

**APPENDIX**

**A. Cut off solvents****Table 19.** The solvents for UV-Visible spectrum and the minimum values for measurement

| Solvents                 | $\lambda$ (nm) |
|--------------------------|----------------|
| $\text{CH}_2\text{Cl}_2$ | 230            |
| $\text{CHCl}_3$          | 245            |
| $\text{CH}_3\text{CN}$   | 195            |
| DMF                      | 270            |
| DMSO                     | 265            |

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

**Table 20.** The bond distances (Å) and angles (°) of the *ctc*-[Ru(azine)<sub>2</sub>Cl<sub>2</sub>] complex

Bond distances

| Atoms       | Angstroms (Å) |
|-------------|---------------|
| Ru(1)-N(8)  | 1.971(2)      |
| Ru(1)-N(4)  | 1.990(2)      |
| Ru(1)-N(5)  | 2.019(2)      |
| Ru(1)-N(1)  | 2.019(2)      |
| Ru(1)-Cl(2) | 2.3830(8)     |
| Ru(1)-Cl(1) | 2.4007(8)     |
| N(1)-C(1)   | 1.334(4)      |
| N(1)-C(4)   | 1.356(4)      |
| N(2)-C(3)   | 1.323(5)      |
| N(2)-C(2)   | 1.327(5)      |
| N(3)-N(4)   | 1.289(3)      |
| N(3)-C(4)   | 1.378(4)      |
| N(4)-C(5)   | 1.435(4)      |
| N(5)-C(11)  | 1.342(4)      |
| N(5)-C(14)  | 1.352(4)      |
| N(6)-C(13)  | 1.315(5)      |
| N(6)-C(12)  | 1.334(5)      |
| N(7)-N(8)   | 1.297(3)      |
| N(7)-C(14)  | 1.377(4)      |
| N(8)-C(15)  | 1.428(4)      |

Table 20. (continued)

| Atoms       | Angstroms (Å) |
|-------------|---------------|
| C(1)-C(2)   | 1.370(5)      |
| C(1)-H(1)   | 0.9300        |
| C(2)-H(2)   | 0.9300        |
| C(3)-C(4)   | 1.392(4)      |
| C(3)-H(3)   | 0.9300        |
| C(5)-C(6)   | 1.373(4)      |
| C(5)-C(10)  | 1.381(4)      |
| C(6)-C(7)   | 1.377(5)      |
| C(6)-H(6)   | 0.9300        |
| C(7)-C(8)   | 1.377(6)      |
| C(7)-H(7)   | 0.9300        |
| C(8)-C(9)   | 1.365(6)      |
| C(8)-H(8)   | 0.9300        |
| C(9)-C(10)  | 1.384(5)      |
| C(9)-H(9)   | 0.9300        |
| C(10)-H(10) | 0.9300        |
| C(11)-C(12) | 1.380(5)      |
| C(11)-H(11) | 0.9300        |
| C(12)-H(12) | 0.9300        |
| C(13)-C(14) | 1.394(5)      |
| C(13)-H(13) | 0.9300        |
| C(15)-C(20) | 1.377(5)      |
| C(15)-C(16) | 1.388(5)      |

Table 20. (continued)

| Atoms        | Angstroms (Å) |
|--------------|---------------|
| C(16)-C(17)  | 1.365(6)      |
| C(16)-H(16)  | 0.9300        |
| C(17)-C(18)  | 1.374(7)      |
| C(17)-H(17)  | 0.9300        |
| C(18)-C(19)  | 1.375(6)      |
| C(18)-H(18)  | 0.9300        |
| C(19)-C(20)  | 1.385(5)      |
| C(19)-H(19)  | 0.9300        |
| C(20)-H(20)  | 0.9300        |
| C(21)-Cl(3)  | 1.694(7)      |
| C(21)-Cl(4)  | 1.716(7)      |
| C(21)-H(211) | 0.9700        |
| C(21)-H(212) | 0.9700        |

Table 20. (continued)

Bond angle (°)

| Atoms             | Angle (°)  |
|-------------------|------------|
| N(8)-Ru(1)-N(4)   | 101.50(10) |
| N(8)-Ru(1)-N(5)   | 77.24(10)  |
| N(4)-Ru(1)-N(5)   | 102.24(10) |
| N(8)-Ru(1)-N(1)   | 99.34(10)  |
| N(4)-Ru(1)-N(1)   | 76.99(10)  |
| N(5)-Ru(1)-N(1)   | 176.32(10) |
| N(8)-Ru(1)-Cl(2)  | 84.66(7)   |
| N(4)-Ru(1)-Cl(2)  | 169.98(7)  |
| N(5)-Ru(1)-Cl(2)  | 86.76(7)   |
| N(1)-Ru(1)-Cl(2)  | 94.31(7)   |
| N(8)-Ru(1)-Cl(1)  | 170.21(7)  |
| N(4)-Ru(1)-Cl(1)  | 85.33(7)   |
| N(5)-Ru(1)-Cl(1)  | 94.55(7)   |
| N(1)-Ru(1)-Cl(1)  | 88.98(7)   |
| Cl(2)-Ru(1)-Cl(1) | 89.60(3)   |
| C(1)-N(1)-C(4)    | 116.8(3)   |
| C(1)-N(1)-Ru(1)   | 130.7(2)   |
| C(4)-N(1)-Ru(1)   | 112.30(19) |
| C(3)-N(2)-C(2)    | 115.8(3)   |
| N(4)-N(3)-C(4)    | 111.6(2)   |
| N(3)-N(4)-C(5)    | 113.9(2)   |
| N(3)-N(4)-Ru(1)   | 119.76(19) |

Table 20. (continued)

| Atoms            | Angle (°)  |
|------------------|------------|
| C(5)-N(4)-Ru(1)  | 125.66(19) |
| C(11)-N(5)-C(14) | 117.1(3)   |
| C(11)-N(5)-Ru(1) | 131.7(2)   |
| C(14)-N(5)-Ru(1) | 111.0(2)   |
| C(13)-N(6)-C(12) | 115.8(3)   |
| N(8)-N(7)-C(14)  | 110.7(2)   |
| N(7)-N(8)-C(15)  | 113.8(2)   |
| N(7)-N(8)-Ru(1)  | 119.5(2)   |
| C(15)-N(8)-Ru(1) | 125.63(19) |
| N(1)-C(1)-C(2)   | 120.1(4)   |
| N(1)-C(1)-H(1)   | 120.0      |
| C(2)-C(1)-H(1)   | 120.0      |
| N(2)-C(2)-C(1)   | 124.4(4)   |
| N(2)-C(2)-H(2)   | 117.8      |
| C(1)-C(2)-H(2)   | 117.8      |
| N(2)-C(3)-C(4)   | 121.8(3)   |
| N(2)-C(3)-H(3)   | 119.1      |
| C(4)-C(3)-H(3)   | 119.1      |
| N(1)-C(4)-N(3)   | 118.3(3)   |
| N(1)-C(4)-C(3)   | 121.1(3)   |
| N(3)-C(4)-C(3)   | 120.6(3)   |
| C(6)-C(5)-C(10)  | 120.8(3)   |
| C(6)-C(5)-N(4)   | 119.9(3)   |
| C(10)-C(5)-N(4)  | 119.3(3)   |

