Electronic Supplementary Information

For

Cobaloxime-Based Artificial Hydrogenases

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Supplementary Figures

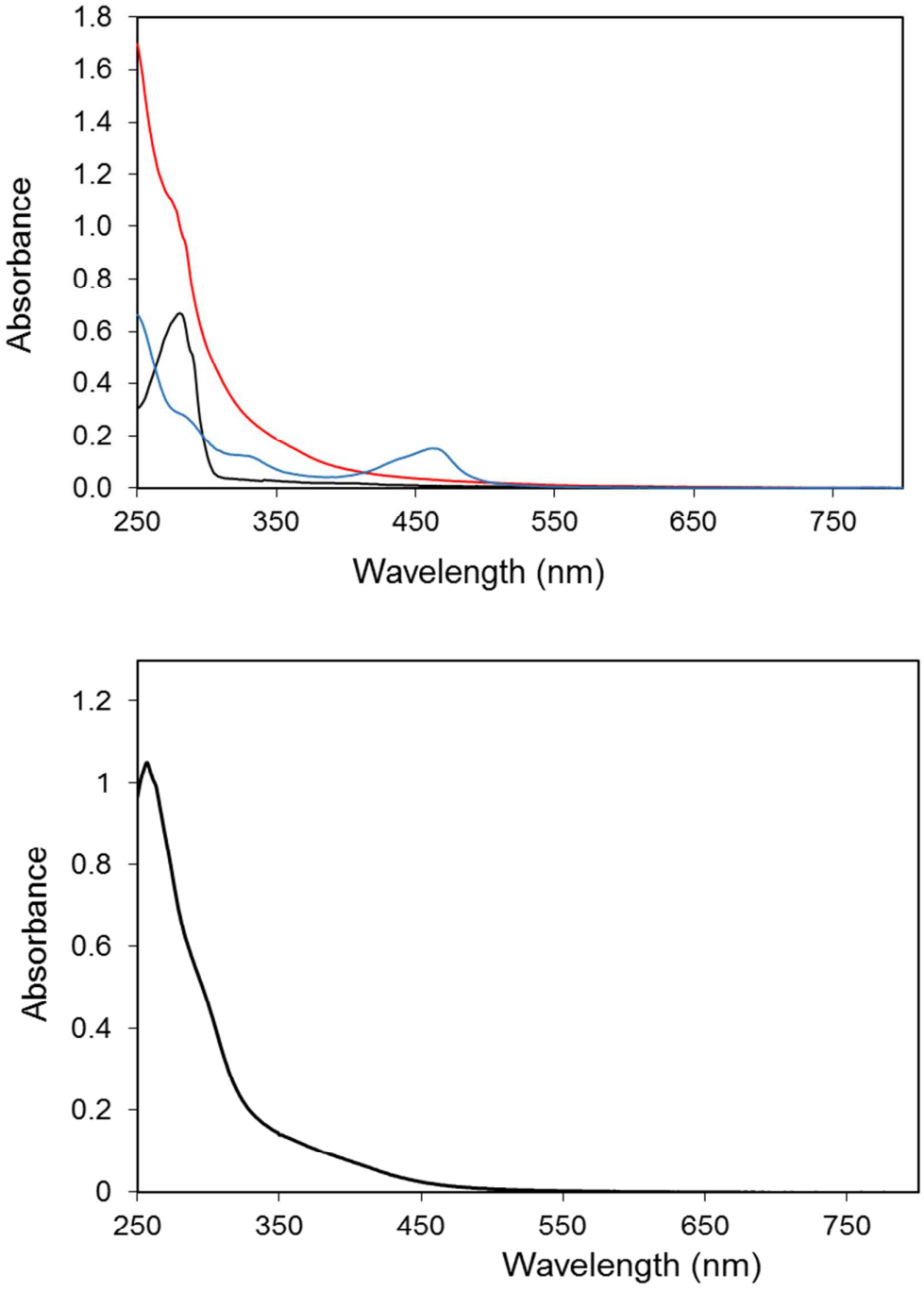

Figure S1. Top: UV-visible spectra of 45 µmol.L^{-1} solutions of apo-SwMb (black trace), **2** (blue trace) and *Sw*Mb·**2** (red trace) in 50 mmol.L^{-1} Tris-HCl pH 7.5; bottom: UV-visible spectra of a 30 µmol.L^{-1} solution of [Co(gh)$_2$pyCl].

