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Synthesis and Reactions of Aminoporphyrazines with Annulated Five- and Seven-Membered Rings

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The novel five- and seven-membered ring appended aminoporphyrazines **3** and **12** have been prepared via mixed Linstead macrocyclization. The structures of both have been unequivocally established by X-ray crystallographic studies. Reductive deselenation of selenadiazole **3** in the presence of 9,10-phenanthrenequinone or 2,3-butanedione results in the formation of pyrazines **6a**,**b,** whereas oxidation of porphyrazine **12** gave the corresponding seco derivative **14**. *seco*-Porphyrazine **14** mediates the generation of singlet oxygen with a quantum yield of 0.74.

Introduction

The wide interest in molecule-based metals[1] and magnets[2] has led us to consider peripherally substituted porphyrazines[3] (pz) as possible precursors to such materials. As a first step, we have prepared donor−acceptor crystals of octakis(dimethylamino)-pzs with TCNQ[4] and C_{60}.[4,5] More recently, we reported the development of a new family of (dimethylamino)-pz/phthalocyanine (pc) hybrids, designed to provide incremental variation of redox chemistry between M[pc] and the octakis(dimethylamino) macrocycle.[6] However, X-ray crystal structural analyses of octakis(dimethylamino)-pzs show that steric clash prevents all adjacent dimethylamino groups from simultaneously conjugating with the pz core.[6,7] We reasoned that if the amino groups were unsubstituted or locked in a cyclic structure they would couple more strongly and therefore make the corresponding porphyrazines more efficient electron donors. Herein, we report our studies toward the synthesis and reactions of "unsubstituted" and "locked" amino-pzs.

Results and Discussion

Until recently, the preparation of free amino-pzs has been unsuccessful due to the failure of diaminomaleonitrile to undergo Linstead[8] macrocyclization reactions. However, Ercolani and co-workers[9a] have recently shown that tetrakis(selenodiazole)-pzs can be reductively converted into their corresponding octa-amino derivatives. Some drawbacks of these symmetrically substituted macrocycles are the poor solubility of the former and low yield and stability of the latter.[10] In addition, they have also reported unsymmetrical porphyrazines with an annulated 1,2,5-selenodiazole ring.[9b] To overcome the limitations presented by the octa-amino derivatives, we also chose to examine related unsymmetrical porphyrazines. Thus, mixed Linstead macrocyclization of 3,4-dicyano-1,2,5-selenodiazole[9] (**1**) with a 7-fold excess of 2,3-dipropylmaleonitrile[11] (**2**) in the presence of magnesium butoxide gave the soluble (chlorinated solvents, MeOH, EtOAc) porphyrazine **3** in 42% yield (Scheme 1).

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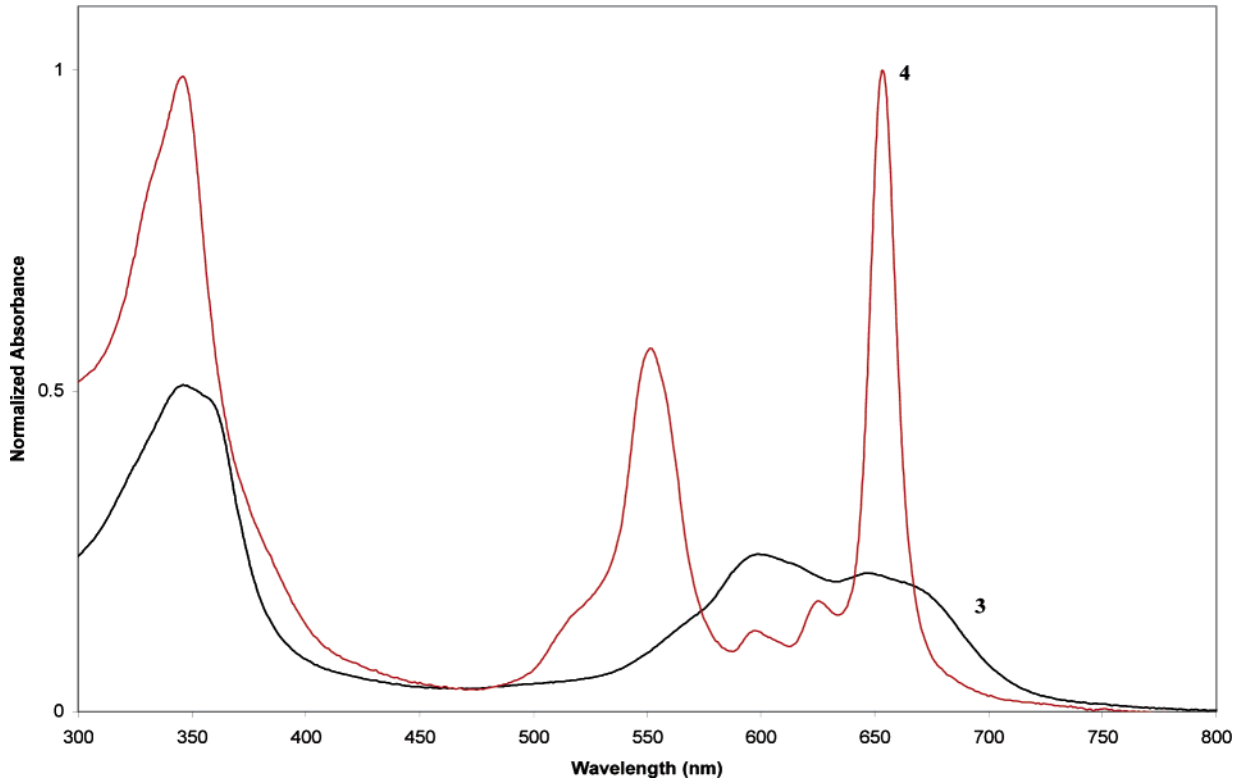
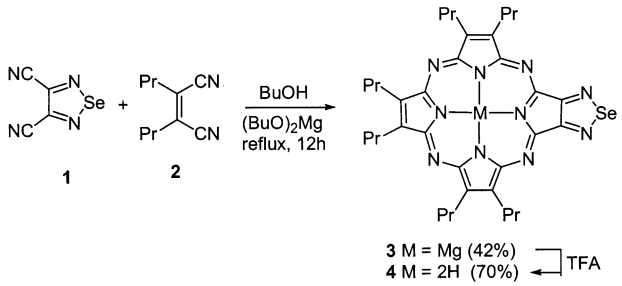


