Porphyrazines with Annulated Diazepine Rings, 1 Synthesis and Characterization of Tetrakis-2,3-(5,7-diphenyl-6*H*-1,4-diazepino)porphyrazine and Its Mg^{II}, Cu^{II}, and Zn^{II} Complexes – X-ray Crystal Structure of 2,3-Dicyano-5,7-diphenyl-6*H*-1,4-diazepine

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A new class of porphyrazine macrocycles carrying peripheral diazepine rings, i.e. tetrakis-2,3-(5,7-diphenyl-6*H*-1,4-diazepino)porphyrazine $[Ph_2DzPzH_2](H_2O)_4$, and its metal derivatives of formula $[Ph_2DzPzM](H_2O)_{x=2-7}$ [M = Mg^{II}-(H_2O), Cu^{II}, Zn^{II}] have been prepared and characterized. Single crystal X-ray work on the monomeric precursor 5,7-diphenyl-2,3-dicyano-6*H*-1,4-diazepine, $Ph_2(CN)_2Dz$, and NMR spectra ($CDCl_3$, $(CD_3)_2SO$) and UV/Vis spectra in solution of different media (basic, neutral, acid) of the monomer and its macrocyclic derivatives have provided information on the conformational flexibility of the diazepine ring as well as on the structural and electronic features of the entire porphyrazine skeleton.

Introduction

Tetrapyrrolic macrocycles such as porphyrins[1] and phthalocyanines (tetrabenzoporphyrazines), substituted phthalocyanines or their aza analogues,[2] object of extensive studies and practical applications for several decades, have been even more intensively investigated during the last 10−20 years. Comparatively, porphyrazines without annulated six-membered aromatic rings (commonly named also as tetraazaporphyrins), a distinct class of novel macrocycles, have been little studied, although the object of recent increasing attention.[3] Very recently, we have reported on the synthesis and characterization of new classes of porphyrazines carrying five-membered S- and Se-containing heterocycles annulated to the pyrrole rings of the central porphyrazine core, namely tetrakis-3,4-(1,2,5-thiadiazole)-[4] and tetrakis-3,4-(1,2,5-selenodiazole)porphyrazines.[5] Definitely, these new macrocycles can be seen as phthalocyanine-like systems in terms of the square-planar molecular geometry, number of π-electrons, and physical properties (low-solubility, high thermal stability, vaporizability). Nevertheless, the presence in the macrocyclic ring of N atoms and of soft atoms such as S and Se certainly determines a different electronic distribution within the skeletal ring. In addition, S and Se can play an important role in affecting the solid state interunit contacts, which are presently deepfully investigated, this probably opening promising perspectives for the new molecular materials in the field of practical applications (electrical conductivity, electrochromism, nonlinear optical properties, etc.).

We have now extended our attention to the synthesis and characterization of porphyrazine macrocycles having peripheral heptaatomic heterocyclic rings, and report here on the X-ray crystal structure of 5,7-diphenyl-2,3-dicyano-6*H*-1,4-diazepine, $Ph_2(CN)_2Dz$, and on the use of this dicyano species as a monomeric precursor for the synthesis of a new class of porphyrazine macrocycles, i.e. tetrakis-2,3-(5,7-diphenyl-6*H*-1,4-diazepino)porphyrazine, Ph_8DzPzH_2, and its complexes with Mg^{II}, Cu^{II}, and Zn^{II} (see Scheme 1). These tetrapyrrolic species, owing to the structural features of the annulated diazepine rings (see below), markedly differ from the S- and Se-porphyrazines mentioned above, and from the phthalocyanines as well, in many respects. First, they are far from being entirely planar, and, hence, the problem is faced of how the central essentially flat porphyrazine core and the peripheral non planar diazepine rings will reciprocally interfere both structurally and electronically. In addition, the presence of the eight peripheral phenyl groups contribute to infer to the new materials specific physical properties, among them solubility, which may diversify the spectrum of the possible practical applications. Special account should be taken of the fact that the physical properties of this new class of complexes can be modulated by operating appropriate substitutions, presumably possible, in the 5, 6, and 7 positions of the external diazepine rings.

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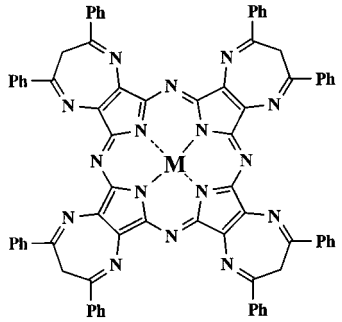
Finally, the N···N···N external cavities can probably be used as the sites for exocyclic metal coordination and formation of multimetallic systems with novel electronic, optical, and redox properties.



Scheme 1

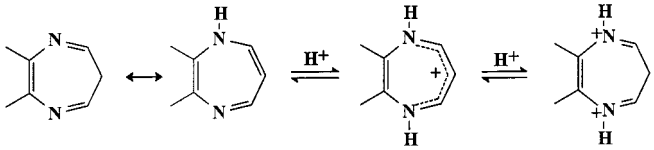
	2	3	4	5
M	Mg	2H	Cu	Zn
Abbreviation	$Ph_8DzPzMg$	Ph_8DzPzH_2	$Ph_8DzPzCu$	$Ph_8DzPzZn$

Results and Discussion

First, we briefly illustrate the structure of the monomeric precursor **1**, and then report on the synthesis and characterization of the macrocycles **2**−**5**.

X-ray Crystal Structure of 5,7-Diphenyl-2,3-dicyano-6*H*-1,4-diazepine, $Ph_2(CN)_2Dz$ (1)

The crystal structure of $Ph_2(CN)_2Dz$ consists of discrete molecules and the crystal packing is determined by van der Waals interactions. Crystal data and details associated with data collection are given in Table 1. The side and front views of the molecule are given in Figure 1 (A, B). Selected bond lengths and angles are quoted in Table 2. The diazepine ring exhibits a boat conformation flattened at the stern, as indicated by the displacements of the C(6), C(2), C(3) atoms from the N(1)−N(4)−C(5)−C(7) mean plane, which are 0.837(2), 0.572(2), 0.588(2) Å, respectively. The dihedral angles formed by the C(5)−C(6)−C(7) and N(1)−C(2)−C(3)−N(4) mean planes with the N(1)−N(4)−C(5)−C(7) mean plane are 119.0 and 148.4°, respectively. The diazepine ring possesses a pseudosymmetry plane running through C(6) and the midpoint of the C(2)−C(3) bond, as indicated by the asymmetry parameter ΔC_s (C4) = 0.011(1). Considering the sequence N(1)−C(2)−C(3)−N(4)−C(5)−C(6)−C(7) the puckering parameters are as follows: q_2 = 0.830(2); q_3 = 0.308(2); Q_T = 0.886(2); φ_2 = 24.3(2); φ_3 = 128.3(4); θ_2 = 69.6(1). The N−C and C−C bond lengths within the diazepine ring appear to be intermediate between those expected for single and double bonds. In fact N(1)−C(2) and N(4)−C(5) lengths are shorter (ca. 1.36 Å) than those in a single bond, while N(1)−C(7) and N(4)−C(5) both 1.301(2) Å], and C(2)−C(3) [1.378(2) Å] are longer than those in a double bond. This indicates that π conjugation permeates the fragment C(7)−N(1)−C(2)−C(3)−N(4)−C(5) internal to the diazepine ring, despite of the fact that the latter is considerably displaced from planarity. The C(51)...C(56) and C(71)...C(76) phenyl rings, which form a dihedral angle of 75.8(1)°, are tilted with respect to the N(1)−N(4)−C(5)−C(7) mean plane by 126.7(1) and 129.0(1)°, respectively.



