Showcasing research from Professor Ryan Chiechi’s laboratory, Stratingh Institute for Chemistry, University of Groningen, Netherlands.

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Controlling destructive quantum interference in tunneling junctions comprising self-assembled monolayers via bond topology and functional groups†

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Quantum interference effects (QI) are of interest in nano-scale devices based on molecular tunneling junctions because they can affect conductance exponentially through minor structural changes. However, their utilization requires the prediction and deterministic control over the position and magnitude of QI features, which remains a significant challenge. In this context, we designed and synthesized three benzodithiophenes based molecular wires; one linearly-conjugated, one cross-conjugated and one cross-conjugated quinone. Using eutectic Ga–In (EGaIn) and CP-AFM, we compared them to a well-known anthraquinone in molecular junctions comprising self-assembled monolayers (SAMs). By combining density functional theory and transition voltage spectroscopy, we show that the presence of an interference feature and its position can be controlled independently by manipulating bond topology and electronegativity. This is the first study to separate these two parameters experimentally, demonstrating that the conductance of a tunneling junction depends on the position and depth of a QI feature, both of which can be controlled synthetically.

Introduction

Molecular electronics is concerned with the transport of charge through molecules spanning two electrodes, the fabrication of which is a challenging area of nanotechnology. In such junctions, π-conjugated molecules influence transport more than a simple, rectangular tunneling barrier; when a tunneling electron traverses the region of space occupied by orbitals localized on these molecules, its wave function can undergo constructive or destructive interference, enhancing or suppressing conductance. When the presence of different pathways in molecular system affects conductance, it is typically described as quantum interference (QI), which was originally adapted from the Aharonov–Bohm effect to substituted benzenes. The concept “quantum interference effect transistor” was also proposed using meta-benzene structures for device application. Solomon et al. further refined the concept in the context of molecular electronics where it is now well established that destructive QI leads to lower conductance in tunneling junctions. We previously demonstrated QI in SAM-based junctions using a series of compounds based on an anthracene core; AC, which is linearly-conjugated; AQ, which is cross-conjugated via a quinone moiety; and AH, in which the cross-conjugation is interrupted by saturated methylene bridges (Fig. S1†). Subsequent studies verified these findings in a variety of experimental platforms and a consensus emerged that, provided the destructive QI feature (anti-resonances in transmission) is sufficiently close to the Fermi level, Ef, cross-conjugation leads to QI. However, experimental studies on conjugation patterns other than AC/AQ are currently limited to ring substitutions such as meta-substituted phenyl rings or varied connectivities in azulene, which differ fundamentally from cross-conjugated bond topologies because they change tunneling pathways, molecular-lengths and bond topology simultaneously (Table S1†). Isolating these variables is however important because the only primary observable is conductance, which varies exponentially with molecular length. More recent work has focused on “gating” QI effects by controlling the alignment of π-systems through-space and affecting the orbital symmetry of aromatic rings with heteroatoms. These studies exclusively study the effects...
of the presence and absence of QI features; to date—and despite recent efforts—\textsuperscript{44–47} the specific effects of bond topology and electronegativity on the depth and position of QI features have not been isolated experimentally.

To address this issue, we designed and synthesized the series of benzodithiophene derivatives (BDT-n); benzo[1,2-b:4,5-b']dithiophene (BDT-1, linearly-conjugated), benzo[1,2-b:4,5-b']dithiophene-4,8-dione (BDT-2, cross-conjugated with quinone), and benzo[1,2-b:5,4-b']dithiophene (BDT-3, cross-conjugated and an isomer of BDT-1). These compounds separate the influence of cross-conjugation (bond topology) from that of the electron-withdrawing effects of the quinone functionality while controlling for molecular formula and length. We investigated the charge transport properties of these molecules in tunneling junctions comprising self-assembled monolayers (SAMs), which are relevant for solid-state molecular-electronic devices.\textsuperscript{48–51} Through a combination of density functional theory (DFT) and transition voltage spectroscopy (TVS) we show that cross-conjugation produces QI features near occupied molecular states and that the position and depth of the QI feature is strongly influenced by the strongly electron-withdrawing quinone functionality, which places these features near unoccupied states while simultaneously bringing those states close to $E_F$. Thus, by controlling bond topology and electronegativity separately, the conductance can be tuned independently of length and connectivity via the relative positions of the QI features and molecular states and not just the presence or absence of such features.

