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1 **Highly Non-Linear Transport Across Single-Molecule Junctions via Destructive Quantum**
2 **Interference**

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13 **To rival the performance of modern integrated circuits, single-molecule devices must**
14 **be designed to exhibit extremely non-linear current-voltage (I-V) characteristics¹⁻⁴. A**
15 **common approach is to design molecular backbones where destructive quantum interference**
16 **(QI) between the highest occupied molecular orbital (HOMO) and the lowest unoccupied**
17 **molecular orbital (LUMO) produces a non-linear energy-dependent tunnelling probability**
18 **near the electrode Fermi energy (E_F)⁵⁻⁸. However, tuning such systems is not**
19 **straightforward, as aligning the frontier orbitals to E_F is hard to control⁹. Here, we instead**
20 **create a molecular system where constructive QI between the HOMO and LUMO is**
21 **suppressed and destructive QI between the HOMO and strongly-coupled occupied orbitals**
22 **is enhanced. We employ a series of fluorene oligomers containing a central**
23 **benzothiadiazole¹⁰ (BT) unit to demonstrate that this strategy can be used to create highly**
24 **non-linear single-molecule circuits. Notably, we are able to reproducibly modulate the**
25 **conductance of a six-nanometer molecule by a factor of more than 10^4 .**

26 Conduction in single-molecule circuits falls within the coherent electron transport regime
27 when the device size is comparable to the electronic phase coherence length¹¹. In this regime,
28 delocalized MOs mediate charge transport, giving rise to non-linear Lorentzian resonances in the

29 transmission spectrum. The energy-dependent transmission amplitude for a single MO, j , is
30 described by the Breit-Wigner formula^{12,13},

$$31 \quad t_j(E) = e^{i\theta_j} \frac{\gamma_j}{E - \varepsilon_j + i\gamma_j} \quad (1)$$

32 where ε_j is the energy of the MO and γ_j is the coupling of the MO to the leads. The phase factor,
33 θ_j , describes the phase relation of the MO with respect to its overlap with states on either lead. The
34 phase factor typically assumes values of 0 or π ¹⁴.

35 While individual resonances yield non-linear I-V characteristics, additional dynamic range
36 can be gained by suppressing current flow at low bias through destructive QI. QI arises due to
37 phase differences among the transmission amplitudes of multiple MOs^{15,16}. In Fig. 1, we present
38 two didactic examples of how destructive QI between two MOs, j and k , can be achieved at E_F .
39 Two MOs with the same phase ($\theta_j - \theta_k \approx 0$) and coupling ($\gamma_j \approx \gamma_k$) will exhibit destructive QI
40 at E_F if their energies straddle E_F (Fig. 1a). Alternatively, two MOs of opposite phase ($\theta_j - \theta_k \approx$
41 π) that are both lower (or equivalently both higher) in energy than E_F (Fig. 1b) will exhibit
42 destructive QI at E_F , provided the level farther from E_F is better coupled to the leads. Notably, the
43 latter type of destructive QI produces a steeper transmission function (Fig. 1c).

44 A common strategy to suppress low-bias current flow is to design molecular backbones
45 where the HOMO and LUMO exhibit destructive QI near E_F ^{5-7,17}, analogous to Fig. 1a. However,
46 to effectively suppress transmission at E_F and achieve a large non-linearity in the transmission
47 spectrum, this strategy requires good alignment between E_F and the transmission minimum, which
48 can be difficult to achieve⁹. Moreover, this type of destructive QI is often implemented in small
49 molecules¹⁸ where through-bond tunnelling via σ orbitals is significant¹⁹. Therefore, transmission
50 at E_F is not adequately suppressed, and the dynamic range of such devices remains poor. In long
51 molecular wires, where σ transmission is negligible, the small energy level spacing between MOs

52 enables orbitals beyond the HOMO and LUMO to influence transmission at E_F ^{16,20}. Successive
53 MOs of opposite phase (e.g., HOMO-1 and HOMO) can produce strong destructive QI at E_F ,
54 analogous to Fig. 1b. However, such destructive QI is typically accompanied by commensurate
55 constructive QI between the HOMO and LUMO, which produces relatively flat transmission near
56 E_F ^{21,22}. We demonstrate that constructive QI between the HOMO and LUMO can be suppressed
57 and destructive QI between occupied Mos enhanced through molecular design using a series of
58 three molecular wires comprising a central para-substituted BT unit flanked by fluorene arms on
59 either side.

