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The new 22- $\pi$ , aromatic "pentaplanar" macrocycle, ozaphyrin (**6**), has been synthesized by a McMurry coupling of 5,5'-diformyl-4,4'-dipropyl-2,2'-bipyrrole (**1**) with 2,5-bis(5-formyl-4-propyl-2-pyrrolyl)furan (**5**). This synthetic pathway to ozaphyrin and its characterization by <sup>1</sup>H nmr spectroscopy, uv-visible spectroscopy, cyclic voltammetry, and X-ray crystallography are described. The structure consists of layers of planar, staggered macrocycles stacked perpendicular to the  $a$ -axis. Ozaphyrin crystallizes with four formula units in the monoclinic space group  $C_{2h}^2-P2_1/n$  in a cell of dimensions  $a = 10.481(7)$  Å,  $b = 17.353(17)$  Å,  $c = 18.726(12)$  Å, and  $\beta = 102.84(5)^\circ$  (108 K). The structure has been refined on  $F^2$  (5171 unique reflections, 411 variables) to  $R_w(F_o^2) = 0.165$ . The conventional agreement index  $R(F)$  is 0.074 for the 3289 reflections have  $F_o^2 > 2\sigma(F_o^2)$ .

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The many investigations of porphyrin-like aromatic macrocycles have recently been reviewed [1]. These macrocycles generally consist of pyrrole rings linked electronically by zero, one, or two  $sp$ -hybridized (methine) carbon atoms to form a cyclic extended aromatic network. Recently we reported the synthesis of a new aromatic "pentaplanar" macrocycle that incorporates thiophene and pyrrole rings [2]. These and other unsaturated macrocycles are of broad interest [3-14]. We report here the synthesis and characterization of a new "pentaplanar" macrocycle that incorporates both a furan and pyrrole rings.

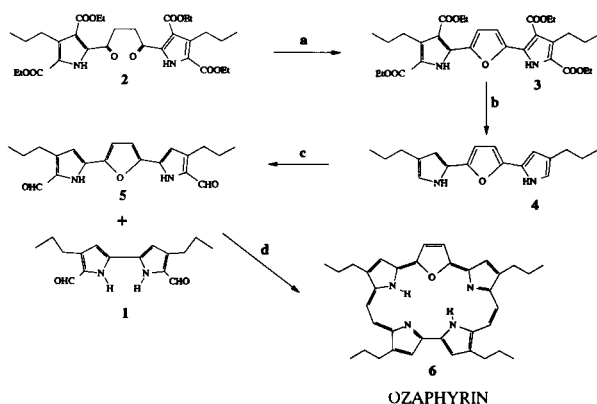
Bipyrrole dialdehyde **1** and dipyrrole dione **2** were prepared as reported previously [2]. The dione **2** was then cyclized with a catalytic amount (0.5 ml) of sulfuric acid in refluxing ethanol to give predominantly the desired dipyrrolylfuran tetraester furan **3** (Scheme). This ester was purified either by recrystallization from ethanol or by chromatography to remove the 1-5% furan by-products. The

tetraester furan **3** was saponified (24 hour reflux) and decarboxylated by heating in ethanol/water (1:1 v/v), and after preliminary purification the solid was recrystallized from hexane to give the dipyrrolylfuran **4**. Diformylation of **4** was achieved with the use of modified Clezy-Vilsmier conditions [15] with a higher temperature (100°) and a longer reaction time (16 hours) to yield the dipyrrolofuran dialdehyde **5**. Macrocycle **6** was prepared by a McMurry coupling [16,17] of an approximately equimolar mixture of bipyrrole dialdehyde **1** and dipyrrolofuran dialdehyde **5**.