I II III IV

Scheme 2

Table 1. Experimental data for the X-ray diffraction studies on crystalline compound **1**

	1
Empirical formula	$C_{19}H_{12}N_4$
Formula mass	296.3
Space group	$P2_1/n$ (#14)
a [Å]	9.595(2)
b [Å]	10.828(2)
c [Å]	14.843(3)
α,γ [°]	90
β [°]	95.07
V [Å^3]	1536.1(5)
Z	4
T [°C]	22
λ(Mo-K_α) [Å]	1.54178
$D_{calcd.}$ [g cm^{-3}]	1.281
μ [cm^{-1}]	5.91
Transmission coefficient	0.974−1.000
Unique total data [$I > 0$]	2862
Unique observed data [$I > 2(I)$]	2492
R	0.055
$wR2$	0.176
GOF	1.162

$R = \Sigma|\Delta F|/\Sigma|F_o|$ calculated on the unique observed data [$I > 2(I)$]; $wR2 = [\Sigma w|F^2|^2/w|F_o{}^2|^2]^{1/2}$ calculated on the unique total data with $I > 0$; $GOF = [\Sigma w|F^2|^2/(NO - NV)]^{1/2}$.

As can be well seen from Figure 1A, two hydrogen atoms of the $-CH_2-$ group are inequivalent: One of them is in the equatorial position while another one, being in the quasi-axial position, is located over the diazepine ring. Thus, in the solid state, **1** exists as 6*H* tautomer of type **I** (Scheme 2).

Macrocycles 2−5: Synthetic and General Aspects

Although 2,3-dicyano-6*H*-1,4-diazepines have been known for a long time[6][7] no attempt, to our knowledge, has so far been made to use them as precursors for the preparation of porphyrazines. We have attempted the template tetramerization in presence of magnesium propylate of both 5,7-dimethyl-2,3-dicyano-6*H*-1,4-diazepine, $Me_2(CN)_2Dz$, and 5,7-diphenyl-2,3-dicyano-6*H*-1,4-diazep-

Table 2. Selected bond lengths [Å] and angles [°] for **1**[a]

Bond lengths			
N(1)−C(2)	1.363(3)	C(2)−C(21)	1.445(2)
N(1)−C(7)	1.301(2)	C(3)−C(31)	1.439(3)
N(4)−C(3)	1.360(2)	C(5)−C(6)	1.505(3)
N(4)−C(5)	1.301(2)	C(5)−C(51)	1.468(2)
N(22)−C(21)	1.140(2)	C(6)−C(7)	1.503(3)
N(32)−C(31)	1.138(3)	C(7)−C(71)	1.468(3)
C(2)−C(3)	1.378(2)		
Bond angles			
C(2)−N(1)−C(7)	120.8(2)	N(4)−C(5)−C(6)	119.3(2)
C(3)−N(4)−C(5)	121.3(2)	C(6)−C(5)−C(51)	121.8(2)
N(1)−C(2)−C(21)	113.8(2)	C(5)−C(6)−C(7)	101.0(2)
N(1)−C(2)−C(3)	126.8(2)	N(1)−C(7)−C(6)	119.8(2)
C(3)−C(2)−C(21)	118.5(2)	C(6)−C(7)−C(71)	121.7(1)
N(4)−C(3)−C(2)	125.5(2)	N(1)−C(7)−C(71)	118.5(2)
C(2)−C(3)−C(31)	119.0(2)	N(22)−C(21)−C(2)	178.3(2)
N(4)−C(3)−C(31)	114.9(1)	N(32)−C(31)−C(3)	177.7(2)
N(4)−C(5)−C(51)	118.8(2)		

[a] Atom numbering corresponds to that shown in Figure 1.

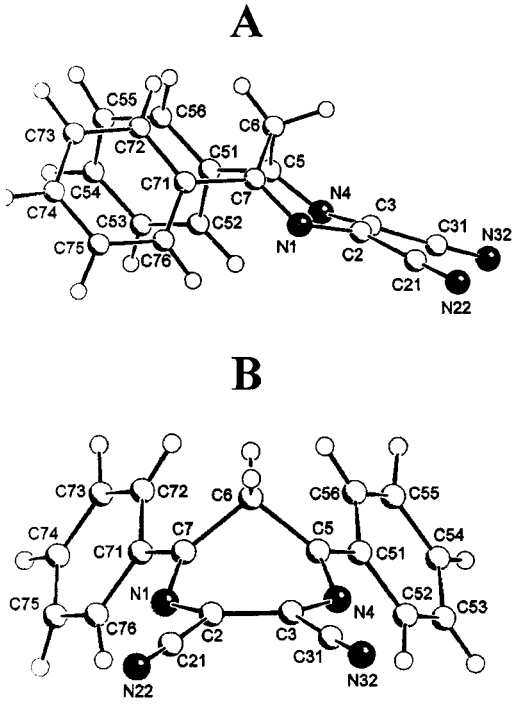


Figure 1. SCHAKAL side (A) and front-top (B) views of $Ph_2(CN)_2Dz$ (**1**)

ine [$Ph_2(CN)_2Dz$, **1**], but only with **1** cyclotetramerization takes place and the Mg^{II} complex $Ph_8DzPzMg$ (**2**) is formed in a high yield as a hydrated bluish-green material.

The Mg complex **2** can be demetallated to the metal-free macrocycle Ph_8DzPzH_2 (**3**) in boiling glacial acetic acid. The use of stronger acids such as CF_3COOH or 96% H_2SO_4 immediately determines demetallation of **2** upon dissolution even at room temperature, as can be evidenced by the UV/Vis spectra (see below). However, these strong acids cannot be used for preparative purposes; in fact, although **3** is stable in 96% H_2SO_4 for days, its precipitation by pouring the solution on ice gives an impure material with low yields, and solutions of **3** in CF_3COOH appear to be not stable enough, and, after even a rapid evaporation of the solvent, an unidentified brown product is obtained (molecular peak in the FAB spectrum at *m*/*z* 1084) instead of the green Ph_8DzPzH_2 (M^+ at 1187.5). A similar brown material, which is presently the object of further investigation, is obtained when non glacial acetic acid is used for preparation of **3** from **2**.

