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Porphyrazine Binaries: Synthesis, Characterization, and Spectroscopy of a Metal-Linked Trinuclear Porphyrazine Dimer

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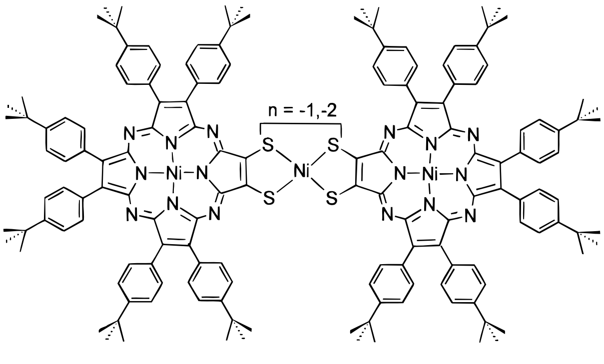
Introduction

Major efforts are under way to design molecular building blocks that allow for the controlled and systematic assembly of supramolecular arrays and polymer systems.[1] The unique electronic, optical, and photophysical properties of porphyrinic macrocycles make them attractive candidates for such a role,[2−6] and we are exploring the use of porphyrazinethiolates[7−10] and related aminoporphyrazines[11] and porphyrazinols[12] to build multi-macrocyclic arrays with novel magnetic or conductive properties.

Peripherally functionalized porphyrazines (pz), of the form $M[pz(((S^-)_2)_n{:}B_{4-n})]$, can be synthesized with $n = 1$ to 4 pyrroledithiolates incorporated into the macrocycle while solubilizing "B" moieties are fused to the remaining $4 - n$ pyrroles. While these porphyrazinethiolates can be "capped" with metal-ion complexes to form *solitaire*-pz's ($n = 1$),[9] *gemini*-pz's ($n = 2$),[10] and *star*-pz's ($n = 4$),[7,8] through straightforward synthetic strategies, they also can be used as building blocks in the assembly of multi-pz arrays through the mutual chelation of metal ions by their peripheral dithiolene moieties. In such arrays, the metal ion in the central macrocyclic cavity and the metal-ion linker can be chosen independently. The conjugated metallomacrocycle core will play an important role in both molecular structure and function, while the redox-switchable metal(bis(dithiolene))[13] linking units, fused directly to the β-pyrrole positions, will permit the regulation of electronic communication between macrocycles.

As a first step toward the assembly of multiporphyrazine arrays, we have linked two porphyrazinedithiolates by the mutual chelation of a nickel ion ion to yield the first trinuclear metal-linked porphyrazine dimer **9**. Crucial to the successful preparation of complex **9** was the preparation and characterization of a pz-dithiolate with a new solubilizing group, B = (4-*tert*-butylphenyl)$_2$, that is compatible with the strategy established previously[9,10] for the synthesis of the unsymmetrical macrocycles but that permits the isolation and purification of macrocyclic arrays.



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Experimental Section

Material and Methods. THF was distilled from sodium benzophenone ketyl. All other solvents were used as supplied. Anhydrous NH_3 (Linde Speciality Gases) was ultra-high-purity grade. Silica gel used for chromatography was Baxter silica gel 60 Å (230−400 mesh). Sodium metal was freshly cut under hexanes immediately prior to use. Bis[(4-((butyloxy)carbonyl)benzyl)thio]maleonitrile, $(BCB)_2mnt$, was prepared as previously reported.[9] All other reagents were used as purchased without further purification. Schlenk-line manipulations were performed on an apparatus purchased from Chemglass with all PTFE valves and with dry argon ($CaSO_4$).

