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Efficient Approach to Functionalized β-Imidazolylporphyrins

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Dedicated to the 90-th anniversary of Academician I. P. Beletskaya

The applicability of the Debus-Radziszewski condensation of 2-formylporphyrins with aromatic α-diketones for the straightforward preparation of 2-functionalized porphyrin derivatives by means of the imidazole heterocyclic bridging unit was investigated in details. The successful transformation of the starting materials was observed regardless the meso-substitution pattern of the porphyrin macrocycle. In contrast, the reactivity and stability of the aromatic α-diketone is revealed to possess considerable influence onto the reaction path. Thus, the application of phenanthrene- and phenanthrolinedione as well as benzil allowed successful preparation of the expected derivatives, while acenaphthene-quinone, naphthoquinone or 3,5-di-tert-butyl-o-quinone demonstrated low stability under reaction conditions and thus low conversion of the formylporphyrin precursor. The obtained compounds were isolated in pure form and characterized with a set of physicochemical methods. The successful demetalation of the representatives of the synthesized family of derivatives opens further access to a variety of metal complexes.

Keywords: Porphyrins, formylporphyrins, β-imidazolylporphyrins, Debus-Radziszewski imidazole synthesis.

Эффективный подход к получению β-имидазолилпорфиринов

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Показана возможность использования реакции конденсации Дебуса-Радзишевского для получения функционализированных 2-имидазолилпорфиринов исходя из 2-формил-замещенных предшественников и ароматических α-дикетонов. Показано, что успешное протекание конденсации практически не зависит от природы мезо-заместителей порфиринового макроцикла. Напротив, природа используемого в реакции ароматического дикетона оказывает значительное влияние на ее протекание. Так, в случае фенантрен- или фенантролиндиона, а также дибензоила была достигнута полная конверсия исходных 2-формилпорфиринов. В то же время аценафтенхинон, 1,2-нафтохинон и 3,5-ди-трет-бутил-о-бензохинон оказались нестабильны в условиях реакции, что приводило к низкой конверсии 2-формилпорфирина. Полученные соединения были выделены в индивидуальном виде и охарактеризованы с использованием набора физико-химических методов анализа. Показана возможность успешного деметаллирования представителей полученного семейства 2-имидазолилпорфиринов, что открывает возможности дальнейшего получения металлокомплексов на их основе.

Ключевые слова: Порфирины, формилпорфирины, β-имидазолилпорфирины, конденсация Дебуса-Радзишевского.

Introduction

Targeted design of polyfunctional molecular building blocks remains an actual task over past decades. A wide diversity of polytopic molecules have been used for the construction of coordination compounds of various architecture. The topology of the rigid molecular building blocks plays a crucial role in the formation of supramolecular systems of desired structure. In this respect convenient molecular scaffolds with multiple modification possibilities are required for development of such building blocks.

Porphyrins have proved their versatility as starting compounds in the mentioned research area.[1] These molecules bring together the rigidity of the macrocyclic core and the possibility of multiple substitution providing access to molecular blocks of specific shape.[2] The unique combination of the physical-chemical properties, *e.g.* optical and electrochemical, makes porphyrins outstanding candidates for the development of the novel functional materials.[3] Thus, the development of selective pathways for the introduction of peripheral substituents to the porphyrin core is of great importance and the modification of porphyrin β-positions is of particular interest allowing to mimic the naturally occurring derivatives.

Among the possible modification paths of the porphyrin, β-positions formylation is a versatile approach, allowing formation of a variety of functional derivatives. Despite the postulated decreased reactivity of formylporphyrins,[4] some transformations were reported for them to date. Thus, formyl group in the β-position of a porphyrin can be smoothly converted to CN-substituent.[5]

The examples of the application of 2-formylporphyrins as components of the heterocyclic condensation are also reported. The interaction of 2-formylporphyrins with a series of aromatic α-diamines and *o*-substituted anilines resulted in formation of the corresponding benzazolo-derivatives in moderate to high yields, including dimeric porphyrin species, connected at β-positions.[6,7] Further investigations revealed the enhanced photoactivity of the cationic forms of β-imidazolylporphyrins in the generation of reactive oxygen species and photoinactivation of gram-negative bacteria.[8,9] The investigation of the interaction of the β-imidazolium-substituted porphyrins and artificial lipid membranes was also performed and the influence of this process onto their photodynamic activity was determined.[10] 2-Formylporphyrins were also successfully introduced to Kröhnke reaction allowing preparation of 2-(4'-terpyridyl)-substituted derivatives.[11] Such terpyridyl-substituted porphyrins were further tested for the application in PDT[12] and aPDT.[13] Changing 2-acetylpyridine with 2,6-diacetylpyridine in the terpyridine synthesis allowed preparation of porphyrin-oligopyridine triades, which are of interest from both coordinational and topological point of view.[14]

