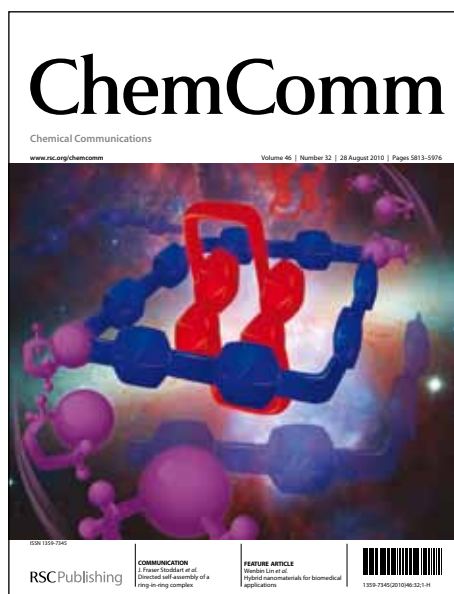


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COMMUNICATION

Unprecedented redox-driven ligand ejection in nickel(II)-diiminosemiquinonate radical complexes

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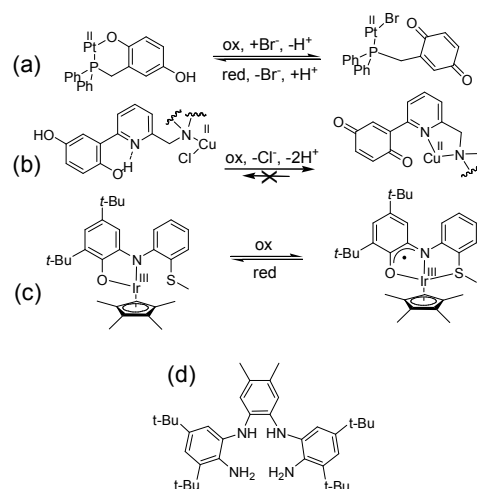
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Nickel(II) complexes of (M:L) stoichiometries 1:1 (1) and 1:2 (2) were prepared from a polydentate ligand involving diiminosemiquinonate radicals. Both were characterized by X-ray diffraction, Vis-NIR and EPR spectroscopy as well as electrochemistry. Ligand-centered oxidation of 1 promotes ligand ejection to give 2.

Molecular switches are at the heart of molecular electronic devices and find applications in numerous fields like biosensors,^[1] drug delivery,^[2] nanotechnologies...^[3] They refer to molecular systems capable of undergoing reversible chemical and physical changes triggered by external stimuli such as electric current, light or pH.^[4] Among the platforms developed for this purpose inorganic complexes play a central role. Redox events on the metal can indeed trigger changes in its geometrical preference, and induce subsequent reorganization of the surrounding ligands.^[5] Inorganic molecular switches that function with ligand-based redox events are rarer,^[6] although organic molecular switches have been widely developed during the past decade.^[4] Prototypical organic moieties that respond to a redox stimulus by molecular motion are viologen pairs.^[7] The viologens do indeed not interact one with each other under their cationic forms, but they readily assemble into donor-acceptor pairs (π -dimers) when one of them is reduced.^[7]

An alternative, yet less common, approach consists in exploiting the redox activity of one chelating moiety of the ligand to labilize a M-L bond (organic-based redox hemilabile ligands, oRHLs) and induce structural changes.^[6] Unfortunately, in these cases rearrangements are often limited to subtle modifications of the metal coordination sphere (Scheme 1a-c), making molecular motions rather small.^[8-10]

We herein describe two nickel(II) complexes **1** and **2** prepared from a polydentate *o*-phenylenediamine ligand H₄L (Fig. 1) and show that **2** is capable of large redox-triggered molecular rearrangements. The process, under the form of a reversible ligand ejection affording **1**, is initiated by electron-transfer from the one-electron oxidized *o*-phenylenediamine group.



Scheme 1 Redox-switchable ligands involving phenols ((a),^[8] (b)^[9] and (c)^[10]) and molecular formula of H₄L (d).

