



An alternative synthesis of β -pyrrolic acetylene-substituted porphyrins

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ABSTRACT

A modified Horner–Emmons condensation reaction has been employed in the synthesis of acetylene-substituted porphyrins at the β -pyrrolic position. This technique was shown to have many advantages over the typically employed Sonogashira coupling method, including negating the requirement for a brominated porphyrin starting material. The electronic spectra of 2-(4'-carboxyphenyl)ethynyl-5,10,15,20-tetraphenylporphyrinato zinc(II) showed a red shift compared to the double bond equivalent, 4-(*trans*-2'-(2''-(5'',10'',15'',20''-tetraphenylporphyrinato zinc(II)yl)ethen-1'-yl)-1-benzoic acid. Comparison of the X-ray structures of 2-((4'-formyl)phenyl)ethynyl-5,10,15,20-tetraphenylporphyrinato zinc(II) and its analogue 4-(*trans*-2'-(2''-(5'',10'',15'',20''-tetraphenylporphyrinato copper(II)yl)ethen-1'-yl)-1-benzaldehyde showed an unexpected decrease in planarity in the analogue with the triple bond as opposed to that with the double bond.

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Plants and bacteria capture solar energy using porphyrin-based chromophores, and convert it into chemical energy. The ability to modify and tune the photophysical properties of synthetic porphyrins via the introduction of specific substituents has led to the understanding and design of numerous porphyrin photonic assemblies, which mimic photosynthetic solar energy transduction by converting solar energy to chemical potential in the form of long-lived charge separated species.^{1–7} We have shown that the efficiency of porphyrin-based dye sensitized solar cells (DSSCs) is dependent on the extent of conjugation between the porphyrin ring and the binding group, and a combination of a diethenyl linker in the β -pyrrolic position and a malonic acid binding group resulted in the highest cell efficiency of 7.1%.⁸ The degree of conjugation is dependent upon the degree of co-planarity between the porphyrin ring and the linker.⁹ X-ray crystallographic results^{10,11} indicated that an ethene-linked bridge between the porphyrin core and binding group at the β -pyrrolic position gave a dihedral angle of 17°. In this work we report the synthesis of several ethyne substituted 5,10,15,20-tetraphenylporphyrins (TPPs), the expectation being that the ethynyl functionality would induce greater planarity and hence a greater photovoltaic efficiency.

Acetylene substitution of porphyrins at the β -pyrrolic position is typically achieved via a Sonogashira^{12–14} or other metal-catalyzed coupling reaction from the corresponding 2-bromoporphyrins.^{15–20} However, Sonogashira coupling reactions on

