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Ni-Centered Coordination-Induced Spin-State Switching Triggered by Electrical Stimulation

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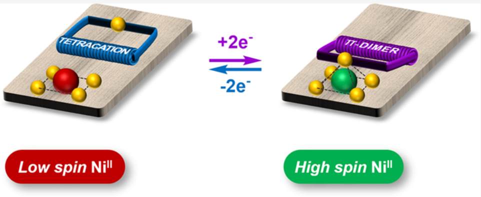
ABSTRACT: We herein report the synthesis and magnetic properties of a Ni(II)-porphyrin tethered to an imidazole ligand through a flexible electron-responsive mechanical hinge. The latter is capable of undergoing a large amplitude and fully reversible folding motion under the effect of electrical stimulation. This redox-triggered movement is exploited to force the axial coordination of the appended imidazole ligand onto the square-planar Ni(II) center, resulting in a change in its spin state from low spin ($S = 0$) to high spin ($S = 1$) proceeding with an 80% switching efficiency. The driving force of this reversible folding motion is the π-dimerization between two electrogenerated viologen cation radicals. The folding motion and the associated spin state switching are demonstrated on the grounds of NMR, (spectro)electrochemical, and magnetic data supported by quantum calculations.



■ INTRODUCTION

Molecules exhibiting switchable magnetic properties have been extensively studied over the last few decades in the context of the miniaturization of electronics, sensors, and memory devices.[1−9] This particular field of magnetic switching has been the subject of major developments fueled by numerous research activities focused on molecular spin crossover (SCO) materials[10−13] and single-molecule magnets.[14−17] Most examples described so far are crystalline solids obtained from first-row transition-metal complexes (d^4 to d^7) capable of undergoing spin-state transition as a response to external physical perturbations such as temperature, pressure, and light.[1,12,18] From a practical point of view, SCO phenomena are quite often difficult to explain from well-defined molecular events and they are also strongly dependent on cooperativity processes that happen to be enhanced in the solid state and at low temperatures.[18,19] SCO systems are therefore usually studied in solid crystals, although recent reports have shown that similar processes can occur in solution and at near-ambient temperatures.[13,20−23]

Alternative concepts aiming at triggering the rearrangement of electrons in discrete metal complexes both at room temperature and in solution have recently emerged. These include the coordination-induced spin-state switching (CISSS) approach,[24−27] where spin state transitions, *e.g.*, from a high-spin (HS) to a low-spin (LS) state, are triggered by rational/drastic modifications of the first coordination sphere of a given metal center upon stimulation. The few examples reported to date in the literature involve a quite limited number of transition metals, namely, Fe(II),[27−29] Mn(V),[30] or Ni(II),[24,25,31−38] selected for their ability to undergo HS ↔ LS transitions following the addition or removal of ligand(s) from the metal center (Figure 1a).[31,39] All of these achievements involve the use of chemicals (pH)[27,40,41] or light[24,31−35,38,42,43] as triggers for molecular motions, leading to an increase or decrease in the coordination number of the metal. In contrast, far less progress has been made in these directions with electron-responsive systems, even though electricity stands as a particularly attractive, controllable, and clean trigger in the perspective of applications in solid-state devices.[44−46] The few examples of redox-triggered magnetic switching reported so far in literature are based on Prussian blue analogues or transition-metal complexes exhibiting valence tautomerism.[47−51]

In this work, we report the syntheses and magnetic properties of an electrically triggered coordination-induced spin-state switch operating on the intramolecular self-locking principle depicted in Figure 1b.[52] The latter shows how the ligancy of a magnetically active nickel(II) center can be reversibly switched between four and five as a result of the reversible folding and unfolding motion of a ligand-tipped electromechanical hinge based on 4,4′-bipyrinium units, best known as viologens.

The redox-responsive Ni(II)-porphyrin complex **9a**$^{4+}$ that was designed to achieve remote control over the ligancy of a nickel center is made out of three key functional elements: (i)

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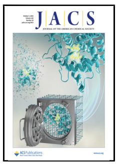

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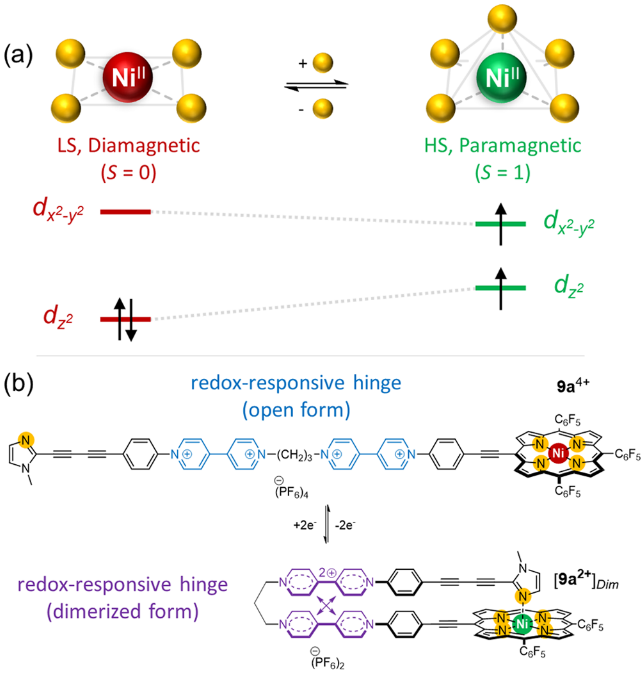


Figure 1. (a) Schematic representation of spin-state switching by coordination/dissociation of an exogenous ligand to/from a Ni(II)-porphyrin. Ligands are represented by yellow spheres (b) Electron-triggered reversible folding/unfolding process in **9a**$^{4+}$ accompanied by coordination/dissociation of the endogenous ligand.

a magnetically active center in the form of a square-planar Ni(II)-porphyrin bearing three electron-withdrawing *meso*-substituents introduced to improve the affinity of the square-planar low-spin (LS) $S = 0$ Ni(II) center for axial coordination;[53] (ii) an electromechanical hinge (actuator) incorporating two dicationic 4,4′-bipyridinium subunits ($\mathbf{V}^{2+}$) linked through a flexible propylene linker in such a way as to promote the formation of intramolecular π-dimers in the reduced state ($2\mathbf{V}^{+\bullet} \rightarrow [\mathbf{V}_2]^{2+}_{\text{Dim}}$);[54,55] and (iii) an endogenously tethered imidazole ligand, selected for its high affinity for the Ni(II) center, introduced at the tip of the actuator through a sequence of ethynyl/phenyl units.[52]

We show in the present article that **9a**$^{4+}$ adopts an elongated conformation in solution, imposed by repulsive electrostatic forces between the dicationic bipyridinium units, wherein the square-planar nickel center lies in a diamagnetic low spin state ($S = 0$). We have then established that this compound undergoes electron-triggered mechanical folding, driven by the dimerization between the electrogenerated bipyridinium cation radicals ($\mathbf{V}^{+\bullet}$),[52,54,56−61] leading to forced coordination of the imidazole ligand coming along with a change in the electronic configuration of the metal LS ($S = 0$) → HS ($S = 1$).[31,53]

