– $C_4H_4O_3$ – H, 70.2), 144 (M^+ – $C_4H_4O_3$ – CH_3, 63), 130 (M^+ – $C_4H_4O_3$ – C_2H_5, 36).

1-Acetyl-2-hydroxy-4-ethyl-3,4,5,6-tetrahydropyrrolo[3,2,1-*ij*]quinoline (31b). Treatment of **29b** with $Rh_2(OAc)_4$ in refluxing CH_2Cl_2 as described above gave **31b**. Yield: 88%. IR: ν_{max} (neat) 1732, 1659, 1614, 1593 cm^{-1}. ^1H NMR: δ_H 1.01 (t, 3 H, J = 7.3 Hz, Me), 1.40–1.95 (m, 3 H, CH_2, H-5), 2.05–2.25 (m, 1 H, H-5′), 2.40 (s, 3 H, COMe), 2.65–2.90 (m, 2 H, H-6), 4.20–4.35 (m, 1 H, H-4), 6.92–7.02 (m, 2 H, Ar H), 7.16 (dd, 1 H, J = 6.3, 2.0 Hz, H-9), 12.90–13.40 (br hump, 1 H, OH). ^{13}C NMR: δ_C 10.51, 20.06, 20.56, 23.85, 25.68, 49.72, 102.50, 117.22, 119.98, 120.68, 121.33, 123.76, 134.40, 169.88, 172.70. Anal. Calcd for $C_{15}H_{17}NO_2$: C, 74.03; H, 7.05; N, 5.76. Found: C, 74.24; H, 7.21; N, 5.69.

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Supplementary Material Available: Spectroscopic and analytical data for compounds **3**, N-substituted carbamates, secondary amines, and compounds **4**, **5**, and **6**, ^1H and ^{13}C NMR spectra for **11h,i,k**, **12h**, and **21a–c**, and NOE spectra for **12h** and **21b,c** (79 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

Synthesis and Characterization of a New 26π-Aromatic Thiophene-Containing Macrocyclic Ligand

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A new porphyrin-like or "pentaplanar" macrocyclic ligand (**9**) has been synthesized by a McMurray coupling of 2,5-bis(5-formyl-4-propyl-2-pyrrolyl)thiophene, followed by air oxidation in chloroform. This highly stable macrocycle is aromatic, as evidenced by its UV–visible and ^1H NMR spectra. The pathway to **9** as well as the synthesis of two asymmetric dipyrrolylthiophenes is also described.

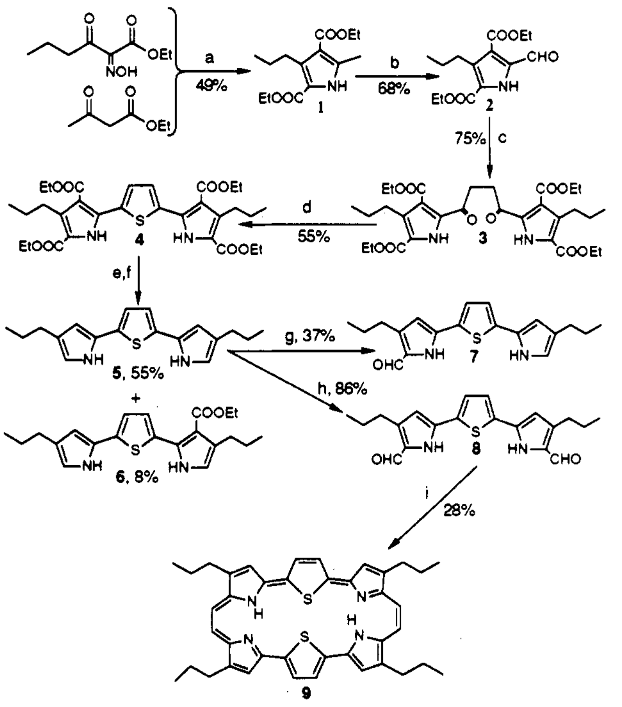
Introduction

Reports of new porphyrin-like, aromatic macrocyclic ligands have appeared in increasing number in the last few years.[1,2] These macrocyclic ligands generally consist of five-membered rings linked electronically by zero, one, or two sp-hybridized (methine) atoms to form a cyclic extended aromatic network. These and other unsaturated ligands have potential uses as one- and two-dimensional conductors,[3] as drugs for photodynamic therapy,[4] as multimetallic chelates for catalysis[5] and magnetic resonance imaging,[6] as media for chemical sensors,[7] and as anion chelands.[8] We report here the synthesis of the new macrocycle **9** and some of its spectroscopic features.