**Results and discussion**

To isolate molecular effects on transport, it is important to control for changes to the width of the tunneling barrier which, in SAMs, is typically defined by the end-to-end lengths of the molecules. Conductance $G$ generally varies exponentially with the barrier-width $d$ such that $G = G_0 \exp(-\beta d)$, where $G_0$ is the theoretical value of $G$ when $d = 0$, and $\beta$ is the tunneling decay coefficient. Since $\beta$ depends on the positions of molecular states relative to $E_F$ and we are comparing compounds with very different redox potentials (orbital energies) we can only ascribe changes to $G$ if $d$ is invariant across the series. Furthermore, to isolate the variable of bond topology experimentally, the electronic properties of the linear- and cross-conjugated compounds must be nearly identical. Fig. 1a shows the structures of the BDT-n series and AQ; the “arms” are linearly-conjugated phenylethynylacetylenes (highlighted in the light blue background) and the cores (Ar, highlighted in the brown background) are substituted by the structures indicated. The variation in the end-to-end lengths of these compounds is within 1 Å and the linear- and cross-conjugated compounds BDT-1 and BDT-3 differ only by the relative position of sulfur atoms; they have the same molecular formula. The synthesis, full characterization and a detailed discussion of their properties are provided in the ESI.\textsuperscript{†} Note that we include AQ in the series as a benchmark for destructive QI effects.

![Fig. 1](image.png)

We measured tunneling charge transport through metal-molecule-metal junctions comprising BDT-1, BDT-2, BDT-3 and AQ using conformal eutectic Ga-In (EGaIn) contacts as top electrodes.\textsuperscript{52} We utilized an established procedure of the \textit{in situ} deprotection of thioacettes\textsuperscript{41,42} to form well-defined SAMs on Au substrates; these substrates served then as bottom electrodes. We refer to the assembled junctions as Au/SAM/EGaIn (Fig. S1*); the “/” and “//” denote a covalent and van der Waals interfaces, respectively. The geometry of the junctions is shown in Fig. 1b. To verify that the structural similarities of the compounds carry over into the self-assembly process, we characterized the SAMs of BDT-n by several complementary techniques, including (high-resolution) X-ray photoelectron spectroscopy (HRXPS/XPS) and angle-resolved near-edge X-ray absorption fine structure (NEXAFS) spectroscopy. These data are discussed in detail in the ESI and summarized in Table 1. The characterization of SAMs of AQ is reported elsewhere.\textsuperscript{16,41} The XPS and NEXAFS data suggest that the molecules in the BDT-n SAMs are assembled upright with the tilt angle of approximately 35°. The molecules are packed densely on the order of $10^{14}$ molecules per cm$^2$ as are similar conjugated molecular wire compounds.\textsuperscript{41}

Fig. 2a shows the current-density \textit{versus} voltage ($J/V$) curves for the BDT-n series and AQ using EGaIn top contacts. BDT-1 is the most conductive across the entire bias window. The conductance of linearly-conjugated BDT-1 and AC (Fig. S1†; a linearly-conjugated analog of AQ), are almost identical (Fig. S21†), meaning that the low-bias conductivity and/or values of $J$ are directly comparable between the AC/AQ and BDT-n series. As expected, the cross-conjugated BDT-2, BDT-3 and AQ are all less conductive than BDT-1 (and AC). The low-bias conductivity (from the ohmic region, $-0.1$ V to $0.1$ V) of
Table 1 Summary of the properties of SAMs of BDT-n and Au/BDT-n//EGaIn junctions

