Reactivity and reducing power of $SmBr_2$-HMPA.

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Supporting Information

Preparation of SmI_2 and $SmBr_2$:

A typical preparation used 5.2 g (0.021 mol) of molecular iodine added to 250 mL of THF. A mass of 4.0 g (0.027 mol) of samarium metal was then added to the solution. The mixture was allowed to stir for 24 hours under nitrogen atmosphere or until the characteristic blue color appeared. Iodometric titration established the concentration of SmI_2.

$SmBr_2$ was prepared using SmI_2 solution and LiBr salts. A four-fold excess of LiBr was utilized to ensure complete conversion of SmI_2 to $SmBr_2$. The mixture of SmI_2 and LiBr has an observable color change, from blue to purple. UV-Vis spectra of this mixture are identical to that of $SmBr_2$ generated by electrochemical reduction of $SmBr_3$.

Synthesis of N-benzyl imine derivative of pinacolone:

Approximately 100 mg of amberlyst was added to a round bottom flask equipped with a stir bar and then attached to a Dean-Stark trap. Next, 50 mL of benzene solvent was added. To this mixture, 6.3 mL of pinacolone (0.050 mol) and 5.8 mL of benzylamine (0.050 mol) were added. The solution was stirred and heated to reflux. This was continued for 40 hours at which point the solid amberlyst was removed by vacuum filtration. Remaining solvent was removed by evaporation under reduced pressure, yielding the crude product as a yellow oil. Kugelrohr distillation removal of unreacted starting materials yielded the final product as a yellow oil. Yield 57%. GCMS: m/z 189 (M^+). ^1H NMR (400 MHz, $CDCl_3$): δ 1.172 (9H, s), 1.866 (3H, s), 4.51 (2H, s), 7.19-7.37 (5H, m)

Synthesis of N-benzyl imine derivative of acetophenone:

Approximately 100 mg of amberlyst was added to 50 mL of benzene in a round bottom flask equipped with a stir bar. To this mixture, 5.5 mL of benzylamine (0.50 mol) and 5.8 mL of acetophenone (0.50 mol) were added. The solution was allowed to stir while heating to reflux for 24 hours. A Dean-Stark trap was employed for collection of water released during the reaction. Solid amberlyst was removed by vacuum filtration. Remaining solvent was removed by evaporation under reduced pressure, yielding the crude product. Removal of unreacted starting material was done by rotary evaporation under vacuum to give the final product. Yield 59 %. GCMS: m/z 208 ($M-1^+$), 91 ($M-118^+$). ^1H NMR (400 MHz, $CDCl_3$): δ 2.304 (3H, s), 4.723 (2H, s), 7.236-7.866 (10H, m).

Pinacol coupling of 2-octanone with $SmBr_2$-HMPA:

To 14.3 mL of 0.07M SmI_2 (1 mmol) in a 50 mL dried round bottom flask equipped with stir bar, 375 mg (4.00 mmol) of LiBr was added. Stirring was performed for 10 minutes, in which time a color change from blue to purple was observed. Exactly 8.7 mL of HMPA (50 mmol) was then added. This solution was stirred for 10 minutes, until a royal purple color was observed. Dropwise addition of 40 μL of 2-octanone (0.25 mmol) was performed. The reaction was allowed to stir for 24 hours at which point it was quenched with saturated ammonium chloride in water. Extraction by diethyl ether was performed. The extract was washed with two 50 mL aliquots of aqueous sodium thiosulfate, followed by three 50 mL aliquots of distilled water. Yield (total coupling) 37%. GCMS: m/z 243 ($M-15^+$), 129 ($M/2^+$).

This reaction was also performed with HMPA distilled from sodium hydride. Yield 69%. GCMS: m/z 243 (M-15$^+$), 129 (M/2$^+$).

