

Supplementary information to be published electronically for the paper: “Mn(II) Complexes Containing the polypyridylic chiral ligand (-)-pinene[5,6]bipyridine. Catalysts for oxidation reactions”

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Table and Figure captions for supplementary information

**Table S1.** Selected bond distances (Å) and angles (deg) for **2**.

**Table S2.** Selected bond distances (Å) and angles (deg) for **3**.

**Table S3.** Selected bond distances (Å) and angles (deg) for **4** and **5**.

**Table S4.** Selected bond distances (Å) and angles (deg) for **6** and **7**.

**Figure S1.** Spacefill representations for the X-Ray structures of complexes a) **5**, b) **6** and c) **7**.

**Figure S2.** CV in CH<sub>3</sub>CN +0.1M [(nBu)<sub>4</sub>N]PF<sub>6</sub> of a solution of ligand (-)-**L**.

**Figure S3.** CV in CH<sub>3</sub>CN +0.1M [(nBu)<sub>4</sub>N]PF<sub>6</sub> of a solution of a) compound **3**, b) compound **4**, c) compound **6** and d) compound **7**, at a platinum electrode (2 mm diameter); scan rate:100 mV/s.

**Figure S4** CV in CH<sub>3</sub>CN +0.1M [(nBu)<sub>4</sub>N]PF<sub>6</sub> of a 0.5 mM solution of a) compound **2**-and b) compound **5** at a platinum electrode (2 mm diameter); scan rate:100 mV/s.

**Table S1.**

|                   |            |                   |            |
|-------------------|------------|-------------------|------------|
| Mn(1)-N(1)        | 2.190(4)   | Mn(2)-Cl(1)       | 2.4519(14) |
| Mn(1)-N(2)        | 2.296(4)   | Mn(2)-N(4)        | 2.295(4)   |
| Mn(1)-Cl(3)       | 2.3293(13) | Mn(2)-Cl(2)       | 2.5526(13) |
| Mn(1)-Cl(2)       | 2.4356(14) | Mn(2)-N(3)        | 2.207(4)   |
| Mn(1)-Cl(1)       | 2.5772(14) | Mn(2)-Cl(4)       | 2.3390(13) |
| Mn(1)···Mn(2)     | 3.736      |                   |            |
| N(1)-Mn(1)-N(2)   | 73.76(15)  | N(3)-Mn(2)-N(4)   | 73.90(15)  |
| N(1)-Mn(1)-Cl(3)  | 115.34(10) | N(3)-Mn(2)-Cl(4)  | 120.22(11) |
| N(2)-Mn(1)-Cl(3)  | 98.82(10)  | N(4)-Mn(2)-Cl(4)  | 98.76(10)  |
| N(1)-Mn(1)-Cl(2)  | 132.10(10) | N(3)-Mn(2)-Cl(1)  | 129.40(11) |
| N(2)-Mn(1)-Cl(2)  | 93.62(10)  | N(4)-Mn(2)-Cl(1)  | 94.90(11)  |
| Cl(3)-Mn(1)-Cl(2) | 112.17(5)  | Cl(4)-Mn(2)-Cl(1) | 110.15(15) |
| N(1)-Mn(1)-Cl(1)  | 90.15(10)  | N(3)-Mn(2)-Cl(2)  | 88.11(10)  |
| N(2)-Mn(1)-Cl(1)  | 155.50(10) | N(4)-Mn(2)-Cl(2)  | 104.71(5)  |
| Cl(3)-Mn(1)-Cl(1) | 104.83(5)  | Cl(4)-Mn(2)-Cl(2) | 83.65(4)   |
| Cl(2)-Mn(1)-Cl(1) | 83.46(4)   | Cl(1)-Mn(2)-Cl(2) | 83.65(4)   |
| Mn(2)-Cl(1)-Mn(1) | 95.91(5)   | Mn(1)-Cl(2)-Mn(2) | 96.97(5)   |

