

Note

One-pot synthesis of nickel porphyrins with 2-pyridine-acetyl substituents: the unexpected Sonogashira cross-coupling products

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Abstract

Nickel porphyrins with 2-pyridine-acetyl substituents were synthesized in one step by the Sonogashira cross-coupling method. The structures of the products were determined by elemental analysis, ¹H NMR, UV–Vis, and X-ray spectroscopic techniques. It is suggested that cross-coupling bromonated nickel porphyrins with 2-pyridine-ethyne first yielded nickel porphyrins with 2-pyridine-ethynyl substituents, followed by in situ hydrolysis to the final products, nickel porphyrins with 2-pyridine-acetyl substituents. © 2004 Elsevier B.V. All rights reserved.

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1. Introduction

2-Acetylpyridine is an important functional group found in many drugs [1], and it also has been widely used as the starting material for supramolecular systems [2], anti-tumor complexes [3], catalysis [4] and helicity study [5]. On the other hand, porphyrins have been extensively studied for multichromophore arrays, catalysis, photodynamic therapy and sensors because of their versatile electronic properties [6]. Combining the two molecules into one substance should bring new aspects and broaden the interests to the research; yet, synthesis of porphyrins with 2-pyridine-acetyl groups has never been reported. This is probably due to the complexity of the synthetic processes. For example, Grignard reagents [7] or the Suzuki coupling method [8] can be employed to connect 2-pyridine-acetyl group to porphyrins; however, both methods require several steps of preparation and separation. We hereby report a con-

venient, one-step synthesis of nickel porphyrins with 2-pyridine-acetyl substituents. Fig. 1 depicts the structures of these porphyrins.

2. Results and discussion

The synthesis of 2-pyridine-acetyl nickel porphyrins involves reacting bromonated biphenylporphinato nickel(II) (NiBPPBr or NiBPPBr₂) with 2-pyridylethyne [9]

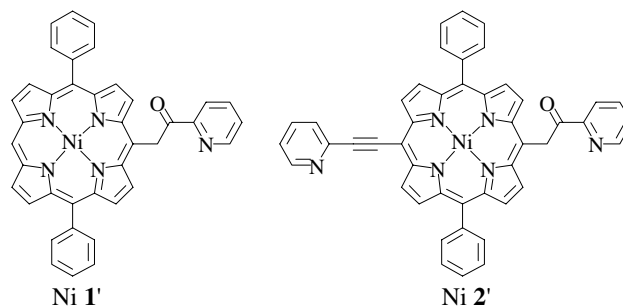


Fig. 1. Structure diagram of Ni porphyrins with 2-pyridine-acetyl substituents.

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according to the Sonogashira cross-coupling method [10]. This method has been widely used to synthesize porphyrins with ethyne-linked functional groups [11–15]. Although porphyrins with 2-pyridine-ethynyl substituents were expected to be the products according to the method, we found that nickel porphyrins with 2-pyridine-acetyl substituents were in fact the major products (Fig. 2). Two such reactions are shown in Fig. 2, and they afforded 55% of Ni **1'** and 46% of Ni **2'**.

The NMR spectra of Ni **1'** and Ni **1** are fairly similar to each other. For example, (1) the ^1H NMR peaks of Ni **1'** differ from those of Ni **1** only by one singlet peak at 6.62 ppm and (2) the other ^1H NMR peaks have similar chemical shifts and spin–spin splitting patterns (please see the characterization section for details). Therefore, the X-ray structure of Ni **1'** was obtained in order to more clearly identify these complexes (Fig. 3, see also Tables 2 and 3). As shown in the figure, the acetyl group is indeed the group that connects the 2-pyridine and the porphine core for Ni **1'**. Based on this, the ^1H NMR spectra of Ni **1'** and Ni **1** were better understood. More importantly, the ^1H NMR peaks of Ni **2'** were properly assigned, namely to distinguish the ^1H NMR peaks of the 2-pyridine-acetyl group and those of the 2-pyridine-ethynyl substituent.

On the other hand, the UV–Vis absorptions of NiBPP, Ni **1** and Ni **1'** reveal different degrees of the interactions between the substituents and the porphine core (Fig. 4): Ni **1** has the most red-shifted absorptions owing to the better resonance interactions via the ethynyl bridge. In contrast, the acetyl group provides less effective π -interactions between the substituents and the porphine ring, resulting in the less red-shifted absorptions of Ni **1'**.