Known for more than a century,[15] the Debus-Radziszewski condensation was recognized as a versatile and convenient tool for the formation of substituted imidazoles.[16] Single example of the application of Debus-Radziszewsky condensation with 2-formylporphyrin is already reported for the formation of 4,5-diphenylimidazol-2-yl fragment.[17] Nevertheless, the mentioned example remains occasional and the potential of employment of α-diketones in the synthesis of β-imidazolylporphyrins is currently unstudied. Moreover, the synthetic availability and chemical stability of aromatic dioxoderivatives in comparison with the corresponding diamines makes them attractive starting compounds for the preparation of a variety of functional porphyrins. In this respect the development of straight-forward approaches to the derivatives bearing various *meso*-substituents and aromatic fragments annulated to the imidazole heterocycle could provide possibilities for the fine tuning of the physicochemical properties of the obtained hetero-dyads.

Our ongoing research is devoted to the development of efficient approaches towards functionalized porphyrin molecular building blocks with special emphasis to the application of classical noble metal-free transformations.[18–21] In this respect the formation of the imidazole heterocycles was shown to be a convenient approach for the conjugation of porphyrins and peripheral coordination centers.[18,22,23] Thus, we have successfully generalized the approaches for the preparation of functionalized *meso*-imidazolyl-,[19,24] β-imidazo-,[18,25,26] β-pyrazino-,[22,27,28] and expanded β-pyrazino-derivatives.[29] In the present work we focused on the determination of the application scope of Debus-Radziszewski condensation for the preparation of a series of porphyrins containing functional β-imidazolyl-substituents.

Experimental

All the chemicals were reagent grade and purchased from commercial suppliers unless otherwise stated. The solvents used in the work were freshly distilled following the conventional methods.[30] Copper(II) and nickel(II) tetraarylporphyrinates **Cu-1a-g**[31–37] and **Ni-1a**[38] were prepared according to published procedures. MALDI-TOF mass spectra were recorded at Bruker Daltonics Ultraflex spectrometer in positive ions mode without matrix. UV-Vis spectra were recorded at Unicam UV-4 spectrophotometer in rectangular quartz cells with 0.1-10 mm optical path in 250-900 nm range. ^{1}H NMR spectra were recorded at Bruker Avance III spectrometer with 600.13 MHz proton frequency in $CDCl_3$ at 303K with the use of the residual solvent signal as an internal reference. The measurements were made at the Shared Facility Centers of the Institute of Physical Chemistry and Electrochemistry RAS.

Preparation of acenaphthenequinone. The procedure was based on the published protocol.[39] Acenaphthene (1.54 g, 10 mmol) was dissolved in CCl_4 (30 mL) and NBS (1.78 g, 10 mmol) was added. The resulting mixture was heated at 85 °C for 1 h, cooled to ambient temperature and filtered. The obtained filtrate was transferred to the distillation setup, diluted with DMSO (30 mL) and heated at 120 °C for 5 h. During the first hour CCl_4 was distilled off. After cooling to ambient temperature the mixture was added dropwise into water (100 mL). The formed crystalline precipitate was filtered, washed successively with water and dried at filter to yield 893 mg (49%) of the acenaphthenequinone. ^{1}H NMR ($CDCl_3$) δ ppm: 8.32 (d, ^{3}J = 8.3 Hz, 1H, CH), 8.15 (d, ^{3}J = 7.0 Hz, 1H, CH), 7.89 (dd, ^{3}J = 8.3 Hz, 7.0, 1H, CH).

