Electronic Supplementary Information for manuscript:

A versatile electronic hole in one-electron oxidized Ni^{II} bis-salicylidene phenylenediamine complexes

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General

All chemicals were of reagent grade and used without purification. Anhydrous CH_2Cl_2 was purchased from Aldrich (anhydrous > 99.8 %).
NMR spectra were recorded on a Bruker AM 300 (^1H at 300 MHz, ^{13}C at 75 MHz). Chemical shifts are given relative to tetramethylsilane (TMS). Mass spectra were recorded on a Thermo finnigan Polaris Q (EI/DCI) apparatus.

UV/Vis spectroscopy

298 K UV/Vis spectra were recorded on a Perkin Elmer Lambda 2 spectrophotometer equipped with a temperature controller unit set at 298 K. The quartz cell path length is 1.000 cm. 238 K UV/Vis spectra were recorded on a Cary 50 spectrophotometer equipped with a Hellma low temperature immersion probe (1.000 cm path length quartz cell) connected to a KNF vacuum pump. The temperature was controlled with a Lauda RK8 KS cryostat.

EPR

X-band EPR spectra were recorded on a BRUKER ESP 300E spectrometer equipped with a BRUKER nitrogen flow cryostat. Spectra were treated using the WINEPR software and simulated using the BRUKER SIMFONIA software.

Electrochemistry

The cyclic, differential pulse and rotating disc electrode voltammograms of each compound (1 mM) in CH_2Cl_2 containing tetra-*n*-butyl ammonium perchlorate (TBAP) 0.1 M as supporting electrolyte, were recorded on a CHI 660 potentiostat at 298 K using a glassy carbon disc as working electrode, a Pt wire as secondary electrode, and an $Ag/AgNO_3$ 0.01 M reference electrode. The potential of the regular ferrocenium / ferrocene (Fc^+/Fc) used as an internal reference is of +0.087 V under our experimental conditions. Experiments were performed under argon atmosphere. Electrolysis at a carbon felt electrode was performed at 233 K, by controlled potential electrolysis, using a PAR 273 potentiostat.

Experimental procedures

2-hydroxy-5-(dimethylamino)-3-tert-butyl-benzaldehyde was prepared according to Ref [S1].
Synthesis of **2** and $\mathbf{3H_2}^{2+}$: *o*-phenylenediamine (85 mg, 0.79 mmol) and the corresponding 2-hydroxybenzaldehyde (1.58 mmol) were stirred together in absolute ethanol (30 mL) for 3h, and then an ethanolic solution (10 mL) of $NiCl_2 \bullet 6H_2O$ (190 mg, 0.79 mmol) was added. The resulting solution was heated to reflux for 3h and then stirred at room temperature overnight.

After evaporation of two thirds of the solvent the solution was stored at –20°C, affording a powder. Washings with cold methanol led to the desired complexes.

2: Yield: 275 mg, (54%). *Anal. Calcd* for $C_{30}H_{34}N_2O_4Ni$: C, 66.08; H, 6.28; N, 5.14; Ni, 10.76. Found: C, 66.21; H, 6.20; N, 5.27; Ni, 10.89. ESI MS: *m/z* 545.3 (M+1). ^1H NMR ($CDCl_3$): 8.21 (s, 2H), 7.69 (s, 2H), 7.18 (s, 2H), 7.06 (s, 2H), 6.56 (s, 2H), 3.78 (s, 6H), 1.45 (s, 18H).

$\mathbf{3H_2}^{2+}$: Yield: 140 mg, (32%). Single crystals were obtained by slow evaporation of CH_2Cl_2. *Anal. Calcd* for $C_{32}H_{42}Cl_2N_4O_2Ni$: C, 59.65; H, 6.57; N, 8.70; Ni, 9.11. *Found*: C, 59.80; H, 6.50, N, 8.62; Ni, 8.94. ESI MS: m/z 571.3 (M-H). ^1H NMR ($CDCl_3$): 8.36 (s, 2H), 8.05 (s, 2H), 7.79 (s, 2H), 7.33 (s, 4H), 3.16 (s, 12H), 1.44 (s, 18H). ^1H NMR for **3** ($CDCl_3$): 8.22 (s, 2H), 7.71 (s, 2H), 7.19 (s, 4H), 6.52 (s, 2H), 2.83 (s, 6H), 1.47 (s,18H).

[S1] M. Braun, R. Fleischer, B. Mai, M.A. Schneider, S. Lachenicht, *Adv. Synth. Catal.* 2004, **346**, 474.

