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Serendipitous Discovery of Conjugated Dipyrromethene-Linked Nitronaphthoporphyrins

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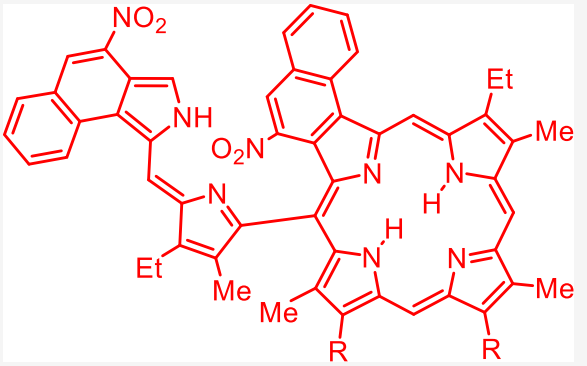
ABSTRACT: Acid-catalyzed condensation of a nitronaphthalene-fused dipyrrylmethane with dipyrrylmethane dialdehydes afforded unique dipyrromethene-naphthoporphyrin conjugates together with expected nitronaphthoporphyrins. The unusual conjugated system retained aromatic porphyrin-type characteristics but afforded highly modified UV−vis spectra with multiple absorptions throughout the visible region.



INTRODUCTION

Numerous approaches to modifying the porphyrin chromophore has been explored, including the synthesis of core modified systems,[1] annulated porphyrinoids,[2] expanded porphyrins[3] and contracted porphyrin-like species.[4] Porphyrin-type structures with absorptions in the red or far red have attracted substantial attention due to potential applications as photosensitizers for photodynamic therapy[5] and in the development of sensors and novel optical materials.[6] Fusion of aromatic rings to the porphyrin nucleus gives mixed results and mononaphtho[1,2-*b*]porphyrins **1**[7] or related phenanthroporphyrins **2**[8] (Figure 1) give only minor bathochromic shifts. However, related structures with additional fusion to *meso*-carbons give far more profound changes as illustrated by recently described porphyrins **3** and **4**.[9,10]

In relation to our investigations into porphyrins with *β*,*β*′-fusion such as **1** and **2**, a series of nitronaphthoporphyrins **5**, **6**, **7** and **8a** were targeted for synthesis (Figure 1).[11] The results from this study showed significant differences in the chromophores depending upon the placement of the nitro substituent. Unfortunately, acidolytic scrambling gave isomeric mixtures in two cases, and this was particularly problematic in the synthesis of **8a**.[11] Although the nitro group is situated next to the porphyrin nucleus in **8a**, its UV−vis spectrum closely resembled the reported values for **1**. During these investigations, a porphyrin-like byproduct was observed in addition to **8a** with an unusual electronic absorption spectrum. This interesting system has now been isolated and fully characterized. These results demonstrate that an unprecedented dipyrromethene-naphthoporphyrin dyad was generated.

RESULTS AND DISCUSSION

Naphthalene-fused pyrroles needed in the synthesis of nitronaphthoporphyrins were prepared from dinitronaphthalenes using a modification of the Barton−Zard reaction (Scheme 1).[12−14] 1,3-Dinitronaphthalene reacted with *tert*-butyl isocyanoacetate to give a mixture of nitronaphtho[1,2-*c*]pyrroles **9** and **10** together with a dipyrrolonaphthalene (structure not shown).[11] Reaction of **10** with acetoxymethylpyrrole **11**[15] in the presence of K-10 Montmorillonite clay[16] gave dipyrrylmethane **12**.[11] The *tert*-butyl ester protective groups were cleaved with trifluoroacetic acid (TFA) and the resulting crude intermediate **13** was reacted with dipyrrylmethane dialdehyde **14a**[21] in the presence of *p*-toluenesulfonic acid. Air oxidation in the presence of zinc acetate, followed by demetalation with TFA, gave the porphyrin products.

Two porphyrin products were identified with similar polarity, but these could be separated by column chromatography. The first fraction corresponded to the expected nitronaphthoporphyrin **8a**, although some isomerization due to acidolytic cleavage-recombination processes[17,18] was evident in the proton NMR spectrum. The second component, isolated in 11−17% yield, was more complex and gave an atypical UV−vis spectrum with strong absorptions at 427 and 548 nm, together with medium-sized absorptions at 599 and

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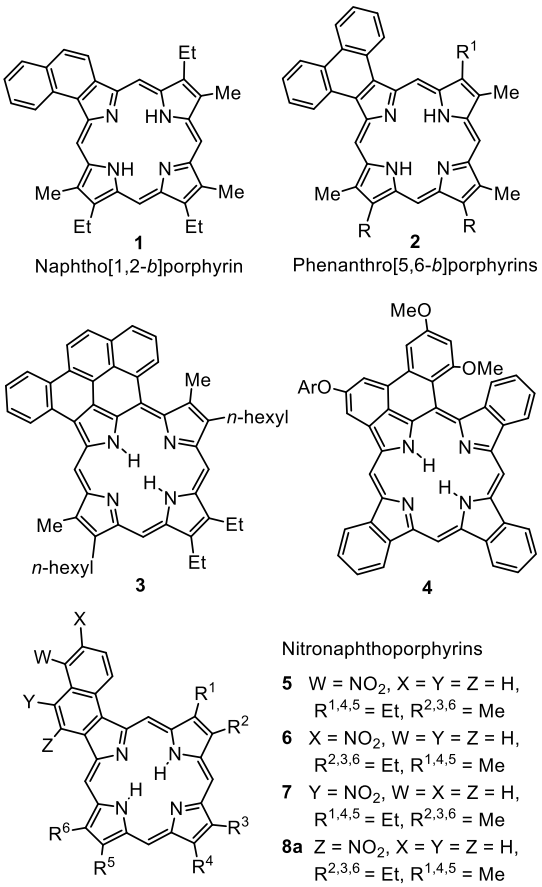
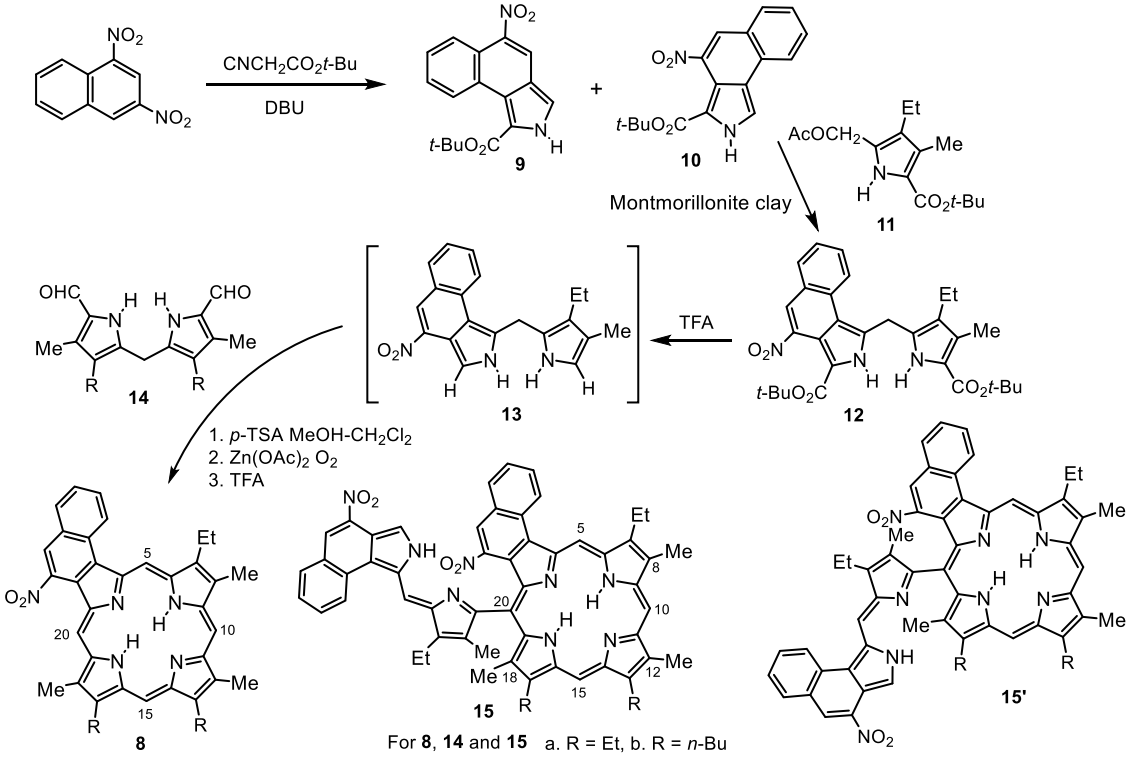