**Table S2.**

|                  |            |                   |            |
|------------------|------------|-------------------|------------|
| Mn(1)-O(3)       | 2.034(4)   | Mn(1)-N(1)        | 2.186(4)   |
| Mn(1)-O(1)       | 2.159(4)   | Mn(1)-N(2)        | 2.234(4)   |
| Mn(1)-O(2*)      | 2.175(4)   | Mn(1)-O(2)        | 2.479(4)   |
| Mn(1)···Mn(1*)   | 3.433(4)   |                   |            |
| O(3)-Mn(1)-O(1)  | 142.87(15) | Mn(1*)-O(2)-Mn(1) | 94.80(16)  |
| O(3)-Mn(1)-O(2*) | 94.45(14)  | C(20)-O(3)-Mn(1)  | 136.3(3)   |
| O(1)-Mn(1)-O(2*) | 87.62(13)  | C(18)-O(1)-Mn(1)  | 99.4(3)    |
| O(3)-Mn(1)-N(1)  | 108.76(14) | C(18)-O(2)-Mn(1*) | 127.6(3)   |
| O(1)-Mn(1)-N(1)  | 108.30(14) | C(18)-O(2)-Mn(1)  | 84.4(3)    |
| O(2*)-Mn(1)-N(1) | 90.08(17)  | N(1)-Mn(1)-O(2)   | 158.12(12) |
| O(3)-Mn(1)-N(2)  | 96.74(13)  | N(2)-Mn(1)-O(2)   | 116.32(15) |
| O(1)-Mn(1)-N(2)  | 91.14(12)  | O(1)-Mn(1)-O(2)   | 54.77(11)  |
| O(2*)-Mn(1)-N(2) | 162.97(11) | O(2*)-Mn(1)-O(2)  | 76.45(17)  |
| N(1)-Mn(1)-N(2)  | 74.19(16)  | O(3)-Mn(1)-O(2)   | 89.67(13)  |

**Table S3.**

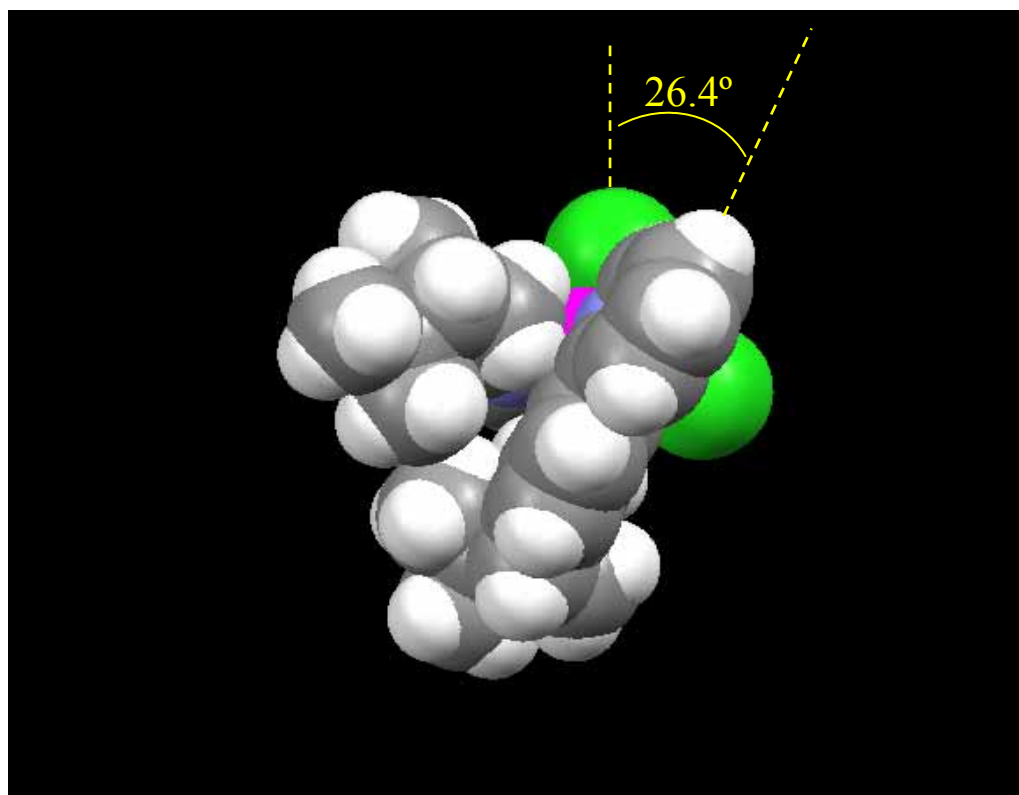
| <b>4</b>          |            | <b>5</b>          |            |
|-------------------|------------|-------------------|------------|
| Mn(1)-O(3)        | 2.189(2)   | Mn(1)-N(1)        | 2.294(7)   |
| Mn(1)-N(1)        | 2.224(2)   | Mn(1)-N(2)        | 2.358(6)   |
| Mn-(1)N(3)        | 2.254(2)   | Mn(1)-N(3)        | 2.290(6)   |
| Mn(1)-Cl(2)       | 2.3698(13) | Mn(1)-N(4)        | 2.387(6)   |
| Mn(1)-Cl(1)       | 2.3822(13) | Mn(1)-Cl(2)       | 2.489(3)   |
| O(3)-Mn(1)-N(1)   | 88.84(8)   | Mn(1)-Cl(1)       | 2.481(3)   |
| O(3)-Mn(1)-N(3)   | 163.28(7)  | N(1)-Mn(1)-N(2)   | 70.3(3)    |
| N(1)-Mn(1)-N(3)   | 74.44(8)   | N(1)-Mn(1)-N(3)   | 179.0(3)   |
| O(3)-Mn(1)-Cl(2)  | 90.52(9)   | N(2)-Mn(1)-N(3)   | 110.6(2)   |
| N(1)-M(1)n-Cl(2)  | 119.96(8)  | N(3)-Mn(1)-N(4)   | 70.4(2)    |
| N(3)-Mn(1)-Cl(2)  | 97.81(7)   | N(1)-Mn(1)-N(4)   | 109.9(2)   |
| O(3)-Mn(1)-Cl(1)  | 90.46(9)   | N(2)-Mn(1)-N(4)   | 84.25(19)  |
| N(1)-Mn(1)-Cl(1)  | 125.05(8)  | N(3)-Mn(1)-Cl(1)  | 91.07(17)  |
| N(3)-Mn(1)-Cl(1)  | 99.00(7)   | N(1)-Mn(1)-Cl(1)  | 88.86(16)  |
| Cl(2)-Mn(1)-Cl(1) | 114.99(5)  | N(2)-Mn(1)-Cl(1)  | 88.48(16)  |
|                   |            | N(4)-Mn(1)-Cl(1)  | 156.05(19) |
|                   |            | N(3)-Mn(1)-Cl(2)  | 89.93(17)  |
|                   |            | N(1)-Mn(1)-Cl(2)  | 89.2(2)    |
|                   |            | N(2)-Mn(1)-Cl(2)  | 153.91(18) |
|                   |            | Cl(1)-Mn(1)-Cl(2) | 107.65(10) |