<table>
<thead>
<tr>
<th>Compound</th>
<th>BDT-1</th>
<th>BDT-2</th>
<th>BDT-3</th>
<th>C18 reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>XPS thickness (Å)</td>
<td>17 ± 3</td>
<td>18 ± 4</td>
<td>19 ± 4</td>
<td>n.d.</td>
</tr>
<tr>
<td>HRXPS thickness (Å)</td>
<td>19.81 ± 0.40</td>
<td>22.30 ± 0.45</td>
<td>17.17 ± 0.34</td>
<td>20.9</td>
</tr>
<tr>
<td>Averaged XPS thickness (Å)</td>
<td>18.4</td>
<td>20.2</td>
<td>18.4</td>
<td>n.d.</td>
</tr>
<tr>
<td>Water contact angle (°)</td>
<td>68.3 ± 4.8</td>
<td>65.8 ± 4.0</td>
<td>62.8 ± 4.6</td>
<td>104.2 ± 2.2</td>
</tr>
<tr>
<td>Density (10^14 molecules per cm²)</td>
<td>2.05</td>
<td>3.30</td>
<td>2.33</td>
<td>4.63</td>
</tr>
<tr>
<td>Area molecules per Å²</td>
<td>48.8 ± 2</td>
<td>30.3 ± 2</td>
<td>43.0 ± 2</td>
<td>21.6</td>
</tr>
<tr>
<td>log</td>
<td>@0.5 V (A cm⁻²)</td>
<td>-2.34 ± 0.17</td>
<td>-4.09 ± 0.23</td>
<td>-3.53 ± 0.20</td>
</tr>
<tr>
<td>Yield of working junctions (%)</td>
<td>88.9</td>
<td>93.8</td>
<td>84.2</td>
<td>79 (ref. 41)</td>
</tr>
<tr>
<td>Num. working EGaIn junctions</td>
<td>32</td>
<td>30</td>
<td>32</td>
<td>28 (ref. 41)</td>
</tr>
<tr>
<td>Total J/V traces</td>
<td>643</td>
<td>626</td>
<td>666</td>
<td>280 (ref. 41)</td>
</tr>
</tbody>
</table>

The quinones (BDT-2 and AQ), however, is even more suppressed than the cross-conjugated BDT-3, while the magnitudes of $J$ for BDT-2, BDT-3 and AQ are similar beyond ~0.5 V. We observed similar behavior in QI mediated by through-space conjugation in which the compound with an interference feature very close to $E_F$ exhibited a sharp rise in $J$, eventually crossing $J/V$ curve of the compound with a feature further from $E_F$. This observation suggests that, as the junction is biased, the transmission probability “climbs” the interference feature rapidly, bringing highly transmissive conduction channels into the bias window at sufficiently low values of $V$ to meet and exceed the total transmission of the compound for which the interference feature is far from $E_F$ at zero bias. Further discussion on the asymmetry of $J/V$ curves is included in the ESI.†

To better compare the conductance of the molecules, we calculated the low-bias conductivities and normalized them to BDT-1. These values are plotted in Fig. 2b, showing that cross-conjugation lowers the conductance of BDT-3 by an order of magnitude compared to BDT-1 and the quinone functionality of BDT-2 and AQ lowers it by two orders of magnitude, in agreement with the analogous behavior of AC and AQ. To control for large-area effects (e.g., if there are defects in the SAM), we measured BDT-n series by conducting-probe atomic force microscopy (CP-AFM) with Au electrodes and found the same trend: BDT-1 > BDT-3 > BDT-2, however, a direct comparison of low-bias conductivities was precluded by the extremely high resistance of BDT-2 and AQ at low bias. These data are discussed in detail in the ESI. Thus, we conclude that quinones suppress conductance more than cross-conjugation alone, irrespective of the measurement/device platform.

