

Electronic Supplementary Information for

**Unsymmetrical one-electron oxidized Ni(II)-
bis(salicylidene) complexes: A protonation-induced
shift of the oxidation site.**

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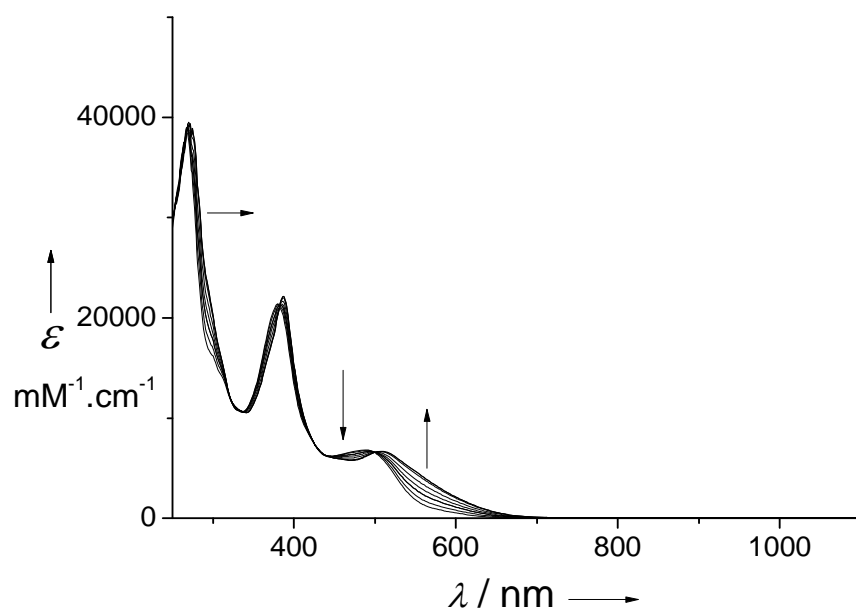


Fig S1. Titration of 2H^+ (0.05 mM in CH_2Cl_2) by 0 to one molar equivalent of NEt_3 (2.5 mM). Arrows indicate spectral changes when NEt_3 is added. $T = 298 \text{ K}$, $l = 1.000 \text{ cm}$.

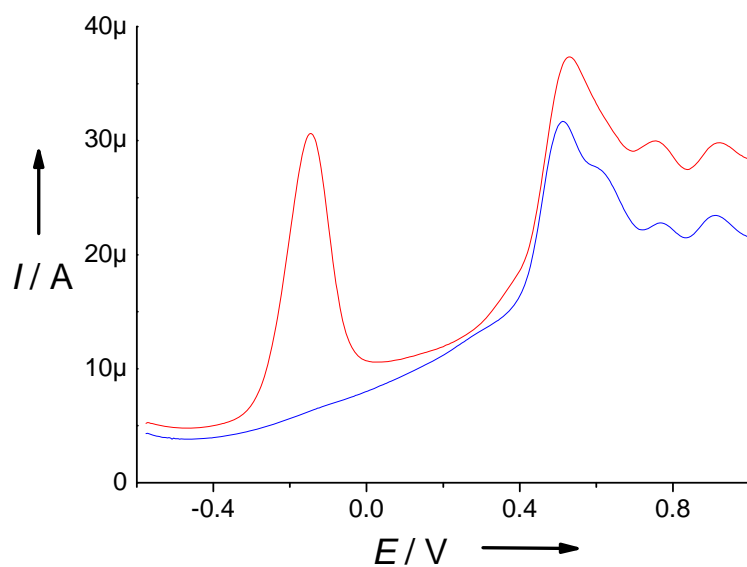


Fig. S2 Differential pulse voltammogram recorded for 1 mM CH_2Cl_2 (+ 0.1 M TBAP) solutions of $2H^+$ (blue) and 2 (red). The potential values are given versus the Fc/Fc^+ couple. $T = 298$ K, pulse amp. 0.05 V.