FIGURE 1. Normalized UV−vis spectra of porphyrazines **3** and **4** in CH_2Cl_2.

SCHEME 1



The structure of the magnesium complex **3** was established by X-ray crystallography (see the Supporting Information). Removal of the Mg ion with trifluoroacetic acid gave the free base porphyrazine **4** in 70% yield. In accordance with Gouterman's four orbital model,[12] both **3** and **4**, having a symmetry lower than D_{4h}, display split Q-bands in their UV−vis spectra having Q_x and Q_y absorbances at 599 and 650 and 552 and 653 nm, respectively (Figure 1).

Reductive deselenation of selenodiazole-pz **3** using the conditions reported by Ercolani and co-workers[9] to elaborate pz-$(NH_2)_8$ (H_2S, pyridine) in the presence of 9,10-phenanthrenequinone or 2,3-butanedione gave, presumably via diamine **5**, the novel pyrazine-pz's **6a**,**b** (Scheme 2). While Mg-pz **6a** was easily obtained (88%), **6b** was best purified after demetalation with trifluoroacetic acid to give the free base pz **7** in good overall yield (78%).

As expected, the UV−vis spectra of **6a**,**b** and **7** are qualitatively the same as those of **3** and **4,** respectively, and again, all other spectroscopic data confirmed their identities. Attempts to isolate the intermediate diamine **5** were unsuccessful and lead to decomposition. Related porphyrazinediol[13] and -dithiol[14] derivatives are also unstable and must be derivatized in situ.

In a parallel approach, commercially available diaminomaleonitrile was readily converted into the 2,3-dicyano-1,4-diazepine **9** via the corresponding diimine **8** following the method reported by Begland et al.[15] (Scheme 3). Although 5,7-diphenyl-2,3-dicyano-6*H*-1,4-diazepine has been reported to undergo macrocyclization,[10] the analogue **8** failed to provide any porphyrazinic products. On the other hand, Linstead macrocyclization of diazepine **9** gave the expected dark blue pigments; unfortunately, all attempts to isolate the presumed macrocycle resulted in decomposition. Thus, diazepine **9** was dimethylated and the product **10** was macrocyclized to provide the more stable Mg-pz. Subsequent demetalation with trifluoroacetic acid gave the stable free base porphyrazine **11** in 25% overall yield as a mixture of stereoisomers. Similarly, mixed Linstead macrocyclization of dinitrile **10** with a 7-fold excess of dipropylmaleonitrile **2** gave, again after demetalation, the stable free base porphyrazine **12** but in an 11% overall yield. Again, this macrocycle was isolated as a mixture of cis and trans stereoisomers as also established by X-ray crystallography (see the Supporting Information).

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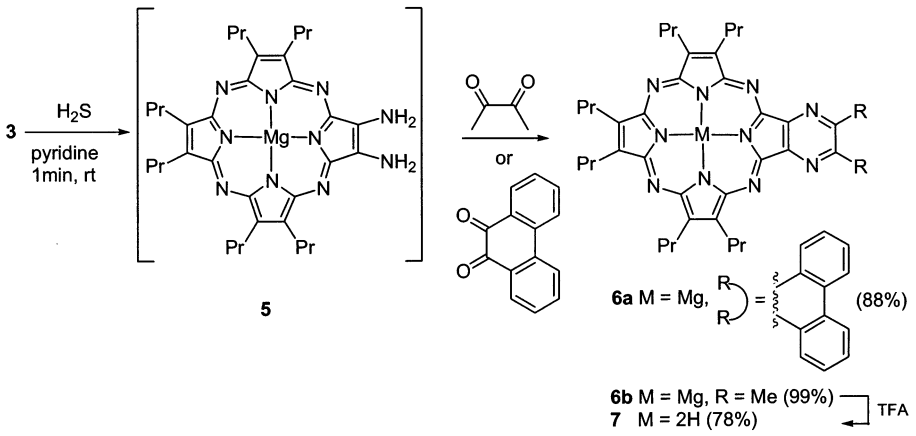
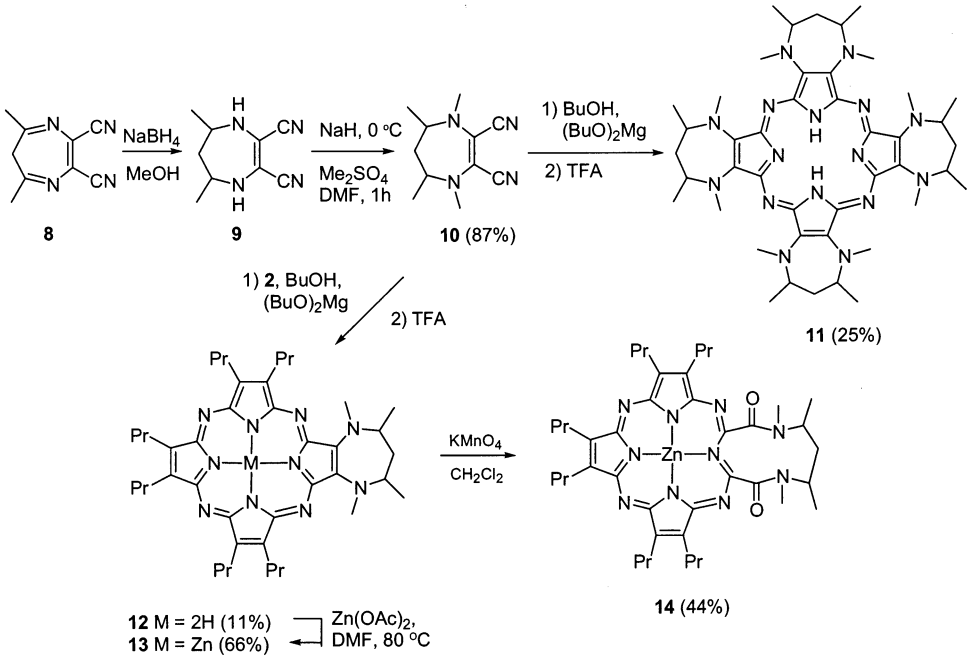
SCHEME 2