Macrocycle **6** is clearly aromatic, as evidenced by both <sup>1</sup>H nmr and uv-visible spectroscopy. The <sup>1</sup>H nmr spectrum shows a sharp peak at  $-2.16$  ppm, consistent with a diamagnetically shielded internal pyrrole proton, and the peaks at 10.31, 10.47, and 10.50 ppm correspond to the external and deshielded methine, pyrrole, and furan protons. The propyl groups are difficult to assign, but are accounted for in the 1.49, 2.60, 4.29, and 4.36 ppm peaks. The uv-visible absorbance of macrocycle **6** shows a split Soret band at 414 and 430 nm, consistent with the  $C_{2v}$  symmetry of the molecule (evident from the crystallographic results, see below), and three intense Q transitions at 640, 677, and 735 nm. The Soret absorbances are of similar intensity ( $\epsilon = 1.2 \times 10^5$  and  $9.9 \times 10^4$ ) to porphyrins [18], porphycenes [19], and other porphyrin-like macrocycles [20]. Macrocycle **6** exhibits Q transitions that are between 20% and 50% as intense as the Soret bands; this is typical of porphycenes [19], but not of porphyrins and metalloporphyrins, where the Q transitions are 1-15% as intense as the Soret bands [18]. Macrocycle **6** is emerald green in color (chloroform solution). In the spirit of the appellation of sapphyrin [21] and rubyrin [20] we christen macrocycle **6** "ozaphyrin", after the Emerald City of Oz [22].

Ozaphyrin **6** is similar to sapphyrin [9,13,14,21,23], porphycene [24-26], rubyrin [20], pentaphyrin [27-29], hexa-

## SCHEME



OZAPHYRIN

a.  $H_2SO_4$  (0.5 ml)/100% EtOH/reflux 8h 88% b.  $KOH/H_2O/EtOH$ /reflux 24h 60%  
c.  $PhCOCl/DMF/100^\circ C$  16h 88% d. (1)  $TiCl_4/Zn/THF$  reflux 17h (2) 10% aqueous  $K_2CO_3$  5%

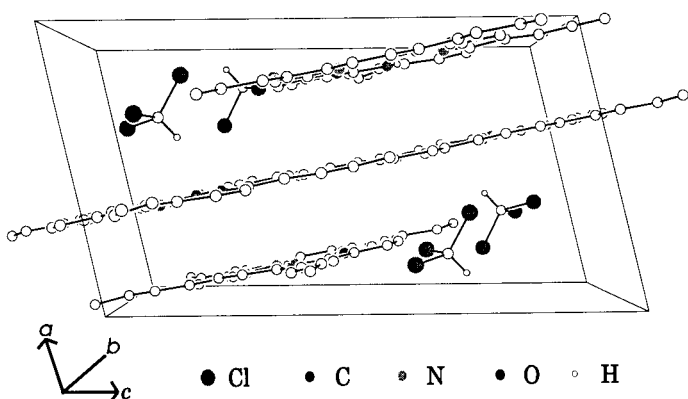
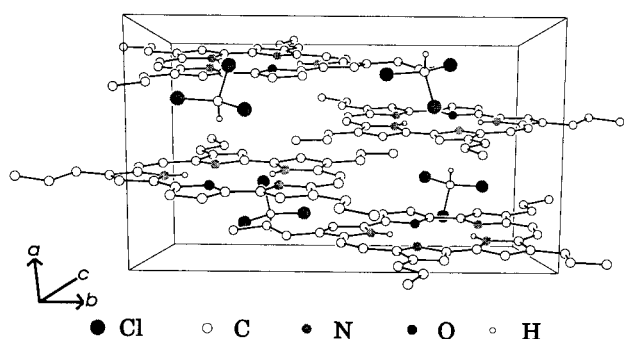
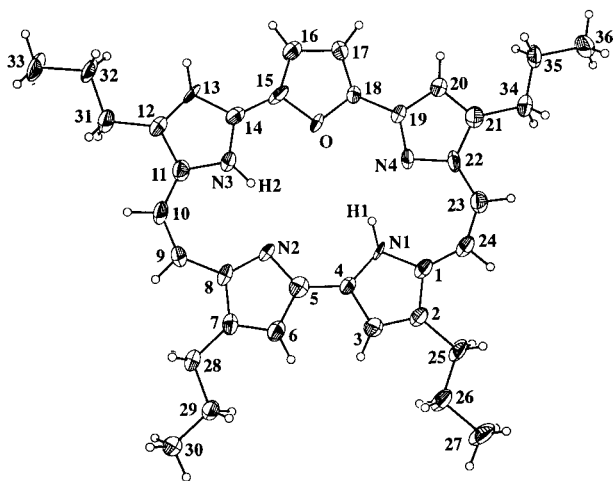
Figure 1. View down the *b*-axis of the ozaphyrin·chloroform structure.Figure 2. View down the *c*-axis of the ozaphyrin·chloroform structure.