Refluxing of the Mg^{II} complex **2** in glacial acetic acid in the presence of excess of copper acetate results in the formation of the Cu^{II} complex $Ph_8DzPzCu$ (**4**). This latter, and the Zn^{II} complex as well, can be obtained by reaction of the metal-free macrocycle **3** with the pertinent metal acetate in dimethyl sulfoxide (DMSO). All samples of the compounds **2**−**5** were obtained as hydrated materials with slightly variable amounts of water molecules depending on the particular samples, as is evidenced by elemental analysis (C,H,N), thermogravimetric measurements, and IR spectra (see Experimental Section). These water molecules can be completely removed by mild heating under vacuum, exception made for one water molecule retained by the Mg complex. It is assumed that such a water molecule is directly and fairly strongly ligated to the metal center, as observed for several similar Mg^{II}−porphyrazines.[4,5,8]

The macrocyclic structure given in Scheme 1 for the present species is confirmed by FAB measurements (see Experimental Section), and is further supported by NMR, IR, and UV/Vis data. The presence of the peripheral 1,4-diazepine rings in this kind of macrocycles requires examination, developed below, of specific problems concerning their structural and conformational flexibility as well as chemical behaviour, since it is known that 1,4-diazepines can exist, depending on substituents, as 6*H* or 1*H* tautomers **I** and **II**, and in acid media they can be protonated forming successively monocations (diazepinium salts) **III** and dications **IV**[9] (Scheme 2).

^{1}H-NMR Spectra of $Ph_2(CN)_2Dz$ (1) and of the Zn^{II} Complex $Ph_8DzPzZn$ (5)

$Ph_2(CN)_2Dz$ (1) in Solution of $CDCl_3$ and $(CD_3)_2SO$

The ^{1}H-NMR spectrum of **1** (Figure 2, Table 3) definitely confirms that its structure in solution of a nonacidic solvent (chloroform, dimethyl sulfoxide) is similar to that found in the solid state. In fact, in addition to the multiplets of the phenyl protons in the low field region (δ = 7.93, 7.50, and 7.41 for *o*-Ph, *p*-Ph and *m*-Ph, respectively), two doublets for the $-CH_2-$ protons are observed at δ = 1.98 and 5.74 in $CDCl_3$ at 293 K (AB system, ^2J = 11.23 Hz). Such a ^{1}H-NMR pattern for **1** is fully consistent with the tautomeric structure **I** (6*H* tautomer). According to the available ^{1}H-NMR data the 6*H* tautomer **I** is also preferred for the dimethyl derivative $Me_2(CN)_2Dz$,[6] and for 5,7-disubstituted 2,3-benzo-1,4-diazepines (R_2BzDz; R = Me, Ph),[10] whilst the 1*H* tautomer **II** is present in 2,3-dihydro-1,4-diazepines.[9c]

An interesting aspect of the observed ^{1}H-NMR spectrum of **1**, worth to be discussed, is that the CH_2 protons appear,

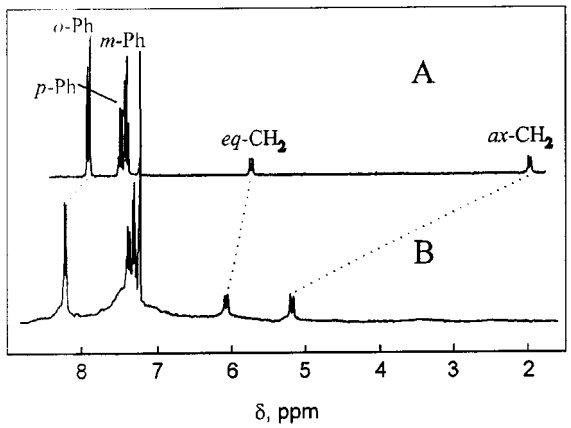


Figure 2. ^{1}H-NMR spectra of (A) $Ph_2(CN)_2Dz$ (**1**) and (B) $Ph_8DzPzZn$ (**5**) in $CDCl_3$

boiling $(CD_3)_2SO$ allowed to explore a wider range of temperatures up to 363 K. As shown in Figure 3 (spectra A−D), the two AB doublets of the CH_2 protons located at δ = 2.32 and 6.19 at 303 K (spectrum A), progressively broaden, completely disappearing at 363 K, thus giving a rough estimation of the coalescence temperature T_c. The high T_c value observed suggests that the ring inversion process for $Ph_2(CN)_2Dz$ is markedly hindered, very likely because of the presence of the two phenyl rings in the 5- and 7-positions.

As far as the position of the CH_2 signals of **1** is concerned, the quasi-axial proton (*ax*-CH_2) is shielded, being located over the plane of the C=N double bonds (Figure 1). Accordingly, the signal is found at higher field than is usual for CH_2 protons adjacent to two sp^2 carbon atoms. The substituents in the diazepine ring appear to have little influence on the resonance position of the *ax*-CH_2 proton

Table 3. Positions of the CH_2 proton signals in the ^{1}H-NMR spectra of compounds containing 1,4-diazepine rings

Compound	Solvent	δ [ppm] *ax*-CH_2	*eq*-CH_2	Splitting ^2J [Hz]	T [°C]
$Ph_2(CN)_2Dz$	$CDCl_3$	1.98	5.74	11.23	293
		1.99	5.73	11.2	313
		2.01	5.70	–	333
	$(CD_3)_2SO$	2.32	6.19	11.18	303
		2.32	6.15	–	323
		2.33	6.14	–	343
		not observed			363 ≈ T_c
$Me_2(CN)_2Dz$[a]	CD_3CN	1.94	4.41	10	243
		singlet		–	T_c ca. room temp.
Ph_2BzDz[b]	C_5D_5N	2.18	5.66	12	223
			3.80	–	353 (T_c = 273±10)
MePhBzDz[b]	CD_3OD	1.97	4.50	12	213
		3.3		–	307 (T_c = 261±7)
Me_2BzDz[b]	CD_3OD	2.04	3.74	11	213
		2.90		–	309 (T_c = 247±8)
$Ph_8DzPzZn$	$CDCl_3$	5.18	6.08	12.6	293
	$(CD_3)_2SO$	5.03	5.99	11.72	373
$Ph_8DzPzMg$	$(CD_3)_2SO$	5.06	5.99	12.10	373

[a] From ref.[6] – [b] From ref.[10]

even at room temperature, as two sharp doublets (again depicted here as an AB system,[9][14] although, owing to their large inequivalence, they might alternatively be considered as an AX system). This means that the inversion of the diazepine ring in this species is slow under these conditions. A different situation is observed in the case of the dimethyl derivative $Me_2(CN)_2Dz$[6] and of 2,3-benzo-1,4-diazepines (R_2BzDz; R = Me, Ph)[10] (Table 3), since for these species the CH_2 protons give a singlet resonance peak at room temperature and only at lower temperatures the peak splits into two doublets (the coalescence temperature T_c is close to room temp. or below, Table 3). Variable temperature ^{1}H-NMR measurements for $Ph_2(CN)_2Dz$ in solution of $CDCl_3$ show that the gradual raising of the temperature from 293 K causes the broadening of the two sharp doublets of the CH_2 protons, and at 333 K two broad unsplit signals are still observed at δ = 2.01 and 5.70 for the axial and equatorial protons, respectively, although clearly the coalescence temperature is not definitely reached. The higher