*General procedure for the preparation of **Ni-2a** and **Cu-2a-g***. The starting metal(II) tetraarylporphyrinate **Ni-1a** or **Cu-1a-g** was dissolved or suspended in 1,2-dichloroethane (DCE, 145 mL per mmol). DMF (2.5 mL per mmol of porphyrin) and $POCl_3$ (2.5 mL per mmol of porphyrin) were added, the mixture was stirred at ambient temperature for 15 min and subsequently heated at 60 °C until the complete consumption of the starting material was detected by TLC (Table 1). Afterwards, the reaction mixture was cooled to ambient temperature and aqueous $NaOAc\cdot 3H_2O$ (10 g *per* 1 mL of $POCl_3$) was added upon vigorous stirring. The resulting two-phase system was transferred to the separating funnel with $CHCl_3$/H_2O mixture and extracted. The organic phase was separated, dried over anhydrous Na_2SO_4 and evaporated. The residue was applied in CH_2Cl_2 to column packed with silica in hexane and eluted with CH_2Cl_2/hexane mixtures (0→100% of DCM). The fraction of the pure product was evaporated to dryness. The spectral characteristics of the obtained compounds **Ni-2a**, **Cu-2b** and **Cu-2d-f** are in consistency with the published ones.[5,40–42]

Cu-2a. Yield: 93%. *m/z*: calcd. for $C_{57}H_{52}CuN_4O$ $[M]^+$ 871.3, found 871.3. UV-Vis ($CHCl_3$) λ_{max} nm (log ε): 309 (4.29), 432 (5.43), 554 (4.16), 596 (4.12).

Cu-2c. Yield: 87%. MS *m/z*: calcd. for $C_{61}H_{60}CuN_4O$ $[M]^+$ 927.4, found 927.4. UV-Vis ($CHCl_3$) λ_{max} nm (log ε): 307 (4.32), 424 (5.37), 548 (4.22), 584 (3.78).

Cu-2g. Yield: 81%. MS *m/z*: calcd. for $C_{45}H_{20}Cl_8CuN_4O$ $[M]^+$ 974.8, found 975.0. UV-Vis ($CHCl_3$) λ_{max} nm (log ε): 312 (4.30), 429 (5.41), 553 (4.19), 597 (4.17).

*Preparation of **2H-2a***. **Cu-1a** (497 mg, 0.588 mmol) was treated with DMF and $POCl_3$ following the procedure for the formylation of metal porphyrins described above. After complete consumption of the starting material and generation of the cationic Vilsmeier adduct the reaction mixture was cooled to ambient temperature and concentrated H_2SO_4 (5.9 mL) was slowly added to reaction mixture upon vigorous stirring. The mixture was stirred for 10 min and the solution of NaOH (12.85 g, 321 mmol) in H_2O (50 mL) was added. The mixture was extracted with water and the organic layer was evaporated. The residue was applied in CH_2Cl_2 to column packed with silica in hexane and eluted with hexane/ CH_2Cl_2 mixture (10→60% of CH_2Cl_2) to afford of **2H-2a**. Yield: 285 mg (60%). The characteristics of the obtained compound are in consistency with the published ones.[43]

*General procedure for the condensation of **2H-2a**, **Ni-2a** and **Cu-2a-g** with α-diketones*. The procedure was based on the previously reported protocol for the preparation of *meso*-imidazolylporphyrins.[19] The starting β-formylporphyrin (0.1 mmol) was dissolved in a mixture of $CHCl_3$ (20 mL) and AcOH (2 mL). Next, α-diketone (2 equiv.) and NH_4OAc (20 equiv.) were added. The mixture was slowly refluxed for 24 h and monitored by TLC. In the cases when complete consumption of the starting material was not achieved within 24 h (Table 2 and 3, additional portions of the diketone (2 equiv.) and NH_4OAc (20 equiv.) were added and refluxing was continued for additional 24 h. After completion of the reaction the mixture was cooled to ambient temperature and extracted with H_2O. The organic layer was separated, dried over anhydrous Na_2SO_4 and evaporated in vacuo. The residue was applied to column packed with silica in hexane (for **2H-3a**, **Cu-3a-f** and **Ni-3a**) or in $CHCl_3$ (for **2H-4a**, **Cu-4a-f** and **Ni-4a**). In the case of phenanthrene-containing porphyrins the column was eluted with hexane/CH_2Cl_2 mixtures (0 → 100% of CH_2Cl_2). The phenanthroline-containing derivatives were eluted with $CHCl_3$/MeOH mixtures (0→5% of MeOH), containing 0.1% of Et_2NH. The fractions containing the target β-areneimidazolyl-porphyrins were evaporated to dryness.

