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Supplementary Material

Cruciform π-systems: Hybrid phenylene-ethynylene/ phenylene-vinylene oligomers

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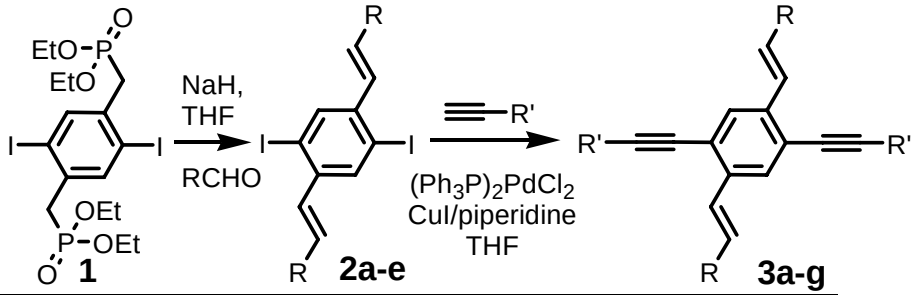
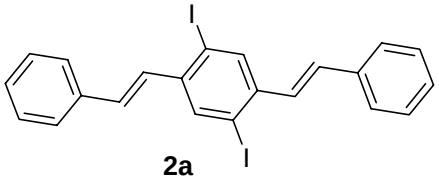


	3a	3b	3c	3d	3e	3f	3g
R							
R'							
2	79%	77%	61%	72%	72%	-	-
3	81%	77%	53%	63%	91%	67%	76%

Scheme 1. Two-step reaction scheme, substituent key and yields of compounds **2a-e** and **3a-g**.

Compounds 2a-e:

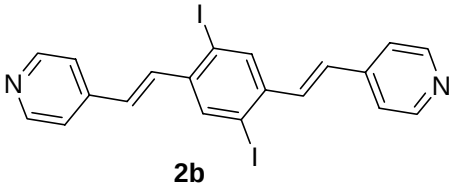
General procedure for compounds 2a-e: An oven-dried Schlenk flask cooled under nitrogen was charged with **1**, NaH (2.5 eq), and dry THF. The flask was closed with a septum, a nitrogen-filled balloon was fitted to the arm and the stopcock was opened. With mild heating (40 °C), the solution turned a vivid purple-red. The aldehyde was introduced in small portions over 1 h with a syringe either as the pure oil or dissolved in dry THF. The reaction was allowed to stir with heat for another 30 min before work-up. The small excess NaH was quenched with water and the mixture was extracted three times with chloroform. The chloroform layer was rinsed with brine and dried with



2a

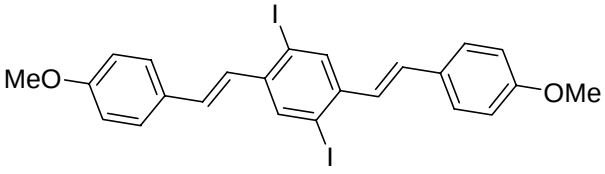
magnesium sulfate and reduced until a precipitate formed. The mixture crystallized from hexanes and was collected by suction filtration and dried under vacuum.

Compound 2a: Following the general procedure, **1** (0.630 g, 1.00 mmol), NaH (60.0 mg, 2.50 mmol), and 25.0 mL THF were combined. Benzaldehyde, (233 mg, 2.20 mmol) was then added. Work up and recrystallization yielded (422 mg, 79%) of pale yellow crystals. MP: 228°C IR: 2915.2, 2840.2, 1458.8, 1437,3, 1348.1, 1069.7, 1041.1, 951.9, 887,6, 855.5, 809.1, 748.4, 691.3, 587.8. ^{1}H NMR ($CDCl_3$): δ8.09 (s, 2H, Ar-H), 7.55 (d, 4H, Ar-H, $J_{H,H}$ = 7.52 Hz), 7.38 (t, 4H, Ar-H, $J_{H,H}$ = 7.33 Hz), 7.30 (t, 2H, Ar-H, $J_{H,H}$ = 7.15 Hz), 7.20 (d, 2H, C=C-H, $J_{H,H}$ = 15.95 Hz), 6.99 (d, 2H, C=C-H, $J_{H,H}$ = 16.13 Hz). ^{13}C NMR ($CDCl_3$): δ140.79, 136.54, 136.34, 135.36, 130.48, 128.82, 128.40, 126.96, 100.28.



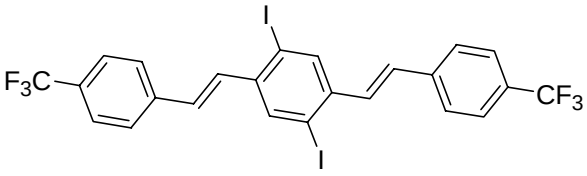
2b

Compound 2b: Following the general procedure, **1** (0.630 g 1.00 mmol), NaH (60.0 mg, 2.50 mmol), and 25.0 mL THF were combined. 4-pyridine carboxaldehyde, (0.236 g 2.20 mmol) was then added. Work up and recrystallization yielded pale yellow crystals (0.413 g, 77.0%). MP: 273°C IR: 3047.4, 3030.7, 3026.6, 1560.1, 1555.6, 1051.9, 956.1, 856.1, 801.9, 731.1, 672.8. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.62 (d, 4H, $J_{H,H}$ = 3.84 Hz, Ar-H), 8.09 (s, 2H, Ar-H), 7.40 (m, 6H, Ar-H, C=C-H), 6.93 (d, 2H, $J_{H,H}$ = 16.2 Hz, C=C-H). ^{13}C-NMR (400 MHz, $CDCl_3$): δ = 150.40, 143.56, 140.62, 136.91, 130.13, 128.32, 121.13, 100.42.



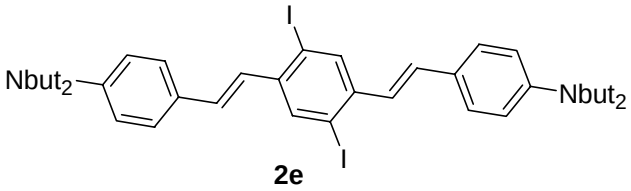
2c

Compound 2c: Following the general procedure, **1** (0.630 g, 1.00 mmol), NaH (60.0 mg, 2.50 mmol), and 25.0 mL THF were combined. 4-Methoxybenzaldehyde, (300 mg, 2.20 mmol) was then added. Work up and recrystallization yielded yellow crystals (362 mg, 60.9%). MP: 213 ^{o} C IR: 2920.6, 2899.3, 1506.7, 1503.1, 1244.3, 1175.0, 1029.3, 956.5, 845.6, 814.4. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.03 (s, 2H, Ar-H), 7.49 (m, H, Ar-H), 7.17 (d, 2H, $J_{3H,H}$ = 23.1 Hz, CH=CH), 7.06 (d, 2H, $J_{3H,H}$ = 23.1 Hz, CH=CH), 6.97 (m, 6H, Ar-H, C=C-H), 3.83 (s, 6H, CO_2CH_3). ^{13}C-NMR (400 MHz, $CDCl_3$): δ = 160.11, 140.91, 136.24, 131.94, 129.67, 128.62, 128.50, 114.49, 100.43, 55.60.



