Electronic Supplementary Material (ESI) for Inorganic Chemistry Frontiers.

Supporting Information
for

Mechanistic Insights into the electrochemical reduction of CO_2 to CO on Ni(salphen) complexes

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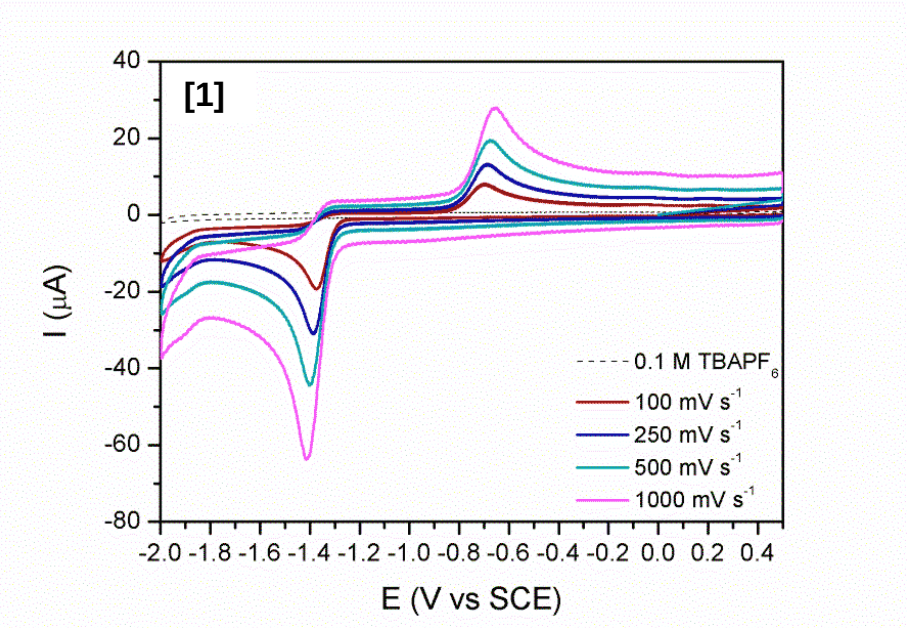

Figure S1. Cyclic voltammograms of complex **1** (1 mM) in DMF, argon saturated solution using $TBAPF_6$ as supporting electrolyte (0.1 M) at different scan rates. Glassy carbon was used as working, platinum wire as counter and SCE as reference electrodes.

