

Supplementary Information (ESI)

**Evaluation of Transition Metal catalysts in Electrochemically
Induced Aromatic Phosphonation**

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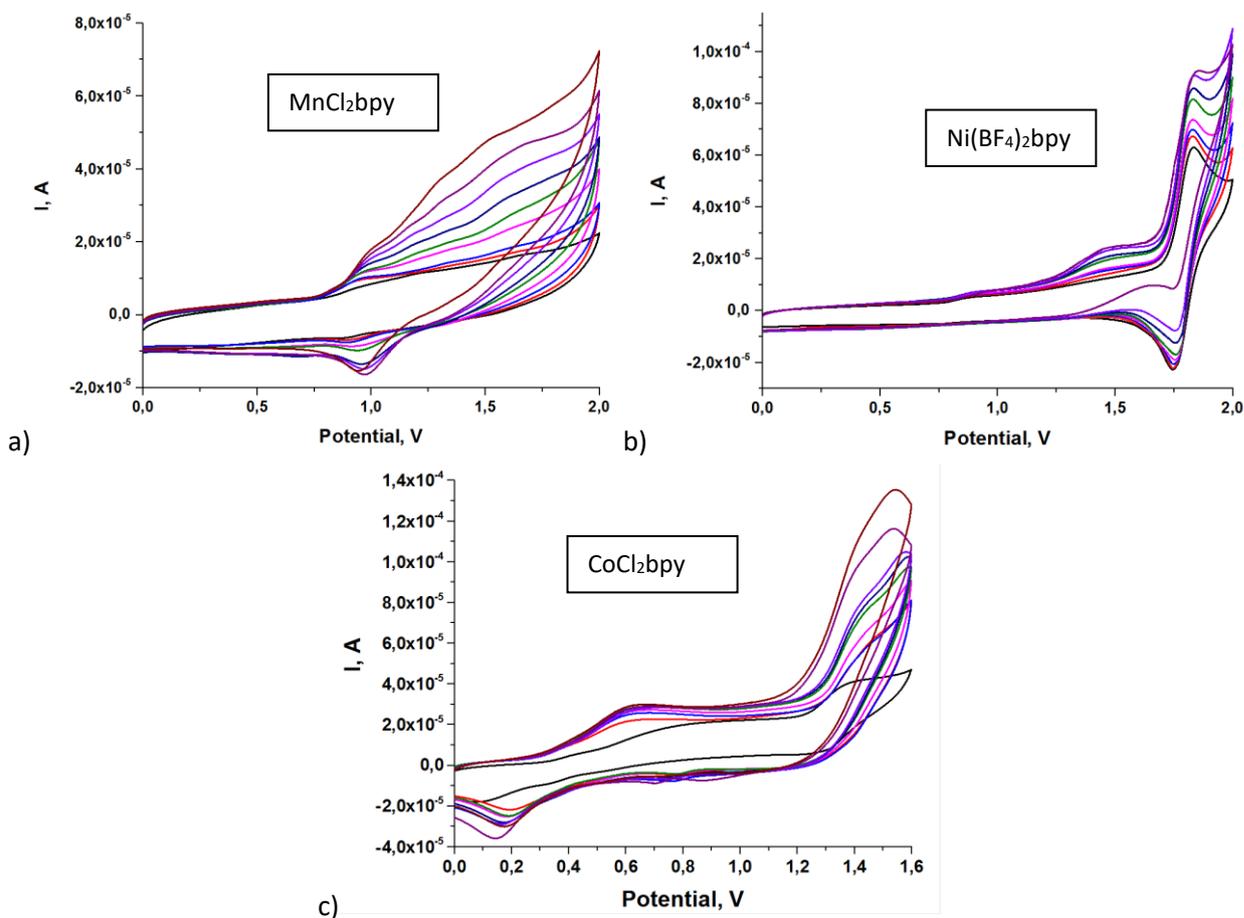