Table 20. (continued)

| Atoms             | Angle (°) |
|-------------------|-----------|
| C(5)-C(6)-C(7)    | 119.5(4)  |
| C(5)-C(6)-H(6)    | 120.3     |
| C(7)-C(6)-H(6)    | 120.3     |
| C(6)-C(7)-C(8)    | 120.2(4)  |
| C(6)-C(7)-H(7)    | 119.9     |
| C(8)-C(7)-H(7)    | 119.9     |
| C(9)-C(8)-C(7)    | 120.0(3)  |
| C(9)-C(8)-H(8)    | 120.0     |
| C(7)-C(8)-H(8)    | 120.0     |
| C(8)-C(9)-C(10)   | 120.6(4)  |
| C(8)-C(9)-H(9)    | 119.7     |
| C(10)-C(9)-H(9)   | 119.7     |
| C(5)-C(10)-C(9)   | 118.9(3)  |
| C(5)-C(10)-H(10)  | 120.6     |
| C(9)-C(10)-H(10)  | 120.6     |
| N(5)-C(11)-C(12)  | 120.0(3)  |
| N(5)-C(11)-H(11)  | 120.0     |
| C(12)-C(11)-H(11) | 120.0     |
| N(6)-C(12)-C(11)  | 123.8(4)  |
| N(6)-C(12)-H(12)  | 118.1     |
| C(11)-C(12)-H(12) | 118.1     |
| N(6)-C(13)-C(14)  | 122.7(4)  |
| N(6)-C(13)-H(13)  | 118.7     |
| C(14)-C(13)-H(13) | 118.7     |



Table 20. (continued)

| Atoms              | Angle (°) |
|--------------------|-----------|
| N(5)-C(14)-N(7)    | 119.0(3)  |
| N(5)-C(14)-C(13)   | 120.6(3)  |
| N(7)-C(14)-C(13)   | 120.3(3)  |
| C(20)-C(15)-C(16)  | 121.1(3)  |
| C(20)-C(15)-N(8)   | 119.5(3)  |
| C(16)-C(15)-N(8)   | 119.4(3)  |
| C(17)-C(16)-C(15)  | 119.2(4)  |
| C(17)-C(16)-H(16)  | 120.4     |
| C(15)-C(16)-H(16)  | 120.4     |
| C(16)-C(17)-C(18)  | 120.3(4)  |
| C(16)-C(17)-H(17)  | 119.8     |
| C(18)-C(17)-H(17)  | 119.8     |
| C(17)-C(18)-C(19)  | 120.7(4)  |
| C(17)-C(18)-H(18)  | 119.7     |
| C(19)-C(18)-H(18)  | 119.7     |
| C(18)-C(19)-C(20)  | 119.8(4)  |
| C(18)-C(19)-H(19)  | 120.1     |
| C(20)-C(19)-H(19)  | 120.1     |
| C(15)-C(20)-C(19)  | 118.9(3)  |
| C(15)-C(20)-H(20)  | 120.5     |
| C(19)-C(20)-H(20)  | 120.5     |
| Cl(3)-C(21)-Cl(4)  | 114.5(4)  |
| Cl(3)-C(21)-H(211) | 108.6     |

**Table 20.** (continued)

| Atoms               | Angle (°) |
|---------------------|-----------|
| Cl(4)-C(21)-H(211)  | 108.6     |
| Cl(3)-C(21)-H(212)  | 108.6     |
| Cl(4)-C(21)-H(212)  | 108.6     |
| H(211)-C(21)-H(212) | 107.6     |

**Table 21.** The bond distances (Å) and angles (°) of the *tcc*-[Ru(azine)<sub>2</sub>Cl<sub>2</sub>] complexBond distances

| Atoms       | Angstroms (Å) |
|-------------|---------------|
| C(13)-N(6)  | 1.330(4)      |
| C(13)-C(14) | 1.390(3)      |
| C(13)-H(13) | 0.92(3)       |
| Ru-N(4)     | 1.9904(18)    |
| Ru-N(8)     | 2.0097(18)    |
| Ru-N(1)     | 2.0935(18)    |
| Ru-N(5)     | 2.0941(19)    |
| Ru-Cl(2)    | 2.3609(6)     |
| Ru-Cl(1)    | 2.3836(6)     |
| N(8)-N(7)   | 1.284(3)      |
| N(8)-C(15)  | 1.442(3)      |
| N(4)-N(3)   | 1.290(3)      |
| N(4)-C(5)   | 1.445(3)      |
| N(5)-C(11)  | 1.337(3)      |
| N(5)-C(14)  | 1.343(3)      |
| N(1)-C(1)   | 1.343(3)      |
| N(1)-C(4)   | 1.345(3)      |
| N(3)-C(4)   | 1.380(3)      |
| N(7)-C(14)  | 1.386(3)      |
| C(4)-C(3)   | 1.398(3)      |
| C(15)-C(20) | 1.380(3)      |
| C(15)-C(16) | 1.385(3)      |

Table 21. (continued)

| Atoms       | Angstroms (Å) |
|-------------|---------------|
| C(5)-C(10)  | 1.380(3)      |
| C(5)-C(6)   | 1.387(3)      |
| C(10)-C(9)  | 1.382(3)      |
| C(10)-H(10) | 0.89(3)       |
| N(2)-C(3)   | 1.323(4)      |
| N(2)-C(2)   | 1.329(4)      |
| C(11)-C(12) | 1.375(4)      |
| C(11)-H(11) | 0.97(3)       |
| C(1)-C(2)   | 1.373(4)      |
| C(1)-H(1)   | 0.97(3)       |
| C(16)-C(17) | 1.379(4)      |
| C(16)-H(16) | 0.90(3)       |
| N(6)-C(12)  | 1.326(4)      |
| C(20)-C(19) | 1.381(3)      |
| C(20)-H(20) | 0.91(2)       |
| C(2)-H(2)   | 0.85(3)       |
| C(12)-H(12) | 0.84(3)       |
| C(6)-C(7)   | 1.376(4)      |
| C(6)-H(6)   | 0.82(3)       |
| C(9)-C(8)   | 1.379(4)      |
| C(9)-H(9)   | 0.95(3)       |
| C(8)-C(7)   | 1.380(4)      |
| C(8)-H(8)   | 0.93(3)       |
| C(3)-H(3)   | 0.96(3)       |

**Table 21.** (continued)

| Atoms       | Angstroms (Å) |
|-------------|---------------|
| C(17)-C(18) | 1.366(5)      |
| C(17)-H(17) | 0.86(3)       |
| C(19)-C(18) | 1.379(4)      |
| C(19)-H(19) | 0.9300        |
| C(7)-H(7)   | 0.95(3)       |
| C(18)-H(18) | 0.88(3)       |

Table 21. (continued)

Bond angle (°)

| Atoms               | Angle (°)  |
|---------------------|------------|
| N(6)-C(13)-C(14)    | 121.8(3)   |
| N(6)-C(13)-H(13)    | 119.8(17)  |
| C(14)-C(13)-H(13)   | 118.4(18)  |
| N(4)-Ru-N(8)        | 104.18(7)  |
| N(4)-Ru-N(1)        | 75.89(7)   |
| N(8)-Ru-N(1)        | 173.03(7)  |
| N(4)-Ru-N(5)        | 172.29(7)  |
| N(8)-Ru-N(5)        | 75.40(7)   |
| N(1)-Ru-N(5)        | 105.49(7)  |
| N(4)-Ru-Cl(2)       | 90.18(6)   |
| N(8)-Ru-Cl(2)       | 97.19(6)   |
| N(1)-Ru-Cl(2)       | 89.77(5)   |
| N(5)-Ru-Cl(2)       | 82.27(5)   |
| N(4)- N(8)-Ru-Cl(1) | 88.92(6)   |
| N(1)-Ru-Cl(1)       | 84.17(5)   |
| N(5)-Ru-Cl(1)       | 90.43(5)   |
| Cl(2)-Ru-Cl(1)      | 168.96(2)  |
| N(7)-N(8)-C(15)     | 110.53(18) |
| Ru-Cl(1)            | 97.26(6)   |
| N(7)-N(8)-Ru        | 121.46(15) |
| C(15)-N(8)-Ru       | 127.86(15) |
| N(3)-N(4)-C(5)      | 109.83(18) |

