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Metal-catalyzed direct heteroarylation of C–H (*meso*) bonds in porphyrins: facile synthesis and photophysical properties of novel *meso*-heteroaromatic appended porphyrins†

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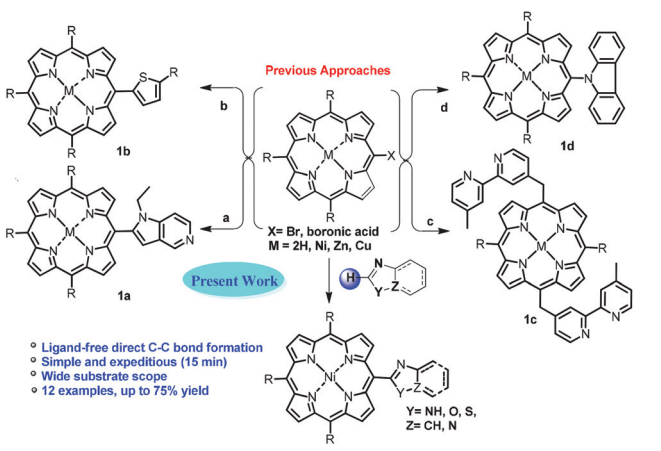
A simple and rapid microwave-assisted synthesis of heteroaromatic appended porphyrins using the Pd/Cu-catalyzed C–C coupling of *meso*-bromoporphyrins with various five- and six-membered heteroaromatic azoles has been successfully developed. The prepared heteroaromatic porphyrins **7a-lNi** were found to exhibit slightly red-shifted (~5–10 nm) Soret and Q bands. The developed reaction conditions are useful for the preparation of diversely substituted heteroaromatic porphyrins (A_3B- and A_2B_2-types).

Introduction

Porphyrins and metalloporphyrins are a distinct class of compounds utilized in various fields such as electron transport, catalysis, photodynamic therapy, optoelectronic devices and building blocks for supramolecular assembly.[1] Due to the interesting photophysical and electrochemical properties of metalloporphyrins, researchers have been making continuous efforts to modify donor–acceptor systems in porphyrins by using highly conjugated peripheral substituents at reactive *meso*- or β-positions.[2] For the modulation of the photophysical properties of parent porphyrins, various extended π-systems or conjugated with heteroaromatic moieties have been explored.[1b] In some of the reported porphyrinoids, structural modifications at the *meso*-position led to the absorption region (~400–800 nm) with the enhanced fluorescence profile (650–900 nm) and redox potential.[3] In recent years, a large number of novel porphyrins have been successfully synthesized by using transition metal-catalyzed cross-coupling reactions of halogenated porphyrins[4] as depicted in Scheme 1. For example, Osuka *et al.* identified highly fluorescence trimeric 5-azaindolylporphyrins **1a** through the Pd and Cu-catalyzed intramolecular cyclization of *meso*-(4-aminopyrid-3-yl) ethynyl porphyrins.[5] Very recently, Sessler's group reported porphyrin–oligothiophene conjugates **1b** involving the Suzuki reaction between bromothiophene and boronate porphyrins.[6] Similarly, the Ullmann coupling[7] of bromoporphyrin with carbazole or amine in the presence of special ligands like Pd-PEPPSI-IPent produced carbazole appended porphyrins **1d**. Therien *et al.* elaborated bipyridyl substituted porphyrins **1c** *via* the metal-mediated coupling reaction of haloporphyrin and dimethylbipyridyl systems.[8] Gryko and Lindsey prepared *meso*-heteroaromatic substituted porphyrins utilizing the TFA catalyzed condensation of heteroaryl-substituted dipyrromethane and dipyrromethane–dicarbinol.[9] Subsequently, Gryko and Tasior reported an efficient synthesis of *trans*-A_2B_2-porphyrins from the reaction of dipyrrane with appropriate pyridine–carboxaldehyde.[10]



Scheme 1 Existing and present methods to prepare heteroaromatic porphyrins. Reaction conditions: (a)(i) *N*-ethyl-3-ethynylpyridin-4-amine, $Pd(PPh_3)_4$, CuI, THF, 17 h, reflux and (ii) $Cu(OAc)_2$, 1,4-dioxane, reflux, 4 days; (b) *meso*-bromoporphyrin, bromoterthiophene, $Pd(PPh_3)_4$, Cs_2CO_3, toluene, 120 °C; (c) *meso*-bromoporphyrin, Bu_3Sn[4-(CH_2)-4′-$(CH_2$-bPy)], $Pd(PPh_3)_4$, THF, 80 °C, 48 h; (d) *meso*-bromoporphyrin, carbazole (10 equiv.), Pd-PEPPSI-IPent, THF, reflux, 42 h.

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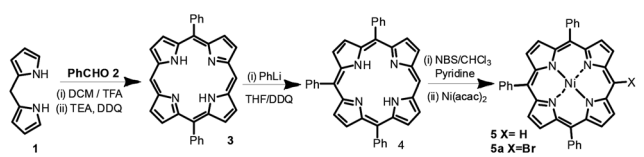
Generally, mixed condensation of two or more aldehydes with pyrrole generates isomeric heteroaromatic porphyrins, thus necessitating chromatographic purification.[2c] Nowadays, various C–C and C–N bond coupling reactions involving haloporphyrins and special ligands like Pd-PEPPSI-IPent, xantphos or DPEPhos are being frequently explored in the preparation of heteroarene linked porphyrins.[11] Despite the development of a few simplified protocols, the synthesis of heteroaromatic porphyrins is a challenging task and warrants the development of a facile and efficient method. In the recent past, metal-catalyzed direct arylation has been pursued with increasing interest to prepare functionalized heterocyclic frameworks. For instance, the arylation of azoles[12] and benzazoles including thiophene,[13] oxazole,[14] oxadiazole,[15] benzoxazole[16] and imidazo[1,2-*a*]pyridine[17] has been achieved from the reaction of heteroarenes with appropriate aryl halides in the presence of transition metal catalysts such as Pd,[18] Ru[19] and Rh.[20]

Given the appealing photophysical and electrochemical properties of porphyrin derivatives, it is desirable to prepare novel azole and benzazole annulated porphyrin frameworks. In continuation of our efforts to identify novel porphyrins with an improved absorption band, recently we prepared thiazolyl and oxadiazolyl porphyrins endowed with efficient DNA photonuclease activity.[21] Although the arylation of five/six-membered heterocycles has been known, however, direct heteroarylation of porphyrins involving haloporphyrins and azoles or benzazoles remains unexplored. To provide a facile route for novel heteroaromatic substituted porphyrin systems, we have developed an efficient microwave-assisted synthetic protocol for the preparation of diverse heteroaromatic appended porphyrins.

