DOI: 10.1002/ejoc.200901310

Synthesis, Characterization, and Electronic Properties of Metalloporphyrins Annulated to Exocyclic Imidazole and Imidazolium Rings

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Keywords: Porphyrinoids / Cyclization / Alkylation / Fused-ring systems / Electrochemistry

meso-Tetraarylporphyrin complexes (M = Ni, Cu, Zn, H_2) fused to an imidazole ring across two neighboring β-pyrrolic positions were synthesized through a cyclization reaction between β,β′-diaminoporphyrins and formic acid or trimethyl orthoformate under acidic conditions. Two synthetic procedures were used to obtain the corresponding porphyrin *N*,*N*′-dimethylimidazolium salts derivatives: alkylation of the imidazole nitrogen atoms with iodomethane and the cyclization reaction between the porphyrin bearing two neighboring β-*N*-methyl groups and trimethyl orthoformate in the presence of ammonium hexafluorophosphate. The electrochemical properties of these porphyrins annulated to an imidazole/imidazolium ring have been investigated by cyclic and rotating disk voltammetry.

Introduction

Tetrapyrrolic macrocycles have been found to be of great interest in various areas such as molecular recognition,[1] molecular sensing,[2] and medicine.[3] Tetrapyrrolic chromophores are widely studied because they are known to play several important biological roles such as catalysis,[4] energy and electron transfer,[5] and light harvesting.[6] These molecules are also promising candidates to be used in the development of new molecular materials with improved photochemical and/or electrochemical properties. The functionalization of tetrapyrrolic macrocycles such as metalloporphyrins is crucial to access new chromophores with additional properties, like optoelectronic properties. Several synthetic procedures have been developed for the preparation of new porphyrins with extended π system.[7] An elegant pathway to extend the π systems of porphyrins is to introduce exocyclic fused rings (benzene, naphthalene, anthracene, pyrene, azulene, quinoline, or pyridine) onto the aromatic core of the macrocycle.[8] Several porphyrins fused to five-membered N-heterocycles (e.g., triazole, pyrrazole, imidazole, or pyrrole) have also been reported.[9] We recently launched a study of porphyrins conjugated with a fused peripheral N-heterocyclic carbene (NHC) group, and the corresponding imidazolium salts are the key precursors of porphyrin–NHC complexes.[10] In this paper, we describe our investigations on the synthesis, characterization, and electrochemical studies of various metalloporphyrins fused to imidazole and imidazolium rings.

Results and Discussion

Porphyrin **1** (Figure 1) fused across the β,β′-pyrrolic positions to a 2′-arylimidazole ring has been described previously by Crossley and co-workers, and it was obtained by the condensation of porphyrin-2,3-dione with an aryl aldehyde in the presence of ammonia.[9f] However, the aryl group of the 2′arylimidazole ring was not suitable to generate the NHC. Thus, we reported another synthetic approach to obtain porphyrin–imidazole derivatives **2** with a nonfunctionalized 2′-imidazole carbon atom. The preparation of porphyrin **3** annulated to an *N*,*N*′-dimethylimidazolium salt has been realized. Deprotonation of the imidazolium salt allowed the formation of carbene **4** and the anchoring of a metal cation such as palladium(II) at the periphery of the porphyrin to obtain porphyrin dimeric species like complex **5** (Figure 1).[10]

To increase the solubility of the different compounds, we synthesized porphyrin derivatives bearing four *meso*-4-*tert*-butylphenyl groups. Condensation of *p*-*tert*-butylbenzaldehyde and pyrrole under Adler–Longo conditions afforded free-base porphyrin **6** in 21% yield, which could be quantitatively metalated with nickel(II) or copper(II).[11] The classical method to prepare imidazole compounds is the condensation reaction between a 1,2-diamine and a carboxylic acid, especially formic acid, to obtain imidazoles containing a nonfunctionalized 2′-carbon atom.[12] Thus, we first con-

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Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/ejoc.200901310.

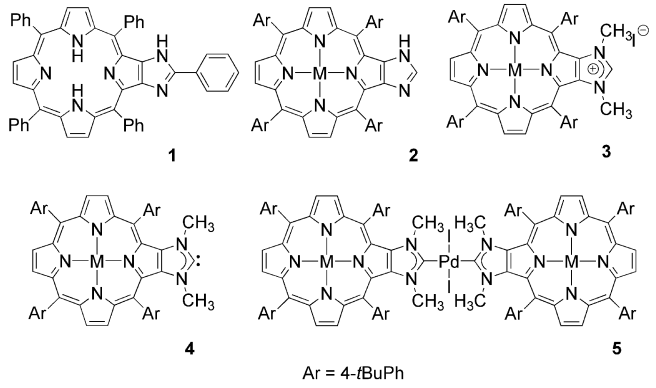
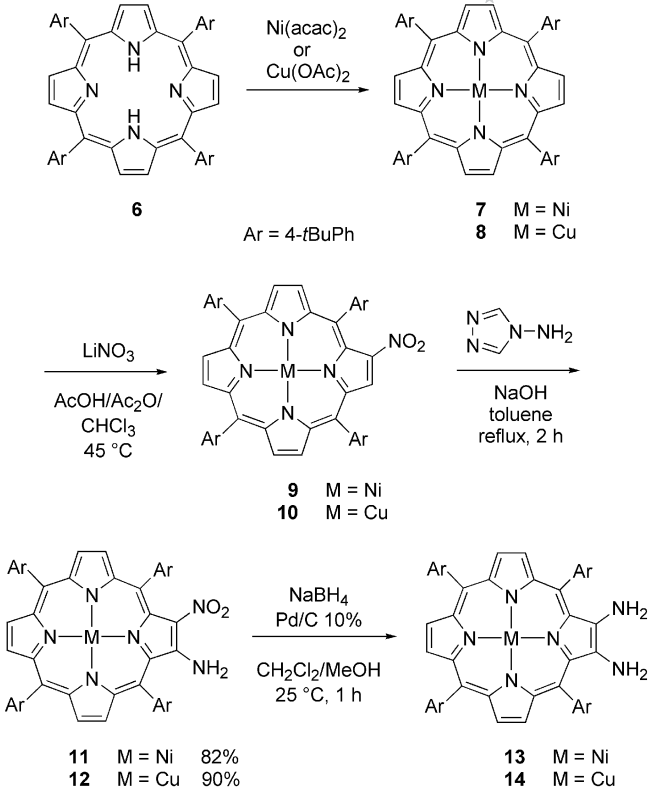


Figure 1. Structures of 2′-arylimidazole **1**, imidazole **2**, imidazolium salt **3**, N-heterocyclic carbene **4**, and palladium complex **5**.

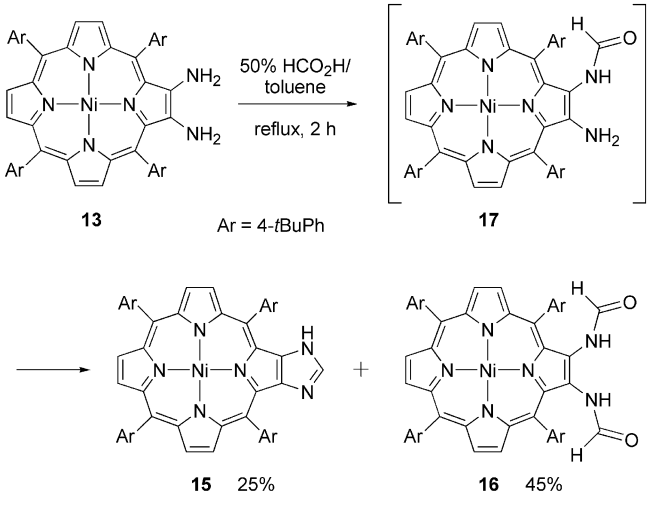
sidered a synthetic route involving the reaction of 2,3-diamino-*meso*-tetraarylporphyrin with formic acid. It is known that 2,3-diamino-*meso*-tetraarylporphyrin derivatives are air sensitive.[13] On the contrary, 2-amino-3-nitroporphyrins appeared to be air stable and can be stored without particular care. β-Nitroporphyrins **9** and **10** were easily obtained in high yield by treating nickel complex **7** and copper complex **8** with lithium nitrate in $CHCl_3$/Ac_2O/AcOH at 45 °C.[14] The electron-withdrawing NO_2 function of **9** and **10** switched the reactivity of the neighboring pyrrolic β-carbon to an electrophilic center. Thus, this β-carbon can be aminated with 4-amino-*4H*-1,2,4-triazole under basic conditions. This reagent was previously used by Callot and co-workers to prepare porphyrins conjugated to enamino ketone and enamino aldehyde functions.[15] Complexes **11** and **12** were obtained in 82 and 90% yield, respectively (Scheme 1).

