Porphyrazines and Norphthalocyanines Bearing Nitrogen Donor Pockets: Metal Sensor Properties

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The amino-functionalized porphyrazines **1**, **2**, and **4** and norphthalocyanines **3** and **5**, which were prepared via Linstead macrocyclization reactions of dinitrile precusors, were subject to UV−vis titrations in the presence of inorganic ions. These polydentate macrocycles are able to bind metal ions by the peripheral ligating diazacrown or vicinal diamine entities in addition to metal ion binding within the porphyrazine (norphthalocyanine) cavity. Although **1** only weakly bound Ag(I) and Hg(II), **2** to **5** were superior polydentate ligands. Surprisingly, porphyrazine **4** was a superior ligand for binding 4 equiv of Co(II), Cu(II), Zn(II), and Cd(II) than the corresponding tetracrowned porphyrazine **2**. Both **2** and **4** were excellent ligands for peripherally complexing 4 equiv of Ag(I) and Hg(II) and only for one metal, Pb(II), was the crowned system **2** superior to **4**. The crowned norphthalocyanine **3** was generally inefficient in the peripheral complexation of inorganic cations, whereas **5** was superior for the peripheral binding of Co(II), Cu(II), Zn(II), Cd(II), and Hg(II) (1 equiv). Again, only with Pb(II) was the crowned system **3** a superior ligand to **5**. X-ray crystallographic characterization of diazacrown **12a**, porphyrazine **1** (M = Mg), and the complexes of crown **12b** with $Cu(BF_4)_2$ and with $HClO_4$ are reported.

Introduction

Phthalocyanines and related tetraazamacrocycles have found wide applications in diverse areas such as biomedical agents for diagnosis and therapy,[1,2] chemical sensors,[3] liquid crystals,[4,5] nonlinear optics,[6] Langmuir−Blodgett films,[7] and ladder polymers[8] and are precursors to new conducting materials. Recently, we reported on the synthesis and novel physical properties of porphyrazines (tetraazaporphyrins) with peripheral heteroatom functionalization, including octathiolates,[9] octa(dialkyl)-amines,[10] and octaol derivatives.[11] These studies have been extended to related macrocycles with two, four,[12] or six peripheral thiols, amines, or alcohols. All these electron-rich porphyrazines show unusual UV−vis spectra, redox chemistry,[13] electrochemistry, magnetic properties, etc. In addition, these porphyrazines exhibit unusual coordination chemistry through binding of metal ions both within the macrocyclic cavity and by the peripheral ligating groups. We have also reported the preparation and full characterization of solitaire-,[14] Gemini,[15] and star-porphyrazines,[16] from the binding of one, two, and four metal ions to peripheral ligating groups. Such binding is apparent by profound changes in the UV−vis spectrum, since the heteroatoms, in contrast to heteroatom-functionalized phthalocyanines, are in direct electronic contact with the core aromatic

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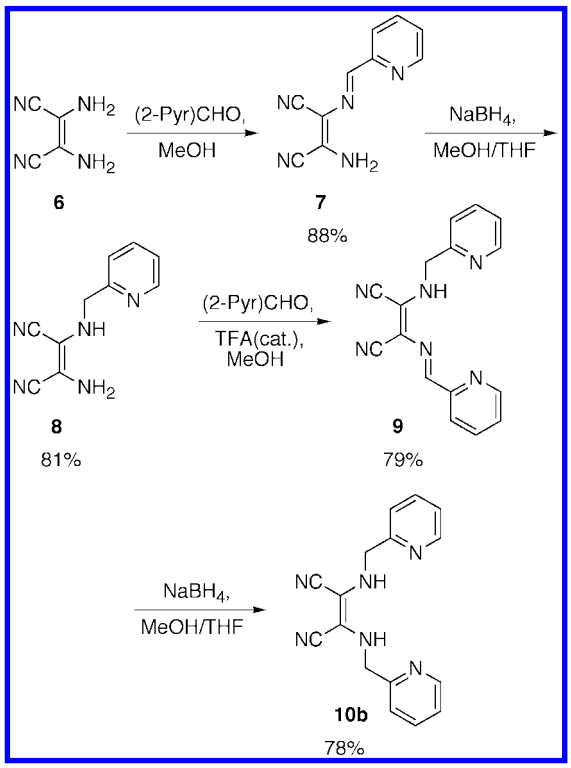
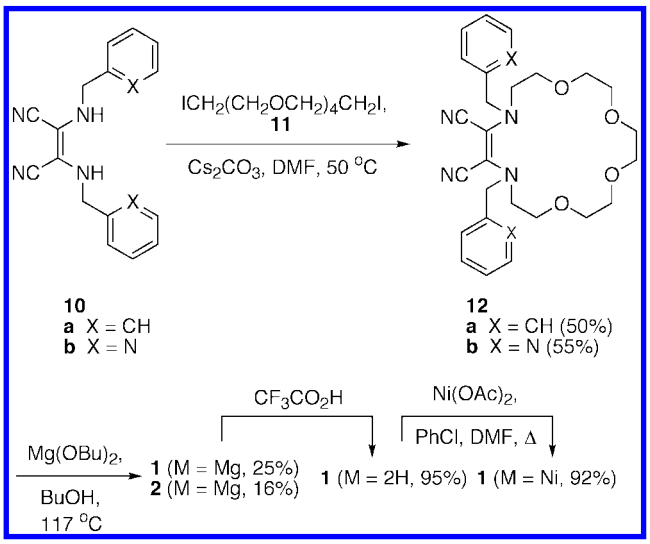
Scheme 1



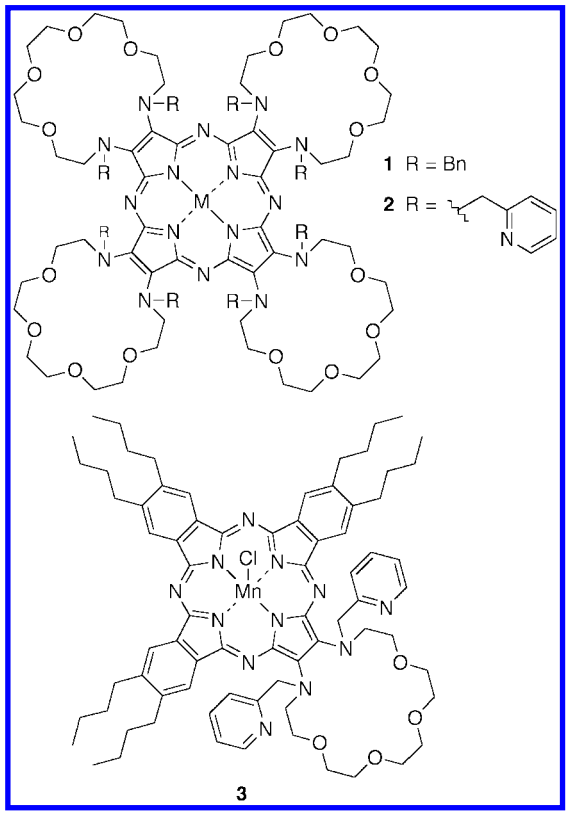
Scheme 2



π-system. As such, these interactions are relevant for the sensing of metal ions in solution. Herein, we now report the synthesis of aza-crowned porphyrazines[17,18] and related multidentate porphyrazines and a study of the selectivity of their interactions with common inorganic cations.

Results and Discussion

Synthesis of Porphyrazines. We set out to prepare five porphyrazine systems endowed with peripheral amino-ligating functionality **1** to **5**. Two of these compounds **1** and **2** contained four diaza-18-crown-6 ring systems, porphyrazine **3** contained a single crown ether entity, and macrocycles **4** and **5** were, respectively, functionalized with eight and two *N*-methyl-*N*-(2-pyridylmethyl)amino units. Porphyrazines **1** and **2** differed in



that **2** contained pendant *N*-(2-pyridylmethyl)amino units rather than the noncoordinating benzylamino group. It is reasonable to expect that these multidentate ligands should, in addition to metal ion coordination within the porphyrazine cavity, be able to peripherally bind up to four (and perhaps more) (**1**, **2**, and **4**) or one (**3** and **5**) metal ions. The tetracrowned porphyrazines **1** and **2** should be able to bind metal ions either within the crown ether cavities and/or within the meso-pockets.[17]

Following the methods of Sheppard[19] for the synthesis of dinitrile **10a**, sequential double-reductive alkylation

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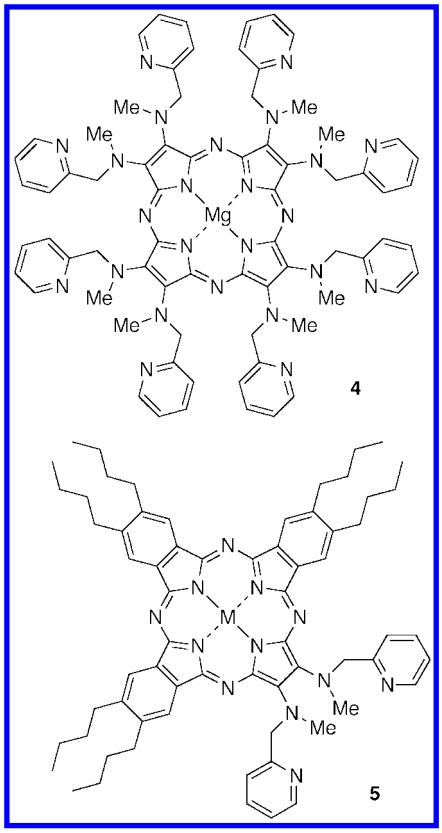
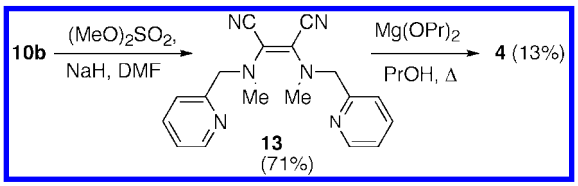


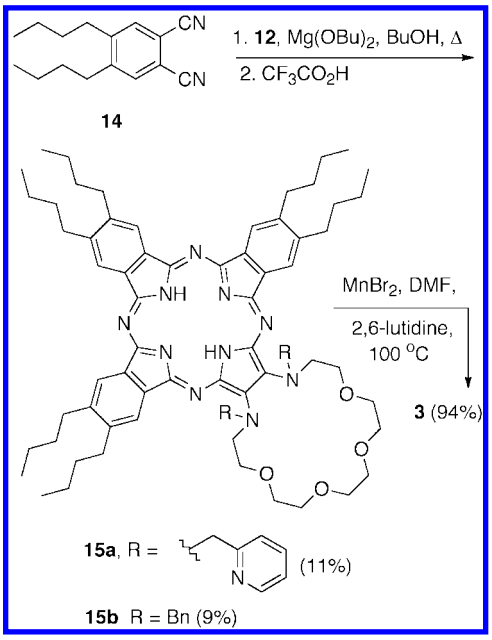
of DAMN (**6**) using 2-pyridinecarboxaldehyde gave 2,3-bis[(2-pyridylmethyl)amino]-2(*Z*)-butene-1,4-dinitrile (**10b**) (Scheme 1). Iodide **11**, which was readily available from pentaethylene glycol, was condensed with diamine **10a** using cesium carbonate in DMF[20] at 50 °C to provide the corresponding diazacrown **12a** as a mixture of *E* and *Z* isomers (50%). Recrystallization gave the corresponding pure *Z* isomer, the structure of which was confirmed by X-ray crystallography (see below). Attempted formation of crown ether **12a** using the ditosylate corresponding to **11** with potassium *tert*-butoxide, sodium or potassium hydrides, or sodium or potassium carbonates as base or from the reaction of **11** using sodium or potassium hydrides as base or at higher temperatures gave significantly reduced yields of crown **12a** (0−15%). Similar to the synthesis of diazaoxocrown ether **12a**, slow addition of a solution of diamine **10b** and diiodide **11** in DMF to a suspension of cesium carbonate in DMF afforded the crystalline crown **12b** in 55% yield (Scheme 2).

