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Synthesis, Structural Characterization, and Electrochemical Studies of Nickel Porphyrins Bearing Two Peripheral Conjugated Chelating Groups

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This Article describes the synthesis of several new nickel porphyrins bearing peripheral chelating groups conjugated with the macrocyclic π system. These monomeric nickel porphyrins display quite unusual chromophoric properties, some of them absorbing in the near-infrared region. Extension of the aromatic core of the porphyrin was realized by connecting *meso*-aryl groups with pyrroles by ketone functionalities. Further functionalizations led to bisenaminoketones or bisenaminothioketones, which are useful building blocks for the elaboration of oligomeric porphyrins linked by metal ions. All new compounds were studied by electrochemistry, some of them showing up to six electron transfers and/or splitting of the first oxidation wave.

Introduction

The expansion and/or functionalization of large aromatic molecules (or more generally π-conjugated molecules) in order to build molecular systems with enhanced optoelectronic properties is a topic of broad current interest.[1] In particular, in the field of oligoporphyrins (or porphyrin analogues, like porphyrazines and phthalocyanines), several research groups have obtained large molecular architectures through covalent or noncovalent linkages.[2-4] Among these new chromophores, fused porphyrins have led to the spectacular enhancement of the electronic properties.[5] Using metal ions as linking units between functionalized porphyrins allowed the easy preparation of oligoporphyrins in a few synthetic steps and with excellent yields.[6] The use of metalloporphyrins or metalloporphyrazines functionalized at the periphery of the macrocycle also allows the anchoring of metal complexes. In such molecules, interactions can be expected between internal and external coordinated metal ions, thus leading to very promising candidates for magnetic

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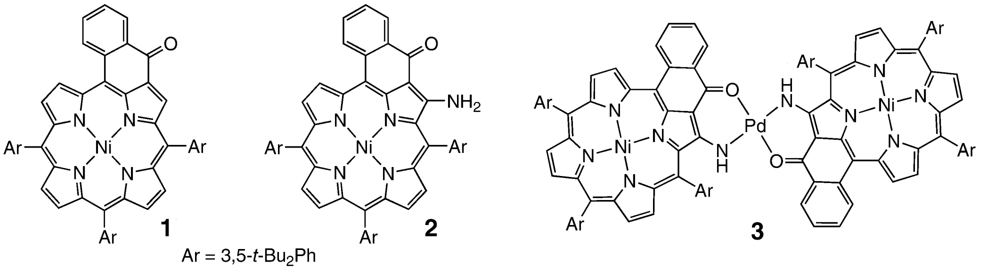
Chart 1. Nickel Ketone **1**, Nickel Enaminoketone **2**, and Palladium(II)-Linked Diporphyrin **3**



molecular materials or to new catalysts where the activity of the external metal ion might be controlled by the central metal ions.[7]

We have described the preparation of nickel porphyrin **2** bearing an enaminoketone conjugated with the aromatic core (see Chart 1).[8] This compound was obtained by amination of the known ketone **1**.[9] The enaminoketone external chelating group was used to assemble metalloporphyrins such as **2** into dimers such as **3** around dicationic metal ions.[10] Strong interactions between the two linked porphyrins were found for these dimers. Compared to the previously used covalent connections (double or triple bonds linking two porphyrins), the electronic spectra and the electrochemical study of these dimers demonstrated that the electronic interactions were in the same range.[11] We have extended this work to porphyrins bearing other external chelating groups (enaminothioketones, enaminoaldehydes, and enaminothioaldehydes), and the interactions between porphyrins found in the dimers built from these monomers were similar.[12]

In order to construct higher oligomers using the same strategy, porphyrins bearing two external chelating groups were needed. In the same series (enaminoketones as external chelating groups) as the initially used porphyrins, this implied that porphyrins bearing two diketones should be aminated. We have described the synthesis of all possible isomeric diketones **4**−**9** (see Chart 2) and the structure of two of them (compound **4** and an analogue of compound **7**, differing only by the *meso*-aryl groups) obtained by X-ray diffraction.[13]

We have already briefly described the use of a nickel porphyrin bearing two external enaminoketones for the preparation of a linear heptametallic porphyrinic trimer.[14] In this Article, we describe the preparation of 14 nickel porphyrins bearing two enaminoketones (NO−NO chelating groups), two enaminothioketones (NS−NS chelating groups), or mixed external functionalizations (NO−NS chelating groups). Two of them gave single crystals suitable for an X-ray structural characterization. The electronic properties and a detailed electrochemical study of these nickel enamino(thio)ketones as well as those of nickel diketones **4**−**9** will be presented.

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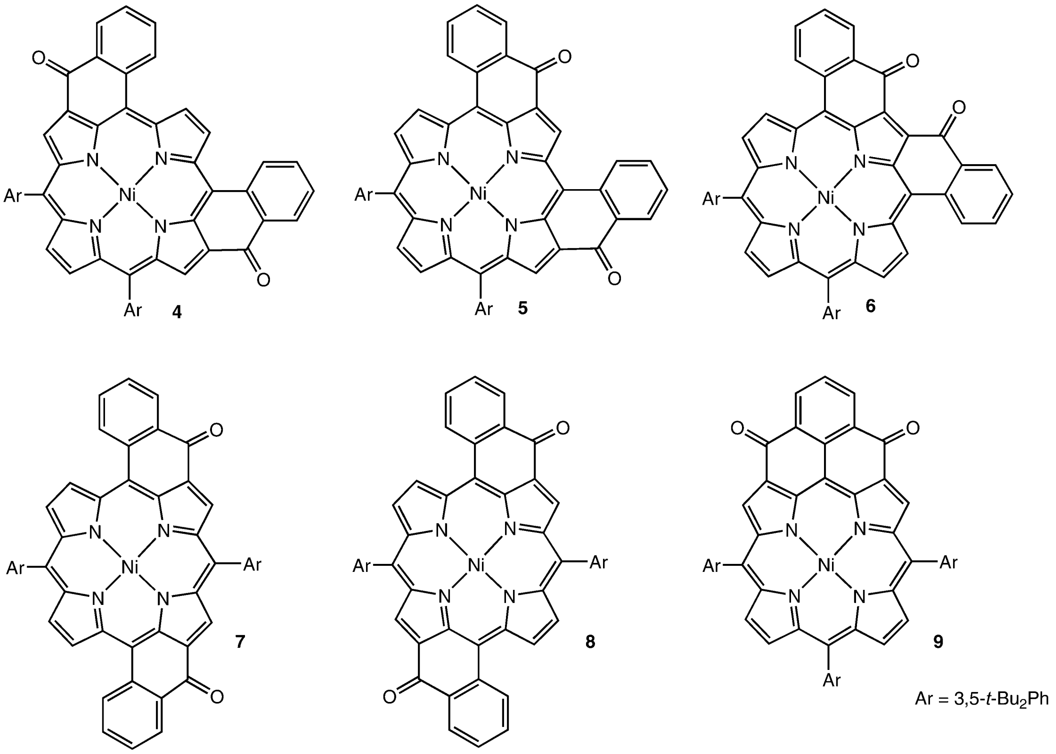
Chart 2. All Possible Isomeric Porphyrinic Diketones (Compounds **4**−**9**)



Experimental Section

General Procedures. UV−vis spectra were acquired with a Hewlett-Packard model 8453 instrument (CH_2Cl_2). NMR ($CDCl_3$ at 25 °C unless otherwise stated, δ (ppm) vs TMS) data acquired on Bruker AC 300, AM 400, and ARX 500 instruments. COSY $^1H-^1H$ NMR have been run on all compounds. Elemental analyses were performed at the Service de Microanalyse, Université Louis Pasteur, Strasbourg. Chromatographic separations were obtained using Merck 9385 silica gel or Merck 1097 alumina. All monomeric porphyrins gave correct masses (Finnigan TSQ 700, EI, 12 eV or MALDI-TOF).

Amination of Diketones 4, 5, and 7−9. To a solution of the diketone (0.18 mmol in 60 mL toluene/ethanol 5/1) was added a large excess of 4-amino-4H-1,2,4-triazole (350 mg, 4.16 mmoles) and sodium hydroxide (500 mg, 12.5 mmol). The solution was heated under reflux, and the progress of the amination was followed by thin layer chromatography (TLC). After full consumption of the starting material (ca. 2 h under reflux), trifluoroacetic acid (4 mL) was added and the mixture heated under reflux for an additional hour. After cooling, dichloromethane (100 mL) was added and the organic phase washed with water (3 × 1 L). The nickel bisenaminoketones **10**−**14** were purified by column chromatography (silica gel, 300 g, dichloromethane as eluent) and crystallized from dichloromethane/methanol.

