Porphyrazinehexamines and Dinitroporphyrazines: Synthesis, Characterization, and Complementary Electrochemistry

Hanlin Nie,[†] Anthony G. M. Barrett,*[,‡] and Brian M. Hoffman*[,†]

Department of Chemistry, Northwestern University, Evanston, Illinois 60208, and Department of Chemistry, Imperial College of Science, Technology and Medicine, London SW7 2AY, U.K.

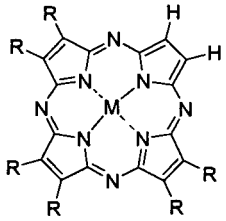
Received May 13, 1999

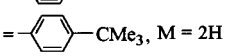
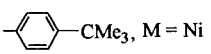
Unsymmetrical porphyrazines, M[pz(H)$_2$(R)$_6$], with three substituted pyrroles (substituents, R = −NMe$_2$, propyl, or 4-*tert*-butylphenyl) at the periphery and one unsubstituted pyrrole have been synthesized from inexpensive and readily available materials. Linstead crossover macrocyclization of **8** with **9**, **11**, and **12** gave pigments **1**, **3**, and **5**, respectively. Subsequent demetalation by treatment with TFA gave free-base porphyrazines **2**, **4**, and **6**. Generally, pyrrolines **11** and **12** are better co-cyclization partners and give higher yields for the desired unsymmetrical porphyrazines compared to maleonitriles **9** and **10** when co-cyclized with **8**. Nickel porphyrazine **7** was obtained by reaction of **6** with Ni(OAc)$_2$ in chlorobenzene and dimethylformamide. Both free-base and nickel porphyrazines (**6** and **7**) were readily nitrated by nitrogen dioxide in CH_2Cl_2, yielding dinitroporphyrazines **18** and **19**, respectively. Electrochemical studies have shown that porphyrazinehexamine **2** is easy to oxidize, having the first oxidation at $E_{1/2} = -0.18$ V, which is 0.91 and 1.04 V lower than that of **4** and **6**, respectively. Dinitroporphyrazine **18**, however, displays a 0.6 V of cathodic shift for the two reversible reduction waves compared to those observed for the parent porphyrazine **6**.

Introduction

Peripherally functionalized porphyrazines (tetraazaporphyrins) and related macrocycles can bind multiple metal ions, having the potential to exhibit novel magnetic and electronic properties and to serve as building blocks in the assembly of higher order polymetallic arrays.[1] Functionalization with a wide range of different β-substituents can provide porphyrazines with novel features and greatly enhanced solubility compared to their phthalocyanine counterparts. Recently, we reported the synthesis and novel physical properties of porphyrazines with peripheral heteroatom functionality, including thiolates,[2−6] dialkylamines,[6−10] and alkoxy moieties[6,11] and the star, solitaire, and gemini metal complexes. All these porphyrazines were totally functionalized at the periphery, with alkyl or aryl moieties attached to the pyrrole β-carbons that did not bear a heteroatom. Herein we report the first preparation of unsymmetrical porphyrazines with a single unsubstituted pyrrole on the macrocycle (Chart 1) and their nitration reactions to provide dinitroporphyrazines.

Chart 1



1 R = -NMe$_2$, M = Mg
2 R = -NMe$_2$, M = 2H
3 R = Pr, M = Mg
4 R = Pr, M = 2H
5 R =  M = Mg
6 R =  M = 2H
7 R =  M = Ni

Results and Discussion

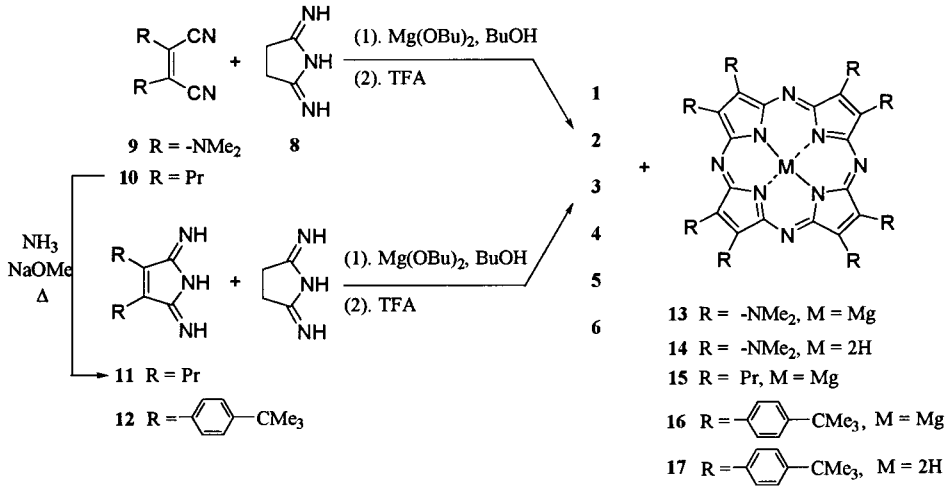
Synthesis of Macrocycles. The general synthesis is shown in Scheme 1. 3,4-Dipropylpyrroline-2,5-diimine (**11**) was prepared from dipropylmaleonitrile (**10**) by passing NH_3 through the methanol solution at reflux for

[†]Northwestern University.
[‡]Imperial College.