To further our understanding to these unexpected products, the reactions were analyzed by systematically changing the experimental conditions. The results are compared in Table 1. As shown in the table, the complex

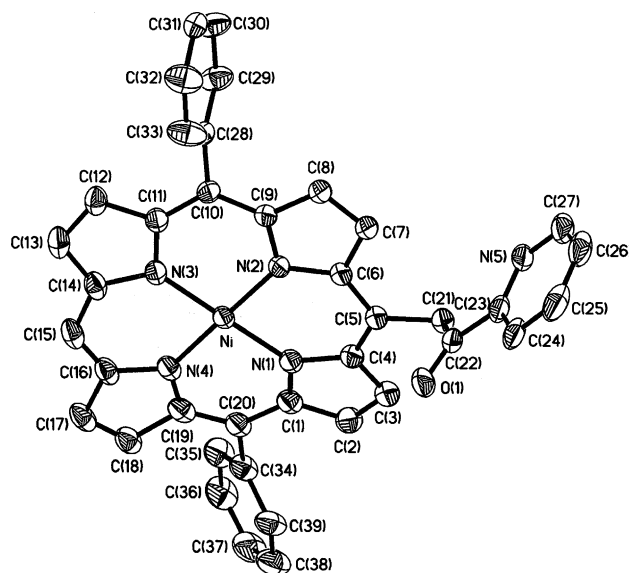


Fig. 3. Crystal structure of Ni **1'**.

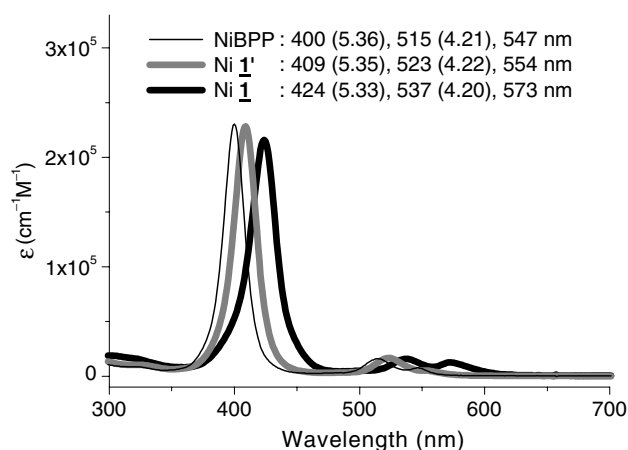


Fig. 4. The absorption spectra of NiBPP, Ni **1'** and Ni **1** in CH_2Cl_2 ($\log \epsilon$ shown in the parentheses).

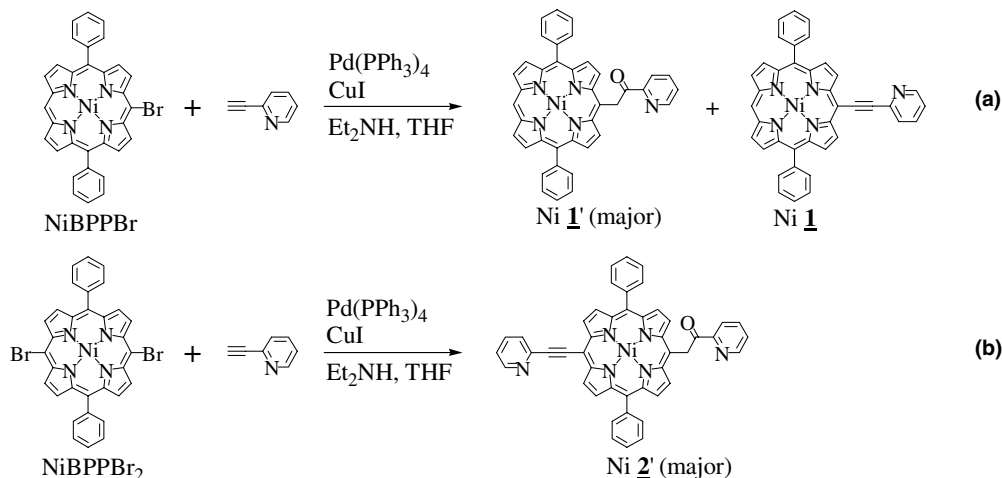


Fig. 2. Reacting brominated NiBPP with 2-pyridylethyne.

