

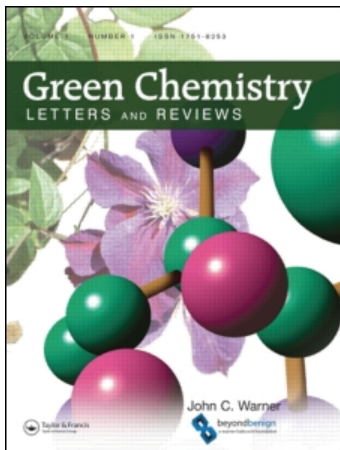
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Green Chemistry Letters and Reviews

Publication details, including instructions for authors and subscription information:

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Rakesh Kumar Sharma^a; Gauri Ahuja^a; Indu Tucker Sidhwani^a

^a Department of Chemistry, Green Chemistry Network Centre, University of Delhi, India

To cite this Article Sharma, Rakesh Kumar , Ahuja, Gauri and Sidhwani, Indu Tucker(2009) 'A new one pot and solvent-free synthesis of nickel porphyrin complex', Green Chemistry Letters and Reviews, 2: 2, 101 – 105

To link to this Article: DOI: 10.1080/17518250903117463

URL: <http://dx.doi.org/10.1080/17518250903117463>

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RESEARCH LETTER

A new one pot and solvent-free synthesis of nickel porphyrin complex

Rakesh Kumar Sharma*, Gauri Ahuja and Indu Tucker Sidhwani

Department of Chemistry, Green Chemistry Network Centre, University of Delhi, Delhi-110007, India

(Received 19 February 2009; final version received 15 June 2009)

A new one pot and solvent-free synthesis of nickel porphyrin complex is described. This is prepared by condensing pyrrole, benzaldehyde, nickel (II) chloride, and 1,8-diazabicyclo [5.4.0] undec-7-ene as a base. This new method allows higher yields, reduced reaction times, ease of handling, and follows principles of green chemistry. The same complex is also prepared by an alternative route, i.e. first, the porphyrin is prepared and then the insertion of metal ion.

Keywords: solvent free; one pot synthesis; nickel porphyrin

Introduction

Porphyryns and metalloporphyryns are synthetically important compounds due to their aromatic character, inner chelating pockets, and varying peripheral carbon chains. These have allowed scientists to discover new and unique chemical reactions. Porphyryns and their metal complexes have also stirred interdisciplinary interest due to a multitude of their intriguing physical, chemical, and biological properties. Due to their importance, a number of papers have been reported in the literature and still continue to attract the attention of researchers. They are also well known optoelectronic as well as biological materials and have been applied in light emitting diodes (1,2). Porphyrin was first synthesized by Fischer (3) in 1920 and has been used as a selective catalyst (4,5), in molecular electronic device (6), as a photodynamic therapy agent (7), in solar cells (8,9), molecular thermometer (10), and various other uses in material chemistry (11).

Traditionally, porphyrin synthesis have been carried out in corrosive, high boiling solvents such as propionic acid (12,13) or in large amount of halogenated solvents containing a corrosive lewis acid catalyst (14–16). In many cases, toxic oxidizing compounds are used to convert the porphyrinogen to porphyrin (17). Recent methods used in the synthesis of tetrarylporphyrin via tetramerization of pyrrole using clays (18), ionic liquids (19), H₂O₂ in acetic acid (20), vapor phase synthesis (21), and mixtures of xylenes and chloroacetic acid (22). These methods suffer from various limitations such as relatively

poor yields, harsh conditions of reactions, high dilution and intractable purification problems, and the use of large amount of corrosive and environmentally harmful solvents. To minimize the usage of various acids, the strategy of microwave induced synthesis in dry media onto solid inorganic support (23) seems to be most adapted. All the reported methods of synthesis give poor yields and are time consuming and use a large amount of solvents. Although a one pot synthesis of the metalloporphyrin has been reported (24), this method suffers on two accounts. Firstly, a large amount of solvent is used and secondly, the preparation requires 8 hours of heating. In the present work, we report a solvent free and microwave assisted synthesis of porphyrin using benzaldehyde and pyrrole which is prepared by a slightly modified method of Loupy (25) followed by the preparation of the nickel porphyrin by a solvent free, microwave assisted reaction using 1,8-diazabicyclo [5.4.0] undec-7-ene (DBU) as a base. We also report a novel one pot method of synthesis for nickel porphyrin starting from pyrrole, benzaldehyde, nickel (II) chloride, and DBU as a base.

