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# Synthesis of 5,10-diphenylporphyrin

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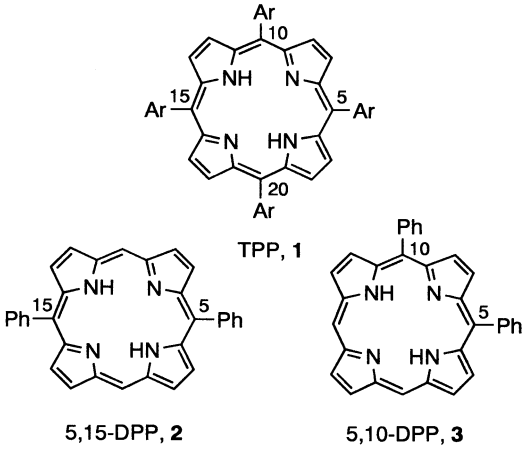
**Abstract**—The synthesis and spectroscopic properties of hitherto unknown 5,10-diphenylporphyrin (**3**) are described. 2+2 and 3+1 Pathways were tested for the making of 5,10-diphenylporphyrin. The most successful method involved the condensation of an appropriately substituted dipyrromethane dicarbinol with dipyrromethane to provide the title compound in up to 20% yield. The structure of **3** was unambiguously established by $^{1}H$ and $^{13}C$ NMR spectroscopy. The UV–vis, fluorescence and NMR data of 5,10-diphenylporphyrin and its Zn(II) and Ni(II) complexes are described and contrasted with those for the isomeric 5,15-diphenyl- and 5,10,15,20-tetraphenylporphyrin.


## 1. Introduction

Arguably, the most studied synthetic porphyrin family are the 5,10,15,20-tetraarylporphyrins (TPP, **1**). The synthetic protocols toward the synthesis of tetraarylporphyrins containing identical or differing aryl groups have developed in recent years to a high degree of sophistication.[1–5] 5,10,15-Triaryl-[6] and 5,15-diaryl-porphyrins (5,15-DPP, **2**)[7–9] are much less studied.




They are, however, interesting because they combine some features of *meso*-tetraarylporphyrins, namely the unsubstituted β-positions and the *meso*-aryl groups, with features of the β-octaalkylporphyrins, namely the unsubstituted *meso*-positions. These features have been utilized in the synthesis of, for instance, benzochlorins,[10] bio-conjugated porphyrins,[10] novel water-soluble *meso*-sulfonated porphyrins,[11] ABCD-[12] and $A_2B_2$-type porphyrins,[5] 5,15-diphenylporphyrin derivatives with non-linear optical properties,[13,14] and multiporphyrin assemblies.[15,16] Modern strategies for the synthesis of 5,15-DPP are available.[8,9,17,18]

The *cis*-isomer to 5,15-DPP, 5,10-diphenylporphyrin (5,10-DPP, **3**) has not been described, though a 5,10-diarylchlorin made via tetrahydrobilene cyclization was recently reported.[19] A retrosynthetic analysis of 5,10-DPP rationalizes this seemingly surprising fact (Fig. 1). Unlike symmetrically substituted 5,15-DPP or TPP, 5,10-DPP cannot be prepared by simple condensation of two identical dipyrrolic subunits. Instead, two more complex approaches are plausible. Option A: a disconnection based on a 3+1 condensation of known 5,10-diphenyltripyrrane **4** with an electrophilic monopyrrolic synthon **5** such as 2,5-diformylpyrrole or its (formal) reduction product 2,5-di(hydroxy-

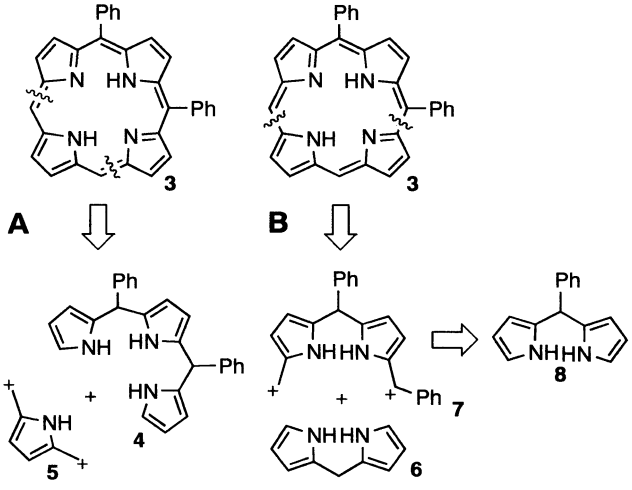



**Figure 1.** Retrosynthetic analysis of **3**.

*Keywords*: 5,10-diphenylporphyrin; dipyrromethane; 2+2 synthesis; 3+1 synthesis.
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methyl)-pyrrole. A number of successful 3+1 approaches toward the synthesis of porphyrins and porphyrin analogs were reported recently.[20–22] Option B: a disconnection based on a 2+2-type condensation of known dipyrromethane **6** with a 1,9-disubstituted dipyrromethane synthon of type **7**, such as the corresponding dicarbinol. Such dicarbinol is accessible by reduction of the corresponding 1-benzoyl-5-phenyl-9-formyl-dipyrromethane, itself perceivably a product of a sequential formylation and benzoylation of known 5-phenyl-dipyrromethane **8**.[18,23,24]

