltage characteristics
in SLM is defined as:

\[ I(V) = G V \frac{e_h^2}{e_h^2 - (\frac{eV}{2})^2} \]  \hspace{1cm} (S2)

where \( G \) is the conductance of the (EGaIn) tunneling junction, defined in terms of the the interface coupling parameter (\( \Gamma \)), conductance quantum (\( G_0 = \frac{2e^2}{\hbar} = 77.48 \mu S \)), and number of molecules in the junction (\( N \)) as:

\[ G = N G_0 \frac{\Gamma^2}{e_h^2} \]  \hspace{1cm} (S3)

Substituting Equation S3 in Equation S2, we obtain:

\[ I(V) = N G_0 \frac{\Gamma^2}{e_h^2 - (\frac{eV}{2})^2} V \]  \hspace{1cm} (S4)

When a molecule has different interaction with the metal electrodes at the two interfaces, the average interface coupling is defined as \( \Gamma = \sqrt{\Gamma_s \Gamma_t} \), where \( \Gamma_s \) and \( \Gamma_t \) are the interface couplings of the molecule with the substrate and the tip, respectively. In symmetric tunneling junctions, \( i.e., \) where the tip and substrate metal are of the same kind, \( \Gamma_s \approx \Gamma_t \), but in our case they are different, namely, EGaIn and Au_{TS}, respectively. Hence, we do not use the geometric average of \( \Gamma_s \) and \( \Gamma_t \).
in this formulation. Furthermore, in the CP-AFM junctions (where the SLM is usually applied), it
is easier to estimate a value for $N$ because of the known dimensions of the probe. This is not so
the case in EGaIn junctions where the number of molecules can vary by a few order of magnitudes
from junction to junction as the junction diameter can be anything between 10 and 100 micrometers.
$N$ will further depend on how the molecules pack in large-area SAMs (i.e., the packing density)
and how well do they wet the EGaIn tip. Same molecules functionalized with different chemical
groups exposed at the EGaIn/molecule interface will result in different EGaIn wetting, and thus
different $N$. This effect, however, can still be consider a manifestation of the nature of the interface
in large-area junctions which our model should take account for. Additional uncertainty in $N$ comes
from the presence of defects in large-area junctions which could contribute with different pathways
resistances to the total charge transport observed. In this sense, in these systems, the total current
does not perfectly describe the sum of all conductance, accounting for the individual contributions
of each of exactly $N$ molecules. In an ensemble junction, the total current is a weighted average of
three major populations of molecules; pristine, high-current defects and low-current defects. The
low-current defects do not contribute to the overall current and have no significant influence on
the transport. The high-current defects only matter when they persist above a certain threshold,
at which point the device becomes defect-mediated. These characteristics of large-area junctions
have been extensively studied\textsuperscript{30,37} and translate in a systematic error which can be ignored when
exploring trends.
Simplified SLM for Large-area Junctions

Considering the points above, the SLM from CP-AFM can be extended to large-area EGaIn junctions, only by keeping the following points under consideration with the provided reasoning:

- The SLM for large-area junctions should only be applied to a series a molecule, where one of them acts as a control, and minimum number of variables (preferably one) vary across the series.

- The interface interaction of the molecules in a series with the bottom electrode ($\Gamma_s$) is taken to be the same for all the molecules as they have the same anchoring group. For example, $\Gamma_s$ is considered the same for all the OPE3-like molecules (i.e., with $R-S/Au^{TS}$ anchor) and all the mOPE3-like molecules (i.e., the ones with the $R-CH_2-S/Au^{TS}$ anchor). The molecules in OPE3 and mOPE3 series should not be compared as they have different anchoring groups.

- Considering these previous points, the packing density of the investigated SAMs is assumed to be similar to that of the control. In our previous studies, we observed that the packing density of SAMs of compounds bearing a similar backbone and an identical anchoring group (and as well a similar molecular volume) was always found to be $2-4 \times 10^{14}$ molecules/cm$^2$ and thus within a factor $2^{16,38,39}$ (which cannot explain the differences of one or two orders of magnitude in the alpha values we extracted and proposed in the main text). In addition, since large-area junctions do not behave as a collection of single molecule junctions in parallel but yield lower current densities, unless we are discussing molecules with dramatically different
nature, we consider $N \approx N^{ref}$ a safe assumption. (Moreover, this assumption allows the use of the model even in the case of published data for which the packing density is unknown.)

- SLM (which is designed for CP-AFM junctions) fails and diverges significantly for EGaIn junctions in the bias window because of the systematically smaller values of $V_{trans}$ obtained in EGaIn experiments compared to CP-AFM data. Thus, here we applied SLM to the low-bias region, i.e., for the limiting case of $V \to 0$.

Considering all these assumptions, we can extend the SLM approach to large-area EGaIn junctions by dividing the $J(V)$ curves of the different SAMs by a known $J^{ref}(V)$ curve of the reference molecules (thus obtaining a current-density ratio, $J_r(V) = \frac{J(V)}{J^{ref}(V)}$). With this approach, although it is not possible to obtain any precise value for $\Gamma$ (contrarily to the ‘exact’ SLM proposed by Baldea and Frisbie, our approach cannot be used to fit $J(V)$ curves and extract parameters), $J_r(V)$ can be used to calculate $\Gamma$ of a series of molecules with respect to that of a control molecule, such as OPE3 or mOPE3. All the current-density ratios for the OPE3 and mOPE3 are shown in ???. The curvature of the plots depends on the relation between the $V_{trans}$ values of the molecules and the control.

Thus, having introduced $J_r(V)$, Equation S2 can be re-written in terms of the reference $J^{ref}(V)$ (either OPE3 or mOPE3) as

$$J_r(V) = \frac{J}{J^{ref}(V)} = \frac{I(V)/A}{I^{ref}(V)/A^{ref}} = \frac{I(V)}{I^{ref}(V)} \cdot \frac{N^{ref}}{N} \quad \text{(S5)}$$
where, \( A \) (or \( A_{\text{ref}} \)) is the junction area of the molecules (and the reference molecule), which can be rewritten as a product of packing density and \( N \) (or \( N_{\text{ref}} \)). As stated above, the packing densities can be assumed to be same for all the molecules throughout a series (or, as mentioned earlier, within uncertainty), thus \( J_r(V) \) depends only on \( I(V) \) (or \( I_{\text{ref}}(V) \)) and \( N \) (or \( N_{\text{ref}} \)), as shown in the Equation S5. Substituting Equation S4 in Equation S5, equation of \( J_r(V) \) can be converted step-by-step into:

\[
J_r(V) = \left( \frac{G}{G_{\text{ref}}} \cdot \frac{\epsilon_h^2}{(\epsilon_{h_{\text{ref}}}^2)^2} \cdot \frac{(\epsilon_{h_{\text{ref}}}^2)^2 - (eV/2)^2}{\epsilon_h^2 - (eV/2)^2} \right) \cdot \frac{N_{\text{ref}}}{N} \tag{S6}
\]

\[
J_r(V) = \frac{\Gamma_t}{\Gamma_{\text{ref} t}} \cdot \frac{3(V_{\text{ref} t}^2 - V^2)}{3V_{\text{trans}}^2 - V^2} \tag{S7}
\]

where \( V_{\text{ref} t} \) is the \( V_{\text{trans}} \) of the reference molecule and the molecule under study. This results in different curvatures of \( I - V \) curve for the two cases: \( V_{\text{ref} t} > V_t \) and \( V_{\text{ref} t} < V_t \). Finally, because of the assumption stated above, \( i.e., \) the breakdown of the above equation for higher bias, we only focus on the limiting case of the low-bias range:

\[
\lim_{V \to 0} J_r(V) = \frac{\Gamma_t}{\Gamma_{\text{ref} t}} \cdot \left( \frac{V_{\text{ref} t}}{V_{\text{trans}}} \right)^2 \tag{S8}
\]