Results and discussion

Synthesis

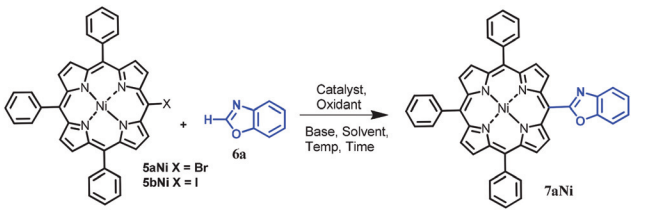
The preparation of 5-(benzoxazol-2′-yl)-10,15,20-triphenylporphyrinato-nickel(II) **7aNi** involves the use of readily available 5-bromo-10,15,20-triphenylporphyrinato-nickel(II) **5aNi** and benzoxazole **6a**. The key intermediate **5aNi** was achieved by the synthetic route as illustrated in Scheme 2. Firstly, in a modified Lindsey method,[22] the reaction of dipyrrane **1** and freshly distilled benzaldehyde **2** in dry DCM with a catalytic amount of trifluoroacetic acid (TFA) produced 5,15-diphenylporphyrin **3**. The treatment of **3** with phenyllithium and DDQ afforded purple coloured *meso*-5,10,15-triphenylporphyrin **4** in 80% yield. A further reaction of **4** with *N*-bromosuccinimide (NBS) afforded free-base *meso*-bromoporphyrin (70% yield) which was metallated with Ni(acac)$_2$ under refluxing conditions to afford **5aNi** in 92% yield.[23]



Scheme 2 Synthesis of bromoporphyrin **5aNi**.

To achieve **7aNi**, our investigation started with **5aNi** and benzoxazole **6a** as model substrates to screen different reaction conditions. Initially, the Pd(OAc)$_2$ catalyzed reaction of **5aNi** and **6a** in the presence of K_3PO_4 and PivOH under conventional as well as microwave (MW) irradiation at 140 °C in DMF exclusively generated dehalogenated porphyrin **5** (Table 1, entries 1 and 2). Next, the combination of Pd(OAc)$_2$ and PPh_3 delivered only a trace amount of **7aNi** (Table 1, entry 3). The use of Cu(OAc)$_2$ with Cs_2CO_3 also did not afford **7aNi** (Table 1, entry 4). To our delight, the combination of CuI and Pd(OAc)$_2$ in the presence of Cs_2CO_3 in DMF at 140 °C (24 h) delivered **7aNi** in 55% yield (Table 1, entry 5). To improve the product yield and efficiency, the reaction of **5aNi** and **6a** was explored

Table 1 Optimization of the reaction conditions



Entry	Base	Catalyst additive	Solvent	Temp [°C]	Time [min]	Yield[c] [%]
1	K_3PO_4	Pd(OAc)$_2$ PivOH	DMF	140	1440	NR[a]
2	K_3PO_4	Pd(OAc)$_2$ PivOH	DMF	140	10	NR[b]
3	K_3PO_4	Pd(OAc)$_2$ PPh_3	DMF	120	1440	Trace
4	Cs_2CO_3	Cu(OAc)$_2$	DMF	120	1440	NR[a]
5	Cs_2CO_3	Pd(OAc)$_2$ CuI	DMF	140	1440	55[a]
6	Cs_2CO_3	Pd(OAc)$_2$ CuI	DMF	120	10	73[b]
7	Cs_2CO_3	Pd(OAc)$_2$ CuBr	DMF	120	10	64[b]
8	Cs_2CO_3	Pd(OAc)$_2$ CuI	DMF	80	10	Trace
9	Cs_2CO_3	Pd(OAc)$_2$ CuI	DMF	140	10	Trace[b]
10	Cs_2CO_3	Pd(OAc)$_2$ CuI	DMF	120	10	40[d]
11	Cs_2CO_3	Pd(OAc)$_2$ CuI	Toluene	120	10	Trace[b]
12	Cs_2CO_3	Pd(OAc)$_2$ CuI	DMSO	120	10	Trace[b]
13	Cs_2CO_3	Pd(OAc)$_2$ CuI	THF	90	10	NR[b]
14	K_2CO_3	Pd(OAc)$_2$ CuI	DMF	120	15	60[b]
15	Na_2CO_3	Pd(OAc)$_2$ CuI	DMF	120	10	Trace[b]

[a] Reaction conditions: **5aNi** (0.0693 mmol), **6a** (0.1386 mmol), Pd(OAc)$_2$ (10 mol%), additive (10 mol%), base (2.0 equiv.), DMF (2.5 mL) 140 °C, 24 h. [b] Reaction performed under MW irradiation (100 W), 120 °C, 10 min. NR = no reaction. [c] Isolated yield. [d] **5bNi** (0.0693 mmol), DMF (2.5 mL), **6a** (0.1386 mmol), Pd(OAc)$_2$ (10 mol%), CuI (10 mol%), Cs_2CO_3 (2.0 equiv.), MW (100 W), 120 °C, 10 min.