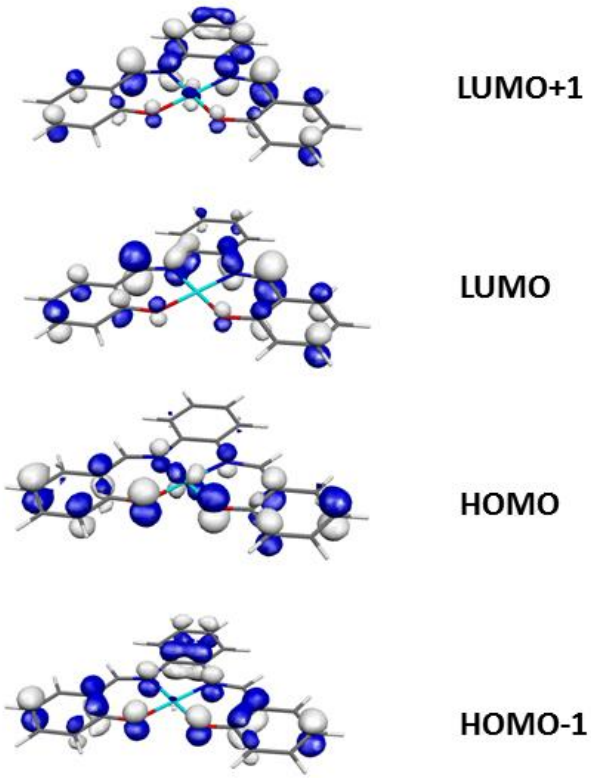

Figure S2. Frontier orbitals of [Ni(salphen)], **[1].**

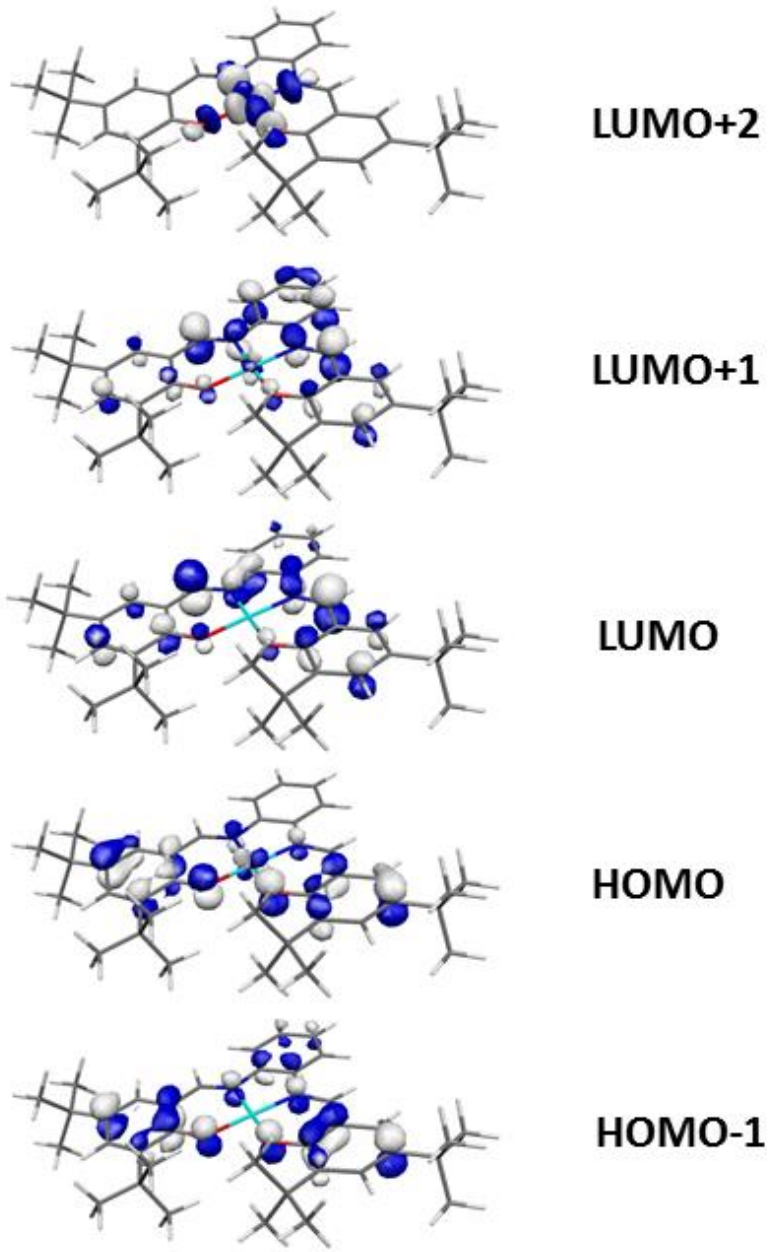

Figure S3. Frontier orbitals of **[2].**

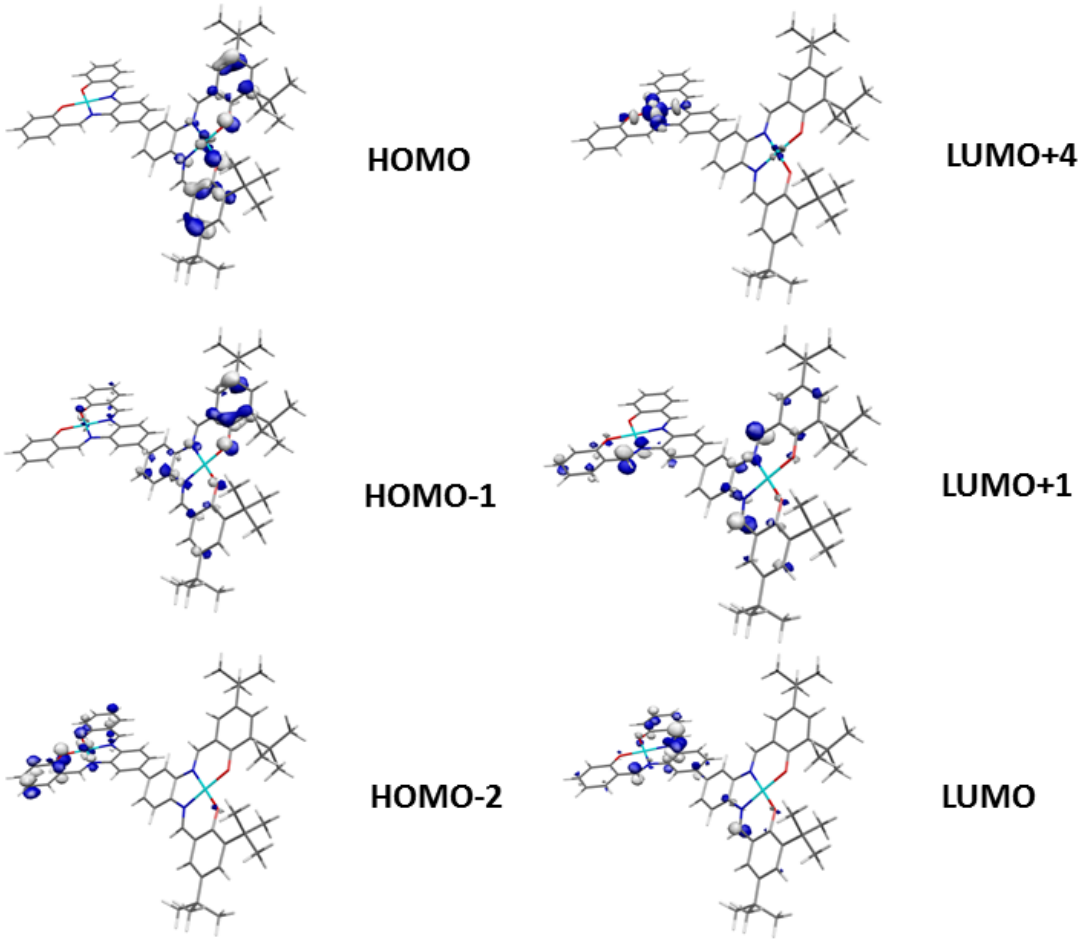

Figure S4. Frontier orbitals of **[3].**

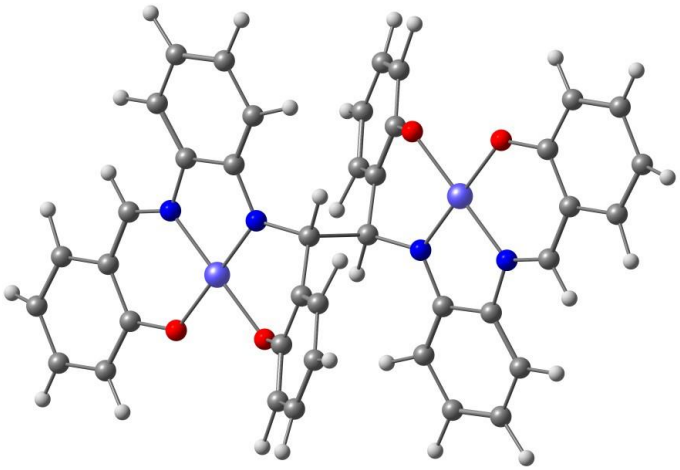

Figure S5. Structure of $[Ni_2(salphen)_2]^{2-}$.[1]

[1] S. Gambarotta, F. Urso, C. Floriani, A. Chiesi-Villa, C. Guastini, Inorg. *Chem.* 1983, 22, 3966-3972

