Bis(dimethylamino)porphyrazines: Synthetic, Structural, and Spectroscopic Investigations

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The synthesis and isolation of unsymmetrical porphyrazines bearing two, four, and six bis(dimethylamino) functionalities has been achieved via the base-catalyzed cross-condensation of 1,2-dicyanobenzene **8** and bis(dimethylamino)maleonitrile **7**. In addition, the benzo-fused hexaaminoporphyrazine dimer **10** was prepared from condensation of dinitrile **7** (in excess) with benzenebis(1,3-diiminopyrroline) **9**. Electrochemical studies reveal that all porphyrazines may be readily oxidized. The X-ray structures of porphyrazines **2b** and **5a** and the cis isomer **3a** are presented. The latter is the first structure of a porphyrazine having a cis-type substitution pattern. The extended π-conjugation in dimer **10** causes a ∼100 nm red-shifted Q-band in the electronic absorption spectrum.

Introduction

Porphyrinic macrocycles are the subject of great interest in areas such as catalysis,[1] photodynamic therapy,[2] and in the fabrication of molecular electronic[3] or magnetic devices.[4] We have been investigating peripherally functionalized tetraazaporphyrins or porphyrazines (pz) as precursors for the development of such materials. The porphyrazine macrocycle is isoelectronic with porphine and has the same shape, but peripherally functionalized porphyrazines form a distinct class of novel compounds with unique properties[5−7] that has been little studied in comparison to functionalized porphyrins[8−14] and phthalocyanines.[5, 15−17] The synthetic route to porphyrazines, the metal-templated cyclization of maleonitrile derivatives, allows for the direct preparation of macrocycles with functional groups attached directly at the β-positions of the pyrrole rings. Functional groups attached in this way can have stronger couplings to the macrocycle core than do those attached to the fused benzo rings of pc and, therefore, exert a greater effect on the physical properties of the compound. Using this strategy, it is possible to prepare compounds in which the solubility, redox, and electronic properties may be tuned. This makes this family of molecules an intriguing target for the development of new charge-transfer complexes[18−21] as precursors to magnetic or conductive materials. Binuclear porphyrazine structures are rigidly constrained in a coplanar arrangement with an extended π-conjugated system and are expected to exhibit different electronic, optical, and photophysical characteristics. Thus, such compounds can play a role in the study of electron transfer in physiological systems[22b] and as potential units for the engineering of novel molecular materials.[6] While several porphyrin[22] and phthalocyanine[23] dimers sharing a common benzene

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(1) Dailey, K. K.; Yap, G. P. A.; Rheingold, A. L.; Rauchfuss, T. B. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1833.
(2) Bonnet, R. *Chem. Soc. Rev.* **1995**, 19. (b) Rosenthal, I. In *Phthalocyanines: Properties and Applications*; Leznoff, C. C., Lever, A. B. P., Eds.; VCH: New York, 1996; Vol. 4; pp 485−507.
(3) (a) Ferraro, J. R.; Williams, J. M. In *Introduction to Synthetic Electrical Conductors*, 1st ed.; Academic Press: Orlando, FL, 1987; p 353. (b) Williams, J. M.; Ferraro, J. R.; Thorn, R. J.; Carlson, K. D.; Geiser, U.; Wang, H. H.; Whangbo, M. H. In *Organic Superconductors (Including Fullerenes): Synthesis, Structure, Properties and Theory*; Prentice Hall: Englewood Cliffs, NJ, 1992. (c) Crossley, M. J.; Burn, P. L.; Langford, S. J.; Prashar, J. K. *J. Chem. Soc., Chem. Commun.* **1995**, 1921.
(4) (a) Kahn, O. In *Molecular Magnetism;* VCH: New York, 1993; Vol. xvi; p 380. (b) Miller, J. S.; Vazquez, C.; Calabrese, J. C.; McLean, R. S.; Epstein, A. *J. Adv. Mater.* **1994**, *6*, 217.
(5) Leznoff, C.; Lever, A. In *Phthalocyanines: Properties and Applications*; Leznoff, C. C., Lever, A. B. P., Eds.; VCH: New York, 1989; Vol. 1.
(6) Gürek, A.; Bekaroglu, Ö. *J. Chem. Soc., Dalton Trans.* **1994**, 1419.
(7) Chabach, D.; Decian, A.; Fischer, J.; Weiss, R. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 898.
(8) Lin, V. S.-Y.; Dimagno, S. G.; Therien, M. J. *Science* **1994**, *264*, 1105.
(9) Wagner, R. W.; Lindsey, J. S.; Seth, J.; Palaniappan, V.; Bocian, D. F. *J. Am. Chem. Soc.* **1996**, *118*, 3996.
(10) Wagner, R.; Johnson, T.; Li, F.; Lindsey, J. *J. Org. Chem.* **1995**, *60*, 5266.
(11) Officer, D. L.; Burrell, A. K.; Reid, D. C. W. *J. Chem. Soc., Chem. Commun.* **1996**, 1657.
(12) Hamilton, A.; Lehn, J.-M.; Sessler, J. L. *J. Am. Chem. Soc.* **1986**, *108*, 5158.
(13) Anderson, H. L. *Inorg. Chem.* **1994**, *33*, 972.
(14) Seth, J.; Palaniappan, V.; Johnson, T. E.; Prathapan, S.; Lindsey, J. S.; Bocian, D. F. *J. Am. Chem. Soc.* **1994**, *116*, 10578.
(15) Kobayashi, N.; Togashi, M.; Osa, T.; Ishii, K.; Yamauchi, S.; Hino, H. *J. Am. Chem. Soc.* **1996**, *118*, 1073.
(16) Kocak, M.; Okur, A. I.; Bekaroglu, Ö. *J. Chem. Soc., Dalton Trans.* **1994**, 323.
(17) Terekhov, D.; Nolan, K.; McArthur, C.; Leznoff, C. *J. Org. Chem.* **1996**, *61*, 3034.
(18) Garrido Montalban, A.; 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.
(19) 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.
(20) Hochmuth, D. H.; Jarrell, W.; Michel, S. L. J.; White, A. J. P.; Williams, D. J.; Barrett, A. G. M.; Hoffman, B. M. Manuscript in preparation.
(21) Chappell, J. S.; Bloch, A. N.; Bryden, W. A.; Maxfield, M.; Poehler, T. O.; Cowan, D. O. *J. Am. Chem. Soc.* **1981**, *103*, 2442.
(22) (a) Kobayashi, N.; Numao, M.; Kondo, R.; Nakajima, S.-i.; Osa, T. *Inorg. Chem.* **1991**, *30*, 2241. (b) Crossley, M. J.; Prashar, J. K. *Tetrahedron Lett.* **1997**, *38*, 6751 and references therein.

