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Synthesis of *meso*-tetraarylthienylporphyrins by Suzuki-Miyaura cross-coupling reaction and studying their UV-Vis absorption spectra

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Dedicated to Professor Jan Bergman for his outstanding contributions to the field of organic chemistry

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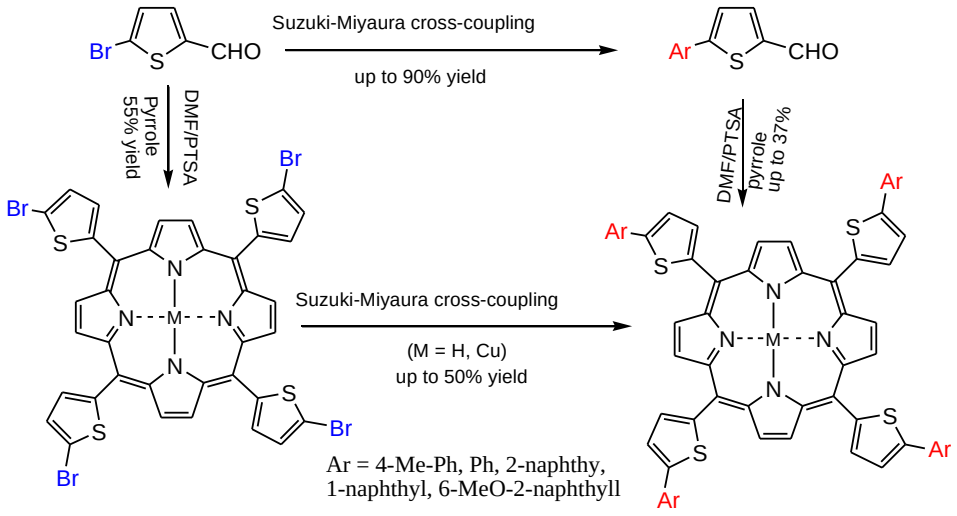
Abstract

meso-Tetra(5-arylthien-2-yl)porphyrins and their copper complexes were synthesized by two different approaches using Suzuki-Miyaura cross-coupling reactions. The first , involving the formation of 5-arylthien-2-yl carbaldehydes, followed by condensation with pyrrole. The second is a direct process that involves the coupling of meso-tetra (5-bromothien-2-yl) porphyrins with the arylboronic acids. The yield of the second approach (40-50 %) was higher than the first approach (28-35 %). The UV-Vis absorption spectra of the synthesized porphyrins revealed bathochromic shifts when compared with the parent porphyrin. Additionally, the products showed no aggregation behaviour in solution (DCM), giving a linear correlation between absorption intensity and the concentration.



Keywords: Suzuki-Miyaura cross-coupling reaction; *meso*-Tetraarylthienylporphyrins; *pi*- Extended porphyrins; Bathochromic shift; Aggregation.

Introduction

Since the first synthesis of *meso*-tetraphenylporphyrin (TPP) as a parent and most popular derivative of *meso*-tetraarylporphyrins (TAP) in 1935 by Rothemund[1] and improved by Adler and Longo in 1967[2] and modified by Lindsey[3], there have been ongoing interests in exploring their physical and chemical characters in addition to their potential applications. TPPs have a robust and versatile platform which give a different opportunity for substitution on the central and the peripheral positions; consequently permits tailoring required for variety of applications. Some of these applications include biomedical and pharmaceutical tenders, multimodal imaging, drug delivery, bio-sensing, phototherapy, probe design for selective anti-body sensors, and electrocatalytic activities can be improved by tuning the substituents on the main scaffold.[4]

The popularity of *meso*-tetraphenyl porphyrins [TPP] arises from their well established and straightforward methods of preparation. On the other hand, porphyrins with heteroaryl rings at *meso*-positions are a relatively unexplored class of porphyrins, and their synthesis is scarcely reported in the literature. For example, only few porphyrins with heteroaryl moieties at the *meso*-positions like pyrrolyl[5] furyl,[6] azulenyl,[7]pyrazolyl,[8,9] imidazoyl[10-12] were reported. Additionally, since the first report for the synthesis of *meso*-tetra(thien-2-yl)porphyrin by Triebs *et al*. in 1968,[13] as an important member of this class of compounds which demonstrated to have unique physical and thermal characters, therefore, it has been used in a diverse range of applications. For example, porphyrins with *meso*-tetrathienyl moieties were used in the light-harvesting and energy-transfer applications,[14-16] in building of ultrathin films of quasi-2D porphyrin materials,[17] organic semiconductor devices,[18] extended electronic systems for supramolecular architectures,[19] incorporated into dithiaporphyrins scaffold for phototoxins applications[20] and recently, it was used as electrocatalyst for water splitting reaction as one of the promising renewable energy sources.[21]

Generally, there are two possible approaches for the synthesis of *meso*-tetrathienylporphyrin compounds can be found in the literature. The first starts by tailoring and preparing the starting materials (either the pyrrole or the thienyl aldehyde derivatives) followed by regular condensation and oxidation in acidic medium.[21,22] While the second involves the synthesis of the parent *meso*-tetrathienyl porphyrins followed by chemical transformations at the peripheral position of both pyrrole and aryl ring systems.[23]

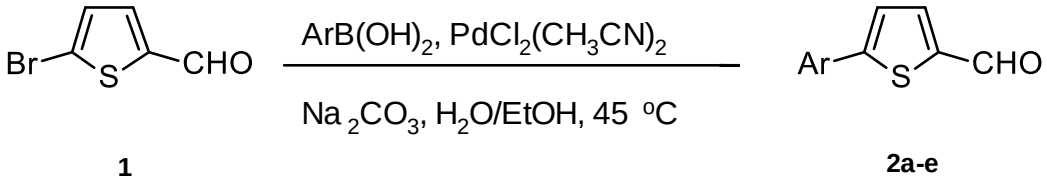
In continuation to our work in designing and preparation of porphyrins for electrochemical and medicinal applications[21], we present in this report synthesis of novel *meso*-tetraarylthien-2-ylporphyrins and its copper complexes *via* two different approaches using Suzuki-Miyaura cross-coupling (SMC), measuring, and studying the insertion of different aryl groups on the UV-Vis absorption spectra as well the aggregation behaviour in solution (DCM) of the synthesized porphyrins. The chemical structure of all the prepared compounds was delineated by spectroscopic techniques (FT-IR, NMR, MS and UV-Vis.)

Results and Discussion

Suzuki-Miyaura cross-coupling (SMC) is one of the powerful approaches to build sp^2-sp^2 carbon-carbon bonds.[24,25] It has been used in the synthesis of many organic molecules with numerous applications in different fields.[26-28]

The work in this study started with the search for a suitable palladium catalyst for (SMC) to prepare the 5-arylthiophene-2-carboxaldehydes (Scheme 1), which are required as building blocks in the synthesis of porphyrin scaffold. At the beginning phosphine-palladium catalyst $Pd(PPh_3)_4$ was used, but unfortunately, the coupling of the bromoaldehyde (**1**) with the arylboronic acids produced the desired product (**2**) in inferior yield

(≤ 10 %). In order to overcome this problem, and after performing literature survey to find an alternative palladium-based catalyst for the SMC reaction, bis(acetonitrile)dichloro palladium(II) [$PdCl_2(CH_3CN)_2$] was found to be the catalyst of choice for this transformation. It was prepared in almost quantitative yield by boiling palladium (II)chloride ($PdCl_2$) in acetonitrile for 20-24 hours in Argon atmosphere.[29] Now, the reaction started by coupling the 5-bromo-2-thiophenecarboxldehyde (**1**) with different arylboronic acid derivatives [$ArB(OH)_2$] in the presence of the prepared palladium catalyst [$PdCl_2(CH_3CN)_2$], sodium carbonate in water/ethanol mixture (2:1) at 45-50 ^oC. The coupling reaction was completed in one hour (the reaction was monitored by TLC) to give the desired 5-arylthiophene-2-carboxaldehydes (**2a-e**) in good to excellent yield (Scheme 1, Table 1). It was noticed that in some cases, a by-product was detected in the reaction medium. This byproduct was isolated and identified as bi-aryl derivatives (Ar-Ar).[29,30] This byproduct was likely produced from the coupling of two aryl boronic acid units under the reaction conditions. The amount of this side product was minimized and prevented to some extent by adjusting the water/ethanol ratio (2:1 was the ideal ratio). Therefore, the desired products were isolated and obtained in pure forms by column chromatography and finally by regular purification with crystallization process (**2a-e**, Scheme 1-Table 1).



1 **2a-e**

Scheme 1. Synthesis of 5-arylthienyl-2-carbaldehyde **(2a-e)** using SMC reaction.