Table S4.

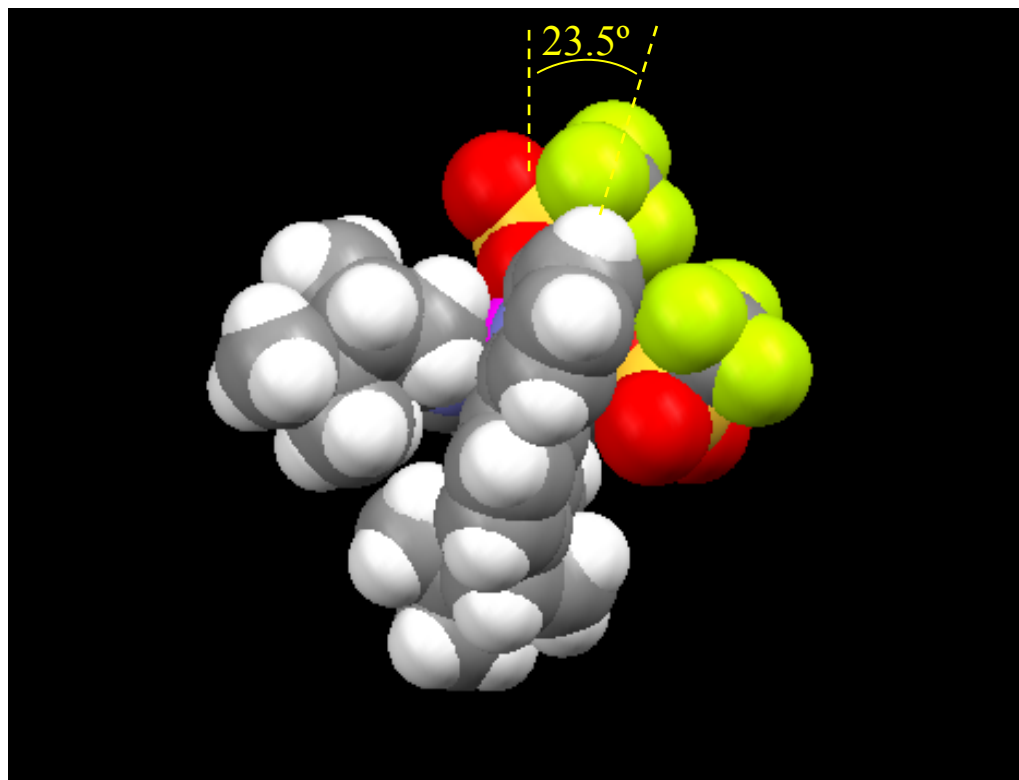
| 6               |             | 7               |            |
|-----------------|-------------|-----------------|------------|
| Mn(1)-O(1)      | 2.168(3)    | Mn(1)-O(1)      | 2.184(4)   |
| Mn(1)-O(4)      | 2.186(3)    | Mn(1)-O(2)      | 2.261(5)   |
| Mn(1)-N(3)      | 2.252(3)    | Mn(1)-N(3)      | 2.347(5)   |
| Mn(1)-N(1)      | 2.265(3)    | Mn(1)-N(4)      | 2.246(5)   |
| Mn(1)-N(2)      | 2.280(3)    | Mn(1)-N(2)      | 2.252(5)   |
| Mn(1)-N(4)      | 2.300(3)    | Mn(1)-N(5)      | 2.321(5)   |
| O(1)-Mn(1)-O(4) | 98.20(11)   | N(4)-Mn(1)-N(2) | 170.42(2)  |
| O(1)-Mn(1)-N(3) | 86.78(11)   | O(1)-Mn(1)-N(4) | 90.57(16)  |
| O(4)-Mn(1)-N(3) | 83.21(11)   | O(1)-Mn(1)-N(2) | 86.53(18)  |
| O(1)-Mn(1)-N(1) | 85.19(11)   | O(1)-Mn(1)-O(2) | 86.93(17)  |
| O(4)-Mn(1)-N(1) | 94.19(11)   | N(4)-Mn(1)-O(2) | 88.23(18)  |
| N(3)-Mn(1)-N(1) | 171.12 (11) | N(2)-Mn(1)-O(2) | 82.45 (17) |
| O(1)-Mn(1)-N(2) | 157.86(11)  | O(1)-Mn(1)-N(5) | 85.12(16)  |
| N(3)-Mn(1)-N(2) | 115.34(11)  | N(4)-Mn(1)-N(5) | 71.7(2)    |
| N(1)-Mn(1)-N(2) | 72.80(11)   | N(2)-Mn(1)-N(5) | 117.12(19) |
| O(1)-Mn(1)-N(4) | 94.09(11)   | O(2)-Mn(1)-N(5) | 158.28(18) |
| O(4)-Mn(1)-N(4) | 152.34(11)  | O(1)-Mn(1)-N(3) | 148.99(17) |
| N(3)-Mn(1)-N(4) | 72.81(11)   | N(4)-Mn(1)-N(3) | 114.71(19) |
| N(1)-Mn(1)-N(4) | 111.53(11)  | N(2)-Mn(1)-N(3) | 71.2(2)    |
| N(2)-Mn(1)-N(4) | 91.86((11)  | O(2)-Mn(1)-N(3) | 110.35(17) |
| O(4)-Mn(1)-N(2) | 86.01(11)   | N(2)-Mn(1)-N(3) | 170.42(2)  |

**Figure S1.**

a)

