

A. Cut off solvents**Table 22.** Solvents for UV-Visible spectrum and the minimum values for measurement

Solvents	λ (nm)
CH_2Cl_2	230
CHCl_3	245
CH_3CN	195
DMF	270
DMSO	265

B. Bond distances (Å) and bond angles (°)

Table 23. Bond distances [Å] and bond angles [°] for *ctc*-[Ru(bsazpy)₂Cl₂]

- Bond distances

Atoms	Bond distances (Å)
Ru(1)-N(6)	1.972(3)
Ru(1)-N(3)	1.980(3)
Ru(1)-N(4)	2.021(3)
Ru(1)-N(1)	2.037(3)
Ru(1)-Cl(2)	2.3839(9)
Ru(1)-Cl(1)	2.3954(9)
N(1)-C(7)	1.328(4)
N(1)-C(1)	1.388(4)
N(2)-N(3)	1.297(3)
N(2)-C(7)	1.360(4)
N(3)-C(8)	1.431(4)
N(4)-C(20)	1.331(4)
N(4)-C(14)	1.389(4)
N(5)-N(6)	1.302(3)
N(5)-C(20)	1.355(4)
N(6)-C(21)	1.428(4)
S(1)-C(7)	1.720(4)
S(1)-C(6)	1.724(4)
S(2)-C(20)	1.723(4)
S(2)-C(19)	1.732(4)

Table 23. (continued)

Atoms	Bond distances (Å)
C(1)-C(2)	1.384(5)
C(1)-C(6)	1.389(5)
C(2)-C(3)	1.361(6)
C(2)-H(2)	0.89(3)
C(3)-C(4)	1.374(7)
C(3)-H(3)	0.95(3)
C(4)-C(5)	1.355(7)
C(4)-H(4)	0.81(4)
C(5)-C(6)	1.389(6)
C(5)-H(5)	0.93(3)
C(8)-C(9)	1.367(5)
C(8)-C(13)	1.381(5)
C(9)-C(10)	1.371(5)
C(9)-H(9)	0.93(3)
C(10)-C(11)	1.358(6)
C(10)-H(10)	0.91(3)
C(11)-C(12)	1.364(6)
C(11)-H(11)	0.83(4)
C(12)-C(13)	1.369(5)
C(12)-H(12)	0.89(3)
C(13)-H(13)	0.88(3)
C(14)-C(15)	1.380(5)

Table 23. (continued)

Atoms	Bond distances (Å)
C(14)-C(19)	1.390(5)
C(15)-C(16)	1.366(5)
C(15)-H(15)	0.88(3)
C(16)-C(17)	1.372(6)
C(16)-H(16)	0.92(3)
C(17)-C(18)	1.347(6)
C(17)-H(17)	0.87(3)
C(18)-C(19)	1.392(6)
C(18)-H(18)	0.83(3)
C(21)-C(22)	1.366(5)
C(21)-C(26)	1.374(5)
C(22)-C(23)	1.388(7)
C(22)-H(22)	0.93(3)
C(23)-C(24)	1.363(8)
C(23)-H(23)	0.84(3)
C(24)-C(25)	1.347(8)
C(24)-H(24)	0.89(4)
C(25)-C(26)	1.376(7)
C(25)-H(25)	0.89(4)
C(26)-H(26)	0.98(3)

Table 23. (continued)

- Bond angles

Atoms	Bond angles (°)
N(6)-Ru(1)-N(3)	103.98(10)
N(6)-Ru(1)-N(4)	77.11(14)
N(3)-Ru(1)-N(4)	97.34(12)
N(6)-Ru(1)-N(1)	97.15(13)
N(3)-Ru(1)-N(1)	76.90(13)
N(4)-Ru(1)-N(1)	170.80(11)
N(6)-Ru(1)-Cl(2)	84.20(8)
N(3)-Ru(1)-Cl(2)	171.36(8)
N(4)-Ru(1)-Cl(2)	87.10(7)
N(6)-Ru(1)-N(3)	103.98(10)
N(6)-Ru(1)-N(4)	77.11(14)
N(3)-Ru(1)-N(4)	97.34(12)
N(6)-Ru(1)-N(1)	97.15(13)
N(3)-Ru(1)-N(1)	76.90(13)
N(4)-Ru(1)-N(1)	170.80(11)
N(6)-Ru(1)-Cl(2)	84.20(8)
N(3)-Ru(1)-Cl(2)	171.36(8)
N(4)-Ru(1)-Cl(2)	87.10(7)
N(1)-Ru(1)-Cl(2)	99.58(10)
N(6)-Ru(1)-Cl(1)	171.38(9)

Table 23. (continued)

Atoms	Bond angles ($^{\circ}$)
N(3)-Ru(1)-Cl(1)	83.95(7)
N(4)-Ru(1)-Cl(1)	98.75(10)
N(1)-Ru(1)-Cl(1)	87.87(7)
Cl(2)-Ru(1)-Cl(1)	88.06(3)
C(7)-N(1)-C(1)	109.9(3)
C(7)-N(1)-Ru(1)	110.6(2)
C(1)-N(1)-Ru(1)	139.4(3)
N(3)-N(2)-C(7)	110.0(3)
N(2)-N(3)-C(8)	114.1(3)
N(2)-N(3)-Ru(1)	119.7(2)
C(8)-N(3)-Ru(1)	124.8(2)
C(20)-N(4)-C(14)	110.5(3)
C(20)-N(4)-Ru(1)	110.5(3)
C(14)-N(4)-Ru(1)	139.1(3)
N(6)-N(5)-C(20)	109.8(3)
N(5)-N(6)-C(21)	114.5(3)
N(5)-N(6)-Ru(1)	119.3(2)
C(21)-N(6)-Ru(1)	124.2(2)
C(7)-S(1)-C(6)	87.8(2)
C(20)-S(2)-C(19)	88.5(2)
C(2)-C(1)-N(1)	126.9(4)