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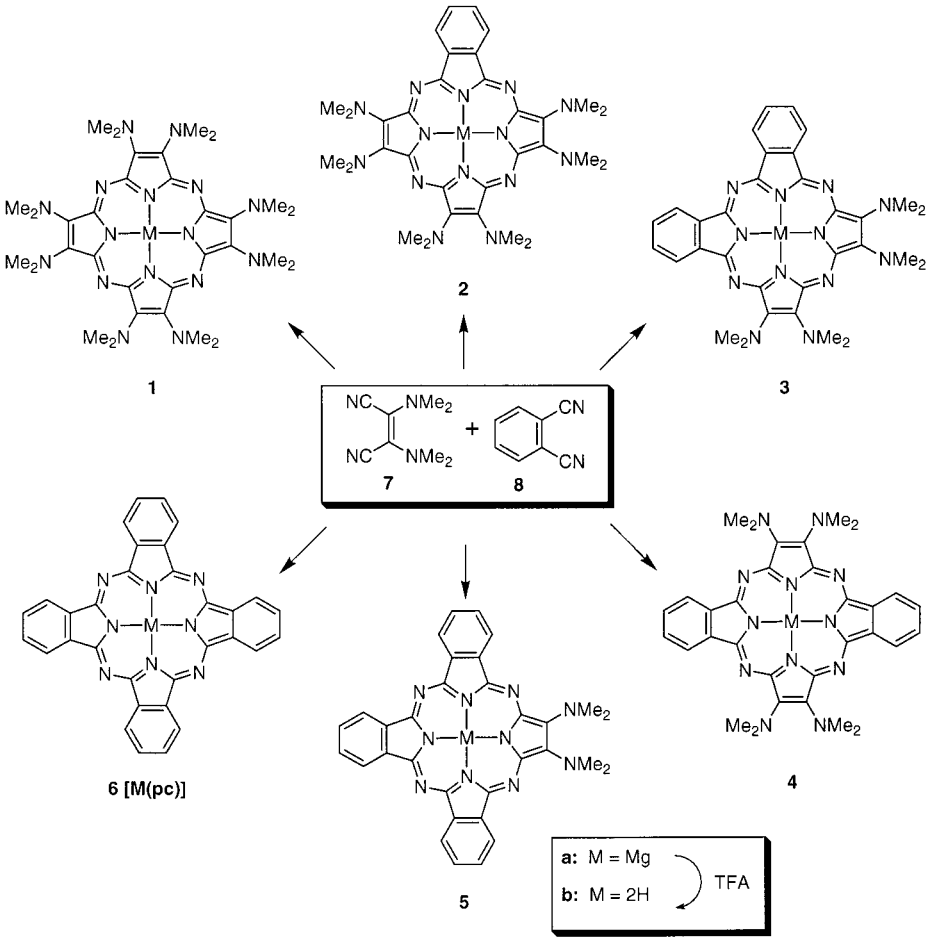
Scheme 1



ring have been reported to date, no studies on related porphyrazine analogues have yet been carried out.

We have recently been investigating unsymmetrical porphyrazines of the form M[pz($\mathbf{A}_n$:$\mathbf{B}_{4-n}$)] in which **A** and **B** represent functional moieties appended to the macrocycle at the β positions.[24−27] The ability to vary the types and numbers (n) of **A** and **B** allows for even greater control over the physical properties of the macrocycles. Herein, we now report the employment of this strategy in the development of a new family of (dimethylamino)-pz/pc hybrids, designed to provide incremental variation of redox chemistry between M[pc] ($n = 0$) and the octakis-(dimethylamino) macrocycle ($n = 4$). To further increase the number of adjustable physicochemical parameters of the subunit, we have also prepared the first planar binuclear porphyrazine containing the bis(dimethylamino) functionalities at the periphery.

Results and Discussion

Syntheses. The synthetic strategy employed for the preparation of the unsymmetrical pz's involves the co-cyclization of bis(dimethylamino)maleonitrile **7** (prepared by the method of Sheppard and co-workers)[28] and 1,2-dicyanobenzene **8** about a magnesium template under the conditions introduced by Linstead[29] (Scheme 1). Following our previously reported strategy for the preparation of *solitaire* porphyrazines,[26,27] bis(dimethylamino)maleonitrile **7** and 1,2-dicyanobenzene **8** were cocyclized in a molar ratio of 25:1, giving a product mixture of **1a** and **2a**. Column chromatography over silica gel, using THF and hexanes (1:4), effectively separated the two macrocycles, and **2a** was isolated as the THF adduct, as shown by the ^{1}H NMR spectrum, in 35% yield.

When the macrocyclization reaction was carried out using a 3:1 molar ratio of starting dinitriles, a mixture of **3a**, **4a**, **5a**, and Mg[pc] (**6**) was obtained. The desired porphyrazines were easily separated from most of the insoluble Mg[pc] by extraction of the crude product mixture with chloroform, filtration, and evaporation. The $n = 1$ compound, **5a**, was partially purified by precipitation from a dichloromethane and methanol solution and further purified by column chromatography, under conditions similar to those used for the purification of **2a**. As before, porphyrazine **5a** was isolated as the THF adduct. Column chromatography of the remaining product mix-

(23) (a) Yang, J.; Mark, R. V. D. *Tetrahedron Lett.* **1993**, *34*, 5223. (b) Lelievre, D.; Damette, O.; Simon, J. *J. Chem. Soc., Chem. Commun.* **1993**, 939 and references therein. (c) Ishii, K.; Kobayashi, N.; Higashi, Y.; Osa, T.; Lelievre, D.; Simon, J.; Yamauchi, S. *Chem. Commun.* **1999**, 969 and references therein.