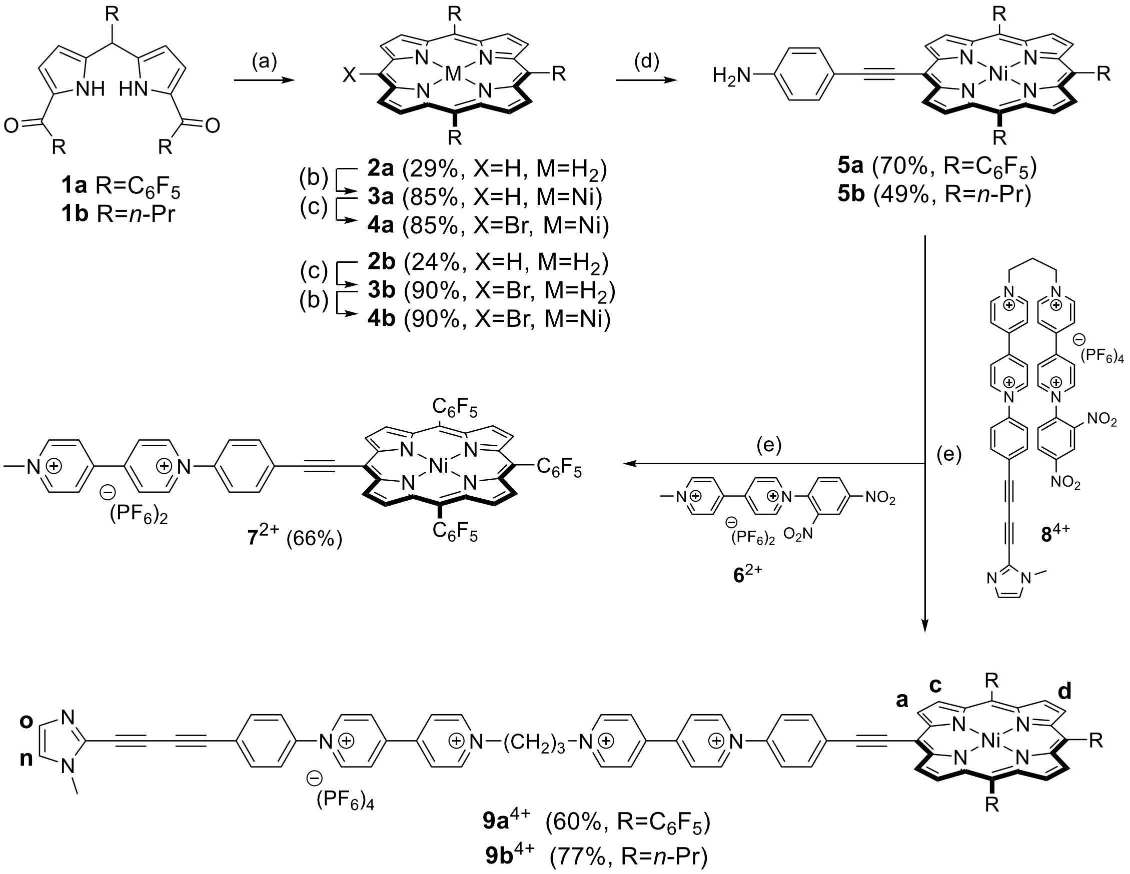
■ RESULTS AND DISCUSSION

Syntheses. Both metalloporphyrin−viologen compounds studied in this work, **9a**$^{4+}$ and **9b**$^{4+}$, differ by the presence of either pentafluorophenyl (electron-withdrawing groups) or propyl (electron-donating groups) substituents at the *meso* positions of the porphyrin ring, respectively. Those substituents were introduced to change the ability of the nickel(II) center to accept axial ligands. **9a**$^{4+}$ and **9b**$^{4+}$ were synthesized in five steps (Scheme 1), starting from the corresponding diaroylated or dialkanoylated dipyrromethanes **1a**[62] or **1b**,[52] building on strategies previously developed in our group.[52,56,63] Reduction of **1a−b** with sodium borohydride afforded the corresponding dicarbinol intermediates that were further condensed with β-free 2,2′-dipyrrolylmethane[62] under inert conditions and then oxidized with DDQ to give the targeted A_3B-type *meso*-substituted porphyrins **2a−b** in 29 and 24% yields, respectively. Subsequent metalation of the inner porphyrin with nickel(II) acetylacetonate[24] and regioselective α-bromination of the remaining *meso*-free position with *N*-bromosuccinimide[62] afforded **4a** in 72% yield over two steps, while a reverse bromination-metalation sequence furnished porphyrin **4b** in 81% yield over two steps. The key amine-substituted intermediates **5a−b** were then obtained in 70 and 49% yields, respectively, as the product of palladium- and copper-catalyzed Sonogashira cross-coupling reactions[64] between **4a−b** and 4-ethynylaniline. The targeted compounds **9a−b**$^{4+}$ were ultimately obtained in 60 and 77% yields, respectively, from a Zincke coupling[56,65] reaction involving the ethynylaniline substituted porphyrins **5a−b** and the previously described 2,4-dinitrophenyl activated bis-viologen precursor **8**$^{4+}$ as reactants.[52] Porphyrin−monoviologen **7**$^{2+}$, used as a reference compound in our investigations, was obtained similarly in 66% yield from monoactivated precursor **6**$^{2+}$.[56]

Characterization of the Open Forms. The structures of **9a**$^{4+}$ and **9b**$^{4+}$ were confirmed by high-resolution mass spectrometry (HRMS) (Figures S35−S37) and spectroscopic measurements. The full ^{1}H NMR spectra of both compounds recorded in deuterated acetonitrile at 1 mM are shown in Figures S20 and S26. All peaks were fully assigned with the help of 1D and 2D (COSY and ROESY) experiments (see the Supporting Information section). The signals attributed to the viologen/phenyl/alkyl subunits are found to resonate at similar frequencies in both compounds. As expected, only the porphyrin-based peaks show noticeable shifts, which can be explained by the drastic difference between the electronic effects of the propyl and pentafluorophenyl substituents. This effect is most apparent for the more deshielded peak attributed to the β-proton H_a (Scheme 1) observed at 10.06 and 9.60 ppm in the spectra of **9a**$^{4+}$ and **9b**$^{4+}$, respectively. To a lesser extent, the imidazole protons (H_n and H_o) follow a similar trend, together with a significant broadening of the signals observed in **9a**$^{4+}$ relative to **9b**$^{4+}$, suggesting an interaction between the available nitrogen atom and the electron-deficient porphyrin Ni complex in **9a**$^{4+}$.

In line with these initial findings, the ability of the imidazole appended nickel(II) complexes to self-assemble in solution, through the formation of intermolecular coordination bonds between imidazole and nickel, was assessed by concentration-dependent ^{1}H NMR measurements performed in MeCN-d_3. Data collected with the propyl-substituted derivative **9b**$^{4+}$ revealed that the signals assigned to the imidazole (H_o and H_n) do not shift significantly upon increasing the concentration from 0.1 to 10 mM (Figure S31), which supports the conclusion that no intermolecular coordination occurs under these conditions. The large broadening and high field shift conversely undergone on this concentration range by all of the signals of the porphyrin (H_a, H_c and H_d) are therefore attributed to the formation of J- or H-type aggregates.[66] The absence of coordination bonds between imidazole and nickel at 1 mM was then further demonstrated by variable-temperature NMR (VT-NMR) measurements, showing that the chemical shifts of both singlets assigned to imidazole do not change upon heating the sample from 273 to 323 K (Figure S32).

