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Peripherally Metalated Secoporphyrazines: A New Generation of Photoactive Pigments

Efstathia G. Sakellariou,[†] Antonio Garrido Montalban,[†] Hubert G. Meunier,[‡] Garry Rumbles,[†] David Phillips,[†] Richard B. Ostler,[†] Klaus Suhling,[†] Anthony G. M. Barrett,*[,†] and Brian M. Hoffman*[,§]

Departments of Chemistry, Imperial College of Science, Technology and Medicine, South Kensington, London, SW7 2AY, U.K., Northwestern University, Evanston, Illinois 60208, and Assumption College, Worcester, Massachusetts 01609

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Base-catalyzed cross condensation of dipropylmaleonitrile **1** with bis(dimethylamino)maleonitrile **2** in an equimolar ratio afforded the porphyrazines **3a**, **4a**, **5a**, **6a** and **7a**. Subsequent demetalation of **5a** with TFA followed by remetalation with $Zn(OAc)_2$ gave ligand **5c** in good yield. Compound **5c** was, in turn, selectively oxidized and further peripherally functionalized using $Pt(PhCN)_2Cl_2$ and $PdCl_2$ to yield the novel seco solitaire porphyrazines **10a** and **10b**. The photophysical profiles of the seco solitaire porphyrazines **10a** and **10b** were evaluated by means of absorption, emission, and transient absorption spectroscopy. The new pigments **10a** and **10b** were found to be photochemically more stable than the solitaire complexes **3d** and **3e** and mediated the generation of singlet oxygen with quantum yields of 0.59 and 0.45, respectively.

Introduction

The diverse chemical reactivity of a macrocyclic structure such as a tetraazaporphyrin (porphyrazine, pz) includes, but it is not limited to, metalation of the core, peripheral functionalization, as well as selective oxidative cleavage of one or more of the pyrrole rings to yield secoporphyrazines.[1,2] The new ligands and metal complexes derived thereof are of potential interest in areas such as nonlinear optics,[3] electron transfer,[4] and photodynamic therapy.[5] In particular, bis(dimethylamino)porphyrazines have proved to be extremely versatile since they can be converted not only to seco analogues but also to new solitaire complexes upon peripheral metalation.[6] In both cases, the new pigments were shown to possess interesting photophysical and photochemical properties such as fluorescence[7] and efficient singlet oxygen generation.[8]

In a continuation of our efforts in this field, the synthesis of the first macrocycles **10a** and **10b** containing both an oxidatively cleaved pyrrole ring and a peripherally coordinated metal species is reported. In addition, full experimental data on the synthesis of solitaire complexes **3d** and **3e** are described. Moreover, we demonstrate that, upon metalation, the photophysical properties of the macrocycles change. Hence, a photophysical evaluation and comparison of the new secoporphyrazines **10a** and **10b** as well as their corresponding precursors with **3c**−**e** and **12** is herein also reported.

Experimental Section

General Procedures. All reactions were conducted in oven- or flame-dried glassware. Reaction temperatures reported refer to external bath temperatures. Hexanes refers to the petroleum fraction

* Authors to whom correspondence should be addressed. E-mail: agmb@ic.ac.uk (A.G.M.B.); bmh@northwestern.edu (B.M.H.).
[†] Imperial College of Science, Technology and Medicine.
[‡] Assumption College.
[§] Northwestern University.

(1) Andersen, K.; Anderson, M.; Anderson, O. P.; Baum, S.; Baumann, T. F.; Beall, L. S.; Broderick, W. E.; Cook, A. S.; Eichhorn, D. M.; Goldberg, D.; Hope, H.; Jarrell, W.; Lange, S. J.; McCubbin, Q. J.; Mani, N. S.; Miller, T.; Garrido Montalban, A.; Rodriguez-Morgade, M. S.; Lee, S.; Nie, H.; Olmstead, M. M.; Sabat, M.; Sibert, J. W.; Stern, C.; White, A. J. P.; Williams, D. B. G.; Williams, D. J.; Barrett, A. G. M.; Hoffman, B. M. *J. Heterocycl. Chem.* **1998**, *35*, 1013.
(2) Michel, S. L. J.; Baum, S.; Barrett, A. G. M.; Hoffman, B. M. *Progress in Inorganic Chemistry*; Karlin, K. D., Ed.; J. Wiley & Sons: New York, 2001.
(3) De la Torre, G.; Vazquez, P.; Agullo-Lopez, F.; Torres, T. *J. Mater. Chem.* **1998**, *8*, 1671.
(4) Lehn, J. M. *Supramolecular Chemistry*; VCH: Weinheim, 1995.
(5) Ali, H.; Van Lier, J. E. *Chem. Rev.* **1999**, *99*, 2379.
(6) Lange, S. J.; Nie, H.; Stern, C. L.; Barrett, A. G. M.; Hoffman, B. M. *Inorg. Chem.* **1998**, *37*, 6435.
(7) Sakellariou, E. G.; Garrido Montalban, A.; Meunier, H. G.; Ostler, R. B.; Rumbles, G.; Barrett, A. G. M.; Hoffman, B. M. *Photochem. Photobiol. A* **2000**, *136*, 185.
(8) Garrido Montalban, A.; Meunier, H. G.; Ostler, R. B.; Barrett, A. G. M.; Hoffman, B. M.; Rumbles, G. *J. Phys. Chem. A* **1999**, *103*, 4352.