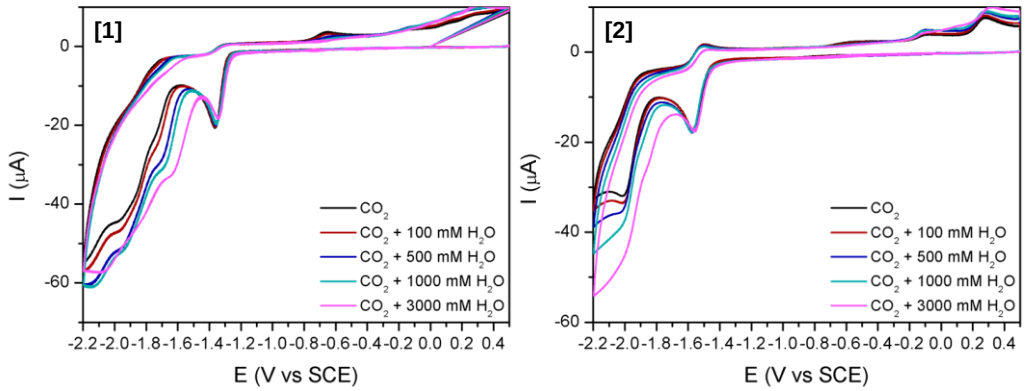

Figure S6. Cyclic voltammograms of complexes **1** and **2** (1 mM) in DMF, carbon dioxide saturated solutions using $TBAPF_6$ as supporting electrolyte (0.1 M) at 100 mV s^{-1}. Different concentrations of Brønsted acid (water) added. Glassy carbon was used as working, platinum wire as counter and SCE as reference electrodes.

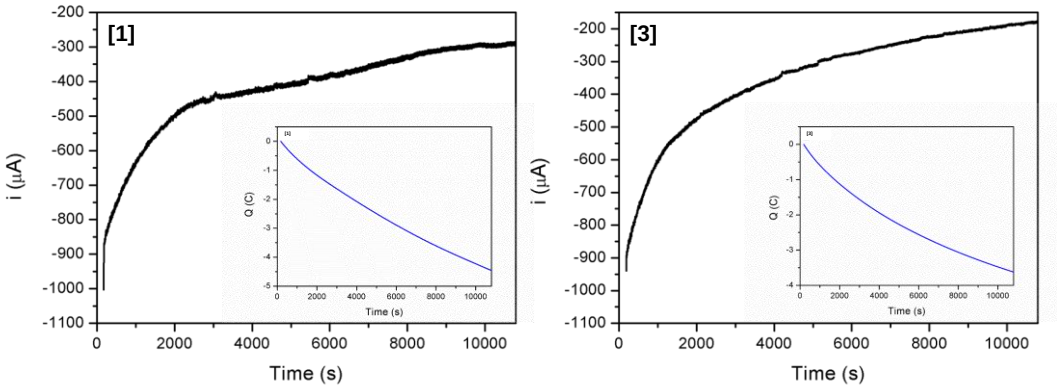

Figure S7. CPE results. Behaviour of current during electrolysis of **1** (left) and **3** right). Inset: Charge passed during electrolysis. Glassy carbon was used as working electrode, platinum wire as counter and SCE as reference electrode.

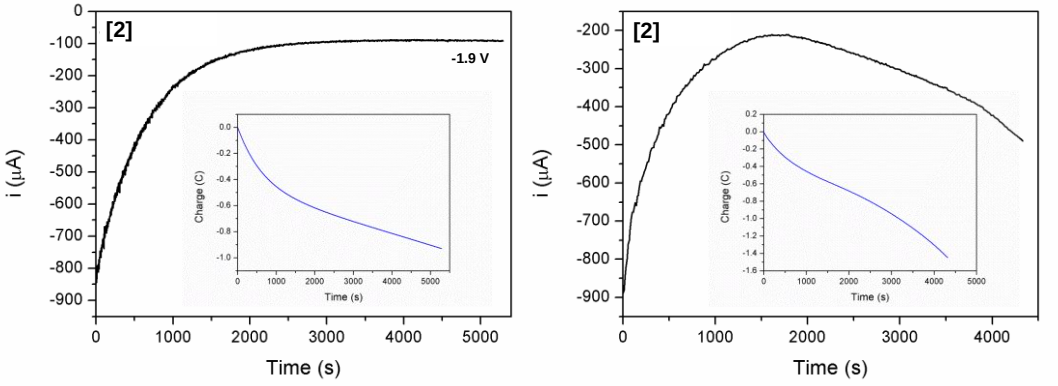

Figure S8. CPE results. Behaviour of current during electrolysis of **2** at -1.9 (left) and 2.1 V (right). Inset: Charge passed during electrolysis. Glassy carbon was used as working electrode, platinum wire as counter and SCE as reference electrode.

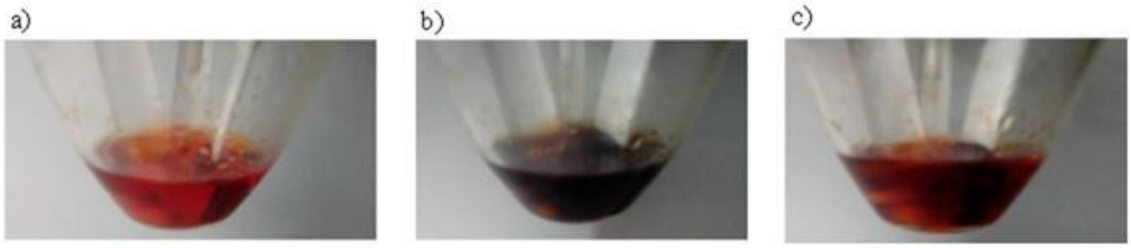

Figure S9. Colour change observation from orange (a) (before electrolysis) to brown (b) (after electrolysis). After air injection into the solution colour reverts back to orange (c).