Linstead macrocyclization[21] of dinitriles **12a** and **12b**, respectively, gave porphyrazine **1** (M = Mg, 25%) and **2** (M = Mg, 16%). Demetalation of **1** (M = Mg) gave porphyrazine **1** (M = 2H), and subsequent remetalation with $Ni(OAc)_2$ gave porphyrazine **1** (M = Ni) (Scheme 2). Dinitrile **13**, prepared by dimethylating dinitrile **10b** (71%), was template macrocyclized to reveal porphyrazine **4** (13%) (Scheme 3). Mixed Linstead macrocyclization reactions of dinitriles **14**[22] with **12a** and **14** with **12b** followed by removal of the magnesium ions with trifluoroacetic acid were successfully used to prepare the

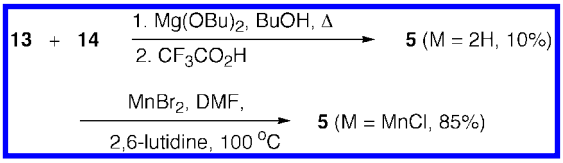
Scheme 3



Scheme 4



Scheme 5



norphthalocyanines **15a** (11%) and **15b** (9%) (Scheme 4). Norphthalocyanine **15a** when heated in the presence of $MnBr_2$ preferentially coordinated Mn(II) within the central cavity, giving metalated norphthalocyanine **3**. The Mn(II) ion readily oxidized within the central cavity and, during the workup of the reaction, exchanged its bromide ligand for chloride when treated with brine, to give exclusively the axial chloride **3**. Mixed Linstead macrocyclization of dinitrile **13** in the presence of excess dinitrile **14** gave, after demetalation, norphthalocyanine **5** (M = 2H) (10%), which was remetalated by reaction with manganese(II) bromide to produce, on workup, norphthalocyanine **5** (M = MnCl) (85%) (Scheme 5).

X-ray Crystallographic Structure Determinations of 12a, 1 (M = Mg), 12b·Cu(BF$_4$)$_2$, and 12b·(HClO$_4$)$_2$. Recrystallization of the mixture of geometric isomers of crown **12a** from ethyl acetate gave the desired *Z* isomer, and its structure was verified by X-ray crystallography (Figure 1). The molecule has crystallographic C_2 symmetry about an axis bisecting both the C=C double bond and the ethylene spacer unit between the second and third oxygen atoms of the polyether chain. This symmetry results in an anti disposition of the two benzyl groups, each of which has its methylene hydrogen atoms directed toward polyether oxygen atoms. The conformation is thus stabilized by a total of four weak C−H···O hydrogen bonds. There are no intermolecular

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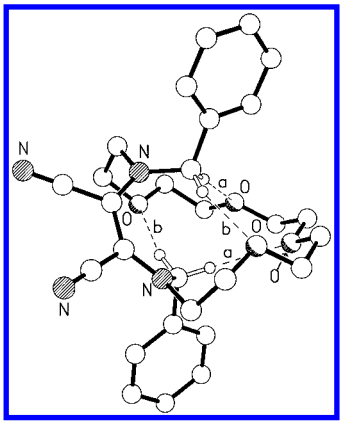


Figure 1. Solid-state molecular structure of **12a** showing also the intramolecular C−H···O stabilizing interactions. The C−H···O hydrogen bonding geometries are as follows: C···O and H···O distances (Å) and C−H···O angles (deg); (a) 3.39, 2.43, 179; (b) 3.27, 2.34, 161 (the C−H distances have been normalized to 0.96 Å).

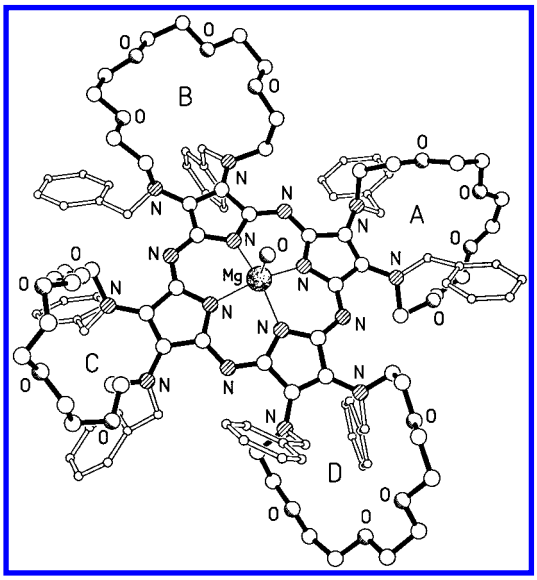


Figure 2. Molecular structure of **1** (M = Mg).

$\pi-\pi$ stacking interactions involving the aromatic rings. All attempts to prepare metal salt complexes [$AgBF_4$, $CdCl_2$, $CoCl_2$, $CaCl_2$, $Zn(BF_4)_2$, KBr, NaBr, $Hg(ClO_4)_2$] of crown **12a**, however, failed to provide crystalline materials suitable for X-ray crystallography.

Crystals of **1** (M = Mg) suitable for X-ray analysis were grown from ethyl acetate/hexanes. The magnesium atom is bound, as expected, to the four central porphyrazine nitrogen atoms in a slightly distorted square pyramidal geometry, the fifth, apical, coordination site being occupied by an aqua ligand (Figure 2). The metal atom lies 0.54 Å out of the basal plane toward the oxygen atom. The Mg−N distances do not differ significantly and are in the range 2.008(7)−2.042(7) Å; the Mg−O bond length is 2.006(7) Å. The porphyrazine core and the eight azapolyether nitrogen atoms are dished away from the magnesium center and its coordinated oxygen atom, the eight outer nitrogen atoms lying, on average, 0.40 Å out of the plane of the central four coordinated nitrogens. The benzyl substituents on the four peripheral azapolyether macrocycles adopt two distinct orientations—in rings **A** and **D** these groups are in an anti disposition (i.e., a geometry analogous to that observed in the structure of

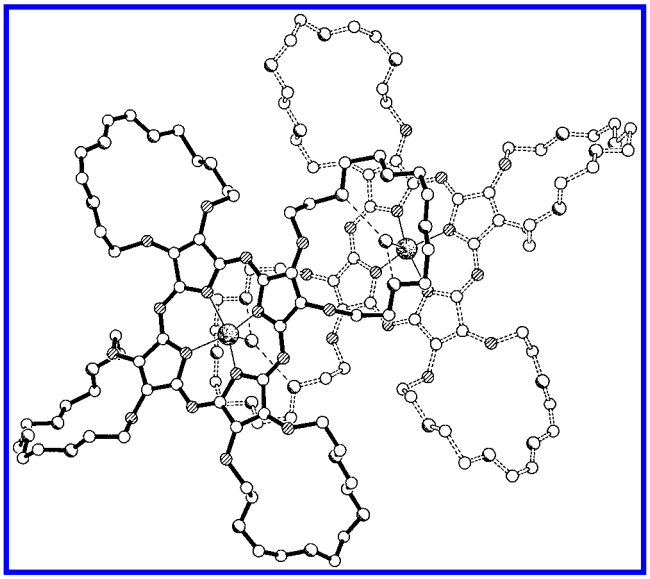


Figure 3. One of the hydrogen-bonded dimer pairs present in the crystals of **1** [M = Mg]. The O···O hydrogen bonding contacts are 2.76 and 2.89 Å (the aqua hydrogen atom positions could not be determined).

12a), whereas in rings **B** and **C** they are syn. In view of the high degree of thermal vibration/disorder present within some of these peripheral macrocycles, we have not attempted to analyze any of the potential intramolecular C−H···O interactions. The only notable feature of the packing of the molecules is the formation of hydrogen-bonded dimer pairs wherein the aqua ligand on one molecule is directed into the center of the diazaoxomacroring **B** of a centrosymmetrically related counterpart and vice versa (Figure 3).

Double-armed diazaoxocrown ethers can bind metals via the macroring alone or in combination with either one or both of the pendant arms. Assuming both arms participate, they may be on the same or opposite sides of the macroring. Upon standing, **12b**·$Cu(BF_4)_2$ formed as a deep blue crystalline solid out of a solution of **12b** and $Cu(BF_4)_2$ in methanol. The crystal structure of this product reveals (Figure 4) that **12b** acts as a pentadentate ligand, binding to copper via the two macroring nitrogen atoms, the two pendant pyridine nitrogen atoms, and one of the macroring oxygen atoms in a distorted square-pyramidal geometry (the oxygen atom occupying the apical position). The four Cu−N distances are in the range 1.970(5)−2.068(6) Å, those to the macroring nitrogen atoms being noticeably longer than those to the pendant pyridyl nitrogen atoms; the Cu−O distance is significantly longer at 2.314(5) Å. The Cu(II) ion lies 0.27 Å above the plane of the four donor nitrogen atoms in the direction of the oxygen atom. There are no intermolecular contacts of note.

In several metalation attempts using transition-metal perchlorate salts, [$Co(ClO_4)_2 \cdot xH_2O$, $Cr(ClO_4)_3 \cdot 6H_2O$, $Ni(ClO_4)_2 \cdot 6H_2O$, $Zn(ClO_4)_2 \cdot 6H_2O$, and as a control $HClO_4$], crystal formation occurred without the characteristic colors of transition metal complexes. These compounds were revealed to be the perchlorate salt of the diprotonated ligand, **12b**·$(HClO_4)_2$ (Figure 5). A noticeable feature of this structure is that the pendant pyridinium moieties lie on opposite sides of the macroring (cf. the same side in **12b**·$Cu(BF_4)_2$ but similar to that adopted in the related species **12a**) emphasizing the conforma-

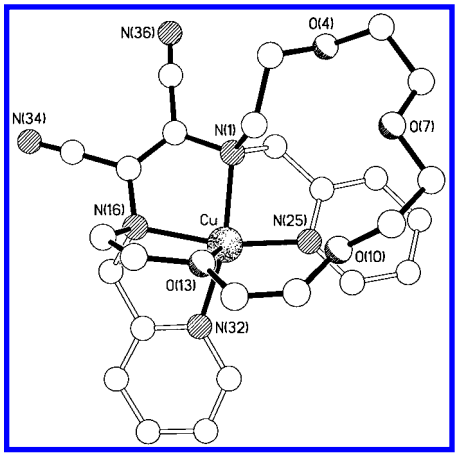


Figure 4. Molecular structure of **12b**·$Cu(BF_4)_2$. Selected bond lengths (Å) and angles (deg): Cu−N(1) 2.068(6), Cu−N(16) 2.046(5), Cu−N(25) 1.970(5), Cu−N(32) 1.994(5), Cu−O(13) 2.314(5); N(1)−Cu−N(16) 84.4(3), N(1)−Cu−N(25) 82.7(2), N(16)−Cu−N(32) 82.6(2), N(25)−Cu−N(32) 106.1(2), N(1)−Cu−O(13) 102.4(2), N(16)−Cu−O(13) 78.3(2), N(25)−Cu−O(13) 115.1(2), N(32)−Cu−O(13) 90.8(2).

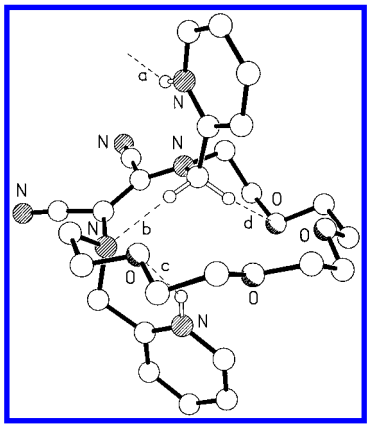


Figure 5. Solid-state structure of the dication of **12b**·$(HClO_4)_2$ showing also the stabilizing intramolecular hydrogen bonding interactions and the intermolecular N−H···O link to one of the perchlorate anions. The N−H···O, C−H···N, and C−H···O hydrogen bonding geometries are as follows for the X···Y and H···Y distances (Å) and X−H···Y angles (deg): (a) 2.78, 1.92, 158; (b) 3.01, 2.26, 135; (c) 3.08, 2.30, 146; (d) 3.09, 2.41, 128 (the N−H and C−H distances have been normalized to 0.90 and 0.96 Å, respectively).

tional flexibility of this new ligand system. As in **12a**, the conformation of the molecule is stabilized via intramolecular hydrogen bonding. Here, this involves the two benzylic methylene hydrogen atoms of one of the pendant groups and the pyridinium N−H hydrogen atom of the other. The pyridinium N−H hydrogen atom of the former is involved in a cation···anion hydrogen bond to one of the perchlorate oxygen atoms. There are no intermolecular $\pi-\pi$ interactions.

