Convenient syntheses of phthalocyanine and tetrabenzotriazaporphyrin (TBTAP) mono-alkynes; unhindered building blocks for click chemistry and beyond

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ABSTRACT: Unsymmetrical phthalocyanines and related macrocycles are often desirable for covalent construction or self-assembly of more complex architectures. Terminal alkynes are versatile in this regard because they are amenable to cross-coupling via Sonagashira type reactions, alkyne-alkyne coupling via Glaser type couplings, and triazole formation via Click reaction with azides. Here we describe two complementary syntheses to conveniently add a single alkyne onto the phthalocyanine peripheral position and onto the *meso*-phenyl group of an (aryl)tetrabenzotriazaporphyrin, here providing a remote link point that is insulated from the macrocycle.

KEYWORDS: Alkynes, Unsymmetrical Phthalocyanines, Phthalocyanine-Porphyrin hybrids, Click Chemistry, Cross-Coupling

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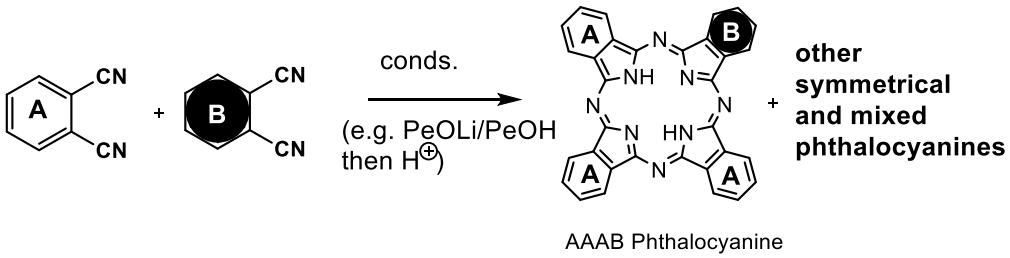
INTRODUCTION

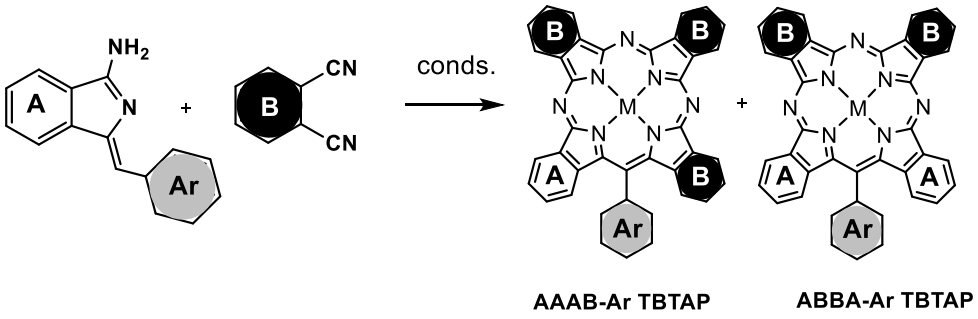
General synthetic strategies for the production of simple and complex phthalocyanines are now well established, in part driven by their intrinsic favourable properties [1]. Variation on the parent phthalocyanine scaffold and metal coordination offers opportunity for tuning their properties for a wide diversity of applications, such as colorants, catalysis, photosensitisers, imaging agents, molecular electronic and photonic components. While the majority of studies and applications of synthetic tetrapyrrole macrocycles have concentrated on simple symmetrically substituted derivatives (or indeed mixtures of regioisomers), defined unsymmetrical systems are very attractive in many cases. In such systems the symmetry is broken. Introduction of complementary functionality, typically at a single site or on a single fragment of the

macrocycle, so called 3:1 or AAAB phthalocyanines, opens new potential for tuning the photophysical properties but also for exploiting the newly introduced functional groups as link points for molecular (covalent synthesis) and supramolecular assembly to produce higher order constructs. A number of strategies have been investigated for the synthesis of AAAB phthalocyanines, including innovative use of solid phase synthesis and sub-phthalocyanine expansion chemistry and the area has been comprehensively reviewed [2-5]. However, statistical mixed cyclisation reactions between different phthalonitrile precursors (or their equivalents) remains the most widely used and general method (Scheme 1).