(24) 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.

(25) (a) Forsyth, T. P.; Williams, D. B. G.; Garrido Montalban, A.; Stern, C. L.; Barrett, A. G. M.; Hoffman, B. M. *J. Org. Chem.* **1998**, *63*, 331. (b) Lange, S. J.; Nie, H.; Stern, C. L.; Barrett, A. G. M.; Hoffman, B. M. *Inorg. Chem.* **1998**, *37*, 6435.

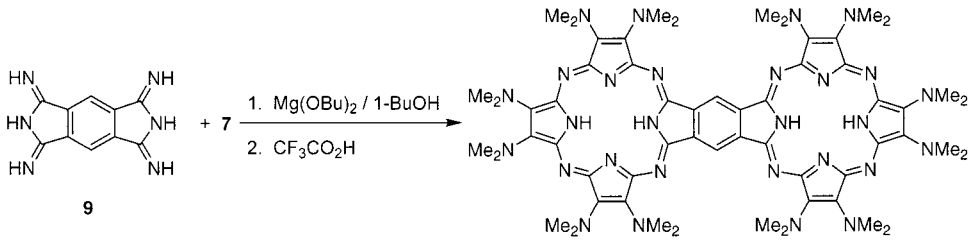
(26) Baumann, T. F.; Sibert, J. W.; Olmstead, M. M.; Barrett, A. G. M.; Hoffman, B. M. *J. Am. Chem. Soc.* **1994**, *116*, 2639.

(27) Baumann, T. F.; Nasir, M. S.; Sibert, J. W.; Olmstead, M. M.; White, A. J. P.; Williams, D. J.; Barrett, A. G. M.; Hoffman, B. M. *J. Am. Chem. Soc.* **1996**, *118*, 10479.

(28) 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.

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

Scheme 2



ture afforded porphyrazines **3a** and **4a** along with a small amount of remaining **5a**. For these two macrocycles, no THF was observed in the ^{1}H NMR spectra. All four macrocycles **2a**, **3a**, **4a**, and **5a** were freely soluble in coordinating solvents such as THF and DMSO. However, with the exception of macrocycle **2a**, their solubility in noncoordinating organic solvents was limited and decreased sharply with decreasing *n*. Crystals of porphyrazines **3a** and **5a** suitable for X-ray analysis were grown by slow evaporation of saturated solutions in deuterated DMSO. To the best of our knowledge, the structure of macrocycle **3a** represents the first solved for a cis-oriented pz.

The internal Mg^{2+} was removed from porphyrazine **2a** by treatment with neat TFA to give the hexamine **2b**. The macrocycle was freely soluble in common organic solvents, thereby facilitating purification by chromatography. Crystals for X-ray structural analysis were grown by slow evaporation of a dichloromethane and 2-propanol solution. Attempts to isolate and purify the free-base pz's **3b**, **4b**, and **5b** were not rigorously pursued due to their poor solubility in common solvents.

Similarly, mixed Linstead[29] macrocyclization of benzobis(1,3-diiminopyrroline) **9**[23] with an excess of bis(dimethylamino)maleonitrile **7** using magnesium butoxide gave a mixture of porphyrazines that were most easily separated after demetalation with trifluoroacetic acid (Scheme 2). Flash chromatography provided the desired benzo-fused porphyrazine dimer **10** along with the octakis(dimethylamino)porphyrazine **1b** (H_2ODMAPz).[18] Most of the octaaminoporphyrazine **1b** could be separated from compound **10** by simply dissolving the crude residue in hexanes, in which only H_2ODMAPz **1b** is soluble. Repeated chromatography gave microanalytically pure dimer **10** (15%). The compound **10** showed three distinct *N*-methyl resonances in the ^{1}H and ^{13}C NMR spectra. These data combined with high-resolution mass ion measurement and elemental analysis were fully consistent with the identity of the dimer **10**.

X-ray Crystallography. The X-ray analysis of **2b** (Figure 1a) shows that, with the exception of the peripheral dimethylamino substituents, the molecule is essentially planar. The N_8C_8 core is planar to within 0.09 Å with the benzpyrrole ring **A** inclined by ca. 3.5° and the pyrrole rings **B**, **C**, and **D** by 2.4, 6.4, and 5.3°, respectively, to this plane. With the exception of the pyrrole ring **B**, the inclinations are all in the same sense. Perhaps the most interesting feature of the solid-state structure is the packing of the molecules (Figure 1b). Centrosymmetrically related pairs of molecules overlay each other with a centroid···centroid offset of ca. 2.57 Å and a shortest intermolecular N···N contact of 3.40 Å. These "dimer pairs" are packed edge-to-face to form a mosaic-like array.

The structure of the magnesium−DMSO complex, **3a**, shows the geometry at magnesium to be slightly distorted square pyramidal (Figure 2a) with the magnesium atom lying 0.44 Å out of the plane of the four pyrrole nitrogen atoms. The N_8C_8 porphyrazine core is planar to within 0.06 Å, and the benzpyrrole rings **A** and **C** and the pyrrole ring **D** are almost coplanar with the coordinated nitrogen atoms (inclinations of ca. 1.6, 2.4, and 2.0°,

