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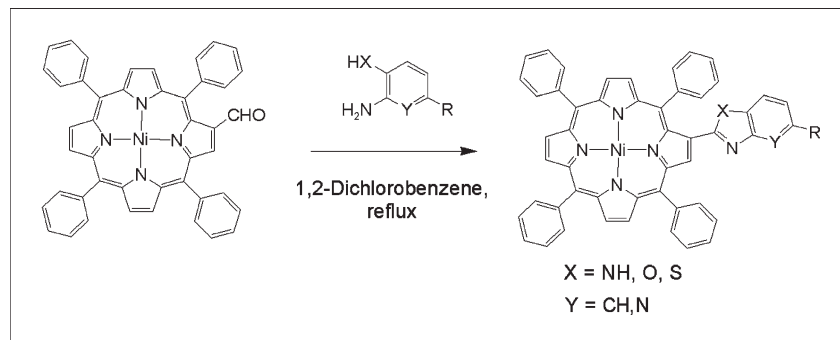
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A simple and efficient synthesis of nickel(II) 2-benzazolo-5,10,15,20-tetraphenylporphyrins from nickel(II) 2-formyl-5,10,15,20-tetraphenylporphyrin and *o*-arylenediamines, *o*-aminophenols or *o*-aminothiophenol in 1,2-dichlorobenzene is described. A diverse range of novel  $\beta$ -substituted azoloporphyrins has been successfully synthesized in good yields and their structures are confirmed on the basis of spectral data.

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## INTRODUCTION

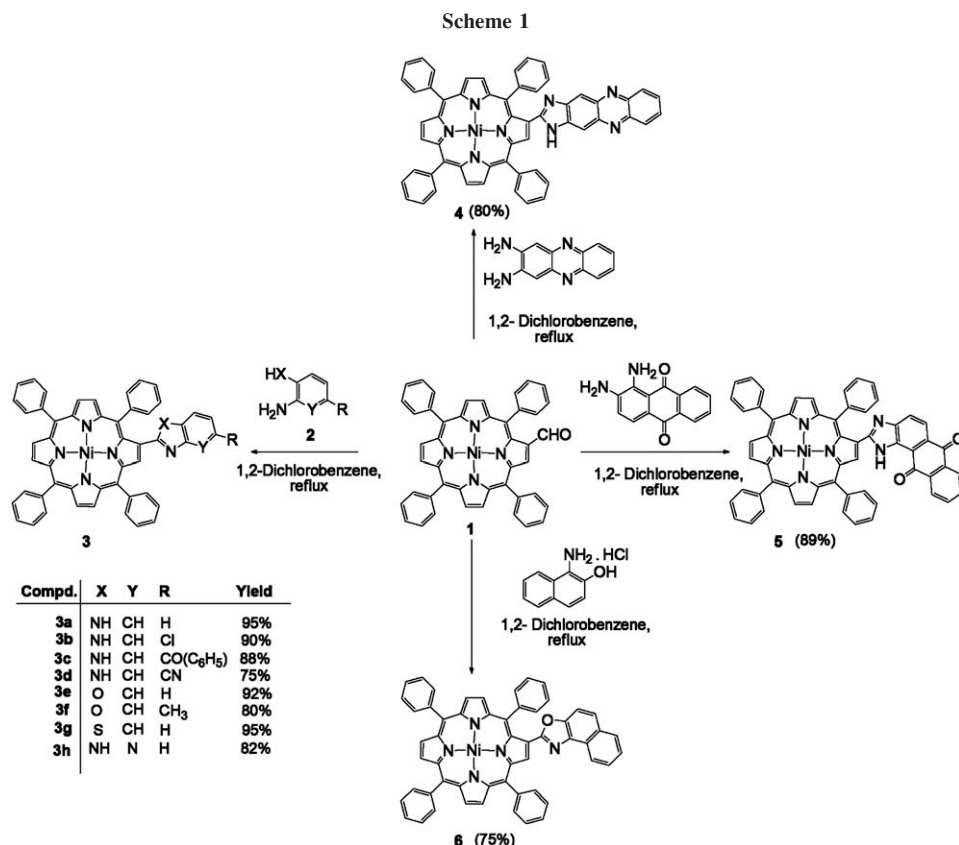
Porphyrins are conjugated tetrapyrrolic macrocycles, which have been found to be of great interest in diverse areas such as catalysis [1], molecular sensing [2], artificial photosynthetic systems [3], and medicine [4]. These chromophores display interesting photophysical, photochemical, and electrochemical properties due to their unusual electronic structure and play vital roles in photosynthesis, cellular respiration, and as a component of metalloenzymes [5]. Furthermore, porphyrin molecules are also promising candidates to be used in the development of new molecular materials with improved electro- and photo-chemical properties. In the past several decades, efforts in synthesizing novel porphyrin macrocycles have made significant contribution toward the other research fields such as electrooptics [6], photovoltaics [7], field-effect transistors [8], and phosphorescent oxygen sensors [9]. The modifications of easily accessible *meso*-tetraarylporphyrins at the *meso*- and  $\beta$ -pyrrolic positions have been extensively explored to gain access to new derivatives especially porphyrins with extended  $\pi$ -systems [10] for applications in a number of areas, ranging from photosensitizer to molecular device for electron transfer processes.