Results and Discussion

The precursor dialdehyde **8** for the synthesis of macrocycle **9** was made by modifications of the method of Merrill and LeGoff[9] (Scheme I). Pyrrole **1**[10] was treated with sulfuryl chloride in acetic acid at 70 °C to give aldehyde **2** in a 68% yield. This aldehyde was then coupled with divinyl sulfone by the method of Stetter[11] to give the 1,4-dipyrrolylbutane-1,4-dione **3**, which precipitated from the cooled reaction mixture in 75% yield and very high

Scheme I[a]



[a] (a) $Zn^0/HOAc/H_2O$; (b) (1) $SO_2Cl_2/HOAc/70$ °C, (2) H_2O; (c) divinyl sulfone, [3,4-dimethyl-5-(2-hydroxyethyl)thiazolium iodide], Et_3N, *p*-dioxane, 70 °C, 20 h; (d) Lawesson's reagent, toluene, reflux 1.5 h; (e) (1) $NaOH/H_2O/EtOH$/reflux, (2) hot $HOAc/H_2O$; (f) 240 °C/(0.2 Torr); (g) PhCOCl/DMF/0 °C; (h) PhCOCl/DMF/75 °C, 10 h; (i) (1) Ti^0/THF/reflux, (2) air oxidation in $CHCl_3$ 1 h.

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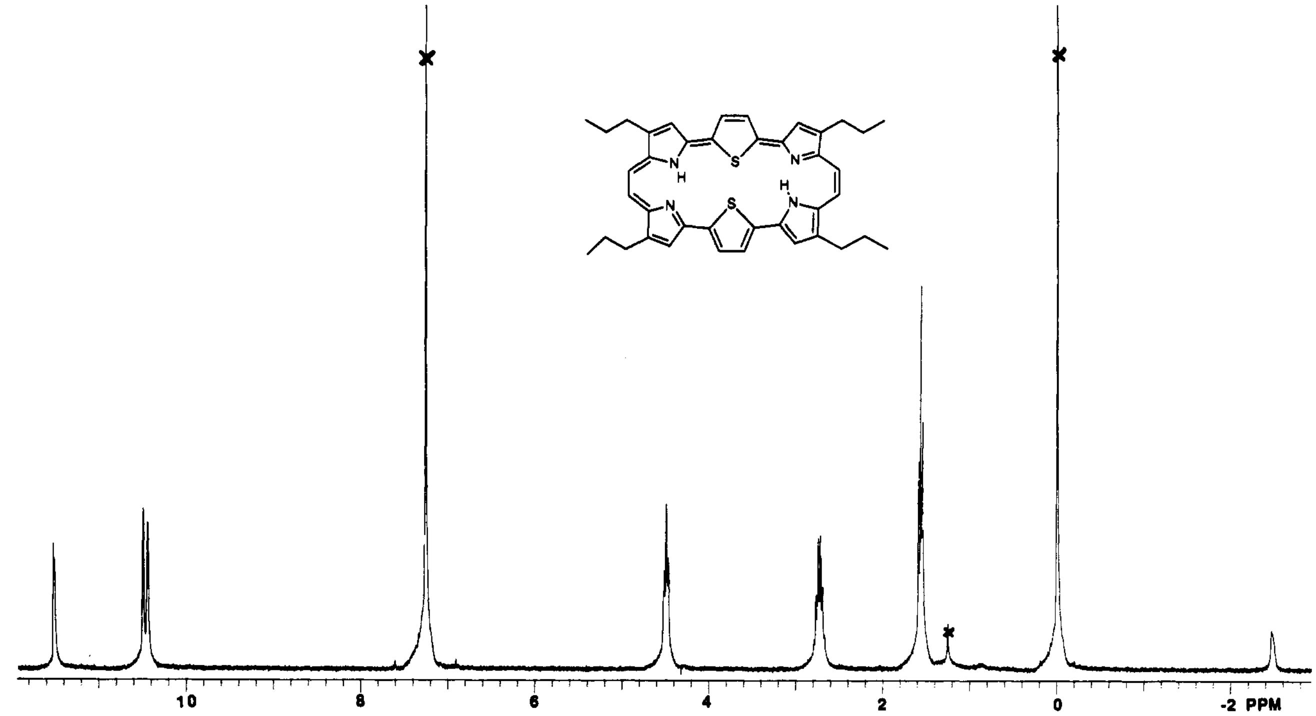

Figure 1. Proton NMR spectrum ($CDCl_3$, 300 MHz) of macrocycle **9**.

purity. Dione **3** was then cyclized with Lawesson's reagent in refluxing toluene to give predominantly the desired dipyrrolylthiophene ester **4**. This product was contaminated with 5–10% of byproduct dipyrrolylfuran,[12] and no satisfactory means of separation of these two products, other than chromatography, was found. Ester **4** was saponified (24-h reflux) and decarboxylated by sublimation of the acid intermediate. In addition to the major product **5**, a substantial amount of monoester **6** was reproducibly obtained, and separation by chromatography was again required.