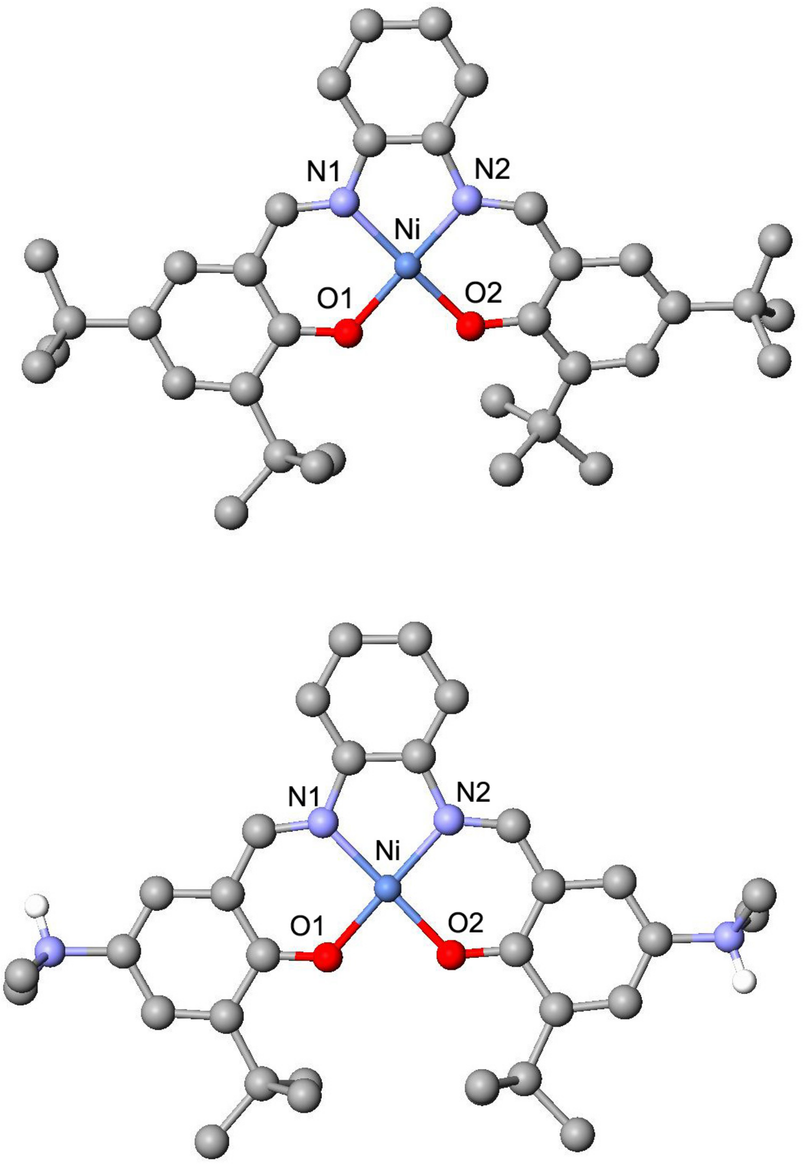

Figure S1: X-Ray crystal structures of **1** (top) and $\mathbf{3H_2}^{2+}$ (bottom). Hydrogen atoms are omitted for clarity (except the ammonium protons). Selected bond lengths (Å) and angles (°) for **1:** Ni-O1 1.854(1); Ni-O2 1.850(1); Ni-N1 1.852(1); Ni-N2 1.857(1); O1-Ni-N1 94.6(1); O2-Ni-N2 94.7(1); O1-Ni-O2 85.9(1); N1-Ni-N2 85.5(1); O1-Ni-N2 174.7(1); O2-Ni-N1 173.2(1). **For** $\mathbf{3H_2}^{2+}$: Ni-O1 1.851(2); Ni-O2 1.846(3); Ni-N1 1.853(3); Ni-N2 1.850(3); O1-Ni-N1 94.4(1); O2-Ni-N2 94.4(1); O1-Ni-O2 85.1(1); N1-Ni-N2 86.1(1); O1-Ni-N2 178.3(1); O2-Ni-N1 178.0(1).

