Synthesis and Investigation of Chalcogen Atom Substituted Dinitriles and Porphyrazines

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A series of chalcogen atom substituted porphyrazines have been assembled and characterized. Oxygen and sulfur chalcogen atoms have been substituted for peripheral methylene groups. Heteroatom-enriched, seven-membered ring dinitriles (**1**–**3**) were synthesized and characterized by IR, MS, UV-vis, ^{1}H NMR, elemental analysis, and X-ray analysis to examine the ring conformations. They were template cyclized in the presence of Mg^{II} to form the Mg^{II} containing porphyrazine macrocycles. The Mg^{II} and metal-free macrocycles (**4**–**9**) were synthesized for all peripherally substituted porphyrazines. The unchalcogen-substituted Ni^{II}, Cu^{II}, and Zn^{II} containing porphyrazine derivatives (**10**–**12**) were also synthesized because of the higher solubility of the metal-free porphyrazine **7**. The macrocycles were characterized and studied using such techniques as UV-vis, IR, elemental analysis, cyclic voltammetry, and electrical conductivity measurements.

Introduction

Phthalocyanines and porphyrins have received considerable attention due to the number of applications that these two families of compounds have been employed, and also for their interesting properties.[1] Among their many applications, phthalocyanines have often been studied for their electrical conductivity,[2] liquid-crystalline properties[3] and use as pigments.[4] Porphyrins for example, have been studied for their magnetic[5] and catalytic[6] properties and their role in biomolecular processes.[7] Another family of similar conjugated macrocycles that have received considerably less attention than the phthalocyanines or porphyrins, are the porphyrazines (also called tetraazaporphyrazines).[8][9] Recently, a significant amount of work has been made with these systems. Hoffman and coworkers for example, have reported the synthesis of polymetallic porphyrazines and a novel metal-linked porphyrazine dimer.[10−13]

Efforts have also been made studying porphyrazines substituted with long alkyl chains for applications in liquid crystals and Langmuir−Blodgett layers.[14] Hemiporphyrazines, a slightly different class of porphyrazines which exhibit a box-like geometry, have also been recently reported. They have been used in the assembly of Langmuir−Blodgett layers[15] and ladder polymers and oligomers.[16]
Bryce and coworkers have applied porphyrazines in supramolecular chemistry by synthesizing pyrazinoporphyrazines with pendant TTF (tetrathiafulvalene) units.[17] Along a similar line, other modifications to the porphyrazine system may be envisioned, for example, a synthetic goal would be to incorporate chalcogen atoms with large diffuse atomic orbitals directly into the periphery of the planar, conjugated porphyrazine macrocycle. An additional related goal would be also to determine their feasibility for use in chalcogen-rich electrically conducting complexes. Despite the enormous amount of research currently being carried out worldwide in the areas of phthalocyanines, porphyrins, and porphyrazines, to our knowledge only the work recently reported by Swager and coworkers[18] has chalcogen-atom incorporation been investigated for these types of macrocycles. This idea has been extensively utilized in the field of the synthesis of chalcogen-rich, planar and fully conjugated organic donor and acceptor molecules. Such well-known examples are TTF, BEDT-TTF (bisethylenedithiotetrathiafulvalene), and square planar metal bis-dmit (dmit = 2-thione-1,3-dithiole-4,5-dithiolato) complexes, which have been used in the assembly of superconducting partial-oxidation state materials.[19] In this paper, we report the findings of a study of the synthesis and characterization of a series of chalcogen-enriched porphyrazine macrocycles and their possible use for future incorporation into electrically conductive materials. Four methylene groups in the periphery of the porphyrazine molecule have been substituted by oxygen and sulfur atoms. Seven-membered ring dinitrile compounds were first synthesized with a methylene (**1**), sulfur (**2**), or oxygen (**3**) group in the five position. Single crystal X-ray structures were obtained for compounds **1**−**3** to understand the ring conformations. The Mg^{II} and

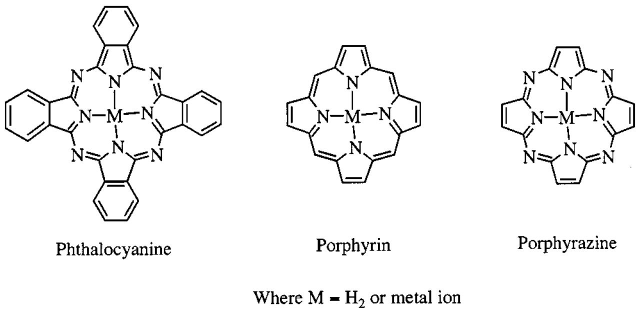

Figure 1. Figure showing general structural differences between phthalocyanines, porphyrins, and porphyrazines