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bp 40−60 °C. Butanol used for reactions was distilled from Mg prior to use, whereas all other reagents were used as commercially supplied. TLC was carried out on E. Merck precoated silica gel 60 F_{254} plates. Plates were visualized using UV radiation (254 nm). Chromatography refers to flash chromatography on E. Merck silica gel 60, 40−60 μm (eluants are given in parentheses).

Steady-State Absorption and Emission Measurements. Electronic absorption spectra were recorded on a dual beam UV/vis spectrometer (Perkin-Elmer Lambda-2) 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 (Instruments SA Fluoromax). Fluorescence quantum yields were determined by the comparative method[9] using chlorophyll a in ether ($\phi_F = 0.32 \pm 0.05$) 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 spectrometer with a femtosecond mode-locked tunable Ti:sapphire laser (Coherent) for excitation.[10,11] The output was frequency-doubled to excite the samples at 355 nm, and the laser repetition rate of 76 MHz was reduced to 3.8 MHz using a pulse picker (APE). The fluorescence decays were measured at 663 nm using a monochromator. The detector was a cooled microchannel plate operated at −3.4 kV (Photek). Instrumental response functions were typically 230 ps full-width half-maximum, and fluorescence decay analysis was performed on reconvolution software from IBH.

Triplet-State Measurements. Transient absorption spectra and singlet oxygen quantum yields were measured on a nanosecond, flash photolysis apparatus. Excitation light at 682 nm and a repetition rate of 10 Hz was provided by a tunable dye laser that was pumped by the frequency-doubled output of a Nd:YAG laser. A 75 W xenon lamp was used as the monitor source of white light and was detected through a monochromator using a photomultiplier tube connected to a computer-interfaced digital oscilloscope. Triplet-state quantum yields were determined by the comparative technique[12] using chorophyll a in diethyl ether as the reference standard ($\phi_T = 0.54 \pm 0.01$[13]). Singlet oxygen phosphorescence decays were detected at 1270 nm using a cooled germanium detector (North Coast). The quantum yield of singlet oxygen formation, ϕ_Δ, was calculated relative to chlorophyll a in the toluene as the reference sample ($\phi_\Delta = 0.6$[14]), with the effect of laser saturation eliminated by measuring the intensity of singlet oxygen phosphorescence as a function of laser power.

[[2,3-Bis(dimethylamino)-7,8,12,13,17,18-hexapropylporphyrazinato]zinc(II)]platinum(II) Chloride (3d). $(PhCN)_2PtCl_2$ (55 mg, 0.12 mmol) and Zn−bis(dimethylamino)hexapropylporphyrazine **3c** (81 mg, 0.11 mmol) in dry 1,2-dichloroethane (25 mL) were heated at reflux for 24 h under N_2. Rotary evaporation and chromatography (hexanes:EtOAc, 9:1; $CHCl_3$:MeOH, 9:1) gave porphyrazine **3d** (44 mg, 40%) as a blue solid: mp > 350 °C; R_f 0.35 ($CHCl_3$:MeOH, 9:1); IR (CH_2Cl_2) 2931, 1727, 1464, 1146, 1081, 1019 cm^{-1}; UV−vis (CH_2Cl_2) λ_{max} (log ϵ) 342 (4.82), 578 (4.68), 605 (4.84) nm; ^{1}H NMR (270 MHz, pyridine-d_5) δ 1.21−1.41 (m, 18H), 2.30−2.58 (m, 12H), 3.85−4.11 (m, 12H), 4.51 (s, 12H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.1, 25.3, 25.4, 25.6, 28.2, 29.7, 53.4, 138.7, 145.0, 145.5, 146.2, 153.1, 156.8, 161.9, 162.1; MS (FAB) *m*/*z* 945 $(M - Cl - H)^+$; HRMS (FAB) calcd for $C_{38}H_{54}Cl_2N_{10}PtZn$ $(M^{\bullet+})$ 979.2849, found $(M^{\bullet+})$ 979.2906. Anal. Calcd for $C_{38}H_{54}Cl_2N_{10}PtZn$: C, 46.46; H, 5.54; N, 14.26. Found: C, 46.42; H, 5.57; N 14.46.