Scheme 1. Synthesis of unsymmetrical phthalocyanines from a mixture of phthalonitriles.

Tetrabenzotriazaporphyrins (TBTAPs) are one of several hybrid structures that lie between phthalocyanines and porphyrins, differing from phthalocyanines in the exchange of just one *meso*-nitrogen atom by a carbon bridge. Hybrids of this type were described for the first time in the late 1930s as part of the first seminal works on phthalocyanines [6], but there remain far fewer studies and reports on them compared to the parent phthalocyanines and porphyrins [7]. The main drawback for TBTAPs, and other hybrid structures, has been the lack of reliable and versatile synthetic strategies to afford them (especially when compared to porphyrins and phthalocyanines). In the last decades, our group and others have developed and studied new synthetic routes, significantly overcoming the initial issues [8-19]. Most recently we have disclosed additional control in the synthesis of TBTAPs that permits direct access to meso-aryl 3:1 (ABBB-Ar) and 2:2 (ABBA-Ar) derivatives [20]. Symmetry in the macrocycle core is intrinsically reduced by exchange of a single nitrogen bridge but, importantly, any *meso*-phenyl substituent lies perpendicular to the core such that further modification at this site has only marginal impact and the properties of the core are therefore preserved.



Scheme 2. Synthesis of meso-aryl tetrabenzotriazaporphyrins (TBTAPS) [20].

The goal of the present research was to produce freely soluble phthalocyanine and TBTAP derivatives with each bearing an unhindered terminal acetylene group. The alkyne fragments on the macrocycles would then be suitably available to act as link points through well-established chemistries, including Sonagashira cross-coupling [21], Glaser coupling [22], Huisgen cycloaddition with azides (“click” chemistry) [23] and others [24]. In the case of phthalocyanines the acetylene fragment was to be located at the peripheral position of an otherwise unsubstituted single isoindolene unit in 3:1 unsymmetrical

phthalocyanine. To aid solubility and characterization, alkyl substituents were selected for inclusion on the remaining isoindolene fragments. For the TBTAP, the acetylene was to be located remotely on the *meso*-phenyl substituent. Further solubilizing substituents were not deemed necessary in this case, based on the known properties of the previously reported simple derivatives.

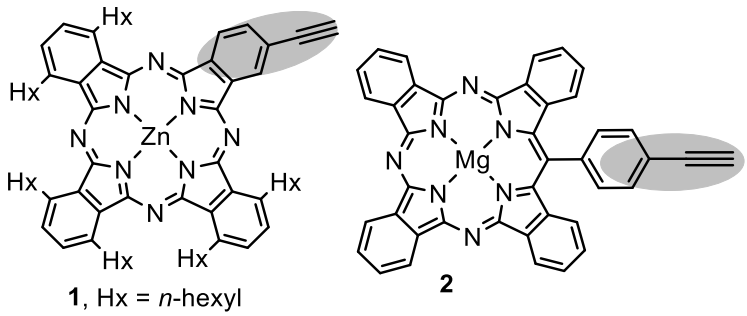


Figure 1. The target unhindered terminal acetylenes of Phthalocyanine (**1**) and TBTAP (**2**).

EXPERIMENTAL

General methods

Reagents and solvents were purchased from commercial sources and used without further purification. ^{1}H (and ^{13}C-NMR) spectra were recorded at 500 (125.7) MHz using a Bruker Ascend^{TM} 500 spectrometer. The residual solvent peaks were used as references. Column chromatography was carried out on silica gel Davisil® LC60A 40-63 micron (Grace GmbH & Co). MALDI-TOF mass spectra were obtained using a Shimadzu Biotech Axima instrument. UV-Vis spectra were recorded in a Hitachi U-3000 spectrophotometer. Melting points were measured using a Reichert Thermovar microscope with a thermopar based temperature control.