^1H and ^{13}C NMR spectra were obtained using a Varian Gemini 300. Electronic spectra were recorded using a Hewlett-Packard HP8452A

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spectrophotometer. Cyclic voltammetry was done on a Cypress Systems 2000 electroanalytical system. Electron paramagnetic resonance (EPR) spectra were measured using a modified Varian E-4 X-band spectrometer, and the field was calibrated using diphenylpicrylhydrazyl (dpph) as a standard. The X-band EPR spectrum (9.132 GHz) of compound **9** was recorded at 77 K, with a modulation amplitude of 8 G and a microwave power of 12 dB. Fast-atom bombardment (FAB) and electric ionization (EI) mass spectra were obtained by Dr. Doris Hung using a VG-70-250E. Elemental analyses were performed by Searle Laboratories, Skokie, IL, and Onieda Research Services, Whitesboro, NY. Melting points were obtained using a Reichert hot-stage microscope and are uncorrected.

Synthetic Details. (4-*tert*-Butylphenyl)acetonitrile (1).[14] 4-*tert*-Butylbenzyl chloride (25 g, 0.137 m), finely-ground NaCN (10.1 g, 0.205 mol), and a substoichiometric amount of NaI (3.0 g, 0.02 mol) were suspended in acetone (30 mL), and the solution was heated to reflux for 48 h. The reaction mixture was filtered hot, and the filtrate was concentrated under vacuum. The residue was taken up in $CHCl_3$, washed with hot water twice, and dried ($MgSO_4$). The $CHCl_3$ was rotary evaporated, yielding a yellow oil. The product was distilled under vacuum at 110 °C to yield a clear oil (21.2 g, 89%). ^1H NMR ($CDCl_3$) [δ (ppm)]: d (7.43, 2H), d (7.28, 2H), s (3.73, 2H), s (1.35, 9H). ^{13}C NMR ($CDCl_3$) [δ (ppm)]: 151.19, 129.08, 127.72, 126.15, 118.19, 34.64, 31.34, 23.19. EI-MS: *m*/*z* 173.

Bis(4-*tert*-butylphenyl)fumaronitrile (2).[14] Freshly-cut Na (5.7 g, 0.246 mol) was added to MeOH (80 mL) cooled to 0 °C. The sodium methoxide was added dropwise over 0.5 h to a solution of **1** (21.2 g, 0.123 mol) and I_2 (31.2 g, 0.123 mol) dissolved in diethyl ether (500 mL) at 0 °C. The dark red color of the solution cleared, and a white precipitate formed, which was collected, washed with MeOH, and dried under vacuum. The filtrate volume was reduced by half and was placed in freezer overnight. A second crop of product was filtered out, washed, and dried under vacuum. Total yield: (14.8 g, 70%. Mp: 231 °C. ^1H NMR ($CDCl_3$) [δ (ppm)]: d (7.80, 4H), d (7.55, 4H), s (1.38, 18H). ^{13}C NMR ($CDCl_3$) [δ (ppm)]: 155.35, 129.35, 128.57, 126.28, 124.45, 117.15, 35.16, 31.15. EI-MS: *m*/*z* 342.

3,4-Bis(4-*tert*-butylphenyl)pyrroline-2,5-diimine (3). Compound **2** (5 g, 0.015 mol) was suspended in ethylene glycol (300 mL) and heated to 115 °C. Two small chunks of Na (∼30 mg) were added to the reaction. When the suspension reached 115 °C, gaseous NH_3 was bubbled through the suspension. After 1.5 h, the solution was filtered hot and the filtrate was poured over ice water (700 mL). A yellow precipitate formed which was collected by filtration and washed with water. The solid was dissolved in $CHCl_3$, dried (Na_2SO_4), treated with activated charcoal, and filtered, and the solvent was removed under vacuum. The product was isolated as a yellow powder (2.7 g, 35%). Mp: 177 °C, cyclizes. ^1H NMR ($CDCl_3$) [δ (ppm)]: d (7.75, 4H), d (7.51, 4H), s (3.51, 3H), s (1.37, 18H). EI-MS: *m*/z 359. The unreacted fumaronitrile that was filtered from the ethylene glycol reaction was dried and reused for the same reaction.