(1) *Phthalocyanines: Properties and Applications*; Leznoff, C. C., Lever, A. P. B., Eds.; VCH: New York, 1989; Vols. 1 and 2.
(2) Velázquez, C. S.; Fox, G. A.; Broderick, W. E.; Andersen, D. A.; Anderson, O. P.; Barrett, A. G. M.; Hoffman, B. M. *J. Am. Chem. Soc.* **1992**, *114*, 7416−7424.
(3) Velázquez, C. S.; Baumann, T. F.; Olmstead, M. M.; Hope, H.; Barrett, A. G. M.; Hoffman, B. M. *J. Am. Chem. Soc.* **1993**, *115*, 9997−10003.
(4) Sibert, J. W.; Baumann, T. F.; Williams, D. J.; White, A. J. P.; Barrett, A. G. M.; Hoffman, B. M. *J. Am. Chem. Soc.* **1996**, *118*, 10487−10493.
(5) Baumann, T. F.; Nasir, M. S.; Sibert, J. W.; White, A. J. P.; Olmstead, M. M.; Williams, D. J.; Barrett, A. G. M.; Hoffman, B. M. *J. Am. Chem. Soc.* **1996**, *118*, 10479−10486.
(6) Forsyth, T. P.; Williams, D. B. G.; Montalban, A. G.; Stern, C. L.; Barrett, A. G. M.; Hoffman, B. M. *J. Org. Chem.* **1998**, *63*, 331−336.
(7) Mani, N. S.; Beall, L. S.; Miller, T.; Anderson, O. P.; Hope, H.; Parkin, S. R.; Williams, D. J.; Barrett, A. G. M.; Hoffman, B. M. *J. Chem. Soc., Chem. Commun.* **1994**, 2095−2096.
(8) Montalban, A. G.; Lange, S. J.; Beall, L. S.; Mani, N. S.; Williams, D. J.; White, A. J. P.; Barrett, A. G. M.; Hoffman, B. M. *J. Org. Chem.* **1997**, *62*, 9284−9289.
(9) Lange, S. J.; Nie, H.; Stern, C. L.; Barrett, A. G. M.; Hoffman, B. M. *Inorg. Chem.* **1998**, *37*, 6435−6443.
(10) Beall, L. S.; Mani, N. S.; White, A. J. P.; Williams, D. J.; Barrett, A. G. M.; Hoffman, B. M. *J. Org. Chem.* **1998**, *63*, 5808−5817.
(11) Cook, A. S.; Williams, D. B. G.; White, A. J. P.; Williams, D. J.; Lange, S. J.; Barrett, A. G. M.; Hoffman, B. M. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 760−761.

10.1021/jo9907890 CCC: $18.00
Published on Web 08/13/1999

Scheme 1



15 h. We have found that heterocycle **11** tends to slowly hydrolyze and oligomerize on standing in methanol or chloroform solution. Thus, the crude sample of **11** that was relatively pure by ^{1}H NMR spectroscopy was used without further purification. 2,5-Diiminopyrrolidine (**8**) was co-macrocyclized with bis(dimethylamino)maleonitrile (**9**) using $Mg(OBu)_2$ in butanol at reflux. The resulting pigment, which contained both the unsymmetrical porphyrazine, $Mg[pz(H)_2(NMe_2)_6]$ (**1**), and the symmetrical porphyrazine $Mg[pz(NMe_2)_8]$ (**13**), was allowed to react with trifluoroacetic acid under a nitrogen atmosphere in the dark, yielding the free-base porphyrazines $H_2[pz(H)_2(NMe_2)_6]$ (**2**) and $H_2[pz(NMe_2)_8]$ (**14**), which were separated by chromatography. In a typical cyclization reaction, 5 equiv of dinitrile **9** was co-cyclized with 2,5-diiminopyrrolidine (**8**) and the desired macrocycle **2** was obtained as a purple solid in 5% overall yield following demetalation.

The magnesium porphyrazine **3** was first prepared by Linstead macrocyclization[12] of 2,5-diiminopyrrolidine (**8**) with 5 equiv of dipropylmaleonitrile (**10**) under the same conditions as described for **1**. The cyclization products, including porphyrazine **3** and $Mg[pz(Pr)_8]$ (**15**),[9] were fairly soluble in chloroform and were separated by chromatography, giving porphyrazine **3** in 3% yield. A much more efficient synthesis of porphyrazine **3** was achieved by co-macrocyclization of 2,5-diiminopyrrolidine (**8**) with 3,4-dipropylpyrroline-2,5-diimine (**11**). The Linstead cyclization of 2,5-diiminopyrrolidine (**8**) with only 3.5 equiv of pyrroline **11** gave porphyrazine **3** in an average of 17% yield after chromatography. The magnesium complex, $Mg[pz(H)_2(Pr)_6]$ (**3**), was demetalated by treatment with trifluoroacetic acid and chromatographed, yielding the free-base porphyrazine $H_2[pz(H)_2(Pr)_6]$ (**4**) (91%).

Porphyrazine **5** was synthesized by co-cyclization of 2,5-diiminopyrrolidine (**8**) with 3.5 equiv of 3,4-bis(4-(*tert*-butyl)phenyl)pyrroline-2,5-diimine (**12**) under similar conditions as described for the synthesis of **3**. The two major products of the reaction, the unsymmetrical porphyrazine $Mg[pz(H)_2(Ar)_6]$ (**5**, Ar = 4-*tert*-butylphenyl) (19% yield) and the symmetrical compound $Mg[pz(Ar)_8]$ (**16**), were separated by chromatography. The free base **6** (95% yield) was obtained by demetalation of magnesium complex **5** with trifluoroacetic acid and purified by chromatography. A dramatic decrease of solubility in dichloromethane and hexanes upon demetalation of magnesium porphyrazines, especially for the free base porphyrazine $H_2[pz(Ar)_8]$ (**17**), made it easier to purify the desired unsymmetrical porphyrazine by chromatography prior to demetalation.

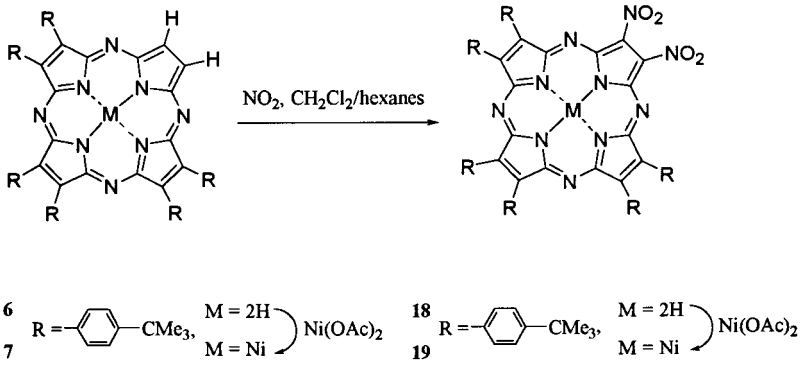
As we showed previously,[9] the yield of an unsymmetrical porphyrazine such as $Mg[pz(H)_2(Ar)_6]$ depends on the ratio of the two cyclization partners and, more importantly, on their relative reactivities. A typical overall yield for the unsymmetrical porphyrazine $H_2[(H)_2(R)_6]$ (**2**, R = $-NMe_2$ or **4**, R = Pr) was only 2−5% from 2,5-diiminopyrrolidine (**8**) when the maleonitrile **9** or **10** was used as the co-macrocyclization partner, whereas the equivalent reactions with pyrroline **11** or **12** gave **4** or **6** in much higher overall yields (15−18%).