Table 1. 5-arylthienyl-2-carboxaldehydes **(2a-e)** and arylboronic acids precursors

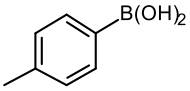
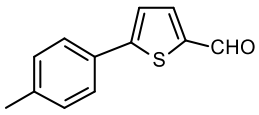
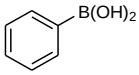
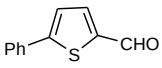
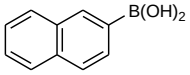
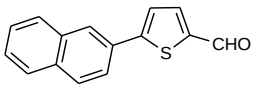
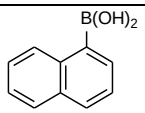
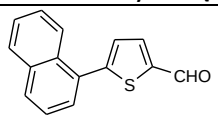
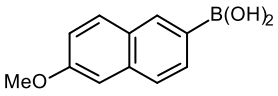
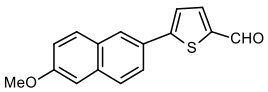
Entry	Arylboronic acid	Product 5-Arylthiophene-2-carbaldehydes **(2)**	Yield (%)	Melting point ($^{\circ}C$)
1		 **2a**	88	96-97
2		 **2b**	95	90-91 [a]
3		 **2c**	60	127-126

Table 1. Continued

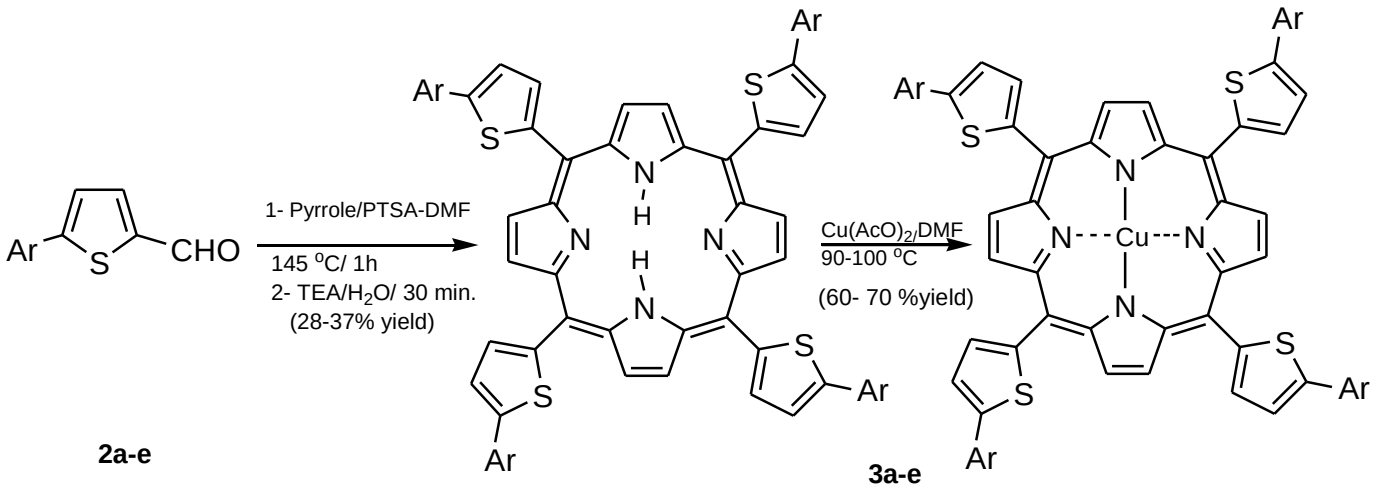
Entry	Arylboronic acid	Product 5-Arylthiophene-2-carbaldehydes **(2)**	Yield (%)	Melting point (°C)
4		 **2d**	90	64
5		 **2e**	55	183

The chemical structure of the synthesized 5-arylthieyl-2-carboxaldehydes **(2a-e)** was confirmed by spectroscopic techniques (FT-IR, ^{1}H-NMR, ^{13}C-NMR and MS). The ^{1}H-NMR spectra of aldehydes **2a-e** revealed a down-field singlet at δ = 9.90, 9.91, 9.91, 9.96, and 9.90 ppm respectively attributed to the formyl hydrogen alongside with the other multiplets of the aromatic protons. Additionally, the ^{13}C-NMR spectra of the syntheisized aldehydes **(2a-e)** showed a very deshielded signal at a range of δ = 184.9-182.5 ppm indorsed to the aldehydic carbon at position two of the thiophene ring. Furthermore, the FT-IR spectra revealed a sharp signal at a range of wave number 1665-1660 cm^{-1} attributed to the aldehyde carbonyl.

We now turn to construct the porphyrin scaffold, which was achieved by two approaches. Firstly, by the direct condensation of pyrrole with the synthesized 5-aryl thiophene-2-carboxaldehydes (**2a-e**) by modifying the previously reported method.[31]. The modification includes using triethylamine (H_2O/TEA 95: 5 v/v) in the work-up stage beside *p*-toluene sulphonic acid (PTSA) as an acidic catalyst and dimethylformamide (DMF) as a solvent. The *meso*-tetraarylthien-2-ylporphyrins (**3a-e**, M = H) were obtained in 28-37 % yield (Scheme 2 Table 2). Subsequently, the complexation reaction of the synthesized free-base porphyrins (**3a-e**, M = H) with copper acetate was readily performed when excess copper acetate $Cu(OAc)_2$ was heated with the *meso*-tetraaryl(thien-2-yl)porphyrins (**3a-e,** M = H) at 90-100 °C in DMF. The porphyrin copper complexes were obtained in a good yield (60-70 %) (Scheme 2).

In addition to the synthesis route mentioned above, another direct approach for the synthesis of porphyrins **3a-e** was investigated. The main aim of this direct approach is to enhance the yield and to shorten the long process of the porphyrin purifications process. Therefore, we have studied the possibility of using the direct coupling of the aryl boronic acids with the tetrabromo derivative the *meso*-tetra (thien-2-yl) porphyrin under Suzuki-Miyaura coupling condensations (SMC). The SMC reaction was successfully used in previous reports for the preparation of other porphyrin derivatives.[32-34] Therefore, the free- base of *meso*-tetra(5-bromothien-2-yl)porphyrin (**4**, M = H, Scheme 3) was prepared following the literature procedure[21] ,and the reactivity toward coupling with the arylboronic acids under SMC reaction conditions was explored.

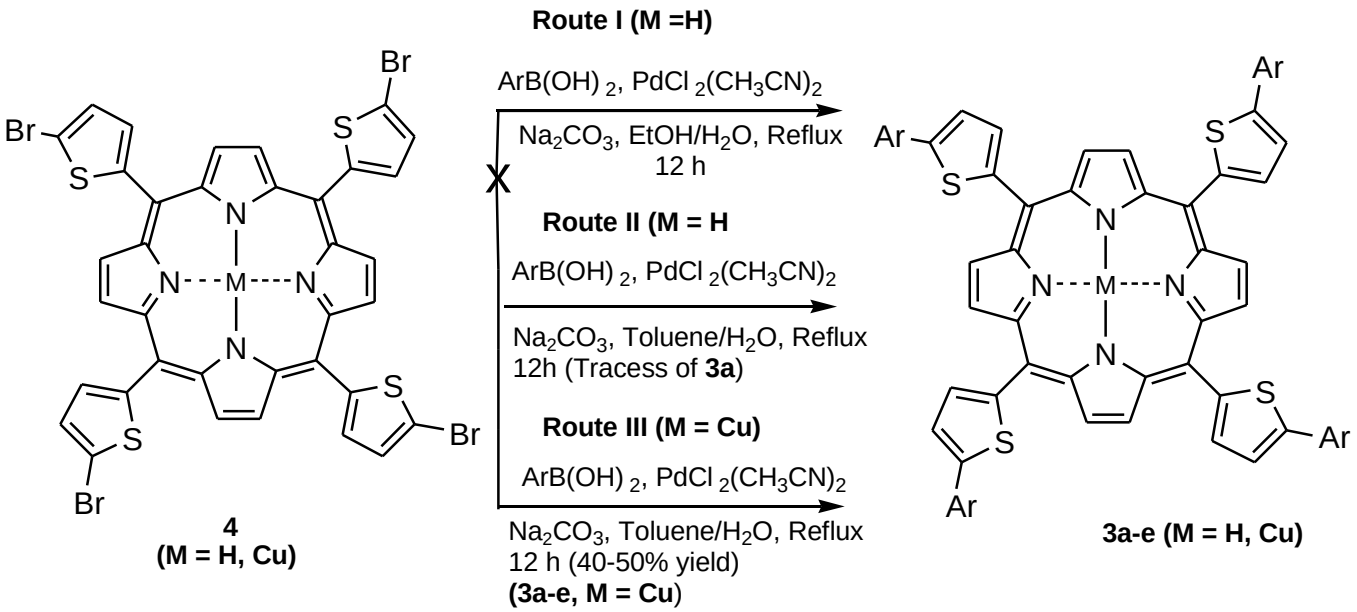
At the beginning, the aforementioned mild SMC reaction conditions with water/ethanol mixture as a solvent was used (Scheme 3, Route I). The *meso*-tetraarylthienyllporphyrin **(3)** was not detected in the reaction medium even after twelve hours of reflux (aliquots were taken from the reaction mixture to monitor it by UV-Vis absorption spectra *via* observing the change on the values of Soret and Q bands of the *meso*-tetra(5-bromothien-2-yl)porphyrin (**4**, M = H, Scheme 3, Route I).



