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An easy one-pot desilylation/copper-free Sonogashira cross-coupling reaction assisted by tetra-butylammonium fluoride (TBAF): synthesis of highly π-conjugated porphyrins

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ABSTRACT

Sonogashira cross-coupling is a key reaction for the synthesis of highly conjugated oligomers. However, its application has well known drawbacks; it requires drastic inert atmosphere conditions, generates homocoupling by-product of the terminal alkyne and others. In this paper, we describe a new and easy procedure using $PdCl_2(PPh_3)_2$ as catalyst assisted by TBAF in a one-pot desilylation/copper-free Sonogashira reaction for the synthesis of highly conjugated porphyrin oligomers.

1. Introduction

Over the past few years, the development of highly conjugated porphyrin oligomers with a strong two-photon absorption (TPA) attracted great attention in a wide range of applications such as chlorophyll antenna mimics,[1] nonlinear optics,[2] organic light-emitting diodes[3] and photodynamic therapy (PDT).[4] PDT is a promising treatment, that is, used clinically to destroy some types of cancers. It relies on the use of a photosensitive drug activated by light to induce cytotoxicity; the photosensitizer (PS) is harmless in the dark.[5] Penetration depth of light into tissue is critical, especially when it comes to reach deep tumours. Unfortunately, the most common PS used in PDT requires visible radiation (600–700 nm) while the therapeutic window is located in the near infrared region (700–950 nm).[6] Two-photon excitation represents an attractive alternative, since it not only allows a deeper penetration of excitation light but also leads to a reduction in photothermal damage caused by light intensity.[7] Clinical porphyrin-based PDT photosensitisers, such as Photofrin®, Verteporfin or Foscan® have a low TPA cross section,[8] in this context the synthesis of new molecular systems specially designed for this purpose appears desirable.

Conjugated porphyrin oligomers have been well studied in the literature and showed to exhibit good to strong TPA.[8–12] The key reaction to synthesize most of these π-conjugated cores seems to be Sonogashira cross-coupling. However, its application on tetrapyrrolic macrocycles has well known drawbacks that restricted its use: a) it requires drastic inert atmosphere conditions to protect unstable Pd(0) and terminal ethynyl porphyrin. b) The reaction is slow and exceeds 14 h at reflux. c) Applying Pd(II) catalyst, such as $Pd_2(PPh_3)_2Cl_2$, $PdCl_2$ requests the use of a reducer, such as CuI that often generates homocoupling product of the terminal alkyne (Glaser cross-coupling).[13] Frequently, Lindsey et al. copper-free Sonogashira conditions that are based on use of Pd(0) ($Pd_2(dba)_3$) as catalyst and triphenylarsine ($AsPh_3$) as ligand are used to avoid undesired by-product.[14] However, although these conditions reduce the formation of Glaser product, they include additional caution in handling unstable $Pd_2(dba)_3$. Also, Senge et al. have applied these conditions to synthesize new ethynyl-linked porphyrin dimers with moderate to good yields (25–68%).[9]

Recently, Mori et al. have reported that tetra-butylammonium fluoride (TBAF) is a useful promoter for palladium-catalyzed copper-free Sonogashira cross-coupling reaction.[15] Then, Li et al. have

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shown that this combined system works solvent-free on aryl chlorides with moderate yields.[16] However, both teams have worked on small aryl species, such as ethenylphenyl and halogenophenyl. TBAF has also been used for deprotection of silylated arylethynyl in one-pot desilylation/Sonogashira coupling reaction,[17] yet authors have applied classical conditions by using copper as co-catalyst (Pd(II)/CuI). To the best of our knowledge, no paper has described the use of TBAF as palladium's promoter in one-pot desilylation/copper-free Sonogashira cross-coupling reaction.

The aim of this work is to describe a simple and new procedure to synthesize highly π-conjugated porphyrins by using a one-pot desilylation/copper-free Sonogashira reaction assisted by TBAF, which can be use as both a desilylate reagent and a base. There is no more need to work in inert atmosphere conditions, reaction time is reduced to 4–6 h at reflux and easy to handle Pd(II) has been used without any copper need. Firstly, various factors have been investigated to find the best conditions to synthesize ethynyl-linked porphyrin dimer. Secondly, these best conditions have been applied in the synthesis of trimeric porphyrin, subsequently a study has been presented to decrease the quantity of TBAF and consequently the amount of solvent used in the reaction.