10 (from **4**, yield 74%): ^1H NMR: $\delta = 9.23$, 8.10 (2s, 2+2H, pyrrole), 8.52 (dd, 2H, $J = 7.7$ and ∼1.5 Hz, cyclized phenyl), 8.08 (dd, 2H, $J = 7.7$ and ∼1.0 Hz, cyclized phenyl), 7.71 (ddd, 2H, $J = 7.7$, 7.7, and ∼1.5 Hz, cyclized phenyl), 7.53 (ddd, 2H, $J = 7.7$, 7.7, and ∼1.0 Hz, cyclized phenyl), 7.75 (t, 2H, $J = 1.8$ Hz, Ar H_{para}), 7.58 (broad d, 4H, $J = 1.8$ Hz, Ar H_{ortho}), 8.21 (broad s, 2H, N−H), 5.12 (broad s, 2H, N−H), 1.41 (s, 36H, *t*-butyl). UV−vis: (CH_2Cl_2) $\lambda_{max} = 318$ ($\epsilon = 38\,400$), 348 (42 400), 480 (66 600), 512 (56 400sh), 544 (69 200), 618 (18 300), 710 (8700) nm. Elem anal. Calcd for $C_{62}H_{58}N_6O_2Ni\cdot 0.5CH_3OH$: C 75.53, H 6.08, N 8.46. Found: C 75.74, H 6.22, N 8.50.

11 (from **5**, yield 56%): ^1H NMR (50 °C): $\delta = 8.84$, 8.45 (2d, 1+1H, $J = 4.8$ Hz, pyrrole), 8.08, 8.05 (d, 1+1H, $J = 4.8$ Hz, pyrrole), 8.52 (dd, 1H, $J = 7.8$ and ∼1.5 Hz, cyclized phenyl), 7.46 (ddd, 1H, $J = 7.8$, 7.8, and ∼1.5 Hz, cyclized phenyl), 7.69 (ddd, 1H, $J = 7.8$, 7.8, and ∼1.5 Hz, cyclized phenyl), 8.12 (dd, 1H, $J = 7.8$ and ∼1.5 Hz, cyclized phenyl), 8.48 (dd, 1H, $J = 7.8$ and ∼1.5 Hz, cyclized phenyl), 7.51 (ddd, 1H, $J = 7.8$, 7.8, and ∼1.5 Hz, cyclized phenyl), 7.63 (ddd, 1H, $J = 7.8$, 7.8, and ∼1.5 Hz, cyclized phenyl), 8.12 (dd, 1H, $J = 7.8$ and ∼1.5 Hz, cyclized phenyl), 8.12 (broad, 1H, Ar H_{ortho}), 7.77 (dd, 1H, $J = 1.8$ and 1.8 Hz, Ar H_{para}), 7.09 (dd, 1H, $J =$ ∼1.8 and ∼1.8 Hz, Ar H_{para}), 8.00−8.05 (broad, 1+1H, Ar H_{ortho}), 7.69 (dd, 1H, $J = 1.8$ and 1.8 Hz, Ar H_{ortho}), 1.56, 1.30 (2s, 18+18H, *t*-butyl), N−H not detected. UV−vis: (CH_2Cl_2) $\lambda_{max} = 368$ ($\epsilon = 37\,800$), 438 (34 600), 536 (64 800), 646 (11 000), 728 (12 300) nm. Elem anal. Calcd for $C_{62}H_{58}N_{10}O_2Ni\cdot H_2O$: C 74.78, H 6.07, N 8.44. Found: C 74.67, H 5.90, N 8.35.

12 (from **7**, yield 69%): ^1H NMR: $\delta = 9.06$, 8.50 (2d, 2+2H, $J = 5.0$ Hz, pyrrole), 8.53 (dd, 2H, $J = 7.8$ and ∼1.0 Hz, cyclized phenyl), 8.15 (dd, 2H, $J = 7.8$ and ∼1.0 Hz, cyclized phenyl), 7.73 (ddd, 2H, $J = 7.8$, 7.8 and ∼1.0 Hz, cyclized phenyl), 7.55 (ddd, 2H, $J = 7.8$, 7.8 and ∼1.0 Hz, cyclized phenyl), 7.88, 7.69 (2t, 1+1H, $J = 1.7$ Hz, Ar H_{para}), 7.20−8.00 (very broad, 4H, Ar H_{ortho}), 1.47, 1.46 (2s, 18+18H, *t*-butyl), N−H not detected. UV−vis: (CH_2Cl_2) $\lambda_{max} = 416$ ($\epsilon = 34\,700$), 502 (85 500), 672 (16 700), 703 (19 000), 758 (24 800) nm. Elem anal. Calcd for $NiC_{62}H_{58}N_6O_2\cdot 0.5CH_3OH$: C 75.53, H 6.08, N 8.46. Found: C 75.56, H 6.00, N 8.38.

13 (from **8**, yield 64%): ^1H NMR: $\delta = 9.01$, 8.45 (2d, 2+2H, $J = 4.9$ Hz, pyrrole), 8.54 (dd, 2H, $J = 7.7$ and ∼1.0 Hz, cyclized phenyl), 8.24 (dd, 2H, $J = 7.7$ and ∼1.0 Hz, cyclized phenyl), 7.74 (ddd, 2H, $J = 7.7$, 7.7, and ∼1.0 Hz, cyclized phenyl), 7.55 (ddd, 2H, $J = 7.7$, 7.7, and ∼1.0 Hz, cyclized phenyl), 7.80 (t, 2H, $J = 1.7$ Hz, Ar H_{para}), 7.40−7.80 (broad, 4H, Ar H_{ortho}), 1.46 (s, 36H, *t*-butyl), N−H not detected. UV−vis: (CH_2Cl_2) $\lambda_{max} = 395$

(ϵ = 24 200), 488 (140 500), 667 (20 000), 757 (38 100) nm. Elem anal. Calcd (%) for $C_{62}H_{58}N_6O_2Ni \bullet CH_3OH$: C 74.93, H 6.19, N 8.32; found: C 75.13, H 6.11, N 8.24.

14 (from **9**, yield 75%): ^1H NMR ($C_2D_2Cl_4$, 60 °C): δ = 8.29 (d, 2H, *J* = 5.1 Hz, pyrrole), 8.11 (2d, 2H, *J* = 4.9 Hz, pyrrole), 8.67 (d, 2H, *J* = 7.5 Hz, cyclized phenyl), 7.62 (t, 1H, *J* = 7.5 Hz, cyclized phenyl), 7.85 (t, 2H, *J* = 1.8 Hz, Ar H_{para}), 7.70−7.72 (m, 7H, Ar $H_{ortho+para}$), 1.49 (s, 36H, *t*-butyl), 1.46 (s, 18H, *t*-butyl), N−H not detected (but observed in $CDCl_3$ at 25 °C: δ = 8.47 and 5.22). UV−vis: (CH_2Cl_2) λ_{max} = 400 (ϵ = 63 300), 492 (70 600), 644 (21 100), 682 (32 500) nm. High-resolution MS calcd for $C_{70}H_{74}N_6O_2Ni + H^+$: 1089.5300; found, 1089.5293.

Thionation of Bisenaminoketones 10−13. A solution of the nickel bisenaminoketone in benzene was heated under reflux, and the Lawesson's reagent was added in small portions (approximatively 1 equiv per addition). The progress of the reaction was followed by TLC, and the reaction was stopped before full consumption of the starting material. After evaporation of the solvent, the residue was chromatographed on a silica gel column (eluent: dichloromethane) allowing the successive isolation of the dithionated, the monothionated, and the starting compound (>90% overall recovery of nickel porphyrins). Crystallization from dichloromethane/methanol afforded the mono- and dithionated products.

15 (from **10**): ^1H NMR: δ = 9.19, 9.17, 8.10, 8.08 (4d, 1+1+1+1H, *J* = 5.0 Hz, pyrrole), 9.06, 8.52, 8.08, 8.01 (4dd, 1+1+1+1H, *J* = 8.0 and ∼1.0 Hz, cyclized phenyl), 7.70, 7.68, 7.53, 7.52 (4ddd, 1+1+1+1H, *J* = 8.0, 8.0, and ∼1.0 Hz, cyclized phenyl), 7.77, 7.75 (2t, 1+1H, *J* = 1.8 Hz, Ar H_{para}), 7.58 (2 broad d, 2+2H, Ar H_{ortho}), 11.77, 5.97 (2d, 1+1H, *J* = 4.0 Hz, NH_2 near S), 8.21, 5.10 (broad, 1+1H, NH_2 near O), 1.41 (2s, 18+18H, *t*-butyl). UV−vis: (CH_2Cl_2) λ_{max} = 356 (ϵ = 37 600), 388 (30 000sh), 468 (39 500), 514 (47 200sh), 566 (61 000), 678 (13 000sh), 742 (9000) nm. Elem anal. Calcd for $NiC_{62}H_{58}N_6SO \bullet H_2O$: C 73.59, H 5.98, N 8.30. Found: C 73.48, H 5.86, N 8.14.