Figure S1. CVs of complexes ($5 \cdot 10^{-3}$ M; for MnCl_2bpy $1.7 \cdot 10^{-3}$ M) in the presence of increasing amount of DEP: **a)** $\text{MnCl}_2\text{bpy} + \text{HP(O)(OEt)}_2$ (1:0, 1:1, 1:6, 1:12, 1:24, 1:48, 1:96, 1:144, 1:168); **b)** $\text{Ni(BF}_4)_2\text{bpy} + \text{HP(O)(OEt)}_2$ (1:0, 1:1, 1:6, 1:12, 1:24, 1:36, 1:72, 1:144); **c)** $\text{CoCl}_2\text{bpy} + \text{HP(O)(OEt)}_2$ (1:0, 1:1, 1:6, 1:12, 1:24, 1:36, 1:72, 1:108, 1:144). Conditions: CH_3CN , 0.1 V/s, 0.1 M Et_4NBF_4 , Ref. electrode – Ag/AgCl, WE – GC.

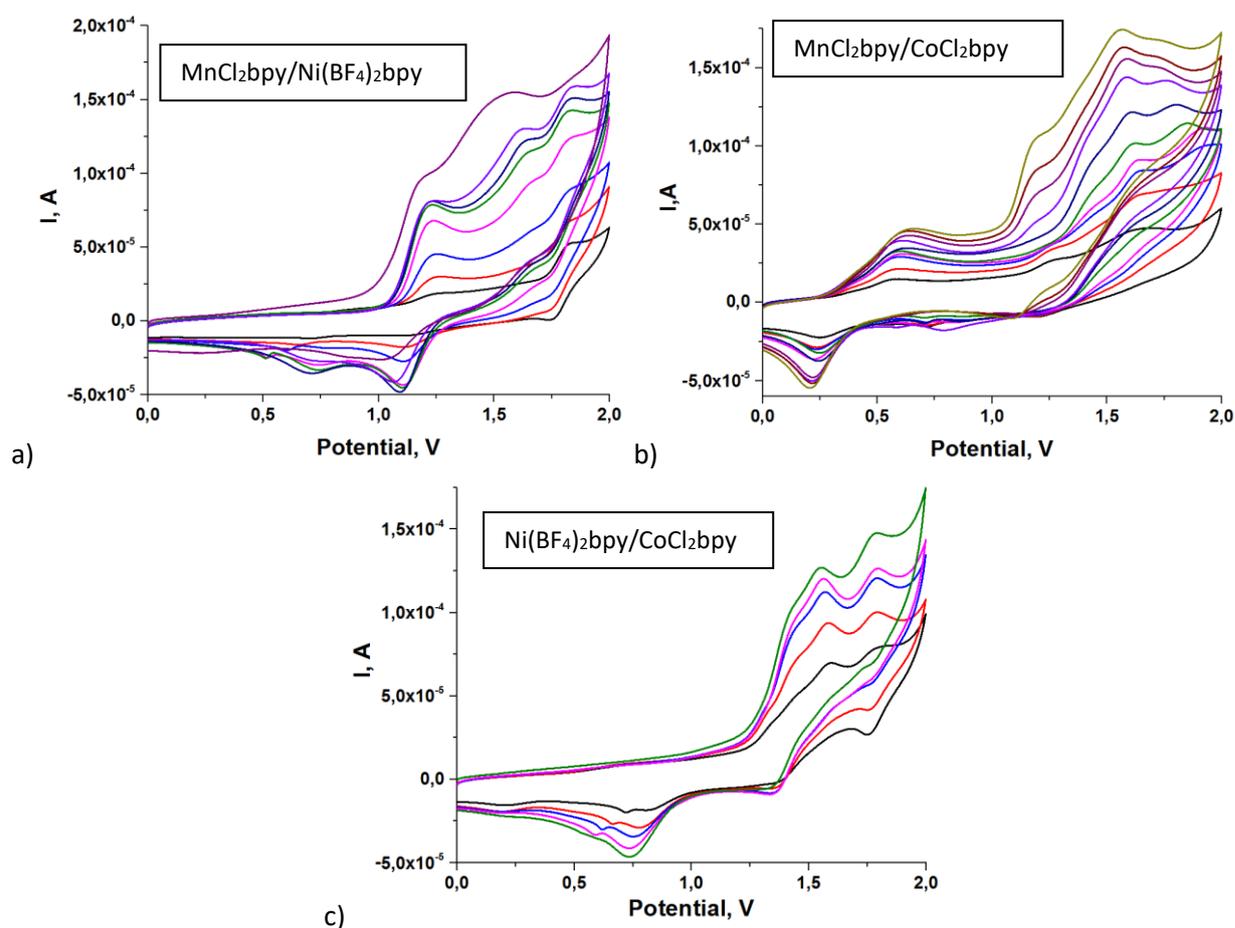


Figure S2. CVs of a mixture of complexes ($5 \cdot 10^{-3}$ M) in the presence of increasing amount of DEP: **a)** $MnCl_2bpy/Ni(BF_4)_2bpy$ (1:0, 1:1, 1:6, 1:12, 1:24, 1:36, 1:72, 1:108, 1:144, 1:180); **b)** $MnCl_2bpy/CoCl_2bpy$ (1:0, 1:1, 1:6, 1:12, 1:24, 1:36, 1:72, 1:108, 1:144, 1:180); **c)** $CoCl_2bpy/Ni(BF_4)_2bpy$ (1:0, 1:1, 1:6, 1:12, 1:24). Conditions: CH_3CN , 0.1 V/s, 0.1 M Et_4NBF_4 , Ref. electrode – Ag/AgCl, WE – GC.

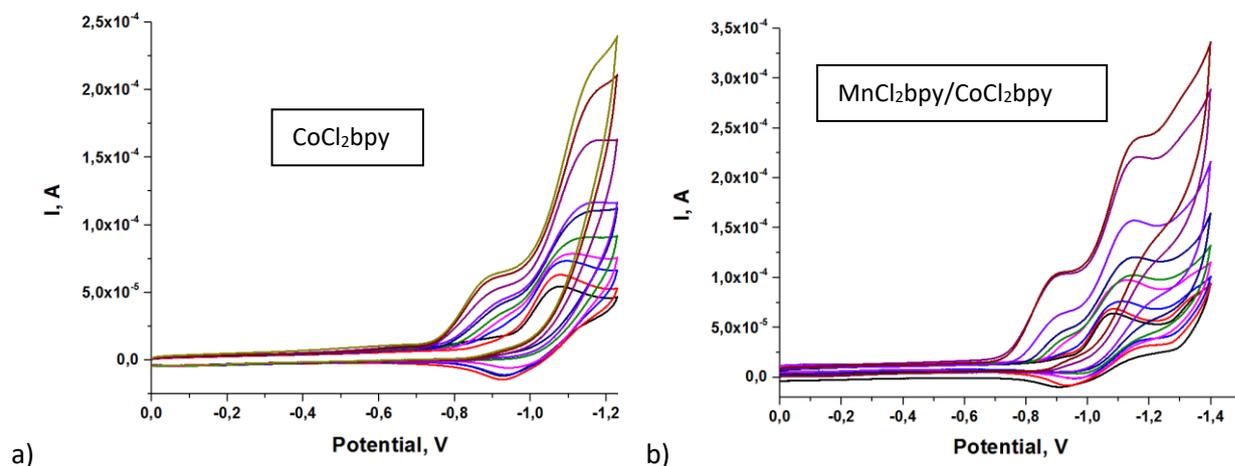


Figure S3. CVs of complexes ($5 \cdot 10^{-3}$ M) in the presence of increasing amount of DEP: **a)** $CoCl_2bpy + HP(O)(OEt)_2$ (1:0, 1:1, 1:3, 1:6, 1:12, 1:24, 1:36, 1:72, 1:144); **b)** $MnCl_2bpy/CoCl_2bpy + HP(O)(OEt)_2$ (1:0, 1:1, 1:6, 1:12, 1:24, 1:36, 1:72, 1:108, 1:144, 1:180). Conditions: CH_3CN , 0.1 V/s, 0.1 M Et_4NBF_4 , Ref. electrode – Ag/AgCl, WE – GC.