H₄L (Scheme 1) was synthesized in a two-step sequence from 3,5-di-*tert*-butyl-2-nitrobromobenzene and 4,5-dimethyl-*o*-phenylenediamine (see ESI for details). H₄L reacted with an equimolar amount Ni(OAc)₂·4 H₂O in the presence of Et₃N to give a brown solution, from which complex **1** precipitated out as a dark solid after exposure to air (yield 76 %). Single crystals of **1** suitable for X-Ray diffraction were grown by slow evaporation of an Et₂O/MeOH solution.

The structure of **1** (Fig. 1a) shows a square planar nickel(II) ion coordinated to a dianionic tetradentate ligand. The Ni-N1, Ni-N2, Ni-N3 and Ni-N4 bond distances (1.809(3), 1.807(2), 1.816(3) and 1.807(3) Å, respectively) are consistent with a diamagnetic low-spin configuration of the metal ion. The peripheral C1-N1, C7-N4 bond lengths (1.343(4) and 1.344(4) Å respectively) and C2-N2, C8-N3 bond lengths (1.366(4) and 1.364(4) Å, respectively) are significantly shorter than the central C13-N2 and C14-N3 ones (1.423(4) and 1.416(4) Å, respectively), but longer than those

expected for C=N bonds. The central ring has thus a dianionic diamidobenzene character, whereas the peripheral rings are diiminobenzosemiquinone (ISQ) radicals.^[11] Noteworthy, the three aromatic rings are coplanar: a strong antiferromagnetic coupling is thus expected between the two radical spins, leading to the observed diamagnetism.

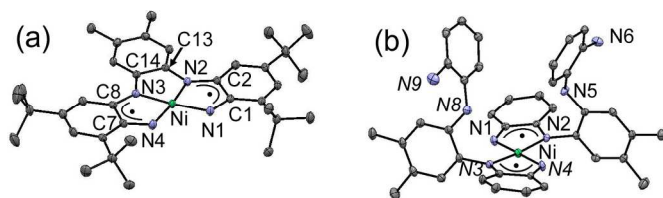


Figure 1 X-Ray crystal structures of: (a) [NiL] (**1**) and (b) [Ni(H₂L)₂] (**2**) shown with 30% thermal ellipsoids. H atoms (**1** and **2**) and *t*-Bu groups (**2**) are omitted for clarity.

During the synthesis of **1** we made the intriguing observation that a green solution formed instead of the brownish one in ten-times more concentrated media. A simple filtration allowed us to isolate a green solid **2** (yield 66 %), whose formulation clearly differs from that of **1** (Fig. 1b). Although we systematically worked with a (1:1) ligand:metal ratio **2** is constituted by a single metal coordinated to two ligands coordinated in a bidentate fashion. The nickel(II) ion lies in a square planar geometry, while the C1-N1, C7-N4, C2-N2 and C8-N3 bond distances (1.343(3), 1.311(3), 1.359(3) and 1.362(3) Å, respectively) compare fairly with those obtained for **1**, confirming that **2** also contains a bis{ISQ} core. The non-coordinating rings exhibit typical diaminobenzene metrical parameters. It is worth noting that H-bonds exist between N2 and H5 (and opposite N3 and H8), as evidenced by the N2-H5-N5 and N3-H8-N8 bond angles of 110(3)° and 113(3)°, respectively, as well as the bond distances N2-N5 and N3-N8 of 2.780(3) and 2.782(3) Å, respectively.

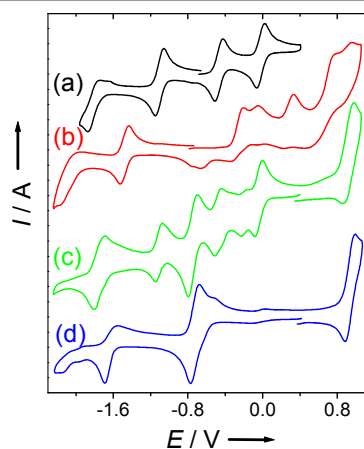
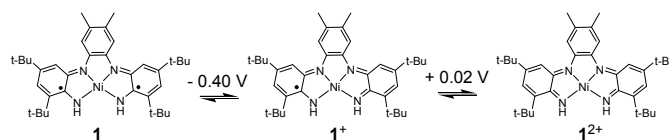


Figure 2. Cyclic voltammograms of (a): **1**; (b): **2**; (c): **2** after electrolysis at 0.21 V; (d): H₄L after electrolysis at 0.21 V. Concentrations are 0.5 mM (**1**) and 0.25 mM (**2**) in CH₂Cl₂ solutions (+ 0.1 M TBAP). *T* = 298 K, scan rate = 0.1 V / s. The potentials are given vs. the Fc⁺/Fc reference.