Table 21. (continued)

| Atoms             | Angle (°)  |
|-------------------|------------|
| N(3)-N(4)-Ru      | 121.43(15) |
| C(5)-N(4)-Ru      | 128.53(14) |
| C(11)-N(5)-C(14)  | 115.9(2)   |
| C(11)-N(5)-Ru     | 131.26(17) |
| C(14)-N(5)-Ru     | 112.16(15) |
| C(1)-N(1)-C(4)    | 115.6(2)   |
| C(1)-N(1)-Ru      | 132.68(17) |
| C(4)-N(1)-Ru      | 111.38(15) |
| N(4)-N(3)-C(4)    | 111.82(19) |
| N(8)-N(7)-C(14)   | 111.93(19) |
| N(1)-C(4)-N(3)    | 119.0(2)   |
| N(1)-C(4)-C(3)    | 121.5(2)   |
| N(3)-C(4)-C(3)    | 119.5(2)   |
| C(20)-C(15)-C(16) | 120.9(2)   |
| C(20)-C(15)-N(8)  | 119.0(2)   |
| C(16)-C(15)-N(8)  | 120.0(2)   |
| C(10)-C(5)-C(6)   | 120.5(2)   |
| C(10)-C(5)-N(4)   | 119.1(2)   |
| C(6)-C(5)-N(4)    | 120.4(2)   |
| C(5)-C(10)-C(9)   | 119.3(2)   |
| C(5)-C(10)-H(10)  | 118.7(16)  |
| C(9)-C(10)-H(10)  | 122.0(16)  |
| C(3)-N(2)-C(2)    | 115.5(2)   |
| N(5)-C(11)-C(12)  | 121.3(3)   |

Table 21. (continued)

| Atoms             | Angle (°) |
|-------------------|-----------|
| N(5)-C(11)-H(11)  | 117.8(17) |
| C(12)-C(11)-H(11) | 120.8(17) |
| N(1)-C(1)-C(2)    | 121.5(2)  |
| N(1)-C(1)-H(1)    | 117.7(15) |
| C(2)-C(1)-H(1)    | 120.7(15) |
| C(17)-C(16)-C(15) | 118.9(3)  |
| C(17)-C(16)-H(16) | 124.3(17) |
| C(15)-C(16)-H(16) | 116.6(17) |
| C(12)-N(6)-C(13)  | 115.7(2)  |
| C(15)-C(20)-C(19) | 119.3(3)  |
| C(15)-C(20)-H(20) | 120.2(16) |
| C(19)-C(20)-H(20) | 120.6(16) |
| N(5)-C(14)-N(7)   | 118.5(2)  |
| N(5)-C(14)-C(13)  | 121.8(2)  |
| N(7)-C(14)-C(13)  | 119.6(2)  |
| N(2)-C(2)-C(1)    | 123.4(3)  |
| N(2)-C(2)-H(2)    | 116.0(18) |
| C(1)-C(2)-H(2)    | 120.6(18) |
| N(6)-C(12)-C(11)  | 123.4(3)  |
| N(6)-C(12)-H(12)  | 121(2)    |
| C(11)-C(12)-H(12) | 116(2)    |
| C(7)-C(6)-C(5)    | 119.5(3)  |
| C(7)-C(6)-H(6)    | 123(2)    |
| C(5)-C(6)-H(6)    | 117(2)    |



Table 21. (continued)

| Atoms             | Angle (°) |
|-------------------|-----------|
| C(8)-C(9)-C(10)   | 120.3(3)  |
| C(8)-C(9)-H(9)    | 121.8(17) |
| C(10)-C(9)-H(9)   | 117.9(17) |
| C(9)-C(8)-C(7)    | 120.0(3)  |
| C(9)-C(8)-H(8)    | 118.4(18) |
| C(7)-C(8)-H(8)    | 121.5(18) |
| N(2)-C(3)-C(4)    | 122.4(3)  |
| N(2)-C(3)-H(3)    | 119.0(17) |
| C(4)-C(3)-H(3)    | 118.6(17) |
| C(18)-C(17)-C(16) | 120.4(3)  |
| C(18)-C(17)-H(17) | 123(2)    |
| C(16)-C(17)-H(17) | 117(2)    |
| C(18)-C(19)-C(20) | 119.7(3)  |
| C(18)-C(19)-H(19) | 120.1     |
| C(20)-C(19)-H(19) | 120.1     |
| C(6)-C(7)-C(8)    | 120.2(3)  |
| C(6)-C(7)-H(7)    | 118.3(18) |
| C(8)-C(7)-H(7)    | 121.5(18) |
| C(17)-C(18)-C(19) | 120.7(3)  |
| C(17)-C(18)-H(18) | 122(2)    |
| C(19)-C(18)-H(18) | 118(2)    |

