Helicity inversion and redox chemistry of chiral manganese(II) cubanes

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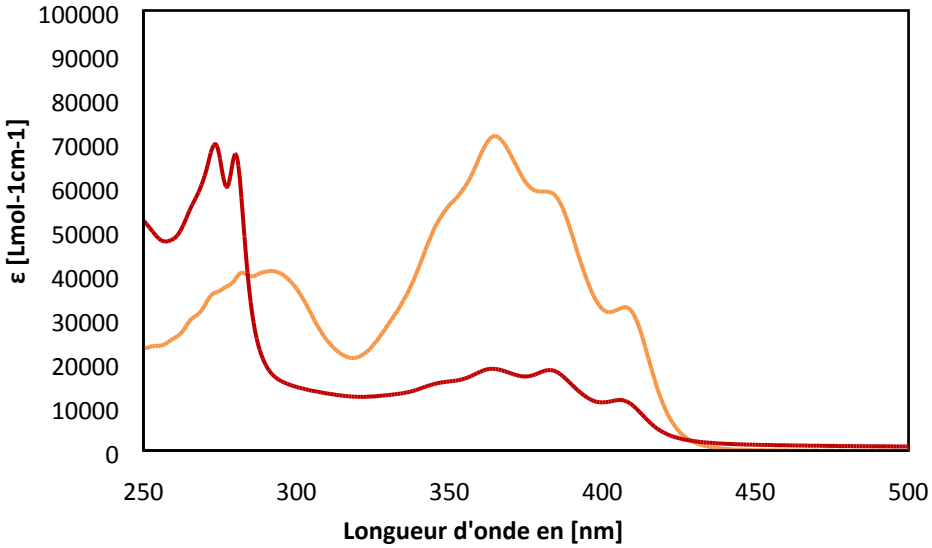
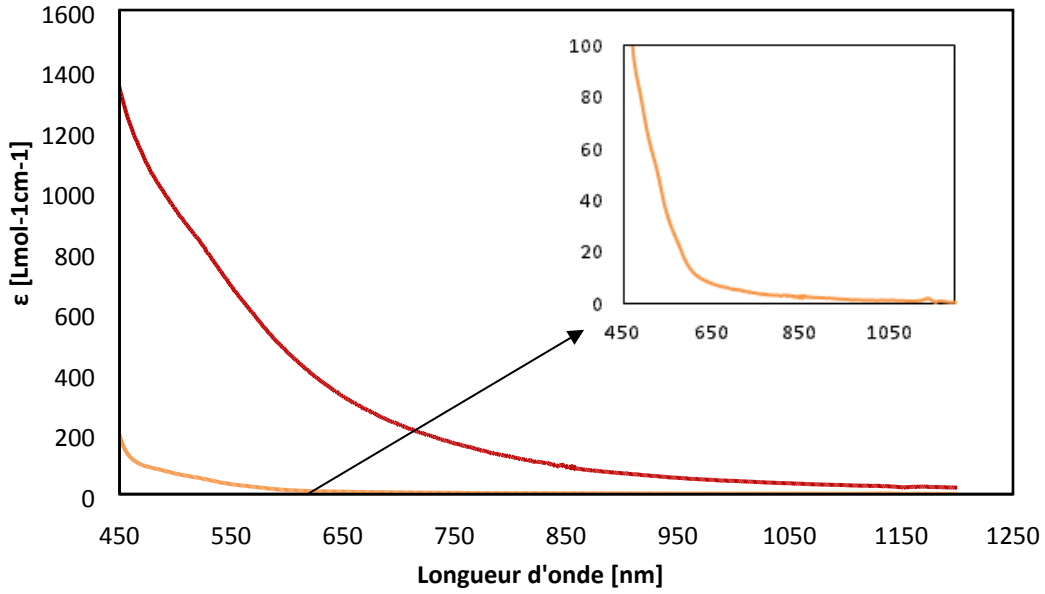
Supplementary material.

Figure S1.