SCHEME 3



Although a meaningful cyclic voltammogram of the rather unstable pz **11** could not be obtained, the electrochemical properties of compound **12** were according to our expectations. The analogous bis(dimethylamino)-porphyrazine, $H_2[pz(Pr)_6(NMe)_2]$, exhibits a first reversible ring oxidation at −0.13 V.[11] On the other hand, the "locked" amino-pz **12** is much easier to oxidize, having a reversible and a quasi-reversible oxidation at $E_{1/2} = -0.30$ and +0.46 V, respectively (vs Fc^+/Fc) (Figure 2).

In fact, the first oxidation of pz **12** occurs 31 mV to lower potential than what was seen for octakis(diemthylamino)porphyrazine (first oxidation potential = −0.27 V),[4] thus making **12** the most easily oxidized porphyrazine reported to date. In addition to the two oxidations, **12** displays a reversible and a quasi-reversible ring reduction at −1.40 and −1.84 V, respectively (vs Fc^+/Fc) (Figure 2).

Attempts to remetalate or to oxidize porphyrazine **11** led only to decomposition. However, reaction of the free base porphyrazine **12** with zinc(II) acetate resulted in selective metalation within the macrocyclic cavity to provide the corresponding zinc complex **13** (66%). Again, all attempts to oxidize the free base porphyrazine **12** to its corresponding seco derivative[16] failed. On the other hand, treatment of the zinc complex **13** with 1 equiv of potassium permanganate gave the requisite novel *seco*-porphyrazine **14** in 44% yield (Scheme 3).

Representative UV−vis spectra of compounds **11**, **13**, and **14** are shown in Figure 3.

While porphyrazines **11** and **13** display broad Q-bands in their UV−vis spectra, *seco*-porphyrazine **14** exhibits a distinct split Soret- and Q-band with absorbances at 335 and 352 and 559 and 644 nm, respectively. The broadening of the Q-band region is presumably due to overlap of underlying n−π* transitions that arise from the nonbonding electrons associated with the peripheral nitrogens. In *seco*-porphyrazine **14**, the peripheral nitrogen lone pairs do not strongly interact with the central ring, and the broadening effect is removed. In addition, the cyclic structure of the amino groups has also a

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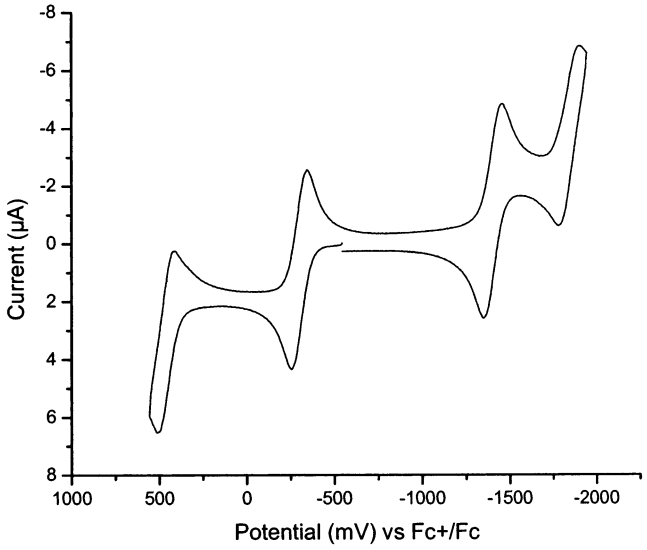

FIGURE 2. Cyclic voltammogram of porphyrazine **12** taken in dichloromethane.

profound effect on the photophysical properties of the macrocycle. While the analogous bis(dimethylamino)-porphyrazine, $Zn[pz(Pr)_6(NMe)_2]$, shows neither fluorescence nor triplet absorption,[17] **13** exhibits fluorescence with a fluorescence quantum yield of $\phi_f = 0.06 \pm 0.01$ and an average fluorescence lifetime of 1.38 ± 0.02 ns. The fixed geometry of the cyclic amino unit may suppress internal conversion followed by vibrational relaxation as the only deactivation pathway for the first singlet excited state, and we therefore observe fluorescence for compound **13**. Similarly, the fluorescence quantum yield, ϕ_f, for *seco*-porphyrazine **14** was determined to be 0.07 ± 0.01 with an average fluorescence lifetime of 1.35 ± 0.02 ns. More importantly, **14** turns out to be the *seco*-porphyrazine with the best singlet oxygen photosensitizing ability reported so far.[17,18] The quantum yield, ϕ_Δ, of the singlet oxygen formation was determined to be 0.74. This final result correlates well with the assumption (vide supra) that due to the rigid cyclic amide-unit the major deactivation pathways for the first singlet and triplet excited states of *seco*-pz **14** are intersystem crossing and quenching of the triplet state by ground-state oxygen with a minor contribution of fluorescence.