with focused MW. The usefulness of MW irradiation in organic transformations is very popular due to its beneficial features such as efficient heating, less energy consumption, shorter reaction time and high product yields.[24] The reaction of **5aNi** and **6a** in DMF under MW irradiation at 120 °C for 10 min afforded **7aNi** in 73% yield (Table 1, entry 6). Changing the additive from CuI to CuBr afforded **7aNi** with a reduced yield (64%) and lowering the temperature (80 °C) failed to afford the desired product (Table 1, entries 7 and 8). The reaction yield dropped at an elevated temperature (140 °C) with the formation of unidentified side products (Table 1, entry 9). Under similar reaction conditions, the use of (5-iodo-10,15,20-triphenylporphyrinato)nickel(II) **5bNi** instead of **5aNi** afforded **7aNi** in low yield (Table 1, entry 10). Attempts to conduct the reaction in solvents like toluene, DMSO and THF were failed (Table 1, entries 11–13) to produce **7aNi** in good yield. Similarly, the use of K_2CO_3 in DMF afforded **7aNi** in moderate yield (60%), whereas Na_2CO_3 offered **7aNi** in a trace amount (Table 1, entries 14 and 15).

Finally, we found that the optimal conditions include the use of $Pd(OAc)_2$ (10 mol%), CuI (10 mol%) and Cs_2CO_3 (2 equiv.) in DMF at 120 °C under MW irradiation for 10 min for the synthesis of **7aNi** from the reaction of **5aNi** with **6a**. HRMS of the porphyrin **7aNi** ionized by MALDI-TOF showed a molecular ion peak for $C_{45}H_{28}N_5NiO$ at *m*/*z* 712.1392 (calc. *m*/*z* 712.1617).

Having the optimized reaction conditions in hand, we performed the reaction of **5aNi** with 6-methylbenzoxazole **6b** to obtain **7bNi** in 70% yield. Next, the reaction of **5aNi** with *N*-substituted benzimidazole **6c** furnished **7cNi** in 65% yield (Table 2). It is noteworthy to mention that we successfully extended the protocol to couple porphyrin **5aNi** with a biologically active molecule, caffeine **6d**,[16c] and furnished **7dNi** in 68% yield (Table 2). The ^{1}H NMR spectrum of **7dNi** showed characteristic singlets at 3.61 ppm and 3.88 ppm for $CONCH_3$ and NCH_3, respectively. The MALDI-MS spectrum of **7dNi** displayed a molecular ion peak corresponding to $C_{46}H_{32}N_8NiO_2$ appearing at *m*/*z* 786.1514 (calc. *m*/*z* 786.2002).

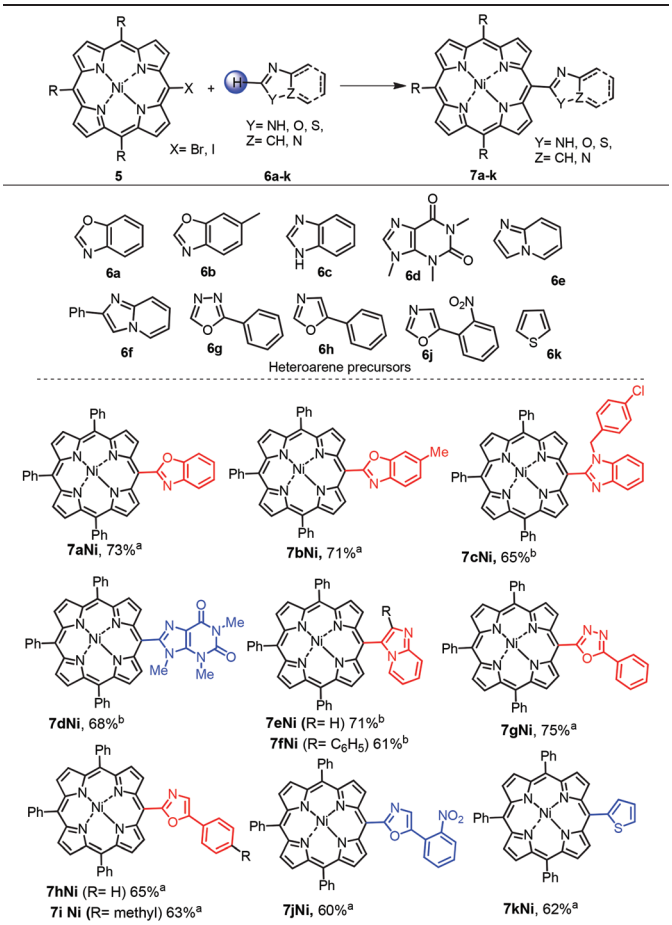
Furthermore, the reaction of **5aNi** with imidazo[1,2-*a*]pyridine **6e**, afforded **7eNi** in moderate yield (58%). But the use of K_2CO_3 as the base with the extended reaction time (10 min) enhanced the reactivity of **5aNi** with **6e** and **6f** to afford porphyrins **7eNi** (70%) and **7fNi** (61%), respectively (Table 2). Similarly, the coupling reactions of **5aNi** with oxadiazole **6g** and oxazoles **6h–j** were also smoothly proceeded to furnish **7gjNi** in good yields (60–75%). Under standard reaction conditions, the thienyl group was also incorporated into porphyrin **7kNi** in 62% yield.

The scope of the reaction was further expanded by preparing [bis(benzoxazolyl)porphyrinato]nickel(II) **7lNi** (64% yield) from the reaction of 5,15-dibromo-10,20-diphenylporphyrin **5c** with 2.5 equivalents of **6a** (Scheme 3).

Photophysical studies

Next, we studied the UV-vis absorption spectra of porphyrins **7a-lNi** using analytical grade chloroform (Fig. 1). Interestingly,

Table 2 Preparation of *meso*-heteroaromatic appended porphyrins **7a-kNi**



[a] Reaction conditions: **5aNi** (0.0693 mmol), **6a–b** or **6g–j** (0.1386 mmol), $Pd(OAc)_2$ (10 mol%), Cs_2CO_3 (2.0 equiv.), CuI (10 mol%), DMF (2.5 mL), MW (100 W), 120 °C. [b] **5aNi** (0.0693 mmol), **6c–f** (0.1732 mmol), $Pd(OAc)_2$ (10 mol%), K_2CO_3 (2.5 equiv.), CuI (10 mol%), DMF (3 mL), MW (100 W), 120 °C, 10 min.