Peripheral Metal Ion Binding by the Porphyrazines 1, 2, and 4 and Norphthalocyanines 3 and 5. UV−vis titrations were performed with several metal salts (see Table 1) to investigate the metal-binding capabilities of porphyrazine **1** (M = Ni). In the UV−vis spectrum of aminoporphyrazines, the disappearance of the n−π* absorbance and a sharpening of the Q-band indicates metal coordination to the peripheral nitrogen atoms. Because the nitrogen n electrons are no longer available to the porphyrazine π system, metal coordination to the peripheral nitrogen atoms ultimately results in a spectrum that resembles an unsubstituted porphyrazine or phthalocyanine.[9,16,17] Binding exactly 4 equiv of a particular metal, one in each of the crown rings, is the maximal result for porphyrazine **1** (M = Ni) unless additional meso-pocket binding is observed.[17] This was realized with $AgBF_4$ (Figure 6) and $Hg(ClO_4)_2$. Unfortunately, to force the total disappearance of the n−π* peak (at 538 nm) and the sharpening of the Q-band (at 602 nm), greater than 100 equiv of either $AgBF_4$ or $Hg(ClO_4)_2$ were required, thus demonstrating that porphyrazine **1** (M = Ni) is not an efficient ligand for peripheral metal-ion binding.

Table 1. Summary of Ability of Porphyrazine 1 (M = Ni), 2, and 4 To Coordinate Metal Cations on the Periphery (Based on Uv−vis Titrations)[a]

	porphyrazine		
metal salt	**1** (M = Ni)	**2** (M = Mg)	**4**
$KClO_4$	−	−	−
$Cr(ClO_4)_3·6H_2O$	−	−	−
$Mn(ClO_4)_2·6H_2O$	−	−	−
$CoCl_2$	−	very good	excellent
$Ni(ClO_4)·6H_2O$	−	−	−
$CuCl_2$	−	very good	excellent
$Zn(ClO_4)_2·6H_2O$	−	good	excellent
$AgBF_4$	poor	excellent	very good
$CdCl_2$	−	good	excellent
$Hg(ClO_4)_2·3H_2O$	poor	excellent	excellent
$Pb(NO_3)_2$	−	excellent	−

[a] Qualitative rankings shown are based on molar equivalents of metal salt per peripheral chelate necessary to effect no further change in the UV−vis titration: −, no effect in UV−vis; poor, 25 equiv; good to very good, 10−2 equiv; excellent, 1 equiv.

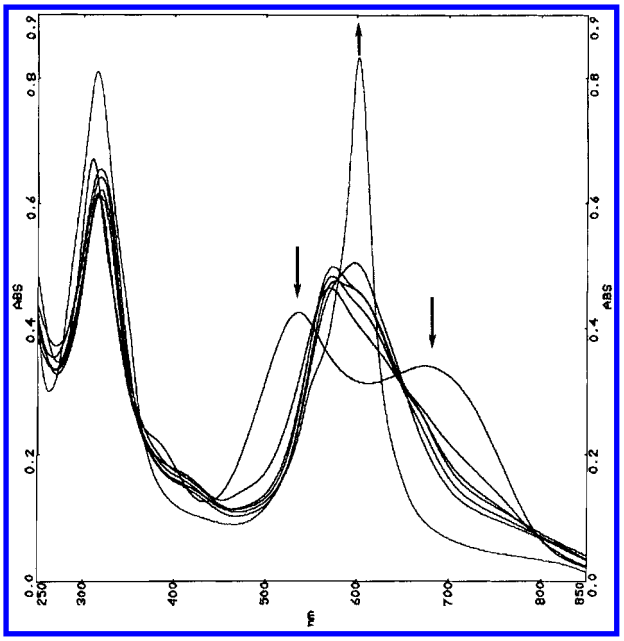


Figure 6. Porphyrazine **1** (M = Ni) titrated with $AgBF_4$ (0, 2, 4, 8, 20, 40, >100 equiv).

Porphyrazine **1** (M = Mg), in the solid state, has two adjacent crown ether rings (A and D in Figure 2) in an orientation similar to that of the starting dinitrile **12a**; the benzyl groups are on opposite sides of the crown ether ring. The other pair of crown ether rings (B and C) adjusts to place the two benzyl groups on the same side of the ring, making the ring more accessible for metal coordination (Figure 2). Evidence suggests that the conformation in solution might be the same. In both the

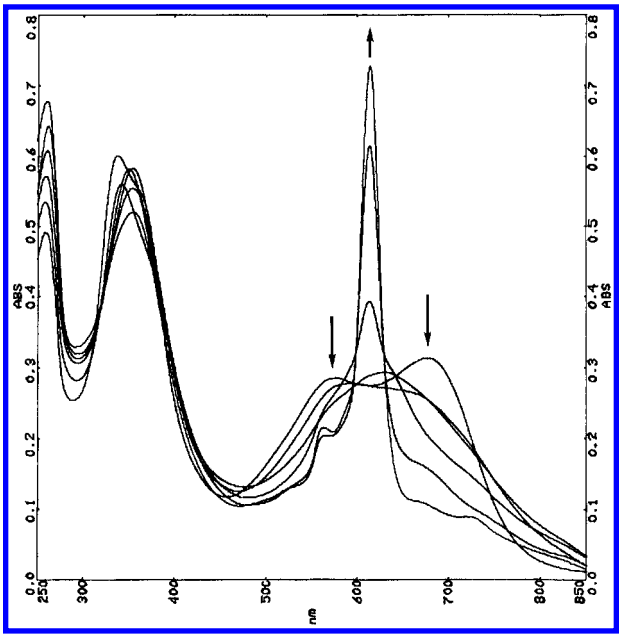


Figure 7. Porphyrazine **2** (M = Mg) titrated with $Hg(ClO_4)_2 \cdot 3H_2O$ (0, 1, 2, 3, 4, 6 equiv).

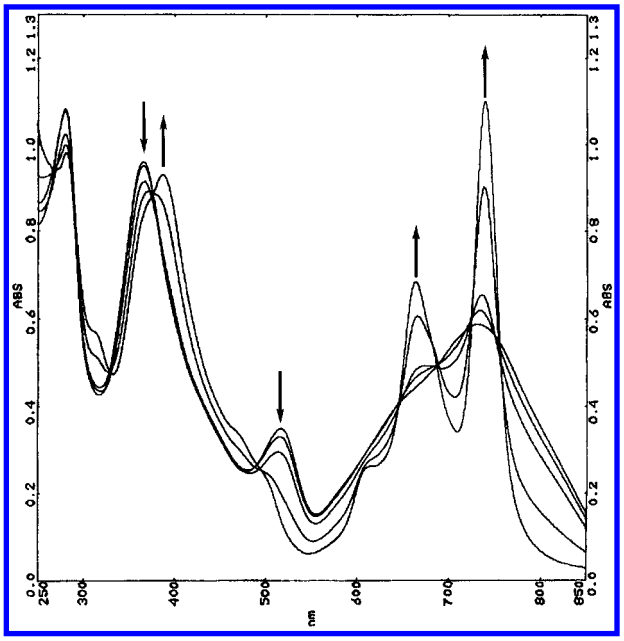


Figure 8. Norphthalocyanine **3** titrated with $Pb(NO_3)_2 \cdot 6H_2O$ (0, 0.5, 1, 2, 4 equiv).

UV−vis titrations of porphyrazine **1** (M = Ni) there is a dramatic change when going from 0 to 2 equiv of a metal salt and comparatively little change until porphyrazine **1** (M = Ni) is treated with greater than 100 equiv of a metal salt (Figure 6). Overall, the benzyl groups may suppress peripheral coordination of metal ions. In contrast, the corresponding porphyrazine **2** (M = Mg) has pendent 2-pyridylmethyl groups, which may themselves enhance peripheral metal ion binding (they are clearly double-armed diazacrown entities) by enveloping the cation in a similar fashion as bicyclic cryptands. Double-armed diazaoxocrown ethers bind a wide range of both alkaline earth and transition-metal cations, and a wealth of examples bearing nitrogens at opposite sides of the macrocycle have been reported.[23] The fusion of a diazacrown ether and an ethylenediamine derivative[24] in **12b** and ultimately **2** (M = Mg) ought to offer enhanced metal ion binding properties. Indeed, as is discussed in the previous section, the crown **12b** forms a square-pyramid complex with copper(II).

Porphyrazine **2** (M = Mg) was titrated with $KClO_4$, $Cr(ClO_4)_3 \cdot 6H_2O$, $Mn(ClO_4)_2 \cdot 6H_2O$, $CoCl_2$, $Ni(ClO_4)_2 \cdot 6H_2O$, $CuCl_2$, $Zn(ClO_4)_2 \cdot 6H_2O$, $AgBF_4$, $CdCl_2$, $Hg(ClO_4)_2 \cdot 3H_2O$, and $Pb(NO_3)_2$. With the exchange of benzyl for 2-pyridylmethyl, the ability of porphyrazine **2** (M = Mg) to coordinate Hg(II) (Figure 7) and Ag(I) improved dramatically. Instead of requiring over 100 equiv of metal salt to effect the disappearance of the n−π* peak and the sharpening of the Q-band, the UV−vis spectrum no longer changed after 6 equiv. Not only does the coordinating ability improve for Hg(II) and Ag(I), but porphyrazine **2** (M = Mg) was able to coordinate Pb(II) as effectively as Hg(II) and Ag(I). UV−vis titrations were consistent with porphyrazine **2** (M = Mg), also being able to coordinate Cu(II), Co(II), Zn(II), and Cd(II) although less effectively than Hg(II), Ag(I), or Pb(II) as 20−40 equiv were needed for the disappearance of the n−π* peak and the sharpening of the Q-band.

Norphthalocyanine **3**, being very soluble in organic solvents, was subject to UV−vis titrations with $Cu(OAc)_2$ and other metal salts. The n−π* transition of the electron lone pairs on the two peripheral nitrogen atoms should disappear if a metal coordinates to these nitrogens because the electron lone pairs would no longer be available to the norphthalocyanine ring system. Similar to porphyrazines **1** and **2**, a sharpening of the Q-band accompanied the disappearance of the n−π* peak ultimately leading to a spectrum that resembled the analogous porphyrazine or phthalocyanine derivative. In norphthalocyanines, however, the Q-band will sharpen to resemble a C_{2v}-symmetric phthalocyanine that has a split Q-band due to the degeneracy of the e_g molecular orbitals. The UV−vis titration with $Cu(OAc)_2$ showed that norphthalocyanine **3** coordinated Cu(II), but 100 equiv of Cu(II) was needed to effect the complete disappearance of the n−π* peak at 512 nm. UV−vis titrations of norphthalocyanine **3** and the metal salts of Pb(II), Hg(II), Ag(I), Zn(II), Co(II), and Cd(II) all resulted in disappearance of the n−π* peak at 512 nm. Binding of exactly one metal on the periphery is the maximal result for the norphthalocyanines. Of all the metals that norphthalocyanine **3** coordinated, Pb(II) exhibited the strongest binding. However, more than 2 equiv of even this metal was required to effect full coordination (Figure 8). Hg(II) and Ag(I) experienced similar binding to Pb(II) and Zn(II), Co(II), and Cd(II) all needed greater than 10 equiv. As in porphyrazine **2** (M = Mg), the crown ring may impede coordination of the metal, and to study its effect the pyridylmethyl−methyl porphyrazine **4** and norphthalocyanine **5** were examined.