Figure 1. Structures of selected annulated porphyrins.

674 nm. The high-resolution TOF-ESI mass spectrum for this species gave a [M + H] peak at m/z 911.4022 that is consistent with the unknown product having the molecular formula $C_{57}H_{50}N_8O_4$. By itself, the molecular formula implied that two nitronaphthodipyrrylmethane units **13** had been incorporated into this structure. The proton NMR spectrum (Figure 2), while complex, showed that this compound, unlike porphyrin **8a**, was isomerically pure.

The proton NMR spectrum of the byproduct showed the presence of five 1H singlets at 10.93, 9.98, 9.80, 8.60 and 8.33 ppm, and the three downfield resonances were assigned as bridging *meso*-protons on a porphyrin ring (Figure 3). NOE difference proton NMR spectroscopy (Figures S27−S30) showed a correlation between the singlet at 8.60 ppm and an aromatic doublet at 8.11 ppm, demonstrating that this peak corresponded to an isolated naphthalene proton. The singlet at 10.03 ppm gave an NOE correlation to a doublet at 10.02 ppm and a multiplet at 4.16 ppm, showing that this corresponded to the 5-H *meso*-proton. Unfortunately, some of the NOE correlations were weak due in part to the low solubility of this compound. Nevertheless, the *meso*-proton at 9.98 ppm interacted with the ethyl group resonances at 3.9−4.0 ppm and could be assigned to the 15-H, while the singlet at 9.80 weakly interacted with the methyl resonances at 3.57 and 3.46 ppm, confirming that this peak could be assigned to the 10-H. Four aromatic 1H doublets and four 1H triplets were noted corresponding to two benzo-units and the assignments for these were confirmed by analysis of the ^{1}H−^{1}H COSY plot (Figure 2). The peak at 8.37 ppm appeared as a weakly coupled doublet, as did the resonance at 8.92 ppm, and these could be assigned to the bridge CH for the dipyrromethene unit and a pyrrolic C−H that were engaged in $^5J_{HH}$ coupling (ca. 1 Hz).

Scheme 1. Synthesis of Nitronaphthoporphyrins and Related Dipyrromethene Adducts



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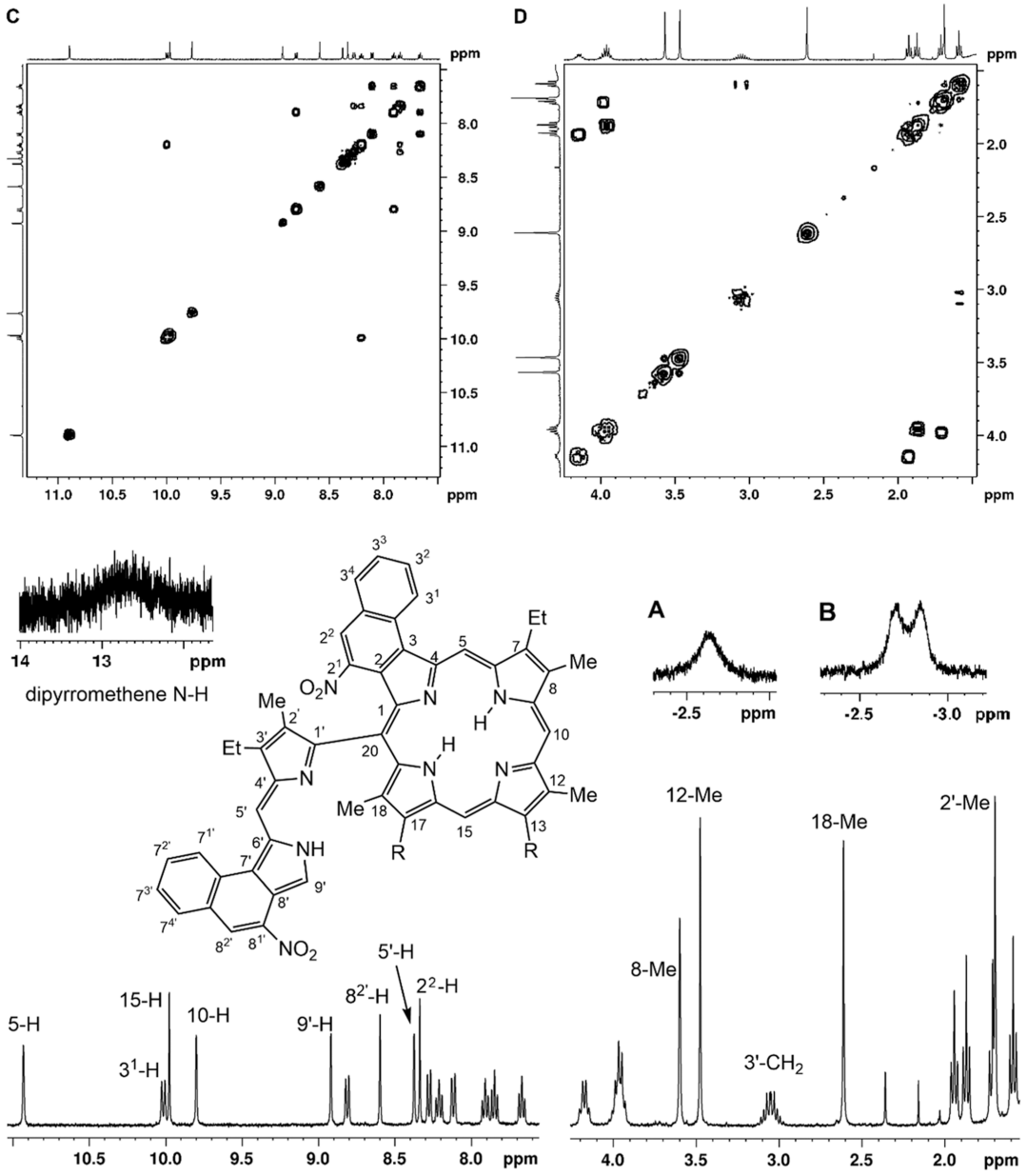

Figure 2. Proton NMR spectrum of nitronaphthoporphyrin byproduct **15a** in $CDCl_3$ at 50 °C. A broad peak between 12 and 13 ppm corresponds to the dipyrromethene N−H. At 50 °C, the internal porphyrin NHs give rise to a broad resonance between −2.5 and −3.0 ppm (insert A), but at 29 °C, this resolves into two separate peaks (insert B). The ^{1}H−^{1}H COSY spectrum for the downfield (C) and upfield (D) regions illustrates the coupling interactions in this unusual system.