Results and discussion

The preparation of a porphyrin complex is a two-step process, which includes synthesis of a ligand and reaction of a ligand with appropriate metal salts. In this paper, the metallation of porphyrin was carried out by two methods: (1) the preparation of tetraphenylporphyrin (TPP) followed by metallation with Ni(II) chloride; (2) one pot synthesis of nickel tetraphenylporphyrin. In the one pot synthesis there

*Corresponding author. Email: rksharmagreenchem@hotmail.com

is an *in situ* generation of the ligand from the starting material followed by the insertion of metal ion to form a complex. The one pot synthesis is effective in porphyrin complexes because of extra stability due to a chelating effect. The one pot synthesis has the following advantages: a reduced number of steps involved in the synthesis, no waste on account of the ligand synthesis, and the completion of the reaction in a short duration of time. Almost 70 porphyrins have been synthesized by conventional method, but less work has been done on porphyrin using microwave. Microwave induces polarization of the starting materials, resulting in not only rapid condensation of pyrrole and aldehyde to porphyrins, but also fast replacement of protons in the porphyrin ring by metal ions.

In the case of the preparation of metalloporphyrins from H_2 (TPP), the role of base DBU is important in the reaction. Without DBU, this reaction does not proceed. The mechanism has been reported, explaining the essential role of DBU in the conversion of metal-free porphyrins into metalloporphyrins (26,27).

The DBU (Figure 1) is a Lewis base since it has two lone pairs of electrons and is an electron-pair donor. However, the hydrogen of porphyrin ring, which is an electron-pair acceptor, is a Lewis acid. Firstly, the DBU captures the hydrogen of the porphyrin ring to produce the porphyrin anion (Por^{2-}). Then the metal source (M^{n+}) is attracted by the Por^{2-} to form a metalloporphyrin.

The characterization data of nickel porphyrins prepared from two different paths discussed above are identical. Under microwave irradiation the reaction duration takes only few minutes. Moreover, the reaction conditions are mild as it includes minimal solvent use (only DBU as catalyst) and waste on account of the ligand is minimized. These improved reaction conditions will allow for a drop in the cost of producing the porphyrin products. This one pot synthesis follows atom economy, less hazardous chemical synthesis, safer solvents and auxiliaries, design for energy efficiency, and reduced derivatives (28).

Mass spectra of porphyrin and nickel porphyrin prepared by Schemes 1 and 2 were performed by using chloroform (of HPLC grade) as a solvent. The presence of strong molecular ion peaks at their specific

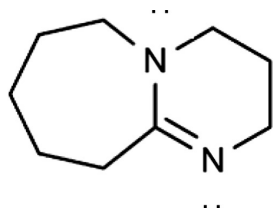
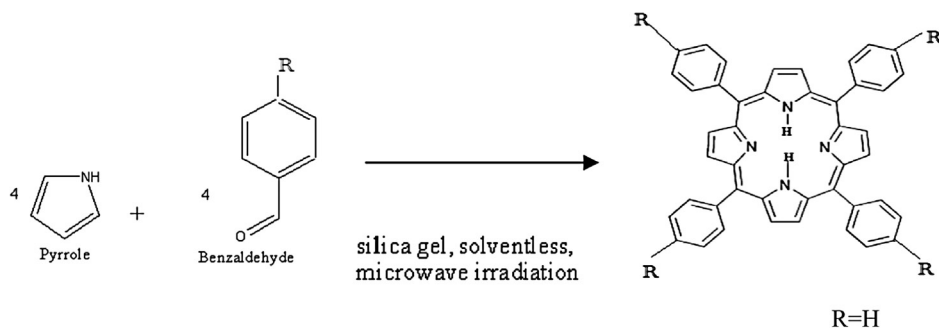


Figure 1. DBU, 1,8-diazabicyclo [5.4.0] undec-7-ene.