UV−vis titrations of porphyrazine **4** with $KClO_4$, $Cr(ClO_4)_3 \cdot 6H_2O$, $Mn(ClO_4)_2 \cdot 6H_2O$, $CoCl_2$, $Ni(ClO_4)_2 \cdot 6H_2O$,

(23) For examples, see: Gandour, R. D.; Fonczek, F. R.; Gatto, V. J.; Minganti, C.; Schultz, R. A.; White, B. D.; Arnold, K. A.; Mazzocchi, D.; Miller S. R., Gokel G. W. *J. Am. Chem. Soc.* **1986**, *108*, 4078. Gokel G. W. *Chem. Soc. Rev.* **1992**, *92*, 39. Tsukube, H.; Yamashita, K.; Iwachido, T.; Zenki, M. *J. Org. Chem.* **1991**, *56*, 268. Tsukube, H.; Minatogawa, H.; Munakata, M.; Toda, M.; Matsumoto, K. *J. Org. Chem.* **1992**, *57*, 542.

(24) Bailey, N. A.; McKenzie, E. D.; Worthington, J. M. *J. Chem. Soc., Dalton Trans.* **1973**, 1227. (b) Li, C.-K.; Tang, W.-T.; Che, C.-M.; Wong, K.-Y.; Wang, R.-J.; Mak, T. C. W. *J. Chem. Soc., Dalton Trans.* **1991**, 1909.

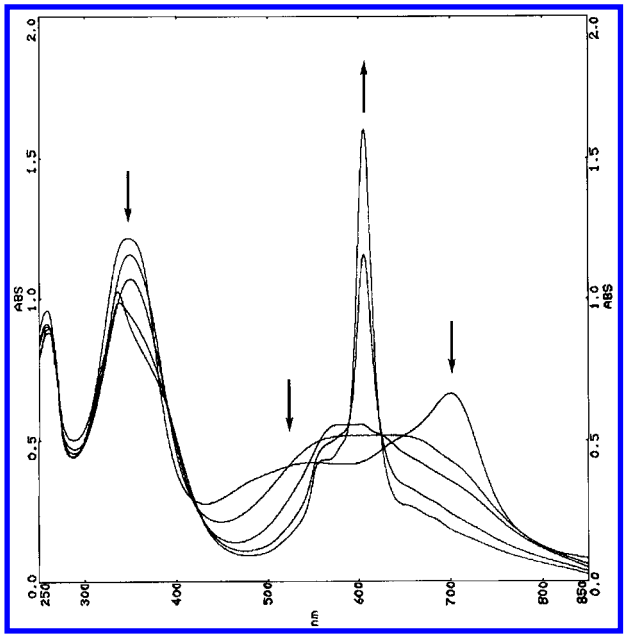


Figure 9. Porphyrazine **4** titrated with $CoCl_2$ (0, 1, 2, 3, 4 equiv).

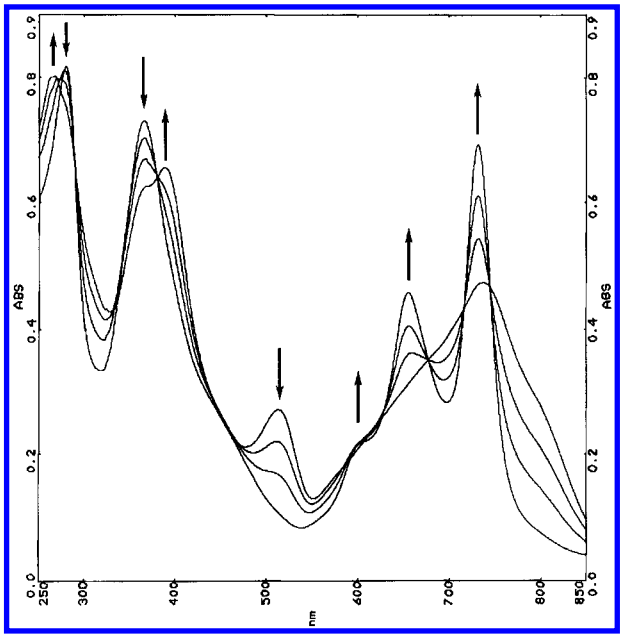
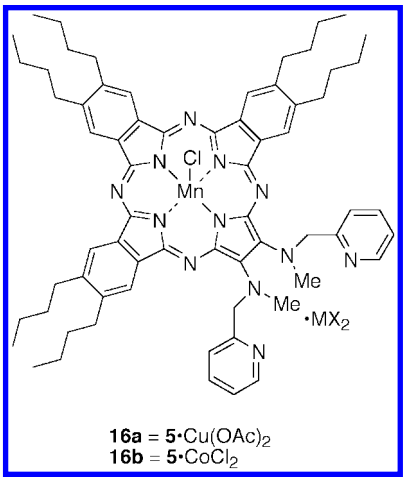


Figure 10. Norphthalocyanine **5** titrated with $Cu(OAc)_2$ (0.0, 0.25, 0.50, 1.0 equiv).

$CuCl_2$, $Zn(ClO_4)_2 \cdot 6H_2O$, $AgBF_4$, $CdCl_2$, $Hg(ClO_4)_2 \cdot 3H_2O$, and $Pb(NO_3)_2$ showed that the crown ether rings in porphyrazine **2** (M = Mg) were necessary only to bind Pb(II). Without the crown ether rings of porphyrazine **2** (M = Mg), porphyrazine **4** readily coordinated the first-row transition metals Co(II), Cu(II), and Zn(II). Only a slight excess of the metal salt was required before the n$-\pi^*$ peak disappeared and the Q-band sharpened [for example, see Figure 9 for Co(II)]. Porphyrazine **4** also coordinated Hg(II), Cd(II), and Ag(I). Both porphyrazines **4** and **2** (M = Mg) fully coordinated Hg(II), and porphyrazine **4** coordinated Cd(II) better than porphyrazine **2** (M = Mg). Porphyrazine **2** (M = Mg) readily coordinated Pb(II) but porphyrazine **4** did not, indicating that the crown ether ring is necessary to bind Pb(II) around the periphery. Porphyrazine **2** (M = Mg) fully coordinated Ag(I) as seen by the disappearance of the n$-\pi^*$ peak and the sharpening of the Q-band. However, in the visible spectrum of porphyrazine **4** in the presence of Ag(I), the n$-\pi^*$ peak disappeared but the Q-band remained broad and only shifted slightly to a shorter wavelength.

A summary of the metal-binding abilities of porphyrazines **1** (M = Ni), **2** (M = Mg), and **4** is shown in the Table 1. In general, compared to porphyrazine **1** (M = Ni), there is an improvement in metal coordinative ability in the series porphyrazine **4** > **2** (M = Mg) > **1** (M = Ni), with Pb(II) being the only exception. The crown ether and 2-pyridylmethyl moieties are necessary to bind Pb(II), whereas only the 2-pyridylmethyl moieties are necessary for the binding of Co(II), Cu(II), Zn(II), Ag(I), Cd(II), and Hg(II).

Since the octakis[*N*-methyl-*N*-(2-pyridylmethyl)amino]-porphyrazine **4** was superior for peripheral metal ion binding than either of the crowned porphyrazines **1** or **2**, the norphthalocyanine system **5** (M = MnCl) was investigated. UV−vis titration of **5** (M = MnCl) with $Cu(OAc)_2$ was complete with 1 equiv (Figure 10). Norphthalocyanine **5** (M = MnCl) also coordinated Cd(II) and Co(II) as effectively as Cu(II); however, full coordination of Zn(II) and Hg(II) required 2 equiv of metal salt. Once again, with the exception of Pb(II), removal of the crown ether ring [compare **3** and **5** (M = MnCl)] dramatically improved the peripheral metal-binding capabilities. Slow evaporation of a 1:1 mixture of norphthalocyanine **5** (M = MnCl) and $Cu(OAc)_2$ or $CoCl_2$ gave the bimetallic complexes **16a** and **16b**. Unfortunately, neither of these



16a = **5**·$Cu(OAc)_2$
16b = **5**·$CoCl_2$

substances were obtained suitably crystalline for X-ray structure determinations. The metal-binding abilities of norphthalocyanines **3** and **5** (M = MnCl) are summarized in Table 2. The results parallel those of porphyrazines **2** (M = Mg) and **4** in that with the removal of the crown ring the ability to coordinate Pb(II) is lost; however, in norphthalocyanine **5** (M = NiCl) the ability to coordinate Ag(I) is lost as well.

Conclusions

It is clear that the porphyrazines **1**, **2**, and **4** and the norphthalocyanines **3** and **5** are able to bind inorganic metal ions to the peripheral ligating functionality with significant changes in the UV−vis spectra. In general, with the exception of the binding of Pb(II), the macrocycles functionalized with pendant *N*-methyl-*N*-(2-pyridylmethyl)amino groups **4** and **5** were superior ligands

Table 2. Summary of the Ability of Norphthalocyanine 3 and 5 (M = MnCl) to Coordinate Metal Cations on the Periphery (Based on UV−vis Titrations)[a]

	norphthalocyanine	
metal salt	**3**	**5** (M = MnCl)
NaBr	−	−
KBr	−	−
$CaCl_2$	−	−
$BaCl_2$	−	−
$Cr(ClO_4)_3 \cdot 6H_2O$	−	−
$Mn(ClO_4)_2 \cdot 6H_2O$	−	−
$Fe(ClO_4)_3 \cdot xH_2O$	−	−
$Co(BF_4)_2 \cdot 6H_2O$	poor	excellent
$Ni(ClO_4)_2 \cdot 6H_2O$	−	−
$Cu(OAc)_2$	very poor	excellent
$Zn(ClO_4)_2 \cdot 6H_2O$	poor	very good
$RuCl_3 \cdot H_2O$	−	−
$AgBF_4$	good	−
$CdCl_2$	poor	excellent
$Hg(ClO_4)_2 \cdot 6H_2O$	good	very good
$Pb(NO_3)_2$	good	−

[a] Qualitative rankings shown are based on molar equivalents of metal salt per peripheral chelate necessary to effect no further change in the UV−vis titration: −, no effect in UV−vis; poor, 100 equiv; good to very good, 25−4 equiv; excellent, 1 equiv.

for the formation of star and solitaire complexes in solution than the corresponding crowned[25] macrocycles **2** and **3**. These results are relevant to the development of selective ion optical sensors.

Experimental Section

Reactions were conducted in oven- or flame-dried glassware under N_2. Reaction temperatures reported refer to external bath temperatures. Solvents used in chromatography were BDH AnalR or GPR grade and were used without further purification. Solvents used for reactions were distilled prior to use: THF, DME, and Et_2O (from sodium−benzophenone ketyl); CH_2Cl_2 and MeCN (from CaH_2); DMF [predried over BaO, distilled from neutral alumina (activity I)]; MeOH, 1-propanol, and 1-butanol (from Mg). All other reagents were purchased from commercial sources and were used without further purification.

TLC was performed on Merck Kieselgel 60 F-254 glass plates. Unless stated to the contrary, chromatography was carried out on Merck Kieselgel 60 (230−400 mesh) (eluants are given in parentheses). Unless stated to the contrary, organic extracts were dried over Na_2SO_4 or $MgSO_4$. All solvents were evaporated at or below 50 °C under reduced pressure using a rotary evaporator.