Scheme 2. Synthesis of *meso*-tetraarylthien-2-yl porphyrins (**3a-e**) and its copper complexes by direct condensation of 5-aryl thiophene-2-carbaldehydes (**2a-e**) with pyrrole.

Table 2. The *meso*-tetraarylthien-2-yl porphyrins (**3a-e**) and aldehyde precursors (**2a-e)**

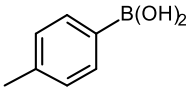
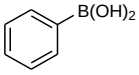
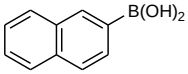
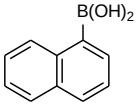
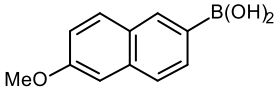
Entry	Aldehydes (precursors)	Porphyrin (products)	Ar	Yield (%)
1	**2a**	**3a**	4-Me-Ph	35
2	**2b**	**3b**	Ph	30
3	**2c**	**3c**	2-naphthyl	32
4	**2d**	**3d**	1-naphthyl	37
5	**2e**	**3e**	6-methoxy-2-naphthyl	28



Scheme 3. Synthesis of the *meso*-tetraarylthien-2-ylporphyrins **(3a-e)** from of the *meso*-tetra(5-bromothien-2-yl)porphyrin **4** using SMC reaction.

Nevertheless, when water/ethanol mixture was replaced by toluene/water (9:1, v/v) as a solvent and the reaction mixture was refluxed for twelve hours, a dark mixture was obtained, and only traces of the *meso*-tetraarylthienyllporphyrin was isolated (**3a** was taken as an example) (Scheme 3, Route II). Presumably, a mixture of different SMC products on the peripheral bromine atoms was formed. Also, the involvement of the palladium catalyst in another complexation reaction with free-base porphyrins instead of catalyzing the coupling reaction cannot be rolled out.[25] Therefore, the copper complex of the *meso*-tetra (5-bromothien-2-yl)porphyrin (**4,** M= Cu) was prepared[21] and used as porphyrin substrate in the SMC reaction instead of the free-base porphyrin **(4,** M= H**)** (Scheme 3, Route III). Under these reaction conditions, the copper complexes of the *meso*-tetraarylthien-2-ylporphyrins **(3a-e,** M = Cu**)** were obtained in better yield (40-50 %) compared to the other approaches. (Scheme 3, Route III, Table 3).

Table 3. The *meso*-tetraarylthien-2-ylporphyrins (**3a-e,** M= Cu) and arylboronic acids precursors (Route III)

Entry	Arylboronic acid (precursors)	Product *meso*-tetraarylthien-2-ylporphyrins **3a-e**, M = Cu	Yield (%)
1		**3a**	42
2		**3b**	45
3		**3c**	46
4		**3d**	50
5		**3e**	40

The chemical structure of *meso*-tetraarylthien-2-yl porphyrins and their copper complexes (**3a-e**) were confirmed by spectroscopic techniques (FT-IR, NMR, MS, and UV-Vis.) and by comparing the spectral data of the porphyrins obtained in both approaches.

The ^{1}H-NMR spectra of the free-base porphyrins (**3a**-e, M = H) revealed a singlet signal at a very up-field and appeared at about -2.52 ppm attributed to the characteristic inner protons of the porphyrin ring (2NH). Which were exchanged by deuterium after adding D_2O to the NMR tube and the signal was completely

disappeared in the ^{1}H-NMR spectra. (Figure 1). ^{1}H-NMR shows the spectrum of porphyrin **3a** after and before adding D_2O).

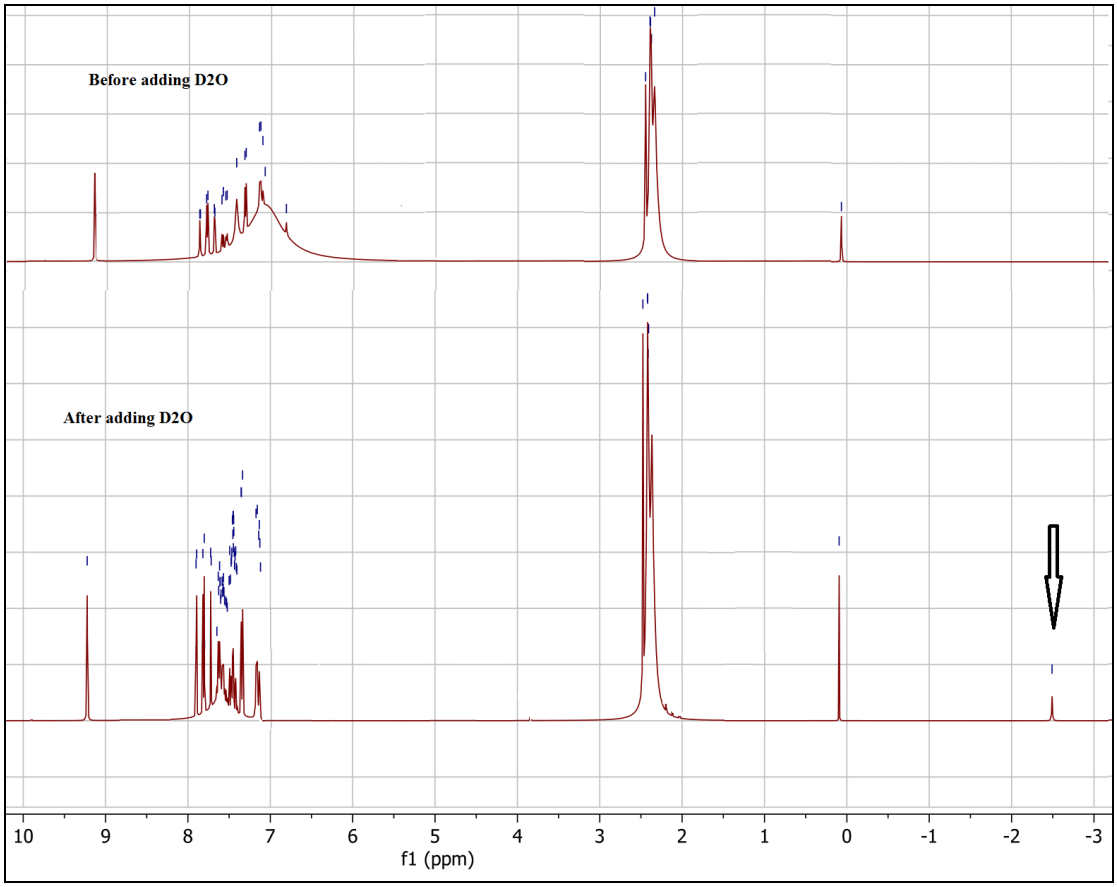


Figure 1. ^{1}H-NMR spectrum of the free base porphyrin (**3a**) in $CDCl_3$ after and before adding D_2O and the disappearance of the signal for exchangeable inner 2NH at about -2.52 ppm.

This signal was disappeared and was not detected in the ^{1}H-NMR spectra of the copper complexes of the *meso*-tetraarylporphyyrins (**3a-e,** M = Cu). Furthermore, all the ^{1}H-NMR spectra of the The free-base meso-tetra-(5-arylthien-2-yl)porphyrins and their copper complexes (**3a-e,** M = H, Cu) exhibited multiplets in the range 8-7 ppm accredited to the other aromatic protons of the thienyl and the substituted aryl rings. Additionally, a downfield signal over 9 ppm recognized to the *beta* hydrogens of the porphyrin ring system.

The FT-IR spectra, of the free-base porphyrins **(3a-e)**, revealed peaks at the range 3415-3400 cm^{-1} which can be attributed to the in-phase stretching vibration mode of the inner N-H bonds. Also, all the investigated porphyrins showed a very weak peak at about 3110 and 1600 cm^{-1} attributed to the stretching vibration mode of the C-H and C=C bonds of the aromatic ring systems respectively.