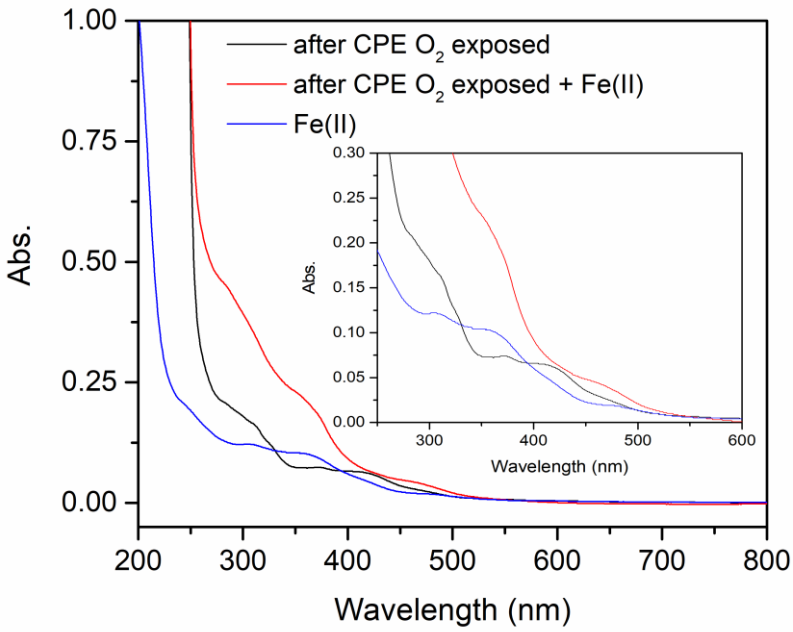

Figure S10. UV-vis spectra in H_2O of: solution of **2** after CPE and injection of O_2 (blue line); same solution after addition of Fe(II) solution (red line); Fe(II) solution.

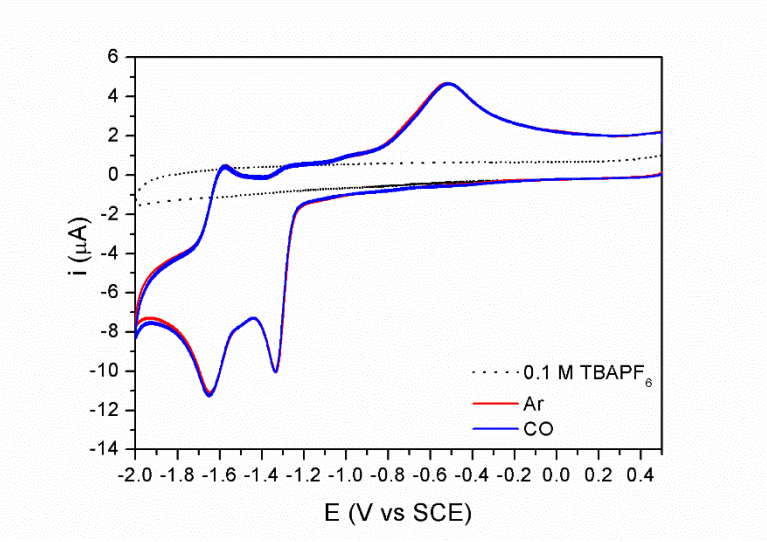

Figure S11. Cyclic voltammograms of complex **3** (1 mM) in DMF, argon and carbon monoxide saturated solutions using $TBAPF_6$ as supporting electrolyte (0.1 M) at 100 mV s^{-1}. Glassy carbon was used as working, platinum wire as counter and SCE as reference electrodes.

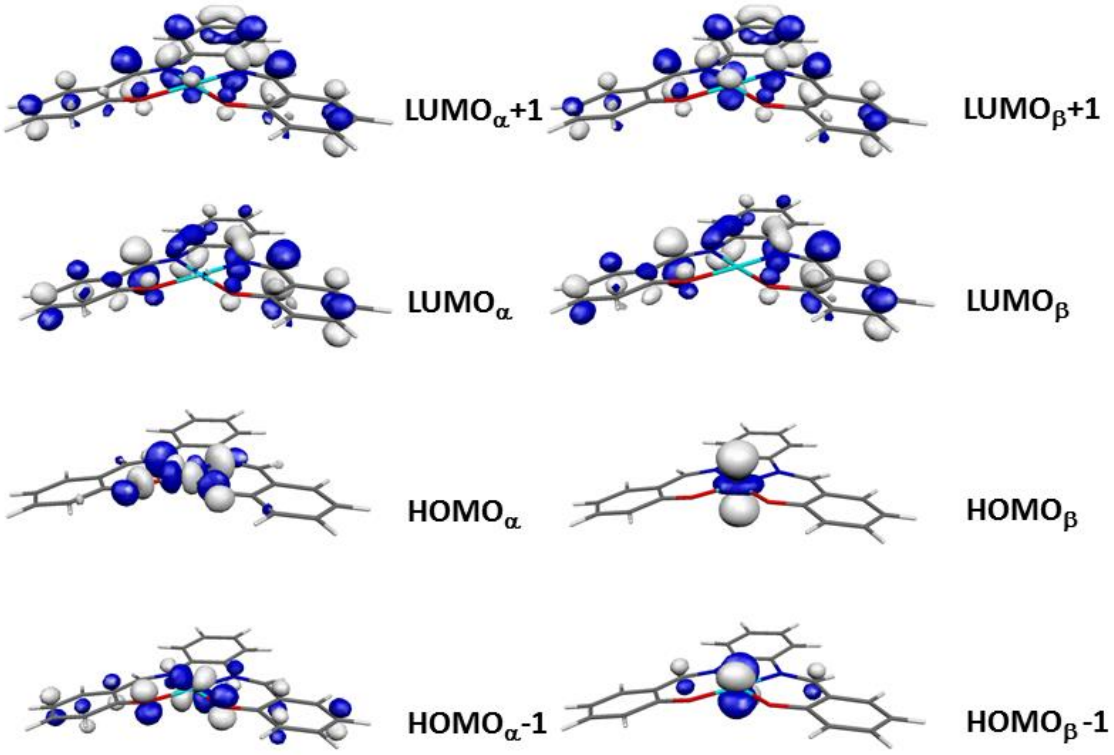

Figure S12. Frontier orbitals of ^{2}**[1]**$^{-}$.