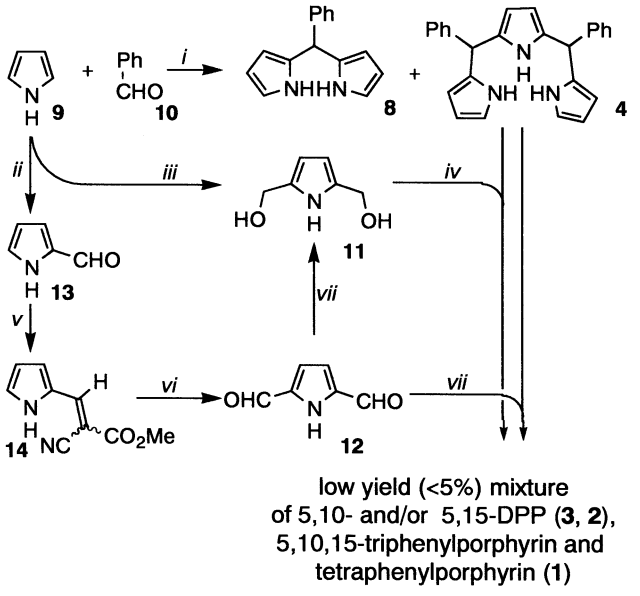
The stepwise syntheses of tetraarylporphyrins carrying four different aryl groups serve as precedent cases for such condensations. The condensation conditions leading to a minimal amount of 'scrambling' of the *meso*-aryl groups for these and related condensations were investigated in detail by Lindsey and co-workers, and served as a starting point in the search for the reaction conditions best suited for the condensations at hand.[25,26]

We present here the results of our investigation to synthesize 5,10-DPP (**3**) using 3+1 and 2+2 approaches. We also report on some notable spectroscopic properties of this novel compound and its zinc(II) and nickel(II) complexes.

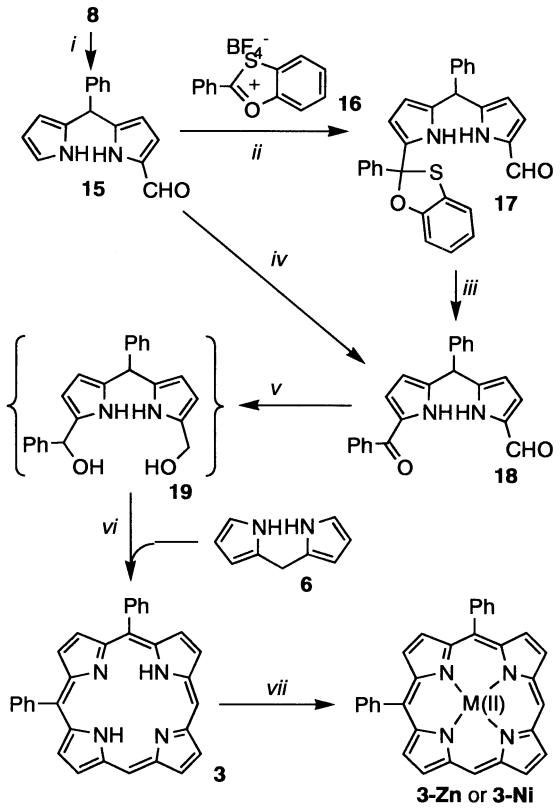
## 2. Results and discussion

### 2.1. 3+1 Synthesis of 5,10-diphenylporphyrin (3)

Following the retrosynthetic analysis detailed above, we sought a 3+1 route for the synthesis of 5,10-DPP (Scheme 1). Condensation of benzaldehyde (**10**) with excess pyrrole (**9**) provides 5-phenyldipyrromethane **8** and diphenyltripyrrane **4** which can be separated by sublimation.[17,27,28] Bisaldehyde **12** is available in 19% overall yield from pyrrole **9**:[20,29–33] Vilsmeyer–Haak formylation of pyrrole,[34] followed by Knoevenagel condensation with




**Scheme 1.** *Reaction conditions*: (i) TFA, room temperature; (ii) (1) DMF, $POCl_3$, (2) aq. $NaHCO_3$; (iii) $CH_2O$, $H_2O$, acetone $K_2CO_3$, 0°C; (iv) (1) $BF_3{\cdot}Et_2O$, 0°C, (2) DDQ; (v) (1) $NCCH_2COOEt$, $NHEt_2$; (vi) (1) DMF, $POCl_3$, (2) aq. NaOH, (3) aq. $H_2SO_4$; (vii) (1) HBr/HOAc, (2) DDQ.



