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One-pot sequential functionalizations of *meso*-tetrathienylporphyrins via Heck–Mizoroki cross-coupling reactions

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ABSTRACT

Synthesis and sequential functionalizations of a new *meso*-tetraiodo(thien-2-yl)porphyrin and its Ni(II) derivative are described. The reactions for the preparation of these new porphyrins were optimized. Subsequently, four successive one-pot Heck–Mizoroki cross-coupling reactions were studied using two acrylates and varied reaction conditions. We describe an optimized protocol for the preparation of highly conjugated thienylporphyrins with the potential to be used as dyes in solar cell devices as demonstrated in our preliminary studies.

Introduction

Highly conjugated porphyrins are considered target molecules with growing interest in materials science.[1] These compounds have very stable structures with a highly conjugated π electronic system,[1] thus presenting applications in photovoltaic cells,[2] catalysis,[3] optical sensors,[4] electronic devices,[5] supramolecular systems,[6] and medicine.[7]

In this sense, thienyl-appended porphyrin derivatives are a relatively unexplored class of aryl-substituted porphyrins, which are under growing investigation due to their important photophysical, photochemical, and chemical properties.[8] Recent publications on thienyl-appended porphyrins have presented a number of applications in eletrocatalysis,[9] electron-transfer studies,[10] biosensors,[11] self-assemblage,[12] and photovoltaic cells,[13] with significant results in this last application.[14]

In addition to the unusual electrochemical properties, thienylporphyrins have been explored in terms of chemical reactivity, and chemo/regio-selective reactions have been found. Bhavana and co-workers[15] reported some electrophilic substitutions in thienyl-porphyrins, and also a number of electrochemical and structural properties of the products. Our group has also reported very selective nitrations followed by cycloaddition reactions, showing that electron-withdrawing groups improve the ability of these thienyl-porphyrins to produce singlet oxygen as well as to avoid photobleaching,[16] which are essential properties for use as photosensitizers in PDT studies.

Thienyl-appended porphyrins substituted with halogens, can be versatile intermediates due to the possibility of performing cross-coupling reactions. These reactions are important tools in synthetic organic chemistry, since they result in new C–C bonds[17] and can yield highly conjugated porphyrins.[18] The synthesis of new functionalized porphyrins, such as dibenzoporphyrins, through the Heck–Mizoroki cross-coupling reactions, has been reported.[18] Nevertheless, single and sequential functionalizations of thienyl-porphyrins through the Heck–Mizoroki cross-coupling reactions have not yet been described in the literature. Herein, we describe the syntheses of the *meso*-tetraiodo(thien-2-yl)porphyrin (**3**) and its Ni(II) derivative (**4**) (Scheme 1). Also, a study on the use of these iodo-thienyl-porphyrins in Heck–Mizoroki cross coupling reactions with acrylates, in different conditions, was performed to obtain new highly conjugated tetrathienylporphyrins; a preliminary study using one of the synthesized derivatives as a dye in solar cell devices is also described.

Results and discussions

In order to obtain the *meso*-tetraiodo(thien-2-yl)porphyrin (**3**) and its Ni(II) derivative **4**, it was first necessary to prepare 5-iodo-2-thiophenecarboxaldehyde (**2**) (Scheme 1). Compound **2** was obtained in 80% yield by the iodination of 2-thiophenecarboxaldehyde (**1**) using a mixture of $NaIO_4$ and I_2, in methanol/H_2SO_4 and then recrystallized from cyclohexane.[19]

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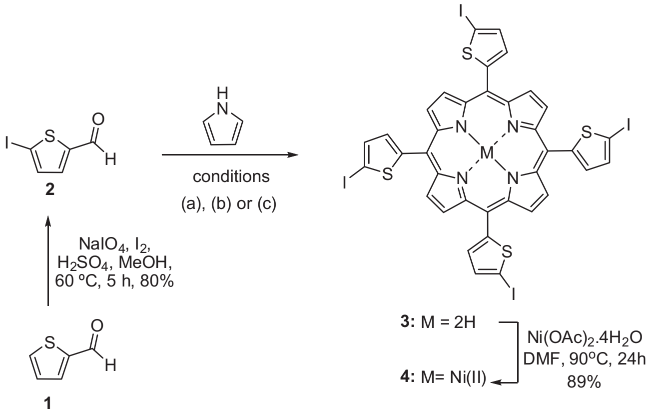