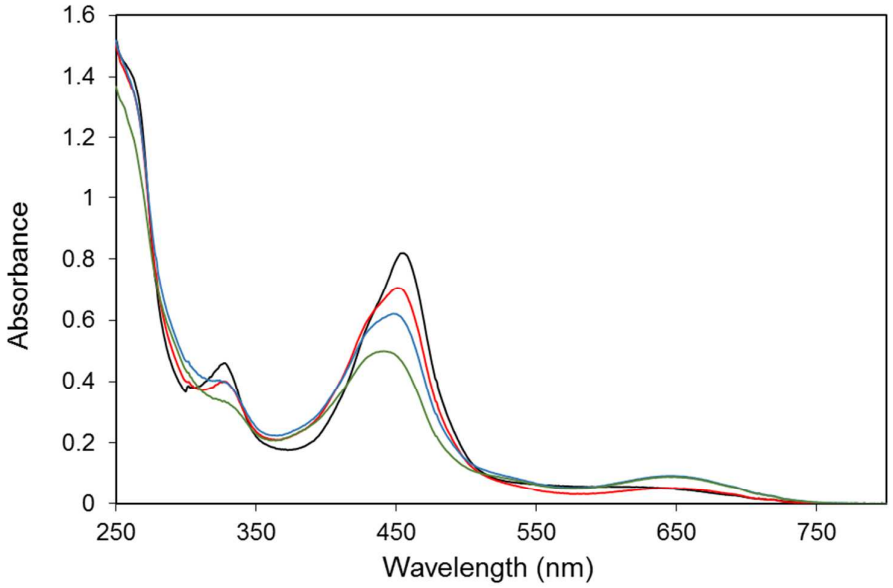

Figure S2. UV-visible spectra of 0.6 mmol.L^{-1} solutions of **1** in the absence (black trace) and in the presence of 1 (red trace), 2 (blue trace) and 5 (green trace) equiv. of imidazole) in 50 mmol.L^{-1} Tris-HCl pH 8.0.