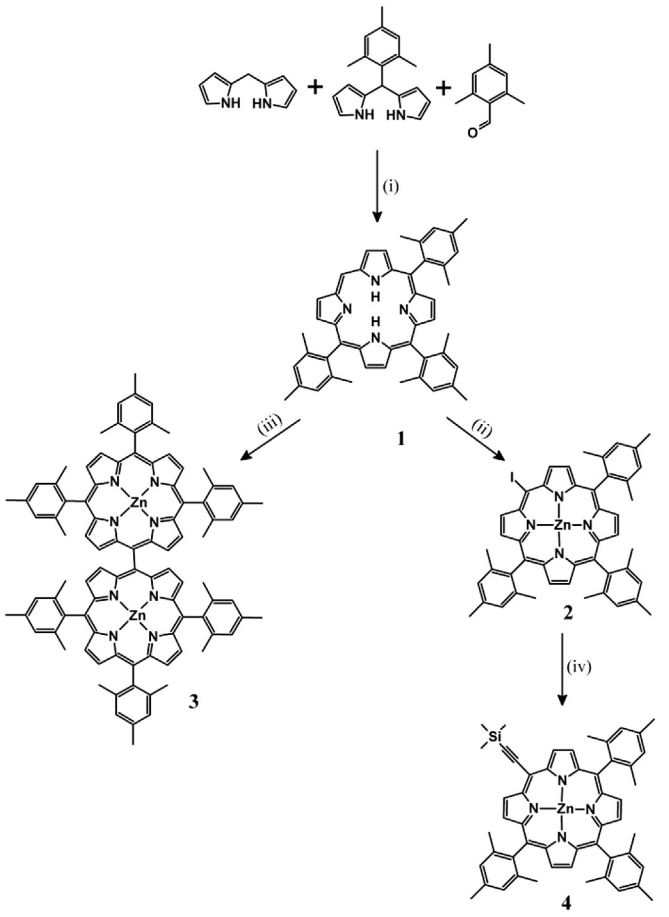
2. Results and discussion

The key parent molecule of most highly π-conjugated porphyrins reported in the literature is silylated *meso*-ethynyl porphyrin,[8–12] herein, we chose to work on porphyrin **4**. It was obtained in two steps starting from porphyrin **1** with one free *meso* position. Compound **1** was accomplished according to Lindsey's method[18] by reaction between dipyrromethane, mesityldipyrromethane with 2 equiv of mesitaldehyde (Scheme 1).

The first step involved halogenation of the free *meso* position, where bromination[19] or iodination[20] routes are widely reported and in both cases a radical mechanism seems to be the most appropriate. We chose the iodination way described by Dolphin where iodine and phenyliodine(III)bis(trifluoroacetate) (I_2/PIFA) are respectively used as reagent and catalyst to iodinate free-base porphyrin.[20] On the other hand, Jin et al. have already shown in bromination case that Zn-metallated porphyrin has given better yield than the free-base, so we investigated iodination of both metallated and free-base porphyrins (Scheme 1).[19] In the instance of free-base porphyrin we have obtained product **2** with an overall yield of iodination and Zn-metallation of 36%. In contrast, applying Dolphin's iodination on already Zn-metallated porphyrin has given surprisingly *meso*,*meso*-linked porphyrin dimer **3** with a good yield without appearance of the desired product on TLC. This simple procedure to synthesize *meso*,*meso*-linked porphyrin dimers seems to have been previously described by Chen et al.[21] using PIFA as catalyst, yet Senge's oxidation or Osuka's oxidation methods are more commonly reported.[22]

The second step was Sonogashira cross-coupling using trimethylsilylacetylene (TMSA) under classical conditions (Pd(II)/CuI) to attach silyl-protected acetylene on porphyrin **2**; porphyrin **4** was obtained with a good yield of 75%.

Several procedures have been then investigated (Table 1) to find the most appropriate method to synthesize ethynyl-linked porphyrin dimer **6** (Scheme 3). Firstly, classical Sonogashira coupling conditions have been applied (Table 1, entry 1) using Pd(II) ($Pd_2(PPh_3)_2Cl_2$) as catalyst and copper(I) iodide (CuI) as palladium's reductant and co-catalyst, in anhydrous and degassed toluene/triethylamine (TEA) at reflux for 18 h. Starting from iodo-porphyrin **2** and terminal ethynyl porphyrin **5**, these conditions have given product **6** with a low yield (26%). Reagent **5** has been obtained by desilylation of porphyrin **4** using 1.1 equiv of TBAF (1 M in THF, 5% water) in THF. It was used directly, after a simple pretreatment with excess $CaCl_2$ to give compound **6**. Indeed, according to various



Scheme 1. Reagents and conditions (i) BF_3OEt_2, $CHCl_3$, 30 min, then DDQ, 1 h, rt, 17%; (ii) $(CF_3CO_2)_2IC_6H_5$, I_2, $CHCl_3$, 1 h, rt, then, $Zn(OAc)_2$, $CHCl_3$/MeOH, 3 h, reflux, 36%; (iii) $Zn(OAc)_2$, $CHCl_3$/MeOH, 3 h, reflux, then, $(CF_3CO_2)_2IC_6H_5$, I_2, $CHCl_3$, 5 min, rt, 75%; (iv) $PdCl_2(PPh_3)_2$, CuI, TMSA, toluene/TEA, 4 h, reflux, 75%.

authors,[10–12] we have not succeeded to isolate compound **5** by silica gel chromatography (substantial decomposition was observed), and we have used this product immediately without purification.

Secondly, Li et al. conditions (Table 1, entry 2) have been applied,[16] involving $Pd_2(PPh_3)_2Cl_2$ as catalyst assisted by an excess of TBAF solution (100 equiv, 1 M in THF, 5% water) used too to dissolve reagents, starting from porphyrins **2** and **4**. Desired dimer **6** was obtained with a low yield (28%), while by-product **7** was formed with a significant yield (12%) resulting from Glaser reaction of terminal ethynyl porphyrin even in copper-free conditions. This kind of homocoupling was also observed during Hiyama cross-coupling reaction.[23] In order to minimize the formation of by-product **7**, $AsPh_3$ was added to the reaction and used as a palladium ligand. Starting from porphyrins **2** and **4** at reflux (60 °C) (Table 1, entry 3) the reaction time (4 h) and by-product **7** (6%) were significantly declined and desired product **6** was obtained with a good yield (57%).