[[2,3-Bis(dimethylamino)-7,8,12,13,17,18-hexapropylporphyrazinato]zinc(II)]palladium(II) Chloride (3e). Porphyrazine **3c** (42 mg, 0.06 mmol), $CHCl_3$ (4.2 mL), CH_3CN (1.4 mL), and $PdCl_2$ (12 mg, 0.07 mmol) were heated to reflux for 8 h under N_2. Rotary evaporation and chromatography (hexanes:EtOAc, 9:1; $CHCl_3$:MeOH, 9:1) gave porphyrazine **3e** (17 mg, 32%) as a blue solid: mp 235−300 °C dec; R_f 0.35 ($CHCl_3$:MeOH, 9:1); IR (CH_2Cl_2) 2928, 1731, 1464, 1264, 1080 cm^{-1}; UV−vis (CH_2Cl_2) λ_{max} (log ϵ) 342 (4.81), 578 (4.65), 605 (4.83) nm; ^{1}H NMR (270 MHz, pyridine-d_5) δ 1.14−1.42 (m, 18H), 2.35−2.55 (m, 12H), 3.85−4.15 (m, 12H), 3.98 (s, 12H); MS (FAB) *m*/*z* 894 $(M^{\bullet+})$, 857 $(M - Cl - H)^+$, 821 $(M - 2Cl - 2H)^+$; HRMS (FAB) calcd for $C_{38}H_{54}N_{10}PdZn$ $(M + H - 2Cl)^+$ 821.2937, found $(M + H - 2Cl)^+$ 821.2934.

2,3,7,8-Tetrakis(dimethylamino)-12,13,17,18-tetrapropylporphyrazine (4b) and 2,3,12,13-Tetrakis(dimethylamino)-7,8,17,-18-tetrapropylporphyrazine (5b). BuOH (20 mL), Mg (0.3 g, 12 mmol), and I_2 (2 small crystals) were heated to reflux for 12 h under N_2. The suspension was cooled, dipropylmaleonitrile **1** (0.15 g, 0.93 mmol) and then bis(dimethylamino)maleonitrile **2** (0.15 g, 0.91 mmol) were added, and the reaction mixture was further heated at reflux for 24 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 residue was dissolved in TFA (3 mL) and stirred at 20 °C for 30 min. It was poured onto ice/water (20 mL) and the resulting suspension brought to pH 10 with 1 M NaOH. The aqueous layer was extracted with CH_2Cl_2 until the washings were colorless. The combined organic layers were dried ($MgSO_4$) and concentrated to yield a dark purple residue. This residue was further purified by chromatography (gravity, CH_2Cl_2). The purification was repeated twice and gave the isolated free base porphyrazines in the order **3b**[6] (16%), **5b** (10%), **4b** (11%), **7b**[15] (21%), and **6b**.[6]

2,3,7,8-Tetrakis(dimethylamino)-12,13,17,18-tetrapropylporphyrazine (4b): dark blue solid; mp 110−120 °C; R_f 0.7 (hexanes:EtOAc, 7:3); IR (CH_2Cl_2) 3300, 2929, 1730, 1588, 1512, 1387, 1085 cm^{-1}; UV−vis (CH_2Cl_2) λ_{max} (log ϵ) 337 (4.53), 563 (br, 4.14) nm; ^{1}H NMR (270 MHz, pyridine-d_5) δ 1.30 (t, $J = 7.3$ Hz, 6H), 1.34 (t, $J = 7.3$ Hz, 6H), 2.34 (sextet, $J = 7.3$ Hz, 4H), 2.45 (sextet, $J = 7.3$ Hz, 4H), 3.76 (s, 12H), 3.79−3.94 (m, 8H), 3.97 (s, 12H); ^{13}C NMR (75 MHz, pyridine-d_5) δ 15.8, 26.7, 26.8, 29.2, 30.8, 44.8, 45.8, 134.1, 141.7, 143.1; MS (FAB) *m*/*z* 654 $(M^{\bullet+})$; HRMS (FAB) calcd for $C_{36}H_{54}N_{12}$ $(M^{\bullet+})$ 654.4594, found $(M^{\bullet+})$ 654.4588.

2,3,12,13-Tetrakis(dimethylamino)-7,8,17,18-tetrapropylporphyrazine (5b): bright purple solid; mp 140−165 °C; R_f 0.8 (hexanes:EtOAc, 7:3); IR (CH_2Cl_2) 3273, 2929, 1722, 1584, 1383, 1139, 1079 cm^{-1}; UV−vis (CH_2Cl_2) λ_{max} (log ϵ) 336 (4.71), 537 (4.46), 625 (sh) nm; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.26 (t, $J =$ 7.5 Hz, 12H), 2.27 (sextet, $J = 7.5$ Hz, 8H), 3.81 (t, $J = 7.5$ Hz,

(9) Williams, A. J. R. *Analyst* **1983**, *108*, 1067.
(10) O'Connor, D. V.; Phillips, D. *Time-Correlated Single Photon Counting*; Academic Press: London, 1983.
(11) Birch, D. J. S.; Imhof, R. E. *Topics in Fluorescence Spectroscopy: Techniques*; Lakowicz, J., Ed.; Plenum Press: New York, 1991.
(12) Bensasson, R.; Goldschmidt, C. R.; Land, E. J.; Truscott, T. G. *Photochem. Photobiol.* **1978**, *28*, 277.
(13) Redmond, R. W.; Heihoff, K.; Braslavsky, S. E.; Truscott, T. G. *Photochem. Photobiol.* **1987**, *45*, 209.
(14) Wilkinson, F.; Helman, W. P.; Ross, A. B. *J. Phys. Chem. Ref. Data* **1993**, *22*, 113.
(15) Garrido Montalban, A.; Lange, S. J.; Beall, L. S.; Mani, N. S.; Williams, D. J.; White, A. J. P.; Barrett, A. G. M.; Hoffman, B. M. *J. Org. Chem.* **1997**, *62*, 9284.