values correspond to the molecular mass viz 614 for $[H_2(p-H)_4 TPP]$ and 671 for both $[Ni^{II}(p-H)_4 TPP]$ Scheme 1, $[Ni^{II}(p-H)_4 TPP]$ Scheme 2. The absorption spectra of porphyrin and its metal complexes were recorded in dimethylformamide (DMF) within the spectral range of $370-700\text{ cm}^{-1}$. The absorption spectra of free porphyrin (Figure 2) revealed one major intense Soret band and four Q-bands in DMF solution in the ultraviolet part of the spectrum. The absorption spectrum of porphyrin metal complex (Figure 3) was depicted on the basis of disappearance of I, II, and III bands. This indicates incorporation of metal ion in the porphyrin ring. The electronic absorptions for both metallated and non-metallated porphyrin have been attributed to porphyrin ring based $\Pi-\Pi^*$ electronic transitions. For Ni (II) porphyrins, as a result of extensive metal (d_{xz} , d_{yz}) to ligand Π^* back bonding an increased energy splitting, ΔE , for porphyrin based $\Pi-\Pi^*$ electronic transition occurs. The increased energy splitting results in hypsochromic shift (29–34). Further coordination with extra ligand causes a general shift of absorption band to higher wavelength. *Meso*-tetraphenylporphyrin shows the presence of a Soret band at 418 nm. The nickel (II) porphyrin complex produces Soret bands at 414 nm, respectively, demonstrating that the trend for increasing red shifts in metalloporphyrins. Absorption of energy manifested in the Soret band is attributable to a single transition affecting the resonating system of the porphyrin ring. Infrared spectra are found to be more useful physical method for investigation and identifying functional groups. The characteristic IR absorption frequencies in the spectral range of $4000-400\text{ cm}^{-1}$ were measured for free porphyrin and its metal complex. The IR absorption spectrum of nickel porphyrin complex indicates that the free porphyrin molecule loses its original characteristics and participates in coordination with the metal ion. The complex indicates no $-NH$ band while ligand exhibited band at 3314 cm^{-1} , suggesting metal nitrogen contribution. The disappearance of the $N-H$ band and the shifting of a few bands indicated the formation of complex. 1H NMR spectral studies have been carried out to verify the formation of porphyrin and its metal derivatives. 1H NMR spectra of products were measured in deuterated chloroform, $CDCl_3$, as a solvent at 300 MHz. The singlet $-NH$ peak (due to rapid exchange of $N-H$ protons) is found to be very high field (-2.79 ppm), since they are located within the shielded core of the porphyrin ring. The resonance signals of coordinated porphyrin are found to have shifted upfield as compared to free porphyrin. The presence of a singlet at 8 ppm corresponds to the hydrogen atoms of the pyrrole ring. This signal is located at a very low field because



Scheme 1. Preparation of 5, 10, 15, 20 meso-tetraphenylporphyrin by microwave method.

of the delocalization of electron of pyrrole ring. The disappearance of the N–H peak indicates the formation of metalloporphyrin. This is the distinguishing factor between porphyrins and metalloporphyrins. All Ni (II) porphyrins display upfield chemical shift with respect to their unmetallated porphyrin counterparts. This trend is particularly evident for pyrrole proton resonances on the porphyrin ring that are located closest to the metal center. The protons in the nickel porphyrin are shifted upfield as a result of shielding due to the presence of metal to ligand π back bonding. A nice correlation of electronic absorption and NMR spectroscopy is evident with regard to the bonding that occurs between the central metal and the porphyrin ring system.

Experimental section

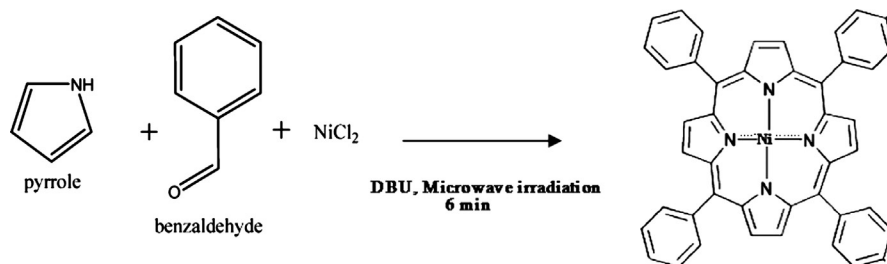
Preparation of 5, 10, 15, 20 meso-tetraphenylporphyrin by microwave method