16 (from **11**): ^1H NMR: δ = 8.78, 8.43, 8.02, 7.98 (4d, 1+1+1+1H, *J* = 4.8 Hz, pyrrole), 9.05, 8.12 (2dd, 1+1H, *J* = 7.8 and ∼1.5 Hz, cyclized phenyl S), 7.70, 7.49 (2ddd, 1+1H, *J* = 7.8, 7.8, and ∼1.5 Hz, cyclized phenyl S), 8.47, 8.21 (2dd, 1+1H, *J* = 7.8 and ∼1.5 Hz, cyclized phenyl O), 7.63, 7.52 (2ddd, 1+1H, *J* = 7.8, 7.8, and ∼1.5 Hz, cyclized phenyl O), 8.00−8.50 (very broad, 2H, Ar), 7.67 (t, 1H, *J* = 1.8 Hz, Ar), 8.09, 7.75, 7.08 (3t, 1+1+1H, *J* = 1.8 Hz, Ar), 12.6, 5.15 (2 broad d, 1+1H, NH_2 near S), ∼1.29 (2s, 18+18H, *t*-butyl), NH_2 near O not detected. UV−vis: (CH_2Cl_2) λ_{max} = 378 (ϵ = 49 000), 452 (47 000), 570 (68 000), 668 (11 000), 766 (7500) nm. Elem anal. Calcd for $NiC_{62}H_{58}N_6SO \bullet H_2O$: C 73.59, H 5.98, N 8.30. Found: C 73.78, H 5.86, N 8.18.

17 (from **11**): ^1H NMR: δ = 8.82, 8.45 (2d, 1+1H, *J* = 4.8 Hz, pyrrole), 8.04 (s, 2H, pyrrole), 9.00, 8.08 (2dd, 1+1H, *J* = 8.0 and ∼1.2 Hz, cyclized phenyl S), 7.66, 7.49 (2ddd, 1+1H, *J* = 8.0, 8.0, and ∼1.2 Hz, cyclized phenyl S), 8.52, 8.13 (2dd, 1+1H, *J* = 7.5 and ∼1.5 Hz, cyclized phenyl O), 7.70, 7.53 (2ddd, 1+1H, *J* = 7.5, 7.5, and ∼1.5 Hz, cyclized phenyl O), 8.00−8.50 (very broad, 2H, Ar), 7.67 (t, 1H, *J* = 1.8 Hz, Ar), 8.10, 7.77, 7.07 (3t, 1+1+1H, *J* = 1.8 Hz, Ar), 11.71, 6.01 (2 broad d, 1+1H, NH_2 near S), 1.55, 1.28 (2s, 18+18H, *t*-butyl), NH_2 near O not detected. UV−vis: (CH_2Cl_2) λ_{max} = 392 (ϵ = 42 000), 458 (42 500), 570 (60 000), 766 (11 400) nm. Elem anal. Calcd for $NiC_{62}H_{58}N_6SO \bullet H_2O$: C 73.59, H 5.98, N 8.30. Found: C 73.74, H 5.97, N 8.02.

18 (from **12**): ^1H NMR: δ = 9.02, 9.01, 8.49, 8.47 (4d, 1+1+1+1H, *J* = 4.8 Hz, pyrrole), 9.07, 8.53, 8.14, 8.11 (4dd, 1+1+1+1H, *J* = 8.0 and ∼1.1 Hz, cyclized phenyl), 7.73, 7.72, 7.55 (3ddd, 1+1+2H, *J* = 8.0, 8.0 and ∼1.1 Hz, cyclized phenyl), 7.91, 7.69 (2t, 1+1H, *J* = 1.8 Hz, Ar H_{para}), 7.40−8.00 (very broad, 4H, Ar H_{ortho}), 11.94, 5.96 (2 broad d, 1+1H, NH_2 near S), 1.55, 1.45 (2s, 18+18H, *t*-butyl), NH_2 near O not detected. UV−vis: (CH_2Cl_2) λ_{max} = 362 (ϵ = 31 700), 386 (35 300), 442 (47 600), 510 (63 800), 700 (22 500sh), 740 (29 000), 794 (24 700) nm. Elem anal. Calcd for $NiC_{62}H_{58}N_6SO \bullet H_2O$: C 73.59, H 5.98, N 8.30. Found: C 73.49, H 5.90, N 8.20.

19 (from **13**): ^1H NMR: δ = 8.99, 8.98, 8.43, 8.40 (4d, 1+1+1+1H, *J* = 4.8 Hz, pyrrole), 9.09, 8.53, 8.24, 8.24 (4dd, 1+1+1+1H, *J* = 7.7 and ∼1.0 Hz, cyclized phenyl), 7.75 (2ddd, 1+1H, *J* = 7.7, 7.7, and ∼1.0 Hz, cyclized phenyl), 7.56 (2ddd, 1+1H, *J* = 7.7, 7.7, and ∼1.0 Hz, cyclized phenyl), 7.82, 7.80 (2 broad t, 2H, *J* = 1.8 Hz, Ar H_{para}), 7.40−7.80 (very broad, 4H, Ar H_{ortho}), 11.95, 6.03 (2 broad d, 1+1H, NH_2 near S), 1.54, 1.46 (2s, 18+18H, *t*-butyl), NH_2 near O not detected. UV−vis: (CH_2Cl_2) λ_{max} = 346 (ϵ = 30 600), 370 (26 600), 436 (38 400sh), 466 (53 800sh), 504 (100 500), 700 (24 200), 738 (18 900sh), 796 (27 100) nm. Elem ana. Calcd for $NiC_{62}H_{58}N_6SO \bullet CH_3OH$: C 73.75, H 6.09, N 8.19. Found: C 73.75, H 6.11, N 7.83.

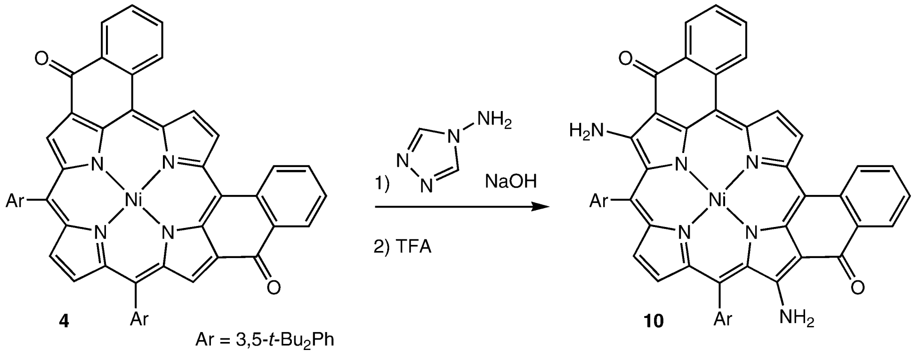
20 (from **10**): ^1H NMR: δ = 9.19, 8.06 (2s, 2+2H, pyrrole), 9.06 (dd, 2H, *J* = 8.0 and 1.1 Hz, cyclized phenyl), 8.05 (dd, 2H, *J* = 8.0 and ∼1 Hz, cyclized phenyl), 7.71 (ddd, 2H, *J* = 8.0, 8.0, and 1.1 Hz, cyclized phenyl), 7.55 (ddd, 2H, *J* = 8.0, 8.0, and 1.1 Hz, cyclized phenyl), 7.77 (t, 2H, *J* = 1.8 Hz, Ar H_{para}), 7.57 (broad d, 4H, *J* = 1.8 Hz, Ar H_{ortho}), 11.72, 5.94 (2 broad d, 2+2H, *J* = 4.0 Hz, NH_2), 1.41 (s, 36H, *t*-butyl). UV−vis: (CH_2Cl_2) λ_{max} = 356 (ϵ = 42 400), 410 (44 400), 540 (51 700), 588 (69 300), 720 (16 300), 772 (10 300) nm. Elem anal. Calcd for $C_{62}H_{58}N_{10}S_2Ni \bullet {}^1/_2H_2O$: C 73.08, H 5.84, N 8.25. Found: C 73.06, H 5.88, N 8.16.