2H-3a. Yield: 96%. ^{1}H NMR ($CDCl_3$) δ ppm: 9.26 (s, 1H, $H_β$), 9.18 (s, 1H, NH), 8.83 (d, ^3J = 8.4 Hz, 1H, H_{Ar}), 8.78 (t, ^3J = 8.0 Hz, 2H, H_{Ar}), 8.69 (d, ^3J = 4.7 Hz, 1H, $H_β$), 8.66 (d, ^3J = 4.7 Hz, 1H, $H_β$), 8.63 (d, ^3J = 4.8 Hz, 1H, $H_β$), 8.62 (d, ^3J = 4.9 Hz, 1H, $H_β$), 8.60 (d, ^3J = 4.7 Hz, 1H, $H_β$), 8.50 (d, ^3J = 4.7 Hz, 1H, $H_β$), 7.83 (d, ^3J = 7.6 Hz, 1H, H_{Ar}), 7.76 (t, ^3J = 7.4 Hz, 1H, H_{Ar}), 7.72 (t, ^3J = 7.3 Hz, 1H, H_{Ar}), 7.68 (t, ^3J = 7.6 Hz, 2H, H_{Ar}), 7.30 (s, 2H, H_{Mes}), 7.28 (s, 2H, H_{Mes}), 7.26 (s, 2H, H_{Mes}), 6.79 (s, 2H, H_{Mes}), 2.64 (s, 3H, $H_{p\text{-}Me}$), 2.62 (s, 3H, $H_{p\text{-}Me}$), 2.58 (s, 3H, $H_{p\text{-}Me}$), 1.96 (s, 6H, $H_{o\text{-}Me}$), 1.94 (s, 6H, $H_{o\text{-}Me}$), 1.91 (s, 6H, $H_{o\text{-}Me}$), 1.88 (s, 6H, $H_{o\text{-}Me}$), 1.56 (s, 3H, $H_{p\text{-}Me}$), -2.26 (s, 2H, NH_{Por}). *m/z*: calcd. for $C_{71}H_{62}N_6$ $[M]^+$ 998.5, found 998.6. UV-Vis ($CHCl_3$) λ_{max} nm (log ε): 261 (4.91), 308 (4.51), 423 (5.38), 520 (4.45), 557 (3.99), 598 (3.95), 653 (3.68).

Ni-3a. Yield: 77%. ^{1}H NMR ($CDCl_3$) δ ppm: 9.17 (s, 1H, $H_β$), 8.81-8.77 (m, 3H, H_{Ar}), 8.75 (d, ^3J = 8.5 Hz, 1H, H_{Ar}), 8.53-8.51 (2d, ^3J = 4.8 Hz, 2H, $H_β$), 8.51-8.49 (2d, ^3J = 4.9 Hz, 2H, H_{Ar}), 8.42 (d, J = 4.8 Hz, 1H, $H_β$), 8.34 (d, ^3J = 4.8 Hz, 1H, $H_β$), 7.74 (t, ^3J = 7.4 Hz, 1H, H_{Ar}), 7.69-7.62 (m, 3H, H_{Ar}), 7.21 (s, 2H, H_{Mes}), 7.19 (s, 2H, H_{Mes}), 7.16 (s, 2H, H_{Mes}), 6.68 (s, 2H, H_{Mes}), 2.57 (s, 3H, $H_{p\text{-}Me}$), 2.55 (s, 3H, $H_{p\text{-}Me}$), 2.51 (s, 3H, $H_{p\text{-}Me}$), 1.90 (s, 6H, $H_{o\text{-}Me}$), 1.88 (s, 6H, $H_{o\text{-}Me}$), 1.87 (s, 6H, $H_{o\text{-}Me}$), 1.86 (s, 6H, $H_{o\text{-}Me}$), 1.48 (s, 3H, $H_{p\text{-}Me}$). The resonance of the imidazole NH fragment is presumably overlapped with multiplets at ~8.52 ppm. *m/z:* calcd. for $C_{71}H_{60}N_6Ni$ $[M]^+$ 1054.4, found 1054.5. UV-Vis ($CHCl_3$) λ_{max} nm (log ε): 260 (4.65), 309 (4.23), 422 (5.17), 535 (4.16), 570 (3.82).

Cu-3a. Yield: 74%. *m/z*: calcd. for $C_{71}H_{60}CuN_6$ $[M]^+$ 1059.4, found 1058.5. UV-Vis ($CHCl_3$) λ_{max} nm (log ε): 422 (5.49), 546 (4.30), 582 (3.76).

Cu-3b. Yield: 66%. *m/z*: calcd. for $C_{63}H_{44}CuN_6$ $[M]^+$ 947.0, found 946.3. UV-Vis ($CHCl_3$) λ_{max} nm (log ε): 261 (4.87), 423 (5.47), 546 (4.34), 585 (3.83).