2,5-Bis(4-propyl-2-pyrrolyl)thiophene **5** rapidly reacts under Clezy-Vilsmieir conditions[13] at 0 °C to give the monoaldehyde **7**, an initial target compound, upon workup. Diformylation of **5** was also achieved, but this required a higher temperature (75–100 °C) and a longer reaction time (10 h), in accord with earlier findings for unsubstituted dipyrrolylthiophene.[8] Macrocycle **9** was then prepared in 28% yield by a McMurray coupling of dialdehyde **8**. The initial coupling product rapidly oxidizes when dissolved in chloroform to give **9**.

Macrocycle **9** is clearly aromatic, as evidenced by both proton NMR (Figure 1) and UV–visible spectroscopy (Figure 2). In Figure 1, a sharp peak at δ −2.2 ppm is consistent with a diamagnetically shielded internal pyrrole proton, and the peaks at 10.53, 10.54, and 11.65 ppm correspond to the external and deshielded pyrrole, thiophene, and methine resonances, respectively. The propyl group resonances are also easily assignable. The UV–visible absorbance of **9** shows a widely split Soret band at 460 and 501 nm, consistent with the pronounced D_{2h} symmetry of the molecule, and four Q transitions at 745, 780, 790, and 859 nm. The Soret absorbances are of similar intensity (ϵ = 2 × 10^5 and 9.5 × 10^4) to porphyrins,[14] porphycenes[15] ($\epsilon \approx (1\text{–}2) \times 10^5$), and other porphyrin-like macrocycles.[2] As for porphycenes, the Q transitions of **9** are very prominent relative to those in the Soret region, being about 30–40% as intense. With porphyrins and metalloporphyrins, the Q bands usually are only about 1–15% as intense.[16]

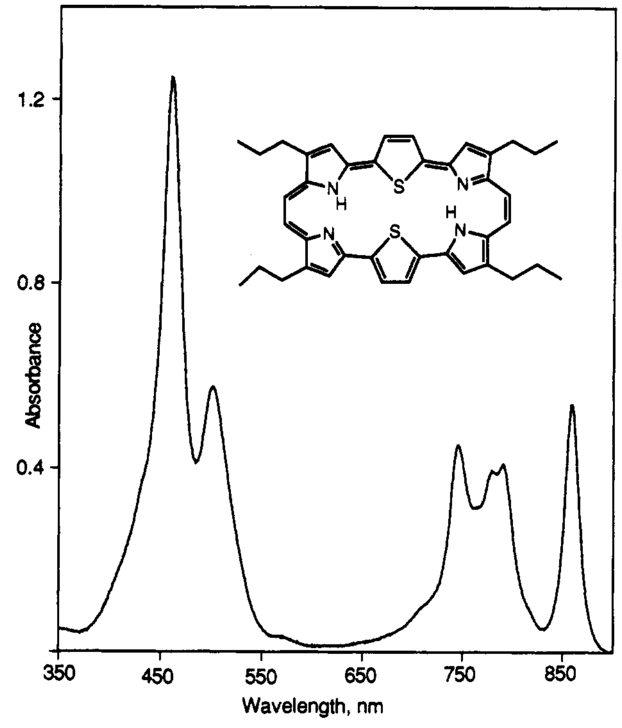

Figure 2. UV–visible absorbance spectrum (THF, 6.5 μmol) of macrocycle **9**.

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Macrocycle **9** is similar to sapphyrin,[8,17] porphycene,[1] rubyrin,[2] pentaphyrin,[18] hexaphyrin,[18] platyrin,[19] and other known aromatic macrocycles, where the aromatic stabilization derives from a diatropic π-network that extends through and between the five-membered rings comprising the parent macrocycle. We suggest that the name "pentaplanar" succinctly describes these two common features, e.g. aromaticity and five-membered ring inclusion, that are shared by all of these macrocycles. Macrocycle **9** is in fact an isomeric analogue of rubyrin, a recently synthesized hexapyrrolic macrocycle[2] with methine groups arranged from the ring in the order [1.1.0.1.1.0.].[20] Macrocycle **9**, by contrast, has methine groups arranged about the ring in the order [2.0.0.2.0.0.] and has two pyrrole groups replaced by thiophene groups. Other thiophene-containing aromatic macrocycles are known,[21,22] and many bind to a range of metals; however, these thiophene-containing macrocycles are all variants of the well-known porphyrin or [1.1.1.1]-type system.