Reduction of ethyl propionate by $SmBr_2$-HMPA:

To 14.3 mL of 0.07M SmI_2 (1 mmol) in a 50 mL dried round bottom flask equipped with stir bar, 375 mg (4.00 mmol) of LiBr was added. Stirring was performed for 10 minutes, in which time a color change from blue to purple was observed. Exactly 8.7 mL of HMPA (50 mmol) was then added. This solution was stirred for 10 minutes, until a royal purple color was observed. To this solution, 29 μL (0.25 mmol) of ethyl propionate was added dropwise. The reaction was allowed to stir for 4.5 hours, after which it was quenched by addition of saturated ammonium chloride in water. Extraction by diethyl ether was followed by two washes of aqueous sodium thiosulfate and three washes of distilled water. GCMS analysis only shows starting material.

Reduction of 1-chlorodecane with $SmBr_2$-HMPA:

To 14.3 mL of 0.07M SmI_2 (1 mmol) in a 50 mL dried round bottom flask equipped with stir bar, 375 mg (4.00 mmol) of LiBr was added. Stirring was performed for 10 minutes, in which time a color change from blue to purple was observed. Exactly 8.7 mL of HMPA (50 mmol) was then added. This solution was stirred for 10 minutes, until a royal purple color was observed. Dropwise addition of 50 μL of 1-chlorodecane (0.25mmol) to this solution was then performed. The reaction was stirred for two hours, at which time it was quenched by addition of an aqueous saturated ammonium chloride solution. The product was extracted into diethyl ether, washed with two 50 mL aliquots of sodium thiosulfate and three rinses of distilled water. Yield >99%. GCMS: m/z 142 (M^+), 113 ($M-29^+$).

Reduction of chlorocyclohexane with $SmBr_2$-HMPA:

In a 50 mL dried round bottom flask equipped with a stir bar, 25.0 mL of 0.08M SmI_2 (2 mmol) and 1.5 g of LiBr (16 mmol) were added. The solution was stirred for 10 minutes, when a color change from blue to purple was observed. Exactly 17.4 mL of HMPA (100 mmol) was then added. The solution was stirred for 10 minutes, until a royal purple color was observed. To this solution, 118 μL of chlorocyclohexane (1.00 mmol) was added. The reaction was allowed to stir for two hours, then quenched with aqueous ammonium chloride and extracted into diethyl ether. The ether extract was washed first with two 50 mL aliquots of aqueous sodium thiosulfate, then with three aliquots of distilled water. Yield >99%. GCMS: m/z 84 (M^+), 56 ($M-28^+$).

Reduction of N-benzyl imine derivative of pinacolone with $SmBr_2$-HMPA:

To 14.3 mL of 0.07M SmI_2 (1 mmol) in a 50 mL dried round bottom flask equipped with stir bar, 375 mg (4.00 mmol) of LiBr was added. Stirring was performed for 10 minutes, in which time a color change from blue to purple was observed. Exactly 8.7 mL of HMPA (50 mmol) was then added. This solution was stirred for 10 minutes, until a royal purple color was observed. Approximately 56 μL (0.30 mmol) of ketimine was then added. The reaction was allowed to stir for 24 hours at which time it was quenched by addition of saturated aqueous ammonium chloride, followed by extraction of the product into diethyl ether. The ether was washed with two 50 mL aliquots of aqueous sodium thiosulfate and then rinsed with three 50 mL aliquots of distilled water. Yield >99%. GCMS: m/z 176 (M-15^+), 134 (M-57^+).

Reduction of N-benzyl imine derivative of acetophenone with $SmBr_2$-HMPA:

To 14.3 mL of 0.07M SmI_2 (1 mmol) in a 50 mL dried round bottom flask equipped with stir bar, 375 mg (4.00 mmol) of LiBr was added. Stirring was performed for 10 minutes, in which time a color change from blue to purple was observed. Exactly 8.7 mL of HMPA (50 mmol) was then added. This solution was stirred for 10 minutes, until a royal purple color was observed. To this solution, 60 μL (0.30 mmol) of ketimine was added. The reaction was allowed to stir for 24 hours after which it was quenched with saturated aqueous ammonium chloride, followed by extraction into diethyl ether. The ether was washed with two 50 mL portions of aqueous sodium thiosulfate followed by three 50 mL rinses with distilled water. Yield >99%. GCMS: m/z 211 (M^+), 196 (M-15^+).