Table 23. (continued)

Atoms	Bond angles (°)
C(2)-C(1)-C(6)	119.9(4)
N(1)-C(1)-C(6)	113.3(4)
C(3)-C(2)-C(1)	118.6(5)
C(3)-C(2)-H(2)	123.1(19)
C(1)-C(2)-H(2)	118.3(19)
C(2)-C(3)-C(4)	121.3(5)
C(2)-C(3)-H(3)	115(2)
C(4)-C(3)-H(3)	124.0(19)
C(5)-C(4)-C(3)	121.2(5)
C(5)-C(4)-H(4)	119(3)
C(3)-C(4)-H(4)	120(3)
C(4)-C(5)-C(6)	118.4(5)
C(4)-C(5)-H(5)	125.4(18)
C(6)-C(5)-H(5)	116.1(18)
C(5)-C(6)-C(1)	120.6(4)
C(5)-C(6)-S(1)	127.4(4)
C(1)-C(6)-S(1)	112.1(3)
N(1)-C(7)-N(2)	121.3(3)
N(1)-C(7)-S(1)	116.9(3)
N(2)-C(7)-S(1)	121.3(3)
C(9)-C(8)-C(13)	120.1(4)

Table 23. (continued)

Atoms	Bond angles (°)
C(9)-C(8)-N(3)	120.1(4)
C(13)-C(8)-N(3)	119.8(4)
C(8)-C(9)-C(10)	119.8(4)
C(8)-C(9)-H(9)	118.2(16)
C(10)-C(9)-H(9)	121.9(16)
C(11)-C(10)-C(9)	119.9(5)
C(11)-C(10)-H(10)	123.5(19)
C(9)-C(10)-H(10)	116.5(19)
C(10)-C(11)-C(12)	120.8(5)
C(10)-C(11)-H(11)	122(3)
C(12)-C(11)-H(11)	117(3)
C(11)-C(12)-C(13)	119.8(5)
C(11)-C(12)-H(12)	121(2)
C(13)-C(12)-H(12)	120(2)
C(12)-C(13)-C(8)	119.5(5)
C(12)-C(13)-H(13)	120(2)
C(8)-C(13)-H(13)	120(2)
C(15)-C(14)-N(4)	126.8(4)
C(15)-C(14)-C(19)	119.5(4)
N(4)-C(14)-C(19)	113.6(4)
C(16)-C(15)-C(14)	118.9(5)
C(16)-C(15)-H(15)	120.8(19)

Table 23. (continued)

Atoms	Bond angles (°)
C(14)-C(15)-H(15)	120.3(19)
C(15)-C(16)-C(17)	121.2(5)
C(15)-C(16)-H(16)	118(2)
C(17)-C(16)-H(16)	121(2)
C(18)-C(17)-C(16)	121.3(5)
C(18)-C(17)-H(17)	119(2)
C(16)-C(17)-H(17)	119(2)
C(17)-C(18)-C(19)	118.5(5)
C(17)-C(18)-H(18)	128(2)
C(19)-C(18)-H(18)	113(2)
C(14)-C(19)-C(18)	120.6(4)
C(14)-C(19)-S(2)	111.3(4)
C(18)-C(19)-S(2)	128.0(4)
N(4)-C(20)-N(5)	121.3(3)
N(4)-C(20)-S(2)	116.1(3)
N(5)-C(20)-S(2)	122.2(4)
C(22)-C(21)-C(26)	120.7(5)
C(22)-C(21)-N(6)	119.9(4)
C(26)-C(21)-N(6)	119.2(5)
C(21)-C(22)-C(23)	119.0(6)
C(21)-C(22)-H(22)	117(2)
C(23)-C(22)-H(22)	124(2)
C(24)-C(23)-C(22)	120.2(6)

Table 23. (continued)

Atoms	Bond angles (°)
C(24)-C(23)-H(23)	126(3)
C(22)-C(23)-H(23)	114(3)
C(25)-C(24)-C(23)	120.3(6)
C(25)-C(24)-H(24)	118(3)
C(23)-C(24)-H(24)	121(3)
C(24)-C(25)-C(26)	120.8(6)
C(24)-C(25)-H(25)	122(3)
C(26)-C(25)-H(25)	117(3)
C(21)-C(26)-C(25)	119.1(6)
C(21)-C(26)-H(26)	117(2)
C(25)-C(26)-H(26)	124(2)

Table 24. Bond distances [\AA] and bond angles [$^\circ$] for *cct*-[Ru(bsazpy)₂Cl₂]- Bond distances

Atoms	Bond distances (\AA)
Ru(1)-N(3)	2.017(3)
Ru(1)-N(4)	2.023(3)
Ru(1)-N(1)	2.024(3)
Ru(1)-N(6)	2.070(3)
Ru(1)-Cl(2)	2.3566(11)
Ru(1)-Cl(1)	2.3873(11)
S(1)-C(7)	1.726(4)
S(1)-C(6)	1.744(4)
S(2)-C(20)	1.730(4)
S(2)-C(19)	1.743(5)
N(1)-C(7)	1.331(5)
N(1)-C(1)	1.393(5)
N(2)-N(3)	1.304(4)
N(2)-C(7)	1.360(5)
N(3)-C(8)	1.432(5)
N(4)-C(20)	1.331(5)
N(4)-C(14)	1.393(5)
N(5)-N(6)	1.304(4)
N(5)-C(20)	1.348(5)
N(6)-C(21)	1.432(5)
C(1)-C(2)	1.391(6)