2d

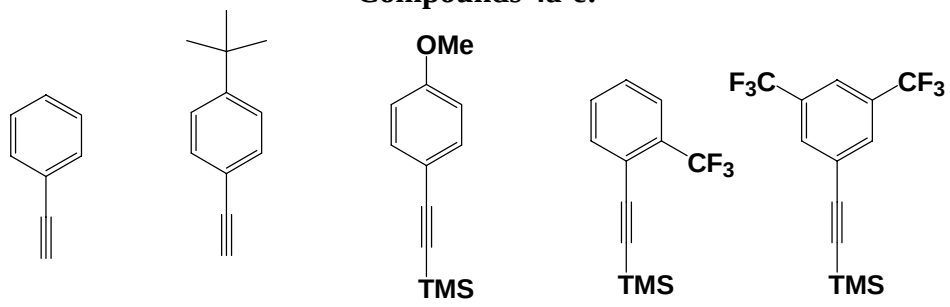
Compound 2d: Following the general procedure, **1** (2.00 g, 3.17 mmol), NaH (228 mg, 9.51 mmol), and 50 mL THF were combined. 4-(trifluoromethyl)-benzaldehyde, (1.22 g, 6.98 mmol) was then added. Work up and crystallization yielded bright yellow crystals (1.53 g, 72%). MP: 213-215^{o} C IR: 3041.5, 2927.7, 1926.8, 1907.5, 1610.5, 1456.2, 1415.7, 1326.9, 1168.8, 1103.2, 1064.6, 956.6, 879.3, 813.9, 756.0, 732.9. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.09 (s, 2H, Ar-H), 7.64 (m, 8H, Ar-H), 7.29 (d, 2H, $J_{3H,H}$ = 16.0 Hz, CH=CH), 7.02 (d, 2H, $J_{3H,H}$ = 16.2 Hz, CH=CH). ^{13}C-NMR (400 MHz, $CDCl_3$): δ = 140.87, 140.04, 136.82, 132.96, 131.24, 131.1-129.8 (m), 128.4-120.2 (m), 127.30, 126.04, 100.66. ^{19}F-NMR (400 MHz, $CDCl_{3)}$: δ = 22.02.



2e

Compound 2e: Following the general procedure, **1** (5.65 g, 8.57 mmol), NaH (1.00 g, 25.0 mmol), and 250 mL THF were combined. 4-Dibutylamino benzaldehyde, (5.00 g, 21.4 mmol) was then added. Work up and crystallization yielded bright orange crystals (5.18 g, 72%). MP: 165° C IR: 2947.0, 2925.8, 2866.0, 1596.9, 1521.7, 1456.2, 1369.4, 1355.9, 1284.5, 1220.9, 1186.1, 1149.5, 1041.5, 954.7, 925.8, 802.3. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.00 (s, 2H, Ar-H), 7.40 (d, 4H, $J_{3H,H}$ = 8.78, Ar-H), 6.92-6.85 (dd, 4H, $J_{3H,H}$ = 16.2 Hz, CH=CH), 6.63 (d, 4H, $J_{3H,H}$ = 8.79 Hz, Ar-H), 3.28 (t, 8H, $J_{3H,H}$ = 7.41 Hz, α-CH_2), 1.60-1.52 (m, 8H, β-CH_2), 1.39-1.31 (m, 8H, γ-CH_2), 0.95 (t, 12H, $J_{3H,H}$ = 7.13 Hz, -CH3). ^{13}C-NMR (400 MHz, $CDCl_3$): δ = 148.16, 140.42, 135.40, 131.89, 128.27, 125.39, 123.78, 111.49, 100.15, 50.77, 29.42, 20.32, 14.01.

Compounds 4a-e:



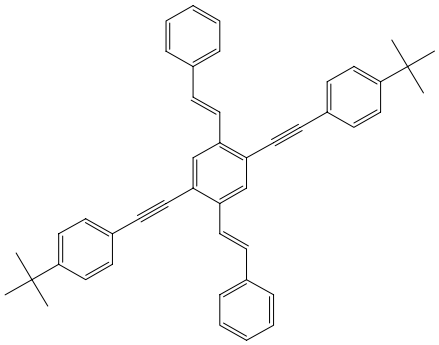
4a **4b** **4c** **4d** **4e**

The compounds **4b-d** have been previously reported and **5a** is commercially available.

Compound **4e**: 3,5-Bis(trifluoromethyl)iodobenzene (2.00g, 5.88 mmol) was combined with $(PPh_3)_2PdCl_2$ (50.0 mg, 72.1 μmol), CuI (50.0 mg, 333 μmol), 2.0 mL THF and 2.0 mL piperidine in a nitrogen-purged Schlenk flask. The mixture was degassed and capped with a septum. trimethylsilylacetylene (0.635 g, 6.47 mmol) was added dropwise. The reaction was allowed to stir in a warm water bath for 12 h. The crude reaction mixture was filtered over a silica plug with hexanes. The hexane mixture was reduced and the product was conveniently re-crystallized by sublimation in its own container at ambient temperature providing crystals suitable for crystallography (1.83 g, 83%). IR: 3087.8, 2960.5, 2900.7, 2173.6, 1834.2, 1807.2, 1786.0, 1608.5, 1460.0, 1409.9, 1373.2, 1300.8, 1249.8, 1181.2, 1130.2, 1107.1, 912.3, 907.7, 896.8, 891.1, 763.8. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.87 (s, 2H), 7.78 (s, 1H), 0.25 (s, 9H). ^{13}C NMR ($CDCl_3$): δ =132.54-131.53 (q, $J_{2C,F}$ = 33.8 Hz), 132.06-132.03 (q, $J_{3C,F}$ = 3.0 Hz),, 127.19-119.06 (q, $J_{1C,F}$ = 272.9 Hz), 125.66, 122.02-121.9 (q, $J_{3C,F}$ = 3.76 Hz), 101.7 , 98.97 , 0.14.

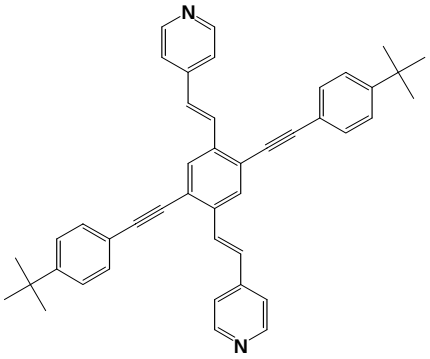
Compounds 3a-g:

3a-g were produced by the Sonagashira coupling of either the free alkyne **4a,b** or by *in-situ* deprotection with potassium hydroxide and ethanol as a co-solvent (**4c-e**). The reaction progress

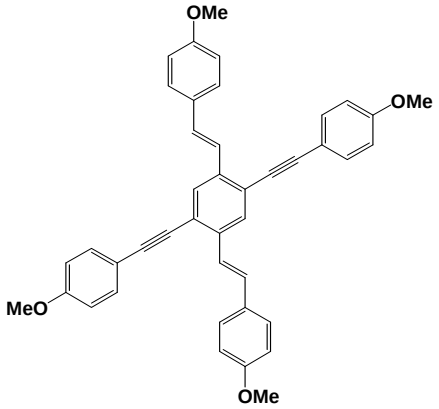


could be monitored by the development of the fluorescent products which were isolated by precipitating twice into non-solvents.

Compound **3a**: **2a** (236 mg, 0.442 mmol) was combined with **4b** (175 mg, 1.11 mmol), $(PPh_3)_2PdCl_2$ (5.0 mg, 7.1 μmol), CuI (5.0 mg, 33 μmol) and dissolved in 4.0 mL of piperidine/THF 1:1. The crude reaction mixture was precipitated twice from dichloromethane into hexane. The resulting yellow powder was recrystallized by evaporation of dichloromethane from hexane yielding 213 mg yellow crystals suitable for crystallographic analysis. Yield: 81% MP: 240°. IR: 3037.7, 2960.5, 2356.6, 2204.4, 1801.4, 1631.7, 1596.9, 1498.6, 1406.0, 1365.5, 1265.2, 1101.3, 1026.1, 956.6, 891.1, 831.3, 752.2, 690.5. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.99 (s, 2H, Ar-H), 7.69 (d, 2H, C=C-H, $J_{3\ H,H}$ = 16.3 Hz), 7.57 (m, 8H), 7.43 (m, 8H), 7.30 (m, 4H), 1.34 (s, 18H, t-butyl). ^{13}C NMR ($CDCl_3$): δ = 152.16, 137.58, 137.50, 131.60, 130.76, 129.02, 128.18, 127.06, 126.00, 125.77, 122.63, 120.38, 65.97, 87.50, 35.12, 31.46. MS (DEP) ($C_{46}H_{42}$): *m/z* = 594.