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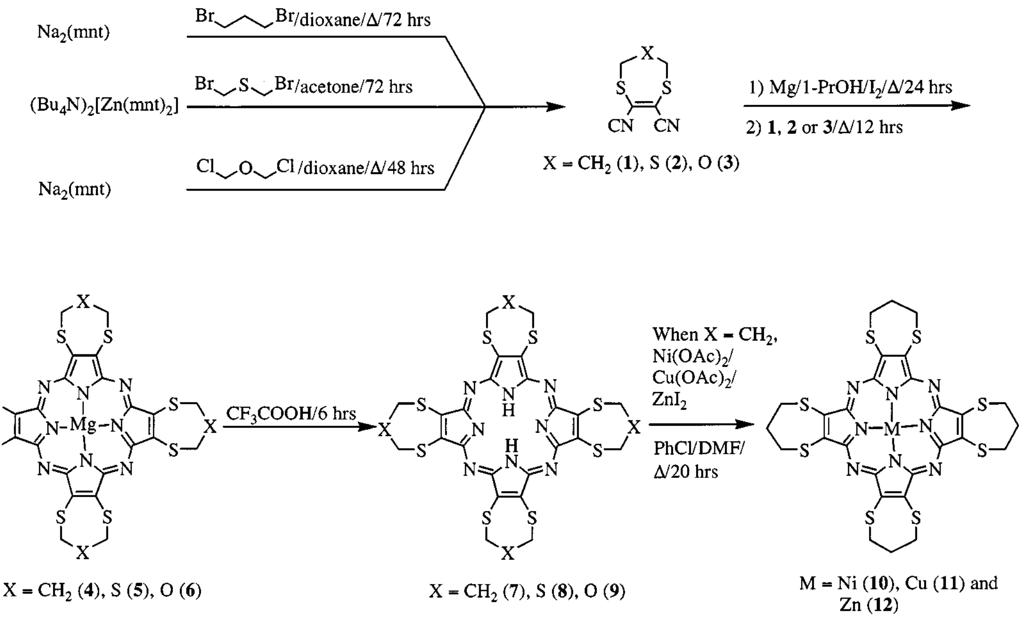


Scheme 1. Synthesis of chalcogen atom substituted dinitriles and related porphyrazines

H_2 containing porphyrazines (**4**−**9**), which were cyclized from the dinitriles, have been synthesized along with the Ni^{II}, Cu^{II}, and Zn^{II} containing macrocycles of the methylene derivative (**10**−**12**). Their electronic spectra and electrochemical properties have been examined and compared to similar reported systems. Also, two-probe pressed-pellet electrical conductivity measurements have been carried out on some of the compounds.

Synthesis of the Porphyrazine Macrocycles

The syntheses of compounds **1**−**12** are shown in Scheme 1. Dinitriles 3,7-dithiacycloheptamaleonitrile (**1**) and 3,7-dithia-5-oxocycloheptamaleonitrile (**3**) were assembled by the reaction of mnt^{2-} ligand with the corresponding dihalide in high dilution conditions in refluxing dioxane over a period of 3 days to obtain yields of 14 and 25% respectively.

3,5,7-trithiacycloheptamaleonitrile (**2**) was synthesized in 67% yield by the reaction of $S(CH_2Br)_2$ with the labile $(Bu_4N)_2[Zn(mnt)_2]$ complex in acetone at room temperature over the same period of time. All three dinitriles had to be purified by column chromatography due to the large amount of dimeric, trimeric and oligomeric side products with similar solubilities. In a previous paper by Spannenberg et al.,[20] compound **1** was synthesized, isolated, and characterized along with the dimeric and trimeric cyclization products. The dimeric and trimeric forms were not of interest in this work. The crystal structures of the three dinitriles **1**−**3** are shown in Figure 2 and selected bond lengths and angles are listed in Table 1.

Their structures were obtained to examine the conformation of the seven-membered rings due to the inability to obtain crystal structures of the ensuing porphyrazine macrocycles. In Figures 2a for 3,7-dithiacycloheptamaleonitrile (**1**) and 2b for 3,5,7-trithiacycloheptamaleonitrile (**2**), both compounds exhibit similar twisted ring conformations. In compound **1**, the dihedral angle between the S1′−C3′−C3−S1 and C2′−C1−C2 planes is 45.48(8)° while for **2** the dihedral angle between the S1−C1−C2−S2 and C5−S3−C6 planes is almost the same at 45.44(17)°. Figures 2c and d each show a different view of the same compound 3,7-dithia-5-oxocycloheptamaleonitrile (**3**). Figure 2c is in the same perspective as for compounds **1** and **2** while Figure 2d is a profile view down the axis of the C1=C2 bond showing a chair-like conformation of the ring unlike that seen for **1** and **2**. This is in contrast to the twisted ring conformations of compounds **1** and **2**. The S1−C5−C6−S2 plane is folded at the sulfur atoms at an angle of 56.76(6)° from the S1−C1−C2−S2 plane and 70.12(15)° from the C5−C6−O1 plane. The square planar metal complexes $(Et_4N)[Cu(pddt)_2]$ (where pddt = $C_5H_6S_4^{2-}$ = 1,3-propanediyldithioethylene-1,2-dithiolato),[21] $(Bu_4N)[Pd(dtdt)_2]$ (where dtdt = $C_4H_4S_5^{2-}$ = 5,7-dihydro-1,4,6-trithiin-2,3-dithiolato),[22] and $(Ph_4P)[Cu(diod)_2]$ (where diod = $C_4H_4OS_4^{2-}$ = 1,4-dithia-6-oxa-2,3-dithiolato)[23] have been reported and the ligands contain the seven-membered rings as compounds **1**−**3** do respectively. It is interesting to note that in every instance, the rings are in a chair-like conformation like compound **3**. For $(Ph_4P)[Cu(diod)_2]$, the fold angles of the planes at the ring sulfur atoms was reported as 61.2° which is greater than for **3** [56.76°(6)]. The angle of the C−O−C plane reported for $(Ph_4P)[Cu(diod)_2]$ is 65.9°, smaller than that found in compound **3** of 70.12(15)°.[23]

The conversion of the dinitriles to the Mg^{II} porphyrazine macrocycles Mg(dtchp) (**4**), Mg(ttchp) (**5**) and Mg(dochp) (**6**) were achieved following slightly modified procedures by Linstead and Whalley[8b] in refluxing Mg alkoxide suspensions. To remove Mg^{II} and to synthesize the metal-free porphyrazines H_2(dtchp) (**7**), H_2(ttchp) (**8**), and H_2(dochp) (**9**),