*Synthesis of protected phthalocyanine **7***

3,6-Dihexylphthalonitrile (0.92 g, 3.1 mmol), 4-(3-hydroxy-3-methyl-1-butynyl)phthalonitrile **6** [25] (0.22 g, 1.0 mmol), zinc acetate dehydrate (excess) and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, 2 drops) were stirred in refluxing *n*-hexanol (10 mL) for 24 h under an argon atmosphere. After precipitation by addition of methanol, the resulting green crude product was then purified by column chromatography eluting with DCM/ EtOH (30:1) to give phthalocyanine **7** as the second green fraction (0.23g, 18 %). Mp > 300 °C; ^{1}H NMR (500 MHz, THF-d_8) δ 9.42 (s,1H), 9.30 (d, *J* = 7.8, 1H), 8.16 (dd, *J* = 7.8 and 1.3,1H), 7.91 (s, 2H), 7.87 (s, 2H), 7.84 (q, *J* = 7.5, 2H), 4.75 (s, 1H), 4.61 (m, 4H), 4.58 – 4.51 (m, 6H), 4.50 – 4.45 (m, 2H), 2.42 (s, 6H), 2.14 – 1.74 (m, 6H), 1.66 – 1.54 (m, 6H), 1.49 – 1.17 (m, 36H), 1.00 – 0.86 (m, 9H), 0.86 – 0.70 (m, 9H); ^{13}C NMR spectra could not be obtained due to aggregation and precipitation at the higher concentrations required for ^{13}C NMR acquisition; UV-Vis (THF) λ_{max} (nm) : 697 and 628; MALDI-MS:1165 [cluster, M^+].

*Deprotection of phthalocyanine **7** to give 1,4,8,11,15,18-hexahexyl-23-ethynyl- phthalocyaninato zinc (II) **1***

A mixture of phthalocyanine **7** (0.23g, 0.2 mmol) and sodium hydroxide (0.2 g, 5 mmol) in dry toluene (5 mL) was heated at reflux for 6 h under argon. After cooling to rt, the solvent was removed, the residue suspended in DCM and washed with water. The organic layer was then dried, and the solvent evaporated. The resulting green-blue product was purified by column chromatography using DCM/EtOH (100: 1) to yield 1,4,8,11,15,18-hexahexyl-23-ethynyl-phthalocyaninato zinc (II) **1** (0.15 g, 68 %); Mp 283 °C; ^{1}H NMR (500 MHz, THF-d_8) δ 9.37 (s, 1H), 9.15 (d, *J* = 7.7 Hz, 1H), 8.15 (d, *J* = 7.7 Hz,

1H), 7.88 (s, 2H), 7.80 – 7.68 (m, 4H), 4.56 (t, *J* = 7.2 Hz, 4H), 4.46-4.44 (m, 4H), 4.42 – 4.36 (m, 2H), 4.34 – 4.28 (m, 2H), 3.94 (s, 1H), 2.39 – 2.13 (m, 12H), 1.52 – 1.23 (m, 36H), 0.99 – 0.86 (m, 9H), 0.86 – 0.77 (m, 9H); ^{13}C NMR spectra could not be obtained due to aggregation and precipitation at the higher concentrations required for ^{13}C NMR acquisition; UV-Vis (THF) λ_{max} (nm): 362, 697; MALDI-MS: 1107 [cluster, M^+].