We can rearrange this equation to extract the ratio \( \Gamma_t/\Gamma_{\text{ref} t} \), which we will indicate as the
Surface Interaction Parameter ($\alpha$), which is a function of the two measurable quantities, namely, the ratio of low-bias current-density ($J_r(V)$) and ratio of the transition voltages:

$$\alpha = \frac{\Gamma_t}{\Gamma_{\text{ref}}} = \lim_{V \to 0} J_r(V) \cdot \left(\frac{V_{\text{trans}}}{V_{\text{trans} \text{ref}}}\right)^2 \quad (S9)$$

To clarify, differences in the packing densities (as mentioned above), which are generally within a factor 2 as long as a good control is chosen, cannot account for the differences observed in alpha values. While a less energetic interaction at the interface could result in lower wetting and thus also affecting the real number of contacted molecules, this effect is to be considered part of the interactions between the SAM and the top electrode in large-area junctions that $\alpha$ is accounting for.
Application of SLM to OPE3 and mOPE3 series

The application of the simplified SLM on the main molecular series in this work, namely, OPE3 and mOPE3 series is discussed in detail in the main text. This provides some useful insight into the molecule//EGaIn interface. The coupling parameter is largest for the molecules with two anchoring sulfur groups which are also most conductive as per the experimental J-V data and theoretical transmission curves. All the mono-thiol fluorinated compounds have a similar coupling to top electrode as the OPE3 and mOPE3 (α = 1). While of the OPEs with methoxy and pyridine groups exposed to EGaIn interface have the lowest α. This can be explained because of the alkyl group that is oriented towards the top electrode in case of the OPE-OMe and mOPE-OMe. These are also individually shown in Figure S11 and Figure S12.

**Figure S11:** (a) Ratio of current-densities ($J_r$) for $J$ of all the molecules with R–S/Au$^{TS}$ anchoring group and $J^\text{ref}$ of the control OPE3. (b) Semilog plot of the relative interfacial coupling for the OPE series. *For diSAc-OPE4F, we used the molecule with similar bottom interface as the reference molecule – TailDown; please refer to Table S2 for the structure and α values.
Figure S12: (a) Ratio of current-densities ($J_r$) for $J$ of all the molecules with R–S/Au$^\text{TS}$ anchoring group and $J^\text{ref}$ of the control mOPE3. (b) Semilog plot of the relative interfacial coupling for the mOPE series.

Extension of SLM to other molecular series

To prove the validity of this approach even further, we applied the same methodology to EGaIn junctions’ data we acquired in our previously published studies:

OPE length-dependent series

In Figure S13 we report the $\alpha$ analysis of the data collected in the study of Carlotti et al.$^3$ in which we investigated the properties of a series of junctions comprising OPE molecules with different lengths and terminations. Remarkably, diSAc-OPE2 and 4 derivatives showed a similar $\alpha$ (about 10) when referenced to their mono-SAe analogues as controls, regardless of their length, just as we reported for OPE3.
Figure S13: (a) $J - V$ plots of the mono- and dithiolated OPE series from our previous work.
(b) Ratio of current-densities ($J_r$) of $J$ of all three diSac-OPE molecules and $J^{\text{ref}}$ of the corresponding control OPE of the same length. (ref) Semilog plot of the relative interfacial coupling for the OPE and diSac-OPE series.

Quantum Interference based series

SLM model was also applied to QI-based fluorenone series with BP as control and benzodithiophene (BDT) series with BDT-1 as reference, from our previous publications are shown in Figure S14.\textsuperscript{38,40}
**Figure S14:** Application of SLM, plotting $\alpha$ on other previous measured series of molecules with respect to the specified references: (a) Linear and cross-conjugated molecules with one and two parallel pathways where FO is the cross-conjugated molecule while the rest are linearly conjugated bearing the same anchoring and top group,\(^{40}\) (b) Series of OPEn molecules with mono- and di-thiols terminal groups where $\alpha$ of every dithiol OPEn molecule is calculated with respect to its monothiol analogue,\(^{3}\) (c) BDT-based series where BDT-1 is a linearly-conjugated molecule, BDT-2 is a cross-conjugated molecule, BDT-3 and AQ are the cross-conjugated molecules with quinoine moiety in the core.\(^{38}\)

**Carboxylic acid - terminated alkanethiols.**

We also investigated the $\alpha$ of saturated molecules. In particular, in the study of Ai et al.\(^{41}\) we compared SAMs of thiolakanes bearing different terminations — methyl, thiol, and carboxylic acid. In particular, we reported that surface bound water molecules on the carboxylic acid-terminated SAM, could induce rectification. The $\alpha$ analysis, reported in Figure S16, highlights that 1) the thiol-terminated SAMs have a higher $\alpha$ (as it is the case of this study); 2) the SAM-COOH//EGaIn interface has a lower $\alpha$ despite the higher J-V current, an observation that we ascribed to the presence of water.
BPT-CH$_3$/BPT-CF$_3$ Binary SAMs.

The $J-V$ raw data was provided by Zharnikov group, Heidelberg University was used to compute $\alpha$ for the binary SAMs with varying composition of CH$_3$ and CF$_3$ in binary SAMs from the recently published work by Asyuda et al.$^{42}$

Miscellaneous Molecular Rectifiers.

The $J-V$ raw data provided by Yoon group, Korea University was used for applying SLM model to NapC11, PheC11, AntC11, PyrC11, BPC11 and BiPyC11,$^{43,44}$ along with the data provided for reference alkanethiol on corresponding metal substrates. For C60C11, we used our own data that was previously published.$^{45}$ For BTTFC11, the data was extracted from graphs using an online tool WebPlotDigitizer$^{46}$ from published work by Han et al.$^{47}$ For FcC11, we used our own $J-V$ data measured in a N$_2$ flowbox environment; $J-V$ data for FcC11 are shown in Figure S15. The Fc-Cn-DPA data was provided by the Nijhuis group at the National University of Singapore (now, University of Twente, NL).$^{48}$
**Figure S15:** $J - V$ plot of the Ferrocene rectifier with undecanethiol as the aliphatic backbone measured on Ag$^{TS}$ using EGaIn as top electrode inside a N$_2$ flowbox environment.

**Figure S16:** (a) $J - V$ plots of the 16-mercaptohexadecanoic acid compared to 1,16-Hexadecanedithiol and 1-hexadecanethiol. (b) Ratio of current-densities ($J_r$) with $J_{ref}$ of the control 1-hexadecanethiol. (ref) Semilog plot of the relative interfacial coupling.
**Table S2:** List of molecules, their structure, functional group at the EGaIn interface, and the values of $\alpha$ for all the series analyzed in this work using the modified SLM. The termini of all the molecules exposed to the EGaIn electrode are highlighted in red. For the rectifiers, $R = C_{11}H_{22}SH$