Macrocycle **9** is potentially capable of acting as a binuclear ligand, and preliminary evidence suggests that this occurs for Cu(II). We will report on the metal-binding, emission, and electrochemical properties of **9** and its analogues in the near future.

Experimental Section

Toluene and *p*-dioxane were dried by refluxing with sodium under argon, followed by distillation. Tetrahydrofuran was dried by distillation under argon from sodium–benzophenone ketyl. Pyridine was stored over NaOH pellets. Anhydrous dimethylformamide was obtained from Burdick and Jackson Co. and stored over 4-Å sieves under N_2 or Ar. All other solvents, acids, and bases were obtained commercially and were used as received. Ethyl butyrylacetate, ethyl acetoacetate, divinyl sulfone, 3,4-dimethyl-5-(2-hydroxyethyl)-1,3-thiazolium iodide, Lawesson's reagent, benzoyl chloride, and titanium tetrachloride were obtained from Aldrich Chemical Co. and were used as received. Sodium nitrite, zinc dust, and sulfuryl chloride were obtained from several commercial sources and used as received.

Melting points were determined on a Mel-Temp melting point apparatus and are uncorrected. Proton and ^{13}C NMR measurements were made with $CDCl_3$ as solvent on a Varian Gemini NMR spectrometer operating at 300 and 75.4 MHz, respectively. NMR chemical shifts are reported in parts per million, with TMS as reference, or the DMSO solvent peak for compound **8**. EI and FAB low- and high-resolution mass spectra were recorded on a VG analytical 70SE quadrupole mass spectrometer by Doris Hung of the Analytical Services Laboratory at Northwestern University. UV–visible spectra were recorded on a Cary-14 spectrophotometer equipped with the hardware/software modification package provided by On-Line Instrument Systems, Inc. Jefferson, GA. Elemental analysis was performed by Galbraith Laboratories, Knoxville, TN.

2-Methyl-4-propyl-3,5-dicarbethoxypyrrole (1). This compound was synthesized by the method of Fischer, Goldschmidt, and Nüssler.[10] A 5-L round-bottom flask was equipped with a paddle, a motor, a dropping funnel, and an ice bath. To the flask was added ethyl butyrylacetate (360 g, 2.27 mol) and acetic acid (1700 mL). The solution was cooled to about 5 °C with an ice bath, and a solution of sodium nitrite (160.8 g, 2.33 mol) in water (430 mL) was dropped in. After the addition was complete, the contents of the flask were allowed to warm to room temperature over a period of 2–24 h. Ethyl acetoacetate (295.2 g, 2.26 mol) was added, followed by portions of zinc dust (finely divided, 300 g total) with vigorous stirring. The zinc dust addition was exothermic, and when 65 °C was reached the flask was cooled with ice and the zinc dust was added more slowly so as to maintain a temperature of 70 °C in the flask. When the zinc dust addition was complete, the ice bath was removed and the flask contents were stirred for an additional 1.5 h at 70 °C. The contents of the flask were poured into a bucket containing 10 kg of crushed ice, stirred well, filtered, washed with water, recrystallized from ethanol/water, and dried to give product **1** (298 g, 1.1 mol, 49%, mp 102–103 °C; lit.[10] mp 102 °C): ^{1}H NMR δ 0.97 (t, J = 5.5 Hz, 3 H, $\mathrm{CH_2CH_2}CH_3$), 1.366, 1.376 (2 t, J = 5.4 Hz, 6 H, 2 $\mathrm{OCH_2}CH_3$), 1.57 (sextet, J = 5.7 Hz, 2 H, $\mathrm{CH_2}CH_2\mathrm{CH_3}$), 2.53 (s, 3 H, CH_3), 3.04 (t, J = 5.7 Hz, 2 H, $CH_2\mathrm{CH_2CH_3}$), 4.31 (m, 4 H, 2 $\mathrm{O}CH_2\mathrm{CH_3}$), 9.45 (br, 1 H, NH); ^{13}C NMR δ 14.13, 14.22, 24.42, 27.63, 59.33, 60.26, 112.71, 117.62, 135.76, 139.71, 162.12, 165.31; MS *m/e* 267 (100), 238 (61), 222 (34), 192 (45); HRMS calcd for $C_{14}H_{21}NO_4$ *m/e* 267.1471, found 267.1454.