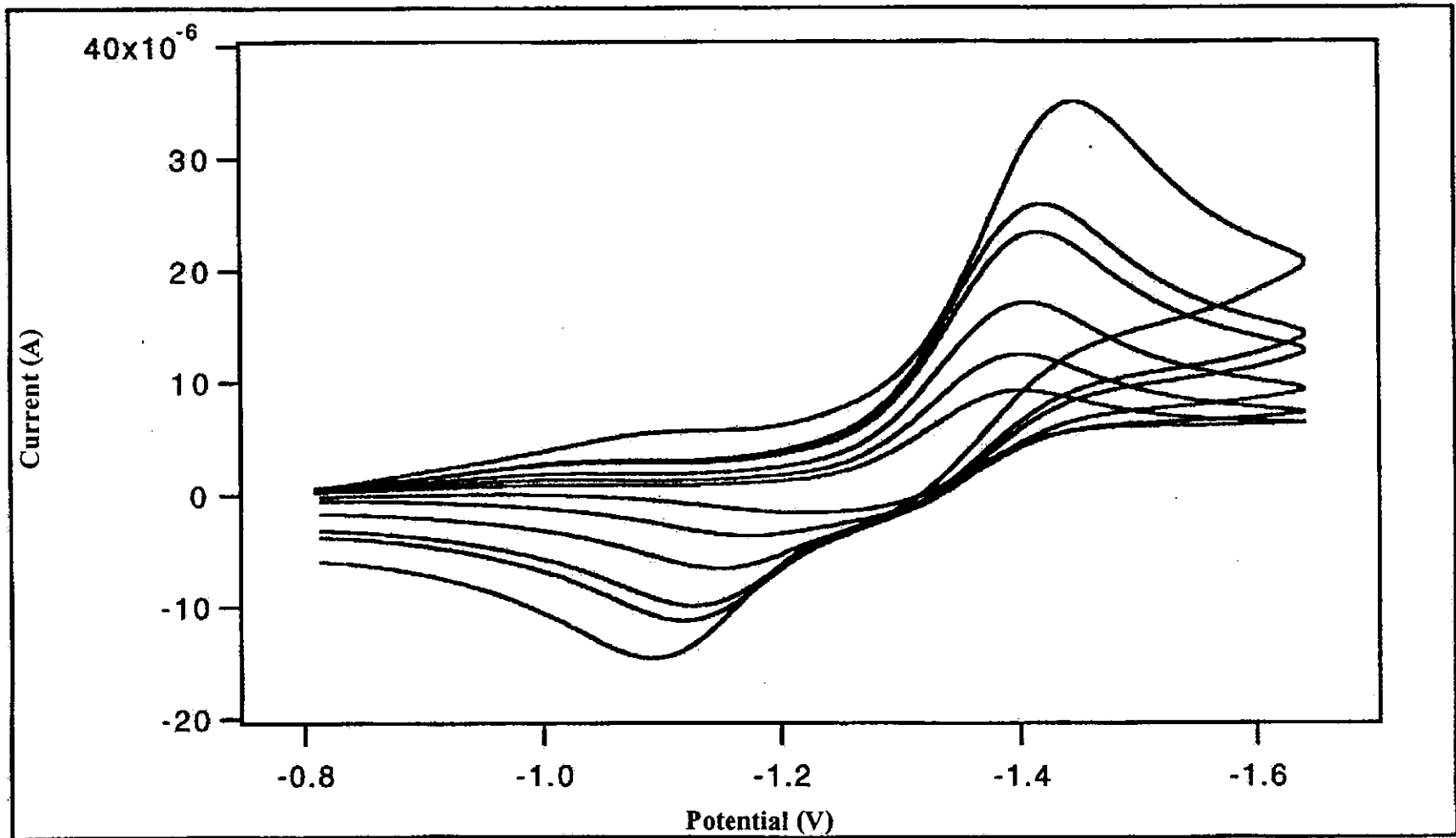


Figure 41. Cyclic voltammogram of azine with various scan rate 50-1000 mV/s in the reduction range.

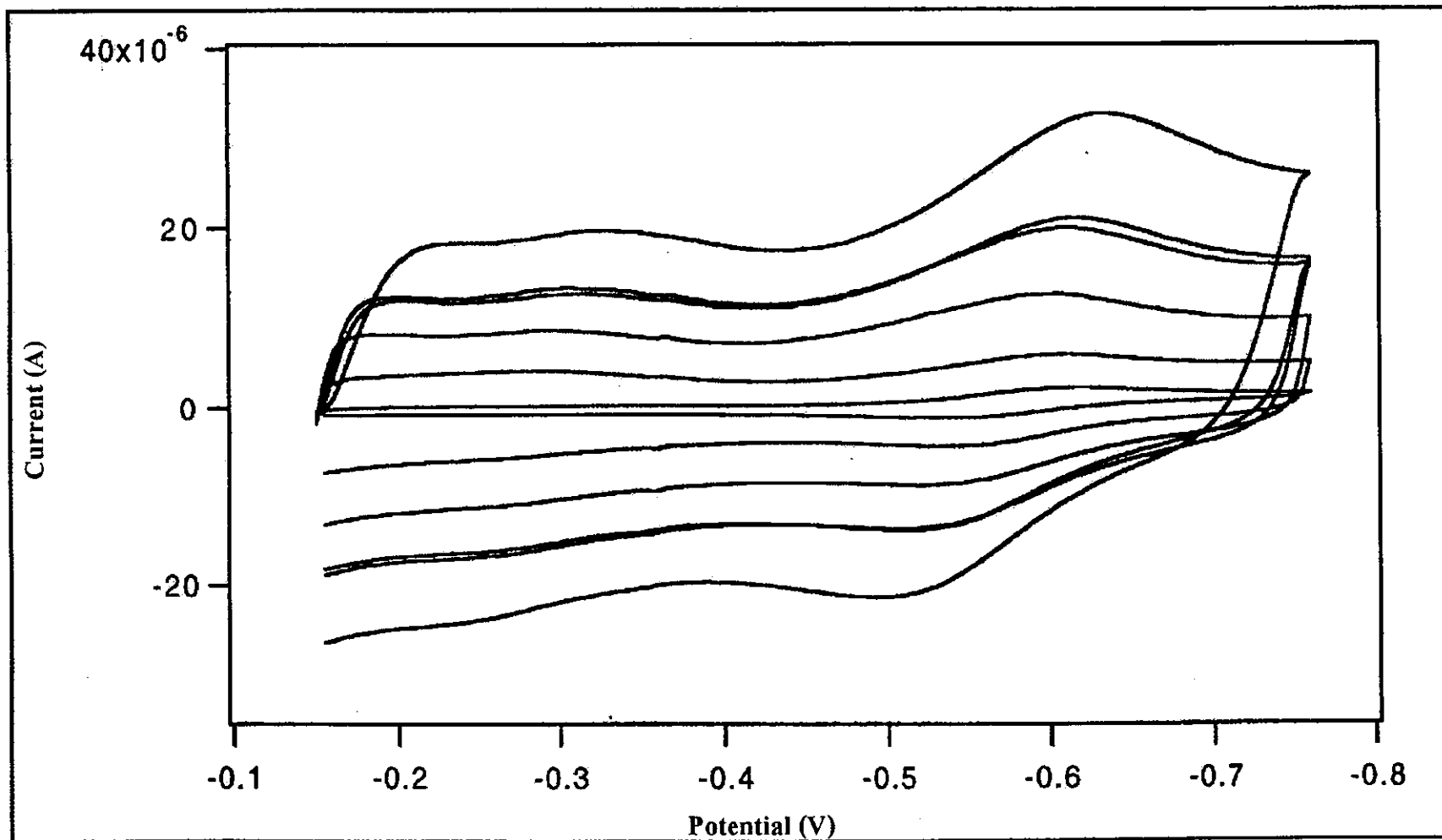


Figure 42. Cyclic voltammogram of *ctc*-[Ru(azine)<sub>2</sub>Cl<sub>2</sub>]-couple I in the reduction range with various scan rate 50-1000 mV/s.