Measuring and studying the UV-Vis absorption spectra

The free-base *meso*-tetra-(5-arylthien-2-ylporphyrins and their copper complexes (**3a-e,** M = H, Cu) are symmetrical porphyrins. Therefore their UV-Vis absorption spectra revealed a typical pattern for the characteristic Soret and Q bands for such ring system.[34] The UV-Vis absorption spectra for the *meso*-tetra-thien-2-ylporphyrins **(3a-e)** were measured and compared with the reported values in the literature of the meso-tetrathien-2-ylporphyrins (**3,** Ar & M = H)[35] and *meso*-tetra-(5-bromothien-2-yl)porphyrins (**4,** M = H &

Cu) and all the data are extracted in Table 4. The UV-Vis spectra are depicted in figure-2 (porphyrin **3b** and its copper complex was taken as an example, and data reported for other synthesized porphyrins are provided in the supporting information).

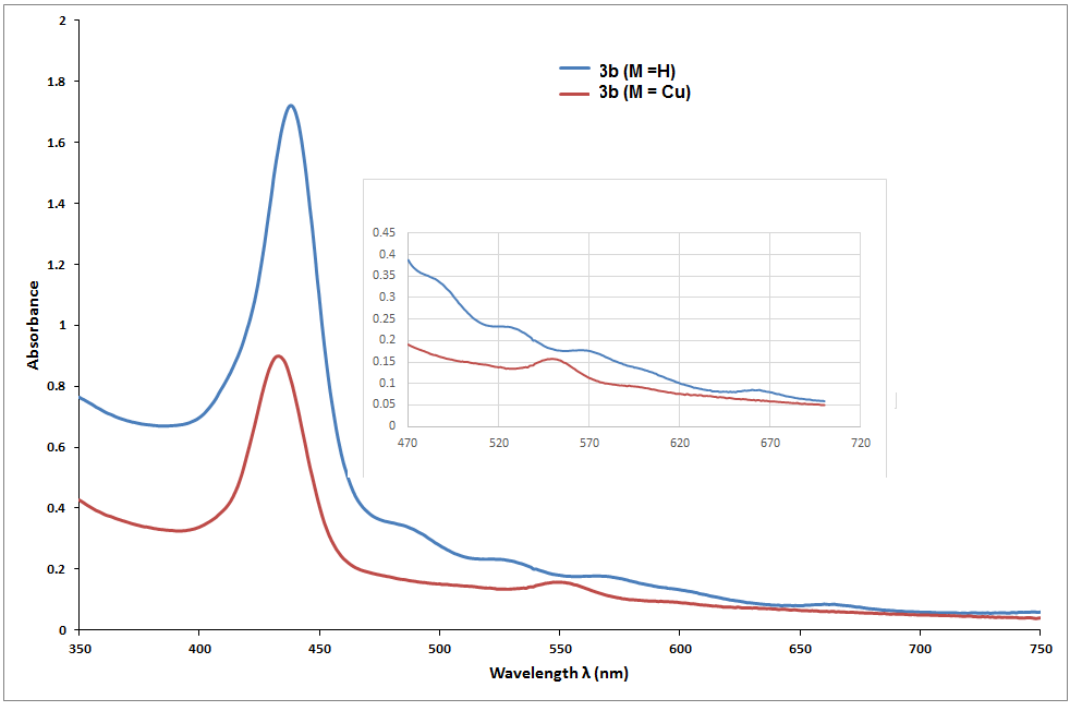


Figure 2.The UV-Vis spectra for the *meso*-tetra-(5-phenyllthien-2-yl) porphyrin (**3b,** M=H) and its copper complex (**3b,** M = Cu) in dichloromethane.

Table 4. The wavelength (λ_{max}) of both Soret and Q-bands and the extinction coefficient (molar absorptivity) (ε) were extracted from the UV-Vis spectra for the the *meso*-tetra-(5-arylthien-2-yl)porphyrins and their copper complexes (**3a-e,** M = H & Cu) and compared with the reported values for the the meso-tetra(thien-2-yl)porphyrins (**3,** Ar = H) and (**4,** M = H & Cu) in chloroform at room temprature

Porphyrins (M)	λ_{max} Soret band (nm)	λ_{max} Q band(s)(nm)	Log ε (Molar absorptivity L mol^{-1} cm^{-1}) [Lit.]
3 (Ar & M = H)	426	523, 558, 594, 661	5.54, 4.25, 3.70, 3.48, 3.40[32]
4 (H)	432	523,563 596,655	5.20, 3.37, 3.08, 2.99, 2.60
3a (H)	441	482, 525, 567,666	5.94, 4.69, 3.46, 2.56, 2.29
3b (H)	439	526, 570,600, 662	5.24,4.23, 3.14,3.02, 2.84
3c (H)	440	529, 570, 620, 667,	5.41,4.30, 3.10,2.90, 2.20
3d (H)	435	484, 526, 573, 663	5.20,4.63, 3.43,2.28, 2.00
3e (H)	440	552, 600, 660	5.62, 4.70, 3.40, 3.10

Table 4. Continued

Porphyrins (M)	λ_{max} Soret band (nm)	λ_{max} Q band(s)(nm)	Log ε (Molar absorptivity L mol^{-1} cm^{-1}) [Lit.]
4 (Cu)	430	548	5.30, 3.44
3a (Cu)	439	549	5.71, 3.05
3b (Cu)	433	550	5.09, 3.33
3c (Cu)	439	548	5.31, 3.51
3d (Cu)	431	550	5.01, 3.20
3e (Cu)	441	548	5.90, 3.39

It was previously reported that, the presence of the 2-thienyl groups on the *meso*-positions of the porphyrin moiety alleviated the saddled conformation of the co-planar shape of the porphyrinoid scaffold when compared with the phenyl group on the *meso*-tetraphenylporphyrin (TPP).[35] While the UV-Vis absorption spectrum of TPP gave λ_{soret} = 417 nm, the *meso*-tetrathien-2-yl (**3,** Ar & M = H) bathochromically shifted to longer wavelength and appeared at 426 nm.[35,36] This shift was initially explained in terms of inductive effects[34]. However, Gupta et al. attributed the shift to the significant *pi*-localization effect of the thien-2-ylporphyrins due to a stronger resonance interaction between the porphyrin moiety and the thienyl groups at the *meso* positions when compared with the phenyl group.[37,38] The insertion of the aryl substituents (Ar) on position five of the thiophene ring on the peripheral *meso*-positions of the porphyrinoid ring systems in the free base *meso*-tetraarylporphyrins **(3a-e)** has affected the values of both Soret and Q-bands compared to the parent *meso*-tetrathien-2-ylporphyrins (**3,** Ar & M = H). While, the later porphyrin with no substituent on the thiophene ring was previously reported to give Soret band with λ_{soret} = 426 nm[36], the insertion of the aryl ring systems (4-Me-Ph**,**-Ph**,** 2-naphthyl, 1-naphthyl, and 6-MeO-2-naphthyl) in **3a, 3b, 3c, 3d**, and **3e** respectively enhanced this value by range of 15-9 nm (Figure 2 &Table 3). Additionally, the observed bathochromic shift in the UV-Vis for *meso*-tetraaryl-2-thienylporphyrins **(3a–e)** compared to the parent *meso*-tetrathien-2-ylporphyrin (**3,** Ar & M=H) can be explained based on increment of the degree of conjugation. The insertion of aryl chromophoresat the thienyl ring at the *meso*-positions of the porphyrin moiety in **3a-e** (4-Me-Ph**,**-Ph**,** 2-naphthyl, 1-naphthyl, and 6-MeO-2-naphthyl) would be extended the thienyl *pi*-electron, which would in turn efficiently increase the p-p overlap between the thienyl ring and the core 18th pi-electron system of the porphyrin scaffold. Hence, extending the effective size of the *pi*- electron system which in turn led to the noticed red shift in the UV-Viv spectra of the studied porphyrins **(3a-e)**.

Aggregation Studies by UV/Vis Spectroscopy

It has been reported that, the porphyrin scaffold with bulky substituents attached to the pophyrinoid core has low tendency for aggregation in solution *via* preventing π-π stacking interactions.[39-43] To assess the aggregation behavior of the synthesized porphyrins **(3a-e)** in solution, we studied this phenomenon by UV/Vis analysis in dichloromethane. It was observed that, firstly no change on the λ_{max} of the studied porphyrins, secondly, a linear increment in the absorption versus the concentration at the study concentration range (15-50 µm). (Figures 3**,** for compound **3b,** M = H as an example, similar behaviour were obtained for other porphyrins and data are provided in the supporting information). These results indicate that, no aggregation behavior for any of the studied porphyrins were observed at the study concentration range (15-50 µm).