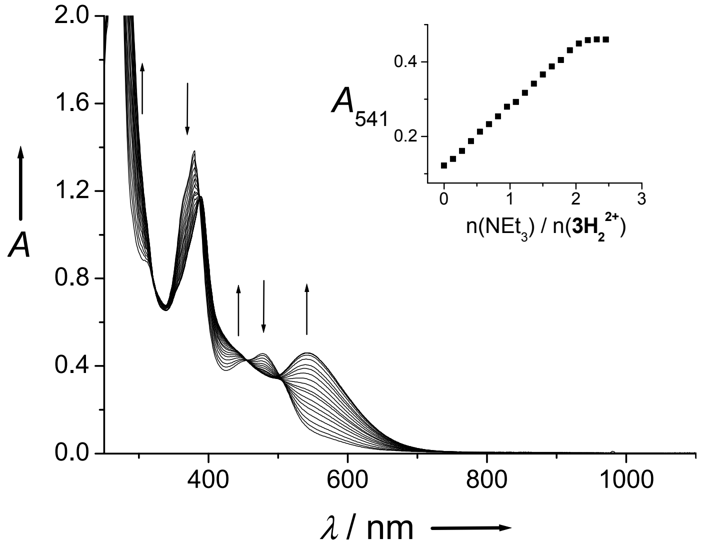

Figure S2. Evolution of the UV-Vis spectrum of a 0.05 mM CH_2Cl_2 solution of $\mathbf{3H_2}^{2+}$ upon addition of NEt_3. Arrows indicate spectral changes upon addition of NEt_3. T = 298 K, l = 1.000 cm. Inset: Absorbance changes at 541 nm as function of the n(NEt_3) / n($\mathbf{3H_2}^{2+}$) ratio.

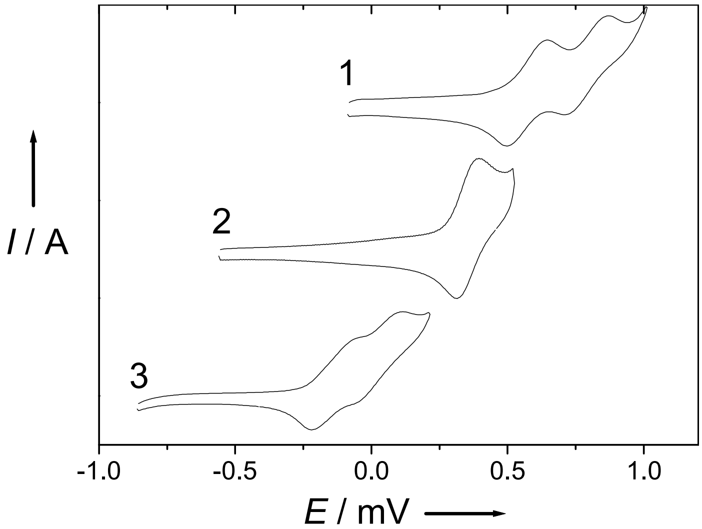

Figure S3: CV curves of 1 mM CH_2Cl_2 solutions (+ 0.1 M TBAP) of **1**, **2** and **3**. Scan rate: 0.1 $V.s^{-1}$, T = 298 K. The potentials are referenced *vs*. Fc/Fc^+. iR was compensated for **2** (iR compensation did not give satisfactory results for the other species).