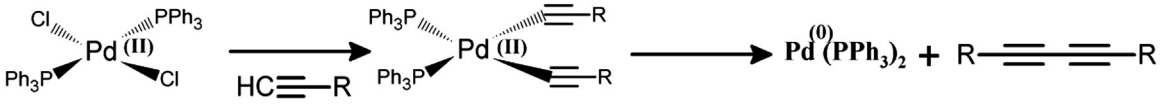
Our explanation is that without ligand ($AsPh_3$) deprotected silyl reagent **5** has been employed in order to reduce Pd(II) to Pd(0) (Scheme 2) and consequently formed the homocoupling product **7**. In fact, it has been shown that Pd(0) species could be readily generated from the reaction of $Pd_2(PPh_3)_2Cl_2$ with solvents, substrates, additives, and/or ligands, etc.[24]

Finally, these results have been compared to those mentioned in the literature, in Table 1 we have chosen the zinc(II) complex of 1,2-bis(5,10,15-triphenylporphyrin-20-yl)ethyne dimer described by Senge et al. (Table 1, entry 4).[9] It is obvious that the new procedure (entry 3) is better and easier to use than classical Sonogashira

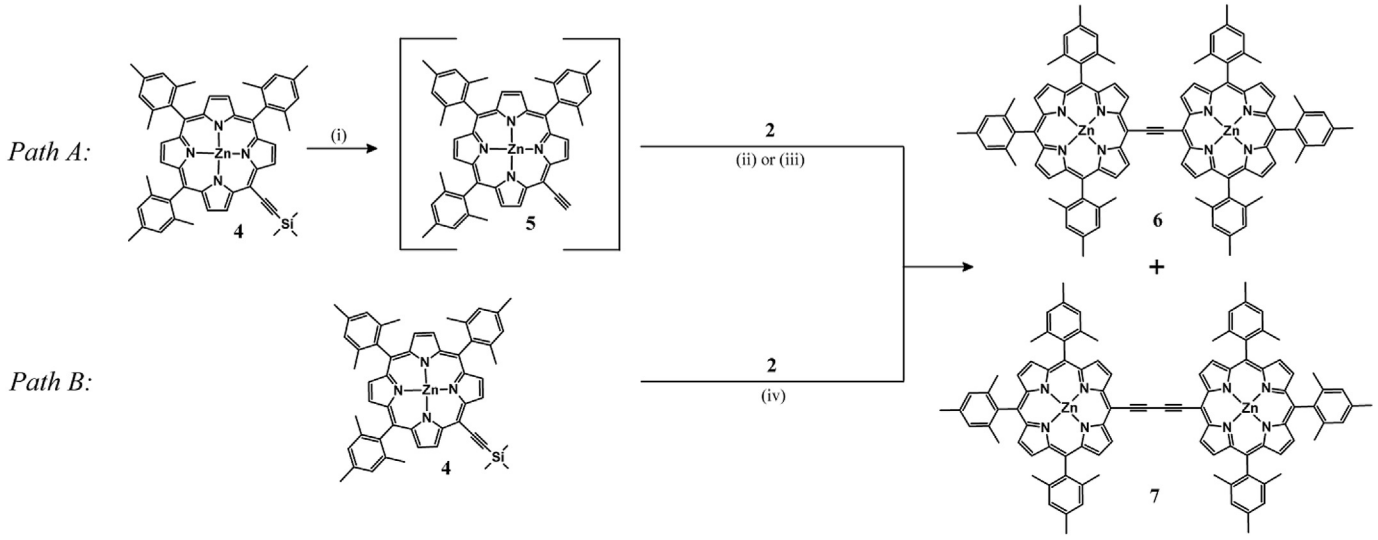
Table 1
Conditions of synthetic routes for Sonogashira coupling[a]

Entry	Path	Catalyst	Step	Solvent	T (°C)	Reaction time (h)	Yield (%)	
							6	**7**
1	*A*	$PdCl_2(PPh_3)_2$/CuI	2	Toluene/TEA	Reflux	18	26	17
2	*B*	$PdCl_2(PPh_3)_2$	1	TBAF (1 M in THF, 5% water)	Reflux	5	28	12
3	*B*	$PdCl_2(PPh_3)_2$/$AsPh_3$	1	TBAF (1 M in THF, 5% water)	Reflux	4	57	6
4[b] (literature)	*A*	$Pd_2(dba)_3$/$AsPh_3$	2	THF/TEA	Reflux	16	47	Not reported

[a] *Path A* summarizes the classical conditions or copper-free Lindsey conditions. *Path B* summarizes the new procedure.
[b] Copper-free Lindsey conditions used by Senge et al. for the synthesis of Zinc(II) complex of 1,2-bis(5,10,15-triphenylporphyrin-20-yl)ethyne dimer.[9]



Scheme 2. Formation of homocoupling product by reducing Pd(II) to catalytically active Pd(0) through terminal alkyne.



