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Synthetic Communications

An International Journal for Rapid Communication of Synthetic Organic Chemistry

ISSN: (Print) (Online) Journal homepage: https://www.tandfonline.com/loi/lsyc20

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To cite this article: Sunaina Singh , Amit Aggarwal , Phillippe H. Mercier , N. V. S. Dinesh K. Bhupathiraju , Michael Landress & Keroles Hanna (2020): An alternate and efficient method for preparation of 2,6-diacetamido-4-formylpyridine for formation of porphyrin appended with hydrogen bonding motifs, Synthetic Communications, DOI: 10.1080/00397911.2020.1799012

To link to this article: https://doi.org/10.1080/00397911.2020.1799012

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https://doi.org/10.1080/00397911.2020.1799012

An alternate and efficient method for preparation of 2,6-diacetamido-4-formylpyridine for formation of porphyrin appended with hydrogen bonding motifs

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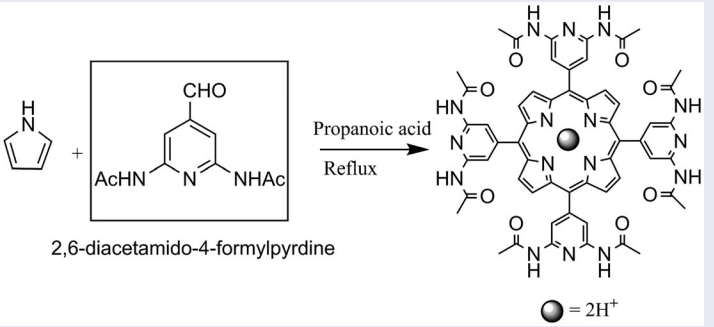
ABSTRACT

We report here an alternate redesigned five-step synthesis of 2,6-diacetamido-4-formylpyridine. The method described here is more convenient where this aldehyde is prepared in commercially viable quantities from simple and easy-to-use reagents and is a key compound required to prepare 5,10,15,20-Tetrakis(3,5-diacetamido-4-pyridyl)porphyrin (I). This porphyrin can be used as an excellent building block for the construction of supramolecular assemblies and is an interesting compound to study the design, principles, and photonic properties such as the extent of electron and energy transfer.

GRAPHICAL ABSTRACT



ARTICLE HISTORY
Received 3 May 2020

KEYWORDS
Pyridine; porphyrins; supramolecular

Introduction

Photofunctional materials can be fabricated by supramolecular chemistry where the well-defined molecular assemblies can be constructed either by specific (such as metal ion coordination and H-bonding) and/or nonspecific (such as van der Waal's and other electrostatic forces) intermolecular interactions. These two types of intermolecular interactions are responsible for the formation of their: (a) self-assembled structures that leads to the formation of discrete, highly ordered systems wherein there is only little tolerance

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of error and (b) self-organized structures that are non-discrete, non-directional and are more tolerant of errors.[1–4] Both of these self-processes are dynamic in nature and highly relies on the molecular conformation and functional groups attached to the component molecules.[4]

The ubiquitous chemical, photophysical and electron transfer properties of the porphyrins and metalloporphyrins makes them an excellent building blocks for the construction of their supramolecular assemblies. These properties can further be easily fine-tuned in several ways. For example, substitution with various electron donating/withdrawing groups or bulky groups at the macrocycle periphery and/or metalation of macrocycle distort the otherwise planar structure of the macrocycle for material applications. The different redox potential of core metal ion may also allow these systems to be used in electron transport and energy transduction and can have applications in optoelectronics.[1,3,5–8]

The rigid structure of porphyrins can also be distorted by appending hydrogen-bonding motifs at the *meso* positions, which can self-assemble into their supramolecular systems to enhance their optoelectronic properties. There are several reports on the synthesis and applications of porphyrinoids bearing various H-bonding motifs.[9–11] However, the substituents bearing N-donor atoms are of great interest as these groups provide sites for metal coordination, H-bonding, and also to improve the hydrophilicity of the porphyrin macrocycle.