Scheme 3 Synthesis of [bis(benzoxazolyl)porphyrinato]nickel(II) **7lNi**.

absorption peaks of **7a-lNi** exhibited a bathochromic shift when compared to those of tetraphenylporphyrin (H2TPP). In particular, porphyrins **7dNi**, **7fNi** and **7jNi** exhibited 5–10 nm red-shifted Soret bands ranging 416–427 nm probably due to electron-rich (metalloporphyrin) and electron-deficient units which may act as push–pull type architectures stabilized by charge-transfer.[25] In the case of porphyrin **7dNi** with caffeine nucleus, a Soret band was observed at 420 nm with increased intensity indicating an efficient energy transfer among the

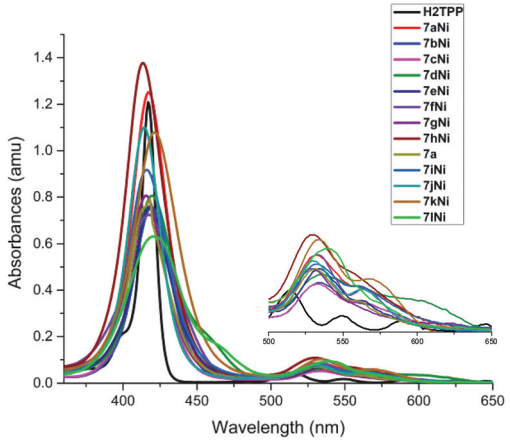
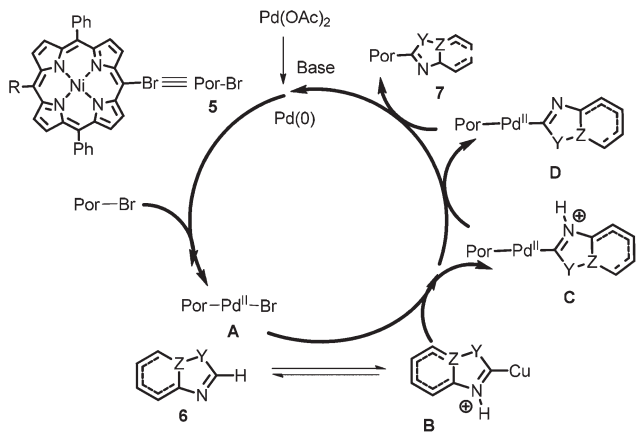


Fig. 1 UV–visible absorption spectra (chloroform) of porphyrins **7a-jNi**.

singlet states of porphyrin and the caffeine moiety. Intense broadening in the Q bands of **7dNi** was observed in the visible region (λ_{max} 500–650 nm) as illustrated in Fig. 1. The incorporation of conjugated imidazo[1,2-*a*]pyridine with porphyrin **7fNi** induced systematic changes both in the Soret and Q bands. Increased π-conjugation in the porphyrin core may cause the splitting of the π–π* level, thereby reducing the HOMO–LUMO gap to induce a bathochromic shift and broadening in the Soret and Q bands.[26] Interestingly, A_2B_2-type porphyrin **7lNi** also showed an intense absorption peak at 421 nm.

Based on the experimental and the literature reports,[18a,27] a plausible mechanism for the formation of **7a-lNi** is depicted in Scheme 4. Initially, oxidative addition of Pd(0) to bromoporphyrin **5a** is believed to produce the porphyrin Pd(II) complex (**A**). Reactive azole–copper species **B**, *in situ* generated from azole **6** and Cu-catalyst, undergoes transmetallation with **A** to furnish Pd(II) complex **C**/**D**. Finally, reductive elimination of **C**/**D** may lead to porphyrins **7** with concomitant regeneration of the active catalyst.



Scheme 4 Plausible pathway for the formation of porphyrins **7**.

Conclusions

In summary, we have developed a MW-assisted rapid and versatile synthesis of diverse *meso*-heteroaromatic appended porphyrins **7a-lNi** by the coupling of *meso*-bromoporphyrins with various azoles **6a–k** in the presence of the Pd–Cu catalytic system. Identified reaction conditions were also extended to assemble bis-heteroarylporphyrins and could be useful for the preparation of A_3B and A_2B_2-types of heteroaromatic appended porphyrins. Porphyrins **7a-lNi** displayed slightly red-shifted (5–10 nm) Soret and Q bands when compared to parent porphyrins. Overall, we have effectively used operationally simple catalytic systems to access π-extended porphyrins possessing impressive electron donor–acceptor chromophoric systems. The developed protocol is believed to be useful in the design and synthesis of new porphyrinoids in fewer steps. Further applications in structural modifications and functionalization of *meso*-heteroaromatic appended porphyrins are presently under progress.

Experimental sections

Materials

All chemicals and reagents were purchased from commercially available sources like Merck, Sigma-Aldrich and Spectrochem. The key intermediate 5-bromo-10,15,20-triphenylporphyrin **5aNi** and 5-iodo-10,15,20-triphenylporphyrin **5bNi** were prepared by a literature procedure.[28] Reactions were performed using CEM Discover focused microwave apparatus in a 10 mL microwave tube, and monitored by thin layer chromatography (TLC) performed using a silica precoated alumina sheet ordered from Merck. The crude products were purified by column chromatography using silica gel of 100–200 mesh size. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker Advance II 400 MHz spectrometer in $CDCl_3$ using tetramethyl silane (TMS) as the internal standard. ^{1}H and ^{13}C NMR chemical shifts are expressed in parts per million (ppm) relative to TMS (0 ppm) and analysis performed at 20 °C. Mass analysis carried out on a MALDI–TOF MS spectrometer was performed using 2,5-dihyrdoxybenzoic acid (DHB) as the matrix. The UV-vis spectra of the synthesized porphyrins derivatives were recorded by using a steady state absorption spectrophotometer (Jasco V-650) in UV spectroscopy grade chloroform.