**Scheme 2.** *Reaction conditions*: (i) DMF, BzCl; (ii) pyridine; (iii) HgO, $HBF_4$; (iv) EtMgBr, BzCl; (v) (1) $NaBH_4$, (2) aq. $NH_4Cl$; (vi) (1) TFA, (2) DDQ; (vii) $Zn(OAc)_2$ or $Ni(OAc)_2$.

methyl cyanomalonate produces pyrrole derivative **14**. Subsequent Vilsmeyer–Haack formylation followed by deprotection produces 2,5-pyrrole bisaldehyde **12**.[35,36] Condensation of **12** with tripyrrane **4** under typical MacDonald conditions (HBr/acetic acid catalysis), followed by DDQ oxidation, resulted in the formation of small amounts (<5%) of porphyrinic materials. ESI-MS of this material analyzed it to be a mixture of di- ($m/z$=463 for $MH^+$), tri- ($m/z$=539 for $MH^+$), and tetraphenylporphyrins ($m/z$=615 for $MH^+$). Evidently, substantial scrambling of the building blocks had taken place under the harshly acidic conditions. As either milder acids failed to bring the bisaldehyde to reaction or other condensation/oxidation protocols also resulted in the formation of low yields of product mixtures,[20,29–33] this 3+1 pathway was abandoned and an alternative pathway sought.

Condensation of biscarbinol **11** with tripyrrane **4** was anticipated to be possible under milder acid catalysis. Biscarbinol **11** is formally available by reduction of bisaldehyde **12** or, more conveniently, in a one-step procedure from pyrrole and formaldehyde under basic conditions.[22] Condensation of **11** with tripyrrane **4** in dry $CH_2Cl_2$ using either $BF_3{\cdot}OEt_2$ or TFA as catalyst, followed by DDQ oxidation and chromatographic work-up, resulted in the formation of a small (<5%) fraction of porphyrins. ESI-MS proved this fraction again to be a mixture of di-, tri- and tetraphenylporphyrins. However, as judged by the $^1H$ NMR of the crude mixture, 5,10-DPP was the main product (vide infra). Scrambling was also observed using the 'low scrambling conditions' (i.e. $CH_3CN$, TFA, 0°C) described by Lindsey

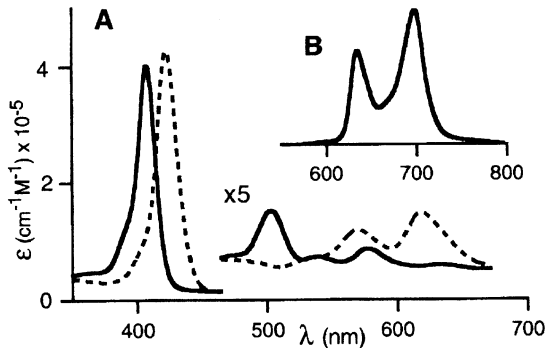



**Figure 2.** (A) (—) UV–vis spectrum of 5,10-DPP (**3**) in $CHCl_3$/trace of $Et_3N$; (- - -) UV–vis spectrum of **3** in $CHCl_3$/1% TFA; (B) uncorrected fluorescence emission spectrum of **3** in $CHCl_3$, $\lambda_{excitation}$=406 nm.

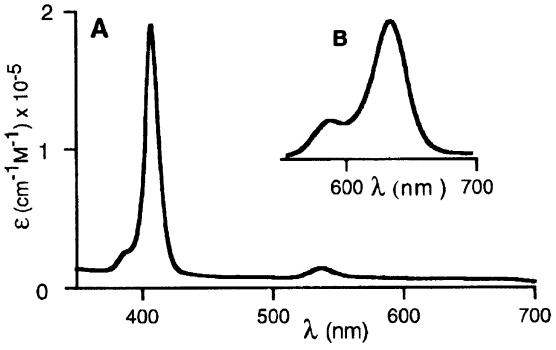



**Figure 3.** (A) UV–Vis spectrum of 5,10-DPPZn (**3**-Zn) in $CHCl_3$; (B) uncorrected fluorescence emission spectrum of **3**-Zn in $CHCl_3$, $\lambda_{excitation}$=411 nm.

and co-workers for related 2+2 condensation.[25] This may indicate the larger susceptibility of tripyrranes to acid-catalyzed scrambling as compared to that of dipyrranes for which the conditions were optimized. Separation of the observed porphyrinic mixture by preparative thin layer chromatography is challenging and impractical at preparative useful scales. As a result, we abandoned the 3+1 routes all together and focused on the development of 2+2 routes toward a practical synthesis of 5,10-DPP.

The type of acid used and the particular reaction conditions were demonstrated to have a profound effect on the outcome of related condensation reactions.[26,37–40] Thus, a thorough screening of different reaction conditions may eventually lead to a more successful 3+1 synthesis of the target molecule.