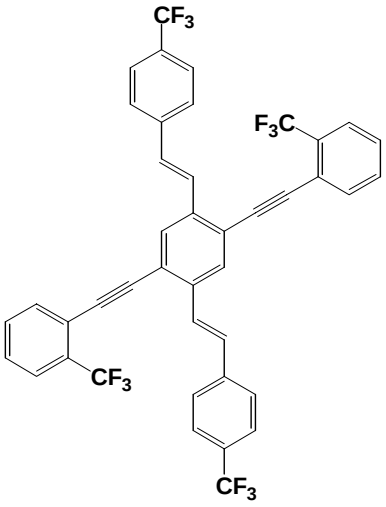


Compound **3b**: Compound **2b** (250 mg, 0.466 mmol) was combined with **4b** (184 mg, 1.17 mmol), $(PPh_3)_2PdCl_2$ (5.0 mg, 7.1 μmol), CuI (5.0 mg, 33 μmol) and dissolved in 4.0 mL of piperidine/THF 1:1. The crude reaction mixture was precipitated twice from dichloromethane into hexane. The resulting yellow powder was recrystallized by evaporation of dichloromethane from hexane yielding 214 mg yellow crystals suitable for crystallographic analysis. Yield: 77% MP: 264°. IR: 2960.5, 2868.0, 2358.8, 2208.3, 1593.1, 1506.3, 1461.9, 1363.6, 1267.1, 1217.0, 1103.2, 1016.4, 962.4, 866.0, 833.2, 800.4. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.61 (bs, pyridine-H), 7.91 (s, 2H, Ar-H), 7.87 (d, 2H, C=C-H, $J_{3\ H,H}$ = 16.5 Hz), 7.54(d, 4H, Ar-H, 8.51), 7.44 (m, 8H), 7.22 (d, 2H, C=C-H, $J_{3\ H,H}$ = 16.5 Hz), 1.34 (s, 18H, t-butyl). ^{13}C NMR ($CDCl_3$): δ = 152.34, 150.22, 144.23, 136.76, 131.31, 129.85, 129.18, 128.06, 125.62, 122.90, 121.20, 119.62, 96.55, 86.53, 34.88, 31.14. MS (DEP) ($C_{44}H_{40}N_2$): *m/z* = 596.

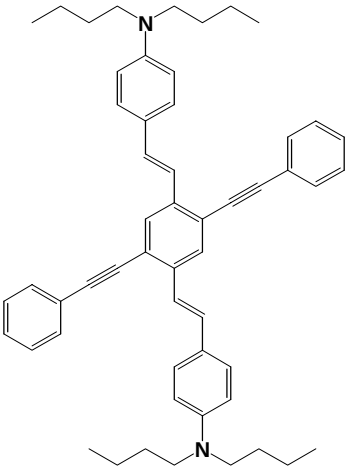


Compound **3c**: Compound **2d** (500 mg, 0.842 mmol) was combined with **4c** (518 mg, 2.53 mmol), $(PPh_3)_2PdCl_2$ (5.0 mg, 7.1 μmol), CuI (5.0 mg, 33 μmol), KOH (0.500 g, 8.9 mmol), 2.0 mL of piperidine, 2.0 mL THF, and 2.0 mL EtOH in a nitrogen purged Schlenk flask. The solution was degassed, capped with a septum and placed in a 50°C water bath for 24 h. The solution was reduced then precipitated twice from dichloromethane into methanol. The resulting yellow powder was recrystallized from xylenes yielding 269 mg yellow crystals. Yield: 53% MP: 199°. IR: 2929.7, 1604.7, 1512.1, 1456.2, 1440.7, 1419.5, 1292.2, 1253.6, 1174.6, 1107.1, 1031.8, 958.6, 852.5, 831.3. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.83 (s, 2H, Ar-H), 7.54 (m, 10H), 7.84 (s, 2H, Ar-H), 7.22 (d, 2H, C=C-H, $J_{3\ H,H}$ = 16.2 Hz), 6.93 (m, 8H), 3.84 (s, 6H, O-CH_3), 3.83 (s, 6H, O-CH_3). ^{13}C NMR ($CDCl_3$): δ = 160.04, 159.75, 137.31, 133.29,

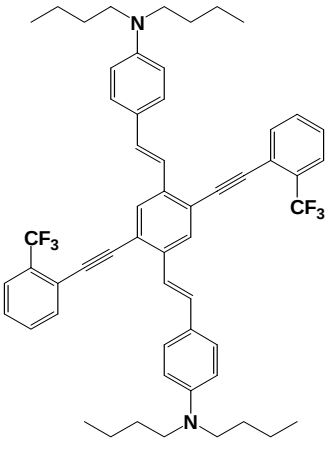
130.49, 130.00, 128.59, 128.26, 123.98, 122.25, 115.65, 114.46, 114.38, 95.53, 87.15, 55.57. MS (DEP) ($C_{42}H_{34}O_4$): *m/z* = 602.



Compound **3d**: Compound **2d** (670 mg, 1.00 mmol) was combined with **4d** (606 mg, 2.50 mmol), $(PPh_3)_2PdCl_2$ (5.0 mg, 7.1 μmol), CuI (5.0 mg, 33 μmol), KOH (0.500 g, 8.9 mmol), 2.0 mL of piperidine, 2.0 mL THF, and 2.0 mL EtOH in a nitrogen purged Schlenk flask. The solution was degassed, capped with a septum and placed in a 50°C water bath for 24 h. The solution was reduced then precipitated twice from dichloromethane into hexane. The resulting green powder was recrystallized from xylenes yielding 475 mg greenish crystals. Yield: 63%. MP: 218-220°. IR: 2358.8, 2341.4, 1610.5, 1569.9, 1496.7, 1415.7, 1334.6, 1313.4, 1259.4, 1182.3, 1132.1, 1107.1, 1070.4, 962.4, 867.9, 823.5, 765.7. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.94 (s, 2H, Ar-H), 7.77 (m, 14H), 7.50 (t, 2H, Ar-H, $J_{3\ H,H}$ = 7.7 Hz), 7.28 (d, 2H, C=C-H, $J_{3\ H,H}$ = 16.5 Hz). ^{13}C NMR (D-TCE, 80°C): δ= 140.44, 137.59, 134.04, 131.45, 131.15 (m), 129.98, 129.74 (m), 129.53, 128.44, 127.66, 126.92, 125.94, 125.47, 125.14, 124.69, 122.96, 122.61, 120.88, 92.69, 91.88. ^{19}F NMR ($CDCl_3$): δ = 22.76, 22.09. MS (DEP) ($C_{42}H_{22}F_{12}$): *m/z* = 754.