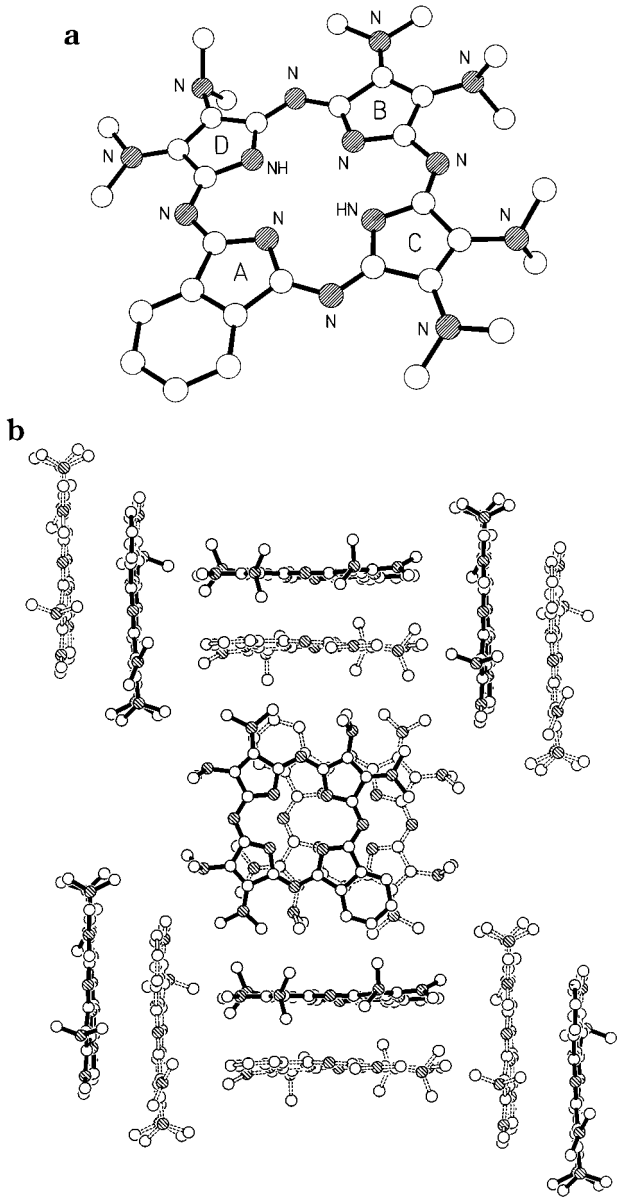


Figure 1. (a) Molecular structure of **2b** and (b) mosaic-like packing of C_i-related π-stacked "dimer pairs" in the structure of **2b**.

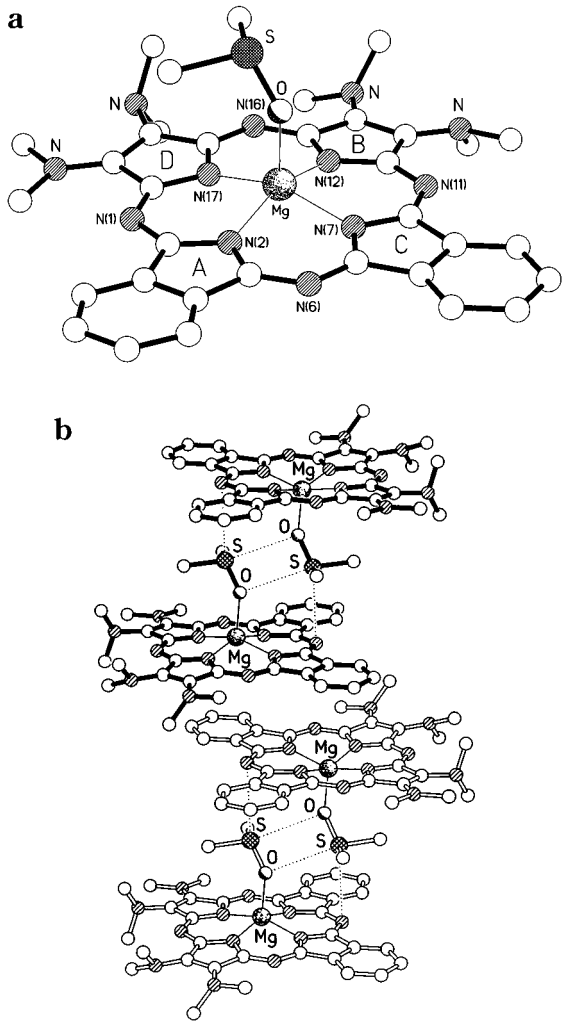


Figure 2. (a) Molecular structure of **3a** showing the distorted square pyramidal coordination at magnesium. Selected bond lengths (Å) and angles (deg): Mg−O 2.025(3), Mg−N(2) 2.030(3), Mg−N(7) 2.032(3), Mg−N(12) 2.013(3), Mg−N(17) 2.026(3), O−Mg−N(2) 101.51(11), O−Mg−N(7) 99.50(10), O−Mg−N(12) 104.19(11), O−Mg−N(17) 105.28(11), N(2)−Mg−N(7) 86.24(11), N(2)−Mg−N(12) 154.24(12), N(2)−Mg−N(17) 87.27(11), N(7)−Mg−N(12) 87.87(11), N(7)−Mg−N(17) 155.17(12), N(12)−Mg−N(17) 87.65(11). (b) The back-to-back and face-to-face stacking of centrosymmetrically related molecules in **3a** showing the short S···O (3.38 Å) and S···N (3.31 Å) contacts between face-to-face oriented molecules.

respectively) while the pyrrole ring **B** is more steeply inclined (by 7.1°) away from the apical oxygen atom. The molecules pack back-to-back and face-to-face to form continuous stacks (Figure 2b), the mean interplanar separation between the back-to-back molecules being ca. 3.35 Å, indicating a degree of $\pi-\pi$ stabilization. The face-to-face arrangement is stabilized by pairs of weak S···O interactions between the DMSO ligands, and S···N approaches between the sulfur atom in one complex and one of the "outer" ring nitrogen atoms [N(6)] in another.

Analysis of the magnesium−DMSO complex, **5a**, shows that the presence of one pyrrole and three benzpyrrole ring systems, as opposed to two and two in **3a**, has little effect on the overall solid-state structure (Figure 3), the geometry at magnesium being distorted square pyramidal with the magnesium atom lying 0.47 Å out of the plane of the four pyrrole nitrogen atoms. The N_8C_8 core is planar to within 0.08 Å, and the benzpyrrole rings **A** and **B** are folded out of this plane away from the DMSO ligand by ca. 11.6 and 3.7°, respectively, while rings **C** and **D** are inclined by ca. 2.3 and 2.2°, respectively, in the opposite sense. The packing of the molecules is also remarkably similar, with the formation of face-to-face and back-to-back stacks analogous to those formed by **3a**. The mean interplanar separation between back-to-back molecules is ca. 3.4 Å, and there are short S···O contacts of 3.42 Å between face-to-face pairs of molecules (there are no analogous short S···N contacts). In both **3a** and **5a** there are no interstack interactions of note.