The nickel(II) complex **7** was prepared readily by a reaction of the free-base porphyrazine **6** with 10 equiv of nickel acetate in a mixture of chlorobenzene and dimethylformamide (3:1) at 100 °C. The metalation process was monitored by UV−vis spectroscopy and stopped when the optical spectrum showed the completion of the reaction (24 h). Porphyrazine **7** was obtained in 98% yield following chromatography.

Nitration by Nitrogen Dioxide. Treatment of porphyrazine **6** in CH_2Cl_2 with a solution of nitrogen dioxide in hexanes at room temperature resulted in the rapid formation, as monitored by UV−vis spectroscopy, of dinitroporphyrazine **18**, which was isolated in 90% yield (Scheme 2) following chromatography. Subsequent reaction with nickel(II) acetate in chlorobenzene and dimethylformamide (3:1) at 100 °C gave nickel(II) dinitroporphyrazine **19** (95%), which was also prepared by direct nitration of nickel(II) porphyrazine **7** with nitrogen dioxide (85%). ^{1}H NMR spectroscopy revealed that both **18** and **19** retained the D_{2h} symmetry as the parent porphyrazines **6** and **7**, and the absence of NMR signals for the two β-pyrrolic hydrogen atoms on the parent porphyrazines showed that the electrophilic aromatic nitration reaction occurred at the periphery. The nickel(II) porphyrazine **7** and the dinitroporphyrazines **18** and **19** have much lower solubilities compared to porphyrazines **1**−**6**, which prevented the recording of ^{13}C NMR spectra for these compounds.

(12) Linstead, R. P.; Whalley, M. *J. Chem. Soc.* **1952**, 4839−4844.

Scheme 2



Unlike porphyrin analogues such as tetrakis(2,6-dichlorophenyl)porphyrins, which were nitrated with fuming nitric acid[13] and acetyl nitrate,[14] both free base and nickel(II) porphyrazines (**2**, **4**, **6** and **7**) underwent decomposition when treated with nitric acid. However, the selectivity and efficiency for the nitration of porphyrazines **6** and **7** by nitrogen dioxide was high compared to that for the related porphyrins,[15−17] where a mixture of mononitro- and dinitroporphyrins is obtained unless stringent precautions are taken. Interestingly, treatment of **4** with nitrogen dioxide gave a mixture of products as the result of nitration at the unsubstituted pyrrole β-carbons and at the α-carbons of the propyl substituents (^{1}H NMR). Such benzylic nitration using nitrogen dioxide is precedented to take place by a hydrogen atom abstraction pathway.[18]

Nitrogen dioxide is known to react with a variety of arenes, giving the corresponding nitro derivatives.[19] Kinetic studies of the reaction of nitrogen dioxide in solution with phenols[20−23] is consistent with a mechanism involving initial hydrogen atom abstraction and subsequent reaction of phenoxy radical with NO_2. However, nitration of polycyclic aromatic hydrocarbons (PAHs) by nitrogen dioxide in dichloromethane most probably occurs via an electron-transfer (ET) pathway.[24,25] NO^+ [$E° = 0.87$ V vs Fc^+/Fc][26] was proposed to be the primary ET oxidant of a PAH using nitrogen dioxide in dichloromethane, which contains N_2O_4, NO_2, and $NO^+NO_3^-$, since the redox potential of $NO_2^•$ itself in dichloromethane [$E°$ ($NO_2^•/NO_2^-$) = −0.39 V vs Fc^+/Fc][26] is not high enough to oxidize PAH's.[25] As shown in Table 1, both free-base porphyrazine **6** ($E_{1/2}$ = 0.86 V vs Fc^+/Fc) and nickel(II) complex **7** ($E_{1/2}$ = 0.83 V vs Fc^+/Fc) should be oxidized to the porphyrazine π-cation radical by the NO^+ in a solution of nitrogen dioxide in dichloromethane. Formation of a cation radical as the first step of nitration also was proposed to occur in the nitration of metalloporphyrins.[17] It is resonable to infer that the mechanism of nitration involves the initial oxidation of the porphyrazines by NO^+ followed by radical combination of the porphyrazine π-cation radical with $NO_2^•$ and subsequent proton loss.[15]

Table 1. Electrochemical Data in Dichloromethane (Volts vs Fc^+/Fc)[a]

	$E_{1/2}$ (ΔE_p, mV)			
compd	Pz^{2+}/Pz^+	Pz^+/Pz	Pz/Pz^{-1}	Pz^{-1}/Pz^{-2}
8	−0.03 (100)	−0.18 (100)	−1.44 (104)	−1.74 (130)
12		0.73 (110)	−1.26 (82)	−1.67 (82)
15		0.86 (82)	−1.05 (80)	−1.42 (74)
17		0.83 (160)	−1.16 (90)	−1.58 (110)
18			−0.47 (80)	−0.82 (80)

[a] Measured in solutions containing ca. 10^{-3} M of compound and 0.1 M [$N(n\text{-}C_4H_9)_4$]PF_6 supporting electrolyte at a Pt disk working electrode with a scan rate of 110 mV s^{-1}.

Treatment of porphyrazinehexamine **2** in dichloromethane with nitrogen dioxide led to a rapid decomposition that was probably due to irreversible oxidation of the macrocycle by nitrogen dioxide. Irreversible oxidation of **2** also occurred upon reaction with osmium tetroxide or *m*-chloroperoxybenzoic acid.