| Series       | Compound acronym | Structure | $\alpha^+$ $V > 0$ | $\alpha^-$ $V < 0$ |
|--------------|------------------|-----------|---------------------|---------------------|
| Carboxylic acid |                 |           |                     |                     |
|              | C16SH (ref)      | ![Structure](image1) | 1                   | 1                   |
|              | C15COOH (H2O)   | ![Structure](image2) | 0.04 ± 0.05         | 0.04 ± 0.02         |
|              | C15COOH         | ![Structure](image3) | 0.005 ± 0.01        | 0.002 ± 0.004       |
|              | C16diSH         | ![Structure](image4) | 5.43 ± 0.22         | 4.49 ± 0.13         |
| OPE          | OPE3 (ref)       | ![Structure](image5) | 1                   | 1                   |
|              | diSAC-OPE3      | ![Structure](image6) | 9.78 ± 0.80         | 10.38 ± 0.84        |
|              | OPEFDown        | ![Structure](image7) | 1.71 ± 0.34         | 1.93 ± 0.40         |
|              | OPEFUp          | ![Structure](image8) | 1.25 ± 0.35         | 1.81 ± 0.51         |
|              | FMidDown        | ![Structure](image9) | 1.43 ± 0.40         | 1.98 ± 0.53         |
|              | FMidUp          | ![Structure](image10)| 1.95 ± 0.41         | 2.83 ± 0.62         |
|              | OPE-OMe         | ![Structure](image11)| 0.4 ± 0.21          | 0.42 ± 0.25         |
|              | OPPy            | ![Structure](image12)| 0.12 ± 0.07         | 0.42 ± 0.15         |
|              | diSAC-OPE4F     | ![Structure](image13)| 11.44 ± 1.24        | 74.99 ± 1.50        |
| TailDown (ref) |                 |           |                     |                     |
|              | TailDown (ref)  | ![Structure](image14)| 1                   | 1                   |
|              | diSAC-OPE4F     | ![Structure](image15)| 58.26               | 74.99               |
| mOPE         | mOPE3 (ref)     | ![Structure](image16)| 1                   | 1                   |
|              | mOPEFDown       | ![Structure](image17)| 0.51 ± 0.21         | 1.09 ± 0.43         |
|              | mOPEFUp         | ![Structure](image18)| 0.53 ± 0.19         | 0.75 ± 0.28         |
|                  | mOPE-OMe | mOPPy | Fluorenone | Fluorenone |
|------------------|----------|-------|------------|------------|
|                  | 0.07 ± 0.22 | 0.15 ± 0.04 | 0.15 ± 0.04 | 0.09 ± 0.02 |
| BP (ref)         |          |       | 1          | 1          |
| BT               | 1.66 ± 0.34 | 2.32 ± 0.49 |          |            |
| FO               | 0.4 ± 0.51  | 0.5 ± 0.67  |          |            |
| FH               | 0.94 ± 0.45 | 1.26 ± 0.63 |          |            |
| OPE3SH (ref)     |          |       | 1          | 1          |
| OPE1SH           | 0.36 ± 0.32 | 0.31 ± 0.20 |          |            |
| OPE2SH           | 0.53 ± 0.30 | 0.57 ± 0.31 |          |            |
| OPE4SH           | 0.57 ± 0.23 | 0.68 ± 0.26 |          |            |
| OPE3SH (ref)     |          |       | 1          | 1          |
| OPE2diSH         | 12.67 ± 0.80 | 8.56 ± 0.28 |          |            |
| OPE3diSH         | 9.78 ± 0.80  | 10.38 ± 0.84 |          |            |
| OPE4SH (ref)     |          |       | 1          | 1          |
| OPE4diSH         | 8.34 ± 0.68  | 8.05 ± 0.50  |          |            |
| Arene-based      | C16SH (AgTS) (ref) |       | 1          | 1          |
| rectifiers       |          |       |            |            |
| NapC11           | 0.77     | –     |            |            |
| PheC11           | 0.71     | –     |            |            |
| AntC11           | 0.72     | –     |            |            |
| PyrC11           | −0.33    | –     |            |            |
**Figure S17:** Energy band schematic showing different rectification mechanisms for several molecular rectifiers in large-area junctions: (a) HOMO-mediated rectifiers FcC11 and Fc-C1-DPA that show thermally-activated rectification. BTTFCl1 (on Au\textsuperscript{TS}) also follows similar mechanism, except the HOMO comes in resonance at positive bias; (b) HOMO-mediated rectifier Fc-C0-DPA in which LUMO localized on diphenylacetylene moiety gates the HOMO in an inverted-Marcus regime causing activationless rectification; (c) LUMO-mediated rectifiers such as C15COOH-H\textsubscript{2}O, BiPyC11 and C60C11 that involve charge-transport in Marcus-normal regimes (except for BiPyC11); the Stark effect lowers the LUMO energies for C15COOH-H\textsubscript{2}O, PyrC11 and BPC11. Straight solid arrows indicate tunneling transport while curved solid arrows suggest hopping transport, and features/MO highlighted in blue and red correspond to positive and negative polarity, respectively.

| Miscellaneous rectifiers | BPC11 | C18SH (Ag\textsuperscript{TS}) (ref) | C60C11 | FcC11 | C18SH (Au\textsuperscript{TS}) (ref) | BTTFCl1 | BiPyC11 | Fc-C0-DPA | Fc-C1-DPA |
|--------------------------|-------|------------------------------------|--------|------|------------------------------------|---------|---------|-----------|-----------|
|                          |       | -0.23                              | 1      | -1.03| 1                                  | -0.58   | 1.26    | -0.54     | -0.93     |
|                          |       |                                    |        |      |                                    |         |         |           |           |
6 DFT Calculations

As a final support for the validity of our experimental observations and their interpretation, we also performed quantum-mechanical calculations using the Density Functional Theory (DFT) software packages. We performed the calculations using the GAUSSIAN 09 software packages\textsuperscript{49} for geometry optimization and calculation of related electronic properties of the molecules. We used Artaios software for computation of transmission spectra in a metal-molecule-metal junction.\textsuperscript{50} The details are given below.

Geometry Optimization

We drew all the molecules in the gaussview program and optimized them with terminal thiol group(s) using the \textit{B3LYP/6-31+g(d,p)} method incorporating the $6-31+g(d,p)$ basis sets in the gaussian package. We used these calculations to extract the energy values of the frontier $\pi$-levels, \textit{i.e.}, the HOMO and LUMO, and also the dipole moment values (total and the x, y and z components), which are tabulated in the main text. Same calculations were also used to generate plots of HOMO and LUMO orbitals for visualization, shown in Figure S18.
Figure S18: HOMO (top) and LUMO (bottom) isoplots (for iso-value = 0.02) calculated for all the molecules under study in this project, as described in section 6. The plots were created using visualization programs VMD\textsuperscript{51} and blender.\textsuperscript{52}
Figure S19: (a) DFT predicted HOMO and LUMO energy values for the OPE and mOPE series on the left axis with the corresponding $V_{\text{trans}}$ for positive and negative bias on the right axis. (b) DFT predicted Dipoles values along the length of the molecule for the molecules in the OPE and mOPE series.

Transmission Calculations

The Gaussian16-optimized geometries were attached between two metal leads with 18 Au atoms each after deleting the one and two hydrogen atoms from the thiol(s) for mono- and di-thiol molecules, respectively. Au(111) crystal planes were used and the molecule-metal distance was kept at a value of 2.48 Å between the sulfur and nearest Au atom, occupying the fcc-site of the Au(111) crystal plane. In other words, vertical orthogonal distance of molecule from the surface of two metal clusters was 1.58 Å. Only for the mono-thiol molecules, the farthest Au atom from S, which was part of the electrode attached directly to the sulfur atom, was deleted to ensure that the system was a closed-shell system. We used B3LYP exchange-correlational functional and LANL2DZ basis sets for the gaussian single-point energy calculations using the keywords $iop(5/33 = 3)$ and $iop(3/33 = 1)$ to generate the hamiltonian and overlap matrices which would then serve as input for the transport calculations. The calculation results are shown in Figure S20. The transmission spectra were
referenced to the experimental fermi level of EGaIn electrode (−4.3 eV).

Figure S20: (a) Transmission Probability as a function of energy referenced to the fermi level of EGaIn computed for molecules without the methylene bridge connected to the thiols. (b) Transmission spectra for rest of the molecules that have a methylene bridge connecting the aromatic part to the thiol anchoring group.