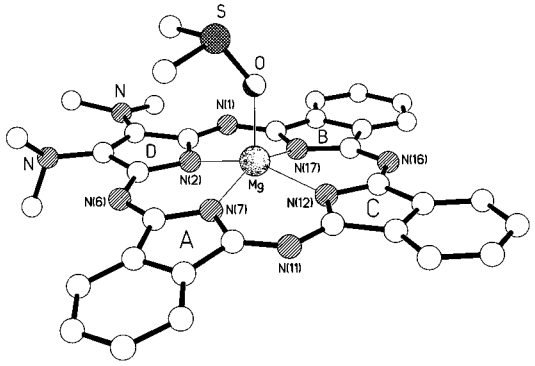


Figure 3. Molecular structure of **5a** showing the distorted square pyramidal coordination at magnesium. Selected bond lengths (Å) and angles (deg): Mg−O 2.015(2), Mg−N(2) 2.033(2), Mg−N(7) 2.029(2), Mg−N(12) 2.042(2), Mg−N(17) 2.026(2), O−Mg−N(2) 104.64(9), O−Mg−N(7) 104.29(9), O−Mg−N(12) 101.70(8), O−Mg−N(17) 102.69(9), N(2)−Mg−N(7) 87.66(8), N(2)−Mg−N(12) 153.63(9), N(2)−Mg−N(17) 86.67(8), N(7)−Mg−N(12) 86.91(8), N(7)−Mg−N(17) 153.00(9), N(12)−Mg−N(17) 86.56(8).

UV/Vis Spectroscopy. Absorption spectra of **1a**−**5a** are each characteristic of tetraazaporphyrins and are shown in Figure 4. Each Mg[pz] shows an intense Soret transition between 300 and 350 nm and a severely broadened Q-band transition between 650 and 700 nm. This broadening obscures the expected "split" of the Q-band, which is normally observed for macrocycles of less than D_{4h} symmetry,[30] and is presumably due to overlap of underlying n−π^* transitions that arise from the nonbonding electrons associated with the peripheral amine moieties. Although aggregation precesses could also be responsible for the broadening effect, credence to the assignment of the n−π^* transition derives from related studies in which we have shown that the Q-band region sharpens greatly upon peripheral metalation.[25b] Thus, the n−π^* peaks are lost completely because the lone pair electrons on the dimethylamino groups are datively bonded to the metal ions and no longer available for charge transfer into the porphyrazine π-system. Additionally, a weaker, broad transition between 500 and 600 nm is visible in the spectrum of each compound, with the exception of **5a**. Upon demetalation, the Soret and Q-bands of **1** and **2** were shifted toward the blue and red, respectively, in agreement with previous observations. The electronic absorption spectrum of the porphyrazine dimer **10** shows a significantly red-shifted Q-band at 839 nm when, for example, compared to H_2ODMAPz **1b** (or the benzo-fused derivative **2b**, which has essentially the same UV−vis spectrum as **1b**), which can be attributed to the extended π conjugated system and the 12 periph-

(30) Gouterman, M. In *The Porphyrins;* Dolphin, D., Ed.; Academic Press: New York, 1978; Vol. 3; pp 1−165.

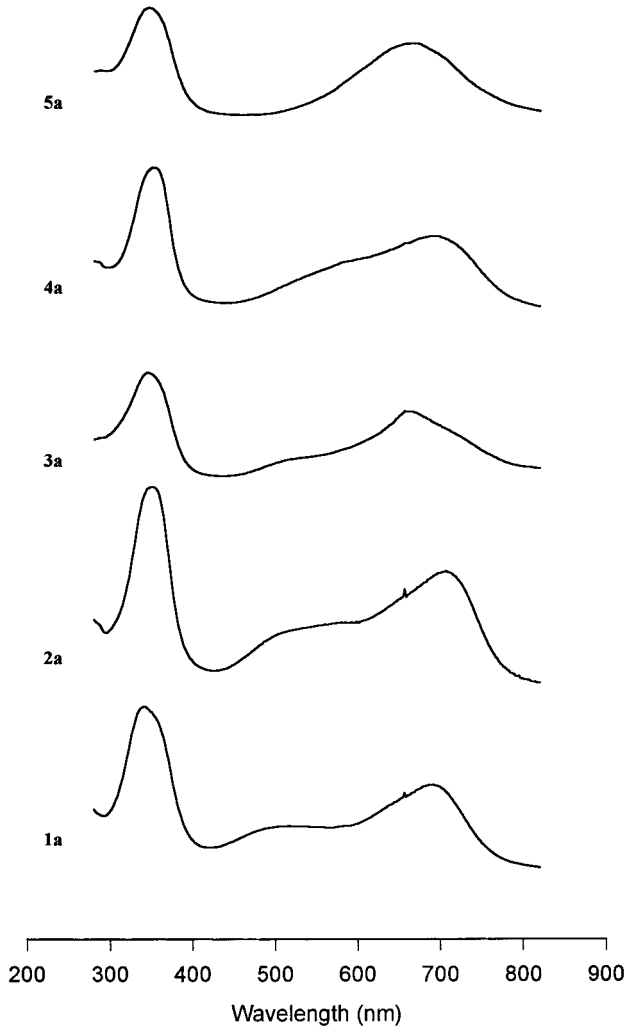


Figure 4. UV−vis spectra of [Mg] porphyrazines **1a**−**5a** in CH_2Cl_2.