2-Amino-3-[(2-pyridylmethylene)amino]-2(*Z*)-butene-1,4-dinitrile (7). 2-Pyridinecarboxaldehyde (29.7 g, 280 mmol) was added to diaminomaleonitrile (**6**) (20.0 g, 185 mmol) in MeOH (125 mL), and the mixture was stirred for 12 h when a yellow solid precipitated out of solution. The solid was collected by vacuum filtration and washed with Et_2O−hexanes (1:1) (500 mL) to yield imine **7** (31.9 g, 88%) as a light tan solid: mp 195−197 °C; R_f 0.40 (EtOAc); IR (DRIFTS) ν_{max} 3371, 2236, 2197, 1636, 1606, 1589, 1562 cm^{-1}; ^1H NMR ($CDCl_3$/DMSO-d_6, 270 MHz) δ 6.94−6.99 (1H, m), 7.15 (2H, br s), 7.35−7.42 (1H, m), 7.83 (1H, d, J = 7.9 Hz), 7.95 (1H, s), 8.25 (1H, d, J = 4.0 Hz); ^{13}C NMR (DMSO, 75 MHz) δ 102.4, 113.8, 114.6, 122.4, 125.8, 128.7, 137.2, 150.1, 154.2, 155.1; MS (CI, NH_3) m/z 198 $(M + H)^+$, 107 $(M - PyrCH_2 + 2H)^+$; HRMS (CI, NH_3) m/z calcd for $C_{10}H_8N_5$ $(M + H)^+$ 198.0778, found 198.0782. Anal. Calcd for $C_{10}H_7N_5$: C, 60.91; H, 3.58; H, 35.51. Found: C, 60.62; H, 3.70; N, 35.32.

2-Amino-3-[(2-pyridylmethyl)amino]-2(*Z*)-butene-1,4-dinitrile (8). $NaBH_4$ (3.9 g, 101.5 mmol) was slowly added to a rapidly stirring solution of imine **7** (20.0 g, 101.5 mmol) in MeOH (250 mL) and THF (375 mL). After the addition was complete, the solution was stirred for 15 min and poured into rapidly stirring ice−H_2O (2.5 L). After 15 min, the solid was collected via vacuum filtration, washed with H_2O (500 mL) and dried under vacuum to give dinitrile **8** (16.4 g, 81%) as a dark tan solid: mp 120−123 °C; R_f 0.50 (EtOAc); IR (DRIFTS) ν_{max} 3387, 3332, 3215, 2219, 2213, 1612, 1598, 1370 cm^{-1}; ^1H NMR ($CDCl_3$/DMSO-d_6, 270 MHz) δ 3.72 (2H, d, J = 6.4 Hz), 4.79 (2H, s), 4.99 (1H, t, J = 6.4 Hz), 6.57−6.62 (1H, m), 6.69 (1H, d, J = 7.7 Hz), 7.06−7.12 (1H, m), 7.90 (1H, d, J = 4.7 Hz); ^{13}C NMR (DMSO, 75 MHz) δ 51.0, 108.4, 108.9, 116.2, 117.2, 121.7, 122.9, 137.4, 149.7, 159.0 (*C*(2)Pyr); MS (CI, NH_3) m/z 200 $(M + H)^+$, 107 $(M - PyrCH_2)^+$; HRMS (CI, NH_3) m/z calcd for $C_{10}H_{10}N_5$ $(M + H)^+$ 200.0936, found 200.0940. Anal. Calcd for $C_{10}H_9N_5$: C, 60.29; H, 4.55; N, 35.15. Found: C, 60.03; H, 4.26; N, 34.78.

2-[(2-Pyridylmethylene)amino]-3-[(2-pyridylmethyl)-amino]-2(*Z*)-butene-1,4-dinitrile (9). CF_3CO_2H (5 drops) was added to dinitrile **8** (15.0 g, 75.4 mmol) and 2-pyridinecarboxaldehyde (12.1 g, 113.1 mmol) in MeOH (150 mL). After 1 h, a precipitate began to form, and after 5 h, the solid was collected by vacuum filtration and was washed with Et_2O (300 mL) to give imine **9** (17.2 g, 79%) as a yellow solid: mp 149−151 °C; R_f 0.20 (EtOAc); IR (DRIFTS) ν_{max} 3262, 2236, 2203, 1606, 1595, 1563, 1435 cm^{-1}; ^1H NMR ($CDCl_3$, 270 MHz) δ 2.20 (1H, br s), 4.77 (2H, s), 7.28−7.38 (3H, m), 7.71−7.81 (2H, m), 8.00 (1H, d, J = 7.9 Hz), 8.50 (1H, s), 8.62 (1H, d, J = 4.5 Hz), 8.69 (1H, d, J = 5.0 Hz); ^{13}C NMR (DMSO, 75 MHz) δ 51.1, 102.7, 113.5, 113.9, 122.0, 122.4, 123.3, 125.9, 137.2, 137.6, 149.8, 150.3, 154.1, 155.5, 157.3; MS (CI, NH_3) m/z 289 $(M + H)^+$, 198 $(M - PyrCH_2 + 2H)^+$; HRMS (CI, NH_3) m/z calcd for $C_{16}H_{13}N_6$ $(M + H)^+$ 289.1202, found 289.1201. Anal. Calcd for $C_{16}H_{12}N_6$: C, 66.66; H, 4.20; N, 29.15. Found: C, 66.70; H, 4.03; N, 28.92.

2,3-Bis[(2-pyridylmethyl)amino]-2(*Z*)-butene-1,4-dinitrile (10b). $NaBH_4$ (2.30 g, 60.1 mmol) was slowly added to imine **9** (17.3 g, 60.1 mmol) in MeOH (150 mL) and THF (225 mL). After the addition was complete, the solution was stirred for 15 min and poured into rapidly stirring ice−H_2O (2.0 L). After 15 min, the solid was collected via vacuum filtration, washed with H_2O (500 mL), and dried under vacuum to give dinitrile **10b** (13.5 g, 78%) as a dark tan solid: mp 90−93 °C; R_f 0.16 (EtOAc); IR (DRIFTS) ν_{max} 3292, 2205, 1605 cm^{-1}; ^1H NMR ($CDCl_3$, 270 MHz) δ 4.43 (4H, d, J = 5.9 Hz), 4.95−4.98 (2H, m), 7.20−7.27 (4H, m), 7.66−7.72 (2H, m), 8.54 (2H, d, J = 5.0 Hz); ^{13}C NMR (DMSO, 75 MHz) δ 50.9, 113.4, 114.7, 122.1, 122.8, 137.0, 149.3, 156.6; MS (CI, NH_3) m/z 291 $(M + H)^+$, 198 $(M - PyrCH_2 + H)^+$; HRMS (CI, NH_3) m/z calcd for $C_{16}H_{15}N_6$ $(M + H)^+$ 291.1358, found 291.1363. Anal. Calcd for $C_{16}H_{14}N_6$: C, 66.19; H, 4.86; N, 28.95. Found: C, 65.93; H, 5.15; N, 28.72.

1,14-Diiodo-3,6,9,12-tetraoxatetradecane (11). With rapid stirring at 0 °C, I_2 (30.4 g, 120 mmol) was slowly added to pentaethylene glycol (10 g, 42 mmol), Ph_3P (28.6 g, 109.1 mmol), and imidazole[26] (7.8 g, 115 mmol) in MeCN (60 mL) and Et_2O (100 mL), resulting in a brown-black slurry. After being stirred at 0 °C for 3 h, the mixture was diluted with Et_2O (900 mL), filtered, and washed with saturated aqueous $Na_2S_2O_3$ (3 × 225 mL), saturated aqueous $CuSO_4$ (3 × 225 mL), and H_2O (3 × 225 mL). The organic layer was dried, filtered, and concentrated to give a white oily solid. Et_2O (100 mL) was added, the resulting suspension was filtered, and the filtrate was concentrated to give another white oily solid. This procedure was repeated with Et_2O (50 mL) to give a clear slightly yellow oil. Chromatography (EtOAc−hexanes 1:2) gave diiodide **11** (18.0 g, 94%) as a clear oil: R_f 0.42 (EtOAc−hexanes 1:1); IR (neat) ν_{max} 1461, 1349, 1107 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 3.19 (4H, t, J = 7.0 Hz), 3.60 (12H, s), 3.69 (4H, t, J = 7.0 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 3.4, 70.6, 71.0, 71.1, 72.3; MS (CI, NH_3) m/z 476 $(M + NH_4)^+$, 459 $(M + H)^+$, 177 $(M - I - CH_2CH_2I + H)^+$; HRMS (CI, NH_3) m/z calcd for $C_{10}H_{24}I_2NO_4$ $(M + NH_4)^+$ 475.9795, found 475.9780.

(25) For an overview of metal ion complexation by crown ethers and related macrocycles, see: Lindoy, L. F. *The Chemistry of Macrocyclic Ligand Complexes*; Cambridge University Press: 1989.

(26) Marshall, J. A.; Cleary, D. G. *J. Org. Chem.* **1986**, *51*, 858.

3,18-Diaza-3,18-dibenzyl-1,2-dicyano-6,9,12,15-tetraoxacyclooctadecene (12a). A solution of dinitrile **10a**[19] (7.2 g, 25 mmol) and diiodide **11** (11.45 g, 25 mmol) in dry DMF (50 mL) was added with stirring over 8 h to Cs_2CO_3 (20.4 g, 62.5 mmol) in dry DMF (1200 mL) at 50 °C. After a further 24 h, the mixture was allowed to cool to room temperature and stirred for 24 h. After the solvent was evaporated, EtOAc (300 mL) was added to the residue. The organic suspension was washed with water (2 × 100 mL) and brine (1 × 100 mL) and the solvent evaporated. Chromatography (EtOAc−hexanes 1:1−1:0) gave dinitrile **12a** (6.13 g, 50%) as a mixture of geometrical isomers. Crystallization from EtOAc gave *Z*-dinitrile **12a** (3.1 g, 25%) as a yellow crystalline solid: mp 108−110 °C (EtOAc); R_f 0.21 (EtOAc−hexanes 1:1); IR ($CHCl_3$) ν_{max} 2201, 1579, 1496, 1125 cm^{-1}; ^1H NMR ($CDCl_3$, 270 MHz) δ 3.31 (4H, t, J = 5.0 Hz), 3.59−3.69 (16H, m), 4.45 (4H, s), 7.11−7.28 (10H, m); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 50.9, 55.1, 69.2, 70.2, 70.6, 70.9, 115.3, 116.5, 127.5, 128.2, 128.6, 137.1; MS (CI, NH_3) m/z 491 $(M + H)^+$, 401 $(M - PhCH_2)^+$, 91 $(PhCH_2)^+$; HRMS (CI, NH_3) m/z calcd for $C_{28}H_{35}N_4O_4$ $(M + H)^+$ 491.2658, found 491.2625. Anal. Calcd for $C_{28}H_{34}N_4O_4$: C, 68.55; H, 6.99; N, 11.42. Found: C, 68.53; H, 6.99; N, 11.41.

3,18-Diaza-1,2-dicyano-3,18-bis(2-pyridylmethyl)-6,9,12,15-tetraoxacyclooctadecene (12b). Dinitrile **10b** (7.25 g, 25.0 mmol) and diiodide **11** (11.5 g, 25.0 mmol) in dry DMF (50 mL) were added over 8 h to a suspension of Cs_2CO_3 (20.4 g, 62.5 mmol) in dry DMF (1200 mL) at 50 °C. After the addition was complete, the mixture was stirred at 50 °C for 24 h, allowed to cool to room temperature, and stirred for a further 24 h. After evaporation, EtOAc (300 mL) was added to the residue, which was washed with H_2O (2 × 100 mL) and brine (1 × 100 mL), and the solvent evaporated. Chromatography (EtOAc−MeOH 95:5) gave dinitrile **12b** (6.13 g, 55%) as a mixture of geometrical isomers. Crystallization of this mixture from EtOAc gave (*Z*)-**12b** (3.1 g, 30%) as a dark-yellow crystalline solid: mp 194−196 °C (EtOAc); R_f 0.18 (EtOAc-MeOH 95:5); IR ($CHCl_3$) ν_{max} 2201, 1589, 1123 cm^{-1}; ^1H NMR ($CDCl_3$, 270 MHz) δ 3.42 (4H, t, J = 5.0 Hz), 3.61−3.70 (16H, m), 4.62 (4H, s), 7.10−7.16 (4H, m), 7.55−7.62 (2H, m), 8.42−8.44 (2H, m); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 51.6, 56.0, 69.3, 70.3, 70.7, 71.0, 115.5, 116.4, 122.3, 122.4, 136.6, 149.5, 157.5; MS (CI, NH_3) m/z 493 $(M + H)^+$, 402 $(M - PyrCH_2 + H)^+$, 94 $(PyrCH_2 + 2H)^+$; HRMS (CI, NH_3) m/z calcd for $C_{26}H_{33}N_6O_4$ $(M + H)^+$ 493.2565, found 493.2584. Anal. Calcd for $C_{26}H_{32}N_6O_4$: C, 63.40; H, 6.55; N, 17.06. Found: C, 63.51; H, 6.25; N, 16.99.