60 Fig. 2a shows the molecular structures of the systems investigated. Synthetic details are
61 provided in Extended Data Fig. 1 and the Supplementary Information. The electron withdrawing
62 BT unit localizes the LUMO and dictates its energy^{10,23}. We use density functional theory (DFT)
63 to calculate the MOs of **1–3** (see Methods). Figure 2b shows the LUMO is localized on the central
64 BT unit, while the HOMO and HOMO-1 are delocalized across the backbone. The HOMO and
65 HOMO-1 have opposite parity, which results in their having opposite phases of transmission. The
66 DFT-calculated energy level diagrams (Fig. 2c) show near-uniform HOMO-LUMO gaps (~ 2.6
67 eV) across all three oligomers, in agreement with cyclic voltammetry data (Extended Data Fig. 2).
68 Although there is a small shift in the oxidation peak, the reduction peak does not shift with length,
69 confirming that the energy of the localized LUMO is dictated by the BT unit. The UV-Vis spectra
70 (Fig. 2d) also show that the optical gap (~ 2.5 eV) does not vary with length, as indicated by the
71 band at ~ 425 nm. The intensity of this band decreases with molecular length, suggesting reduced
72 orbital overlap between the HOMO and LUMO as molecular length increases. The shorter
73 wavelength band (~ 350 nm), which is characteristic of the oligofluorene unit¹⁰, experiences a red
74 shift as a function of molecular length, indicating an increased delocalization of the HOMO across

75 the backbone from **1–3**. Thus, we expect transport in **1–3** will be coherent, mediated by the
76 delocalized HOMO while the LUMO is effectively absent.

77 To measure the conductance of **1–3**, we use the scanning tunnelling microscope-based
78 break-junction (STM-BJ) technique as described in the Methods section. We collect 2,600 STM-
79 BJ traces and compile the traces into logarithmically-binned one-dimensional (1D) histograms
80 (Fig. 3a). The most probable conductance values for each oligomer are determined by fitting each
81 1D histogram with a Gaussian. The conductance values, G , are then plotted against molecular
82 length, L (S-to-S distance from DFT optimized structures), on a semi-logarithmic scale (Fig. 3a
83 inset) and fit with an exponential, $G \sim e^{-\beta L}$. We obtain a decay constant, β , of 0.19 \AA^{-1} , which is
84 comparable to the decay constant observed for polyene²⁴ and other molecular wires^{25,26} and
85 suggests transport is coherent across all three oligomers (see Supplementary Fig. 1 for details).
86 Since the applied bias (1.25 V) is smaller than the optical (Fig. 2d) and electrochemical gaps (\sim
87 2.6 V) (Extended Data Fig. 2), transport is likely still in the off-resonant regime.

88 To confirm that junctions are formed by bridging the entire molecule between the two
89 electrodes, we construct two-dimensional (2D) conductance-versus-displacement histograms. The
90 2D histogram for **3** is shown in Fig. 3b, with an individual conductance trace inset (see
91 Supplementary Fig. 2 for 2D histograms for **1** and **2**). The observed junction elongation, ~ 6 nm,
92 is consistent with the length of **3**. While the length of **3** approaches the length at which hopping
93 transport becomes relevant²⁷, coherent transport has been observed in other systems of similar
94 length^{28,29}. Additionally, temperature-dependent measurements (Supplementary Fig. 3) show that
95 conductance does not vary with temperature, consistent with a coherent transport mechanism.