The tessellation of 2-dimensional arrays mediated by complementary H-bonding groups on two different porphyrins results in a checkerboard pattern wherein donor chromophores and acceptor chromophores alternate. These types of systems promote electron transfer and are of particular interest because of their relevance to light harvesting arrays. These porphyrin arrays can be deposited on the glass surface where the domain size and defect density are strongly influenced by the surface energetics, solvent, and rate of solvent evaporation.[6,9] By adjusting the number of H-bonds and their relative orientation, supramolecular assemblies formed by porphyrins through hydrogen bonds can be tuned.[12–15] For these reasons, 5,10,15,20-Tetrakis(3,5-diacetamido-4-pyridyl)porphyrin (**I**) (Figure 1) is an interesting compound to study the design, principles, and photonic properties such as the extent of electron and energy transfer in supramolecular systems. However, the synthesis of the diacetamidopyridylporphyrin (**I**) is challenging because of the difficulty in preparing the aldehyde precursor, 2,6-diacetamido-4-formylpyridine (**6**) due to the significant electronic effects at the 4 position.[6,9] In the previously reported six step method to form **6,**[7] the first step involves the conversion of 4-methylpyridine to 2,6-diamino-4-methylpyridine using tetralin and sodamide. This compound was further treated with strong oxidant peracetic acid at elevated temperature to yield 2,6-diacetamido-4-methylpyridine-1-oxide. Refluxing of this oxide in acetic anhydride to yield 2-diacetamido-6-acetamido-4-acetoxymethylpyridine, that was further hydrolyzed using K_2CO_3 in methanol/water to afford 2,6-diacetamido-4-hydroxymethylpyridine. This compound was oxidized using PCC under ultrasound conditions. Using this procedure, we were not able to isolate 2,6-diamino-4-methylpyridine in significant amount despite using freshly dried tetralin, inert atmosphere and pure reagents thus resulting in very low overall yield of 2,6-diacetamido-4-formylpyridine. We found this strategy practically not efficient.

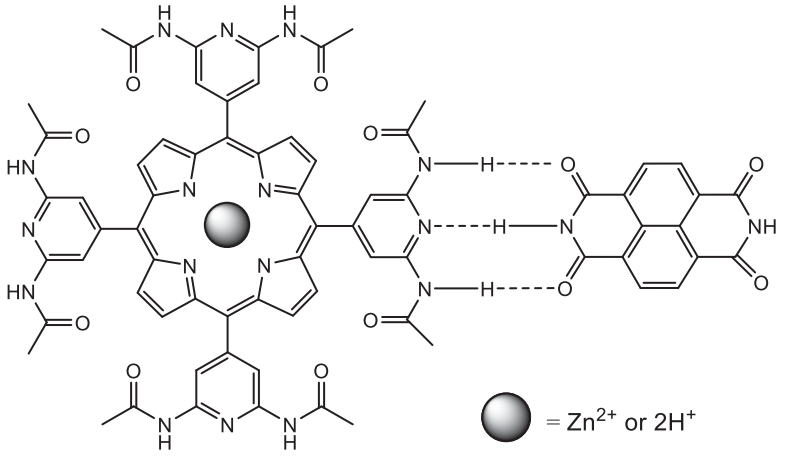
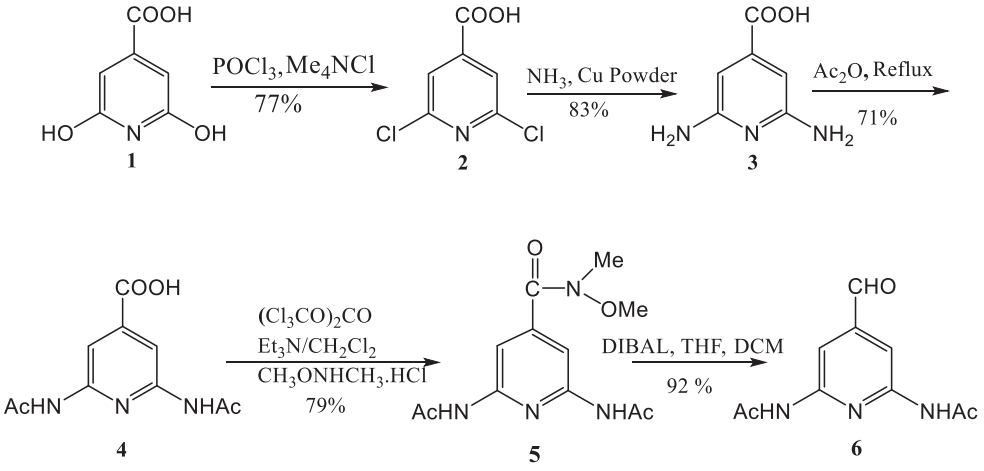