Electronic Absorption Spectra. The UV−vis spectra of **2**, **4**, **6**, **7**, **18**, and **19** are shown in Figure 1. The nickel(II) porphyrazine, **7**, exhibits an intense B (Soret) band at λ_{max} = 343 nm and a Q band at λ_{max} = 613 nm. The spectrum of the free base porphyrazine **6** with the same peripheral substituents is qualitatively similar, but with the expected[27,28] split Q band having Q_x and Q_y absorbances at 586 and 656 nm (λ_{max}). The absorption bands at λ_{max} 467 and 435 nm are assigned to the n−π* transitions of the nonbonding electrons on the meso nitrogen atoms to the macrocycles **6** and **7**, respectively. The propyl-substituted porphyrazine, **4**, displays an electronic absorption spectrum with a split Q band at

(13) Bartoli, J. F.; Battioni, P.; Foor, W. R. D.; Mansuy, D. *J. Chem. Soc., Chem. Commun.* **1994**, 23−24.
(14) Ozette, K.; Leduc, P.; Palacio, M.; Bartoli, J. F.; Barkigia, K. M.; Fajer, J.; Battioni, P.; Mansuy, D. *J. Am. Chem. Soc.* **1997**, *119*, 6442−6443.
(15) Catalano, M. M.; Crossley, M. J.; Harding, M. M.; King, L. G. *J. Chem. Soc., Chem. Commun.* **1984**, 1535−1536.
(16) Crossley, M. J.; Govenlock, L. J.; Prashar, J. K. *J. Chem. Soc., Chem. Commun.* **1995**, 2379−2380.
(17) Crossley, M. J.; King, L. G.; Newsom, I. A.; Sheehan, C. S. *J. Chem. Soc., Perkin Trans. 1* **1996**, 2675−2684.
(18) Titov, A. I. *Tetrahedron* **1963**, *19*, 557−580.
(19) Olah, G. A.; Malhotra, R.; Narang, S. C. *Nitration, Methods and Mechanism*; VCH: New York, 1989.
(20) Coombes, R. G.; Diggle, A. W.; Kempsell, S. P. *Tetrahedron Lett.* **1994**, *35*, 6373−6376.
(21) Coombes, R. G.; Diggle, A.; Kempsell, S. P. *Tetrahedron Lett.* **1986**, *27*, 2037−2040.
(22) Brunton, G.; Cruse, H. W.; Riches, K. M.; Whittle, A. *Tetrahedron Lett.* **1979**, 1093−1094.
(23) Fischer, A.; Mathivanan, N. *Tetrahedron Lett.* **1988**, *29*, 1869−1872.
(24) Eberson, L.; Radner, F. *Acta Chem. Scand., Ser. B* **1985**, *39*, 357−374.
(25) Eberson, L.; Radner, F. *Acta Chem. Scand., Ser. B* **1985**, *39*, 343−356.
(26) For comparison, the electrochemical data in dichloromethane that were originally reported as $E°$ vs NHE were converted to E vs Fc^+/Fc using $E = E° - 0.64$.
(27) Gouterman, M. In *The Porphyrins*; Dolphin, D., Ed.; Academic Press: New York, 1978; Vol. 3, pp 1−165.
(28) Kobayashi, N.; Konami, H. In *Phthalocyanines: Properties and Applications*; Leznoff, C. C., Lever, A. P. B., Eds.; VCH: New York, 1996; Vol. 4, pp 343−404.

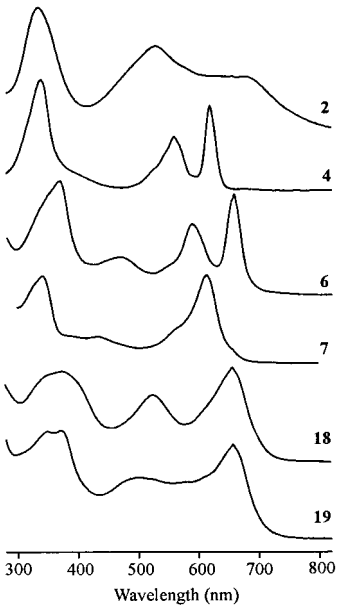


Figure 1. UV−vis spectra for porphyrazines **2**, **4**, **6**, **7**, **18**, and **19**.

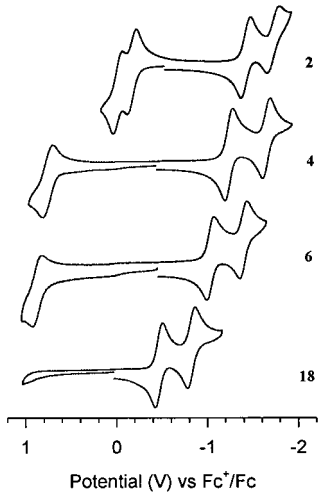


Figure 2. Cyclic voltammograms of porphyrazines **2**, **4**, **6**, and **18** taken in dichloromethane.

λ_{max} = 559 and 617 nm, blue-shifted about 33 nm compared to that of **6**. The spectrum of **2** is typical for porphyrazines with β-dimethylamino substituents.[7−9] The extreme broadening of the split Q band (λ_{max} 528 and 679 nm) is attributed to the n−π* transitions of the nonbonding electrons on the peripheral nitrogen atoms to the macrocycles.

Porphyrazines **6** and **7** undergo a rapid color change from blue to purple upon the dinitration in dichloromethane. The dinitroporphyrazines **18** and **19** are somewhat unusual in showing similar absorption spectra with split B bands (λ_{max} 353 and 373 nm for **18**, 348 and 370 nm for **19**) as well as split Q bands (λ_{max} 523 and 657 nm for **18**, 582 and 659 nm for **19**).