Synthesis of $H_2[pz((SR)_2:B_3)]$ (R = BCB) (4), 2,3-Bis((4-((butyloxy)carbonyl)benzyl)thio)-7,8,12,13,17,18-hexakis(4-(*tert*-butyl)phenyl)porphyrazine. Magnesium metal (0.09 g, 0.004 mol) and *n*-BuOH (25 mL) were heated to reflux under N_2 for 8 h to form a magnesium butoxide suspension. A small chip of I_2 was added to initiate the reaction. When $(BCB)_2$mnt (1.04 g, 0.002 mol) and **3** (3.59 g, 0.01 mol) was added to the suspension and the reaction mixture was heated for another 12 h, the mixture turned dark green. The BuOH was removed under vacuum, and the residue was washed with EtOH until the washings were colorless. The residual crude solid was dried under vacuum, dissolved in an excess of CF_3CO_2H (30 mL), and stored in the dark for 1 h. The purple slurry was poured over ice water (300 mL) and neutralized with concentrated NH_4OH. The green solid was collected by filtration and washed thoroughly with water and MeOH and dried under vacuum. This solid was chromatographed on silica gel using 10% hexanes/$CHCl_3$ as the eluent with porphyrazine **4** the second major green band to elute. The product was recrystallized from CH_2Cl_2/MeOH to yield microcrystalline material (0.48 g, 16% yield, based on $(BCB)_2$mnt). Anal. Found (calc for $C_{100}H_{110}N_8O_4S_2$): C, 77.02 (77.38); H, 7.34 (7.15); N, 7.24 (7.22). ^1H NMR ($CDCl_3$) [δ (ppm)]: d (8.24, 4H), d (8.14, 4H), d (8.04, 4H), d (7.70, 4H), m (7.52, 12H), d (7.13, 4H), s (4.95, 4H), t (4.29, 4H), q (1.62, 4H), s (1.52, 18H), s (1.49, 18H), s (1.38, 18 H), sx (1.35, 4 H), t (0.89, 6H), s (−2.91, 2H-internal). UV/vis ($CHCl_3$): λ_{max} 372, 474, 614, 682 nm. FAB-MS: *m*/*z* 1552 $(M + H^+)$.

$Ni[pz((SR)_2:B_3)]$ (R = BCB) (5), [2,3-Bis((4-butyloxy)carbonyl)benzyl)thio)-7,8,12,13,17,18-hexakis(4-*tert*-butylphenyl)porphyrazinato]nickel(II). Macrocycle **4** (0.20 g, 0.13 mmol), anhydrous $Ni(OAc)_2$ (0.23 g, 1.3 mmol), PhCl (20 mL), and DMF (10 mL) were heated to 100 °C under nitrogen for 5 h. The solvent was removed under vacuum, and the solid was washed with 5% HCl in MeOH and then MeOH. Recrystallization from CH_2Cl_2/MeOH afforded 0.2 g of microcrystalline product (95%). Anal. Found (calc for $C_{100}H_{108}N_8NiO_4S_2$): C, 74.08 (74.69); H, 6.67 (6.77); N, 6.92 (6.97). ^1H NMR ($CDCl_3$) [δ (ppm)]: m (8.09, 8H), d (7.87, 4H), d (7.67, 4H), m (7.49, 8H), d (7.05, 12H), s (4.80, 4H), t (4.18, 4H), q (1.62, 4H), s (1.50, 18H), s (1.46, 18H), s (1.37, 18 H), sx (1.36, 4 H), t (0.89, 6H). UV/vis ($CHCl_3$): λ_{max} 348, 462, 600, 642. FAB-MS: *m*/*z* 1609 $(M + H^+)$.

$Na_2Ni(pz((S^-)_2:B_3))$ (6), Disodium [2,3-Dithiolato-7,8,12,13,17,18-hexakis(4-*tert*-butylphenyl)porphyrazinato]nickel(II). Macrocycle **5** (0.200 g, 0.129 mmol) was suspended in liquid NH_3 (25 mL) at −78 °C. Sodium metal (0.036 g, 1.55 mmol), freshly cut under hexanes, was added in small pieces and, once dissolved, THF (10 mL) was added to solubilize the porphyrazine. The mixture turned from purple to a green color. After 1 h, NH_4Cl (0.055 g, 1.0 mmol) was added to quench the excess sodium and sodium amide. The NH_3 and THF were vented off under a stream of argon yielding a fine green powder containing sodium chloride and the disodium salt of the porphyrazinedithiolate. Due to the air sensitive nature of the dithiolate, no attempt at determining a yield for the deprotection was made.