2,4-Dicarbethoxy-3-propylpyrrole-5-carboxaldehyde (2). In a fume hood a 250-mL three-necked round-bottom flask was equipped with a thermometer, a dropping funnel, and an optional nitrogen inlet, and was charged with acetic acid (150 mL) and 2,4-dicarbethoxy-5-methyl-3-propylpyrrole (**1**; 26.7 g, 0.1 mol). The contents of the flask were stirred and heated to about 50 °C, and sulfuryl chloride (28 g, 0.21 mol) was dropped in over a 15-min time period. After the addition was complete, the flask contents were stirred and heated to 50–70 °C for an additional 30 min, and water (60 mL) was dropped in over 1 min. Some crystal deposition was observed at this point. The contents of the flask were poured into a 2-L beaker containing water (1 L). The contents of the beaker were stirred until the solid mass all settled to the bottom. The aqueous layer was decanted off; the solid was washed with water (500 mL) and dissolved in hot ethanol (150 mL). The solution so obtained was treated with $NaHCO_3$ until no more effervescence was observed at the boiling point, and the hot ethanolic liquid was poured into a 250-mL beaker. The 2-L beaker was filled with water (800 mL), and the ethanolic solution was poured into it with vigorous stirring. The contents were stirred for 10 min. The solid product **2** was collected by filtration, washed with water, and recrystallized from hexane: yield 19 g (67 mmol, 67%); mp 91–92 °C; ^{1}H NMR δ 0.98 (t, J = 5.5 Hz, 3 H, $\mathrm{CH_2CH_2}CH_3$), 1.405, 1.414 (2 t, J = 5.4 Hz, 6 H, 2 $\mathrm{OCH_2}CH_3$), 1.59 (sextet, J = 5.7 Hz, 2 H, $\mathrm{CH_2}CH_2\mathrm{CH_3}$), 3.07 (m, 2 H, $CH_2\mathrm{CH_2CH_3}$), 4.39 (q, J = 5.4 Hz, 4 H, 2 $\mathrm{O}CH_2\mathrm{CH_3}$), 10.02 (br, 1 H, NH), 10.28 (s, 1 H, CHO); ^{13}C NMR δ 13.92, 14.05, 24.13, 26.78, 60.58, 61.11, 120.50, 123.60, 133.51, 135.57, 160.28, 163.33, 182.60; MS *m/e* 281 (100), 252 (40), 235 (65), 224 (28), 206 (60); HRMS calcd for $C_{14}H_{19}NO_5$ *m/e* 281.1263, found 281.1260.

1,4-Bis(3,5-bis(ethoxycarbonyl)-4-propyl-2-pyrrolyl)-1,4-butanedione (3). A three-necked 2-L round-bottom flask equipped with a stir paddle was charged with aldehyde **2** (150 g, 0.53 mol) and anhydrous 1,4-dioxane (1200 mL). The aldehyde was stirred under an N_2 flow until it dissolved, and 3,4-dimethyl-5-(2-hydroxyethyl)thiazolium iodide (22.25 g, 0.078 mol) was added, followed by divinyl sulfone (30.82 g, 0.26 mol), and triethylamine (16.2 g, 0.16 mol). The flask contents were heated to 70 °C under N_2 and stirred at 68–72 °C for 20 h. The contents were cooled with stirring to 40 °C and filtered, and the filtrate was concentrated to 500 mL on a rotary evaporator. The flask contents were cooled to about 14 °C, and the product so obtained was collected by filtration and compressed with a rubber dam. This crude product was washed with a minimum of very cold 25% CH_2Cl_2/75% hexane (cooled to −50 to −78 °C with dry ice) and dried to yield the pure product **3** (106 g, 0.18 mol, 68%) as a white powder, mp 129–130 °C. An additional 11.3 g of impure product was recovered from the various mother liquors: total yield 75%; ^{1}H NMR δ 0.96 (t, J = 7.4 Hz, 6 H, $\mathrm{CH_2CH_2}CH_3$), 1.37 (t, J = 7.2 Hz, 6 H, $\mathrm{OCH_2}CH_3$), 1.42 (t, J = 7.2 Hz, 6 H, $\mathrm{OCH_2}CH_3$), 1.58 (sextet, J = 7.6 Hz, 4 H, $\mathrm{CH_2}CH_2\mathrm{CH_3}$), 2.91 (t, J = 7.8 Hz, 4 H, $CH_2\mathrm{CH_2CH_3}$), 3.37 (s, 4 H, $\mathrm{O{=}C}CH_2CH_2\mathrm{C{=}O}$), 4.37 (q, J = 7.2 Hz, 4 H, $\mathrm{O}CH_2\mathrm{CH_3}$), 4.40 (q, J = 7.2 Hz, 4 H, $\mathrm{O}CH_2\mathrm{CH_3}$), 9.89 (br, 2 H, NH); ^{13}C NMR δ 14.04, 14.09, 14.21, 24.38, 27.24, 34.70, 60.95, 61.21, 119.70, 121.87, 131.54, 134.07, 160.23, 164.98, 190.71; MS *m/e* 588 (100), 543 (25), 496 (67), 450 (14), 423 (12); HRMS

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calcd for $C_{30}H_{40}N_2O_{10}$ *m/e* 588.2683, found 588.2661.