Electrochemistry. The electrochemical properties of the porphyrazines with one unsubstituted pyrrole and the dinitroporphyrazines were studied by cyclic voltammetry in dichloromethane. As shown in Figure 2, H_2[pz-$(H)_2(NMe_2)_6$] (**2**) is easy to oxidize, having two reversible ring oxidations at potentials −0.18 and −0.03 V, which are very similar to those observed for other dimethylamino-substituted porphyrazines.[9,29] In fact, the first oxidation of **2** occurs at a potential only 90 mV higher than that for octakis(dimethylamino)tetraazaporphyrin (**14**) (first oxidation $E_{1/2}$ = −0.27 V), the most easily oxidized porphyrazine prepared to date.[29] Replacement of dimethylamino moieties by propyl groups shifts E^o by +0.91 V for **4** ($E_{1/2}$ = +0.73 V). The hexakis(4-*tert*-butylphenyl) porphyrazine **6** exhibits one reversible ring oxidation ($E_{1/2}$ = +0.86 V), which is 130 mV higher than that of **4**. Metalation of **6** with Ni(II) ion causes no significant changes in the oxidation potential ($E_{1/2}$ = +0.83 V). All porphyrazines with one unsubstituted pyrrole (**2**, **4**, **6,** and **7**) display two reversible ring reductions, with the order for reduction potentials as **2** > **4** > **7** > **6**, exactly the opposite of the order for the ring oxidations. These data are collected in Table 1.

The cyclic voltammogram of **18** shows that dinitration of the ring shifts oxidations out of the measurable region. The potentials for the two reversible ring reductions ($E_{1/2}$ = −0.47 and −0.82 V) are approximately 0.6 V lower (easier to reduce) than those for the parent porphyrazine **6**, due to the introduction of the two electron-withdrawing nitro groups. Similar cathodic shifts have been observed for the related nitroporphyrins[14] and β-octachloroporphyrin or β-octabromoporphyrin analogues,[30] and **18** is the most readily reduced porphyrazine prepared to date.

Conclusions

We have described a simple convenient synthesis of porphyrazines, abbreviated as M[pz$(H)_2(R)_6$], with three substituted pyrroles (substituents, R = −NMe_2, propyl, or 4-*tert*-butylphenyl) at the periphery and one unsubstituted pyrrole, starting from inexpensive and readily available materials. This method is sufficiently mild so that a wide range of functionality and heteroatoms can be tolerated. These macrocycles have both favorable solubility and an open site for possible peripheral functionalizations such as nitration, halogenation,[30,31] hydroxylation and subsequent oxidations,[32] Diels−Alder reactions,[33,34] formylation,[35,36] and other reactions associated with normal isolated alkenes and aromatic ring systems. We have further shown that both free base and nickel(II) porphyrazines (**6** and **7**) with one unsubstituted pyrrole can be nitrated by nitrogen dioxide with high efficiency and selectivity, resulting in the formation of macrocycles with dramatically altered electrochemical properties. This method will provide a synthon for a number of peripherally functionalized porphyrazines,

(29) Eichhorn, D. M.; Yang, S.; Jarrell, W.; Baumann, T. F.; Beall, L. S.; White, A. J. P.; Williams, D. J.; Barrett, A. G. M.; Hoffman, B. M. *J. Chem. Soc., Chem. Commun.* **1995**, 1703−1704.
(30) Hodge, J. A.; Hill, M. G.; Gray, H. B. *Inorg. Chem.* **1995**, *34*, 809−812.
(31) Hoffmann, P.; Labat, G.; Robert, A.; Meunier, B. *Tetrahedron Lett.* **1990**, *31*, 1991−1994.
(32) Nie, H.; Stern, C. L.; Barrett, A. G. M.; Hoffman, B. M. *Chem. Commun.* **1999**, 703−704.
(33) Tomé, A. C.; Lacerda, P. S. S.; Neves, M. G. P. M. S.; Cavaleiro, J. A. S. *Chem. Commun.* **1997**, 1199−1200.
(34) Vicente, M. G. H.; Cancilla, M. T.; Lebrilla, C. B.; Smith, K. M. *Chem. Commun.* **1998**, 2355−2356.
(35) Yeung, M.; Ng, A. C. H.; Drew, M. G. B.; Vorpagel, E.; Breitung, E. M.; McMahon, R. J.; Ng, D. K. P. *J. Org. Chem.* **1998**, *63*, 7143−7150.
(36) Senge, M. O.; Gerstung, V.; Ruhlandt-Senge, K.; Runge, S.; Lehmann, I. *J. Chem. Soc., Dalton Trans.* **1998**, 4187−4199.

nitroporphyrazine **18**, for instance, which cannot be prepared by direct cyclizaton of heteroatom-appended dinitriles or their pyrroline derivatives.

Currently, we are utilizing the compounds described here to prepare new peripherally functionalized porphyrazines and higher order porphyrazine arrays and will report these investigations in due course.

Experimental Section

General Information. 2,5-Diiminopyrrolidine (**8**),[37] bis(dimethylamino)maleonitrile (**9**),[38] dipropylmaleonitrile (**10**),[9] and 3,4-bis(4-*tert*-butylphenyl)pyrroline-2,5-diimine (**12**)[39] were prepared following the previously reported procedures. All other reagents and solvents were obtained from commercial suppliers and used without further purification. TLC was carried out on E. Merck precoated silica gel 60 F_{254} plates. Chromatography was carried out on Whatman 60 (230−400 mesh) silica gel (eluants are given in parentheses). Elemental analyses were performed by Oneida Research Services, Inc., Whitesboro, NY. Cyclic voltammetric measurements were carried out using a Cypress Systems 1087 computer-controlled potentiostat. A single compartment cell was used with a platinum disk working electrode, Ag/AgCl reference electrode, and a silver wire as auxiliary electrode. Measurements were carried out in CH_2Cl_2 with 0.1 M tetra-*n*-butylammonium hexafluorophosphate as supporting electrolyte. Solutions containing approximately 10^{-3} M analyte were deaerated for several minutes by purging with N_2. All $E_{1/2}$ values were calculated from $(E_{pa} + E_{pc})/2$ at a scan rate of 110 mV s^{-1} and no correction for junction potentials. Ferrocene was added as an internal reference for all measurements.