Figure 3. A drawing [52] of the ozaphyrin (6) molecule. The labeling scheme is shown. The thermal ellipsoids are drawn at their 75% probability levels, except for hydrogen atoms which are drawn artificially small.

pyrrole [27-29], platyrin [30,31], and other known aromatic macrocycles, where according to Hückel's  $4n + 2$  rule the aromatic stabilization derives from a diatropic  $\pi$ -network of 18, 22, or 26 electrons that extends through and between the five-membered rings comprising the macrocycle. Previously, we have suggested the term "pentaplanar" to describe succinctly the common features of all

Table 1  
Selected Bond Lengths (Å) and Angles (deg) for Ozaphyrin 6

O(1)-C(18)	1.363(6)	O(1)-C(15)	1.382(6)
N(1)-C(4)	1.369(6)	N(1)-C(1)	1.390(6)
N(2)-C(8)	1.375(6)	N(2)-C(5)	1.380(6)
N(3)-C(14)	1.359(6)	N(3)-C(11)	1.380(6)
N(4)-C(19)	1.344(6)	N(4)-C(22)	1.368(6)
C(1)-C(24)	1.384(7)	C(1)-C(2)	1.430(7)
C(2)-C(3)	1.356(7)	C(3)-C(4)	1.430(7)
C(4)-C(5)	1.426(7)	C(5)-C(6)	1.441(7)
C(6)-C(7)	1.351(7)	C(7)-C(8)	1.448(7)
C(8)-C(9)	1.426(7)	C(9)-C(10)	1.366(7)
C(10)-C(11)	1.367(7)	C(11)-C(12)	1.443(7)
C(12)-C(13)	1.360(7)	C(12)-C(31)	1.505(7)
C(13)-C(14)	1.409(7)	C(14)-C(15)	1.405(7)
C(15)-C(16)	1.364(7)	C(16)-C(17)	1.392(7)
C(17)-C(18)	1.363(7)	C(18)-C(19)	1.428(7)
C(19)-C(20)	1.417(7)	C(20)-C(21)	1.363(7)
C(21)-C(22)	1.440(7)	C(22)-C(23)	1.402(7)
C(23)-C(24)	1.373(7)	C(18)-O(1)-C(15)	105.8(4)
C(4)-N(1)-C(1)	109.7(4)	C(8)-N(2)-C(5)	104.0(4)
C(14)-N(3)-C(11)	109.2(4)	C(19)-N(4)-C(22)	103.7(4)
C(24)-C(1)-N(1)	130.1(5)	C(24)-C(1)-C(2)	123.2(5)
N(1)-C(1)-C(2)	106.8(4)	C(3)-C(2)-C(1)	107.9(4)
C(2)-C(3)-C(4)	108.8(5)	N(1)-C(4)-C(5)	132.8(4)
N(1)-C(4)-C(3)	106.9(4)	C(5)-C(4)-C(3)	120.3(4)
N(2)-C(5)-C(4)	131.1(4)	N(2)-C(5)-C(6)	110.6(4)
C(4)-C(5)-C(6)	118.2(4)	C(7)-C(6)-C(5)	108.1(5)
C(6)-C(7)-C(8)	104.8(4)	N(2)-C(8)-C(9)	129.4(5)
N(2)-C(8)-C(7)	112.5(4)	C(9)-C(8)-C(7)	118.1(5)
C(10)-C(9)-C(8)	134.5(5)	C(11)-C(10)-C(9)	132.5(5)
C(10)-C(11)-N(3)	125.8(5)	C(10)-C(11)-C(12)	127.8(5)
N(3)-C(11)-C(12)	106.4(4)	C(13)-C(12)-C(11)	107.9(4)
C(13)-C(12)-C(31)	128.9(5)	C(12)-C(13)-C(14)	107.7(5)
N(3)-C(14)-C(15)	124.5(5)	N(3)-C(14)-C(13)	108.8(5)
C(15)-C(14)-C(13)	126.8(5)	C(16)-C(15)-O(1)	109.6(4)
C(16)-C(15)-C(14)	132.9(5)	O(1)-C(15)-C(14)	117.5(4)
C(15)-C(16)-C(17)	107.3(5)	C(18)-C(17)-C(16)	106.7(5)
O(1)-C(18)-C(17)	110.7(4)	O(1)-C(18)-C(19)	118.9(4)
C(17)-C(18)-C(19)	130.5(5)	N(4)-C(19)-C(20)	113.3(4)
N(4)-C(19)-C(18)	124.0(5)	C(20)-C(19)-C(18)	122.7(5)
C(21)-C(20)-C(19)	105.9(5)	C(20)-C(21)-C(22)	105.3(4)
N(4)-C(22)-C(23)	123.8(5)	N(4)-C(22)-C(21)	111.7(4)
C(23)-C(22)-C(21)	124.5(5)	C(24)-C(23)-C(22)	131.8(5)
C(23)-C(24)-C(1)	135.2(5)		