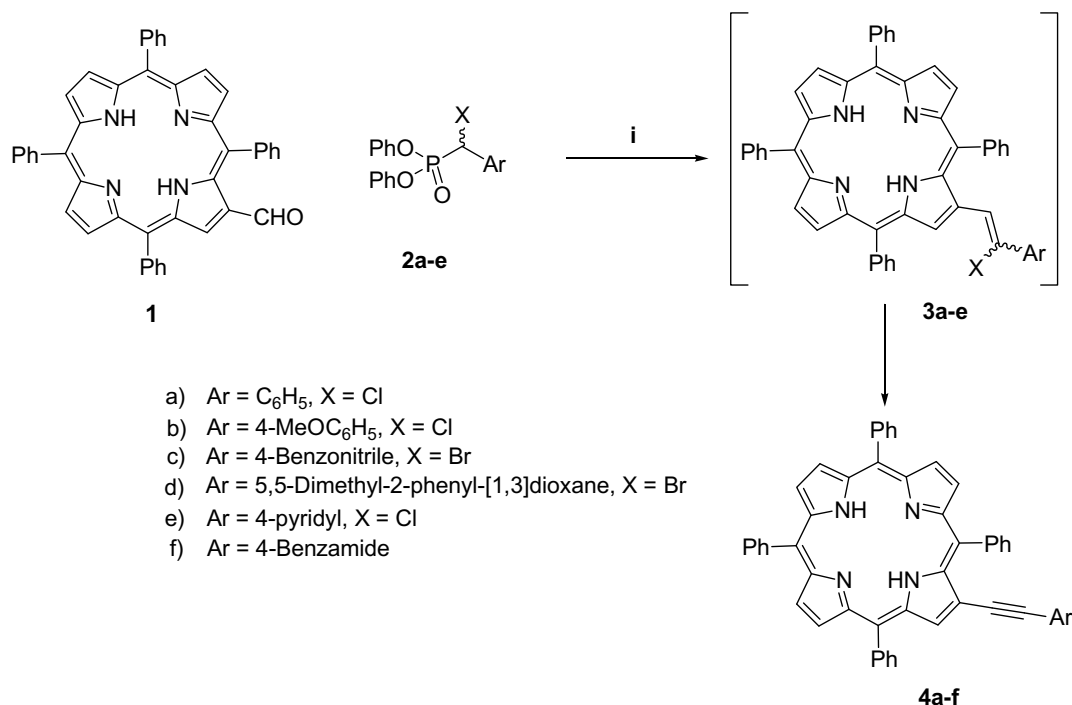
2-bromo-5,10,15,20-tetraphenylporphyrin are restricted to small scale,²¹ relatively low yielding reactions,^{15,12,22–25} and the target compounds are difficult to purify. Sonogashira coupling also requires the use of a copper catalyst, which has the potential to metalate/transmetalate the porphyrin.²⁶ Alternative copper-free coupling has been performed using Pd catalysts¹⁵ and ligands such as AsPh₃.^{27,15,12} However, the restriction imposed by the expense and toxicity of the reagents, together with the harsh reaction conditions (high reaction temperatures for extended times), restricts the application of this approach and possible future scale-up.

In this work β -pyrrolic substituted porphyrins were derived from a modified Horner–Emmons reaction. This method has been shown to have generic applicability in the synthesis of a range of symmetrical and non-symmetrical substituted diaryl acetylenes,^{28–31} and negates the requirement for both a brominated starting material and a metal catalyst. The reaction conditions were also amenable to scale-up, and in the current application the target compounds could be produced in high yield from the readily synthesized and high yielding, 2-formylporphyrin **1** (Scheme 1).³² To the best of our knowledge, the Horner–Emmons reaction has not been used previously for the synthesis of acetylene modified porphyrins.

A typical Horner–Emmons reaction uses equimolar amounts of reactants and 2 equiv of base. However, in the synthesis of acetylene-functionalized porphyrins **4a–d** these conditions resulted in the isolation of starting material **1** as well as an inseparable mixture of the halovinyl intermediates **3** and the desired products **4**. Moderate to high yields of the desired products

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Scheme 1. Synthesis of TPP derivatives with an acetylene linker at the β -pyrrolic position. Reagents and conditions: (i) THF, *t*-BuOK (10% soln.), rt.

Table 1
Product yields

Substituent (Ar)	Product	Yield (%)
Phenyl	4a	54
4-Methoxyphenyl	4b	84
4-Benzonitrile	4c	26
5,5-Dimethyl-2-phenyl-[1,3]dioxane	4d	88
4-Pyridyl	4e	70
4-Benzamide	4f	36

