Supporting Information for:

Topological radical pairs produce ultrahigh conductance in long molecular wires

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1. Experimental Methods

1) Synthesis

All reactions were carried out under an atmosphere of pre-purified nitrogen using Schlenk techniques unless otherwise noted. All solvents used for experiments were purchased dry and deoxygenated from Sigma-Aldrich and used without further purification. All reagents used in the synthesis were purchased from Sigma-Aldrich and used without further purification. ¹H-NMR and ¹³C NMR spectra were recorded on a Bruker Avance III 500 (500 MHz) and a Bruker Avance III 500/w Ascend magnet (500 MHz) spectrometer. The mass spectrometry data were obtained at the Columbia University mass spectrometry facility using a Waters Xevo G2-XS QTOF + H-Class Plus UPLC mass spectrometer.

Generally, naming protocols are as follows:

n is used to denote the number of secondary amines in the backbone of the polymer chain.

PA[n] is the name given to intermediates along the step whereas OE[n] is the name of the final system.

 $PA[2]-(NO_2)_2^1$, N-(tert-butoxycarbonyl)-4,4'-dibromodiphenylamine², and $PA[3](Boc)-(NH_2)_2^3$ were synthesized using published procedures.



PA[1](Boc)-(Br,SMe): To a flame-dried 250 mL round-bottom flask equipped with a stir bar, N-(tert-butoxycarbonyl)-4,4'-dibromodiphenylamine (2.00 g, 4.68 mmol, 1.00 equiv.), and THF (100 mL) were added. The flask was cooled to $-78 \,^{\circ}$ C for 30 min after which *n*BuLi (2.44 mL, 2.3 M in hexanes, 5.62 mmol, 1.20 equiv.) was added dropwise. After stirring for 2 hours at $-78 \,^{\circ}$ C, anhydrous dimethyl disulfide [Aldrich®] (1.25 mL, 14.05 mmol, 3.00 equiv.) was added dropwise. The reaction mixture stirred for 15 h and slowly warmed to RT. Solvent was removed *in vacuo* and water (50 mL) was added. The mixture was extracted with dichloromethane (50 mL×3), and the combined organic layer was dried over anhydrous sodium sulfate. Solvent was removed *in vacuo*. The compound was purified via silica column chromatography with 40% DCM/hexanes as a white solid (0.75 g, 41% yield). ¹**H NMR** (500 MHz, CDCl₃) δ 7.41 (d, *J* = 9.3 Hz, 2H), 7.20 (d, *J* = 8.7 Hz, 2H), 7.13 – 7.05 (m, 4H), 2.47 (s, 3H), 1.45 (s, 9H). ¹³C NMR (126 MHz, CDCl₃) δ 153.42, 142.09, 139.84, 136.11, 131.77, 128.70, 128.25, 127.49, 127.09, 125.62, 118.85, 81.66, 28.23, 16.07. **HRMS** (ESI+) calculated [M+Na]⁺ 416.0296, found 416.0303.



PA[2](Boc)-(NO₂)₂: To a flame-dried 250 mL round-bottom flask equipped with a stir bar, **PA[2]-(NO**₂)₂ (2.00 g, 5.71 mmol, 1.00 equiv.), DMAP [Aldrich®] (1.40g, 11.43 mmol, 2.00 equiv.), Boc₂O [Aldrich®] (0.81 g, 28.57 mmol, 5.00 equiv.), and anhydrous THF (100 mL) were added. The reaction mixture was heated to 60 °C for 9 h after which it was cooled to RT and DCM (100mL) was added. The mixture was washed with HCl (1 M, 3×50 mL) and aq. NaHCO₃ (sat. 3×50 mL). The organic layer was dried over anhydrous sodium sulfate and solvent was removed *in vacuo*. The compound was isolated as a dark yellow solid (3.08 g, 98% yield). ¹H NMR (500 MHz, DMSO) δ 8.22 (d, *J* = 9.1 Hz, 4H), 7.45 (d, *J* = 9.1 Hz, 4H), 7.32 (s, 4H), 1.41 (s, 18H). ¹³C NMR (126 MHz, DMSO) δ 152.65, 148.93, 144.19, 140.56, 129.27, 126.26, 124.76, 82.36, 28.11. HRMS (ESI+) calculated [M+Na]⁺ 573.1961, found 573.1956.



PA[2](Boc)-(NH₂)₂: To a flame-dried two-necked 250 mL round-bottom flask equipped with a stir bar, **PA[2](Boc)-(NO₂)₂** (1.00 g, 1.81 mmol), Pd/C [Aldrich®] (10%, 100 mg), EtOH (100 mL), and EtOAc (80 mL) were added. The mixture was purged five times with H₂ gas. Four balloons filled with H₂ were fitted to the flask and the mixture stirred at RT for 72 h. Subsequently, the mixture was filtered over a celite plug and the filtrate was collected. Solvent was removed *in vacuo* to yield the compound as an off-white solid (0.49 g, 55% yield). ¹H NMR (500 MHz, DMSO) δ 7.08 (s, 4H), 6.83 (d, *J* = 8.6 Hz, 4H), 6.50 (d, *J* = 8.6 Hz, 4H), 5.10 (s, 4H), 1.35 (s, 18H). ¹³C NMR (126 MHz, DMSO) δ 153.95, 147.53, 140.81, 131.61, 128.67, 126.49, 114.29, 80.15, 28.37. HRMS (ESI+) calculated [M+Na]⁺ 513.2478, found 513.2477.



OE[2]: In a nitrogen atmosphere glovebox, *p*-Phenylenediamine [Aldrich®] (14.0 mg, 0.13 mmol, 1.00 equiv.), 4-Bromothioanisole [Aldrich®] (50.0 mg, 0.25 mmol, 1.90 equiv.), Tris(dibenzylideneacetone)dipalladium(0) [Aldrich®] (11.9 mg, 0.01 mmol, 0.01 equiv.), XPhos (12.4 mg, 0.02 mmol, 0.2 equiv.), Cs₂CO₃ (169.5 mg, 0.52 mmol, 4.00 equiv.), were added to a 20 mL vial equipped with a stir bar. Toluene (10 mL) was added to the vial which was then capped and removed from the glovebox. The reaction mixture stirred at 80 °C for 72 h, was cooled to RT, and water was added. The mixture was extracted with dichloromethane (20 mL×3), and the combined organic layer was dried over anhydrous sodium sulfate. Solvent was removed *in vacuo*. The compound was then purified via silica column chromatography with 40% EtOAc/hexanes as a gray solid (16.7 mg, 38% yield). ¹H NMR (500 MHz, DMSO) δ 7.94 (s, 2H), 7.17 (d, *J* = 8.2 Hz, 4H), 7.01 (s, 4H), 6.93 (d, *J* = 8.2 Hz, 4H), 2.40 (s, 6H). ¹³C NMR (126 MHz, DMSO) δ 143.73, 136.84, 130.24, 125.62, 120.18, 116.35, 17.80. HRMS (ESI+) calculated [M]⁺ 352.1068, found 352.1077.