The transmission spectra shown in Figure S20 support the experimental observations described in this work. The OPE-OMe and mOPE-OMe are least conductive and have smallest transmission in HOMO-LUMO gap, with the resonance peaks not reaching to the value 1. This reduced transmission could be because of the exposed aliphatic OMe group at the top molecule-metal interface, unlike the aromatic-metal or thiol-metal interfaces in the rest of the molecules. The OPE3 and mOPE3 along with the diSAc- molecules are the most conductive. Both OPPy and mOPPy have similar feature showing an extra peak above fermi level; this goes together with the obser-
vation of rectification in these two pyridine-terminated molecules (and a peak in the NDC plots). This demands for further future study on pyridine-terminated molecular wires. The fluorinated molecules on the other hand all show similar transmission probability as OPE3 and mOPE3, in agreement with the EGaIn measurements. Thus, we show here that the single-molecular model of metal-molecule-metal tunneling junction can be successfully used as a model to predict and support the experimental conductance observations from large-area molecular junctions, which otherwise are very computationally expensive to model.
Optimized Geometry Coordinates

Below are the cartesian coordinates of the DFT-optimized geometries for all the molecular wires and their analogues using Gaussian16, described above in this study:

Coordinates for mOPE3:

C  1.30120286  1.23772529  0.74842764
C -0.08189889  1.24148855  0.86992048
C -0.80441148  0.03044470  0.93874197
C -0.08750408 -1.18449469  0.88058426
C  1.29557162 -1.18818993  0.75892650
C  2.01821872  0.02282576  0.69060100
C -2.22218379  0.03418656  1.06429119
C -3.43588538  0.03720351  1.17242383
C  3.43623667  0.01893660  0.56634426
C  4.65005563  0.01545357  0.46032439
C -4.85509540  0.04027635  1.29827708
C -5.57425492 -1.17013155  1.38337442
C -5.57278565  1.25356437  1.34352560
C -6.96001269 -1.16069143  1.51099845
H -5.03505632 -2.11126558  1.35065218
C -6.95870100  1.24979969  1.47106182
H -5.03261994  2.19253973  1.27963042
C -7.67416981  0.04616990  1.56069444
C  6.07044110  0.01132819  0.33657587
C  6.78925945  1.22383736  0.27548840
C  6.78199764 -1.20535605  0.27341411
C  8.17758588  1.21481898  0.15514591
H  6.24769724  2.16310614  0.32346222
C  8.17034880 -1.20442446  0.15303269
H  6.23481942 -2.14145039  0.31969484
C  8.87359412  0.00315808  0.09356361
H  8.71822349  2.15573630  0.10928640
H  8.70534728 -2.14847524  0.10546088
H  9.95551829 -0.00000000  0.00000000
H  1.84426776  2.17576208  0.69663452
H  1.83428548 -2.12914366  0.71525285
H -0.63058838 -2.12255447  0.93192278
H -0.62062524  2.18249292  0.91307512
| Element | X         | Y         | Z         |
|---------|-----------|-----------|-----------|
| C       | -9.17416151 | 0.04918445 | 1.69068005 |
| H       | -9.51396684 | -0.82420635 | 2.25199683 |
| H       | -9.51437850 | 0.95298617 | 2.20123052 |
| S       | -9.95551829 | 0.00000000 | 0.00000000 |
| H       | -7.49496623 | 2.19469763 | 1.50131600 |
| H       | -7.49728775 | -2.10347483 | 1.57260262 |

Coordinates for mOPE-OMe:

| Element | X         | Y         | Z         |
|---------|-----------|-----------|-----------|
| C       | -1.30587627 | -1.25795460 | -0.75288700 |
| C       | 0.07727518  | -1.26493332 | -0.87420050 |
| C       | 0.80162836  | -0.05594333 | -0.95229183 |
| C       | 0.08677330  | 1.16093741  | -0.90388707 |
| C       | -1.29633547 | 1.16775704  | -0.78223444 |
| C       | -2.02081130 | -0.04150260 | -0.70436855 |
| C       | 2.21957748  | -0.06253438 | -1.07692369 |
| C       | 3.43339382  | -0.06813257 | -1.18370334 |
| C       | -3.43886536 | -0.03432219 | -0.57931910 |
| C       | -4.65197913 | -0.02791904 | -0.47195198 |
| C       | 4.85276722  | -0.07392479 | -1.30740079 |
| C       | 5.57260529  | 1.13456520  | -1.41252896 |
| C       | 5.57027013  | -1.28795410 | -1.33019479 |
| C       | 6.95857009  | 1.12255072  | -1.53745088 |
| H       | 5.03359617  | 2.07625902  | -1.39745916 |
| C       | 6.95647453  | -1.28679323 | -1.45508412 |
| H       | 5.02971353  | -2.22551515 | -1.25071689 |
| C       | 7.67251132  | -0.08517629 | -1.56441859 |
| C       | -6.07355527 | -0.02041499 | -0.34554217 |
| C       | -6.77882665 | -1.23540263 | -0.28473540 |
| C       | -6.76570790 | 1.20194833  | -0.28182018 |
| C       | -8.16932330 | -1.21812666 | -0.16079764 |
| H       | -6.26016497 | -2.18520867 | -0.33262585 |
| C       | -8.15629169 | 1.19932949 | -0.15764265 |
| H       | -6.23683511 | 2.14623147  | -0.32720107 |
| C       | -8.87423030 | -0.00564813 | -0.09573456 |
| H       | -9.95020398 | 0.00000000  | 0.00000000 |
| H       | -1.85079174 | -2.19447247 | -0.69372293 |
| H       | -1.83388120 | 2.10968044  | -0.74586822 |
| H       | 0.63140789  | 2.09769418  | -0.96253850 |
| H       | 0.61454541  | -2.20708383 | -0.90989817 |
| C       | 9.17281356  | -0.09088267 | -1.69081727 |
| H       | 9.51441180  | -1.00677059 | -2.17839020 |
| H       | 9.51390949  | 0.76868523  | -2.27237277 |
| Element | X          | Y          | Z          |
|---------|------------|------------|------------|
| S       | 9.95020398 | 0.00000000 | 0.00000000 |
| H       | -10.3890833 | 3.58367645 | 0.04908477 |
| H       | 7.49621643  | 2.06398069 | -1.61469317|
| H       | 7.49253650  | -2.23223202| -1.46756426|
| O       | -8.74501457 | 2.43251784 | -0.10296528|
| O       | -8.77131042 | -2.44503796| -0.10951982|
| C       | -10.18523429| -2.51569708| 0.01743727 |
| H       | -10.68930174| -2.04539951| -0.83648919|
| H       | -10.42787715| -3.57883971| 0.03727204 |
| H       | -10.52872752| -2.04865376| 0.94926735 |
| C       | -10.15794488| 2.51804361 | 0.02576969 |
| H       | -10.66798573| 2.05580180 | -0.82900846|
| H       | -10.50432222| 2.05190362 | 0.95657137 |