For insight into the shapes of the $J/V$ curves and the conductance, we simulated the transmission spectra, $T(E)$ vs. $E - E_F$ ($E_F$ value of ~−4.3 eV, see Experimental section), of the BDT-n series using density functional theory (DFT) and compared the resulting curves with AQ (Fig. 3). These calculations, which are discussed in more detail in the Computational methodology section of the ESI,‡ simulate the transmission spectra through isolated molecules in vacuum at zero bias and are useful for predicting trends in conductance. There are three important features of these curves: (1) only the compounds with cross-conjugation (including quinones) show sharp dips (anti-resonances or QI features) in the frontier orbital gap; (2) the dips occur near $E_F$ only for the two quinones; and (3) the QI

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Fig. 2 (a) Plots of log|$J$ (A cm⁻²)| versus $V$ for Au/SAM//EGaIn junctions comprising SAMs of BDT-1 (salmon up-triangles), BDT-2 (purple down-triangles), BDT-3 (pink diamonds) and AQ (grey circles). Each datum is the peak position of a Gaussian fit of log|$J$ for that voltage. The error bars are 95% confidence intervals taking each junction as a degree of freedom. (b) Normalized low bias conductance, linearly conjugated BDT-1 (salmon ball) features the highest values, the quinone BDT-2 (purple ball) and AQ (grey ball) the lowest and cross conjugated BDT-3 (pink ball) is in between.
features are more pronounced for the molecules in which the cross-conjugation is caused by a quinone moiety as opposed to the carbon–carbon bond topology. When bias is applied to a junction, the \( E \)–axis of the transmission plot shifts and \( E_F \) broadens such that an integral starting at \( E - E_F = 0 \) eV and widening to larger ranges of \( E - E_F \) is a rough approximation of how \( T(E) \) translates into current, \( I(V) \). This relationship is apparent in the slightly lower conductance of \( AQ \) compared to \( BDT-2 \) (Fig. 2b) and the slightly lower values of \( T(E) \) for \( AQ \) compared to \( BDT-2 \) across the entire range of \( E - E_F \). The proximities of the QI features to \( E_F \) are also apparent in the \( J/V \) curves (Fig. 2a). As the junction is biased, the minimum of the QI feature shifts such that, by 0.5 V, the transmission probabilities are roughly equal for \( BDT-n \) and \( AQ \).

The shape of \( T(E) \) near \( E - E_F = 0 \) eV is roughly traced by differential conductance plots of \( \log \left( \frac{dI}{dV} \right) \) vs. \( V \). The shapes of these plots are different between the resonances (\( T(E) \rightarrow 1 \)) near the frontier orbitals. The sharp dips in the spectra of \( BDT-2 \) (purple), \( BDT-3 \) (pink) and \( AQ \) (grey) indicated with arrows are destructive QI features. The colors on the bottom axis are with respect to the \( E_F \) value of \(-4.3\) eV.

Fig. 3 Transmission spectra for isolated molecules of \( BDT-n \) and \( AQ \). The spectrum of \( BDT-1 \) (salmon) is featureless between the resonances (\( T(E) \rightarrow 1 \)) near the frontier orbitals. The sharp dips in the spectra of \( BDT-2 \) (purple), \( BDT-3 \) (pink) and \( AQ \) (grey) indicated with arrows are destructive QI features. The energies on the bottom axis are with respect to the \( E_F \) value of \(-4.3\) eV.

Fig. 4 Differential conductance heatmap plots of Au/SAM/EGaIn junctions comprising \( BDT-1 \) (top-left), \( BDT-2 \) (top-right), \( BDT-3 \) (bottom-left) and \( AQ \) (bottom-right) showing histograms binned to \( \log \left( \frac{dI}{dV} \right) \) (differential conductance, \( Y \)-axis) versus potential (\( V \), \( X \)-axis). The colors correspond to the frequencies of the histograms and lighter (more yellow) colors indicate higher frequencies. The bright spots near \( \pm 1 \) V are due to the doubling of data that occurs in the forward/return \( J/V \) traces. The plots for both \( BDT-2 \) and \( AQ \), which contain quinones, are \( V \)-shaped at low bias and exhibit negative curvature, indicating a destructive QI feature near \( E_F \), while the plots of \( BDT-1 \) and \( BDT-3 \) are \( U \)-shaped.
such that the J/V characteristics and transmission plots of AQ and BDT-2 are nearly indistinguishable despite the presence of two thienyl groups in BDT-2. These results also suggest that tunneling transport is mediated by the HOPS (hole-assisted tunneling) for BDT-1 and BDT-3 and by the LUPS (electron-assisted tunneling) for BDT-2 and AQ because tunneling current is dominated by the resonance(s) closest to $E_F$.