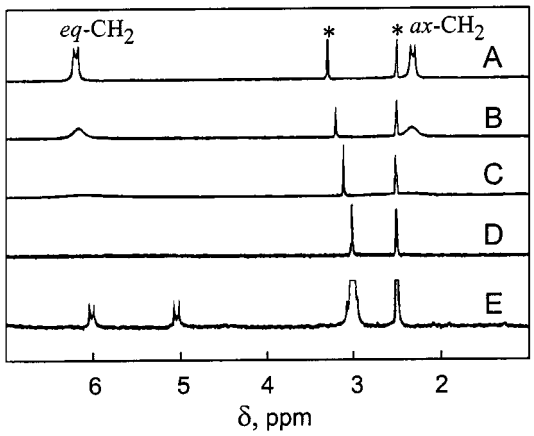


Figure 3. ^{1}H-NMR spectra of $Ph_2(CN)_2Dz$ (**1**) (A−D) and $Ph_8DzPzZn$ (**5**) (E) in $(CD_3)_2SO$ at 313 K (A), 333 K (B), 353 K (C), and 373 K (D, E); signals of nondeuterated solvent and water traces are marked with an asterisk

(Table 3). As to the equatorial proton (*eq*-CH_2), the substituents (especially in 5- and 7-positions) strongly affect the position of its resonance. In $Ph_2(CN)_2Dz$ the *eq*-CH_2 proton is deshielded by the adjacent C=N double bonds and, additionally, by the π-electron ring current of the phenyl rings. Hence, its resonance shifts downfield as compared with that of $Me_2(CN)_2Dz$.

$Ph_8DzPzZn$ (5) in Solution of $CDCl_3$, $(CD_3)_2SO$, CF_3COOH, and H_2SO_4

The ^{1}H-NMR spectrum of $Ph_8DzPzZn$ (**5**) in $CDCl_3$ shows general features similar to those of the monomeric compound $Ph_2(CN)_2Dz$ (compare A and B, Figure 2). At 293 K the phenyl protons give resonances at δ = 8.23, 7.32, and 7.37 for *o*-Ph, *m*-Ph and *p*-Ph, respectively. As to the CH_2 protons, two doublets appear at δ = 5.18 and 6.08 (^2J = 12.5 Hz), which means that in $CDCl_3$ and in $(CD_3)_2SO$ as well (Table 3), all diazepine rings of the Zn^{II} complex **5** are present in the form of the 6*H* tautomer **I**. It can be seen from Figure 2 that in going from $Ph_2(CN)_2Dz$ (**1**) to $Ph_8DzPzZn$ (**5**) a downfield shift is observed for the resonances of the *o*-Ph and CH_2 protons, due to their close position to the porphyrazine macrocycle. These downfield shifts are probably the result of combined structural and electronic effects, since annulation of the diazepine rings very likely implies an increased planarity of the C(7)−N(1)−C(2)−C(3)−N(4)−C(5) moiety, thus allowing an extension of the π-electron conjugation and this, in turn, the deshielding effect of the strong π-electron ring current of the formed porphyrazine macrocycle to which the diazepine rings are attached in this case. The unusually large downfield shift of the axial methylene proton (δ = 3.2) to the new position of δ = 5.18 is especially remarkable and indicates its proximity to the macrocycle. In fact, the distance of this axial methylene hydrogen atom from the center of the porphyrazine macrocycle (ca. 5.3 Å, as can be estimated from the MM+ geometry optimization procedure of the Hyperchem[11]), is 1.7 Å shorter than that of the equatorial hydrogen. Furthermore, such distance is comparable with that of the aromatic pyrrole protons for the Zn complex of unsubstituted porphyrazine (ca. 5.1 Å, singlet at δ = 9.4 in its ^{1}H-NMR spectrum[12]). It is remarkable that in the ^{1}H-NMR spectrum of $Ph_8DzPzZn$ in $(CD_3)_2SO$ even at 373 K (Figure 3, spectrum E) the CH_2 protons give two sharp doublets of the AB system, whilst approximately at the same temperature the monomeric precursor **1** showed coalescence. This means that annulation to the porphyrazine macrocycle very strongly reduces the conformational flexibility of the diazepine ring.

The ^{1}H-NMR spectra of $Ph_8DzPzZn$ in trifluoroacetic and sulfuric acids (Figure 4) differ from those taken in $CDCl_3$ or $(CD_3)_2SO$. This is not surprising, because it is known[9] that 1,4-diazepines exhibit strong basic properties, forming easily (e.g. in CF_3COOH) monocations **III** of diazepinium salts ($pK_{a1} \approx 9$ and 13 for 2,3-benzo- and for 2,3-dihydro-1,4-diazepines, respectively), and, under much more severe conditions (conc. H_2SO_4), diprotonated forms **IV** ($pK_{a2} \approx -1$ and −3 for 2,3-benzo- and for 2,3-dihydro-1,4-diazepines, respectively). The signals of the *m*-Ph and *p*-Ph protons are shifted downfield in CF_3COOH (δ = 8.03 and ca. 8.25, respectively) as compared to their position in the $CDCl_3$ solution. Whilst no AB doublets attributable to the CH_2 protons are observed, two singlets of equal intensity (4 H each) are found present at δ = 4.90 and 8.32.[13] These two resonances can be assigned to the −CH= and NH protons. Their position and relative intensity prove that diazepine rings of $Ph_8DzPzZn$ in the CF_3COOH solution are present in the form of the 1*H* tautomer **II**, rather than in the form of a type-**III** cation. In support of this: a) the olefinic −CH= and NH protons of the 1*H* tautomer **II** of 2,3-dihydro-5,7-dimethyl-1*H*-1,4-diazepine give, similarly, resonances of equal intensity at δ = 4.40 and 7.76 for solution in CCl_4;[9c] b) for the corresponding cation of type **III** in the case of 2,3-dihydro-5,7-diphenyl-1,4-diazepine occurring in CF_3COOH, signals of the −CH= and NH protons are observed at lower fields and have intensity ratio 1:2 [δ = 5.95 (1 H) and 8.1 (2 H)[14]]. Hence, if the tetracation $[Ph_8(DzH)PzZn]^{4+}$ with diazepine rings in form **III** were the case, the −CH= and especially NH resonances should appear at lower fields (due to the influence of the macrocyclic π-electron ring current) and have relative intensity 1:2. Transformation of the diazepine rings of $Ph_8DzPzZn$ from 6*H* tautomer **I** in neutral $CDCl_3$ solution to the 1*H* tautomer **II** in CF_3COOH occurs evidently because of the specific acid solvation of the second nitrogen atom of the diazepine rings and *meso*-nitrogen atoms of the porphyrazine macrocycle by molecules of trifluoroacetic acid. Unlike