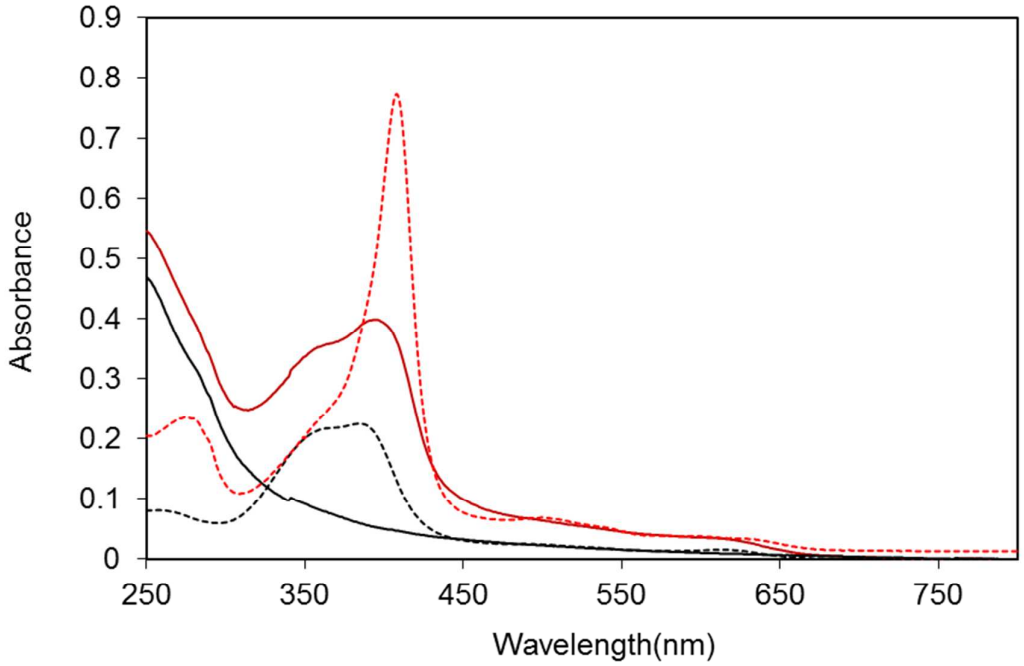

Figure S3. UV-visible spectra of 10 µmol.L^{-1} solutions (50 mmol.L^{-1} Tris-HCl pH 7.5) of hemin (black dotted trace), *Sw*Mb•**2** (black plain trace), holo-*Sw*Mb (red dotted trace) and *Sw*Mb•**2** reacted for 4h with 1 equiv. hemin (red plain trace)

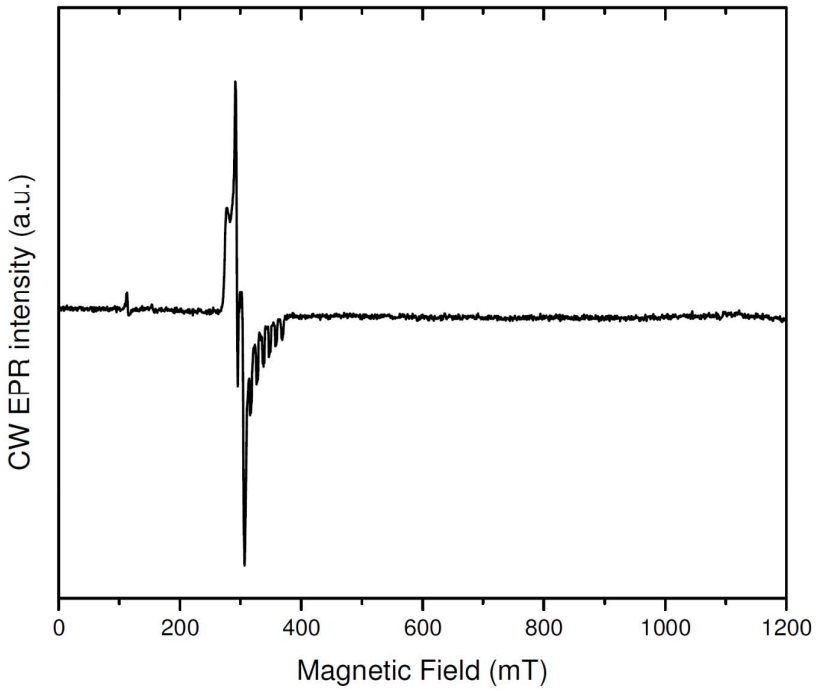

Figure S4. CW X-band (9.34 GHz) EPR spectra of *Sw*Mb•**1.** T=5 K. For experimental details, see Experimental Section.