Pyrrole (0.29 g, 4.32 mmol) was added to benzaldehyde (0.44 g, 4.12 mmol) in a 25 ml Erlenmeyer flask with constant shaking for 5 minutes, followed by the addition of 0.63 g of silica gel. The solution was constantly stirred for half an hour. This was irradiated in a domestic microwave oven (500 W) for 5 minutes with a one-minute interval in between, in a silica gel bath. The reaction was monitored by TLC in 7:1 hexane and ethylacetate. The mixture was cooled at room temperature until silica gel was evenly and completely covered with the reaction mixture. Ethyl

acetate (15 mL) was added to the mixture, the mixture was then filtered in order to remove the silica gel. Then ethyl acetate was evaporated with the help of rotary evaporator leading to the formation of black colored viscous residue. The residue was passed through a silica gel column and eluted with hexane and ethylacetate. The porphyrin fractions were collected and evaporated. Purple colored crystals were obtained. Yield: 67%, m.pt $> 300^\circ\text{C}$, ($\lambda_{\text{max}}/\text{cm}^{-1}$: 418 (2.26), 513.7 (0.708), 548 (0.377), 591.7 (0.283), 648.2 (0.267), $^1\text{HNMR}$: py-H (8.84, 8H, s), o-Ph(8.22, 8H, d), m-Ph, p-ph (7.74, 12H), –NH(–2.79, 2H, s), m/z: 614, $\nu_{\text{max}}/\text{cm}^{-1}$: 3314, 3051, 3019, 1594, 1471, 1440, 1349, 1070, 978, 964, 791, 730, 699.

Preparation of (5, 10, 15, 20 tetraphenylporphyrinato) nickel (II), NiTPP by microwave method

Porphyrin (0.25 g, 0.4 mmol), synthesized above was ground with NiCl_2 (1.7 g, 7.15 mmol) and poured into about 5ml of DBU to give a slurry in 25 ml Erlenmeyer flask. Both were kept for constant stirring for 10–15 minutes. The solution was irradiated (750 W) for 6 minutes with one-minute interval in silica gel bath. The reaction was monitored by TLC in 7:1 hexane and ethylacetate. The solution was then cooled and kept stirring for 4 hours. DBU was evaporated with the help of rotary evaporator leading to the formation of black viscous paste. The residue was passed through a silica gel column and eluted with hexane and ethylacetate. The porphyrin fractions were collected and evaporated. Dark purple



Scheme 2. One pot synthesis of (5, 10, 15, 20 tetraphenylporphyrinato) nickel (II), NiTPP by microwave.

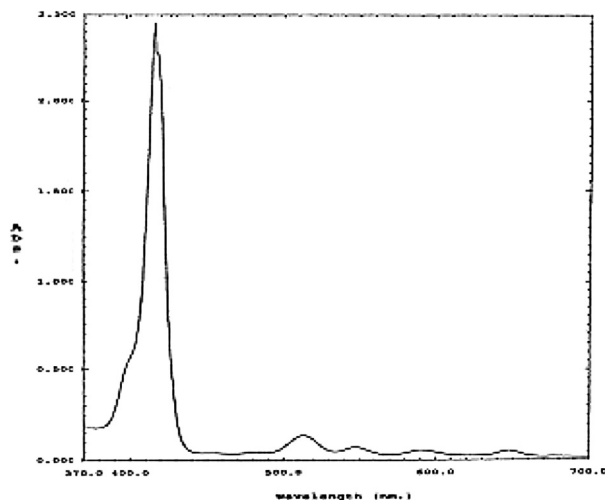


Figure 2. Absorption spectra of 5, 10, 15, 20-tetraphenylporphyrin in DMF solution.

colored crystals were obtained. Yield: 57%, m.pt > 300°C, $\lambda_{\max}/\text{cm}^{-1}$: 414 (2.099), 527 (0.181), $^1\text{H-NMR}$: py-H (8.74, 8H, s), o-Ph (7.99, 8H, d), m-ph, p-ph (7.67, 12H, d), m/z: 671, $\nu_{\max}/\text{cm}^{-1}$: 3051, 3018, 1439, 1349, 1070, 965, 982, 833, 792, 741, 707, 695 (Scheme 1).