these macrocycles [2]. Ozaphyrin is a hetero analogue of saphyrin, which has methine groups arranged around the ring in the order [1.1.1.1.0] [32]. Ozaphyrin, in contrast, has methine groups arranged in the order [2.0.0.2.0], with one of the pyrrole rings replaced with a furan ring. Some examples of furan-containing macrocycles do exist, for example, the furan analogues of porphycene [33-35] and porphyrin [36,37]. However, ozaphyrin is one of the first examples of a mixed furan-pyrrole macrocycle.

The crystal structure of ozaphyrin consists of the packing of four ozaphyrin molecules and four chloroform solvate molecules. The structure of ozaphyrin·chloroform can be most aptly described as consisting of layers of staggered macrocycles stacked perpendicular to the *a*-axis, as shown in Figure 1, with the average intralayer distance being 3.4 Å. The solvated chloroform molecules fill the remaining space between the ozaphyrin macrocycles. The

Table 2  
Crystallographic Data for Ozaphyrin 6

empirical formula	C <sub>36</sub> H <sub>40</sub> N <sub>4</sub> O•ClICl <sub>3</sub>
formula weight, amu	664.09
space group	C <sub>2h</sub> <sup>5</sup> -P2 <sub>1</sub> /m
a, Å	10.481(7)
b, Å	17.353(17)
c, Å	18.726(12)
$\beta$ , deg	102.84(5)
V, Å <sup>3</sup>	3321(4)
Z	4
T, K	108
D <sub>calcd</sub> , g/cm <sup>3</sup>	1.328
$\mu$ , cm <sup>-1</sup>	3.13
crystal size, mm	0.43 x 0.22 x 0.19
transmission factors	0.938-0.962
radiation ( $\lambda$ (K $\alpha$ )), Å	graphite monochromated 0.7093
scan range, deg	4<2 $\theta$ <48
scan width, deg	1.3 in $\omega$
scan speed, deg/min	1.0 to 2.0
detector aperture, mm	3.0 horizontal, 4.0 vertical
background counts	static 1/4 time each side
data collected	$\pm h + k + l$
measured reflections	5329
unique data	5171
variables	411
R(I <sup>2</sup> ) (F <sub>o</sub> <sup>2</sup> >2 $\sigma$ (F <sub>o</sub> <sup>2</sup> ))	0.074
R <sub>w</sub> (I <sup>2</sup> )	0.165
goodness of fit	1.59
$\Delta\rho$ : max.-min, e•Å <sup>-3</sup>	0.65 and -0.55

macrocycles are staggered with slight overlap of adjacent propyl arms, so that no macrocycle is directly above the other (Figure 2). The closest approach of ozaphyrin to chloroform is 2.52 Å between atom H(37) (chloroform) and atom N(2). Figure 3 shows the labeling scheme and the structure of the ozaphyrin molecule. Bond distances and angles are reported in Table 1. The aromaticity of ozaphyrin is confirmed by its planarity. The average deviation from the mean least-squares plane of the core atoms of the macrocycle is 0.037 Å and of all non-hydrogen atoms (including those of the propyl arms) is 0.044 Å, small compared with deviations from planarity in other macrocycles [38]. Note that in porphycene [39] two of the propyl arms are coplanar with the macrocycle and two propyl arms are roughly perpendicular to the plane.

The planarity of ozaphyrin leads to a highly distorted cavity that can be described as a flattened pentagon, with the hetero atoms forming the vertices. While the N(1)-N(2) distance is 3.264(6) Å, the other four sides of the pentagon are in the narrow range 2.814(6) to 2.867(6) Å. The size of the cavity (~5.0 Å) of ozaphyrin is larger than that of most porphyrins (3-4 Å), but is comparable to that in sapphyrin [40], superphthalocyanine [41-43], pentaphyrin [44], and texaphyrin [45,46]. As opposed to the symmetrical cavities of sapphyrin and texaphyrin, the cavity of ozaphyrin is unsymmetrical. Thus, the distances from