Cu-3c. Yield: 97%. *m/z*: calcd. for $C_{75}H_{68}CuN_6$ $[M]^+$ 1115.5, found 1115.9. UV-Vis ($CHCl_3$) λ_{max} nm (log ε): 307 (4.32), 424 (5.37), 548 (4.22), 584 (3.78).

Cu-3d. Yield: 89%. *m/z*: calcd. for $C_{63}H_{44}CuN_6O_4$ $[M]^+$ 1011.3, found 1011.5. UV-Vis ($CHCl_3$) λ_{max} nm (log ε): 256 (4.87), 425 (5.46), 548 (4.34), 583 (3.86).

Cu-3e. Yield: 98%. *m/z*: calcd. for $C_{75}H_{68}CuN_6O_4$ $[M]^+$ 1179.5, found 1178.5. UV-Vis ($CHCl_3$) λ_{max} nm (log ε): 265 (4.78), 301 (4.62), 426 (5.08), 549 (4.53), 584 (4.07).

Cu-3f. Yield: 67%. *m/z*: calcd. for $C_{67}H_{44}CuN_6O_8$ $[M]^+$ 1123.3, found 1123.7. UV-Vis ($CHCl_3$) λ_{max} nm (log ε): 284 (4.53), 306 (4.47), 421 (5.49), 545 (4.28), 579 (3.76).

Cu-3g. Yield: 60%. *m/z*: calcd. for $C_{59}H_{28}Cl_8CuN_6$ $[M]^+$ 1162.9, found 1162.9. UV-Vis ($CHCl_3$) λ_{max} nm (log ε): 259 (4.79), 311 (4.36), 419 (5.03), 546 (4.25), 584 (3.91).

2H-4a. Yield: 89%. ^{1}H NMR ($CDCl_3$) δ ppm: 9.47 (s, 1H, NH), 9.26 (s, 1H, $H_β$), 9.26-9.21 (m, 2H, H_{Ar}), 9.10 (d, ^3J = 8.0 Hz, 1H, H_{Ar}), 8.72 (d, ^3J = 4.8 Hz, 1H, $H_β$), 8.69 (d, ^3J = 4.7 Hz, 1H, H_b), 8.65-8.60 (m, 3H, $H_β$), 8.51 (d, ^3J = 4.8 Hz, 1H, $H_β$), 8.25 (d, ^3J = 7.9 Hz, 1H, H_{Ar}), 7.79 (dd, ^3J = 8.0, ^4J = 4.3 Hz, 1H, H_{Ar}), 7.76 (dd, ^3J = 8.0, ^4J = 4.3 Hz, 1H, H_{Ar}), 7.32 (s, 2H, H_{Mes}), 7.30 (s, 3H, H_{Mes}), 7.27 (s, 2H, H_{Mes}), 6.82 (s, 2H, H_{Mes}), 2.66 (s, 3H, $H_{p\text{-}Me}$), 2.64 (s, 3H, $H_{p\text{-}Me}$), 2.60 (s, 3H, $H_{p\text{-}Me}$), 1.97 (s, 6H, $H_{o\text{-}Me}$), 1.94 (s, 6H, $H_{p\text{-}Me}$), 1.92 (s, 6H, $H_{p\text{-}Me}$), 1.89 (s, 6H, $H_{p\text{-}Me}$), 1.65 (s, 3H, $H_{o\text{-}Me}$), -2.26 (s, 2H, NH_{Por}). *m/z*: calcd. for $C_{69}H_{60}N_8$ $[M]^+$1000.5, found 1000.6.

Ni-4a. Yield: 98%. ^{1}H NMR ($CDCl_3$) δ ppm: 9.20-9.17 (m, 3H, H_{Ar}), 9.16 (s, 1H, $H_β$), 9.07 (dd, ^3J = 8.0, ^4J =1.7 Hz, 1H, H_{Ar}), 8.54-8.49 (m, 4H, $H_β$), 8.43 (d, ^3J = 4.9 Hz, 1H, $H_β$), 8.32 (d, ^3J = 4.9 Hz, 1H, $H_β$), 7.74 (dd, ^3J = 8.0, ^4J = 4.3 Hz, 1H, H_{Ar}), 7.67 (dd, ^3J = 8.1, ^4J = 4.3 Hz, 1H, H_{Ar}), 7.21 (s, 2H, H_{Mes}), 7.19 (s, 2H, H_{Mes}), 7.16 (s, 2H, H_{Mes}), 6.68 (s, 2H, H_{Mes}), 2.57 (s, 3H, $H_{p\text{-}Me}$), 2.55 (s, 3H, $H_{p\text{-}Me}$), 2.51 (s, 3H, $H_{p\text{-}Me}$), 1.89 (s, 6H, $H_{o\text{-}Me}$), 1.87 (s, 12H, $H_{o\text{-}Me}$), 1.85 (s, 6H, $H_{o\text{-}Me}$), 1.54 (s, 3H, $H_{p\text{-}Me}$). *m/z*: calcd. for $C_{69}H_{59}N_8Ni$ $[M]^+$ 1057.4, found 1057.5. UV-Vis ($CHCl_3$) λ_{max} nm (log ε): 291 (4.49), 423 (5.26), 535 (4.20), 569 (3.86).