Table 24. (continued)

Atoms	Bond distances (Å)
C(1)-C(6)	1.396(5)
C(2)-C(3)	1.371(6)
C(2)-H(2)	0.85(4)
C(3)-C(4)	1.391(7)
C(3)-H(3)	0.92(5)
C(4)-C(5)	1.371(7)
C(4)-H(4)	0.94(5)
C(5)-C(6)	1.392(6)
C(5)-H(5)	0.86(5)
C(8)-C(9)	1.372(6)
C(8)-C(13)	1.383(6)
C(9)-C(10)	1.375(7)
C(9)-H(9)	0.91(5)
C(10)-C(11)	1.362(8)
C(10)-H(10)	0.78(5)
C(11)-C(12)	1.363(8)
C(11)-H(11)	0.86(5)
C(12)-C(13)	1.369(7)
C(12)-H(12)	0.90(5)
C(13)-H(13)	0.84(5)
C(14)-C(15)	1.395(6)
C(14)-C(19)	1.402(6)

Table 24. (continued)

Atoms	Bond distances (Å)
C(15)-C(16)	1.364(6)
C(15)-H(15)	0.87(4)
C(16)-C(17)	1.382(8)
C(16)-H(16)	0.90(5)
C(17)-C(18)	1.352(8)
C(17)-H(17)	0.84(5)
C(18)-C(19)	1.392(7)
C(18)-H(18)	0.88(4)
C(21)-C(22)	1.374(6)
C(21)-C(26)	1.391(6)
C(22)-C(23)	1.380(7)
C(22)-H(22)	0.85(4)
C(23)-C(24)	1.368(8)
C(23)-H(23)	0.89(5)
C(24)-C(25)	1.366(9)
C(24)-H(24)	0.90(6)
C(25)-C(26)	1.380(7)
C(25)-H(25)	0.84(5)
C(26)-H(26)	0.87(5)
C(27)-Cl(3)	1.674(9)
C(27)-Cl(4)	1.732(9)
C(27)-H(27A)	0.9700
C(27)-H(27B)	0.9700

Table 24. (continued)- Bond angles

Atoms	Bond angles (°)
N(3)-Ru(1)-N(6)	175.62(12)
N(4)-Ru(1)-N(6)	76.09(13)
N(1)-Ru(1)-N(6)	105.97(12)
N(3)-Ru(1)-Cl(2)	95.47(9)
N(4)-Ru(1)-Cl(2)	91.15(9)
N(1)-Ru(1)-Cl(2)	170.29(9)
N(6)-Ru(1)-Cl(2)	82.60(9)
N(3)-Ru(1)-Cl(1)	85.30(9)
N(4)-Ru(1)-Cl(1)	174.63(9)
N(1)-Ru(1)-Cl(1)	85.89(9)
N(6)-Ru(1)-Cl(1)	98.54(9)
Cl(2)-Ru(1)-Cl(1)	88.33(4)
C(7)-S(1)-C(6)	88.62(19)
C(20)-S(2)-C(19)	88.66(19)
C(7)-N(1)-C(1)	110.8(3)
C(7)-N(1)-Ru(1)	111.9(2)
C(1)-N(1)-Ru(1)	137.0(3)
N(3)-N(2)-C(7)	109.9(3)
N(2)-N(3)-C(8)	113.1(3)
N(2)-N(3)-Ru(1)	119.4(2)
C(8)-N(3)-Ru(1)	127.2(2)
C(20)-N(4)-C(14)	110.5(3)

Table 24. (continued)

Atoms	Bond angles ($^{\circ}$)
C(20)-N(4)-Ru(1)	111.8(3)
C(14)-N(4)-Ru(1)	137.7(3)
N(6)-N(5)-C(20)	110.9(3)
N(5)-N(6)-C(21)	111.5(3)
N(5)-N(6)-Ru(1)	116.9(2)
C(21)-N(6)-Ru(1)	130.2(3)
C(2)-C(1)-N(1)	126.0(4)
C(2)-C(1)-C(6)	120.4(4)
N(1)-C(1)-C(6)	113.6(3)
C(3)-C(2)-C(1)	118.1(4)
C(3)-C(2)-H(2)	119(3)
C(1)-C(2)-H(2)	123(3)
C(2)-C(3)-C(4)	121.3(5)
C(2)-C(3)-H(3)	121(3)
C(4)-C(3)-H(3)	117(3)
C(5)-C(4)-C(3)	121.5(5)
C(5)-C(4)-H(4)	122(3)
C(3)-C(4)-H(4)	116(3)
C(4)-C(5)-C(6)	117.6(4)
C(4)-C(5)-H(5)	121(3)
C(6)-C(5)-H(5)	121(4)
C(5)-C(6)-C(1)	121.2(4)

Table 24. (continued)