Scheme 1. Synthesis of 7^{2+}, $9a^{4+}$, and $9b^{4+}$[a]



[a]Reaction conditions: (a) $NaBH_4$, MeOH/THF, 25 °C; then 2,2′-dipyrrolylmethane, $Yb(OTf)_3$ or TFA, CH_2Cl_2 or CH_3CN, 34 or 25 °C; then DDQ, 25 °C. (b) $Ni(acac)_2$, toluene, reflux. (c) NBS, pyridine, $CHCl_3$, 0 °C. (d) 4-Ethynylaniline, $PdCl_2(PPh_3)_2$, CuI, Et_3N, THF, 40 °C. (e) EtOH, CH_3CN, THF, 80 °C; then KPF_6, H_2O.[63] The lowercase letters shown on the final product will be used to discuss the attribution of the ^1H NMR signals to specific protons, *i.e.*, H_a, H_c, H_d, H_o, and H_n.

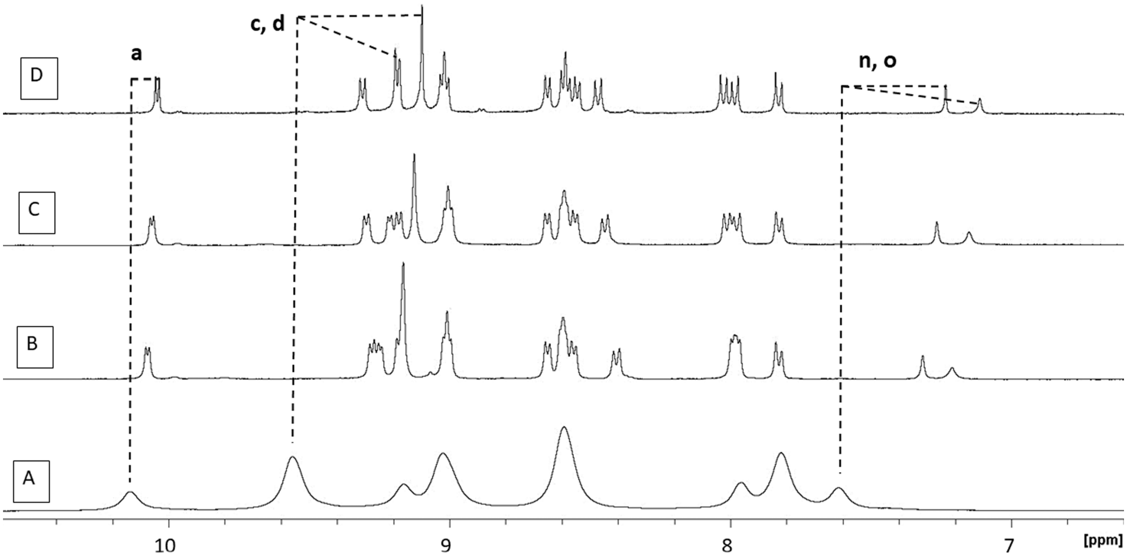


Figure 2. Partial ^1H NMR signature of **9a**$^{4+}$ in the aromatic region at (A) 10, (B) 2, (C) 1, and (D) 0.1 mM. The dotted lines represent the shifts of the porphyrin- and imidazole-based peaks (298 K, MeCN-d_3, 400 MHz).

Similar investigations were carried out on C_6F_5-substituted analogue **9a**$^{4+}$, featuring an "activated" nickel center, more inclined to accept one or two additional ligands in the axial position.[41,53,67] The spectra recorded over the 0.1−10 mM concentration range are shown in Figure 2. The two major differences with the data collected in the same condition with **9b**$^{4+}$ are the simultaneous downfield shift of the signals assigned to the imidazole and porphyrin units. These changes observed for concentrations greater than 1 mM have been attributed to the formation of short coordination oligomers in solution favored by the electron-withdrawing effect of the three C_6F_5 substituents. The large concentration required to trigger these changes is however consistent with the weak affinity of imidazole for the metal center, a conclusion that was eventually confirmed by the quite weak binding constants estimated from NMR titration experiments involving 1-methylimidazole and 7^{2+} as the reference ligand and metal complex, respectively (see the Supporting Information section for details). The ability of **9a**$^{4+}$ to self-assemble in solution was further investigated by diffusion-ordered spectroscopy (DOSY) measurements conducted at room temperature in MeCN-d_3 over a concentration range of 1−10 mM. Here, again, the limited evolution of the calculated diffusion coefficient over this concentration range, decreasing from 614 (for the most diluted sample) to 505 $\mu m^2 \cdot s^{-1}$ (for the most concentrated sample), suggests the formation of small assemblies involving only a few monomers ($n = 2$ at 10 mM using a spherical model, see the Supporting Information section).

On the other hand, further analyses revealed significant solvent dependence of the absorption spectra of **9a**$^{4+}$, the most notable feature being a significant bathochromic shift of the Soret band going from $\lambda_{max} = 421$ nm in the least coordinating solvent MeCN and 428 in DMF up to 441 nm in the most coordinating solvent DMSO (Figure S39A). The coordination ability of DMSO, and to a lesser extent of DMF, on the Ni center was further demonstrated by ^{1}H NMR measurements with a broadening and downfield shift of $\delta(H_a)$ from 10.06 ppm in MeCN-d_3 up to 10.98 ppm in DMF-d_7 and 26.4 ppm in DMSO-d_6 (Figure S28). The particular behavior observed in DMSO, and most particularly the large low field shift of $\delta(H_a)$, was thus attributed to partial conversion of the first coordination sphere of the Ni(II) center from tetra-coordinated square planar to penta-coordinated square-based pyramid (with one molecule of DMSO in axial position) or hexacoordinated bipyramidal (with two molecules of DMSO in axial position), coming along with a partial change in the electronic configuration of the metal from low spin ($S = 0$) to high spin ($S = 1$).

These solvent effects proved to be far less marked with **9b**$^{4+}$, whose ^{1}H NMR spectra recorded in deuterated DMF or DMSO showed well-defined/sharp signals resonating between 0 and 10 ppm (Figure S30). Opposite to the case of **9a**$^{4+}$, the most deshielded proton peaks were assigned to protons from the viologen units (H_b and H_e) rather than from the porphyrin (H_a). We also found that $\delta(H_a)$ undergoes only a minor shift between MeCN-d_3 (9.60 ppm) and DMSO-d_6 (9.64 ppm). This solvent-independent behavior was also demonstrated by UV/vis experiments (Figure S39B).

Characterization of the Electron-Triggered Folding Process. **9a**$^{4+}$, **9b**$^{4+}$, and the reference compound 7^{2+} were submitted to detailed electrochemical analyses carried out in DMF (+0.1 M electrolyte concentration) to ensure the solubility of all investigated species both at their oxidized and reduced states and to minimize the solvent effects discussed above affecting both the first coordination sphere and the magnetic properties of the metal center. Some key data collected with these compounds are given in Table 1.

