

## Supplementary Information

### Aromaticity Decreases Single-Molecule Junction Conductance

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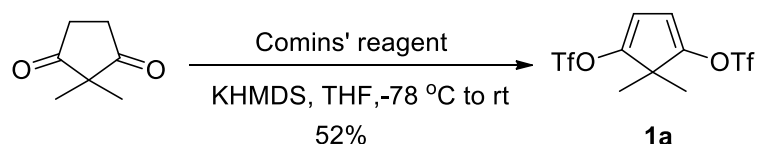
- 1. Synthesis Information, NMR and X-Ray Structure Determination**
- 2. Measurement, Data Analysis and Additional Data**
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## Synthesis Information:

Chemicals: Solvents, inorganic salts, and organic reagents were purchased from commercial sources and used without further purification unless otherwise mentioned.

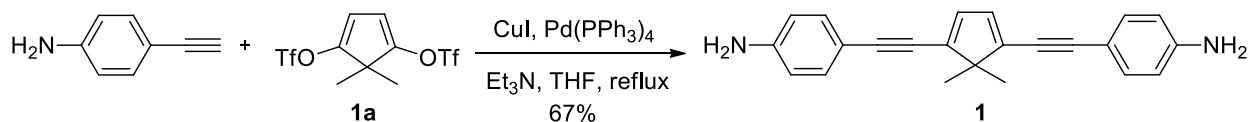
Chromatography: Merck pre-coated 0.25 mm silica plates containing a 254 nm fluorescence indicator were used for analytical thin-layer chromatography. Flash chromatography was performed on 230-400 mesh silica (SiliaFlash® P60) from Silicycle. Spectroscopy: NMR spectra were obtained on a Bruker DPX 300 or 400 MHz spectrometer. Spectra were analyzed with the MestreNova Software (Version 6.1). CI-MS spectra were taken on a Nermag R-10-10 instrument. Compounds **1**, **2**, **3** were prepared by the Sonogashira coupling of 4-ethynylaniline with 2,5-dibromofuran, 2,5-dibromothiophene and **1a**, respectively. 2,5-bis(4-aminophenyl)furan (**5**)<sup>1</sup>, 2,5-bis(4-aminophenyl)thiophene (**6**)<sup>2</sup> were prepared according to the known procedures.

### 1,4-Bis[(trifluoromethanesulfonyl)oxy]-5,5-dimethylcyclopenta-1,3-diene (**1a**)



To a stirred solution of 2,2-dimethylcyclopentane-1,3-dione<sup>3</sup> (989 mg, 7.85 mmol) and *N*-(5-chloro-2-pyridyl)triflimide (Comins' reagent)<sup>4</sup> (6.55 g, 16.6 mmol) in dry THF (45 mL) at  $-78^{\circ}\text{C}$ , a solution of potassium hexamethyldisilazide (0.5 M in toluene, 17.5 mmol) was added dropwise. The reaction mixture was stirred at this temperature for 1 h and then it was slowly warmed to room temperature. The mixture was diluted with hexane, washed with water, 10% NaOH and brine. The organic phase was dried ( $\text{Na}_2\text{SO}_4$ ) and concentrated under reduced pressure. The crude compound was further purified by flash chromatography (hexane) to give the title compound **1a** as a solid (1.62 g, 52%). <sup>1</sup>H NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  6.04 (s, 2H), 1.29 (s, 6H); <sup>13</sup>C NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  154.4, 118.5 (q,  $J = 318.8$  Hz), 110.8, 48.9, 18.9; <sup>19</sup>F NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -72.2 (s).

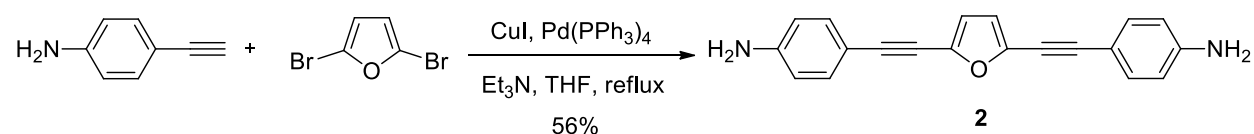
### 1,4-bis(4-aminophenylethynyl)-5,5-dimethylcyclopenta-1,3-diene (**1**)



Degassed  $\text{Et}_3\text{N}$  (987 mg, 9.77 mmol, 4.5eq) and 4-ethynylaniline (500 mg, 4.27 mmol, 2eq) was added to the mixture of **1a** (833 mg, 2.13 mmol, 1eq),  $\text{Pd}(\text{PPh}_3)_4$  (123 mg, 0.106 mmol, 5%),  $\text{CuI}$