Conclusions

In summary, novel five- and seven-membered ring appended aminoporphyrazines have been prepared and their reactivities studied. Cyclic voltammetry measurements have shown that the rigid organization of the peripheral amino groups renders the seven-membered ring family of macrocycles more electron rich than acyclic analogues, thus making them an intriguing target for the development of new molecule based metals and magnets. In addition, oxidative cleavage of the cyclic amino-pz unit in **13** to give **14** results in the *seco*-porphyrazine with the highest singlet oxygen quantum yield reported so far ($\phi_\Delta = 0.74$). Such compounds could potentially be used as agents for diagnosis and therapy, and further work is currently in progress.

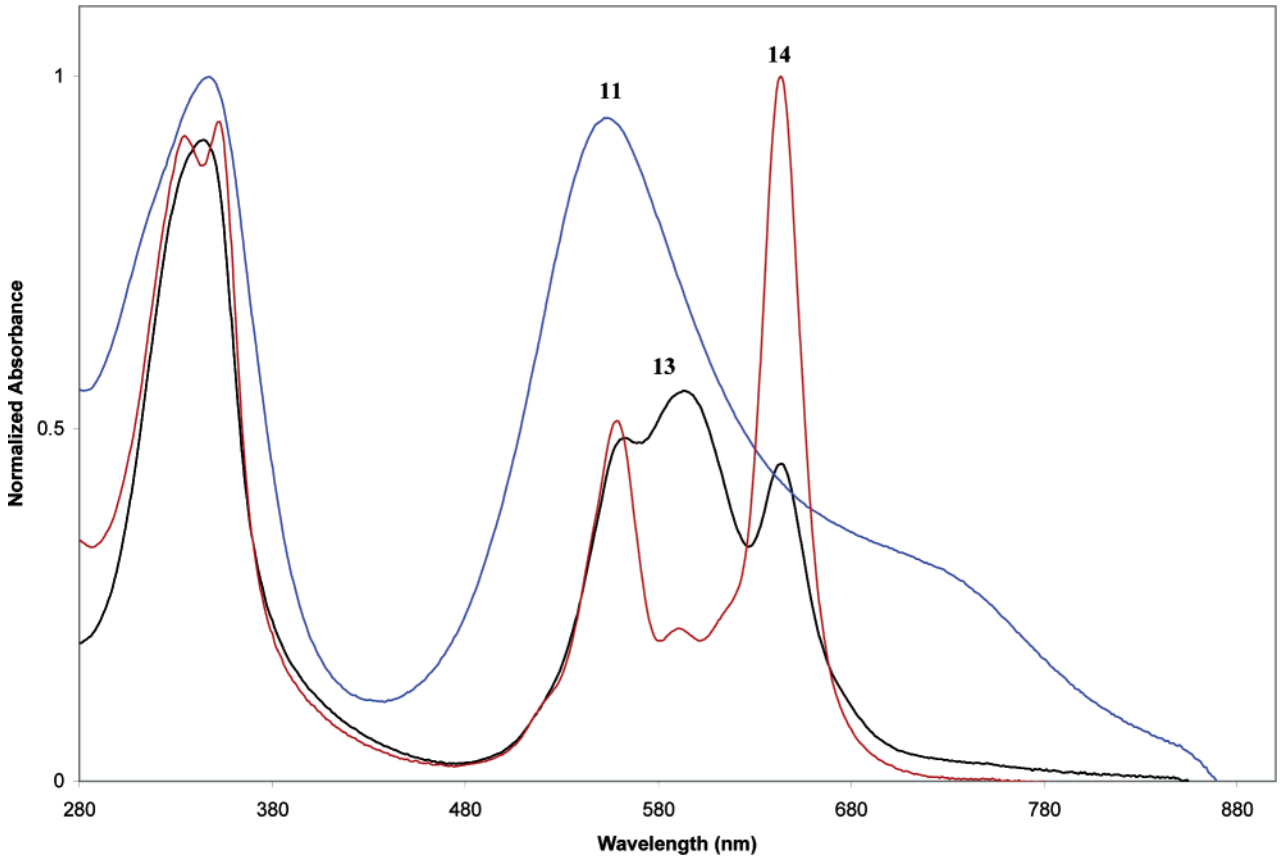

FIGURE 3. Normalized UV−vis spectra of porphyrazines **11**, **13**, and **14** in CH_2Cl_2.