Synthesis of (Z)-1(4-ethynylphenylmethylene)-1H-isoindol-3-amine ***11***

A mixture of 2-bromobenzamidine hydrochloride [26] (260 mg, 1.1 mmol), BINAP (41 mg, 0.055 eq) and $PdCl_2$(MeCN) (14.5 mg, 0.05 eq) was sealed in a microwave vessel with a magnetic bar and then purged and refilled with N_2 three times. Then, a solution of 1,4-diethynylbenzene (465 mg, 3 eq) and DBU (0.41 ml, 2.5 eq) in dry DMF (4 ml) was added. The mixture was stirred under N_2 for 5 min and then irradiated in a microwave reactor at 120 ºC for 1 h. After cooling, 25 ml of ethyl acetate were added and the mixture washed with a saturated solution of $NaHCO_3$ (3 x 50 ml). The organic layer was dried ($MgSO_4$), filtered and concentrated. The residue was finally purified by column chromatography using ethyl acetate as eluent to afford a yellow amorphous solid (140 mg, 52%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.06 (br d, 2H, *J* = 8.3 Hz,), 7.78 (br d, 1H, *J* = 7.6 Hz), 7.50 (br d, 2H), 7.47-7.45 (m, 2H), 7.38 (br t, 1H, *J* = 7.4 Hz), 6.70 (s, 1H), 5.7 – 4.5 (br s, 2H, NH_2), 3.14 (s, 1H). ^{13}C NMR (125.7 MHz, $CDCl_3$): δ 165.6, 148.3, 142.9, 137.4, 132.3, 131.1, 130.3, 129.6, 127.6, 120.6, 120.0, 119.2, 114.3, 84.3, 78.0; UV-Vis (MeOH) λ_{max} (nm): 373; MALDI-MS: 245.2 $[M+H]^+$.

Synthesis of (Z)-1(4-(2-Hydroxy-2-methylbut-3-ynyl)phenylmethylene)-1H-isoindol-3-amine ***12***

A mixture of 2-bromobenzamidine hydrochloride [26] (250 mg, 1.05 mmol), BINAP (40 mg, 0.055 eq) and $PdCl_2$(MeCN) (14 mg, 0.05 eq) was sealed in a microwave vessel with a magnetic bar and then purged and refilled with N_2 three times. Then, a solution of 4-(4-ethynylphenyl)-2-methylbut-3-yn-2-ol [27] (215 mg, 1.1 eq) and DBU (0.4 ml, 2.5 eq) in dry DMF (4 ml) was added. The mixture was stirred under N_2 for 5 min then irradiated in a microwave reactor at 120 ºC for 1 h. After cooling, 50 ml of ethyl acetate was added and the mixture washed with a saturated solution of $NaHCO_3$ (3 x 75ml). The organic layer was dried ($MgSO_4$), filtered and concentrated. The residue was finally purified by column chromatography using petroleum ether:AcOEt (1:1) → AcOEt → AcOEt:EtOH:H_2O (90:5:3) as eluents to afford an amorphous yellow solid (177 mg, 55%). ^{1}H NMR (500 MHz, MeOD): δ 7.97 (d, 2H, *J* = 8.0 Hz) 7.84 (dt, 1H, *J* = 7.5, 0.9 Hz), 7.68 (dt, 1H, *J* = 7.5, 0.9 Hz), 7.50 (td, 1H, *J* = 7.5, 0.9 Hz), 7.41 (td, 1H, *J* = 7.5, 0.9 Hz), 7.37 (2H, *J* = 8.0 Hz), 6.72 (s, 1H) 1.57 (s, 6H). ^{13}C NMR (125.7 MHz, MeOD): δ 168.2, 149.2, 144.1, 138.3, 132.4, 132.3, 131.1, 130.8, 128.7, 122.6, 121.4, 120.8, 113.5, 95.9, 82.9, 66.0, 31.8. UV-Vis (MeOH) λ_{max} (nm): 377; MALDI-MS: 303.1 $[M+H]^+$.

Synthesis of [20-(4-(trifluoromethanesulfonyl)phenyl)-tetrabenzo[*b,g,q,l*]-5,10,15-triazaporphyrinato]magnesium(II) **16**

