## Supplementary Information

**Table S1.** IR spectra for trinuclear racemic copper compound

| Vibration | $\nu$(-OH)$_{st}$ | $\nu$(CH)$_{st}$ aromatic | $\nu_{as}$( -COO$^-$)$_{st}$ | $\nu_s$(–COO-)$_{st}$ | $\Delta\nu$ | $\nu$ (C-OH)$_{st}$ |
|---|---|---|---|---|---|---|
| Ligand | 3063 | 2988 | 1633 | 1384 | ------- | 1041 |
| **AO biomimetic model** | 3214 | 2825 | 1615 | 1385 | 230 (Monodentade) | --- |

**Table S2.** IR spectra for polymeric manganese compounds

| Vibration | $\nu$(-OH)$_{st}$ | $\nu$(CH)$_{st}$ aromatic | $\nu_{as}$( -COO$^-$)$_{st}$ | $\nu_s$(–COO-)$_{st}$ | $\Delta\nu$ | $\nu$ (C-OH)$_{st}$ | M-ClO$_4$ |
|---|---|---|---|---|---|---|---|
| Ligand | 3063 | 2988 | 1633 | 1384 | ------- | 1041 | ------- |
| [Mn$_2$(R,R(-)Hcpse)$_4$(NaClO$_4$)$_2$(NaOH)(MeOH)]n·(EtOH)$_{2n}$·(MeOH)$_n$H$_2$O$_n$ | 3217 | 2880 | 1569 | 1443 | 126 (Bridge) | --- | $\nu_2$(1019) $\nu_3$ (1082) $\nu_4$ (927) |
| [Mn$_2$(S,S(-)Hcpse)$_4$(NaClO$_4$)$_2$(NaOH)(MeOH)]n·(EtOH)$_{2n}$·(MeOH)$_n$H$_2$O$_n$ | 3588 | 2979 | 1569 | 1414 | 155 (Bridge) | --- | $\nu_2$(1021) $\nu_3$ (1092) $\nu_4$ (932) |