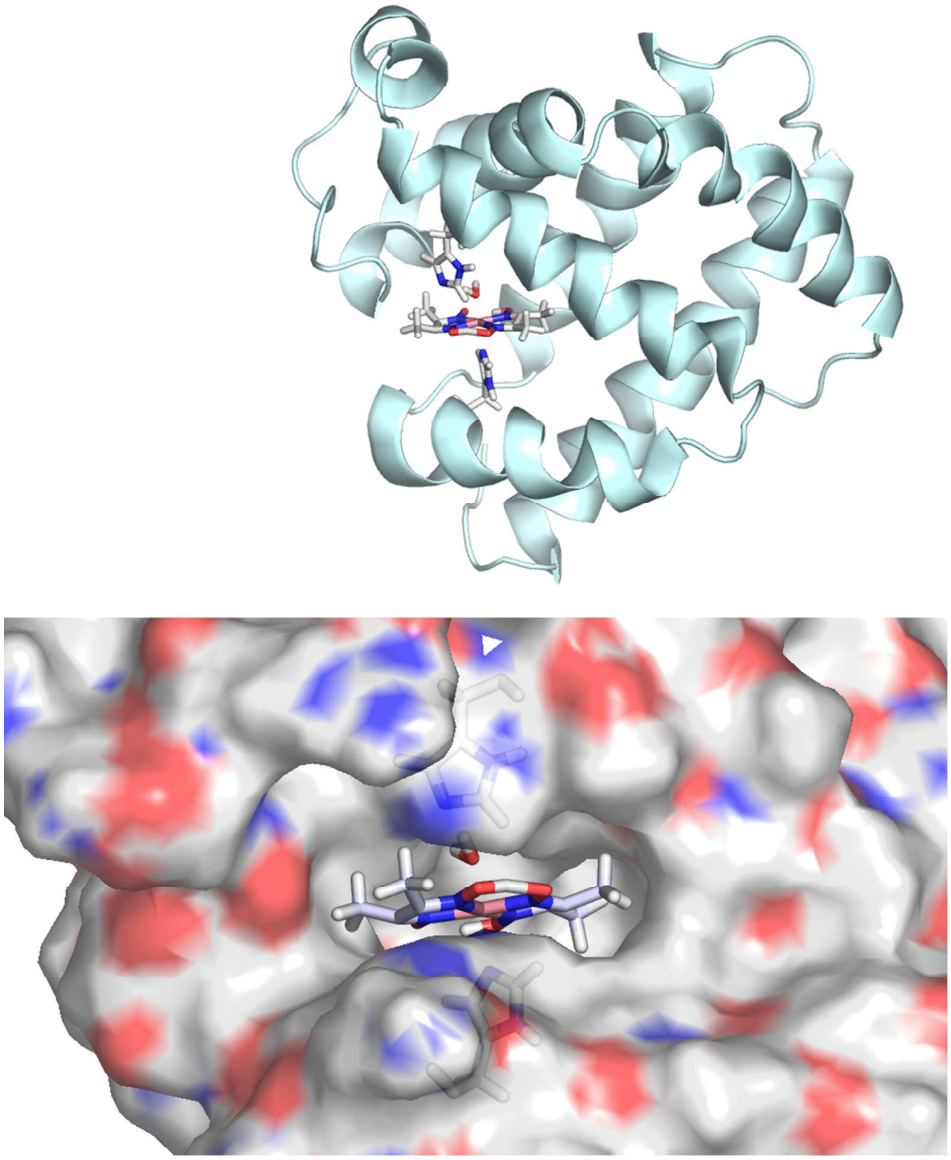

Figure S5. Top: structure of *Sw*Mb·**2** as computed at the (QC)/MM level; bottom: electrostatic representation of the protein environment around **2** in *Sw*Mb·**2** (hydrophilic regions are shown in red (oxygen atoms) and blue (nitrogen atoms) while hydrophobic regions are shown in grey. The cobalt atom is depicted in pink.