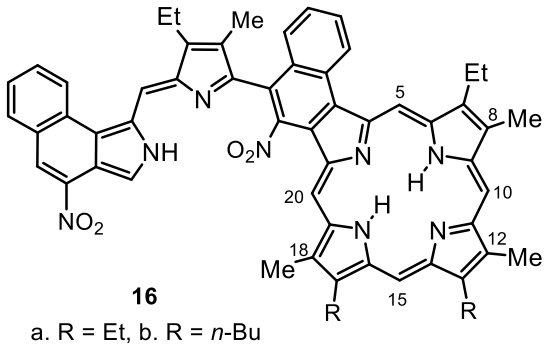

Figure 3. Initially proposed structures **16** for byproducts.

Four 3H singlets were present at 3.60, 3.48, 2.61, and 1.69 ppm. The diamagnetic ring current of porphyrins strongly deshields directly connected alkyl substituents and porphyrin-methyl groups generally show up near 3.6 ppm.[19] Therefore, while two resonances are present in this region, the other two peaks diverge considerably from the expected values. A 2H quartet and a 4H multiplet between 4.20 and 3.90 ppm fall into the expected range for porphyrin-CH_2 units and the ^{1}H−^{1}H COSY spectrum showed that these protons couple with 3H triplets at 1.94, 1.87, and 1.71 ppm, confirming that at least three ethyl substituents are present (Figure 2). In addition, a 2H multiplet at 3.12−2.98 ppm is consistent with a diastereotopic methylene unit and this also coupled with a 3H triplet at 1.59 ppm. NOE difference proton NMR spectroscopy showed that the CH_2 was placed next to the

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bridging methine resonance of the dipyrromethene unit at 8.37 ppm. At 50 °C, a broad 2H resonance is observed at −2.64 ppm that is consistent with the internal NHs for a porphyrin macrocycle, but the very broad downfield peak at 13 ppm indicates that a strongly hydrogen bonded OH or NH is present; this is due to the dipyrromethene NH. At 29 °C, the porphyrin NH protons resolved into two broad peaks showing that proton exchange was slow enough to provide different chemical environments for the two protons (Figure 2). Some ambiguity arose because the singlet at 8.33 ppm did not show any NOE correlations. Initially the byproduct was assigned as structure **16** (Figure 3) as the species could plausibly arise by conjugative nucleophilic attack by a second dipyrrylmethane unit onto the nitronaphthalene moiety. A problem with this assignment is that the *meso*-proton at position 20 would have to correspond to the relatively upfield peak at 8.33 ppm. In addition, the resonance for the methyl group at position 18 appears at 2.61 ppm, which is about 1 ppm upfield from the expected value. This can be rationalized as being due to shielding due to the 20-H and 18-Me protons lying under the nitro substituent's π-system. The HSQC spectrum was also a cause for concern as the proton signal at 8.33 ppm corresponded to a carbon-13 resonance at 123.1 ppm. Unsubstituted *meso*-carbons in porphyrins usually show up between 90 and 105 ppm and indeed the remaining *meso*-protons appeared at 100.6, 98.1, and 97.1 ppm. Therefore, there would of necessity have to be a profound electronic effect to shift the *meso*-carbon resonance so far downfield. This type of shift is seen in core modified porphyrinoids such as thiaporphyrins[19] and once again this possibility appears to be reasonable. The only alternative was that the dipyrromethene unit had been regioselectively introduced at position 20. The formation of this species, structure **15**, Scheme 1, would require substitution at a sterically hindered site. The UV−vis spectrum (see below) was also quite different from previously described *meso*-linked dipyrromethene-porphyrin dyads.[20] A second example of this system with *n*-butyl substituents was prepared by reacting **13** with dialdehyde **14b**. Unexpectedly, this version (**15b**) was far less soluble in organic solvents even though longer alkyl substituents are present. It was possible to obtain the proton NMR spectrum for **15b** but the low solubility prevented us from obtaining a high quality carbon-13 NMR spectrum. In fact, **15a** is also not very soluble and a noisy carbon-13 NMR spectrum could only be obtained at 50 °C when run for approximately 16 h.

The UV−vis spectra of **15a** and **15b** show strong absorptions in the near UV and most of the visible region (Figure 4). Although falling slightly short of being a panchromatic system, porphyrins with these types of absorption spectra are being sought for applications in dye-sensitized solar cells.[21] Previously reported porphyrins with *meso*-dipyrromethene substituents gave very different electronic spectra showing strong Soret band and much weaker absorptions at longer wavelengths. Addition of trace amounts of TFA to **15a,b** resulted in the formation of a protonated species with strong absorptions at 437, 562, and 728 nm. At much higher concentrations of TFA, a third species was generated with peaks at 410, 435, 574, and 692 nm. Nitronaphthoporphyrins **8** have reduced basicity compared to regular porphyrins and it is speculated that the initial protonation occurs on the dipyrromethene unit.

As the formation of **15** requires 2 M equivalents of **13** to 1 M equivalent of dialdehydes **14**, the reaction was repeated with

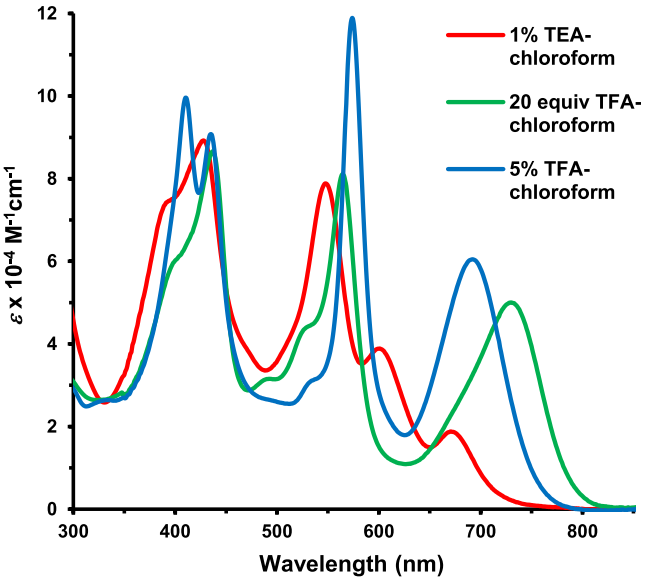
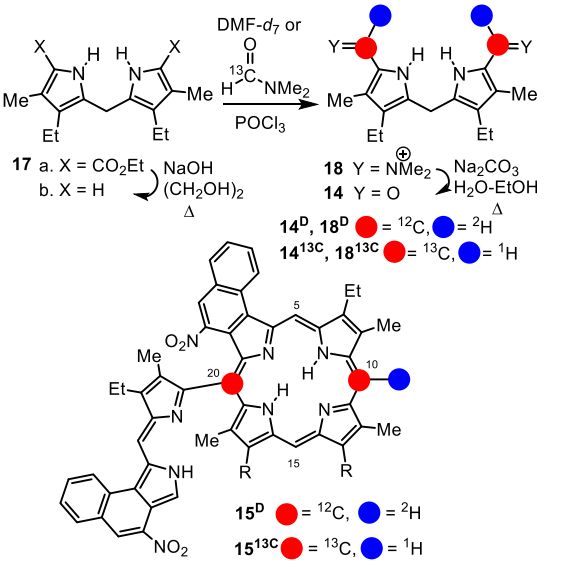


Figure 4. UV−vis spectra of dipyrromethene-appended nitronaphthoporphyrin **15a** in 1% Et_3N−$CHCl_3$ (red line), in $CHCl_3$ with 20 equiv of TFA (green line) and in 5% TFA-$CHCl_3$ (blue line).

up to two equivalents of the nitronaphthodipyrrylmethane. However, there was no significant improvement in the yields compared to reacting the dipyrrolic precursors in a 1:1 molar ratio. In addition, attempts to react nitronaphthoporphyrin **8** with **13** under the same conditions failed to give any formation of **15**. This result indicates that **8** is not a precursor to **15** and the observation is supported by the spectroscopic results as **8** is a mixture of isomers but **15** is not significantly contaminated with isomeric structures.