Table 1. Electrochemical Data Collected for 1 mM Solutions (in Viologen) of 9a^{4+}, 9b^{4+}, and 7^{2+} in DMF + TBAP (0.1 M)[a]

	E^{4c}	E^{3c}	E^{2c}	E^{1c}	E^{1a}
compound	$P^{-\bullet}/P^{2-}$	$P/P^{-\bullet}$	$V^{+\bullet}/V^0$	$V^{2+}/V^{+\bullet}$	$P/P^{+\bullet}$
9a^{4+}	−1.77[b] (86)[d]	−1.23[b] (60)[d]	−1.05[b] (40)[d]	−0.51[b] (48)[d]	0.78[c]
9b^{4+}	−2.51[c]	−1.58[b] (63)[d]	−1.01[b] (40)[d]	−0.55[b] (72)[d]	0.62[c]
7^{2+}	−1.76[b] (62)[d]	−1.23[b] (64)[d]	−0.96[b] (62)[d]	−0.67[b] (64)[d]	0.81[c]

[a] Glassy carbon WE, $\Phi = 3$ mm, E *vs* E_{ref} [$Ag^+(10^{-2}$ M)/Ag], $\nu = 0.1$ $V \cdot s^{-1}$. "P" and "V" stand for "porphyrin" and "viologen", respectively. [b] Half-wave potential value ($E_{1/2}$ in V). [c] Peak potential value (E_{pa} or E_{pc} in V). [d] Peak-to-peak potential shift ($\Delta E_p = |E_{pa} - E_{pc}|$ in mV).

As can be seen in Figure 3A, the cyclic voltammogram of **9a**$^{4+}$ exhibits one irreversible oxidation wave at $E_p^{1a} = 0.78$ V and four consecutive reversible reduction processes in the accessible potential range, *i.e.*, above −2 V. The first two higher-intensity waves observed at $E_{1/2}^{1c} = -0.51$ and $E_{1/2}^{2c} = -1.05$ V are attributed to the one-electron/viologen reductions, yielding successively dicationic bis-radical **9a**$^{2(+\bullet)}$ and neutral quinonic **9a**^{0} species. These processes are followed by two waves of lower intensities at $E_{1/2}^{3c} = -1.23$ and $E_{1/2}^{4c} = -1.77$ V attributed to the consecutive one-electron reductions of the porphyrin ring, affording a porphyrin anion radical and a porphyrin dianion (Figure S49B).[68] This attribution is consistent with the relative intensities of the first two reduction waves that are twice as high as the two last ones and with the stoichiometry of the viologens (V) and porphyrin (P) units involved in **9a**$^{4+}$.

A similar signature was observed for the propyl-substituted analogues **9b**$^{4+}$. In agreement with the presence of electron-donating *meso*-substituents, we found the porphyrin unit to be much easier to oxidize, and conversely much harder to reduce, in **9b**$^{4+}$ than in **9a**$^{4+}$ (Figures S48 and S49A). This difference is best revealed by the 350 mV shift observed for the reversible porphyrin-based reduction wave ($P/P^{\bullet-}$) at E^{3c} (Table 1) in **9a**$^{4+}$ than in **9b**$^{4+}$. These substituents were conversely found to have less influence on the viologen-centered reduction processes that are observed at similar potential values in both compounds ($\Delta E^{1c} = \Delta E^{2c} = 40$ mV).

The ability of **9a**$^{4+}$ and **9b**$^{4+}$ to dimerize following the one-electron reduction of the viologen units involved in the hinge was first revealed by comparing their electrochemical signatures to that of the monoviologen reference compound 7^{2+} (dashed line in Figures 3 and S49C). The latter displays the expected four reversible waves attributed to the successive one-electron reduction of the viologen and porphyrins units. A quick look at the CV curves of 7^{2+} and **9a**$^{4+}$ however reveals that the porphyrin ring is reduced at similar potential values in both compounds, while the viologen units are much easier to reduce into the radical species, by about 160 mV, in **9a**$^{4+}$ than in 7^{2+}. Another striking difference is the stability domain of the $V^{+\bullet}$ state ($\Delta E = |E_{1/2}^{2c} - E_{1/2}^{1c}|$), which is found to be much larger for **9a**$^{4+}$ (540 mV) or **9b**$^{4+}$ (460 mV) than for 7^{2+} (290 mV). Both the ease of reduction of the viologens (V^{2+}) and the stabilization of the cation radical state $V^{+\bullet}$ are in fact well-known phenomenological indicators revealing the existence of a π-dimerization reaction coupled to the first viologen-centered electron transfer (Scheme 2).[54,69] This intramolecular dimerization process only occurs in the bis-viologen derivatives **9a**$^{4+}$ and **9b**$^{4+}$ due to the presence of a flexible propyl linker capable of adopting either an *anti*-conformation in the open tetracationic forms (**9a**$^{4+}$ and **9b**$^{4+}$) or a *syn* conformation in

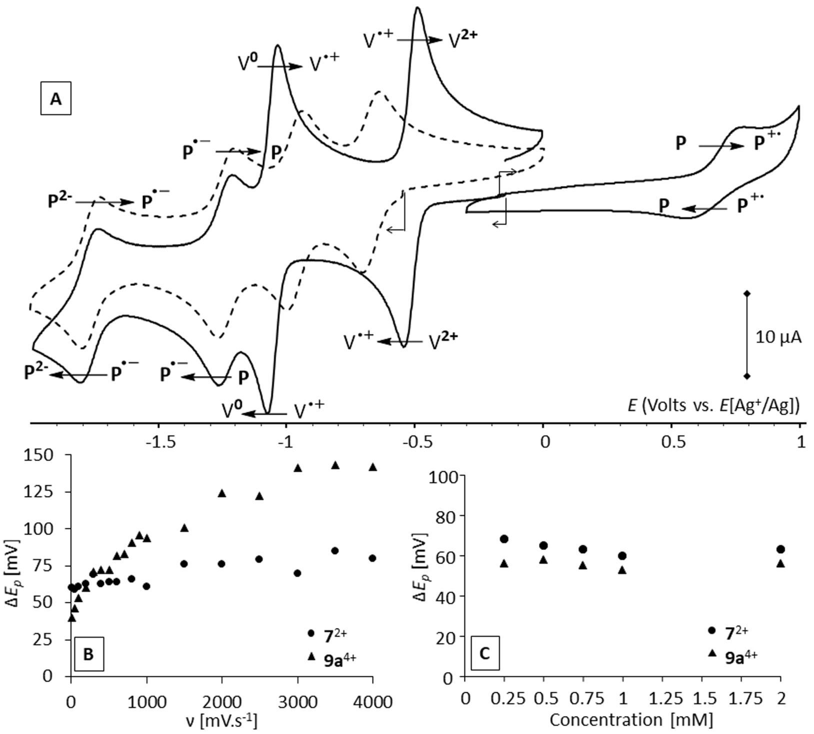
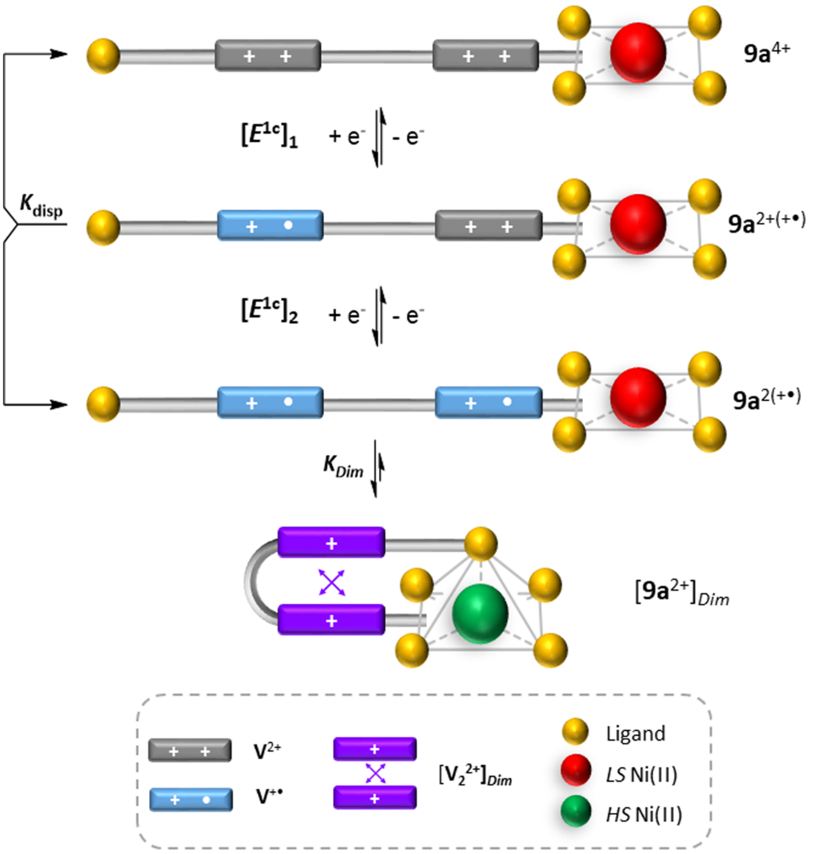