$[(dppf)Pd][Ni(pz((S^-)_2:B_3))]$ (7), [(1,1′-Diphenylphosphino)ferrocene]palladium(II) [2,3-Dithiolato-7,8,12,13,17,18-hexakis(4-*tert*-butylphenyl)porphyrazine]nickel(II). The reaction residue containing **6** was dissolved in deaerated acetone (50 mL) and treated with (dppf)-$PdCl_2$ (0.1 g, 0.136 mmol) at which time a green solid formed. The solid was collected by filtration and washed well with MeOH. The solid was then chromatographed on silica gel using $CHCl_3$ as the eluent, and the major green-blue band was collected. Recrystallization from CH_2Cl_2/MeOH yielded 0.12 g of product (40% yield, based on **5**). Anal. Found (calc for $C_{110}H_{106}FeN_8NiPdP_2S_2$): C, 69.72 (70.04); H, 5.95 (5.67); N, 5.94 (5.94). UV/vis ($CHCl_3$): λ_{max} 342, 481, 623, 639 nm. FAB-MS: *m*/*z* 1888 $(M + H^+)$.

$Ni[pz((SR)_2:B_3)]$ (R = Piv) (8), [2,3-Bis((2,2-dimethylpropanoyl)thio)-7,8,12,13,17,18-hexakis(4-*tert*-butylphenyl)porphyrazinato]nickel(II). Macrocycle **5** (0.20 g, 0.15 mmol) was deprotected by the procedure described above, and the resulting porphyrazinedithiolate was taken up in deaerated acetone (50 mL). An excess of *t*-BuCOCl (0.055 g, 0.45 mmol) was added to the green solution at which point a fine green precipitate formed. Excess *t*-BuCOCl was quenched with water, and the product was collected by filtration and dried. The solid was dissolved in CH_2Cl_2 and chromatographed on silica gel eluting with 30% hexanes in CH_2Cl_2. The major green band was collected and recrystallized from CH_2Cl_2/MeOH to yield 0.095 g of product (55% yield, based on **5**). Anal. Found (calc for $C_{86}H_{96}N_8NiS_2O_2$): C, 73.86 (74.00); H, 6.85 (6.97); N, 7.92 (8.03). ^1H NMR ($CDCl_3$) [δ (ppm)]: m (8.09, 8H), d (7.87, 4H), d (7.67, 4H), m (7.49, 8H), d (7.05, 12H), s (1.55, 18H), s (1.50, 36H), s (1.43, 18H). UV/vis($CHCl_3$): λ_{max} 349, 451, 636 nm. FAB-MS: *m*/*z* 1403 $(M + H^+)$.

$[N(C_4H_9)_4]Ni[Ni(pz((S^-)_2:B_3))]_2$ (9). Porphyrazine **8** (0.050 g, 0.04 mmol) was dissolved in THF (10 mL), and sodium methoxide in degassed MeOH (2 M; 1 mL) was added. After 15 min, a solution of $NiCl_2\cdot 6H_2O$ (4.0 mg, 0.02 mmol) and $(C_4H_9)_4NBr$ (12.0 mg, 0.04 mmol) in MeOH (10 mL) was added dropwise to the reaction mixture. The mixture was stirred for 1 h as a dark green precipitate formed. The solid was collected by filtration, washed thoroughly with water and MeOH, dried, washed with hexanes, and dried again. The filter cake was extracted with CH_2Cl_2, and the solution was filtered and rotary evaporated to yield an amorphous green powder. Recrystallization from CH_2Cl_2/MeOH gave a black microcrystalline precipitate (0.026 g, 50%). Anal. Found (calc for $C_{152}H_{156}N_{16}S_4Ni_3\cdot C_{16}H_{36}N\cdot CH_2Cl_2$): C, 71.31

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(14) Alternative syntheses for compounds **1** and **2** has been reported: Marinina, L. E.; Mikhalenko, S. A.; Luk'yanets, E. A. *Zh. Obshch. Khim.* **1973**, *43*, 2025−2029.