Thorough literature survey revealed that several porphyrins fused to five membered nitrogen heterocycles at  $\beta, \beta'$ -positions [11] and  $\beta$ -substituted azoloporphyrins containing pyrrazole and isoxazole ring systems have

previously been reported [12] but the  $\beta$ -substituted benzazoloporphyrins have not been synthesized yet. We recently developed an efficient synthetic strategy for the preparation of a series of nickel(II) 2-benzazolo-5,10,15,20-tetraphenylporphyrins from nickel(II) complex of 2-formyl-5,10,15,20-tetraphenylporphyrin, which is one of the useful building blocks for the construction of modified porphyrin analogues [13]. In this article, we describe our investigations on the synthesis and spectroscopic characterization of various nickel porphyrins bearing imidazole, oxazole, and thiazole ring systems at the  $\beta$ -position.

## RESULTS AND DISCUSSION

For the synthesis of new nickel(II) complexes of 2-benzazolo-5,10,15,20-tetraphenylporphyrins (**3a–h**, **4–6**) and bis-benzimidazoloporphyrins (**7** and **8**); firstly, nickel(II) 2-formyl-5,10,15,20-tetraphenylporphyrin (**1**) was prepared [14] from nickel(II) *meso*-tetraphenylporphyrin by using Vilsmeier-Haack formylation reaction. Later, a model reaction was carried out with precursor (**1**) and *o*-phenylenediamine in 1,2-dichlorobenzene at reflux condition. The progress of the reaction was observed by TLC. After completion of the reaction, the mixture was allowed to cool at room temperature and directly loaded on silica gel column. On elution with hexane, 1,2-dichlorobenzene was recovered back from the column

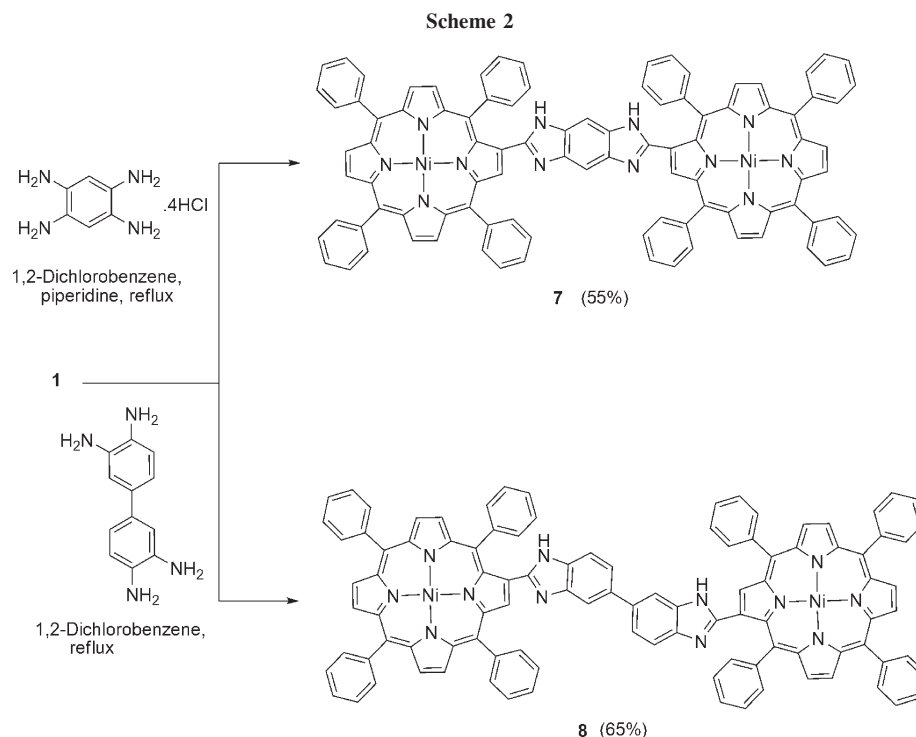


and can be recycled. The desired product (**3a**) was obtained by using 1% MeOH in chloroform as eluent in 95% yield. Instead, a reaction was also performed in refluxing DMF but it was found to be sluggish and produced side products which are difficult to separate by column chromatography. The use of 1,2-dichlorobenzene as a solvent has advantage because no unwanted side reactions have been observed and desired products were formed in high yields. The reaction seems to proceed through initial formation of an iminoporphyrin intermediate, which on intramolecular oxidative cyclization in the presence of atmospheric air affords desired products in good to excellent yields.