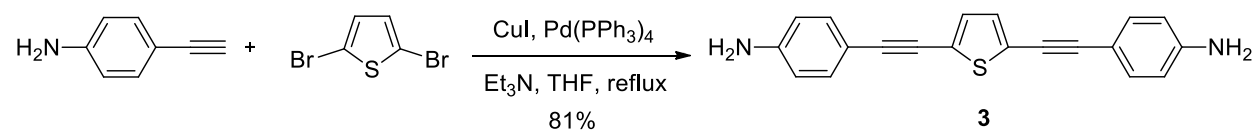
(21 mg, 0.109 mmol, 5%) in 15 mL of dry THF under Argon. The mixture was refluxed 16 h and then cooled down. The mixture was quenched by H<sub>2</sub>O and then extracted with ethyl acetate. The organic extract was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered and evaporated under reduced pressure. The crude compound was purified by flash column chromatography (gradient elution, dichloromethane then hexane: ethyl acetate=1:1) over silica gel (neutralized by 2% Et<sub>3</sub>N in hexane) to afford the compound **1** as a yellow solid in 67% yield (471 mg). <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) δ 7.15 (d, *J* = 8.4 Hz, 4H), 6.55-6.53 (m, 6H), 5.57 (s, 4H), 1.18 (s, 6H); <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>) δ 149.4, 139.0, 132.4, 131.5, 113.6, 108.4, 98.9, 82.7, 56.2, 22.4; HRMS (FAB+) calcd for C<sub>23</sub>H<sub>20</sub>N<sub>2</sub>: 324.1626; found 324.1641.

### 2,5-bis(4-aminophenylethynyl)furan (**2**)



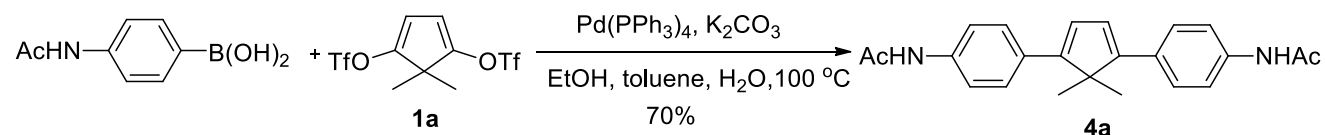
The compound **2** was prepared by a similar procedure to the preparation of compound **1**. <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) δ 7.21 (d, *J* = 8.4 Hz, 4H), 6.78 (s, 2H), 6.56 (d, *J* = 8.4 Hz, 4H), 5.70 (s, 4H); <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>) δ 150.2, 137.0, 132.6, 115.5, 113.6, 106.3, 95.9, 76.6; HRMS (FAB+) calcd for C<sub>20</sub>H<sub>14</sub>ON<sub>2</sub>: 298.1106; found 298.1107.

### 2,5-bis(4-aminophenylethynyl)thiophene (**3**)



The compound **3** was prepared by a similar procedure to the preparation of compound **1**. <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) 7.21-7.19 (m, 6H), 6.55 (d, *J* = 8.4 Hz, 4H), 5.66 (s, 4H); <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>) δ 149.9, 132.6, 131.4, 123.6, 113.6, 107.0, 96.0, 79.4; HRMS (FAB+) calcd for C<sub>20</sub>H<sub>14</sub>N<sub>2</sub>S: 314.0878; found 314.0875.

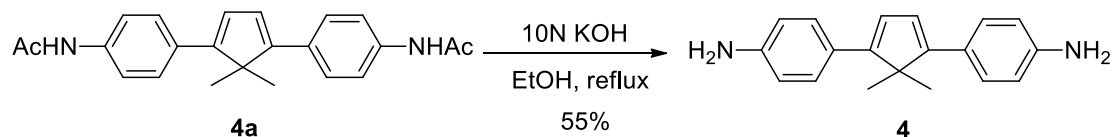
### 1,4-bis(4-acetamidophenyl)-5,5-dimethylcyclopenta-1,3-diene (**4a**)



A mixture of **1a** (426 mg, 1.09 mmol), 4-acetamidophenylboronic acid (489 mg, 2.73 mmol), Pd(PPh<sub>3</sub>)<sub>4</sub> (125 mg, 0.108 mmol), and K<sub>2</sub>CO<sub>3</sub> (753 mg, 5.46 mmol) in 21 mL of nitrogen-purged ethanol:toluene:water (1:1:1) was stirred at 100°C overnight. The resulting mixture was cooled