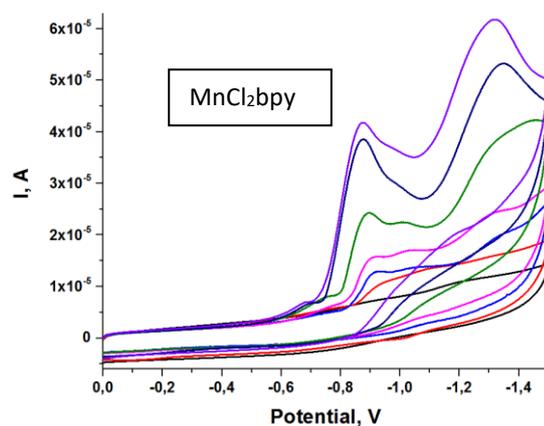


Figure S4. CVA of MnCl_2bpy ($1.7 \cdot 10^{-3} \text{ M}$) in the presence of increasing amount of DEP (1:0, 1:1, 1:3, 1:6, 1:12, 1:24, 1:36, 1:72, 1:144). Conditions: CH_3CN , 0.1 V/s, 0.1 M Et_4NBF_4 , Ref. electrode – Ag/AgCl, WE – CC.

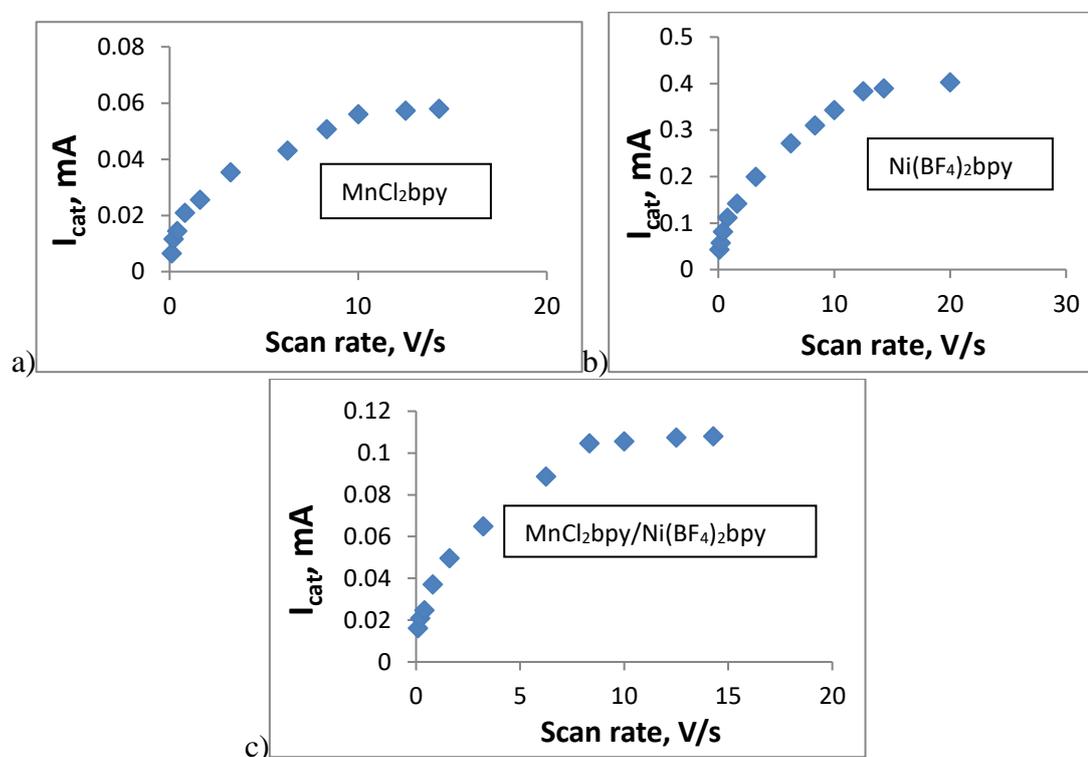


Figure S5. Dependence i_{cat} vs the scanning rate ν for the oxidation wave (in the presence of excess amount of $\text{HP}(\text{O})(\text{OEt})_2$), corresponding to: **a)** Mn(II/III) $[\text{Mn}(\text{II})\text{bpy}] = 1.7 \text{ M}$; **b)** Ni(II/III) $[\text{Ni}(\text{II})\text{bpy}] = 5 \cdot 10^{-3} \text{ M}$; **c)** Mn(II/III)/Ni(II) $[\text{Mn}(\text{II})\text{bpy}] = [\text{Ni}(\text{II})\text{bpy}] = 5 \cdot 10^{-3} \text{ M}$.