(71.58); H, 6.68 (6.90); N, 8.23 (8.40). UV/vis (CH_2Cl_2): λ_{max} 365, 476, 596, 640, 676 nm.

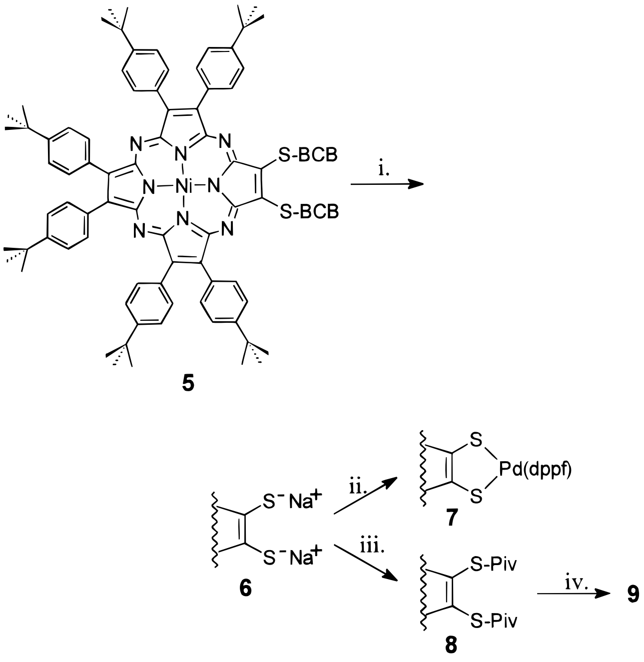
Results and Discussion

Synthesis of Porphyrazinethiolates and Their Metal Complexes. The preparation of soluble porphyrazinethiolates begins with the design of a compatible pair of dinitrile derivatives that can be cocyclized. Following the strategy for the synthesis of the *gemini*-porphyrazines,[10] the functional groups on the pair of dinitriles should have disparate polarities so as to allow for the separation of each porphyrazine product formed in the cyclization. The previously-reported porphyrazines with $n = 1, 2$ peripheral dithiolates were synthesized through the mixed condensation of 4-((butyloxy)carbonyl)benzyl-protected dithiomaleonitrile ($(BCB)_2$mnt) with 1,2-dicyanobenzene.[9,10] However, while these macrocycles can be studied as individual molecules, the benzene ring fused to the the β-positions of the noncoordinating pyrroles tends to lower the macrocyclic solubility, which makes higher-order arrays of these porphyrazines insufficiently soluble for study. Hence we designed a dinitrile functionalized with a noncoordinating component that would help solubilize the porphyrazine but remain compatible with the strategy established for the synthesis of the unsymmetrical macrocycles. The 3,4-bis(4-*tert*-butylphenyl)pyrroline-2,5-diimine, **3**, was selected as the new nonpolar coreactant with the expectation that the *tert*-butylphenyl substituents would enhance the solubility of the resulting porphyrazines and their respective metal complexes. For the cocondensation, the BCB-protected dithiomaleonitrile remains the polar component due to its stability under the cyclization conditions while the BCB group is readily cleaved under reductive conditions.[9]