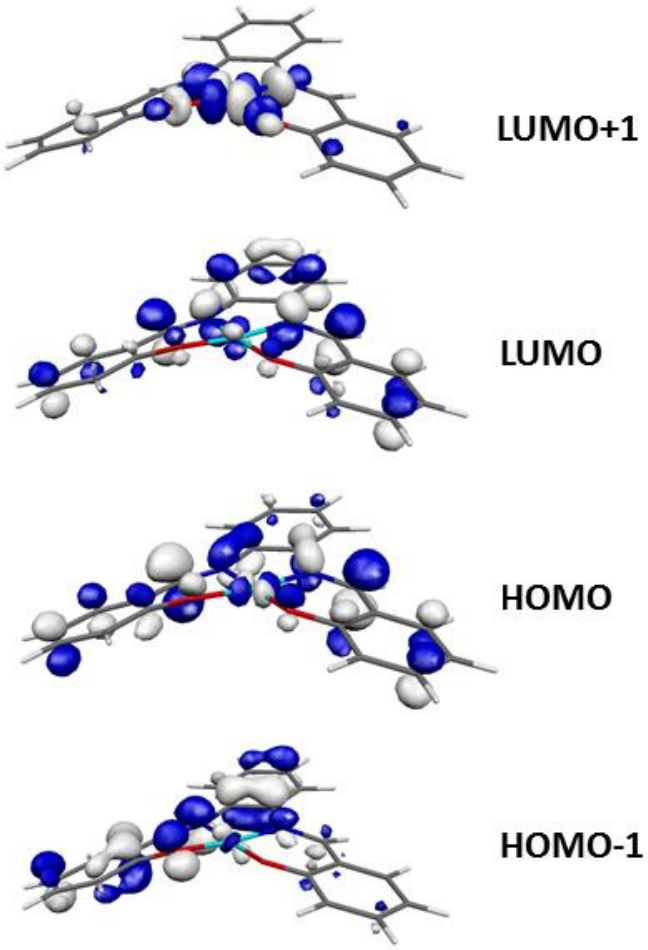

Figure S13. Frontier orbitals of ^{1}**[1]**$^{2-}$.

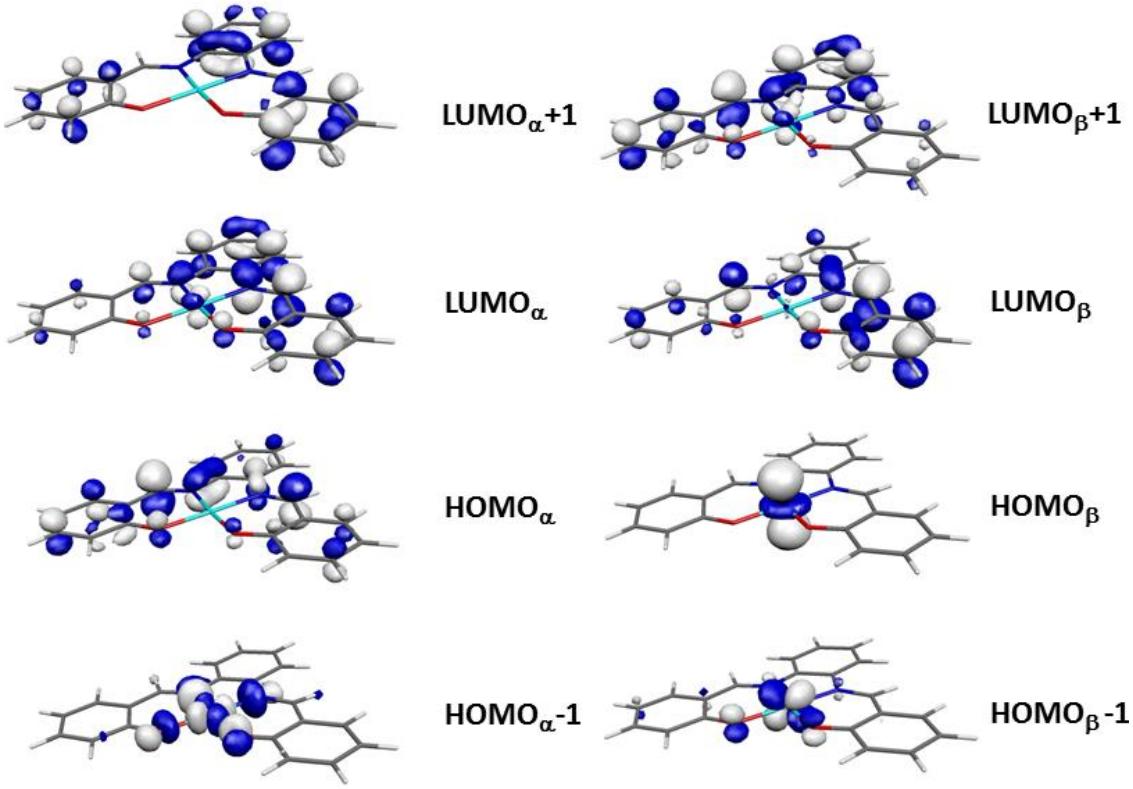

Figure S14. Frontier orbitals of ^{3}**[1]**$^{2-}$.

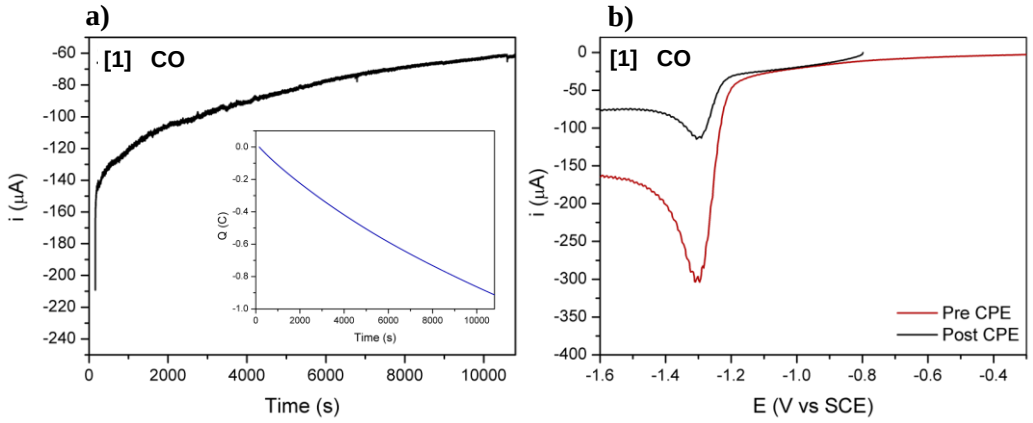

Figure S15. a) Current and charge (inset) behavior during CPE of complex **1** under CO at -1.6 V vs SCE. b) Linear voltammograms before and after electrolysis of **1** in DMF using $TBAPF_6$ as supporting electrolyte (0.1 M) at 10 mV s^{-1}. Glassy carbon was used as working electrode, platinum wire as counter and SCE as reference electrode.