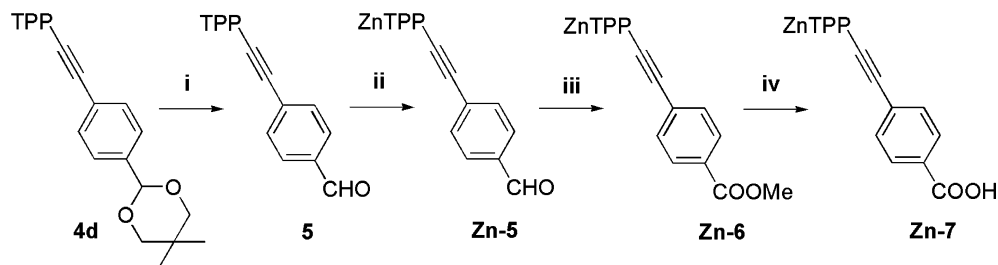
(Table 1) were obtained by significantly reducing the reaction time and dramatically increasing the concentration of base to a 10% solution of *t*-BuOK (ca. 80 equiv). This resulted in only trace amounts of the halovinyl intermediate **3**, as confirmed by the NH signal at -2.6 ppm in the ¹H NMR spectra. Further treatment of the isolated products with *t*-BuOK resulted in spectroscopically pure materials, although in significantly lower yield. The pure form of the aldehyde **5** was obtained directly via hydrolysis of the crude **4d** (Scheme 2).

Phosphonates **2a**, **2b** and **2e** were synthesized from the corresponding aldehydes using diphenyl phosphite²⁹ followed by conversion to the chlorophosphonates with phosphorus oxychloride and *N,N*-diethylaniline.³³ In the cases of **2c** and **2d**, the bromophospho-

nates were prepared as the chloro analogues could not be synthesized via the above method. Compounds **2c** and **2d** were obtained using milder conditions (tetrabutylammonium bromide, 2,3-dichloro-5,6-dicyanobenzoquinone and triphenylphosphine³⁴), which also prevented hydrolysis of the 1,3-dioxane ring in **2d**.

The modified Horner–Emmons reaction provided a means of attaching a range of acetylene-linked aromatic substituents, but was restricted to substituents on the aryl ring that did not react with the *t*-BuOK. As such, the reaction of **1** with diphenyl chloro(4-methoxycarbonylphenyl)methylphosphonate or diphenyl chloro(4-nitrophenyl)methylphosphonate failed to produce the desired product but instead gave an intractable mixture of multiple products. However, in the case of **4c**, the reaction afforded a readily separated mixture of the desired product and the unexpected 2-(4'-benzamide)ethynyl-5,10,15,20-tetraphenylporphyrin (**4f**, cf. Table 1). Although not a common method, the use of base for the reduction of nitriles to amides has been previously reported.^{35–37}

In order to demonstrate the versatility of the synthetic method even for base-sensitive acetylene-substituted porphyrins, the synthesis of the zinc porphyrin carboxylic acid **Zn-7** (Scheme 2) was carried out from the protected aldehyde **4d**. The chelation of zinc by these porphyrins provided the opportunity to compare the spectroscopic properties of the acetylene-linked porphyrins directly with their ethene analogues.



Scheme 2. Reagents and conditions: (i) DCM, TFA, H₂O, rt, 1 h, 81% (ii) DCM, MeOH, Zn(OAc)₂·2H₂O, rt, 1 h, 99% (iii) THF, MeOH, NaCN, MnO₂, reflux overnight, 88% (iv) THF, MeOH, KOH, H₂O, reflux overnight, 73%.

All products were characterized using 1-D and 2-D ^1H and ^{13}C NMR spectroscopy, mass spectrometry and UV–visible spectroscopy. All the data collected (cf. Supplementary data) were consistent with the proposed structures.

The electronic spectra (Fig. 1) showed that both the Soret and the two Q bands of the carboxylic acid derivative **Zn-7** were red shifted to 1.5, 2.5 and 5.5 nm, respectively, relative to the equivalent ethene compound.⁶ Although the red shift is less than in previous examples, this is consistent with observations in other β -alkyne porphyrin derivatives.^{38,12} Single crystals of **Zn-5** suitable for X-ray diffraction were obtained by slow diffusion of methanol into a solution of **Zn-5** in dichloromethane (Fig. 2).³⁹ Against expectations, the dihedral angle between the plane of the benzene ring and the plane of best fit made by the porphyrin core was $31.98(16)^\circ$, and almost twice that of the value of the corresponding angle in 4-(*trans*-2'-(5'',10'',15'',20''-tetraphenylporphyrinato copper(II)yl)ethen-1'-yl)-1-benzaldehyde of $17(2)^\circ$.¹⁰ A density functional theory (DFT) study is currently being undertaken in an attempt to account for these observations.