Reaction of 4-*tert*-butylbenzyl chloride with sodium cyanide produced the (4-*tert*-butylphenyl)acetonitrile, **1**, in good yield (89%). Reaction of **1** with sodium methoxide and iodine, following Linstead's procedure for the oxidative coupling of substituted acetonitriles,[15] yielded the bis(4-*tert*-butylphenyl)-fumaronitrile, **2**, in 70% yield. The temperature required for the Mg(II)-templated cyclization of **2** is too high (~150 °C) for the dinitrile to be a compatible coreactant with $(BCB)_2$mnt, which starts to decompose at temperatures over 130 °C. This problem was solved by activation of the fumaronitrile[16] to the corresponding pyrrolinediimine, **3**, which cyclizes quite quickly in refluxing *n*-butanol ($T = 120$ °C), the preferred solvent for the cocyclization reaction. Cocondensation of 5 equiv of **3** and 1 of $(BCB)_2$mnt using the Mg(II)-template method[17] followed by treatment of the crude product with trifluoroacetic acid gave a mixture of free-base products, which can be easily separated in one chromatographic step. The BCB-protected porphyrazine **4** shows high solubility in most organic solvents and is isolated in a relatively high yield (16%).

The remaining members of this series, the $n = 2$ (*cis* and *trans*) and 3 porphyrazines, containing the 4-*tert*-butylphenyl solubilizing group, also have been prepared through the equimolar cocondensation of **3** and $(BCB)_2$mnt. Because our primary focus here is the design of a soluble pz-dimer complex, this paper concentrates on derivatives of the $n = 1$ porphyrazine **4**. The synthesis and characterization of the $n = 2$ and 3 porphyrazinethiolates and their resulting metal complexes, including new *cis*- and *trans*-*gemini*-porphyrazines, can be found in the Supporting Information.

Scheme 1[a]



[a] Key: (i) Na, NH_3, THF, −33 °C; (ii) (dppf)$PdCl_2$, acetone; (iii) PivCl, acetone; (iv) (a) Na(OMe), MeOH, THF, (b) $NiCl_2 \cdot 6H_2O$, $(C_4H_9)_4NBr$.

Metalation of the free-base macrocycle, **4**, with $Ni(OAc)_2$ proceeds smoothly using a standard procedure[18] to give **5** in near quantitative yield. The peripheral sulfur atoms of **5** were reductively deprotected using sodium metal in liquid ammonia (Scheme 1).[9] The resulting porphyrazinedithiolate **6** was air sensitive and Schlenk techniques were used for all the following manipulations. To confirm the metal-binding ability of the deprotection product, the porphyrazinedithiolate was dissolved in acetone to give a blue-green solution that was subsequently treated with (dppf)$PdCl_2$ to give the air-stable *solitaire*-porphyrazine product **7** (40%).

Direct preparation of a trinuclear porphyrazine dimer by addition of $NiCl_2$ to **6** proved inconvenient because the deprotection step generates several porphyrazine byproducts. Instead, the porphyrazinedithiolate **6** was treated with pivaloyl chloride to produce the Piv-protected porphyrazine **8** which is readily purified using silica gel chromatography in a 50% yield (Scheme 1). Deprotection of **8** using sodium methoxide in methanol[9] cleanly regenerates the porphyrazinedithiolate **6**. The monoanionic, formally nickel(III), metal-bridged dimer **9** is then prepared *in situ* through the addition of $NiCl_2$ to **6** and concommitant air-oxidation of the resulting dianion; the monoanion was isolated as the tetrabutylammonium salt. Such ready oxidation of the dianionic form is also seen with the $[Ni(bdt)_2]^{n-}$ complex (bdt = benzene-1,2-dithiolate).[19]

The cyclic voltammogram of **9** shows that the half-wave potential for one-electron reduction of the Ni(III)-bridged dimer to the Ni(II)-bridged dimer ($[S_2NiS_2]^- \rightarrow [S_2NiS_2]^{2-}$) is −0.62 V vs Fc^+/Fc.[20] This value is comparable to that reported for the reduction of $[Ni(bdt)_2]^-$ ($E_{1/2} = -0.74$ V vs Fc^+/Fc).[13d] The reduction potentials for these two monoanions are significantly