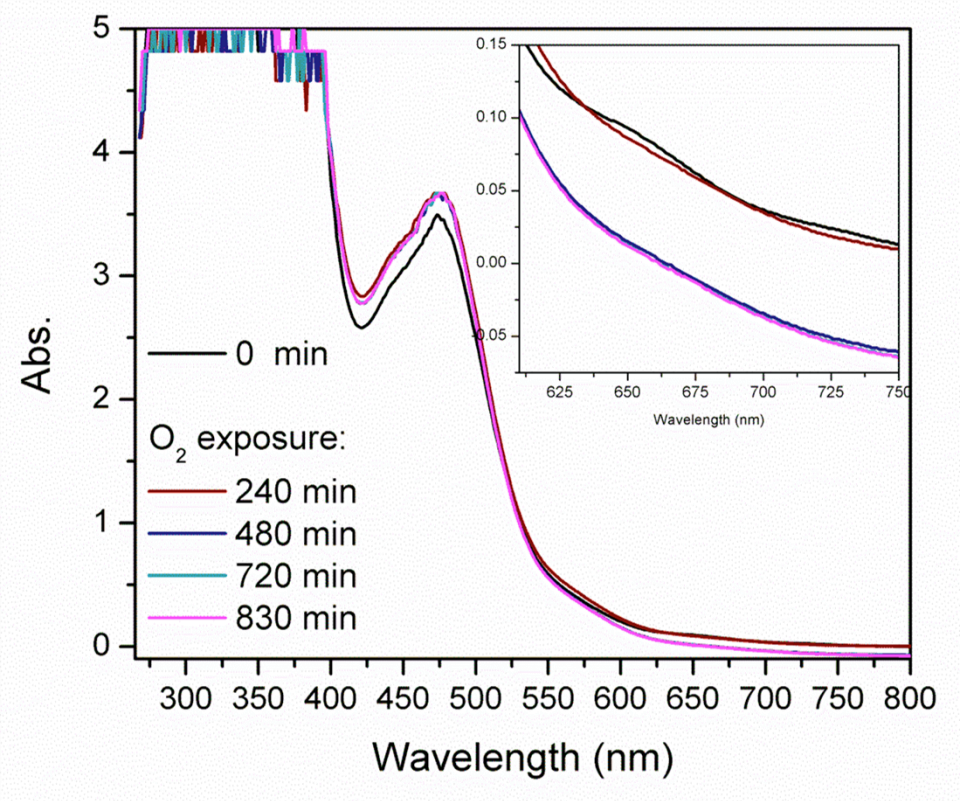

Figure S16. UV-vis spectra obtained for **1** after CPE under CO before and during exposure of the solution to atmospheric O_2.

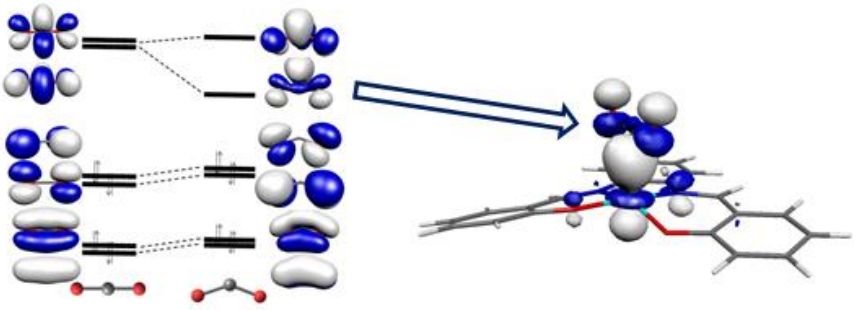

Figure S17. Walsh diagram for the conversion of linear into angular CO_2: the π orbitals (left) and H_β-1 Ni-C σ bonding orbital depicting the back donation from the metal to the LUMO of CO_2 (right) in ^{3}**[1(CO$_2$)]**$^{2-}$.

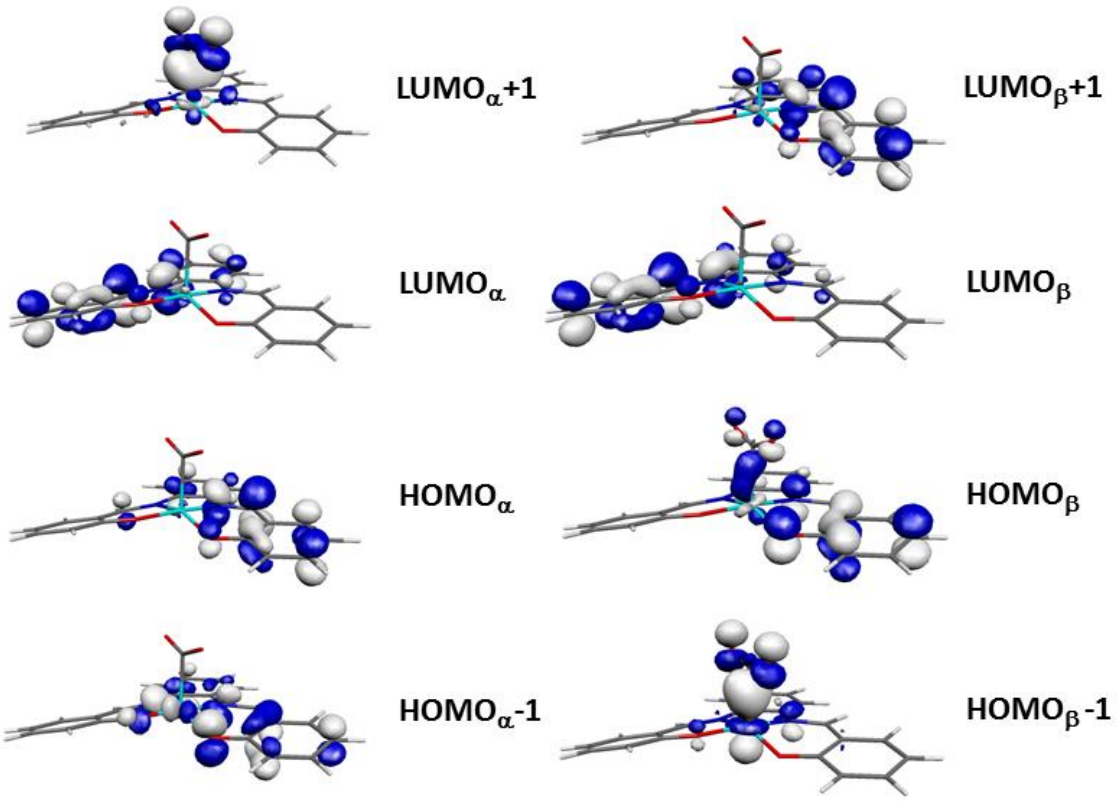

Figure S18. Frontier orbitals of ^{3}**[1(CO$_2$)]**$^{2-}$.