Figure 3. (A) Voltammetric curves of a DMF (0.1 M TBAP) solution of **9a**$^{4+}$ (solid lines) and **7**$^{2+}$ (dashed line). (B) Peak-to-peak potential (ΔE_p) measured for **9a**$^{4+}$ and **7**$^{2+}$ at various scan rates (1 mM). (C) Peak-to-peak potential (ΔE_p) measured for **9a**$^{4+}$ and **7**$^{2+}$ at various concentrations (ν = 0.1 V s^{-1}, VC, Φ = 3 mm, E (volt) *vs* E_{ref} [Ag$^+$(10^{-2} M)/Ag]).

Scheme 2. Representative Scheme of the Stepwise Viologen-Centered Reductions of 9a^{2+} and the Consecutive Dimerization and Disproportionation Equilibria Involved



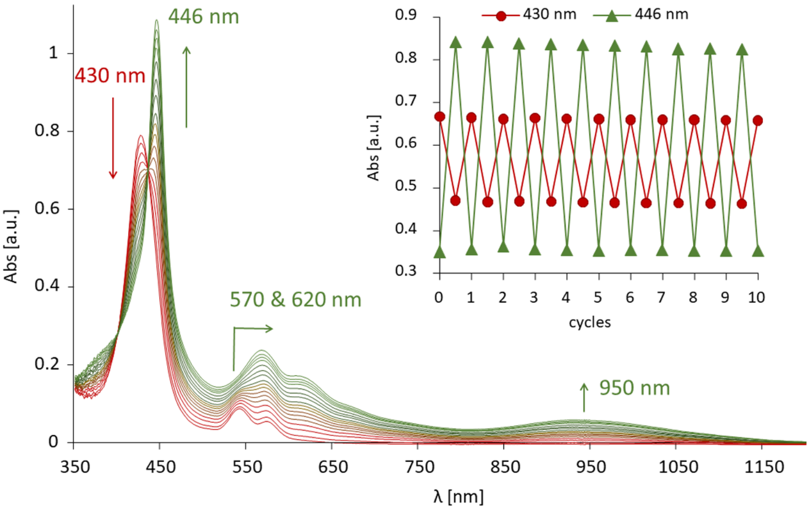


Figure 4. UV/vis spectra recorded during the exhaustive electrolysis (1 e^-/viologen) of $\mathbf{9a}^{4+}$ at 4.5×10^{-5} mol L^{-1} in DMF (0.1 M $TBAPF_6$) (working electrode: Pt, $E_{app} = -0.65$ V, 10 mL, $l = 1$ mm, $t \approx 1$ h). Increment: Switching cycles of $\mathbf{9a}^{4+}$ on thin-layer spectroelctrochemistry during alternating reduction ($E_{app} = -0.85$ V) and reoxidation ($E_{app} = 0$ V). The UV/vis-NIR absorptions at 430 (red; square-planar Ni-porphyrin) and 446 nm (green; square pyramidal Ni-porphyrin) are plotted as a function of the number of switching cycles.

the folded π-dimerized forms ($[\mathbf{9a}^{2+}]_{Dim}$ or $[\mathbf{9b}^{2+}]_{Dim}$, see Scheme 2). Then, the facts that the viologen units are more easily reduced in $\mathbf{9a}^{4+}$ ($E^{1c}_{1/2} = 0.51$ V) than in $\mathbf{9b}^{4+}$ ($E^{1c}_{1/2} = 0.55$ V) and that the stability domain of the viologen cation radical is larger for $\mathbf{9a}^{4+}$ (540 mV) than for $\mathbf{9b}^{4+}$ (460 mV) are compelling experimental proofs demonstrating that the *meso* substituents of the porphyrin ring have an influence on the π-dimerization constant (K_{Dim} in Scheme 2), which provide the first evidence that the coordination of imidazole on the nickel center provides additional stability to the closed isomers $[\mathbf{9a}^{2+}]_{Dim}$ or $[\mathbf{9b}^{2+}]_{Dim}$. These initial hypotheses were eventually confirmed by spectroelectrochemical studies discussed in the following section.

The existence of a dimerization step coupled to electron transfer was further revealed by studying the influence of scan rate and concentration on the shape and potential of the first viologen-centered reduction wave of $9a^{4+}$ and 7^{2+}. We first established that the calculated peak-to-peak potential shift calculated for 7^{2+} does not vary over the studied concentration and scan rate ranges (Figure 3B,C), indicating that 7^{2+} undergoes, on these time scales, fully reversible (fast) reduction and that the electrogenerated species $7^{+\bullet}$ do not form intermolecular dimers under these conditions. By subjecting $9a^{4+}$ to similar studies, we found conversely that the $E_{1/2}$ and ΔE_p values calculated for the first reduction wave do not change over the concentration range 2×10^{-4}–2×10^{-3} but that the scan rate applied at the electrode has a profound influence on the peak-to-peak potential difference ΔE_p (Figure 3B,C). This value goes from 140 mV measured at 4 V/s down to 40 mV measured at 10 mV/s, which is consistent with the existence of a chemical step coupled to "fast" (Nernstian) electron transfer ($[E^{1c}]_1$ and $[E^{1c}]_2$ shown in Scheme 2). In other words, the electrochemical response is here controlled by diffusion and the kinetics of the chemical steps involved in the process, which are the intramolecular dimerization (K_{Dim} in Scheme 2) of the doubly reduced species $\mathbf{9a}^{2(+\bullet)} \leftrightarrow [\mathbf{9a}^{2+}]_{Dim}$ and the associated disproportionation reaction (K_{Disp} in Scheme 2) $\mathbf{9a}^{2+(+\bullet)} \leftrightarrow \mathbf{9a}^{2(+\bullet)}{}_{+}\ \mathbf{9a}^{4+}$, which is driven by the continuous consumption/stabilization of $\mathbf{9a}^{2+(+\bullet)}$ as a dimer. The 40 mV ΔE_p value calculated at low scan rates can thus be simply explained by the fact that the second electron transfer $[E^{1c}]_2$ can be achieved at a more positive potential than the first one $[E^{1c}]_1$.[69] In the first approximation based on the work of Richardson and Taube,[70] a K_{Disp} value of 1.44 was calculated from the experimental ΔE_p values measured at 10 mV/s by cyclic voltammetry. Then, a dimerization constant of about 5250 could be estimated from the CV data recorded with $\mathbf{9a}^{4+}$ and reference compound 7^{2+} (see the Supporting Information section for details).