96 Next, we measure the I-V characteristics of **1–3** (see Methods). Fig. 3c shows a 2D current
97 versus time histogram for **3** (see Extended Data Fig. 3 for corresponding 2D histograms for **1** and

98 **2**). For each oligomer, traces in which the current exceeds 5×10^{-8} A at the maximum applied bias
99 (± 2.0 V) are selected ($\sim 20\%$ of traces). The cyclic I-V histograms show that junctions are stable
100 for more than 1.7 s at room temperature in solution and do not rupture as the bias is repeatedly
101 swept between ± 2 V at a rate of 20 V s^{-1} . The average I-V curves for **1–3** are all highly non-linear
102 (Fig. 3d). (See Supplementary Fig. 4 for average I-V histograms for **1–3**.) The curve for **1** is
103 uniformly steep on a logarithmic scale, whereas the curves for **2** and **3** manifest two distinct
104 regions. At low bias, the I-V curves for **2** and **3** are linear because the through-molecule current is
105 lower than the through-solvent current (Supplementary Fig. 5). Once the molecular junction
106 current exceeds the solvent current, the I-V curves for **2** and **3** increase rapidly as the bias
107 approaches ± 2 V, indicating that we may be approaching, but have not yet reached, the resonant
108 transport regime. This is further corroborated by the numerical differential conductance curves,
109 which do not show a peak within the bias range (Supplementary Fig. 6).

110 To highlight the stability of the junctions at high bias and the nonlinearity of transmission,
111 we modify the STM-BJ measurement to enable rapid switching of the applied bias while holding
112 the molecule in the junction (see Methods). Fig. 3e shows a 2D current-time histogram for bias
113 switching measurements of **3** without data selection. (See Extended Data Fig. 4 for sample traces
114 and Extended Data Fig. 5 for analogous histograms for **1** and **2**.) We observe high junction
115 formation probabilities and large conductance ratios in the bias switching measurements of all
116 three oligomers. The junction formation probabilities for **1**, **2** and **3** are 93%, 99% and 100%,
117 respectively (Supplementary Fig, 7). In each of the six cycles, the molecule (**1–3**) is held at high
118 bias for 12.5 ms without the junction rupturing, and in many traces, the current exceeds 10^{-7} A.
119 The stability of the junctions at high bias indicates no irreversible changes occur, as might be
120 expected when entering the resonant transport regime³⁰ or charging of the molecule in the hopping

121 regime³¹. In many of the traces in Fig. 3e, the current at high bias (2.0 V) is more than 30,000
122 times larger than the current at low bias (0.5 V). Since the current at low bias is through-solvent
123 rather than through-molecule current, we stress that 30,000 represents the lower bound of the
124 enhancement factor and underscores the extreme nonlinearity of circuits formed with **3**.

125 We calculate transmission functions for junctions created with **1–3** (Fig. 4a) to elucidate
126 the relationship between destructive QI and the non-linear I-V characteristics observed
127 experimentally (see Methods for calculation details). The transmission functions show that, from
128 **1** to **3**, the HOMO resonances shift closer to E_F while the LUMO resonances shift farther from E_F .
129 Thus, the transmission functions qualitatively agree with the optical and electrochemical data,
130 insofar as the calculated HOMO-LUMO gap (~ 1.7 eV) does not vary significantly with molecular
131 length. However, we note that these transmission functions do not capture the magnitude of the
132 HOMO-LUMO gap accurately, due to errors inherent to DFT as discussed in Supplementary
133 Information Section 4. Furthermore, despite the large applied bias, calculations including an
134 applied electric field do not indicate a sizable Stark effect (see Supplementary Fig. 9).

135 Importantly, the DFT calculations demonstrate the LUMO is effectively decoupled in **1–3**.
136 Fig. 4b shows that for all three oligomers, the HOMO and HOMO-1 are both more than an order
137 of magnitude better coupled than the LUMO. In other highly conjugated systems, where the
138 coupling of the HOMO and LUMO are similar, higher transmission is observed at low bias²² due
139 to constructive QI. In Fig. 4c, we overlay the HOMO resonance for **3** with a single-level model to
140 show that, at E_F , DFT-based transmission, which accounts for all MOs, is 350 times lower than
141 transmission assuming HOMO-dominated transport. Since the LUMO is decoupled, destructive
142 QI among multiple pairs of resonances of opposite phase, e.g. HOMO–HOMO-1, HOMO-1–
143 HOMO-2, etc., suppresses transmission near E_F . (See Extended Data Fig. 6 for visualization of

144 destructive QI contributions.) The inset to Fig. 4c shows that such destructive QI increases with
145 molecular length. To experimentally confirm that the LUMO does not contribute to transport
146 within the applied bias range, we perform two-electrode electrochemical gating measurements of
147 **1** (see Methods). These measurements demonstrate conductance is mediated by the HOMO
148 (Supplementary Fig. 8) and the transmission function is quite asymmetric. By contrast, the LUMO
149 is not decoupled in a control molecule lacking BT (Extended Data Fig. 7). Furthermore, two-
150 electrode gating measurements of the control molecule suggest a more symmetric transmission
151 function (Extended Data Fig. 8).