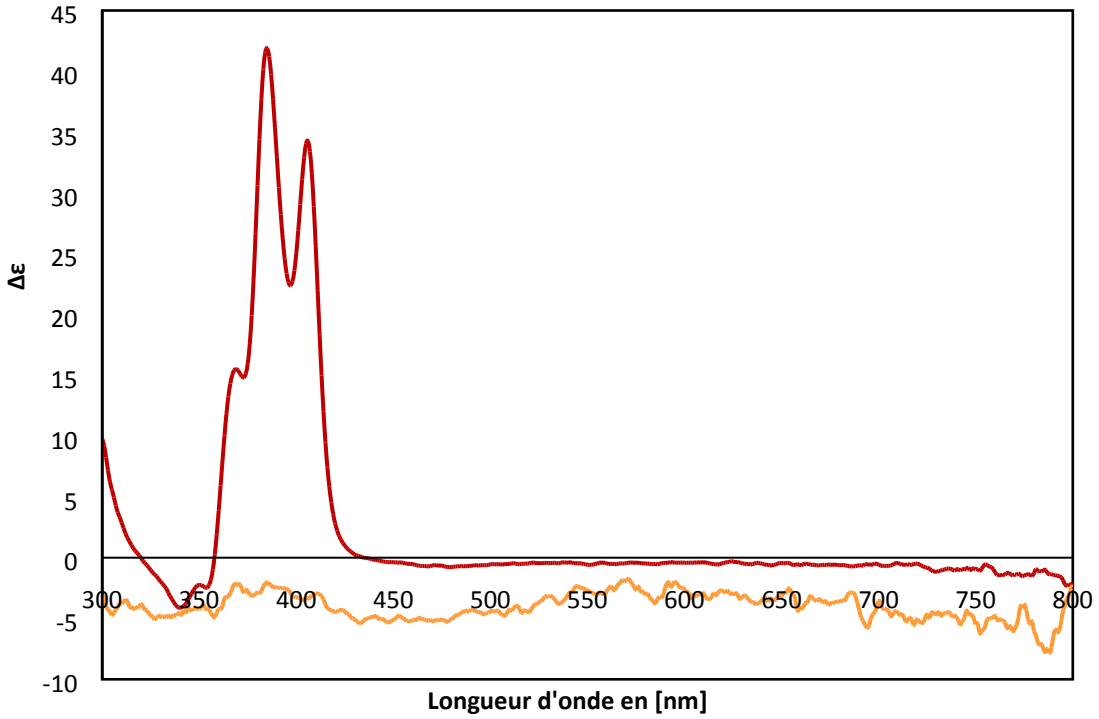


a) UV-visible spectra of $[Mn_4(\mathbf{1}\text{-}H)_4(OH)_2(MeCN)_2](ClO_4)_4.MeCN(EtOH)_2$, **4**, brown, and $[Mn_4(\mathbf{5}\text{-}H)_4(DPP)_2](DPP)_2.5EtOH$, **6**, orange. **4** was measured in MeCN at $3*10^{-5}$ M, **6** $1*10^{-5}$ M in $EtOH/CH_2Cl_2$ 50/50.



b) Measurements at higher concentrations: **4** in MeCN at $3*10^{-4}$ M, **6** at $3*10^{-3}$ M in $EtOH/CH_2Cl_2$ 50/50.

Figure S2



CD spectra of **4 (**$3*10^{-5}$ M in MeCN, brown) and **6** ($1*10^{-5}$ M in $EtOH/CH_2Cl_2$ 50/50, orange).

Figure S3. IR-spectra for Mn_4(S-**2**-H)$_4$ cubanes with various capping ligands: DPP (green), $PhCO_2^-$ (violet), *m*-$(NO_2)C_6H_4CO_2^-$ (blue), *p*-$(NO_2)C_6H_4CO_2^-$ (red).