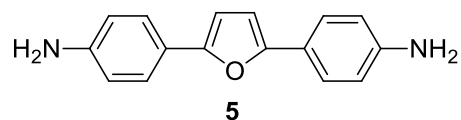
down, quenched with water, and extracted with ethyl acetate. The combined organic layers were washed with brine, dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated in vacuum. Purification by flash chromatography on silica gel (gradient elution hexane: ethyl acetate 1:1 to 0:1) afforded the coupling product **4a** as a red solid in 70% yield (272 mg). <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) δ 9.98 (s, 2H), 7.61-7.55 (m, 8H), 6.83 (s, 2H), 2.05 (s, 6H); 1.43 (s, 6H); <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>) δ 168.1, 155.6, 137.8, 129.5, 126.3, 124.6, 118.9, 52.4, 24.0, 23.2; HRMS (FAB<sup>+</sup>) calcd for C<sub>23</sub>H<sub>24</sub>O<sub>2</sub>N<sub>2</sub>: 360.1838; found 360.1852.

#### 1,4-bis(4-aminophenyl)-5,5-dimethylcyclopenta-1,3-diene (**4**)



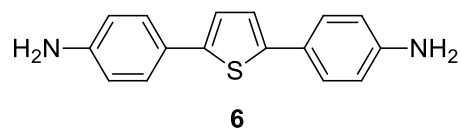
To a solution of compound **4a** (94 mg, 0.26 mmol) in 5 mL of ethanol was added 10 N KOH (1.0 mL, 10.0 mmol) and the mixture was stirred at 100°C for 24 h. The resulting mixture was cooled down, quenched with water, and extracted with ethyl acetate. The combined organic layers were dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated in vacuum. Purification by flash chromatography on silica gel (ethyl acetate: hexane= 1:1) afforded the product **4** in 55% yield (40 mg). <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) δ 7.29 (d, *J* = 8.4 Hz, 4H), 6.57-6.55 (m, 6H), 5.14 (s, 4H), 1.36 (s, 6H); <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>) δ 155.0, 147.2, 126.7, 123.1, 121.4, 113.8, 52.0, 23.6; HRMS (FAB<sup>+</sup>) calcd for C<sub>19</sub>H<sub>20</sub>N<sub>2</sub>: 276.1626; found 276.1637.

#### 2,5-bis(4-aminophenyl)furan (**5**)

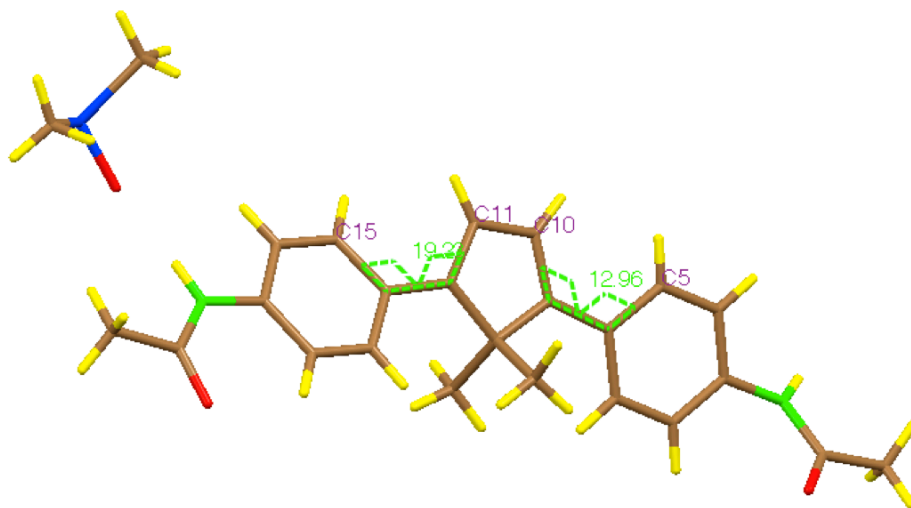


<sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) δ 7.40 (d, *J* = 8.8 Hz, 4H), 6.59 (d, *J* = 8.4 Hz, 4H), 6.56 (s, 2H), 5.28 (s, 4H); <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>) δ 152.2, 148.0, 124.3, 118.8, 113.9, 103.7; MS (FAB<sup>+</sup>): 250 (M<sup>+</sup>, 100).