### 2.2. 2+2 Synthesis of 5,10-diphenylporphyrin (3)

The key intermediate in the 2+2 routes toward the target porphyrin is benzoylformyl-dipyrromethane **18** (Scheme 2). We found that known monoformyl-5-phenyl-dipyrromethane **15**, available from dipyrromethane **8** in 57% yield adopting established methods,[41] can be benzoylated in pyridine using 3 equiv. of the 2-phenyl-1,3-benzoxathiolium tetrafluoro-borate salt (**16**) as the benzoylating agent.[3,42–44] Masked benzoylformyldipyrromethane **17** was then deprotected using $HgO/HBF_4$,[45] affording key intermediate **18** in 66% yield from dipyrromethane **15**. Alternate benzoylation methods are available.[46,47]

Following established procedures,[4,47] dicarbonyl **18** was reduced with $NaBH_4$ to the corresponding dicarbinol-dipyrromethane **19**. Due to its high reactivity and low stability, the dicarbinol was generally not isolated and purified but immediately condensed under acid catalysis with known dipyrromethane **6**[7,17,41] at low scrambling conditions ($CH_3CN$, 2.5 mM reactant concentrations, 30 mM TFA, 25°C, 10 min).[4] Oxidation with DDQ followed by column chromatography and recrystallization afforded 5,10-DPP **3** in 10–20% yield in analytical purity. Crystallization experiments with the goal of obtaining crystals for X-ray diffractometry studies resulted only in the formation of unsuitably thin needles. ESI mass spectrometry of the recrystallized product indicated the absence of tri- or tetraphenylporphyrin. Conversion of free base **3** to the corresponding Ni(II)- (**3**-Ni) and Zn(II)-complexes (**3**-Zn) using standard metal insertion protocols proceeded in near-quantitative yields.