Table 3  
Atomic coordinates ( $\times 10^4$ ) and equivalent isotropic displacement parameters (Å<sup>2</sup>  $\times 10^3$ ) for Ozaphyrin 6. U(eq) is defined as one third of the trace of the orthogonalized U<sub>ij</sub> tensor

Atom	x	y	z	U(eq)
Cl(1)	1687(2)	2210(1)	7688(1)	36(1)
Cl(2)	3538(2)	2669(1)	9001(1)	57(1)
Cl(3)	3098(2)	1058(1)	8669(1)	37(1)
O(1)	-1580(3)	-3135(2)	5371(2)	20(1)
N(1)	-987(4)	-1413(2)	6961(2)	17(1)
N(2)	-792(4)	-3172(2)	7593(2)	18(1)
N(3)	-1256(4)	-4299(2)	6443(2)	20(1)
N(4)	-1558(4)	-1499(2)	5412(2)	18(1)
C(1)	-993(5)	-612(3)	6986(3)	19(1)
C(2)	-688(5)	-400(3)	7743(3)	19(1)
C(3)	-498(5)	-1057(3)	8146(3)	21(1)
C(4)	-701(5)	-1702(3)	7659(3)	17(1)
C(5)	-612(5)	-2468(3)	7942(3)	20(1)
C(6)	-336(5)	-2567(3)	8726(3)	20(1)
C(7)	-384(5)	-3329(3)	8868(3)	18(1)
C(8)	-659(5)	-3695(3)	8156(3)	18(1)
C(9)	-756(5)	-4515(3)	8126(3)	20(1)
C(10)	-928(5)	-5048(3)	7575(3)	21(1)
C(11)	-1115(5)	-4981(3)	6832(3)	19(1)
C(12)	-1232(5)	-5592(3)	6299(3)	20(1)
C(13)	-1439(5)	-5264(3)	5624(3)	22(1)
C(14)	-1452(5)	-4459(3)	5716(3)	21(1)
C(15)	-1658(5)	-3899(3)	5160(3)	21(1)
C(16)	-1935(5)	-3946(3)	4414(3)	24(1)
C(17)	-2049(5)	-3196(3)	4145(3)	22(1)
C(18)	-1814(5)	-2719(3)	4738(3)	18(1)
C(19)	-1790(5)	-1897(3)	4780(3)	17(1)
C(20)	-2000(5)	-1420(3)	4151(3)	21(1)
C(21)	-1897(5)	-681(3)	4404(3)	20(1)
C(22)	-1631(5)	-746(3)	5190(3)	18(1)
C(23)	-1483(5)	-118(3)	5672(3)	21(1)
C(24)	-1225(5)	-79(3)	6423(3)	21(1)
C(25)	-580(5)	413(3)	8039(3)	23(1)
C(26)	-309(6)	435(3)	8873(3)	25(1)
C(27)	-273(6)	1260(3)	9174(3)	33(2)
C(28)	-197(5)	-3706(3)	9603(3)	20(1)
C(29)	20(5)	-3143(3)	10238(3)	20(1)
C(30)	330(5)	-3529(3)	10978(3)	25(1)
C(31)	-1115(5)	-6433(3)	6502(3)	24(1)
C(32)	-1487(6)	-6972(3)	5846(3)	26(1)
C(33)	-1291(6)	-7826(3)	6078(3)	33(2)
C(34)	-2078(5)	53(3)	3954(3)	22(1)
C(35)	-2326(5)	-83(3)	3136(3)	23(1)
C(36)	-2550(6)	665(3)	2701(3)	29(1)
C(37)	3187(6)	1988(3)	8299(3)	32(2)

the center of the cavity to atoms N(3), N(4), N(1), N(2), and O are 2.77, 2.71, 2.50, 2.40, and 1.95 Å. It may be possible to bind two first-row transition metals or a lanthanide in this cavity.

Ozaphyrin exhibits two quasi-reversible electrochemical reductions at -0.907 V and -1.138 V and one quasi-reversible oxidation at +0.628 V versus SCE [47]. Three other irreversible oxidations are found at higher potentials. While the potentials for the two reductions are similar to those reported for porphycenes [48], the potential for the oxidation is lower than those found in most porphycenes and porphyrins [49].