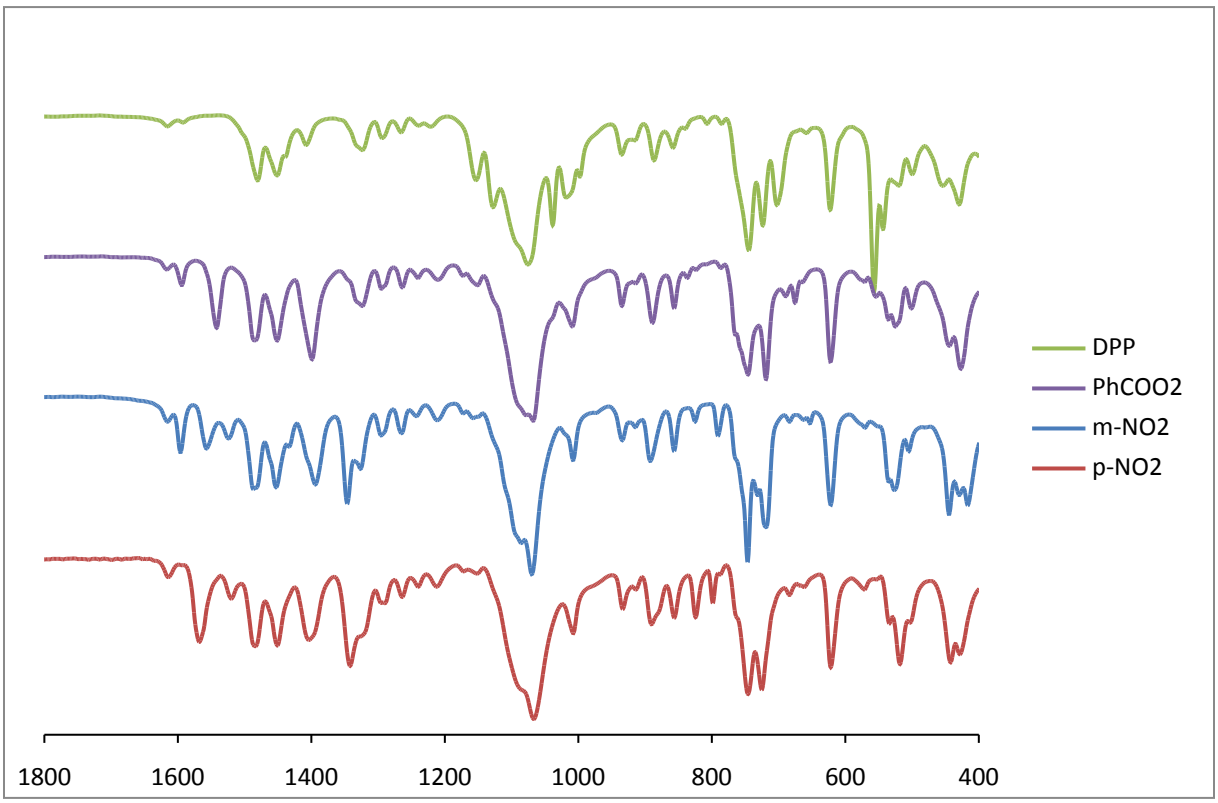


Figure S4 Comparison of $[Mn_4(S\text{-}\mathbf{3}\text{-}H)_4]^{4+}$ cores in **8** (left) and **9** (right).