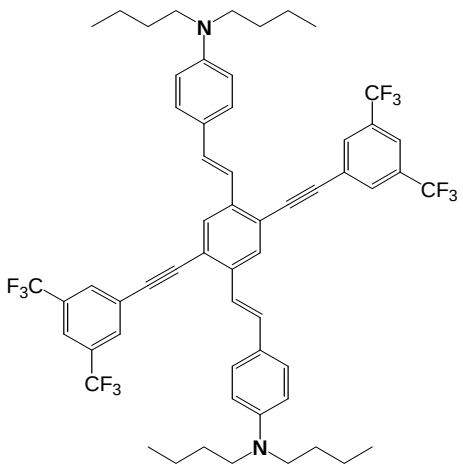


Compound **3e**: Compound **2e** (330 mg, 0.418 mmol) was combined with phenylacetylene **4a** (107 mg, 1.05 mmol), $(PPh_3)_2PdCl_2$ (5.0 mg, 7.1 μmol), CuI (5.0 mg, 33 μmol) and dissolved in 4.0 mL of piperidine/THF 1:1. The crude reaction mixture was precipitated twice from dichloromethane into methanol. The resulting orange powder was recrystallized from methanol yielding 280 mg orange crystals. Yield: 91%. MP: 164-168°. IR: 3033.8, 2929.7, 1795.6, 1600.8, 1521.7, 1461.9, 1400.2, 1367.4, 1257.5, 1220.9, 1147.9, 1109.0, 925.8, 804.3, 752.2, 688.5. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.84 (s, 2H, Ar-H), 7.84 (d, 4H, Ar-H, $J_{3\ H,H}$ = 7.7 Hz), 7.44 (m, 12H), 7.19 (d, 2H, C=C-H, $J_{3\ H,H}$ = 16.5 Hz), 6.64 (d, 4H, Ar-H, $J_{3\ H,H}$ = 8.8 Hz), 3.31 (t, 8H, α-C-H, $J_{3\ H,H}$ = 7.41 Hz), 1.63 (m, 8H, β-C-H), 1.39 (m, 8H, γ-C-H,), 0.97 (t, 12H, -CH_3, $J_{3\ H,H}$ = 7.4 Hz). ^{13}C NMR ($CDCl_3$): δ = 147.97, 137.29, 131.57, 130.38, 128.38, 128.25, 128.09, 128.07, 124.49, 123.48, 121.41, 120.50, 111.59, 94.78, 88.51, 50.74, 29.46, 20.32, 14.00. MS (DEP) ($C_{54}H_{60}N_2$): *m/z* = 736.



Compound **3f**: Compound **2e** (250 mg, 0.317 mmol) was combined with **4d** (192 mg, 0.792 mmol), $(PPh_3)_2PdCl_2$ (5.0 mg, 7.1 μmol), CuI (5.0 mg, 33 μmol), KOH (0.500 g, 8.9 mmol), 2.0 mL of piperidine, 2.0 mL THF, and 2.0 mL EtOH in a nitrogen purged Schlenk flask. The solution was degassed, capped with a septum and placed in a 50°C water bath for 24 h. The crude reaction mixture was dissolved in dichloromethane and washed three times with water. The solution was reduced then precipitated twice from dichloromethane into methanol.

The resulting orange powder was recrystallized from methanol yielding 186 mg orange crystals. Yield: 67% MP: 182°. IR: 3030.0, 2954.7, 2869.9, 2208.3, 1600.8, 1521.7, 1469.7, 1398.3, 1369.4, 1315.4, 1286.4, 1259.4, 1220.9, 1174.6, 1136.0, 1109.0, 1055.0, 1031.8, 962.4, 806.2, 765.7. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.86 (s, 2H, Ar-H), 7.77 (d, 2H, Ar-H, $J_{3\ H,H}$ = 7.69 Hz), 7.73 (d, 2H, Ar-H, $J_{3\ H,H}$ = 7.69 Hz), 7.58 (t, 2H, Ar-H, $J_{3\ H,H}$ = 7.68 Hz), 7.45 (m, 8H), 7.17 (d, 2H, C=C-H, $J_{3\ H,H}$ = 16.47 Hz), 6.64 (d, 4H, Ar-H, $J_{3\ H,H}$ = 8.78 Hz), 3.31 (t, 8H, α-C-H, $J_{3\ H,H}$ = 6.59 Hz), 1.60 (m, 8H, β-C-H), 1.39 (m, 8H, γ-C-H,), 0.97 (t, 12H, -CH_3, $J_{3\ H,H}$ = 7.14 Hz). ^{13}C NMR ($CDCl_3$): δ = 148.32, 137.94, 134.69, 131.71, 131.60, 131.19, 131.11, 128.64, 128.52, 128.21, 126.18, 126.11, 124.66, 121.95, 121.68, 120.32, 111.81, 94.29, 90.85, 51.00, 29.74, 20.59, 14.25. MS (DEP) ($C_{56}H_{58}F_6N_2$): *m/z* = 872.



Compound **3g**: Compound **2e** (182 mg, 0.25 mmol) was combined with **4e** (177 mg, 0.624 mmol), $(PPh_3)_2PdCl_2$ (5.0 mg, 7.1 μmol), CuI (5.0 mg, 33 μmol), KOH (0.500 g, 8.9 mmol), 2.0 mL of piperidine, 2.0 mL THF, and 2.0 mL EtOH in a nitrogen purged Schlenk flask. The solution was degassed, capped with a septum and placed in a 50°C water bath for 24 h. The crude reaction mixture was dissolved in dichloromethane and washed three times with water. The solution was reduced then precipitated twice from dichloromethane into methanol. The resulting orange powder was recrystallized from methanol yielding 192 mg orange crystals. Yield: 76% MP: 191°. IR: 3039.6, 2960.5, 2931.6, 2864.1, 2208.3, 1600.8, 1521.7, 1373.2, 1286.4, 1182.3, 1137.9, 956.6, 893.9, 804.3, 684.7. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.02 (s, 4H, Ar-H), 7.86 (s, 2H, Ar-H), 7.84 (s, 2H, Ar-H), 7.43 (d, 4H, Ar-H, $J_{3\ H,H}$ = 8.78 Hz), 7.37 (d, 2H, C=C-H, $J_{3\ H,H}$ = 16.2 Hz), 7.19 (d, 2H, C=C-H, $J_{3\ H,H}$ = 16.3 Hz), 6.65 (d, 4H, Ar-H, $J_{3\ H,H}$ = 8.51 Hz), 3.32 (t, 8H, α-C-H, $J_{3\ H,H}$ = 6.59 Hz), 1.58 (m, 8H, β-C-H), 1.39 (m, 8H, γ-C-H,), 0.97 (t, 12H, -CH_3, $J_{3\ H,H}$ = 7.14 Hz). ^{13}C NMR ($CDCl_3$): δ = 148.29, 137.80, 132.53-131.53 (m), 131.30, 131.21, 128.22, 128.13, 127.06-118.9 (m), 125.70, 123.98, 121.62, 120.82, 119.66, 111.59, 92.07, 91.94. MS (DEP) ($C_{56}H_{56}F_{12}N_2$): *m/z* = 1008.

UV-vis/Fluorescence:

	3a	**3b**	**3c**	**3d**	**3e**	**3f**	**3g**
Chloroform							
Ab	331, 365 sh	330	339,374 sh	330, 363 sh	339, 439	342, 444	345, 458
Em	420, 442	446, 526 sh	432, 454	419, 434 sh	514	543	563
ϕ	0.83	0.28	0.88	0.92	0.16	0.20	0.14
Hexane							
Ab	326, 352 sh	324, 348 sh	334, 376 sh	-	332, 422	344, 416	346, 420
Em	414, 432	424, 444 sh	420, 442	-	472, 498	502, 526 sh	524
ϕ	0.78	0.45	0.78	-	0.94	0.70	0.53

Cyclic Voltametry:

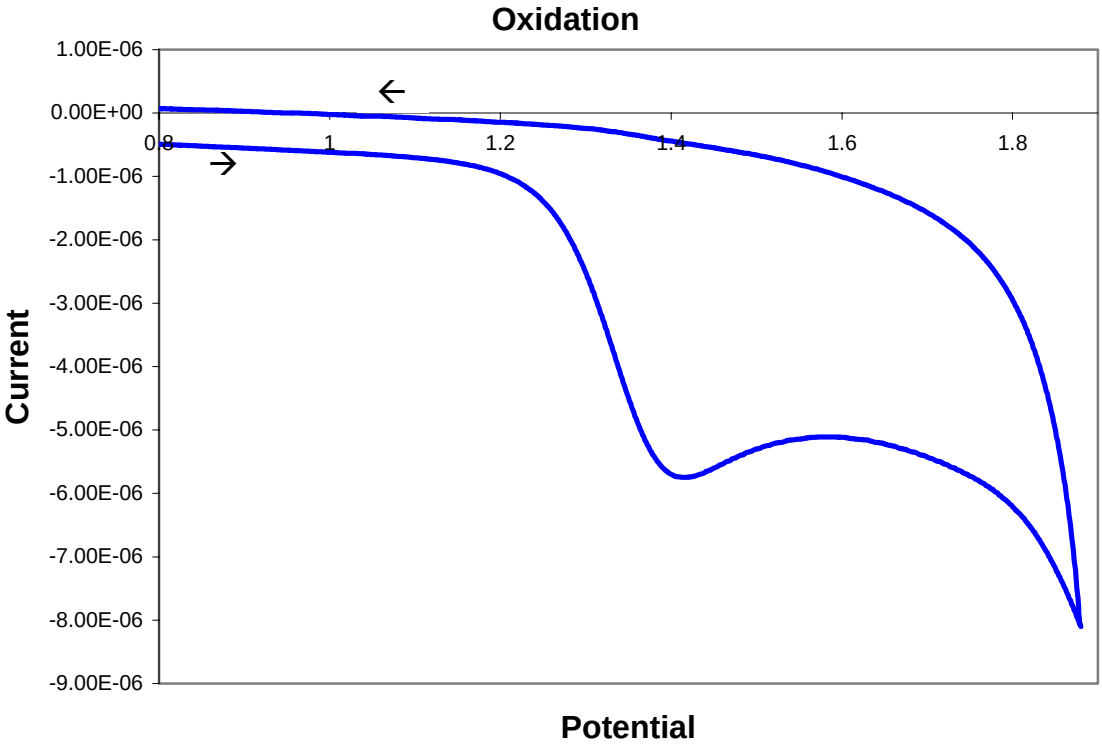
Electrochemical experiments were carried out with CH Instruments model 660 electrochemical workstation. Cyclic voltammograms (CV) were obtained by using a conventional three-electrode system. A platinum foil was used as the counter electrode. A platinum disk electrode (ϕ = 1.2 mm) from Bioanalytical Systems serves as a working electrode. Reference electrode **A**, Ag/0.1 M $AgNO_3$ in CH_2Cl_2, was separated from the test by a fritted bridge containing the background electrolyte (0.1 M Bu_4NPF_6 in CH_2Cl_2 or 0.1 M Bu_4NPF_6 in THF). The reference electrode was calibrated before each experiment with the ferrocene/ferrocenium (Fc/Fc^+) redox system. The $E_{1/2}$ of 5 mM of Fc/Fc^+ in 0.1 M Bu_4NPF_6 in in CH_2Cl_2 was 0.89 V and in 0.1 M 0.1 M Bu_4NPF_6 in THF 0.141 V. The standard redox potential of the Fc/Fc^+ system has been determined to be 0.190 V [Bard, AJ., Faulkner LR. Electrochemical Methods; John Wiley & Sons: New York 1980 p.701].. Therefore, the potential of our reference electrode **A** was 0.289 V and 0.331 in CH_2Cl_2 and THF respectively vs. S.H.E. For additional experiments (oxidation of **3d**), the working and reference electrodes (reference electrode **B**) were a platinum wires with a platinum foil counter electrode. The reference electrode was calibrated before each experiment with the ferrocene/ferrocenium (Fc/Fc^+) redox system. The $E_{1/2}$ of 5 mM of Fc/Fc^+ in 0.1 M Bu_4NPF_6 in in CH_2Cl_2 was 0.205 V. Therefore, the potential of our reference electrode **B** was 0.395 V vs. S.H.E. All solutions were purged prior to electrochemical measurements using nitrogen gas. All solvents were dried with molecular sieves (3 Å). All the salts were used as received from Aldrich.

Table: Reduction and oxidation potentials of 3a-g

	3a	**3b**	**3c**	**3d**	**3e**	**3f**	**3g**
Reduction:							
onset	-0.80	-1.44	-0.83	-1.46	-1.8*	-1.8*	-1.8*
$E_{1/2}$	-1.02	-1.57	-1.12	-1.57	-	-	-
peak	-1.26	-1.67	-1.15	-1.65	-	-	-
Oxidation:							
onset	1.21	1.40	1.07	1.45	0.41, 1.47	0.47, 1.45	0.50, 1.54
$E_{1/2}$	1.32	1.51	1.12	1.52	0.53	0.53	0.57
peak	1.42	1.68	1.19	1.61	0.61	0.62	0.66

***** only onsets of reduction were observed.

3a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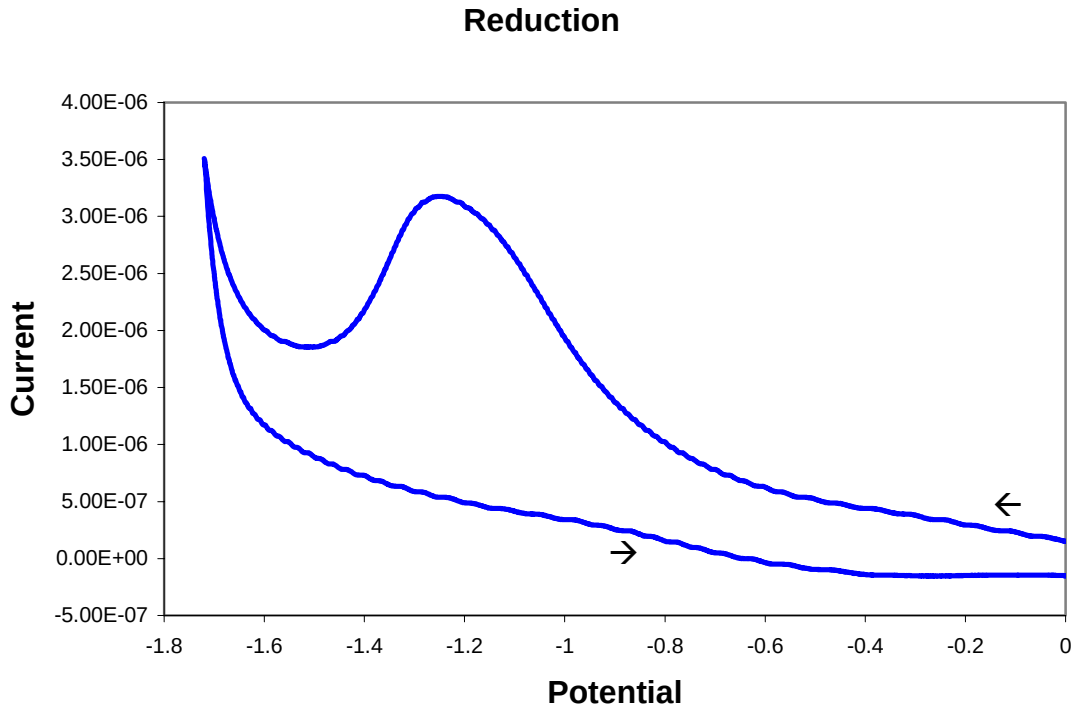
-3.00E-06
-4.00E-06
-5.00E-06
-6.00E-06
-7.00E-06
-8.00E-06
-9.00E-06
0.8
1
1.2
1.4
1.6
1.8
Current
Potential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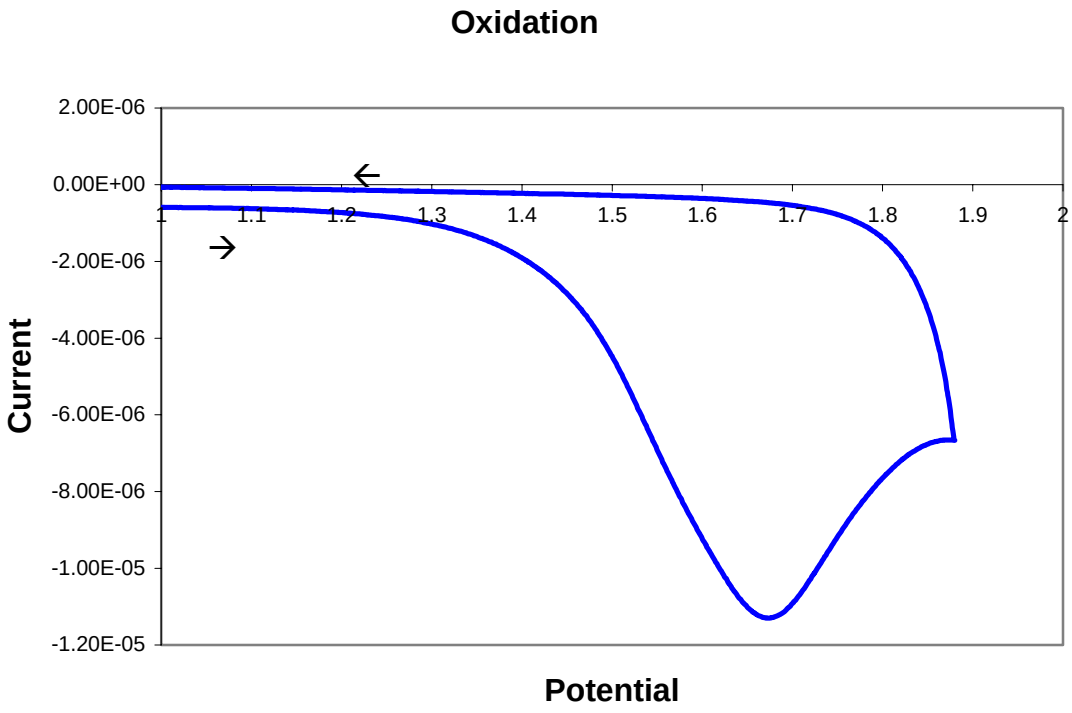
2.00E-06
1.50E-06
1.00E-06
5.00E-07
0.00E+00
-5.00E-07
-1.8
-1.6
-1.4
-1.2
-1
-0.8
-0.6
-0.4
-0.2
0
Current
Potential