## EXPERIMENTAL

Toluene and *p*-dioxane were dried by refluxing with sodium under dinitrogen, followed by distillation. Tetrahydrofuran was dried by distillation under dinitrogen from sodium-benzophenone ketyl. Pyridine was dried by refluxing with calcium hydride under dinitrogen, followed by distillation. Pyridine was stored over either sodium hydroxide pellets or 4-Å molecular sieves. The dichloromethane used for electrochemical measurements was dried by refluxing over calcium hydride under dinitrogen. Anhydrous dimethylformamide was obtained from Burdick and Jackson Co. and stored over 4-Å sieves under dinitrogen or argon. 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, benzoyl chloride, titanium tetrachloride, and zinc dust were obtained from Aldrich Chemical Co. and were used as received. Sodium nitrite and sulfuric acid were obtained from several commercial sources and were used as received. Electrochemical grade tetrabutylammonium perchlorate and tetrabutylammonium hexafluorophosphate were purchased from Fluka and were used as received.

Melting points were determined on a Mel-Temp melting point apparatus and are uncorrected. Proton and <sup>13</sup>C nmr measurements were made with deuteriochloroform as solvent on a Varian Gemini nmr spectrometer operating at 300 and 75.4 MHz, respectively. Chemical shifts (δ) are reported in parts per million, with tetramethylsilane as the reference. Electron-impact and fast-atom-bombardment 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. The uv-visible spectra were recorded on a Cary 1E spectrophotometer. Electrochemical measurements were carried out on a Model CS-1087 Computer Controlled Electro-analytical System, made by Cypress Systems, Inc. A conventional three-electrode system was used, comprising a platinum working electrode, a silver wire counter electrode, and a saturated SCE as the reference electrode. The potential scan rate was varied from 100 mV/s to 1500 mV/s. Infrared measurements were made on an upgraded Mattson Alpha Centauri Fourier-transform infrared spectrometer. Elemental analyses were carried out by Searle Microanalytical Services at Northwestern University.

## Crystallography.

Crystals of ozaphyrin suitable for diffraction studies were obtained from a chloroform/methanol solution that was cooled to 5°. The final cell dimensions of *a* = 10.481(7) Å, *b* = 17.353(17) Å, *c* = 18.726(12) Å, β = 102.84(5)° at 108 K were found by a least-squares refinement of the setting angles of 25 reflections that had been automatically centered on an Enraf-Nonius CAD4 diffractometer. Intensity data were collected at 108 K by the ω-2θ scan technique and were processed by methods standard to this laboratory [50]. The intensities of 6 standard reflections were measured every 3 hours of X-ray exposure time. A total of 5329 reflections were measured, 5171 of which are unique. An absorption correction was applied [51]. Experimental details and crystal data are shown in Table 2. The structure was solved by direct methods [52], and refined by full-matrix least-squares calculations [53], the function Σ(*F<sub>o</sub>*<sup>2</sup> - *F<sub>c</sub>*<sup>2</sup>)<sup>2</sup> being minimized. A difference electron density map allowed the assignment of the internal hydrogen atoms to atoms N(1) and N(3). The final refinement on

*F<sub>o</sub>*<sup>2</sup>, including anisotropic thermal parameters of all non-hydrogen atoms and a riding model for the hydrogen atoms (411 variables, 5157 observations), resulted in a value of *R<sub>w</sub>*(*F<sub>o</sub>*<sup>2</sup>) of 0.165. For those 3289 reflections having *F<sub>o</sub>*<sup>2</sup> > 2σ(*F<sub>o</sub>*<sup>2</sup>), *R*(*F*) is 0.074. Final positional and equivalent isotropic displacement parameters are given in Table 3. Anisotropic displacement parameters for the non-hydrogen atoms are given in Table S1 [54], while final positional and thermal parameters for hydrogen atoms are reported in Table S2. Bond lengths and angles for all atoms are given in Table S3, while Table S4 provides a listing of structure amplitudes. These supplementary tables have been deposited [54].

5,5'-Diformyl-4,4'-dipropyl-2,2'-bipyrrole (**1**).

This compound was prepared as previously reported [2].

1,4-Bis(3,5-bis(ethoxycarbonyl)-4-propyl-2-pyrrolyl)-1,4-butanedi-one (**2**).

This compound was prepared as previously reported [2].

2,5-Bis(3,5-bis(ethoxycarbonyl)-4-propyl-2-pyrrolyl)furan (**3**).