The electrochemical behaviour of **1** and **2** has been investigated by cyclic voltammetry (CV) (Fig. 2). **1** undergoes four reversible monoelectronic transfers (Fig. 2a); two in oxidation at $E_{1/2}^{ox,1} = -0.40$ V, $E_{1/2}^{ox,2} = 0.02$ V and two in reduction at $E_{1/2}^{red,1} = -0.93$ V, $E_p^{c,2} = -1.57$ V vs. Fc⁺/Fc. The oxidation processes are assigned to the

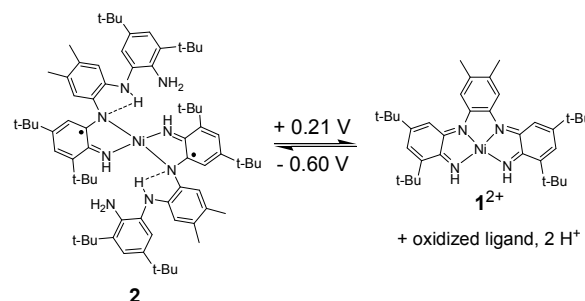
successive oxidation of the ISQ moieties^[12] into diiminobenzoquinone (IBQ) (Scheme 2).



Scheme 2. Sequential oxidation of **1**.

The CV curve of **2** contrast sharply with that of **1**: Oxidation waves were indeed observed at $E_p^{a,1} = -0.18$, $E_p^{a,2} = -0.04$ V, $E_p^{a,3} = 0.28$ V (Fig. 2b), but they were found to be surprisingly irreversible. This prompted us to investigate the electrochemical behaviour of the free ligand H₄L (see ESI). H₄L also showed irreversible oxidation waves in this potential range ($E_p^{a,1} = 0.02$, $E_p^{a,2} = 0.13$ V, $E_p^{a,3} = 0.36$ V), supporting the assignment of the first anodic waves of **2** to the oxidation of the uncoordinated diaminobenzene moieties. The anodic shift of the coordinated-IBQ/ISQ redox wave when **2** is compared to **1**, most likely results from the presence of H-bonds between N2 and H5 as well as N3 and H8.

After exhaustive electrolysis at +0.21 V the CV curve of **2** was dramatically different than the original one (Fig 2c); it displays a single reversible bielectronic oxidation wave at $E_{1/2}^{ox,1} = 0.78$ V, and five reversible reduction wave at $E_{1/2}^{red,1} = -0.03$ V, $E_{1/2}^{red,2} = -0.40$ V, $E_{1/2}^{red,3} = -0.62$ V, $E_{1/2}^{red,4} = -0.93$ V and $E_{1/2}^{red,5} = -1.47$ V. $E_{1/2}^{red,3}$ corresponds to a bielectronic process, whereas the other reduction waves are monoelectronic processes. The four monoelectronic redox waves are reminiscent of **1** (or its oxidation products). Owing to the electrolysis potential (+0.21 V), which is higher than $E_{1/2}^{ox,2}$ of **1**, the oxidation product is the cation **1**²⁺, a fact confirmed by Vis-NIR spectroscopy. Generation of **1**²⁺ implies that free ligand is released in solution. A pure sample of H₄L was thus subjected to electrolysis under similar conditions. The CV curve recorded after electrolysis shows two reversible two-electron redox waves at $E_{1/2}^{ox,1} = 0.79$ V and $E_{1/2}^{red,3} = -0.61$ V (Fig. 2d). Both match the bielectronic waves observed for **2** after oxidation at +0.21 V, confirming that oxidation of **2** is accompanied by release of free oxidized ligand (Scheme 3).



Scheme 3. Redox-driven structural changes in **2**.