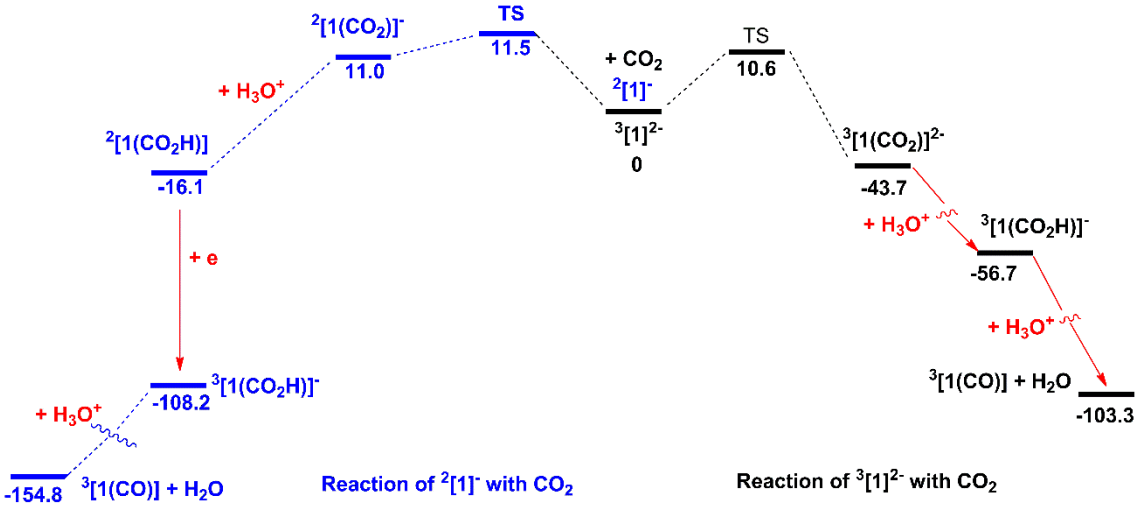

Figure S19. Energy profile for the reactions of the reduced complexes ^{2}**[1]**$^-$ and ^{3}**[1]**^{2} with CO_2 in DMF (relative energies, ΔG, in kcal mol^{-1}).

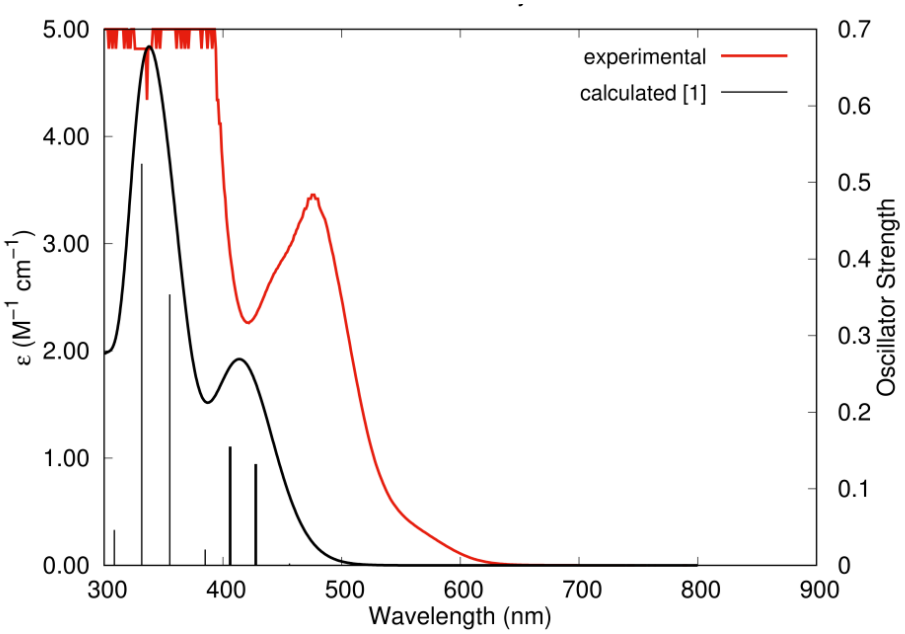

Figure S20. Experimental and calculated (TDDFT, black line) spectra of [Ni(salphen)] **[1]**. The sticks correspond to the calculated wavelengths.

Table S1. Relevant TD-DFT excitation energies (λ), oscillator strengths (*f*) and compositions, for complexes [Ni(salphen)], **[1]**.

Complex	λ (nm)	*f*	Composition	λ_{exp} (nm)
[1]	428	0.1323	H → L (98%)	
	406	0.1551	H-1→L (70%), H→L+1 (26%)	476