A solution of **2** (20 g, 34 mmoles) in ethanol (100 ml) containing concentrated sulfuric acid (0.5 ml) was held at reflux under dinitrogen for 8 hours. When the solution was cooled to 0° a precipitate was obtained. This precipitate was collected by filtration, washed with ethanol, and dried to give the product tetraester furan **3** (17 g, 30 mmole, 88%) as a fluorescent yellow solid, mp 165-166°. The tetraester furan **3** is moderately light sensitive in solution and must be protected from light. If the product tetraester furan **3** was not of sufficient purity, as indicated by nmr or tlc measurements, it was further purified by eluting through silica gel with (25:1 v/v) chloroform/ethyl acetate as the eluent; <sup>1</sup>H nmr: δ 0.99 (t, *J* = 7.3 Hz, 6H, CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 1.40 (t, *J* = 7.1 Hz, 12H, OCH<sub>2</sub>CH<sub>3</sub>), 1.61 (sextet, *J* = 7.6 Hz, 4H, CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 3.06 (m, 4H, CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 4.37 (q, *J* = 7.1 Hz, 8H, OCH<sub>2</sub>CH<sub>3</sub>), 7.46 (s, 2H, furan CH), 9.72 (br, 2H, NH); <sup>13</sup>C nmr: δ 14.2, 14.3, 24.5, 27.9, 60.2, 60.8, 112.7, 114.6, 119.8, 129.3, 135.9, 144.8, 151.3, 161.9, 164.6; ms (chloroform): *m/z* 570 (100%), 524 (55%), 478 (7.8%); hrms Calcd. for C<sub>30</sub>H<sub>38</sub>N<sub>2</sub>O<sub>6</sub>; *m/z* 570.2577. Found: 570.2578.

*Anal.* Calcd. for C<sub>30</sub>H<sub>38</sub>N<sub>2</sub>O<sub>6</sub>; C, 63.15; H, 6.71; N, 4.91. Found: C, 63.10; H, 7.01; N, 4.85.

2,5-Bis(4-propyl-2-pyrrolyl)furan (**4**).

Tetraester furan **3** (1.3 g, 2.2 mmoles), potassium hydroxide (10 g, 178 mmoles), water (10 ml), and ethanol (10 ml) were held at reflux under dinitrogen for 24 hours. The ethanol was then boiled off to leave a tan oil and an aqueous base. After 8 hours the reflux was stopped, and when the solution was cooled a green oil solidified. This oil was collected, passed through a silica plug (methylene chloride eluent), and evaporated down with hexane on a rotary evaporator. When solid appeared, the flask contents were filtered, washed with hexane, and dried to give dipyrrolyl-furan **4** as white waxy flakes (0.45 g, 1.6 mmoles, 60%), mp 114°; <sup>1</sup>H nmr: δ 0.96 (t, *J* = 5.4 Hz, 6H, CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 1.61 (sextet, *J* = 5.7 Hz, 4H, CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 2.45 (t, *J* = 5.7 Hz, 4H, CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 6.30 (d, *J* = 2.4 Hz, 2H, CHNH), 6.32 (s, 2H, furan CH), 6.58 (s, 2H, pyrrole CH), 8.23 (br, 2H, CHNH); <sup>13</sup>C nmr: δ 14.0, 24.2, 29.1, 103.9, 105.7, 115.4, 123.7, 126.1, 146.2; ms (chloroform): *m/z* 282 (100%), 253 (21%), 112 (21%); hrms Calcd. for C<sub>18</sub>H<sub>22</sub>N<sub>2</sub>O; *m/z* 282.1732. Found: 282.1719.

*Anal.* Calcd. for  $C_{18}H_{22}N_2O$ : C, 76.56; H, 7.85; N, 9.92. Found: C, 76.15; H, 7.90; N, 9.72.