21 (from **11**): ^1H NMR: δ = 8.76, 8.40 (2d, 1+1H, *J* = 4.5 Hz, pyrrole), 7.98 (s, 2H, pyrrole), 9.04 (dd, 1H, *J* = 8.0 and ∼1.5 Hz, cyclized phenyl), 7.50 (ddd, 1H, *J* = 8.0, 8.0, and ∼1.5 Hz, cyclized phenyl), 7.70 (ddd, 1H, *J* = 8.0, 8.0, and ∼1.2 Hz, cyclized phenyl), 8.13 (dd, 1H, *J* = 8.0 and ∼1.2 Hz, cyclized phenyl), 8.98 (dd, 1H, *J* = 8.0 and ∼1.5 Hz, cyclized phenyl), 7.53 (ddd, 1H, *J* = 8.0, 8.0, and ∼1.5 Hz, cyclized phenyl), 7.63 (ddd, 1H, *J* = 8.0, 8.0, and ∼1.5 Hz, cyclized phenyl), 8.17 (dd, 1H, *J* = 8.0 and ∼1.5 Hz, cyclized phenyl), ∼8.00−8.50 (very broad, 2H, Ar), 7.67 (t, 1H, *J* = 1.8 Hz, Ar), 8.06, 7.77, 7.09 (3t, 1+1+1H, *J* = 1.8 Hz, Ar), 12.40 (broad d, 1H, N−H), 11.70, 5.98 (2 broad d, 1+1H, *J* ∼ 5.0 Hz, N−H) 1.55, 1.29 (2s, 18+18H, *t*-butyl), one N−H not detected. UV−vis: (CH_2Cl_2) λ_{max} = 398 (ϵ = 58 000), 474 (42 000), 600 (67 000), 796 (9700) nm. Elem anal. Calcd for $C_{62}H_{58}N_6S_2Ni \bullet 2H_2O$: C 71.19, H 5.97, N 8.03. Found: C 71.12, H 5.66, N 7.82.

22 (from **12**): ^1H NMR (50 °C): δ = 8.97, 8.45 (2d, 2+2H, *J* = 4.8 Hz, pyrrole), 9.06 (dd, 2H, *J* = 8.0 and 1.1 Hz, cyclized phenyl), 8.11 (dd, 2H, *J* = 8.0 and 1.1 Hz, cyclized phenyl), 7.70 (ddd, 2H, *J* = 8.0, 8.0 and 1.1 Hz, cyclized phenyl), 7.54 (ddd, 2H, *J* = 8.0, 8.0, and 1.1 Hz, cyclized phenyl), 7.96, 7.71 (2t, 1+1H, *J* = 1.8 Hz, Ar H_{para}), 7.60−7.90 (very broad, 4H, Ar H_{ortho}), 11.94, 5.86 (2 broad d, 2+2H, NH_2), 1.48, 1.46 (2s, 18+18H, *t*-butyl). UV−vis: (CH_2Cl_2) λ_{max} = 358 (ϵ = 37 800), 404 (46 500), 436 (42 300), 490 (57 800sh), 516 (72 700), 726 (21 800sh), 772 (33 900), 821 (23 800) nm. Elem anal. Calcd for $NiC_{62}H_{58}N_{10}S_2 \bullet H_2O$: C 72.44, H 5.88, N 8.17. Found: C 72.70, H 5.96, N 8.16.

23 (from **13**): ^1H NMR: δ = 8.95, 8.38 (2d, 2+2H, *J* = 4.8 Hz, pyrrole), 9.08 (dd, 2H, *J* = 7.8 and ∼1.0 Hz, cyclized phenyl), 8.23 (dd, 2H, *J* = 7.8 and ∼1.0 Hz, cyclized phenyl), 7.75 (ddd, 2H, *J* = 7.8, 7.8, and ∼1.0 Hz, cyclized phenyl), 7.57 (ddd, 2H, *J* = 7.8, 7.8, and ∼1.0 Hz, cyclized phenyl), 7.82 (broad t, 2H, *J* = 1.8 Hz, Ar H_{para}), 7.40−7.80 (very broad, 4H, Ar H_{ortho}), 11.88, 5.98 (2 broad d, 2+2H, NH_2), 1.53 (s, 36H, *t*-butyl). UV−vis:

Scheme 1. Amination Reaction Leading to Bisenaminoketones (Shown Here on Compound **4**)



(CH_2Cl_2) λ_{max} = 362 (ϵ = 41 900), 396 (29 800), 468 (46 100sh), 508 (108 300), 728 (30 400), 765 (24 400), 827 (27 100) nm. Elem anal. Calcd for $C_{62}H_{58}N_6S_2Ni{\cdot}CH_3OH$: C 72.62, H 6.00, N 8.06. Found: C 72.77, H 5.97, N 7.63.

Electrochemical Studies. Spectroscopic grade dichloromethane was purchased from Merck, dried over molecular sieves (4 Å), and stored under argon prior to use. Electrochemical grade NBu_4PF_6 was purchased from Fluka and used as received. The electrochemical experiments were carried out at room temperature in dichloromethane containing 0.1 M NBu_4PF_6 in a three-electrode cell. The working electrode was either a glassy-carbon disk electrode (3 mm diameter) or a platinum-disk electrode (2 mm diameter) used either in motionless mode for cyclic voltammetry (CV: 10 $mV{\cdot}s^{-1}$ to 10 $V{\cdot}s^{-1}$) or as rotating disk electrode for rotating disk voltammetry (RDV). The electrochemical cell was connected to a computerized multipurpose electrochemical device AUTOLAB (Eco Chemie BV-Utrecht, The Netherlands) driven by *GPES* software running on a personal computer. All potentials are referenced to the ferrocene/ferricinium (Fc/Fc^+) couple used as an internal standard. The auxiliary electrode was a Pt wire, and a Pt wire was also used as a pseudo-reference electrode. The accessible potentials ranged from +1.2 to −2.4 V vs Fc/Fc^+ in dichloromethane.

Crystal Data for 10: $C_{62}H_{58}N_6NiO_2{\cdot}CH_2Cl_2$, M = 1062.84, triclinic, space group $P\bar{1}$; a = 13.563(2) Å, b = 13.818(2) Å, c = 17.639(5) Å, α = 70.870(5)°, β = 84.605(5)°, γ = 60.888(5)°, V = 2720(1) Å^3, Z = 2, D_c = 1.30 $g{\cdot}cm^{-3}$. A total of 10 121 ± h ± $k + l$ reflections was collected on a brown crystal of dimensions 0.10 × 0.06 × 0.06 mm^3, using a KappaCCD diffractometer, graphite-monochromated Mo Kα radiation, $2.5 < \theta < 29.99$, T = 173 K. Unique reflections numbering 5622 having $I > 3\ \sigma(I)$ were used to determine and refine the structure. Final results: R = 0.102, R_w = 0.127, GOF = 1.101, largest peak in final difference = 0.916 e·Å^{-3}.

Crystal Data for 23: $C_{124}H_{116}N_{12}Ni_2S_4{\cdot}CH_2Cl_2{\cdot}H_2O{\cdot}C_4H_8O$, M = 2195.12, monoclinic, space group $C2/c$; a = 29.5565(2) Å, b = 15.2293(1) Å, c = 30.1660(3) Å, β = 116.492(5)°, V = 12152.7(2) Å^3, Z = 4, D_c = 1.20 $g{\cdot}cm^{-3}$. A total of 18 275 ± h ± $k + l$ reflections was collected on a violet crystal of dimensions 0.10 × 0.08 × 0.08 mm^3, using a KappaCCD diffractometer, graphite-monochromated Mo Kα radiation, $2.5 < \theta < 30.06$, T = 173 K. Unique reflections numbering 12086 having $I > 3\ \sigma(I)$ were used to determine and refine the structure. Final results: R = 0.098, R_w = 0.129, GOF = 1.484, largest peak in final difference = 1.145 e·Å^{-3}.

Results and Discussion

Synthesis of Bisenaminoketones. Diketones **4**−**8** were obtained by the condensation of *o*-carbomethoxybenzaldehyde, 3,5-di-*tert*-butylbenzaldehyde, and pyrrole under Lindsey's conditions,[15] followed by metalation of the porphyrins with nickel(II), hydrolysis of the esters, transformation of the diacids into acid chlorides, and finally, an intramolecular Friedel−Crafts reaction. Diketone **9** was obtained following the same strategy, starting from an *o,o′*-dicyano-substituted *meso*-phenyl group. These diketones in our hands, we first tried to aminate these compounds with the reagents previously used for the amination of monofunctionalized porphyrins (hydrazine, tosylhydrazine, hydroxylamine, or hydroxylamine *O*-sulfonic acid).[8] Unfortunately, we obtained either complex mixtures or no reaction products instead of the expected bisenaminoketones.

Reaction with 4-amino-4H-1,2,4-triazole, an amination reagent described by Katritzky and Laurenzo,[16] allowed us to prepare all bisenaminoketones in good yields (56−74%). It was, however, necessary to add a strong Brønsted acid (such as trifluoroacetic acid) to favor the elimination of triazole after the 1,4-addition (see Scheme 1).