### 2.3. UV–Vis and fluorescence spectroscopic properties of 5,10-diphenylporphyrin (3) and its metal complexes

As expected, the UV–vis spectrum of **3** is porphyrin-like

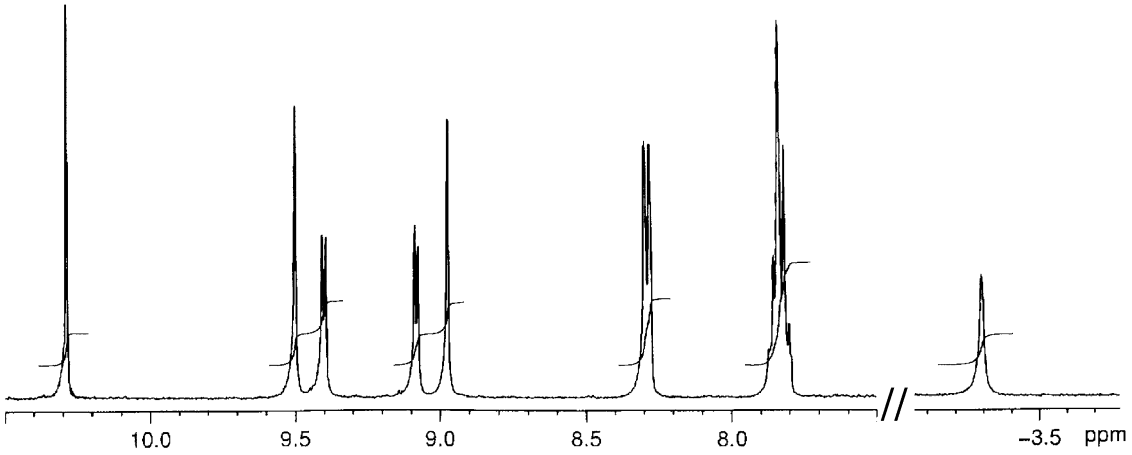



**Figure 4.** $^1H$ NMR spectrum (400 MHz, $CDCl_3$, 25°C) of 5,10-DPP (**3**).

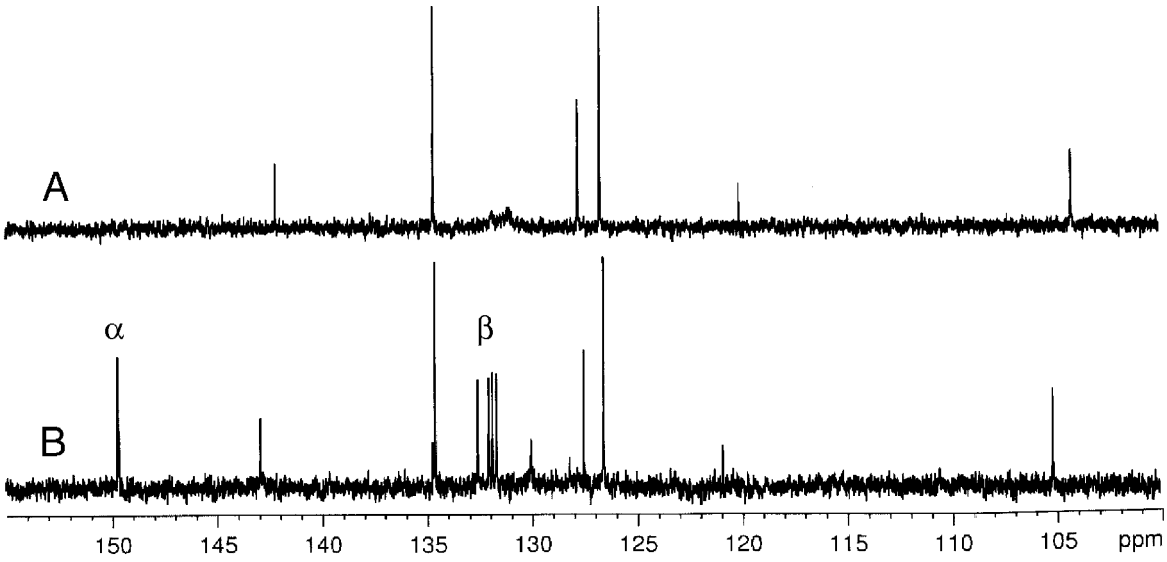



**Figure 5.** Comparison of the $^{13}C$ NMR spectra (100 MHz, $CDCl_3$, 25°C) spectra of **3** (A) and **3**-Zn (B).

with a Soret band at 406 nm and four Q bands (502, 534, 576, 630 nm) (Fig. 2(A)). Surprisingly, however, the spectrum is a phyllo-type spectrum, i.e. the intensity of the Q-bands follows the order I>III>II>IV.[48]

The fluorescence spectrum of **3** (Fig. 2(B)) displays emission bands at 634 and 698 nm. Comparable emission wavelengths but with reversed intensity ratios are observed for 5,15-DPP and TPP.[49] The electronic spectra for the fluorescent Zn-complex **3**-Zn (Fig. 3) and (non-fluorescent) **3**-Ni are as expected.

### 2.4. $^1H$ and $^{13}C$ NMR spectroscopic properties of 5,10-diphenylporphyrin 3 and its metal complexes

The $^1H$ NMR spectrum of **3** is shown in Fig. 4. Most diagnostic for the presence of *meso*-protons in **3** is the singlet at 10.25 ppm (cf. singlet at 10.3 ppm in 5,15-DPP). The 5,10-disubstitution pattern of **3** can be deduced from the resulting (idealized) point group $C_{2v}$, mandating two singlets (2H each), and two doublets (also 2H each) for the β-protons (region 9–9.5 ppm). 5,15-DPP **2** of higher point group $D_{2h}$, on the other hand, displays only two doublets (4H each). The remaining signals can be assigned to the *o*-protons (8.3 ppm), and *m*- and *p*-protons (7.85 ppm) of the two equivalent phenyl groups. The highly shielded pyrrolic NH protons are observed at −3.34 ppm.

The $^{13}C$ NMR spectrum of free base 5,10-diphenylporphyrin **3** is shown in Fig. 5(A). Remarkably, of the 14 non-equivalent carbons, only six provide well-defined signals. All other signals are severely broadened even when recording 10*k* scans using long (2.5 s) delay times. The spectrum of the diamagnetic metal complex **3**-Zn is shown in Fig. 5(B). In contrast to the free base porphyrin spectrum, 12 sharp signals are observable, even using relatively fast scans (1.0 s delay time). This severe line broadening, especially for the α-pyrrolic carbon signals (around 149–150 ppm), is due to either extremely long relaxation times or NH-tautomerism effects. This broadening was observed before in free base TPP, among other porphyrins.[50] In contrast, Edwards and co-workers reported in a recent contribution that the carbon NMR spectrum of free base 5,15-DPP is not broadened.[51] They attributed this effect to a faster tautomeric NH exchange rate promoted by the lower symmetry of DPP as compared to that of TPP (medium rate of tautomeric exchange rate—line broadening). Following their arguments (which we cannot agree with), 5,10-DPP **3** of even lower symmetry than 5,15-DPP ought to display a non-broadened $^{13}C$ NMR. This, however, is clearly not observed. Thus, the observed line broadening effect in free base porphyrins still awaits full explanation.

Fig. 6 shows the assignments of $^1H$ NMR and $^{13}C$ NMR signals for **3**-Zn. These were determined using 2D NMR experiments: HETCOR, HMBC, and NOE. The tertiary *meso*-carbon (105.1 ppm) was unambiguously identified by HETCOR while the quaternary *meso*-carbon (120.9 ppm) was assigned using HMBC through its two-bond coupling with the *ortho*-carbon of the phenyl ring (134.6 ppm). The assignments for the two singlet β-protons (9.01 and 9.34 ppm) were verified by NOE experiment. Irradiation at 9.34 ppm (β-H) exhibited a through-space