8H), 3.87 (s, 24H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.8, 25.5, 28.2, 44.4, 136.7, 141.7, 150.4, 152.4; MS (FAB) *m*/*z* 654 ($M^{\bullet+}$); HRMS (FAB) calcd for $C_{36}H_{54}N_{12}$ ($M^{\bullet+}$) 654.4594, found ($M^{\bullet+}$) 654.4593. Anal. Calcd for $C_{36}H_{54}N_{12}$: C, 66.02; H, 8.31; N, 25.66. Found: C, 66.09; H, 8.25; N, 25.49.

[2,3,7,8-Tetrakis(dimethylamino)-12,13,17,18-tetrapropylporphyrazinato]zinc(II) (4c). Porphyrazine **4b** (29 mg, 0.04 mmol) and anhydrous $Zn(OAc)_2$ (8.3 mg, 0.04 mmol) in dry DMF (13 mL) were heated at 100 °C for 16 h under N_2. Rotary evaporation and chromatography (hexanes:EtOAc, 7:3) gave zinc−porphyrazine **4c** (26 mg, 91%) as a dark blue solid: R_f 0.6 (hexanes:EtOAc, 7:3); IR (CH_2Cl_2) 2928, 1724, 1579, 1457, 1379, 1304, 1264 cm^{-1}; UV−vis (CH_2Cl_2) λ_{max} (log ϵ) 337 (4.54), 625 (4.17) nm; ^{1}H NMR (270 MHz, pyridine-d_5) δ 1.30 (t, J = 7.4 Hz, 6H), 1.34 (t, J = 7.4 Hz, 6H), 2.39 (sextet, J = 7.4 Hz, 4H), 2.50 (sextet, J = 7.4 Hz, 4H), 3.84 (s, 12H), 4.03 (s, 12H), 3.90−4.08 (m, 8H); ^{13}C NMR (67.5 MHz, pyridine-d_5) δ 14.9, 25.9, 26.0, 28.49, 28.54, 30.0, 44.1, 45.1, 141.5, 142.8, 154.5, 155.5, 156.6; MS (FAB) *m*/*z* 717 ($M - H)^+$; HRMS (FAB) calcd for $C_{36}H_{52}N_{12}Zn$ ($M^{\bullet+}$) 716.3729, found ($M^{\bullet+}$) 716.3725.

[2,3,12,13-Tetrakis(dimethylamino)-7,8,17,18-tetrapropylporphyrazinato]zinc(II) (5c). Porphyrazine **5b** (27 mg, 0.04 mmol) and anhydrous $Zn(OAc)_2$ (7.8 mg, 0.04 mmol) in dry DMF (10 mL) were heated at 100 °C for 16 h under N_2. Rotary evaporation and chromatography (hexanes:EtOAc, 7:3) gave zinc−porphyrazine **5c** (27 mg, 93%) as a purple-blue solid: mp 170−250 °C; R_f 0.7 (hexanes:EtOAc, 7:3); IR (CH_2Cl_2) 2928, 1722, 1572, 1462, 1383, 1312, 1142, 1081 cm^{-1}; UV−vis (CH_2Cl_2) λ_{max} (log ϵ) 342 (4.77), 628 (4.40) nm; ^{1}H NMR (270 MHz, pyridine-d_5) δ 1.29 (t, J = 7.4 Hz, 12H), 2.39 (sextet, J = 7.4 Hz, 8H), 3.94 (s, 24H), 3.90−3.99 (m, 8H); ^{13}C NMR (67.5 MHz, pyridine-d_5) δ 14.9, 25.9, 28.5, 44.4, 137.5, 142.6, 154.6, 156.8; MS (FAB) *m*/*z* 718 ($M^{\bullet+}$); HRMS (FAB) calcd for $C_{36}H_{52}N_{12}Zn$ ($M^{\bullet+}$) 716.3729, found ($M^{\bullet+}$) 716.3730.

[2,3,7,8-Tetrakis(dimethylamino)-12,13,17,18-tetrapropyl-2-seco-2,3-dioxoporphyrazinato]zinc(II) (8). Porphyrazine **4c** (49 mg, 0.07 mmol) in CH_2Cl_2 and CCl_4 (1:1, 10 mL) was left standing at 20 °C in air while being monitored by TLC. Upon formation of the secoporphyrazine product, the solvent was evaporated and the residue chromatographed (hexanes:EtOAc, 7:3). The starting material **4c** was redissolved under the same conditions, and the same procedure was repeated 3 times until complete conversion to the secoporphyrazine **8** (45 mg, 86%) was achieved: R_f 0.15 (hexanes:EtOAc, 7:3); UV−vis (CH_2Cl_2) λ_{max} 342, 580, 671 nm; ^{1}H NMR (270 MHz, pyridine-d_5) δ 1.14 (t, J = 7.4 Hz, 3H), 1.19−1.38 (m, 9H), 2.10 (sextet, J = 7.4 Hz, 2H), 2.25−2.49 (m, 6H), 3.42 (s, 3H), 3.43 (s, 3H), 3.44 (s, 6H), 3.62 (t, J = 7.4 Hz, 2H), 3.74−3.97 (m, 6H), 3.93 (s, 6H), 4.02 (s, 3H), 4.04 (s, 3H); MS (FAB) *m*/*z* 750 ($M^{\bullet+}$); HRMS (FAB) calcd for $C_{36}H_{53}N_{12}O_2Zn$ ($M + H)^+$ 749.3706, found ($M + H)^+$ 749.3694.