Reductive coupling of alkyl halide with π-bond by $SmBr_2$-HMPA:

To 14.3 mL of 0.07M SmI_2 (1 mmol) in a 50 mL dried round bottom flask equipped with stir bar, 375 mg (4.00 mmol) of LiBr was added. Stirring was performed for 10 minutes, in which time a color change from blue to purple was observed. Exactly 8.7 mL of HMPA (50 mmol) was then added. This solution was stirred for 10 minutes, until a royal purple color was observed. To this solution, 94 μL of 1-bromodecane (0.45 mmol) and 71 μL of 2-octanone (0.45 mmol) were added simultaneously. The solution was allowed to stir for 15 minutes. The reaction was then quenched by addition of saturated aqueous ammonium chloride, followed by extraction into diethyl ether. Two 50 mL washes of aqueous sodium thiosulfate followed by three 50 mL rinses of distilled water were then performed. Coupling yield 52%. GCMS: m/z 255 ($M-15^+$), 185 ($M-85^+$).

Isolation of product from reduction of N-benzyl imine of pinacolone

To 14.3 mL of 0.07M SmI_2 (1 mmol) in a 50 mL dried round bottom flask equipped with stir bar, 375 mg (4.00 mmol) of LiBr was added. Stirring was performed for 10 minutes, in which time a color change from blue to purple was observed. Exactly 8.7 mL of HMPA (50 mmol) was then added. This solution was stirred for 10 minutes, until a royal purple color was observed. To this, 75 uL of ketimine (0.37 mmol) was added. The reaction was allowed to stir for 1 hour. The reaction was then quenched by addition of saturated aqueous ammonium chloride, followed by extraction into diethyl ether. Two 50 mL washes of aqueous sodium thiosulfate followed by three 50 mL rinses of distilled water were then performed. Removal of HMPA was performed by addition of florisil to the ether extract. This florisil was then removed by gravity filtration and washed with ether once. The ether extracts were then collected in a tared round bottom flask. The ether was removed by rotary evaporation, yielding the product in 90 % yield.

UV-Vis Spectroscopy Studies

All UV-Vis studies employed a 5Q quartz cuvette of pathlength 1 cm. All solutions were made in a nitrogen atmosphere dry box and sealed in cuvettes with glass stoppers edged with Apiezon grease. These solutions were analyzed within 15 minutes of removal from the nitrogen atmosphere.

a) THF blanks:

THF was used as a background for all UV-Vis studies. A cuvette was filled with distilled, degassed THF, capped and sealed to prevent contamination from water/O_2, and immediately analyzed.

b) SmI_2 solutions:

Approximately 5 mL of 0.07 M SmI_2 (0.35 mmol) was placed in a 50 mL round bottom flask. This was then diluted until only a pale blue color could be observed (approximately a 5-fold dilution). Cuvettes were then filled with this solution, sealed, and analyzed.

c) SmI_2-HMPA solutions:

Approximately 5 ml of 0.07 M SmI_2 (0.4 mmol) was placed in a 50 mL round bottom flask equipped with a stir bar. To this, 3.00 mL of HMPA (17.5 mmol, 50 eq.) was added. The solution was stirred until a royal purple color appeared. An approximate 1:5 ratio of SmI_2-HMPA : THF was placed in a cuvette, sealed, and analyzed.

d) $SmBr_2$ solutions:

Approximately 5 mL of 0.07 M SmI_2 (0.4 mmol) was placed in a 50 mL round bottom flask equipped with a stir bar. To this, 1.4 g of LiBr (1.4 mmol, 4 eq.) was added. The solution was allowed to stir for 10 minutes at which point a purple color was observed. An approximate 1 : 5 ratio of $SmBr_2$: THF was placed in a cuvette, sealed, and analyzed.