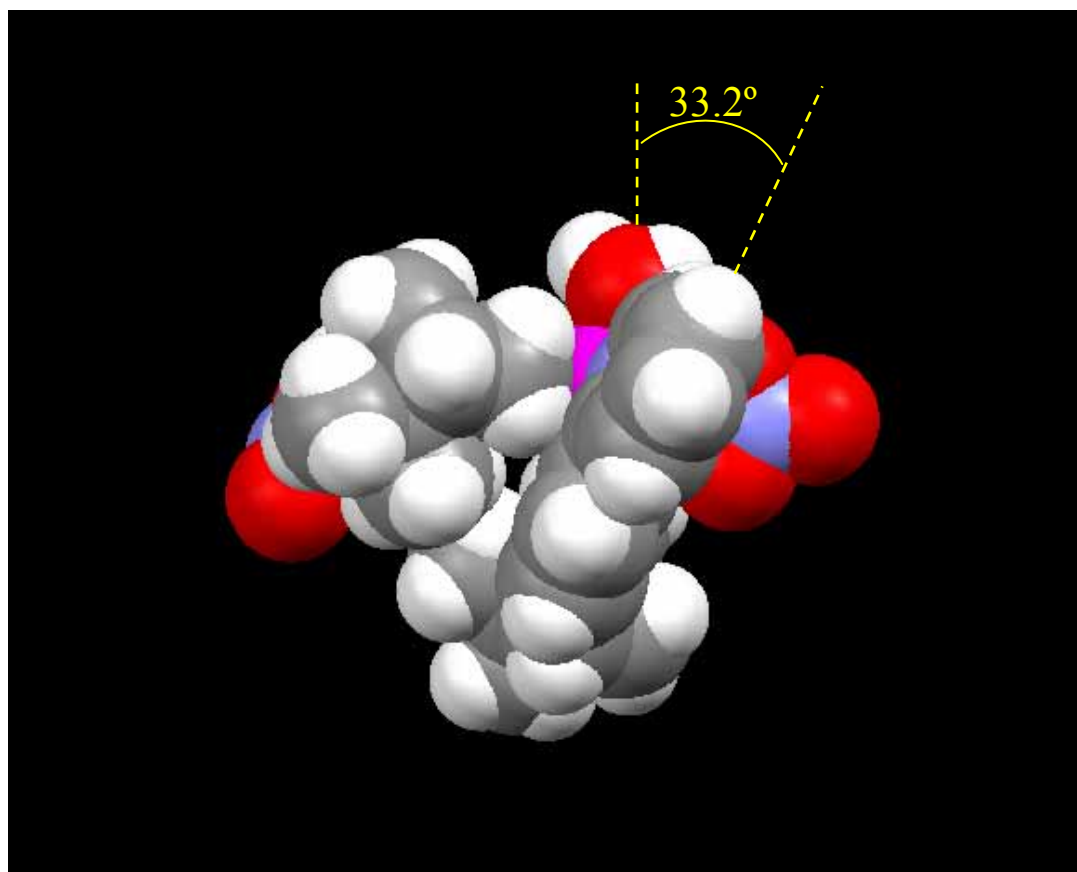


b)



c)