Figure 1. Structure of the rigid coplanar dyad, assembled by three-point hydrogen bonding which may mediate electron transfer processes, can be formed by mixing 5,10,15,20-Tetrakis(3,5-diacetamido-4-pyridyl)porphyrin (**I**)and napthalene diimide (NDI) in different aprotic solvents.

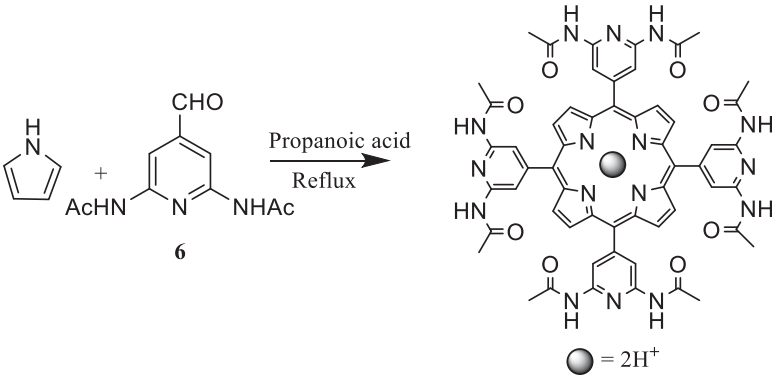


Scheme 1. Synthesis of 2,6-diacetamido-4-formylpyridine **6**.

So we embarked upon developing a simple method for the synthesis of precursor 2,6-diacetamido-4-formylpyridine (**6**) which can be produced in fewer steps, better yield, prevents the use of peracetic acid at high temperature and is more convenient that can avoid much of the problems associated with the earlier synthesis.

Results and discussion

The method reported herein (Scheme 1) involves conversion of commercially available citrazinic acid **1** to the 2,6-dichloroisonicotinic acid **2** in 77% yield by treatment with phosphorous oxychloride and tetramethylammonium chloride.[16,17] Compound **2** was reacted with ammonia in presence of copper catalyst, at high temperature and pressure (~180 °C, 20 bar). The copper powder was filtered out from the solution and the compound was precipitated from the filtrate by treatment with an acid to pH 5. The overall yield of the free



Scheme 2. Synthesis of porphyrin **I**.

acid, 2,6-diaminopyridine-4-carboxylic acid **3** was about 83%.[18] The compound **3** was then treated with acetic anhydride at refluxing conditions resulting in compound **4** which was filtered and washed with water several times, to yield 71% of 2,6-diacetamido-4-pyridinecarboxylic acid. Compound **4** was then treated with triphosgene to form an acid chloride, followed by addition of *N,O*-dimethylhydroxylamine to yield the desired Weinreb amide **5** in about 79% yield.[19] This is a versatile method for direct conversion of carboxylic acids to the corresponding Weinreb amides. The direct conversion relies on *in situ* activation of carboxylic acids with *N,O*-dimethylhydroxylamine.[20–22] Reduction of Weinreb amide **5** to aldehyde **6** was obtained in 92% yield by treatment with DIBAL-H (see ESI).[23] The overall yield of this aldehyde starting from compound **1** is 33% which is reasonable since the starting compounds are inexpensive and yield is higher than the previously reported method where the overall yield reported was 17%.[7]