Overall, these electrochemical data reveal that (i) the kinetics of electron transfer centered on the viologen units (one electron per viologen) remains reversible (fast) in the investigated time scale (10 mV to 4 V/s), (ii) the electrochemical response of $\mathbf{9a/b}^{4+}$ is driven by the kinetics of the coupled chemical steps, (iii) there are no concentration effects and thus no intermolecular chemical association involved in solution in the concentration range (2×10^{-4}–2×10^{-3} M) neither with $\mathbf{9a}^{4+}$ nor with any of the in situ electrochemically generated species $\mathbf{9a}^{2+(+\bullet)}$ or $\mathbf{9a}^{2(+\bullet)}$, and (iv) the doubly reduced species $\mathbf{9a}^{2(+\bullet)}$ is greatly stabilized by intramolecular π-dimerization of the two viologen radicals involved in the hinge, yielding the folded species $[\mathbf{9a}^{2+}]_{Dim}$.

The dimerization process yielding the intramolecular dimer $[\mathbf{9a}^{2+}]_{Dim}$ was then further characterized by spectroelectrochemistry (SEC) measurements performed at platinum electrodes using either a thin layer or a large volume (~10 mL) of SEC cells. The advancement of the electrochemical reactions and the stability of the *in situ* generated reduced species (1 e^-/viologen) at the electrolysis time scale (~hour) were systematically checked by rotating disk voltammetry measurements (see Figure S50). Preliminary studies focused on the spectroscopic response of the reference compound 7^{2+} to an exhaustive electrochemical reduction at $E_{app} = -0.8$ V. As expected, one-electron reduction of the viologen led to the development of a broad signal at 670 nm ($\varepsilon = 1.5 \times 10^4$ L·mol^{-1}·cm^{-1}) attributed to the electrogenerated free viologen radicals coming along with a minor decrease (2%) in the intensity of the Soret band (Figure S52). Similar analyses were then carried out with $\mathbf{9a}^{4+}$ and $\mathbf{9b}^{4+}$ to gain insights into the folding process. As can be seen in Figure 4, the exhaustive

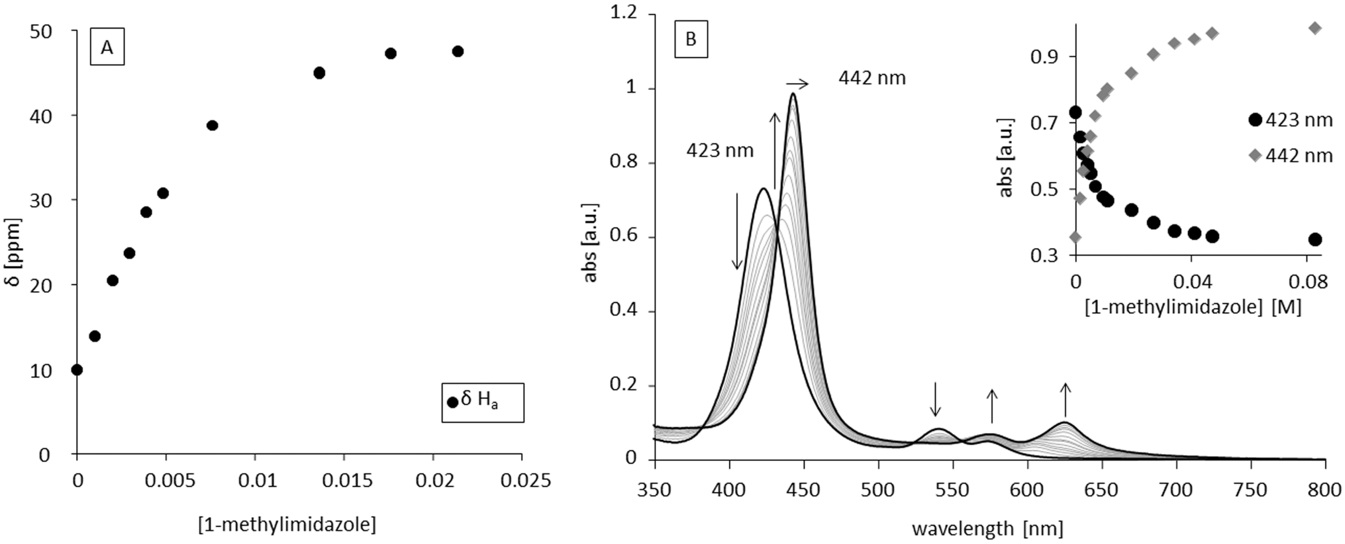


Figure 5. (A) Variation of δ_{Ha} *vs* concentration in 1-methylimidazole for 7^{2+} (1 mM MeCN-d_3, 400 MHz, 298 K). (B) UV/vis spectra recorded during the progressive addition of 1-methylimidazole to a solution of 7^{2+} (MeCN, 5.92×10^{-5} M, l = 1 mm). Increment: Variation of the absorption at $\lambda_{\max}$ = 423 and 442 nm *vs* concentration of 1-methylimidazole.

electrolysis of a DMF (0.1 TBAPF$_6$) solution of **9a**$^{4+}$ at E_{we}= −0.65 V led to major changes in the 300−1200 nm range. It includes a broad diagnostic band developing in the NIR region, at $\lambda_{\max}$ = 950 nm (ε = 6700 L·mol^{-1}·cm^{-1}), revealing the redox-triggered formation of the expected intramolecular π-dimers and whose energy provides direct information on the electronic-coupling between both bipyridinium radicals.[71]

Then, the ability of the terminal imidazole ligand to bind the nickel center, now brought nearby following redox-triggered mechanical folding, was demonstrated by the disappearance of the initial Soret band at 430 nm ($\varepsilon = 1.1 \times 10^5$ L·mol^{-1}·cm^{-1}) at the expense of a new red-shifted band centered at 446 nm ($\varepsilon = 1.3 \times 10^5$ L·mol^{-1}·cm^{-1}). This quite large 16 nm bathochromic shift of the Soret band proceeding through a well-defined isosbestic point at 436 nm is here fully consistent with a clean conversion of the open complex **9a**$^{4+}$ into its folded isomer stabilized by both π-dimerization of the two viologen radicals and axial coordination of the imidazole on the nickel center ([**9a**$^{2+}$]$_{\mathrm{Dim}}$ in Scheme 2).