Boc-OE[3]: In а nitrogen atmosphere glovebox, 4,4'-dibromo-N-(tertbutoxycarbonyl)phenylaniline (0.500)1.17 1.00 mmol, equiv.), g, Tris(dibenzylideneacetone)dipalladium(0) [Aldrich®] (0.11 g, 0.12 mmol, 0.1 equiv.), XPhos [Aldrich®] (0.11 g, 0.23 mmol, 0.2 equiv.), Cs₂CO₃ (1.52 g, 4.68 mmol, 4.00 equiv.), were added to a 20 mL vial equipped with a stir bar. Toluene (10 mL) was added to the vial which was then capped and removed from the glovebox. To the vial was added 4-(Methylthio)aniline [Aldrich®] (0.81 g, 5.85 mmol, 5.00 equiv.). The reaction mixture stirred at 80 °C for 72 h, was cooled to RT, and water was added. The mixture was extracted with dichloromethane (50 mL×3), and the combined organic layer was dried over anhydrous sodium sulfate. Solvent was removed in vacuo. The compound was then purified via alumina column chromatography with 90% DCM/Hexanes as a dark brown solid (0.25 g, 39% yield). ¹H NMR (500 MHz, DMSO) δ 8.21 (s, 2H), 7.20 (d, J = 8.7 Hz, 4H), 7.08 (d, J = 8.9 Hz, 4H), 7.05 - 6.98 (m, 8H), 2.42 (s, 6H), 1.38 (s, 9H). ¹³C NMR (126 MHz, DMSO) δ 153.99, 141.92, 141.46, 135.74, 129.64, 128.32, 127.48, 117.98, 117.13, 80.17, 28.41, 17.25. **HRMS** (ESI+) calculated [M]⁺ 543.2014, found 543.2018.



Boc-OE[4]: In a nitrogen atmosphere glovebox, PA[2](Boc)-(NH₂)₂ (0.30 g, 0.61 mmol, 1.00 4-Bromothioanisole [Aldrich®] (0.24)1.16 mmol. 1.90 equiv.), g, equiv.), Tris(dibenzylideneacetone)dipalladium(0) [Aldrich®] (0.06 g, 0.06 mmol, 0.1 equiv.), XPhos (0.06 g, 0.12 mmol, 0.2 equiv.), Cs₂CO₃ (0.80 mg, 2.44 mmol, 4.00 equiv.), were divided equally and added to two 20 mL vials equipped with stir bars. Toluene (10 mL) was added to each vial which were then capped and removed from the glovebox. The reaction mixtures stirred at 80 °C for 72 h, were cooled to RT, and water was added. The mixtures were combined, extracted with dichloromethane (50 mL \times 3), and the combined organic layer was dried over anhydrous sodium sulfate. Solvent was removed in vacuo. The compound was then purified via alumina column chromatography with 2.5% MeOH/DCM as a dark brown solid (0.12 g, 28% yield). ¹H NMR (500 MHz, CD₃CN) δ 7.23 (d, J = 8.6 Hz, 4H), 7.19 (s, 4H), 7.10 (d, J = 8.6 Hz, 4H), 7.07 – 7.00 (m, 8H), 6.72 (s, 2H), 2.45 (s, 6H), 1.44 (s, 18H). ¹³C NMR (126 MHz, CD₃CN) δ 153.78, 141.66, 141.40, 140.83, 135.67, 129.31, 128.47, 126.80, 117.30, 117.05, 80.49, 27.44, 16.58. HRMS (ESI+) calculated [M+Na]⁺ 757.2858, found 757.2832.



Boc-OE[5]: In a nitrogen atmosphere glovebox, $PA[3](Boc)-(NH_2)_2$ (0.40 g, 0.59 mmol, 1.00 equiv.), 4-Bromothioanisole [Aldrich®] (0.23 g, 1.11 mmol, 1.90 equiv.), Tris(dibenzylideneacetone)dipalladium(0) [Aldrich®] (0.05 g, 0.06 mmol, 0.1 equiv.), XPhos (0.05 g, 0.12 mmol, 0.2 equiv.), Cs₂CO₃ (0.77 mg, 2.36 mmol, 4.00 equiv.), were divided equally and added to two 20 mL vials equipped with stir bars. Toluene (10 mL) was added to each vial which were then capped and removed from the glovebox. The reaction mixtures stirred at 80 °C for 72 h, were cooled to RT, and water was added. The mixtures were combined, extracted with

dichloromethane (50 mL×3), and the combined organic layer was dried over anhydrous sodium sulfate. Solvent was removed *in vacuo*. The compound was then purified via alumina column chromatography with 2.5% MeOH/DCM as a light orange solid (0.37 g, 72% yield). ¹H NMR (500 MHz, DMSO) δ 8.25 (s, 2H), 7.23 – 7.12 (m, 12H), 7.09 – 6.97 (m, 12H), 2.41 (s, 6H), 1.37 (s, 27H). ¹³C NMR (126 MHz, DMSO) δ 153.67, 153.40, 142.00, 141.67, 141.19, 140.07, 134.85, 129.54, 128.81, 127.72, 127.58, 127.14, 118.21, 117.02, 80.98, 80.62, 28.31, 28.25, 17.17. HRMS (ESI+) calculated [M]⁺ 925.3907, found 925.3867.



Boc-OE[6]: In a nitrogen atmosphere glovebox, PA[2](Boc)-(NH₂)₂ (0.20 g, 0.41 mmol, 1.00 PA[1](Boc)-(Br,SMe) g, 0.77 mmol. 1.90 equiv.). (0.30)eauiv.). Tris(dibenzylideneacetone)dipalladium(0) [Aldrich®] (0.04 g, 0.04 mmol, 0.1 equiv.), XPhos (0.04 g, 0.08 mmol, 0.2 equiv.), Cs₂CO₃ (0.53 mg, 1.64 mmol, 4.00 equiv.), were added to a 20 mL vial equipped with a stir bar. Toluene (10 mL) was added to the vial which was then capped and removed from the glovebox. The reaction mixture stirred at 80 °C for 72 h, was cooled to RT, and water was added. The mixture was extracted with dichloromethane (50 mL \times 3), and the combined organic layer was dried over anhydrous sodium sulfate. Solvent was removed in vacuo. The compound was then purified via alumina column chromatography with 2.5% MeOH/DCM as a light orange solid (0.35 g, 82% yield). ¹H NMR (500 MHz, DMSO) δ 8.27 (s, 2H), 7.22 (d, J = 8.9 Hz, 4H), 7.17 – 7.13 (m, 8H), 7.08 – 6.99 (m, 16H), 2.45 (s, 6H), 1.38 (m, 36H). ¹³C NMR (126 MHz, DMSO) δ 153.71, 153.66, 141.84, 141.68, 140.79, 140.71, 135.29, 135.23, 135.07, 128.77, 128.64, 127.59, 127.07, 126.76, 117.29, 117.21, 80.58, 28.35, 15.41. HRMS (ESI+) calculated [M+Na]⁺ 1139.4751, found 1139.4691.