[2,3,12,13-Tetrakis(dimethylamino)-7,8,17,18-tetrapropyl-2-seco-2,3-dioxoporphyrazinato]zinc(II) (9). The same procedure as above, using porphyrazine **5c**, gave porphyrazine **9** (49 mg, 93%) as a dark blue solid: mp 280−320 °C dec; R_f 0.23 (hexanes:EtOAc, 7:3); IR (CH_2Cl_2) 2928, 1724, 1631, 1487, 1461, 1385, 1138 cm^{-1}; UV−vis (CH_2Cl_2) λ_{max} (log ϵ) 330 (4.38), 362 (4.35), 553 (4.15), 661 (3.93) nm; ^{1}H NMR (270 MHz, pyridine-d_5) δ 1.13 (t, J = 7.4 Hz, 6H), 1.23 (t, J = 7.4 Hz, 6H), 2.13 (sextet, J = 7.4 Hz, 4H), 2.27 (sextet, J = 7.4 Hz, 4H), 3.41 (s, 6H), 3.68 (t, J = 7.4 Hz, 4H), 3.78 (t, J = 7.4 Hz, 4H), 3.87 (s, 12H), 4.04 (s, 6H); ^{13}C NMR (67.5 MHz, pyridine-d_5) δ 14.7, 14.9, 25.7, 25.8, 27.9, 28.4, 34.9, 39.6, 44.3, 137.2, 140.7, 143.6, 152.8, 153.0, 153.7, 156.2, 169.4; MS (FAB) *m*/*z* 750 ($M^{\bullet+}$); HRMS (FAB) calcd for $C_{36}H_{51}N_{12}O_2Zn$ ($M - H)^+$ 749.3518, found ($M - H)^+$ 749.3528. Anal. Calcd for $C_{36}H_{52}N_{12}O_2Zn$: C, 57.63; H, 6.98; N, 22.40. Found: C, 57.56; H, 7.07; N, 22.28.

[[2,3,12,13-Tetrakis(dimethylamino)-7,8,17,18-tetrapropyl-2-seco-2,3-dioxoporphyrazinato]zinc(II)]platinum(II) Chloride (10a). Porphyrazine **9** (15 mg, 0.02 mmol) and $(PhCN)_2PtCl_2$ (10 mg, 0.02 mmol) in dry 1,2-dichloroethane (10 mL) were heated to reflux for 2.5 h under N_2. Rotary evaporation followed by chromatography (CH_2Cl_2:MeOH, 19:1) gave porphyrazine **10a** (15 mg, 71%) as a blue solid: mp > 300 °C dec; R_f 0.18 (CH_2Cl_2:MeOH, 19:1); IR (CH_2Cl_2) 2928, 1725, 1640, 1465, 1137, 1085 cm^{-1}; UV−vis (CH_2Cl_2) λ_{max} (log ϵ) 344 (4.72), 581 (4.60), 619 (4.47) nm; ^{1}H NMR (270 MHz, pyridine-d_5) δ 1.16 (t, J = 7.4 Hz, 6H), 1.21 (t, J = 7.4 Hz, 6H), 2.08−2.24 (m, 8H), 3.42 (s, 6H), 3.55−3.65 (m, 8H), 4.05 (s, 6H), 4.37 (s, 12H); ^{13}C NMR (67.5 MHz, pyridine-d_5) δ 14.6, 14.7, 25.3, 25.5, 27.6, 27.9, 35.0, 39.7, 55.7, 138.0, 142.5, 146.4, 151.4, 155.2, 158.7, 162.3, 168.2. Anal. Calcd for $C_{36}H_{52}Cl_2N_{12}O_2PtZn$: C, 42.54; H, 5.16; N, 16.54. Found: C, 42.65; H, 5.00; N, 16.37.