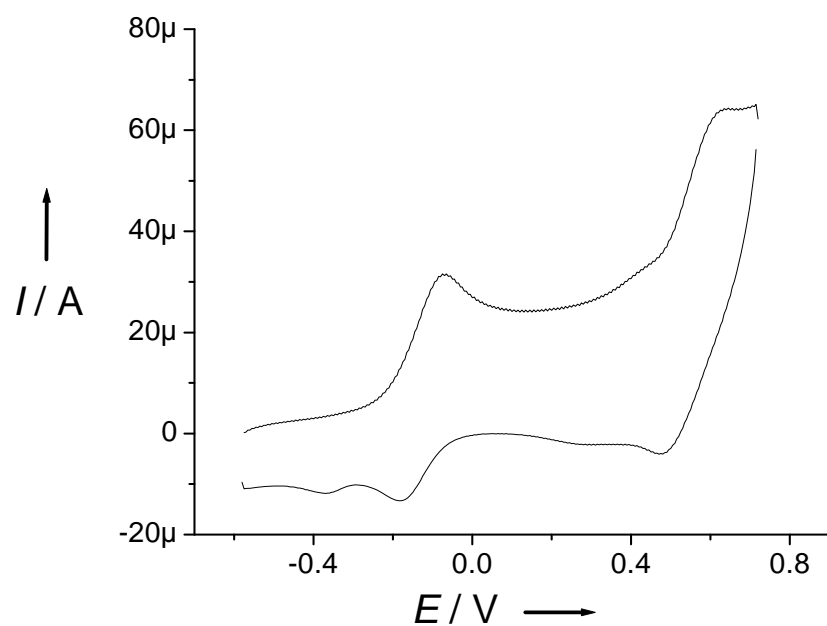


Fig. S3 Cyclic voltammetry curves of a 1 mM CH_2Cl_2 solution (+ 0.1 M TBAP) of complex 2 . Scan rate: 0.1 V s^{-1} , $T = 298$ K. The potentials are referenced versus the Fc/Fc^+ couple.

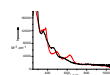


Fig S4. UV-Vis spectra of $(2\bullet)^+$ (red) and $(2H\bullet)^{2+}$ (black) in CH_2Cl_2 (+0.005 M TBAP). $T = 243$ K, $l = 1.000$ cm.

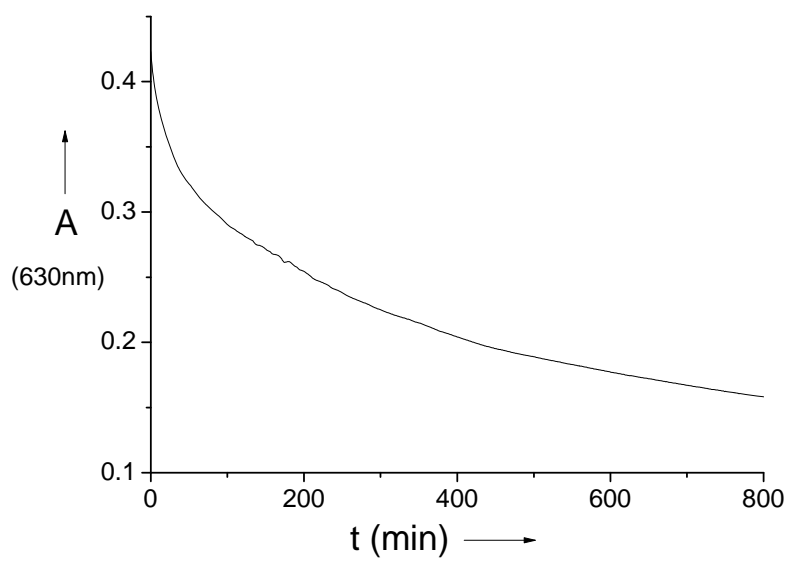


Fig S5. Decay pattern of $(2\bullet)^+$ in CH_2Cl_2 at 298 K, $l = 1.000$ cm.

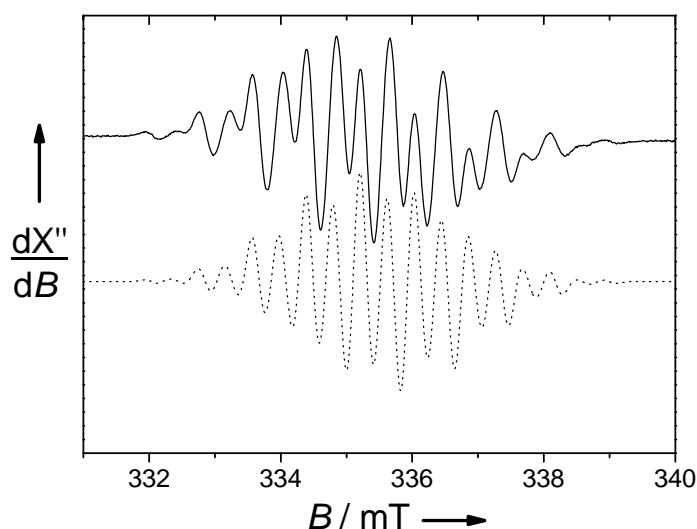


Fig S6. Isotropic X-Band EPR spectra of a 1 mM CH_2Cl_2 solution (containing 0.1 M TBAP) of $(2')^+$. Solid lines is experimental spectrum, dotted lines a simulation using the parameters given in the text. $T = 223$ K, microwave frequency 9.42 GHz, power 20 mW, modulation frequency 100 KHz, amplitude 0.1 mT.