**Figure S2**

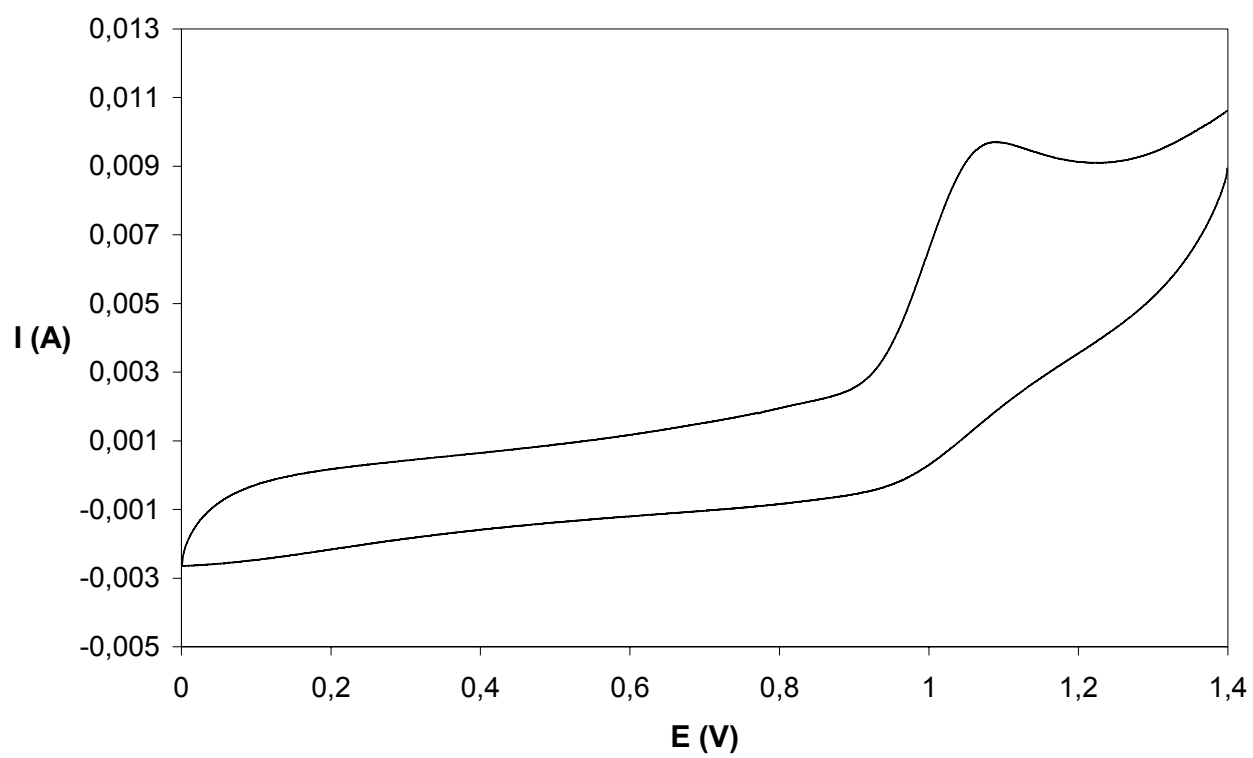