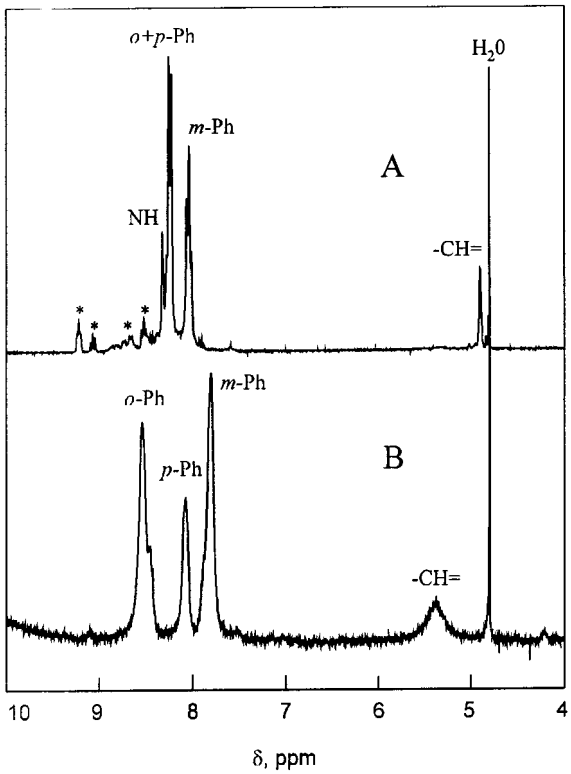


Figure 4. ^{1}H-NMR spectra of $Ph_8DzPzZn$ (**5**) in CF_3COOH (A) and in H_2SO_4 (B); signals of decomposition products are marked with an asterisk

monomeric 1,4-diazepine derivatives, protonation of the diazepine rings in the macrocyclic complex **5** with formation of the tetracation $[Ph_8(DzH)PzZn]^{4+}$ is not favourable under these conditions. Noteworthy, in the case of monomer **1**, due to two electron-withdrawing CN groups present and strongly reducing its basicity, the diazepinium salt $Ph_2(CN)_2DzH^+$ of type **III** is also not formed in CF_3COOH. Accordingly, the ^{1}H-NMR spectral pattern remains characteristic for the 6*H* tautomer **I**, although all signals, because of the acidic solvation, appear at lower fields [multiplets at δ = 8.35, 8.02, 7.87 for *o*-, *p*- and *m*-Ph and two AB doublets (^2J = 11 Hz) at δ = 2.77 and 6.51 for the axial and equatorial CH_2 protons].

The ^{1}H-NMR spectrum of the Zn^{II} complex **5** in H_2SO_4 contains nonresolved multiplets of the phenyl protons (δ = 8.54, 8.07, 7.80 for *o*-, *p*- and *m*-Ph, respectively) and one broad signal at δ = 5.39. The intensity ratio of this signal to the signals of the phenyl protons is 1:10, which allows us to assign it to the olefinic −CH= proton of the monoprotonated diazepine rings in form **III**. For a structure containing doubly protonated diazepine rings **IV** this ratio should be 1:5. Resonances of the NH protons which should be present for both possible structures **III** and **IV** have not been observed. The NH groups located close to the aromatic porphyrazine macrocycle should be strongly deshielded by its π-electron ring current and give resonances downfield with respect to their position in mono- and diprotonated 2,3-dihydro- or 2,3-dibenzo-1,4-diazepines (for 2,3-dihydro-1,4-diazepinium salts **III** δ_{NH} = 8.5−9.5[14][15] and for form **IV** of Me_2BzDz in H_2SO_4 δ_{NH} = 13.4[9c]). No signals are present in the lowfield region (δ > 12.6), where resonances of the NH protons for the structure with doubly protonated diazepine rings **IV** could be expected. Therefore, the octacationic structure $Ph_8(DzH_2)PzZn^{8+}$ can be excluded for the H_2SO_4 solution. For the tetracation $Ph_8(DzH)PzZn^{4+}$ with monoprotonated diazepine rings (form **III**), the NH resonances, expected in the region δ = 9−12, are very likely underneath the intense absorption of H_2SO_4 at δ = 9.3−12.6. In the spectrum taken in deuterated sulfuric acid, the signal of the −CH= proton is not present. This is easily explained by deuterio exchange which is facilitated by the quasi-aromatic properties of the diazepinium salt **III** and hence its reactivity in electrophylic substitution.[16][17]

Although *meso*-nitrogen atoms of the porphyrazine macrocycle can also take part in the acid-base interaction processes,[18] no signal attributable to the $^+N_{meso}$−H resonance was found either in CF_3COOH or in H_2SO_4. It is not surprising that the ^{1}H-NMR spectra provide no evidence of protonation of *meso*-nitrogen atoms. Low relative intensity and broadness (due to the rapid exchange with media) make difficult the detection of these signals, expected in the low field region (possibly nearby the OH absorption of the solvent). UV/Vis spectroscopy in some cases can provide more definite information about acid-base interaction of *meso*-nitrogen atoms.[18]

The ^{1}H-NMR spectra of the Mg^{II} complex **2** in weakly donor solvents show features strictly similar to those observed for the Zn^{II} complex [see data in Table 3 for $(CD_3)_2SO$)]. Similar spectra are also obtained for the free ligand as to the presence of the Ph and CH_2 groups, although the spectra are of poor quality because of low solubility. In strong acids such as H_2SO_4 (96%) complex **2** undergoes demetallation to the free ligand, whose spectra did not allow identification of the central NH groups.

UV/Vis Spectra

UV/Vis spectra of the macrocyclic compounds **2**−**5**, which show strong absorptions in the ranges 250−410 (Soret region) and 600−700 nm (*Q*-band region), deserve some detailed discussion.

Spectra in Basic, Neutral, and Slightly Acidic Solvents

Remarkably, the UV/Vis spectra of the metal-free ligand **3** and the metal complexes **2**, **4**, and **5** in basic, neutral and slightly acidic solvents [pyridine (Table 4), $CHCl_3$, $(CH_3)_2SO$, alcohols, acetic acid] show two well distinct bands in the *Q*-band region (see Figure 5A, B, C for the free ligand, and Figure 5F, G, H for the Cu^{II} complex), i.e. an intense sharp short-wave band with $\lambda_{max} \approx 630-640$ nm (split for the free ligand **3** because of its lower symmetry, i.e. D_{2h}) accompanied by a slightly broader less intense well separated satellite with $\lambda_{max} \approx 660-680$ nm (ca. 800−1000 cm^{-1}).

These two bands cannot be considered as two components of the split *Q*-band originating from considerable lowering of the symmetry of the molecule, since annulation of the four nonplanar diazepine rings cannot significantly disturb the overall D_{4h} symmetry of the chromophore. A split *Q*-band could alternatively originate from dimer formation caused by strong π-interaction,[19] and, indeed, such type of splitting (800−1000 cm^{-1}) has been observed for macrocyclic units brought very close to one another and firmly held together, as occurs, for instance, for the diphthalocyanine systems $(PcRh)_2$,[20] $(PcFe)_2(-C)$ and $(PcRu)_2(-C)$.[21] This is not, however, the case for the present species, for which, noteworthy, the ^{1}H-NMR spectra in $CDCl_3$ give no indication of molecular association even at high concentrations of the species. Clearly, then, the two peaks in the *Q*-band region have a different origin. We suggest that the sharp more intense band at 630−640 nm is associated with the lowest π→π* transition ("normal" *Q*-band), and the less intense long-wave band at 660−680 nm is due to the low lying n→π* transition (Q_n-band), as it is further discussed below.