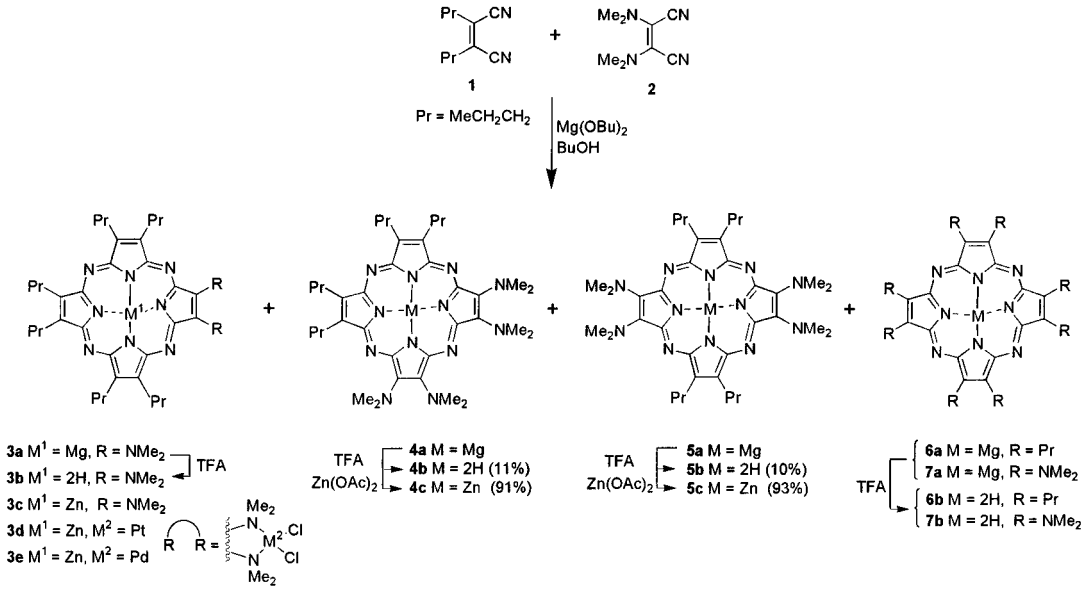
[[2,3,12,13-Tetrakis(dimethylamino)-7,8,17,18-tetrapropyl-2-seco-2,3-dioxoporphyrazinato]zinc(II)]palladium(II) Chloride (10b). Porphyrazine **9** (8.6 mg, 0.01 mmol) and $PdCl_2$ (2.4 mg, 0.01 mmol) in $CHCl_3$:CH_3CN (4:1, 10 mL) were heated to reflux for 2.5 h under N_2. Rotary evaporation followed by chromatography (CH_2Cl_2:MeOH, 19:1) gave porphyrazine **10b** (6.1 mg, 66%) as a dark blue solid: mp > 250 °C dec; R_f 0.17 (CH_2Cl_2:MeOH, 19:1); IR (CH_2Cl_2) 2927, 1717, 1639, 1465, 1134, 1087 cm^{-1}; UV−vis (CH_2Cl_2) λ_{max} (log ϵ) 347 (4.79), 584 (4.61), 631 (4.51) nm; ^{1}H NMR (270 MHz, pyridine-d_5) δ 1.17 (t, J = 7.4 Hz, 6H), 1.27 (t, J = 7.4 Hz, 6H), 2.17 (m, 4H), 2.30 (m, 4H), 3.45 (s, 6H), 3.72 (t, J = 7.5 Hz, 4H), 3.82 (t, J = 7.6 Hz, 4H), 3.91 (s, 12H), 4.08 (s, 6H); ^{13}C NMR (67.5 MHz, pyridine-d_5) δ 14.7, 14.9, 25.7, 25.8, 27.9, 28.4, 34.9, 39.6, 44.3, 137.4, 140.7, 143.6, 152.8, 153.0, 153.7, 156.2, 169.4; MS (FAB) *m*/*z* 856 ($M - 2Cl)^+$; HRMS (FAB) calcd for $C_{36}H_{53}N_{12}O_2PdZn$ ($M - 2Cl + H)^+$ 855.2741, found ($M - 2Cl + H)^+$ 855.2725. Anal. Calcd for $C_{36}H_{52}Cl_2N_{12}O_2PdZn$: C, 48.28; H, 5.85; N, 18.76. Found: C, 48.35; H, 6.00; N, 18.66.

Results and Discussion

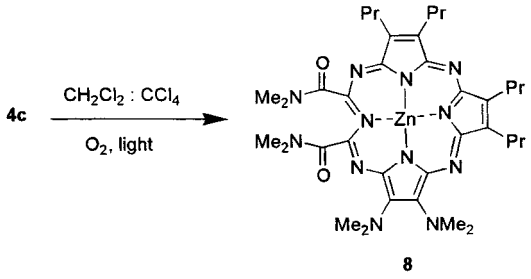
Synthesis. The Linstead[16] crossover macrocyclization of dinitriles **1**[6] and **2**[17] using an excess of **1** and magnesium butoxide in butanol, followed by demetalation with TFA, has previously been reported for the synthesis of porphyrazines **3a**[6] and **6a**.[6] We now report an extension of this reaction to the alternative macrocycles **4a**,**b** and **5a**,**b**. Thus, macrocyclization using an equimolar ratio of dinitriles **1** and **2** gave the "cis" and "trans" Mg−porphyrazines **4a** and **5a** along with porphyrazine **3a**[6] and the corresponding symmetrical porphyrazines **6a**[6] and **7a**[15] (Scheme 1). The macrocyclization mixture was further demetalated since the very similar polarities of the porphyrazines rendered their separation extremely difficult as the magnesium complexes. Thus, the free base porphyrazines **4b** (11%) and **5b** (10%) were obtained upon treatment with trifluoroacetic acid along with porphyrazines **3b** (16%) and **6b** and **7b** (21%) and subsequently separated by column chromatography. Porphyrazine **6b** was not isolated due to its low solubility in

(16) Linstead, R. P.; Whalley, M. *J. Chem. Soc.* **1952**, 4839.
(17) Begland, R. W.; Hartter, D. R.; Jones, F. N.; Sam, D. J.; Sheppard, W. A.; Webster, O. W.; Weigert, F. J. *J. Org. Chem.* **1974**, *39*, 2341.