(a) Synthesis of (5,15-dibromo-10,20-diphenylporphyrinato)nickel(II) 5cNi. To a solution of 5,15-diphenylporphyrin **3** (200 mg) in chloroform (250 mL) was added pyridine (4 mL). After stirring the contents for 5 min, a solution of *N*-bromosuccinimide (2.2 equivalent) in chloroform (100 mL) was added dropwise over a period of 30 min. The reaction mixture was quenched with acetone (50 mL) and concentrated under reduced pressure. The residue thus obtained was purified by column chromatography on silica gel (100–200 mesh) and eluted with hexane/chloroform to isolate free-base 5,15-dibromoporphyrin in 80% yield. Next, $Ni(acac)_2$ (5 mmol) was added to a solution of 5,15-bromoporphyrin (1 mmol) in

toluene (30 mL) and the mixture was heated at 110 °C for 3 h. After the completion of metallation, toluene was evaporated and extracted with chloroform (200 mL). The organic layer was washed with water (250 mL), dried over sodium sulphate and distilled at reduced pressure. The crude product was purified by column chromatography using silica (100–200 mesh) and chloroform : hexane (1 : 9) as the eluent to afford **5cNi**. Yield 85% ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.45 (d, J = 5.0 Hz, 4H), 8.74 (d, J = 5.0 Hz, 4H), 7.95 (dd, J = 7.8, 6.3 Hz, 4H), 7.84–7.62 (m, 6H). UV/vis ($CHCl_3$): λ_{max} (ε, L Mol^{-1} cm^{-1}) nm = 417 (457 000), 534 (32 600) nm; the spectral data of **5cNi** were in good agreement with the literature.[29]

(b) Synthesis of [5-(benzoxazol-2′-yl)-10,15,20-triphenylporphyrinato]nickel(II) 7aNi. A microwave vial containing a magnetic stir bar was charged with **5aNi** (0.069 mmol, 46.5 mg), **6a** (0.083 mmol, 9.88 mg), cesium carbonate (0.1386 mmol, 45 mg), $Pd(OAc)_2$ (10 mol%), CuI (10 mol%) and DMF (2.5 mL). The reaction mixture was irradiated with focused MW (100 W) at 120 °C for 10 min. The progress of the reaction was monitored by TLC. Upon completion of the reaction, the contents were filtered over silica gel and washed with chloroform (50 mL). The filtrate was concentrated using a rotary evaporator and the residue was purified by column chromatography using chloroform : hexane : triethylamine (20 : 80 : 1 to 50 : 50 : 1) as an eluent to afford the pure product **7aNi**. Yield 73%. mp > 300 °C; UV/vis ($CHCl_3$): λ_{max} (ε, L Mol^{-1} cm^{-1}) nm = 418 (397 000), 535 (35 000) nm; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.44 (d, J = 5.1 Hz, 2H), 8.84 (d, J = 5.1 Hz, 2H), 8.72 (d, J = 4.9 Hz, 2H), 8.68 (d, J = 4.9 Hz, 2H), 8.14–8.12 (m, 1H), 8.03–7.95 (m, 6H), 7.82–7.81 (m, 1H), 7.72–7.67 (m, 9H), 7.58–7.50 (m, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.4, 152.2, 143.5, 142.8, 142.3, 142.2, 140.5, 140.4, 133.9, 133.7, 133.6, 132.9, 132.2, 132.1, 128.0, 127.0, 126.9, 120.9, 119.9, 111.0, 101.6 ppm; IR (neat, ATR) ν_{max} (cm^{-1}) = 3160, 3020, 2956, 2360, 2260, 1951, 1720, 1597, 1437, 1720, 1597, 1437, 1360, 1273, 995, 794, 694, 563; MALDI-MS m/z calcd for $C_{45}H_{28}N_5NiO$ $[M + H]^+$: 712.1647; found 712.1392.

[5-(6′-Methylbenzoxazol-2′-yl)-10,15,20-triphenylporphyrinato]nickel(II) 7bNi. Prepared by following the same procedure as for **7aNi** and **7bNi** was isolated as a purple solid. Yield 70%; mp > 300 °C; UV/vis ($CHCl_3$): λ_{max} (ε, L Mol^{-1} cm^{-1}) nm = 419 (377 500), 534 (27 500) nm; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.40 (d, J = 5.1 Hz, 2H), 8.84 (d, 5.0 Hz, 2H), 8.78–8.70 (m, 2H), 8.68 (d, J = 4.9 Hz, 2H), 8.00–7.98 (m, 7H), 7.71–7.62 (m, 10 H), 7.36 (d, J = 8.2 Hz, 1H), 2.61 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.7, 143.5, 142.8, 142.2, 140.4, 136.0, 133.6, 132.8, 132.1, 130.9, 128.8, 127.9, 126.9, 121.1, 120.2, 119.8, 111.1, 101.8, 21.9 ppm; IR (neat, ATR) ν_{max} (cm^{-1}) = 3165, 3023, 2959, 2361, 2265, 1960, 1725, 1600, 1440, 1597, 1437, 1375, 1273, 998, 795, 691, 562; MALDI-MS m/z calcd for $C_{46}H_{30}N_5NiO$ $[M + H]^+$: 726.1804; found 726.1558.