The nitro function of complexes **11** and **12** could be quantitatively reduced with sodium borohydride and 10% Pd/C in a dichloromethane/methanol mixture to obtain 2,3-diaminoporphyrins **13** and **14** (Scheme 1).[16] Imidazole rings with a nonfunctionalized 2′-carbon atom are easily obtained in high yield by a cyclization reaction between a 1,2-diamine and an excess amount of formic acid, which is usually used as the solvent.[12] In our case, toluene was added to the reaction mixture, as the porphyrin derivatives were not soluble enough in formic acid. The cyclization reaction was first performed between 2,3-diaminoporphyrin **13** and formic acid in toluene (50%) for 2 h (Scheme 2). Two major compounds were obtained: imidazole **15** and bis(formamide) **16**, respectively, in 25 and 45% yield. Both compounds **15** and **16** are issued from two competitive reactions on the same intermediate, which is monoformamide **17**. The low yield obtained for imidazole **15** indicates that the intramolecular cyclization process was more difficult to realize than the formation of the second amide bond, which was favored by the excess amount of formic acid. The yield of imidazole **15** can be increased by decreasing the concentration of formic acid (5%). After heating at reflux for 2 h, TLC revealed that monoformamide **17** was the major product, accompanied by trace amounts of imidazole **15** and



Scheme 1. Synthetic route to 2,3-diamino-*meso*-tetraarylporphyrins.

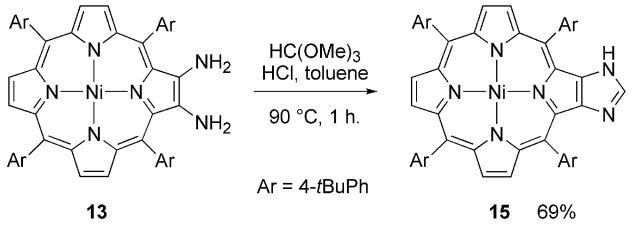
bis(formamide) **16**. At this stage, formic acid was eliminated and monoformamide **17** was treated with trifluoroacetic acid in toluene to favor the intramolecular cyclization reaction. Following this procedure, the yield of imidazole **15** was increased to 55%.



Scheme 2. Cyclization reaction with formic acid.

However, there are two major drawbacks for the formation of the imidazole ring with formic acid: (1) Quite low yields were obtained. (2) Undesired bis(formamide) **16** was always formed (Scheme 2). Thus, we explored another synthetic procedure excluding the use of formic acid as reagent.

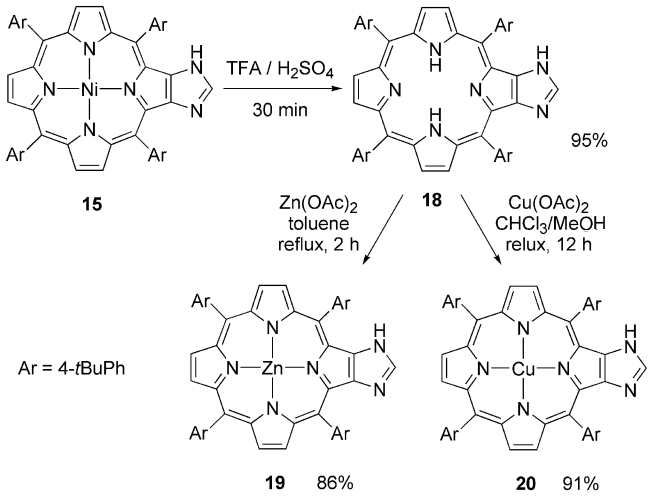
After the reduction of the nitro function of **11**, $HC(OMe)_3$ was added to an acidified (HCl) solution of 2,3-diaminoporphyrin **13** in toluene, and the mixture was heated to 90 °C.[17] Following this simple procedure, imidazole **15** was obtained in 69% yield (Scheme 3). The formation of the imidazole ring could be easily deduced from the FAB^+ MS (m/z = 963.46 $[M + H]^+$) data and ^1H NMR spectra. Broad signals were observed at room temperature, showing slow equilibration of the tautomerization on the ^1H NMR timescale.[9f] Sharp signals were observed at 55 °C in $CDCl_3$ and the C(2′)-*H* signal was clearly observed as a singlet at δ = 7.90 ppm.



Scheme 3. Cyclization reaction with $HC(OMe)_3$ under acidic conditions.

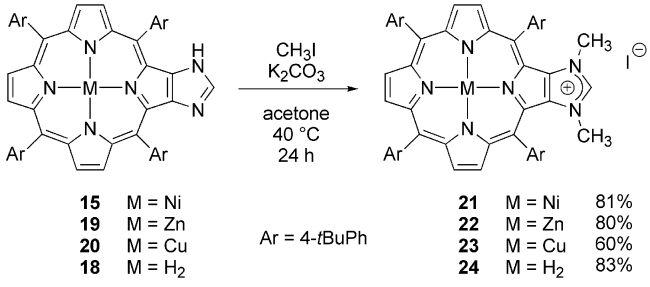
These reactions were performed on porphyrins containing nickel(II) as the inner metal. It rapidly appeared that it was the best choice, as it was not possible to prepare the copper(II) porphyrin fused to the imidazole ring starting from copper(II) complex **14**. However, we could easily obtain other metalloporphyrins annulated to the imidazole, since nickel complex **15** could be demetalated with a TFA/H_2SO_4 (9:1) mixture, and free-base porphyrin **18** was obtained in 95% yield (Scheme 4). The typical ^1H NMR signal due to the internal N*H* of the free-base porphyrin was observed as a singlet at δ = –2.87 ppm, and the broad signals due to slow imidazole tautomerization were observed by ^1H NMR spectroscopy, showing that the macrocycle and the exocyclic imidazole ring did not suffer from the acidic conditions. Remetalation reactions with other metals such as zinc(II) or copper(II) were realized to obtain porphyrin complexes **19** and **20** in 86 and 91% yield, respectively (Scheme 4).

We recently reported the synthesis of porphyrins with a fused peripheral NHC group. The corresponding imidazolium salts are the key precursors of such porphyrin–NHC systems.[10] Our primary focus was on the synthesis of porphyrins fused to *N*,*N*′–dimethylimidazolium salts, which were obtained by two different synthetic procedures. The first one was the alkylation of the nitrogen atoms of the imidazole ring with an excess amount of iodomethane under basic conditions. Imidazolium salts **21** (M = Ni), **22** (M = Zn), **23** (M = Cu), and **24** (M = H_2) were obtained by following this procedure, respectively, from imidazole **15**, **19**, **20**, and **18** in similar yields in the range of ca. 80% (Scheme 5). Purification of these imidazolium salts by column chromatography on SiO_2 was feasible and allowed the separation of the trace amounts of the corresponding unreacted imidazole and monomethylated imidazole derivatives (both eluted with dichloromethane). The imidazolium salts



Scheme 4. Demetalation/remetalation sequence for the synthesis of Zn and Cu complexes **19** and **20**.

were the most polar fractions and were eluted with 5% methanol/dichloromethane. Imidazolium salts **21**–**24** have similar and simple ^1H NMR spectra because of the high symmetry of the molecules. The ^1H NMR spectrum of free-base imidazolium salt **24** in $CDCl_3$ (25 °C) is presented in Figure 2. It clearly shows the downfield signal of the electron-deficient C(2′)–*H* at δ = 10.77 ppm and the upfield signal of the inner N–*H* at δ = –2.94 ppm. The chemical shift of the signals corresponding to the iminium proton is due to the charged hydrogen bond between the electron-deficient imidazolium ring of porphyrin **24** and the I^- anion.[18]



Scheme 5. Synthesis of porphyrins annulated to imidazolium salts **21**–**24**.