Further measurements performed on the propyl-substituted analogue **9b**$^{4+}$ led to similar changes in the NIR region with the development of a broad band attributed to the formation of the intramolecular dimer [**9b**$^{2+}$]$_{\mathrm{Dim}}$. On the other hand, as observed with 7^{2+}, the electrochemical reduction of the viologens proved to have very little influence on the Soret band, which only features an intensity increase of about 10% without significant displacement of the absorption maximum (3 nm red shift). Comparison of these changes with those obtained under the same conditions with **9a**$^{4+}$ thus led us to conclude that **9b**$^{2(+\bullet)}$ undergoes an effective intramolecular dimerization yielding [**9b**$^{2+}$]$_{\mathrm{Dim}}$ but that this folding does not lead to the coordination of the imidazole to the electron-rich (relative to **9a**$^{4+}$) nickel center.

In agreement with the proposed intramolecular process yielding [**9a**$^{2+}$]$_{\mathrm{Dim}}$, we also checked that the intensities of the dimer band at $\lambda_{\max}$ = 950 nm and the Soret band at 446 nm evolve linearly with concentration ($\varepsilon_{950\mathrm{nm}}$ = 6700 L·mol^{-1}·cm^{-1}; $\varepsilon_{446\mathrm{nm}} = 1.3 \times 10^5$ L·mol^{-1}·cm^{-1}, see Figure S42). We next established that this species can also be easily produced using excess zinc powder as a chemical reducing agent and that the efficiency of the electron-triggered folding process can be assessed by ESR measurements. The spectra recorded after exhaustive (chemical) reduction of **9a**$^{4+}$ and of 7^{2+}, used as a reference, are shown in Figure S54. The intense and broad signal recorded after reduction of 7^{2+} is consistent with the quantitative formation of free radicals unable to interact in these experimental conditions, while the residual signal observed from **9a**$^{4+}$ attests to the strong displacement of the dimerization equilibrium (K_{Dim} in Scheme 2) in favor of the silent diamagnetic complex [**9a**$^{2+}$]$_{\mathrm{Dim}}$, the weak signal being attributed to the amount of nonassociated bis radicals **9a**$^{2(+\bullet)}$ (Scheme 2) that remains in solution.

The reversibility of the redox-triggered folding motion (**9a**$^{4+}$ ↔ [**9a**$^{2+}$]$_{\mathrm{Dim}}$) was eventually checked by thin-layer spectroelectrochemistry by carrying out reduction/oxidation cycles. As can be seen in the inset of Figure 4, the system showed no fatigue after ten consecutive reduction (E_{app} = −0.85 V) and backoxidation (E_{app} = 0 V) cycles, as revealed by the complete recovery of the absorption at 430 and 446 nm throughout the process.

It has also been shown that both dimerization and coordination of the appended 1-methylimidazole to Ni are favorable enough to occur even in the presence of an excess of competing exogenous ligand like 1-methylimidazole (Figure S53). This was revealed from the concomitant growth of the characteristic π-dimer band at 950 nm together with the 6 nm bathochromic shift of the Soret band (441−447 nm), which can be attributed to the ejection of one exogenous ligand initially bound to nickel in the open form and the coordination of the covalently linked terminal imidazole brought right above the metal by the folding process.

These SEC data discussed above thus provide clear evidence supporting the conclusion that the electrochemical reduction of **9a**$^{4+}$ (one electron/viologen) triggers a large amplitude folding motion allowing to force the axial coordination of the tethered 1-methylimidazole ligand on the nickel center. This process is fully reversible and comes with a change in the coordination sphere of the metal center going from square planar to square pyramidal. This increase in coordination

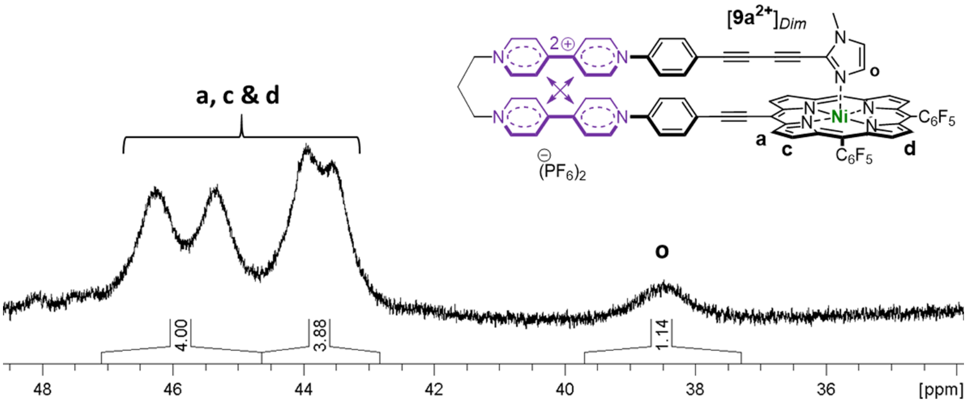


Figure 6. Selected window of the ^{1}H NMR spectrum of $[\mathbf{9a}^{2+}]_{\mathrm{Dim}}$ upon chemical reduction showing the downfield shifted proton peaks (1 mM, MeCN-d_3, 293 K).

number is however only observed when the porphyrin ring is depleted by electron-withdrawing substituents (Figure S51).

Magnetic Properties. Further studies aimed at studying the change in magnetic properties associated with the electron-triggered metamorphic process. In agreement with the schematic drawing shown in Figure 1a, it was indeed expected that the folding motion and the resulting change in the coordination number of the Ni(II) center, going from tetra-coordinated square planar in $\mathbf{9a}^{4+}$ to penta-coordinated square pyramidal in $[\mathbf{9a}^{2+}]_{\mathrm{Dim}}$, could trigger a drastic change in the spin state of the metal from low spin ($S = 0$) to high spin ($S = 1$).[41,53,72] These assumptions were confirmed by NMR measurements performed before and after reduction of $\mathbf{9a}^{4+}$ in MeCN-d_3. The diamagnetic LS state of this tetracationic species was first demonstrated by the ^{1}H NMR spectrum recorded at 1 mM (see Figure 2C), mainly through the observation of all of the expected well-resolved signals within a fairly standard window (0−10 ppm). The influence of axial coordination on the magnetic state of the Ni(II) center was also initially checked by running ^{1}H NMR of $\mathbf{9a}^{4+}$ in pyridine-d_5 (Figure S29) or upon addition of 1-methylimidazole in excess to the reference compound $\mathbf{7}^{2+}$ (see titration curves displayed in Figure 5 and the Supporting Information section for details).

As an illustration of that behavior, we found that the gradual addition of 1-methylimidazole leads to large broadening/shifting or even disappearance of the ^{1}H NMR signals, including a 43 ppm downfield shift, from $\delta_i = 10$ ppm to $\delta_f = 53$ ppm (recorded after addition of 120 molar equivalents of the 1-methylimidazole ligand), of the singlet attributed to one of the β-proton atoms H_a. Similar titrations followed by UV−visible absorbance spectroscopy showed that the binding of 1-methylimidazole results in the progressive decrease in the intensity of the initial Soret band at 423 nm at the expense of a new band at 442 nm, reaching full development after addition of about 1600 molar equivalents of the 1-methylimidazole ligand. Fitting the NMR data with a 2:1 (L:M) binding model,[41] based on the well-accepted idea that the coordination of one axial ligand (K_1) promotes the addition of a second (K_2) on the opposite face of Ni-porphyrin, led us to estimate the association constants K_1 and K_2 to be 110 and 90 M^{-1}, respectively. The slightly higher K_1 value can be correlated to the electron deficiency of the porphyrin ring surrounded by three C_6F_5 units and a viologen unit as EWGs.[41] These preliminary studies carried out with the reference compound $\mathbf{7}^{2+}$ thus revealed that imidazole has a fairly moderate affinity for the nickel center and that its addition leads to strong downfield shifts of the ^{1}H NMR signals, reaching up to 53 ppm for the protons of the porphyrin, accompanied by a bathochromic 19 nm shift of the Soret band in MeCN, a behavior that is strongly reminiscent to that observed during the reduction of $\mathbf{9a}^{4+}$ in DMF (0.1 M $\mathrm{TBAPF_6}$) (Figure 4).