To a solution of [20-(4-hydroxyphenyl)-tetrabenzo[b,g,q,l]-5,10,15-triazaporphyrinato]magnesium(II) [15] (52 mg, 83 µmol) and pyridine (10 µL, 1.5 eq) in DCM (3 mL), triflic anhydride (15.4 µL, 1.1 eq) was added at 0 °C under a nitrogen atmosphere. The mixture was stirred for 2 h while allowing the temperature to reach rt. Then, more DCM (20 mL) was added and the solution was washed with distilled water (2 x 25 mL). The organic solvents were removed under vacuum and the crude purified by flash chromatography using Petroleum Ether:THF:MeOH (10:3:1) as eluent. As a final step, size exclusion chromatography (Biobeads SX-3 in THF) was performed to give **16** as purple crystals (60 mg, 95%). ^{1}H NMR (500 MHz, THF-d_8): δ 9.60 (ddd, 2H, *J* = 7.6, 1.2, 0.8 Hz), 9.54-9.48 (m, 4H), 8.35 (d, 2H, *J* = 8.2 Hz), 8.18-8.15 (m, 4H), 8.04 (dd, 2H, *J* = 8.2, 2.5 Hz); 7.93 (dt, 2H, *J* = 6.9, 0.8 Hz), 7.60 (dt, 2H, *J* = 8.1, 0.8 Hz) 7.08 (dt, 2H, *J* = 8.1, 0.8 Hz). ^{13}C NMR (125.7 MHz, THF-d_8): δ 157.0, 153.8, 152.6, 151.6, 144.6, 142.1, 141.1, 140.8, 140.6, 140.1, 135.3, 130.1, 129.8,

128.1, 127.4, 125.0, 124.5, 123.8, 123.7, 123.6, 123.1, 120.3 (q, $^{1}J_{C\text{-}F}$ = 321 Hz). UV-Vis (dist. THF) λ_{max} (nm): 669, 647, 593, 442, 396; MALDI-MS: 760 [Cluster M^{+}].