All nickel bisenaminoketones (see Chart 3) were able to be characterized by NMR. The amination of the pyrrolic positions was clearly established by the disappearence of the diketone pyrrolic singlet signal in ^{1}H NMR. In addition, the two N−H protons were well-separated (δ = 8.21 and 5.12 ppm for compound **10**) indicating an intramolecular hydrogen bond between one N−H and the carbonyl oxygen atom. In the electronic spectra of nickel bisenaminoketones **10**−**14** compared with those of the corresponding nickel diketones **4**−**9**, a hypsochromic shift was observed (except for compounds **7** and **12**). For example, the lowest energy bands for compound **4** and **10** were located at 736 and 710 nm, respectively.

We could finally obtain single crystals suitable for an X-ray diffraction study of compound **10** (shown in Figure 1). The nickel porphyrin is best described as ruffled. The nickel ion and the four pyrrolic nitrogen atoms are coplanar, and the four nickel to nitrogen distances are almost identical (1.90−1.91 Å). The intramolecular hydrogen bond between one N−H and the carbonyl oxygen expected from the NMR

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(15) Lindsey, J. S.; Schreiman, I. C.; Hsu, H. C.; Kearney, P. C.; Marguerettaz, A. M. *J. Org. Chem.* **1987**, *52*, 827. Littler, B. J.; Ciringh, Y.; Lindsey, J. S. *J. Org. Chem.* **1999**, *64*, 2864. Lindsey, J. S. In *The Porphyrin Handbook*; Kadish, K. M., Smith, K. M., Guilard, R., Eds; Academic Press: Boston, MA, 2000; Vol. 1, p 45.

(16) Katritzky, A. R.; Laurenzo, K. S. *J. Org. Chem.* **1986**, *51*, 5039. Katritzky, A. R.; Laurenzo, K. S. *J. Org. Chem.* **1988**, *53*, 3978.

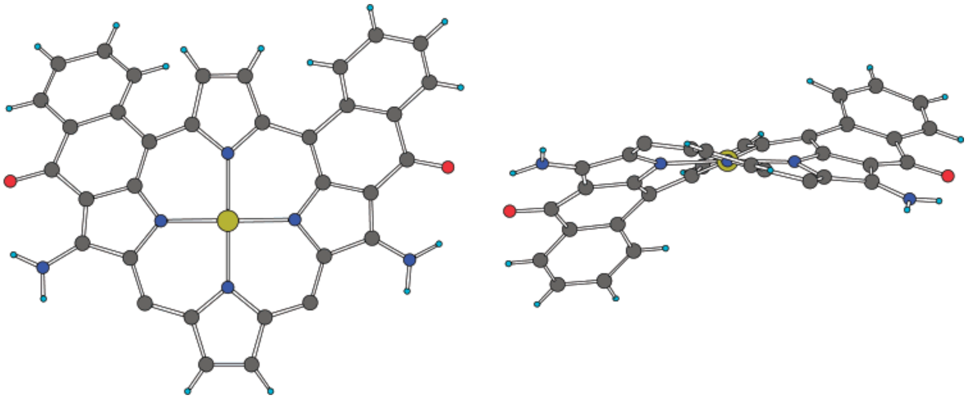
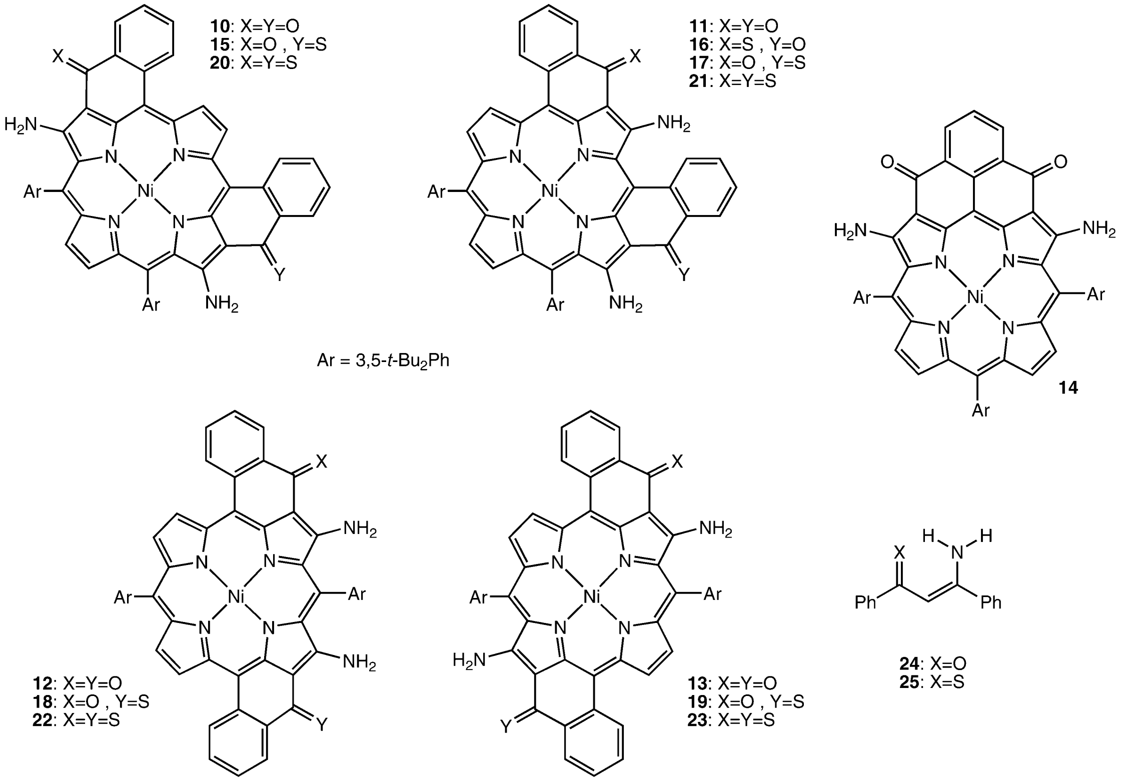


Figure 1. X-ray structure of nickel enaminoketone **10** (two *meso*-aryl groups omitted for clarity, two orthogonal views).

Chart 3. Structures of Nickel Porphyrins **10**−**23** and of Enamino(thio)ketone **24** (**25**)



data is indeed observed: the distance between the N−H hydrogen atom and oxygen is found equal to 2.3 Å. In addition, the six-membered rings formed by the atoms involved in the two enaminoketone functions (OCCCNH) are almost planar.

Thionation of Porphyrins Bearing Two Enaminoketone Groups. In the case of the monofunctionalized nickel porphyrins, we have shown that replacing enaminoketones by enaminothioketones gave much stronger complexes with soft metal ions.[12] Even dimers built around nickel(II) were stable enough to allow purification by chromatography. Therefore, it was obvious that the thionation of doubly functionalized nickel porphyrins could lead to more stable oligomers if the assembling was done with soft metal ions. Treatment of the bisenaminoketones with Lawesson's reagent in refluxing benzene led cleanly to bisenaminothioketones.[17] In addition, by controlling the amount of reagent and the progress of the reaction it was possible to isolate the monothionated analogue (see Scheme 2 for compound **10**).

The reaction mixture (compounds **10**, **15**, and **20** in the example shown) was easily purified by chromatography because replacement of the oxygen atom by sulfur induced a drastic decrease in polarity. In the case of the unsymmetrical compound **5**, two monofunctionalized isomers (compounds **16** and **17**) were isolated and their respective structures determined by ^{1}H NMR nuclear Overhauser effect experiments. In this way, we isolated and characterized five monothionated (compounds **15**−**19**) and four dithionated nickel porphyrins (compounds **20**−**23**) (see Chart 3).

The thionation of the enaminoketones could be easily confirmed from the ^{1}H NMR spectra. The two NH protons

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(17) Pedersen, B. S.; Schreibye, S.; Nilsson, N. H.; Lawesson, S. O. *Bull. Soc. Chim. Belg.* **1978**, *87*, 223. Cava, M. P.; Levinson, M. I. *Tetrahedron* **1985**, *41*, 5061.