The final structural identification of these byproducts relied upon the introduction of isotopic labels. A deuterated dipyrrylmethane dialdehyde was prepared using the Vilsmeier−Haack reaction (Scheme 2). Diester **17a**[22] was heated with sodium hydroxide in ethylene glycol to afford **17b** and this was reacted with the Vilsmeier complex derived from phosphorus

Scheme 2. Synthesis of Isotopically Labeled Dipyrrylmethane Dialdehydes and Porphyrinoid Products



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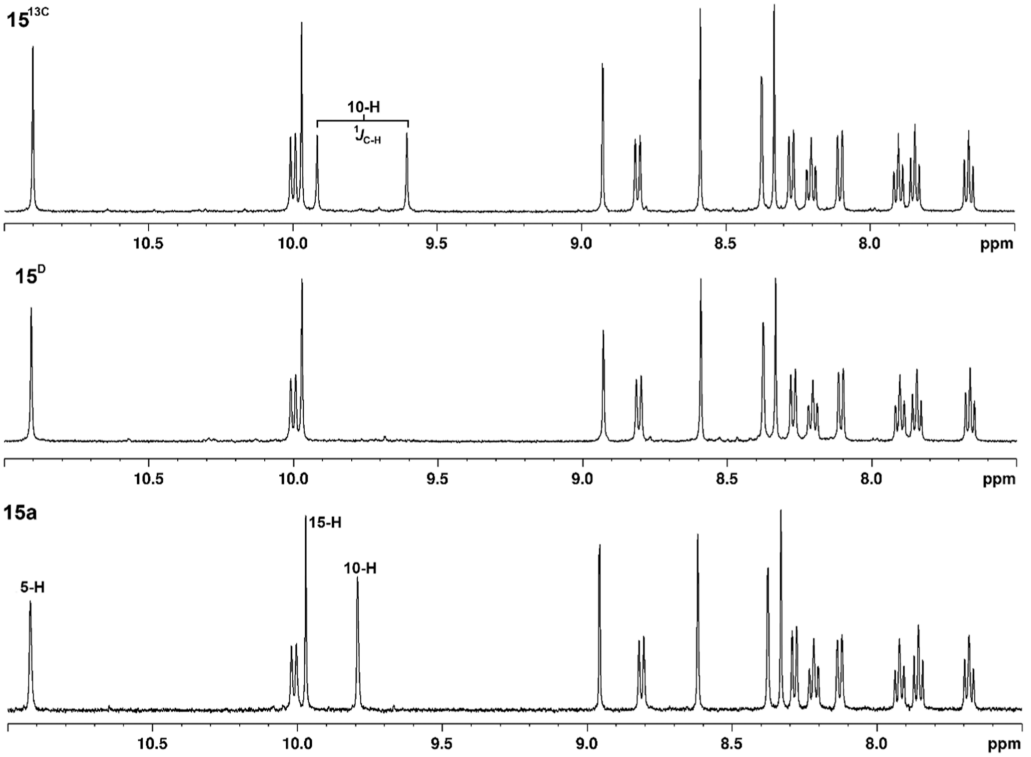
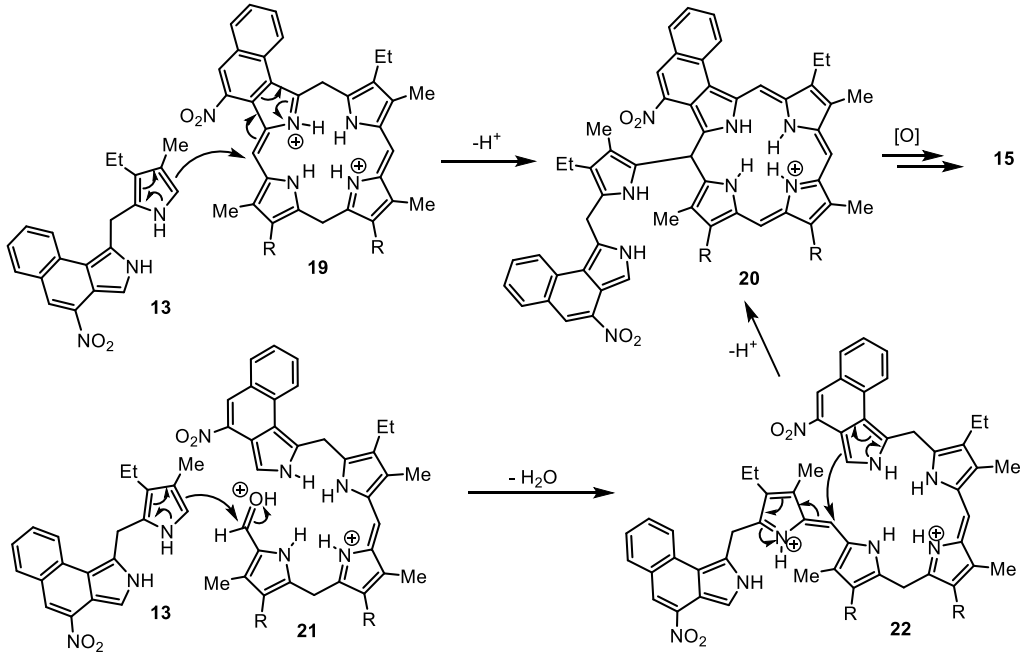


Figure 5. Proton NMR spectra of byproduct **15** (bottom), deuterated byproduct **15**^{D} (middle) and ^{13}C-labeled byproduct **15**^{13C} (top) showing details of the aromatic region.

Scheme 3. Potential Mechanisms for the Formation of Dipyrromethene-Appended Nitronaphthoporphyrins 15



oxychloride and DMF-d_7 to give imine salt **18**^{D}; subsequent hydrolysis afforded labeled dialdehyde **14**^{D}. Reaction of **14**^{D} with **13** as described above (Scheme 1) gave nitronaphthoporphyrin **8a** and deuterated byproduct **15**^{D}. The proton NMR spectrum for the isolated byproduct showed the loss of the resonance at 9.80 ppm but the peak at 8.33 ppm was still present (Figure 5). If this corresponded to a *meso*-proton, as would be expected if the product were in fact **16**, this resonance should also be lost. However, this study did not allow an unambiguous assignment to be made. Examination of the proton NMR spectrum for the nitronaphthoporphyrin **8a** formed in this reaction showed that no deuterium incorporation was present. This observation was confirmed by high resolution TOF-ESI mass spectrometry. Hence, proton exchange with the *meso*-protons must have occurred and could potentially take place in the byproduct as well. In order to address this issue, carbon-13 labeled dialdehyde **14**^{13C} was prepared from 1-^{13}C DMF (Scheme 2). Reaction with **13** as

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before gave carbon-13 labeled nitronaphthoporphyrin $\mathbf{8}^{13C}$ and byproduct $\mathbf{15}^{13C}$. As expected, the nitronaphthoporphyrin was contaminated with isomeric impurities. However, incorporation of the ^{13}C-label was also evident. The proton NMR spectrum for $\mathbf{15}^{13C}$ (Figure 5) gave rise to a doublet for the 10-H resonance ($^{1}J_{CH}$ = 155.7 Hz); however, the peak at 8.33 ppm was unaffected, demonstrating that structure **16** cannot be correct. The carbon-13 NMR spectrum showed a labeled methine carbon at 97.1 ppm and a quaternary carbon at 105.4 ppm. The latter signal corresponds to *meso*-carbon C-20 in structure **15**. The observed upfield shift to the methyl substituent at position 18 can be ascribed to it lying under the π-system for the dipyrromethene unit. Two conjugated conformations, **15** and **15′** (Scheme 1), are feasible. In the former, hydrogen bonding to a nitro substituent may be possible.