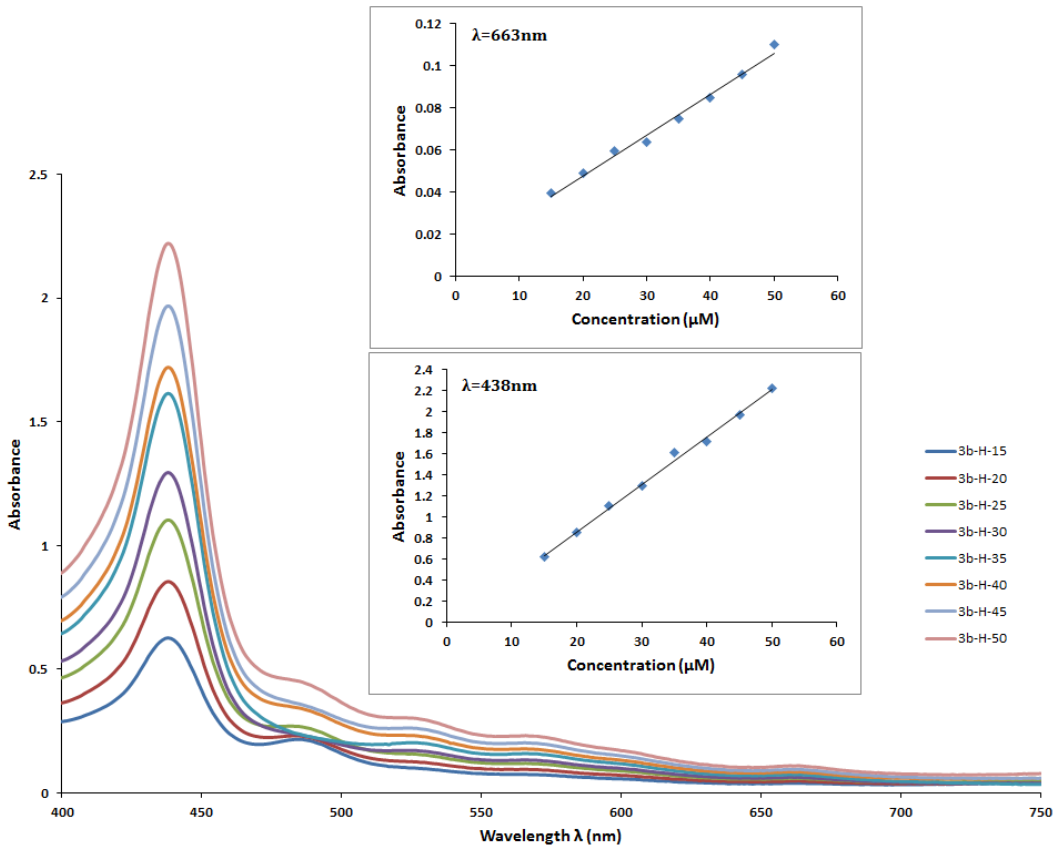


Figure 3. Aggregation study for compound **3b** (M = H) in dichloromethane (DMC).

Conclusions

meso-Tetra(5-arylthien-2-yl)porphyrins and their copper complexes (**3a-e** M= H & Cu) were synthesized by two different approaches using Suzuki-Miyaura cross-coupling reactions (SMC). Either by two-step via tailoring the 5-arylthien-2-yl carbaldehydes followed by condensation with pyrrole in dimethylformamide (DMF) as a solvent and p-toluene sulphonic acid (PTSA) as a catalyst or by one-step-direct coupling of the *meso*-tetra(5-bromothien-2-yl)porphyrins with the arylboronic acids. The yield of the second approach (40-50 %) was relatively better than the second (28-35 %). The UV-Vis absorption spectra of the synthesized porphyrins revealed bathochromic shifts in both Soret and Q bands (up to 15 nm), compared to the parent porphyrin (**3,** Ar & M = H) , as a result of extension of the pi-electron system of the core porphyrin moiety after insertion of the aryl chromophores as peripheral substituents. Additionally, the synthesized porphyrins showed no aggregation behavior in the DCM solution and gave a linear correlation of the absorption versus the concentration at the study concentration range (10-50 µm).

Experimental Section

General. All the reagents and solvents were purchased from commercial suppliers and used directly without further purification. Melting points were measured using a capillary tube with SANYO Gallen-Kamp

instrument. The ultraviolet–visible (UV-Vis) spectra were measured on GENESYS 10S UV-VIS spectrophotometer. Infrared spectroscopy (IR) spectra were recorded using an Agilent Technologies Cary 630 FTIR spectrometer. The NMR spectra were measured with BRUKER nuclear magnetic resonance 850 MHT spectrometer in $CDCl_3$ as a solvent, and the chemical shift was given in δ \ (ppm). EI-MS spectra were recorded on SHIMADZU QP-2010 PULS spectrometer. Chromatographic separations were performed either using palates (15x20 cm) or columns with silica gel (200) and (400) mesh, respectively. All the reactions were monitored by TLC using Merck silica gel 60 PF_{245} cards and the compound were visualised by UV lamp (245-365 nm).

Synthesis of bis(acetonitrile)dichloro palladium (II) catalyst [$PdCl_2(CH_3CN)_2$]. Palladium (II) chloride (0.5 g, 2.81 mmol) was dissolved in acetonitrile (100 mL) in a round-bottomed flask under argon and heated to reflux overnight. The solution was filtered to remove unreacted palladium chloride and washed with diethyl ether. The solvent was removed under vacuum to give (0.57 g), yield 78 % of the desired catalyst as yellowish-brown crystal, which was used directly without any further purification.[29]

Synthesis of 5-arylthienyl-2-carbaldehyde (2a-e). General procedure. A mixture of aryl boronic acid(s) (3.2 mmol), sodium carbonate (0.31g, 2.9 mmol), acetonitrile-dichloro palladium (II) (0.02g, 0.077mmol) and 5-bromothiophene-2-carbaldehyde (**1**) (0.3 mL, 2.61 mmol), were dissolved in H_2O (6 mL) and ethanol (3 mL). The reaction mixture was stirred and heated at (45-50 ^oC) for 10-12 hours. The resulting black solution was poured into cooled water and extracted with ethyl acetate (4 × 15 mL). The organic layer was dried over anhydrous Na_2SO_4, filtered and evaporated under vacuum. The solid product was collected then column chromatographed (petroleum ether: ethyl acetate, 10:1) and crystallized from petroleum ether-benzene mixture (1:1).

5-(4-Methylphenyl)thiophene-2-carbaldehyde (2a). It was obtained as pale yellow crystals from petroleum ether (0.662 g), 88 % yield, mp 96-97° C[41]. IR (cm^{-1}): 1660 (CHO). ^{1}H-NMR ($CDCl_3$): δ = 9.90(s,1H, C<u>H</u>O), 7.76-7.25 (m, Ar-H), 2.42 (s, 3H, CH_3). ^{13}C-NMR ($CDCl_3$): δ = 184.98, 155.98, 146.08, 143.25, 141.72, 132.95, 131.66, 130.98, 130.61, 127.63, 21.23. Ms (EI): *m/z* for $C_{12}H_{10}OS$; (2002) Calcd C, 71.25; H, 4.98; O, 7.91; S, 15.85 % Found: 71.05; H, 4.79; O, 7.76; S, 15.81 %

5-Phenylthienyl-2-carbaldehyde (2b). It was obtained as yellow crystals (0.48g) 95 % yield, mp 90-91 ^oC, Literature mp (92-93°C)[26]. IR (cm^{-1}): 1655.408 (CHO). ^{1}H-NMR ($CDCl_3$): δ = 9.91(s, 1H, CHO), 7.74-725 (m, Ar-H),. ^{13}C-NMR ($CDCl_3$): δ = 182.86, 154.34, 142.48, 137.43, 135.66, 132.72, 129.47, 129.23, 128.08, 126.47. Ms (EI): *m/z* for $C_{11}H_8OS$, M^+ (188) M+1 (189).