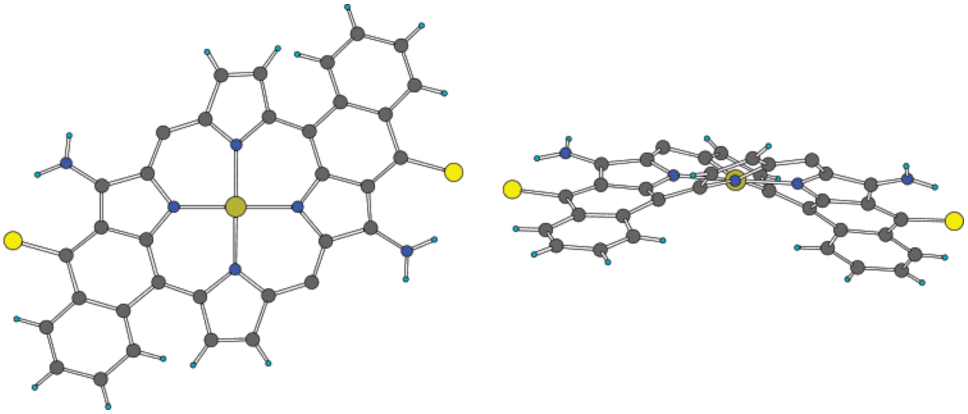
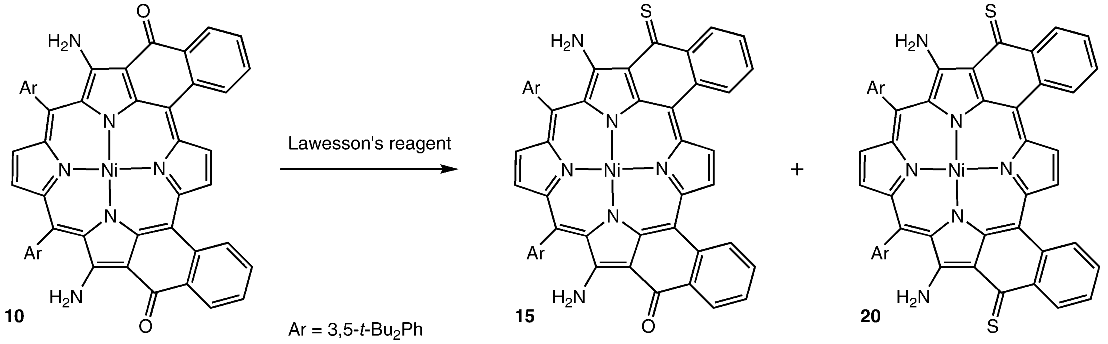


Figure 2. X-ray structure of compound **23** (two *meso*-aryl groups omitted for clarity, two orthogonal views).

Scheme 2. Thionation of Bisenaminoketone **10**



were even more differentiated in the case of the enaminothioketones. In compound **15**, for example (NO and NS chelating groups present), the signals were found at 8.21 and 5.10 ppm for the NO chelating group and at 11.77 and 5.97 ppm for the NS chelating group. The aromatic protons next to the NS chelating group were also shifted downfield (for compound **15**, 9.06 and 8.52 ppm, respectively, for the protons next to sulfur or oxygen). The replacement of oxygen by sulfur had also a dramatic influence on the electronic spectra of the nickel porphyrins. In the sequence shown in Scheme 2 (enaminoketone **10** giving compounds **15** and **20**), the lowest energy band was bathochromically shifted by ca. 30 nm for each replacement of oxygen by sulfur (from 710 to 742 and 772 nm). To compare these data with that of simpler compounds, we prepared the known enaminoketone **24**[18] and enaminothioketone **25**.[19] The replacement of oxygen by sulfur induced an even larger bathochromic shift (from $\lambda_{max} = 352$ nm for **24** to $\lambda_{max} = 412$ nm for **25**).

These chromophores (lowest energy bands λ_{max} of 796, 821, and 827 nm for compounds **21**−**23**) are quite unusual for monomeric nickel porphyrins (which absorb generally below 600 nm) and even for nickel porphyrins with extended π systems. The electronic data of all new compounds are summarized in Table 1. Two highly extended porphyrins described recently show absorbances in the near-infrared region up to over 1000 nm.[20a,b] However, in general, even nickel porphyrins with two additional fused aryl groups do not show such a large bathochromic shift (lowest energy band at λ_{max} of 636 nm for recently published examples).[20c,d]

In the case of bisenaminothioketone **23**, we could grow single crystals suitable for an X-ray diffraction study (see Figure 2). The porphyrin geometry is again ruffled. The nickel coordination is square planar with the four nickel to nitrogen bond lengths almost equal (from 1.89 to 1.91 Å). The intramolecular hydrogen bond lengths (N−H/S) are equal to 2.36 Å. As expected, the C═S bond is longer than the C═O bond in the enaminoketones (1.69 Å instead of 1.34 Å).

Electronic Properties and Electrochemical Studies. The electrochemical properties of nickel porphyrins are well-documented.[21] In general, the nickelporphyrins are oxidized in two one-electron steps and reduced in two one-electron steps (sometimes a third oxidation or reduction step might

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(18) Preparation of enaminoketone **24** according to Bredereck, H.; Gompper, R.; Morlock, G. *Chem. Ber*. **1957**, *90*, 942.

(19) Thionation of **24** was realized with Lawesson's reagent, and the spectroscopic data of **25** obtained in this way were identical to the ones described previously: Duguay, G. *C. R. Acad. Sci., Ser. C* **1975**, *281*, 1077.

(20) (a) Gill, H. S.; Harmjanz, M.; Santamaria, J.; Finger, I.; Scott, M. J. *Angew. Chem., Int. Ed*. **2004**, *43*, 485. (b) Kurotobi, K.; Kim, K. S.; Noh, S. B.; Kim, D.; Osuka, A. *Angew. Chem., Int. Ed*. **2006**, *45*, 3944. (c) Aihara, H.; Jaquinod, L.; Nurco, D. J.; Smith, K. M. *Angew. Chem., Int. Ed*. **2001**, *40*, 3439. (d) Nath, M.; Huffman, J. C.; Zaleski, J. M. *J. Am. Chem. Soc*. **2003**, *125*, 11484. (e) Fox, S.; Boyle, R. W. *Tetrahedron* **2006**, *62*, 10039. (f) Cammidge, A. N.; Scaife, P. J.; Berber, G.; Hughes, D. L. *Org. Lett*. **2005**, *7*, 3413. (g) Shen, D.-M.; Liu, C.; Chen, Q.-Y. *Chem. Commun*. **2005**, 4982. (h) Fox, S.; Boyle, R. W. *Chem. Commun*. **2004**, 1322. (i) Yamane, O.; Sugiura, K.-I.; Miyasaka, H.; Nakamura, K.; Fujimoto, T.; Nakamura, K.; Kaneda, T.; Sakata, Y.; Yamashita, M. *Chem. Lett*. **2004**, *33*, 40. (j) McCarthy, J. R.; Hyland, M. A.; Brückner, C. *Chem. Commun*. **2003**, 1738. (k) Tanaka, M.; Hayashi, S.; Eu, S.; Umeyama, T.; Matano, Y.; Imahori, H. *Chem. Commun*. **2007**, 2069. (l) Jasinski, S.; Ermilov, E. A.; Jux, N.; Röder, B. *Eur. J. Org. Chem*. **2007**, 1075.

Table 1. Electronic Spectra of Nickel Porphyrins

compound	wavelength ($\lambda > 400$ nm)	optical gap (eV)
4	412, 480, 524, 736	1.68
10	480, 512, 544, 618, 710	1.74
15	468, 514, 566, 678, 742	1.67
20	410, 540, 588, 720, 772	1.60
5	402, 500, 540, 646, 750	1.65
11	438, 536, 646, 728	1.70
16	452, 570, 668, 766	1.61
17	458, 570, 766	1.61
21	474, 600, 796	1.55
6	480, 516, 738, 826	1.50
7	420, 490, 550, 726	1.70
12	416, 502, 672, 703, 758	1.63
18	442, 510, 700, 740, 794	1.56
22	404, 436, 490, 516, 726, 772, 821	1.51
8	472, 698, 776	1.59
13	488, 667, 757	1.63
19	436, 466, 504, 700, 738, 796	1.55
23	468, 508, 728, 765, 827	1.50
9	482, 522, 698	1.77
14	400, 492, 644, 682	1.82

be observed, but close to the electrolyte oxidation or reduction potential). In most cases, the initial oxidations and reductions are localized on the aromatic π system and do not involve the nickel(II) ion. We have studied by cyclic voltammetry the electrochemical behavior of the porphyrins described in this Article and of the six isomeric diketones **4**−**9** described previously.[13] All data are summarized in Table 2.

In the case of the first nickelporphyrins studied, i.e., diketones **4**−**9**, instead of the expected usual reversible two oxidation and reduction steps, we observed several additional steps indicative of either the participation of the reducible keto functionalities to the reduction steps (especially for diketone **6**) or an aggregation due to the flattening of the conjugated system of some diketones (for compounds **5** and **8**). A good agreement (except for compound **9** whose low solubility led to electrode inhibition) was found between the optical gap values and the electrochemical gap between the first oxidation and the first reduction step.