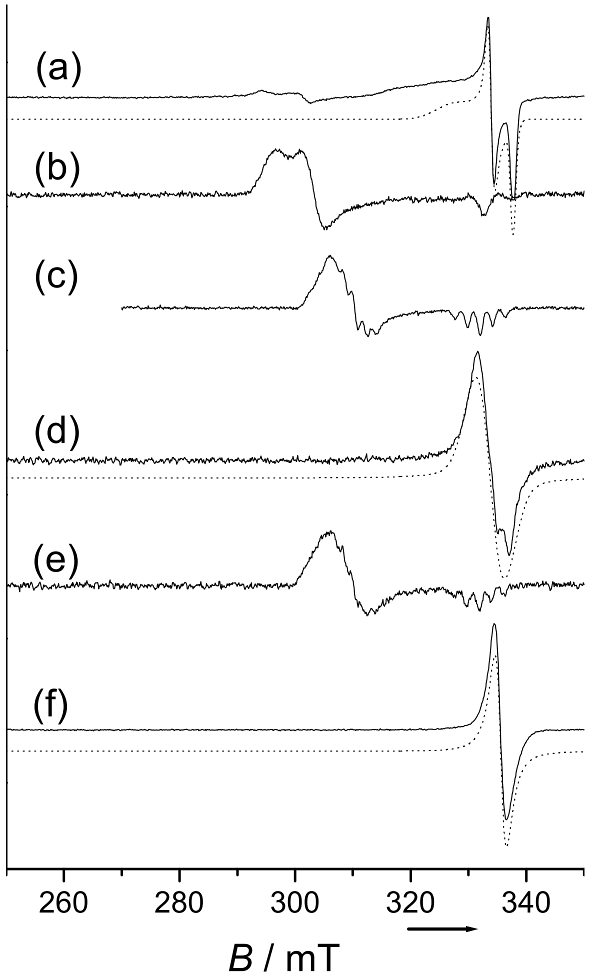

Figure S4. 100 K X-Band EPR spectra of: **(a)** 1mM solution of $\mathbf{1}^+$ in anhydrous CH_2Cl_2 (+ 0.1 M TBAP), the Ni(III) impurity accounts for less than 8% of the total signal; dotted line: simulation of the spectrum of $\mathbf{1}^+$ using parameters given in the text **(b)** 1mM solution of $\mathbf{1}^+$ in standard CH_2Cl_2 distilled prior to electrolysis (+ 0.1 M TBAP); **(c)** 1mM solution of $\mathbf{1}^+$ in CH_2Cl_2 (+ 0.1 M TBAP) containing 0.1 M pyridine; **(d)** 0.5 mM solution of $\mathbf{2}^+$ in anhydrous CH_2Cl_2 (+ 0.1 M TBAP); dotted line: simulation of the spectrum of $\mathbf{1}^+$ using g = 2.017; **(e)** 0.5 mM solution of $\mathbf{2}^+$ in anhydrous (>99.8) CH_2Cl_2 containing 0.2 M pyridine (+ 0.1 M TBAP); **(f)** 1mM solution of $\mathbf{3}^+$ in anhydrous CH_2Cl_2 (+ 0.1 M TBAP); dotted line: simulation of the spectrum of $\mathbf{1}^+$ using g = 2.006. Microwave Freq : 9.42 GHz, power: 20 mW, Mod. Freq: 100 KHz, Amp. 0.05 mT (**a, c, d, e, f**), 0.4 mT (**b**).

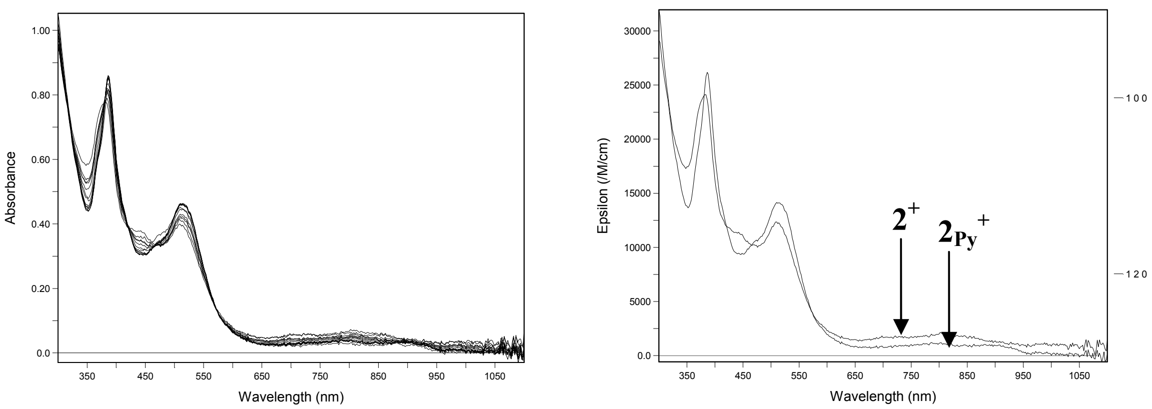

Figure S5. Evolution of the UV-Vis spectrum of a 0.033 mM CH_2Cl_2 solution (+0.005 TBAP) of **2**$^+$ upon addition of pyridine (left) and calculated spectra for **2**$^+$ and $\mathbf{2}_{\mathbf{Py}}^{+}$ using the logβ values given in the text (right). T = 236 K, l = 1.000 cm.