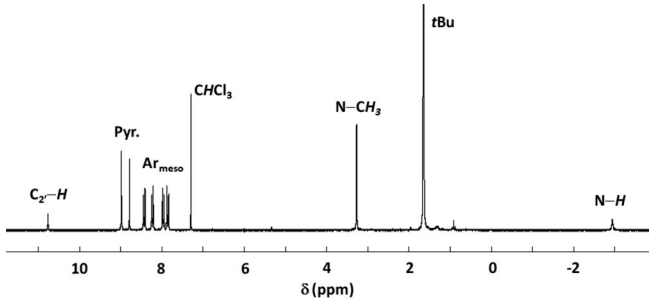
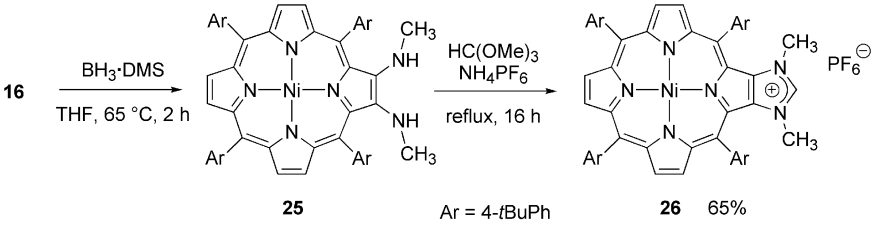


Figure 2. ^1H NMR spectrum (200 MHz, $CDCl_3$, 25 °C) of free-base porphyrin imidazolium salt **24**.

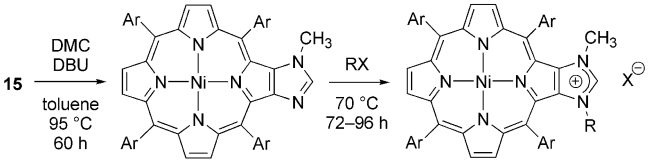


Scheme 6. Synthesis of a porphyrin annulated to imidazolium salt **26**.

The second synthetic strategy was based on a cyclization reaction between *N*,*N*′-dimethylaminoporphyrin **25** bearing two neighboring β *N*–CH_3 functions and $HC(OMe)_3$ in the presence of NH_4PF_6 (Scheme 6).[19] The synthesis of *N*,*N*′-dimethylaminoporphyrin **25** was realized through the reduction of the two carbonyl functions of bis(formamide) **16** with the neat borane dimethyl sulfide (DMS) complex.[20] Porphyrin **25** was not isolated, but used immediately for the cyclization reaction with $HC(OMe)_3$ in the presence of NH_4PF_6. Imidazolium salt **26** was obtained in 65% yield. The ^{1}H NMR (200 MHz) spectra of imidazolium salts **26** and **21** in $CDCl_3$ at 25 °C are similar (some signals are broad for **26**), and the signal of the iminium C(2′)–*H* appears at δ = 8.90 and 11.07 ppm for **26** and **21**, respectively. The significantly large difference of $\Delta\delta$ ca. 2 ppm in the chemical shifts of the signals corresponding to the iminium proton is due to the fact that PF_6^- is a weakly complexing anion in comparison to I^-.[21]

The synthesis of porphyrins annulated to imidazolium rings containing two different N-alkyl groups was also realized. During the alkylation of porphyrin imidazole **15** with iodomethane, we observed by TLC the formation of intermediate monomethylated imidazole **27** (Scheme 7), which can be isolated after column chromatography separation. However, this procedure was not suitable for the preparation of monomethylated imidazole **27** in high yield, as it was not possible to prevent the formation of imidazolium salt **21** and to selectively obtain monomethylated compound **27**. Thus, we applied a synthetic procedure previously described by Shieh et al. for the *N*-methylation of benzimidazole derivatives with dimethyl carbonate (DMC) and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) under conventional thermal conditions (Scheme 7).[22] Following this procedure (60 h in toluene at 95 °C), we obtained monomethylated porphyrin imidazole **27** in very high yield (95%), and more interestingly, it was not necessary to purify this compound by column chromatography. Well-resolved signals were observed by ^{1}H NMR spectroscopy, showing the absence of slow tautomerism equilibrium for **27**. The second nitrogen atom of the monomethyl imidazole ring could be alkylated with an excess amount of other reagents such as iodobutane and benzyl bromide to obtain the corresponding porphyrin imidazolium salts **28** and **29**.

UV/Vis spectroscopic data are summarized in Table 1. UV/Vis spectra of **18** and **24** are represented in Figure 3. The annulation of the porphyrin to an exocyclic imidazole ring across two neighboring β-pyrrolic positions has a minor effect on the electronic properties of the porphyrin,



Scheme 7. Synthesis of porphyrins annulated to imidazolium rings containing two different *N*-alkyl groups **28** and **29**.

as, for example, *meso*-tetraarylporphyrin complex **6** and imidazole **18** have similar UV/Vis spectra. The absorption spectra of imidazole porphyrins have the typical features of porphyrins involving a sharp Soret band and two Q-bands (four Q-bands for free-base porphyrin **18**, Figure 3). Bathochromic shifts (5–20 nm for the lowest-energy Q-bands) of the absorption bands were observed upon alkylation of the imidazole ring as it is illustrated by nickel complexes **15** (imidazole, 568 nm), **27** (*N*-methylimidazole, 573 nm), and **21** (imidazolium salt, 575 nm).

Table 1. UV/Vis data for imidazoles **15**, **18**–**20**, and **27** and imidazolium salts **21**–**24** and **26**.

Compound	λ_{max} Soret band (nm)	λ_{max} Q-band (nm)
15 Ni–imidazole	419	531, 568
27 Ni–methylimidazole	422	536, 573
19 Zn–imidazole	424	551, 588
20 Cu–imidazole	417	538, 575
18 H_2–imidazole	420	516, 552, 587, 644
21 Ni–imidazolium I^-	425	537, 575
26 Ni–imidazolium PF_6^-	426	537, 575
22 Zn–imidazolium I^-	432	563, 608
23 Cu–imidazolium I^-	425	547, 584
24 H_2–imidazolium I^-	428	528, 568, 595, 657

The electrochemical properties of the imidazole and imidazolium porphyrins were investigated by cyclic voltammetry (CV; Table 2 and Supporting Information) and rotating-disc voltammetry (RDV, Supporting Information). Reproducible results were obtained on freshly polished electrodes. Redox potential for the nickel, copper, and zinc imidazoles **15**, **18**–**20**, and **27** and imidazolium derivatives **21**–**24** and **26** are reported in Table 2. As a general trend, two reversible one-electron oxidations as well as two reversible one-electron reductions occurred for the porphyrins fused to an imidazole ring as observed for porphyrins.[23] Electrode deposit and/or inhibition at low scan rates were observed in some cases like for free-base imidazole **18**. For the latter, only the first reduction step and the first oxi-