To demonstrate the versatility of this methodology, synthesis of various novel nickel(II) complexes of 2-benzazolo-5,10,15,20-tetraphenylporphyrins (**3b–g**), 2-(1*H*-imidazo-[4,5-*b*]pyridin-2-yl)-5,10,15,20-tetraphenylporphyrin (**3h**), 2-(1*H*-imidazo[4,5-*b*]phenazin-2-yl)-5,10,15,20-tetraphenylporphyrin (**4**), 2-(1*H*-imidazo[4,5-*b*]anthraquinone-2-yl)-5,10,15,20-tetraphenylporphyrin (**5**), and 2-(naphtho[1,2-*d*]oxazol-2-yl)-5,10,15,20-tetraphenylporphyrin (**6**) has been carried out by condensing the corresponding *o*-arylenediamines, *o*-aminophenols, *o*-aminothiophenol, and 1-amino-2-naphthol with nickel(II) 2-formyl-5,10,15,20-tetraphenylporphyrin in 1,2-dichlorobenzene at reflux in 75–95% yields (Scheme 1).

Under standardized reaction conditions, the scope of the reaction was then further explored by reacting 1,2,4,5-benzenetetraamine tetrahydrochloride in the presence of 4 equivalents of piperidine and 3,3'-diaminobenzidine with nickel(II) 2-formylporphyrin (**1**) in 1,2-dichlorobenzene at reflux separately to obtain bis-benzimidazoloporphyrins (**7** and **8**) in 55% and 65% yields, respectively (Scheme 2).

All the newly synthesized  $\beta$ -substituted benzazolo-5,10,15,20-tetraphenylporphyrins were purified by column chromatography on silica gel and characterized on the basis of <sup>1</sup>H-NMR, IR, UV-vis, and mass spectral data. <sup>1</sup>H-NMR of nickel(II) 2-imidazoloporphyrins (**3a–d** and **4**) showed a singlet for NH proton of imidazole ring between  $\delta$  8.0 and  $\delta$  8.8 ppm. For compounds **3h** and **5**, NH proton appears at  $\delta$  10.25 ppm and 10.04 ppm, respectively. A singlet for one  $\beta$ -pyrrolic proton appeared at around  $\delta$  9.2 ppm and characteristic signals for the rest of  $\beta$ -pyrrolic protons were present in the proton NMR as a singlet or doublet or multiplet at  $\delta$  8.3–8.9 ppm for all the nickel(II) 2-benzazoloporphyrins. An additional singlet for three protons was observed at  $\delta$  2.49 due to the presence of CH<sub>3</sub> group in nickel(II) 2-(6-methylbenzoxazol-2-yl)-5,10,15,20-tetraphenylporphyrin (**3f**). The infrared absorption spectra of novel 2-imidazoloporphyrins (**3a–d**, **3h**, **4**, **5**, **7**, and **8**) exhibited



characteristic band at around  $3400\text{ cm}^{-1}$  due to the stretching of NH bond. In addition, porphyrins (**3c** and **5**) showed characteristic strong absorption peak at  $1653\text{ cm}^{-1}$  and  $1664\text{ cm}^{-1}$ , respectively, due to the stretching of the C=O bond whereas a strong absorption band was observed at  $2224\text{ cm}^{-1}$  in the IR spectrum of nickel(II) 2-(6-cyano-1*H*-benzimidazol-2-yl)-5,10,15,20-tetraphenylporphyrin (**3d**) due to the presence of C≡N functionality. The electronic absorption spectra of all the newly synthesized porphyrins exhibited a typical Soret band at around 420–430 nm and two Q bands at around 538 and 570 nm.

## CONCLUSIONS

In summary, we have shown an efficient methodology for the preparation of a variety of novel nickel(II) 2-benzazolo-5,10,15,20-tetraphenylporphyrins from nickel(II) 2-formyl-5,10,15,20-tetraphenylporphyrin in good to excellent yields. This synthetic protocol provides a convenient approach for the construction of diverse porphyrinic architectures which may be useful for various applications in a number of areas, ranging from medicine to molecular device for electron transfer process.

## EXPERIMENTAL

All the reactions were performed in the presence of air using water condenser. *o*-Arylenediamines, *o*-aminophenols,

and *o*-aminothiophenol were purchased from Aldrich and used without further purification. Solvents were purchased from Merck and dried according to literature procedures. Thin layer chromatography (TLC) was performed using silica gel 60 F254 (precoated aluminum sheets) from Merck. Reactions were monitored by TLC and products were purified by column chromatography using silica gel (60–120 mesh size).  $^1\text{H-NMR}$  spectra were obtained in  $\text{CDCl}_3$ , using a Bruker 300 MHz NMR spectrometer. Chemical shifts are expressed in parts per million (ppm) relative to tetramethylsilane (TMS; 0 ppm) as an internal standard. Coupling constants (*J*) are reported in hertz (Hz). Infrared spectra were recorded on Perkin Elmer IR spectrometer and absorption maxima ( $\nu_{\text{max}}$ ) are given in  $\text{cm}^{-1}$ . Mass spectra were recorded on ESI-MS (micromass LCT, waters) mass spectrometer. Elemental analyses for all compounds were performed on Elementar Analysensysteme GmbH VarioEL elemental analyzer and data of C, H, and N is within  $\pm 0.4\%$  of calculated value. UV–vis spectra were recorded on Analyticjena Specord 250 UV–vis spectrophotometer using  $\text{CHCl}_3$  as a solvent.