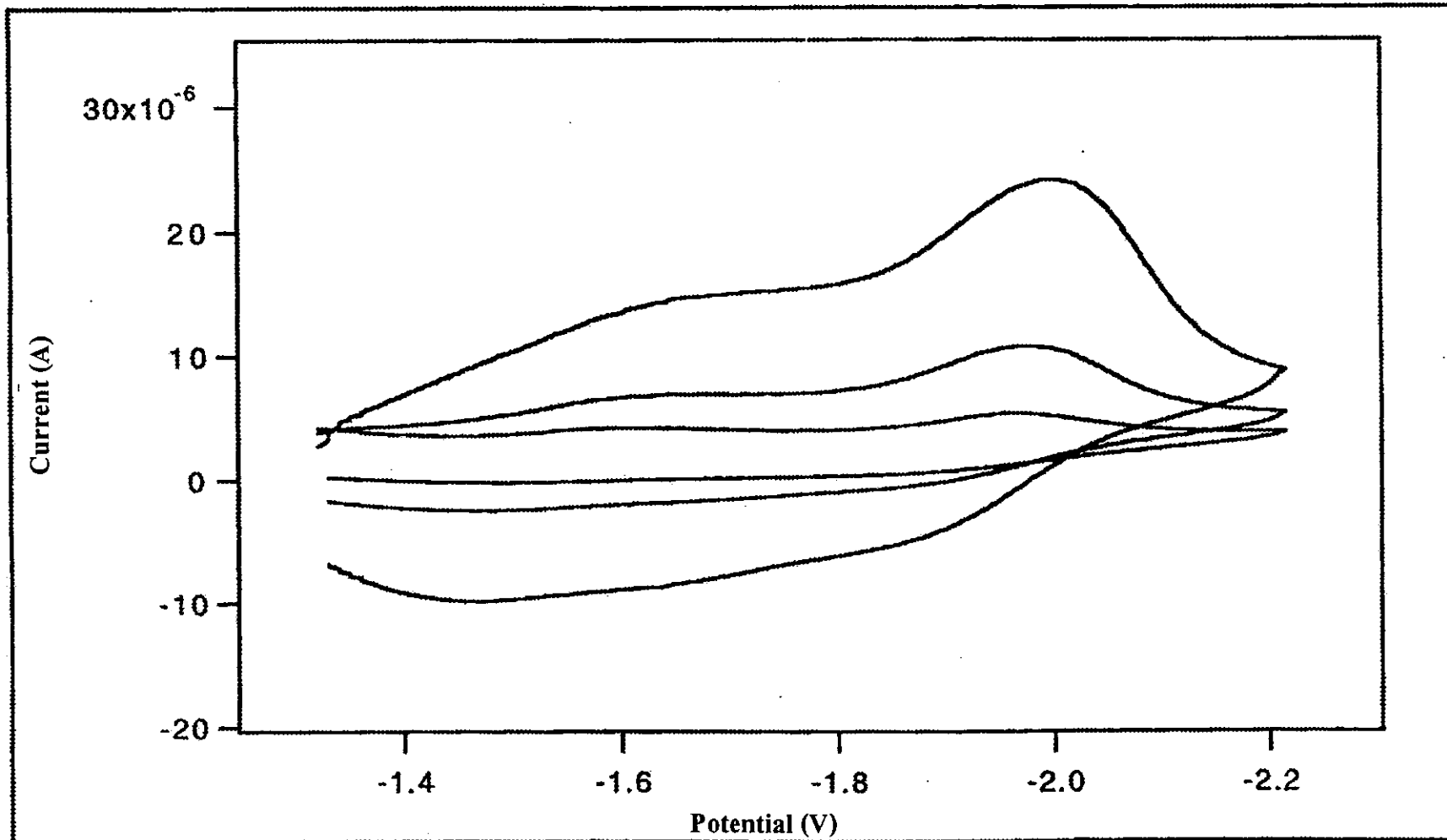


Figure 43. Cyclic voltammogram of *ctc*-[Ru(azine)<sub>2</sub>Cl<sub>2</sub>]-couple II in the reduction range with various scan rate 100-400 mV/s.

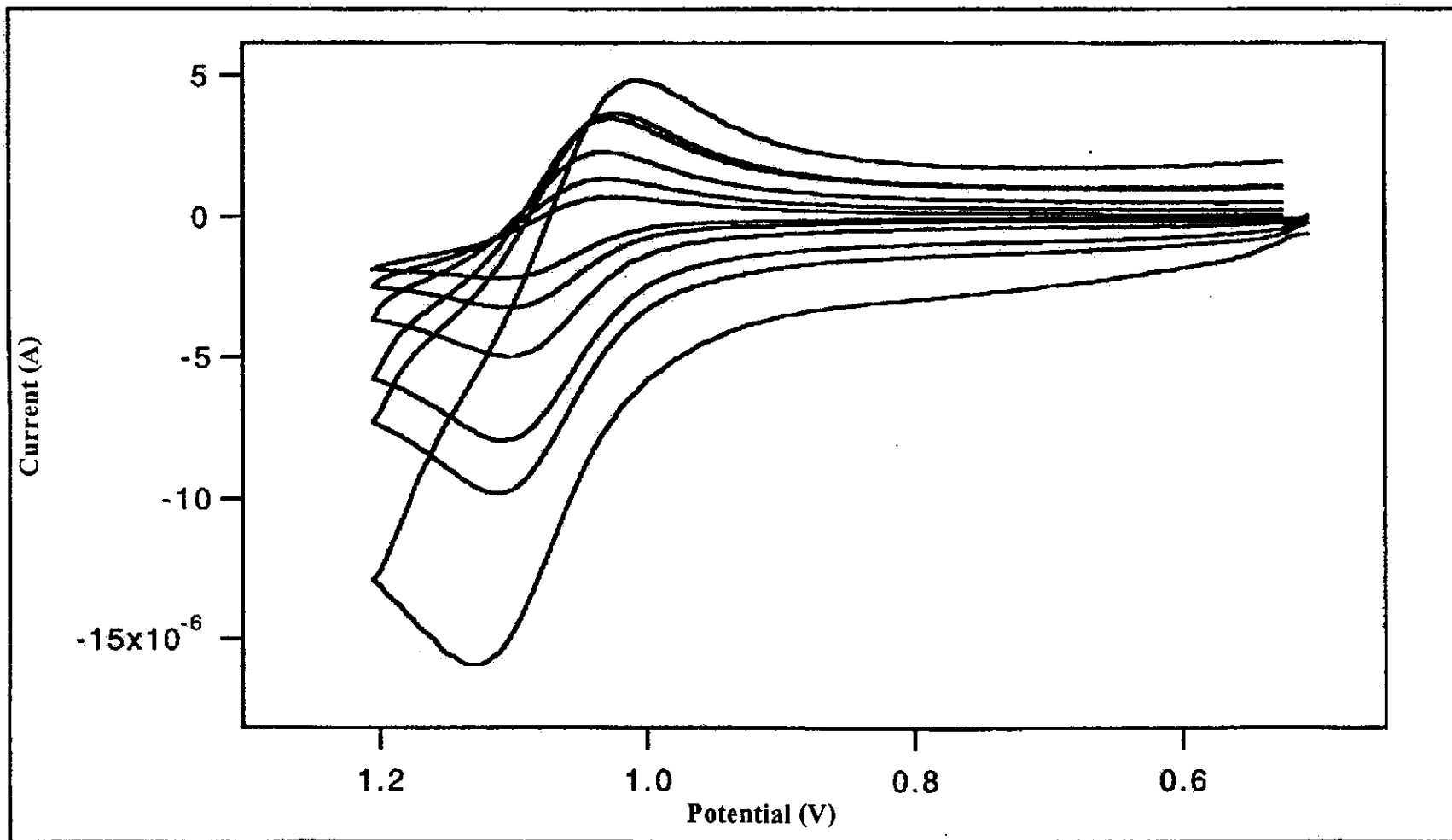


Figure 44. Cyclic voltammogram of *ctc*-[Ru(azine)<sub>2</sub>Cl<sub>2</sub>] in the oxidation range with various scan rate 50-1000 mV/s.