Table 1
Selected reaction conditions and yields

Starting materials	Reaction conditions	Reaction time	Products
NiBPPBr/2PyCCH	Pd(PPh ₃) ₄ /CuI/Et ₂ NH/THF	38 h ^a	41% Ni 1' + 21% Ni 1
NiBPPBr/2PyCCH	Pd(PPh ₃) ₄ /CuI/Et ₂ NH/THF	5 days	55% Ni 1'
Ni 1	Pd(PPh ₃) ₄ /CuI/Et ₂ NH/THF ^b	5 days	55% Ni 1'
NiBPPBr ₂ /2PyCCH	Pd(PPh ₃) ₄ /CuI/Et ₂ NH/THF	43 h ^c	46% Ni 2'
ZnBPPBr/2PyCCH	Pd(PPh ₃) ₄ /CuI/Et ₂ NH/THF	5 days	<2% Zn 1' + 21% Zn 1
ZnBPPBr/2PyCCH	Pd(PPh ₃) ₄ /CuI/Et ₂ NH/THF + 1 drop H ₂ O ^d	5 days	<5% Zn 1' + 21% Zn 1 ^e

^a NiBPPBr was not completely consumed at this point.

^b None of the reagent alone converted Ni **1** to Ni **1'**.

^c Prolonged reaction time decomposes the porphyrins, and multiple bands were observed in column.

^d Adding one drop of water did not significantly affect the nickel porphyrin reactions.

^e Prolonged reaction time decreased the overall yields of the porphyrins. The yields were higher if shortened the reaction time [18].

Ni **1** was found to be one of the reaction products at 38 h in the cross-coupling reactions (Entry 1). However, this compound completely disappeared after prolonged reaction and the yield of Ni **1'** increased from 41% to 55%. More importantly, although very stable in THF, Ni **1** was converted to Ni **1'** at 55% yield after standing in the cross-coupling environment for five days (Entry 3). These results suggest that (1) Ni **1** was the initial product of the cross-coupling reactions, and (2) Ni **1** was gradually converted to Ni **1'** in situ and (3) the conversion rate from Ni **1** to Ni **1'** was 55% (see Tables 2 and 3).

Many acid-hydrolysis reactions of pyridylethyne have been well documented [16], therefore, it is logical to assume that Ni **1** transforms to Ni **1'** via the hydrolysis mechanism. Furthermore, the conversion rate of 2-pyridylethyne has been reported to be 60%; this is quite close to the Ni **1'** conversion rate (55%, from Ni **1**). Note-worthily, converting Ni **1** to Ni **1'** does not require the intro-

duction of acids. In addition, the source of water for hydrolysis in the reaction solutions could be from the crystallized porphyrins or the palladium catalyst [17]. We found that such trace amount of water was enough for the conversion, and adding extra water did not increase the yield of Ni **1'** nor shorten the reaction time.

We also examined the same reactions with different porphyrins: reacting 2-pyridylethyne with NiBPPBr₂ yielded 46% of Ni **2'** after 43 h of reaction (Table 1, Entry 4). In this case, prolonging reaction time decomposed the porphyrins and numerous bands were found during chromatographic separation. Also, the same phenomenon is far less effective for the zinc analogues, and the yields were less than those observed for the nickel complexes (Table 1, Entry 5). Interestingly, adding extra water seemed to increase the yield of Zn **1'** (Entry 6). The difference between the nickel and the zinc porphyrin reactions is possibly due to the facts that: (1) zinc(II) is a d¹⁰ close-shell ion and nickel(II) is a d⁸ open-shell ion, and (2) zinc(II) porphyrins form the 5- or 6-coordinated complex fairly easily [19] while nickel(II) porphyrins are usually 4-coordinated unless dissolved in strongly ligating solvents, such as pyridine or piperidine [20]. These two factors are likely to affect the geometry, the energy and the electronic structure of these porphyrins, resulting in the difference in the reactivities.

In summary, we report a one-pot synthesis of nickel porphyrins with 2-pyridine-acetyl substituents by the Sonogashira cross-coupling method. It is suggested that porphyrins with 2-pyridine-ethynyl substituents were first generated, and were gradually converted to porphyrins with 2-pyridine-acetyl substituents via in situ hydrolysis.

3. Experimental

3.1. Materials

Air-sensitive solids were handled in an MBraun Uni-lab glove box. A vacuum line and standard Schlenk techniques were employed to process air-sensitive solu-

Table 2
Crystal data for Ni **1'**

<i>Crystallizes from CH₂Cl₂/hexane as dark-red blocks</i>	
Formula	C ₃₉ H ₂₅ N ₅ NiO
Formula weight	638.35
Temperature (K)	150(1)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	C2/c
Unit cell dimensions	
<i>a</i> (Å)	25.4032(4)
<i>b</i> (Å)	13.1159(2)
<i>c</i> (Å)	17.8961(3)
Volume (Å ³)	5846.85(16)
<i>Z</i>	8
Density (calculated) (mg/m ³)	1.450
Absorption coefficient (mm ⁻¹)	0.707
<i>F</i> (000)	2640
Crystal size (mm ³)	35 × 30 × 25
θ Range for data collection (°C)	1.64–27.50
Reflections collected	49,721
Independent reflections	6722 (<i>R</i> _{int} = 0.0827)
Goodness-to-fit on <i>F</i> ²	1.188
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0749, <i>wR</i> ₂ = 0.2001
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.1012, <i>wR</i> ₂ = 0.2249
Extinction coefficient	0.0126(9)