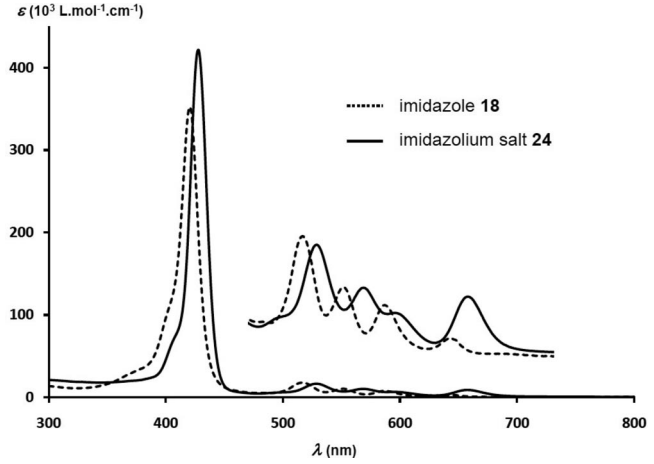


Figure 3. UV/Vis spectra of imidazole **18** (dashed line) and imidazolium salt **24** (solid line) in CH_2Cl_2.

dation step are well resolved, whereas further reduction and oxidation steps were unresolved. However, well-resolved signals were obtained at higher scan rates ($>1\ V\,s^{-1}$). The potentials are dependent on the electronegativity (EN) of the central metal, and therefore, the potential of zinc complex **19** (EN = 1.65) is slightly shifted to more negative potentials relative to that of nickel (EN = 1.91) and copper (EN = 1.90) complexes **15** and **20**.

Table 2. Cyclic voltammetry data for imidazoles **15**, **18**–**20**, and **27** and imidazolium salts **21**–**24** and **26**.[a]

	$E°_{red2}$	$E°_{red1}$	$E°_{ox1}$	$E°_{ox2}$	E_p[b]
15	–2.27	–1.73	+0.44	+0.65	
	(80)	(90)	(100)	(100)	
27	–2.22	–1.76	+0.43	+0.73	
	(90)	(70)	(70)	(90)	
19	–2.15	–1.81	+0.28	+0.61	
	(110)	(60)	(90)	(90)	
20	–2.14	–1.74	+0.44	+0.77	
	(90)	(60)	(60)	(90)	
18		–1.65	+047	+0.69[c]	–2.05
		(60)	(60)	(170)	
21	–2.18	–1.54	+0.64[d]		–2.03
	(80)	(60)	(70)		–0.01
					+0.33
26	–2.01	–1.56	+0.66[d]		
	(60)	(60)	(100)		
22	–2.24	–1.69	+0.36	+0.66	–1.93
	(90)	(80)	(60)	(60)	–0.04
					+0.28
23	–1.99	–1.59	+0.54	+0.90	+0.00
	(60)	(60)	(100)	(60)	+0.35
24	–1.73	–1.48	+0.57	+0.75	+0.00
	(70)	(60)	(60)	(60)	+0.38

[a] Potentials are given in volt vs. the Fc^+/Fc couple used as an internal standard and measured at a scan rate of $0.1\ V\,s^{-1}$. Values indicated in parentheses correspond to the peak potential differences ($\Delta E_p = E_{pa} - E_{pc}$ in mV). See the Experimental Section for details of the conditions. [b] E_p = irreversible peak potentials. [c] Reversible electron transfer observed at a scan rate of $2\ V\,s^{-1}$. [d] Two-electron process.

For the imidazolium salts, several reduction and oxidation potentials were also observed. For nickel and zinc complexes **21** and **22**, three reductions are observed at low scan rates, and the first and third ones are reversible electron transfers, whereas the second reduction was irreversible. Increasing the scan rates up to $10\ V\,s^{-1}$ showed that the second reduction became reversible for scan rates higher than $1\ V\,s^{-1}$ and that, at the same time, the third reduction step decreased in amplitude and vanished. Such an evolution is in agreement with an electrochemical chemical (EC) electron-transfer process for the second reduction step. The generated species, being electroactive, is reduced reversibly at –2.18 V for **21** and –2.24 V for **22**. Up to now we were unable to identify the generated species obtained after the second reductive electron transfer. For copper complex **23**, the generated dianion is much more stable and did not undergo a follow up chemical reaction in contrast to **21** and **22**. It has to be mentioned that the imidazolium ring is a reducible substituent,[24] but its reduction occurs at rather negative potentials. Therefore, none of the electron transfers observed for the imidazolium derivatives involve the imidazolium substituent. Only reduction steps occurring on the porphyrin were observed. For imidazolium salts **21**–**24** with I^- as the anion, the two first oxidations behave as irreversible processes at around 0 and +0.30 V and are attributed to the oxidation of iodide (dissociation of the iodide salt) occurring in two steps, namely, a first oxidation corresponding to $3\ I^- \rightarrow I_3^- + 2\ e^-$ and a second oxidation of $I_3^- \rightarrow 3/2\ I_2 + e^-$.[25] As expected, these two first oxidation steps of iodide were not observed for imidazolium **26** with PF_6^- as the anion. The electrochemical properties of the imidazolium salts are drastically different compared to those of the corresponding imidazoles, as it is clearly illustrated by comparing nickel complexes **15** (imidazole) and **21** (imidazolium salt). The redox potentials of nickel imidazolium salt **21** are shifted to more positive potentials (200 mV for the first oxidation and the first reduction) compared to the redox potentials of nickel imidazole **15**. This is due to the electron-accepting character of the imidazolium ring. In oxidation, a drastic change was also observed, as two reversible one-electron oxidations occurred for imidazole **15** (+0.44 and +0.65 V vs. Fc^+/Fc), whereas the two one-electron oxidations merged into a single two-electron step for imidazolium salt **21** (+0.64 V vs. Fc^+/Fc). The data obtained also showed that the influence of the imidazolium ring on the shifts of the redox potentials was dependent on the nature of the inner metal of the porphyrin. For example, the redox potentials of nickel complex **21** are shifted to more positive potentials by 200 mV for the first oxidation and the first reduction, whereas those of zinc complex **22** are shifted to more positive potentials by 100 mV for the first oxidation and 150 mV for the first reduction. Thus, although identical structural modifications have been brought to the porphyrin core, that is, the methylation of the nitrogen atoms of the imidazole ring, the redox potentials were strongly dependant of the inner metal of the porphyrin when going from the imidazoles to the imidazolium salts.

Conclusions

Several porphyrins annulated to imidazole and imidazolium rings were synthesized starting from a *meso*-tetraarylporphyrin, which can be obtained at the gram scale. The functionalization of two neighboring β-carbon atoms with amino groups was achieved in three steps, namely, the nitration of one β-carbon followed by the amination of the electrophilic neighboring β-carbon, and the reduction of the NO_2 group. Several cyclization reactions were explored to obtain porphyrins fused to an imidazole ring: we found that the better one was the cyclization reaction between the nickel 2,3-diaminoporphyrin complex and trimethyl orthoformate under acidic conditions (around 70% yield). The nickel complex can be demetalated and remetalated with other metal ions. Alkylation of the nitrogen atoms of these imidazoles with iodomethane afforded the corresponding *N*,*N*′-dimethylimidazolium salts. Imidazolium salts bearing two different *N*-alkyl groups were also obtained. The electrochemical properties of the imidazolium salts are different than those of the corresponding imidazoles. Moreover, the influence of the imidazolium ring on the shifts of the redox potentials was strongly dependant of the inner metal of the porphyrin. To conclude, we now have access to a wide panel of ligands by varying (i) the inner metal of the porphyrin and (ii) the groups on the nitrogen atoms. We are currently investigating the coordination properties of these molecules, especially the properties of metal complexes that can be anchored at the periphery of the porphyrin through the NHC ligand issued from the imidazolium salts.

