Supplementary Information

Aromaticity Decreases Single-Molecule Junction Conductance

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Contents:

1. Synthesis Information, NMR and X-Ray Structure Determination

2. Measurement, Data Analysis and Additional Data

3. References
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), 2,5-bis(4-aminophenyl)thiophene (6) 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\(^{3}\) (989 mg, 7.85 mmol) and \(N\)-(5-chloro-2-pyridyl)triflimide (Comins' reagent)\(^{4}\) (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 (Na\(_2\)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%).\(^{1}\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 6.04 (s, 2H), 1.29 (s, 6H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 154.4, 118.5(q, \(J\) = 318.8 Hz), 110.8, 48.9, 18.9; \(^{19}\)F NMR (376 MHz, CDCl\(_3\)) \(\delta\) -72.2 (s).

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

Degassed Et\(_3\)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), Pd(PPh\(_3\))\(_4\) (123 mg, 0.106 mmol, 5%), 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 H₂O and then extracted with ethyl acetate. The organic extract was dried over anhydrous Na₂SO₄, 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% Et₃N in hexane) to afford the compound 1 as a yellow solid in 67% yield (471 mg).

1H NMR (400 MHz, DMSO-d₆) δ 7.15 (d, J = 8.4 Hz, 4H), 6.55-6.53 (m, 6H), 5.57 (s, 4H), 1.18 (s, 6H); 13C NMR (100 MHz, DMSO-d₆) 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 C23H20N₂: 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. 1H NMR (400 MHz, DMSO-d₆) 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); 13C NMR (100 MHz, DMSO-d₆) δ 150.2, 137.0, 132.6, 115.5, 113.6, 106.3, 95.9, 76.6; HRMS (FAB+) calcd for C20H14ON: 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. 1H NMR (400 MHz, DMSO-d₆) δ 7.21-7.19 (m, 6H), 6.55 (d, J = 8.4 Hz, 4H), 5.66 (s, 4H); 13C NMR (100 MHz, DMSO-d₆) δ 149.9, 132.6, 131.4, 123.6, 113.6, 107.0, 96.0, 79.4; HRMS (FAB+) calcd for C20H14N2S: 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(PPh₃)₄ (125 mg, 0.108 mmol), and K₂CO₃ (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$_2$SO$_4$ 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). $^1$H NMR (400 MHz, DMSO-$d_6$) $\delta$ 9.98 (s, 2H), 7.61-7.55 (m, 8H), 6.83 (s, 2H), 2.05 (s, 6H); 1.43 (s, 6H); $^{13}$C NMR (100 MHz, DMSO-$d_6$) $\delta$ 168.1, 155.6, 137.8, 129.5, 126.3, 124.6, 118.9, 52.4, 24.0, 23.2; HRMS (FAB+) calcd for C$_{23}$H$_{24}$O$_2$N$_2$: 360.1838; found 360.1852.

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

![Diagram of 4a](image1)

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$^\circ$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$_2$SO$_4$ 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). $^1$H NMR (400 MHz, DMSO-$d_6$) $\delta$ 7.29 (d, $J$ = 8.4 Hz, 4H), 6.57-6.55 (m, 6H), 5.14 (s, 4H), 1.36 (s, 6H); $^{13}$C NMR (100 MHz, DMSO-$d_6$) $\delta$ 155.0, 147.2, 126.7, 123.1, 121.4, 113.8, 52.0, 23.6; HRMS (FAB+) calcd for C$_{19}$H$_{20}$N$_2$: 276.1626; found 276.1637.

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

![Diagram of 5](image2)

$^1$H NMR (400 MHz, DMSO-$d_6$) $\delta$ 7.40 (d, $J$ = 8.8 Hz, 4H), 6.59 (d, $J$ = 8.4 Hz, 4H), 6.56 (s, 2H), 5.28 (s, 4H); $^{13}$C NMR (100 MHz, DMSO-$d_6$) $\delta$ 152.2, 148.0, 124.3, 118.8, 113.9, 103.7; MS (FAB$^+$): 250 (M$^+$, 100).

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

![Diagram of 6](image3)
$^1$H NMR (400 MHz, DMSO-$d_6$) δ 7.29 (d, $J = 8.8$ Hz, 4H), 7.10 (s, 2H), 6.57 (d, $J = 8.4$ Hz, 4H), 5.29 (s, 4H); $^{13}$C NMR (100 MHz, DMSO-$d_6$) δ 148.3, 141.3, 125.9, 121.8, 121.2, 114.0; MS (FAB$^+$): 266 (M$^+$, 100).

**Figure S1.** Crystal structure of 4a (crystallized in DMSO). Dihedral angle Between C5-C10 is 13° and C11-C15 is 19°. 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 ~0.2mM 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.](image)

**References:**