Diketone **6** showed quite unusual optical properties for a monomeric nickelporphyrin ($\lambda_{max} = 826$ nm), and the close proximity of the two oxygen atoms ($d_{O-O} = 2.86$ Å) led to an easy protonation of the diketone (quantitative protonation was observed with *p*-toluenesulfonic acid), reminiscent of the one found for 1,8-bis(dialkylamino)naphthalene (proton sponge).[13] This conjugated 1,4-diketone might also be seen as a quinone, and the electrochemical results validated this comparison. The reduction of compound **6** occurred in four one-electron steps (see the cyclic voltammetry curves in Figure 3), with the second one being irreversible even at high scan rates (up to 5 V/s).

The first two reduction steps were similar to the reduction of a quinone, as detailed in Scheme 3. After the uptake of the first electron, protonation of the radical anion occurred, leading to a species which was further reduced by one electron. Protonation gave the neutral nickel dihydroxyporphyrin, which then underwent the expected two one-electron reduction steps (at more cathodic potentials) observed for nickelporphyrins.

This behavior was confirmed by spectroelectrochemical experiments (see the Supporting Information for spectra and experimental conditions). Coulometry at potentials R_1 or R_2 (see arrows in Figure 3) left the porphyrin core intact (no significant decrease of the Soret band) whereas the reduction at R_3 led to a large intensity decrease of the Soret band indicative of the generation of the nickel porphyrin radical anion delocalized over the aromatic core. The dihydroxy compound obtained after the two-electron reduction gave back the initial diketone only if the reoxidation was carried out at a much more positive potential (at O_1, see arrow in Figure 3). Reduction of diketone **6** could also be carried out chemically with sodium dithionite, leading to a compound possessing the same electronic spectra as the one resulting from the electrochemical reduction at potential R_2.

A quinone-like behavior also seemed to occur on reduction of compound **5** (see Figure 4, cyclic voltammetry of compound **5**), but in this case the nickel porphyrin was reduced first (see the Supporting Information; the spectroelectrochemical study clearly showed the generation of the porphyrin radical anion after the first reduction step). The fourth reduction step was irreversible due to the protonation steps involved, as seen before for the first two reduction waves of compound **6.**

Compounds **5** and **8** presented an unusual behavior during oxidation, i.e., the splitting of the first oxidation step into two waves with an intensity approximately corresponding to that of 0.5 electron (see Figures 4 and 5). However, the relative intensities of the two waves varied strongly with the scan rate used, indicative of an association due to π stacking of two entities (porphyrin−porphyrin or porphyrin−porphyrin radical cation). We had never before observed significant π stacking between neutral molecules for this type of compounds (NMR or UV−vis measurements), but the concentrations used and the high ionic strength required to run the electrochemical experiments prompted us to check by NMR the presence or absence of π stacking between neutral molecules under conditions close to those of the electrochemical conditions.

NMR experiments were carried out on compound **5** by varying the nickel porphyrin concentration (from 6.10^{-5} to 3.10^{-3} mol/L, which was close to the solubility limit) or by varying the amount of supporting electrolyte present for a given concentration of nickelporphyrin (NBu_4PF_6 from 0 to 8.10^{-2} mol/L with 10^{-3} mol/L of nickel porphyrin). In all cases, the chemical shifts measured did not change significantly (≤ 0.02 ppm chemical shift differences were observed), demonstrating clearly the absence of association due to π stacking between two neutral molecules. Therefore, the association probably takes place between the radical cation generated at the anode and a neutral molecule present in close proximity. Under our conditions, this kind of association seems to be almost quantitative in the medium used since

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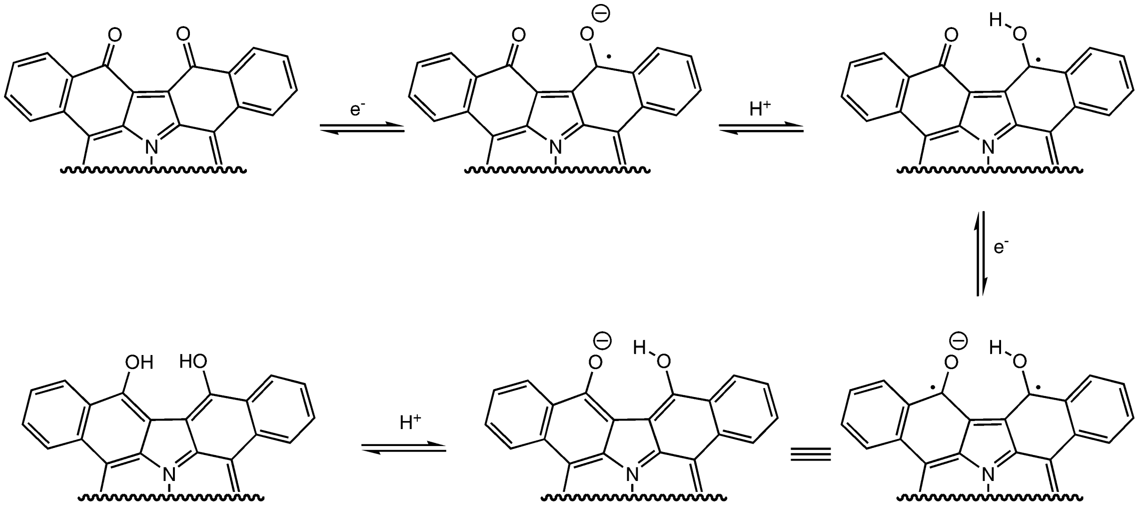
Table 2. Cyclic Voltammetry Data[a]

compound	reduction E'° in V vs Fc/Fc^{+} (number of electrons exchanged)				oxidation E'° in V vs Fc/Fc^{+} (number of electrons exchanged)		
4	−2.12(1i)	−1.84(1)	−1.33(1)	−0.99(1)	0.71(1)		1.12(1i)
5	−2.15(li)	−1.77(1)	−1.35(1)	−1.00(1)	0.64(0.5)	0.73(0.5)	1.05(1)
6	−2.18(1)	−1.73(1)	−1.17(1i)	−0.78(1)	0.70(1)		1.12(1i)
7		−1.82(1)	−1.32(1)	−1.01(1)	0.72(1)		1.08(1i)
8			−1.16(1)	−0.88(1)	0.64(0.5)	0.75(0.5)	1.04(1)
9[b]		−2.11	−1.29	−0.95	0.94		
10	−2.23(1)	−2.01(1)	−1.67(1)	−1.37(1)	0.40(1)	0.83(1)	
11	−2.19(1)	−2.00(1)	−1.52(1)	−1.21(1)	0.39(1)	0.69(1)	
12		−2.37(i)	−1.49(1)	−1.15(1)	0.40(1)	0.81(1)	1.26(i)
13		−2.38(i)	−1.51(1)	−1.16(1)	0.38(1)	0.69(1)	
14		−2.41(1)	−1.66(1)	−1.31(1)	0.41(0.5)	0.52(0.5)	0.83(1)
15	−2.20(1i)	−1.92(1i)	−1.52(1)	−1.25(1)	0.38(i)	0.68(1)	
16	−2.25(i)	−1.87(1i)	−1.40(1)	−1.07(1)	0.37(1i)	0.72(1i)	0.87(1i)
17	−2.19(1)	−1.91(1)	−1.38(1)	−1.15(1)	0.39(1i)	0.68(1)	0.80(1)
18		−2.19(1)	−1.35(1)	−1.05(1)	0.41(i)	0.65(1)	0.76(1)
19		−2.23(1)	−1.32(1)	−1.00(1)	0.39(i)	0.69(1)	0.84(1)
20	−2.13(2i)	−1.74(1)	−1.40(1)	−1.17(1)	0.37(i)	0.62(i)	0.97(i)
21	−2.11(i)	−1.75(1)	−1.33(1)	−1.05(1)	0.39(i)	0.66(i)	0.81(1)
22	−2.15(i)	−2.00(1)	−1.23(1)	−0.96(1)	0.42(i)	0.65(i)	0.89(2)
23		−2.04(1)	−1.24(1)	−0.95(1)	0.36(i)	0.65(i)	1.00(i)

[a] Experimental conditions: see Experimental Section. The number of exchanged electrons is indicated in parenthesis following the peak potential when it could be determined accurately and confirmed by RDV experiments. All reduction or oxidation steps are electrochemically reversible ($\Delta E_p \approx 60-80$ mV) except when indicated by the letter "i" next to the number of exchanged electrons. [b] Approximative values due to the low solubility of compound **9**.