Atoms	Bond angles (°)
C(5)-C(6)-S(1)	127.9(3)
C(1)-C(6)-S(1)	111.0(3)
N(1)-C(7)-N(2)	121.3(3)
N(1)-C(7)-S(1)	116.0(3)
N(2)-C(7)-S(1)	122.5(3)
C(9)-C(8)-C(13)	120.4(4)
C(9)-C(8)-N(3)	119.3(4)
C(13)-C(8)-N(3)	120.4(4)
C(8)-C(9)-C(10)	119.4(4)
C(8)-C(9)-H(9)	119(3)
C(10)-C(9)-H(9)	121(3)
C(11)-C(10)-C(9)	120.6(5)
C(11)-C(10)-H(10)	121(4)
C(9)-C(10)-H(10)	117(4)
C(10)-C(11)-C(12)	119.6(5)
C(10)-C(11)-H(11)	117(4)
C(12)-C(11)-H(11)	123(4)
C(11)-C(12)-C(13)	121.2(5)
C(11)-C(12)-H(12)	120(3)
C(13)-C(12)-H(12)	118(3)
C(12)-C(13)-C(8)	118.8(4)
C(12)-C(13)-H(13)	125(3)

Table 24. (continued)

Atoms	Bond angles (°)
C(8)-C(13)-H(13)	116(3)
N(4)-C(14)-C(15)	126.4(4)
N(4)-C(14)-C(19)	113.8(4)
C(15)-C(14)-C(19)	119.7(4)
C(16)-C(15)-C(14)	118.2(4)
C(16)-C(15)-H(15)	122(3)
C(14)-C(15)-H(15)	120(3)
C(15)-C(16)-C(17)	121.4(5)
C(15)-C(16)-H(16)	120(3)
C(17)-C(16)-H(16)	119(3)
C(18)-C(17)-C(16)	122.1(5)
C(18)-C(17)-H(17)	122(4)
C(16)-C(17)-H(17)	116(4)
C(17)-C(18)-C(19)	117.8(5)
C(17)-C(18)-H(18)	128(3)
C(19)-C(18)-H(18)	114(3)
C(18)-C(19)-C(14)	120.9(4)
C(18)-C(19)-S(2)	128.3(4)
C(14)-C(19)-S(2)	110.7(3)
N(4)-C(20)-N(5)	122.1(4)
N(4)-C(20)-S(2)	116.2(3)
N(5)-C(20)-S(2)	121.5(3)

Table 24. (continued)

Atoms	Bond angles ($^{\circ}$)
C(22)-C(21)-C(26)	120.0(4)
C(22)-C(21)-N(6)	119.8(4)
C(26)-C(21)-N(6)	120.1(4)
C(21)-C(22)-C(23)	119.5(5)
C(21)-C(22)-H(22)	122(3)
C(23)-C(22)-H(22)	118(3)
C(24)-C(23)-C(22)	120.5(6)
C(24)-C(23)-H(23)	121(4)
C(22)-C(23)-H(23)	118(4)
C(25)-C(24)-C(23)	120.3(5)
C(25)-C(24)-H(24)	121(4)
C(23)-C(24)-H(24)	118(4)
C(24)-C(25)-C(26)	120.1(5)
C(24)-C(25)-H(25)	124(4)
C(26)-C(25)-H(25)	115(4)
C(25)-C(26)-C(21)	119.5(5)
C(25)-C(26)-H(26)	124(3)
C(21)-C(26)-H(26)	116(3)
Cl(3)-C(27)-Cl(4)	114.8(4)
Cl(3)-C(27)-H(27A)	108.6
Cl(4)-C(27)-H(27A)	108.6
Cl(3)-C(27)-H(27B)	108.6
Cl(4)-C(27)-H(27B)	108.6