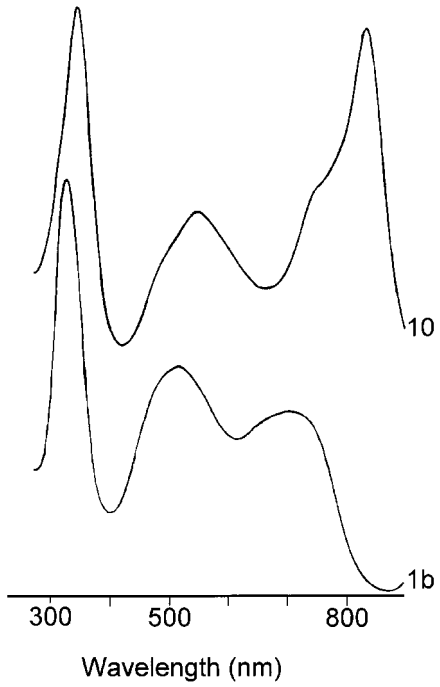


Figure 5. UV−vis spectra of porphyrazines **1b** and **10** in CH_2Cl_2.

Table 1. Electrochemical Data in Dichloromethane

	$E_{1/2}$ (volts vs Fc^+/Fc)			
compd	Pz^{2+}/Pz^+	Pz^+/Pz	Pz/Pz^-	Pz^-/Pz^{2-}
1a		−0.35		
2a	−0.076	−0.27		
3a		−0.27		
4a		−0.25		
5a		−0.18	−1.82	
1b	−0.063	−0.27	−1.61	
2b	0.021	−0.22	−1.55	−1.82
10	0.099	−0.18	−1.44	−1.56

eral auxochromic dimethylamino groups (Figure 5). Similarly red-shifted Q-bands have also been observed for other well-characterized benzo-fused phthalocyanine dimers.[23b] In addition, a less intense peak appears at 548 nm (vide supra) and the Soret band at 346 nm.

Cyclic Voltammetry. Each of the Mg[pz]'s **1a**−**5a** was examined by cyclic voltammetry in dichloromethane, and the results are summarized in Table 1. Because the central metal ion is not redox active, all observed transitions may be assigned to ring redox processes. Additionally, it is expected that ligation of the THF molecule observed in **2a** and **5a** would have no significant effect upon the ring redox processes, as axial ligation has been shown to have very little effect on ring-localized redox processes, even with transition-metal MPc species.[31]

The cyclic voltammogram of each macrocycle showed a first ring oxidation significantly lower in potential than that of ferrocene, used as internal standard. Reported potentials are referenced to the Fc^+/Fc couple. For the Mg[pz]'s, there was a significant increase in the first oxidation potential going from **1a** ($n = 4$, $E°_{1/2} = -0.35$ V) to **2a** ($n = 3$, $E°_{1/2} = -0.27$ V). Surprisingly, there was no significant difference in $E°_{1/2}$ values among the $n = 3$ and 2 macrocycles, but another increase was apparent for **5a**, where $n = 1$ ($E°_{1/2} = -0.18$ V). Compound **2a** was the only Mg[pz] that showed a second ring oxidation, which appeared at $E°_{1/2} = -0.076$ V. The $n = 1$ macrocycle, **5a**, was likewise the only Mg[pz] to show a ring reduction, appearing at $E°_{1/2} = -1.82$ V.

Removal of the internal Mg from pz's **1** and **2** had a pronounced effect on the redox potentials of each. Compound **1b** showed two reversible oxidations at potentials of −0.27 and −0.063 V, respectively, and **2b** at −0.22 and +0.021 V. The electrochemical properties of dimer **10** reveals similar first and second oxidation potentials centered at −0.18 and +0.099 V. A reversible ring reduction for compound **1b** is centered at −1.61 V (vs Fc^+/Fc), while compound **10** exhibits two ring reductions at $E°_{1/2} = -1.44$ and −1.56 V, which we assign to the $[H_2Pz]/[H_2Pz]^-$ and $[H_2Pz]^-/[H_2Pz]^{2-}$ couples, respectively. Compound **2b** displays also two ring reductions at $E°_{1/2} = -1.55$ and −1.82 V.

Conclusions

The synthesis of unsymmetrical porphyrazines bearing two, four, and six bis(dimethylamino) functionalities and the first planar homodimer of a peripherally heterosubstituted porphyrazine has been achieved. Due to the extended π-conjugated system and the 12 peripheral

(31) Lever, A. B. P.; Milaeva, E. R.; Speier, G. In *Phthalocyanines: Properties and Applications*; Lezuoff, C. C., Lever, A. B. P., Eds.; VCH: New York, 1993; Vol. 3; pp 1−70.

dimethylamino residues in the dimer, the Q-band in the UV−vis spectrum is significantly red-shifted to a long wavelength that may result in **10** being of biomedical application. Furthermore, the electron-donating amino substituents render the macrocycles very electron rich. This makes this family of molecules ideally suited for the development of new charge-transfer complexes and as precursors to magnetic or conductive materials. In addition, the external amino groups provide the molecules with the capability of binding metal ions. We are currently investigating the coordination chemistry of compounds **1**−**5** and **10** and the synthesis of related heterodimers. Such work will be reported in due course.

Experimental Section

General Procedures. All reactions were conducted in oven- or flame-dried glassware. Hexanes refers to the petroleum fraction bp 40−60 °C. Butanol used for reactions was distilled from Mg prior to use, whereas all other reagents were used as commercially supplied. TLC was carried out on E. Merck precoated silica gel 60 F_{254} plates. Chromatography refers to flash chromatography on E. Merck silica gel 60, 40−60 μm (eluants are given in parentheses). Cyclic voltametric measurements were carried out with a Cypress Systems 1087 computer-controlled potentiostat.