The φ_n orbitals of the *meso*-nitrogen atoms of the porphyrazine macrocycle and the pyridine-type nitrogen atoms of the annulated heterocyclic rings (e.g. in tetrapyrazinoporphyrazines) have a lower energy than the HOMO, and corresponding n→π* transitions are observed in the Soret band region.[22] The lone pairs of these nitrogen atoms are located in the plane of the porphyrazine skeleton. Differently, the lone pairs of the imido nitrogen atoms in the diazepine rings of compounds **2**−**5** are not coplanar with the macrocycle forming an angle with its mean plane of about

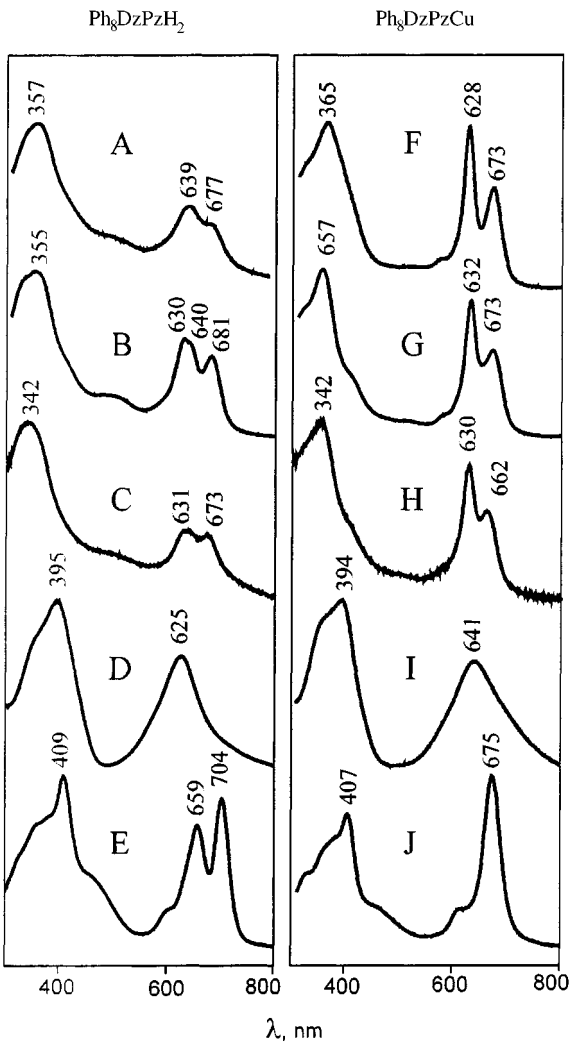


Figure 5. UV/Vis spectra of Ph_8DzPzH_2 (A−E) and $Ph_8DzPzCu$ (F−J) in pyridine (A, F), $CHCl_3$ (B, G), CH_3COOH (C, H), CF_3COOH (D, I) and H_2SO_4 (E, J)

only negligibly affected. This is clear for our species looking at Figure 5 (see spectra B and C, and also F, G, and H).

Spectra in Strong Acids (CF_3COOH, H_2SO_4)

The UV/Vis spectra in CF_3COOH (Figures 5, D and I) show a Soret band at λ_{max} = 394−401 nm, and a broad *Q*-band at λ_{max} = 625−664 nm. No distinct Q_n-band is observed. This type of spectrum is consistent with diazepine rings being present in the 1*H*-tautomeric form **II** as was concluded on the basis of the ^{1}H-NMR data. Strong acidic solvation of the diazepine imido and amino nitrogen atoms and *meso*-nitrogen atoms of the porphyrazine macrocycle is responsible for the diffuse character of the *Q*-band envelope.

The spectra of the Cu and Zn complexes **4** and **5** and of the metal-free macrocycle **3** in solution of conc. H_2SO_4 (96%) are very similar to the spectra of the corresponding unsubstituted, alkyl- or aryl-substituted, and benzo-annulated porphyrazines in neutral solvents[18][19] in that they show a single *Q*-band for complexes **4** and **5** ($\lambda_{max} \approx$ 675−690 nm), and two well-resolved Q_x and Q_y components (659 and 704 nm) for the metal-free ligand **3**. The main maximum in the Soret band envelope is considerably moved towards higher wavelengths (Figure 5, E and J). Such spectra are in full agreement with the symmetrical structure of the macrocycle containing protonated diazepine rings in form **III,** as was also suggested on the basis of the ^{1}H-NMR data. In this structure there is no lone pair on the nitrogen atoms of the diazepine rings and hence the Q_n-band is absent in the spectra. Usually at least one of the *meso*-nitrogen atoms of metalloporphyrazines is protonated in H_2SO_4, which results in a bathochromic shift of the *Q*-band and its observed splitting (in case of interaction with one, two or three *meso*-nitrogen atoms).[18] For our metal complexes, although the maximum of the *Q*-band is shifted bathochromically as compared with neutral solvents by ca. 1000 cm^{-1}, there is no splitting observed due to nonsym-

Table 4. UV/Vis data for Ph_8DzPzH_2, and its Mg^{II}, Cu^{II} and Zn^{II} derivatives in pyridine solution

Compound		λ [nm] (lg ε)					
		Soret region			Q-band region		
Ph_8DzPzH_2	**3**		339sh (4.83)	357 (4.86)	484sh	639 (4.55)	677sh (4.44)
$Ph_8DzPzMg$	**2**		351sh (5.01)	374 (5.05)	589 (4.22)	639 (5.12)	680 (4.83)
$Ph_8DzPzCu$	**4**		323sh (4.82)	365 (4.94)	577 (4.24)	628 (4.93)	673 (4.73)
$Ph_8DzPzZn$	**5**	348sh (4.96)	367 (5.02)	384sh (5.01)	585 (4.20)	637 (5.07)	678 (4.80)

35−40° (as can be estimated from the X-ray data on **1**, and MM+ geometry optimization of Ph_8DzPz^{2-}). As a result the φ_n orbitals of the diazepine imido nitrogen atoms should rise in their energy over HOMO, thus causing the corresponding n→π* electronic transition to appear as a Q_n-band in the long-wave region, as indeed it occurs. The solvatochromic effect is normally large on the peak position of the n→π* transitions, whereas the π→π* transitions are metrical protonation. Symmetrical acid-base interaction with all four *meso*-nitrogen atoms which should give a single bathochromically shifted *Q*-band (e.g. by more than 2500 cm^{-1} for metallophthalocyanines in H_2SO_4)[18] is also impossible. In fact, four positively charged diazepine rings acting as strong electron acceptors should decrease the basicity of the *meso*-nitrogen atoms as compared with unsubstituted porphyrazines in which only two *meso*-nitrogen

atoms can be protonated in H_2SO_4. Thus, in tetra(2,3-pyridino)porphyrazines only one *meso*-nitrogen atom can be protonated in addition to four pyridinium rings.[18] The observed strong bathochromic shift of the Soret band maximum allows to discard protonation of *meso*-nitrogen atoms in H_2SO_4 (and in CF_3COOH as well), because the *B*-band ($a_{2u} \rightarrow e_g$ transition), which is the strongest in the Soret envelope, should be hypsochromically shifted upon protonation.[23]

Conclusion

A new class of porphyrazine macrocycles carrying seven-membered diazepine rings annulated at the periphery of the "internal" tetrapyrrolic macrocycle is reported. This new class of complexes shows specific structural (displacement from planarity of the external diazepine rings, presence of peripherally attached phenyl rings) and UV/Vis spectral features in the *Q*-band region. Further synthetic work is presently being extended to other metal derivatives. Alternative peripheral substitution is possible on the diazepine rings and attempts are in due course for the preparation of new macrocyclic diazepine materials showing better solubility, either in donor or nondonor solvents, and original chemical and physical properties.