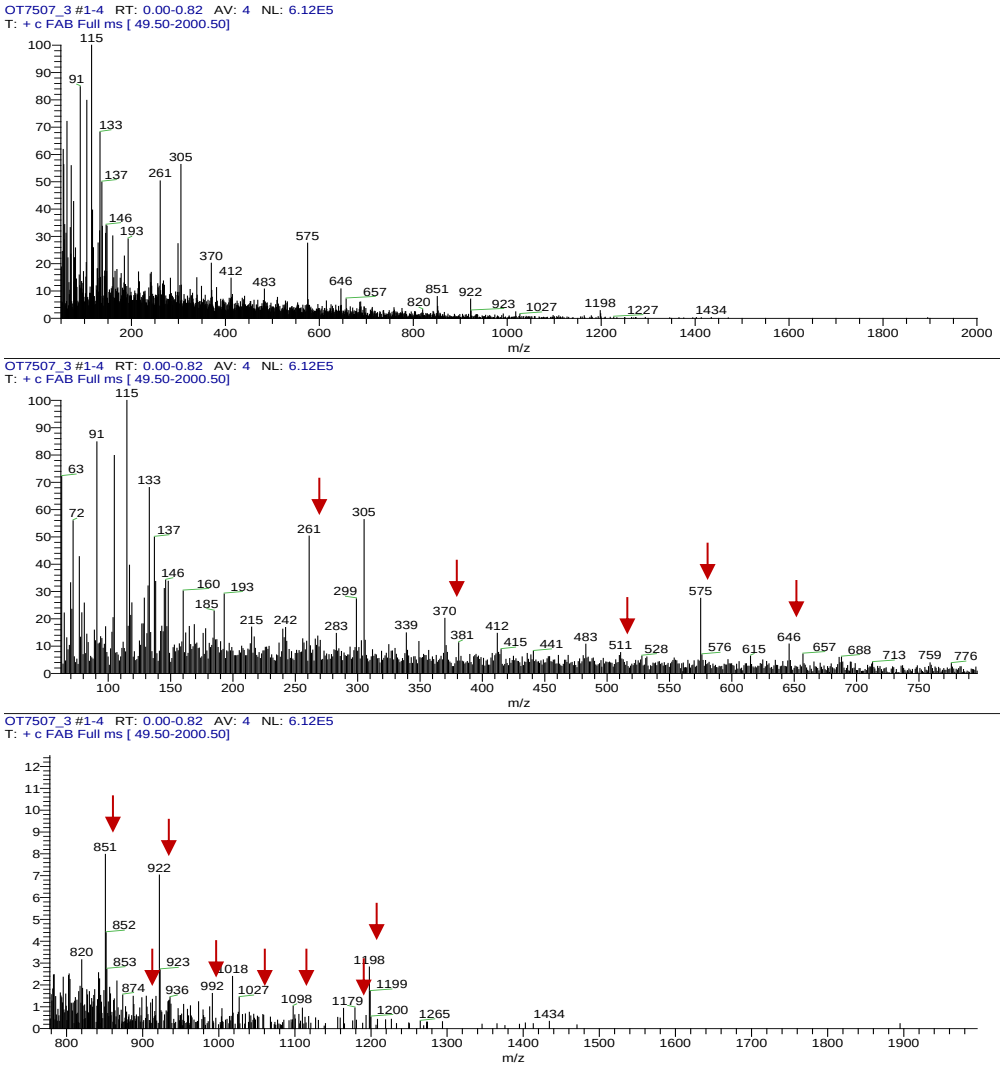


**Figure S3.** Mass spectrum FAB$^+$ of $[Mn_2(R,R(-)Hcpse)_4(NaClO_4)_2(NaOH)(MeOH)]n\cdot (EtOH)_{2n}\cdot(MeOH)_nH_2O_n$

**Table S4**. Fragmentation pattern for Mass spectrum corresponding to $[Mn_2(R,R(-)Hcpse)_4(NaClO_4)_2(NaOH)(MeOH)]n\cdot (EtOH)_{2n}\cdot(MeOH)_nH_2O_n$

| Peake | (m/z) | Assignation |
|---|---|---|
| 1322 | Dimeric unit 1323.20 | $(C_{48}H_{67}Cl_2Mn_2N_4Na_4O_{22})$ |
| 1198 | 121.94 ($ClNaO_4$) | $(C_{48}H_{67}ClMn_2N_4Na_3O_{18})$ |
| 1179 | 149 ($ClNa_2O_4$) | $(C_{48}H_{67}ClMn_2N_4Na_2O_{18})$ |
| 1098 | 219($Cl_2Na_2O_8$) | $(C_{48}H_{67}ClMn_2N_4Na_3O_{14})$ |
| 1027 | 274.9 ($Cl_2Na_3O_9CH_3$) | $(C_{47}H_{64}Mn_2N_4NaO_{13})$ |
| 992 | 306.92 ($Cl_2Na_3O_9CH_3$) | 993.29 ($C_{46}H_{59}Mn_2N_4NaO_{12}$) |
| 922 | 403 ($Cl_2Na_3O_{10}C_8H_{20}$) | 920.18($C_{41}H_{56}Mn_2N_4NaO_{12}$) |
| 874 | 445.19($Cl_2Na_3O_{10}C_8H_{20}$) | 877.13($C_{38}H_{39}Mn_2N_4NaO_{12}$) |
| 851 | 472.06 ($Cl_2Na_3O_{10}C_{10}H_{27}$) | 851.11($C_{36}H_{39}Mn_2N_4NaO_{12}$) |
| 657 | 669.12 ($ClNaO_{12}MnN_2C_{25}H_{36}$) | 654.07 ($C_{23}H_{31}ClMnN_8O_{10}$) |
| 575 | 744.87($C_{24}H_{34}MnN_2Na_3O_{15}$) | 574.13 ($C_{24}H_{33}ClMnN_2NaO_7$) |
| 511 | 824.07 ($Cl_2Na4O_{16}MnN_2\ C_{25}H_{39}$) | 499.16 ($C_{24}H_{32}MnN_2O_6$) |
| 483 | 839.09 ($Cl_2Na_4O_{15}MnN_2C_{26}H_{42}$) | 484.14 ($C_{23}H_{29}MnN_2O_6$) |
| 412 | 913.13 ($Cl_2Na_4O_{17}MnN_2C_{29}H_{48}$) | 410.10 ($C_{20}H_{23}MnN_2O_4$) |
| 370 | 928.15 ($Cl_2Na_4O_{17}MnN_2C_{30}H_{51}$) | 369.06 ($C_{17}H_{18}MnN_2O_4$) |
| 115 | ($C_{47}H_{63}Cl_2Mn_2N_4Na_3O_{17}$) | ($CH_4NaO_5$) |