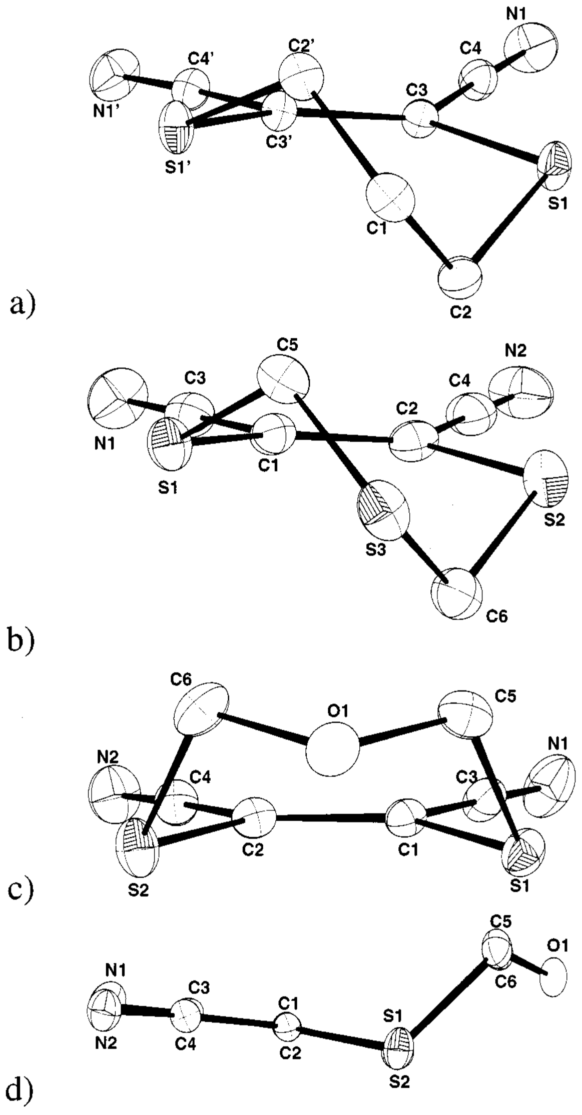


Figure 2. Thermal ellipsoids drawings (30% probability) and numbering schemes for the dinitriles (a) 3,7-dithiacycloheptamaleonitrile (**1**), (b) 3,5,7-trithiacycloheptamaleonitrile (**2**), (c) 3,7-dithia-5-oxocycloheptamaleonitrile (**3**), (d) Profile view down the axis of the C1−C2 double bond of **3** showing the chair-like conformation of the seven-membered ring. Hydrogen atoms have been omitted for clarity.

compounds **4**−**6** were treated with trifluoroacetic acid followed by aqueous precipitation and neutralization with ammonia.[10b] This method resulted in clean demetallation and yielded compounds **7**−**9** in up to 83% yield.

Purification of H_2(dtchp) (**7**) was achieved using column chromatography. The sulfur and oxygen peripherally substituted compounds H_2(ttchp) (**8**) and H_2(dochp) (**9**) could not be purified with column chromatography due to their rather low solubility in common organic solvents. Sublimation was attempted as it has been shown to purify phthalocyanines.[16] In both cases though, black insoluble materials resulted and no sublimation products were observed. Nevertheless, **8** and **9** can be purified through exhaustive washing.

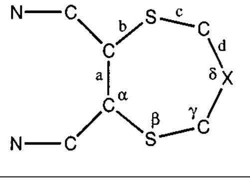
Due to the adequate solubility of H_2(dtchp) (**7**), facile insertion of Ni^{II}, Cu^{II}, and Zn^{II} ions into the core of the macrocycle was accomplished to assemble compounds **10**−**12**. This was completed by refluxing anhydrous $Ni(OAc)_2$, $Cu(OAc)_2$, and ZnI_2 respectively with the metal-free porphyrazine in a mixture of PhCl/DMF over a period of 20 hours.[12]

Electronic Absorption Spectroscopy

Phthalocyanines and porphyrazines give similar and characteristic absorption spectra as it is a valuable tool in determining their synthesis.[4b] This is important in this study due to the inability to obtain single-crystal X-ray structures of the macrocycles. Table 2 lists the electronic band maxima for all compounds synthesized. Figure 3 shows the spectra for compounds **4** and **7** which are representative of all of the Mg^{II} and metal-free compounds assembled in this study along with the Ni^{II}, Cu^{II} and Zn^{II} containing macrocycles of the methylene derivative, **10**−**12**.

The optical spectra for the four-fold symmetric Mg^{II} derivatives Mg(dtchp) (**4**), Mg(ttchp) (**5**), and Mg(dochp) (**6**) are nearly identical. They exhibit an intense single Soret band at approximately 368−370 nm, a weak shoulder absorption at 510−538 nm and an intense Q band at 656−664 nm. This is similar to that seen for metal phthalocyanines.[1] The Soret and Q band region absorptions are attributed to

Table 1. Selected and averaged bond lengths [Å] and angles [°] for compounds **1**−**3** [where X = CH_2 (**1**), S (**2**), or O (**3**)]



	1	2	3		1	2	3
a	1.352(3)	1.367(6)	1.354(3)	α	130.59(5)	130.9(3)	126.38(15)
b	1.7558(15)	1.745(4)	1.7524(19)	β	101.98(7)	102.4(2)	104.15(10)
c	1.8149(16)	1.799(5)	1.818(2)	γ	113.59(10)	115.2(3)	115.28(15)
d	1.5155(19)	1.794(5)	1.403(3)	δ	112.71(18)	98.2(2)	113.70(16)

Table 2. Electronic band maxima (λ_{max}, nm) and log ε values for compounds **4**−**12** along with M(pc) (where M = Mg, H_2, Ni, Cu, or Zn)[4b] values for comparison (measured in CH_2Cl_2 unless noted otherwise)