152 In conclusion, we have shown that constructive QI between the HOMO and LUMO can be
153 suppressed in long molecular wires by decoupling the LUMO through chemical design. As a result,
154 destructive QI between strongly-coupled occupied MOs of opposite parity gives rise to highly non-
155 linear current-voltage characteristics. Notably, destructive QI increases as a function of molecular
156 length because the energy level spacing between MOs decreases. Using this novel design strategy,
157 we are able to modulate the conductance of a six-nanometer molecule by a factor of over 10^4 ,
158 suggesting a promising approach to developing functional, room temperature molecular
159 electronics.

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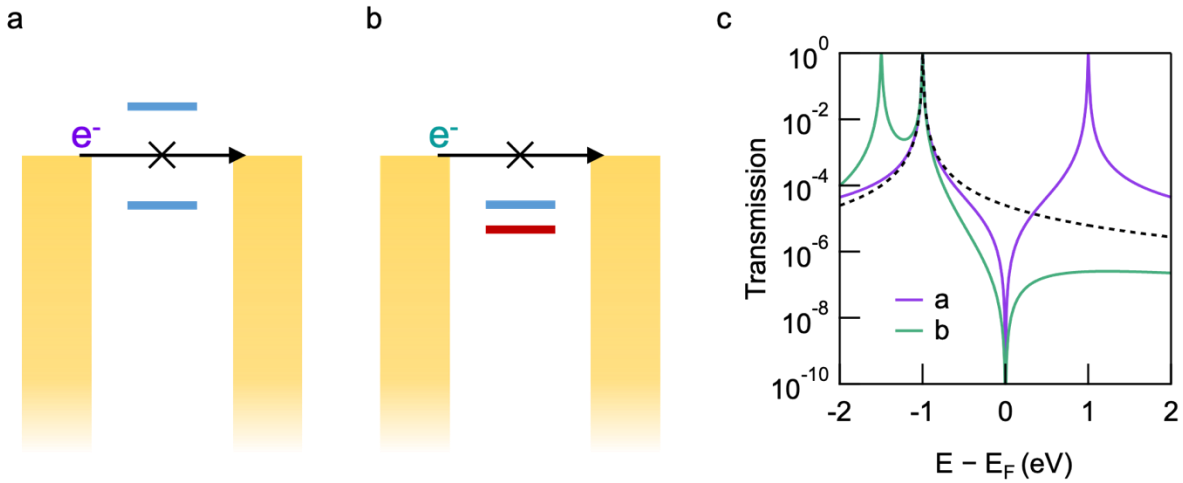
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234 contributions from all authors. L.V. and P.J.S. oversaw the project.