*Synthesis of protected phthalocyanine **13***

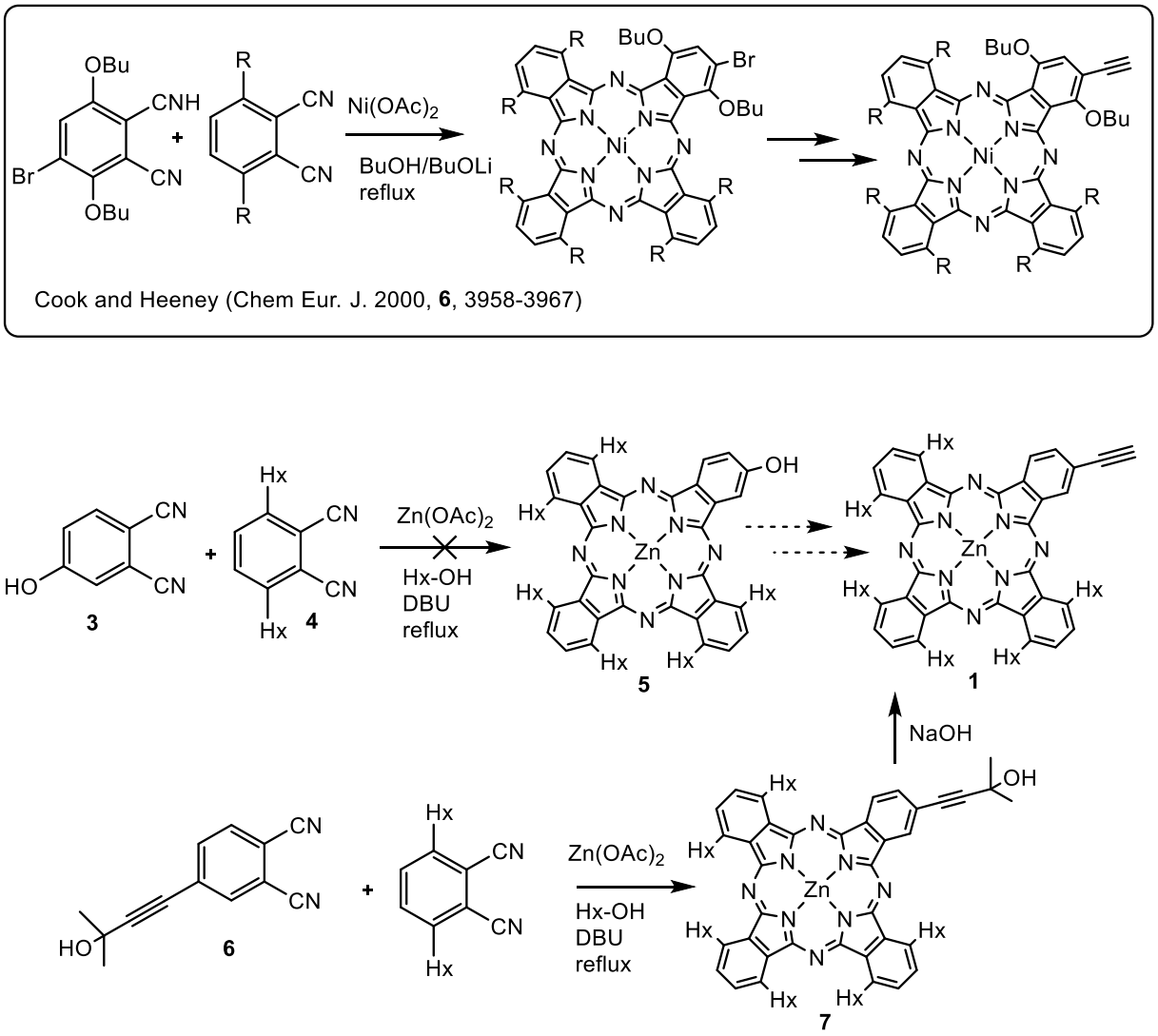
A mixture of [20-(4-(trifluoromethanesulfonyl)phenyl)-tetrabenzo[*b,g,q,l*]-5,10,15-triazaporphyrinato]magnesium(II) **16** (57 mg, 75 μmol), 3-hydroxy-3-methylbut-1-yne (37 μL, 5 eq), $Pd(PPh_3)_4$ (8.6 mg, 0.1 eq), CuI (2.9 mg, 0.2 eq) and Et_3N (0.5 mL) in DMF (2 mL), was stirred at 80 °C under argon atmosphere for 20 h. Then, the solvents were removed under vacuum and the crude mixture purified by flash chromatography using Petroleum Ether:THF:MeOH (10:3:1) and recrystallisation from acetone:ethanol to give **13** as purple crystals (28 mg, 54%). ^{1}H NMR (500 MHz, THF-d_8): δ 9.60 (ddd, 2H, *J* = 7.6, 1.2, 0.8 Hz), 9.53-9.48 (m, 4H), 8.18-8.15 (m, 4H), 8.14 (d, 2H, *J* = 8.2 Hz), 8.04 (dd, 2H, *J* = 8.2, 1.8 Hz); 7.92 (dt, 2H, *J* = 6.9, 0.8 Hz), 7.62 (dt, 2H, *J* = 8.1, 0.8 Hz) 7.18 (dt, 2H, *J* = 8.2, 1.8 Hz), 4.77 (s, 1H, OH); 1.70 (s, 6H). ^{13}C NMR (125.7 MHz, THF-d_8): δ 156.7, 153.6, 152.5, 143.5, 142.4, 141.0, 140.8, 140.1, 133.2, 132.8, 130.0, 129.7, 128.1, 127.3, 126.0, 125.5, 125.4, 123.8, 123.6, 123.5, 97.9, 81.6, 65.0, 32.2. UV-Vis (dist. THF) λ_{max} (nm): 670, 647, 594, 443, 396; MALDI-MS: 694 [Cluster M^{+}].

Synthesis of [20-(4-(ethynyl)phenyl)-tetrabenzo[b,g,q,l]-5,10,15-triazaporphyrinato]magnesium(II) **2**.