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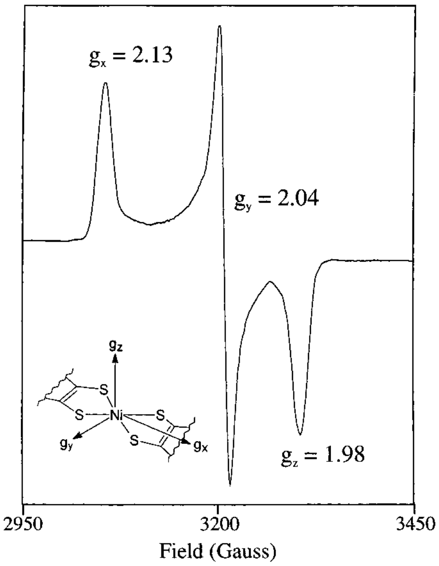

Figure 1. X-band frozen solution EPR spectrum (9.132 GHz) of porphyrazine dimer **9**, recorded at 77 K.

more negative than that reported for $[Ni(mnt)_2]^-$ ($E_{1/2} = 0.1$ V vs Fc^+/Fc).[13d] Thus, the porphyrazinedithiolate **6** and benzenedithiolate behave similarly in stabilizing the $[S_2Ni^{III}S_2]^-$ bridging unit, as opposed to the more electron-withdrawing mnt^{2-} ligand, which substantially favors the dianion bridge.

EPR Spectroscopy of the Trinuclear Porphyrazine Dimer 9. The classical spectroscopic signature of Ni(III) bis(dithiolene) complexes is their EPR spectrum.[21] The frozen-solution EPR spectrum of dimer **9** in CH_2Cl_2/toluene, Figure 1, exhibits the rhombic symmetry typical of Ni(III) bis(dithiolene) complexes[13,21] with **g**-tensor values ($g_x = 2.13$, $g_y = 2.04$, and $g_z = 1.98$) that are essentially indistinguishable from those reported for (n-Bu_4N)[$Ni^{III}(mnt)_2$] ($g_x = 2.16$, $g_y = 2.04$, and $g_z = 1.99$).[21] Thus, from the perspective of the linking moiety, the dimer **9** can be viewed as a classical bis(dithiolene) complex. By analogy with the results of Maki et al.,[21] one concludes that $Ni[Ni(pz(c{:}b_3))]_2^-$ anion has a $^2B_{3g}$ ground state where the odd electron orbital is composed primarily of a metal d_{yz} orbital and sulfur $2p_z$ orbitals. As expected, the Ni(II)-bridged dianion formed by reduction of **9** is EPR silent.

Electronic Absorption Spectroscopy. The optical spectrum of the unsymmetrically-substituted $Ni[pz((S\text{-}BCB)_2{:}B_3)]$ (**5**) is typical for porphyrazines in that it exhibits two intense $\pi \rightarrow \pi^*$ absorbances, a low-energy Q band at 640−680 nm that is accompanied by a slightly higher energy shoulder at 590−620 nm and the high-energy B (Soret) band at 340−350 nm (Figure 2). The Gouterman four orbital model[22] for porphyrinic macrocycles assigns the B and Q transitions to excitations from the two highest-occupied MO's (a_{1u} and a_{2u}) into the e_g LUMO. Commonly, the reduction from 4-fold symmetry caused by an unsymmetrical substitution pattern leads to a split of the Q band,[9,10] but this is not the case for **5**. However, in the free-base porphyrazine **4**, the lowered symmetry is enhanced, giving rise to two distinct absorbances, Q_x and Q_y (614 and 682 nm).

Figure 2, which includes the absorption spectra of the *solitaire*-porphyrazine **7** and porphyrazine dimer **9**, shows that coordination of a transition metal to the peripheral sulfurs atoms has a significant effect on the electronic structure of the porphyrazine. Although the spectra of both **7** and **9** exhibit the usual Soret and Q bands, their Q bands are split and shifted to longer wavelength relative to the BCB-protected precursor **5** and, most importantly, the effect is greater for the dimer than the *solitaire*-porphyrazine.