Experimetal Section

General Procedures. All reactions were conducted in oven- or flame-dried glassware. Hexanes refers to the petroleum fraction bp 40−60 °C. Solvents used for reactions were distilled prior to use: DMF [predried over BaO, distilled from alumina (activity I)]; dichloromethane (from CaH_2); butanol (from Mg). All other reagents were used as commercially supplied. TLC was carried out on precoated silica gel 60 F_{254} plates. Chromatography refers to flash chromatography on silica gel 60, 40−60 μm (eluants are given in parentheses). 3,4-Dicyano-1,2,5-selenodiazole (**1**),[9] 2,3-dipropylmaleonitrile (**2**),[11] 2,3-dicyano-5,7-dimethyl-6*H*-1,4-diazepine (**8**),[15] and 2,3-dicyano-4,5,6,7-tetrahydro-5,7-dimethyl-1*H*-1,4-diazepine (**9**)[15] were prepared according to literature procedures. Cyclic voltammetry data were recorded with a computer-controlled potentiostat. A three-electrode configuration was employed: a platinum disk working electrode, a silver wire counter electrode, and a silver−silver chloride reference electrode. Measurements were made in CH_2Cl_2, freshly distilled from CaH_2, with $Bu_4N{\cdot}PF_6$ as the supporting electrolyte. All measurements were calibrated by addition of ferrocene as an internal reference, and $E_{1/2}$ values were calculated from $(E_{pa} + E_{pc})/2$ at a scan rate of 110 mVs^{-1}.

Steady-State Absorption and Emission Measurements. Electronic absorption spectra were recorded on a dual beam UV−vis spectrometer with fixed 2 nm resolution. Fluorescence emission and excitation spectra were recorded on a spectrometer with xenon arc lamp excitation and a photon-counting detection system. Fluorescence quantum yields were determined by the comparative method[19] using chlorophyll a in ether ($\phi_F = 0.32 \pm 0.05$[20]) as the reference standard. To avoid unwanted reabsorption effects, all fluorescence measurements were recorded on solutions with Q-band absorbances of less than 0.1 in 1 cm path length cells.

Time-Resolved Fluorescence Measurements. Fluorescence decays were recorded using a time-correlated single-photon counting with a femtosecond mode-locked tunable Ti:sapphire laser for excitation.[21,22] The output was frequency-doubled with an angle tuned BBO crystal to excite the samples at 400 nm, and the laser repetition rate of 76 MHz was reduced to 3.8 MHz using a pulse picker. The fluorescence decays were measured at 660 nm using a monochromator. The detector was a cooled microchannel plate operated at −3.4 kV. Instrumental response functions were typically 230 ps full-width half-maximum, and fluorescence decay analysis was performed on reconvolution software.

Singlet-Oxygen Measurements. Singlet oxygen quantum yields were measured on a nanosecond flash photolysis apparatus. Excitation light at 570 nm and a repetition rate of 10 Hz was provided by a tuneable pulsed dye laser that was pumped by the frequency doubled output of a Nd:YAG laser. Singlet oxygen phosphorescence decays were detected at 1270 nm using a liquid nitrogen-cooled germanium detector. The signal from the detector was averaged and recorded by a digital storage oscilloscope. The quantum yield of singlet oxygen formation, ϕ_Δ, was calculated relative to chlorophyll a in toluene as the reference sample ($\phi_\Delta = 0.6$[23]), with the effect of laser saturation eliminated by measuring the intensity of singlet oxygen phosphorescence as a function of laser power.

Mg[pz(selenodiazole)Pr$_6$] (3). A mixture of butanol (10 mL), Mg (21 mg, 0.86 mmol), and I_2 (1 small crystal) was heated to reflux for 12 h under N_2. The suspension was cooled, 3,4-dicyano-1,2,5-selenodiazole (**1**) (46 mg, 0.25 mmol) and dipropylmaleonitrile **2** (0.29 g, 1.8 mmol) were added simultaneously, and the mixture was further heated at reflux for 12 h. The deep blue suspension was allowed to cool and was filtered (Celite), and the solids were washed with CH_2Cl_2. Rotary evaporation and chromatography ($CHCl_3$/MeOH 49:1) gave Mg-pz **3** (72 mg, 42%) as a dark blue solid: R_f 0.7 ($CHCl_3$/MeOH 9:1); mp 57−67 °C ($CHCl_2$); IR (CH_2Cl_2) ν_{max} 1573, 1463, 1008, 950 cm^{-1}; UV−vis (CH_2Cl_2) λ_{max} (log ϵ) 346 (4.52), 599 (4.19), 650 (4.12) nm; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 3.98−3.74 (m, 12H), 2.53−2.19 (m, 12H), 1.42−1.20 (m, 18H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 169.0, 159.3, 158.4, 157.7, 145.3, 144.7, 142.6, 141.0, 28.7, 28.4, 27.3, 25.8, 25.3, 15.04, 15.00, 14.3; MS (FAB) *m*/*z* 695 $[M + H]^+$; HRMS (FAB) calcd for $C_{34}H_{42}MgN_{10}Se$ $[M^{\bullet+}]$ 694.2610, found $[M^{\bullet+}]$ 694.2603. **Crystal data for 3:** $C_{34}H_{42}MgN_{10}Se{\cdot}H_2O{\cdot}CH_2Cl_2$, M = 797.0, triclinic, $P\bar{1}$ (no. 2), a = 9.226(1) Å, b = 13.660(2) Å, c = 16.894(4) Å, α = 70.44(1)°, β = 75.67(1)°, γ = 87.19(1)°, V = 1942.5(6) Å^3, Z = 2, D_c = 1.363 g cm^{-3}, μ(Cu Kα) = 30.7 cm^{-1}, T = 203 K, purple reflecting needle shaped crystals; 5205 independent measured reflections, F^2 refinement, R_1 = 0.077, wR_2 = 0.153, 3183 independent observed absorption corrected reflections [$|F_o| > 4\sigma(|F_o|)$, $2\theta \le 115°$], 468 parameters. CCDC 200086.