[Tetrakis(1,16-diaza-1,16-dibenzyl-4,7,10,13-tetraoxacyclooctadeceno)[14,15-*b*:14′,15′-*g*:14″,15″-*l*:14‴,15‴-*q*]-porphyrazinato]magnesium(II) [1 (M = Mg)]. Mg turnings (12.4 mg, 0.51 mmol), a crystal of I_2, and 1-butanol (20 mL) were heated at reflux for 24 h. After the mixture was cooled to room temperature, dinitrile **12a** (500 mg, 1.02 mmol) was added and the solution heated at reflux for a further 36 h. After being allowed to cool to room temperature, the mixture was diluted with $CHCl_3$ (20 mL), vacuum filtered through Celite, and evaporated. Chromatography (EtOAc−MeOH 99:1−95:5) gave porphyrazine **1** (M = Mg) (125 mg, 25%) as a dark blue solid: mp 187−190 °C; R_f 0.34 ($CHCl_3$−MeOH 95:5); IR ($CHCl_3$) ν_{max} 1559, 1453, 1290, 1115 cm^{-1}; UV−vis ($CHCl_3$) λ_{max} (log ϵ) 334 (4.67), 363 (4.71), 566 (4.37), 709 (4.58) nm; ^1H NMR ($CDCl_3$, 270 MHz) δ 2.90−3.90 (64H, br m), 4.20−4.60 (16H, br m), 5.20−5.60 (16H, br m), 6.70−7.60 (40H, br m); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 51.9, 56.3, 71.1, 126.5, 128.4, 128.6, 137.5, 141.8, 152.6; FABMS m/z 1986 $(M)^+$, 993 $(M)^{2+}$. Anal. Calcd for $C_{112}H_{136}MgN_{16}O_{16}$: C, 67.71; H, 6.90; N, 11.28. Found: C, 67.71; H, 6.90; N, 11.08.

Tetrakis(1,16-diaza-1,16-dibenzyl-4,7,10,13-tetraoxacyclooctadeceno)[14,15-*b*:14′,15′-*g*:14″,15″-*l*:14‴,15‴-*q*]porphyrazine [1 (M = 2H)]. In the dark, CF_3CO_2H (2 mL) was added to porphyrazine **1** (M = Mg) (107 mg, 0.054 mmol), and after 20 min, the solution was added to rapidly stirring ice−H_2O (50 mL) and neutralized with 1 M NaOH. The suspension was vacuum filtered through Celite, and the solids were washed with distilled water. Chromatography ($CHCl_3$−MeOH 97.5:2.5) gave porphyrazine **1** (M = 2H) (101 mg, 95%) as a dark blue solid: mp 190−193 °C; R_f 0.57 ($CHCl_3$−MeOH 95:5); IR ($CHCl_3$) ν_{max} 1572, 1549, 1121 cm^{-1}; UV−vis ($CHCl_3$) λ_{max} (log ϵ) 326 (4.58), 358 (4.55), 562 (4.58), 668sh, 740sh nm; ^1H NMR ($CDCl_3$, 270 MHz) δ −1.03 (2H, s), 3.52−3.79 (64H, br m), 4.45 (16H, br s), 5.40 (16H, s), 7.03−7.08 (24H, m), 7.37−7.39 (16H, m); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 50.6, 55.3, 70.2, 70.6, 70.8, 71.0, 126.3, 128.0, 128.5, 136.2, 140.6, 148.1; FABMS m/z 1964 $(M)^+$, 1873 $(M - PhCH_2)^+$, 1782 $(M - 2PhCH_2)^+$. Anal. Calcd for $C_{112}H_{138}N_{16}O_{16}$: C, 68.48; H, 7.08; N, 11.41. Found: C, 68.58; H, 7.27; N, 11.38.

[Tetrakis(1,16-diaza-1,16-dibenzyl-4,7,10,13-tetraoxacyclooctadeceno)[14,15-*b*:14′,15′-*g*:14″,15″-*l*:14‴,15‴-*q*]-porphyrazinato]nickel(II) (1 (M = Ni)). Porphyrazine **1** (M = 2H) (40 mg, 0.02 mmol) and $Ni(OAc)_2$ (50.7 mg, 0.204 mmol) in DMF (1.5 mL) and PhCl (4 mL) were heated at reflux for 12 h and cooled to room temperature, and the blue suspension was vacuum filtered through Celite and the solvent evaporated. Chromatography ($CHCl_3$−MeOH 100:0−97.5:2.5) gave porphyrazine **1** (M = Ni) (38 mg, 92%) as a dark blue solid: mp 172−175 °C ($CHCl_3$−MeOH); R_f 0.42 ($CHCl_3$−MeOH 95:5); IR ($CHCl_3$) ν_{max} 1576, 1451, 1192 cm^{-1}; UV−vis ($CHCl_3$) λ_{max} (log ϵ) 312 (4.69), 380sh, 541 (4.51), 671 (4.41) nm; ^1H NMR ($CDCl_3$, 300 MHz) δ 3.55−3.81 (64H, m), 4.44 (16H, br s), 5.39 (16H, s), 7.09−7.15 (24H, m), 7.41−7.43 (16H, m); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 50.8, 55.8, 70.2, 70.6, 70.8, 70.9, 126.4, 128.1, 128.5, 137.3, 140.7, 143.4; FABMS m/z 2020 $(M)^+$, 1010 $(M)^{2+}$. Anal. Calcd for $C_{112}H_{136}N_{16}NiO_{16}$: C, 66.56; H, 6.78; N, 11.09. Found: C, 66.48; H, 6.69; N, 10.80.

[Tetrakis[1,16-diaza-1,16-bis(2-pyridylmethyl)-4,7,10,13-tetraoxacyclooctadeceno][14,15-*b*:14′,15′-*g*:14″,15″-*l*:14‴,15‴-*q*]porphyrazinato]magnesium(II) [2 (M = Mg)]. Mg turnings (5.3 mg, 0.22 mmol), a crystal of I_2, and 1-butanol (5 mL) were heated at reflux for 24 h and cooled to room temperature when dinitrile **12b** (220 mg, 0.44 mmol) was added and the solution heated at reflux for a further 24 h. After being allowed to cool to room temperature, the mixture was diluted with $CHCl_3$ (6 mL) and vacuum filtered through Celite and the solvent evaporated. Chromatography ($CHCl_3$−MeOH−NH_4OH 97.25:2.5:0.25−83.5:15:1.5) gave porphyrazine **2** (M = Mg) (35 mg, 16%) as a dark green solid: mp 115−118 °C; R_f 0.16 ($CHCl_3$−MeOH−NH_4OH) 94:5:1); IR ($CHCl_3$) ν_{max} 1591, 1569, 1108 cm^{-1}; UV−vis ($CHCl_3$) λ_{max} (log ϵ) 257 (4.54), 342 (4.58), 580 (4.25), 664 (4.29) nm; ^1H NMR ($CDCl_3$, 400 MHz) δ 2.90−3.86 (64H, m), 4.06−4.64 (16H, m), 5.56 (16H, br s), 6.61−7.98 (24H, m), 8.26−8.93 (8H, m); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 51.8, 58.1, 69.7, 70.1, 70.4, 70.6, 121.4, 122.6, 136.3, 137.1, 148.7, 152.1, 160.7; FABMS m/z 1995 $(M + H)^+$.

2,3-Bis[methyl(2-pyridylmethyl)amino]-2(*Z*)-butene-1,4-dinitrile (13). Dinitrile **10b** (1.0 g, 3.5 mmol) in 1,2-dimethoxyethane (DME) (10 mL) was added to a cooled (−22 °C) suspension of NaH (60% dispersion in mineral oil; 350 mg, 8.6 mmol) in DME (10 mL). After 30 min, Me_2SO_4 (1.0 g, 7.9 mmol) in DME (5 mL) was added, and the brown mixture was cooled to −45 °C and then allowed to warm slowly to room temperature. H_2O (5 mL) was carefully added and the aqueous layer extracted with EtOAc (3 × 30 mL). The combined organic layers were washed with H_2O (2 × 25 mL) and brine (1 × 25 mL), dried, and evaporated. Chromatography (EtOAc to EtOAc−MeOH 97.5:2.5) gave dinitrile **13** (780 mg, 71%) as a brown oil: R_f 0.23 (EtOAc−MeOH 95:5); IR (neat) ν_{max} 2185, 1591, 761 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 2.83 (6H, s), 4.40 (4H, s), 7.16−7.28 (4H, m), 7.64−7.69 (2H, m), 8.53−8.56 (2H, m); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 41.8, 60.2, 45.5, 118.2, 123.3, 123.4, 137.5, 150.4, 157.0; MS (CI, NH_3) m/z 319 $(M + H)^+$, 228 $(M - PyrCH_2 + 2H)^+$, 94 $(PyrCH_2 + 2H)^+$; HRMS (CI, NH_3) m/z calcd for $C_{18}H_{19}N_6$ $(M + H)^+$ 319.1671, found 319.1686. Anal. Calcd for $C_{18}H_{18}N_6$: C, 67.91; H, 5.70; N, 26.40. Found: C, 67.94; H, 5.48; N, 26.15.

[2,3,7,8,12,13,17,18-Octa[methyl(2-pyridylmethyl)amino]porphyrazinato]magnesium(II) (4). Dry 1-propanol (5 mL) and a crystal of I_2 were added to Mg turnings (10 mg, 0.41 mmol), and the suspension was heated at reflux for 24 h. After the mixture was cooled to room temperature, dinitrile **13** (350 mg, 1.10 mmol) in dry 1-propanol (2 mL) was added. The resulting suspension was heated at reflux for 24 h, cooled

to room temperature, diluted with $CHCl_3$ (10 mL), and filtered through Celite and the solvent evaporated. Chromatography ($CHCl_3$−MeOH−NH_4OH 94:5:1) followed by gel permeation chromatography on Bio-Beads S-X3 ($CHCl_3$) gave porphyrazine **4** (45 mg, 13%) as a dark blue solid: mp 92−95 °C; IR ($CHCl_3$) ν_{max} 1571, 1473, 1434 cm^{-1}; UV−vis ($CHCl_3$), λ_{max} (log ϵ) 258 (4.48), 352, (4.65), 531, (4.16), 702 (4.48) nm; ^1H NMR ($CDCl_3$, 300 MHz) δ 3.56 (24H, br s), 5.09 (16H, br s), 6.84−6.86 (8H, m), 7.22−7.31 (16H, m), 7.94 (8H, br s); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 42.9, 61.5, 121.5, 122.2, 136.4, 138.3, 148.4, 152.4, 160.2; FABMS *m/z* 1298 $(M)^+$, 1259 $(M - Mg - Me)^+$, 1071 $(M - Mg - Me - 2(PyrCH_2))^+$.