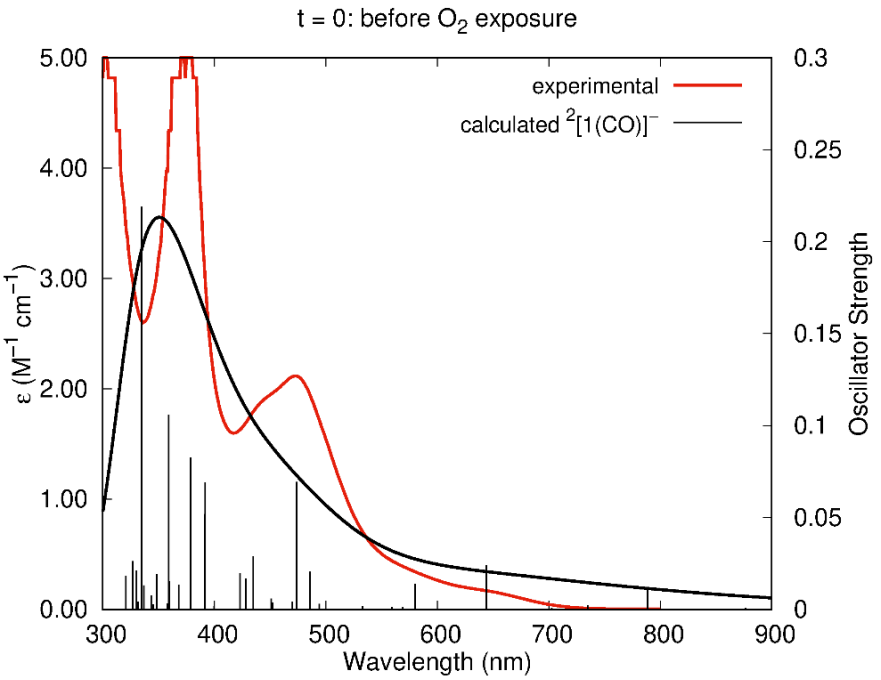

Figure S21. Absorption spectrum of the CO container species **^{2}[1(CO)]$^-$**: experimental (red line) and calculated (TDDFT, black line) spectra. The sticks correspond to the calculated wavelengths.

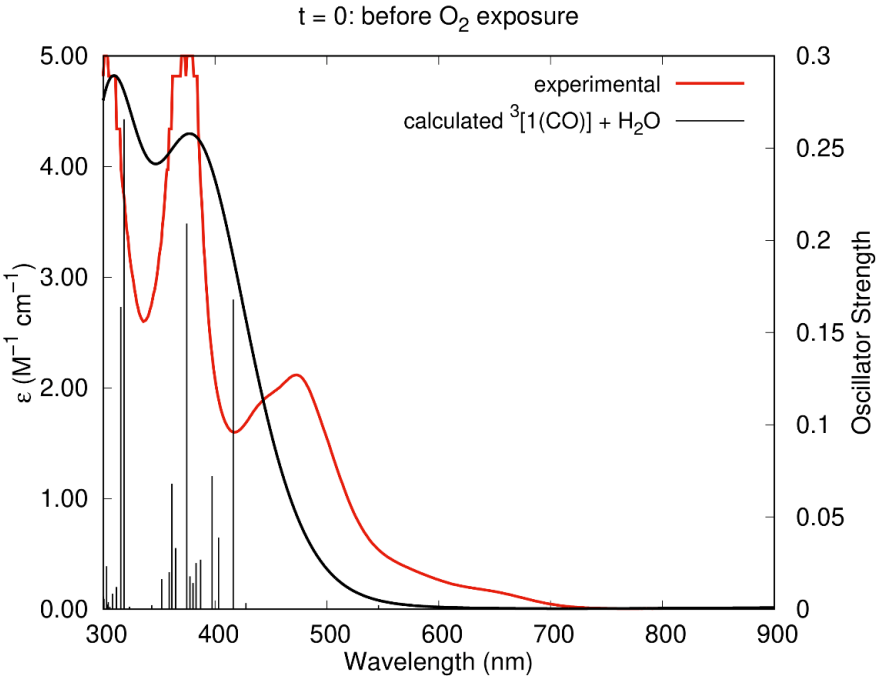

Figure S22. Absorption spectrum of the CO container species **^{3}[1(CO)] + H_2O**: experimental (red line) and calculated (TDDFT, black line) spectra. The sticks correspond to the calculated wavelengths.

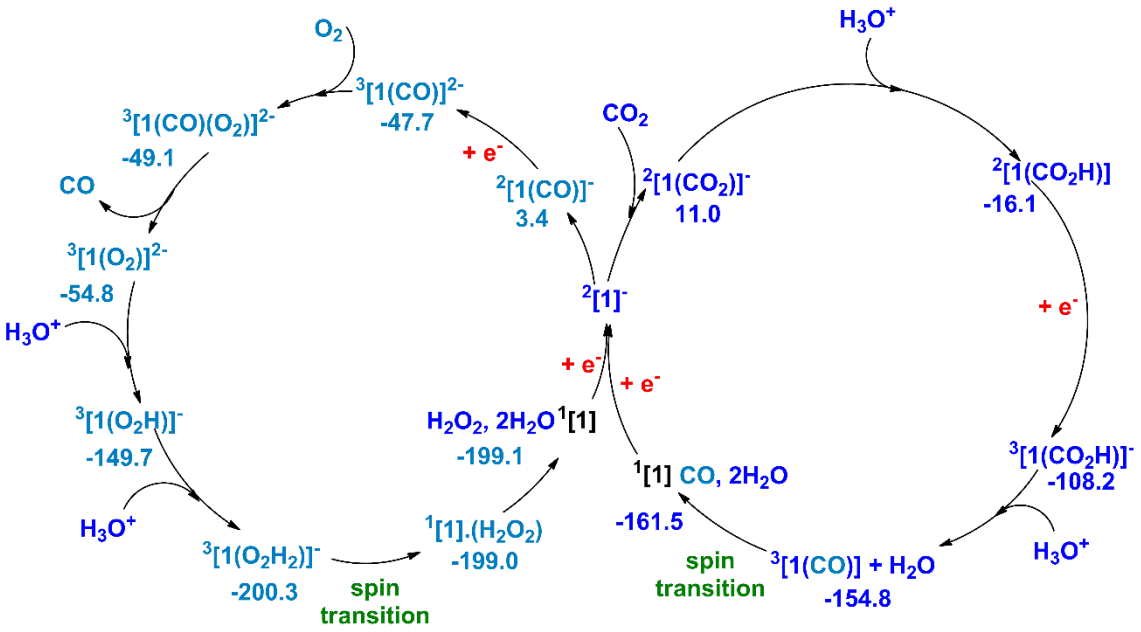

Figure S23. Energy profile for the reactions of the reduced complexes **^{2}[1]$^{-}$** with CO_2 (right side, blue) and CO (left side, turquoise). The free energies, ΔG, are given in kcal $mol^{-1}$and the reference 0 is the energy of **^{2}[1]$^{-}$**. The two reduction and the spin transition steps are highlighted in both cycles.