H$_2$[pz(selenodiazole)Pr$_6$] (4). TFA (2 mL) was added to porphyrazine **3** (10 mg, 14 μmol) and the mixture stirred at 20 °C for 15 min under N_2. The solution was poured onto ice and water (30 mL), neutralized with $NaHCO_3$, and filtered. The purple precipitate was taken up in CH_2Cl_2 (250 mL), dried ($MgSO_4$), rotary evaporated, and chromatographed ($CHCl_3$) to give porphyrazine **4** (7.0 mg, 70%) as a dark purple solid: R_f 0.7 ($CHCl_3$/MeOH 49:1); mp 297−98 °C ($CHCl_3$); IR (film) ν_{max} 1523, 1462, 1290, 1200 cm^{-1}; UV−vis (CH_2Cl_2) λ_{max} (log ϵ) 346 (4.81), 552 (4.60), 653 (4.87) nm; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 4.08−3.93 (m, 8H), 3.79 (t, J = 7.6 Hz, 4H), 2.42−2.20 (m, 12H), 1.32−1.20 (m, 18H), −2.56 (br s, 2H); MS (FAB) *m*/*z* 673 $[M + H]^+$; HRMS (FAB) calcd for $C_{34}H_{45}N_{10}Se$ $[M + H]^+$ 673.2994, found $[M + H]^+$ 673.2994. Anal. Calcd for $C_{34}H_{44}N_{10}Se$: C, 60.79; H, 6.60; N, 20.85. Found: C, 60.64; H, 6.45; N, 20.98.

Mg[pz(pyrazine)Pr$_6$] (6a). H_2S was bubbled through a solution of Mg-pz **3** (15 mg, 22 μmol) in pyridine (7.5 mL) for 1 min at 20 °C. The solvent was immediately distilled off under reduced pressure, and the resulting blue oil was taken up in CH_2Cl_2 (3 mL). To this solution was immediately added a solution of 9,10-phenanthrenequinone (5.4 mg, 26 μmol) in CH_2Cl_2 (1.5 mL), and the resulting mixture was stirred for 3 h at 20 °C under N_2. Rotary evaporation and repeated chromatography ($CHCl_3$/MeOH 49:1; hexanes/EtOAc 9:1; $CHCl_3$; $CHCl_3$/MeOH 49:1) gave porphyrazine **6a** (15 mg, 88%) as a dark blue solid: R_f 0.7 (EtOAc); IR (film) ν_{max} 1722, 1460, 1363, 1011 cm^{-1}; UV−vis (CH_2Cl_2) λ_{max} (log ϵ) 355 (4.75), 627 (4.59) nm; ^{1}H NMR (pyridine-d_5, 270 MHz) δ 10.42 (dd, J = 7.2, 2.1 Hz, 2H), 8.87 (d, J = 7.2 Hz, 2H), 7.93 (m, 4H), 4.32 (t, J = 7.6 Hz, 4H), 4.12 (m, 8H), 2.68 (m, 4H), 2.57 (m, 8H), 1.41 (t, J = 7.3 Hz, 12H), 1.40 (t, J = 7.2 Hz, 6H); ^{13}C NMR (pyridine-d_5, 100 MHz) δ 161.3, 161.2, 161.0, 146.8, 146.5, 146.4, 143.7, 134.1, 133.2, 132.2, 130.0, 128.8, 30.6, 30.4, 30.3, 27.8, 27.6, 16.79, 16.78, 16.7; MS (FAB) *m*/*z* 791 $[M^{\bullet+}]$; HRMS (FAB) calcd for $C_{48}H_{50}N_{10}Mg$ $[M^{\bullet+}]$ 790.4070, found $[M^{\bullet+}]$ 790.4068.

H$_2$[pz(pyrazine)Pr$_6$] (7). H_2S was bubbled through a solution of Mg-pz **3** (10 mg, 14 μmol) and 2,3-butanedione (0.10 g, 1.16 mmol) in pyridine (5 mL) for 1 min at 20 °C. Rotary evaporation and chromatography ($CHCl_3$/MeOH 49:1; hexanes/EtOAc 9:1−2.3:1) gave porphyrazine **6b** (9.5 mg, 99%) as a dark blue solid: R_f 0.3 ($CHCl_3$/MeOH 49:1); mp 223−27 °C ($CHCl_3$); IR (film) ν_{max} 1722, 1462, 1009 cm^{-1}; UV−vis (CH_2Cl_2) λ_{max} (log ϵ) 349 (4.47), 587 sh (4.11), 610 (4.27), 627 (4.29)

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nm; MS (FAB) *m/z* 669 $[M + H]^+$; HRMS (FAB) calcd for $C_{38}H_{49}MgN_{10}$ $[M + H]^+$ 669.3992, found $[M + H]^+$ 669.3985. TFA (2 mL) was added to porphyrazine **6b** (4.0 mg, 6 μmol) and the mixture stirred at 20 °C for 20 min under N_2. The solution was poured onto ice and water (30 mL), neutralized with $NaHCO_3$, and filtered. The purple precipitate was taken up in CH_2Cl_2 (250 mL), dried ($MgSO_4$), rotary evaporated, and chromatographed ($CHCl_3$/MeOH 49:1) to give porphyrazine **7** (3.0 mg, 78%) as a dark purple solid: R_f 0.5 ($CHCl_3$/MeOH 9:1); mp 298 °C dec; IR (film) ν_{max} 1734, 1462, 1333, 1196, 1108 cm^{-1}; UV−vis (CH_2Cl_2) λ_{max} (log ϵ) 340 (4.74), 565 (4.57), 634 (4.71) nm; ^1H NMR ($CDCl_3$, 300 MHz) δ 4.19 (t, J = 7.7 Hz, 4H), 4.06 (t, J = 7.4 Hz, 4H), 3.85 (t, J = 7.4 Hz, 4H), 3.21 (s, 6H), 2.48−2.24 (m, 12H), 1.40−1.20 (m, 18H), −2.36 (s, 2H); MS (FAB) *m/z* 647 $[M + H]^+$; HRMS (FAB) calcd for $C_{38}H_{51}N_{10}$ $[M + H]^+$ 647.4298, found $[M + H]^+$ 647.4297. Anal. Calcd for $C_{38}H_{50}N_{10}$: C, 70.56; H, 7.79; N, 21.65. Found: C, 70.74; H, 7.62; N, 21.47.