Boc-OE[7]: In a nitrogen atmosphere glovebox, PA[3](Boc)-(NH₂)₂ (0.40 g, 0.59 mmol, 1.00 equiv.), PA[1](Boc)-(Br,SMe) (0.44)1.11 mmol, 1.90 equiv.), g, Tris(dibenzylideneacetone)dipalladium(0) [Aldrich®] (0.05 g, 0.06 mmol, 0.1 equiv.), XPhos (0.05 g, 0.12 mmol, 0.2 equiv.), Cs₂CO₃ (0.77 mg, 2.36 mmol, 4.00 equiv.), were divided equally and added to two 20 mL vials equipped with stir bars. Toluene (10 mL) was added to each vial which were then capped and removed from the glovebox. The reaction mixtures stirred at 80 °C for 72 h, were cooled to RT, and water was added. The mixtures were combined, extracted with dichloromethane (50 mL \times 3), and the combined organic layer was dried over anhydrous sodium sulfate. Solvent was removed in vacuo. The compound was then purified via alumina column chromatography with 2.5% MeOH/DCM as a light orange solid (0.57 g, 78% yield). ¹H NMR (500 MHz, DMSO) δ 8.28 (s, 2H), 7.21 (d, *J* = 8.7 Hz, 4H), 7.15 (m, 12H), 7.08 – 7.00 (m, 16H), 2.45 (s, 6H), 1.37 (m, 45H). ¹³C NMR (126 MHz, DMSO) δ 153.68, 141.88, 141.67, 141.19, 140.79, 140.11, 135.32, 135.25, 134.99, 128.81, 128.66, 127.62, 127.20, 126.75, 117.31, 117.22, 81.00, 80.65, 80.61, 56.33, 55.41, 28.37, 28.33, 28.27, 15.41. HRMS (ESI+) calculated [M+H]⁺ 1308.5878, found 1308.5887.

General Boc Deprotection Procedure: To a quartz tube was added Boc-OE[n] powder which was then placed under vacuum. The tube was placed in a tube furnace with the portion containing the solid in the middle of the furnace. The furnace was heated to 150 °C for 15 h, after which it was cooled to RT and the tube was opened to air. The deprotected OE[n] was isolated as a dark brown solid in quantitative yield.



OE[3]: Prepared via the general Boc deprotection procedure. ¹H NMR (500 MHz, DMSO) δ 7.86 (s, 2H), 7.71 (s, 1H), 7.16 (d, J = 8.5 Hz, 4H), 7.01 – 6.93 (m, 8H), 6.89 (d, J = 8.5 Hz, 4H), 2.39 (s, 6H). ¹³C NMR (126 MHz, DMSO) δ 144.34, 138.91, 135.37, 130.43, 125.05, 121.01, 118.25, 115.87, 17.98. HRMS (ESI+) calculated [M-2H+H]⁺ 442.1412, found 442.1432.



OE[4]: Prepared via the general Boc deprotection procedure. ¹H NMR (500 MHz, DMSO) δ 7.81 (s, 2H), 7.60 (s, 2H), 7.15 (d, J = 8.7 Hz, 4H), 6.99 – 6.91 (m, 12H), 6.87 (d, J = 8.8 Hz, 4H), 2.38 (s, 6H). ¹³C NMR (126 MHz, DMSO) δ 144.53, 139.62, 137.44, 134.87, 130.48, 124.86, 121.26, 119.09, 117.59, 115.72, 18.03. HRMS (ESI+) calculated [M-2H+H]⁺ 533.1833, found 533.1812.



OE[5]: Prepared via the general Boc deprotection procedure. ¹H NMR (500 MHz, DMSO) δ 7.80 (s, 2H), 7.57 (s, 2H), 7.51 (s, 1H), 7.16 (d, J = 8.9 Hz, 4H), 7.02 – 6.83 (m, 20H), 2.38 (s, 6H). ¹³C NMR (126 MHz, DMSO) δ 144.60, 139.87, 138.17, 134.71, 130.50, 124.79, 121.35, 119.39, 118.41, 117.37, 115.67, 18.05. HRMS (ESI+) calculated [M]⁺ 625.2334, found 625.2303.



OE[6]: Prepared via the general Boc deprotection procedure. ¹H NMR (500 MHz, DMSO) δ 7.79 (s, 2H), 7.55 (s, 2H), 7.47 (s, 2H), 7.15 (d, *J* = 8.6 Hz, 4H), 6.98 – 6.84 (m, 24H), 2.38 (s, 6H). ¹³C NMR (126 MHz, DMSO) δ 144.58, 139.92, 138.41, 137.66, 136.77, 134.67, 130.48, 124.81, 121.37, 119.48, 118.69, 118.18, 117.32, 115.67, 40.42, 18.01. HRMS (ESI+) calculated [M]⁺ 716.2756, found 716.2717.



OE[7]: Prepared via the general Boc deprotection procedure. ¹H NMR (500 MHz, DMSO) δ 7.79 (s, 2H), 7.55 (s, 2H), 7.45 (d, *J* = 11.0 Hz, 3H), 7.15 (d, *J* = 8.7 Hz, 4H), 7.05 – 6.78 (m, 28H), 2.38 (s, 6H). ¹³C NMR (126 MHz, DMSO) δ 144.63, 139.98, 138.51, 137.92, 137.49, 136.70, 134.63, 130.51, 127.40, 126.75, 124.77, 121.39, 119.52, 118.79, 118.45, 118.09, 117.27, 115.64, 55.38, 31.16, 28.38, 18.05. HRMS (ESI+) calculated [M-4H+H]⁺ 804.2943, found 804.2923.

General STM-BJ Acidified Sample Preparation Procedure: To a 20 mL vial was added OE[n] (Approximately 0.1 mg), propylene carbonate (1.0 mL), and trifluoroacetic acid (0.1 mL), after which the solution went from light yellow to dark green over 5 min. The solution was heated to reflux under vacuum for 10 min, cooled to room temperature, and measured under high bias in the junction.