#### 2, 5-bis(4-aminophenyl)thiophene (**6**)



$^1\text{H}$  NMR (400 MHz,  $\text{DMSO-}d_6$ )  $\delta$  7.29 (d,  $J = 8.8$  Hz, 4H), 7.10 (s, 2H), 6.57 (d,  $J = 8.4$  Hz, 4H), 5.29 (s, 4H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{DMSO-}d_6$ )  $\delta$  148.3, 141.3, 125.9, 121.8, 121.2, 114.0; MS ( $\text{FAB}^+$ ): 266 ( $\text{M}^+$ , 100).



**Figure S1.** Crystal structure of **4a** (crystallized in DMSO). Dihedral angle Between C5-C10 is  $13^\circ$  and C11-C15 is  $19^\circ$ . Brown = Carbon; Yellow = Hydrogen; Red = Oxygen; Green = Nitrogen; Blue = Sulfur.

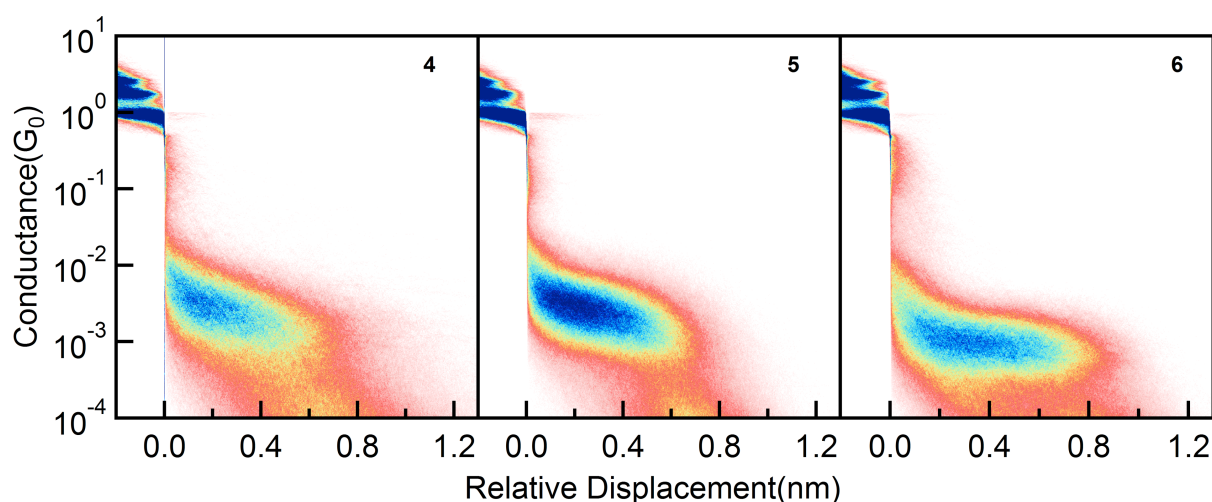
## Measurement, Data Analysis and Additional Data

Single molecule conductance measurements are performed using a home-built modified Scanning Tunneling Microscope (STM). The STM tip is a 0.25mm diameter gold wire (99.998%, Alfa Aesar). The substrate is a gold-coated (99.999%, Alfa Aesar) mica surface. A commercial single-axis piezoelectric positioner (Nano-P15, Mad City Labs) is used to achieve sub-angstrom level control of the tip-substrate distance. The STM is controlled using a custom program using IgorPro (Wavemetrics, Inc.). All of the experiments are conducted at room temperature in ambient conditions.

In the STM-Break Junction technique, the tip is repeatedly brought in and out of contact with the substrate, while a constant bias is applied and current is measured. A gold metal contact with a conductance of at least  $5 G_0$  is formed before pulling out. Tip is withdrawn from the

substrate at a speed of about 16nm/s, and current is recorded at a fixed applied bias voltage of 225mV at a 40kHz data acquisition rate. The target molecules are introduced in solution with the same concentration  $\sim 0.2\text{mM}$  in solvent 1,2,4-Trichlorobenzene. Right after the contact breaks, a target molecule in the vicinity can bridge the gap so that its conductance ( $G=I/V$ ) can be measured. Tens of thousands of conductance vs. displacement traces were obtained for each molecule studied and conductance histograms are constructed without any sort of data selection.

Below we show the 2d conductance histograms of molecule 4, 5 and 6. The same data sets are used to create the log-binned histograms included in the manuscript.



**Figure S2** 2D histograms for 4, 5 and 6 showing conductance peak extending over a distance of around 0.8 nm relative to the break of the  $G_0$  contact.

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