3b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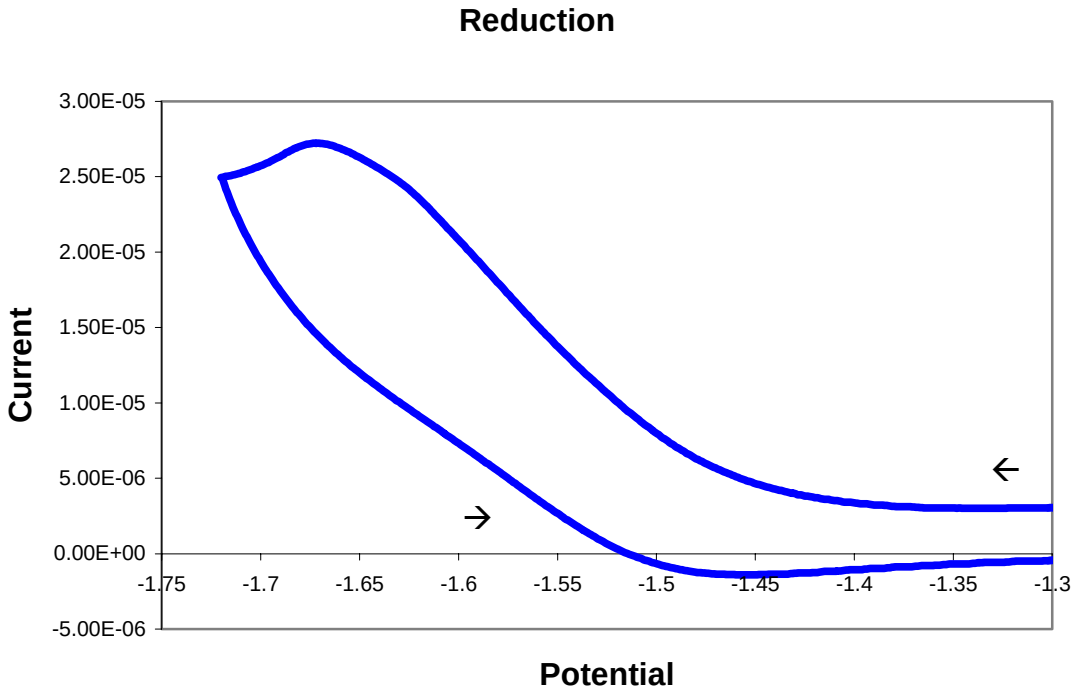
-6.00E-06
-8.00E-06
-1.00E-05
-1.20E-05
Current
1
1.1
1.2
1.3
1.4
1.5
1.6
1.7
1.8
1.9
2
Potential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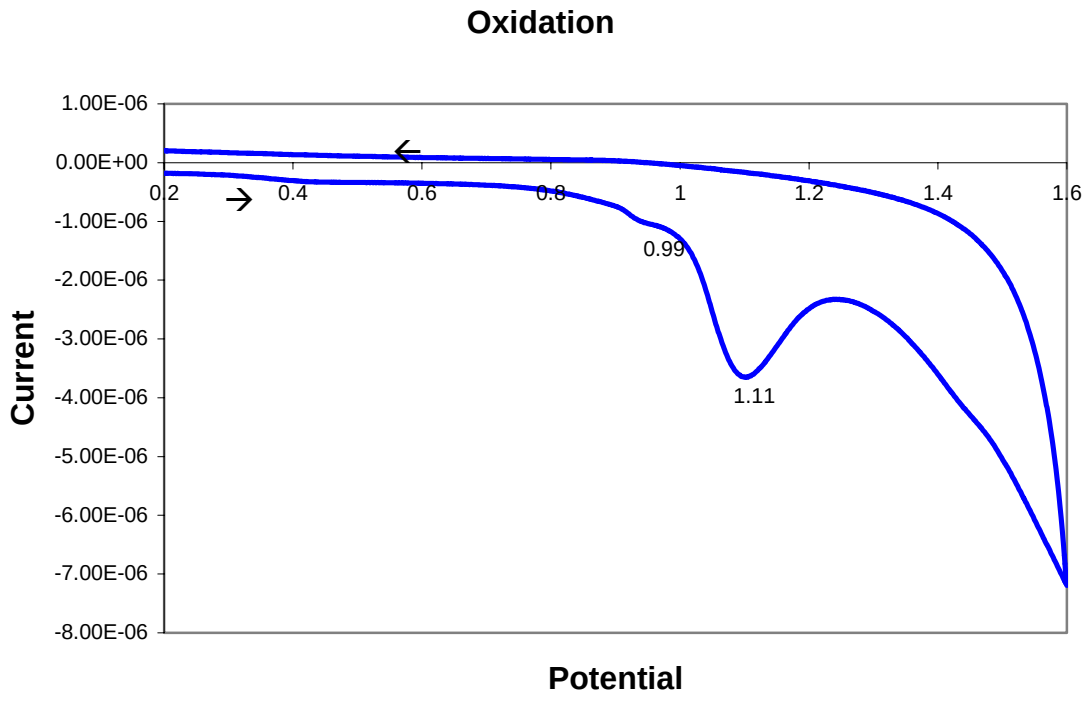
1.00E-05
5.00E-06
0.00E+00
-5.00E-06
Current
-1.75
-1.7
-1.65
-1.6
-1.55
-1.5
-1.45
-1.4
-1.35
-1.3
Potential