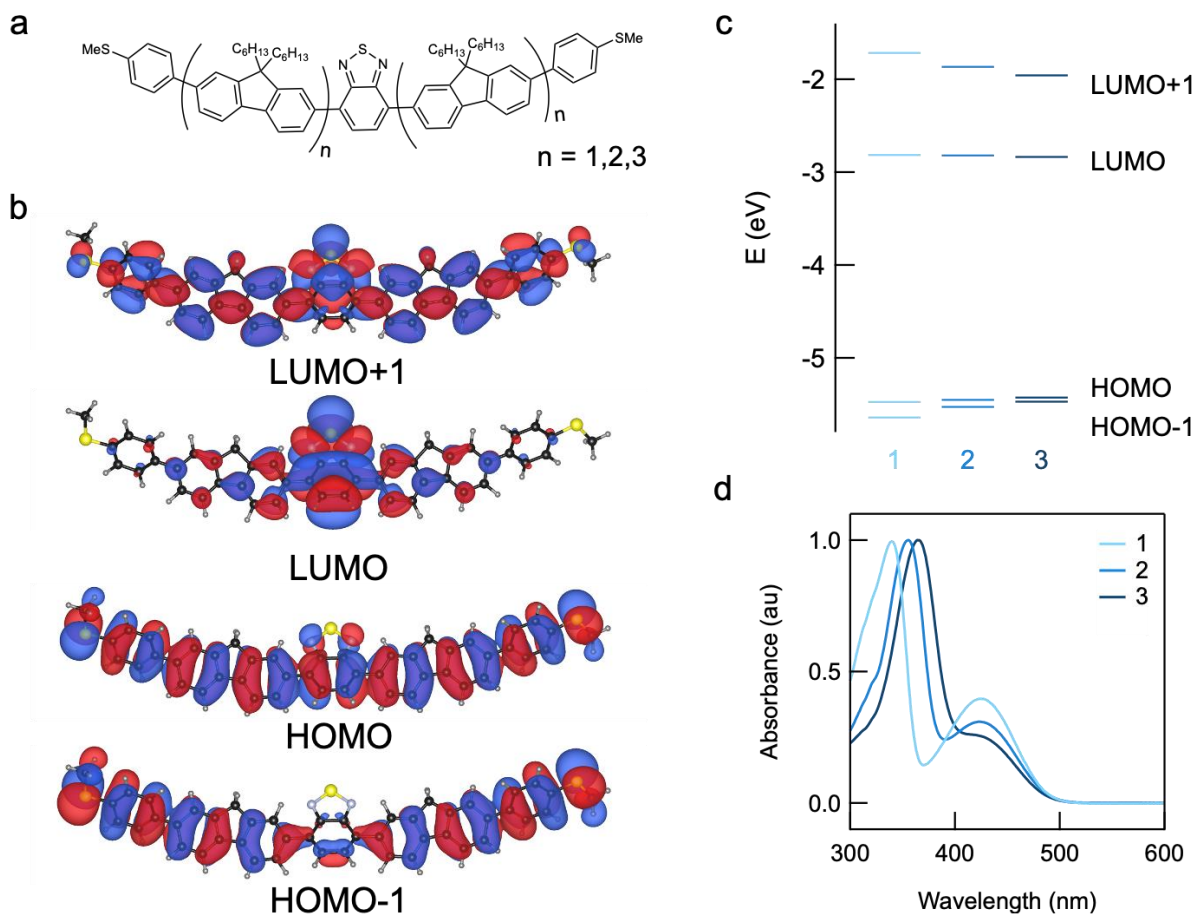
235 **Competing Financial Interests.** Authors declare no competing financial interests.

236 **Additional Information.** Supplementary information is available in the online version of the
 237 paper. Reprints and permission information is available online at www.nature.com/reprints.
 238 Correspondence and requests for materials should be addressed to L.V. and P.J.S.
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240

241 **Fig. 1. Destructive QI between two MOs at the Fermi energy, E_F .** a,b) Schematic illustrating
 242 QI with two levels. The MO phase for each level (θ_j) is indicated by blue ($\theta_j = 0$) vs. red ($\theta_j = \pi$).
 243 c) Transmission functions corresponding to (a) and (b) calculated as $T(E) = |t_1 + t_2|^2$. Note in (a)
 244 the two levels straddle E_F ($\epsilon_{1(2)} = \pm\epsilon_0$) and are equally coupled to the electrodes ($\gamma_1 = \gamma_2$), while
 245 in (b) the lower energy level ($\epsilon_2 = 1.5\epsilon_0$, $\gamma_2 = 1.5\gamma_0$) is better coupled than the higher energy
 246 level ($\epsilon_1 = \epsilon_0$, $\gamma_1 = \gamma_0$). A single-level model, calculated as $T(E) = |t_0|^2$ with $\epsilon_0 = -1$ eV and $\gamma_0 =$
 247 0.005 eV, is presented for comparison (dashed).



248

249 **Fig. 2. Structure and Electronic Properties of Molecules 1–3.** a) Molecular structure of 1–3.