Experimental Section

Experimental Details: ^{1}H NMR spectra were recorded with a Bruker DPX-200 spectrometer and referenced to $SiMe_4$ in ppm. Abbreviations for ^{1}H NMR spectra used are as follows: s, singlet; d, doublet; m, multiplet. UV/Vis spectra were recorded with a Perkin–Elmer Lambda 35 spectrophotometer in quartz cuvettes and CH_2Cl_2 was used as the solvent. IR spectra were recorded with an Avatar 320 FTIR spectrometer as KBr discs. FAB mass spectra were recorded with a SX 102 Jeol 1993 MS instrument and 3-nitrobenzyl alcohol was used as matrix. ESI mass spectra were recorded with a Q-Tof Waters 2001 MS instrument and CH_2Cl_2 was used as solvent. Elemental analyses were realized at the Service Central d'Analyse du Centre National de la Recherche Scientifique of Solaize (France). All reagents and solvents were of commercial reagent grade and used without further purification except where noted. Dry CH_2Cl_2 was obtained by distilling from CaH_2. Dry toluene was obtained by distilling from Na. Dry THF was obtained by distilling from CaH_2, then Na/benzophenone. Preparative separations were performed by silica gel flash column chromatography (Baeckeroot-Labo 60*M*).

Synthesis of the Starting Compounds: Porphyrins **6**–**8**, β-nitroporphyrins **9** (M = Ni) and **10** (M = Cu), and 2-amino-3-nitroporphyrins **11** (M = Ni) and **12** (M = Cu) were prepared according to our previously published procedures.[10]

Nickel 2-Amino-3-Nitroporphyrin 11: A solution of β-nitroporphyrin **9** (1 g, 1.06×10^{-3} mol), sodium hydroxide (0.2 g, 5×10^{-3} mol), and 4-amino-4*H*-1,2,4-triazole (0.943 g, 1.12×10^{-2} mol) in a mixture of toluene (200 mL) and ethanol (10 mL) was heated under reflux for 1 h. After cooling and evaporation, dichloromethane was added, and the organic phase was then washed with water (3×) and dried with sodium sulfate. Chromatography on silica gel (dichloromethane/pentane, 7:3) and crystallization from dichloromethane/methanol afforded **11** in 82% yield (0.83 g). ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C): δ = 8.71 (d, J = 5.0 Hz, 1 H, pyrrole), 8.67 (d, J = 5.0 Hz, 1 H, pyrrole), 8.57 (d, J = 5.0 Hz, 1 H, pyrrole), 8.56 (s, 2 H, pyrrole), 8.47 (d, J = 5.0 Hz, 1 H, pyrrole), 8.01–7.89 (m, 8 H, Ar_{ortho}), 7.87–7.63 (m, 8 H, Ar_{meta}), 6.55 (br. s, 2 H, NH_2), 1.58 (s, 36 H, *t*Bu) ppm. UV/Vis (CH_2Cl_2): λ (ε, L mol^{-1} cm^{-1}) = 444 (131600), 558 (12600), 601 (8900) nm. MS (FAB$^+$): m/z = 954 [$NiC_{60}H_{61}N_6O_2^+$]. $C_{60}H_{60}N_6NiO_2 \cdot H_2O$ (973.87): calcd. C 74.00, H 6.42, N 8.63; found C 74.03, H 6.39, N 8.58.

Copper 2-Amino-3-nitroporphyrin 12: Same procedure as for **11**. Copper complex **12** was obtained in 90% yield. UV/Vis (CH_2Cl_2): λ (ε, L mol^{-1} cm^{-1}) = 443 (170100), 564 (14500), 601 (10600) nm. MS (ESI$^+$): m/z = 960.6 [$CuC_{60}H_{61}N_6O_2^+$]. $CuC_{60}H_{60}N_6O_2 \cdot H_2O$ (978.72): calcd. C 73.63, H 6.39, N 8.59; found C 73.80, H 6.32, N 8.69.

Synthesis of Nickel Imidazole 15 and Nickel Bis(formamide) 16

Method A – Cyclization with Formic Acid: A solution of **11** (500 mg, 5.23×10^{-4} mol) and palladium on activated carbon (10%, 20 mg, 1.88×10^{-4} mol) in a mixture of dichloromethane (125 mL) and methanol (15 mL) was prepared and degassed. Sodium borohydride (500 mg, 1.32×10^{-2} mol) was added, and the mixture was stirred under an atmosphere of argon for 1 h. Completion of the reduction was verified by silica gel TLC (one red spot corresponding to 2,3-diaminoporphyrin **13**). After evaporation of the solvents, formic acid (25 mL) and toluene (25 mL) were added to the residue, and the reaction mixture was heated at reflux under an atmosphere of argon for 2 h. After cooling, the mixture was neutralized with K_2CO_3, washed with water (3×), and concentrated. The residual mixture was purified by silica gel column chromatography (CH_2Cl_2). The first fraction containing a mixture of brown nonpolar unidentified compounds was eliminated. The second fraction contained red-pink **15**, and the third more polar fraction eluted with CH_2Cl_2/MeOH (95:5) contained **16**. After evaporation of the solvents and crystallization from CH_2Cl_2/MeOH, compounds **15** and **16** were obtained as purple solids in 25 (125 mg) and 45% (231 mg) yield, respectively.

Method B – Cyclization with HC(OMe)$_3$]: A solution of nickel(II) porphyrin **11** (500 mg, 5.23×10^{-4} mol) and palladium on 10% activated carbon (20 mg, 1.88×10^{-4} mol) in a mixture of dichloromethane (125 mL) and methanol (15 mL) was prepared and degassed. Sodium borohydride (500 mg, 1.32×10^{-2} mol) was added, and the mixture was stirred under an atmosphere of argon for 1 h. Completion of the reduction was verified by silica gel TLC (one red spot corresponding to 2,3-diaminoporphyrin **13**). After evaporation of the solvents, $HC(OMe)_3$ (7 mL, 6.4×10^{-2} mol), toluene (25 mL), and hydrochloric acid (0.5 mL) were added to the residue, and the mixture was degassed. The solution was heated at 90 °C for 1 h under an atmosphere of argon. After cooling, chloroform (40 mL) and water (80 mL) were added. The mixture was neutralized with K_2CO_3, washed with water (3×), and concentrated. After purification by silica gel column chromatography (CH_2Cl_2), crystallization from CH_2Cl_2/MeOH afforded **15** in 69% yield (338 mg).

Nickel Imidazole 15: ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C): δ = 8.90–8.70 (br. s, 4 H, pyrrole), 8.79 (s, 2 H, pyrrole), 8.52 (br. s, 1 H, NH imidazole), 8.10–7.90 (m, 8 H, Ar_{ortho}), 7.94 (s, 1 H, CH imid-

azole), 7.90–7.75 (br. s, 4 H, Ar_{meta}), 7.72 (d, J = 8.2 Hz, 4 H, Ar_{meta}), 1.62 (br. s, 18 H, *t*Bu), 1.59 (s, 18 H, *t*Bu) ppm. UV/Vis (CH_2Cl_2): λ (ε, $L\,mol^{-1}\,cm^{-1}$) = 419 (248600), 531 (14500), 568 (7700) nm. MS (FAB^+): m/z = 935 [$NiC_{61}H_{61}N_6^+$]. $C_{61}H_{60}N_6Ni{\cdot}H_2O$ (953.88): calcd. C 76.81, H 6.55, N 8.81; found C 77.13, H 6.48, N 8.90.

Nickel Bis(formamide) 16: ^1H NMR (200 MHz, $CDCl_3$, 25 °C): δ = 8.75 (s, 2 H, pyrrole), 8.73 (s, 4 H, pyrrole), 7.94 (d, J = 7.9 Hz, 4 H, Ar_{ortho}), 7.87 (m, 4 H, Ar_{ortho}), 7.75 (br. s, 2 H, CHO), 7.71 (d, J = 7.5 Hz, 8 H, Ar_{meta}), 7.09 (br. s, 2 H, NH), 1.47 (s, 18 H, *t*Bu), 1.46 (s, 18 H, *t*Bu) ppm. UV/Vis (CH_2Cl_2): λ (ε, $L\,mol^{-1}\,cm^{-1}$) = 424 (232100), 538 (17400) nm. IR (KBr): $\tilde{\nu}$ = 1704 (CO) cm^{-1}. MS (ESI^+): m/z = 981.3 [$NiC_{62}H_{63}N_6O_2^+$]. $C_{62}H_{62}N_6NiO_2$ (981.89): calcd. C 75.84, H 6.36, N 8.56; found C 75.73, H 6.41, N 8.50.