3c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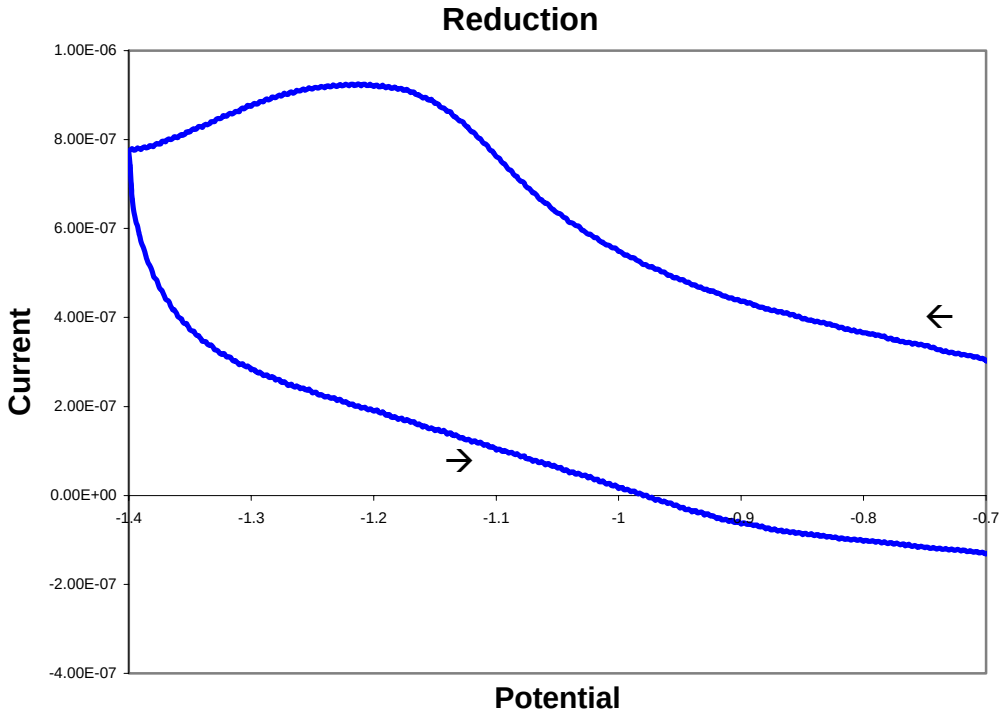
-4.00E-06
-5.00E-06
-6.00E-06
-7.00E-06
-8.00E-06
0.2
0.4
0.6
0.8
1
1.2
1.4
1.6
0.99
1.11
Current
Potential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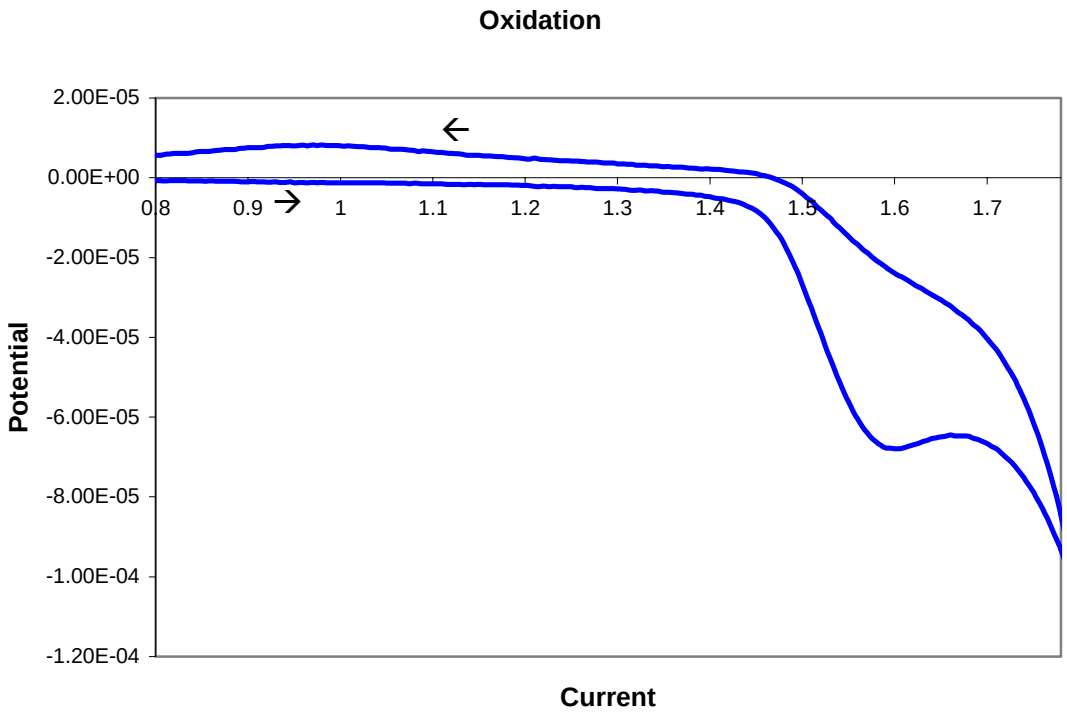
-4.00E-07
-1.4
-1.3
-1.2
-1.1
-1
-0.9
-0.8
-0.7
Current
Potential

3d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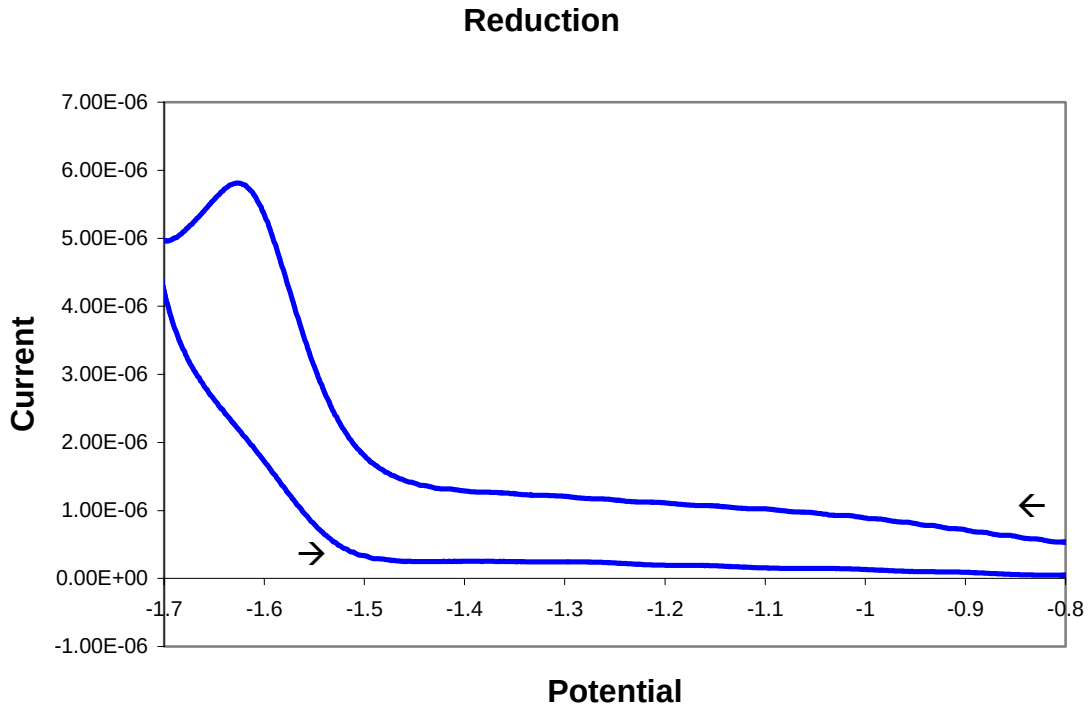
-1.20E-04
0.8
0.9
1
1.1
1.2
1.3
1.4
1.5
1.6
1.7
Potential
Current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-1.00E-06
-1.7
-1.6
-1.5
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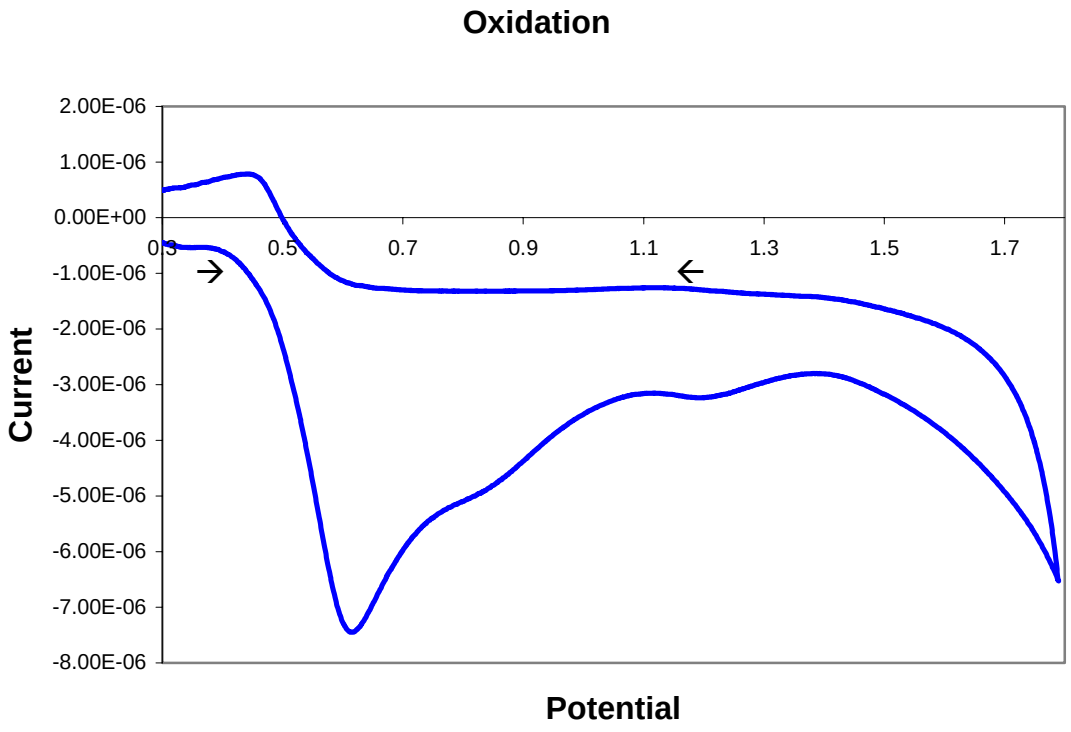
-1.3
-1.2
-1.1
-1
-0.9
-0.8
Current
Potential