Compound	λ_{max} (log ε)
Mg(dtchp) (**4**)	370 (4.30), 538 (3.69), 612 (3.82), 664 (4.15)
Mg(ttchp) (**5**)	368 (4.50), 514 (4.10) 610 (4.15), 656 (4.29)
Mg(dochp) (**6**)	370 (4.32), 518 (3.93), 610 (3.99), 656 (4.15)
Mg(pc)[a]	347 (4.73), 610 (4.45), 647 (4.39), 674 (4.94)
H_2(dtchp) (**7**)	358 (4.37), 526 (4.02), 614 (3.99), 700 (3.98)
H_2(ttchp) (**8**)[b]	346 (5.10), 518 (4.81), 610 (4.81), 680 (4.75)
H_2(dochp) (**9**)[b]	346 (6.10), 514 (5.84), 616 (5.84), 686 (5.77)
H_2(pc)[c]	350 (4.74), 602 (4.43), 638 (4.62), 665 (5.18), 698 (5.21)
Ni(dtchp) (**10**)[d]	342 (4.85), 508 (4.55), 640 (4.61)
Ni(pc)[c]	351 (4.57), 643 (4.51), 671 (5.10)
Cu(dtchp) (**11**)[b]	352 (4.80), 536 (4.49), 656 (4.60)
Cu(pc)[c]	351 (4.57), 643 (4.51), 671 (5.10)
Zn(dtchp) (**12**)[b]	372 (4.73), 556 (4.20), 666 (4.56)
Zn(pc)[a]	348 (4.81), 607 (4.59), 646 (4.56), 672(5.45)

[a] Measured in pyridine. − [b] In DMF. − [c] In chloronapthalene. − [d] In chlorobenzene.

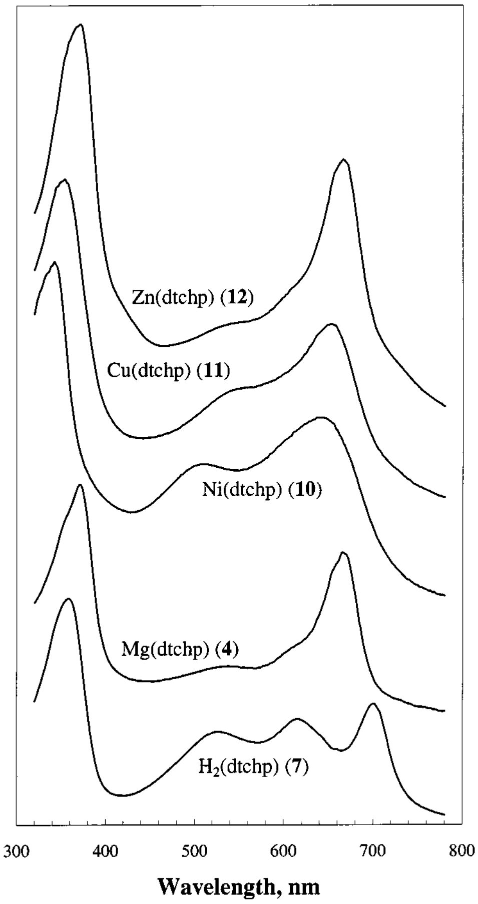


Figure 3. Comparison of the UV-vis absorption spectra for the metal-free derivative H_2(dtchp) (**7**) and metal-containing derivatives Mg(dtchp) (**4**), Ni(dtchp) (**10**), Cu(dtchp) (**11**), and Zn(dtchp) (**12**)

$\pi\rightarrow\pi^*$ transitions from the a_{1u}, a_{2u} HOMOs to the doubly degenerate (e_g) LUMOs.[12] The optical spectra of H_2(dtchp) (**7**), H_2(ttchp) (**8**), and H_2(dochp) (**9**) which are also very similar, show a splitting of the Q band found at 656−664 nm for compounds **4**−**6**. This is due to the lowering of symmetry from four-fold (D_{4h}) to two-fold (D_{2h}) symmetry for the metal-free derivatives **7**−**9**, and removal of the degeneracy of the e_g LUMOs.[4b] Also observed in each is a slight red-shift of the Soret band in the metal-free compounds. This behavior observed in the Soret and Q band regions is typical for substituted porphyrazines.[8][10−12][14][24] In difference to metal and metal-free phthalocyanines, we observe a definite broadening of the absorptions in compounds **4**−**9**.[4b] This has also been observed in several instances in other sulfur-containing porphyrazines. With 8 sulfur atoms in the periphery of the CH_2 derivative and more so with 12 sulfur and oxygen atoms in the periphery of the other new porphyrazine derivatives reported here, there are probably significant contributions to the spectra from underlying $n\rightarrow\pi^*$ transitions from the lone pair electrons of the heteroatoms.[12] Like Mg(dtchp) (**4**), the D_{4h} Ni^{II}, Cu^{II}, and Zn^{II} derivatives, Ni(dtchp) (**10**), Cu(dtchp) (**11**), and Zn(dtchp) (**12**), show similar spectra with an intense Soret band and Q band with a weaker absorption in the 500−560 nm region. In the case of the Ni^{II} derivative, the Soret band at 342 nm, the weak absorption at 508 nm and the Q band region absorption at 640 nm are the most red-shifted absorptions of all the new metal derivatives presented here. In comparison to the Mg^{II} derivative, this is not observed in metal phthalocyanines as the Mg^{II} and Ni^{II} derivatives give absorptions at nearly the same wavelengths (Table 2). This effect has been seen in other thio-substituted porphyrazines.[24]

Redox Properties of H_2(dtchp) (7)

The redox properties of H_2(dtchp) (**7**) have been investigated with cyclic voltammetry. The $E_{1/2}$ values are found in Table 3 along with other related porphyrazine and phthalocyanine systems for comparison. Potentials as high as +0.90 V were reached (vs. SCE, CH_2Cl_2, 0.1 M Bu_4NPF_6) with **7** but no oxidation process were found. Upon scanning cathodically, two low-potential redox couples were observed with $E_{1/2}$ values of −0.95 and −1.29 V (vs. Fc/Fc^+ couple; $E_a - E_c$ = 120 and 250 mV and $i_{p,a}/i_{p,c}$ = 0.80 and 0.91 respectively).