To further investigate the mechanism of transport, we measured transition voltages, $V_{\text{trans}}$ (Table S3, Fig. S17 and S18†), which provide information about the energy offset between $E_F$ and the dominant frontier orbital. Fig. 5a shows the levels for the BDT-$n$ series calculated by DFT with respect to $E_F$ (−4.3 eV), clearly predicting LUPS-mediated tunneling for BDT-2 and AQ. Fig. 5b compares the experimental values of $V_{\text{trans}}$ to the energy differences between $E_F$ and the frontier orbitals. The salient feature of Fig. 5b is that the trend in $|E_{\text{HOPS}} - E_F|$ opposes the trend in $V_{\text{trans}}$ such that the trend in experimental values of $V_{\text{trans}}$ agrees with DFT only when we compare $V_{\text{trans}}$ with $|E_{\text{HOPS}} - E_F|$ for BDT-1 and BDT-3, and with $|E_{\text{LUPS}} - E_F|$ for BDT-2 and AQ. Thus, DFT calculations combined with experimental values of $V_{\text{trans}}$ predict electron-assisted tunneling for BDT-2 and AQ. This degree of internal consistency between the experiment and theory is important because, ultimately, the only primary observable is conductance, which we plot as J/V curves, differential conductance heatmaps and Fowler–Nordheim plots (from which we extract $V_{\text{trans}}$). And we find remarkable agreement between these direct and indirect observations and DFT calculations on model junctions comprising single molecules.

**Conclusion**

The key question of this work is how cross-conjugation and electronegativity affect QI features. Based on our experimental observations and calculations, we assert that destructive QI induced by cross-conjugation is highly sensitive to the functional groups that induce the cross-conjugation and that quinones are, therefore, a poor testbed for tuning QI effects (beyond switching them on and off†) because their strong electron-withdrawing nature places a deep, destructive feature near $E_F$ irrespective of other functional groups (in our case, two fused thiophene rings barely make a difference). Comparing a quinine to a hydrocarbon also compares HOPS-mediated tunneling to LUPS-mediated tunneling between molecules with significantly different band-gaps and absolute frontier orbital energies. In contrast, BDT-1 and BDT-3 are heterocyclic isomers with no functional groups, identical molecular formulas, nearly-identical HOPS, identical lengths that translate into SAMs of identical thicknesses, and transport is dominated by the HOPS. They isolate the single variable of conjugation patterns, allowing us to separate bond topology (cross-conjugation) from electronic properties (functional groups), giving experimental and theoretical insight into the relationship between bond topology and QI. Our results suggest that there is a lot of room to tune the conductance of moieties derived from BDT-3 by including pendant groups (e.g., halogens, CF$_3$ groups or acidic/basic sites) that shift the QI feature gradually towards $E_F$ synthetically and/or in response to chemical signals.

**Experimental**

**Synthesis**

**Reagents.** All reagents and solvents were commercial and were used as received. Benzo[1,2-b:4,5-b']dithiophene was purchased from TCI. 2,6-dibromobenzof[1,2-b:4,5-b']dithiophene-4,8-dione,$^{58}$ 2,6-dibromobenzof[1,2-b:4,5-b']dithiophene,$^{59}$ 4-ethyl-1-thioacetylbenzene$^{60}$ and 1-tert-butylthio-4-ethylbenzene$^{61}$ were synthesized according to literature procedures.