[2,3,7,8,12,13-Hexakis(dimethylamino)-17,18-benzporphyrazinato]magnesium(II) (2a). Mg turnings (0.416 g, 17.1 mmol) were stirred in butanol (105 mL) at reflux under nitrogen for 24 h. Bis(dimethylamino)maleonitrile **7**[28] (8.00 g, 48.8 mmol) and 1,2-dicyanobenzene **8** (0.254 g, 1.78 mmol) were added to the resulting magnesium butoxide suspension, and the reaction mixture was stirred at reflux under nitrogen for 3 days and allowed to cool to room temperature. Following rotary evaporation, the resulting blue-black residue was dissolved in $CHCl_3$ and filtered, and the solids were further washed with $CHCl_3$ until the washing became colorless. Rotary evaporation and chromatography (THF/hexanes 1:4) gave **2a** (0.115 g, 35%) as the THF adduct: mp >350 °C; R_f 0.33 (THF/hexanes 1:4); IR (thin film) 1574, 1379 cm^{-1}; UV−vis (CH_2Cl_2) λ_{max} (log ϵ) 343 (4.80), 707 (4.59); ^{1}H NMR (300 MHz, DMSO-d_6) δ 1.75 (m, 4H, THF), 3.60 (m, 4H, THF), 3.69 (s, 12H), 3.77 (s, 12H), 3.94 (s, 12H), 8.06 (dd, 2H, J = 3, 5 Hz), 9.11 (dd, 2H, J = 3, 5 Hz); HRMS (APCI) calcd for $C_{32}H_{41}MgN_{14}$ (M + H)$^+$, 645.3489, found (M + H)$^+$ 645.3439.

2,3,7,8,12,13-Hexakis(dimethylamino)-17,18-benzporphyrazine (2b). Porphyrazine **2a** (0.050 g, 0.078 mmol) was dissolved in TFA (20 mL), and the purple solution was stirred in the absence of light under N_2 for 12 h and poured onto crushed ice containing an excess of aqueous NH_3. The resulting dark precipitate was collected by vacuum filtration and washed with H_2O and MeOH until the washings were nearly colorless. The crude product mixture was purified by chromatography ($NH_4OH_{(aq)}$/MeOH/$CHCl_3$ 3:7:990) to give porphyrazine **2b** (0.036 g, 74%) as a dark purple solid: mp >350 °C; R_f 0.70 (MeOH/$CHCl_3$ 1:19); IR (thin film) 1574, 1390 cm^{-1}; UV−vis (CH_2Cl_2) λ_{max} (log ϵ) 336 (4.75), 538 (4.53), 696 (4.41) nm; ^{1}H NMR (300 MHz, $CDCl_3$) δ −0.89 (s, 2H), 3.74 (s, 12H), 3.76 (s, 12H), 3.98 (s, 12H), 7.94 (dd, 2H, J = 3, 5 Hz), 9.03 (dd, 2H, J = 3, 5 Hz); MS (FAB) m/z 623 (M$^{\cdot+}$). Anal. Calcd for $C_{32}H_{42}N_{14}$: C, 61.74; H, 6.75; N, 31.51. Found: C, 61.71; H, 6.57; N, 31.50. Crystal data for **2b**: $C_{32}H_{42}N_{14}\cdot{}^1/_3H_2O$, M = 628.8, rhombohedral, $R\bar{3}$ (no. 148), $a = b$ = 28.242(4) Å, c = 22.215(3) Å, V = 15345(4) Å^3, Z = 18, D_c = 1.225 g cm^{-3}, μ(Mo Kα) = 0.80 cm^{-1}, F(000) = 6036, T = 293 K; purple iridescent prisms, 0.72 × 0.53 × 0.51 mm, Siemens P4/PC diffractometer, ω-scans, 5824 independent reflections. The structure was solved by direct methods, and the non-hydrogen atoms were refined anisotropically using full matrix least-squares based on F^2 to give R_1 = 0.057, wR_2 = 0.164 for 3243 independent observed reflections [$|F_o| > 4\sigma(|F_o|)$, $2\theta \le 50°$] and 430 parameters.

Porphyrazines 3a, 4a, and 5a. Bis(dimethylamino)maleonitrile **7**[28] (5.08 g, 31.0 mmol) and 1,2-dicyanobenzene **8** (2.00 g, 15.6 mmol) were added to magnesium butoxide (21.5 mmol) in butanol (100 mL), prepared as above. The reaction mixture was stirred at reflux under nitrogen for 2 days, cooled to room temperature, and rotary evaporated. The remaining dark residue was dissolved in $CHCl_3$, filtered, and evaporated, and the crude, dark product mixture was redissolved in a 1:1 mixture of CH_2Cl_2/MeOH and rotary evaporated until most of the CH_2Cl_2 had been removed. The crude Mg[pz(NMe$_2$)$_2$(pc)$_3$] **5a** was collected by filtration. Rotary evaporation of the remaining filtrate and chromatography (THF/hexanes 1:4) gave the purified pz's in the order **5a**, **3a**, and **4a**.

[2,3-Bis(dimethylamino)norphthalocyaninato]magnesium(II) (5a). The crude solid collected above was dissolved in a minimal amount of THF and chromatographed (THF/hexanes 1:4) to give porphyrazine **5a** (1.06 g, 9%) as the THF chelate: mp >350 °C; R_f 0.19 (THF/hexanes 1:4); IR (thin film) 1582, 1383 cm^{-1}; UV−vis (CH_2Cl_2) λ_{max} (log ϵ) 350 (4.73), 670 (4.61) nm; ^{1}H NMR (300 MHz, DMSO-d_6) δ 1.77 (m, 4H, THF), 3.61 (m, 4H, THF), 3.95 (s, 12H), 8.20 (m, 6H), 9.26 (m, 2H), 9.40 (m, 4H); MS (FAB) m/z 573 (M$^{\cdot+}$). HRMS (APCI) calcd for $C_{32}H_{25}MgN_{10}$ (M + H)$^+$ 573.2114, found (M + H)$^+$ 573.2109. Crystal data for **5a**: $C_{34}H_{30}MgN_{10}OS$, M = 651.1, triclinic, $P\bar{1}$ (no. 2), a = 10.586(1) Å, b = 12.827(2) Å, c = 13.141(1) Å, α = 107.29(1)°, β = 99.98(1)°, γ = 104.79(1)°, V = 1586.1(4) Å^3, Z = 2, D_c = 1.363 g cm^{-3}, μ(Cu Kα) = 14.7 cm^{-1}, F(000) = 680, T = 293 K; purple iridescent rhombs, 0.37 × 0.33 × 0.23 mm, Siemens P4/PC diffractometer, ω-scans, 4946 independent reflections. The structure was solved by direct methods and the non-hydrogen atoms were refined anisotropically using full-matrix least-squares methods based on F^2 to give R_1 = 0.051, wR_2 = 0.133 for 4202 independent observed reflections [$|F_o| > 4\sigma(|F_o|)$, $2\theta \le 125°$] and 425 parameters.