Table 3. Cyclic voltammetric half-wave potentials (V, reported vs. Fc/Fc^+ couple) for the reduction of H_2(dtchp) (**7**)[a] and similarly related compounds for comparison

Compound	$E_{1/2}{}^1$	$E_{1/2}{}^2$
H_2(dtchp) (**7**)	−0.95	−1.29
H_2(obtp)[b]	−0.85	−1.19
H_2(obcbp)[c]	−0.8	−1.2
H_2(pc)[d]	−1.20	−1.54

[a] Conditions: scan rate, 100 mV/s; reference electrode, standard calomel; working electrode, Au plate; 0.1 M Bu_4NPF_6 electrolyte in CH_2Cl_2 under argon at room temperature. − [b] Ref.[11b] − [c] Ref.[12] − [d] Ref.[25]

These values are slightly lower than the tetrathioether-substituted porphyrazines H_2(obcbp) [obcbp = octa(4-butyloxycarbonylbenzylthio) porphyrazine, −0.8 and −1.2 V] and H_2(obtp) [obtp = octa(benzylthio) porphyrazine, −0.85 and −1.19 V] reported by Hoffman and coworkers.[11b][12] These compounds were also reported to exhibit no oxidation processes as seen in the H_2(dtchp) (**7**) system. This is in contrast to phthalocyanines which can exhibit oxidation processes that are typically irreversible along with their reversible reduction couples. The $E_{1/2}$ values for the ring reductions for H_2(pc) (−1.20 and −1.54 V) are lower than the values for the porphyrazines reported and discussed here.[12,25]

Conductivity Measurements

As said above, one side goal of this work was to determine the feasibility for use of the chalcogen-rich porphyrazines studied here in the preparation of electrically conducting complexes. Preliminary electrical conductivity studies have been completed and measurements of compounds H_2(dtchp) (**7**), Ni(dtchp) (**10**), and Cu(dtchp) (**11**) exhibited pressed-pellet conductivities of $<10^{-12}$ S/cm. It is thus clear that this result doesn′t live up the expectations. Moreover, even the metal-free H_2(dtchp) is not oxidized at potentials below 0.9 V/SCE, and the lack of solubility of most of the studied porphyrazines severely limits a more detailed analysis.

Conclusions

We have synthesized a series of chalcogen-substituted dinitrile isologues and they have been characterized and investigated using a variety of techniques including single-crystal X-ray analysis. Compounds **1** and **2** show a twisted conformation of the seven-membered rings while **3** exhibits a chair conformation. The dinitriles were cyclized in Mg propoxide suspensions to assemble the macrocyclic Mg^{II} porphyrazines. The metal-free porphyrazines were obtained by treatment with trifluoroacetic acid. The electronic spectra of the Mg^{II} and metal-free porphyrazines show very little variance with the substitution of O or S for a methylene group in the periphery. Due to the low-solubility of the peripherally substituted oxygen and sulfur derivatives, only the higher soluble methylene substituted porphyrazine H_2(dtchp) (**7**) could be further studied. Compound **7** could be purified via column chromatography and cyclic voltammetry studies showed it exhibits two low-potential reduction couples. The Ni^{II}, Cu^{II}, and Zn^{II} containing porphyrazines were then assembled and characterized. Due to the fact that the solubility of the porphyrazines studied here is lowered when chalcogen atoms are incorporated into the structure, future directions must also consist of the addition of solubility improving groups, such as long alkyl chains. This may then allow chalcogen atom enhanced porphyrazine derivatives to be further studied for metal coordination, electrochemical, and electrical conductivity studies.

Experimental Section

General Procedures and Chemicals: All reactions unless otherwise noted were carried out under an argon atmosphere. All solvents were purified following standard procedures. Compounds Na_2mnt and $(Bu_4N)_2$[Zn(mnt)$_2$] were synthesized according to Davison et al.[26] Bis(chloromethyl) ether and bis(bromomethyl) thioether were synthesized following Buc[27] and Komoto et al.,[28] respectively. − Column chromatography was carried out using silica gel 60 (Merck, 63−200 μm particle size), and POLGRAM SIL G/UV 254 (Macherey-Nagel, 0.25 mm thickness) was used for TLC experiments. − Elemental analyses were performed by the Microanalysis Service at the LCC-CNRS, Toulouse. − Mass spectra were obtained at the Joint Mass Spectrometry Service at Paul Sabatier University, Toulouse. − Melting points were obtained using a Stuart Scientific SMP1 melting point apparatus and are uncorrected. − UV-vis spectra were recorded on a Hewlett Packard 8452A spectrophotometer. − IR spectra were obtained on a Perkin Elmer 1725X FT-IR spectrometer as KBr pellets. − NMR spectra were recorded on a Bruker AC 200 MHz instrument.

Preparation of 3,7-Dithiacycloheptamaleonitrile (1): Compound **1** was prepared, isolated, and purified according to Spannenberg et al.,[20] and its elemental analysis was in agreement with that reported.