**General procedure for the synthesis of porphyrins (3a–h, 4, and 5).** To a solution of nickel(II) 2-formyl-5,10,15,20-tetraphenylporphyrin (0.050 g, 0.071 mmol) in 1,2-dichlorobenzene (10 mL), *o*-arylenediamine/*o*-aminophenol/*o*-aminothiophenol (0.106 mmol) was added and the mixture was refluxed at  $160^\circ\text{C}$  (8 h for compounds **3a–h** and 16 h for compounds **4** and **5**). After completion of the reaction, the mixture was cooled to room temperature and loaded on silica gel column. 1,2-Dichlorobenzene was removed by eluting the column with hexane. The desired product was isolated by using 1% MeOH in chloroform as solvent.

**Nickel(II) 2-(1*H*-benzimidazol-2-yl)-5,10,15,20-tetraphenylporphyrin (3a).** Yield: 95%; UV:  $\lambda_{\text{max}}$  ( $\epsilon$ ,  $\text{M}^{-1}\text{ cm}^{-1}$ ) 424 (396200), 538 (39700), 568 (15100) nm; IR (film): 3400,

1598, 1441, 1351, 1272, 1073, 1008, 796, 750, 700  $\text{cm}^{-1}$ ;  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  7.08–7.13 (m, 4H, ArH), 7.55–7.69 (m, 10H, *meso*-ArH), 7.75–7.81 (m, 3H, *meso*-ArH), 7.91–7.98 (m, 7H, *meso*-ArH), 8.14 (s, 1H, NH), 8.39 (d, 1H,  $\beta$ -pyrrolic H,  $J = 4.98$  Hz), 8.61 (d, 1H,  $\beta$ -pyrrolic H,  $J = 4.98$  Hz), 8.67–8.74 (m, 4H,  $\beta$ -pyrrolic H), 9.21 (s, 1H,  $\beta$ -pyrrolic H) ppm; HRMS: mass calculated for  $\text{C}_{51}\text{H}_{32}\text{N}_6\text{Ni}$  ( $\text{M}^+$ ): 786.2043; found: 786.4633. Anal. Calcd. for  $\text{C}_{51}\text{H}_{32}\text{N}_6\text{Ni}\cdot 0.5\text{H}_2\text{O}$ : C, 76.90; H, 4.18; N, 10.55. Found: C, 76.64; H, 4.53; N, 10.33.

**Nickel(II) 2-(6-chloro-1H-benzimidazol-2-yl)-5,10,15,20-tetraphenylporphyrin (3b).** Yield: 90%; UV:  $\lambda_{\text{max}}$  ( $\epsilon$ ,  $\text{M}^{-1} \text{cm}^{-1}$ ) 425 (608600), 538 (53800), 569 (21000) nm; IR (film): 3370, 1594, 1439, 1405, 1349, 1258, 1302, 1214, 1070, 1008, 902, 847, 795, 752, 700  $\text{cm}^{-1}$ ;  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  7.12–7.20 (m, 3H, ArH), 7.64–7.76 (m, 12H, *meso*-ArH), 7.855 (d,  $J = 5.4$  Hz, 2H, *meso*-ArH), 7.94–8.04 (m, 6H, *meso*-ArH), 8.09 (s, 1H, NH), 8.43 (d, 1H,  $\beta$ -pyrrolic H,  $J = 4.8$  Hz), 8.64 (d, 1H,  $\beta$ -pyrrolic H,  $J = 4.5$  Hz), 8.70–8.74 (m, 4H,  $\beta$ -pyrrolic H), 9.22 (s, 1H,  $\beta$ -pyrrolic H) ppm; HRMS: mass calculated for  $\text{C}_{51}\text{H}_{32}\text{ClN}_6\text{Ni}$  ( $\text{M} + \text{H}^+$ ): 821.1660; found: 821.4358. Anal. Calcd. for  $\text{C}_{51}\text{H}_{31}\text{ClN}_6\text{Ni}$ : C, 74.52; H, 3.80; N, 10.22. Found: C, 74.39; H, 3.65; N, 9.89.