Then, our attention focused on the ^{1}H NMR signature of the folded species $[\mathbf{9a}^{2+}]_{\mathrm{Dim}}$ produced by chemical or electrochemical reduction of the open form of $\mathbf{9a}^{4+}$. The ^{1}H NMR spectrum recorded after chemical reduction (1 e^-/viologen) of a 1 mM solution of $\mathbf{9a}^{4+}$ in deuterated acetonitrile (Figures 6 and S55 and S56) displays distinct features including five peaks observed between 40 and 50 ppm, one broad singlet at −2 ppm, and several broad and unresolved signals still resonating in the 0−10 ppm window. Based on literature data reported for similar C_6F_5-substituted HS Ni porphyrins,[24,31] these four broad peaks observed above 43 ppm were attributed to the resonances of H_a, H_c, and H_d in the HS nickel complex $[\mathbf{9a}^{2+}]_{\mathrm{Dim}}$.[73] The less intense broad singlet at 38.5 ppm integrating for one proton was then attributed to the imidazole proton H_o, which ends up being in close proximity to the paramagnetic center in the folded isomer.

Using eq (1),[31] which gives the molar ratio of the HS paramagnetic complex $[\mathbf{9a}^{2+}]_{\mathrm{Dim}}$ (n_{para}) as a function of the chemical shifts of $[\mathbf{9a}^{2+}]_{\mathrm{Dim}}$ (δ) and $\mathbf{9a}^{4+}$ (δ_{dia} in MeCN-d_3 and δ_{para} in pyridine-d_5), we were able to calculate the switching efficiency at 80% and then the effective magnetic moment, including Pascal's diamagnetic correction, at $\mu_{\mathrm{eff}} = 3.05\mu_{\mathrm{B}}$ (see the Supporting Information section for details) at 293 K, following the Evans method, which is within the range expected for a divalent HS Ni complex ($S = 1$).[24,74,75]

$$n_{\mathrm{para}} = \frac{\delta - \delta_{\mathrm{dia}}}{\delta_{\mathrm{para}} - \delta_{\mathrm{dia}}} = \frac{47.9 - 10.1}{57.1 - 10.1} = 0.80 \qquad (1)$$

Theoretical Calculations. The folding process was further characterized by computational chemistry. DFT calculations were performed at the CAM-B3LYP/6-31+G(d,p)/SDD level of theory on the oxidized and reduced forms of the folded and unfolded isomers. As expected, we found that the folding of the fully oxidized form $\mathbf{9a}^{4+}$ is energetically disfavored, by about +5.3 kcal·mol^{-1}, under the effect of repulsive electrostatic forces arising between the two viologen units. The folded isomer was conversely found to be strongly stabilized (−36.1 kcal·mol^{-1}, see Figure 7) in the reduced state (1e$^-$/viologen) by two complementary processes: (i) the overlap of SOMO

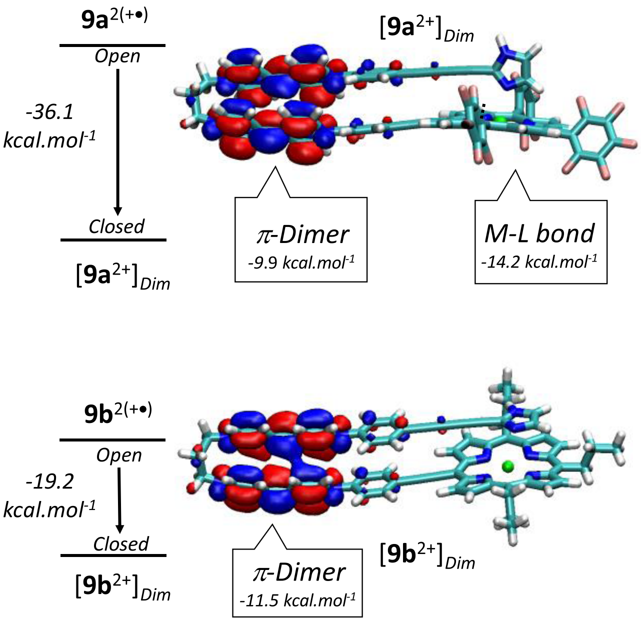


Figure 7. Schematic representation of the energy difference between the open $\mathbf{9a/b}^{2(+\bullet)}$ and closed $[\mathbf{9a/b}^{2+}]_{\mathrm{Dim}}$ isomers, and the energy-minimized π-dimers $[\mathbf{9a/b}^{2+}]_{\mathrm{Dim}}$.

centered on the viologen moieties yielding a sandwichlike π-dimer with an interplanar distance of about 3.2 Å and (ii) by the formation of a 2.06 Å Ni−N coordination bond involving the terminal imidazole ligand.

TDDFT calculations performed at the same level of theory (CAM-B3LYP/6-311+G(d,p)/SDD) led to 50 states lying in good agreement with the experimental spectrum shown in Figure 4, in particular for the characteristic band centered at 960 nm (see Figures S57 and S58).

In agreement with the experimental data discussed above, we found that substitution of the $-C_6F_5$ groups by $-C_3H_7$ leads to the formation of a folded architecture featuring an unbound imidazole ligand lying flat with respect to the porphyrin plane (Figure 7). The absence of the M−L bond in the folded isomer results in a significant decrease in the stabilization energy down to -19.2 kcal·mol^{-1}. These major differences allow us to conclude that both π-dimerization of viologen cation radicals and the N−Ni coordination bond contribute by about 10 and 14 kcal·mol^{-1} to the total stabilization energy of $[\mathbf{9a}^{2+}]_{\mathrm{Dim}}$, respectively.

■ CONCLUSIONS

We have reported the synthesis and the magnetic properties of a redox-responsive tweezer-like molecule featuring a Ni(II) porphyrin tethered to an imidazole ligand through a flexible mechanical hinge capable of undergoing large amplitude and fully reversible folding motion under the effect of electrical stimulation. On the grounds of NMR, (spectro)-electrochemical, and magnetic studies supported by quantum calculations, we have shown that this well-mastered and fully reversible molecular motion can be exploited to force the axial coordination of the appended imidazole ligand onto the square-planar Ni(II) center, thereby triggering a change in its spin state from low spin (S = 0) to high spin (S = 1). We believe that this first example of electron-triggered CISSS, involving large amplitude molecular motion triggered by simple reduction of the viologen units, opens up new opportunities for the development of electronic and spintronic devices.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/jacs.2c07196.

> Equipment and methods, experimental procedures and characterizations, electrochemical data, Evans measurements, and computational details (PDF)

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Notes

The authors declare no competing financial interest.

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