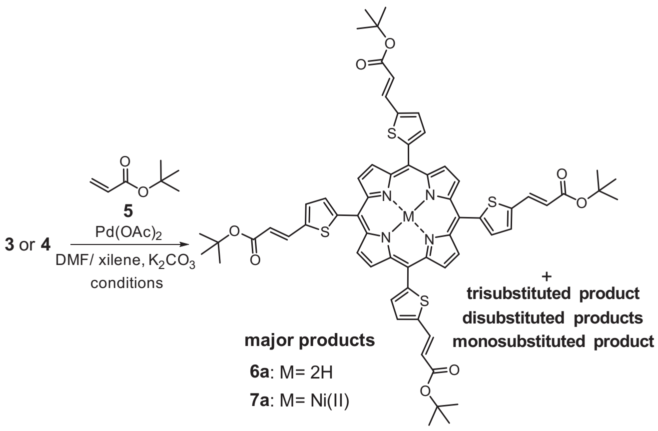
Scheme 1. Synthesis of the *meso*-tetraiodo(thien-2-yl)porphyrin (**3**) and its Ni(II) derivative **4**. Reagents and conditions: (a) propionic acid, reflux, 1 h, 12%. (b) BF_3·Et_2O, CH_2Cl_2, 24 h, rt, then *p*-chloranil, 6 h, 13%. (c) BF_3·OEt_2, CH_2Cl_2, 24 h, −10 °C, then *p*-chloranil, rt, 12 h, 38%.

Subsequently, compound **2** was reacted with pyrrole under reflux in propionic acid (open air system), thus obtaining the porphyrin **3** (12% yield) after three recrystallizations from a 3:1 $MeOH/CH_2Cl_2$ mixture.[20] We have also found more efficient conditions for the synthesis of **3** using Lindsey's methodology.[21] The reaction of aldehyde **2** and pyrrole in CH_2Cl_2 at room temperature, with 10% mol catalysis of BF_3·OEt_2 yielded the porphyrinogen intermediate, which after oxidation with *p*-chloranil and purifications furnished **3** in 13% yield. Even better, when the porphyrinogen generation was carried out at −10 °C using these last conditions, the porphyrin **3** was obtained in 38% yield after recrystallizations.

The Ni(II) derivative **4**, was also obtained in 89% yield by heating **3** in DMF (90 °C) with nickel(II) acetate tetrahydrate, after extraction with CH_2Cl_2/H_2O and crystallization from MeOH.[22]

The *meso*-tetraiodo(thien-2-yl)porphyrin (**3**) and its Ni(II) derivative **4** were then subjected to the Heck–Mizoroki cross-coupling reaction with *tert*-butyl acrylate (**5**) (Scheme 2). The acrylate **5** was chosen first since it contains the bulky *tert*-butyl group, which can prevent aggregation of porphyrin derivatives in solution, thus simplifying the complete NMR spectral assignment of the products.

First, the cross-coupling reactions (Scheme 2) were studied using 50 equiv of *tert*-butyl acrylate (**5**), PPh_3 (17% mol for each position) and $Pd(OAc)_2$ (7% mol for each position) at three different temperatures for 24 h (Table 1, entries 1–3).



Scheme 2. Sequential one-pot Heck–Mizoroki reactions of porphyrins **3** and **4** with *tert*-butyl acrylate (**5**).

These reactions were carried out in a glass pressure tube under an argon atmosphere and a 1:1 mixture of degassed xylene/DMF as solvent. At 150 °C (entry 1, Table 1) we observed mainly degradation of the starting material/products, but the tetrasubstituted derivative **6a** was obtained in 10% yield after purification using preparative TLC. At 130 °C compound **6a** was obtained in 26% and a mixture of tri-substituted products **6b** + **6c** (Fig. 1) was isolated in 3% yield (entry 2, Table 1).

The product **6c**, where the iodine atom was replaced by the hydride group, was probably obtained from the hydrodehalogenation reaction as observed in similar systems by Pyo and co-workers.[23] These authors have found that at high temperatures formaldehyde can be a hydride source with Pd(II) catalysis, and in our case DMF decomposition can generate formaldehyde in situ.

The ligand XPhos (18% mol for each position) was also tested (entries 4–5, Table 1) to compare the efficiency of different phosphine ligands. At 130 °C compound **6a** was obtained in 35% yield and the mixture of **6b** + **6c** in 8% yield. At 110 °C only the *mono* **6d** and *di*-substituted derivatives **6e** + **6f** mixture (Fig. 1) were obtained in 28% and 5% yields, respectively.