#### 2,5-Bis(5-formyl-4-propyl-2-pyrrolyl)furan (5).

Dipyrrolylfuran **4** (2.82 g, 10 mmoles) was dissolved in anhydrous dimethylformamide (250 ml) under nitrogen. Benzoyl chloride (14 g, 100 mmoles) was then added. The resulting orange solution was stirred for 5 minutes, then held at 100° for 16 hours. The solution was then poured into 500 g of crushed ice and made basic with 50% sodium hydroxide. The resulting fine suspension was heated to 80°, saturated with salt, then cooled and filtered through a medium fritted glass filter. The yellow solid so obtained was washed with water and dissolved in 400 ml of hot chloroform. The traces of water were separated and the chloroform solution was concentrated on a rotary evaporator to a volume of about 10 ml. The solid was then separated by filtration, washed with chloroform and ether, and dried to give the product dipyrrolefuran dialdehyde **5** (2.7 g, 8.75 mmoles, 88%) as a yellow to light green powder, mp 254°. A second crop (0.3 g, 0.09 mmole, 9%) was obtained from the chloroform liquors; <sup>1</sup>H nmr:  $\delta$  1.00 (t, J = 7.2 Hz, 6H,  $CH_2CH_2CH_3$ ), 1.72 (sextet, J = 7.5 Hz, 4H,  $CH_2CH_2CH_3$ ), 2.78 (t, J = 7.5 Hz, 4H,  $CH_2CH_2CH_3$ ), 6.44 (d, J = 2.5 Hz, 2H,  $CHNH$ ), 6.76 (s, 2H, furan CH), 9.74 (s, 2H, CHO), 10.57 (br, 2H,  $CHNH$ ); <sup>13</sup>C nmr:  $\delta$  13.9, 24.7, 27.3, 108.7, 109.4, 129.5, 130.0, 139.8, 146.1, 177.4; ms (chloroform): m/z 338 (100%), 323 (18%); hrms Calcd. for  $C_{20}H_{22}N_2O_3$ : m/e 338.1630. Found: 338.1635.

*Anal.* Calcd. for  $C_{20}H_{22}N_2O_3$ : C, 70.98; H, 6.55; N, 8.28. Found: C, 70.70; H, 6.97; N, 8.19.

#### Ozaphyrin 6.

A solution of titanium tetrachloride (3.85 g, 20.3 mmoles) in tetrahydrofuran (275 ml) was added under an argon atmosphere to zinc dust (2.8 g, 42.4 mmoles) with stirring, and the suspension was held at reflux for 1.5 hours. Dipyrrolefuran dialdehyde **5** (0.25 g, 0.74 mmole), bipyrrole dialdehyde **1** (0.22 g, 0.81 mmole) and pyridine (3 ml) in tetrahydrofuran (500 ml) were then added dropwise over a 4-hour period to the gently refluxing suspension. The resulting mixture was refluxed with stirring for 17 hours. A quenching solution of 10% potassium carbonate in water (75 ml) was then carefully introduced. The reaction mixture was filtered through Celite, and chloroform (300 ml) was added. The water layer was separated and the resulting chloroform/tetrahydrofuran solution was concentrated on a rotary evaporator. This solution was eluted through several silica gel columns with (1:2 v/v) chloroform/hexanes as the eluent. Porphycene was collected as a fast-running purple band and ozaphyrin **6** was collected as the third green band. Ozaphyrin was crystallized from chloroform/methanol, and dried *in vacuo* (20 mg, 0.036 mmole, 5.0%) as purple pentagonal blocks, mp 164-166°; uv visible (methylene chloride):  $\lambda$  max (log  $\epsilon$ ) 259 (4.03), 360 (4.30), 414 (5.06), 430 (5.00), 640 (4.53), 677 (4.33), 735 (4.76); <sup>1</sup>H nmr:  $\delta$  -2.16 (s, 2H, NH), 1.49 (t, J = 7.4 Hz, 12H,  $CH_2CH_2CH_3$ ), 2.60 (m, 8H,  $CH_2CH_2CH_3$ ), 4.29 and 4.36 (t, J = 7.6 Hz, 8H,  $CH_2CH_2CH_3$ ), 9.86 (s, 2H, pyrrole CH), 10.31 (q, 4H, J = 11.8 Hz, methine CH), 10.47 and 10.50 (s, 4H, pyrrole and furan CH); <sup>13</sup>C nmr:  $\delta$  14.8, 14.8, 25.3, 25.6, 30.9, 31.5, 107.1, 110.3, 117.5, 121.6, 129.8, 131.6, 134.6, 142.0, 143.0, 143.4, 144.2, 144.4; ms (chloroform): m/z 501 (100%), 545 (89%), 459 (23%), 443 (20%); hrms Calcd. for  $C_{36}H_{41}N_4O$ : m + 1/e 545.3280. Found: 545.3309.

*Anal.* Calcd. for  $C_{36}H_{40}N_4O$ : C, 79.38; H, 7.40; N, 10.28. Found:

C, 77.56; H, 7.79; N, 9.94.

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