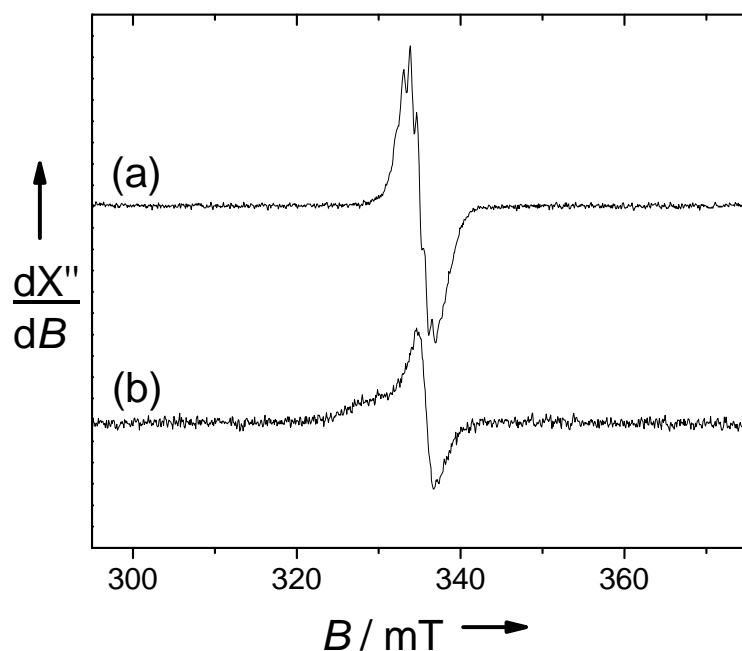


Fig. S7 X-Band EPR spectra of 0.5 mM CH_2Cl_2 solutions (containing 0.1 M TBAP) of $(2')^+$ (a) and $(2')^+$ in the presence of three equivalents of HClO_4 (b, spectrum multiplied by a three factor). * $T = 100$ K, microwave frequency 9.42 GHz, power 20 mW, modulation frequency 100 KHz, amplitude 0.4 mT.

*: In the presence of three equivalents of HClO_4 protonation is not fully achieved, likely due to the enhanced acidity of the dimethylaminophenoxyl radical moiety with respect to the dimethylaminophenolate. Under these conditions the EPR signal is less intense, suggesting some decomposition promoted by the excess of acid.

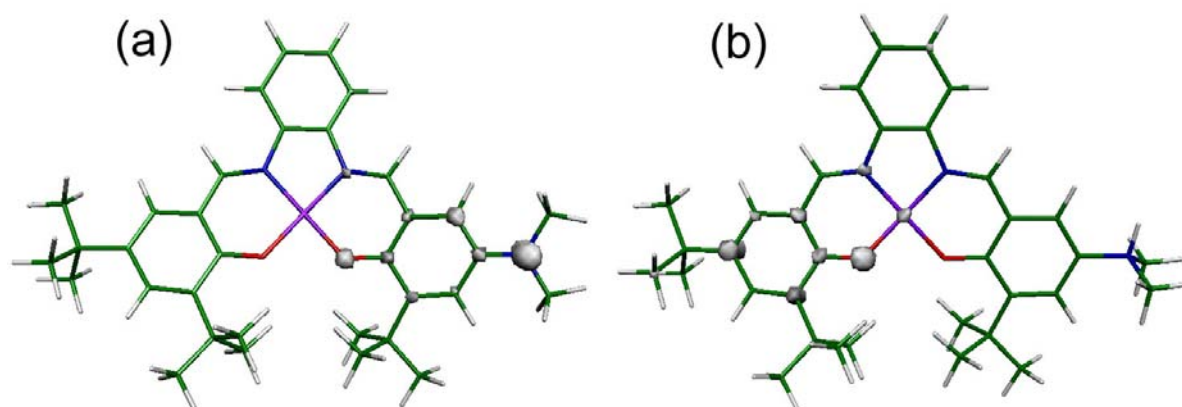


Fig S8. Spin density plots for $(2')^+$ (a) and $(2H')^{2+}$ (b).

Table S1. Computed nitrogen and proton hyperfine coupling constants (MHz) for $(2')^+$ *

	N33	H42	H43	H76	H77	H78	H81	H82	H83
A ₁	-0.42	-3.95	1.49	-1.29	30.84	34.57	-1.31	35.50	37.35
A ₂	-0.55	-14.02	-2.07	-1.56	32.43	35.93	-1.67	36.43	38.27
A ₃	50.56	-17.34	-3.62	5.61	37.86	41.46	5.53	42.41	44.21
A _{iso}	16.53	-11.77	-1.40	0.92	33.71	37.32	0.85	38.11	39.94

* Note that our calculations highlight the non-equivalence of the protons of the $N(CH_3)_2$ group. On one hand, we observe that H76 and H81 have an almost zero value due to their specific in-plane orientation with respect to the phenoxy ring. On the other hand, {H77,H78} and {H82, H83} both feature an angle of 60 degrees with the phenoxy ring, which is in line with larger hyperfine coupling constants. Since the experimental A values were obtained by simulation of an isotropic EPR spectrum (free rotation of the methyl groups of the N-dimethylamino substituent), a better comparison could be made by using the averaged value A_{iso} of the computed hyperfine couplings of {H76, H77, H78, H81, H82, H83}, which is 25.14 MHz.

The following labelling is used (where (a) denotes $(2')^+$ and (b) $(2H')^{2+}$):