The formation of dyads **15** was unexpected and difficult to fully rationalize. MacDonald condensation of **13** with dialdehydes **14** would be expected to generate porphodimethenes **19** and these may be more prone to nucleophilic attack from a second equivalent of **13** at position **20** due to the electron-withdrawing nature of the fused nitroarene unit (Scheme 3). Subsequent air oxidation of intermediate **20** would then afford the observed product. However, this does not explain why byproducts **15** are obtained in isomerically pure form, while nitronaphthoporphyrins **8** exhibit a significant degree of scrambling. The conjugate addition could take place prior to porphyrin formation but the methine linkage is likely to initially form at position 10 due to the reduced nucleophilicity of the nitronaphthopyrrole component. This would lead to the formation of an open-chain tetrapyrrole **21** that could undergo an intermolecular attack from **13** to give, following elimination of water, a hexapyrrolic intermediate **22**. Cyclization would generate **20** and subsequent oxidation would again produce **15**.

CONCLUSIONS

A unique dipyrromethene-naphthoporphyrin conjugate has been synthesized by acid-catalyzed condensations of a nitronaphthodipyrrylmethane with dipyrrylmethane dialdehydes. The dipyrromethene and porphyrin components appear to strongly interact as the resulting UV−vis spectrum for this system gives atypical absorptions over most of the visible region. The formation of this novel porphyrin derivative indicates that other interesting architectures may be accessible when electron-deficient subunits are present.

EXPERIMENTAL SECTION

Melting points are uncorrected. NMR spectra were recorded using a 400 or 500 MHz NMR spectrometer and were run at 302 K unless otherwise indicated. ^{1}H NMR values are reported as chemical shifts δ, relative integral, multiplicity (s, singlet; d, doublet; t, triplet; q, quartet; p, pentet; m, multiplet; br, broad peak), and coupling constant (J). Chemical shifts are reported in parts per million (ppm) relative to $CDCl_3$ ^{1}H residual $CHCl_3$ singlet δ 7.26 ppm, ^{13}C $CDCl_3$ triplet δ 77.23 ppm, and coupling constants were taken directly from the spectra. Structural assignments were made with additional information from gCOSY, gHSQC, and NOE difference NMR experiments Mass spectral data were acquired using positive-mode electrospray ionization (ESI^+) and a high-resolution time-of- flight mass spectrometer. ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra for all new compounds are reported in Supporting Information.

Deuterated 3,3′-Diethyl-4,4′-Dimethyl-2,2′dipyrrylmethane-5,5′-Dicarbaldehyde 14^{D}. A mixture of dipyrrylmethane diethyl ester **17a**[22] (770 mg. 2.06 mmol), ethylene glycol (10 mL), sodium hydroxide (1.0 g) and 2 drops of hydrazine was placed in a preheated oil bath at 200 °C and stirred under reflux for 2 h. The mixture was cooled, poured into water (100 mL) and extracted with hexanes. The organic solution was dried over sodium sulfate, filtered and the solvent evaporated under reduced pressure to give deprotected dipyrrylmethane **17b** as a pale yellow oil. DMF-d_7 (0.50 g) was placed in a 25 mL round-bottom flask and cooled in a salt ice bath to <10 °C. Phosphorus oxychloride (1.05 g) was added dropwise to the stirred liquid while maintaining the temperature between 10 and 20 °C. The resulting Vilsmeier complex, which solidified, was allowed to stand at room temperature for 15 min and then dissolved in dichloromethane (2.5 mL) and cooled to 10 °C. Dipyrrylmethane **17b** was dissolved in dichloromethane (2.5 mL) and added dropwise to the Vilsmeier reagent. The resulting mixture was stirred under reflux by heating the flask with a hot water bath for 15 min. The solvent was removed on a rotary evaporator and the residue refluxed with sodium carbonate (1.0 g) and a 1:1 ethanol−water mixture (16 mL) on a boiling water bath. The mixture was cooled, diluted with water (20 mL) and the resulting precipitate collected by suction filtration. The solid was dried in vacuo and recrystallized from chloroform-hexanes to give $\mathbf{14}^{D}$ (443 mg, 1.54 mmol, 75%) as a pale yellow solid, mp 215−216 °C. IR (ATR): ν/cm^{-1} 3217 (N−H stretch), 2117 (C−D stretch), 1593 (C═O stretch). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 10.55 (br s, 2H, 2 × NH), 3.95 (s, 2H, bridge-CH_2), 2.47 (q, 4H, J = 7.5 Hz, 2 × CH_2CH_3), 2.29 (s, 6H, 2 × pyrrole-CH_3), 1.08 (t, 6H, J = 7.5 Hz). $^{13}C\{H\}$ NMR ($CDCl_3$, 125 MHz): δ 176.7 (t, $^{1}J_{C-D}$ = 25.7 Hz, 2 × CDO), 134.7, 132.3, 129.2 (5,5′-C), 125.2, 23.1 (bridge-CH_2), 17.3 (2 × CH_2CH_3), 15.3 (2 × CH_2CH_3), 9.0 (2 × pyrrole-CH_3). HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{17}{}^{1}H_{19}{}^{2}H_2N_2O_2$, 287.1723, found, 287.1723.

Carbon-13 Labeled 3,3′-Diethyl-4,4′-Dimethyl-2,2′dipyrrylmethane-5,5′-Dicarbaldehyde 14^{13C}. Following the procedure detailed above, 1-^{13}C-DMF (0.50 g; 67.5 mmol) and dipyrrylmethane **17a**[22] (0.830 g, 2.22 mmol) afforded ^{13}C-labeled dialdehyde $\mathbf{14}^{13C}$ (500.5 mg, 1.74 mmol, 78%) as a pale gray solid, mp 218−219 °C. IR (ATR): ν/cm^{-1} 3217 (N−H stretch), 1584 (C═O stretch). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 10.73 (br s, 2H, 2 × NH), 9.49 (d, 2H, $^{1}J_{C-H}$ = 72.3 Hz, 2 × CHO), 3.95 (s, 2H, bridge-CH_2), 2.47 (q, 4H, J = 7.5 Hz, 2 × CH_2CH_3), 2.29 (s, 6H, 2 × pyrrole-CH_3), 1.07 (t, 6H, J = 7.5 Hz). $^{13}C\{H\}$ NMR ($CDCl_3$, 125 MHz): δ 176.9, 134.8, 132.4 (br), 129.1 (d, $^{1}J_{C-C}$ = 67.8 Hz, 5,5′-C), 125.2 (d, $^{2}J_{C-C}$ = 3.3 Hz), 22.9 (bridge-CH_2), 17.3 (2 × CH_2CH_3), 15.5 (2 × CH_2CH_3), 9.0 (2 × pyrrole-CH_3). HRMS (ESI) m/z: $[M + H]^+$ calcd for $^{12}C_{15}{}^{13}C_2H_{21}N_2O_2$, 287.1665, found, 287.1660.