**Nickel(II) 2-(6-benzol-1H-benzimidazol-2-yl)-5,10,15,20-tetraphenylporphyrin (3c).** Yield: 88%; UV:  $\lambda_{\text{max}}$  ( $\epsilon$ ,  $\text{M}^{-1} \text{cm}^{-1}$ ) 425 (456500), 538 (44300), 570 (19300) nm; IR (film): 3360, 1653, 1617, 1598, 1441, 1350, 1308, 1238, 1073, 1008, 797, 753, 701  $\text{cm}^{-1}$ ;  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  7.02–7.13 (m, 5H, ArH), 7.46–7.49 (m, 3H, ArH), 7.61–7.72 (m, 12H, *meso*-ArH), 7.79–7.86 (m, 2H, *meso*-ArH), 7.90–7.93 (m, 6H, *meso*-ArH), 8.21–8.24 (m, 1H,  $\beta$ -pyrrolic H), 8.39 (m, 1H,  $\beta$ -pyrrolic H), 8.52 (s, 1H, NH), 8.59–8.71 (m, 4H,  $\beta$ -pyrrolic H), 9.20 (s, 1H,  $\beta$ -pyrrolic H) ppm; HRMS: mass calculated for  $\text{C}_{58}\text{H}_{36}\text{N}_6\text{NiO}$  ( $\text{M}^+$ ): 890.2304; found: 890.2327. Anal. Calcd. for  $\text{C}_{58}\text{H}_{36}\text{N}_6\text{NiO}\cdot\text{H}_2\text{O}$ : C, 76.58; H, 4.21; N, 9.24. Found: C, 76.55; H, 4.42; N, 9.53.

**Nickel(II) 2-(6-cyano-1H-benzimidazol-2-yl)-5,10,15,20-tetraphenylporphyrin (3d).** Yield: 75%; UV:  $\lambda_{\text{max}}$  ( $\epsilon$ ,  $\text{M}^{-1} \text{cm}^{-1}$ ) 425 (589500), 538 (70100), 569 (37000) nm; IR (film): 3400, 2224, 1599, 1441, 1350, 1306, 1073, 1007, 797, 753, 701  $\text{cm}^{-1}$ ;  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  7.36–7.39 (m, 2H, ArH), 7.57–7.68 (m, 13H, *meso*-ArH and ArH), 7.91–7.97 (m, 8H, *meso*-ArH), 8.08 (s, 1H, NH), 8.40 (d, 1H,  $\beta$ -pyrrolic H,  $J = 5.1$  Hz), 8.61 (d, 1H,  $\beta$ -pyrrolic H,  $J = 4.8$  Hz), 8.67–8.73 (m, 4H,  $\beta$ -pyrrolic H), 9.20 (s, 1H,  $\beta$ -pyrrolic H) ppm; HRMS: mass calculated for  $\text{C}_{52}\text{H}_{32}\text{N}_7\text{Ni}$  ( $\text{M} + \text{H}^+$ ): 812.2008; found: 812.9039. Anal. Calcd. for  $\text{C}_{52}\text{H}_{31}\text{N}_7\text{Ni}$ : C, 76.86; H, 3.85; N, 12.07. Found: C, 77.21; H, 3.53; N, 11.81.

**Nickel(II) 2-(benzoxazol-2-yl)-5,10,15,20-tetraphenylporphyrin (3e).** Yield: 92%; UV:  $\lambda_{\text{max}}$  ( $\epsilon$ ,  $\text{M}^{-1} \text{cm}^{-1}$ ) 425 (435400), 538 (40900), 574 (23700) nm; IR (film): 1598, 1453, 1351, 1242, 1076, 1008, 850, 796, 752, 700  $\text{cm}^{-1}$ ;  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  6.99 (m, 1H, ArH), 7.14–7.16 (m, 3H, ArH), 7.67–7.68 (m, 12H, *meso*-ArH), 7.89 (d, 2H, *meso*-ArH,  $J = 6.99$  Hz), 7.99 (s, 6H, *meso*-ArH), 8.55 (d, 1H,  $\beta$ -pyrrolic H,  $J = 4.89$  Hz), 8.65 (d, 1H,  $\beta$ -pyrrolic H,  $J = 4.89$  Hz), 8.68–8.75 (m, 4H,  $\beta$ -pyrrolic H), 9.22 (s, 1H,  $\beta$ -pyrrolic H) ppm; HRMS: mass calculated for  $\text{C}_{51}\text{H}_{31}\text{N}_5\text{NiO}$  ( $\text{M}^+$ ): 787.1882; found: 787.0692. Anal. Calcd. for  $\text{C}_{51}\text{H}_{31}\text{N}_5\text{NiO}$ : C, 77.68; H, 3.96; N, 8.88. Found: C, 77.95; H, 4.31; N, 9.20.