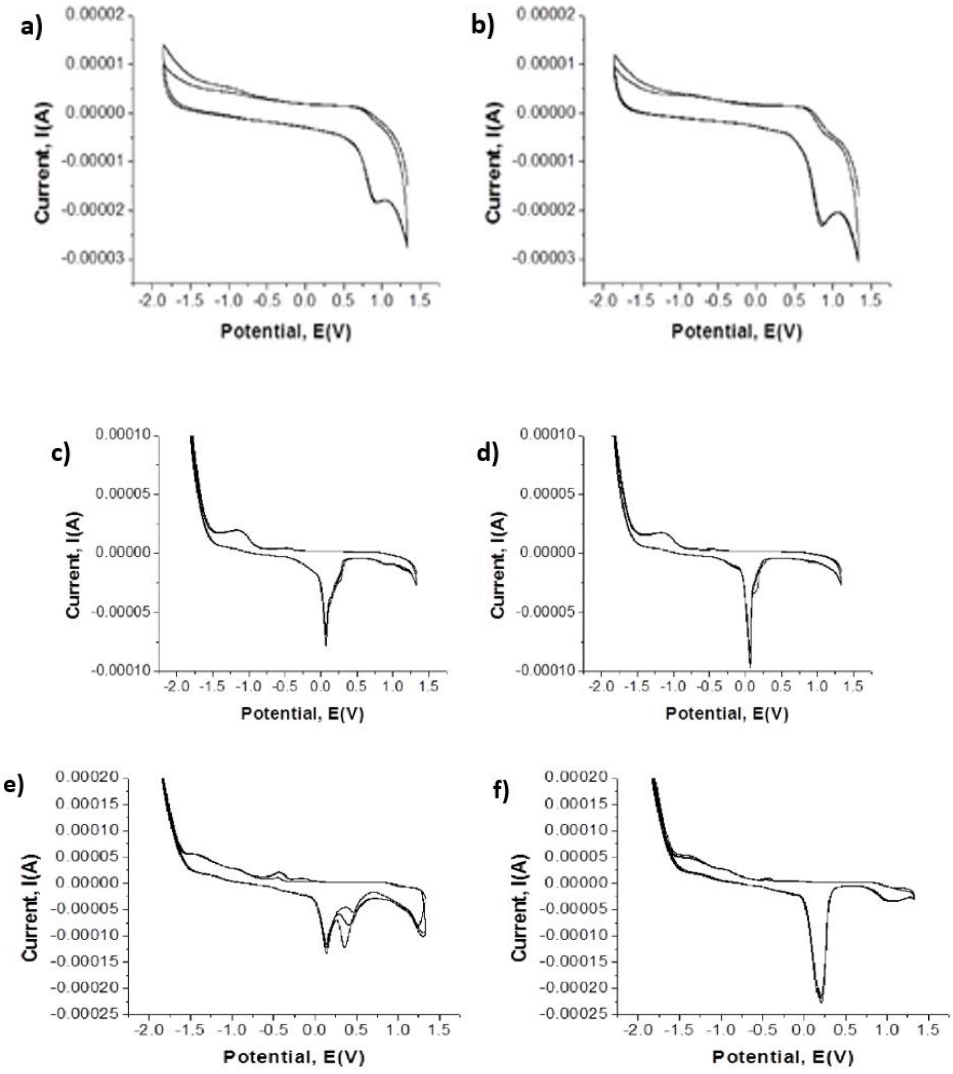


**Figure S5.** Electrochemical analyses for compound **1**. a). Cyclic voltammograms vs. NHE for the ligands (+)*S*,*S*-$H_2$cpse (1 mM), b). (-)*R*,*R*-$H_2$cpse (1 mM), c). [Cu(*S*,*S*(+)Hcpse)$_2$] (1 mM) d). [Cu(*R*,*R*(-)Hcpse)$_2$] (1 mM), e). [$Cu_3$(*S*,*S*(+)-cpse)$_3$](1 mM), and f). [$Cu_3$(*R*,*R*(-)-cpse)$_3$] (1 mM) in methanol with 0.1 M tetrabutylammonium hexafluorophosphate (*n*-$Bu_4NPF_6$) as supporting electrolyte.

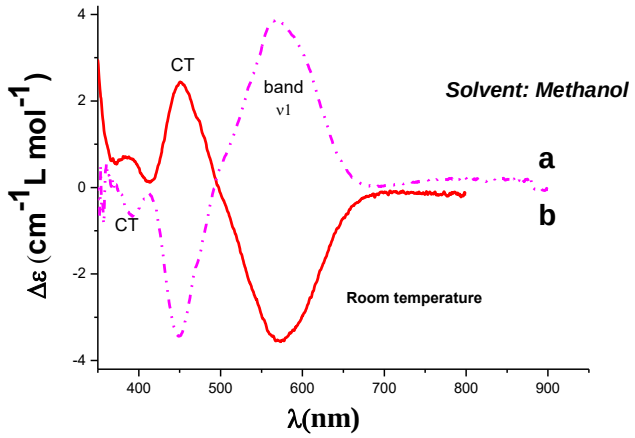


**Figure S6.** CD spectra for the manganese polymeric compounds.
**a.** $[Mn_2(R,R(-)Hcpse)_4(NaClO_4)_2(NaOH)(MeOH)]_n \cdot (EtOH)_{2n} \cdot (MeOH)_n H_2O_n$ and
**b.** $[Mn_2(S,S(-)Hcpse)_4(NaClO_4)_2(NaOH)(MeOH)]_n \cdot (EtOH)_{2n} \cdot (MeOH)_n H_2O_n$