In conclusion, the use of modified Horner–Emmons conditions has provided a versatile method for synthesizing acetylene-linked substituents on the β -pyrrolic position of TPP. This resulted in a high yielding, scalable methodology that negated the need for a metal catalyst and 2-bromo-5,10,15,20-tetraphenylporphyrin as

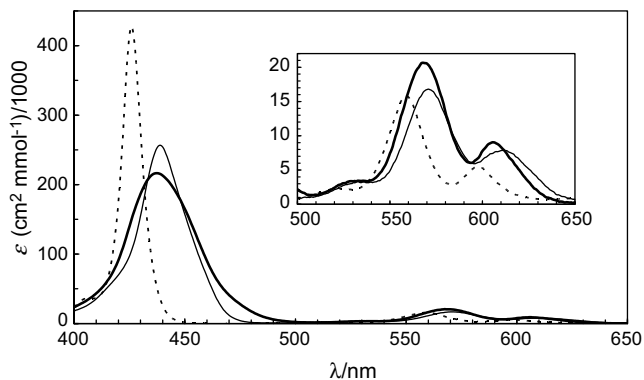


Figure 1. Electronic absorption spectra of 2-(4'-carboxyphenyl)ethynyl-5,10,15,20-tetraphenylporphyrinato zinc(II) **Zn-7** (thinner line), 4-(*trans*-2'-(2''-(5'',10'',15'',20''-tetraphenylporphyrinato zinc(II)yl)ethen-1'-yl)-1-benzoic acid (thicker line) and 2-(4'-carboxyphenyl)ethynyl-5,10,15,20-tetraphenylporphyrinato zinc(II) (dotted line) in DMF at 25 °C. The inset is an expansion of the Q-band region.

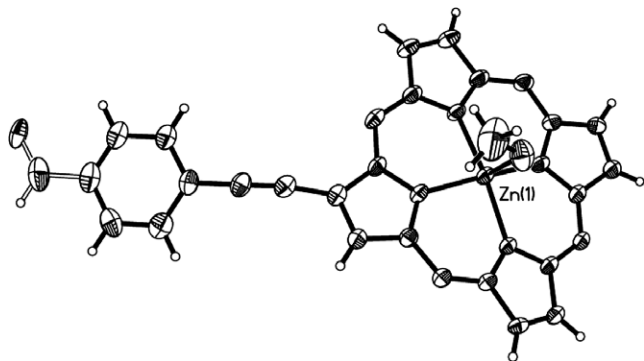


Figure 2. Crystal structure of 2-((4'-formyl)phenyl)ethynyl-5,10,15,20-tetraphenylporphyrinato zinc(II) (**Zn-5**) with methanol coordinated to zinc. The angle between the benzene ring and the plane of best fit made by the porphyrin ring is $31.98(16)^\circ$ (benzene rings omitted for clarity). The thermal ellipsoids were set at 50% probability level. The hydrogen atoms are drawn as spheres of arbitrary radii.

the starting material. The X-ray crystal data showed that the dihedral angle between the plane of the porphyrin core and the plane of the aryl substituent was greater in the acetylene-linked molecule compared to that in an ethylene analogue. Also, the electronic properties indicated only a slight bathochromic shift of the acetylene analogue compared to the corresponding ethylene analogue. Both these observations are the focus of an on-going DFT investigation.

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2008.07.059.

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39. Crystallographic data for **Zn-5** have been deposited at the Cambridge Crystallographic Data Centre as Supplementary Publication Number CCDC 673558. Copies of these data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: +44 1223 336033 or e-mail: deposit@ccdc.cam.ac.uk].