[5-(1-(4-Chlorobenzyl)-benzo[*d*]imidazole-2′-yl)-10,15,20-triphenylporphyrinato]nickel(II) 7cNi. A microwave vial containing a magnetic stir bar was charged with **5aNi** (45.6 mg, 0.0693 mmol), **6c** (84 mg, 0.345 mmol), potassium carbonate (23.90 mg, 0.1732 mmol), $Pd(OAc)_2$ (10 mol%), CuI (10 mol%) and DMF (3 mL). The reaction mixture was irradiated with focused MW (100 W) at 120 °C for 10 min. The progress of the reaction was monitored by TLC in 50% hexane/chloroform. After completion of the reaction, the mixture was filtered over silica gel and washed with chloroform (2 × 50 mL). The filtrate was concentrated and the residue was purified by column chromatography using chloroform : hexane : TEA (20 : 80 : 1 to 70 : 30 : 1) as an eluent to afford a pure purple coloured solid. Yield 65% (36.5 mg), mp > 300 °C; UV/vis ($CHCl_3$): λ_{max} (ε, L Mol^{-1} cm^{-1}) nm = 417 (380 550), 533 (265 400) nm; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.80 (t, J = 4.3 Hz, 4H), 8.78 (d, J = 1.9 Hz, 1H), 8.76 (s, 1H), 8.71 (d, J = 4.9 Hz, 2H), 8.26 (d, J = 8.0 Hz, 1H), 8.01 (d, J = 6.0 Hz, 2H), 7.84 (d, J = 7.8 Hz, 1H), 7.76–7.68 (m, 10H), 7.57 (d, J = 6.7 Hz, 1H), 7.50–7.47 (m, 2H), 7.43 (dd, J = 6.0, 3.5 Hz, 2H), 7.25 (d, J = 7.7 Hz, 1H), 6.71 (t, J = 7.6 Hz, 2H), 6.32 (d, J = 8.4 Hz, 2H), 4.84 (s, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.2, 151.7, 143.5, 142.8, 142.6, 140.7, 140.5, 136.1, 135.0, 133.8, 133.7, 132.8, 132.4, 131.9, 130.8, 128.4, 128.1, 128.0, 127.0, 126.9, 119.9, 116.0, 115.1, 110.4, 103.7, 99.1, 48.1 ppm; IR (neat, ATR) ν_{max} (cm^{-1}) = 3010, 2919, 2376, 2376, 2291, 1751, 1696, 1620, 1620, 1535, 1450, 1450, 1342, 1249, 1157, 1095, 1010, 802, 702, 646, 470; MALDI-MS m/z calcd for $C_{52}H_{34}ClN_6Ni$ $[M + 2H]^+$: 836.1665; found 836.5734.

[5-(1′,3′,7′-Trimethyl-xanthin-8′yl)-10,15,20-triphenylporphyrinato]nickel(II) 7dNi. Purple colour solid, yield 68%; mp > 300 °C; UV/vis ($CHCl_3$): λ_{max} (ε, L Mol^{-1} cm^{-1}) nm = 420 (402 700), 532 (35 150), 559 (17 500) and 550–600 nm boarding of the Q-band; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.96 (s, 1H), 9.20 (d, J = 4.4 Hz, 2H), 8.97–8.89 (m, 4H), 8.77 (d, J = 4.9 Hz, 3H), 7.78 (br, 10H), 7.56 (d, J = 8.5 Hz, 1H), 7.37 (d, J = 2.0 Hz, 1H), 7.31 (s, 1H), 3.88 (s, 3H), 3.61 (s, 6H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.8, 151.4, 150.6, 147.1, 142.6, 141.9, 141.7, 141.6, 139.4, 132.9, 132.7, 131.8, 131.8, 127.00, 125.9, 118.6, 107.6, 105.6, 101.1, 32.9, 28.9 ppm; IR (neat, ATR) ν_{max} (cm^{-1}) = 3120, 2930, 2885, 2500, 2144, 2013, 1751, 1697, 1620, 1522, 1396, 1219, 1096, 1026, 948, 810, 771, 632; MALDI-MS m/z calcd for $C_{46}H_{33}N_8NiO_2$ $[M + H]^+$: 787.2080; found 787.1574.

[5-(Imidazo[1,2-*a*]pyridin-3′yl)-10,15,20-triphenylporphyrinato]nickel(II) 7eNi. Prepared by following the same procedure as for **7cNi** and **7eNi** was isolated as a purple solid. Yield 70%; mp > 300 °C; UV/vis ($CHCl_3$): λ_{max} (ε, L Mol^{-1} cm^{-1}) nm = 418 (377 450), 532 (35 000), 559 (17 000) nm; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.94 (s, 1H), 9.59 (s, 1H), 9.21 (dd, J = 4.8 Hz, 2H), 9.16 (s, 1H), 8.99 (d, J = 4.8 Hz, 1H), 8.91 (d, 4.8 Hz, 1H), 8.95 (d, J = 4.7 Hz, 1H), 8.85 (d, J = 4.8 Hz, 1H), 8.13–8.00 (m, 5H), 7.93 (d, J = 9.1 Hz, 1H), 7.82 (dd, J = 8.1, 1.7 Hz, 2H), 7.78–7.66 (m, 6H), 7.36–7.32 (m, 1H), 7.07–6.93 (m, 3H), 6.72–6.69 (m, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.9, 143.5, 143.4, 143.2, 143.0, 142.9, 142.7, 141.8, 140.7, 140.6, 140.3, 134.2, 133.9, 133.8, 133.7, 132.9, 132.8, 132.7, 132.6, 132.5, 132.4, 132.3, 128.3, 127.9, 127.8, 127.5, 127.1, 126.9, 125.7, 124.2, 118.9, 118.6, 117.6, 115.4, 105.3, 104.1 ppm; IR (neat, ATR) ν_{max} (cm^{-1}) = 3012, 2954, 2916, 2846, 2384, 2291, 2074, 1743, 1697, 1635, 1535, 1460, 1342, 1257, 1010, 981, 802, 632;

MALDI-MS *m*/*z* calcd for $C_{45}H_{29}N_6Ni$ $[M + H]^+$: 711.1807; found 711.1891.