The reaction between the Ni(II) derivative **4** and *tert*-butyl acrylate (**5**) was studied in four different conditions. Using PPh_3 with the same previous conditions, the *tetra*-substituted compound **7a** was obtained at 130 °C in 29% yield, after purification by preparative TLC (entry 6, Table 1). Also, the *tri*-substituted compound **7b** (Fig. 1) was obtained in 5% yield.

At 110 °C, compounds **7a** and **7b** were isolated in 20% and 14% yields, respectively. The use of XPhos in the reactions of **4** and **5** gave the *tetra*-substituted derivative **7a** in better yields. At 130 °C compounds **7a** and **7b** were obtained in 35% and 6% yields, respectively (entry 8, Table 1) and at 110 °C in 41% and 11% yields, respectively (entry 9, Table 1). In general, we have found that the reaction between porphyrin **4** and *tert*-butyl acrylate (**5**) showed good performance to produce the *tetra*-substituted derivatives when it was conducted at both 110 °C and 130 °C.

Also, the use of Xphos provided better yields when compared to PPh_3. It is important to mention that in all the studied conditions (Table 1) the starting materials **3** or **4** were completely consumed after 24 h, or recovered only as traces during the purifications.

We have also studied the Heck–Mizoroki cross-coupling reaction of porphyrins **3** and **4** and methyl acrylate (**8**), aiming at obtaining substituted thienylporphyrins with methyl ester groups which are easily hydrolyzable in basic conditions (Scheme 3), thus allowing further applications of the corresponding carboxylic derivatives in solar cell devices.[24,25] The experiments were carried out at 110 °C and 130 °C in the presence of PPh_3 or XPhos and $Pd(OAc)_2$, similarly to the previous studies. The results are provided in Table 2. In comparison with *tert*-butyl acrylate (**5**) we established the reaction time

Table 1
Cross-couplings between porphyrins **3**, **4** and *tert*-butyl acrylate (**5**)

Entry	Porphyrin	Phosphine	*T* (°C)	Yield
1	**3**[a]	PPh_3	150	**6a** (10%)
2	**3**[b]	PPh_3	130	**6a** (26%)/**6b + 6c** (3%)
3	**3**[b]	PPh_3	110	**6a** (20%)/**6b + 6c** (9%)
4	**3**[b]	XPhos	130	**6a** (35%)/**6b + 6c** (8%)
5	**3**[b]	XPhos	110	**6d** (28%)/**6e** + **6f** (5%)
6	**4**[b]	PPh_3	130	**7a** (29%)/**7b** (5%)
7	**4**[b]	PPh_3	110	**7a** (20%)/**7b** (14%)
8	**4**[b]	XPhos	130	**7a** (35%)/**7b** (6%)
9	**4**[b]	XPhos	110	**7a** (41%)/**7b** (11%)

[a] Experiment carried out with 10 mg of **3**.
[b] Experiments carried out with 30 mg of **3** and **4**.

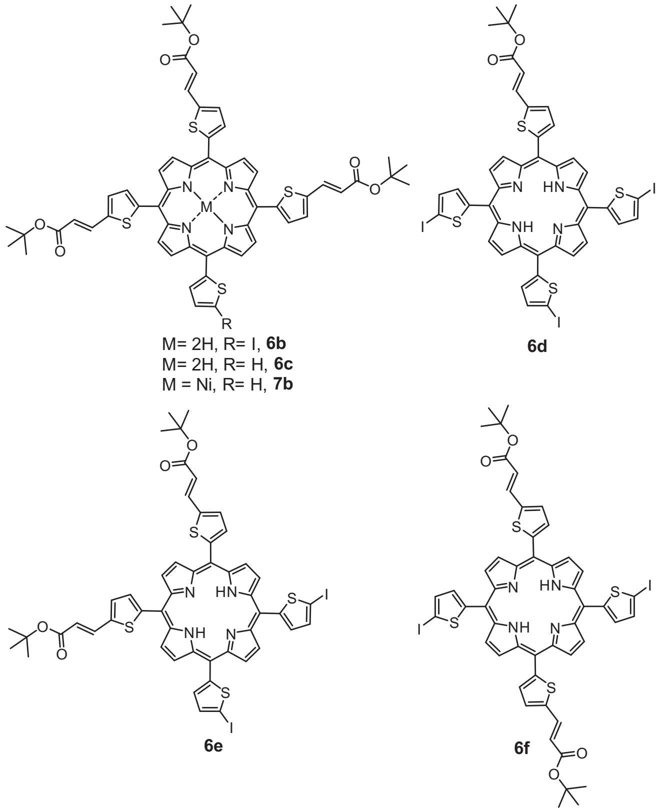


Figure 1. *Mono*, *di*, and *tri*-substituted products derived from the reaction of porphyrins **3** and **4** with *tert*-butyl acrylate (**5**) in different reaction conditions.