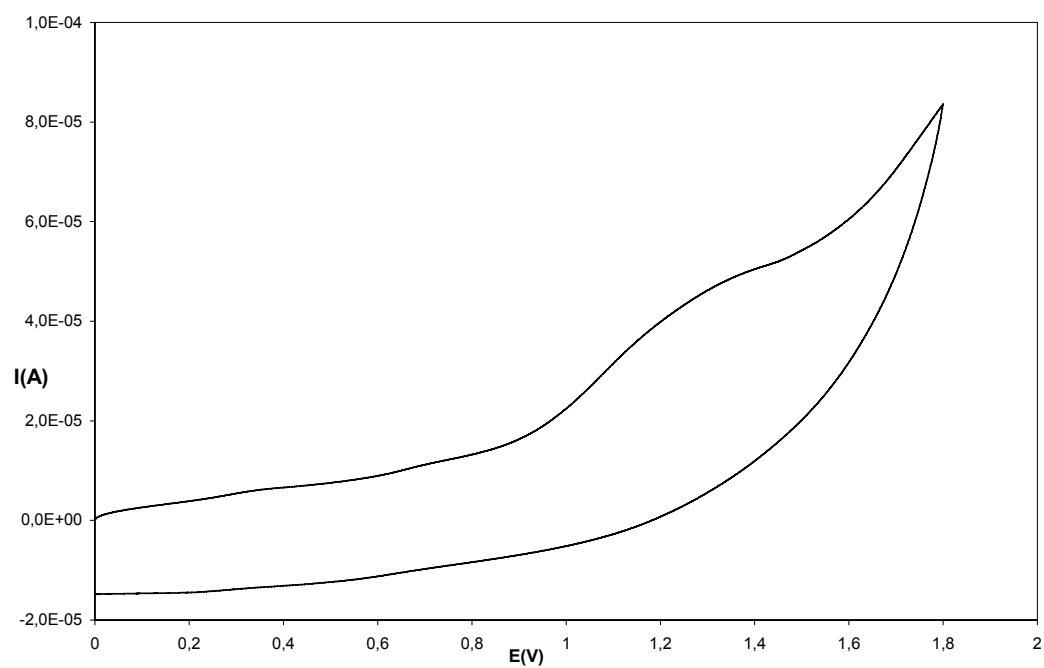
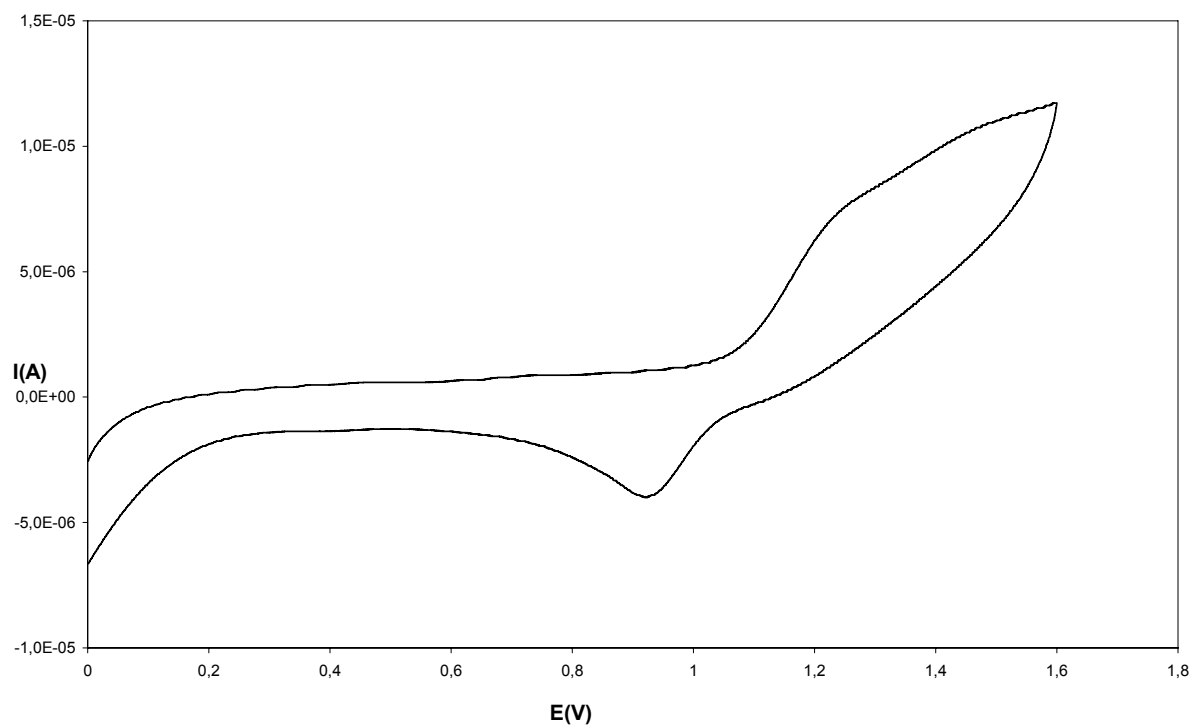