General STM-BJ Basified Sample Preparation Procedure: To a 20 mL vial was added OE[n] (Approximately 0.1 mg), propylene carbonate (1.0 mL), and triethylamine (0.1 mL), after which the solution went from light yellow to light purple over 5 min. The solution was heated to reflux under vacuum for 10 min, cooled to room temperature, and measured under high bias in the junction.

2) SC-XRD Data

The crystallographic structures of OE[2] from single-crystal X-ray diffraction (SC-XRD) data. Structures were collected on an Agilent SuperNova diffractometer using mirror-monochromated Cu K α radiation. Single crystals of OE[2] were successfully obtained by slow evaporation of a solution of the compound in 40% ethyl acetate/hexanes.



Crystallographic data for **OE**[2].

	OE [2]
CCDC Deposition number	2190696
Chemical formula	$C_{20}H_{20}N_2S_2$
Formula weight	352.51
Crystal system	Trinclinic
Space group	<i>P</i> -1
<i>a</i> (Å)	9.6978(9)
<i>b</i> (Å)	9.7406(9)
<i>c</i> (Å)	18.339(3)
α (°)	82.549(9)
$\beta(^{\circ})$	82.491(9)
$\gamma(^{\circ})$	89.991(7)
Volume (Å ³)	1702.7(4)
Z	4
$ ho_{ m calc}$ (g/cm ³)	1.375
Temperature (K)	100
$\mu (\mathrm{mm}^{-1})$	2.842
F(000)	744
Radiation (Å)	Cu Kα (λ =1.54184)
2θ range (°)	4.579 to 72.510
Index ranges	$-8 \leqslant h \leqslant 11, -11 \leqslant k \leqslant 12, -22 \leqslant l \leqslant 22$
Total/independent reflections	6495/3504
Data/restraints/parameters	3504/0/425
Goodness-of-fit	1.015
$R_1^{\mathrm{a}}/\mathrm{w}R_2^{\mathrm{b}}$	10.64/31.48
Largest diff. peak, hole (e ⁻ Å ⁻³)	1.552, -1.000
${}^{a}R_{1} = \sum F_{0} - F_{2} / \sum F_{0} $	

 $\overline{{}^{a}R_{1} = \Sigma ||F_{0}| - |F_{c}|| / \Sigma |F_{0}|}$ ${}^{b}wR_{2} = [\Sigma w (F_{0}^{2} - F_{c}^{2})^{2} / \Sigma w (F_{0}^{2})^{2}]^{1/2}$

3) UV-Vis Spectra

The ultraviolet-visible-near infrared spectra were collected on a Shimadzu 1800 spectrophotometer and a Varian Cary 5000 spectrophotometer. All measurements were taken using a quartz cuvette with a path length of 1 cm.

In the UV-Vis spectra figures and other supporting figures below, the imine-linked OE[n] is denoted by i-OE[n] (see below, and Figure S2).



i-**OE**[*n*=odd]

General UV-Vis Neutral Sample Preparation Procedure: A 2.0×10^{-5} M solution of OE[*n*] in DMSO was prepared prior to obtaining absorbance measurements.

General UV-Vis Acidified Sample Preparation Procedure: A 2.0 x 10⁻⁵ M solution of **OE**[*n*] in 5% TFA/DMSO was prepared prior to obtaining absorbance measurements.

General UV-Vis Oxidized Basified Sample Preparation Procedure: A 2.0×10^{-5} M solution of OE[*n*] in 5% triethylamine/DMSO was prepared. Approximately 2 mg of NH₄S₂O₈ was added to the solution, after which the mixture went from clear to blue over 30min. The sample was filtered using a syringe filter prior to obtaining absorbance measurements.

General UV-Vis Oxidized Acidified Sample Preparation Procedure: A 2.0×10^{-5} M solution of OE[*n*] in 5% TFA/DMSO was prepared. Approximately 2 mg of NH₄S₂O₈ was added to the solution, after which the mixture went from clear to dark green over 30min. The sample was filtered using a syringe filter prior to obtaining absorbance measurements.

OE[2] UV-Vis Acid/Base Titration Procedures: OE[2] was dissolved in 5% TFA/DCM to approximately a concentration of 10^{-5} M. A dilute solution of triethylamine in DCM was prepared and added dropwise to the solution of **OE**[2]. Absorbance spectra were obtained after each addition of triethylamine. Once **OE**[2] was in its fully basified form, a dilute solution of TFA in DCM was added dropwise and absorbance spectra were obtained after each addition until the spectrum returned to its original acidified state.

We measured steady-state UV-Vis spectra for (A-B) trivial OE[n] with (A) acid (trifluoroacetic acid, TFA) and (B) without acid, (C) t-OE[n], and (D) i-OE[n], in dimethyl sulfoxide (DMSO).



A photo of t-OE[2] (left, green) and i-OE[2] (right, red) in PC solutions.



We obtained the extinction coefficients (ε) of **OE**[n], i-**OE**[n] and t-**OE**[n] at their respective λ_{max} (A). The increased ε and red-shifted absorbance indicate electronic coupling between the nitrogen sites. We then calculated the optical band gaps of **OE**[n], i-**OE**[n] and t-**OE**[n], obtained from Tauc analysis. The band gap value of t-**OE**[2] is not applicable from the measured UV-Vis spectrum.



The UV-Vis spectra under trifluoroacetic acid (TFA) titration of OE[2] shows a transmission between the basified and the acidified forms. The isosbestic points indicates clean interconversion.



4) Cyclic Voltammograms

Cyclic voltammograms for OE[2]-OE[7] acidified (TFA) solutions. The CV data has many board peaks that are not clearly defined. However, all the peaks are relatively close to the oxidation potential of Fc and thus clearly accessible in the STM-BJ setup. In STM-BJ measurement absent of reference electrode, the instrumental bias is relative to the potential of the Au tip. Thus, it varies a bit from tip to tip. The grey shaded area marks the possible range of 500 mV instrumental bias versus the oxidation potential of Fc. For every t-OE[n], the conductance with tip bias higher than 500 mV does not significantly change from the conductance at 500 mV, as seen in the I-V measurement of t-OE[7] (Figure 3B in the main article).



Cyclic voltammograms of OE[5] during base titration. The peaks don't shift significantly.