Experimental Section

Solvents and Chemicals: Solvents (1-propanol, $CHCl_3$, CH_3COOH, CF_3COOH, pyridine, ethyl alcohol, dimethyl sulfoxide (DMSO), ethyl acetate, acetonitrile, 96% H_2SO_4) and reagents [diaminomaleodinitrile, dibenzoylmethane, P_2O_5, Mg turnings, $Cu(OCOCH_3)_2 \cdot H_2O$, $Zn(OCOCH_3)_2 \cdot 2H_2O$] were pure chemicals (Carlo Erba, Aldrich, Merck).

Chemical Physical Measurements: IR spectra were taken with a Perkin−Elmer 783 spectrophotometer in the range 4000−200 cm^{-1} by using Nujol mulls between CsI disks or KBr pellets. − UV/Vis solution spectra were taken with a Varian Cary 5E spectrometer. − Thermogravimetric analyses were carried out with a Stanton Re Model STA-781 analyzer in N_2 (0.5 L/min). − FAB experiments were carried out with a multiple quadrupole instrument (VG quattro). − Elemental analyses (C, H, N) were provided by the "Servizio di Microanalisi" at the Dipartimento di Chimica, Università "La Sapienza" (Rome).

2,3-Dicyano-5,7-dimethyl-6*H*-1,4-diazepine, $Me_2(CN)_2Dz$: This species has been prepared from diaminomaleodinitrile and acetylacetone according to a known procedure.[6]

2,3-Dicyano-5,7-diphenyl-6*H*-1,4-diazepine, $Ph_2(CN)_2Dz$ (1): Diaminomaleodinitrile (2.4 g, 20 mmol) and dibenzoylmethane (5.0 g, 20 mmol) were condensed in absolute ethanol (80 mL) in the presence of P_2O_5 following closely the procedure reported in the literature.[7] Yield 88%. This material was used for the synthesis of the macrocyclic compounds without further purification. − $Ph_2(CN)_2Dz$ (**1**): $C_{19}H_{12}N_4$ (296.3): calcd. C 77.01, H 4.08, N 18.91; found C 76.94, H 3.88, N 18.80. − ^1H NMR ($CDCl_3$): δ = 1.98 (d, *J* = 11.27 Hz, 1 H, *ax*-CH_2), 5.74 (d, *J* = 11.18 Hz, 1 H, *eq*-CH_2), 7.41 (m, 4 H, *m*-Ph), 7.50 (m, 2 H, *p*-Ph), 7.93 (m, 4 H, *o*-Ph). − ^{13}C NMR ($CDCl_3$): δ = 39.22 (CH_2), 115.04 (CN), 123.68 ($C_{2,3}$), 129.13 (*o*-Ph), 129.82 (*m*-Ph), 133.13 (*p*-Ph), 133.40 (*ipso*-Ph), 149.20 ($C_{5,7}$).

Substituted Porphyrazinatomagnesium Pentahydrate, $[Ph_8DzPzMg(H_2O)] \cdot 4H_2O$ (2): Magnesium metal (0.54 g, 22.2 mmol) was suspended, with stirring, in propyl alcohol (25 mL) in the presence of a small amount of I_2 and the mixture was refluxed for 10 h to complete the conversion of Mg into its corresponding propylate. $Ph_2(CN)_2Dz$ (**1**) (1.5 g, 5.06 mmol) was then added and the mixture kept refluxing for further 8 h. During the reaction the gray mixture changed to dark green, and then to dark blue. At the end of the reaction, propanol was evaporated under reduced pressure and the solid material was suspended in 50% aqueous acetic acid and stirred for 3 h to dissolve the residual unchanged magnesium propylate. The dark bluish-green solid, separated by filtration, was washed with water to neutrality, then with 3 portions of methanol, and brought to constant weight in a vacuum dessicator. Yield 1.42 g (93%). The product can be recrystallized from pyridine/ethyl acetate. All samples obtained from different preparations contained variable amounts of weakly ligated water molecules (4−7). − Representative sample of formula $[Ph_8DzPzMg(H_2O)] \cdot 4H_2O$: $C_{76}H_{58}MgN_{16}O_5$ (1299.71): calcd. C 70.23, H 4.50, N 17.24; found C 69.68, H 4.68, N 16.82. − Thermogravimetric analysis revealed a featureless loss of four water molecules for this sample in the temperature range 25−200°C (found 5.76%, calculated for 4 molecules of H_2O 5.54%), whereas the fifth molecule is more strongly retained, being most likely directly ligated to the central metal. − MS (FAB); *m*/*z* (%): 1210.5 (100) $[M - 5H_2O]^+$, 1227.9 (7) $[M - 4H_2O]^+$, 2418.9 (20) $[M - 5H_2O]_2^+$. − UV/Vis (pyridine): λ_{max} (lg ε) = 351 nm sh, 374 (5.05), 589 (4.22), 639 (5.12), 680 (4.83). − IR (KBr): $\tilde{\nu}$ = 3060 cm^{-1} w, 1645 m, 1600 w, 1580 w, 1527 vs, 1498 w, 1470 w, 1448 s, 1395 w, 1320 m, 1305 w, 1277 m, 1175 s, 1120 s, 1043 m, 1027 w, 1003 w, 983 m, 952 w, 925 vw, 875 w, 840 w, 782 vw, 760 s, 740 w, 710 vs, 690 s, 420 w. − ^1H NMR [$(CD_3)_2SO$ 373 K]: δ = 5.06 (d, *J* = 12.21 Hz, 4 H, *ax*-CH_2), 5.99 (d, *J* = 11.99 Hz, 4 H, *eq*-CH_2), 7.41 (m, 16 H, *m*-Ph), 7.49 (m, 8 H, *p*-Ph), 8.13 (d, *J* = 7.92 Hz, 16 H, *o*-Ph).