5-(Naphth-2-yl)thienyl-2-carbaldehyde (2c). It was obtained as yellow crystals (0.36g) 60 % yield, mp 126-127 ^oC [42]**.** IR (cm^{-1}): 1650.905 (CHO). ^{1}H-NMR ($CDCl_3$): δ = 9.91 (s, 1H,CHO), 8.15-7.52 (m, Ar-H). ^{13}C-NMR ($CDCl_3$): δ = 182.77, 154.36, 142.56, 137.51, 133.76, 133.68, 133.37, 132.68, 130.40, 129.04, 128.54, 128.42, 128.25, 127.83, , 127.69, Ms (EI): *m/z* for $C_{15}H_{10}OS$, M^+ (238), M+1 (239). Found C, 75.31 %, H, 4.03 %, O, 6.41 %, S, 13.15 % Calcd C, 75.60 %, H, 4.23 %, O, 6.71 %, S, 13.46 %

5-(Naphth-1-yl) thienyl-2-carbaldehyde (2d). It was obtained as yellow crystals (0.60g) 90% yield, mp 64 °C [43]. IR (cm^{-1}): 1655 (CHO), 1520 (C=C aromatic). ^{1}H-NMR ($CDCl_3$): δ = 9.96 (s,1H,CHO), 8.15(-736 (m, Ar-H). ^{3}C-NMR ($CDCl_3$): δ = 182.98, 152.35, 143.58, 136.64, 133.86, 131.18,131.12, 129.82, 128.68,128.62, 128.38, 128.18, 127.92, 127.85, 127.09. Ms(EI): *m/z* for $C_{15}H_{10}OS$, M^+(238), M+1 (239). Found C, 75.43 %, H, 4.03 %, O, 6.52 %, S, 13.33 % Calcd C, 75.60 %, H, 4.23 %, O, 6.71 %, S, 13.46 %

5-(6-Methoxynaphth-2-yl) thienyl-2-carbaldehyde (2e). It was obtained as yellow crystals (0.26g) 55 % yield, mp 183 ^oC. IR (cm^{-1}): 1670 (CHO), 1500 (C=C aromatic). ^{1}H-NMR ($CDCl_3$): δ = 9.90 (s,1H, CHO), 8.07-7.14(m, Ar-H), 3.94 (s,3H,OC<u>H</u>$_3$)**.** ^{13}C-NMR ($CDCl_3$): δ =182.75, 158.63, 154.81, 142,06, 137.62, 135,00 129.96, 128.79,

128.27, 127.76, 125.52, 124.54, 123.80, 119.91, 55.41. Ms(EI): *m/z* for $C_{16}H_{12}O_2S$, M^+ (268), M+1 (269). Found C, 71.44 %, H, 4.42 %, O, 11.70 %, S ,12.05 % . Calcd C, 71.62 %, H, 4.51 %, O, 11.93 %, S, 11.95 %.

Synthesis of 5,10,15,20- tetrakis(5-arylthien-2-yl) porphyrins (3a-e, M = H)

A mixture of pyrrole (1 ml, 14.9 mmol), and 5-arylthiophene-2-carbaldehyde (**2a-e**) (14.8 mmol) in dimethylformamide DMF (10 ml) was heated at 100 ^oC under argon atmosphere. Then, *p*-toluene sulphonic acid (PTSA) (2.82 g, 16.37 mmol) was added, the reaction mixture was heated up gradually to 145 ^oC and kept at this temperature for one hour. The obtained dark violet solution was left to cool to room temperature. Subsequently, poured into a mixture of cooled water and triethylamine (H_2O/TEA 95: 5 v/v) and left for 30 min. with stirring. The solid precipitate was filtered, washed several times with water and methanol, air-dried and purified by column chromatography MeOH (1 %). / crystallization from $CHCl_3$

5,10,15,20- Tetra(5-(4-methylphenyl)thien-2-yl) porphyrin (3a, M= H). It was obtained as dark purple crystals (0.15g) 35 % yield, mp >350 ^oC. IR (cm^{-1}):3400 (NH). ^{1}H-NMR ($CDCl_3$): δ = 9.27 (s, 8H, β-H), 7.95 -7.34 (m, Ar-H of the phenyl and thienyl-H), 2.42 (m, 3H, Me), -2.52 (s, 2H,inner porphyrin NH). ^{13}C-NMR ($CDCl_3$): δ = 154.98, 147.00, 142.90, 139.29, 137.48, 131.56, 130.99, 129.68, 129.53, 127.05, 126.09, 125.67, 124.96, 123.14, 122.41. Ms (EI): *m/z* for $C_{64}H_{46}N_4S_4$ M.Wt = 999.34, Found C, 76.73 %; H, 4.44 %; N, 5.34 %; S, 13.05 %. Calcd. C, 76.92 %; H, 4.64 %; N, 5.61 %; S, 12.83 %. UV–Vis (CH_2Cl_2), λ_{max} (nm): 441, 482, 525, 567, and 660.

5,10,15,20- Tetra(5-phenylthien-2-yl)porphyrin (3b, M = H). It was obtained as dark purple crystals, 30 % yield, mp > 350 ^oC . IR (cm^{-1}): 3426.75 (NH). ^{1}H-NMR ($CDCl_3$): δ = 9.20(s,8H, β-H),7.90-7.39 (m, Ar-H of the phenyl and thienyl-H), -2.56(s,2H,inner porphyrin NH). ^{13}C-NMR ($CDCl_3$): δ =147.1, 141.9, 135, 134.2, 133.9, 130.1, 129.1, 128.8, 127.9, 125.8, 123.4, 122.5. Ms (EI): *m/z* for $C_{60}H_{38}N_4S_4$ M.wt 943.23. Found C, 76.27 %, H, 3.89 %, N, 5.77 %, S, 13.58 %. Calcd. C, 76.40 %, H, 4.06 %, N, 5.94 %, S, 13.60 %. UV–Vis (CH_2Cl_2), λ_{max} (nm): 439 nm (Soret band) , 526 nm ,570 nm , 600 nm , 662 nm (Q bands)

5,10,15,20-Tetra(5-(2-naphthyl)thien-2yl)porphyrin (3c, M = H). It was obtained as dark purple crystals 32 % yield, mp > 350 ^oC . IR (cm^{-1}): 3440 (NH). ^{1}H-NMR ($CDCl_3$): δ = 9.25 (s,8H, β-H),8.33-6.91 (m, Ar-H of the naphthyl and thienyl-H), -2.47(s, 2H, inner porphyrin NH). ^{3}C-NMR ($CDCl_3$): δ = 142.2, 133.77, 132.6, 131.6, 128.8, 128.5, 127.8, 127.6, 126.7, 126.3, 124.2, 123.3. Ms (EI): *m/z* for $C_{76}H_{46}N_4S_4$ M.wt 1143.47. Found C, 79.67 %, H, 3.93 %, N, 4.85 %, S, 11.01 %. Calcd C,79.83 %, H,4.05 %, N,4.90 %, S,11.22 %. UV–Vis (CH_2Cl_2), λ_{max} (nm): 440 nm (soret band) 529 nm ,570 nm, 667 nm (Q bands)

5,10,15,20-Tetrakiss (5-(1-naphthyl)thien-2yl) porphyrin (3d, M = H). It was obtained as dark purple crystals 37 % yield, mp > 350 ^oC . IR (cm^{-1}): 3424.565 (NH). ^{1}H-NMR ($CDCl_3$): δ = 9.36 (s, 8H, β-H), 8.76-7.26 (m, Ar-H of the naphthyl and thienyl-H), -2.45(s, 2H, inner porphyrin NH). ^{13}C-NMR ($CDCl_3$): δ =144.8, 143, 141.2, 134.3, 133.8, 132.8 , 131.9, 131.7, 128.5, 126.8,125.9,125.2,112.6. Ms (EI) *m/z* for $C_{76}H_{46}N_4S_4$ M.wt 1143.47 . Found: C, 79.62 %, H, 3.85 %, N, 5.02 %, S, 10.98 % . Calcd: C,79.83 %,H,4.05 %,N,4.90 % , S,11.22 %. UV–Vis (CH_2Cl_2), λ_{max} (nm): 435 nm (soret bands) , 484 nm, 526 nm , 573 nm , 663 nm (Q bands)

5,10,15,20-Tetrakis (5-(6-methoxy-2-naphthylthien-2yl) porphyrin (3e, M = H). It was obtained as dark purple crystals 28 % yield, mp > 350 ^oC. IR (cm^{-1}) : 3420(NH), ^{1}H-NMR ($CDCl_3$): δ = 9.15-9.04(m, 8H, β-H), 8.07-7.49 (m, Ar-H, for the naphthyl and thienyl-H),), 3.95 (s,12H,OCH_3), -2.3 (m,2H,inner porphyrin NH). ^{13}C-NMR($CDCl_3$): δ =157.9, 143.6, 136.3, 134.1, 133.6, 129.7, 129.5, 129.4, 127.6,127.3, 126.1, 125.95, 124.7, 11.1, 105.6, 55.3. Ms (EI): *m/z* for $C_{80}H_{54}N_4O_4S_4$ M.wt 1263.57. Found C, 75.93 % H, 4.20 %, N, 4.31 %, O, 4.89 %, S, 10.01 % . Calcd C, 76.04 %; H, 4.31 %; N, 4.43 %; O, 5.06 %; S, 10.15 %. UV–Vis (CH_2Cl_2), λ_{max} (nm): 440 nm (soret bands) , 552 nm, 600 nm (Q bands).

Synthesis of porphyrin copper complexes (3a-e, M =Cu). A mixture of porphyrin (**3a**, M = H) (100 mg, 0.09 mmol) and metal acetate (0.3 mmol) was dissolved in DMF (5 ml). The reaction mixture was heated-up and kept at 100 ^{o}C under argon atmosphere for 3 hours, left to cool then poured into cooled water. The solid product was collected by filtration, washed by water several times, air dried, purified by column chromatography ($CHCl_3$/MeOH 99:1 v/v) and crystallization from $CHCl_3$/MeOH.