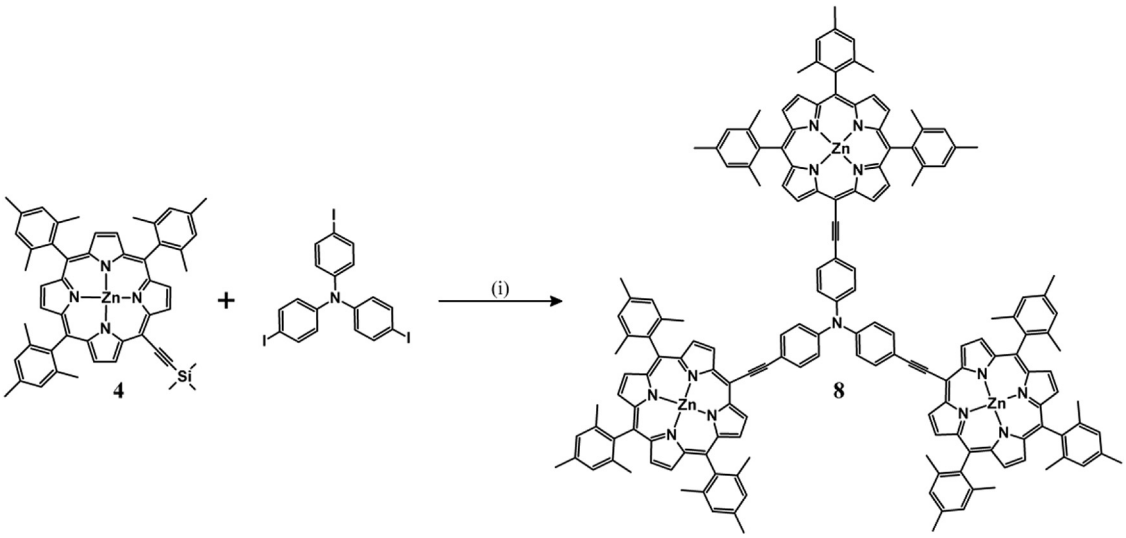
Scheme 3. Synthetic routes for Sonogashira coupling. *Path A* illustrates the classical conditions or copper-free Lindsey conditions (i) TBAF, 15 min, rt, then excess $CaCl_2$, 15 min, rt, (ii) $PdCl_2(PPh_3)_2$/CuI, toluene/TEA, 18 h, reflux, (iii) $Pd_2(dba_3)_2$/Ph_3As, THF/TEA, 16 h, reflux. *Path B* illustrates the new procedure, (iv) $PdCl_2(PPh_3)_2$/Ph_3As, TBAF (1 M in THF, 5% water), 4 h, reflux.

reaction conditions (entry 1) or Lindsey copper-free conditions (entry 4): 1) It is a one-pot instead of 2-step reaction. 2) It is no longer necessary to work in inert atmosphere neither to use degassed anhydrous solvents. 3) Easy to handle $Pd_2Cl_2(PPh_3)_2$ has been employed without copper(I), which often generate homocoupling product. 4) Yield is close or higher than the best ones described in the literature. 5) Reaction time significantly decreased to 4 h, compared to 16 h. It is worth noting that we tried to reduce even more the reaction time by using microwave irradiation but all assays have furthered Glaser reaction.

Once the best conditions have been obtained, they have been committed in the synthesis of trimer **8** (Scheme 4). Starting from tris(4-iodophenyl)amine and porphyrin **4**, using $PdCl_2(PPh_3)_2$ as catalyst assisted by an excess of TBAF (100 equiv, 1 M in THF, 5% water) at reflux for 6 h (Table 2, entry 1). However, in order to justify TBAF excess, we decided to investigate the effect of the amount of solution employed in the reaction. This large excess of TBAF is justified by experimental data collected in Table 2. The use of smaller amounts of TBAF solution (1 M in THF, 5% water) resulted in drastic yield reductions, particularly when the minimum necessary of 3.6 equiv was tested (entry 3); this amount corresponds to the total quantity of silylporphyrin **4** used in the reaction. So, excess TBAF (1 M in THF, 5% water) solution allowed solubilization of the reagents, 100 equiv lead to completely dissolving of all species, but the increase of this amount of TBAF did not give a better yield. Moreover, TBAF permits also to activate the palladium catalyst. Indeed, even if the mechanism of the Sonogashira reaction assisted by TBAF is not well known,[25] some works report that this ammonium fluoride salt acts as a base and also as a stabilizer of possible active palladium nanoparticles generated in the decomposition of the catalyst.[26,27]

Photophysical analyses were carried out on all synthesized porphyrins. Scheme 5 shows the UV–vis absorption spectra of oligomers **3**, **6**, **7**, **8** and corresponding monomer **4** in $CHCl_3$ at 298 K, selected data are reported in Table 3. As expected porphyrin dimers **3**, **6** and **7** show splitting of the Soret band, which is due to the excitonic coupling between the two parallel strong dipole transitions of each porphyrin ring.[9,28] Absence of excitonic coupling between porphyrin units in compound **8** explains why, in this instance, the electronic spectrum does not display this splitting.[28] Moreover, dimers **6**, **7** and trimer **8** exhibit bathochromic shifts of Q-bands compared to monomer **4**; it can be explained by a decrease of the energy gap between **HOMO** and **LUMO** as a result of the extension of the π-conjugated system.[29]