[2,3,7,8-Tetrakis(dimethylamino)-12,13;17,18-dibenzporphyrazinato]magnesium(II) (3a): yield 0.36 g (4.8%); mp > 350 °C; R_f 0.28 (THF/hexanes 1:4); IR (thin film) 1572, 1381 cm^{-1}; UV−vis (CH_2Cl_2) λ_{max} (log ϵ) 350 (4.65), 684 (4.43) nm; ^{1}H NMR (300 MHz, DMSO-d_6) δ 3.75 (s, 12H), 3.97 (s, 12H), 8.16 (m, 4H), 9.19 (m, 2H), 9.32 (m, 2H); MS (FAB) m/z 609 (M$^{\cdot+}$); HRMS (APCI) calcd for $C_{32}H_{33}MgN_{12}$ (M + H)$^+$ 609.2802, found (M + H)$^+$ 609.2759. Crystal data for **3a**: $C_{34}H_{38}MgN_{12}OS$, M = 687.1, triclinic, $P\bar{1}$ (no. 2), a = 10.014(1) Å, b = 12.074(2) Å, c = 14.367(1) Å, α = 94.82(1)°, β = 98.34(1)°, γ = 98.63(1)°, V = 1689.2(4) Å^3, Z = 2, D_c = 1.351 g cm^{-3}, μ(Cu Kα) = 14.3 cm^{-1}, F(000) = 724, T = 293 K; purple iridescent prisms, 0.23 × 0.13 × 0.10 mm, Siemens P4/RA diffractometer, ω-scans, 5004 independent reflections. The structure was solved by direct methods, and the non-hydrogen atoms were refined anisotropically using full-matrix least-squares based on F^2 to give R_1 = 0.058, wR_2 = 0.147 for 4049 independent observed absorption corrected reflections [$|F_o| > 4\sigma(|F_o|)$, $2\theta \le 120°$] and 443 parameters. The crystallographic data (excluding structure factors) for **2b**, **3a**, and **5a** have been deposited with the Cambridge Crystallographic Data Centre. Copies of the data can be obtained free of charge, upon request, from the Director, CCDC, 12 Union Road, Cambridge, CB12 1EZ, UK (Fax: Int. code +(1223) 336-033; e-mail: teched@chemcrys.cam.ac.uk).

[2,3,12,13-Tetrakis(dimethylamino)-7,8;17,18-dibenzporphyrazinato]magnesium(II) (4a): yield 0.023 g (0.3%); mp >350 °C; R_f 0.36 (THF/hexanes 1:4); IR (thin film) 1574, 1381 cm^{-1}; UV−vis (CH_2Cl_2) λ_{max} (log ϵ) 352 (4.71), 694 (4.42) nm; ^{1}H NMR (300 MHz, DMSO-d_6) δ 3.91 (s, 24H), 8.15 (dd, 4H, J = 5.3 Hz), 9.19 (dd, 4H, J = 3.5 Hz); MS (FAB) m/z 609 (M$^{\cdot+}$); HRMS (APCI) calcd for $C_{32}H_{33}MgN_{12}$ (M + H)$^+$ 609.2802, found (M + H)$^+$ 609.2866.

Bis[7,8,12,13,17,18-hexakis(dimethylamino)porphyrazino][*b,e*]benzene (10). A mixture of BuOH (70 mL), Mg (0.24 g, 10 mmol), and I_2 (1 small crystal) was heated to reflux for 12 h under N_2. The suspension was cooled, benzobis(1,3-diiminopyrroline) **9**[23] (0.22 g, 1.0 mmol) followed by bis(dimethylamino)maleonitrile **7**[28] (1.15 g, 7.0 mmol) were added, and the reaction mixture was further heated at reflux for 48 h. The deep purple suspension was allowed to cool and was filtered (Celite), and the solids were washed with CH_2Cl_2. After rotary evaporation, the dark purple residue was dissolved in

TFA (50 mL) and, after 1 h at 20 °C, poured onto ice and water (200 mL) and the resulting suspension brought to pH 7.0−7.5 with 2 M NaOH. The aqueous layer was extracted with CH_2Cl_2 until the washings were colorless. The combined organic layers were dried ($MgSO_4$) and concentrated to yield a dark purple residue. Hexanes were added (to dissolve most of the unwanted octakis(dimethylamino)porphyrazine **1b**), and the suspension was filtered. The resulting filtrate was rotary evaporated and chromatographed twice ($CHCl_3$/MeOH 9:1) providing the dimer **10** (0.175 g, 15%) as a dark purple solid: mp >350 °C; R_f 0.87 ($CHCl_3$/MeOH 9:1); IR (CH_2Cl_2) 3690, 3303, 1595, 1573, 1385, 1081 cm^{-1}; UV−vis (CH_2Cl_2) λ_{max} (log ϵ) 346 (4.93), 548 (4.64), 839 (4.90) nm; ^1H NMR (300 MHz, $CDCl_3$) δ −0.45 (s, 4H), 3.79 (s, 24H), 3.81 (s, 24H), 4.21 (s, 24H), 10.61 (s, 2H); ^{13}C NMR (75 MHz, pyridine-d_5) δ 46.1, 47.1, 47.4; MS (FAB) *m*/*z* 1166 ($M^{\cdot+}$); HRMS (FAB) calcd for $C_{58}H_{79}N_{28}$ $(M + H)^+$ 1167.7043, found $(M + H)^+$ 1167.7054. Anal. Calcd for $C_{58}H_{78}N_{28}$: C, 59.67; H, 6.73; N, 33.59. Found: C, 59.85; H, 6.34; N, 33.30.

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Supporting Information Available: Copies of ^1H NMR spectra of **2a**, **3a**, **4a**, and **5a** and X-ray data of **2b**, **3a**, and **5a**. This material is available free of charge via the Internet at http://pubs.acs.org.

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