Phthalocyanine **13** (16.6 mg, 24 μmol) was dissolved in dry toluene (10 mL) and ground NaOH (5 mg, 0.12 mmol, 5 eq) was added. The mixture was stirred at reflux under argon for 5 h. Then, the solvent was removed under vacuum and the crude mixture purified by flash chromatography using Petroleum Ether:THF (5:1) as eluent to give a purple solid (14 mg, 94%). ^{1}H NMR (500 MHz, THF-d_8): δ 9.59 (d, 2H, *J* = 7.6 Hz), 9.53-9.48 (m, 4H), 8.18-8.15 (m, 6H), 8.06 (d, 2H, *J* = 7.5 Hz); 7.92 (dt, 2H, *J* = 6.9, 0.8 Hz), 7.62 (dt, 2H, *J* = 8.1, 0.8 Hz) 7.17 (dt, 2H, *J* = 8.2, 1.8 Hz), 3.95 (s, 1H). ^{13}C NMR (125.7 MHz, THF-d_8): δ 156.7, 153.6, 152.5, 143.5, 142.3, 141.1, 140.8, 140.1, 133.4, 130.0, 129.7, 128.2, 127.3, 125.8, 125.3, 125.4, 123.8, 123.6 (2), 84.3, 80.5. UV-Vis (dist. THF) λ_{max} (nm): 670, 647, 593, 443, 396; MALDI-MS: 636 [Cluster M^{+}].

RESULTS AND DISCUSSION

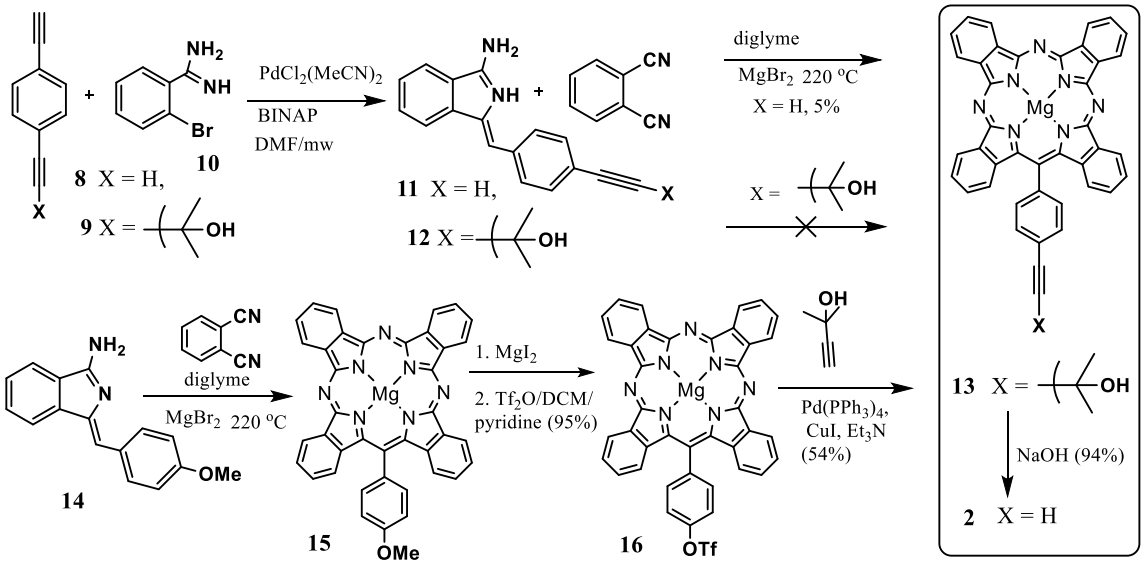
The synthesis of target phthalocyanine **1** is shown in scheme 3. Initial attempts focused on mixed cyclisation reactions between 4-hydroxyphthalonitrile **3** and 3,6-dihexylphthalonitrile **4**, reasoning that the monohydroxyphthalocyanine **5** would be relatively easy to separate from the symmetrical side product. Transformation to the monoalkyne could then be achieved by conversion to a halide-equivalent (e.g. triflate) and then cross-coupling with a protected acetylene in a sequence similar to those adopted for the synthesis of hindered phthalocyanine monoalkynes by Cook (scheme 3, inset, [28]) and Kobayashi [29]. Unfortunately, the mixed cyclisation failed to yield any significant proportion of the unsymmetrical phthalocyanine, and this observation proved to be general for mixed reactions involving 4-hydroxyphthalonitrile, indicating its likely low reactivity compared to (alkyl) phthalonitriles.