5,10,15,20-Tetrakiss (5-(4-methylphenyl)thien-2-yl) porphyrin copper complex (3a, M = Cu). It was obtained as dark violet-green crystals, 65 % yield. ^{1}H-NMR ($CDCl_3$): δ =8.99 (s, 8H, β-H), 7.85-7.12 (m, Ar-H, for phenyl and thienyl-H), 2.37 (s, C$\underline{H}_3$). ^{13}C-NMR ($CDCl_3$): δ = 154.9, 147.0, 142.9, 139.3, 137.5, 131.6, 130.1, 129.7, 129.5, 127.1, 126.1, 125.7, 124.9, 123.3, 21.23.

5,10,15,20-Tetra(5-phenylthien-2-yl) porphyrin copper complex (3b, M = Cu). It was obtained as dark violet-green crystals, 70 % yield. ^{1}H-NMR ($CDCl_3$): δ = 8.41(s, 8H, β-H), 7.77-7.30 (m, Ar-H).^{13}C-NMR ($CDCl_3$): δ = 154.2, 144.1, 142.3, 139.7, 135.3, 130.5, 134.3, 129.7, 129.1, 127.7, 125.6. Ms (EI): *m/z* for $C_{60}H_{36}CuN_4S_4$ (M.wt 1004.76).UV–Vis (CH_2Cl_2), λ_{max} (nm): 433 nm (soret bands), 504 nm, 550 nm (Q bands).

5,10,15,20-Tetra(5-(2-naphthyl)thien-2-yl) porphyrin copper(3c, M = Cu)). It was obtained as dark violet crystals 60 % yield. ^{1}H-NMR ($CDCl_3$): δ =8.25-8.17(s, 8H, β-H), 7.94-7.77(m, Ar-H). ^{13}C-NMR ($CDCl_3$): δ = 147.11,145.6, 143.6, 140.6, 138.4, 133.7, 132.7,131.5,128.5, 127.6, 126.6, 124.1. Ms (EI): *m/z* for $C_{76}H_{44}CuN_4S_4$ (M.wt 1205.00)..UV–Vis (CH_2Cl_2), λ_{max} (nm): 439 nm (soret band) , 548 nm (Q bands) .

5,10,15,20-Tetra (5-(1-naphthyl)thien-2-yl) porphyrin copper(3d, M = Cu)). It was obtained as dark violet crystals 60 % yield. ^{1}H-NMR ($CDCl_3$): δ = 8.57(s, 8H, β-H), 7.95-7.40 (m,Ar-H). ^{13}C-NMR ($CDCl_3$): δ = 143, 137.4, 134.5, 133.5, 132.8, 132.2, 131.7, 128.2, 127.8, 126.6, 126.1, 125.9, 125.3. Ms (EI): *m/z* $C_{76}H_{44}CuN_4S_4$ (M.wt 1205.00). UV–Vis (CH_2Cl_2), λ_{max} (nm): 431 nm (soret bands) , 550 nm (Q bands).

5,10,15,20-Tetra (5-(6-methoxy-2-naphthyl)thien-2-yl) porphyrin copper(3e, M = Cu)). It was obtained as dark violet crystals 62 % yield. ^{1}H-NMR ($CDCl_3$): δ =8.07(s, 8H, β-H), 7.76-7.71(m,Ar-H), 3.93(s,OC$\underline{H}_3$). ^{13}C-NMR ($CDCl_3$): δ = 182.7, 158.6, 154.7, 157.8, 154.7, 142, 137.6, 133.6, 129.9, 125.5, 124.4 123.7, 119.1, 105.6, 55.3. Ms (EI): *m/z* for $C_{80}H_{52}CuN_4O_4S_4$ (M.Wt 1325.10). UV–Vis (CH_2Cl_2), λ_{max} (nm): 441 nm (soret bands) , 548 nm (Q bands).

Synthesis of 5,10,15,20- tetra(5-bromothiophen-2-yl) porphyrin and its copper complex (4, M = H & Cu).

It was prepared using a modified literature procedure.[21] The free base porphyrin (**4,** M = H) was obtained as dark violet crystals in 55 % yield (1.77 g), m.p. over 250 ^{o}C. FT-IR (cm^{-1}): 3415 (NH). ^{1}H-NMR ($CDCl_3$): δ in ppm : 9.23 (8 β–H), 7.42-6.56 (m, Ar-H the thiophene rings), -2.52 (2H,inner NH of the porphyrin ring). Ms**;** *m/z* for $C_{36}H_{18}Br_4N_4S_4$ M.wt 954 (M^+), 955 (M^{+1}) ,638 (100 %). UV–Vis (CH_2Cl_2**)**, λ_{max} (nm): 432 nm (soret bands), 523 nm, 563 nm, 596 nm, 655 nm (Q bands)

5,10,15,20-Tetra(5-bromothien-2-yl)porphyrinato copper (II) (4, M =Cu). It was obtained as dark violet crystals, over 90 % yield. ^{1}H-NMR ($CDCl_3$): δ = 8.17-7.26 ppm (m, Ar-H). Ms (EI): *m/z* for $C_{36}H_{16}Br_4CuN_4S_4$, 1015 (M^+), 1016 (M+1), 1017 (M+2), 1018 (M+3). UV–Vis ($CHCl_3$), λ_{max} (nm): 430 nm (soret bands), 548 nm (Q bands).

Synthesis of the *meso*-tetraarylthien-2-ylporphyrins (3a, M = H) from of the *meso*-tetra(5-bromothien-2-yl) porphyrin (4, M = H) using SMC reaction (Route II). A mixture of aryl boronic acid (3.2 mmol), sodium carbonate (0.31g, 2.9 mmol), acetonitrile-dichloro palladium (II) (0.02g, 0.077mmol) and 5,10,15,20-tetrakis(5-bromothiophen-2-yl) porphyrin (**4,** M = H). (2.61 mmol), were suspended in toluene/water (10mL (9/1). The reaction mixture was refluxed for 10-12 hours. The resulting black solution was poured into cooled water and (4 × 15 mL), extracted with DCM. The organic layer was dried over anhydrous Na_2SO_4, filtered and evaporated under vacuum. The solid product was collected then column chromatographed ($CHCl_3$/MeOH 99:1 v/v) and crystallized from $CHCl_3$/MeOH. Traces of *meso*-tetrakiss (4-methylphenylthien-2-yllporphyrin (**3a,** M

=H) was isolated and purified (less than 1 % after purification), and the spectroscopic data were compared with the obtained from the method in scheme 3.

Synthesis of the *meso*-tetraarylthienyllporphyrins (3a-e, M = Cu) from of the *meso*-tetra (5-bromothien-2-yl) porphyrin (4, M = Cu) using SMC reaction (Route III). A mixture of aryl boronic acid (3.2 mmol), sodium carbonate (0.31g, 2.9 mmol), acetonitrile-dichloro palladium (II) (0.02g, 0.077mmol) and 5,10,15,20- tetra(5-bromothiophen-2-yl) porphyrin copper complex (**4,** M = Cu) (2.61 mmol), were suspended in toluene/water (10 mL (9/1). The reaction mixture was refluxed for 10-12 hours. The resulting black solution was poured into cooled water and (4 × 15 mL), extracted with DCM. The organic layer was dried over anhydrous Na_2SO_4, filtered and evaporated under vacuum. The solid product was collected then column chromatographed ($CHCl_3$/MeOH 99:1 v/v) and crystallized from $CHCl_3$/MeOH. The *meso*-tetraarylthienyllporphyrin copper complexes (**3a-e,** M = Cu) were isolated 40-50 5 % yield.

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Supplementary Material

All the spectroscopic data for all compounds can be found using the link "Supplementary Material" on the Publisher's web site.