Coordinates for mOPPy:

| Element | X            | Y            | Z            |
|---------|--------------|--------------|--------------|
| C       | 2.03122596   | -1.84055947  | 0.00176076   |
| C       | 0.64782242   | -1.95667710  | 0.00184260   |
| C       | -0.17320571  | -0.80782971  | 0.00066188   |
| C       | 0.44449274   | 0.46197079   | -0.00060404  |
| C       | 1.82789840   | 0.57816961   | -0.00068595  |
| C       | 2.64789382   | -0.57079230  | 0.00049485   |
| C       | -1.59130094  | -0.92681183  | 0.00074568   |
| C       | -2.80556276  | -1.0273195   | 0.00081539   |
| C       | 4.06636420   | -0.45163704  | 0.00041290   |
| C       | 5.28015740   | -0.34929322  | 0.00034041   |
| C       | -4.22572082  | -1.14367273  | 0.00089761   |
| C       | -5.04482469  | 0.00059447   | -0.00026266  |
| C       | -4.84712289  | -2.41108164  | 0.00214914   |
| C       | -6.43458361  | -0.11690069  | -0.00017664  |
| H       | -4.58497374  | 0.98346531   | -0.00123428  |
| C       | -6.23279574  | -2.51549641  | 0.00222367   |
| H       | -4.23219059  | -3.30524377  | 0.00305719   |
| C       | -7.05220440  | -1.37305989  | 0.00106516   |
| C       | 6.69926995   | -0.23190330  | 0.00022317   |
| C       | 7.52879990   | -1.37000579  | 0.00137974   |
| C       | 7.33146785   | 1.02656770   | -0.00104852  |
| C       | 8.91136586   | -1.19648159  | 0.00120968   |
| H       | 7.09673042   | -2.36497573  | 0.00238664   |
| C       | 8.72389140   | 1.08130449   | -0.00109812  |
| H       | 6.74249045   | 1.93749436   | -0.00197209  |
| H       | 9.56766265   | -2.06411400  | 0.00209216   |
| H       | 9.22952778   | 2.04454165   | -0.00207081  |
H  2.65138031  -2.73100157  0.00267635
H  2.29064729   1.55964745 -0.00166417
H  -0.17561389  1.35233609 -0.00151855
H   0.18505234 -2.93806785  0.00282173
H  -6.68954889 -3.50247078  0.00320131
H  -7.03400437  0.78771927 -0.00109939
N   9.51741765   0.00000000  0.00000000
C  -8.55435849 -1.57729287  0.00121600
H  -8.84025037 -2.15594792 -0.88274350
H  -8.84025374 -2.15458751  0.88606301
S  -9.51741765   0.00000000  0.00000000

Coordinates for diSAc-OPE3:
C   7.58954322  -1.27041959  0.00064550
C   6.19817298  -1.25913202  0.00072871
C   5.48245423  -0.4434150   0.00031246
C   6.21681346   1.16027826 -0.00018616
C   7.60710881   1.14976426 -0.00026839
C   8.30949758  -0.06610220  0.00014467
H   8.11243872  -2.22236420  0.00097299
H   5.65246507  -2.19720171  0.00112200
H   5.68499057   2.10617972 -0.00050678
H   8.14915469   2.0908520   -0.00065474
S  10.09135309  -0.00000000  0.00000000
C   4.05886891  -0.03381657  0.00041722
C   2.84008792  -0.02305956  0.00046889
C   1.41716289  -0.01149585  0.00034065
C   0.70402591   1.20727825  0.00017444
C   0.68424586  -1.21848416  0.00040130
C  -0.68425126   1.21856020  0.00073700
H   1.25440333   2.14250369  0.00013222
C  -0.70403032  -2.12070221  0.00029856
H   1.21929635  -2.16256425  0.00053396
C  -1.41716729   0.01157189  0.00012935
H  -1.21930175   2.16264030 -0.00005196
H  -1.25440773  -2.14242765  0.00035178
C  -2.84009230   0.02313760  0.00002711
C  -4.05887444   0.03387561 -0.00006122
C  -5.48245886   0.04438854 -0.00008546
C  -6.21681013  -1.16023828 -0.00065384
C  -6.19818768   1.25917213  0.00052229
C  -7.60710456  -1.14973429 -0.00065861
H  -5.68498019  -2.10613480  -0.00108322
C   -7.58955901   1.27044771   0.00054050
H   -5.65248974   2.19724691   0.00099700
C   -8.30950539   0.06612627  -0.00008467
H   -8.14914147  -2.09096130  -0.00114526
H   -8.11245955   2.22239036   0.00105601
S   -10.09135309   0.00000000  -0.00000000

Coordinates for OPE3:
C   1.04245633  -1.17416138  -0.00020127
C   -0.34592252  -1.16835072  -0.00017292
C   -1.06366354   0.04766385  -0.00018270
C   -0.33555675   1.25749917  -0.00022293
C    1.05282324   1.25147850  -0.00022293
C    1.77047970   0.03557228  -0.00024050
C    -2.48670386   0.05367460  -0.00015229
C    -3.70546453   0.05942492  -0.00012622
C     3.19389764   0.02946989  -0.00027491
C     4.41235861   0.02403690  -0.00029998
C    -5.12909799   0.06393709  -0.00009681
C    -5.85002472   1.27563869  -0.00010358
C    -5.85838796  -1.14374336  -0.00006058
C    -7.24141134   1.28102367  -0.00007523
H    -5.30836396   2.1605707   -0.00013150
C    -7.24868967  -1.13911583  -0.00003122
H    -5.32263606  -2.08742858  -0.00005449
C    -7.95629170   0.07370715  -0.00003802
C     5.83810228   0.01761706  -0.00021239
C     6.55058894  -1.20018199  -0.00014360
C     6.56156208   1.22892844  -0.00020261
C     7.94414623  -1.20150484  -0.00006796
H     5.99997539  -2.13540763  -0.00015167
C     7.95507463   1.21766769  -0.00012697
H     6.01941468   2.16908885  -0.00025669
C     8.65190182   0.00490888  -0.00005916
H     8.47970499  -2.14644328  -0.00001688
H     8.49915394   2.15772715  -0.00012189
H     9.73785783   0.00000000  0.00000000
S    -9.73785783   0.00000000  0.00000000
H    -1.58131656  -2.11606433  -0.00019319
H    -1.59972511   2.18874138  -0.00028320
H    -7.76831740   2.23074868  -0.00008133

S-65
Coordinates for mOPEFDown:

H -0.87427160  2.19949453  -0.00023201
H -0.89266475 -2.10570225  -0.00014199
H -7.78671116 -2.08264416  -0.00000331

C  1.29832562  1.24064288  -0.74938386
C -0.08463436  1.24407345  -0.87096138
C -0.80650265  0.03244769  -0.93978835
C -0.09077606 -1.18338057  -0.88168603
C  1.29215817  -1.18802012 -0.75993354
C  2.01210374  0.0241662  -0.69179388
C -2.22414284  0.03650855  -1.06542005
C -3.43778422  0.03982719  -1.17361752
C  3.42921413  0.02004062  -0.56748572
C  4.64143610  0.01636524  -0.46145893
C -4.85697889  0.04329045  -1.29945520
C -5.57599489 -1.16700798  -1.38643040
C -5.57421024  1.25687643  -1.34260747
C  -6.96174152 -1.15715590  -1.51389554
C  -6.96011223  1.25347173  -1.46997321
C  -7.67560026  0.04997808  -1.56147238
C  6.05326051  0.01201739  -0.33851431
C  6.80798998  1.19931593  -0.27354056
C  6.80061627  -1.17990659 -0.27298802
C  8.18898710  1.21959346  -0.15372666
C  8.18145610 -1.20867888  -0.15311611
C  8.87493150  0.00333175  -0.09364558
H  9.95586350  0.00000000  -0.00000000
H  1.84310829  2.17758829  -0.69743024
H  1.83217134 -2.12813428  -0.71606304
H  -0.63455541 -2.12093554  -0.93310611
H  -0.62365092  2.18478607  -0.91418859
H  -7.49634334  2.19841052  -1.49858170
H  -7.49919854 -2.09970611  -1.57699813
H  -5.03384831  2.19562110  -1.27717558
H  -5.03685862 -2.10821831  -1.35529326
C  -9.17566740  0.05338738  -1.69097286
H  -9.51564958 -0.81859787  -2.25433928
H  -9.51593391  0.95848851  -2.19915584
S  -9.95586350 -0.00000000  0.00000000
F  6.14311103  2.37475724  -0.33184358
H  8.69127016 -2.16426784  -0.10826667
Coordinates for OPEFDown:
C  1.03974728  -1.17701102  -0.00041922
C  -0.34847727  -1.17064092  -0.00040972
C  -1.06539676   0.04606464   0.00007620
C  -0.33827300  1.25670046   0.00055379
C   1.04995308  1.25143436   0.00054476
C   1.76472634   0.03418859   0.00058611
C  -2.48828635   0.05200772   0.0008549
C  -3.70701099   0.05776556   0.00009188
C   3.18719985   0.02822621   0.00049311
C   4.40408964   0.02299889   0.0004115
C  -5.13055349   0.06251232   0.0008166
C  -5.85087689  1.27460880   0.00051261
C  -5.85991374  -1.14506234  -0.00035562
C  -7.24216287  1.28039244   0.00049886
C  -7.25017870  -1.1400988   -0.00035768
C  -7.95732776   0.07311765   0.00006872
C   5.82122258   0.01690638   0.00029791
C   6.57004016  -1.17591462  -0.00045292
C   6.58030696   1.20321210   0.00050204
C   7.95602887  -1.20641276  -0.00047371
C   7.96650355   1.22175951   0.00050115
C   8.65362828   0.00468499   0.00008051
H   8.46659143  -2.16266393  -0.00059812
H   8.48530742   2.17356544   0.00088025
H   9.73860019  -0.0000000   -0.00000001
S  -9.73860019   0.0000000    0.00000000
H   1.58020599  -2.11790551  -0.00079474
H   1.59831575   2.18774909   0.00091428
F   5.91437672   2.37959146   0.00077812
H  -0.87757203   2.19824521   0.00092960
H  -0.89566863  -2.10761445  -0.00077952
H  -7.78847302  -2.08333893  -0.00068419
H  -7.76887806   2.23017474   0.00082319
H  -5.32444705  -2.08888143  -0.00068640
H  -5.30880754   2.21476335   0.00085377
F   5.89398998  -2.34647230  -0.00091839

Coordinates for mOPEFUp:

S-67
Coordinates for OPEFUp:

C 1.03749124 -1.17570897 0.00010405
| Atoms | Coordinates             |   |
|-------|-------------------------|---|
| C     | 1.41490616, 0.01580271, -0.00003549 |
| C     | -2.83768798, -0.03066176, -0.00002491 |
| C     | -4.05577082, -0.04248970, -0.00002106 |
| C     | 2.83769308, 0.03088500, -0.00004380 |
| C     | 4.05577422, 0.04255491, -0.00004481 |
| C     | -5.47821647, -0.05022790, -0.00001902 |
| C     | -6.18921118, -1.26759601, -0.00124847 |
| H     | -5.67239321, 2.21968116, -0.00221779 |
| C     | -7.58285506, 1.12155979, 0.00118668 |
| H     | -5.69340592, 2.11791719, 0.00218216 |
| C     | -8.32825799, -0.06400785, -0.00001012 |
| C     | 5.47822897, 0.05016113, 0.00000300 |
| C     | 6.18925487, 1.26750647, 0.00125744 |
| C     | 6.20072821, -1.16090946, -0.00120806 |
| C     | 7.57242569, 1.24254165, 0.00126811 |
| H     | 5.67245281, 2.2196277, 0.00221077 |
| C     | 7.58280500, -1.12168016, -0.00113276 |
| H     | 5.69336961, -2.11800737, -0.00219320 |
| C     | 8.32822915, 0.06386063, 0.00009002 |
| S     | -10.09792888, -0.00013376, 0.00006889 |
| H     | 1.21313420, 2.16701923, 0.00213180 |
| H     | 1.26082636, -2.1393242, -0.00220435 |
| S     | 10.09787103, -0.00013376, 0.00006889 |
| H     | -1.21311800, -2.16680891, -0.00219852 |
| H     | -1.26083216, 2.13954356, 0.00213763 |
| F     | -8.23949426, -2.42783528, -0.00240891 |
| F     | -8.26938489, 2.29053646, 0.00237825 |
| F     | 8.23961452, 2.42767630, 0.00248779 |
| F     | 8.26929102, -2.29068021, -0.00230334 |

Coordinates for OPE-OMe:

| Atoms | Coordinates             |   |
|-------|-------------------------|---|
| C     | 1.04600873, 1.17437035, 0.00007800 |
| C     | -0.34242430, 1.16860572, 0.00009100 |
| C     | -1.06002787, -0.04743570, 0.00014700 |
| C     | -0.32205563, -1.25729914, 0.00018500 |
| C     | 1.05637715, -1.25123051, 0.00017000 |
| C     | 1.77391335, -0.03534137, 0.00011700 |
| C     | -2.48319717, -0.05345000, 0.00017700 |
| C     | -3.70195080, -0.05920284, 0.00019500 |
| C     | 3.19745833, -0.02924951, 0.00011000 |
|   |   |   |   |
|---|---|---|---|
| C | 4.41534962 | -0.02390124 | 0.00010300 |
| C | -5.12561514 | -0.06375618 | 0.00014000 |
| C | -5.84661891 | -1.27540462 | -0.00001300 |
| C | -5.85502113 | 1.14386532 | 0.00024200 |
| C | -7.23806945 | -1.28081273 | -0.00005800 |
| H | -5.30494372 | -2.21581629 | -0.00010400 |
| C | -7.24537190 | 1.13924176 | 0.00020200 |
| H | -5.31926263 | 2.08754830 | 0.00036300 |
| C | -7.95292282 | 1.14386532 | 0.00024200 |
| C | 5.84252844 | -0.01752035 | 0.00008200 |
| C | 6.53864700 | 1.20428225 | 0.00007100 |
| C | 6.54959877 | -1.2330930 | 0.00007900 |
| C | 7.93472821 | 1.20059044 | 0.00005000 |
| H | 6.00854822 | 2.14896984 | 0.00009000 |
| C | 7.94560864 | -1.21679324 | 0.00004400 |
| H | 6.02802112 | -2.18242867 | 0.00009200 |
| C | 8.65449327 | -0.00489391 | 0.00004200 |
| H | 9.73472826 | 0.00000000 | 0.00000000 |
| S | -9.73472826 | 0.00000000 | 0.00000000 |
| H | 1.58521246 | 2.11606856 | 0.00003400 |
| H | 1.60362548 | -2.18828110 | 0.00019500 |
| H | 10.21090616 | -3.57948714 | 0.00031300 |
| H | -0.87081814 | -2.19929153 | 0.00022500 |
| H | -0.89921088 | 2.10595622 | 0.00005600 |
| H | -7.78340998 | 2.08277750 | 0.00029200 |
| H | -7.76496076 | -2.23056609 | -0.00018700 |
| O | 8.52691045 | 2.43337526 | 0.00008500 |
| O | 8.54881263 | -2.44426287 | 0.00004800 |
| C | 9.94572715 | 2.51786123 | 0.00003000 |
| H | 10.37595105 | 2.05335267 | 0.89644200 |
| H | 10.37584792 | 2.05338325 | -0.89650100 |
| H | 10.17881734 | 3.58333341 | 0.0000500 |
| C | 9.96832603 | -2.51613336 | 0.00017700 |
| H | 10.3944920 | -2.04793590 | -0.89630400 |
| H | 10.39428736 | -2.04773257 | 0.89662600 |

Coordinates for OPPy:

|   |   |   |   |
|---|---|---|---|
| C | 1.57873353 | 1.17690741 | 0.00208431 |
| C | 0.19054152 | 1.17067235 | 0.00206172 |
| C | -0.52617094 | -0.04618916 | -0.00002754 |
| C | 0.20153578 | -1.25650423 | -0.00209189 |
| C | 1.58973146 | -1.25019415 | -0.00206917 |

S-71
References

(1) Valkenier-van Dijk, E. Molecular Conductance: Synthesis, Self-assembly, and Electrical Characterization of Alpha-conjugated Wires and Switches, English, Relation: https://www.rug.nl/ Rights: University of Groningen, Ph.D. Thesis, 2011.