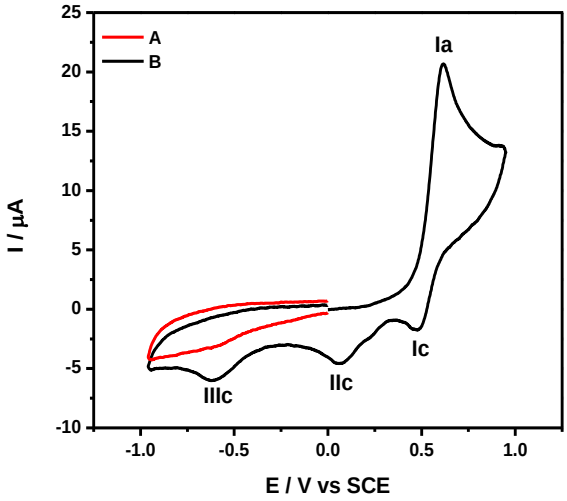


**Figure S7.** Cyclic voltammetry for compound **3** at ~1 mM, on glassy carbon electrode (ϕ = 3 mm), in acetonitrile containing *n*-$Bu_4NPF_6$ 0.1 M. a) positive direction starting scan, b) negative direction starting scan. Scan rate: 0.1 V $s^{-1}$ for $[Mn_2(R,R(-)Hcpse)_4(NaClO_4)_2(NaOH)(MeOH)]_n \cdot (EtOH)_{2n} \cdot (MeOH)_n H_2O_n$

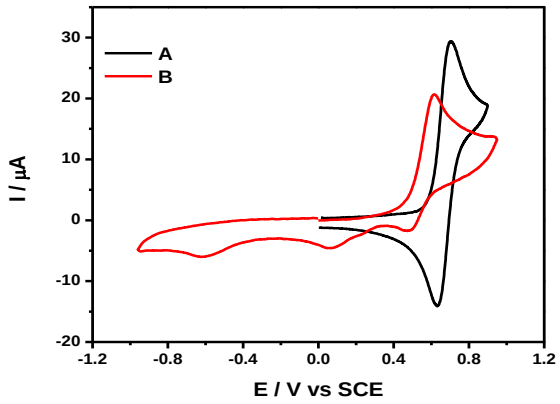


**Figure S8.** Comparison of the current due to the oxidation of ferrocenecarboxaldehyde 1 mM (A) and compound **3** at ~1mM (B), on glassy carbon electrode (ϕ = 3 mm), in acetonitrile containing *n*-$Bu_4NPF_6$ 0.1 M, at a scan rate of 0.1 $Vs^{-1}$ for $[Mn_2(R,R(-)Hcpse)_4(NaClO_4)_2(NaOH)(MeOH)]_n \cdot (EtOH)_{2n} \cdot (MeOH)_n H_2O_n$

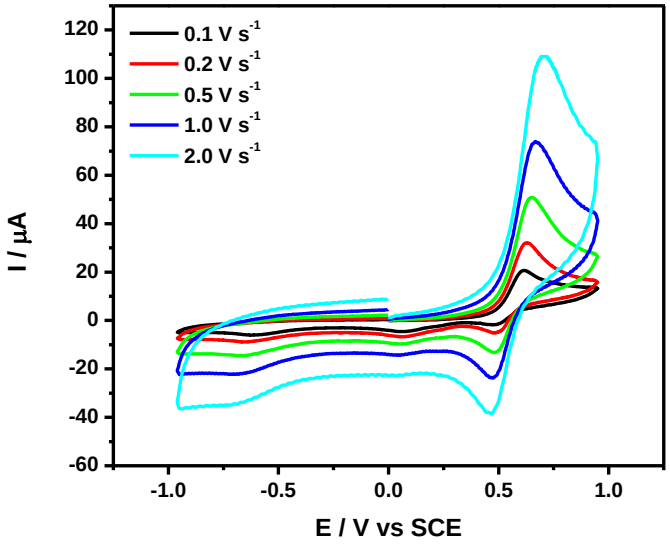


**Figure S9**. Cyclic voltammetry at different scan rates for compound **3** at ~1 mM, on glassy carbon electrode (ϕ = 3 mm), in acetonitrile containing *n*-$Bu_4NPF_6$ 0.1 M for $[Mn_2(R,R(-)Hcpse)_4(NaClO_4)_2(NaOH)(MeOH)]_n \cdot (EtOH)_{2n} \cdot (MeOH)_n H_2O_n$