5) EPR Spectra

The X-band electron paramagnetic resonance spectra were collected on a Bruker EMX spectrometer. with microwave frequency of 9.736 GHz at 298 K. The spectra were acquired at 0.98 G modulation and 100 kHz modulation frequency. Both **OE** forms are oxidized by O_2 in air in the presence of trifluoroacetic acid (TFA) to generate t-**OE**[*n*] (A), while the i-**OE**[*n*] (B) is generated in the presence of triethylamine (TEA). We observed paramagnetic radical feature for t-**OE**[*n*], but diamagnetic feature for i-**OE**[*n*].



6) Conductance Measurement

STM-BJ conductance measurements were carried out using a custom-built Scanning Tunneling Microscope (STM)⁴. We used 0.25 mm diameter cut gold wire (99.95%, Alfa Aesar) as the STM tip, and ~100 nm thick gold-coated (99.999%, Alfa Aesar) steel pucks as the substrates. A commercially available single-axis piezoelectric positioner (P-840.10, PI) was used to control the tip-substrate distance at sub-angstrom level. The STM setup was controlled using a custom software written in IgorPro (Wavemetrics, Inc.) and operated under ambient conditions at room temperature. The gold substrates were UV/ozone cleaned for 20 minutes before use. The gold tip is coated by Apiezon wax to minimize background current during the measurement. For each measurement, 1000 traces were collected before adding molecular solutions to check the cleanliness of the tip and substrate surface. Propylene carbonate (PC) solutions of OE[n] at 0.1 mM concentration with equivalent (2 eq. for OE[2] and OE[3], 4 eq. for OE[4] and OE[5], and 6 eq. for OE[6] and OE[7]) trifluoroacetic acid (TFA) were added to the substrate for STM-BJ measurements. After the formation of each gold-gold contact junction with a conductance greater than $5G_0$, the piezoelectric positioner moved the tip at a speed of 20 nm/s to break the junction. The current and voltage across the junction were measured at 40 kHz with a voltage applied across the junction in series with a 97 k Ω resistor to avoid saturating the current amplifier. During the retraction of the STM tip, a gold point contact is formed with a conductance close to $1G_0$. When this contact is broken in a solution of molecules with gold-binding groups, such as the thioanisole groups for trivial OE[n] and t-OE[n], and the amine groups specifically for trivial OE[n], molecular conductance plateaus are observed below $1G_0$. The measured conductance (current/voltage) traces were then collected and compiled into logarithmically binned 1D conductance histograms, while 2D conductance-displacement histograms were obtained by overlaying all the measured traces after aligning them at a conductance of $0.5G_0$. All the conductance measurement shown in the main text and the supporting information were measured for 2000 traces without data selection.

6) Current-Voltage Measurement

The current data in Figure 3A and Figure 3B is measured by withdrawing the gold tip at 20 nm/s to form a gap between the tip and substrate at 500 mV applied bias. Next, the tip is held in a fixed position when the external bias is ramped continuously at a rate of 40 V/s for 10 cycles. Within each cycle, the bias was first ramped from 0.5 V to 1 V, then from 1 V to -1 V, and finally from -1 V to 0.5 V. Then the tip was further withdrawn at 20 nm/s to break the junction. Traces are selected where the conductance at the beginning and at the end of the holding is between $10^{-1.5}$ and $10^{-3}G_0$, and the 2D current versus time histogram is constructed from the hold section of the selected traces using logarithmically binned current and linearly binned time.

2. Calculation Methods

1) Tight-binding Analysis

This section draws from standard tight-binding derivations that are also presented in these books⁵⁻⁶. In the molecular junction model, H_0 describes the Hamiltonian of the isolated single molecule. When two Au electrodes are appended to the molecule, it becomes an open system. The Hamiltonian of such system includes the interaction between the molecule and electrodes,

$$\widetilde{\mathbf{H}} = \mathbf{H}_0 + \mathbf{\Sigma} = \mathbf{H} + \mathbf{\Sigma}_{\mathrm{L}} + \mathbf{\Sigma}_{\mathrm{R}} \tag{1}$$

where $\Sigma_L = \langle 1 | \mathbf{\Sigma}_L | 1 \rangle$ and $\Sigma_R = \langle N | \mathbf{\Sigma}_R | N \rangle$ are the self-energies from the left and right electrodes to the two terminal sites of the molecule, 1 and *N*, respectively. These self-energy terms are non-Hermitian, and represented by Γ_L and Γ_R , the scattering rates at molecule-electrode interfaces:

$$\Gamma_{\rm L} = i \left(\Sigma_{\rm L} - \Sigma_{\rm L}^{\dagger} \right) = -2 \operatorname{Im}[\Sigma_{\rm L}] = \langle 1 | \Gamma_{\rm L} | 1 \rangle \tag{2}$$

$$\Gamma_{\rm R} = i \left(\Sigma_{\rm R} - \Sigma_{\rm R}^{\dagger} \right) = -2 \operatorname{Im}[\Sigma_{\rm R}] = \langle N | \mathbf{\Gamma}_{\rm R} | N \rangle \tag{3}$$

We then obtain the energy-dependent Green's function:

$$\mathbf{G}(E) = \left[E\mathbf{I} - \widetilde{\mathbf{H}}\right]^{-1} = \left[E\mathbf{I} - \mathbf{H}_0 - \mathbf{\Sigma}_{\mathrm{L}} - \mathbf{\Sigma}_{\mathrm{R}}\right]^{-1}$$
(4)

where I is the identity matrix and E is the energy of the transmitting electrons. The transmission function is calculated by:

$$T(E) = \operatorname{Tr}[\mathbf{\Gamma}_{\mathrm{L}}\mathbf{G}(E)\mathbf{\Gamma}_{\mathrm{R}}\mathbf{G}^{\dagger}(E)]$$
(5)

where G(E) and $G^{\dagger}(E)$ are the retarded and advanced Green's functions, respectively.

For the tight-binding simulations, we assumed the wide-band limit i.e. the coupling between the molecule and the electrodes is energy-independent. In the weak coupling regime, the self-energies become:

$$\Sigma_{\rm L} = -\frac{i}{2}\Gamma_{\rm L} \tag{6}$$

and

$$\Sigma_{\rm R} = -\frac{i}{2}\Gamma_{\rm R} \tag{7}$$

To model the prototypical multi-radical polyacetylene system, we construct (6m-2)*(6m-2) matrices for m = 1-3, where *m* is the number of the SSH TI units shown in the middle structure of Figure 1B. The matrix for m = 1 is shown below:

$$\widetilde{\mathbf{H}}_{1} = \begin{pmatrix} -\frac{iI_{L}}{2} & t_{1} & 0 & 0\\ t_{1} & 0 & t_{2} & 0\\ 0 & t_{2} & 0 & t_{1}\\ 0 & 0 & t_{1} & -\frac{i\Gamma_{R}}{2} \end{pmatrix}$$
(8)

Here, the parameters t_1 and t_2 represent the coupling of each single bond and double bond of the chain. We can set $t_1 = e^{-0.5}$ and $t_2 = e^{0.5}$ without loss of generality.⁷ The on-site energy of carbon is set to zero, which is also the Fermi energy, to make sure that the Fermi energy is in the middle of the calculated HOMO and LUMO resonances.