3,5,7-Trithiacycloheptamaleonitrile (2): An 8.0 g ($9.63 \cdot 10^{-3}$ mol) amount of $(Bu_4N)_2$[Zn(mnt)$_2$] was dissolved in 350 ml of acetone. Dropwise was added 4.30 g (0.020 mol) of bisbromomethyl thioether to the rapidly stirring solution. The stirring was continued and the solution turned from a pale yellow to a deep red color after 3 days. At this time, the solvent was evaporated to leave a dark-red oil. The product was isolated with column chromatography using CH_2Cl_2 as eluent (R_f = 0.73). The solid was recrystallized using CH_2Cl_2/hexane to yield 2.60 g of **2** (67%) as yellow platelets, m. p. 91−92°C. − $C_6H_4N_2S_3$ (200.29): calcd. C 35.98, H 2.01, N 13.99; found C 35.95, H 1.55, N 13.69. − ^1H NMR ($CDCl_3$): δ = 4.82 (s, 4 H). − IR (KBr): $\tilde{\nu}$ = 2996 cm^{-1} m, 2937 m, 2220 m, 1496 s, 1386 s, 1227 s, 1198 s, 1158 vs, 1117 m, 1033 m, 1008 m, 984 w, 850 m, 780 m, 734 vs, 490 vs. − UV/Vis (CH_2Cl_2): λ_{max} (lg ε) = 256 nm (4.46), 300 (4.46), 364 (4.43), 386 (4.42). − MS (FAB); *m/z* (%): 201 (100) [M + H$^+$].

3,7-Dithia-5-oxocycloheptamaleonitrile (3): Compound **3** was prepared similar to **1**. A 5.58 g (0.030 mol) sample of Na_2mnt was placed in 600 ml of dioxane under an argon atmosphere allowed to react with 3.45 g (0.030 mol) of bis(chloromethyl) ether. The crude product was purified by column chromatography using CH_2Cl_2 as eluent (R_f = 0.88). The pale yellow microcrystalline product was recrystallized in CH_2Cl_2/hexane to yield 1.09 g (25%) of **3** as cream-colored plates, m. p. 133−134°C. $C_6H_4N_2OS_2$ (184.23): calcd. C 39.12, H 2.19, N 15.21; found C 39.36, H 1.64, N 15.13. − ^1H-NMR ($CDCl_3$): δ = 5.45 (s, 4 H). − IR (KBr): $\tilde{\nu}$ = 3006 cm^{-1} m, 2927 m, 2220 m, 1511 s, 1441 vs, 1401 sh, 1335 s, 1322 s, 1242 s, 1147 vs, 1067 vs, 998 s, 970 vs, 932 vs, 682 vs, 510 s. − UV/Vis (CH_2Cl_2): λ_{max} (lg ε) = 258 nm (2.38), 300 (2.40), 358 (2.38). − MS (EI, 70 eV); *m/z* (%): 184 (100) [M$^+$].

[Tetrakis(dithiacyclohepta)porphyrazinato]magnesium(II) [Mg(dtchp) (4)], [Tetrakis(trithiacyclohepta)porphyrazinato]magnesium(II) [Mg(ttchp) (5)], and [Tetrakis(dithiaoxocyclohepta)porphyrazinato]magnesium(II) [Mg(dochp) (6)]: The synthesis of the following Mg containing derivatives **4**−**6** were completed following previously reported procedures.[8b] Under an argon atmosphere, magnesium (Aldrich, 98%) was refluxed with 15 ml of 1-propanol with

Table 4. Crystallographic and acquisition data and refinement for compounds **1**−**3**

Compound	**1**	**2**	**3**
Formula	$C_7H_6N_2S_2$	$C_6H_4N_2S_3$	$C_6H_4N_2OS_2$
Molecular mass	182.26	200.29	184.23
Crystal system	Tetragonal	Orthorhombic	Monoclinic
Space group	$P4_12_12$	$I2cb$	$P2_1/c$
a [Å]	8.3297(10)	6.7361(9)	6.9920(10)
b [Å]	8.3297(10)	12.1566(18)	13.3750(16)
c [Å]	12.161(2)	20.332(3)	8.9440(12)
α [°]	90	90	90
β [°]	90	90	112.880(15)
γ [°]	90	90	90
U [Å^3]	843.8(2)	1665.0(4)	770.62(18)
Z	4	8	4
ρ (calcd.) [g cm^{-3}]	1.435	1.598	1.588
μ [mm^{-1}]	0.563	0.820	0.627
F (000)	376	816	376
T [K]	180(2)	180(2)	180(2)
Crystal size [mm^3]	0.38 × 0.38 × 0.25	0.45 × 0.40 × 0.13	0.38 × 0.25 × 0.25
θ Range for data collection [°]	3.84→24.23	1.95→24.39	2.90→24.20
hkl range:	$-9 \le h \le 9$; $-9 \le k \le 9$; $-13 \le l \le 14$	$-7 \le h \le 7$; $-14 \le k \le 13$; $-23 \le l \le 23$	$-7 \le h \le 8$; $-15 \le k \le 15$; $-10 \le l \le 10$
Data collected	6643	5120	4772
No. of measured reflections	671	1327	1219
No. of refined parameters	51	100	100
Min./max. height in final $\Delta\rho$ map [eÅ^{-3}]	−0.116/0.120	−0.341/0.325	−0.228/0.263
S : Goodness-of-fit on F^2	1.111	1.190	1.084
Final R [a,b] indices [$I > 2\sigma(I)$]	$R_1 = 0.0173$, $wR_2 = 0.0464$	$R_1 = 0.0356$, $wR_2 = 0.1074$	$R_1 = 0.0289$, $wR_2 = 0.0777$
R indices (all data)	$R_1 = 0.0174$, $wR_2 = 0.0465$	$R_1 = 0.0372$, $wR_2 = 0.1120$	$R_1 = 0.0320$, $wR_2 = 0.0795$
a and b values used in w	0.0243; 0.2028	0.0663; 2.02115	0.0321; 0.2856