3e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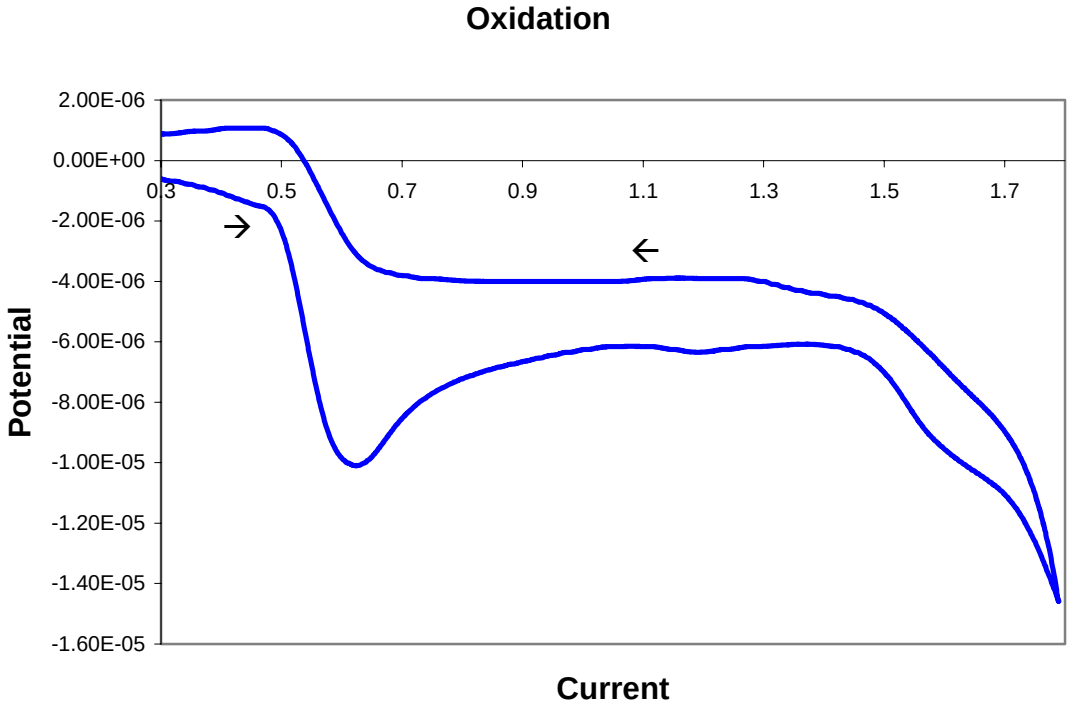
-3.00E-06
-4.00E-06
-5.00E-06
-6.00E-06
-7.00E-06
-8.00E-06
0.3
0.5
0.7
0.9
1.1
1.3
1.5
1.7
Current
Potential

3f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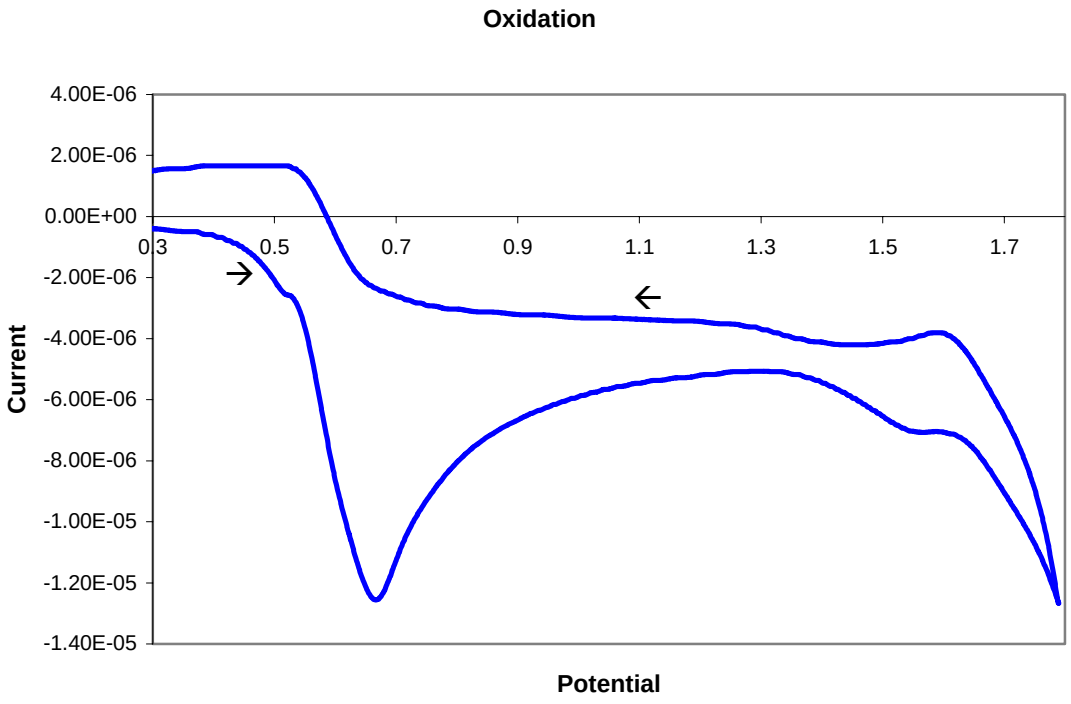
0.5
0.7
0.9
1.1
1.3
1.5
1.7
Potential
Current

3g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1.5
1.7
Current
Potential