

Supplementary Information

“Electronics and Chemistry: Varying Single Molecule Junction Conductance Using Chemical Substituents”

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Synthetic Procedures:

Starting materials and reagents were obtained from commercial sources or synthesized by procedures noted below. Tetramethyl 1,4-diaminobenzene (**1**), 2,5-dimethyl 1,4-diaminofluorene (**2**), 1,4-diaminobenzene (**5**) and 2-Chloro 1,4-diamino benzene (**9**) were purchased from Sigma-Aldrich. 2,5-dichloro 1,4-diaminobenzene (**6**) and tetrafluoro 1,4-diaminobenzene (**12**) were purchased from TCI-America. 2-Trifluoromethyl 1,4-diaminobenzene (**8**) was purchased from Alfa Aesar and 2-cyano 1,4-diaminobenzene (**10**) was purchased from Frinton Labs. All commercial molecules were used as purchased (typically 98% purity or higher). 2-Methoxy 1,4-diaminobenzene (**3**), 2-methyl 1,4-diaminobenzene (**4**) 2-Bromo 1,4-diaminobenzene (**7**) and 2-Fluoro 1,4-diaminobenzene (**11**) were synthesized as detailed below. All measurements were performed in trichlorobenzene purchased from Sigma-Aldrich.

Compound 3:

2-methoxy-1,4-diaminobenzene was prepared as previously reported¹
¹H NMR (300MHz) and ¹³C NMR (75MHz) were recorded on a Bruker DRX 300. ¹H NMR resonances were referenced to the respective solvent peak.

Compound 4:

A solution of 2-methyl-4-nitroaniline (Aldrich, 1.00 g, 6.57 mmol) dissolved in 1,4-dioxane (100 mL) was treated with PtO₂·H₂O (Lancaster, 0.050 g, 0.220 mmol) and stirred under hydrogen (3 bar) for 12 h. The solution was filtered through celite and the solvent was removed under vacuum revealing a light yellow oil which solidified on standing. Recrystallization from benzene afforded the diamine as a pure white solid (0.658 g, 82%).

¹H NMR (300 MHz, DMSO-d₆) δ 6.37 (d, *J* = 8.1 Hz, 1H), 6.19-6.30 (m, 2H), 4.05 (bs, 4H), 1.96 (s, 3H) ppm; ¹³C NMR (75 Mhz, DMSO-d₆) 139.98, 137.71, 123.38, 117.77, 116.40, 113.86, 18.453 ppm; HRMS (EI+, [M+]) calcd for C₇H₁₀N₂ 122.0844 *m/z*; found 122.0850 *m/z*.

Compound 7:

To a solution of 4-nitroaniline (27.6g, 0.20mol) in acetic acid (300mL) was added bromine (10.3mL, 0.20mol) in acetic acid (50mL). The reaction mixture was stirred at room temperature for 4hours. The reaction mixture was poured to 1L of ice slurry. The yellow precipitate was collected by filtration. Purification by recrystallization with water and ethanol (9:1) mixture as a solvent afforded 2-bromo-4-nitroaniline as a yellow solid (24.2g, 56%).

¹H-NMR (300MHz, CDCl₃) δ 8.39 (d, *J*=2.4Hz, 1H), 8.04 (dd, *J*=9.0, 2.4Hz, 1H), 6.75 (d, *J*=9.0Hz, 1H), 4.85 (bs, 2H).

To a mixture of 2-bromo-4-nitroaniline (2.17g, 10mmol) and tin powder (1.78g, 15mmol) was added slowly conc. HCl (25mL). The mixture was refluxed in water bath for 2hours. The reaction mixture was basified by addition of aq. NaOH, filtered through celite and washed with methylene chloride. The organic layer was collected and dried over MgSO₄. After removal of solvent in vacuum, white crystals (0.54, 29%) were obtained by recrystallization in methylene chloride and hexane mixture.

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$^1\text{H-NMR}$ (300MHz, CDCl_3) δ 6.87 (d, $J=2.4\text{Hz}$, 1H), 6.66 (d, $J=8.4\text{Hz}$, 1H), 6.55 (dd, $J=8.4, 2.4\text{Hz}$, 1H), 3.69 (bs, 2H), 3.38 (bs, 2H).

Compound 11:

To a mixture of 2-fluoro-4-nitroaniline (2.17g, 10mmol, Matrix Scientific) and tin powder (1.78g, 15mmol) was added slowly conc. HCl (25mL). The mixture was refluxed in a water bath for 2 hours. The reaction mixture was basified by addition of aqueous NaOH, filtered through celite and washed with methylene chloride. The organic layer was collected and dried over MgSO_4 . After removal of solvent in vacuo, pink crystals (0.44g, 35%) were obtained by recrystallization in methylene chloride and hexane mixture.

$^1\text{H-NMR}$ (300MHz, CDCl_3) δ 6.65 (t, $J=9.6\text{Hz}$, 1H), 6.44 (dd, $J=12.5, 2.4\text{Hz}$, 1H), 6.35 (dd, $J=8.1, 2.4\text{Hz}$, 1H), 3.38 (bs, 4H).

Theoretical Procedures

The generalized gradient approximation (GGA) as formulated by Perdew, Burke and Ernzerhof (PBE) was used². The molecular calculations were done with Jaguar v5.0³ using a 6-31g** basis for the light atoms and a lacvp** basis for Au⁴. The molecular geometry was fully relaxed. Each amine-Au link was modeled using a single Au atom. The amine-Au link is characterized by a N-Au bond length of 2.43-2.46 Å and a Au-N-C bond angle of 121-126 degrees. For 1,4-diaminobenzene, Au binds to the amines in a trans configuration. All of the molecules considered in the experiments were studied in this configuration.

References:

1. Tietze, L. F.; Looft, J.; Feuerstein, T. *European Journal of Organic Chemistry* **2003**, (15), 2749-2755.
2. Perdew, J. P.; Burke, K.; Ernzerhof, M. *Physical Review Letters* **1996**, 77, (18), 3865-3868.
3. Jaguar *Jaguar* 5.0; Schrodinger, L.L.C., Portland, OR, 1991-2003.
4. Wadt, W. R.; Hay, P. J. *Journal of Chemical Physics* **1985**, 82, (1), 284-298.