2,3-[14′,15′-[1′,16′-Diaza-1′,16′-bis(2-pyridylmethyl)-4′,7′,-10′,13′-tetraoxacyclooctadeceno]]-9,10,18,19,27,29-hexabutylnorphthalocyanine [15a (M = 2H)]. A rapidly stirred mixture of Mg turnings (23 mg, 0.91 mmol), 1-butanol (8.0 mL), and I_2 (1 crystal) was heated at reflux for 24 h. Solid I_2 was slowly added to this refluxing mixture until a uniform white suspension was obtained. Dinitrile **14**[22] (500 mg, 2.1 mmol) and dinitrile **12b** (210 mg, 0.42 mmol) were added to the suspension at room temperature, which was heated at reflux for 24 h and then allowed to cool to room temperature. After evaporation, CH_2Cl_2 (25 mL) was added, and the resulting blue-green suspension was vacuum-filtered through Celite and concentrated to give the crude magnesium norphthalocyanine **15a** (M = Mg) as a dark gummy solid. CF_3CO_2H (7.5 mL) was added to the crude residue, which was allowed to stand protected from light for 2 h, added to ice−H_2O (100 mL) and neutralized with 1 M NaOH. The resulting suspension was extracted with $CHCl_3$ (3 × 25 mL), and the combined organic layers were dried, filtered, and concentrated to yield the crude 2*H*-norphthalocyanine. The residue was chromatographed twice (MeOH−$CHCl_3$ 0:100−5:95; hexanes (60−80 °C)−acetone−NH_4OH 80:19:1 to 75:24:1 dried over $CaCl_2$) to give norphthalocyanine **15a** (M = 2H) (54 mg, 11%) as a dark blue solid: mp 182−185 °C; R_f 0.33 ($CHCl_3$−MeOH 95:5); IR ($CHCl_3$) ν_{max} 1553, 1321, 1108, 1016 cm^{-1}; UV−vis ($CHCl_3$) λ_{max} (log ϵ) 299 (4.60), 345 (4.92), 519sh, 590sh, 654 (4.67), 685sh, 730 (4.75) nm; ^1H NMR ($CDCl_3$, 300 MHz) δ −0.44 (2H, br s), 1.12−1.18 (18H, m), 1.64−1.76 (12H, m), 1.88−2.01 (12H, m), 3.10−3.23 (12H, m), 3.55 (4H, s), 3.61−3.67 (8H, m), 4.14 (4H, br s), 4.89 (4H, br s), 5.93 (4H, s), 7.04 (2H, app t), 7.36 (2H, app t), 7.63 (2H, d, J = 7.8 Hz), 8.57 (2H, d, J = 4.3 Hz), 8.71 (2H, s), 9.07 (2H, s), 9.33 (2H, s); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 14.2, 23.1, 23.18, 23.20, 33.5, 33.6, 33.7, 33.8, 34.0, 34.1, 53.0, 59.4, 70.3, 70.4, 70.6, 70.8, 121.6, 122.6, 122.7, 122.9, 123.3, 132.3, 133.8, 136.2, 137.5, 138.2, 140.6, 142.7, 142.8, 143.7, 144.5, 149.0, 155.9, 159.3, 160.4; FABMS *m/z* 1215 $(M + H^+)$, 1123 $(M - (2\text{-Pyr})CH_2 + H)^+$, 1031 $(M - 2((2\text{-Pyr})CH_2 + H)^+$, 93 $((2\text{-Pyr})CH_2 + H)^+$; HRFABMS *m/z* calcd for $C_{74}H_{95}N_{12}O_4$ $(M + H)^+$ 215.7559, found 1215.7589. Anal. Calcd for $C_{74}H_{94}N_{12}O_4$: C, 73.12; H, 7.79; N, 13.83. Found: C, 73.22; H, 7.61; N, 13.70.

2,3-[14′,15′-(1′,16′-Diaza-1′,16′-dibenzyl-4′,7′,10′,13′-tetraoxacyclooctadeceno)]-9,10,18,19,27,29-hexabutylnorphthalocyanine [15b (M = 2H)]. A rapidly stirring mixture of Mg turnings (35 mg, 1.4 mmol), 1-butanol (11.5 mL), and I_2 (1 crystal) was heated at reflux for 24 h, when further I_2 was slowly added to this refluxing mixture until a uniform white suspension was obtained. At room temperature, dinitriles **14**[22] (750 mg, 3.1 mmol) and **12a** (310 mg, 0.63 mmol) were added as solids to the suspension, which was heated at reflux for 24 h and then allowed to cool to room temperature. After evaporation, CH_2Cl_2 (25 mL) was added, and the resulting blue-green suspension was vacuum-filtered through Celite and concentrated to give the crude magnesium norphthalocyanine **15b** (M = Mg) as a dark gummy solid. CF_3CO_2H (7.5 mL) was added to the crude residue, and the mixture was allowed to stand protected from light for 2 h, added to ice−H_2O (100 mL), and neutralized with 1 M NaOH. The resulting suspension was extracted with $CHCl_3$ (3 × 25 mL), and the combined organic layers were dried, filtered, and concentrated to yield the crude 2*H*-norphthalocyanine. The residue was chromatographed twice ($CHCl_3$; EtOAc−hexanes (60−80 °C) 1:4−1:3) to give norphthalocyanine **15b** (M = 2H) (68 mg, 9%) as a dark blue solid: mp 186−189 °C; R_f 0.35 (EtOAc−hexanes 1:3); IR ($CHCl_3$) ν_{max} 1551, 1496, 1453, 1320, 1108, 1016 cm^{-1}; UV−vis ($CHCl_3$) λ_{max} (log ϵ) 299 (4.59), 345 (4.91), 527sh, 602sh, 658 (4.65), 688sh, 733 (4.69) nm; ^1H NMR ($CDCl_3$, 300 MHz) δ −0.65 (2H, br s), 1.10−1.20 (18H, m), 1.67−1.77 (12H, m), 1.97 (12H, br s), 3.12 (12H, br s), 3.60 (12H, app d), 4.06 (4H, br s), 4.81 (4H, br s), 5.85 (4H, s), 7.28−7.37 (6H, m), 7.71 (4H, d, J = 7.2 Hz), 8.69 (2H, s), 9.01 (2H, s), 9.19 (2H, s); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 14.2, 23.1, 23.2, 33.5, 33.6, 33.8, 33.9, 34.0, 34.1, 52.3, 57.5, 70.35, 70.44, 70.7, 70.8, 122.5, 122.9, 123.4, 126.6, 128.2, 128.6, 132.3, 134.2, 137.5, 138.3, 140.2, 140.7, 142.69, 142.73, 143.3, 144.5, 156.1, 159.3; FABMS *m/z* 1212 $(M)^+$, 1122 $(M - PhCH_2 + H)^+$, 1031 $(M - 2(PhCH_2) + H)^+$, 91 $(PhCH_2)^+$; HRFABMS *m/z* calcd for $C_{76}H_{97}N_{10}O_4$ $(M + H)^+$ 1213.7694, found 1213.7705. Anal. Calcd for $C_{76}H_{96}N_{10}O_4$: C, 75.21; H, 7.97; N, 11.54. Found: C, 74.95; H, 7.91; N, 11.25.

[2,3-[14′,15′-(1′,16′-Diaza-1′,16′-bis(2-pyridylmethyl)-4′,7′,10′,13′-tetraoxacyclooctadeceno)]-9,10,18,19,27,29-hexabutylnorphthalocyanato]manganese(III) Chloride (3). $MnBr_2$ (3.0 mg, 1.4 μmol) and 2,6-lutidine (1 drop) were added to a suspension of norphthalocyanine **15a** (11 mg, 9 μmol) in DMF (3 mL). The resulting suspension was heated at 100 °C for 2 h. After the suspension was cooled to room temperature, brine (4 mL) was added to the dark green solution and the mixture was stirred for 1 h, poured into H_2O (3 mL) and extracted with $CHCl_3$ (3 × 10 mL). Evaporation and chromatography ($CHCl_3$−MeOH 90:10) gave norphthalocyanine **3** (11 mg, 94%) as a dark green solid: mp 87−90 °C; R_f 0.43 ($CHCl_3$−MeOH 90:10); IR ($CHCl_3$) ν_{max} 1563, 1466, 1337, 1101, 750 cm^{-1}; UV−vis ($CHCl_3$) λ_{max} (log ϵ) 279 (4.74), 367sh, 381 (4.64), 524 (4.20), 661sh, 730 (4.50) nm; FABMS *m/z* 1267 $(M - Cl)^+$, 1176 $(M - Cl - (PyrCH_2) + 2H)^+$, 634 $(M)^{2+}$; HRFABMS *m/z* calcd for $C_{74}H_{92}N_{12}O_4Mn$ $(M - Cl)^+$ 1267.674, found 1267.683. Anal. Calcd for $C_{74}H_{92}ClMnN_{12}O_4 \cdot CHCl_3$: C, 63.29; H, 6.59; N, 11.81. Found: C, 63.52; H, 6.71; N, 11.96.

2,3-Bis[methyl(2-pyridylmethyl)amino]-9,10,18,19,27,-28-hexabutylnorphthalocyanine [5 (M = 2H)]. A rapidly stirring mixture of Mg turnings (30 mg, 1.2 mmol), 1-butanol (10.0 mL), and I_2 (1 crystal) was heated at reflux for 24 h. Further I_2 was slowly added to this refluxing mixture until a uniform white suspension was obtained. Dinitrile **14** (670 mg, 2.8 mmol), as a solid, and dinitrile **13** (180 mg, 0.56 mmol), as a solution in 1-butanol (1 mL), were added at room temperature, and the suspension was heated at reflux for 24 h and allowed to cool to room temperature. After evaporation, CH_2Cl_2 (25 mL) was added, and the resulting blue-green suspension was vacuum-filtered through Celite and concentrated to give the crude magnesium norphthalocyanine **5** (M = Mg) as a dark gummy solid. CF_3CO_2H (7.5 mL) was added, and the solution was allowed to stand protected from light for 2 h, added to ice−H_2O (100 mL), and neutralized with 1 M NaOH. The resulting suspension was extracted with $CHCl_3$ (3 × 25 mL), and the combined organic layers were dried, filtered, and concentrated to yield the crude 2*H*-norphthalocyanine. The residue was chromatographed twice (MeOH−$CHCl_3$ 0:100−5:95; hexanes (60−80 °C)−acetone−NH_4OH 80:19:1−75:24:1 dried over $CaCl_2$) to give norphthalocyanine **5** (M = 2H) (58 mg, 10%) as a dark blue solid: mp 172−175 °C; R_f 0.35 ($CHCl_3$−MeOH) 90:10); IR ($CHCl_3$) ν_{max} 1571, 1321, 1110, 1012 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHs) δ −1.25 (2H, br s), 1.13−1.21 (18H, m), 1.58−1.79 (12H, m), 1.89−2.00 (12H, m), 2.97−3.18 (12H, m), 3.88 (6H, s), 5.97 (4H, s), 7.18 (2H, app t), 7.51 (2H, app t), 7.60 (2H, d, J = 7.7 Hz), 8.29 (2H, s), 8.71 (2H, d, J = 4.5 Hz), 8.85 (2H, s), 9.15 (2H, s); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 14.2, 23.3, 33.6, 33.8, 33.9, 34.1, 42.4, 62.4, 121.8, 122.5, 122.6, 122.7, 123.3, 132.3, 134.5, 136.4, 137.3, 138.0, 142.5, 142.7, 144.4, 149.2, 155.7, 158.9, 160.2 (*C*(Pyr)); FABMS *m/z* 1041 $(M + H)$,$^+$ 920 $(M - 2(CH_3) - PyrCH_2 + 2H)^+$, 829 $(M - 2(CH_3) - 2(PyrCH_2) + 3H)^+$, 93 $(PyrCH_2 + H)^+$; HRFABMS *m/z* calcd for $C_{66}H_{81}N_{12}$ $(M + H)^+$ 1041.6707, found 1041.6660. Anal. Calcd for $C_{66}H_{80}N_{12}$: C, 76.12; H, 7.74; N, 16.14. Found: C, 76.41; H, 7.53; N, 15.87.