Table 2
Cross-Couplings between porphyrins **3**, **4** and methyl acrylate (**8**)

Entry	Porphyrin	Phosphine	*T* (°C)	Yield
1	**3**	PPh_3	130	**9a** (16%)/**9b** (7%)
2	**3**	PPh_3	110	**9a** (39%)/**9b** (14%)
3	**3**	XPhos	130	**9a** (41%)/**9b** (11 %)
4	**3**	XPhos	110	**9a** (47%)/**9b** (16%)
5	**4**	PPh_3	130	**10a** (24%)/**10b** (8%)
6	**4**	PPh_3	110	**10a** (36%)/**10b** (11%)
7	**4**	XPhos	130	**10a** (35%)/**10b** (8%)
8	**4**	XPhos	110	**10a** (46%)/**10b** (10%)

All the experiments carried out starting from 30 mg of **3** and **4**.

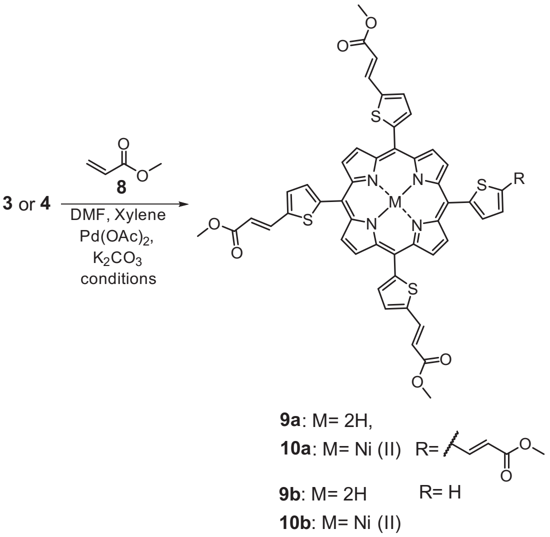
of 24 h and the use of an excess of methyl acrylate (**8**) (50 equiv) with respect to porphyrins **3** and **4**.

The reaction between porphyrin **3** and methyl acrylate (**8**) using PPh_3 at 130 °C yielded the *tetra*-substituted product **9a** in 16% as shown in Table 2, entry 1. Also, in this reaction compound **9b** was obtained in 7% yield, after purification with preparative TLC. When the reaction was carried out at 110 °C (entry 2, Table 2) we observed a significant increase in the overall yield with **9a** as major product (39% yield). Better results were obtained when the ligand PPh_3 was replaced by XPhos at 130 °C and 110 °C (entries 3–4, Table 2). At 130 °C compounds **9a** and **9b** were isolated in 41% and 11% yields, and at 110 °C 47% and 16% yields, respectively. Comparing the entries 1–4 (Table 2) we have found that not only the ligand XPhos can improve the efficiency of the reaction in sequential cross-couplings, but the lower temperature (110 °C) also gave better results. Subsequently, we also studied the cross-coupling reaction of the Ni(II) porphyrin **4** with **8** using similar reaction conditions (entries 5–8, Table 2). The reaction between **4** and **8** at 130 °C and in the presence of PPh_3 provided **10a** and **10b** in 24% and 8% yields, respectively (entry 5, Table 2). At 110 °C the same reaction gave **10a** and **10b** in 36% and 11% yields, respectively (entry 6, Table 2), thus allowing a good improvement in overall yields by using a lower temperature. The use of XPhos also improved the efficiencies of the sequential cross-couplings yielding **10a** and **10b** in 35% and 8% yields at 130 °C and 46% and 10% at 110 °C, respectively (entries 7–8, Table 2).

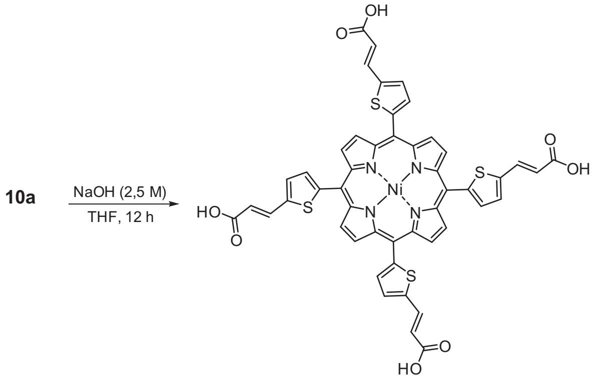
In general, methyl acrylate (**8**), the Ni(II) derivative **4**, the lower temperature (110 °C) and the ligand XPhos gave the best results in these sequential cross-coupling reactions. It is important to mention that non-significant red shifts were obtained with these functionalizations (no more 6 nm, see the UV–Vis analyses in Supp. Info.). However, all of these compounds present good potential for studies in solar cell devices and opened up perspectives for the synthesis of supramolecular thienyl-appended porphyrin systems.