Mathematica Code

```
t0 = 1; \delta = 0.5; t1 = t0 * Exp[ - \delta]; t2 = t0 * Exp[\delta]; \Gamma = 0.1;
H1 = \{\{0, t1, 0, 0\}, \{t1, 0, t2, 0\}, \{0, t2, 0, t1\}, \{0, 0, t1, 0\}\};
H2 = \{ \{0, t1, 0, 0, 0, 0, 0, 0, 0, 0\}, \{t1, 0, t2, 0, 0, 0, 0, 0, 0, 0\}, \{0, t2, 0\}, \{0, t2, 0\}, \{0, t3, 0\}, \{0
t1, 0, 0, 0, 0, 0, 0}, {0, 0, t1, 0, t1, 0, 0, 0, 0, 0}, {0, 0, 0, t1, 0, t2, 0, 0, 0,
0}, {0, 0, 0, 0, t2, 0, t1, 0, 0, 0}, {0, 0, 0, 0, 0, t1, 0, t1, 0, 0}, {0, 0, 0, 0, 0,
0, 0, t1, 0, t2, 0}, {0, 0, 0, 0, 0, 0, 0, t2, 0, t1}, {0, 0, 0, 0, 0, 0, 0, 0, t1,
0}};
0, t1, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0}, {0, 0, 0, t1, 0, t2, 0, 0, 0, 0, 0, 0, 0, 0, 0,
0, 0}, {0, 0, 0, 0, t2, 0, t1, 0, 0, 0, 0, 0, 0, 0, 0, 0}, {0, 0, 0, 0, 0, 0, t1, 0, t1,
0, 0, 0, 0, 0, 0, 0, 0}, {0, 0, 0, 0, 0, 0, 0, t1, 0, t2, 0, 0, 0, 0, 0, 0}, {0, 0, 0, 0, 0}, {0, 0, 0, 0}, {0, 0, 0}, {0, 0, 0}, {0, 0, 0}, {0, 0, 0}, {0, 0, 0}, {0, 0, 0}, {0, 0, 0}, {0, 0, 0}, {0, 0, 0}, {0, 0, 0}, {0, 0, 0}, {0, 0, 0}, {0, 0, 0}, {0, 0, 0}, {0, 0, 0}, {0, 0}, {0, 0}, {0, 0}, {0, 0}, {0, 0}, {0, 0}, {0, 0}, {0, 0}, {0, 0}, {0, 0}, {0, 0}, {0, 0}, {0, 0}, {0, 0}, {0, 0}, {0, 0}, {0, 0}, {0, 0}, {0, 0}, {0, 0}, {0, 0}, {0, 0}, {0, 0}, {0, 0}, {0, 0}, {0, 0}, {0, 0}, {0, 0}, {0, 0}, {0, 0}, {0, 0}, {0, 0}, {0, 0}, {0, 0}, {0, 0}, {0, 0}, {0, 0}, {0, 0}, {0, 0}, {0, 0}, {0, 0}, {0, 0}, {0, 0}, {0, 0}, {0, 0}, {0, 0}, {0, 0}, {0, 0}, {0, 0}, {0, 0}, {0, 0}, {0, 0}, {0, 0}, {0, 0}, {0, 0}, {0, 0}, {0, 0}, {0, 0}, {0, 0}, {0, 0}, {0, 0}, {0, 0}, {0, 0}, {0, 0}, {0, 0}, {0, 0}, {0, 0}, {0, 0}, {0, 0}, {0, 0}, {0, 0}, {0, 0}, {0, 0}, {0, 0}, {0, 0}, {0, 0}, {0, 0}, {0, 0}, {0, 0}, {0, 0}, {0, 0}, {0, 0}, {0, 0}, {0, 0}, {0, 0}, {0, 0}, {0, 0}, {0, 0}, {0, 0}, {0, 0}, {0, 0}, {0, 0}, {0, 0}, {0, 0}, {0, 0}, {0, 0}, {0, 0}, {0, 0}, {0, 0}, {0, 0}, {0, 0}, {0, 0}, {0, 0}, {0, 0}, {0, 0}, {0, 0}, {0, 0}, {0, 0}, {0, 0}, {0, 0}, {0, 0}, {0, 0}, {0, 0}, {0, 0}, {0, 0}, {0, 0}, {0, 0}, {0, 0}, {0, 0}, {0, 0}, {0, 0}, {0, 0}, {0, 0}, {0, 0}, {0, 0}, {0, 0}, {0, 0}, {0, 0}, {0, 0}, {0, 0}, {0, 0}, {0, 0}, {0, 0}, {0, 0}, {0, 0}, {0, 0}, {0, 0}, {0, 0}, {0, 0}, {0, 0}, {0, 0}, {0, 0}, {0, 0}, {0, 0}, {0, 0}, {0, 0}, {0, 0}, {0, 0}, {0, 0}, {0, 0}, {0, 0}, {0, 0}, {0, 0}, {0, 0}, {0, 0}, {0, 0}, {0, 0}, {0, 0}, {0, 0}, {0, 0}, {0, 0}, {0, 0}, {0, 0}, {0, 0}, {0, 0}, {0, 0}, {0, 0}, {0, 0}, {0, 0}, {0, 0}, {0, 0}, {0, 0}, {0, 0}, {0, 0}, {0, 0}, {0, 0}, {0, 0}, {0, 0}, {0, 0}, {0, 0}, {0, 0}, {0, 0}, {0, 0}, {0, 0}, {0, 0}, {0, 0}, {0, 0}, {0, 0}, {0, 0}, {0, 0}, {0, 0}, {0, 0}, {0, 0}, {0, 0}, {0, 0}, {0, 0}, {0, 0}, {0, 0}, {0, 0}, {0, 0}, {0, 0}, {0, 0}, {0, 0}, {0, 0}, {0, 0}, {0, 0}, {0, 0}, {0, 0}, {0, 0}, {0, 0}, {0, 0}, {0, 0}, {0, 0}, {0, 0}, {0, 0}, {0, 0}, {0, 0}, {0, 0}, {0, 0}, {0, 0}, {0, 0}, {0, 0
H1//MatrixForm:
H2//MatrixForm;
H3//MatrixForm;
G1L = SparseArray[\{\{1, 1\} \rightarrow \Gamma\}, \{4, 4\}];
G1R = SparseArray[\{\{4, 4\} - >\Gamma\}, \{4, 4\}];
G2L = SparseArray[\{\{1, 1\} \rightarrow \Gamma\}, \{10, 10\}];
G2R = SparseArray[\{\{10, 10\} - >\Gamma\}, \{10, 10\}];
G3L = SparseArray[\{\{1, 1\} \rightarrow \Gamma\}, \{16, 16\}];
G3R = SparseArray[\{\{16, 16\} - >\Gamma\}, \{16, 16\}];
G1[E_]:=Inverse[E IdentityMatrix[4] - (H1 - I / 2(G1L + G1R))];
G2[E_]:=Inverse[E IdentityMatrix[10] - (H2 - I / 2(G2L + G2R))];
G3[E]:=Inverse[E IdentityMatrix[16] - (H3 - I / 2(G3L + G3R))];
T1[E ]:=Tr[G1L.G1[E].G1R.G1[E] \ [ConjugateTranspose]];
T2[E_]:=Tr[G2L.G2[E].G2R.G2[E] \setminus [ConjugateTranspose]];
T3[E_]:=Tr[G3L.G3[E].G3R.G3[E] \setminus [ConjugateTranspose]];
LogPlot[{T1[x], T2[x], T3[x]}, {x, -1, 1}];
```