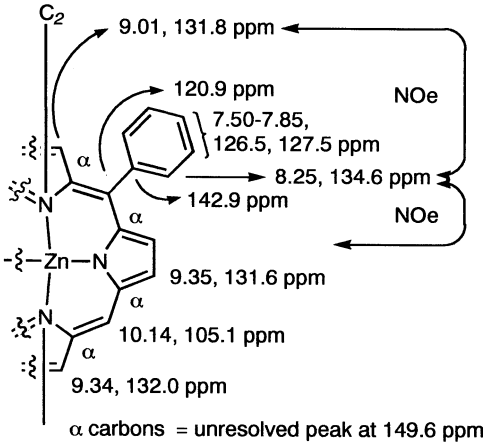



**Figure 6.** Assignment of $^1H$ and $^{13}C$ NMR signals ($CDCl_3$, 25°C) in **3**-Zn as determined by 2D NMR techniques.

coupling with the peak at 10.14 ppm (*meso*-carbon) while irradiation at 8.24 ppm (*ortho*-carbon of phenyl substituent) gave a through-space coupling with the peak at around 9.01 ppm (β-H). The α-carbons, however, were not resolved enough to assign them to particular α-positions in the macrocycle.

In summary, 5,10-DPP **3** can be synthesized using a 3+1 methodology. However, due to the formation of a number of hard to separate scrambling products, this method proved to be impractical. A 2+2 strategy produced pure product in moderate yields. The NMR, UV–vis and fluorescent spectroscopic properties of 5,10-DPP were distinctly different from those of the isomeric 5,15-DPP. This observation highlights the effects *meso*-substituents have on the electronic properties of porphyrins.[52] It is hoped that this contribution will pave the path toward the synthesis of 5,10-DPP derivatives for applications which take advantage of the orthogonal arrangement of the two phenyl substituents.

## 3. Experimental

### 3.1. Materials and instrumentation

$CH_2Cl_2$, THF, and pyrrole were dried over and distilled from $CaH_2$, Na/benzophenone ketyl, and KOH, respectively. All other solvents and reagents were used as received. The alumina used was Selecto Scientific Alumina B, Super I, 63–150 μm. The flash column silica gel used was Geduran Silica Gel 60, 35–75 μm, the analytical TLC plates were Silicycle ultra pure silica gel 60, 250 μm, with F-254 indicator. $^1$H and $^{13}$C NMR spectra were recorded on a Bruker DRX400. UV–vis spectra were recorded on Cary 50 and fluorescence spectra on a Cary Eclipse spectrophotometer. IR spectra were measured on a Jasco 410 FT-IR. Elemental analysis of compound **3** was provided by Numega Resonance Labs Inc., San Diego, CA, high resolution mass spectra were obtained by the University of Notre Dame, Chem. Dept. mass spectrometry facility (B. Boggess).

**3.1.1. 1-Formyl-5-phenyldipyrromethane (15).** Benzoyl chloride (1.7 mL, 14 mmol) was added to a cooled mixture of DMF (2.8 mL, 36 mmol) and 5-phenyl-dipyrromethane **8** (2.0 g, 9.0 mmol) under an atmosphere of dry $N_2$. The mixture was stirred at 0°C for 2 h and then another 2 h at room temperature. The reaction mixture was quenched by addition of $Na_2CO_3$ (2.0 g) dissolved in 50% aq. EtOH (150 mL). The resulting solution was extracted with $CH_2Cl_2$ (2×100 mL). The organic phase was dried ($Na_2SO_4$) and evaporated to dryness under vacuum. The residue was separated using flash column chromatography (silica gel, $CH_2Cl_2$/10% ethyl acetate). The first fraction contained the desired product ($R_f$=0.73, silica gel–$CH_2Cl_2$/20% EtOAc). Evaporation of the solvent produced **15** in 57% yield (1.3 g) as a tan solid. Spectroscopic and analytical data were comparable to those described before.[17] A second fraction eluting from the column was identified to be the 1,9-bisformyl-5-phenyldipyrrane ($R_f$=0.30, silica gel–$CH_2Cl_2$/20% EtOAc).[17]

**3.1.2. 1-[2-(2-Phenyl-1,3-benzoxathiolyl)]-5-phenyl-9-formyldipyrromethane (17).** 1-Formyl-5-phenydipyrromethane **15** (50 mg, 0.20 mmol) was dissolved in a mixture of pyridine (0.16 mL) and acetonitrile (5 mL). 2-Phenyl-1,3-benzoxathiolium tetrafluoroborate salt (60 mg, 0.60 mmol) was added to the solution.[42] After 1 h at room temperature, $H_2O$ (50 mL) was added and the reaction mixture was extracted with $CHCl_3$ (3×50 mL). The combined organic layers were washed with 5% aq. NaOH, $H_2O$ and dried ($Na_2CO_3$). The solvent was evaporated under vacuum to produce a red solid in quantitative yield. The product was found sufficiently pure to be used in the next step without further purification (see procedure below). $^1$H NMR (400 MHz, $CDCl_3$): δ 9.70–9.90 (m, 1H), 9.24 (s, 1H), 8.98–8.87 (m, 1H), 7.69 (d, *J*=7.7 Hz, 2H), 7.40–7.30 (m, 7H), 7.10–6.80 (m, 5H), 6.13 (m, 1H), 5.80–5.90 (m, 2H), 5.54 (s, 1H); $^{13}$C NMR ($CDCl_3$): δ 178.7, 154.0, 142.3, 142.0, 140.0, 133.4, 132.4, 131.1, 128.9, 128.6, 128.4, 127.8, 127.5, 126.5, 126.2, 125.9, 122.8, 121.8, 112.0, 110.9, 108.2, 98.4; IR (KBr) $\nu_{max}$: 1638 (C=O) cm$^{-1}$. LR-MS (APCI+) *m/z* 463 [MH$^+$]; HRMS-FAB *m/z* calcd (found) for $C_{29}H_{23}N_2O_2S^+$: 463.1480 (463.1496).