[5-(2′-Phenylimidazo[1,2-*a*]pyridin-3′-yl)-10,15,20-triphenylporphyrinato]nickel(II) 7fNi. Purple solid: yield 61%; mp > 300 °C; UV/vis ($CHCl_3$): λ_{max} (ε, L Mol^{-1} cm^{-1}) nm = 418 (366 000), 533 (41 500), 556 (42 500) nm; ^1H NMR (400 MHz, $CDCl_3$) δ 9.82 (s, 1H), 9.11 (d, J = 4.7 Hz, 2H), 8.88 (d, J = 4.7 Hz, 2H), 8.81 (d, J = 4.8 Hz, 2H), 8.77–8.72 (m, 2H), 8.77–8.64 (m, 2H), 8.46 (br, 1H), 7.99 (br, 5H), 7.76–7.68 (m, 10H), 7.49–7.47 (m, 2H), 7.38–7.33 (m, 2H), 6.62 (t, J = 6.7 Hz, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.8, 143.5, 143.4, 143.3, 142.9, 142.8, 140.5, 140.4, 133.8, 133.7, 133.0, 132.9, 130.8, 127.0, 119.9, 119.8, 119.4, 117.3, 115.6, 113.4, 106.1, 100.0, 99.6 ppm; IR (neat, ATR) ν_{max} (cm^{-1}) = 3012, 2954, 2916, 2384, 2291, 2074, 1743, 1697, 1635, 1535, 1460, 1342, 1010, 981, 802, 632; MALDI-MS *m*/*z* calcd for $C_{51}H_{33}N_6Ni$ $[M + H]^+$: 787.2120; found 787.1453.

[5-(2′-Phenyl-1,3,4-oxadiazol-5′-yl)-10,15,20-triphenylporphyrinato]nickel(II) 7gNi. Purple solid: yield 75%; mp > 300 °C; UV/vis ($CHCl_3$): λ_{max} (ε, L Mol^{-1} cm^{-1}) nm = 418 (402 950), 535 (35 050) nm; ^1H NMR (400 MHz, $CDCl_3$) δ 9.39 (d, J = 5.1 Hz, 2H), 8.86 (d, J = 5.1 Hz, 2H), 8.74 (d, J = 4.9 Hz, 2H), 8.70 (d, J = 4.9 Hz, 2H), 8.31 (d, J = 7.4, 2H), 8.02–7.98 (m, 6H), 7.70 (m, 8H), 7.58–7.60 (m, 4H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.5, 166.0, 143.6, 142.5, 142.3, 140.3, 137.6, 134.2, 133.7, 133.6, 133.0, 132.4, 132.0, 131.5, 130.9, 130.0, 129.3, 129.1, 128.9, 128.3, 128.0, 127.2, 127.1, 127.0, 126.9, 124.1, 123.5, 121.6, 120.1, 97.4 ppm; IR (neat, ATR) ν_{max} (cm^{-1}) = 3120, 3110, 2956, 2360, 1951, 1805, 1597, 1442, 1327, 1257, 995, 1027, 995, 884, 786, 748, 694, 104; MALDI-MS *m*/*z* calcd for $C_{46}H_{29}N_6NiO$ $[M + H]^+$: 739.1756; found 739.1260.

[5-{(5′-Phenyl)-oxazol-2′-yl}-10,15,20-triphenylporphyrinato]nickel(II) 7hNi. Purple solid: yield 63%; mp > 300 °C; UV/vis ($CHCl_3$): λ_{max} (ε, L Mol^{-1} cm^{-1}) nm = 417 (458 667), 540 (36 000) nm; ^1H NMR (400 MHz, $CDCl_3$) δ 8.77 (d, J = 4.9 Hz, 2H), 8.66 (d, J = 4.9 Hz, 2H), 8.02 (t, J = 7.2 Hz, 3H), 7.85–7.63 (m, 5H), 7.65–7.49 (m, 5H), 7.53–7.42 (m, 3H), 7.41–7.33 (m, 2H), 7.20–7.25 (m, 2H), 7.08–6.82 (m, 4H), 6.57–6.62 (m, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.2, 143.2, 142.9, 142.6, 142.0, 140.9, 136.5, 133.8, 132.9, 132.4, 132.3, 131.2, 130.8, 130.4, 128.3, 127.8, 126.7, 125.7, 118.9, 114.4, 114.2, 114.1, 113.4, 110.7, 105.7 ppm; IR (neat, ATR) ν_{max} (cm^{-1}) = 3363, 2985, 2831, 2250, 1728, 1458, 1373, 1219, 1103, 817, 748, 663; MALDI-MS *m*/*z* calcd for $C_{47}H_{30}N_5NiO$ $[M]^+$: 737.1724; found 737.1238.

[5-{(5′-*p*-Tolyl)-oxazol-2′-yl}-10,15,20-triphenylporphyrinato]nickel(II) 7iNi. Purple solid, yield 65%, mp > 300 °C; UV/vis ($CHCl_3$): λ_{max} (ε, L Mol^{-1} cm^{-1}) nm = 417 (305 667), 543 (2500) nm; ^1H NMR (400 MHz, $CDCl_3$) δ 9.86 (s, 1H), 9.44 (d, J = 4.7 Hz, 2H), 9.15 (d, J = 4.4 Hz, 2H), 8.95–8.85 (m, 4H), 8.06 (d, J = 6.2 Hz, 3H), 7.94 (d, J = 7.7 Hz, 2H), 7.82–7.66 (m, 10H), 7.54 (d, J = 7.4 Hz, 2H), 7.32 (d, J = 7.8 Hz, 3H), 2.44 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.9, 143.1, 142.8, 142.5, 142.3, 140.9, 140.8, 136.5, 133.8, 133.7, 133.0, 132.3, 132.0, 131.4, 130.9, 130.3, 128.3, 127.8, 127.7, 127.7, 126.9, 125.7, 120.0, 119.2, 114.4, 114.2, 114.0, 112.9, 110.7, 29.7 ppm; IR (neat, ATR) ν_{max} (cm^{-1}) = 3161, 2951, 2916, 2846, 1735, 1612, 1573, 1465, 1315, 1148, 1080, 1010, 964, 802, 604; MALDI-MS *m*/*z* calcd for $C_{48}H_{33}N_5NiO$ $[M]^+$: 751.1882; found 751.2351.