Scheme 3. Proposed Detailed Electron and Proton Uptake for Compound **6**



the two electrochemical waves were of equal intensity (0.5 + 0.5 electron at the scan rate of 100 mV/s). This phenomenon is not very common but is known for compounds where large flat aromatic systems are present. For example, for the ruthenium complexes of eilatin or isoeilatin (extended bipyridines), an analogous splitting (two waves accounting for 0.5 electron) was observed for the first reduction wave (Ru^{II}/Ru^{I}).[22] Splitting of the first oxidation wave was also described for several metal complexes (M = Mn, Co, Ni, Cu) of octaethylcorrole.[23] The authors studied extensively the mechanism of the oxidations and came to the conclusion that, in these examples, the splitting was due to the association of two neutral molecules prior to oxidation. The structure of the corrole used (octaethyl-substituted corrole) favored this type of association, since the molecules might be roughly described as flat. In our case, the nickel porphyrins are substituted in at least two meso positions with 3,5-di-*tert*-butyl phenyl groups, thus making such associations between two neutral molecules much less favorable. However, association between one neutral and one charged nickel porphyrin should be much stronger and is known even for encumbered meso-substituted tetraarylporphyrins. X-ray structures have been reported for mixed-valence species (one neutral and one radical cation molecule) or between two radical cations, leading to dimeric entities or even to polymeric materials.[24] Therefore, a strong interaction between a radical cation generated at the anode and the starting material is the most plausible explanation for the peculiar behavior observed for some compounds during the initial oxidation step.

In the case of the bisenaminoketones **10**−**14**, all potentials are considerably shifted toward negative potentials when

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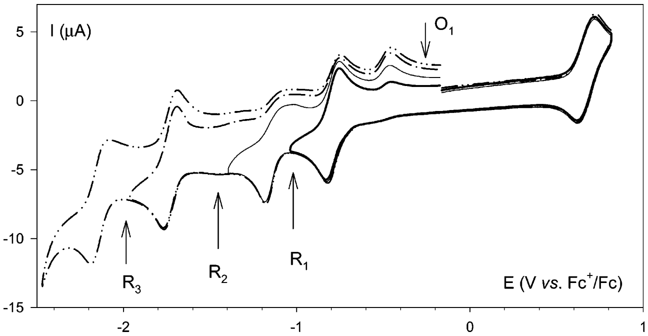

Figure 3. Cyclic voltammetry of compound **6** (see Experimental Section for conditions).

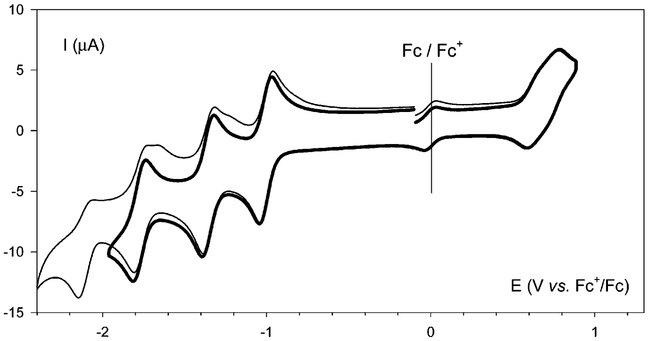

Figure 4. Cyclic voltammetry of compound **5** (see Experimental Section for conditions).

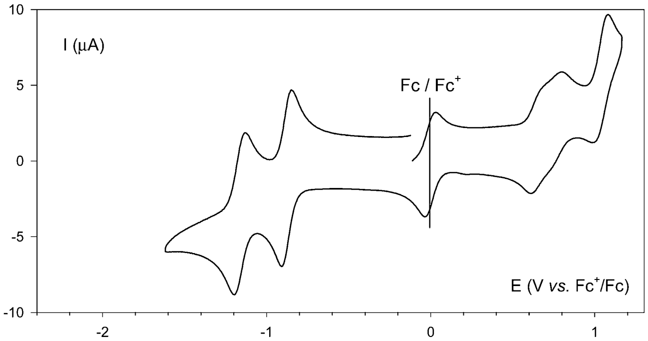

Figure 5. Cyclic voltammetry of compound **8** (see Experimental Section for conditions).

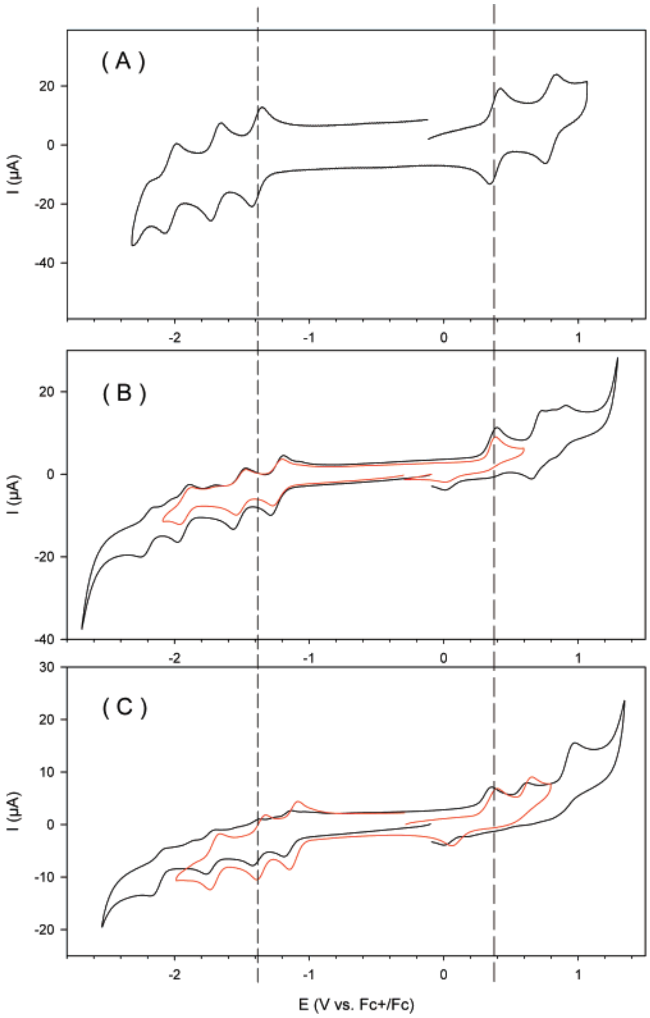

Figure 6. Comparison of compounds **10**, **15**, and **20** (cyclic voltammetry curves A, B, and C respectively. See Experimental Section for conditions). For the thionated compounds **15** and **20**, different scanning limits shows the irreversibility of the first oxidation waves.

compared with those of the analogous diketones **4**−**9** (for example, a cathodic shift of 380 mV was observed for the first reduction potential of enaminoketone **10** when compared with the first reduction potentials of diketone **4**), except for compounds **7** and **12**. These electrochemical data correlate with the shifts of their respective electronic spectra.

The opposite is true after replacement of the oxygen atom by sulfur. In all series of compounds, the general trend was the same as the one observed for the series shown in Figure 6 (compounds **10**, **15**, and **20**). The values of the first oxidation potentials did not vary much within the same series. By contrast, the first reduction potential is anodically shifted by approximatively 100 mV for each replacement of an oxygen atom by sulfur (see in the Supporting Information a schematic representation of the potential evolution for three series of compounds).

The splitting of the first oxidation waves was no longer observed for the bisenaminoketones **10**−**13** or their thionated analogues (except for the sparingly soluble compound **14**, but the low solubility did not allow us to study this compound correctly). As soon as one thioenaminoketone moiety was present in the structure, the first oxidation potential was always irreversible, as observed before for the monofunctionalized nickel porphyrins.[12]

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Conclusion

For all compounds studied (**4**−**23**), the electrochemical data were in good agreement with the electronic spectra recorded in dichloromethane. Some compounds showed, in addition to the classical two oxidation and two reduction waves generally measured for nickel porphyrins, quinone-like (two electrons + two protons) reduction steps, which were observed before or after the porphyrin core reduction depending on the structure of the extended nickel porphyrins. In addition, some compounds showed a splitting of the first oxidation waves that might be due to the stacking of the generated radical cation with the starting neutral molecule.

For all different structures, the electronic influence might be summarized by the following: (a) Bisamination of the diketones led to a hypsochromic shift in the electronic spectra, an increase of the HOMO−LUMO gap, and a cathodic shift of all electrochemical potentials (with the exception of compounds **7** and **12**). (b) Thionation of the enaminoketones led to a bathochromic shift, a decrease of the HOMO−LUMO gap, and an anodic shift of all reduction potentials.

These nickelporphyrins bearing two external enamino(thio)ketone functionalities are well-suited for the construction of oligoporphyrins linked by metal ions. Furthermore, the presence of a hard external ligand (NO chelate) and a soft ligand (NS chelate) in the same molecules should allow selective complexation of soft or hard metal ions on each site of the porphyrins. This should permit much more efficient and elegant synthetic pathways toward oligomers than the one used previously with the bis NO chelates.

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Supporting Information Available: CV voltammetry and spectroelectrochemical studies of compounds **5** and **6**; evolution of the reduction and oxidation potential for three series of compounds in PDF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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