**3.1.3. 1-Benzoyl-5-phenyl-9-formylphenyldipyrromethane (18)—two-step, one-pot procedure from 1-formyl-5-phenyl-dipyrromethane (15).** 2-Phenyl-1,3-benzoxathiolium tetrafluoroborate (0.80 g, 2.7 mmol) was added under stirring into a solution of 1-formyl-5-phenyldipyrromethane **15** (0.22 g, 0.9 mmol) and pyridine (0.22 mL, 2.7 mmol) in dry acetonitrile (20 mL). After 1 h at room temperature, a mixture of HgO (0.58 g, 2.7 mmol), 48% aq. $HBF_4$ (1 mL), and DMSO (20 mL) were added. The stirred reaction mixture was warmed to 60°C for 1 h. TLC monitoring of the reaction was performed using aliquots treated with aq. KI. Upon the disappearance of starting material, the mixture was treated with 10% aq. KI (6 mL) and extracted with $CHCl_3$ (3×50 mL). The organic layers were collected, washed with 10% aq. KI (2×20 mL), water (2×20 mL), 5% aq. NaOH (2×20 mL), and then water again, and dried ($Na_2SO_4$). The crude product was concentrated and separated by column chromatography (silica gel, $CHCl_3$/5–10% ethyl acetate). The second fraction was collected and the solvent was evaporated under vacuum to afford **18** as a lightly colored foamy solid in 66% yield (0.21 g). The product is susceptible to slow decomposition at room temperature. $R_f$=0.61 (silica gel–$CH_2Cl_2$/20% EtOAc); $^1$H NMR (400 MHz, $CDCl_3$): δ 11.34–11.26 (m, 2H), 9.17 (s, 1H), 7.83–7.80 (m, 2H), 7.60–7.33 (m, 8H), 6.81 (m, 1H), 6.70 (m, 1H) 6.10–6.00 (m, 2H), 5.70 (s, 1H); $^{13}$C NMR ($CDCl_3$): δ 184.6, 179.0, 171.2, 142.5, 140.8, 139.8, 138.0, 132.6, 131.8, 131.0, 129.6, 128.9, 128.7, 128.1, 127.5, 122.6, 120.8, 111.8, 111.3, 44.7; IR (KBr) $\nu_{max}$: 1643 (C=O, aldehyde), 1609 (C=O, ketone) cm$^{-1}$; LR-MS (APCI+): *m/z* 355 [MH$^+$]; HRMS-FAB *m/z* calcd (found) for $C_{23}H_{19}N_2O_2^+$: 355.1447 (355.1421).

**3.1.4. 5,10-Diphenylporphyrin (3).** To a stirred solution of diacyldipyrromethane **18** (50 mg, 0.14 mmol) in THF/methanol (10:1, 6 mL) was added, under $N_2$, $NaBH_4$ (0.11 g, 2.8 mmol) in small portions (~every 2 min). After 40 min at room temperature, the reaction mixture was poured into a mixture of saturated aq. $NH_4Cl$ and $CHCl_3$ (1:1, 20 mL). The organic phase was isolated,