Cu-4a. Yield: 76%. *m/z*: calcd. for $C_{69}H_{58}CuN_8$ $[M]^+$ 1061.4, found 1061.4. UV-Vis ($CHCl_3$) λ_{max} nm (log ε): 289 (4.50), 422 (5.46), 545 (4.28), 581 (3.75).

Cu-4b. Yield: 94%. *m/z*: calcd. for $C_{61}H_{42}CuN_8$ $[M]^+$ 949.3, found 949.4. UV-Vis ($CHCl_3$) λ_{max} nm (log ε): 242 (4.67), 286 (4.55), 424 (5.45), 546 (4.28), 581 (3.80).

Cu-4c.Yield: 94%. *m/z*: calcd. for $C_{73}H_{66}CuN_8$ $[M]^+$ 1117.5, found 1117.8. UV-Vis ($CHCl_3$) λ_{max} nm (log ε): 280 (4.68), 425 (5.47), 547 (4.24), 584 (3.82).

Cu-4d. Yield: 95%. *m/z*: calcd. for $C_{61}H_{42}CuN_8O_4$ $[M]^+$ 1014.3, found 1014.5. UV-Vis ($CHCl_3$) λ_{max} nm (log ε): 285sh (4.61), 428 (5.40), 548 (4.24), 584 (3.78).

Cu-4e. Yield: 93%. *m/z*: calcd. for $C_{73}H_{66}CuN_8O_4$ $[M]^+$ 1181.5, found 1181.8. UV-Vis ($CHCl_3$) λ_{max} nm (log ε): 287 (4.68), 427 (5.54), 548 (4.41), 585 (3.98).

Cu-4f. Yield: 35%. *m/z*: calcd. for $C_{65}H_{42}CuN_8O_8$ $[M]^+$ 1125.2, found 1126.4. UV-Vis ($CHCl_3$) λ_{max} nm (log ε): 269 (4.64), 306 (4.43), 424 (5.55), 546 (4.26), 582 (3.84).

Cu-4g. Yield: 37%. *m/z*: calcd. for $C_{57}H_{26}Cl_8CuN_8$ $[M]^+$ 1165.9, found 1166.3. UV-Vis ($CHCl_3$) λ_{max} nm (log ε): 306sh (4.28), 422 (5.44), 547 (4.25), 587 (3.98).

Ni-5a. Yield: 6%. *m/z*: calcd. for $C_{69}H_{58}N_6Ni$ $[M]^+$ 1028.4, found 1027.6.

Ni-6a. Yield: 3%. *m/z*: calcd. for $C_{67}H_{58}N_6Ni$ $[M]^+$ 1004.4, found 1005.5.

Ni-7a. Yield: 10%. *m/z*: calcd. for $C_{71}H_{72}N_6Ni$ $[M]^+$ 1066.5, found 1065.7. UV-Vis ($CHCl_3$) λ_{max} nm (log ε): 421 (5.39), 533 (4.33), 564 (3.85).

Ni-8a. Yield: 94%. ^{1}H NMR ($CDCl_3$) δ ppm: 9.07 (s, 1H, H_β), 8.60-8.53 (m, 4H, H_β), 8.48 (d, ^3J = 4.7 Hz, 1H, H_β), 8.37 (d, ^3J = 4.9 Hz, 1H), 8.23 (s, 1H, NH), 7.72 (d, ^3J = 7.5 Hz, 2H, $H_{o\text{-}Ph}$), 7.42-7.36 (m, 4H, H_{Ph}), 7.35-7.30 (m, 4H, H_{Ph}), 7.24 (s, 2H, H_{Mes}), 7.23 (s, 2H, H_{Mes}), 7.18 (s, 2H, H_{Mes}), 6.88 (s, 2H, H_{Mes}), 2.59 (s, 3H, $H_{p\text{-}Me}$), 2.58 (s, 3H, $H_{p\text{-}Me}$), 2.54 (s, 3H, $H_{p\text{-}Me}$), 1.97 (s, 3H, $H_{p\text{-}Me}$), 1.92 (s, 6H, $H_{o\text{-}Me}$), 1.91 (s, 12H, $H_{o\text{-}Me}$), 1.90 (s, 6H, $H_{o\text{-}Me}$). *m/z*: calcd. for $C_{71}H_{62}N_6Ni$ $[M]^+$ 1056.4, found 1055.5. UV-Vis ($CHCl_3$) λ_{max} nm (log ε): 296 (4.42), 419 (5.36), 534 (4.28), 568 (3.88).