(2) Kovalchuk, A. Dipoles, Conjugation and Molecular Electronics, English, Ph.D. Thesis, University of Groningen, 2018.

(3) Carlotti, M.; Degen, M.; Zhang, Y.; Chiechi, R. C. Pronounced Environmental Effects on Injection Currents in EGaIn Tunneling Junctions Comprising Self-Assembled Monolayers. *J. Phys. Chem. C* **2016**, *120*, 20437–20445.

(4) Weiss, E. A.; Kaufman, G. K.; Kriebel, J. K.; Li, Z.; Schalek, R.; Whitesides, G. M. Si/SiO$_2$-templated Formation of Ultraflat Metal Surfaces on Glass, Polymer, and Solder Supports: Their Use as Substrates for Self-Assembled Monolayers. *Langmuir* **2007**, *23*, 9686–9694.

(5) Qiu, X.; Ivasyshyn, V.; Qiu, L.; Enache, M.; Dong, J.; Rousseva, S.; Portale, G.; Stöhr, M.; Hummelen, J. C.; Chiechi, R. C. Thiol-free self-assembled oligoethylene glycols enable robust air-stable molecular electronics. *Nature Materials* **2020**, *19*, 330–337.

(6) Laboratory of the Facultés Universitaires Notre-Dame de la Paix, L. 2021.

(7) Shirley; D. A. High-Resolution X-Ray Photoemission Spectrum of the Valence Bands of Gold. *Phys. Rev. B* **1972**, *5*, 4709–4714.

(8) Moulder, J.; Stickle, W.; Sobol, P. Handbook of X-Ray Photoelectron Spectroscopy, Perkin-Elmer, Physical Electronics Division. 1993.
(9) Kumar, S.; van Herpt, J. T.; Gengler, R. Y. N.; Feringa, B. L.; Rudolf, P.; Chiechi, R. C. Mixed Monolayers of Spiropyrans Maximize Tunneling Conductance Switching by Photoisomerization at the Molecule–Electrode Interface in EGaIn Junctions. *J. Am. Chem. Soc.* 2016, *138*, 12519–12526.

(10) Munir, A.; ul Haq, T.; Qurashi, A.; ur Rehman, H.; Ul-Hamid, A.; Hussain, I. Ultrasmall Ni/NiO Nanoclusters on Thiol-Functionalized and -Exfoliated Graphene Oxide Nanosheets for Durable Oxygen Evolution Reaction. *2018*, 2, 363–371.

(11) Kumar, S.; Soni, S.; Danowski, W.; van Beek, C. L. F.; Feringa, B. L.; Rudolf, P.; Chiechi, R. C. Correlating the Influence of Disulfides in Monolayers across Photoelectron Spectroscopy Wettability and Tunneling Charge-Transport. *Journal of the American Chemical Society* 2020, *142*, 15075–15083.

(12) Carlotti, M.; Soni, S.; Kumar, S.; Ai, Y.; Sauter, E.; Zharnikov, M.; Chiechi, R. C. Two-Terminal Molecular Memory Through Reversible Switching of Quantum Interference Features in Tunneling Junctions. *Angew. Chem., Int. Ed.* 2018, *57*, 15681–15685.

(13) Antonova, I. V.; Kurkina, I. I.; Gutakovskii, A. K.; Kotin, I. A.; Ivanov, A. I.; Nebogatikova, N. A.; Soots, R. A.; Smagulova, S. A. Fluorinated graphene suspension for flexible and printed electronics: Flakes, 2D films, and heterostructures. *2019, 164*, 107526.

(14) Krounbi, L.; Enders, A.; Anderton, C. R.; Engelhard, M. H.; Hestrin, R.; Torres-Rojas, D.; Dynes, J. J.; Lehmann, J. Sequential Ammonia and Carbon Dioxide Adsorption on Pyrolyzed Biomass to Recover Waste Stream Nutrients. *2020*, 8, 7121–7131.
(15) Ma, Y.; Yang, H.; Guo, J.; Sathe, C.; Agui, A.; Nordgren, J. Structural and electronic properties of low dielectric constant fluorinated amorphous carbon films. 1998, 72, 3353–3355.

(16) Carlotti, M.; Kovalchuk, A.; Wächter, T.; Qiu, X.; Zharnikov, M.; Chiechi, R. C. Conformation-Driven Quantum Interference Effects Mediated by Through-Space Conjugation in Self-Assembled Monolayers. Nat. Commun. 2016, 7, 13904.

(17) Hellgren, N.; Haasch, R. T.; Schmidt, S.; Hultman, L.; Petrov, I. Interpretation of X-ray photoelectron spectra of carbon-nitride thin films: New insights from in situ XPS. Carbon 2016, 108, 242–252.

(18) Boucly, A.; Rochet, F.; Arnoux, Q.; Gallet, J.-J.; Bournel, F.; Tissot, H.; Marry, V.; Dubois, E.; Michot, L. Soft X-ray Heterogeneous Radiolysis of Pyridine in the Presence of Hydrated Strontium-Hydroxyhectorite and its Monitoring by Near-Ambient Pressure Photoelectron Spectroscopy. Scientific Reports 2018, 8, DOI: 10.1038/s41598-018-24329-8.

(19) Rani, J. R.; Lim, J.; Oh, J.; Kim, D.; Lee, D.; Kim, J.-W.; Shin, H. S.; Kim, J. H.; Jun, S. C. Substrate and buffer layer effect on the structural and optical properties of graphene oxide thin films. RSC Advances 2013, 3, 5926.

(20) Ivashenko, O.; Logtenberg, H.; Areephong, J.; Coleman, A. C.; Wesenhagen, P. V.; Geertsema, E. M.; Heureux, N.; Feringa, B. L.; Rudolf, P.; Browne, W. R. Remarkable Stability of High Energy Conformers in Self-Assembled Monolayers of a Bistable Electro- and Phototwitchable Overcrowded Alkene. The Journal of Physical Chemistry C 2011, 115, 22965–22975.
Enhancing lithium-sulphur battery performance by strongly binding the discharge products on amino-functionalized reduced graphene oxide. *Nature Communications* **2014**, *5*, DOI: 10.1038/ncomms6002.

Fabrication of pH-sensitive graphene oxide–drug supramolecular hydrogels as controlled release systems. *Journal of Materials Chemistry* **2012**, *22*, 24856.

The Route to Functional Graphene Oxide. *ChemPhysChem* **2010**, *11*, 2131–2139.

The characterization of Co-nanoparticles supported on graphene. *RSC Advances* **2015**, *5*, 75600–75606.

High Resolution X-Ray Photoelectron Spectroscopy Measurements of Octadecanethiol Self-Assembled Monolayers on Au(111). *Langmuir* **1998**, *14*, 2092–2096.

UV/Vis and NIR Light-Responsive Spiropyran Self-Assembled Monolayers. *Langmuir* **2013**, *29*, 4290–4297.

Spectroscopic characterization of thiol-derived self-assembling monolayers. *Journal of Physics: Condensed Matter* **2001**, *13*, 11333–11365.
(28) Rodriguez-Douton, M. J.; Mannini, M.; Armelao, L.; Barra, A.-L.; Tancini, E.; Sessoli, R.; Cornia, A. One-step covalent grafting of Fe4single-molecule magnet monolayers on gold. *Chem. Commun.* **2011**, *47*, 1467–1469.