Nickel Monoformamide 17: A solution of **11** (500 mg, 5.23×10^{-4} mol) and palladium on activated carbon (10%, 20 mg, 1.88×10^{-4} mol) in a mixture of dichloromethane (125 mL) and methanol (15 mL) was prepared and degassed. Sodium borohydride (500 mg, 1.32×10^{-2} mol) was added, and the solution was stirred under an atmosphere of argon for 1 h. Completion of the reduction was verified by silica gel TLC (one red spot corresponding to 2,3-diaminoporphyrin **13**). After evaporation of the solvents, formic acid (2.5 mL) and toluene (47.5 mL) were added to the residue, and the reaction mixture was heated at reflux under an atmosphere of argon for 2 h. After cooling, the mixture was neutralized with K_2CO_3, washed with water (3×), and concentrated. The residual mixture was purified by silica gel column chromatography (CH_2Cl_2). The first fraction containing a mixture of brown nonpolar unidentified compounds was eliminated. The second fraction contained red **17**, followed by trace amounts of **15**. Trace amounts of bis(formamide) can be eluted with CH_2Cl_2/MeOH, 95:5. After evaporation of the solvents and crystallization from CH_2Cl_2/MeOH, monoformamide **17** was obtained as a purple solid in 58% yield (290 mg). ^1H NMR (200 MHz, $CDCl_3$, 25 °C): δ = 8.75 (m, 6 H, pyrrole), 7.90 (m, 8 H, Ar_{ortho}), 7.85 (br. s, 1 H, CHO), 7.77 (m, 8 H, Ar_{meta}), 7.07 (br. s, 1 H, NH), 6.99 (br. s, 2 H, NH_2), 1.58 (s, 36H *t*Bu), 1.57 (s, 36 H, *t*Bu) ppm. λ (ε, $L\,mol^{-1}\,cm^{-1}$) = 419 (211000), 538 (14600), 580 (7500) nm. IR (KBr): $\tilde{\nu}$ = 1704 (CO), 3389, 3457 (NH_2) cm^{-1}. MS (ESI^+): m/z = 953.0 [$NiC_{61}H_{63}N_6O^+$]. $C_{61}H_{62}N_6NiO$ (953.88): calcd. C 76.81, H 6.55, N 8.81; found C 75.07, H 6.63, N 8.26.

Free-Base Imidazole 18: Nickel imidazole **15** (460 mg, 4.91×10^{-4} mol) was dissolved in TFA/H_2SO_4 (16/4 mL), and the solution was stirred at room temperature for 30 min. It was then poured on ice, diluted with chloroform (200 mL), neutralized with saturated K_2CO_3, washed with water, dried (Na_2SO_4), and concentrated. Crystallization from CH_2Cl_2/MeOH afforded **18** in 95% yield (410 mg). ^1H NMR (200 MHz, $CDCl_3$, 25 °C): δ = 9.00 (d, J = 4.8 Hz, 2 H, pyrrole), 8.88 (d, J = 4.8 Hz, 2 H, pyrrole), 8.85 (s, 2 H, pyrrole), 8.22 (d, J = 8.3 Hz, 4 H, Ar_{ortho}), 8.20 (d, J = 8.3 Hz, 4 H, Ar_{ortho}), 8.01 (s, 1 H, CH imidazole), 7.90 (d, J = 8.2 Hz, 4 H, Ar_{meta}), 7.80 (d, J = 8.3 Hz, 4 H, Ar_{meta}), 1.69 (s, 18 H, *t*Bu), 1.65 (s, 18 H, *t*Bu), –2.89 (s, 2 H, internal NH) ppm. UV/Vis (CH_2Cl_2): λ (ε, $L\,mol^{-1}\,cm^{-1}$) = 420 (350800), 516 (16200), 552 (9400), 587 (7100), 644 (3180) nm. MS (ESI^+): m/z = 879.5 [$C_{61}H_{63}N_6^+$].

Zinc Imidazole 19: Free-base imidazole **18** (185 mg, 2.10×10^{-4} mol) was mixed with $Zn(OAc)_2{\cdot}2H_2O$ (100 mg, 4.46×10^{-4} mol) in toluene (25 mL). The mixture was heated at reflux for 2 h. After solvent evaporation and purification by silica gel column chromatography (CH_2Cl_2), crystallization from CH_2Cl_2/pentane afforded **19** in 86% yield (171 mg). ^1H NMR (200 MHz, $CDCl_3$ + 10% CD_3OD, 25 °C): δ = 8.86 (d, J = 4.6 Hz, 2 H, pyrrole), 8.83 (s, 2 H, pyrrole), 8.71 (d, J = 4.6 Hz, 2 H, pyrrole), 8.03 (d, J = 8.1 Hz, 4 H, Ar_{ortho}), 7.95 (d, J = 8.0 Hz, 4 H, Ar_{ortho}), 7.64 (d, J = 8.0 Hz, 4 H, Ar_{meta}), 7.61 (d, J = 8.1 Hz, 4 H, Ar_{meta}), δ = 7.51 (s, 1 H, CH imidazole), 1.53 (s, 36 H, *t*Bu) pm ppm. UV/Vis (CH_2Cl_2): λ (ε, $L\,mol^{-1}\,cm^{-1}$) = 424 (554000), 551 (20900), 590 (9800) nm. MS (ESI^+): m/z = 941.5 [$ZnC_{61}H_{61}N_6^+$]. $C_{61}H_{60}N_6Zn{\cdot}H_2O$ (960.59): calcd. C 76.27, H 6.51, N 8.75; found C 76.46, H 6.43, N 8.90.

Copper Imidazole 20: Free-base imidazole **18** (400 mg, 4.55×10^{-4} mol) was mixed with $Cu(OAc)_2{\cdot}2H_2O$ (220 mg, 1.10×10^{-3} mol) in $CHCl_3$/methanol (40/5 mL). The mixture was heated at reflux for 12 h. After solvent evaporation and purification by silica gel column chromatography (CH_2Cl_2), crystallization from CH_2Cl_2/methanol afforded **20** in 91% yield (390 mg). UV/Vis (CH_2Cl_2): λ (ε, $L\,mol^{-1}\,cm^{-1}$) = 417 (418300), 538 (19100), 575 (8300) nm. MS (ESI^+): m/z = 940.0 [$CuC_{61}H_{61}N_6^+$]. $CuC_{61}H_{60}N_6{\cdot}2H_2O$ (976.75): calcd. C 75.01, H 6.60, N 8.60; found C 74.94, H 6.52, N 8.66.

Nickel Imidazolium Salt 21 (Alkylation with Iodomethane): Nickel imidazole **15** (125 mg, 1.33×10^{-4} mol) was dissolved in acetone (30 mL). Iodomethane (5 mL) and K_2CO_3 (0.5 g) were added, and the solution was stirred at 40 °C under an atmosphere of argon for 24 h. Completion of the alkylation was verified by silica gel TLC, and the solvent was evaporated. The residue was purified by silica gel column chromatography (CH_2Cl_2 to CH_2Cl_2/MeOH, 95:5). Nickel imidazolium salt **15** was the most polar compound. Crystallization from pentane afforded **21** in 81% yield (116 mg). ^1H NMR (200 MHz, $CDCl_3$, 25 °C): δ = 11.07 (s, 1 H, CH imidazolium), 8.78 (s, 2 H, pyrrole), 8.75 (d, J = 5.0 Hz, 2 H, pyrrole), 8.70 (d, J = 5.0 Hz, 2 H, pyrrole), 8.09 (d, J = 8.3 Hz, 4 H, Ar_{ortho}), 7.99 (d, J = 8.3 Hz, 4 H, Ar_{ortho}), 7.84 (d, J = 8.3 Hz, 4 H, Ar_{meta}), 7.76 (d, J = 8.3 Hz, 4 H, Ar_{meta}), 3.30 (s, 6 H, methyl), 1.60 (s, 18 H, *t*Bu), 1.59 (s, 18 H, *t*Bu) ppm. UV/Vis (CH_2Cl_2): λ (ε, $L\,mol^{-1}\,cm^{-1}$) = 425 (276100), 537 (18000), 575 (sh., 3800) nm. MS (FAB^+): m/z = 963 [$NiC_{63}H_{65}N_6^+$]. $C_{63}H_{65}IN_6Ni{\cdot}H_2O$ (1109.84): calcd. C 68.18, H 6.08, I 11.43, N 7.57; found C 67.48, H 6.05, I 11.19, N 7.55.