**Nickel(II) 2-(6-methylbenzoxazol-2-yl)-5,10,15,20-tetraphenylporphyrin (3f).** Yield: 80%; UV:  $\lambda_{\text{max}}$  ( $\epsilon$ ,  $\text{M}^{-1} \text{cm}^{-1}$ ) 425

(586800), 538 (51100), 574 (27700) nm; IR (film): 1597, 1460, 1442, 1351, 1260, 1215, 1180, 1075, 1009, 850, 797, 754, 701  $\text{cm}^{-1}$ ;  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  2.49 (s, 3H,  $\text{CH}_3$ ), 6.90–7.06 (m, 2H, ArH), 7.15–7.20 (m, 2H, *meso*-ArH), 7.47 (s, 1H, ArH), 7.66–7.68 (m, 10H, *meso*-ArH), 7.88 (d, 2H, *meso*-ArH,  $J = 7.2$  Hz), 7.99–8.01 (m, 6H, *meso*-ArH), 8.50 (d, 1H,  $\beta$ -pyrrolic H,  $J = 5.01$  Hz), 8.64 (d, 1H,  $\beta$ -pyrrolic H,  $J = 4.8$  Hz), 8.67–8.76 (m, 4H,  $\beta$ -pyrrolic H), 9.20 (s, 1H,  $\beta$ -pyrrolic H) ppm; HRMS: mass calculated for  $\text{C}_{52}\text{H}_{34}\text{N}_5\text{NiO}$  ( $\text{M} + \text{H}^+$ ): 802.2117; found: 802.2360. Anal. Calcd. for  $\text{C}_{52}\text{H}_{33}\text{N}_5\text{NiO}\cdot\text{H}_2\text{O}$ : C, 76.11; H, 4.30; N, 8.53. Found: C, 76.54; H, 4.66; N, 8.88.

**Nickel(II) 2-(benzthiazol-2-yl)-5,10,15,20-tetraphenylporphyrin (3g).** Yield: 95%; UV:  $\lambda_{\text{max}}$  ( $\epsilon$ ,  $\text{M}^{-1} \text{cm}^{-1}$ ) 422 (420800), 539 (22700), 572 (6400) nm; IR (film): 1598, 1441, 1351, 1261, 1214, 1178, 1074, 1009, 968, 899, 799, 753, 700  $\text{cm}^{-1}$ ;  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  6.99–7.04 (m, 2H, ArH), 7.25–7.40 (m, 2H, ArH), 7.59–7.62 (m, 12H, *meso*-ArH), 7.92–7.94 (m, 8H, *meso*-ArH), 8.45 (d, 1H,  $\beta$ -pyrrolic H,  $J = 4.9$  Hz), 8.56 (d, 1H,  $\beta$ -pyrrolic H,  $J = 4.9$  Hz), 8.61–8.67 (m, 4H,  $\beta$ -pyrrolic H), 8.92 (s, 1H,  $\beta$ -pyrrolic H) ppm; HRMS: mass calculated for  $\text{C}_{51}\text{H}_{31}\text{N}_5\text{NiS}$  ( $\text{M}^+$ ): 803.1654; found: 803.1700. Anal. Calcd. for  $\text{C}_{51}\text{H}_{31}\text{N}_5\text{NiS}\cdot 2\text{H}_2\text{O}$ : C, 72.87; H, 4.20; N, 8.33. Found: C, 72.56; H, 4.36; N, 8.53.

**Nickel(II) 2-(1H-imidazo[4,5-b]pyridin-2-yl)-5,10,15,20-tetraphenylporphyrin (3h).** Yield: 82%; UV:  $\lambda_{\text{max}}$  ( $\epsilon$ ,  $\text{M}^{-1} \text{cm}^{-1}$ ) 425 (773100), 538 (64700), 569 (34000) nm; IR (film): 3367, 3400, 1598, 1414, 1350, 1263, 1072, 1008, 794, 776, 699  $\text{cm}^{-1}$ ;  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  6.98–7.05 (m, 3H, ArH), 7.57–7.69 (m, 12H, *meso*-ArH), 8.02 (s, 8H, *meso*-ArH), 8.45 (s, 1H,  $\beta$ -pyrrolic H), 8.65 (s, 1H,  $\beta$ -pyrrolic H), 8.72–8.78 (m, 4H,  $\beta$ -pyrrolic H), 9.2370 (s, 1H,  $\beta$ -pyrrolic H), 10.25 (s, 1H, NH) ppm; HRMS: mass calculated for  $\text{C}_{50}\text{H}_{31}\text{N}_7\text{Ni}$  ( $\text{M}^+$ ): 787.1994; found: 787.1434. Anal. Calcd. for  $\text{C}_{50}\text{H}_{31}\text{N}_7\text{Ni}$ : C, 76.16; H, 3.96; N, 12.43. Found: C, 76.26; H, 4.32; N, 11.88.