General procedure for the demetalation of ***Cu-3a****,* ***Cu-4a****,* ***Ni-3a*** *and* ***Ni-4a****.* H_2SO_4 (0.12 mL) was added to a solution of metal(II) porphyrin (0.02 mmol) in TFA (0.83 mL) and the obtained mixture was stirred at ambient temperature for 5 min. Afterwards the mixture was diluted with $CHCl_3$ (5 mL) and water (5mL). The mixture was neutralized with NaOH, transferred to separating funnel with $CHCl_3$ (50 mL) and water (50 mL) and extracted. The organic phase was separated, evaporated to dryness and the obtained free-base porphyrin was purified at silica as described above for the corresponding metal complexes.

Results and Discussion

The strategy for the introduction of the heterocyclic fragment to the β-position of the porphyrin core implies the preliminary preparation of β-formyl derivatives and their subsequent interaction with α-dicarbonyl compounds under Debus-Radziszewski conditions. In the present work, we have selected a representative series of porphyrins, bearing *meso*-substituent with different electronic and steric properties, as well as a set of α-dicarbonyl compounds of different origin. The starting compounds used in the present research are shown in Chart 1.

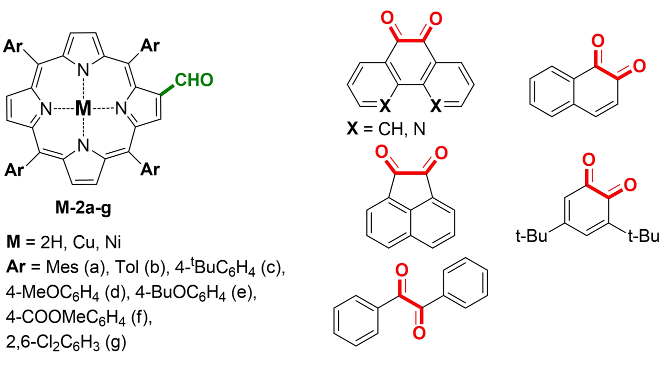
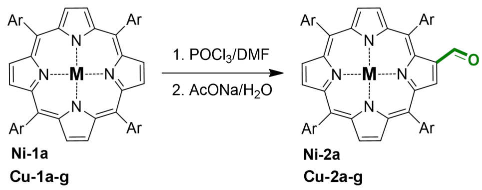


Chart 1. The designation of the compounds used in the work.

Table 1. The synthesis of β-formylporphyrins.

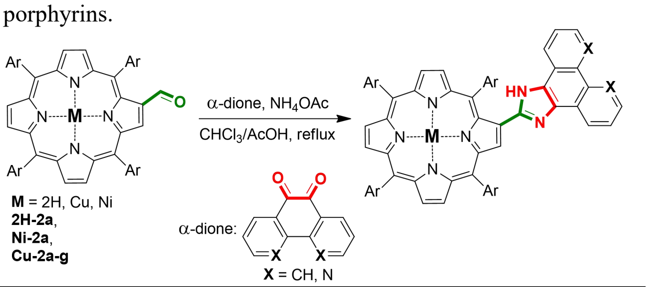


Substrate	Vilsmeier reagent, equiv.	Time, h	t, °C	Product, yield, %
Ni-1a	28	48	60	**Ni-2a**, 95
Cu-1a	11	72	90	**Cu-2a**, 93
Cu-1b	45	72	60	**Cu-2b**, 85
Cu-1c	45	72	60	**Cu-2c**, 87
Cu-1d	45	72	60	**Cu-2d**, 48
Cu-1e	45	24	60	**Cu-2e**, 74
Cu-1f	45	24	80	**Cu-2f**, 71
Cu-1g	22	48	80	**Cu-2g**, 81