Reaction of Nitronaphthodipyrrylmethane 12 with Dialdehyde 14a. Dipyrrylmethane **12**[11] (100 mg, 0.187 mmol) was stirred with TFA (2 mL) under nitrogen for 10 min. The mixture was then diluted with chloroform (50 mL) and washed sequentially with water, 5% aqueous sodium bicarbonate solution and water. The organic layer was dried over sodium sulfate, the solution filtered and the solvent removed under reduced pressure. The residue and dialdehyde **14a**[22] (48.2 mg, 0.168 mmol) were dissolved in dichloromethane (206 mL) and methanol (10 mL), a solution of *p*-toluenesulfonic acid (225 mg) in methanol (10 mL) was added, and the resulting mixture was stirred at room temperature open to the air for 16 h. A saturated solution of zinc acetate in methanol (10 mL) was then added and the mixture was stirred open to the air for 2 additional days. The mixture was then washed with water and the solvent was removed under reduced pressure. The residue was dissolved in TFA and allowed to stand for 5 min. Following dilution with chloroform, the solution was washed with water, 5% aqueous sodium bicarbonate solution and water. The solvent was removed under reduced pressure and the residue purified on a grade 3 alumina column eluting with dichloromethane. The colored fractions corresponding to the porphyrin products were evaporated to dryness, loaded onto a grade 3 alumina column and eluted with 50−80% v/v toluene-hexanes. The initial red-colored fraction was recrystallized from chloroform−methanol to give nitronaphthoporphyrin **8a** (15.2−16.6 mg, 0.0261−0.0285 mmol, 15−17%) as purple crystals, mp 257−259 °C. This compound has

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been reported previously[11] and is contaminated with isomeric impurities. ^{1}H NMR (TFA-$CDCl_3$, 500 MHz): δ 11.57 (s, 1H, 20-H), 11.46 (s, 1H, 5-H), 10.60 (s, 2H, 10,15-H), 9.96 (d, 1H, J = 8.5 Hz, 3^1-H), 9.45 (s, 1H, 2^2-H), 8.66 (d, 1H, J = 7.9 Hz, 3^4-H), 8.50 (t, 1H, J = 7.7 Hz, 3^2-H), 8.19 (t, 1H, J = 7.7 Hz, 3^3-H), 4.19−4.10 (m, 6H, 3 × CH_2CH$_3$), 3.66 (s, 3H, 18-CH_3), 3.65 (s, 3H), 3.63 (s, 3H) (8,12-CH_3), 1.75 (t, 3H, J = 7.8 Hz), 1.73−1.69 (m, 6H) (3 × CH_2CH_3), −2.52 (br s, 1H, NH), −2.89 (br s, 1H, NH), −3.54 (br s, 1H, NH). A second dark fraction was collected and recrystallized from chloroform−methanol to give dipyrromethene-porphyrin dyad **15a** (9.5−14.4 mg, 0.0104−0.0158 mmol, 11−17%) as dark crystals, mp > 300 °C. UV−vis (1% Et_3N−$CHCl_3$): λ_{max}/nm (log ε) 392 (sh, 4.87), 428 (4.95), 548 (4.90), 601 (4.59), 671 (4.27). UV−vis (20 equiv TFA-$CHCl_3$): λ_{max}/nm (log ε) 293 (4.50), 437 (4.93), 489 (sh, 4.49), 525 (sh, 4.63), 564 (4.90), 730 (4.69). UV−vis (5% TFA-$CHCl_3$): λ_{max}/nm (log ε) 410 (5.00), 435 (4.96), 533 (sh, 4.49), 574 (5.07), 692 (4.78). ^{1}H NMR ($CDCl_3$, 50 °C, 500 MHz): δ 12.6 (v br, 1H), 10.93 (s, 1H, 5-H), 10.02 (d, 1H, J = 8.5 Hz, 3^1-H), 9.98 (s, 1H, 15-H), 9.80 (s, 1H, 10-H), 8.92 (d, 1H, J = 1.4 Hz, 9′-H), 8.81 (d, 1H, J = 8.5 Hz, $7^{1\prime}$-H), 8.60 (s, 1H, $8^{2\prime}$-H), 8.37 (d, 1H, J = 0.8 Hz, 5′-H), 8.33 (s, 1H, 2^2-H), 8.27 (d, 1H, J = 8.0 Hz, 3^4-H), 8.20 (t, 1H, J = 7.7 Hz, 3^2-H), 8.11 (d, 1H, J = 8.2 Hz, $7^{4\prime}$-H), 7.90 (t, 1H, J = 7.6 Hz, $7^{2\prime}$-H), 7.84 (t, 1H, J = 7.5 Hz, 3^3-H), 7.66 (t, 1H, J = 7.6 Hz, $7^{3\prime}$-H), 4.19−4.11 (m, 2H), 4.02−3.90 (m, 4H) (3 × porphyrin-CH_2), 3.57 (s, 3H, 8-Me), 3.46 (s, 3H, 12-Me), 3.12−2.98 (m, 2H, 3′-CH_2), 2.61 (s, 3H, 18-Me), 1.93 (t, 3H, J = 7.7 Hz, 7-CH_2CH_3), 1.87 (t, 3H, J = 7.7 Hz, 17-CH_2CH_3), 1.71 (t, 3H, J = 7.7 Hz, 13-CH_2CH_3), 1.69 (s, 3H, 2′-Me), 1.59 (t, 3H, J = 7.6 Hz, 3′-CH_2CH_3), −2.64 (br s, 2H, 2 × NH). ^{13}C{^{1}H} NMR ($CDCl_3$, 50 °C, 125 MHz): δ 156.5, 154.2, 152.7, 146.6, 146.15, 146.08, 144.8, 142.03, 142.00, 141.2, 141.1, 140.6, 139.0, 138.7, 138.5, 136.8, 136.3, 135.3, 135.3, 133.4, 132.8, 132.64, 132.59, 132.1, 131.9 ($7^{4\prime}$-CH), 131.3, 131.1, 131.0, 130.8, 130.5, 129.3, 127.30, 127.22, 127.07, 126.96, 125.9, 124.2, 124.0, 123.9 ($8^{2\prime}$-CH), 123.1 (2^2-CH), 105.4 (20-C), 100.6 (5-CH), 98.1 (15-CH), 97.1 (10-CH), 20.1, 19.9, 18.9, 17.7, 17.5, 17.1, 16.3, 13.0, 11.7, 11.3, 9.6. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{57}H_{51}N_8O_4$, 911.4028, found, 911.4022.

Reaction of Nitronaphthodipyrrylmethane 12a with Deuterium Labeled Dialdehyde 14^D. The foregoing experiment was repeated by reacting dipyrrylmethane **12a**[11] (100 mg, 0.187 mmol) with isotopically labeled dialdehyde **14^D** (48.4 mg, 0.168 mmol) to give nitronaphthoporphyrin **8a** (16.0 mg, 0.027 mmol, 16%) as dark maroon crystals and monodeuterated dyad **15^D** (9.9 mg, 0.011 mmol, 11%) as dark purple crystals. As was the case for the previous reaction, porphyrin **8a** was contaminated with isomeric impurities; the sample did not retain significant levels of deuterium incorporation. **8a**: mp > 260 °C. ^{1}H NMR (TFA-$CDCl_3$, 500 MHz): δ 11.57 (s, 1H, 20-H), 11.46 (s, 1H, 5-H), 10.60 (s, 2H, 10,15-H), 9.96 (d, 1H, J = 8.5 Hz, 3^1-H), 9.45 (s, 1H, 2^2-H), 8.66 (d, 1H, J = 7.9 Hz, 3^4-H), 8.50 (t, 1H, J = 7.7 Hz, 3^2-H), 8.19 (t, 1H, J = 7.7 Hz, 3^3-H), 4.19−4.10 (m, 6H, 3 × CH_2CH$_3$), 3.66 (s, 3H, 18-CH_3), 3.65 (s, 3H), 3.63 (s, 3H) (8,12-CH_3), 1.75 (t, 3H, J = 7.8 Hz), 1.73−1.69 (m, 6H) (3 × CH_2CH_3), −2.52 (br s, 1H, NH), −2.89 (br s, 1H, NH), −3.54 (br s, 1H, NH). HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{37}H_{36}N_5O_2$, 582.2864, found, 582.2841.