3,4-Dipropylpyrroline-2,5-diimine (11). Na metal (80 mg, 3.4 mmol) was added to dipropylmaleonitrile (**10**) (3.0 g, 18.6 mmol) in MeOH (300 mL) when NH_3 was bubbled through the solution at 65 °C for 15 h. The resulting purple solution was cooled to room temperature and filtered. Rotary evaporation gave a residue that was taken up in CH_2Cl_2 (100 mL). After being washed with brine (2 × 100 mL) and water (100 mL), the solution was dried over Na_2SO_4. Evaporation under reduced pressure yielded a greenish solid that was used without further purification. Recrystallization of a sample from MeOH gave a white solid: mp 133−135 °C dec; IR ν_{max}/cm^{-1} 1650, 1108; ^1H NMR (400 MHz, $CDCl_3$) δ 0.90 (t, 6H), 1.46 (m, 4H), 2.26 (t, 4H), 8.23 (s, exchangeable with D_2O, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 15.2, 23.8, 26.8, 139.4, 167.5; HRMS (EI, 3-NBA) *m*/*z* 180.149 6 ($M + H^+$), calcd for $C_{10}H_{18}N_3$ 180.150 1. Anal. Calcd for $C_{10}H_{17}N_3$: C, 67.00; H, 9.56; N, 23.44. Found: C, 66.64; H, 9.25; N, 23.48.

2,3,7,8,12,13-Hexakis(dimethylamino)porphyrazine (2). Mg turnings (0.29 g, 11.8 mmol) and a small crystal of I_2 in *n*-butanol (180 mL) were heated to reflux under N_2 for 15 h. The resulting suspension of magnesium butoxide was cooled to 80 °C, and bis(dimethylamino)maleonitrile (**9**) (2.0 g, 12.2 mmol) and 2,5-diiminopyrrolidine (**8**) (0.34 g, 3.5 mmol) were added. The reaction mixture was heated to reflux for an additional 15 h when the solution became deep violet. After removal of *n*-butanol by vacuum distillation, the residue was dissolved in $CHCl_3$ (200 mL) and filtered through Celite. After rotary evaporation, the resulting violet solid was dissolved in CF_3CO_2H (25 mL) under N_2, stirred in the absence of light for 3 h at room temperature, and poured onto crushed ice. The slurry containing the purple precipitate was made basic by addition of concentrated $NH_3 \cdot H_2O$. The resultant solid was collected by filtration and washed copiously with MeOH until the washings were colorless. After evaporation, the crude product was chromatographed (0.2% $NH_3 \cdot H_2O$ in $CHCl_3$) to remove other pigments including octakis(dimethylamino)porphyrazine, $H_2[Pz(NMe_2)_8]$ (**14**).[7,8,29] Recrystallization from a mixture of MeOH and hexanes gave **2** as purple microcrystals (0.11 g, 5.5%): mp 194−196 °C; R_f (1% MeOH in $CHCl_3$) 0.47; IR ν_{max}/cm^{-1} 3286, 1575, 1527, 1392, 1327, 1082, 781; UV−vis (CH_2Cl_2) λ_{max} (log ϵ) 334 (4.37), 528 (4.21), 614 (sh), 679 (4.02) nm; ^1H NMR (400 MHz, $CDCl_3$) δ −0.04 (s, 2H), 3.56 (s, 12H), 3.78 (s, 12H), 3.99 (s, 12H), 8.63 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 44.7, 45.8, 46.6, 129.7, 130.9, 138.7, 145.8, 147.2, 151.5, 154.5, 155.9; FAB MS *m*/*z* 573 ($M + H^+$), calcd for $C_{28}H_{41}N_{14}$ 573. Anal. Calcd for $C_{28}H_{40}N_{14} \cdot 0.5H_2O$: C, 57.81; H, 7.10; N, 33.71. Found: C, 57.92; H, 6.97; N, 33.95.

[2,3,7,8,12,13-Hexakis(propyl)porphyrazine]magnesium(II) (3). Method 1. Mg turnings (0.45 g, 18.5 mmol) and a small crystal of I_2 in *n*-butanol (200 mL) were heated to reflux under N_2 for 15 h. The resulting magnesium butoxide suspension was cooled to 80 °C, and 3,4-dipropylpyrroline-2,5-diimine (**11**) (4.0 g, 22.3 mmol) and 2,5-diiminopyrrolidine (**8**) (0.68 g, 7.0 mmol) were added. The reaction mixture was heated to reflux for an additional 15 h when the solution turned to dark purple. After removal of *n*-butanol by vacuum distillation, the residue was taken up in $CHCl_3$ (400 mL) and filtered through Celite. Rotary evaporation gave **3** as a purple solid that was chromatographed (1% MeOH in $CHCl_3$) to yield a crystalline material (0.71 g, 17%): mp 181−185 °C; R_f (10% MeOH in $CHCl_3$) 0.52; IR ν_{max}/cm^{-1} 1462, 1145, 990, 949, 771; UV−vis (CH_2Cl_2) λ_{max} (log ϵ) 346 (4.83), 560 (sh), 592 (sh), 600 (4.80) nm; ^1H NMR (400 MHz, DMSO-d_6) δ 1.22 (m, 18H), 2.28 (m, 12H), 3.82 (t, 12H), 9.23 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.3, 15.0, 15.1, 25.0, 25.7, 25.8, 27.4, 28.5, 28.6, 131.2, 143.4, 144.6, 144.8, 155.8, 157.2, 159.8, 160.0; FAB MS *m*/*z* 589 ($M^{\bullet+}$), calcd for $C_{34}H_{44}MgN_8$ 589. Anal. Calcd for $C_{34}H_{44}MgN_8 \cdot H_2O$: C, 67.27; H, 7.64; N, 18.46. Found: C, 66.89; H, 7.64; N, 18.07.

Method 2. Co-cyclization of 2,5-diiminopyrrolidine (**8**) with dipropylmaleonitrile (**10**) under the same conditions described in Method 1 and subsequent chromatography (1% MeOH in $CHCl_3$) gave porphyrazine **3** (3%), which had ^1H NMR, UV−vis, and FAB MS spectra identical to a sample prepared by Method 1.