The aldehyde **6** prepared here was not soluble in solvents ideal for Lindsey method[24–26] conditions, therefore, we only could use Adler method for the preparation of porphyrin **I**.[27] Pyrrole and 2,6-diacetamido-4-formylpyridine (**6**) were added in 1:1 ratio to boiling propionic acid and the reaction mixture was refluxed for 2 h (Scheme 2). After purification the free base porphyrin **I** was obtained in a yield of about 29%.

The porphyrin **I** synthesized and reported here can form a supramolecular assembly with naphthalene diimide (NDI) (Figure 1). In this system, the porphyrin can act as a donor and NDI as an acceptor. Having NDI motif directly attached at the meso position of a diacetamidoporphyrin provides a suitable through-bond pathway for electron transfer since it reduces the conformational flexibility of the assembly.[28] Naphthalene diimides are electron deficient species and possesses unique photophysical, electronic properties and enhanced solubility [29,30] and therefore can be used as an ideal candidates in the design of conducting materials.[31,32]

Experimental procedure

Materials and methods

General

^{1}H and ^{13}C NMR spectra were recorded in a Brüker Avance 500 MHz spectrometer. Electrospray ionization mass spectrometric analyses were performed at the CUNY Mass

Spectrometry Facility at Hunter College using an Agilent Technologies HP-1100 LC/MSD instrument. The electrospray ionization was run in methanol, with 0.1% formic acid. UV-visible spectra were recorded on a Varian Bio3 spectrophotometer. All reagents were obtained from commercial sources and used without further purification. Flash column chromatography was performed using silica gel-60, and the analytical TLC was carried out on precoated sheets with silica gel (0.2 mm thick), both from Sorbent Technologies.

Synthesis of 5,10,15,20-tetrakis(3, 5-diacetamido-4-pyridyl)porphyrin (I)

Compound **1** was purchased from Sigma Aldrich Co. Compounds **2** (2,6-dichloro-4-pyridinecarboxylic acid) and **3** (2,6-diamino-4-pyridinecarboxylic acid) were synthesized by previously described procedures.[16–18]

2,6-Diacetamido-4-pyridinecarboxylic acid (4)

10.0 mL of acetic anhydride was added to 2.0 g (13.0 mmol) of the diamine **3**. The resultant solution was stirred for 4 h at refluxing conditions and 2.2 g (71%) of a brown amorphous solid **4** was collected by filtration, washed with water, mp 195-197 °C. ^{1}H NMR (DMSO-d_6) δ13.53 (s, 1H), 10.28 (s, 2H), 8.21 (s, 2H), 2.13 (s, 6H); ^{13}C NMR (DMSO-d_6) δ170.03, 166.64, 151.57, 142.50, 108.77, 24.53; HRMS calcd. for $C_{10}H_{12}N_3O_4$ $(M+H)^+$ 238.0828, found, 238.0825.

2,6-Diacetamido-4-pyridine-N-methoxy-N-methyl amide (5)

To a solution of the carboxylic acid (**4**) 0.5 g (2 mmol) in CH_2Cl_2 (10 mL) at 0 °C were added triphosgene 0.3 g (1 mmol) and triethylamine 0.15 mL (10 mmol). The N,O-dimethylhydroxylamine hydrochloride 0.2 g (2 mmol) was added to the above solution and the ice bath was removed. The reaction mixture was then stirred at room temperature and monitored by TLC. After completion of reaction, the triethylamine was removed by filtration. The filtrate was collected and the solvent was removed under reduced pressure. The solid obtained was subjected to column chromatography on flash silica gel, eluted with dichloromethane/methanol 9:1, 0.44 g of product was obtained in 79% yield, mp >300 °C. ^{1}H NMR (MeOD-d_4) δ7.93 (s, 2H), 3.65 (s, 3H), 3.31 (s, 3H), 2.17 (s, 6H); ^{13}C NMR (MeOD-d_4) δ170.64, 150.39, 146.17, 106.91, 60.59, 56.07, 22.65; HRMS calcd. for $C_{12}H_{16}N_4O_4$ (M^+) 280.1176, found 280.1172.