[a] $R = \Sigma\ ||F_o| - |F_c||/\Sigma\ F_o$. − [b] $wR_2 = \{\Sigma[\ w(F_o^2-F_c^2)^2\ ]/\Sigma[w(F_o^2)^2\ ]\}^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP\ ]$ where P is $[2\ F_c^2 + \mathrm{Max}(F_o^2,0)\ ]/3$. S = GoF = $\{\Sigma\ [\ w(F_o^2-F_c^2)^2\ ]/(n-p)\}^{1/2}$ where n is the number of reflections and p is the total number of parameters refined.

a crystal of iodine as initiator for 24 hours. To the grayish suspension was then added the dicyano compound **1**−**3** as a slurry in a small amount of 1-propanol. The mixture was stirred and refluxed for a minimum of 12 hours. The solution was filtered hot and the precipitate was washed with CH_2Cl_2 until the washings were pale blue. The filtrate and washings were combined and evaporated to dryness to give a blue-black product. The product was washed with water until the washings were clear followed by copious amounts of EtOH also until the washings were clear. The solid was dried under vacuum and recrystallized in CH_2Cl_2/2-propanol. − Mg(dtchp) (**4**): Yield 33%, dark-blue microcrystals. − IR (KBr): ṽ = 2962 cm^{-1} m, 2926 m, 1654 m, 1560 m, 1459 m, 1384 m, 1300 m, 1255 w, 1220 w, 1104 m, 1026 s, 802 s, 560 w. − $C_{28}H_{24}MgN_8S_8$ (753.34): calcd. C 44.64, H 3.21, N 14.87; found C 44.30, H 2.80, N 14.65. − UV/Vis (CH_2Cl_2): λ_{max} (lg ε) = 370 nm (4.30), 538 (3.69), 612 (3.82), 664 (4.15). − Mg(ttchp) (**5**): Yield 19%, dark-blue microcrystals. − IR (KBr): ṽ = 2963 cm^{-1} m, 2930 w, 2073 w, 1617 m, 1459 m, 1384 m, 1262 s, 1097 s, 1022 s, 801 vs, 559 w. − $C_{24}H_{16}MgN_8S_{12}$ (825.47): calcd. C 34.92, H 1.95, N 13.57; found C 34.20, H 1.30, N 13.41. − UV/Vis (CH_2Cl_2): λ_{max} (lg ε) = 368 nm (4.50), 514 (4.10), 610 (4.15), 656 (4.29). − Mg(dochp) (**6**): Yield 27%, dark-blue microcrystals. − IR (KBr): ṽ = 2950 cm^{-1} m, 2919 m, 1701 sh, 1623 s, 1472 m, 1372 w, 1310 s, 1245 w, 1215 w, 1034 vs, 897 s, 794 m, 756 m, 661 w, 558 s. − $C_{24}H_{16}MgN_8O_4S_8$ (761.22): calcd. C 37.87, H 2.12, N 14.72; found C 37.20, H 1.71, N 14.56. − UV/Vis (CH_2Cl_2): λ_{max} (lg ε) = 370 nm (4.32), 518 (3.93), 610 (3.99), 656 (4.15).

Tetrakis(dithiacyclohepta)porphyrazine [H_2(dtchp) (7)], Tetrakis(trithiacyclohepta)porphyrazine [H_2(ttchp) (8)], and Tetrakis(dithiaoxocyclohepta)porphyrazine [H_2(dochp) (9)]: The following procedure for the synthesis of the metal free derivatives is similar to that reported by Hoffman and coworkers.[11b] A sample of the Mg containing macrocycles **4**−**6** was dissolved in a minimal amount of trifluoroacetic acid and was placed in the dark for 6 hrs. The solution was filtered, slowly poured into ice water, neutralized with concentrated ammonia, and filtered again. The precipitate was washed extensively with 5% HCl/MeOH, distilled water followed by MeOH until the washings were clear. The product was dried under vacuum and for H_2(dtchp) (**7**), purified with column chromatography (R_f = 0.90) with 5% MeOH/CH_2Cl_2 as eluent. − H_2(dtchp) (**7**): Yield 75%, blue-black powder. − IR (KBr): ṽ = 2962 cm^{-1} m, 2924 m, 2347 w, 1711 m, 1697 w, 1560 w, 1412 m, 1301 m, 1261 vs, 1098 s, 1018 vs, 864 m, 798 vs, 739 m, 660 w. − $C_{28}H_{26}N_8S_8$ (731.05): calcd. C 46.00, H, 3.59, N 15.33, S 35.08; found C, 45.70, H 3.40, N 15.25, S 34.94. − UV/Vis (CH_2Cl_2): λ_{max} (lg ε) = 358 nm (4.37), 526 (4.02), 614 (3.99), 700 (3.98). − MS (FAB); *m/z* (%): 731 (100) [M$^+$]. − H_2(ttchp) (**8**): Yield 80%, blue-black powder. − IR (KBr): ṽ = 2961 cm^{-1} m, 2928 m, 2347 vw, 1697 m, 1681 m, 1560 w, 1453 w, 1375 m, 1288 m, 1218 s, 1015 vs, 866 m, 798 s, 729 s, 669 m. − $C_{24}H_{18}N_8S_{12}$ (803.18): calcd. C 35.89, H 2.26, N 13.95, S 47.90; found C 36.22, H 2.06, N 13.60, S 47.42. − UV/Vis (DMF): λ_{max} (lg ε) = 346 nm (5.10), 518 (4.81), 610 (4.81), 680 (4.75). − H_2(dochp) (**9**): Yield 83%, blue-black powder. − IR (KBr): ṽ = 2961 cm^{-1} m, 2926 m, 1711 m, 1618 m, 1470 m, 1424 s, 1384 m, 1306 s, 1226 s, 1047 vs, 898 vs, 786 s, 739 m, 713 m, 663 m, 483 s. − $C_{24}H_{18}N_8O_4S_8$ (738.93): calcd. C 39.01, H 2.46, N 15.17, O 8.66, S 34.71; found C 38.40, H 2.13, N 14.84, S 34.23. − UV/Vis (DMF): λ_{max} (lg ε) = 346 nm (6.10), 514 (5.84), 616 (5.84), 686 (5.77). − FAB-MS; *m/z* (%): 739 (100) [M^+].