C. Cyclic Voltammograms

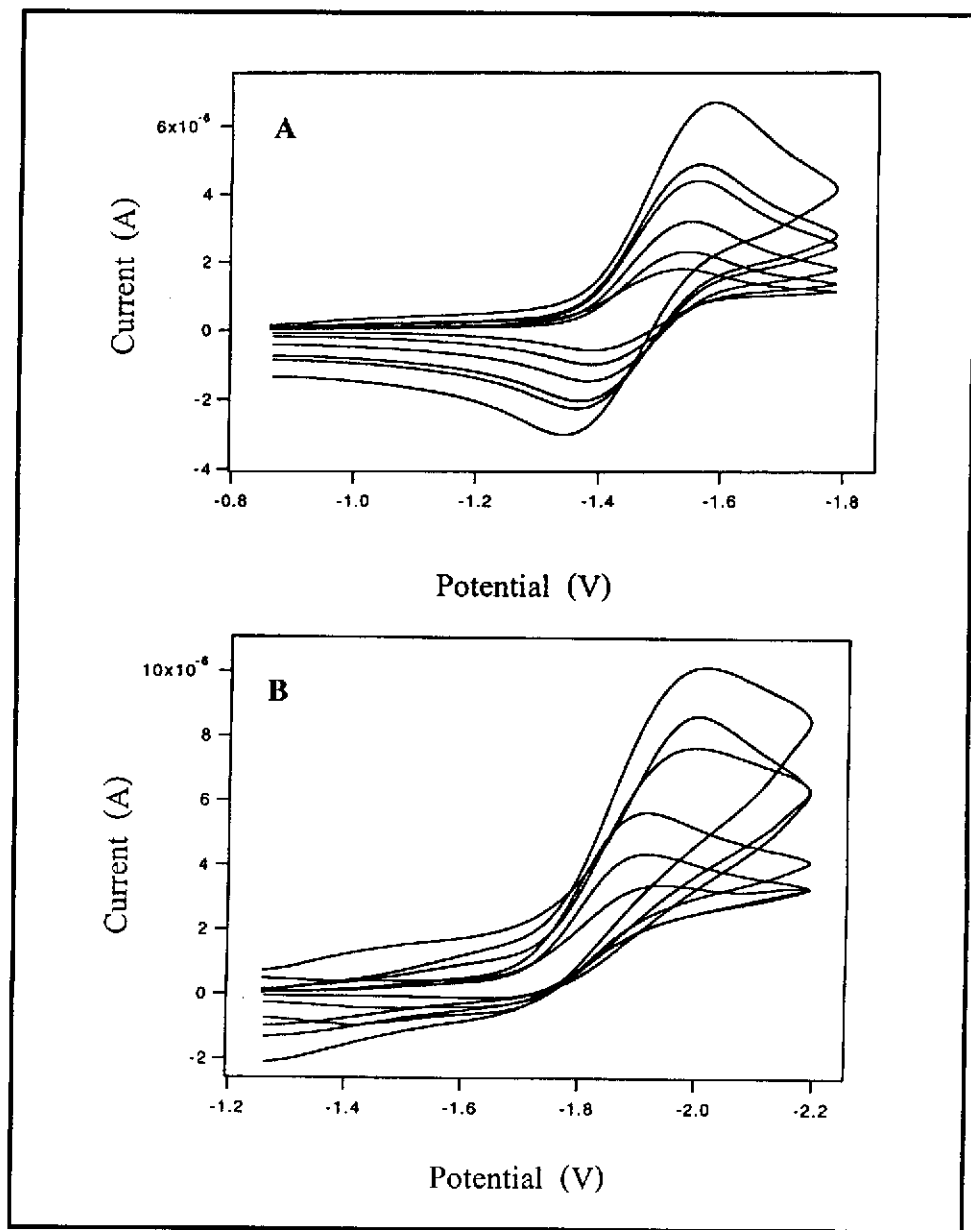


Figure 46. Cyclic voltammogram of bsazpy (A) and azpy (B) with various scan rates 50-1000 mV/s in the reduction range.

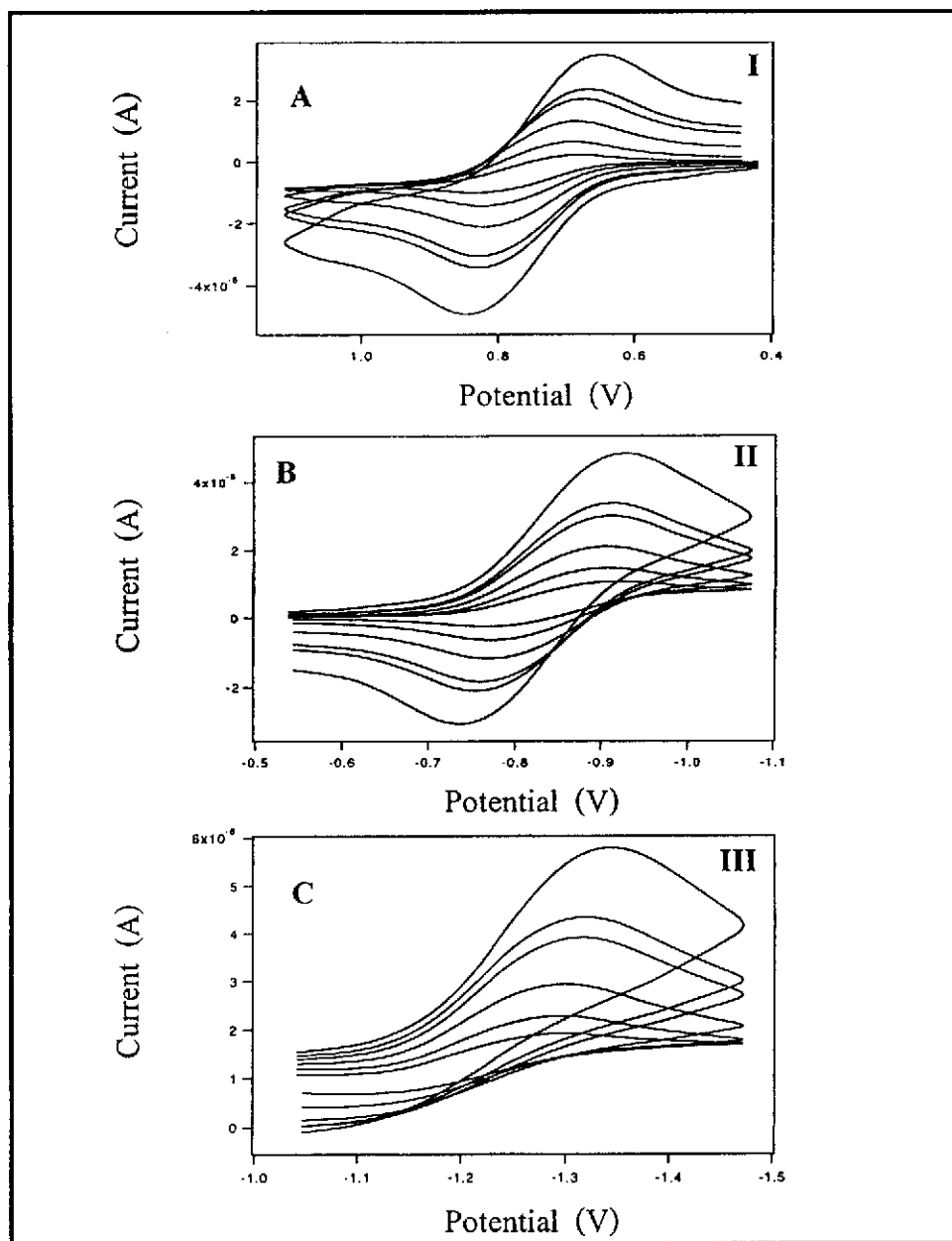


Figure 47. Cyclic voltammogram of *ctc*-[Ru(bsazpy)₂Cl₂] – couple I (Ru^{III}/Ru^{II})

(A) in the oxidation range and couple II (B), couple III (C) in the reduction range with various scan rates 50-1000 mV/s .