[5-{5′-(2-Nitrophenyl)-oxazol-2′-yl}-10,15,20-triphenylporphyrinato]nickel(II). Faint green solid: yield 60%; mp > 300 °C; UV/vis ($CHCl_3$): λ_{max} (ε, L Mol^{-1} cm^{-1}) nm = 418 (361 667), 530 (26 000) nm; ^1H NMR (400 MHz, $CDCl_3$) δ 9.85 (s, 1H), 9.39 (d, J = 3.9 Hz, 2H), 9.14 (d, J = 3.7 Hz, 2H), 8.94 (dd, J = 14.1, 4.3 Hz, 2H), 8.87 (d, J = 4.0 Hz, 2H), 8.05 (d, J = 5.8 Hz, 2H), 7.98 (d, J = 8.0 Hz, 2H), 7.88 (d, J = 8.0 Hz, 2H), 7.77–7.66 (m, 8H), 7.58–7.52 (m, 3H), 7.32 (d, J = 2.4 Hz, 1H), 7.09 (dd, J = 8.2, 2.4 Hz, 1H), 6.62 (d, J = 8.2 Hz, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.6, 143.4, 142.6, 140.5, 139.3, 134.0, 133.9, 133.8, 133.7, 132.8, 132.7, 132.6, 132.6, 131.7, 130.07, 129.97, 129.87, 128.1, 128.0, 127.9, 127.0, 126.9, 124.6, 124.7, 124.5, 123.5, 121.9, 119.4, 115.6, 114.1 ppm; IR (neat, ATR) ν_{max} ($cm^{-1)}$ = 3363, 2985, 2831, 2250, 1728, 1540, 1458, 1373, 1249, 1103, 817, 748, 663; MALDI-MS *m*/*z* calcd for $C_{47}H_{28}N_6NiO_3$ $[M]^+$ 782.1576; found 782.9997

[5-(2-Thienyl)-10,15,20-triphenylporphyrinato]nickel(II) 7kNi. Purple solid; yield 62%; mp > 300 °C; UV/vis ($CHCl_3$): λ_{max} (relative intensity) = 421 (0.631), 545 (0.065), 588 nm; ^1H NMR (400 MHz, $CDCl_3$) δ 9.31 (d, J = 4.9 Hz, 1H), 9.07 (d, J = 5.0 Hz, 2H), 8.82–8.80 (m, 3H), 8.54–8.56 (m, 6H), 8.08–806. (m, 1H), 8.03 (d, J = 5.1 Hz, 1H), 7.85–7.78 (m, 1H), 7.71–7.61 (m, 8H), 7.47–7.49 (d, J = 1.8 Hz, 1H) ppm;^{13}C NMR (100 MHz, $CDCl_3$) δ 163.7, 143.5, 142.8, 142.2, 140.4, 136.0, 133.6, 132.8, 132.1, 130.9, 128.8, 127.9, 126.9, 126.1, 121.1, 120.2, 119.8, 111.1, 101.8 ppm; IR (neat, ATR) ν_{max} (cm^{-1}): 3445, 2925, 2362, 1630, 1520, 1480, 1430, 790, 1011; MALDI-MS *m*/*z* calcd for $C_{42}H_{26}N_4NiS$ $[M]^+$: 676.1232; found 676.0805.

(C) Synthesis of [5,15-bis(benzoxazolyl)-10,20-diphenylporphyrinato]nickel(II) 7lNi. A microwave vial containing a magnetic stir bar was charged with **5cNi** (50 mg, 0.073 mmol), **6a** (21.97 mg, 0.184 mmol), cesium carbonate (45 mg, 0.184 mmol), $Pd(OAc)_2$ (20 mol%), CuI (10 mol%) and DMF (2.5 mL). The reaction mixture was irradiated with focused MW (100 W) at 120 °C for 15 min. The progress of the reaction was monitored by TLC. Upon completion of the reaction, the contents were filtered over silica gel and washed with chloroform (50 mL). The filtrate was concentrated using a rotary evaporator and the obtained residue was purified by column chromatography using chloroform : hexane (9 : 1) as an eluent to afford pure **7lNi**. Yield 64%, mp > 300 °C; UV/vis ($CHCl_3$): λ_{max} (ε, L Mol^{-1} cm^{-1}) nm = 420 (270 000), 535 (35 000) nm; ^1H NMR (400 MHz, $CDCl_3$) δ 9.44 (d, J = 5.1 Hz, 2H), 8.84 (d, J = 5.1 Hz, 2H), 8.72 (d, J = 4.9 Hz, 2H), 8.68 (d, J = 4.9 Hz, 2H), 8.14–8.12 (m, 1H), 8.03–7.95 (m, 4H), 7.82–7.81 (m, 1H), 7.72–7.67 (m, 6H), 7.58–7.50 (m, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.4, 152.2, 143.5, 142.8, 142.3, 142.2, 140.5, 140.4, 133.9, 133.7, 133.6, 132.9, 132.2, 132.1, 128.0, 127.0, 126.9, 120.9, 119.9, 111.0, 101.6 ppm; IR (neat, ATR) ν_{max} (cm^{-1}) = 3160, 3023, 2960, 2362, 1955, 1720, 1597, 1725, 1598, 1437, 1363, 1273, 995, 794, 694, 563; MALDI-MS *m*/*z* calcd for $C_{48}H_{28}N_8NiO_2$ $[M + H]^+$: 753.2333; found *m*/*z* (calcd for *m*/*z* 753.4474).

Conflicts of interest

There are no conflicts to declare.

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