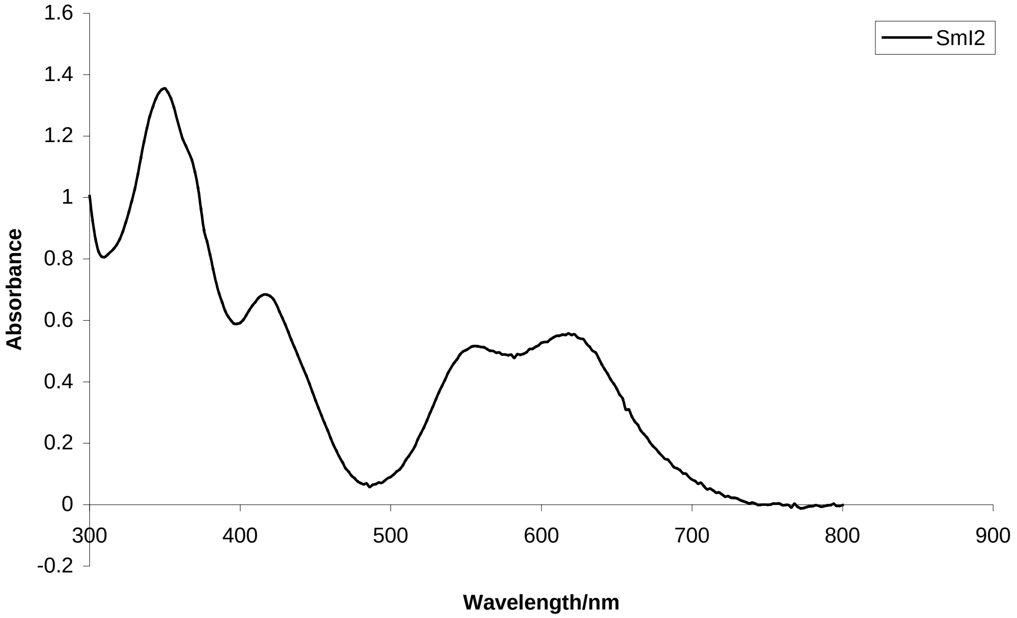
e) $SmBr_2$-HMPA solutions:

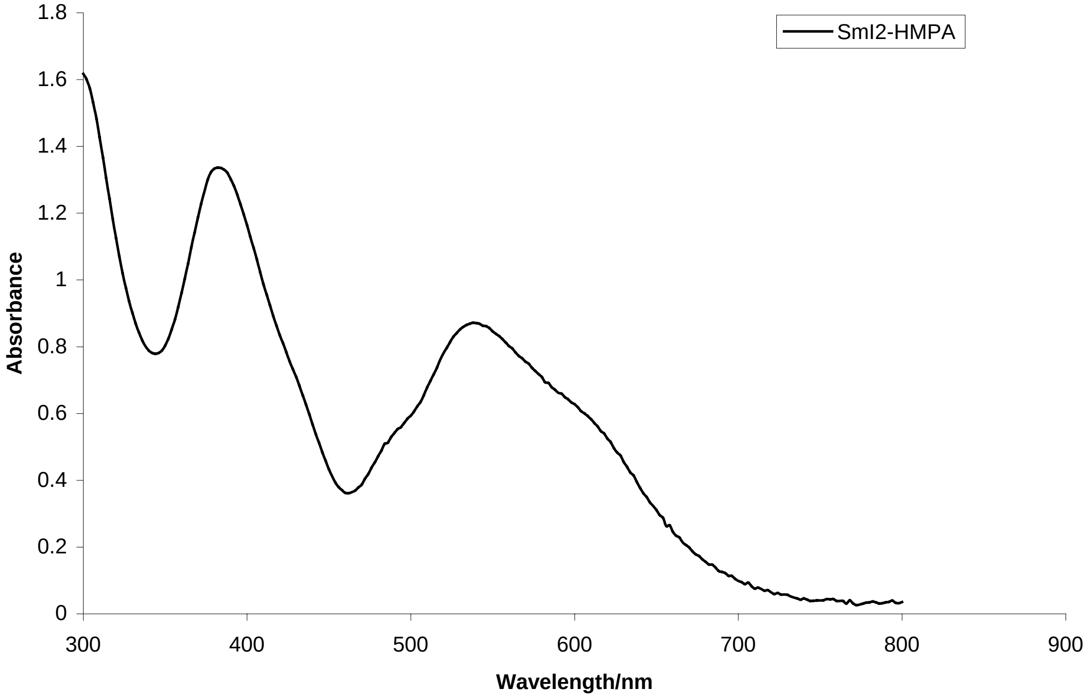
Approximately 5 mL of 0.07 M SmI_2 (0.4 mmol) was placed in a 50 mL round bottom flask equipped with a stir bar. To this, 1.4 g of LiBr (1.4 mmol, 4 eq.) was added. The solution was allowed to stir for 10 minutes at which point a purple color was observed. To this solution, 3.00 mL of HMPA (17.5 mmol, 50 eq.) was added. The solution was allowed to stir until a royal purple color observed. A 1 : 5 ratio of $SmBr_2$-HMPA solution : THF was placed in a cuvette, sealed, and analyzed.