15^D. Mp > 300 °C. ^{1}H NMR ($CDCl_3$, 50 °C, 500 MHz): δ ^{1}H NMR ($CDCl_3$, 50 °C): δ 10.91 (s, 1H, 5-H), 10.00 (d, 1H, J = 8.5 Hz, 3^1-H), 9.97 (s, 1H, 15-H), 8.93 (d, 1H, J = 1.2 Hz, 9′-H), 8.80 (d, 1H, J = 8.4 Hz, $7^{1\prime}$-H), 8.59 (s, 1H, $8^{2\prime}$-H), 8.37 (d, 1H, J = ca. 1.0 Hz, 5′-H), 8.33 (s, 1H, 2^2-H), 8.27 (d, 1H, J = 7.9 Hz, 3^4-H), 8.20 (t, 1H, J = 7.7 Hz, 3^2-H), 8.11 (d, 1H, J = 8.2 Hz, $7^{4\prime}$-H), 7.90 (t, 1H, J = 7.6 Hz, $7^{2\prime}$-H), 7.84 (t, 1H, J = 7.4 Hz, 3^3-H), 7.66 (t, 1H, J = 7.6 Hz, $7^{3\prime}$-H), 4.19−4.11 (m, 2H), 4.03−3.91 (m, 4H) (3 × porphyrin-CH_2), 3.57 (s, 3H, 8-Me), 3.46 (s, 3H, 12-Me), 3.12−2.98 (m, 2H, 3′-CH_2), 2.61 (s, 3H, 18-Me), 1.92 (t, 3H, J = 7.7 Hz, 7-CH_2CH_3), 1.87 (t, 3H, J = 7.7 Hz, 17-CH_2CH_3), 1.71 (t, 3H, J = 7.6 Hz, 13-CH_2CH_3), 1.69 (s, 3H, 2′-Me), 1.59 (t, 3H, J = 7.6 Hz, 3′-CH_2CH_3), −2.68 (br s, 2H, 2 × NH). HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{57}H_{50}{}^2HN_8O_4$, 912.4091, found, 912.4061.

Reaction of Nitronaphthodipyrrylmethane 12a with Carbon-13 Labeled Dialdehyde 14^{13C}. The foregoing experiment was repeated by reacting dipyrrylmethane **12a**[11] (100 mg, 0.187 mmol) with isotopically labeled dialdehyde **14^{13C}** (48.4 mg, 0.168 mmol) to give nitronaphthoporphyrin **8^{13C}** (16.5 mg, 0.028 mmol, 17%) as dark maroon crystals and dyad **15^{13C}** (7.9 mg, 0.0087 mmol, 9.2%) as dark purple crystals, mp 259−260 °C. As expected, porphyrin **8^{13C}** was contaminated with isomeric impurities. ^{1}H NMR (TFA-$CDCl_3$, 500 MHz): δ 11.61 (d, 1H, $^1J_{C-H}$ = 164.7 Hz, 20-H), 11.50 (s, 1H, 5-H), 10.65 (d, 1H, $^1J_{C-H}$ = 162.7 Hz, 10-H), 10.65 (s, 1H, 15-H), 9.97 (d, 1H, J = 8.5 Hz, 3^1-H), 9.49 (s, 1H, 2^2-H), 8.69 (d, 1H, J = 8.0 Hz, 3^4-H), 8.52 (t, 1H, J = 7.7 Hz, 3^2-H), 8.21 (t, 1H, J = 7.5 Hz, 3^3-H), 4.21−4.12 (m, 6H, 3 × CH_2CH$_3$), 3.67 (s, 3H, 18-CH_3), 3.66 (s, 3H), 3.64 (s, 3H) (8,12-CH_3), 1.78−1.70 (m, 9H, 3 × CH_2CH_3), −2.83 (br s, 1H, NH), −3.15 (br s, 1H, NH), −3.82 (br s, 1H, NH). HRMS (ESI) m/z: $[M + H]^+$ calcd for $^{12}C_{35}{}^{13}C_2H_{36}N_5O_2$ 584.2931, found 584.2939.

15^{13C}. Mp > 300 °C. ^{1}H NMR ($CDCl_3$, 50 °C, 500 MHz): δ 10.90 (s, 1H, 5-H), 10.00 (d, 1H, J = 8.5 Hz, 3^1-H), 9.97 (s, 1H, 15-H), 9.76 (d, 1H, $^1J_{C-H}$ = 155.7 Hz, 10-H), 8.93 (d, 1H, J = 1.3 Hz, 9′-H), 8.80 (d, 1H, J = 8.3 Hz, $7^{1\prime}$-H), 8.59 (s, 1H, $8^{2\prime}$-H), 8.37 (d, 1H, J = 1.3 Hz, 5′-H), 8.33 (s, 1H, 2^2-H), 8.27 (d, 1H, J = 7.9 Hz, 3^4-H), 8.21 (t, 1H, J = 7.7 Hz, 3^2-H), 8.10 (d, 1H, J = 8.1 Hz, $7^{4\prime}$-H), 7.90 (t, 1H, J = 7.6 Hz, $7^{2\prime}$-H), 7.84 (t, 1H, J = 7.5 Hz, 3^3-H), 7.66 (t, 1H, J = 7.5 Hz, $7^{3\prime}$-H), 4.19−4.10 (m, 2H), 4.02−3.92 (m, 4H) (3 × porphyrin-CH_2), 3.57 (s, 3H, 8-Me), 3.46 (s, 3H, 12-Me), 3.12−2.98 (m, 2H, 3′-CH_2), 2.61 (s, 3H, 18-Me), 1.92 (t, 3H, J = 7.7 Hz, 7-CH_2CH_3), 1.87 (t, 3H, J = 7.7 Hz, 17-CH_2CH_3), 1.71 (t, 3H, J = 7.7 Hz, 13-CH_2CH_3), 1.69 (s, 3H, 2′-Me), 1.59 (t, 3H, J = 7.6 Hz, 3′-CH_2CH_3), −2.68 (br s, 2H, 2 x NH). HRMS (ESI) m/z: $[M + H]^+$ calcd for $^{12}C_{55}{}^{13}C_2H_{51}N_8O_4$, 913.4095, found, 913.4073.