One pot synthesis of (5, 10, 15, 20 tetraphenylporphyrinato) nickel (II), NiTPP by microwave method

Pyrrole (0.48 g, 7.21 mmol), benzaldehyde (0.65 g, 6.19 mmol) and NiCl_2 (2 g, 8.41 mmol) were ground together and poured into about 6ml of DBU in 25 ml Erlenmeyer flask. The mixture was stirred for 10–15 minutes and irradiated (500 W) for 8 minutes with a

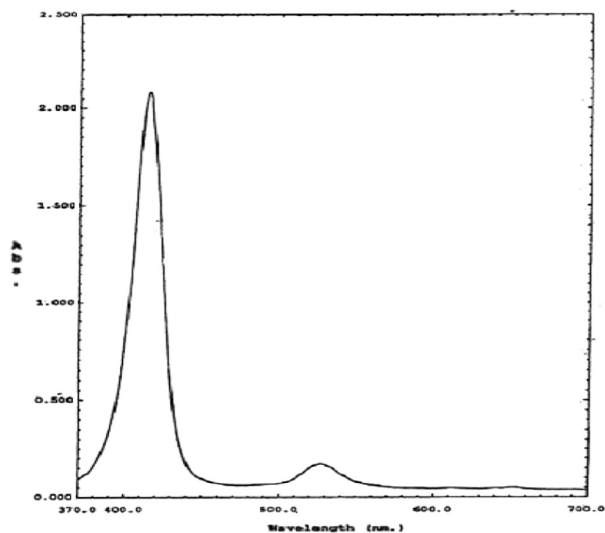


Figure 3. Absorption spectrum of nickel porphyrin complex (one-pot synthesis).

two-minute interval in between in a silica gel bath. The reaction was monitored by TLC in 7:1 hexane and ethylacetate. The solution was cooled to room temperature and kept stirring for 3 hours. DBU was evaporated on rotary evaporator forming black viscous residue. The residue was passed through silica gel column eluted with hexane and ethylacetate. The porphyrin fractions were collected and evaporated. Dark purple colored crystals were obtained. Yield: 60%, m.pt > 300°C, $\lambda_{\max}/\text{cm}^{-1}$: 418 (1.006), 525 (0.886), $^1\text{H-NMR}$: py-H (8.74, 8H, s), o-Ph (7.99, 8H, d), m-ph, p-ph (7.67, 12H, d), m/z: 671, $\nu_{\max}/\text{cm}^{-1}$: 3052, 3022, 1598, 1439, 1350, 1071, 1006, 834, 792, 742, 708, 695 (Scheme 2).

Measurements

SL-159 ELICO spectrophotometer was used to obtain the electronic spectra in the region 370–700 nm in DMF as a solvent. TOF-MS Mass spectrometry has been successfully used to investigate the molecular ion species in solution on Waters (USA) K-455 model with ES^+ mode in chloroform (HPLC grade) solvent. FTIR spectra were recorded on a Perkin-Elmer spectrometer at room temperature using KBr pellet technique. The pellet was used to record the IR spectrum in the range of 400–4000 cm^{-1} under the atmospheric conditions with a resolution of 1 cm^{-1} . $^1\text{H-NMR}$ spectra were obtained in a Bruker 300 MHz machine, using deuterated chloroform (CDCl_3) as solvent and tetramethylsilane (TMS) as a reference.

Conclusion

The synthesis of nickel porphyrin was performed in a green method; the metallation of porphyrin was carried out by two methods: (1) the preparation of TPP followed by metallation; (2) one pot synthesis of nickel tetraphenylporphyrin. In the one pot synthesis, there is an *in-situ* generation of the ligand from the starting material followed by the insertion of metal to form a complex. The reported processes follow green chemistry principles and have the advantages of the ease of preparation, a reduced number of steps involved in the synthesis, and the completion of the reaction in a short duration of time, along with improved yields.

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