Scheme 3. Synthesis of target phthalocyanine **1**.

The target phthalocyanine was instead prepared by first synthesizing a protected alkynylphthalonitrile precursor. To achieve this, 4-iodophthalonitrile was first coupled with 3-hydroxy-3-methylbut-1-yne under Sonagashira conditions to give protected alkynylphthalonitrile **6**. This protecting group was chosen because of its robustness (it is known to tolerate phthalocyanine-forming reaction conditions form the work of Torres and coworkers [25]), and because we again expected that the hydroxyl functionality would make the required unsymmetrical derivative separable from symmetrical octahexyl phthalocyanine. Indeed, mixed cyclisation proceeded smoothly in hexanol/DBU with zinc acetate, and the resulting mixture was separated by chromatography to give the unsymmetrical phthalocyanine **7**. Deprotection with sodium hydroxide smoothly yielded the unhindered phthalocyanine monoacetylene **1**, whose electronic spectrum is almost identical to that of the parent octaalkyl analogue [30]. Unlike many symmetrical octaalkyl phthalocyanines [31], however, unsymmetrical phthalocyanine **1** does not show any liquid crystal behavior. It is freely soluble in most organic solvents, displaying unaggregated UV-Vis and 1H NMR spectra so further reactions and processing will be straightforward. However, aggregation is evident at the high concentrations required for acquisition if ^{13}C NMR spectra.

Ethynyl-TBTAP **2** was synthesized following two routes (Scheme 4). The first approach was to install the acetylene unit early in the synthesis and carry it through to the final hybrid. Aminoisoindolenes **11** and **12** were prepared from 1,4-diethynylbenzene **8** and its singly protected derivative **9** by reaction with 2-bromobenzamidine **10** under palladium catalysis and microwave heating. The resulting aminisoindolenes **11** and **12** were reacted with phthalonitrile and magnesium bromide using our previously optimized reaction conditions for formation of TBTAP hybrids [15]. A low yield only (5%) of ethynyl-TBTAP **2** was obtained when the unprotected aminoisondolene **11** was used, and use of the protected analogue **12** was worse still, with no TBTAP product being isolated. In both cases the dominant macrocyclic product was simple magnesium phthalocyanine.



Scheme 4. Syntheses of target TBTAP **2**.

The target ethynyl-TBTAP **2** was more conveniently prepared through modification of a pre-formed macrocycle. *Meso*-4-methoxyTBTAP-Mg **15** was synthesized as reported [15] and smoothly demethylated using magnesium iodide [15]. The resulting phenol was converted to the corresponding triflate **16** in high yield by simple treatment with trifluoromethane sulfonic acid anhydride (triflic anhydride) and triethylamine. TBTAP triflate **16** is clearly a highly versatile intermediate that can react as a partner in many cross-coupling reactions. In our case we converted the triflate to the target acetylene by first cross-coupling with protected acetylene (3-hydrox-3-methylbut-1-yne) under palladium-copper catalysis, followed by deprotection with sodium hydroxide. TBTAP **2** is also freely soluble in organic solvents and, as expected, the introduction of the acetylene group on the *meso*-phenyl has negligible effect on the absorption spectrum of the hybrid.

In conclusion, we have described complementary strategies that yield freely soluble phthalocyanine and tetrabenzotriazaporphyrin derivatives that bear a single unhindered and versatile terminal acetylene functional group. They are designed to be easily employed in both click chemistry and in cross-coupling strategies to attach and link with molecular and macromolecular substrates. In the phthalocyanine case the acetylene unit provides a conjugating bridge that provides electronic communication to the macrocycle, while in the TBTAP the acetylene bridge is also rigid but now insulated from the core itself due to the twisted conformation of the *meso*-phenyl group.

Acknowledgements

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