2,3-Dicyano-4,5,6,7-tetrahydro-1,4,5,7-tetramethyl-1*H*-1,4-diazepine (10). Tetrahydrodiazepine **9** (0.53 g, 3.0 mmol) in DMF (30 mL) was added rapidly to a suspension of NaH (60% in mineral oil, 0.27 g, 6.6 mmol) in DMF (30 mL), and the mixture was stirred at 0 °C for 1 h. Me_2SO_4 (0.66 mL, 7.0 mmol) in DMF (10 mL) was added dropwise within 1 h and the suspension further stirred at 0 °C for 2 h. The reaction mixture was poured onto ice and water (200 mL) and extracted with CH_2Cl_2 (3 × 100 mL), and the combined organic layers were dried ($MgSO_4$). Rotary evaporation and chromatography (hexanes/EtOAc 2.3:1) gave dinitrile **10** (0.53 g, 87%) as a colorless solid: R_f 0.2 (hexanes/EtOAc 2.3:1); mp 52 °C (EtOAc); IR (film) ν_{max} 2205, 1594, 1562, 1395, 1091 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 3.55−3.42 (m, 2H), 2.79 (s, 6H), 1.84−1.74 (m, 1H), 1.47−1.36 (m, 1H), 1.16 (d, J = 6.8 Hz, 6H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 115.6, 114.9, 56.0, 37.9, 34.4, 19.4; MS (EI) *m/z* 204 $[M^{\bullet+}]$; HRMS (EI) calcd for $C_{11}H_{16}N_4$ $[M^{\bullet+}]$ 204.1375, found $[M^{\bullet+}]$ 204.1373.

H_2[pz(diazepine)$_4$] (11). Butanol (200 mL), Mg (48 mg, 2.0 mmol), and I_2 (1 small crystal) were heated to reflux for 12 h under N_2. The suspension was cooled, diazepine **10** (0.40 g, 2.0 mmol) added, and the mixture further heated at reflux for 16 h. The deep blue suspension was allowed to cool and was filtered (Celite), and the solids were washed with CH_2Cl_2. After rotary evaporation, the dark blue residue was filtered through silica (hexanes/EtOAc 1:1), rotary evaporated, and dissolved in TFA (10 mL). After 30 min at 20 °C under N_2, the mixture was poured onto ice and water (50 mL), neutralized with 4 M NaOH, and filtered. The purple precipitate was taken up in CH_2Cl_2 (10 mL), dried ($MgSO_4$), rotary evaporated, and chromatographed (hexanes/EtOAc 2.3:1) to give porphyrazine **11** (0.10 g, 25%) as a dark purple solid: R_f 0.7 (EtOAc); mp 300 °C dec; IR (film) ν_{max} 1565, 1440, 1414, 1300, 1069 cm^{-1}; UV−vis (CH_2Cl_2) λ_{max} (log ϵ) 350 (4.74), 551 (4.75) nm; ^1H NMR ($CDCl_3$, 300 MHz) δ 4.28−3.60 (br m, 32 H), 2.20−1.93 (br m, 8H), 1.60−1.40 (m, 24 H), −1.45 (s, 2H); MS (FAB) *m/z* 819 $[M^{\bullet+}]$; HRMS (FAB) calcd for $C_{44}H_{67}N_{16}$ $[M + H]^+$ 819.5735, found $[M + H]^+$ 819.5747. Anal. Calcd for $C_{44}H_{66}N_{16}$: C, 64.52; H, 8.12; N, 27.36. Found: C, 64.67; H, 8.15; N, 27.27.