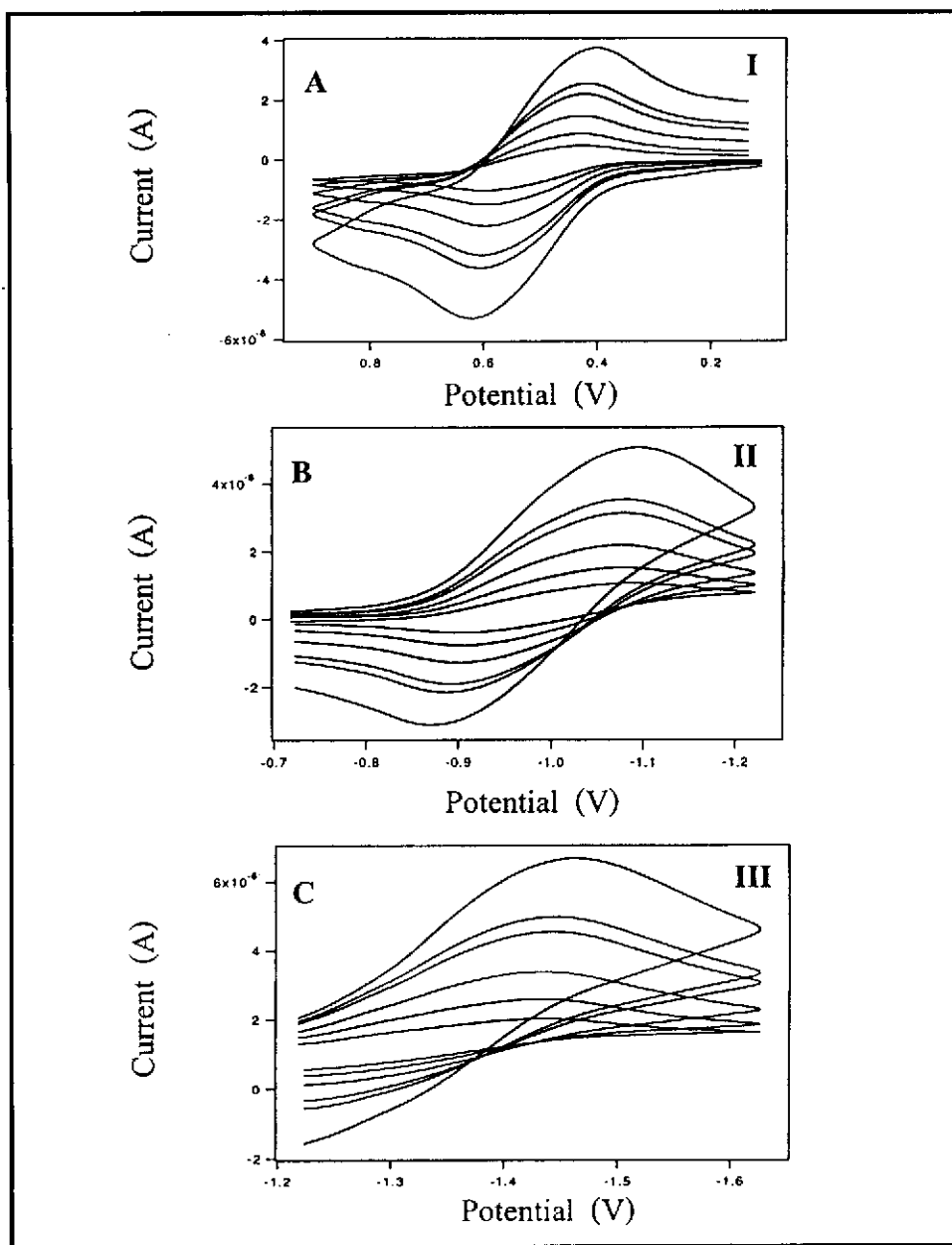


Figure 48. Cyclic voltammogram of $cct-[Ru(bsazpy)_2Cl_2]$ – couple I (Ru^{III}/Ru^{II})

(A) in the oxidation range and couple II (B), couple III (C) in the reduction range with various scan rates 50-1000 mV/s .