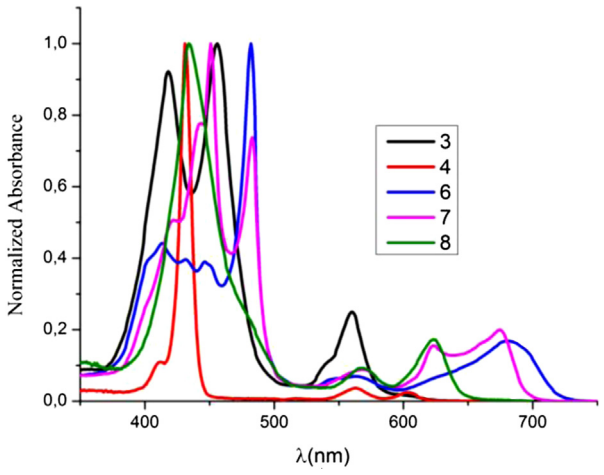
Emission measurements were carried out in order to study the electronic interactions between the porphyrin subunits in the



Scheme 4. Synthesis of trimer **8**, (i) $PdCl_2(PPh_3)_2/Ph_3As$, TBAF (1 M in THF, 5% water), reflux, 6 h.

Table 2
Effects of TBAF amount on reaction yield

Entry	TBAF (1 M in THF, 5% water)	Yield (%)
1	100 equiv	81
2	10 equiv	45
3	3.6 equiv	24



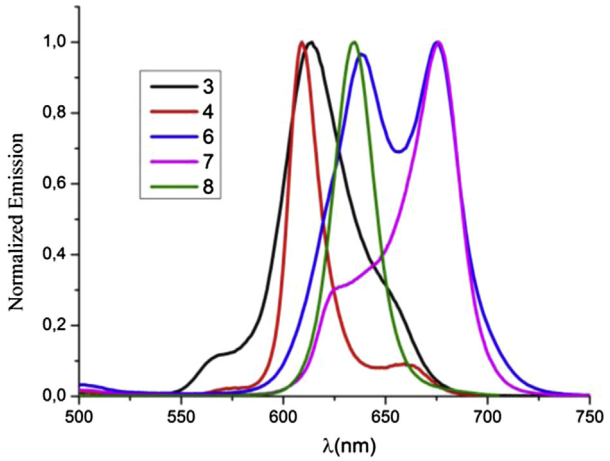
Scheme 5. Normalized absorption spectra of monomer **4** and oligomers **3**, **6**, **7** and **8** in $CHCl_3$ at 298 K ($c<10^{-6}$ M).

excited state. Fluorescence spectra of oligomers **3**, **6**, **7**, **8** and corresponding monomer **4** in $CHCl_3$ are presented in Scheme 6 and the corresponding photophysical parameters are summarized in Table 3. Dimer **3** shows a broadening of the emission bands, but no bathochromic shift was observed, compared, to monomer **4** as there is no conjugation between the porphyrin units. On the other hand, the emission maxima of oligomers **6**, **7** and **8** have been red shifted compared to monomer **4**. Indeed, the enlargement of the π-conjugation system in these three oligomers has significant influences on the emission characteristics. All these electronic absorption and emission spectra are the hallmarks of electronic interactions between porphyrin units in oligomers **6**, **7** and **8**.

Table 3
Photophysical parameters of porphyrins: monomer **4** and oligomers **3**, **6**, **7** and **8** in $CHCl_3$[a]

Compound	λ_{abs} [nm]	ε [10^{-3} M^{-1} cm^{-1}]	λ_{em} [nm]	Φ
3	418	187	569	0.02
	456	203	614	
	560	50		
4	431	514	609	0.03
	563	18	660	
	603	12		
6	414	122	638	0.006
	482	277	676	
	563	19		
	680	46		
7	451	270	627	0.007
	483	199	676	
	568	24		
	623	42		
	674	54		
8	434	389	635	0.05
	567	36		
	624	67		

[a] λ_{abs}=absorption peak wavelength; ε=molar extinction coefficient; λ_{em}=emission peaks (λ_{exc}=450 nm); Φ=emission quantum yield versus cresyl violet in methanol (0.54[29]).



Scheme 6. Normalized emission spectra of monomer **4** and oligomers **3**, **6**, **7** and **8** in $CHCl_3$ at 298 K ($c<10^{-6}$ M, λ_{exc}=450 nm).

3. Conclusion

A simple one-pot desilylation/copper-free Sonogashira cross-coupling reaction has been reported for the synthesis of highly π-conjugated porphyrin oligomers. $Pd_2Cl_2(PPh_3)_2$ assisted by TBAF has been used, yet results showed the importance of using Ph_3As as ligand in order to decrease the formation of Glaser by-product.