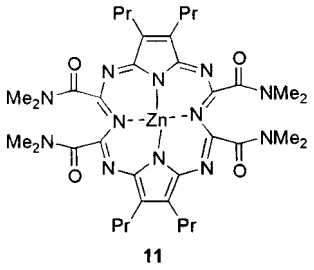
Scheme 1



Scheme 2



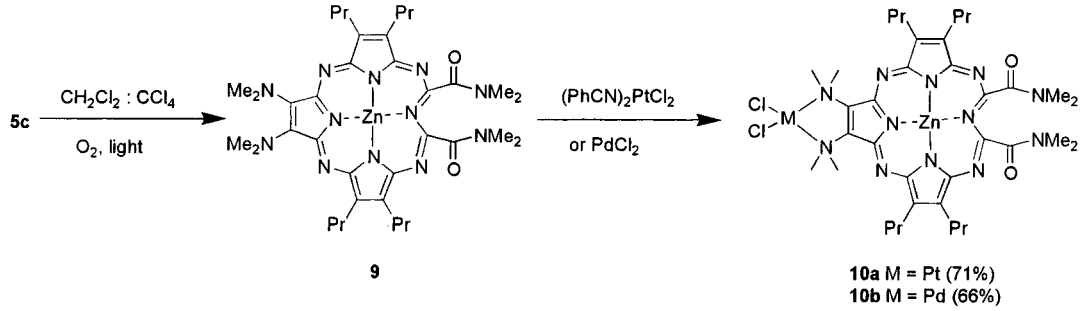
disecoporphyrazine **11**.[15] Unfortunately, the "cis" secoporphyrazine **8** was also found to be unstable in the solid state and under inert atmosphere for more than 2 days. Efforts were therefore concentrated to the synthetically more accessible "trans" analogue. Thus, upon treatment of porphyrazine **9** with $Pt(PhCN)_2Cl_2$ in 1,2-dichloroethane, the desired metalated product **10a** was isolated in a 71% yield. Similarly, reflux of **9** with palladium(II) chloride in acetonitrile and chloroform (4:1) gave the seco solitaire porphyrazine **10b** (66%). The lower yield of the palladium complex when compared to its platinum analogue correlates well with the previously reported yields for the solitaire complexes **3d** (40%) and **3e** (32%).[7] On the other hand, the significantly higher yields of the platinum and the palladium secoporphyrazines **10a** and **10b** when compared to pigments **3d** and **3e** indicate that the presence of the carboxamide units confers stability and favors the complexation reaction.



organic media. However, its formation was confirmed by means of mass spectroscopy. The novel free base porphyrazines **4b** and **5b** were separately allowed to react with zinc acetate in dry DMF to afford the corresponding porphyrazines **4c** and **5c**.

In an attempt to obtain the corresponding monosecoporphyrazines, porphyrazines **4c** and **5c** in carbon tetrachloride and dichloromethane (1:1) were allowed to stand under ambient light in air (Schemes 2 and 3). Porphyrazine **5c** was found to undergo oxidation much faster than **4c**. On the other hand, 4 days were required for a significant amount of porphyrazine **8** to be isolated. In both cases, the newly formed seco derivatives were separated from the corresponding starting materials since both were unstable in solution for prolonged times. Indeed, photolytic oxygenation of secoporphyrazine **9** gave the overoxidation product the

Scheme 3



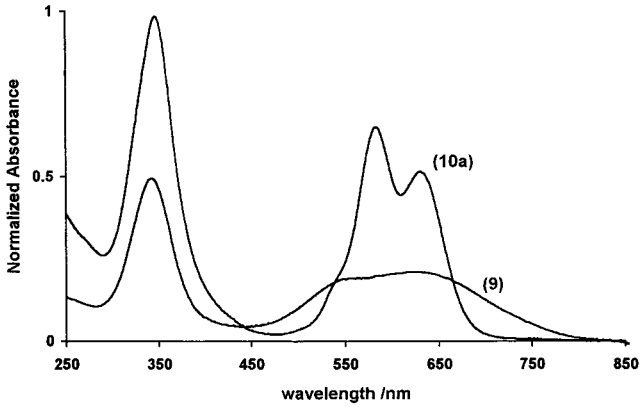
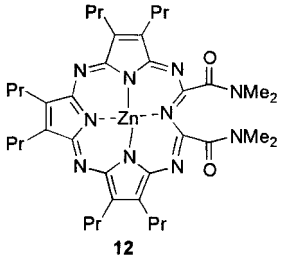


Figure 1. UV−vis absorption spectra of porphyrazines **9** and **10a** in CH_2Cl_2.