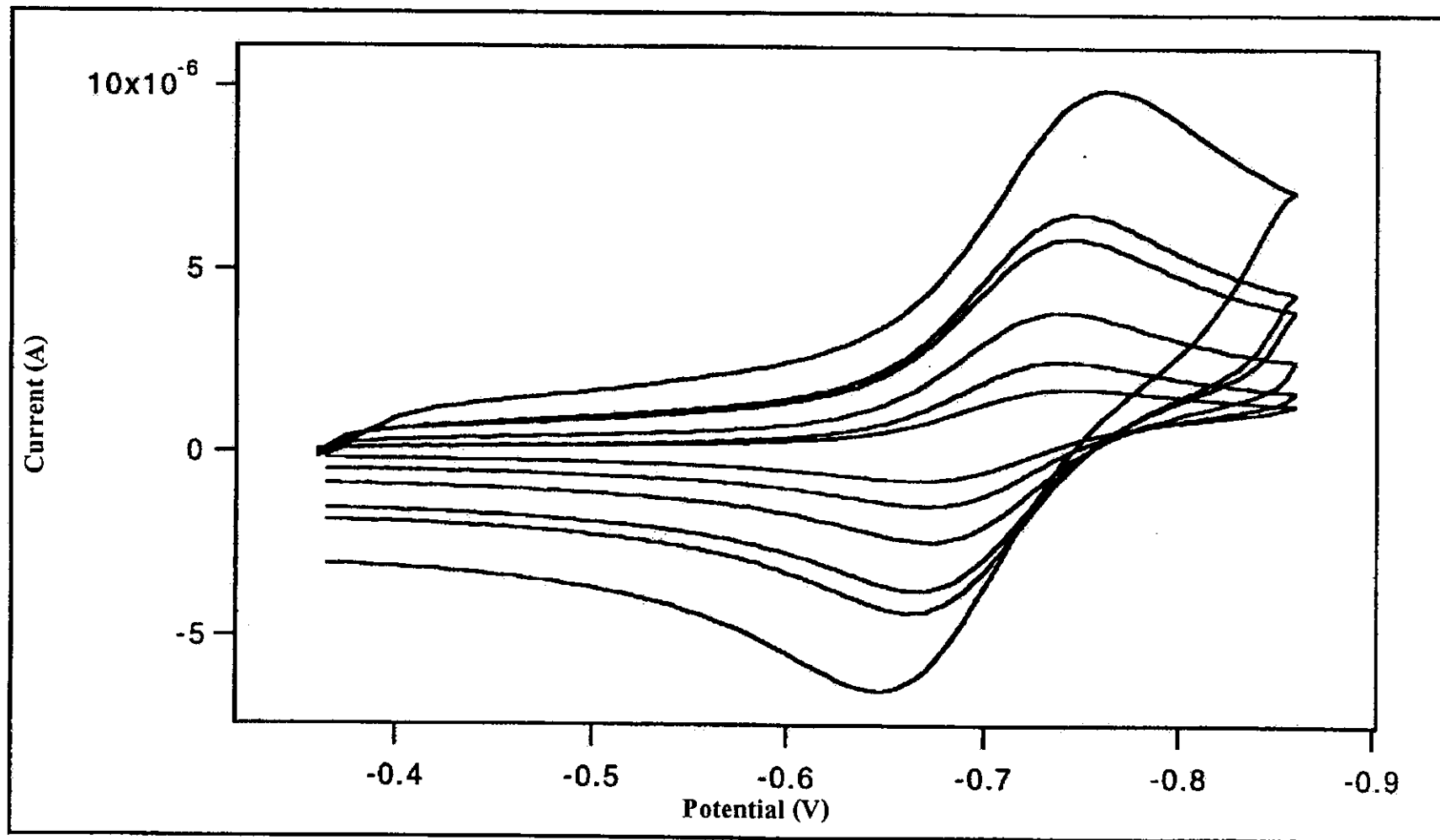


Figure 45. Cyclic voltammogram of *ccc*-[Ru(azine)<sub>2</sub>Cl<sub>2</sub>]-couple I in the reduction range with various scan rate 50-1000 mV/s.

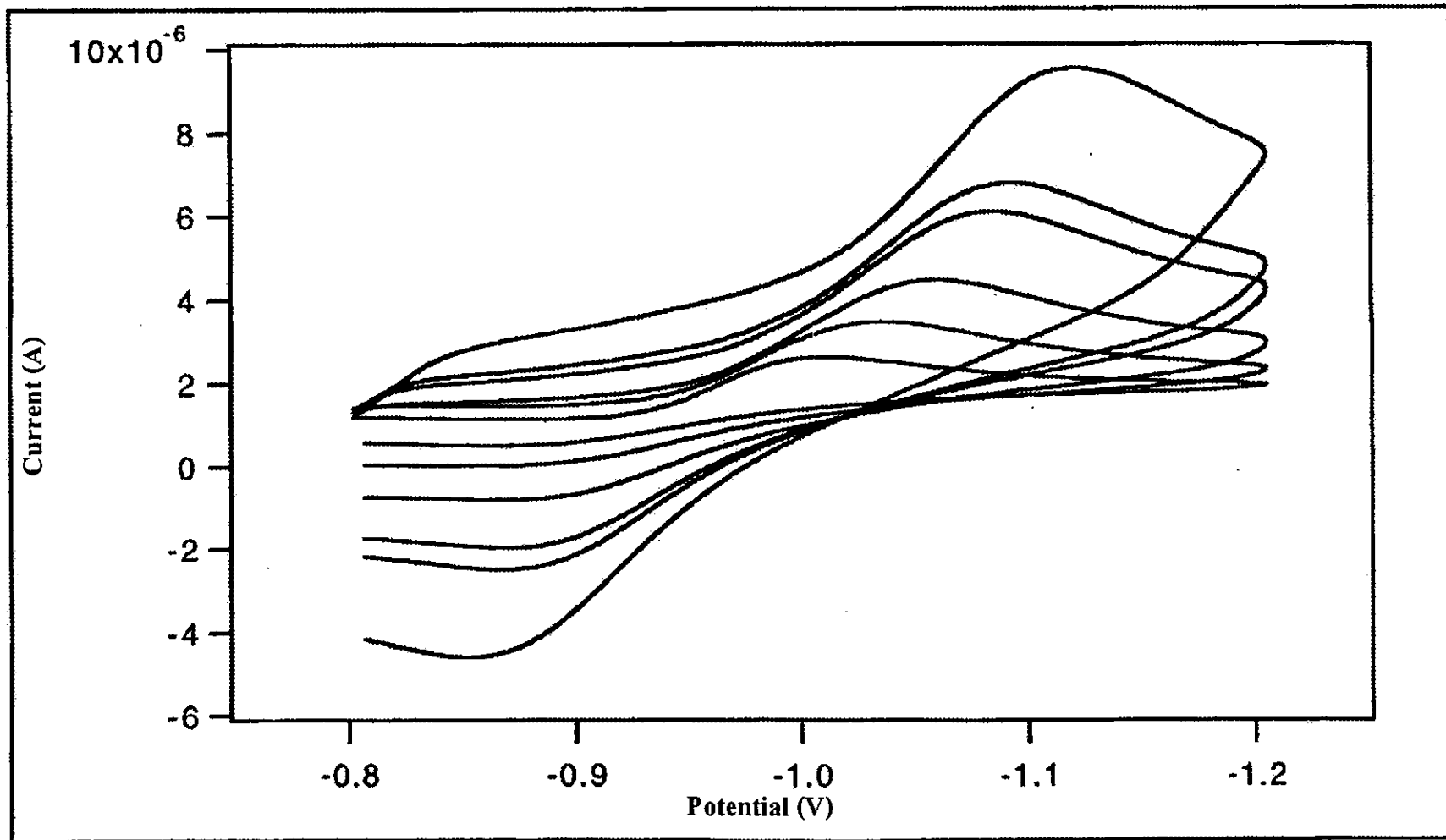


Figure 46. Cyclic voltammogram of *ccc*-[Ru(azine)<sub>2</sub>Cl<sub>2</sub>]-couple II in the reduction range with various scan rate 50-1000 mV/s.