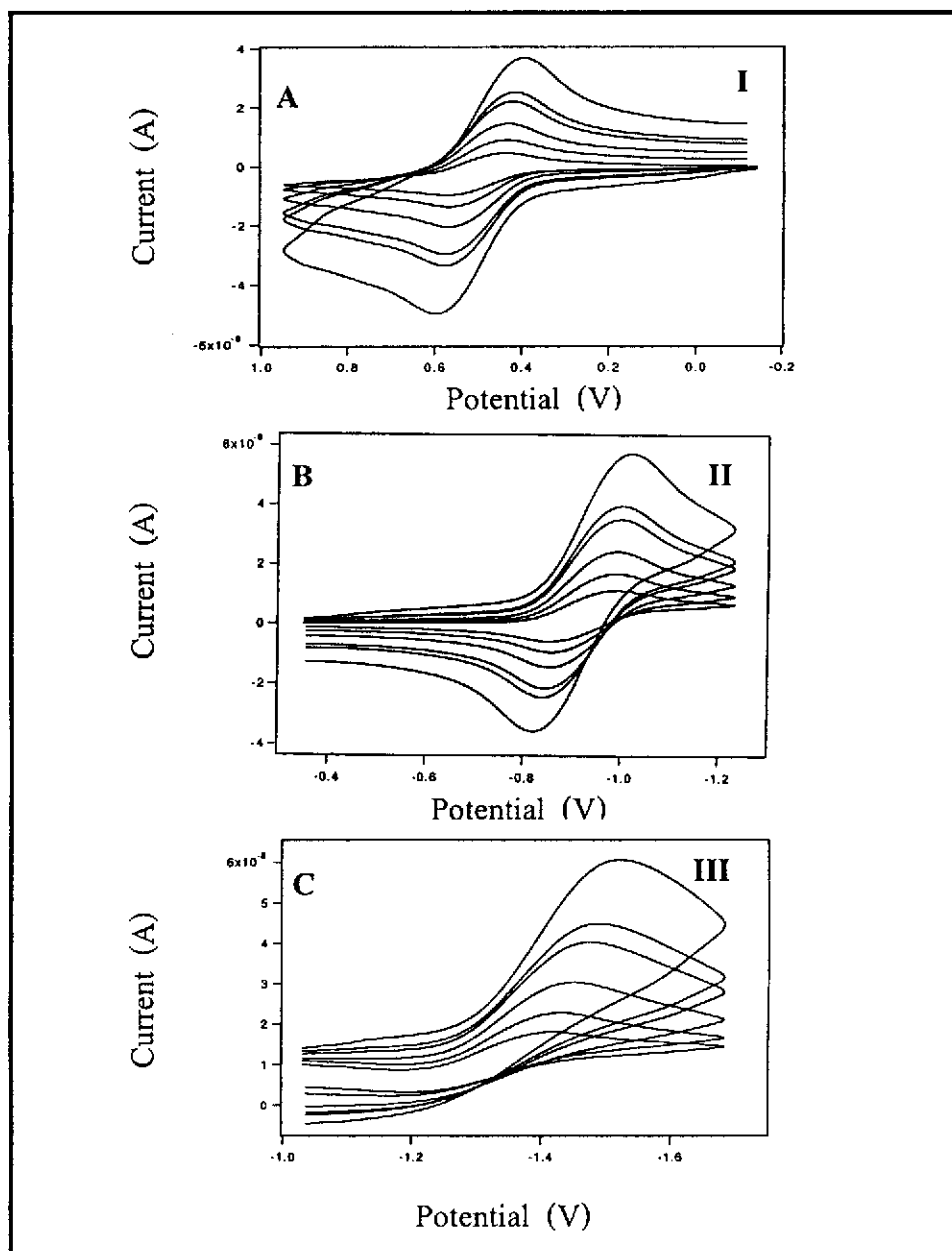


Figure 49. Cyclic voltammogram of *ttt*-[Ru(bsazpy)₂Cl₂] – couple I (Ru^{III}/Ru^{II})

(A) in the oxidation range and couple II (B), couple III (C) in the reduction range with various scan rates 50-1000 mV/s .