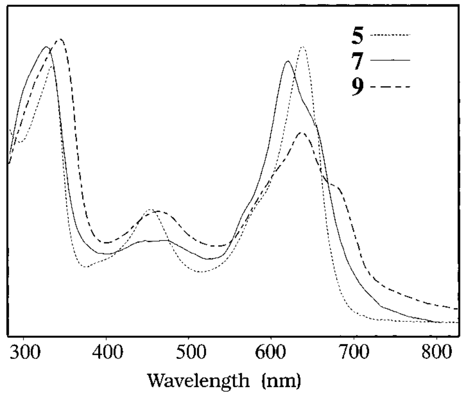

Figure 2. Optical absorption spectra of BCB-protected porphyrazine **5** (short dashed line), *solitaire*-porphyrazine complex **7** (solid line), and porphyrazine dimer **9** (long dashed line) in CH_2Cl_2.

In both the *solitaire*-porphyrazine and the dimer complex, the splitting of the Q band can be explained by an extension of the π-conjugated system and resulting departure of the macrocyclic symmetry from the effective D_{4h} symmetry of **5**. The splitting in the spectrum of the C_{2v}-symmetric **7** is $\sim$400 cm^{-1} and is comparable to that reported for aryl-substituted porphyrazines ($\sim$550 cm^{-1}) in which a single pyrrole is functionalized with a fused benzene ring.[23] It appears the peripheral five-membered chelate ring of the *solitaire*-porphyrazine has extended the π-conjugation of the porphyrazine core in a fashion analogous to that done by a fused benzo group. The Q band of the Ni(III)-bridged dimer **9** is broader than that of the monomeric precursor **5** with larger splitting ($\sim$790 cm^{-1}) and is more red-shifted than that of the *solitaire*-porphyrazine **7**. This is not the consequence of intramolecular exciton coupling between the two macrocycles.[24] Within the simple point−dipole exciton coupling theory developed by Kasha,[25] the exciton splitting for a coplanar porphyrinic dimer is given by the approximate equation $\Delta E = \mu^2/2\pi\epsilon_0 R^3$, where μ is the transition dipole moment and R is the center to center chromophore separation. Given the large separation between the centers of the porphyrazine rings ($\sim$14 Å) in the metal-linked dimer **9**, and plausible values of μ, the contribution of the exciton coupling to the splitting of the Q band is far too small to account for the spectra. Instead, the optical effects are attributed to enhanced π-conjugation into the open-shell $[S_2NiS_2]$ spacer and quite possibly throughout both porphyrazine rings. Analogous conclusions were reached regarding the red-shift broadening of the Q band observed in the optical spectra of planar, conjugated porphyrin[26] and phthalocyanine[27] dimers.

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Summary

This report presents the synthesis and characterization of a soluble porphyrazinedithiolate ligand and its metal complexes. As a first step toward the assembly of metal-linked multiporphyrazine arrays, we have linked two of the porphyrazinedithiolates by a metal ion (Ni(III)) to form a novel trimetallic metal-linked porphyrazine dimer. Future work includes the insertion of paramagnetic metals into the macrocyclic cavities of the dimer to examine the degree to which the porphyrazine ring mediates the electronic interaction between the central and linking metal ions.

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Supporting Information Available: Text describing the synthesis and characterization (^{1}H NMR, EA, FAB-MS, UV/vis) of the series M[pz(((S-BCB)$_2$)$_n$:B$_{4-n}$)], where $n = 2$ (*cis* and *trans*) and 3 and M = 2H and Ni, and of the trimetallic *cis*- and *trans*-gemini porphyrazines [(Et$_3$P)$_2$Pt]$_2$[Ni[*cis*-pz(((S$^-$)$_2$)$_2$:B$_2$)]] and [(Et$_3$P)$_2$Pt]$_2$[Ni[*trans*-pz(((S$^-$)$_2$)$_2$:B$_2$)]] and UV/vis spectra for this family of porphyrazines (Figure S1) including a discussion of their optical properties (6 pages). Ordering information is given on any current masthead page.

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