**NMR and mass spectra.** $^1$HNMR and $^{13}$C NMR were performed on a Varian Unity Plus (400 MHz) instrument at 25 °C, using tetramethylsilane (TMS) as an internal standard. NMR shifts are reported in ppm, relative to the residual protonated solvent signals of CDC$_1$: (δ = 7.26 ppm) or at the carbon absorption in CDC$_1$: (δ = 77.0 ppm). Multiplicities are denoted

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**Fig. 5** (a) Energy offsets of the frontier orbitals calculated using DFT with respect to $E_F$ value of −4.3 eV. (b) The energy offsets (salmon and purple lines, right axis) plotted with the measured values of $V_{\text{trans}}$ (black line, left axis). The salmon line plots the energy offsets of the HOPS. The purple line plots the smallest energy difference (purple arrows in (a)): $|E_{\text{HOPS}} - E_{\text{Fermil}}|$ for BDT-1 and BDT-3, $|E_{\text{LUPS}} - E_{\text{Fermil}}|$ for BDT-2 and AQ. The exact values of $V_{\text{trans}}$ and the orbital energies are shown in Tables S3 and S5.$^\dagger$
as: singlet (s), doublet (d), triplet (t) and multiplet (m). High Resolution Mass Spectroscopy (HRMS) was performed on a JEOL JMS 600 spectrometer.

**UV-Vis and cyclic voltammetry.** UV-Vis measurements were carried out on a Jasco V-630 spectrometer. Cyclic voltammetry (CV) was carried out with a Autolab PGSTAT100 potentiostat in a three-electrode configuration.

**General.** Unless stated otherwise, all crude compounds were isolated by bringing the reaction to room temperature, extracting with CH2Cl2, washing with saturated NaHCO3 water and then brine. The organic phase was then collected and dried over Na2SO4 and the solvents removed by rotary evaporation.

Synthetic schemes and NMR spectra are provided in the ESI.

**2,6-Dibromobenz[1,2-b:4,5-b]dithiophene (1).** Benzo[1,2-b:4,5-b’]dithiophene (540 mg, 2.84 mmol) were dissolved in 70 mL anhydrous THF under an atmosphere of N2, cooled to −78 °C and n-butyllithium (8.5 mmol, 5.3 mL, 1.6 M in hexane) was added drop-wise. The solution was stirred for 30 min in the cold bath before being warmed to room temperature and stirred for and additional 20 min. The mixture was cooled to −78 °C again and a solution of CBr4 (2.8 g, 8.5 mmol) in 5 mL anhydrous THF was added. The solution was stirred for 30 min in the cold bath before being quenched with concentrated sodium bicarbonate solution (10 mL) at −78 °C. The crude solid was purified by recrystallization from CHCl3 to give 1 (890 mg, 90%) as colorless platelets. 1HNMR (400 MHz, CDCl3) δ: 7.97 (d, J = 8.2, 4H), 7.53 (d, J = 2.8, 4H), 7.59 (s, 1H), 7.52 (d, J = 4, 4H), 4.75 (s, 2H); 13CNMR (100 MHz, CDCl3) δ: 138.36, 136.88, 125.63, 116.00, 115.10.

**2,6-Dibromobenz[1,2-b:4,5-b]dithiophene (BDT-1).** 2,6-Dibromobenz[1,2-b:4,5-b]dithiophene (125 mg, 0.36 mmol) and 4-ethylthiophen-2-yl acetyl chloride (100 mg, 0.71 mmol) were dissolved in mixture of fresh distilled Et3N (5 mL) and anhydrous THF (10 mL). After degassing with dry N2, the catalysts Pd[PPh3]4 (58 mg, 0.05 mmol) and CuI (10 mg, 0.05 mmol) were added. The reaction mixture was refluxed overnight under N2. The crude solid was purified by column chromatography to give BDT-1 (78 mg, 40%). 1HNMR (400 MHz, CDCl3) δ: 8.17 (s, 2H), 7.59 (d, J = 2.8, 4H), 7.55 (s, 2H), 7.43 (d, J = 2.8, 4H), 2.45 (s, 6H); 13CNMR (100 MHz, CDCl3) δ: 195.88, 140.66, 140.46, 136.90, 136.90, 136.74, 136.51, 130.89, 126.53, 126.25, 119.27, 97.57, 87.31, 32.97. HRMS (ESI) calcd for C30H18O2S4 [M + H]+: 539.0264, found: 539.0247.