2,6-Diacetamido-4-formylpyridine (6)

To a solution of compound **5** (0.5 g, 1.78 mmol) in CH_2Cl_2 (65 mL) was added DIBALH (1 M in THF, 14 ml, 14 mmol) at −78 °C, and the mixture was stirred at the same temperature for 2 h. After that, methanol was added to quench the DIBALH, the resulting mixture was partitioned between $CHCl_3$ and 1 N HCl and the organic layer was washed with brine solution, dried with Na_2SO_4 and solvent was removed under reduced pressure. The residue was purified by column chromatography (silica gel, ethylacetate/ethanol (9:1)) to give 360 mg, 92% of the solid, mp 222-224 °C. ^{1}H NMR (DMSO-d_6) δ10.33 (s, 2H), 9.96 (s,1H), 8.11 (s, 2H), 2.10 (s, 6H); ^{13}C NMR (DMSO-d_6) δ194.1, 170.7,

152.6, 146.5, 108.9, 25.3; HRMS calcd. for $C_{10}H_{12}N_3O_3$, $(M+H)^+$ 222.0879, found 222.0876.

5, 10, 15, 20-Tetrakis(3,5-diacetamido-4-pyridyl)porphyrin (I)

Pyrrole (69.5 µL, 1.0 mmol) and 2, 6-diacetamido-4-formylpyridine **6** (221 mg, 1.0 mmol) were added to boiling propionic acid (10.0 mL). The reaction mixture was refluxed for 2 h and then dried under vacuum. The resulting solid was purified by column chromatography on silica gel eluting with ethanol/ethylacetate (1:1) to yield 70 mg (29%) of porphyrin. ^{1}H NMR (DMSO-d_6) δ10.52 (s, 8H), 8.99 (s, 8H), 8.60 (s, 8H), 2.16 (s, 24H), −3.10 (s, 2H); ^{13}C NMR (DMSO-d_6) δ170.25, 152.67, 149.50, 130.12, 118.82, 115.80, 24.53. HRMS calcd. for $C_{56}H_{50}N_{16}O_8$ $(M+H)^+$1075.4076, found 1075.4043; UV/visible (DMSO) λ_{max}= 422.6, 514.8, 549.0, 587.2 and 642.3 nm

Conclusions

We have developed a new method for the synthesis of 2,6-diacetamido-4-formylpyridine, a key molecule to form porphyrin **I** bearing rigid H-bonding moieties at the meso positions. This protocol provides a practical alternative and improved synthetic route to the previously reported method[7] for the synthesis of this aldehyde and avoids much of the problems associated with the reported synthetic method. The meso-substituted pyridyl porphyrin can be used for constructing supramolecular structures with molecules bearing hydrogen bonding motifs through hetero-complementary assembly where porphyrin can act as a donor and other molecules can serve as an acceptor. These supramolecular materials are expected to have unique optical and physical properties e.g., redox and optoelectronic properties. Further studies of this H-bonded porphyrin- naphthalene diimide systems for their electron transfer properties are currently under investigation.

Acknowledgments

AA, SS, ML, and KH acknowledge CUNY Research Scholar Program (CRSP) for their support to this project.

Funding

AA (PSC-CUNY Award #62251-00 50) and SS (PSC-CUNY Award # 61356-00 49) would like to thank Professional Staff Congress (PSC) -CUNY Research Award Program to support this work.

Dedication

This work is dedicated to the memory of Dr. Charles Michael Drain for being a wonderful mentor, advisor and colleague through the years.

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