4. Experimental section

4.1. General

All solvents and reagents were purchased from Aldrich, Prolabo or Acros. Chloroform used in the UV–vis and fluorescence measurements is of spectroscopy quality and it was stored in a dark place to avoid its acidification. Analytical thin layer chromatography (TLC) was performed on Merck 60F254 silica gel. Column chromatography was carried out with a Combiflash® COMPANION®/TS using Grace-Resolv™ silica cartridges. ^1H and ^{13}C NMR spectroscopies were performed with a Brüker DPX 400 spectrometer. Chemical shifts are reported as δ (parts per million), downfield from internal TMS. UV–vis spectra were recorded on a SPECORD® 210 double beam spectrophotometer using 10 mm quartz cells. Fluorescence spectra were recorded on a PTI quanta master spectrofluorimeter equipped with a xenon short arc lamp (Ushio) and a photomultiplier tube (Hamamatsu R1527P). Porphyrin fluorescence quantum yields (Φ) were determined using cresyl violet in MeOH (Φ=0.54) as a standard.[30] MALDI-TOF mass spectra were recorded with a Voyager Elite (Framingham MA, USA) time-off light mass spectrometer equipped with a 337 nm nitrogen laser (VSL 337ND) (IRCOF, University of Rouen – France). It was operated in the reflection-delayed extraction mode at an acceleration voltage of 20 kV.

*4.1.1. 5,10,15-Trimesitylporphyrin (**1**).* Dipyrromethane (1 equiv, 578 mg, 3.95 mmol), *meso*-mesityldipyrromethane (1 equiv, 1.045 g, 3.95 mmol) and mesitaldehyde (2 equiv, 1.2 g, 7.9 mmol) were dissolved in 450 mL of dry chloroform under argon atmosphere. $BF_3(OEt)_2$ (0.6 equiv, 242 μL, 2.37 mmol) was added to the solution and the reaction was stirred in the dark for 30 min. Then, DDQ (3 equiv, 2.7 g, 11.95 mmol) was added and the solution was stirred for an additional 1 h at room temperature. The reaction was quenched by addition of TEA (10 mL), the mixture was poured over silica (120 μm) and eluted with DCM until elution of all porphyrins. Porphyrins were then separated by flash chromatography (silica gel, petroleum ether/DCM: gradient ranging from 0 to 25%). Porphyrin **1** was obtained as a purple solid (450 mg, 17%): ^1H NMR ($CDCl_3$, 400 MHz) **δ** ppm 10.23 (s, 1H), 9.39 (d, 2H, *J*=4.6 Hz), 8.99 (d, 2H, *J*=4.6 Hz), 8.86 (s, 4H), 7.46 (s, 4H), 7.43 (s, 2H), 2.78 (s, 6H), 2.76 (s, 3H), 2.03 (s, 18H), −2.60 (s, 2H); ^{13}C NMR ($CDCl_3$) **δ** ppm 139.4, 138.5, 137.9, 137.7, 131.5, 130.4, 130.1, 127.8, 127.7, 118.1, 117.4, 104.0, 21.7, 21.4; UV–vis ($CHCl_3$) λ_{max} nm (ε, 10^{-3} L mol^{-1} cm^{-1}) 414 (431), 509 (17), 541 (4.6), 583 (5.0), 639 (1.1); MS(MALDI-TOF) calcd for $C_{47}H_{44}N_4$ 664.356, $[M+H]^+$ found: 665.459.

*4.1.2. Zinc(II) 5-iodo-10,15,20-trimesitylporphyrin (**2**).* 5,10,15-Trimesitylporphyrin **1**(1 equiv, 103 mg, 0.155 mmol), $CHCl_3$ (10 mL), bis-(trifluoroacetoxy)iodobenzene (0.7 equiv, 50 mg, 0.11 mmol) and iodine (0.6 equiv, 24 mg, 0.093 mmol) were stirred for 1 h under argon at room temperature. The mixture was poured into DCM, washed with saturated aqueous $Na_2S_2O_3$ (200 mL) then with water (300 mL) and dried over $MgSO_4$. Next, the residue and zinc (II) acetate (42 mg, 0.23 mmol) were dissolved in a solution of $CHCl_3$/MeOH (10 mL/2 mL). The mixture was heated to a gentle reflux for 3 h. After solvent evaporation, the product was purified by flash chromatography (silica gel, petroleum ether/DCM: gradient ranging from 0 to 30%), to obtain compound **2** as a pale purple solid (48 mg, 36%). ^1H NMR ($CDCl_3$, 400 MHz) **δ** ppm 9.70 (d, 2H, *J*=4.6 Hz), 8.77 (d, 2H, *J*=4.6 Hz), 8.66 (m, 4H), 7.27 (s, 4H), 7.25 (s, 2H), 2.63 (s, 6H), 2.60 (s, 3H), 1.83 (s, 6H), 1.81 (s, 12H); ^{13}C NMR ($CDCl_3$, 400 MHz) **δ** ppm 151.8, 150.7, 150.2, 139.2, 139.1, 138.7, 137.9, 137.5, 132.1, 131.5, 131.4, 127.6, 119.6, 79.8, 21.7, 21.6, 21.4; UV–vis ($CHCl_3$) λ_{max} nm (ε, L mmol^{-1} cm^{-1}) 425 (477), 554 (21), 593 (4); MS(MALDI-TOF) calcd for $C_{47}H_{41}IN_4Zn$ 852.166, $[M+H]^+$ found: 853.203.