Table 3
Selected bond lengths and bond angles of Ni **1'**

Bond lengths (Å)					
Ni–N2	1.932(3)	N5–C23	1.341(6)	C12–C13	1.341(6)
Ni–N4	1.940(3)	C1–C20	1.406(5)	C13–C14	1.414(7)
Ni–N1	1.952(3)	C1–C2	1.434(6)	C14–C15	1.384(6)
Ni–N3	1.958(3)	C2–C3	1.334(6)	C15–C16	1.359(7)
O1–C22	1.212(5)	C3–C4	1.440(6)	C16–C17	1.437(6)
N1–C1	1.370(5)	C4–C5	1.387(6)	C17–C18	1.340(8)
N1–C4	1.392(5)	C5–C6	1.391(6)	C18–C19	1.442(5)
N2–C6	1.378(5)	C5–C21	1.513(5)	C19–C20	1.390(6)
N2–C9	1.387(5)	C6–C7	1.433(6)	C21–C22	1.517(7)
N3–C11	1.376(5)	C7–C8	1.347(7)	C22–C23	1.495(5)
N3–C14	1.378(5)	C8–C9	1.426(6)	C23–C24	1.387(8)
N4–C19	1.374(6)	C9–C10	1.384(6)	C24–C25	1.388(7)
N4–C16	1.400(5)	C10–C11	1.376(5)	C25–C26	1.390(11)
N5–C27	1.334(6)	C11–C12	1.439(6)	C26–C27	1.375(11)
Bond angle (°)					
N2–Ni–N4	179.22(15)	C2–C3–C4	107.0(4)	C15–C14–C13	123.8(4)
N2–Ni–N1	90.43(13)	C5–C4–N1	125.1(4)	C16–C15–C14	124.2(4)
N4–Ni–N1	88.94(14)	C5–C4–C3	124.3(4)	C15–C16–N4	125.7(4)
N2–Ni–N3	89.42(13)	N1–C4–C3	110.5(4)	C15–C16–C17	124.3(4)
N4–Ni–N3	91.21(14)	C4–C5–C6	121.8(4)	N4–C16–C17	109.9(4)
N1–Ni–N3	179.18(12)	C4–C5–C21	121.0(4)	C18–C17–C16	107.7(4)
C1–N1–C4	103.8(3)	C6–C5–C21	117.3(3)	C17–C18–C19	106.8(4)
C1–N1–Ni	128.4(3)	N2–C6–C5	126.5(4)	N4–C19–C20	125.6(3)
C4–N1–Ni	127.7(3)	N2–C6–C7	110.7(4)	N4–C19–C18	111.1(4)
C6–N2–C9	104.9(3)	C5–C6–C7	122.7(4)	C20–C19–C18	123.3(4)
C6–N2–Ni	127.4(3)	C8–C7–C6	106.7(4)	C19–C20–C1	120.6(4)
C9–N2–Ni	127.7(2)	C7–C8–C9	107.8(4)	C5–C21–C22	111.4(4)
C11–N3–C14	104.3(3)	C10–C9–N2	126.5(3)	O1–C22–C23	119.9(4)
C11–N3–Ni	128.8(2)	C10–C9–C8	123.4(4)	O1–C22–C21	120.8(4)
C14–N3–Ni	126.9(3)	N2–C9–C8	110.0(3)	C23–C22–C21	119.3(4)
C19–N4–C16	104.5(3)	C11–C10–C9	121.9(4)	N5–C23–C24	124.6(4)
C19–N4–Ni	129.4(3)	C10–C11–N3	125.0(4)	N5–C23–C22	117.0(5)
C16–N4–Ni	126.0(3)	C10–C11–C12	124.5(4)	C24–C23–C22	118.3(4)
C27–N5–C23	116.4(6)	N3–C11–C12	110.4(3)	C23–C24–C25	118.2(6)
N1–C1–C20	125.9(4)	C13–C12–C11	106.8(4)	C24–C25–C26	117.3(7)
N1–C1–C2	111.6(3)	C12–C13–C14	107.1(4)	C27–C26–C25	120.4(5)
C20–C1–C2	122.5(4)	N3–C14–C15	124.8(4)	N5–C27–C26	123.1(6)
C3–C2–C1	106.9(4)	N3–C14–C13	111.4(4)		