**2,6-Bis[4-acetylthiophenyl]ethyl]benzo[1,2-b:4,5-b’]dithiophene (BDT-3).**2 TiCl4 (0.042 mL, 0.388 mmol) was added drop-wise to a solution of compound (7) (100 mg, 0.176 mmol) and CH3(CO)Cl (0.03 mL, 0.377 mmol) in CH2Cl2 at 0 °C. The resulting mixture was stirred at room temperature for 10 min and the conversion was monitored by TLC (hexanes/CH2Cl2, 2:1). Upon completion the reaction was quenched with water (10 mL). The crude solid was purified by column chromatography to give BDT-3 (25 mg, 26%). 1HNMR (400 MHz, CDCl3) δ: 8.17 (s, 1H), 8.15 (s, 1H), 7.59 (d, J = 7.2, 4H), 7.58 (s, 2H), 7.43 (s, 1H), 7.35 (d, J = 8.2, 4H), 2.45 (s, 3H); 13CNMR (100 MHz, CDCl3) δ: 195.88, 141.43, 140.03, 136.90, 134.76, 131.51, 131.48, 126.27, 126.50, 120.94, 117.42, 87.15, 32.97. HRMS(ESI) calcd for C30H18O2S4 [M + H]+: 539.0264, found: 539.0247.

**Self-assembled monolayers**

The SAMs of BDT-n were formed via in situ deprotection41,42 on template-stripped Au substrates.43 Freshly template-stripped substrates were immersed into 3 mL of 50 μM solutions of the thiocarbonyl precursors in freshly distilled toluene inside a nitrogen-filled glovebox and sealed under a nitrogen atmosphere. The sealed vessels were kept inside a nitrogen flow box (O2 below 3%, RH below 15%) overnight; all subsequent handling and EAgIn measurements were performed inside the flowbox. 1.5 h prior to measurement, 0.05 mL of 17 mM diazabicyclocoundec-7-ene (DBU) in toluene was added to the precursor/substrate solution. The substrates were then rinsed with toluene and allowed to dry for 30 min before performing the measurements.

**Characterization**

The SAMs of BDT-n were characterized by XPS (laboratory and synchrotron), NEXAFS spectroscopy, UPS and water contact angle goniometry. In some cases, SAMs of CH3(CH2)15SH or...
CH$_3$(CH$_2$)$_{17}$SH on Au were used as a reference. See ESI† for details.

**Transport measurements**

EGaIn. For each SAM, at least 10 junctions were measured on each of three different substrates by applying a bias from 0.00 V to 1.00 V → −1.00 V → 0.00 V with steps of 0.05 V. At least 20 trace/re-trace cycles were measured for each junction; only junctions that did not short over all 20 cycles were counted as “working junction” for computing yields.

CP-AFM. $I$–$V$ measurements were performed on a Bruker AFM Multimode MMAFM-2 equipped with a Peak Force TUNA Application Module. The Au on mica substrates were removed from the flowbox immediately prior to measurement, which occurred under ambient conditions by contacting the SAM with an Au-coated Si$_3$N$_4$ tip with a nominal radius of 30 nm (NPG-10, Bruker; resonant frequency: 65 kHz, spring constant: 0.35 N m$^{-1}$). The AFM tip was grounded and the samples were biased from −1.0 V → 1.0 V → −1.0 V on Au$^{\text{Mica}}$. 11 trace/re-trace cycles per junction were performed and the top electrode was removed from SAMs between junctions.

**Processing.** All raw data were processed algorithmically using Scientific Python to generate histograms, Gaussian fits, extract transition voltages and construct differential conductance heatmap plots.

**DFT calculations**

Calculation were performed using the ORCA 4 software package$^{65,66}$ and the ARTAIOS-030417 software package.$^{67,68}$ The molecules terminating with thiols were first minimized to find the gas-phase geometry and then attached to two 18-atom Au(111) clusters via the terminal sulfur atoms with a distance of 1.75 Å at hexagonal close-pack hollow sites (hydrogen atom from the thiol was deleted before attaching the electrodes).

Single-point energy calculations were performed on this model junction using B3LYP/G and LANL2DZ basis sets according to the detailed step-wise procedure for all the calculations involved is further described in ESI†.

**Conflicts of interest**

There are no conflicts to declare.

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**References**