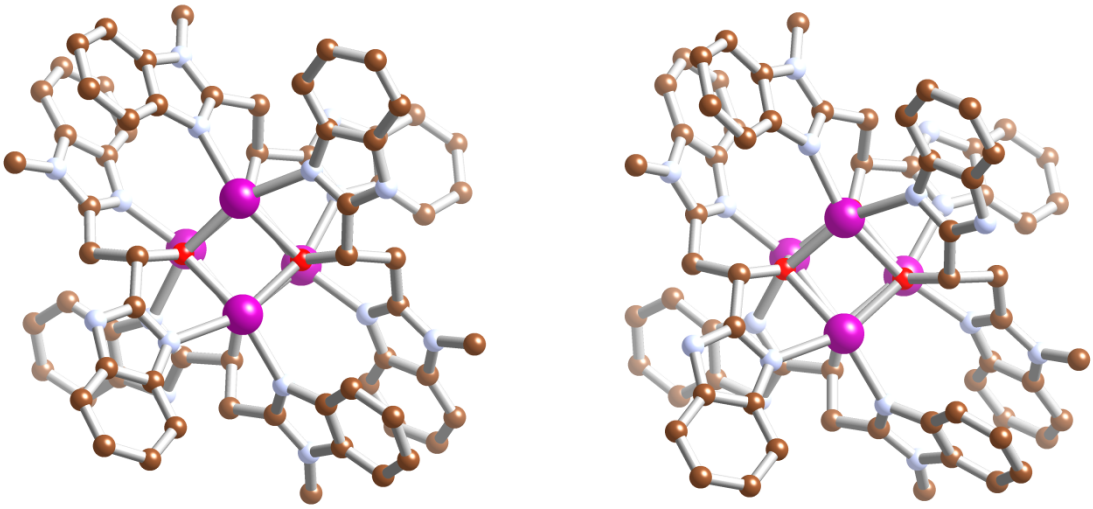


Table S1. Bond distances in $[Mn_4(\mathbf{1}\text{-}H)_4(OH)_2(MeCN)_2](ClO_4)_4.MeCN(EtOH)_2$, **4**.

Bond to Mn(III)	Distance, Å	Bond to Mn(II)	Distance, Å
Mn1-O1A	1.888(3)	Mn(3)-O13	2.040(4)
Mn1-O1B	2.102(4)	Mn3-N4B	2.146(4)
Mn1-N2A	2.160(4)	Mn3-N4A	2.152(4)
Mn2-O13	1.855(3)	Mn3-O1A	2.177(3)
Mn2-N1B	2.101(4)	Mn3-N1S	2.388(5)
Mn2-O1B	2.166(4)	Mn3-O1B	2.433(3)

Table S2 Hydrogen Bonds.

$[Mn_4(\mathbf{1}\text{-}H)_4(OH)_2(MeCN)_2](ClO_4)_4.MeCN(EtOH)_2$, **4**.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1*A*—H1*C*···O8*PB*	0.88	2.21	2.93 (2)	139
N3*A*—H3*C*···O1*S*^{iv}	0.88	1.89	2.731 (6)	160
N2*B*—H2*D*···O4*E*^{v}	0.88	2.20	3.029 (13)	157
N3*B*—H3*D*···O2*P*^{v}	0.88	2.06	2.909 (6)	161
O13—H19···O3*D*^{iv}	0.86	2.00	2.835 (17)	162.3

$[Mn_4(\mathbf{5}\text{-}H)_4(DPP)_2](DPP)_2.5EtOH$, **6.**

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N21*B*—H21*B*···O2*D*^{ii}	0.86	1.95	2.763 (5)	158
N11*B*—H11*B*···O1	0.86	1.95	2.797 (6)	170
N11*A*—H11*A*···O3*D*^{iii}	0.86	1.89	2.739 (5)	167
O1—H1*A*···O2*D*^{ii}	0.82	1.91	2.732 (5)	176

Symmetry codes: (ii) $-x+3/2, -y+1/2, -z$; (iii) $-x+3/2, y+1/2, -z+1/2$.

$[Mn_4(\mathit{S}\text{-}\mathbf{3}\text{-}H)_4(DPP)_2](ClO_4)_2$, **8**

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N11*A*—H11*A*···O4	0.86	2.21	3.062 (5)	170
N11*B*—H11*B*···O5	0.91	2.30	3.026 (5)	137

$[Mn_4(\mathit{S}\text{-}\mathbf{3}\text{-}H)_4(m\text{-}C_6H_4(NO_2)CO_2)_2](ClO_4)_2$, **9**

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N11*A*—H11*A*···O7	0.84 (3)	2.25 (4)	3.074 (6)	168 (5)
N11*B*—H11*B*···O1	0.85 (3)	2.13 (4)	2.894 (6)	148 (5)
N11*C*—H11*C*···O3	0.85 (3)	2.25 (4)	3.092 (6)	170 (5)
N11*D*—H11*D*···O5	0.85 (3)	2.11 (4)	2.851 (6)	145 (5)

Symmetry codes: (iv) $x-1/2, y+1/2, z$; (v) $x-1/2, y+1/2, z+1$.