250 The compounds 1, 2 and 3 correspond to the number of fluorene units, n . b) MOs of 1 calculated

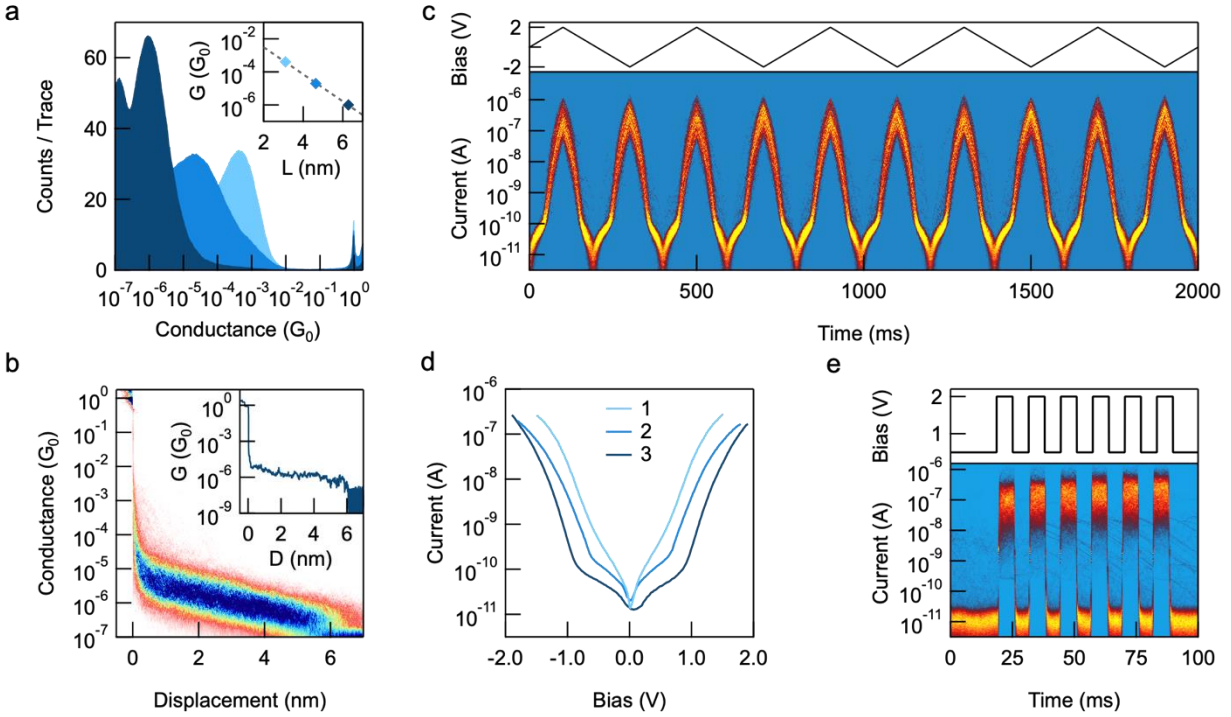
251 using DFT with B3LYP functional. Note the HOMO and HOMO-1 have opposite parity,

252 indicating their MO phase factors will be different. White, black, yellow, and light blue atoms

253 represent H, C, S, and N, respectively. c) Energy level diagram for 1–3 constructed from DFT

254 calculations. The energy gap between HOMO and HOMO-1 decreases with increasing molecular

255 length. d) Normalised absorption spectra for 1–3 recorded in dichloromethane (10^{-5} M).



256

257 **Fig. 3. Conductance and Current-Voltage (I-V) Measurements of 1–3.** a) Logarithmically-

258 binned 1D conductance histograms for **1**, **2** and **3**. Histograms are compiled from 2,600 STM-BJ

259 traces collected using 1.25 V applied bias. The peak at $10^{-7} G_0$ corresponds to the instrument noise

260 floor. Inset: Conductance versus length for **1–3**. Fit line: $G \sim e^{-\beta L}$, where G is conductance, L is the

261 DFT-based molecular S-S length, and $\beta = 0.19 \text{ \AA}^{-1}$. b) 2D conductance-displacement histogram

262 and sample trace (inset) for **3**. Histogram is compiled from a subset of $\sim 1,000$ traces that evidence

263 a plateau at $1 G_0$. Counts increase from red to blue. c) Cyclic I-V measurements of **3**. Top: Bias

264 applied across the junction with a $100 \text{ k}\Omega$ resistor in series while tip-substrate gap is held constant.