2,5-Bis(3,5-bis(ethoxycarbonyl)-4-propyl-2-pyrrolyl)thiophene (4). The dipyrrolylbutanedione **3** (5.13 g, 8.7 mmol) and Lawesson's reagent (2.35 g, 5.8 mmol) were refluxed under N_2 in toluene (50 mL) for 4 h. After the toluene was removed under reduced pressure, the residue was taken up in CH_2Cl_2, filtered, and eluted through a 5- × 30-cm column of silica with pure CH_2Cl_2 as the initial eluent and then 5% ethyl acetate/CH_2Cl_2 as eluent. An initial fraction of byproduct dipyrrolylfuran was followed by the main product **4**, which was concentrated to dryness on a rotary evaporator to give pure **4** (2.8 g, 4.8 mmol, 55%) as a yellow solid that exhibits blue fluorescence: mp 156–157.5 °C; ^{1}H NMR δ 0.99 (t, J = 7.3 Hz, 6 H, $\mathrm{CH_2CH_2C}H_3$), 1.34 (t, J = 7.1 Hz, 6 H, $\mathrm{OCH_2C}H_3$), 1.40 (t, J = 7.1 Hz, 6 H, $\mathrm{OCH_2C}H_3$), 1.62 (sextet, J = 7.7 Hz, 4 H, $\mathrm{CH_2C}H_2\mathrm{CH_3}$), 3.06 (m, 4 H, $\mathrm{C}H_2\mathrm{CH_2CH_3}$), 4.30 (q, J = 7.1 Hz, 4 H, $\mathrm{OC}H_2\mathrm{CH_3}$) 4.36 (q, J = 7.1 Hz, 4 H, $\mathrm{OC}H_2\mathrm{CH_3}$), 7.42 (s, 2 H, thiophene CH), 9.10 (br, 2 H, NH); ^{13}C NMR δ 14.20, 14.36, 24.48, 27.67, 60.17, 60.66, 114.31, 119.86, 128.17, 131.74, 133.76, 135.63, 160.97, 164.62; MS *m/e* 586 (100), 540 (65), 494 (30); HRMS calcd for $C_{30}H_{38}N_2O_8S$ *m/e* 586.2349, found 586.2328.

2,5-Bis(4-propyl-2-pyrrolyl)thiophene (5) and 2-(3-Carbethoxy-4-propyl-2-pyrrolyl)-5-(4-propyl-2-pyrrolyl)thiophene (6). The above ester **4** (4 g, 6.8 mmol), NaOH (11 g, 275 mmol), water (50 mL), and ethanol (50 mL) were held at reflux under N_2 for 24 h. The solution was concentrated on a rotary evaporator, diluted to 150 mL with water, and acidified with HOAc. The precipitate was collected by filtration, dissolved in hot HOAc (50 mL), and filtered, and the filtrate was poured into water (250 mL). The precipitate was again collected by filtration, washed with water, and dried (80 °C (0.1 Torr)) to give the crude tetraacid (2.3 g). Sublimation of this acid (240 °C (0.1 Torr)) gave ≈1.3 g of crude product **5**, which contained some monoester **6**. The two products were separated by column chromatography (3 × 40 cm, CH_2Cl_2 eluent). Product **5** and monoester **6** fluoresce blue and green, respectively, and the progress of the fractions down the column was so monitored. Product **5** was collected and recrystallized from CH_2Cl_2/hexane to give waxy white flakes (1.1 g, 3.7 mmol, 54%): mp 176–180 °C; ^{1}H NMR δ 0.97 (t, J = 7.3 Hz, 6 H, $\mathrm{CH_2CH_2C}H_3$), 1.61 (sextet, J = 7.4 Hz, 4 H, $\mathrm{CH_2C}H_2\mathrm{CH_3}$), 2.45 (t, J = 7.5 Hz, 4 H, $\mathrm{C}H_2\mathrm{CH_2CH_3}$), 6.25 (m, 2 H, C*H*NH), 6.57 (m, 2 H, CH), 6.86 (s, 2 H, thiophene CH), 8.01 (br, 2 H, CHN*H*); ^{13}C NMR δ 14.04, 24.14, 29.10, 106.95, 115.80, 120.81, 126.35, 113.30; MS *m/e* 298 (100), 269 (30), 239 (8); HRMS calcd for $C_{18}H_{22}N_2S$ *m/e* 298.1504, found 298.1497.