Electronic Spectra. The UV−vis spectra of both solitaire complexes **10a** and **10b** display analogous bands in the Soret (B) and Q regions. While no significant change is observed for the B-band of these complexes with respect to the free ligand **9**, the Q-band is clearly split and less broadened. As previously described for **3c**−**e** and **12**, the removal of the broadening of the Q-band is directly associated with the peripheral metalation since the nitrogen lone pairs can no longer interact with the porphyrazine core.[7,8] Thus,



"sharpening" of the Q-band is clearly observed upon formation of pigments **10a** and **10b** both exhibiting Q_x and Q_y absorbances at 581, 619 and 581, 630 nm, respectively (Figure 1). Moreover, since the symmetry of both compound **9** and complexes **10a** and **10b** remains the same (C_{2v}), the sharp change in the UV−vis spectra can solely be attributed to the decoupling of the amine nitrogens by the platinum and palladium metals from the central ring.

In contrast to the free ligand **3c**,[8] porphyrazine **9** was found to be very weakly fluorescent ($\phi_f = 1.1 \times 10^{-3}$) while, as previously observed with **3d**,**e**,[7] upon peripheral metalation the derived platinum and palladium complexes **10a** and **10b** exhibited fluorescence with quantum yields of 0.07 and 0.08 ± 0.01, respectively. The lifetimes were on the order of 0.54 ± 0.05 ns. A characteristic fluorescence emission spectrum of porphyrazine **10a** is given in Figure 2.

More interestingly, for the photochemically more stable (compared to **3d**,**e**) novel seco solitaire porphyrazines **10a** and **10b**, triplet states could be detected, and the quantum yield for this process was determined to be 0.56 for complex **10a** (Figure 3). Although determination of the quantum yield for the seco palladium porphyrazine **10b** was not carried out, a similar result is expected as indicated from its singlet oxygen quantum yield. These new complexes proved to

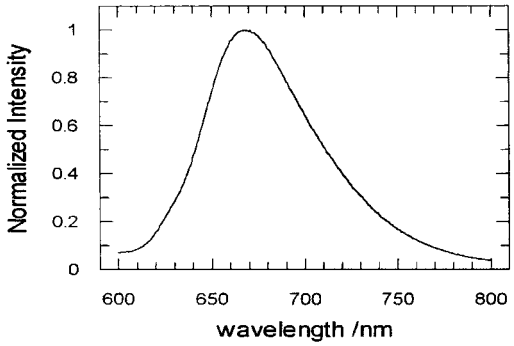


Figure 2. Fluorescence emission spectrum of porphyrazine **10a** in CH_2Cl_2. Excitation wavelength = λ_{ex} = 581 nm.

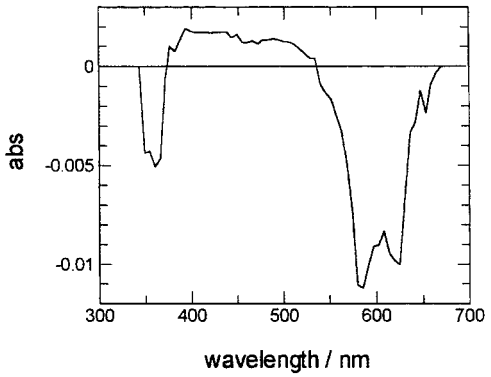


Figure 3. Transient absorption spectrum of peripherally metalated secoporphyrazine **10a**. Excitation wavelength = λ_{ex} = 550 nm.

enhance not only intersystem crossing but also the photosensitization of singlet oxygen formation. Thus, quantum yields of the singlet oxygen formation were determined to be 0.59 and 0.45 for compounds **10a** and **10b**, respectively. These values are in good agreement with the previously reported value for singlet oxygen generation by the secoporphyrazine **12** with $\phi_\Delta = 0.54$.[8] In addition, peripheral metalation induces higher fluorescence in compounds **10a**,**b** when compared to **12**, for which a quantum yield could not be determined due to the weak intensity of the process.

Both triplet-state and singlet oxygen quantum yields were determined by the comparative technique using chlorophyll a as the reference.[12] Ideally, measurements are carried out in the same solvent for which a standard value is known. However, the different solubilities of chlorophyll a and complexes **9**, **10a**, and **10b** precluded using the same solvent since there are only a limited number of values reported in the literature; consequently, chlorophyll a was measured in toluene[14] and the ligands in dichloromethane, thus accounting for the slightly higher oxygen quantum yield of complex **10a** (0.59) versus the triplet-state yield (0.56).

A most significant result was the singlet oxygen generation yield recorded for precursor **9** contrasted with complexes **10a** and **10b**. The process was of weak intensity and measured at the limit of detection to give a value of 0.03. This final result correlates well with our assumption that the nitrogen lone pair of the dimethylamino groups enhances nonradiative decay through electronic coupling with the macrocycle.

Conclusion

We have successfully carried out the synthesis and chemical characterization of the new platinum and palladium seco solitaire porphyrazines **10a** and **10b**. In addition, we have shown that the peripheral complexation and the oxidative cleavage of one of the pyrrole rings have a profound effect on the electronic properties of the porphyrazines. Thus, the photophysical profile of each of the newly prepared complexes was evaluated, following a series of experiments using emission, absorption, and transient absorption spectroscopy, and compared with compounds **3c**−**e** and **12**. The results reported herein indicate that these complexes could potentially be used as agents for diagnosis and therapy. Such studies are currently in progress.

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