Zinc Imidazolium Salt 22: Same procedure as for **21**. Zinc imidazolium salt **22** was obtained in 80% yield. ^1H NMR (200 MHz, $CDCl_3$, 25 °C): δ = 10.17 (br. s, 1 H, CH imidazolium), 8.93 (s, 2 H, pyrrole), 8.92 (d, J = 4.8 Hz, 2 H, pyrrole), 8.81 (d, J = 4.7 Hz, 2 H, pyrrole), 8.29 (d, J = 8.2 Hz, 4 H, Ar_{ortho}), 8.13 (d, J = 8.1 Hz, 4 H, Ar_{ortho}), 7.85 (d, J = 8.2 Hz, 4 H, Ar_{meta}), 7.77 (d, J = 7.9 Hz, 4 H, Ar_{meta}), 3.22 (s, 6 H, methyl), 1.63 (s, 18 H, *t*Bu), 1.62 (s, 18 H, *t*Bu) ppm. UV/Vis (CH_2Cl_2): λ (ε, $L\,mol^{-1}\,cm^{-1}$) = 432 (463900), 563 (18250), 608 (7800) nm. MS (ESI^+): m/z = 969.5 [$ZnC_{63}H_{65}N_6^+$]. $C_{63}H_{65}IN_6Zn{\cdot}H_2O$ (1116.56): calcd. C 67.77, H 6.05, N 7.53; found C 67.41, H 6.02, N 7.54.

Copper Imidazolium Salt 23: Same procedure as for **21**. Copper imidazolium salt **23** was obtained in 60% yield. UV/Vis (CH_2Cl_2): λ (ε, $L\,mol^{-1}\,cm^{-1}$) = 425 (331200), 547 (17700), 584 (4200) nm. MS (ESI^+): m/z = 968.5 [$CuC_{63}H_{65}N_6^+$]. $C_{63}H_{65}CuIN_6$ (1096.68): calcd. C 69.00, H 5.97, N 7.66; found C 68.89, H 6.38, N 7.67.

Free-Base Imidazolium Salt 24: Same procedure as for **21**. Free-base imidazolium salt **24** was obtained in 83% yield. ^1H NMR (200 MHz, $CDCl_3$, 25 °C): δ = 10.77 (s, 1 H, CH imidazolium), 8.98 (s, 4 H, pyrrole), 8.79 (s, 2 H, pyrrole), 8.43 (d, J = 8.2 Hz, 4 H, Ar_{ortho}), 8.23 (d, J = 8.2 Hz, 4 H, Ar_{ortho}), 7.97 (d, J = 8.3 Hz, 4 H, Ar_{meta}), 7.86 (d, J = 8.3 Hz, 4 H, Ar_{meta}), 3.27 (s, 6 H, methyl), 1.66 (s, 18 H, *t*Bu), 1.64 (s, 18 H, *t*Bu), –2.94 (s, 2 H, internal NH)

ppm. UV/Vis (CH_2Cl_2): λ (ε, $L\,mol^{-1}\,cm^{-1}$) = 428 (421500), 528 (16300), 568 (9900), 595 (6100), 657 (7600) nm. MS (ESI^+): *m*/*z* = 907.4 [$C_{63}H_{67}N_6^+$]. $C_{63}H_{67}IN_6{\cdot}2H_2O$ (1071.18): calcd. C 70.64, H 6.68, N 7.85; found C 70.56, H 6.58, N 7.79.

Nickel Imidazolium Salt 26: A solution of nickel bis(formamide) **16** (260 mg, 2.65×10^{-4} mol) in anhydrous THF was prepared and degassed. $BH_3{\cdot}DMS$ (2 M in THF, 0.9 mL, 1.8×10^{-3} mol) was added under an atmosphere of argon, and the solution was stirred at 65 °C for 2 h. Completion of the reduction was verified by silica gel TLC. Then, methanol (1 mL) was added to neutralize the excess amount of the borane/dimethyl sulfide complex. After evaporation of the solvents, $HC(OMe)_3$ (10 mL, 9.1×10^{-2} mol) and NH_4PF_6 (50 mg, 3.07×10^{-4} mol) were added to the residue, and the reaction mixture was degassed and heated at reflux for 16 h under an atmosphere of argon. After cooling, the mixture was poured into a saturated aqueous solution of NH_4PF_6. The obtained solid was filtered, dried, and purified by alumina column chromatography (CH_2Cl_2 to CH_2Cl_2/EtOH, 95:5). Nickel imidazolium salt **26** was the most polar compound. Crystallization from pentane afforded **26** in 65% yield (191 mg). ^1H NMR (200 MHz, $CDCl_3$, 25 °C): δ = 8.90 (s, 1 H, CH imidazolium), 8.76 (s, 2 H, pyrrole), 8.73 (d, *J* = 5.1 Hz, 2 H, pyrrole), 8.70 (d, *J* = 5.1 Hz, 2 H, pyrrole), 8.09 (d, *J* = 8.3 Hz, 4 H, Ar_{ortho}), 7.98 (d, *J* = 8.3 Hz, 4 H, Ar_{ortho}), 7.83 (d, *J* = 8.3 Hz, 4 H, Ar_{meta}), 7.75 (d, *J* = 8.3 Hz, 4 H, Ar_{meta}), 3.10 (s, 6 H, methyl), 1.58 (s, 18 H, *t*Bu), 1.56 (s, 18 H, *t*Bu) ppm. UV/Vis (CH_2Cl_2): λ (ε, $L\,mol^{-1}\,cm^{-1}$) = 426 (234900), 537 (19400), 575 (sh., 4100) nm. MS (FAB^+): *m*/*z* = 963 [$NiC_{63}H_{65}N_6^+$]. $C_{63}H_{65}F_6N_6NiP{\cdot}H_2O$ (1127.90): calcd. C 67.09, H 5.99, F 10.11, N 7.45, P 2.75; found C 67.25, H 5.96, F 10.79, N 7.53, P 3.01.

Nickel *N*-Methylimidazole 27: A solution of nickel imidazole **15** (1 g, 1.07×10^{-3} mol) in toluene (200 mL) was prepared. Dimethyl carbonate (50 mL, 0.594 mol) and 1,8-diazabicyclo[5.4.0]undec-7-ene (2 g, 1.31×10^{-2} mol) were added, and the reaction mixture was degassed and heated at 95 °C for 72 h. After evaporation of toluene, **27** was precipitated by adding methanol to the residue. After filtration, **27** was obtained in 95% yield (965 mg). ^1H NMR (200 MHz, $CDCl_3$, 25 °C): δ = 8.77 (s, 2 H, pyrrole), 8.76 (s, 2 H, pyrrole), 8.75 (d, *J* = 4.6 Hz, 1 H, pyrrole), 8.62, (d, *J* = 4.6 Hz, 1 H, pyrrole), 8.05 (d, *J* = 8.2 Hz, 4 H, Ar_{ortho}), 7.97 (d, *J* = 8.4 Hz, 4 H, Ar_{ortho}), 7.80 (s, 1 H, CH imidazole), 7.73 (d, *J* = 8.2 Hz, 4 H, Ar_{meta}), 7.71 (d, *J* = 8.4 Hz, 4 H, Ar_{meta}), 2.99 (s, 3 H, methyl), 1.60 (s, 9 H, *t*Bu), 1.59 (s, 18 H, *t*Bu), 1.56 (s, 9 H, *t*Bu) ppm. UV/Vis (CH_2Cl_2): λ (ε, $L\,mol^{-1}\,cm^{-1}$) = 422 (243400), 536 (14800), 573 (7700) nm. MS (ESI^+): *m*/*z* = 949.3 [$NiC_{62}H_{63}N_6^+$]. $C_{62}H_{62}N_6Ni{\cdot}H_2O$ (967.90): calcd. C 76.94, H 6.66, N 8.68; found C 76.82, H 6.65, N 8.73.