265 Bottom: 2D current-time histogram constructed from 282/1,000 traces (see Extended Data Fig. 3

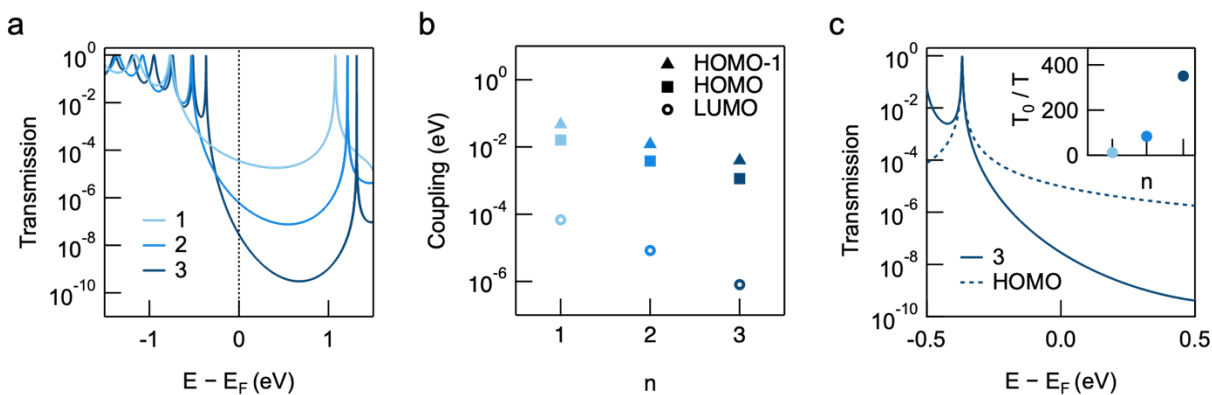
266 for cyclic I-V histograms for **1** and **2**). d) Average I-V curves for **1–3** generated by fitting cyclic

267 I-V histograms (see Supplementary Fig. 4 for corresponding average I-V histograms). e) Bias

268 switching measurements of **3**. Top: Bias applied across the junction with a $100 \text{ k}\Omega$ resistor in series

269 while tip-substrate gap is held constant. Bottom: 2D current-time histogram compiled from 1,046

270 traces measured consecutively (54 traces where no gap formed during the hold were excluded).
271 Counts increase from dark red to yellow in (c) and (e).



272
273 **Fig. 4. Transmission Function Calculations for Au-Molecule-Au Junctions.** **a)** Transmission
274 functions for molecular junctions of **1–3** calculated using DFT. **b)** Coupling between MO and leads
275 for **1–3**. Coupling values extracted from DFT-based transmission calculations. **c)** Transmission
276 function of **3** (solid line) overlaid with a single-level model of the HOMO (dashed). Inset: Ratio
277 of transmission at E_F for single-level model of HOMO, T_0 , to DFT-based transmission, T , for **1–**
278 **3**. The increase in T_0/T indicates destructive QI increases with molecular length. See Extended
279 Data Fig. 9 for analogous overlays for **1** and **2**.

280 Methods

281 **Conductance Measurements.** The STM-BJ technique has been described previously^{32,33}. In brief,
282 we prepare $\sim 30 \mu\text{M}$ solutions of **1**, **2** and **3** in UV-treated 1-bromonaphthalene (see Supplemental
283 Information Section 5 for solvent details). The solution is deposited on an Au-coated steel
284 substrate. An Au tip is then repeatedly brought into contact with and retracted from the substrate.
285 As the tip is retracted, an atomic point contact forms, and subsequently breaks, yielding a
286 nanometer-scale gap. The terminal thiomethyl linkers of **1–3** bind to the tip and substrate, forming
287 an Au-molecule-Au junction. As the tip is retracted further, the junction breaks once the gap is too

288 large for the molecule to bridge. A bias is applied across the tip/sample junction with a 200 k Ω
289 resistor in series with the junction. The current and voltage measured across the junction are
290 recorded as a function of tip displacement to generate conductance ($G = I/V$) versus displacement
291 traces. The conductance of the atomic point contact is roughly 1 G_0 ($G_0 = 2e^2/h$). Plateaus at
292 conductance values lower than 1 G_0 in the conductance versus displacement traces indicate the
293 formation of molecular junctions. For the two-electrode gating experiments³⁴, a coated STM tip
294 and 100 k Ω series resistor are used. Conductance measurements of **1** and **C1** are performed in ~
295 40 μ M solutions of propylene carbonate with added supporting electrolyte (~ 0.1 M TBAPF₆).