Figure S3

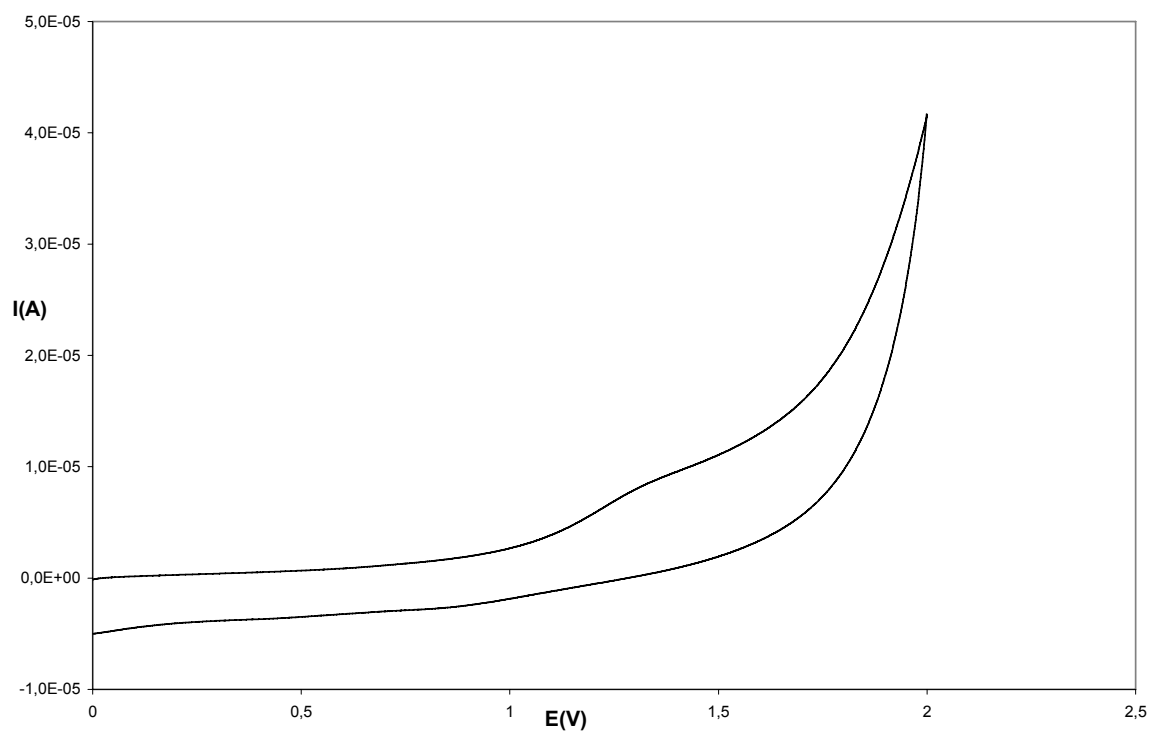
a)