tions. Tetrahydrofuran (THF) was obtained from Merck (Darmstadt, Germany), and all other chemicals were ordered from Acros Organics (New Jersey, USA). THF was distilled from Na/benzophenone under N₂. Diethylamine (Et₂NH) was dried over KOH pellets and distilled under vacuum. All NMR solvents were purchased from Cambridge Isotope Lab., Inc. (MA, USA) and were used as received. Pd(PPh₃)₄ was prepared according to the literature [17]. Chromatographic purification was performed with Silica Gel 60 (230–400 mesh, Merck).

3.2. Synthesis

One hundred milligram of brominated NiBPP under nitrogen was mixed with 2–4 equivalents of 2-pyridylethyne (2 eq. for reacting with NiBPPBr and 4 eq. for reacting with NiBPPBr₂), 20 mol% of Pd(PPh₃)₄, 10 mol% of CuI, 5 ml of Et₂NH and 80 ml of THF.

The de-gassed reaction mixtures were stirred under nitrogen at 40 °C and monitored with TLC and UV–Vis spectroscopy. NH₄Cl_(aq) washes were applied to quench the reactions. Porphyrin products were obtained after separation by chromatography on silica gel then crystallization from CH₂Cl₂/hexanes. The reaction yields are listed in Table 1.

Other characterization data:

Ni **1'**: ¹H NMR (CDCl₃ at 7.26 ppm), porphine: 9.75(s, 1H), 9.31(d, *J* = 5 Hz, 2H), 9.08(d, *J* = 5 Hz, 2H), 8.83(d, *J* = 5 Hz, 2H), 8.81(d, *J* = 5 Hz, 2H), 8.01(m, 4H), 7.70(m, 6H); 2-pyridine-acetyl: 8.93(d, *J* = 5 Hz, 1H), 8.14(d, *J* = 7 Hz, 1H), 7.90(t, *J* = 7 Hz, 1H), 7.60(t, *J* = 6 Hz, 1H), 6.62(s, 2H). Elemental analysis, C₃₉H₂₅N₅ONi · ½ H₂O, calculated C 72.36%, H 4.05%, N 10.82%; Found C 72.70%, H 3.99%, N 10.55%.

Ni **1**: ¹H NMR (CDCl₃ at 7.26 ppm), porphine: 9.73(s, 1H), 9.69(d, *J* = 5 Hz, 2H), 9.03(d, *J* = 5 Hz, 2H), 8.84(d, *J* = 5 Hz, 2H), 8.79(d, *J* = 5 Hz, 2H), 8.01(m, 4H), 7.71(m, 6H); 2-pyridine-ethynyl: 8.82(overlapped, 1H),

7.95(d, $J = 8$ Hz, 1H), 7.87(t, $J = 8$ Hz, 1H), 7.39(t, $J = 6$ Hz, 1H). Elemental analysis, $C_{39}H_{23}N_5Ni \cdot H_2O$, calculated C 73.38%, H 3.95%, N 10.97%; Found C 73.56%, H 3.79%, N 10.36%.

Ni **2'**: 1H NMR ($CDCl_3$ at 7.26 ppm), porphine: 9.59(d, $J = 5$ Hz, 2H), 9.21(d, $J = 5$ Hz, 2H), 8.76(d, $J = 5$ Hz, 2H), 8.70(d, $J = 5$ Hz, 2H), 7.97(m, 4H), 7.68(m, 6H); 2-pyridine-acetyl: 8.91(d, $J = 5$ Hz, 1H), 8.14(t, $J = 7$ Hz, 1H), 7.85(t, $J = 7$ Hz, 1H), 7.60(t, $J = 6$ Hz, 1H), 6.51(s, 2H); 2-pyridine-ethynyl: 8.91(d, $J = 5$ Hz, 1H), 7.92(d, $J = 8$ Hz, 1H), 7.68(overlapped, 1H), 7.37(t, $J = 6$ Hz, 1H). Elemental analysis, $C_{46}H_{28}N_6ONi \cdot \frac{1}{2}H_2O$, calculated C 73.82%, H 3.91%, N 11.23%; Found C 73.95%, H 3.88%, N 11.22%.

4. Supplementary material

Crystallographic data for the structural analysis of Ni **1'** has been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 221509. Copies of this information may be obtained free of charge from: The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ UK (fax: +44 1223 336 033, e-mail: deposit@ccdc.cam.ac.uk or www:<http://www.ccdc.cam.ac.uk>).

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