[Tetrakis(dithiacyclohepta)porphyrazinato]nickel(II) [Ni(dtchp) (10)], [Tetrakis(dithiacyclohepta)porphyrazinato]copper(II) [Cu(dtchp) (11)], and [Tetrakis(dithiacyclohepta)porphyrazinato]zinc(II) [Zn(dtchp) (12)]: Compounds **10**−**12** were synthesized similar to previously reported procedures found in refs.[10−12] After the reaction of **7** with anhydrous $Ni(OAc)_2$, $Cu(OAc)_2$, or ZnI_2 respectively in a 3:1 mixture of PhCl/DMF at 100°C for 20 hours under an argon atmosphere, the solvents were removed under vacuum. The remaining solids were washed thoroughly with water and 5% HCl/MeOH to remove excess metal salts followed by MeOH until the washings were clear then dried under vacuum. − Ni(dtchp) (**10**): Yield 92%, blue-black powder. − IR (KBr): $\tilde{\nu}$ = 2993 cm^{-1} m, 2922 m, 1683 m, 1538 w, 1517 m, 1412 m, 1302 m, 1254 s, 1244 s, 1078 m, 1047 vs, 875 m, 815 s, 750 s, 690 w. − $C_{28}H_{26}NiN_8S_8$ (787.72): calcd. C 42.69, H 3.33, N 14.23, S 32.56; found C 42.21, H 3.04, N 14.13, S 32.40. − UV/Vis (PhCl): λ_{max} (lg ε) = 342 nm (4.85), 508 (4.55), 640 (4.61). − Cu(dtchp) (**11**): Yield 95%, blue-black powder. − IR (KBr): $\tilde{\nu}$ = 2960 cm^{-1} m, 2923 m, 1654 w, 1560 w, 1488 w, 1414 m, 1302 s, 1260 s, 1236 m, 1091 s, 1043 s, 907 w, 864 w, 805 vs, 745 s, 678 w, 503 w. − $C_{28}H_{26}CuN_8S_8$ (792.58): calcd. C 42.43, H 3.05, N 14.14, S 32.36; found C 42.05, H 2.98, N 14.10, S 32.15. − UV/Vis (DMF): λ_{max} (lg ε) = 354 nm (4.80), 550 (4.49), 654 (4.60). − Zn(dtchp) (**12**): Yield 94%, green-black powder. − IR (KBr): $\tilde{\nu}$ = 2963 cm^{-1} m, 1653 m, 1613 m, 1413 w, 1380 w, 1262 s, 1098 s, 1022 s, 864 w, 800 vs, 687 w. − $C_{28}H_{26}N_8S_8Zn$ (794.41): calcd. C 42.33, H 3.05, N 14.11; found C 42.10, H 2.98, N 14.02. − UV/Vis (DMF): λ_{max} (lg ε) = 372 nm (4.73), 556 (4.20), 666 (4.56).

Electrochemical Methods: Cyclic voltammetry was performed using a ISMP Model Elektrokemat 400 potentiostat equipped with microcomputer-controlled instrumentation with positive feedback ohmic resistance compensation following previously described techniques.[29] Methylene chloride was dried, distilled, and degassed with argon prior to use and tetrabutylammonium hexafluorophosphate was used as the supporting electrolyte (0.1 M). A standard calomel electrode was used for the reference electrode with a 2 mm gold plate as the working electrode and the electrochemical experiments were completed under an argon atmosphere.

Electrical Conductivity Measurements: Two-probe pressed powder, AC electrical resistance measurements were carried out with an in-house assembled powder press using a Hewlett Packard 4263A LCR meter.

Crystal Structure Determinations: Suitable crystals of compounds **1** (pale green diamonds), **2** (yellow plates), and **3** (clear hexagons) were obtained from slow evaporation of 1:1 solutions of hexane/dichloromethane. Data were collected on an imaging plate IPDS-STOE diffractometer [Mo-K_α radiation, λ(Mo-K_α) = 0.71073 Å]. The cell parameters were determined from 5000 reflections over the whole θ range. Data for all structures were corrected for Lorentz-polarization effects. Data reduction were performed with X-Red.[30] The structures were solved by direct methods (SHELXS-86)[31] followed by normal heavy-atom procedures. For every compound, full matrix least-squares refinement on F^2 with all non-H atoms anisotropic. H-atoms were placed geometrically at 0.99 Å and included in the calculations as riding the adjacent C atom with an isotropic displacement parameter 50% higher than the one of the adjacent C atom. All crystallographic calculations were performed using SHELXL-97 (Sheldrick, 1997)[32] Neutral atom scattering factors were taken from ref. 33. Molecular graphics were obtained using Cameron.[34] The crystallographic data are compiled in Table 4. Crystallographic data (excluding structure factors) for the structures reported in this manuscript have been deposited with the Cambridge Crystallographic Data Centre. The deposition number for compounds **1**, **2**, and **3** is 101472. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, GB-Cambridge CB12 1EZ [Fax: (internat.) +44 (0)1223/ 336-033, E-mail: deposit@ccdc.cam.ac.uk].

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