2) DFT Transmission Calculation

All the DFT calculations were carried out using close-shell Kohn-Sham formulation of density functional theory with FHI-aims software⁸. A non-empirical generalized gradient-corrected approximation (Perdew-Burke-Ernzerhof, PBE) for the exchange-correlation functional⁹ was used. Scalar relativistic corrections to the kinetic energy were incorporated into the first-principles calculations at the atomic zeroth-order regular approximation (ZORA) level¹⁰. The Kohn-Sham states were represented in an optimized all-electron numeric atom-centered basis set with "tight" computational settings (roughly equivalent to "double zeta + polarization" quality for the molecular atoms and "double zeta" quality for the gold atom from the electrodes in the transmission calculations). The calculation results were obtained using standard convergence criteria in the self-consistent field cycle for the difference in the particle density (10^{-5} electrons/Å³), total energy (10⁻⁶ eV), sum for Kohn-Sham eigenvalues (10⁻⁴ eV) and forces (10⁻⁴ eV/Å). For the charge constraint on the t-OE[n], we use point charges arranged on two parallel squares above and below the molecule with the inter-sheet distance of 6 Å, consisting of 15×15 evenly distributed point charges. The edge length of the point-charge squares varies with different length of the molecule (see Table S1). The energy-dependent transmission functions were calculated using the non-equilibrium Green's function formalism with the transport package AITRANSS¹¹⁻¹³. The junction electrodes were modeled by tetrahedral clusters each consisting of 22 gold atoms with fixed interatomic distance of 2.88 Å. The self-energy of the electron reservoirs was constructed by a Markovian spatially local function ($\Sigma(\mathbf{r}, \mathbf{r}') = i\eta(\mathbf{r})\delta(\mathbf{r} - \mathbf{r}')$). The local absorption rate $\eta(\mathbf{r})$ was adjusted to guarantee the smooth change in $\eta(\mathbf{r})$ doesn't affect the electronic transmission. The Fermi level for transport calculations on charged molecules is set in the middle between HOMO and LUMO resonance peaks for t-OE[n]. The resulting trends of the zero-bias conductance with increasing wire length is identical over a major energy window and does not depend on the exact location of the Fermi level.

3. Additional Figures



Figure S1. The four resonant structures of t-**OE**[7]. The location of TI units is different for each resonant structure. The real electronic structure of t-**OE**[7] should be considered as a linear combination of these four resonant structures. Similarly, t-**OE**[3] and t-**OE**[5] have three and two resonant structures with different locations of TI units respectively.



Figure S2. The interconversion between trivial, t- and i-OE[7].



Figure S3. (A) The 1D histograms of the i-**OE**[n] when n is even. (B) The 1D histograms of the i-**OE**[n] when n is odd. (C) The measured conductance of the i-**OE**[n] against n. For even n, a reversed conductance decay is observed. For odd n, an exponential decay in conductance is observed.



Figure S4. The 2D histograms of i-OE[2] to i-OE[7] measured at 500 mV.



Figure S5. The 2D histograms of t-OE[2] to t-OE[7] measured at 500 mV.



Figure S6. The 1D histograms of trivial **OE**[2] and **OE**[3] measured at -250 mV.



Figure S7. The 2D histograms of trivial **OE**[2]-**OE**[7] measured at -250 mV.



Figure S8. The molecular structures correspond to the experimental current data in Figure 3C.



Figure S9. Geometries of t-OE[n] with charge constraints in transmission calculations.



Figure S10. The HOMO- and LUMO-derived molecular conductance orbitals (MCOs) of t-**OE**[n] with two Au₂₂ tetrahedral clusters appended to the terminal linkers. The molecular region of the MCOs is the same as the corresponding HOMO or LUMO of the isolated molecules.



Figure S11. The HOMO and LUMO orbitals of isolated t-OE[n].



Figure S12. (A) The calculated transmission function of trivial OE[n], showing off-resonance transmission feature. (B) Transmission at Fermi (E_F) of trivial OE[n], with $\beta = 2.09$.

Figure S13. The HOMO and LUMO orbitals of isolated trivial **OE**[n].

i- OE [<i>n</i>]	НОМО	LUMO
<i>n</i> = 2		- Part Contractor
<i>n</i> = 3		Part Contractor
n = 4	EUDSEUDSEUDS	QUE CONTRACTOR DE
n = 5	QUI SAI SAI VIS	Real Contraction of the second
<i>n</i> = 6	-2013200220022002	P 4260 560 560 508
n = 7	Constrant Constrants	Stand Ball Barks

Figure S14. The HOMO and LUMO orbitals of isolated i-OE[n].



Figure S15. The HOMO- and LUMO-derived molecular conductance orbitals (MCOs) of i-**OE**[n] with two Au_{22} tetrahedral clusters appended to the terminal linkers. The molecular region of the MCOs is the same as the corresponding HOMO or LUMO of the isolated molecules.



Figure S16. (A) The calculated transmission function of *i*-**OE**[*n*]. (B) Transmission at Fermi (E_F) of *i*-**OE**[*n*], with $\beta_{even} = -0.36$ and $\beta_{odd} = 0.28$.