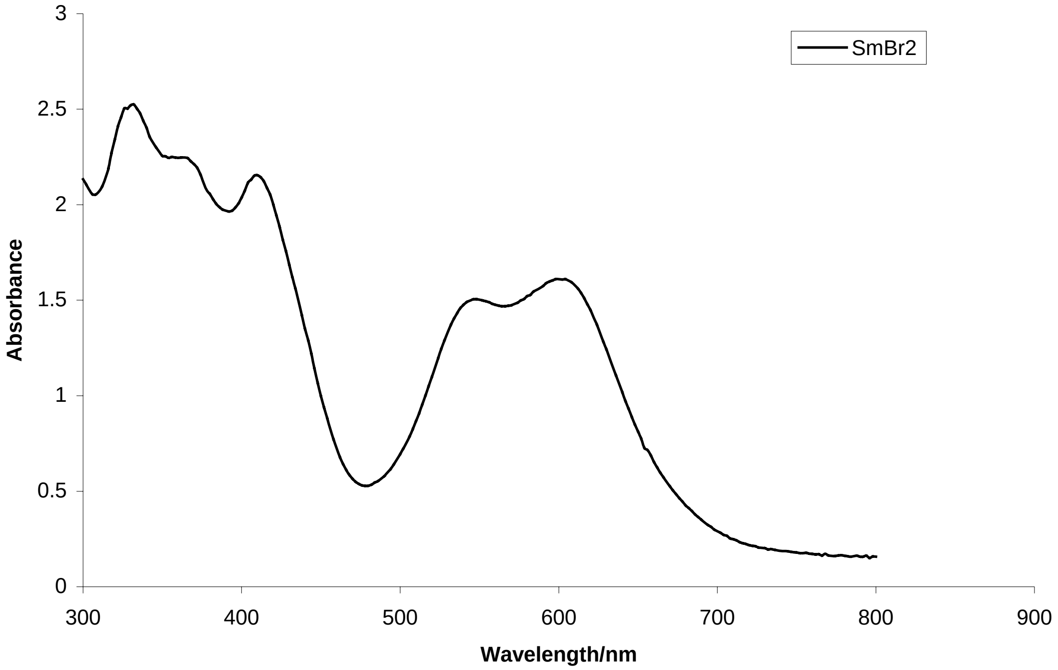
Cyclic Voltammetry Experiments

Cyclic voltammetry was performed using platinum wire auxiliary electrodes, glassy carbon working electrodes, and $Ag/AgNO_3$ reference electrodes. Working and auxiliary electrodes were cleansed by immersion in 95% ethanol for 24 hours prior to use. Working electrodes were further cleaned by use of polishing alumina followed by rinsing with acetone immediately preceding usage.