Nickel Imidazolium Salt 28 [R = $(CH_2)_3CH_3$]: A solution of *N*-methylimidazole **27** (120 mg, 1.27×10^{-4} mol) and 1-iodobutane (4 mL, 0.035 mol) in chloroform (30 mL) was prepared. The mixture was degassed and heated at 70 °C under an atmosphere of argon for 72 h. Completion of the reaction was verified by silica gel TLC, and the solvent was then evaporated. The residue was purified by silica gel column chromatography (CH_2Cl_2 to CH_2Cl_2/MeOH, 95:5). Nickel imidazolium salt **28** was the most polar compound. After evaporation of the solvent, crystallization from pentane afforded **28** in 36% yield (51 mg). ^1H NMR (200 MHz, $CDCl_3$, 25 °C): δ = 11.10 (s, 1 H, CH imidazolium), 8.87 (d, *J* = 5.0 Hz, 1 H, pyrrole), 8.83 (d, *J* = 5.0 Hz, 1 H, pyrrole), 8.79 (d, *J* = 5.0 Hz, 1 H, pyrrole), 8.71 (d, *J* = 5.0 Hz, 1 H, pyrrole), 8.70 (d, *J* = 5.0 Hz, 1 H, pyrrole), 8.56 (d, *J* = 5.0 Hz, 1 H, pyrrole), 8.11 (d, *J* = 8.4 Hz, 2 H, Ar_{ortho}), 8.09 (d, *J* = 8.4 Hz, 2 H, Ar_{ortho}), 8.01 (d, *J* = 8.4 Hz, 2 H, Ar_{ortho}), 8.00 (d, *J* = 8.4 Hz, 2 H, Ar_{ortho}), 7.87 (d, *J* = 8.4 Hz, 2 H, Ar_{ortho}), 7.84 (d, *J* = 8.4 Hz, 2 H, Ar_{ortho}), 7.77 (d, *J* = 8.4 Hz, 2 H, Ar_{ortho}), 3.38 (s, 3 H, methyl), 3.19 (t, *J* = 7.5 Hz, 2 H, $CH_2CH_2CH_2CH_3$), 1.23 (m, 2 H, $CH_2CH_2CH_2CH_3$), 0.86 (m, 2 H, $CH_2CH_2CH_2CH_3$), 0.58 (t, *J* = 7.2 Hz, 2 H, $CH_2CH_2CH_2CH_3$), 1.60 (s, 18 H, *t*Bu), 1.59 (s, 18 H, *t*Bu) ppm. UV/Vis (CH_2Cl_2): λ (ε, $L\,mol^{-1}\,cm^{-1}$) = 427 (244000), 539 (17900), 573 (5400) nm. MS (ESI^+): *m*/*z* = 1005.6 [$NiC_{63}H_{66}N_6^+$]. $C_{66}H_{71}IN_6Ni{\cdot}4H_2O$ (1586.68): calcd. C 65.73, H 6.60, N 6.97; found C 65.71, H 6.22, N 6.96.

Nickel Imidazolium Salt 29 [R = (CH_2Ph)]: A solution of *N*-methylimidazole **27** (150 mg, 1.58×10^{-4} mol) and benzyl bromide (15 mL, 0.126 mol) in chloroform (30 mL) was prepared. The mixture was degassed and heated at 70 °C under an atmosphere of argon for 96 h. Completion of the reaction was verified by silica gel TLC, and the solvent was then evaporated. The residue was purified by silica gel column chromatography (CH_2Cl_2 to CH_2Cl_2/MeOH, 95:5). Nickel imidazolium salt **29** was the most polar compound. Crystallization from dichloromethane/pentane afforded **29** in 46% yield (81 mg). ^1H NMR (200 MHz, $CDCl_3$, 25 °C): δ = 11.38 (s, 1 H, CH imidazolium), 8.89, (d, *J* = 5.0 Hz, 1 H, pyrrole), 8.84 (d, *J* = 5.0 Hz, 1 H, pyrrole), 8.79 (d, *J* = 5.0 Hz, 1 H, pyrrole), 8.70 (d, *J* = 5.0 Hz, 1 H, pyrrole), 8.68 (d, *J* = 5.0 Hz, 1 H, pyrrole), 8.51 (d, *J* = 5.0 Hz, 1 H, pyrrole), 8.08 (d, *J* = 8.4 Hz, 2 H, Ar_{ortho}), 8.03 (d, *J* = 8.4 Hz, 2 H, Ar_{ortho}), 8.00 (d, *J* = 8.4 Hz, 2 H, Ar_{ortho}), 7.98 (d, *J* = 8.4 Hz, 2 H, Ar_{ortho}), 7.83 (d, *J* = 8.4 Hz, 2 H, Ar_{meta}), 7.82 (d, *J* = 8.4 Hz, 2 H, Ar_{meta}), 7.77 (2 d, *J* = 8.4 Hz, 2 H, Ar_{meta}), 6.92 (m, 3 H, Ph), 6.72 (m, 2 H, Ph), 4.43 (s, 2 H, CH_2), 3.38 (s, 3 H, methyl), 1.59 (s, 18 H, *t*Bu), 1.56 (s, 18 H, *t*Bu) ppm. UV/Vis (CH_2Cl_2): λ (ε, $L\,mol^{-1}\,cm^{-1}$) = 428 (280000), 539 (17500), 572 (5300) nm. MS (ESI^+): *m*/*z* = 1039.6 [$NiC_{69}H_{69}N_6$]$^+$. $C_{69}H_{69}BrN_6Ni{\cdot}2H_2O$ (1156.95): calcd. C 71.63, H 6.36, N 7.26; found C 71.65, H 6.25, N 7.25.

Electrochemical Studies: Spectroscopic-grade dichloromethane was purchased from Merck, dried with molecular sieves (4 Å), and stored under an atmosphere of argon prior to use. Electrochemical-grade Bu_4NPF_6 was purchased from Fluka and used as received. Electrochemical measurements were carried out at room temperature in CH_2Cl_2 containing 0.1 M Bu_4NPF_6 in a classical three-electrode cell by cyclic voltammetry (CV) and rotating-disk voltammetry (RDV). The working electrode was a glassy carbon disk (3 mm in diameter), the auxiliary electrode a Pt wire, and the reference electrode a Pt wire used as pseudoreference electrode. The electrodes were polished before each measurement, otherwise irreproducible CVs. were obtained due to insulating film formation either during oxidation or reduction. The cell was connected to an Autolab PGSTAT30 potentiostat (Eco Chemie, Holland) driven by a GPSE software running on a personal computer. All potentials are given vs. Fc^+/Fc used as internal reference and uncorrected from ohmic drop.

Supporting Information (see footnote on the first page of this article): ^1H NMR spectra of the compounds, rotating disk data, and cyclic voltammograms.

Acknowledgments

We are grateful to the Centre National de la Recherche Scientifique (CNRS), the French Ministry of Research, and the Agence National de la Recherche (ANR) for financial support of the research project ANR-09-JCJC-0089-01.

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Received: November 16, 2009
Published Online: February 15, 2010