4. Additional Tables

	<i>n</i> = 2	<i>n</i> = 3	<i>n</i> = 4	<i>n</i> = 5	<i>n</i> = 6	<i>n</i> = 7
Edge Length of the Charge Squares (l, Å)	6	12	16	22	28	34
Distance between the Squares (d, Å)	6	6	6	6	6	6
Total Charge (Q)	-2.6	-2.7	-7.2	-7.6	-14.0	-14.8
Charge of the molecule (Q')	+2.025	+2.006	+4.038	+3.998	+5.988	+5.972

Table S1. Parameters related to the charge constraint of t-**OE**[n].

Table S2. The energy of HOMO, LUMO and HOMO-LUMO gap of isolated t-**OE**[n].

Isolated t-OE[n]

Energy (eV)	<i>n</i> = 2	<i>n</i> = 3	<i>n</i> = 4	<i>n</i> = 5	<i>n</i> = 6	<i>n</i> = 7
НОМО	-10.69	-9.61	-14.05	-12.92	-16.30	-15.26
LUMO	-10.26	-9.33	-13.60	-12.59	-15.94	-14.95
HOMO-LUMO gap	0.43	0.28	0.45	0.33	0.44	0.31

Table S3. The energy of HOMO, LUMO and HOMO-LUMO gap of isolated trivial **OE**[n].

Isolated Trivial OE[n]							
Energy (eV)	<i>n</i> = 2	<i>n</i> = 3	<i>n</i> = 4	<i>n</i> = 5	<i>n</i> = 6	<i>n</i> = 7	
НОМО	-4.18	-4.10	-4.05	-3.97	-3.91	-3.85	
LUMO	-1.53	-1.56	-1.60	-1.58	-1.54	-1.52	
HOMO-LUMO gap	2.65	2.54	2.45	2.40	2.37	2.33	

Isolated i- OE [<i>n</i>]						
Energy (eV)	<i>n</i> = 2	<i>n</i> = 3	<i>n</i> = 4	<i>n</i> = 5	<i>n</i> = 6	<i>n</i> = 7
НОМО	-4.70	-4.43	-4.71	-4.50	-4.70	-4.55
LUMO	-3.51	-3.37	-3.76	-3.68	-3.92	-3.83
HOMO-LUMO gap	1.19	1.06	0.95	0.82	0.78	0.72

*Table S4. The energy of HOMO, LUMO and HOMO-LUMO gap of isolated i-***OE**[*n*]*.*

5. NMR Spectra

¹H-NMR of **PA**[1](Boc)-(Br, SMe)



¹³C-NMR of **PA**[1](Boc)-(Br, SMe)



¹H-NMR of **PA**[2](Boc)-(NO₂)₂



¹³C-NMR of **PA**[2](Boc)-(NO₂)₂



¹H-NMR of $PA[2](Boc)-(NH_2)_2$



¹³C-NMR of **PA**[2](Boc)-(NH₂)₂



¹H-NMR of **OE**[2]



¹³C-NMR of **OE**[2]



¹H-NMR of Boc-**OE**[3]



¹³C-NMR of Boc-**OE**[3]



¹H-NMR of Boc-**OE**[4]



¹³C-NMR of Boc-**OE**[4]



¹H-NMR of Boc-**OE**[5]



¹³C-NMR of Boc-**OE**[5]



¹H-NMR of Boc-**OE**[6]



¹³C-NMR of Boc-**OE**[6]



¹H-NMR of Boc-**OE**[7]



¹³C-NMR of Boc-**OE**[7]



¹H-NMR of **OE**[3]



¹³C-NMR of **OE**[3]



¹H-NMR of **OE**[4]



¹³C-NMR of **OE**[4]



¹H-NMR of **OE**[5]



¹³C-NMR of **OE**[5]



¹H-NMR of **OE**[6]



¹³C-NMR of **OE**[6]



¹H-NMR of **OE**[7]



¹³C-NMR of **OE**[7]



6. References

(1) Yepez, G.; Poyil, A. N.; Bugarin, A., Large-Scale Synthesis of Aniline Trimers in Different Oxidation States. *Synthesis* **2019**, *51*, 3611-3616.

(2) Sadighi, J. P.; Singer, R. A.; Buchwald, S. L., Palladium-Catalyzed Synthesis of Monodisperse, Controlled-Length, and Functionalized Oligoanilines. *J. Am. Chem. Soc.* **1998**, *120*, 4960-4976.

(3) Eelkema, R.; Anderson, H. L., Synthesis of End-Functionalized Polyanilines. *Macromolecules* **2008**, *41*, 9930-9933.

(4) Venkataraman, L.; Klare, J. E.; Tam, I. W.; Nuckolls, C.; Hybertsen, M. S.; Steigerwald, M. L., Single-Molecule Circuits with Well-Defined Molecular Conductance. *Nano Lett.* **2006**, *6*, 458-462.

(5) Datta, S., Electronic transport in mesoscopic systems. 1995.

(6) Scheer, E.; Cuevas, J. C., Molecular electronics: an introduction to theory and experiment. 2017.

(7) Li, L.; Gunasekaran, S.; Wei, Y.; Nuckolls, C.; Venkataraman, L., Reversed Conductance Decay of 1D Topological Insulators by Tight-Binding Analysis. *J. Phys. Chem. Lett.* **2022**, *13*, 9703-9710.

(8) Blum, V.; Gehrke, R.; Hanke, F.; Havu, P.; Havu, V.; Ren, X.; Reuter, K.; Scheffler, M., Ab Initio Molecular Simulations with Numeric Atom-Centered Orbitals. *Comp. Phys. Commun.* **2009**, *180*, 2175-2196.

(9) Perdew, J. P.; Burke, K.; Ernzerhof, M., Generalized Gradient Approximation Made Simple. *Phys. Rev. Lett.* **1996**, *77*, 3865.

(10) Lenthe, E. v.; Baerends, E.-J.; Snijders, J. G., Relativistic Regular Two-Component Hamiltonians. J. Chem. Phys. **1993**, *99*, 4597-4610.

(11) Arnold, A.; Weigend, F.; Evers, F., Quantum Chemistry Calculations for Molecules Coupled to Reservoirs: Formalism, Implementation, and Application to Benzenedithiol. *J. Chem. Phys.* **2007**, *126*, 174101.

(12) Bagrets, A., Spin-Polarized Electron Transport across Metal–Organic Molecules: A Density Functional Theory Approach. J. Chem. Theory Comput. **2013**, *9*, 2801-2815.

(13) Wilhelm, J.; Walz, M.; Stendel, M.; Bagrets, A.; Evers, F., Ab Initio Simulations of Scanning-Tunneling-Microscope Images with Embedding Techniques and Application to C₅₈-Dimers on Au (111). *Phys. Chem. Chem. Phys.* **2013**, *15*, 6684-6690.