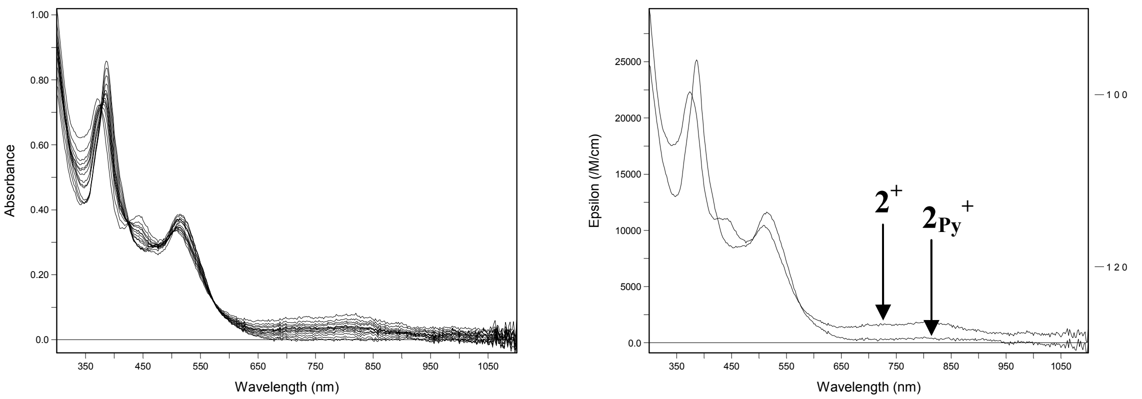

Figure S6. Evolution of the UV-Vis spectrum of a 0.033 mM CH_2Cl_2 solution (+0.005 TBAP) of **2**$^+$ upon addition of pyridine (left) and calculated spectra for **2**$^+$ and $\mathbf{2}_{\mathbf{Py}}^{+}$ using the logβ values given in the text (right). T = 263 K, l = 1.000 cm.

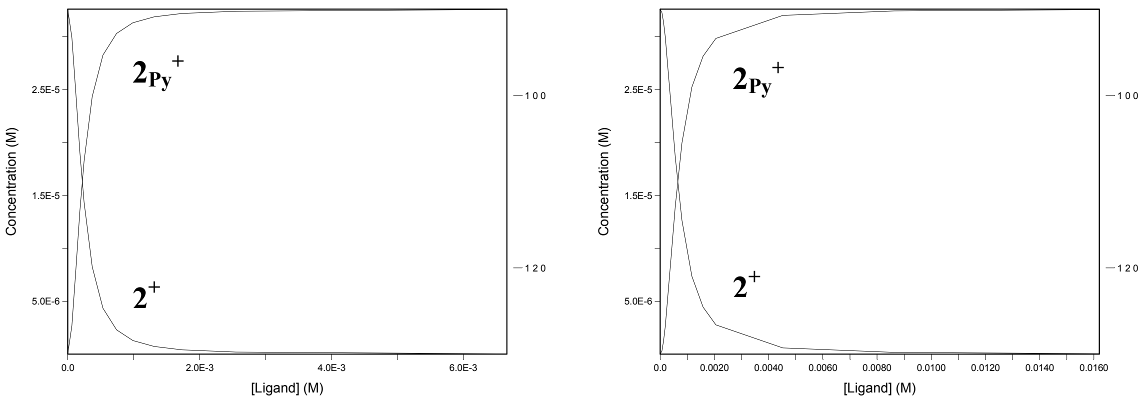

Figure S7. Evolution of the amounts of $\mathbf{2}^+$ and $\mathbf{2}_{\mathbf{Py}}^+$ as function of pyridine concentration at 236 K (left) and 263 K (right). Initial $\mathbf{2}^+$ concentration is 0.033 mM.

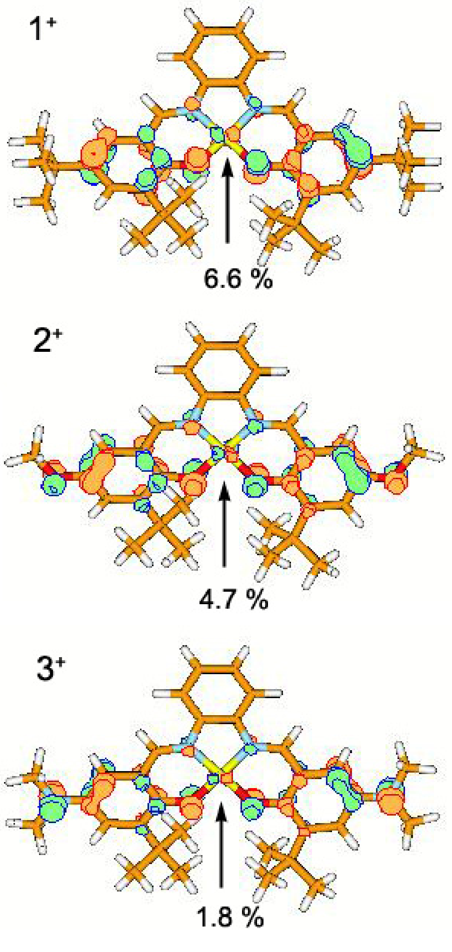

Figure S8 Optimized structures and calculated SOMO for $\mathbf{1}^+$, $\mathbf{2}^+$ and $\mathbf{3}^+$; The Mulliken contribution of the nickel orbitals (mainly the d_{yz}) to the total spin density is indicated.