(29) Hamoudi, H.; Esaulov, V. A. Self-assembly of α, ω-dithiols on surfaces and metal dithiol heterostructures. *Annalen der Physik* **2016**, *528*, 242–263.

(30) Simeone, F. C.; Yoon, H. J.; Thuo, M. M.; Barber, J. R.; Smith, B.; Whitesides, G. M. Defining the Value of Injection Current and Effective Electrical Contact Area for EGaIn-Based Molecular Tunneling Junctions. *J. Am. Chem. Soc.* **2013**, *135*, 18131–18144.

(31) Batra, A.; Meisner, J. S.; Darancet, P.; Chen, Q.; Steigerwald, M. L.; Nuckolls, C.; Venkataraman, L. Molecular Diodes Enabled by Quantum Interference. *Faraday Discuss.* **2014**, *174*, 79–89.

(32) Vilan; A. Revealing Tunnelling Details by Normalized Differential Conductance Analysis of Transport Across Molecular Junctions. *Phys. Chem. Chem. Phys.* **2017**, *19*, 27166–27172.

(33) Zhang, Y.; Soni, S.; Krijger, T. L.; Gordiichuk, P.; Qiu, X.; Ye, G.; Jonkman, H. T.; Herrmann, A.; Zojer, K.; Zojer, E.;chiechi, R. C. Tunneling Probability Increases With Distance in Junctions Comprising Self-Assembled Monolayers of Oligothiophenes. *J. Am. Chem. Soc.* **2018**, *140*, 15048–15055.

(34) Bâldea, I. Ambipolar Transition Voltage Spectroscopy: Analytical Results and Experimental Agreement. *Phys. Rev. B* **2012**, *85*, 035442.
(35) Xie, Z.; Bâldea, I.; Smith, C. E.; Wu, Y.; Frisbie, C. D. Experimental and Theoretical Analysis of Nanotransport in Oligophenylene Dithiol Junctions as a Function of Molecular Length and Contact Work Function. *ACS Nano* 2015, 9, 8022–8036.

(36) Xie, Z.; Bâldea, I.; Oram, S.; Smith, C. E.; Frisbie, C. D. Effect of Heteroatom Substitution on Transport in Alkanedithiol-Based Molecular Tunnel Junctions: Evidence for Universal Behavior. *ACS Nano* 2016, 11, 569–578.

(37) Weiss, E. A.; Chiechi, R. C.; Kaufman, G. K.; Kriebel, J. K.; Li, Z.; Duati, M.; Rampi, M. A.; Whitesides, G. M. Influence of Defects on the Electrical Characteristics of Mercury-Drop Junctions: Self-Assembled Monolayers of N-Alkanethiolates on Rough and Smooth Silver. *J. Am. Chem. Soc.* 2007, 129, 4336–4349.

(38) Zhang, Y.; Ye, G.; Soni, S.; Qiu, X.; Krijger, T. L.; Jonkman, H. T.; Carlotti, M.; Sauter, E.; Zharnikov, M.; Chiechi, R. C. Controlling Destructive Quantum Interference in Tunneling Junctions Comprising Self-Assembled Monolayers via Bond Topology and Functional Groups. *Chem. Sci.* 2018, 9, 4414–4423.

(39) Carlotti, M.; Soni, S.; Qiu, X.; Sauter, E.; Zharnikov, M.; Chiechi, R. C. Systematic Experimental Study of Quantum Interference Effects in Anthraquinoid Molecular Wires. *Nanoscale Advances* 2019, 1, 2018–2028.

(40) Soni, S.; Ye, G.; Zheng, J.; Zhang, Y.; Asyuda, A.; Zharnikov, M.; Hong, W.; Chiechi, R. C. Understanding the Role of Parallel Pathways via in-Situ Switching of Quantum Interference in Molecular Tunneling Junctions. *Angew. Chem., Int. Ed.* 2020, 59, 14308–14312.
(41) Ai, Y.; Kovalchuk, A.; Qiu, X.; Zhang, Y.; Kumar, S.; Wang, X.; Kühnel, M.; Nørgaard, K.; Chiechi, R. C. In-Place Modulation of Rectification in Tunneling Junctions Comprising Self-Assembled Monolayers. *Nano Lett.* **2018**, *18*, 7552–7559.

(42) Asyuda, A.; Wan, X.; Zharnikov, M. Binary Aromatic Self-Assembled Monolayers: Electrostatic Properties and Charge Tunneling Rates Across the Molecular Framework. *Phys. Chem. Chem. Phys.* **2020**, *22*, 10957–10967.

(43) Yoon, H. J.; Liao, K.-C.; Lockett, M. R.; Kwok, S. W.; Baghbazadeh, M.; Whitesides, G. M. Rectification in Tunneling Junctions: 2,2’-Bipyridyl-Terminated N-Alkanethiolates. *J. Am. Chem. Soc.* **2014**, *136*, 17155–17162.

(44) Cho, S. J.; Kong, G. D.; Park, S.; Park, J.; Byeon, S. E.; Kim, T.; Yoon, H. J. Molecularly Controlled Stark Effect Induces Significant Rectification in Polycyclic-Aromatic-Hydrocarbon-Terminated N-Alkanethiolates. *Nano Lett.* **2018**, *19*, 545–553.

(45) Qiu, L.; Zhang, Y.; Krijger, T. L.; Qiu, X.; van’t Hof, P.; Hummelen, J. C.; Chiechi, R. C. Rectification of Current Responds to Incorporation of Fullerenes Into Mixed-Monolayers of Alkanethiolates in Tunneling Junctions. *Chem. Sci.* **2017**, *8*, 2365–2372.

(46) Rohatgi, A. Webplotdigitizer: Version 4.4, 2020.

(47) Han, Y.; Maglione, M. S.; Cabanes, V. D.; Casado-Montenegro, J.; Yu, X.; Karuppannan, S. K.; Zhang, Z.; Crivillers, N.; Mas-Torrent, M.; Rovira, C.; Cornil, J.; Veciana, J.; Nijhuis, C. A. Reversal of the Direction of Rectification Induced by Fermi Level Pinning at MoleculeElectrode Interfaces in Redox-Active Tunneling Junctions. *ACS Appl. Mater. Interfaces* **2020**, *12*, 55044–55055.

S-79
(48) Yuan, L.; Wang, L.; Garrigues, A. R.; Jiang, L.; Annadata, H. V.; Antonana, M. A.; Barco, E.; Nijhuis, C. A. Transition From Direct to Inverted Charge Transport Marcus Regions in Molecular Junctions via Molecular Orbital Gating. Nat. Nanotechnol. 2018, 13, 322–329.

(49) Frisch, M. J. et al. Gaussian09 Revision E.01, Gaussian Inc. Wallingford CT 2009, 2009.

(50) Herrmann, C.; Gross, L.; Steenbock, T.; Deffner, M.; Voigt, B. A.; Solomon, G. C. ARTAIOS - A Transport Code for Postprocessing Quantum Chemical Electronic Structure Calculations, Available From https://www.chemie.uni-hamburg.de/ac/herrmann/software/index.html, 2020.

(51) Humphrey, W.; Dalke, A.; Schulten, K. VMD – Visual Molecular Dynamics. J. Mol. Graphics 1996, 14, 33–38.

(52) Community, B. O. Blender - a 3D modelling and rendering package; Blender Foundation, Stichting Blender Foundation, Amsterdam, 2018.

(53) Herrmann, C.; Solomon, G. C.; Subotnik, J. E.; Mujica, V.; Ratner, M. A. Ghost Transmission: How Large Basis Sets Can Make Electron Transport Calculations Worse. J. Chem. Phys. 2010, 132, 024103.