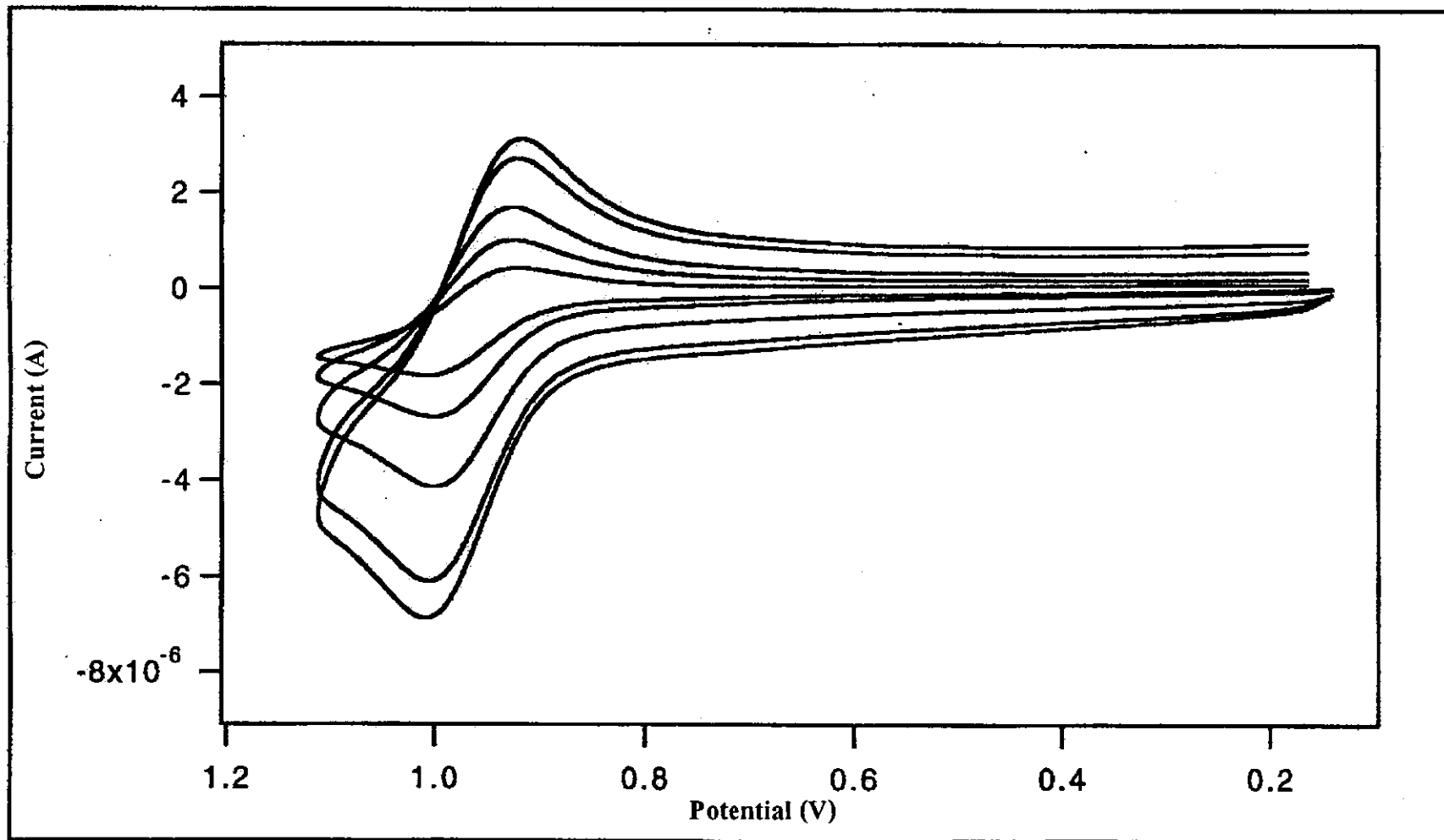


Figure 47. Cyclic voltammogram of *ccc*-[Ru(azine)<sub>2</sub>Cl<sub>2</sub>] in the oxidation range with various scan rate 50-1000 mV/s.



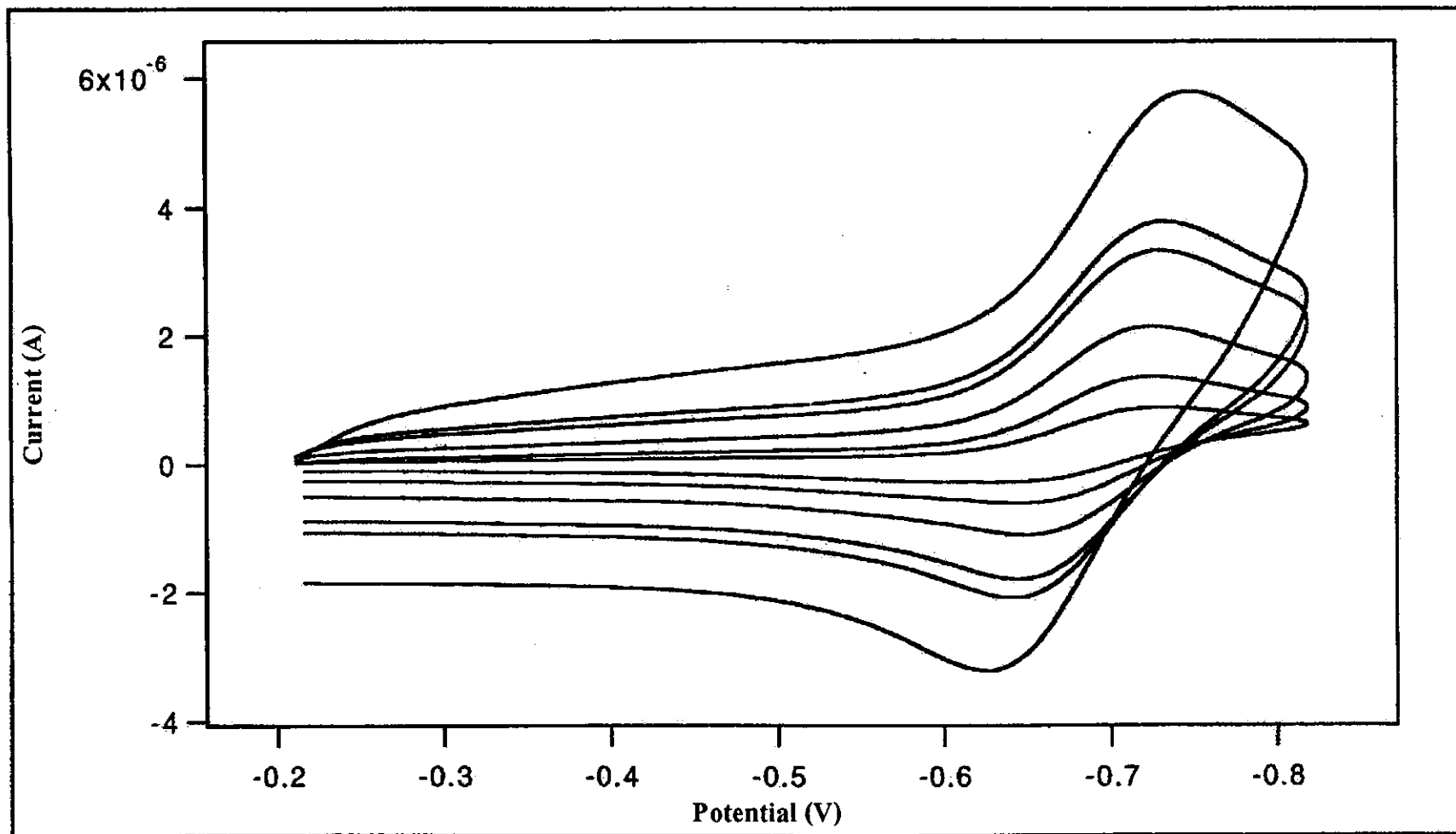


Figure 48. Cyclic voltammogram of *tcc*-[Ru(azine)<sub>2</sub>Cl<sub>2</sub>]-couple I in the reduction range with various scan rate 50-1000 mV/s.