*4.1.3. Zinc (II) dimer **3**.* 5,10,15-Trimesitylporphyrin **1** (50 mg, 0.075 mmol) and zinc(II) acetate (5 equiv, 83 mg, 0.37 mmol) were dissolved in a solution of $CHCl_3$/MeOH (10 mL/2 mL). The mixture was stirred for 3 h at reflux and solvent was evaporated. The crude was washed twice with water (100 mL) and dried over $MgSO_4$. Next, zinc–porphyrin (53 mg, 0.073 mmol), iodine (0.6 equiv, 11 mg, 0.043 mmol) and bis-(trifluoroacetoxy)iodobenzene (0.7 equiv, 22 mg, 0.051 mmol) were dissolved in $CHCl_3$ (11 mL) and the solution was stirred at room temperature for 5 min under argon. The resulting yellow-brown mixture was then washed several times with water and dried with anhydrous $MgSO_4$. The product was purified by flash chromatography (silica gel, petroleum ether with DCM, gradient ranging from 0 to 30%), to give **3** (35 mg, 75%). ^1H NMR ($CDCl_3$, 400 MHz) δ ppm 8.74 (d, *J*=4.5 Hz, 4H), 8.71 (d, *J*=4.5 Hz, 4H), 8.41 (d, *J*=4.6 Hz, 4H), 8.02 (d, *J*=4.6 Hz, 4H), 7.31 (s, 4H), 7.17 (s, 8H), 2.65 (s, 6H), 2.51 (s, 12H), 1.94 (s, 12H), 1.88 (s, 24H); ^{13}C NMR ($CDCl_3$, 400 MHz) δ ppm 154.8, 150.1, 149.6, 149.2, 139.3, 139.2, 137.3, 137.1, 130.9, 130.6, 130.0, 127.6, 127.5, 119.3, 119.0, 118.8, 21.8, 21.5, 21.3; UV–vis ($CHCl_3$) λ_{max} nm (ε, 10^{-3} L mol^{-1} cm^{-1}) 418 (187), 456 (203), 560 (50); MS(MALDI-TOF) calcd for $C_{94}H_{82}N_8Zn_2$ 1454.523, $[M+H]^+$ found: 1455.468.

*4.1.4. (5,10,15-Trimesityl-20-trimethylsilylethynylporphyrinato)zinc (II) (**4**).* Porphyrin **2** (1 equiv, 220 mg, 0.26 mmol), $PdCl_2(PPh_3)_2$ (0.2 equiv, 38 mg, 0.05 mmol), CuI (0.1 equiv, 6 mg, 0.03 mmol) and TMSA (5 equiv, 128 mg, 1.3 mmol) were combined in a 250-mL Schlenk flask. Dry toluene and freshly distilled TEA (11 mL, 10:1) were added and the solution was freeze–pump–thaw degassed. Then, the mixture was stirred for 4 h at 50 °C. After solvent removing, the crude product was dissolved in DCM, washed twice with water (75 mL) and dried over $MgSO_4$. The residue was purified by flash chromatography (silica gel, petroleum ether/DCM: gradient ranging from 0 to 30%). The title compound was obtained as a dark green solid in 75% yield (169 mg). ^1H NMR ($CDCl_3$, 400 MHz) δ ppm 9.66 (d, *J*=4.5 Hz, 2H), 8.78 (d, *J*=4.5 Hz, 2H), 8.62 (m, 4H), 7.27 (s, 4H), 7.22 (s, 2H), 2.63 (s, 6H) 2.60 (s, 3H), 1.84 (s, 6H), 1.82 (s, 12H), 0.59 (s, 9H); UV–vis (DCM) λ_{max} nm (ε, 10^{-3} L mol^{-1} cm^{-1}) 431 (514), 563 (18), 603 (12). MS(MALDI-TOF) calcd for $C_{52}H_{50}N_4SiZn$ 822.309, $[M+H]^+$ found: 823.352.

*4.1.5. Zinc (II) complex of 1,2-bis(5,10,15-trimesitylporphyrin-20yl) ethyne (**6**) and zinc (II) complex of 1,4-bis(5,10,15-trimesitylporphyrin -20yl)-buta-1,3-diyne (**7**)*

4.1.5.1. Classical procedure. Porphyrin **4** (1 equiv, 60 mg, 0.072 mmol) was dissolved in anhydrous THF (12 mL) under argon atmosphere in a 25 mL-Schlenk flask. TBAF (1.4 equiv, 100 μL, 1 M in THF) was added in the solution and the mixture was stirred for 15 min at room temperature. Then, anhydrous calcium chloride (3 g) was added and the solution was stirred for an additional 15 min. The mixture was filtered into another Schlenk flask and the solvent was evaporated. Deprotected TMS compound **5** (1.4 equiv, 0.072 mmol) was combined with zinc-(II)5-iodo-10,15,20-trimesitylporphyrin **2** (1 equiv, 41 mg, 0.049 mmol), $PdCl_2(PPh_3)_2$ (0.2 equiv, 7 mg, 0.009 mmol) and CuI (0.1 equiv, 1 mg, 0.005 mmol). Degassed anhydrous toluene/TEA (11 mL, 10/1) was added and the mixture was stirred for 18 h under argon atmosphere at reflux. Then, the solvent was removed; the crude product was dissolved in DCM, washed twice with water (75 mL) and dried

over $MgSO_4$. The residue was purified by preparative silica gel (petroleum ether/$CHCl_3$: 60/40), to give **6** as a green solid (27 mg, 26%). The remainder of the material was a mixture of **6** and **7**.