**Nickel(II) 2-(1H-imidazo[4,5-b]phenazin-2-yl)-5,10,15,20-tetraphenylporphyrin (4).** Yield: 80%; UV:  $\lambda_{\text{max}}$  ( $\epsilon$ ,  $\text{M}^{-1} \text{cm}^{-1}$ ) 430 (346200), 540 (51600), 578 (29700) nm; IR (film): 3400, 1598, 1420, 1351, 1305, 1218, 1160, 1073, 1009, 796, 752, 701  $\text{cm}^{-1}$ ;  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  7.05–7.10 (t, 2H, ArH,  $J = 7.30$  Hz), 7.49–7.61 (m, 12H, *meso*-ArH), 7.69–7.72 (m, 2H, ArH), 7.80–7.90 (m, 8H, *meso*-ArH), 8.10 (s, 1H, ArH), 8.18 (s, 1H, ArH), 8.32 (d, 1H,  $\beta$ -pyrrolic H,  $J = 5.1$  Hz), 8.37 (s, 1H, NH), 8.53–8.66 (m, 5H,  $\beta$ -pyrrolic H), 9.24 (s, 1H,  $\beta$ -pyrrolic H) ppm; HRMS: mass calculated for  $\text{C}_{57}\text{H}_{36}\text{N}_8\text{Ni}$  ( $\text{M} + 2\text{H}^+$ ): 890.2416; found: 890.3008. Anal. Calcd. for  $\text{C}_{57}\text{H}_{34}\text{N}_8\text{Ni}$ : C, 76.95; H, 3.85; N, 12.60. Found: C, 76.74; H, 3.65; N, 11.45.

**Nickel(II) 2-(1H-imidazo[4,5-b]anthraquinone-2-yl)-5,10,15,20-tetraphenylporphyrin (5).** Yield: 89%; UV:  $\lambda_{\text{max}}$  ( $\epsilon$ ,  $\text{M}^{-1} \text{cm}^{-1}$ ) 420 (369500), 540 (47800), 576 (24200) nm; IR (film): 3384, 1664, 1647, 1589, 1491, 1440, 1350, 1325, 1291, 1160, 1074, 1007, 798, 753, 702  $\text{cm}^{-1}$ ;  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  6.58–6.62 (m, 1H, ArH), 6.85–6.90 (m, 2H, ArH), 7.36 (s, 2H, ArH), 7.45 (s, 1H, ArH), 7.67 (s, 8H, *meso*-ArH), 7.73 (s, 4H, *meso*-ArH), 7.89–8.00 (m, 6H, *meso*-ArH), 8.21 (s, 2H, *meso*-ArH), 8.33 (d, 1H,  $\beta$ -pyrrolic H,  $J = 4.76$  Hz), 8.52 (d, 1H,  $\beta$ -pyrrolic H,  $J = 4.69$  Hz), 8.80–8.67 (m, 4H,  $\beta$ -pyrrolic H), 9.12 (s, 1H,  $\beta$ -pyrrolic H), 10.04 (s, 1H, NH) ppm; HRMS: mass calculated for  $\text{C}_{59}\text{H}_{34}\text{N}_6\text{NiO}_2$  ( $\text{M}^+$ ): 916.2097; found: 916.2141. Anal. Calcd. for  $\text{C}_{59}\text{H}_{34}\text{N}_6\text{NiO}_2\cdot\text{H}_2\text{O}$ : C, 75.57; H, 4.08; N, 8.96. Found: C, 75.42; H, 3.88; N, 8.57.

**Nickel(II) 2-(naphtho[1,2-*d*]oxazol-2-yl)-5,10,15,20-tetraphenylporphyrin (6).** To a solution of nickel(II) 2-formyl-5,10,15,20-tetraphenylporphyrin (0.050 g, 0.071 mmol) in 1,2-dichlorobenzene (10 mL), 1-amino-2-naphthol hydrochloride (0.027 g, 0.142 mmol) was added followed by addition of piperidine (0.005 mL). The reaction mixture was stirred at reflux for 16 h. After completion of the reaction, the mixture was cooled to room temperature and loaded on silica gel column. 1,2-Dichlorobenzene was removed on elution with hexane and desired product was isolated from the column by using chloroform as eluent. Yield: 75%; UV:  $\lambda_{\text{max}}$  ( $\epsilon$ ,  $\text{M}^{-1} \text{cm}^{-1}$ ) 425 (355900), 539 (33600), 575 (19600) nm; IR (film): 1598, 1441, 1351, 1281, 1218, 1176, 1075, 1008, 845, 798, 753, 700  $\text{cm}^{-1}$ ;  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  6.83 (t, 1H, ArH,  $J = 7.2$  Hz), 7.05–7.10 (m, 2H, ArH), 7.33 (d, 1H, ArH,  $J = 9$  Hz), 7.57 (t, 1H, ArH,  $J = 7.2$  Hz), 7.68–7.73 (m, 12H, *meso*-ArH), 7.90 (d, 2H, *meso*-ArH,  $J = 7.2$  Hz), 7.98 (d, 1H, ArH,  $J = 9$  Hz), 8.01 (s, 6H, *meso*-ArH), 8.50–8.54 (m, 2H,  $\beta$ -pyrrolic H), 8.64–8.77 (m, 4H,  $\beta$ -pyrrolic H), 9.28 (s, 1H,  $\beta$ -pyrrolic H) ppm; HRMS: mass calculated for  $\text{C}_{55}\text{H}_{34}\text{N}_5\text{NiO}$  ( $\text{M} + \text{H}$ ) $^+$ : 838.2117; found: 838.3940. Anal. Calcd. for  $\text{C}_{55}\text{H}_{33}\text{N}_5\text{NiO} \cdot 1.5\text{H}_2\text{O}$ : C, 76.32; H, 4.19; N, 8.09. Found: C, 76.39; H, 4.45; N, 8.25.