References

1. Rothemund, P. *J. Am. Chem. Soc.* **1936**, 58, 625–627. https://doi.org/10.1021/ja01295a027.
2. Adler, A.D, Longo,F. R., Finarelli,J. D., Goldmacher,J., Assour, J., Korsakoff, L., *J. Org. Chem.* **1967**, *32*, 476. https://doi.org/10.1021/jo01288a053.
3. Kadish, K. M., Smith, K. M., Guilard, R., Eds.; Academic Press: Boston, 2000; Vol. 1, pp 45–118.
4. Boyle, N.M., Rochford, J., Pryce, M. T., *Coordination Chem. Rev.* **2010**, *254*, 77–102. https://doi.org/10.1016/j.ccr.2009.09.001.
5. Furuta, H., Maeda, H., Furuta, T., Osuka, A. *Org. Lett.* **2000**, 2 187–189. https://doi.org/10.1021/ol9912783.
6. Gupta, I., Ravikanth, M., *Tetrahedron* **2003**, 59, 6131–6139. https://doi.org/10.1 016/S0040-4020(03)00950-5.
7. Kurotobi,K., Osuka,A., *Org. Lett.* **2005**, 7, 1055–1058. https://doi.org/10.1021/ol047336o.
8. Werner, A., Sanchez-Migallon, A. Fruchier, A., Elguero, J., *Tetrahedron* **1995**, 51, 4779. https://doi.org/10.1016/0040-4020(95)00159-6.
9. Guo, C.-C., Ren, T, G., Wang, J., Li, C.-Y., Song, J.-X. *J. Porphyrins and Phthalocyanines* **2005**, 09, 430–435. https://doi.org/10.1142/S1088424605000538.
10. Tjahjono, D.H., Akutsu, T., Yoshioka, N., Inoue, N. *Biochimica et Biophysica Acta (BBA) - General Subjects* **1999**, 1472, 333–343. https://doi.org/10.1016/S0304-4165(99)00139-7.

11. Kobuke, Y., Miyaji, H., *J. Am. Chem. Soc.* **1994**, 116, 4111–4112. https://doi.org/10.1021/ja00088a070.
12. Milgrom, L.R., Dempsey, P.J.F, Yahioglu, G. *Tetrahedron* **1996**, 52, 9877–9890. https://doi.org/10.1016/0040-4020(96)00520-0.
13. Treibs, A., Häberle, N., *Liebigs Ann.* **1968**, 718, 183–207. 10.1002/jlac.19687180118.
14. Collis, G.E., Campbell, W.M., Officer, D.L., Burrell, A.K. , *Org*. Biomol. *Chem.* **2005**, 3, 2075. https://doi.org/10.1039/b502517f.
15. Vollmer, M.S., Würthner,, F. Effenberger, F., Emele, P., Meyer, D.U., Stümpfig, T., Port, , H., Wolf, H.C. *Chem. Eur. J.* **1998**, 4 260–269. https://doi.org/10.1002/(SICI)1521-3765(19980210)4:2<260::AID-CHEM260>3.0.CO;2-9.
16. Odobel, F., Suresh,S., Blart, E., Nicolas, .Y,. Quintard, J.-P., Janvier, P., Le Questel, J.-Y.,. Illien, B., Rondeau, D., Richomme, P., Häupl, T. , Wallin, S., Hammarström, L. *Chem. Eur. J.* **2002**, 8 3027. https://doi.org/10.1002/1521-3765(20020703)8:13<3027::AID-CHEM3027>3.0.CO;2-Z.
17. Maruyama, H. Segawa, H., Sotoda, S., Sato, T., Kosai, N., Sagisaka, S., Shimidzu, T., Tanaka, . *Synthetic Metals* **1998,** 96, 141–149. https://doi.org/10.1016/S0379-6779(98)00081-2.
18. Shimidzu, T., Segawa, H., Wu, F., Nakayama, N., *J. Photochem. Photobiol. A: Chemistry* 1**995**, 92, 121–127. https://doi.org/10.1016/1010-6030(95)04168-2.
19. Friedlein, R., von Kieseritzky,F., Braun, S., Linde, C., Osikowicz, W., Hellberg, J., , Salaneck, W.R. *Chem. Commun*. **2005**, 1974. https://doi.org/10.1039/b418866g.
20. You, Y., Gibson, S.L., Hilf, R., Ohulchanskyy, T.Y., Detty, M.R. *Bioorg. Med. Chem. Lett.* **2005**, 13, 2235–2251. https://doi.org/10.1016/j.bmc.2004.12.048.
21. Elghamry, I., Ibrahim, S.S., Abdelsalam, M., Al-Faiyz, Y., Al-Qadri, M. *Int. J. Electrochem. Sci.* **2018**, 10233–10246. https://doi.org/10.20964/2018.11.70.
22. Prasath, R., Bhavana, P. *J. Heterocycl. Chem.* **2012** , 49, 1044–1049. https://doi.org/10.1002/jhet.923.
23. Betoni Momo, P., Pavani, C., Baptista, M.S., Brocksom, T.J., Thiago de Oliveira, K. *Eur. J. Org. Chem.* **2014**, 4536–45 47. https://doi.org/10.1002/ejoc.201402227.
24. Ben Halima, T., Zhang, W., Yalaoui, I., Hong, X., . Yang, Y.-F., Houk, K.N., Newman, S.G., *J. Am. Chem. Soc.* **2017**, 139, 1311–1318. https://doi.org/10.1021/**acs**.orglett.9b03434.
25. Pijeat,J., Dappe, Y.J., Thuéry, P., Campidelli, S., *Org. Biomol. Chem.* **2018**, 16, 8106–8114. https://doi.org/10.1039/C8OB02150C.
26. Maluenda, I., Navarro, O. *Molecules* **2015,** 20, 7528 –7557. https://doi.org/10.3390/molecules20057528.
27. Ward, A.C.R. *Catal. Lett.* **2016**, 146, 820 –840. https://doi.org/10.1007/s10562-016-1707-8.
28. Len, C., Bruniaux, S., Delbecq, F., Parmar, V. *Catalysts* **2017**, 7, 146. https://doi.org/10.3390/catal7050146.

29. Ganesamoorthy,S., Shanmugasundaram, K., Karvembu, R., *J. Mol. Catal. A-Chem.* **2013**, 371, 118–124. https://doi.org/10.1016/j.molcata.2013.01.029.
30. Yano, J.K., Denton, T.T., Cerny, M.A., Zhang, X., Johnson, E.F. Cashman, J.R. *J. Med. Chem.* **2006**, 49, 6987–7001. https://doi.org/10.1021/jm060519r.
31. Fadda, A.A., E. El-Mekawy, ., El-Shafei, A.I., Freeman, H. *Archiv Der Pharmazie* **2013**, 346, 53 –61. https://**doi**.org/10.1002/ardp.201200313.
32. Sooambar, C., Troiani, V., Bruno, C., Marcaccio, ., Paolucci, F., Listorti, A., Belbakra, A., Armaroli, N., Magistrato, A., De Zorzi, S. Geremia, R., Bonifazi, D. *Org. Biomol. Chem.* **2009,** 7, 2402. https://doi.org/10.1039/B820210A.
33. Davis, N.K.S., Thompson, A.L., Anderson, H.L. *Org. Lett.* **2010,** 12, 2124–2127. https://doi.org/10.1021/acs.inorgchem.9b03329.
34. Kadish, R. Smith, K. M., Guiard, K. M. in the *Handbook of Porphyrin Science: With Applications to Chemistry, Physics, Materials Science, Engineering, Biology and Medicine* World Scientific Publishing Pte. Ltd 26 **2014.**
35. Brückner, C., Foss, P.C.D., Sullivan, J.O., Pelto, .R., Zeller, M., Birge, R.R., Crundwell, G., *Phys. Chem. Chem. Phys.* **2006**, 8, 2402–2412. https://doi.org/10.1039/B600010J.
36. Thomas, D.W., Martell, A.E. *J. Am. Chem. Soc.* **1956**, 78, 1338–1343. https://doi.org/10.1021/ja01588a020.
37. Ono, N. Miyagawa, H., Ueta, T., Ogawa, T., Tani, H. J. *Chem. Soc. Perkin Trans. I.* **1998**, 1595–1602. https://doi.org/10.1039/A801185K.
38. Gupta, I., Ravikanth, M. *J. Photochem. Photobiol. A: Chemistry* **2006,** 177, 156–163. https://doi.org/10.1016/j.jphotochem.2005.05.020.
39. Uchoa, A.F., de Oliveira, K.T., Baptista, M.S, Bortoluzzi, A.J., Iamamoto, Y., Serra, O.A. *J. Org. Chem.* **2011**, 76 8824–8832. https://doi.org/10.1021/jo201568n.
40. de Souza, J.M., de Assis, F.F. Carvalho, C.M.B., Cavaleiro, J.A.S., Brocksom, T.J., de Oliveira, K.T. *Tetrahedron Lett.* **2014**, 55, 1491–1495. https://doi.org/10.1016/j.tetlet.2014.01.049.
41. Goswami, L. Neog, K. , Sharma, K. Gogoi, P. Organic and Biomolecular Chemistry, **2017**, 15,31, 6470 – 6473. https://doi.org/10.1039/C7OB01641G
42. Bolliger, J. L., Frech, C. M. Advanced Synthesis and Catalysis, **2010**, 352, # 6, 1075 – 1080. https://doi.org/10.1002/adsc.200900848.
43 Borg, R. E., Hatamimoslehabadi, M., Bellinger, S. La, Jeffrey; M. F., Yelleswarapu, C., Rochford, J. Photochemistry and Photobiology, **2019**, 95, # 1, 280 – 292. https://doi.org/10.1111/php.12980.