2,3,7,8,12,13-Hexakis(propyl)porphyrazine (4). Porphyrazine **3** (0.71 g, 1.2 mmol) was dissolved in CF_3CO_2H (25 mL), stirred for 2 h at room temperature under N_2, and poured onto crushed ice. The slurry containing the purple precipitate was made basic by addition of concentrated aqueous NH_3. The solid was collected by filtration and washed copiously with MeOH until the washings were colorless. The pure product (0.62 g, 91%) was obtained following chromatography ($CHCl_3$): mp 270−275 °C dec; R_f ($CHCl_3$) 0.32; IR ν_{max}/cm^{-1} 3298, 1488, 1463, 1145, 798, 714; UV−vis (CH_2Cl_2) λ_{max} (log ϵ) 338 (4.67), 559 (4.38), 617 (4.57) nm; ^1H NMR (400 MHz, $CDCl_3$) δ −2.71 (s, 2H), 1.27 (m, 18H), 2.31 (m, 12H), 3.82 (m, 4H), 3.90 (m, 8H), 9.10 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 15.8, 15.9, 26.5, 26.55, 26.6, 29.1, 29.2, 29.3, 135.1, 143.8, 144.4, 145.8, 149.2, 157.3, 159.5, 161.5; FAB MS *m*/*z* 567 ($M + H^+$), calcd for $C_{34}H_{46}N_8$ 567. Anal. Calcd for $C_{34}H_{46}N_8$: C, 72.05; H, 8.18; N, 19.77. Found: C, 72.19; H, 8.29; N, 19.49.

[2,3,7,8,12,13-Hexakis(4-(*tert*-butyl)phenyl)porphyrazine]magnesium(II) (5). Mg turnings (0.18 g, 7.4 mmol) and a small crystal of I_2 in *n*-butanol (100 mL) were heated to reflux under N_2 for 15 h. The resulting magnesium butoxide suspension was cooled to 80 °C, and 3,4-bis(4-*tert*-butylphenyl)-pyrroline-2,5-diimine (**12**) (3.0 g, 8.3 mmol) and 2,5-diiminopyrrolidine (**8**) (0.27 g, 2.8 mmol) were added. The reaction mixture was heated to reflux for an additional 15 h when the solution turned dark green. After removal of *n*-butanol by vacuum distillation, the residue was dissolved in $CHCl_3$ (400 mL) and filtered through Celite. Rotary evaporation gave a dark green solid that was chromatographed ($CHCl_3$) to yield **5** as a greenish blue solid (0.60 g, 19%): mp >300 °C; R_f (2% MeOH in $CHCl_3$) 0.50; IR ν_{max}/cm^{-1} 1464, 1364, 1268, 1107, 982, 837; UV−vis (CH_2Cl_2) λ_{max} (log ϵ) 372 (4.86), 466, 591 (sh), 629 (4.88) nm; ^1H NMR (400 MHz, DMSO-d_6) δ 0.83 (s, 18H), 0.95 (s, 18H), 1.47 (s, 18H), 6.81 (d, J = 6.0 Hz, 4H), 6.92 (d, J = 6.8 Hz, 4H), 7.67 (d, J = 8.4 Hz, 4H), 7.84 (d, J = 7.6 Hz, 4H), 7.90 (d, J = 7.6 Hz, 4H), 8.01 (d, J = 8.0 Hz, 4H), 9.26 (s,

(37) Elvidge, J. A.; Linsted, R. P. *J. Chem. Soc.* **1954**, 442−448.
(38) Begland, R. W.; Hartter, D. R.; Jones, F. N.; Sam, D. J.; Sheppard, W. A.; Webster, O. W.; Weigert, F. J. *J. Org. Chem.* **1974**, *39*, 2341.
(39) Baumann, T. F.; Barrett, A. G. M.; Hoffman, B. M. *Inorg. Chem.* **1997**, *36*, 5661−5665.

2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 32.9, 36.1, 125.2, 126.3, 132.9, 131.8, 133.0, 134.1, 136.9, 143.6, 151.6, 158.5, 159.9, 161.7; FAB MS *m/z* 1130 ($M + H^+$), calcd for $C_{76}H_{81}MgN_8$ 1130. Anal. Calcd for $C_{76}H_{80}MgN_8 \cdot 2H_2O$: C, 78.30; H, 7.26; N, 9.61. Found: C, 78.54; H, 7.21; N, 9.43.

2,3,7,8,12,13-Hexakis(4-*tert*-butylphenyl)porphyrazine (6). Porphyrazine **5** (0.60 g, 5.3 mmol) was dissolved in CF_3CO_2H (25 mL), stirred for 2 h under N_2 at room temperature, and poured onto crushed ice. The slurry containing the blue precipitate was made basic by addition of concentrated aqueous NH_3, and the solid was collected by filtration and washed copiously with MeOH until the washings were colorless. Pure **6** (0.56 g, 95%) was obtained by chromatography (1/1 CH_2Cl_2/hexanes): mp >300 °C; R_f (3/2 CH_2Cl_2/hexanes) 0.48; IR ν_{max}/cm^{-1} 3284, 1481, 1367, 1266, 1108, 962, 837, 798, 713; UV−vis (CH_2Cl_2) λ_{max} (log ϵ) 366 (4.84), 467 (4.37), 586 (4.63), 656 (4.81) nm; ^{1}H NMR (300 MHz, $CDCl_3$) δ −2.41 (s, 2H), 1.52 (s, 18H), 1.53 (s, 18H), 1.54 (s, 18H), 7.57 (d, J = 8.4 Hz, 4H), 7.60 (d, J = 8.4 Hz, 4H), 7.70 (d, J = 8.4 Hz, 4H), 8.20 (d, J = 8.4 Hz, 4H), 8.25 (d, J = 8.1 Hz, 4H), 8.28 (d, J = 8.1 Hz, 4H), 9.10 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 32.6, 32.7, 35.9, 36.0, 126.1, 126.2, 126.5, 128.0, 131.5, 131.7, 131.8, 133.5, 133.7, 133.8, 134.7, 141.8, 142.0, 149.1, 151.8, 151.9, 152.0, 158.6, 160.1, 164.2; FAB MS *m/z* 1107 ($M^{\bullet+}$), calcd for $C_{76}H_{82}N_8$ 1107. Anal. Calcd for $C_{76}H_{82}N_8$: C, 82.42; H, 7.46; N, 10.12. Found: C, 82.55; H, 7.48; N, 10.13.