**2,6-Di(nickel(II) 5,10,15,20-tetraphenylporphyrin-2-yl) benzo[1,2-*d*;4,5-*d'*]diimidazole (7).** To a solution of nickel(II) 2-formyl-5,10,15,20-tetraphenylporphyrin (0.050 g, 0.071 mmol) in 1,2-dichlorobenzene (10 mL), 1,2,4,5-benzene-tetraamine tetrahydrochloride (0.010 g, 0.035 mmol) was added followed by the addition of piperidine (0.014 mL). The reaction mixture was then refluxed for 16 h under stirring. After completion of the reaction, the mixture was allowed to cool at room temperature and loaded on silica gel column. 1,2-Dichlorobenzene was removed by eluting the column with hexane. The desired product was isolated from the column using 5% MeOH in  $\text{CHCl}_3$  as eluent. Yield: 55%; UV:  $\lambda_{\text{max}}$  ( $\epsilon$ ,  $\text{M}^{-1} \text{cm}^{-1}$ ) 426 (410000), 538 (61700), 575 (35300) nm; IR (film): 3410, 1591, 1440, 1350, 1072, 1008, 835, 796, 752, 700  $\text{cm}^{-1}$ ;  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  6.73 (br s, 2H, ArH), 7.58–7.69 (s, 24H, *meso*-ArH), 7.78–7.88 (m, 14H, *meso*-ArH), 8.23 (br s, 4H, 2NH and *meso*-ArH), 8.45–8.67 (m, 12H,  $\beta$ -pyrrolic H), 9.08 (s, 2H,  $\beta$ -pyrrolic H), ppm; HRMS: mass calculated for  $\text{C}_{96}\text{H}_{59}\text{N}_{12}\text{Ni}_2$  ( $\text{M} + \text{H}$ ) $^+$ : 1495.3693; found: 1495.9106. Anal. Calcd. for  $\text{C}_{96}\text{H}_{58}\text{N}_{12}\text{Ni}_2 \cdot 0.5\text{H}_2\text{O}$ : C, 76.56; H, 3.95; N, 11.16. Found: C, 76.40; H, 4.14; N, 11.04.

**Bis-benzimidazoloporphyrin (8).** To a solution of nickel(II) 2-formyl-5,10,15,20-tetraphenylporphyrin (0.050 g, 0.071 mmol) in 1,2-dichlorobenzene (10 mL), 3,3'-diaminobenzidine (0.007 g, 0.035 mmol) was added. The reaction mixture was then refluxed for 16 h under stirring. After completion of the reaction, mixture was cooled to room temperature and loaded on silica gel column using hexane as a solvent. The desired product was obtained by eluting the column with 5% MeOH in  $\text{CHCl}_3$ . Yield: 65%; UV:  $\lambda_{\text{max}}$  ( $\epsilon$ ,  $\text{M}^{-1} \text{cm}^{-1}$ ) 426 (74410), 538 (76400), 568 (35200) nm; IR (film): 3410, 1598, 1441, 1351, 1304, 1073, 1008, 836, 796, 752, 700  $\text{cm}^{-1}$ ;  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  6.78–7.14 (m, 6H, ArH), 7.42–7.66 (m, 24H,

*meso*-ArH), 7.84–8.00 (m, 16H, *meso*-ArH), 8.49–8.91 (m, 14H,  $\beta$ -pyrrolic H and NH), 9.16 (s, 2H,  $\beta$ -pyrrolic H) ppm; HRMS: mass calculated for  $\text{C}_{102}\text{H}_{63}\text{N}_{12}\text{Ni}_2$  ( $\text{M} + \text{H}$ ) $^+$ : 1571.4006; found: 1571.5747. Anal. Calcd. for  $\text{C}_{102}\text{H}_{62}\text{N}_{12}\text{Ni}_2 \cdot 2\text{H}_2\text{O}$ : C, 76.14; H, 4.13; N, 10.45. Found: C, 76.26; H, 4.46; N, 9.87.

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