Byproduct **6** was eluted with 1% acetone/CH_2Cl_2 and recrystallized from CH_2Cl_2/hexane: yield 200 mg (0.5 mmol, 8%); mp 116–118 °C; ^{1}H NMR δ 0.960, 0.968 (2 t, J = 7.3 Hz, 6 H, $\mathrm{CH_2CH_2C}H_3$), 1.31 (t, J = 7.1 Hz, 3 H, $\mathrm{OCH_2C}H_3$), 1.60 (sextet, J = 7.4 Hz, 4 H, $\mathrm{CH_2C}H_2\mathrm{CH_3}$), 2.44 (t, J = 7.5 Hz, 2 H, $\mathrm{C}H_2\mathrm{CH_2CH_3}$), 2.67 (t, J = 7.5 Hz, 2 H, $\mathrm{C}H_2\mathrm{CH_2CH_3}$), 4.26 (q, J = 7.1 Hz, 2 H, $\mathrm{OC}H_2\mathrm{CH_3}$), 6.27 (s, 1 H, C*H*NH), 6.51 (d, J = 1.8 Hz, 1 H, CH of ester pyrrole), 6.54 (m, 1 H, CH of nonester pyrrole), 6.87 (d, J = 3.8 Hz, 1 H, thiophene CH), 7.19 (d, J = 3.8 Hz, 1 H, thiophene CH); 8.12 (br, 1 H, NH), 8.30 (br, 1 H, NH); ^{13}C NMR δ 14.01, 14.11, 14.26, 23.65, 24.11, 29.06, 29.13, 59.70, 107.30, 111.18, 116.14, 116.44, 120.19, 126.11, 126.31, 127.47, 127.79, 130.30, 130.49, 136.77, 165.59; MS *m/e* 370 (100), 342 (12), 295 (15); HRMS calcd for $C_{21}H_{26}N_2O_2S$ *m/e* 370.1715, found 370.1710.

2-(5-Formyl-4-propyl-2-pyrrolyl)-5-(4-propyl-2-pyrrolyl)thiophene (7). Benzoyl chloride (2.35 g, 16.7 mmol) was added dropwise to a solution of **5** (500 mg, 1.67 mmol) in DMF (15 mL) with stirring under N_2 at ≈0 °C. The suspension was stirred for 1 h at 0 °C, and the precipitate was collected by filtration. This solid was dissolved in water and made basic (aqueous NaOH) with stirring. The precipitate was redissolved in ethanol (40 mL) and further basified with aqueous NaOH. The product was reprecipitated as a metallic green tar by pouring the ethanolic solution into water (100 mL), followed by the addition of salt with stirring. This tar was dissolved in CH_2Cl_2 and eluted through silica (1% Et_3N/CH_2Cl_2 eluent). The product was collected and recrystallized from CH_2Cl_2/hexane to give a green powder (200 mg, 0.6 mmol, 37%): mp 143–144 °C; ^{1}H NMR δ 0.964, 0.980 (2 t, J = 7.2–7.3 Hz, 6 H, $\mathrm{CH_2CH_2C}H_3$), 1.64 (m, 4 H, $\mathrm{CH_2C}H_2\mathrm{CH_3}$), 2.44 (t, J = 7.5 Hz, 2 H, $\mathrm{C}H_2\mathrm{CH_2CH_3}$), 2.71 (t, J = 7.5 Hz, 2 H, $\mathrm{C}H_2\mathrm{CH_2CH_3}$), 6.288, 6.298 (s, s, 2 H, CH), 6.59 (s, 1 H, C*H*NH), 6.92 (d, J = 3.8 Hz, 1 H, thiophene CH), 7.26 (d, J = 3.8 Hz, 1 H, thiophene CH), 8.46 (br, 1 H, NH), 9.57 (s, 1 H, CHO), 10.0 (br, 1 H, NH); ^{13}C NMR δ 13.84, 13.99, 24.12, 24.60, 27.27, 29.00, 107.76, 109.45, 116.66, 121.05, 125.22, 125.81, 126.50, 129.38, 129.91, 134.46, 136.98, 140.06, 176.42; MS *m/e* 326 (100), 311 (10), 297 (23); HRMS calcd for $C_{19}H_{22}N_2OS$ *m/e* 326.1453, found 326.1454.