UV-Vis Spectra:






SmBr2
Absorbance
Wavelength/nm
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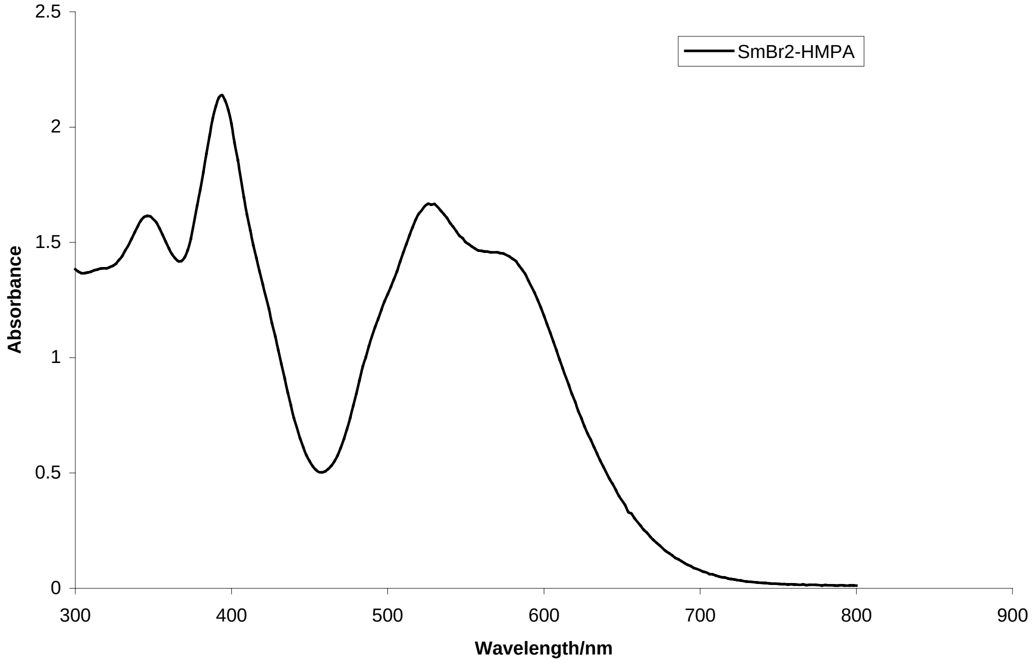
0.5
1
1.5
2
2.5
3
300
400
500
600
700
800
900