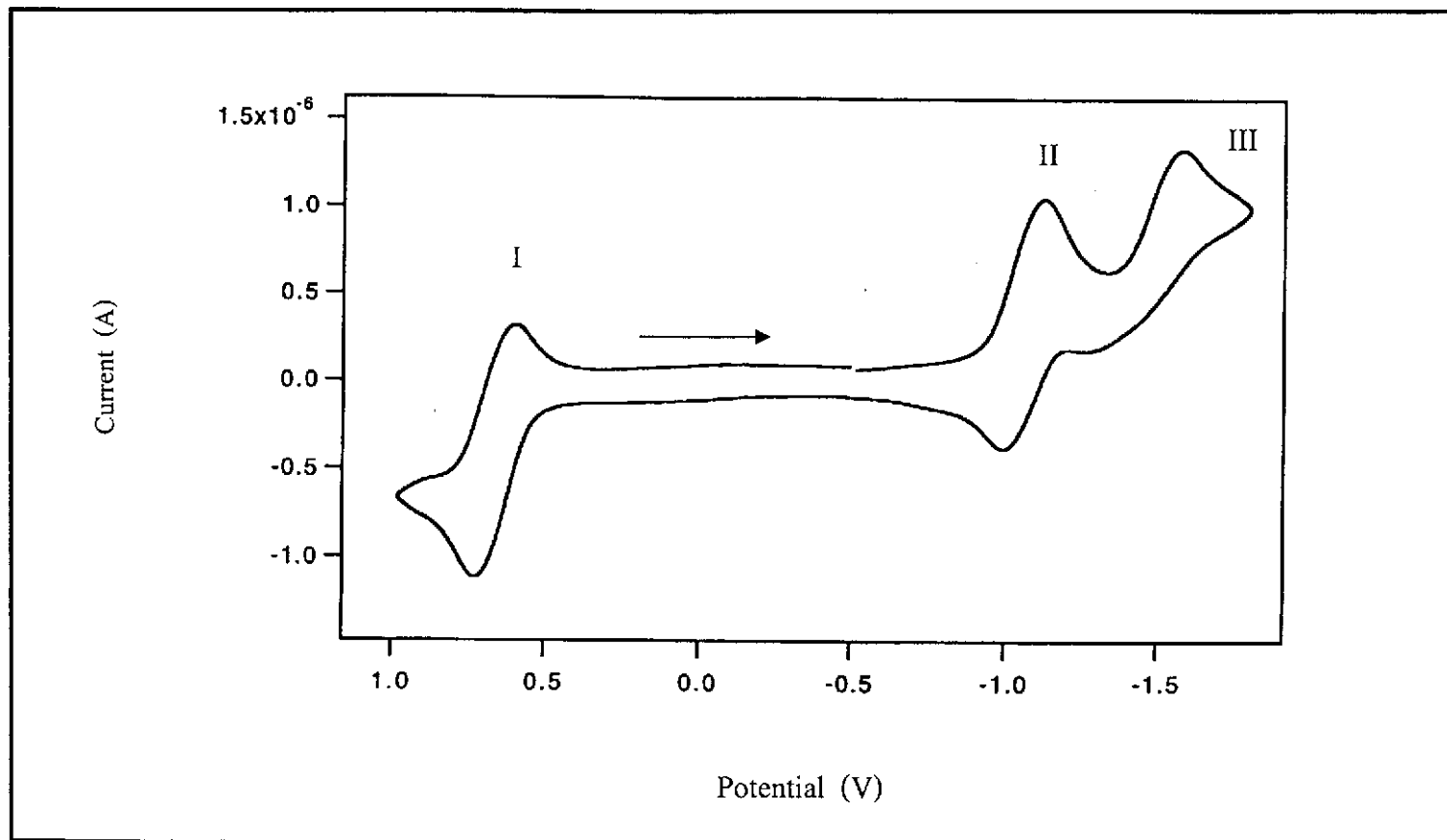


Figure 50. Cyclic voltammogram of *ctc*-[Ru(azpy)₂Cl₂] in 0.1 M TBAH CH₂Cl₂ at scan rate 50 mV/s.

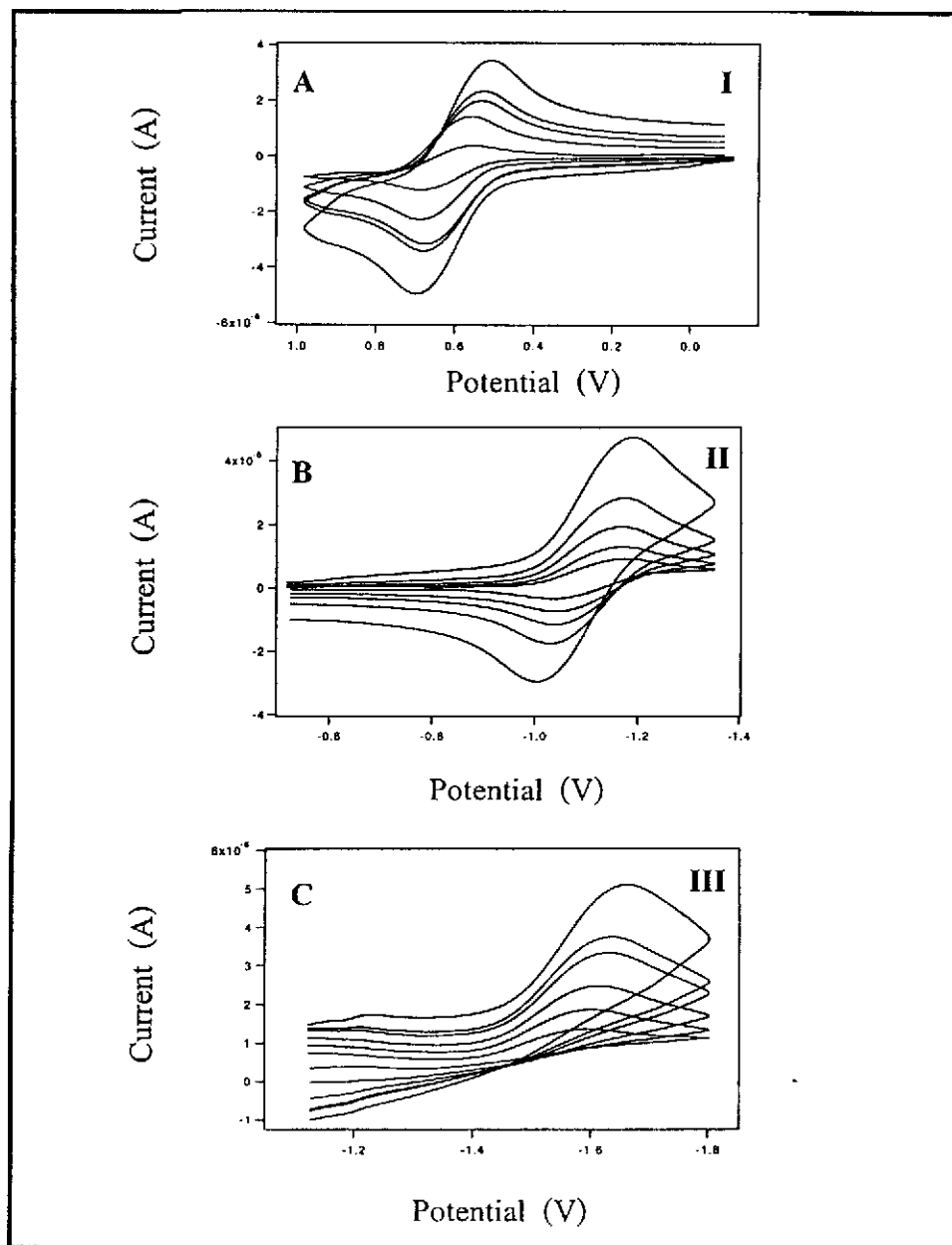


Figure 51. Cyclic voltammogram of *ctc*-[Ru(azpy)₂Cl₂] – couple I (Ru^{III}/Ru^{II}) (A) in the oxidation range and couple II (B), couple III (C) in the reduction range with various scan rates 50-1000 mV/s .