# Oxidation Potentials Correlate with Conductivities of Aromatic Molecular Wires

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## Supplementary Information

**1. Synthetic Procedures**
**2. Electrochemistry Methods**
**3. CV Data and Voltammograms**

## 1. Synthetic Procedures:

Reagents and starting materials obtained from commercial sources were typically ≥97% purity and were used without further purification unless stated otherwise. 2,6-Diaminonaphthalene,[1] 2,6-diaminoanthracene[2] and 9,10-diaminoanthracene[3] were synthesized according to published methods and were sublimed under vacuum (<200 ºC) prior to use.

**4,4'-(1,4-naphthalenediyl)bisbenzamine (8).** To a solution of 188 mg (0.657 mmol) of 1,4-dibromonaphthalene in 10 mL of toluene was added 120 mg (0.104 mmol) of tetrakis(triphenylphosphine) palladium and the mixture was stirred at room temperature for 30 min. To the solution was added 1.3 mL (2M, 2.6 mmol) of aqueous sodium carbonate followed by 288 mg (1.31 mmol) of 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-aniline (Aldrich) in 10 mL of ethanol. The resulting mixture was heated at reflux for 5.5 h. The mixture was cooled to room temperature and partitioned between 25 mL of water and 25 mL of ethyl acetate. The organic layer was removed and the aqueous layer was extracted with 25 mL of ethyl acetate. The combined organic layers were dried over sodium sulfate, filtered, concentrated in vacuo and purified by flash chromatography on silica gel using 3:1 hexane:ethyl acetate to 1:1 hexane:ethyl acetate. The oily product fraction was dissolved in 2 mL of ethyl acetate and was treated with ca. 10 mL of hexanes until the solution became slightly cloudy. The product precipitated as a pale yellow solid (91 mg, 45% yield). A portion was sublimed at 200-220 ºC under vacuum for conductance and electrochemical measurements. $^1$H NMR (CDCl$_3$, 400 MHz) δ 8.03-8.01 (m, 2H), 7.42-7.32 (m, 8H), 6.84-6.82 (m, 4H), 3.77 (br s, 4H); APCI-MS (MeOH/Me$_2$CO): 311 (M+H$^+$).

[1] Chatt, J.; Wynne, W. P. *J. Chem. Soc.* **1943**, 33-36.
[2] Rabjohns, M. A.; Hodge, P.; Lovell, P. A. *Polymer* **1997**, *38*, 3395-3407.
[3] Schiedt, v. B. *J. Prakt. Chem.* **1941**, *157*, 203-224. Campbell, T. W.; Mccoy, V. E.; Kauer, J. C.; Foldi, V. S. *J. Org. Chem.* **1961**, *26*, 1422-1426.

## 2. Electrochemistry Methods:

Electrochemistry was performed on a BAS CV-50W voltammetric analyzer with a three electrode cell. Each diamine was dissolved in acetonitrile containing 0.1 M tetrabutylammonium perchlorate (TBAP) as supporting electrolyte to give 1.0 mM final concentration in diamine. Sample solutions were sparged with argon for 5 min. prior to use. A platinum disc working electrode (BAS, d = 1.6 mm) and platinum wire counter electrode were used. The reference electrode contained a silver wire with 10 mM silver nitrate in TBAP electrolyte solution. Cyclic voltammetry experiments were carried out at ambient temperature and were recorded at 100 mV $s^{-1}$. Potentials were swept from -0.5V to +2.0V or from -1.5V to +1.5V. Ferrocene was used as an external calibrator and gave $E_{1/2} = 90$ mV (vs Ag/AgNO$_3$) for each experiment.

## 3. Conductance Data, CV Data and Voltammograms[a]:

| compound | number | conductance ($G_0$ x $10^{-3}$) | $E_{1/2}$ (V) vs Fc/Fc$^+$ | distance N-N (Å) |
|---|---|---|---|---|
| diaminophenylnaphthalene | **8** | 0.035 | *0.370* | 14.2 |
| terphenyldiamine | **7** | 0.18 | *0.262* | 14.2 |
| tetrachlorobenzidine | **S11** | 0.4 | *0.870* | 9.9 |
| octafluorobenzidine | **10** | 0.5 | *1.088* | 10.0 |
| dichlorobenzidine | **S12** | 0.9 | 0.371 | 9.9 |
| benzidine | **6** | 1.1 | 0.133 | 9.9 |
| tolidine | **S13** | 1.3 | 0.084 | 9.9 |
| tetramethylbenzidine | **S14** | 1.4 | 0.042 | 9.9 |
| 2,7-diaminofluorene | **S15** | 1.5 | -0.037 | 9.6 |
| 2,6-diaminoanthracene | **5** | 1.6 | *-0.020* | 10.1 |
| 2,6-diaminonaphthalene | **4** | 2.6 | *-0.024* | 7.8 |
| tetrafluorphenylenediamine | **9** | 5.5 | 0.400 | 5.6 |
| chlorophenylenediamine | **S16** | 6.0 | 0.052 | 5.6 |
| cyanophenylenediamine | **S17** | 6.0 | *0.170* | 5.6 |
| dichlorophenylenediamine | **S18** | 6.1 | 0.217 | 5.6 |
| trifluoromethylphenylenediamine | **S19** | 6.1 | *0.120* | 5.6 |
| 1,4-diaminobenzene | **3** | 6.4 | -0.122 | 5.6 |
| dimethylphenylenediamine | **S20** | 6.7 | -0.189 | 5.6 |
| chloromethylphenylenediamine | **S21** | 7.1 | 0.019 | 5.6 |
| tetramethylphenylenediamine | **S22** | 8.2 | -0.259 | 5.6 |
| 1,4-diaminonaphthalene | **2** | 9.0 | -0.220 | 5.6 |
| 9,10-diaminoanthracene | **1** | 17 | -0.412 | 5.6 |

[a]Conductivities ($G_0$ x $10^{-3}$) are generally within 5% of the indicated value. Half-wave potentials ($E_{1/2}$) are first oxidation potentials (± 10 mV). Italicized $E_{1/2}$ values were estimated by subtracting 59/2 mV from first anodic peak potentials when irreversibility was observed (where 59 mV is the expected difference between the first anodic peak potential and the second cathodic peak potential for a one-electron redox process). Nitrogen-to-nitrogen (N-N) distances were approximated from MMFF-minimized geometries.[4]

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[4] Spartan '04, Wavefunction, Inc. Irvine, CA.

In the voltammograms below, the y-axis is current (A) and x-axis is potential ($E$, mV vs. Ag/Ag$^+$):