washed with water (2×) and dried ($Na_2CO_3$). The solvent was evaporated under vacuum. The residue was dissolved in acetonitrile (56 mL), dipyrromethane (21 mg, 0.14 mmol) was added. The resulting mixture was stirred for 5 min at room temperature, TFA (0.13 mL, 1.7 mmol) was added, and the mixture was stirred for 10 min. DDQ (0.10 g, 0.44 mmol) in toluene (~10 mL) was then added. After mixing for 1 h at room temperature, triethylamine (0.24 mL, 1.7 mmol) was added. The crude mixture was filtered through a pad of alumina. $CHCl_3$ (~50 mL) was used to extract the filter cake. The porphyrin-containing fractions (as assessed by UV–vis) were concentrated and passed through a plug of silica (eluted with $CHCl_3$). The DPP fractions were combined. Evaporation of the solvent in vacuo afforded up to 20% yield of microcrystalline purple product (13 mg). An experiment using 0.30 g (0.85 mmol) of dipyrrane **18** gave 37 mg (9.5 % yield) of 5,10-DPP **3**. $R_f$=0.58 (silica gel–$CH_2Cl_2$/50% pet. ether 30–60). UV–vis ($CDCl_3$) $\lambda_{max}$ (log $\varepsilon$): 406 (5.6), 502 (4.2), 534 (3.4), 576 (3.7), 630 (2.9) nm; UV–vis ($CDCl_3$+drops of TFA) $\lambda_{max}$ (log $\varepsilon$): 423 (5.63), 570 (4.37), 617.6 (4.47) nm; $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 10.25 (s, 2H), 9.46 (s, 2H), 9.36 (d, $J$=4.6 Hz, 2H), 9.04 (d, $J$=4.6 Hz, 2H), 8.93 (s, 2H), 8.27–8.20 (m, 4H), 7.85–7.75 (m, 6H), −3.34 (br s, 2H); $^{13}$C NMR ($CDCl_3$): $\delta$ 142.2, 134.7, 132.0–130.0 (multiple broadened and weak signals), 127.8, 126.7, 120.1; LR-MS (APCI+): $m/z$ 463 [$MH^+$]; $m/z$ expected for $C_{32}H_{23}N_4$: 463.2; Anal. calcd (found) for $C_{32}H_{22}N_4$: C, 83.09 (82.70); H, 4.79 (4.66); N, 12.11 (11.71).

**3.1.5. [5,10-Diphenylporphyrinato]zinc(II) (3-Zn).** A suspension of zinc(II) acetate·$2H_2O$ (5.2 mg, 0.024 mmol) in methanol (6 mL) was added to a stirred solution of 5,10-diphenylporphyrin **3** (6 mg, 0.013 mmol) in $CHCl_3$ (6 mL) and heated to reflux for about 10 min. To the mixture was added water (10 mL) and the organic layer was isolated and dried ($Na_2SO_4$). The solvent was evaporated by vacuum to provide a red violet residue. This residue was recrystallized from $CHCl_3$/pentane to yield purple microcrystals of **3**-Zn. $R_f$=0.46 (silica gel–$CH_2Cl_2$/50% pet. ether 30–60); UV–vis ($CDCl_3$) $\lambda_{max}$ (log $\varepsilon$): 411 (5.4), 539 (4.1) nm; $^1$H NMR ($CDCl_3$): $\delta$ 10.14 (s, 2H), 9.45–9.32 (m, 4H), 9.09 (d, $J$=4.3 Hz, 2H), 9.01 (s, 2H), 8.30–8.17 (m, 4H), 7.85–7.70 (m, 6H); $^{13}$C NMR ($CDCl_3$): $\delta$ 149.7, 149.6, 142.9, 134.6, 132.5, 132.0, 131.8, 131.6, 127.5, 126.5, 120.9, 105.1; LR-MS (APCI+): $m/z$ 524 [$M^+$], expected isotope cluster for $C_{32}H_{22}N_4Zn$ is observed; HRMS-FAB $m/z$ calcd (found) for $C_{32}H_{22}N_4Zn$: 524.0979 (524.0973).

**3.1.6. [5,10-Diphenylporphyrinato]nickel(II) (3-Ni).** To a boiling solution of 5,10-diphenylporphyrin **3** (10 mg, 0.022 mmol) in DMF (5 mL) was added a solution of nickel(II) acetate·$4H_2O$ (11 mg, 0.044 mmol) in DMF (5 mL). The mixture was refluxed for 1 h. The volume of reaction mixture was reduced under vacuum to 50% of its original volume, diluted with $CHCl_3$ (20 mL), washed with $H_2O$ repeatedly and finally dried ($Na_2SO_4$). Removal of the solvent in vacuo gave **3**-Ni as a red solid. $R_f$=0.84 (silica gel–$CH_2Cl_2$/50% pet ether 30–60); UV–vis ($CDCl_3$) $\lambda_{max}$ (log $\varepsilon$): 401 (5.2), 516 (4.1) 547 (3.8) nm; $^1$H NMR (400, MHz, $CDCl_3$): $\delta$ 9.90, (s, 2H), 9.25 (s, 2H), 9.17 (d, $J$=4.78 Hz, 2H), 8.92 (d, $J$=4.78 Hz, 2H), 8.82 (s, 2H), 8.10–8.0 (m, 4H), 7.80–7.65 (m, 6H); $^{13}$C NMR ($CDCl_3$): $\delta$ 143.0 142.9, 142.6, 142.5, 141.2, 133.8, 132.5, 132.0, 131.9, 127.7, 126.8, 119.1, 104.3; LR-MS (APCI+): $m/z$=518.6 [$M^+$], expected isotope cluster for $C_{32}H_{22}N_4Ni$ is observed; HRMS-FAB $m/z$ calcd (found) for $C_{32}H_{22}N_4Ni$: 518.1041 (518.1019).

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