We additionally examined the oxidation processes by spectroelectrochemistry (Fig. 3-4). The electronic spectrum of **1** is characterized by an intense LLCT transition involving the ISQ radical at 952 nm [12 050 M⁻¹ cm⁻¹], which shifts to 899 nm [11 320 M⁻¹ cm⁻¹] in **1**⁺.^[13] Not surprisingly the dication **1**²⁺ does not exhibit strong ISQ radical band above 850 nm, but simply CT transitions involving the IBQ moieties at 738 nm [7510 M⁻¹ cm⁻¹] and 466 nm

[26380 $M^{-1} cm^{-1}$]. Interestingly the LLCT transition in **2** is four-times more intense than for **1** [877 nm, 55 160 $M^{-1} cm^{-1}$]. This enhancement may reflect the involvement of the coordinated diaminobenzene bridge in the transition for **1**. During electrolysis of **2** the 877 nm band disappeared at the expense of two intense transitions at 410 [26 100 $M^{-1} cm^{-1}$] and 494 nm [22 600 $M^{-1} cm^{-1}$], and a broad band at ca. 700 nm (Fig. 4b). The latter two bands correspond to 1^{2+} (Fig. 3c), whereas the former originates from the oxidized free ligand (see ESI). These spectroscopic results again support a redox-driven ligand ejection, consistent with electrochemical data.

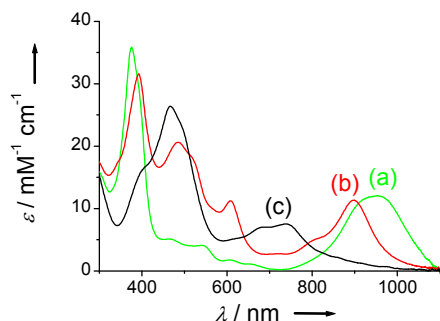


Figure 3. Vis-NIR spectra of (a) **1**, (b) 1^+ , (c) 1^{2+} . Concentrations = 0.5 mM in CH_2Cl_2 (+ 0.1 M TBAP). $T = 298$ K.

We monitored the reversibility of the system by applying to **2** the required potential to eject one ligand (exhaustive electrolysis at +0.21 V), and then a cathodic potential (-0.60 V). The Vis-NIR spectrum recorded just after electrolysis (Fig. 4c) was clearly different than that of **2**, with a maximum peak at 894 nm [18 460 $M^{-1} cm^{-1}$] and a shoulder at 950 nm. However, after 15 h the NIR band has both shifted to 877 nm and increased in intensity (Fig. 4d), giving spectral features reminiscent of **2**. Thus, although the reaction occurs slowly the ejected ligand can rebind the nickel ion after reduction (Scheme 3).^[14]

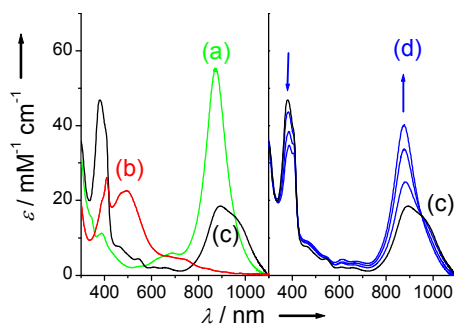


Figure 4. Vis-NIR spectra of (a) **2**; (b) **2** after electrolysis at 0.21 V; (c-d) **2** after electrolysis at 0.21 V followed by reduction at -0.60 V [(c) 5 min after reduction, (d) after 30 min, 2 h and 15 h]. Arrows indicate spectral changes. Concentrations = 0.25 mM in CH_2Cl_2 (+ 0.1 M TBAP). $T = 298$ K.

In conclusion we herein describe the first example of electrochemically driven ejection of a redox hemilabile ligand involving diiminosemiquinonate moieties. Both the intramolecular H-bonds and the attenuated negative charge at the terminal chelating atoms in **2** labilize sufficiently the M-

diiminosemiquinonate bonds to allow for redox-triggered ligand ejection, while keeping rebinding possible. The effect of the pH and substituents on the process are currently investigated in our laboratory.

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Notes and references

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† Electronic Supplementary Information (ESI) available: CCDC-927235-6, experimental procedures, EPR, NMR, UV-Vis spectra and cyclic voltammetry curves. See DOI: 10.1039/c000000x/

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14 The potential of -0.60 V is not sufficient to reduce the oxidized free ligand. The driving force for the conversion $1^{2+} \rightarrow 2$ is therefore not electron transfer to the free ligand, but rather to the complex. This

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assumption is confirmed by the conversion of **1** into **2** upon addition of H₄L (see ESI).