[2,3,7,8,12,13-Hexakis(4-(*tert*-butyl)phenyl)porphyrazine]nickel(II) (7). Porphyrazine **6** (0.24 g, 0.21 mmol) and $Ni(OAc)_2 \cdot 4H_2O$ (0.52 g, 2.1 mmol) in a mixture of PhCl (45 mL) and DMF (15 mL) were heated to 100 °C for 24 h. The solvent was removed under reduced pressure, and the purple solid was washed with 5% HCl in MeOH followed by MeOH. Chromatography ($CHCl_3$/hexanes 7/3) gave **7** (0.24 g, 98%): mp >300 °C; R_f (3/2 CH_2Cl_2/hexanes) 0.59; IR ν_{max}/cm^{-1} 1463, 1364, 1268, 1107, 982, 838, 799; UV−vis (CH_2Cl_2) λ_{max} (log ϵ) 343 (4.74), 435 (4.25), 564 (sh), 613 (4.76) nm; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.52 (s, 18H), 1.53 (s, 18H), 1.54 (s, 18H), 7.55 (d, J = 8.5 Hz, 4H), 7.57 (d, J = 8.3 Hz, 4H), 7.71 (d, J = 8.3 Hz, 4H), 8.11 (d, J = 8.4 Hz, 4H), 8.15 (d, J = 8.4 Hz, 4H), 8.18 (d, J = 8.3 Hz, 4H), 8.95 (s, 2H); FAB MS *m/z* 1164 ($M^{+\cdot}$), calcd for $C_{76}H_{80}N_8Ni$ 1164. Anal. Calcd for $C_{76}H_{80}N_8Ni \cdot 0.5H_2O$: C, 77.81; H, 6.96; N, 9.55. Found: C, 77.91; H, 6.86; N, 9.64.

2,3-Dinitro-7,8,12,13,17,18-hexakis(4-(*tert*-butyl)phenyl)-porphyrazine (18). A saturated solution of N_2O_4 in hexanes (5 mL) was added to porphyrazine **6** (0.12 g, 0.11 mmol) in CH_2Cl_2 (40 mL). The mixture was stirred when the color changed from blue to reddish purple immediately. TLC and UV−vis spectroscopy were used to monitor the nitration process, which was stopped after 10 min, and the solution was poured into H_2O (100 mL). The organic layer was separated and dried over Na_2SO_4. After filtration and rotary evaporation, the purple residue was chromatographed (3/2 CH_2Cl_2/hexanes) to give **18** (0.12 g, 90%): mp >300 °C; R_f (3/2 CH_2Cl_2/hexanes) 0.38; IR ν_{max}/cm^{-1} 3301, 1608, 1534, 1483, 1341, 1269, 1109, 1081, 832, 797; UV−vis (CH_2Cl_2) λ_{max} (log ϵ) 353 (sh), 373 (4.64), 523 (4.49), 657 (4.66) nm; ^{1}H NMR (300 MHz, CD_2Cl_2) δ −1.05 (s, 2H), 1.49 (s, 18H), 1.50 (s, 18H), 1.51 (s, 18H), 7.59 (d, J = 8.4 Hz, 4H), 7.64 (d, J = 8.4 Hz, 4H), 7.72 (d, J = 8.7 Hz, 4H), 8.08 (d, J = 8.7 Hz, 4H), 8.16 (s, J = 8.4 Hz, 4H), 8.30 (d, J = 8.4 Hz, 4H); FAB MS *m/z* 1197 ($M^{+\cdot}$), calcd for $C_{76}H_{80}N_{10}O_4$ 1197. Anal. Calcd for $C_{76}H_{80}N_{10}O_4 \cdot 0.5H_2O$: C, 75.66; H, 6.77; N, 11.61. Found: C, 75.54; H, 6.79; N, 11.41.

[2,3-Dinitro-7,8,12,13,17,18-hexakis(4-(*tert*-butyl)phenyl)porphyrazine]nickel(II) (19). Method 1. Dinitroporphyrazine **18** (0.10 g, 0.08 mmol) and $Ni(OAc)_2 \cdot 4H_2O$ (0.20 g, 0.8 mmol) in PhCl (30 mL) and DMF (10 mL) were heated at100 °C for 24 h. The solvent was removed under reduced pressure, and the purple solid was washed with 5% HCl in MeOH and then MeOH. Evaporation and chromatography (8/3 $CHCl_3$/hexanes) of the residue gave **19** (0.095 g, 95%) as a dark blue solid: mp >300 °C; R_f (3/2 CH_2Cl_2/hexanes) 0.38; IR ν_{max}/cm^{-1} 1609, 1534, 1490, 1341, 1269, 1109, 836, 561; UV−vis (CH_2Cl_2) λ_{max} (log ϵ) 348 (4.14), 370 (4.15), 502 (3.87), 582 (sh), 659 (4.03) nm; ^{1}H NMR (600 MHz, CD_2Cl_2) δ 1.47 (s, 18H), 1.48 (s, 18H), 1.49 (s, 18H), 7.59 (d, J = 8.4 Hz, 4H), 7.61 (d, J = 8.4 Hz, 4H), 7.67 (d, J = 8.0 Hz, 4H), 8.04 (d, J = 8.0 Hz, 4H), 8.06 (s, J = 8.0 Hz, 4H), 8.16 (d, J = 8.4 Hz, 4H); FAB MS *m/z* 1254 ($M^{\bullet+}$), calcd for $C_{76}H_{78}N_{10}NiO_4$ 1254. Anal. Calcd for $C_{76}H_{78}N_{10}NiO_4 \cdot H_2O$: C, 71.75; H, 6.34; N, 11.01. Found: C, 72.00; H, 6.50; N, 10.80.

Method 2. Nickel dinitroporphyrazine **19** was also prepared from nickel porphyrazine **7** by the same procedure as described for the synthesis of **18**. The dark blue product (85% yield) obtained after purification by chromatography was identical in all respects to the sample prepared by Method 1.

Acknowledgment. This work was supported by the National Science Foundation (CHE9727590 (B.M.H. and A.G.M.B.)), DMR (9523228 (B.M.H.)), the Materials Research Laboratory of Northwestern University, the EPSRC, Glaxo Wellcome for endowment support (A.G.M.B.), the Wolfson Foundation (A.G.M.B.), and NATO.

JO9907890