It is known that carboxyl groups have a strong interaction with TiO_2 films when employed in photovoltaic experiments.[24,25] Thus hydrolysis of **10a** in the presence of a 2.5 M NaOH aqueous solution using THF as co-solvent furnished **11** with free carboxyl groups appended to the porphyrin core in 72% yield (Scheme 4).[26]

In order to evaluate the photovoltaic performance of **11**, a TiO_2 film of 10 μm was immersed in a solution of 15 mg L^{-1} of **11** in THF for 24 h, and then the film was removed from the solution and washed with acetone in order to remove the excess of the dye. After that, the device was closed and its performance was



Scheme 3. Heck–Mizoroki cross-coupling reactions of porphyrins **3** and **4** and methyl acrylate (**8**).



Scheme 4. Hydrolysis of the methyl ester **10a**.

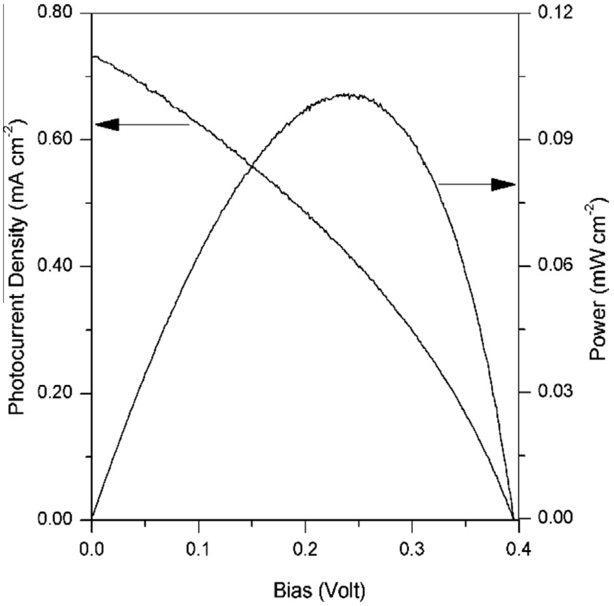


Figure 2. Photocurrent and power density versus bias for **11**.

Table 3
Dye sensitized solar cell parameters

Parameters	Value
V_{oc}	400 mV
I_{sc}	0.73 mA
FF	0.34
PCE	0.10%

evaluated. For more information about the device assembly, see the Supporting information.

To evaluate the performance of the dye **11** in a typical dye sensitized solar cell device, we evaluated three parameters: the open circuit voltage, the short circuit current, and the fill factor. All the parameters were extracted from the curves presented in Figure 2 and are shown in Table 3. We can observe that porphyrin **11** shows photovoltaic activity but its performance is not appreciable. However, we believe that after the optimization of some parameters like film thickness, dye concentration, and electrical contact improvements, the efficiency of these devices can be significantly increased.

The major parameters responsible for the low efficiency of the dye-synthesized solar cell assembly with the dye **11** were the low values of currents and the fill factor. As the device presents an appreciable V_{oc}, without electron flow, the cell was able to show an interesting photo-conversion. The low current observed can be associated to charge transference and recombination processes. Further studies will be conducted to identify the problems described above as well as other substituted derivatives will be designed in order to explore better the photoactivity of substituted thienyl-porphyrins in these systems.

Conclusions

The synthesis of the new *meso*-tetraiodothienylporphyrin (**3**) and its Ni(II) derivative **4** was successfully achieved from 5-iodo-2-thiophenecarboxaldehyde (**2**) and pyrrole. Porphyrin **3**, and its Ni(II) derivative **4**, were reacted in sequential one-pot Heck–Mizoroki cross-coupling reactions with two different acrylates, in different reaction conditions, thus furnishing new highly conjugated porphyrins in a very constructive way. Preliminary studies using **11** in solar cell devices were performed, and although we have found low efficiency in the tested systems, we believe that some improvements in the device assembly and dye-structures can significantly increase the photoactivity of these high substituted thienyl-porphyrins as suggested in the recent literature.[14]

Acknowledgments

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.tetlet.2016.05.106.

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