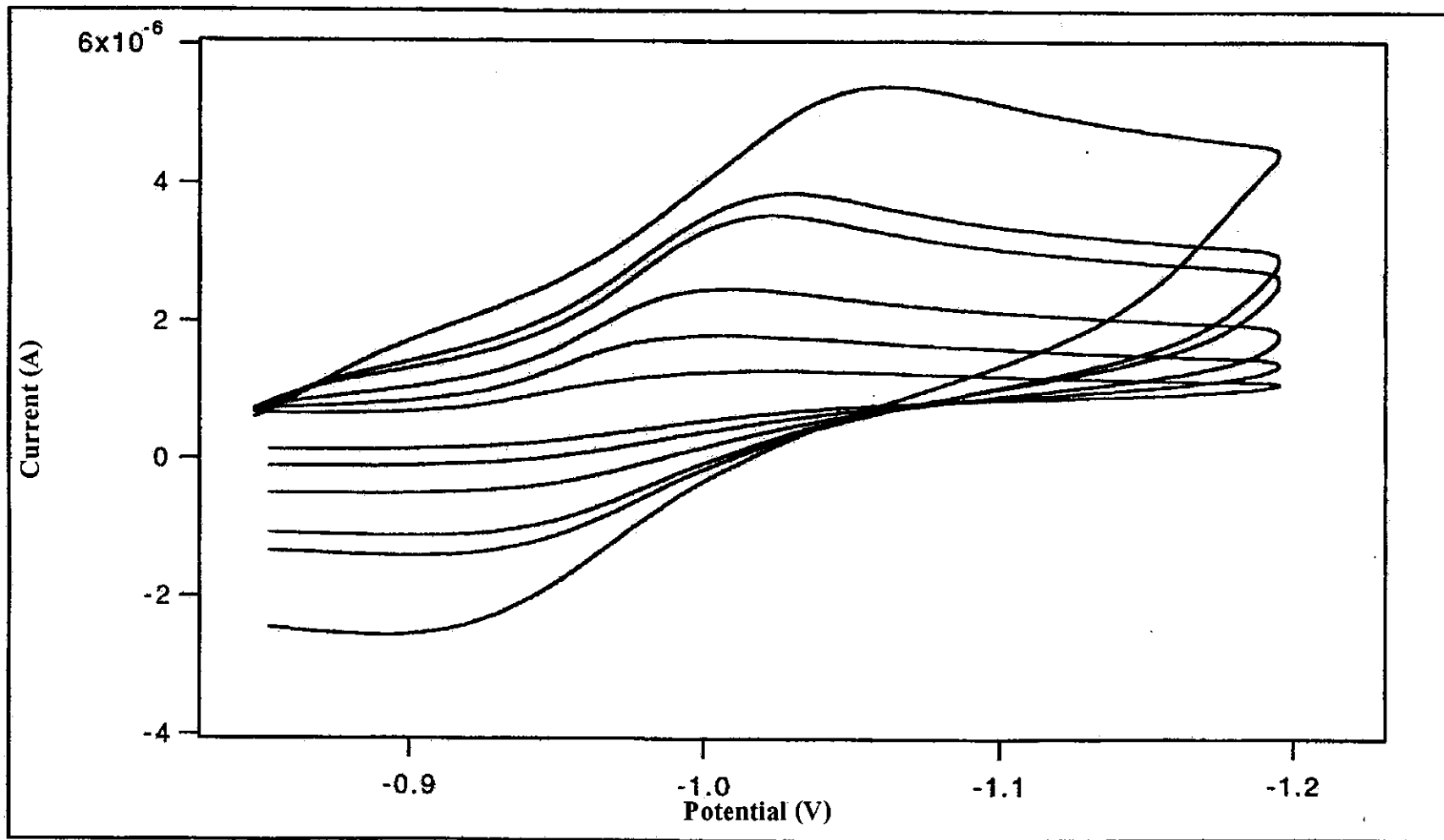


Figure 49. Cyclic voltammogram of *tcc*-[Ru(azine)<sub>2</sub>Cl<sub>2</sub>]-couple II in the reduction range with various scan rate 50-1000 mV/s.

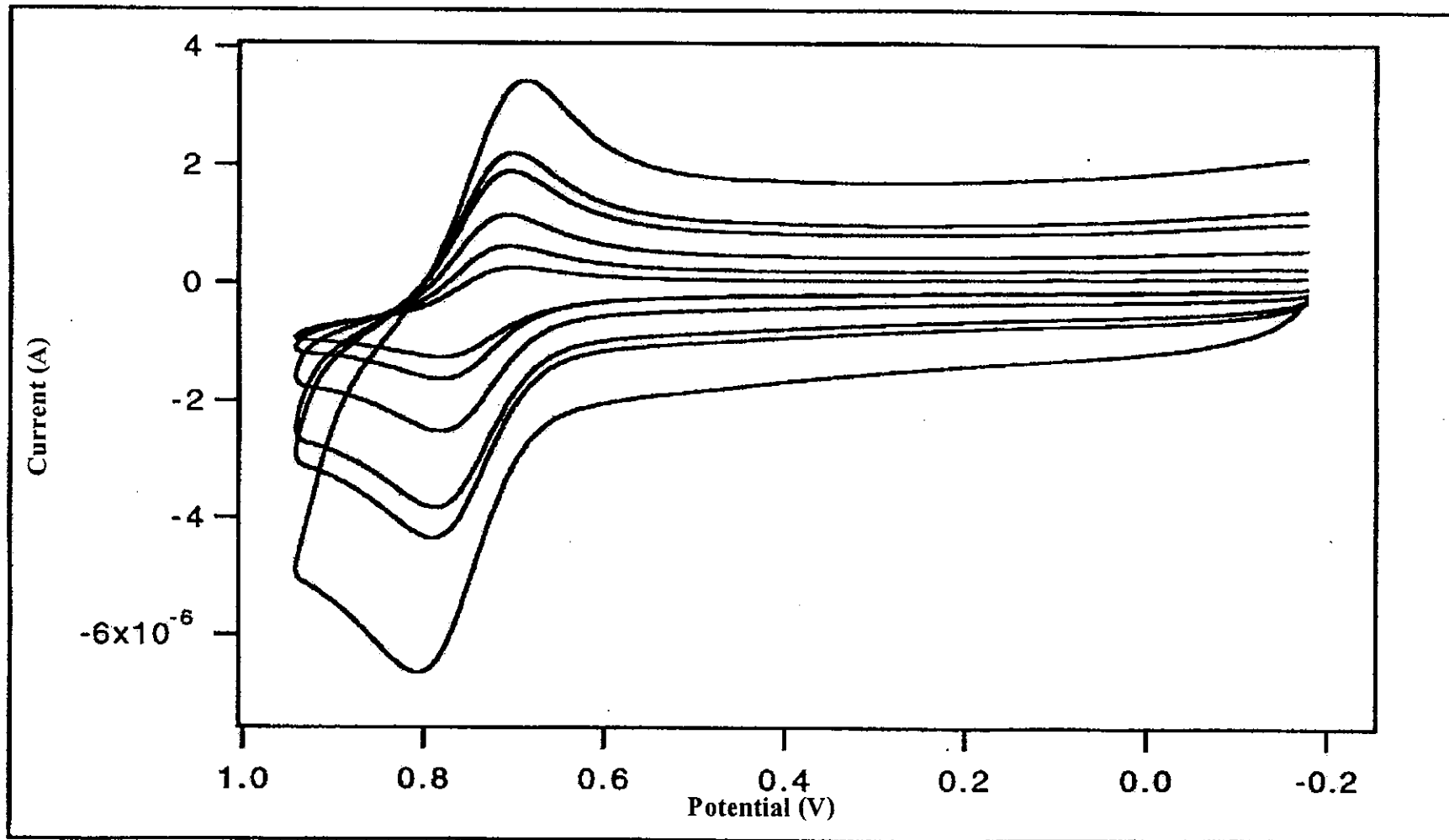


Figure 50. Cyclic voltammogram of *tcc*-[Ru(azine)<sub>2</sub>Cl<sub>2</sub>] in the oxidation range with various scan rate 50-1000 mV/s.