SmBr2-HMPA
Absorbance
Wavelength/nm
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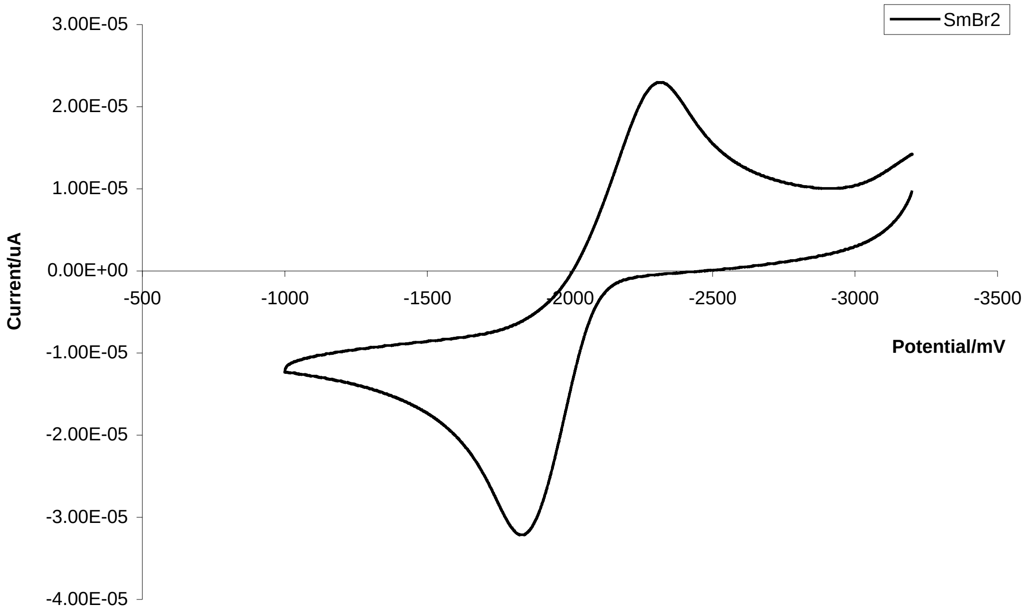
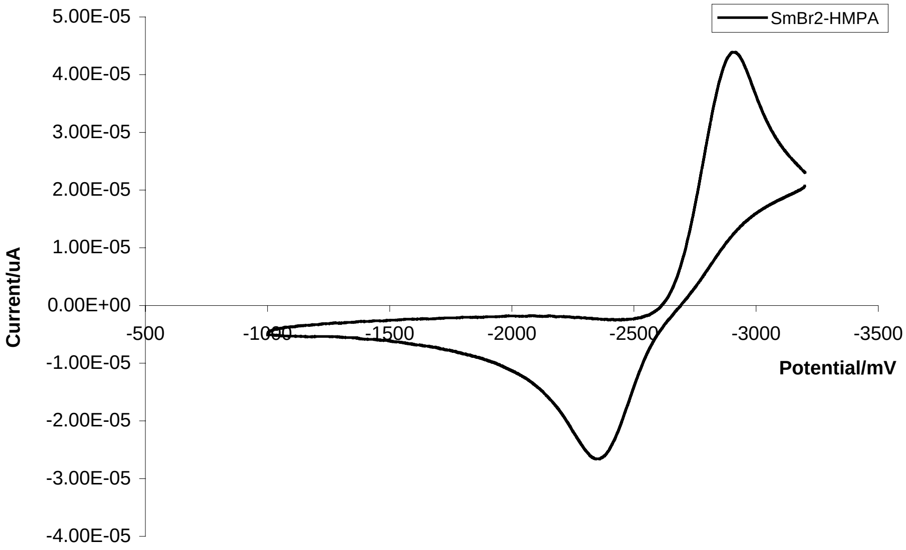
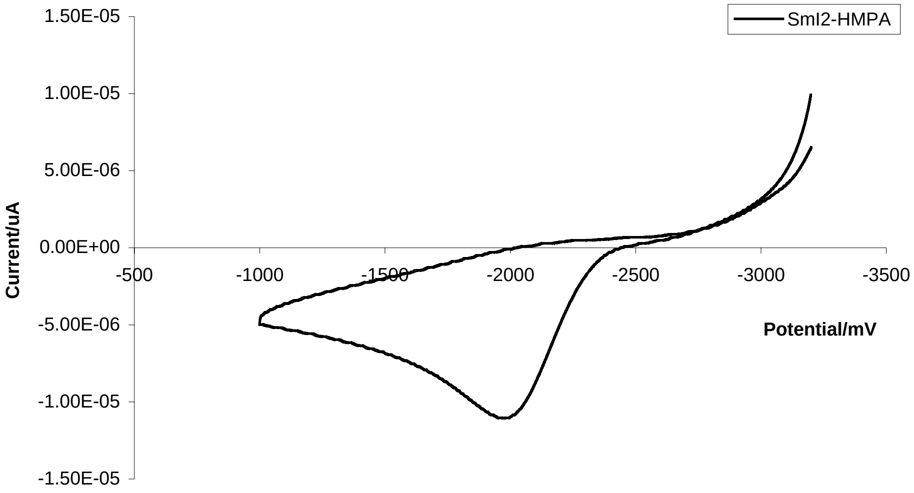
0.5
1
1.5
2
2.5
300
400
500
600
700
800
900

Cyclic Voltammograms






SmI2-HMPA
1.50E-05
1.00E-05
5.00E-06
0.00E+00
-5.00E-06
-1.00E-05
-1.50E-05
Current/uA
-500
-1000
-1500
-2000
-2500
-3000
-3500
Potential/mV