Substituted Porphyrazine Tetrahydrate, $[Ph_8DzPzH_2] \cdot 4H_2O$ (3): Solvated magnesium complex **2** (310 mg, 0.24 mmol) was suspended in glacial acetic acid (15 mL) and the mixture refluxed for 16 h. After cooling, the reaction mixture was poured into water. The precipitated dark green solid formed was separated by filtration, washed with H_2O, then with acetone, and brought to constant weight in a vacuum dessicator. Yield 233 mg (77%). − $[Ph_8DzPzH_2] \cdot 4H_2O$: $C_{76}H_{58}N_{16}O_4$ (1259.40): calcd. C 72.48, H 4.64, N 17.79; found C 72.22, H 4.21, N 17.74. − MS (FAB); *m*/*z* (%): 1187.5 (100) $[M - 4H_2O]^+$. − UV/Vis (pyridine): λ_{max} (lg ε) = 339 nm sh, 357 (4.86), 490 sh, 639 (4.55), 677 (4.44). − IR (KBr): $\tilde{\nu}$ = 3298 cm^{-1} w (NH), 3060 m, 1650 m, 1600 vw, 1535 vs, 1498 w, 1480 vw, 1448 s, 1390 vw, 1320 m, 1306 vw, 1285 m, 1187 m, 1120 s, 1080 w, 1040 vw, 1025 m, 1000 w, 975 m, 945 w, 845 w, 790 w, 753 m, 688 vs, 660w, 610 vw, 415 w.

Substituted Porphyrazinatocopper Dihydrate, $[Ph_8DzPzCu] \cdot 2H_2O$ (4): A mixture of $[Ph_8DzPzH_2] \cdot 4H_2O$ (**3**) (250 mg, 0.20 mmol) and anhydrous copper acetate (463 mg, 2.55 mmol) in pyridine (10 mL) was kept refluxing for 6 h. After cooling, the solid separated by centrifugation was washed with water to remove the unchanged Cu^{II} acetate, and dried in a vacuum dessicator. Yield 111 mg (44%). − $[Ph_8DzPzCu] \cdot 2H_2O$: $C_{76}H_{52}CuN_{16}O_2$ (1284.90): calcd. C 71.04, H 4.08, Cu 4.94, N 17.44; found C 70.77, H 4.11, Cu 4.68, N 17.64. − UV/Vis (pyridine): λ_{max} (lg ε) = 323 nm sh, 365 (4.94), 577 (4.24), 628 (4.93), 674 (4.73). − IR (KBr): $\tilde{\nu}$ = 3060 w, *1645 s*, 1600 w, 1585 w, 1530 vs, 1500 m, 1485 m, 1447 s, 1410 w, 1319 m, 1304 m, 1280 m, 1188 s, 1128 vs, 1080 vw, 1050 m, 1028 m, 1000 w, 980m, 952 m, 880 w, 840 vw, 782 vw, 758 s, 737 w, 712 vs, 688 s, 652 w, 622 w, 592 vw, 558 vw, 468 w, 418 m. − Alternatively, the

Cu complex can be prepared by refluxing a mixture of the corresponding Mg^{II} complex (160 mg, 0.125 mmol) and anhydrous copper acetate (176 mg, 0.97 mmol) in glacial acetic acid (10 mL) for 5 h. Yield 83 mg (52%). − $[Ph_8DzPzCu]\cdot 4H_2O$: $C_{76}H_{56}CuN_{16}O_4$ (1320.93): calcd. C 69.11, H 4.27, Cu 4.81, N 16.97; found C 68.14, H 3.62, Cu 5.39, N 17.13.

Substituted Porphyrazinatozinc Heptahydrate, $[Ph_8DzPzZn]\cdot 7H_2O$ (5): A mixture of $[Ph_8DzPzH_2]\cdot 4H_2O$ (**3**) (274 mg, 0.22 mmol) and zinc acetate (380 mg, 1.73 mmol) in pyridine (10 mL) was refluxed for 6 h. After cooling, water (10 mL) was added, and the solid material, separated by centrifugation, was washed with water to remove the excess of the unchanged Zn^{II} salt, and dried in a vacuum dessicator. Yield 192 mg (67%). − $[Ph_8DzPzZn]\cdot 7H_2O$: $C_{76}H_{62}N_{16}ZnO_7$ (1376.80): calcd. C 66.30, H 4.54, N 16.29; found C 65.70, H 4.00, N 16.02. − MS (FAB); *m/z*: 1252 $[M - 7H_2O]^+$. − UV/Vis (pyridine): λ_{max} (lg ε) = 348 nm sh, 367 (5.02), 384 sh, 585 (4.20), 637 (5.07), 678 (4.80). − IR (KBr): $\tilde{\nu}$ = 3055 cm^{-1} w, *1645 s*, 1600 vw, 1582 vw, 1527 vs, 1498 w, 1473 w, 1447 s, 1400 w, 1320 m, 1305 w, 1278 m, 1220 vw, 1178 s, 1127 vs, 1080 vw, 1062 vw, 1043 m, 1027 w, 1002 w, 982 m, 952 w, 872 w, 842 w, 782 wv, 760 s, 748 w, 710 vs, 690 s, 652 w, 623 w, 422 m. − ^1H NMR ($CDCl_3$, 293 K): δ = 5.18 (d, *J* = 12.7 Hz, 4 H, *ax*-CH_2), 6.08 (d, *J* = 12.5 Hz, 4 H, *eq*-CH_2), 7.31 (m, 16 H, *m*-Ph), 7.39 (m, 8 H, *p*-Ph), 8.23 (d, *J* = 7.4 Hz, 16 H, *o*-Ph); [$(CD_3)_2SO$ 373 K]: δ = 5.03 (d, *J* = 12.2 Hz, 4 H, *ax*-CH_2), 5.99 (d, *J* = 12.23 Hz, 4 H, *eq*-CH_2), 7.42 (m, 16 H, *m*-Ph), 7.50 (m, 8 H, *p*-Ph), 8.13 (d, *J* = 7.33 Hz, 16 H, *o*-Ph).

X-ray Crystal Structure Determination of $Ph_2(CN)_2Dz$ (1): Single crystals of **1** were obtained as light-yellow hexagonal prisms during recrystallization of $Ph_2(CN)_2Dz$ from hot acetonitrile. A suitable colorless crystal with the approximate dimensions 0.31×0.34×0.55 mm was mounted on a glass fiber. The reduced cell was obtained with use of TRACER.[24] Data were collected at 295 K with a Siemens AED single-crystal diffractometer. For intensities and background the individual reflection profiles were analyzed.[25] The structure amplitudes were obtained after the usual Lorentz and polarization corrections[26] and the absolute scale was established by the Wilson method.[27] The crystal quality was tested by ψ scans showing that crystal absorption effects could be neglected. The function minimized during the least-square refinements was $\Sigma w(\Delta F^2)^2$. Anomalous scattering corrections were included in all structure factor calculations.[28b] Scattering factors for neutral atoms were taken from ref.[28a] for nonhydrogen atoms and from ref.[29] for H. Structure solution was based on the observed reflections [$I > 2(I)$] while the refinement was based on the unique reflections having $I > 0$. The structure was solved by the direct methods using SIR92.[30] Refinement was done by full-matrix least-squares first isotropically and then anisotropically for all non-H atoms using SHELX93.[31] The hydrogen atoms were located from a difference Fourier map and introduced in the refinements as fixed atoms contributions (U_{iso} = 0.10 $Å^2$). In the last stage of refinement the weighting scheme $w = 1/[\sigma^2(F_o^2) + (aP)^2]$ [with $P = (F_o^2 + 2F_c^2)/3$] was applied with *a* resulting in the value of 0.1001. The final difference map showed no unusual features, with no significant peaks above the general background.[32]

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