2,5-Bis(5-formyl-4-propyl-2-pyrrolyl)thiophene (8). Benzoyl chloride (6.35 g, 45.2 mmol) was added dropwise to a solution of **5** (1.35 g, 4.52 mmol) in DMF (100 mL) at −20 °C with stirring under N_2. A precipitate was observed after 2 min. After 10 min the flask contents were held at 100 °C until the solid dissolved (about 1 h) and then held at 75 °C for 10 h. The dark yellow solution was poured into water (200 mL) and made basic with concentrated NaOH. The precipitate so obtained was collected by filtration, washed with water, and dissolved in 400 mL of boiling ethanol. A solution K_2CO_3 (12% w/v) in water (100 mL) was then added dropwise. The flask contents were refluxed for 2 h, and the ethanol was removed by rotatory evaporation. The yellow powder was collected by filtration and recrystallized from chloroform to give product **8** (1.4 g, 3.9 mmol, 86%): mp 224–226 °C; ^{1}H NMR δ 1.01 (t, J = 7.3 Hz, 6 H, $\mathrm{CH_2CH_2C}H_3$), 1.71 (sextet, J = 7.4 Hz, 4 H, $\mathrm{CH_2C}H_2\mathrm{CH_3}$), 2.75 (t, J = 7.5 Hz, 4 H, $\mathrm{C}H_2\mathrm{CH_2CH_3}$), 6.38 (d, J = 2 Hz, 2 H, CH), 7.29 (s, 2 H, thiophene CH), 9.64 (s, 2 H, CHO), 9.81 (br, 2 H, NH); ^{13}C NMR δ (DMSO-d_6) 13.67, 24.05, 26.71, 109.58, 125.66, 129.82, 132.48, 133.21, 137.63, 177.34. MS *m/e* 354 (100), 339 (21), 326 (22), 297 (10); HRMS calcd for $C_{20}H_{22}N_2O_2S$ *m/e* 354.1402, found 354.1377.

Macrocycle 9. A solution of $TiCl_4$ (8.59 g, 45.3 mmol) in THF (800 mL) was added under an argon atmosphere to zinc dust (6 g, 92 mmol) with stirring, and the suspension was held at reflux for 1 h. Aldehyde **8** (1.61 g, 4.5 mmol) and pyridine (6 mL) in THF (600 mL) were then added dropwise over 1.5-h period to the gently refluxing suspension. The resulting mixture was refluxed with stirring for 16 h. A quenching solution of 10% K_2CO_3 in water (125 mL) was then carefully introduced. The reaction mixture was filtered, and the filtrate was concentrated on a rotary evaporator almost to dryness. Chloroform (250 mL) was added, and the rapidly darkening solution was washed with water (200 mL) and stirred in air for 1 h to effect complete oxidation of the intermediate. The $CHCl_3$ solution was dried (Na_2SO_4), concentrated to 100 mL, and eluted through several silica gel columns ($CHCl_3$). The fast-running dark-orange band was collected, recrystallized from $CHCl_3$/MeOH, and dried in vacuo to give the product **9** (409 mg, 0.64 mmol, 28%) as metallic green needles: mp 330 °C dec; UV–visible λ_{max} (log ϵ) (THF) 460 (5.28), 501 (4.95), 745 (4.84), 780 (4.78), 790 (4.80), 858 (4.92); ^{1}H NMR δ −2.23 (s, 2 H, NH), 1.57 (t, J = 7.4 Hz, 12 H, $\mathrm{CH_2CH_2C}H_3$), 2.75 (sextet, J = 7.4 Hz, 8 H, $\mathrm{CH_2C}H_2\mathrm{CH_3}$), 4.53 (t, J = 7.7 Hz, 8 H, $\mathrm{C}H_2\mathrm{CH_2CH_3}$), 10.54, 10.55 (s, s, 4 H, 4 H, pyrrole and thiophene CH), 11.65 (s, 4 H, methine CH); ^{13}C NMR ($CDCl_3$ at 50 °C) δ 14.80, 25.61, 31.28, 107.97, 122.70, 129.73, 130.96, 138.45, 141.76, 143.89; FAB MS (3-nitrobenzyl alcohol) *m/e* 643 (100); FAB HRMS calcd for $C_{40}H_{42}N_4S_2$ 642.2851, found 642.2894. Anal. Calcd for $C_{40}H_{42}N_4S_2$: C, 74.73; H, 6.58; N, 8.71; S, 9.97. Found: C, 74.43; H, 6.58; N, 8.39; S, 9.78.

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Supplementary Material Available: ^{13}C NMR spectra of **1–9** and ^{1}H NMR spectra of **1–8** (17 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.