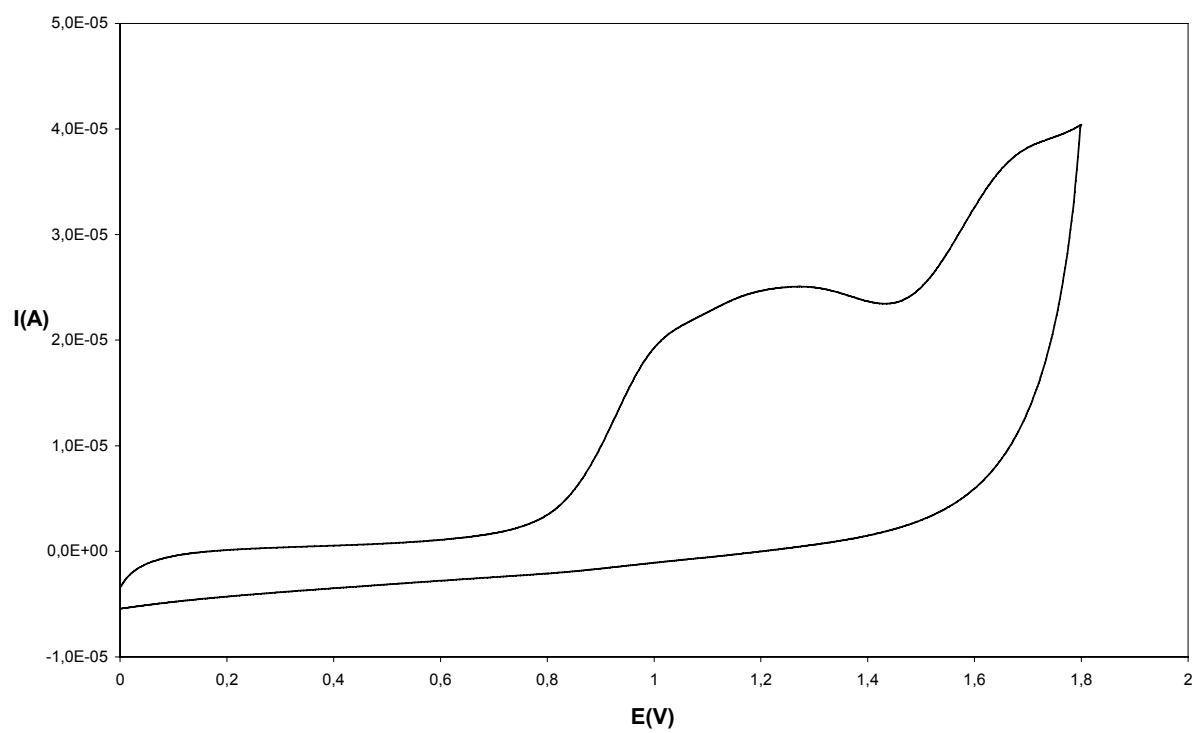
b)



c)

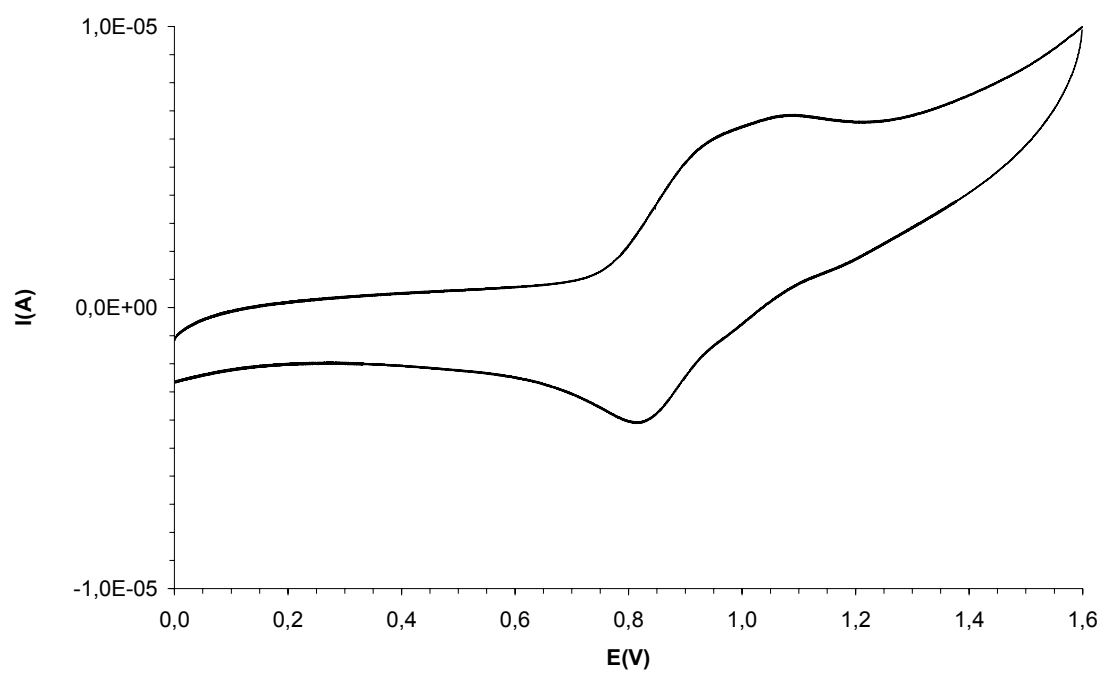


d)



**Figure S4.**

a)



b)