296 **Current-Voltage Measurements.** I-V characteristics of **1–3** are measured by withdrawing the tip
297 at a rate of 16 nm s⁻¹ to form a gap between the tip and substrate while applying a bias of 0.1 V.
298 The tip is then held in a fixed position as the bias is ramped continuously at a rate of 20 V s⁻¹ for
299 five cycles (for **1**, the bias was ramped from +1.8 V to -1.8 V, while for **2** and **3** from +2.0 V to -
300 2.0 V). The tip is then further withdrawn at a rate of 16 nm s⁻¹ to rupture the junction. All biases
301 are applied across the junction using a 100 k Ω resistor in series with the junction. Traces are
302 selected where the current exceeds 5×10^{-8} A at the maximum applied bias (i.e. ± 1.8 V for **1** and
303 ± 2.0 V for **2** and **3**), and histograms are constructed from the hold portion of each selected trace.
304 2D current versus time histograms are constructed using logarithmically binned current (57 bins
305 dec⁻¹) and linearly binned time (4000 bins s⁻¹). Average 2D current versus voltage histograms are
306 constructed from the hold portion of each trace using logarithmically binned current (57 bins dec⁻¹
307 ¹) and linearly binned voltage (100 bins V⁻¹). Average I-V curves are generated by fitting the
308 current data in each voltage bin with a Gaussian. Since the series resistor reduces the voltage
309 applied across the junction when the current exceeds $\sim 2.5 \times 10^{-7}$ A, the highest positive bias

310 portions of the average I-V curves are omitted (i.e., max bias for **1** is ± 1.5 V, max bias for **2** is \pm
311 1.8 V, max bias for **3** is ± 1.9 V).

312 **Bias Switching Measurements.** Instead of continuously retracting the tip from the substrate, the
313 tip is withdrawn at a rate of 16 nm s^{-1} to form a molecular junction. The tip is then held in a fixed
314 position while the applied bias is pulsed between a high and low value for six cycles (lasting 100
315 ms). Finally, the tip is withdrawn again at the same rate to rupture the junction. The bias is applied
316 across the junction using a $100 \text{ k}\Omega$ resistor in series with the junction. For **1** and **2**, the applied high
317 bias is 1.5 V. For **3**, the applied high bias is 2.0 V. For all three, 0.5 V is applied while pulling and
318 during the low bias portion of the hold.

319 **DFT Calculations.** Density functional theory (DFT) simulations are conducted with the FHI-
320 AIMS package^{35,36} using the B3LYP and PBE exchange-correlation functionals³⁷ for the isolated
321 molecule and transmission calculations, respectively. For each molecule, we first optimize the
322 structure (alkyl chains are replaced with hydrogens to facilitate computation) with a maximum
323 residual force per atom of $10^{-2} \text{ eV}\cdot\text{\AA}^{-1}$. For the transmission calculation, the optimized structure is
324 used to construct an Au_1 -molecule- Au_1 structure which is relaxed to determine the optimal Au-S
325 bond length and orientation. Two tetrahedral Au_{60} clusters are then added, maintaining the optimal
326 Au-S bond. The Au_{60} clusters have (111) lattice surfaces and represent the gold electrodes in the
327 single-molecule junction. We use the Au_{60} -molecule- Au_{60} structure to calculate the energy-
328 dependent transmission function of the molecule. The transmission functions are calculated with
329 the AITRANSS package based on a non-equilibrium Green's function formalism^{38,39}.

330 **Data Availability.** Data associated with the synthesis and characterisation of **1–3** and **C1** are
331 available at <http://dx.doi.org/10.5525/gla.researchdata.1062>. Additional data that support the

332 findings of this study not included in the supplementary information document are available from
333 the corresponding authors upon reasonable request.

334 **Code Availability.** The data that support the findings were acquired using a custom instrument
335 controlled by custom software (Igor Pro, Wavemetrics). The software is available from the
336 corresponding author upon reasonable request.

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