[2,3-Bis[methyl(2-pyridylmethyl)amino]-9,10,18,19,27,-28-hexabutylnorphthalocyanato]manganese(III) Chlo-

Table 3. Crystal Data, Data Collection, and Refinement Parameters[a]

data	**12a**	**1** (M = Mg)	**12b**·$Cu(BF_4)_2$	**12b**·$(HClO_4)_2$
formula	$C_{28}H_{34}N_4O_4$	$C_{112}H_{136}N_{16}O_{17}Mg$	$C_{26}H_{32}N_6O_4Cu·2BF_4$	$C_{26}H_{34}N_6O_4Cu·2ClO_4$
solvent		0.75EtOAc		q
formula wt	490.6	2068.8	729.7	693.5
color, habit	yellow cubes	deep red blocks	deep blue plates	pale yellow needles
cryst size/mm	0.37 × 0.33 × 0.33	0.43 × 0.33 × 0.27	0.40 × 0.37 × 0.20	0.57 × 0.08 × 0.07
cryst syst	monoclinic	monoclinic	monoclinic	monoclinic
space grp symbol, no.	*C*2/*c*, 15	$P2_1/n$, 14	$P2_1$, 4	$P2_1/c$, 14
T/K	293	203	293	293
cell dimensions				
a/Å	14.203(3)	24.419(9)	8.082(3)	19.714(5)
b/Å	11.753(3)	17.824(8)	9.797(3)	8.041(1)
c/Å	16.923(5)	25.512(10)	20.206(11)	21.380(5)
β/deg	112.13(2)	99.43(3)	96.84(4)	112.62(2)
V/Å^3	2617(1)	10954(7)	1589(1)	3129(1)
Z	4 [b]	4	2	4
D_c/g cm^{-3}	1.245	1.254	1.526	1.472
F(000)	1048	4416	746	1448
radiatn used	Cu Kα	Cu Kα[c]	Cu Kα	Cu Kα[c]
μ/mm^{-1}	0.68	0.75	1.78	2.50
θ range/deg	5.1−62.5	2.3−56.1	2.2−62.5	2.4−60.0
no. of unique reflns				
measured	2097	14288	2801	4625
obsd, $\lvert F_o\rvert > 4\sigma(\lvert F_o\rvert)$	1799	7682	2717	3788
absorptn correctn			Gaussian	
max, min transmission		∧c	0.71, 0.52	
no. of variables	152	1328	425	424
R_1[d]	0.093	0.148	0.055	0.049
wR_2[e]	0.255	0.402	0.150	0.131
weighting factors *a*, *b*[f]	0.186, 2.484	0.301, 22.245	0.098, 1.530	0.074, −0.35
largest diff peak, hole/e Å^{-3}	0.51, −0.44	0.85, −0.58	0.57, −0.57	0.52, −0.35

[a] Details in common: graphite monochromated radiation, ω scans, Siemens P4 diffractometer, refinement based on F^2. [b] The molecule has crystallographic C_2 symmetry. [c] Rotating anode source. [d] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$. [e] $wR_2 = \sqrt{\{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}}$. [f] $w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$.

ride [5 (M = MnCl)]. $MnBr_2$ (10 mg, 4.7 μmol) and 2,6-lutidine (1 drop) were added to a suspension of norphthalocyanine **5** (M = 2H) (25 mg, 2.4 μmol) in DMF (10 mL), and the mixture was heated at 100 °C for 2.5 h. After the mixture was cooled to room temperature, brine (5 mL) was added to the dark green solution, and the mixture was allowed to stir at room temperature for 1 h. The mixture was poured into H_2O (10 mL) and extracted with $CHCl_3$ (3 × 10 mL) and the extract evaporated. Chromatography ($CHCl_3$−MeOH 95:5) gave norphthalocyanine **5** (M = MnCl) (23 mg, 85%) as a dark green solid: mp 230−233 °C; R_f 0.43 ($CHCl_3$−MeOH 95:5); IR ($CHCl_3$) ν_{max} 1567, 1335, 745 cm^{-1}; UV−vis ($CHCl_3$) λ_{max} (log ϵ) 279 (4.70), 367sh, 381 (4.60), 521 (4.15), 684sh, 737 (4.48) nm; FABMS *m*/*z* 1093 (M − Cl)$^+$, 1002 (M − Cl − (PyrCH$_2$) + H)$^+$, 909 (M − Cl − 2(PyrCH$_2$) + H)$^+$; HRFABMS *m*/*z* calcd for $C_{66}H_{78}N_{12}Mn$ (M − Cl)$^+$ 1093.585, found 1093.589. Anal. Calcd for $C_{66}H_{78}ClMnN_{12}$: C, 70.16; H, 6.96; N, 14.88. Found: C, 69.99; H, 7.09; N, 14.58.

General Procedure for UV−vis Titrations of Porphyrazines 1, 2, and 4 and Norphthalocyanines 3 and 5. $CHCl_3$ solutions of known concentration of porphyrazine or norphthalocyanine (3 mL) were subject to UV−vis titrations with MeOH solutions of varying concentrations (0, 0.25, 0.5, 1, 2, 3, 4, 6, 8, 20, 40, >100 molar equiv) of the metal salt of interest. For each titration, the solvent ratio was always $CHCl_3$:MeOH = 3:1. Blank UV−vis spectra (in the absence of metal salt) were run for each of the porphyrazines and norphthalocyanines to determine any solvent effect (of which there were none). Blank UV−vis spectra (in the absence of porphyrazine or norphthalocyanine) were also run for each metal salt to make sure that there was no significant absorbance in the window of interest (300−850 nm).

Complex 12b·Cu(BF$_4$)$_2$. A solution of dinitrile **12b** (10 mg, 20 μmol) in MeOH (1 mL) was added to a solution of $Cu(BF_4)_2$·xH$_2$O (25 mg, 70 μmol) in MeOH (1 mL). The layers were mixed and allowed to stand at room temperature. Complex **12b**·$Cu(BF_4)_2$ was obtained as a dark blue crystalline solid: mp > 190 °C dec; IR (DRIFTS) ν_{max} 2227, 1613, 1448, 1057 cm^{-1}; FABMS *m*/*z* 555 (M)$^+$, 493 (M − Cu + H)$^+$; HRFABMS *m*/*z* calcd for $C_{26}H_{32}N_6O_4Cu$ 555.1781, found 555.1815. Anal. Calcd for $C_{26}H_{32}B_2CuF_8N_6O_4$: C, 42.79; H, 4.42; N, 11.52. Found: C, 42.57; H, 4.24; N, 11.35.

Complex 12b·(HClO$_4$)$_2$. A solution of dinitrile **12b** (20 mg, 40 μmol) in MeOH (1 mL) was added to a solution of $HClO_4$ (12 mg, 120 μmol) in MeOH (1 mL). The layers were mixed and allowed to stand at room temperature to provide **12b**·$(HClO_4)_2$ as a pale yellow crystalline solid: mp 93−95 °C; IR (DRIFTS) ν_{max} 2193, 1617, 1098, 767, 623 cm^{-1}; FABMS *m*/*z* 493 (M + H)$^+$, 402 (M − PyrCH$_2$ + 2H)$^+$, 93 (PyrCH$_2$ + H)$^+$; HRFABMS *m*/*z* calcd for $C_{26}H_{33}N_6O_4$ (M + H)$^+$ 493.2563, found 493.2580. Anal. Calcd for $C_{26}H_{34}Cl_2N_6O_{12}$: C, 45.03; H, 4.93; N, 12.12. Found: C, 45.05; H, 4.99; N, 12.11.

([2,3-Bis[methyl(2-pyridylmethyl)amino]-9,10,18,19,-27,28-hexabutylnorphthalocyanato]manganese(III)chloride)·Copper(II) Acetate (16a). Slow evaporation of a solution of norphthalocyanine **5** (M = MnCl) (6 mg, 5.3 μmol) and Cu(OAc)$_2$·H$_2$O (1.1 mg, 5.3 μmol) in $CHCl_3$ and MeOH (1:1, 6 mL) gave complex **16a** as a dark green solid: mp 128−130 °C; IR (DRIFTS) ν_{max} 1573, 1459, 1337, 1048, 749 cm^{-1}; UV−vis ($CHCl_3$/MeOH 3:1) λ_{max} (log ϵ) 267 (4.67), 284sh, 367sh, 390 (4.58), 607sh, 656 (4.43), 733 (4.60) nm; FABMS *m*/*z* 1193 (M − 2(CH$_3$CO$_2$))$^+$, 1156 (M − Cl − 2(CH$_3$CO$_2$))$^+$, 1093 (M − Cl − Cu − (2CH$_3$CO$_2$))$^+$, 578 (M − Cl − 2(CH$_3$CO$_2$))$^{2+}$; HRFABMS *m*/*z* calcd for $C_{66}H_{78}N_{12}ClMnCu$ (M − 2(CH$_3$CO$_2$))$^+$ 1191.484, found 1191.486. Anal. Calcd for $C_{70}H_{84}ClCuMnN_{12}O_4$: C, 64.11; H, 6.46; N, 12.82. Found: C, 64.23; H, 6.16; N, 12.69.

([2,3-Bis[methyl(2-pyridylmethyl)amino]-9,10,18,19,-27,28-hexabutylnorphthalocyanato]manganese(III)chloride)·Cobalt(II) Chloride (16b). Slow evaporation of a solution of norphthalocyanine **5** (M = MnCl) (6 mg, 5.3 μmol) and $CoCl_2$ (0.7 mg, 5.3 μmol) in $CHCl_3$ and MeOH (1:1, 6 mL) gave complex **16b** as a dark green solid: mp dec; IR (DRIFTS) ν_{max} 1461, 1337, 1046, 753 cm^{-1}; UV−vis ($CHCl_3$−MeOH 1:1) λ_{max} (log ϵ) 281 (4.77), 373sh, 386 (4.72), 615sh, 664 (4.57), 735 (4.74) nm; FABMS *m*/*z* 1224 (M − Cl)$^+$, 1187 (M − 2Cl)$^+$. Anal. Calcd for $C_{66}H_{78}Cl_3CoMnN_{12}$: C, 62.93; H, 6.24; N, 13.34. Found: C, 62.68; H, 5.95; N, 13.48.

Table 3 provides a summary of the crystal data, data collection, and refinement parameters for **12a**, **1** (M = Mg), **12b**·$Cu(BF_4)_2$, and **12b**·$(HClO_4)_2$. The structures were solved by direct methods and were refined by full-matrix least-squares [blocked in the case of **1** (M = Mg)] on the basis of F^2. In **1** (M = Mg), disorder was found in the polyether chain of ring D, and this was resolved into two 50:50 partial occupancy orientations. In all four structures, all of the non-hydrogen atoms were refined anisotropically [including the 75% occupancy ethyl acetate solvent molecule in **1** (M = Mg)] with, in **12a** and **1** (M = Mg), the pendant phenyl rings being refined as optimized rigid bodies. In **12b**·$(HClO_4)_2$, the N−H hydrogen atoms were located from a ΔF map and refined isotropically subject to an N−H distance constraint. The C−H hydrogen atoms in each structure were placed in calculated positions, assigned isotropic thermal parameters, $U(H) = 1.2U_{eq}(C)$ [$U(H) = 1.5U_{eq}(CMe)$], and allowed to ride on their parent atoms. Computations were carried out using the SHELXTL PC program system.[27] The absolute structure of **12b**·$Cu(BF_4)_2$ was determined by use of the Flack parameter, which refined to a value of 0.06(7).

(27) SHELXTL PC version 5.03, Siemens Analytical X-ray Instruments, Inc., Madison, WI, 1994.

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Supporting Information Available: Copies of the ^1H (300 MHz, $CDCl_3$) and ^{13}C (75 MHz, $CDCl_3$) NMR spectra of diiodide **11** and porphyrazines **2** (M = Mg) and **4**; X-ray data for **12a**, **1** (M = Mg), **12b**·$Cu(BF_4)_2$, and **12b**·$(HClO_4)_2$; and UV−vis titrations of ligand **1** (M = Ni) with $Hg(ClO_4)_2$, ligand **2** with $AgBF_4$, $Pb(NO_3)_2$, $CuCl_2$, $CoCl_2$, $Zn(ClO_4)_2$, and $CdCl_2$, ligand **3** with $Cu(OAc)_2$, $Hg(ClO_4)_2$, $AgBF_4$, $Zn(ClO_4)_2$, $Co(BF_4)_2$, and $CdCl_2$, ligand **4** with $CuCl_2$, $Zn(ClO_4)_2$, $Hg(ClO_4)_2$, $CdCl_2$, and $AgBF_4$, and ligand **5** with $CdCl_2$, $Co(BF_4)_2$, $Zn(ClO_4)_2$, and $Hg(ClO_4)_2$ (49 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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