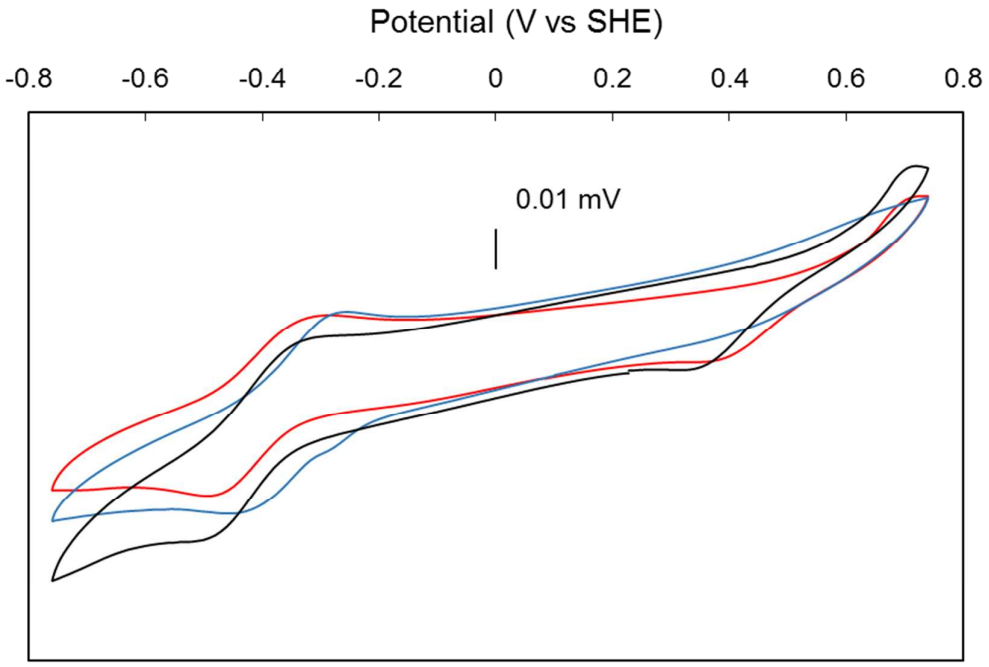

Figure S6. Cyclic voltammograms of **1** (1 mmol.L^{-1}) recorded in 100 mmol.L^{-1}Tris-HCl pH 7.5 buffer , 100 mmol.L^{-1}, NaCl on a glassy carbon electrode in the absence (red trace) and in the presence of 10 equiv. of imidazole (blue trace). Scan rate 100 mV.s^{-1}.

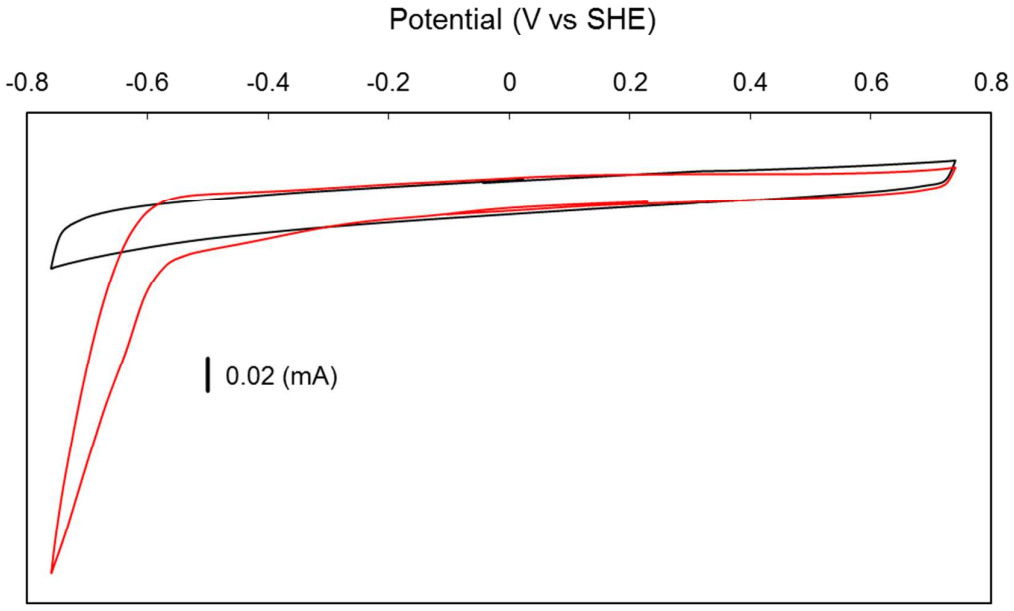

Figure S7. Cyclic voltammograms recorded in 100 mmol.L^{-1} Tris-HCl pH 7.5 buffer (100 mmol.L^{-1} NaCl of *Sw*Mb·**2** (red trace) adsorbed on MWCNTs and coated with Nafion. The data recorded on a similar electrode without *Sw*Mb·**2** are shown in black. Scan rate: 100 mV.s^{-1}.

References

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