Reaction of Nitronaphthodipyrrylmethane 12a with Dialdehyde 14b. Dipyrromethane **12a**[11] (100 mg, 0.187 mmol) was stirred with TFA (2 mL) under nitrogen for 10 min. The mixture was then diluted with chloroform (50 mL) and washed sequentially with water, 5% aqueous sodium bicarbonate solution and water. The organic layer was dried over sodium sulfate, filtered and the solvent was removed under reduced pressure. The residue and dialdehyde **14b**[22] (57.8 mg, 0.169 mmol) were dissolved in dichloromethane (206 mL) and methanol (10 mL), a solution of *p*-toluenesulfonic acid (225 mg) in methanol was added, and the resulting mixture was stirred at room temperature open to the air for 16 h. A saturated solution of zinc acetate in methanol (10 mL) was then added and the mixture was stirred open to the air for 2 additional days. The mixture was washed with water and the solvent was removed under reduced pressure. The residue was dissolved in TFA and allowed to stand for 5 min. Following dilution with chloroform, the solution was washed with water, 5% aqueous sodium bicarbonate solution and water. The solvent was removed under reduced pressure and the residue purified on a grade 3 alumina column eluting with dichloromethane. The colored fractions corresponding to the porphyrin products were evaporated to dryness and taken up in a minimal amount of toluene. The solution was placed on a grade 3 alumina column and eluted with 1:1 v/v hexanes-toluene. The initial red-colored fraction was recrystallized from chloroform−methanol to give nitronaphthoporphyrin **8b** (21.2 mg, 0.0332 mmol, 20%) as a magenta-colored powder, mp 258−260 °C. UV−vis ($CHCl_3$): λ_{max}/nm (log ε) 396 (sh, 4.83), 418 (5.22), 521 (3.91), 557 (4.42), 577 (4.12), 670 (2.49). UV−vis (5% TFA-$CHCl_3$): λ_{max}/nm (log ε) 403 (4.96), 424 (5.34), 565 (4.17), 613 (4.17). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 10.28 (s, 1H), 10.26 (s, 1H) (5, 20-H), 9.75 (s, 1H), 9.65 (s, 1H) (10, 15-H), 9.59 (d, 1H, J = 8.5 Hz, 2^1-H), 8.59 (s, 1H, 3^2-H), 8.28 (d, 1H, J = 7.9 Hz), 8.06 (t, 1H, J = 7.5 Hz), 7.80 (t, 1H, J = 7.3 Hz), 3.99 (t, 2H, J = 7.9 Hz), 3.86 (t, 2H, J = 7.8 Hz), 3.78 (q, 2H, J = 7.8 Hz), 3.56 (s, 3H), 3.44 (s, 6H), 2.28−2.18 (m, 4H), 1.81−1.73 (m, 4H), 1.71 (t, 3H, J = 7.8 Hz), 1.15−1.11 (2 overlapping triplets, 6H), −4.71 (br s, 2H). ^{1}H NMR (500 MHz, TFA-$CDCl_3$): δ 11.58 (s, 1H), 11.48 (s, 1H) (5,20-H), 10.62 (s, 1H), 10.61 (s, 1H) (10,15-H), 9.96 (d, 1H, J = 8.4 Hz), 9.47 (s, 1H), 8.67 (d, 1H, J = 7.9 Hz), 8.51 (t, 1H, J = 7.7 Hz), 8.20 (t, 1H, J = 7.5 Hz), 4.17 (q, 2H, J = 7.8 Hz), 4.10 (t, 4H, J =

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7.8 Hz), 3.66 (s, 3H), 3.65 (s, 3H), 3.63 (s, 3H) (3 × porphyrin-CH_3), 2.17−2.06 (m, 4H), 1.74−1.61 (m, 4H), 1.71 (t, 3H, J = 7.8 Hz), 1.10−1.05 (2 overlapping triplets, 6H), −2.68 (br s, 1H), −3.04 (br s, 1H), −3.70 (br s, 1H). $^{13}C\{^1H\}$ NMR (TFA-$CDCl_3$, 500 MHz): δ 145.0, 144.2, 144.0, 143.5, 143.3, 143.2, 142.5, 142.1, 139.5, 138.9, 138.3, 136.9, 133.8, 133.6, 133.5, 132.3, 131.6, 130.8, 130.1, 129.8, 127.0, 123.4, 101.6, 99.2, 98.92, 98.89, 34.48, 34.46, 26.7, 23.2, 20.5, 16.3, 13.92, 13.89, 12.2, 12.0, 11.8. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{41}H_{44}N_5O_2$, 638.3490, found, 638.3511. A second dark fraction was collected and recrystallized from chloroform−methanol to give dipyrromethene-appended naphthoporphyrin **15b** (10.3 mg, 0.0106 mmol, 11%) as dark green crystals, mp > 300 °C. UV−vis ($CHCl_3$): λ_{max}/nm (log ε) 393 (sh, 4.77), 427 (4.90), 493 (sh, 4.46), 548 (4.81), 599 (4.49), 674 (4.08). UV−vis (25 equiv TFA-$CHCl_3$): λ_{max}/nm (log ε) 402 (4.72), 436 (4.87), 489 (sh, 4.49), 493 (sh, 4.46), 528 (sh, 4.63), 562 (4.86), 726 (4.62). UV−vis (10% TFA-$CHCl_3$): λ_{max}/nm (log ε) 411 (4.92), 436 (4.91), 574 (4.97), 689 (4.68). ^1H NMR ($CDCl_3$, 55 °C, 500 MHz): δ 10.95 (s, 1H, 5-H), 10.03 (d, 1H, J = 8.5 Hz, 3^1-H), 9.98 (s, 1H, 15-H), 9.80 (s, 1H, 10-H), 8.92 (d, 1H, J = 1.3 Hz, 9′-H), 8.82 (d, 1H, J = 8.3 Hz, $7^{1\prime}$-H), 8.61 (s, 1H, $8^{2\prime}$-H), 8.38 (d, 1H, J = 1.2 Hz, 5′-H), 8.34 (s, 1H, 2^2-H), 8.28 (d, 1H, J = 7.9 Hz, 3^4-H), 8.21 (t, 1H, J = 7.6 Hz, 3^2-H), 8.13 (d, 1H, J = 8.1 Hz, $7^{4\prime}$-H), 7.92 (t, 1H, J = 7.6 Hz, $7^{2\prime}$-H), 7.85 (t, 1H, J = 7.5 Hz, 3^3-H), 7.68 (t, 1H, J = 7.6 Hz, $7^{3\prime}$-H), 4.19 (q, 2H, J = 7.8 Hz), 4.01−3.85 (m, 4H) (3 × porphyrin-CH_2), 3.61 (s, 3H, 8-Me), 3.46 (s, 3H, 12-Me), 3.10−3.00 (m, 2H, 3′-CH_2), 2.60 (s, 3H, 18-Me), 2.28 (p, 2H, J = 7.3 Hz), 2.15 (p, 2H, J = 7.2 Hz) (13,17-CH_2CH_2), 1,95 (t, 3H, J = 7.8 Hz, 7-CH_2CH_3), 1.84−1.73 (m, 4H, 2 × $CH_2CH_2CH_3$), 1.71 (s, 3H, 2′-Me), 1.59 (t, 3H, J = 7.6 Hz, 3′-CH_2CH_3), 1,16 (t, 3H, J = 7.4 Hz), 1.13 (t, 3H, J = 7.4 Hz) (2 × $CH_2CH_2CH_3$), −2.59 (br s, 2H, 2 × NH). HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{61}H_{59}N_8O_4$, 967.4654, found, 967.4651.

■ ASSOCIATED CONTENT

Data Availability Statement

The data underlying this study are available in the published article and its online Supporting Information.

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.joc.4c00824.

Selected UV−vis (Figures S1−S15), IR spectra of isotopically labeled dipyrrylmethane dialdehydes (Figure S16), ^1H NMR, $^1H-^1H$ COSY, HSQC, DEPT-135, $^{13}C\{^1H\}$ NMR (Figures S11−S59), and mass spectra (Figures S60−S69) (PDF)

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Notes

The authors declare no competing financial interest.

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