H_2[pz(diazepine)Pr$_6$] (12). Butanol (60 mL), Mg (48 mg, 2.0 mmol), and I_2 (1 small crystal) were heated to reflux for 12 h under N_2. The suspension was cooled, dipropylmaleonitrile **2** (0.32 g, 2.0 mmol) and diazepine **10** (58 mg, 0.28 mmol) were added simultaneously, and the mixture was further heated at reflux for 16 h. The deep blue suspension was allowed to cool and was filtered (Celite), and the solids were washed with CH_2Cl_2. Rotary evaporation and chromatography (hexanes.EtOAc 19:1) gave the Mg-pz [R_f 0.7 (hexanes/EtOAc 2.3:1); UV−vis (CH_2Cl_2) λ_{max} 351, 594 nm; MS (FAB) *m/z* 714 $[M - H]^+$. The Mg-porphyrazine was dissolved in TFA (2 mL) and, after 30 min at 20 °C under N_2, poured onto ice and water (50 mL), neutralized with 4 M NaOH, and filtered. The purple precipitate was taken up in CH_2Cl_2 (5 mL), dried ($MgSO_4$), rotary evaporated, and chromatographed (hexanes/EtOAc 19:1) to give porphyrazine **12** (21 mg, 11%) as a dark purple solid: R_f 0.9 (hexanes/EtOAc 2.3:1); mp 105 °C (EtOAc); IR (film) ν_{max} 3289, 1583, 1461, 1141 cm^{-1}; UV−vis (CH_2Cl_2) λ_{max} (log ϵ) 340 (4.68), 566 (4.63), 630 (4.27) nm; ^1H NMR ($CDCl_3$, 300 MHz) δ 4.30−4.10 (br m, 8H), 3.95−3.80 (m, 12H), 2.44−2.26 (m, 12H), 2.20−2.10 (m, 2H), 1.60 (d, J = 6.5 Hz, 6H), 1.36−1.25 (m, 18H), −1.97 (s, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 155.9, 149.1, 143.5, 142.7, 141.7, 58.5, 41.8, 38.5, 31.0, 29.8, 28.3, 28.1, 25.7, 25.6, 20.9, 14.8; MS (FAB) *m/z* 692 $[M^{\bullet+}]$; HRMS (FAB) calcd for $C_{41}H_{60}N_{10}$ $[M^{\bullet+}]$ 692.5002, found $[M^{\bullet+}]$ 692.4982. **Crystal data for 12:** $C_{41}H_{60}N_{10}$, M = 693.0, triclinic, $P\bar{1}$ (no. 2), a = 12.196(2) Å, b = 16.856(3) Å, c = 23.660(5) Å, α = 97.10(2)°, β = 104.64(2)°, γ = 109.94(1)°, V = 4305(2) Å^3, Z = 4 (two crystallographically independent molecules), D_c = 1.069 g cm^{-3}, μ(Cu Kα) = 5.07 cm^{-1}, T = 293 K, purple reflecting flattened needle shaped crystals; 9447 independent measured reflections, F^2 refinement, R_1 = 0.088, wR_2 = 0.255, 4525 independent observed reflections [$|F_o| > 4\sigma(|F_o|)$, $2\theta \leq 120°$], 980 parameters. CCDC 200087.

Zn[pz(diazepine)Pr$_6$] (13). Porphyrazine **12** (50 mg, 72 μmol) and anhydrous $Zn(OAc)_2$ (13 mg, 72 μmol) in dry DMF (10 mL) were heated at 80 °C for 10 h under N_2. The mixture was allowed to cool and was filtered (Celite), and the solids were washed with CH_2Cl_2. Rotary evaporation and chromatography (hexanes/EtOAc 19:1) gave Zn-pz **13** (36 mg, 66%) as a dark blue solid: R_f 0.7 (hexanes/EtOAc 9:1); mp 151 °C (EtOAc); IR (film) ν_{max} 1580, 1462, 1374, 1147 cm^{-1}; UV−vis (CH_2Cl_2) λ_{max} (log ϵ) 344 (4.72), 596 (4.61), 648 (4.18) nm; ^1H NMR (pyridine-d_5, 300 MHz) δ 5.03−4.89 (br m, 2H), 4.31 (s, 6H), 4.22−3.99 (m, 12H), 2.61−2.39 (m, 12H), 2.05−1.86 (m, 2H), 1.49 (d, J = 6.6 Hz, 6H), 1.43−1.21 (m, 18H); ^{13}C NMR (pyridine-d_5, 75 MHz) δ 159.5, 158.9, 158.5, 157.7, 145.2, 144.5, 144.4, 138.3, 59.7, 43.1, 39.2, 31.3, 30.0, 29.9, 27.4, 27.3, 22.2, 16.3; MS (FAB) *m/z* 754 $[M^{\bullet+}]$; HRMS (FAB) calcd for $C_{41}H_{58}N_{10}Zn$ $[M^{\bullet+}]$ 754.4137, found $[M^{\bullet+}]$ 754.4117.

Zn-seco[pz(diazepine)Pr$_6$] (14). $KMnO_4$ (7.5 mg, 47 μmol) was added to Zn-pz **13** (36 mg, 47 μmol) in CH_2Cl_2 (10 mL), and the mixture was stirred at 20 °C for 8 h. The resulting purple solution was filtered (Celite) and washed with CH_2Cl_2. Rotary evaporation and chromatography (hexanes/EtOAc 19:1) gave zinc-*seco*-pz **14** (16 mg, 44%) as a dark purple solid: R_f = 0.6 (EtOAc); mp 174 °C (EtOAc); IR (CH_2Cl_2) ν_{max} 1635, 1454, 1248, 1113 cm^{-1}; UV−vis (CH_2Cl_2) λ_{max} (log ϵ) 335 (4.73), 352 (4.74), 559 (4.47), 592 (4.12), 644 (4.76) nm; ^1H NMR (pyridine-d_5, 300 MHz) δ 4.19−3.89 (m, 12H), 3.64−3.50 (m, 2H), 3.41 (s, 6H), 2.56−1.95 (m, 14H), 1.42−1.13 (m, 24 H); ^{13}C NMR (pyridine-d_5, 75 MHz) δ 169.4, 157.7, 157.3, 156.1, 153.4, 146.0, 144.0, 142.4, 57.3, 32.8, 31.3, 29.9, 29.8, 29.4, 27.7, 27.4, 27.3, 27.2, 21.2, 16.3, 16.1; MS (FAB) *m/z* 787 $[M - H]^+$; HRMS (FAB) calcd for $C_{41}H_{59}N_{10}O_2Zn$ $[M + H]^+$ 787.4114, found $[M + H]^+$ 787.4153. Anal. Calcd for $C_{41}H_{58}N_{10}O_2Zn$: C, 62.46; H, 7.42; N, 17.77. Found: C, 62.37; H, 7.58; N, 17.65.

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Supporting Information Available: Copies of ^1H NMR spectra of **6a**, **10**, and **12**; ^{13}C NMR spectra of **3**, **6a**, **10**, **12**, and **13**; a fluorescence spectrum of **14**; and ORTEPS and tables of **3** and **12**. This material is available free of charge via the Internet at http://pubs.acs.org.

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