4.1.5.2. New procedure. Porphyrin **2** (1 equiv, 17 mg, 0.02 mmol), **4** (1.2 equiv, 20 mg, 0.024 mmol), $PdCl_2(PPh_3)_2$ (0.14 equiv, 2 mg, 0.0028 mmol), Ph_3As (0.6 equiv, 3.5 mg, 0.011 mmol) and TBAF (100 equiv, 2 mL, 1 M in THF 5% water) was combined in a ground flask. The mixture was stirred at reflux for 4 h until disappearance of compound **5** on TLC. The reaction was quenched by adding DCM; the solution was washed with water (75 mL) and dried over $MgSO_4$. The residue was purified by preparative silica gel (petroleum ether/$CHCl_3$: 60/40), to give **6** (17 mg, 57%).

*4.1.6. Zinc (II) complex of 1,2-bis(5,10,15-trimesitylporphyrin-20yl) ethyne (**6**).* ^{1}H NMR ($CDCl_3$, 400 MHz) δ ppm 10.37 (d, J=4.5 Hz, 4H), 8.96 (d, J=4.5 Hz, 4H), 8.67 (s, 8H), 7.30 (s, 8H), 7.28 (s, 4H), 2.65 (s, 12H), 2.62 (s, 6H), 1.92 (s, 24H), 1.90(s, 12H); ^{13}C NMR ($CDCl_3$, 400 MHz) δ ppm 152.6, 150.2, 149.9, 149.5, 139.2, 138.8, 137.5, 131.7, 131.3, 131.0, 127.7, 127.6, 120.1, 105.0, 21.8, 21.7 21.6; UV–vis ($CHCl_3$) λ_{max} nm (ε, 10^{-3} L mol^{-1} cm^{-1}) 414 (122), 482 (277), 563 (19), 680 (46); MS(MALDI-TOF) calcd for $C_{96}H_{82}N_8Zn_2$ 1478.523, $[M+H]^+$ found: 1479.476.

*4.1.7. Zinc (II) complex of 1,4-bis(5,10,15-trimesitylporphyrin-20yl)-buta-1,3-diyne (**7**).* ^{1}H NMR ($CDCl_3$, 400 MHz) δ ppm 9.91 (d, J=4.5 Hz, 4H), 8.87 (d, J=4.5 Hz, 4H), 8.63 (q, 8H), 7.3 (s, 12H), 2.64 (s, 12H), 2.62 (s, 6H), 1.87 (s, 24H), 1.86 (s, 12H); ^{13}C NMR ($CDCl_3$, 400 MHz) δ ppm 153.2, 150.4, 149.6, 149.4, 139.1, 138.7, 137.5, 131.9, 131.7, 131.4, 131.2, 131.1, 130.9, 128.4, 128.2, 127.7, 127.6, 120.3, 68,0 21.7, 21.6, 21.4; UV–vis ($CHCl_3$) λ_{max} nm (ε, 10^{-3} L mol^{-1} cm^{-1}) 451 (5.43), 483 (5.29), 568 (4.37), 623 (4.62), 674 (4.73); MS(MALDI-TOF) calcd for $C_{98}H_{82}N_8Zn_2$ 1502.523, $[M+H]^+$ found: 1503.386.

*4.1.8. Zinc(II) trimer **8**.* It was obtained according to the new procedure, starting from tris(4-iodophenylamine) (5 mg, 0.008 mmol), **4** (3.6 equiv, 24 mg, 0.03 mmol), $PdCl_2(PPh_3)_2$ (0.4 equiv, 2.2 mg,0.0032 mmol), Ph_3As (1.5 equiv, 3.8 mg, 0.012 mmol) and TBAF (100 equiv, 0.8 mL, 1 M in THF 5% water). The mixture was stirred at reflux for 6 h. The reaction was quenched by adding DCM; the solution was washed twice with water (100 mL) and dried over $MgSO_4$. The crude was purified by preparative silica gel (petroleum ether/DCM: 50/50), to give **8** as a dark green solid (17 mg, 81%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ ppm 9.80 (d, J=4.5 Hz, 6H), 8.83 (d, J=4.5 Hz, 6H), 8.64 (q, 12H), 8.06 (d, J=8.5 Hz, 6H), 7.52 (d, J=8.5 Hz, 6H), 7.29 (s, 18H), 2.64 (s, 18H), 2.61 (s, 9H), 1.86 (s, 54H); ^{13}C NMR ($CDCl_3$, 400 MHz) δ ppm 152.0, 150.1, 149.7, 149.4, 146.9, 139.2, 138.8, 137.4, 132.9, 131.4, 131.2, 131.0, 130.9, 127.6, 124.5, 120.2, 119.8, 119.3, 99.4, 95.8, 92.8, 21.7, 21.6, 21.4; UV–vis ($CHCl_3$) λ_{max} nm (ε, 10^{-3} L mol^{-1} cm^{-1}) 434 (389), 567 (36), 624 (67); MS(MALDI-TOF) calcd for $C_{165}H_{135}N_{13}Zn_3$ 2495.884, $[M+H]^+$ found: 2496.727.

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