The starting Cu^{II} and Ni^{II} porphyrins were smoothly converted to the corresponding β-formyl derivatives upon interaction with Vilsmeier reagent in 1,2-dichloroethane (Table 1). At this step we have found that the preliminary preparation of the formylating agent is not required for the successful transformation of the starting metal(II) porphyrins and the experimental implementation allows the subsequent addition of DMF and $POCl_3$ directly to the solution of the porphyrin. Moreover, the application of low amount of the Vilsmeier reagent allowed to prepare the formyl derivatives **M-2a-g** in high yields. The decreased yield of **Cu-2d** possibly could be assigned to the poor solubility of the corresponding Cu^{II} tetra(4-methoxyphenyl)porphyrin **Cu-1d** in the reaction medium. The formylation of **Cu-1f**,**g** bearing peripheral electron-with-drawing groups did not reveal any considerable decrease of their reactivity and was also performed successfully. The demetalation of **Cu-2a** upon *in situ* treatment with H_2SO_4 provided the corresponding free-base β-formylporphyrin **2H-2a** in 60% overall yield.

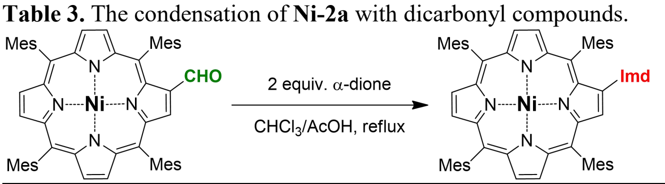
First, the interaction of the prepared series of metal(II) 2-formylporphyrins with phenanthrene- and phenanthroline-diones was investigated (Table 2) for the testification of the generality of the process. The free-base 2-formyl-tetramesitylporphyrin was also involved into the inter-action, allowing to evaluate the influence of the metal center on the reactivity of the porphyrin component of the condensation. The used conditions of the condensation were based on our previously reported protocol, developed for *meso*-formylporphyrins,[19] which consisted in prolonged reflux of formylporphyrin substrates in the $CHCl_3$/AcOH mixture in the presence of the excess of α-diketone and NH_4OAc. Thus, in all cases the interaction successfully provided the corresponding β-areneimidazolylporphyrins. The yields of the products were found to be virtually independent from the nature of the *meso*-substituents except for the 2,6-dichlorophenyl ones. Application of the latter porphyrin showed the decrease of the product yield presumably originating from the steric effects of *o*-chlorine atoms. Generally, it can be concluded, that the reactivity of 2-formylporphyrins substrates considerably exceeds the one of *meso*-formyl derivatives,[19] that could be implicitly observed by the comparison of reaction time and reagent ratio, required for the complete conversion of the starting material.

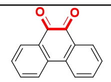
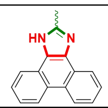
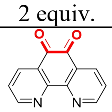
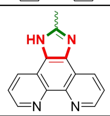
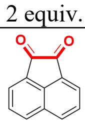
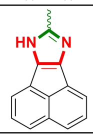
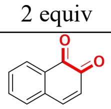
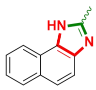
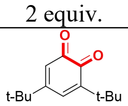
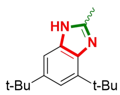
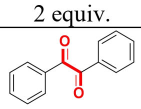
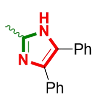
Table 2. The synthesis of β-areneimidazolyl substituted porphyrins.



Substrate	X, equiv.	Time	Product, yield, %
2H-2a	CH, 2	24 h	**2H-3a**, 96
	N, 2	24 h	**2H-4a**, 89
Cu-2a	CH, 4	48 h	**Cu-3a**, 74
	N, 2	24 h	**Cu-4a**, 76
Ni-2a	CH, 4	48 h	**Ni-3a**, 77
	N, 4	48 h	**Ni-4a**, 58
Cu-2b	CH, 4	48 h	**Cu-3b**, 66
	N, 4	48 h	**Cu-4b**, 94
Cu-2c	CH, 2	24 h	**Cu-3c**, 97
	N, 4	48 h	**Cu-4c**, 94
Cu-2d	CH, 2	24 h	**Cu-3d**, 89
	N, 2	48 h	**Cu-4d**, 95
Cu-2e	CH, 4	48 h	**Cu-3e**, 98
	N, 4	48 h	**Cu-4e**, 93
Cu-2f	CH, 4	48 h	**Cu-3f**, 67
	N, 4	48 h	**Cu-4f**, 35
Cu-2g	CH, 4	48 h	**Cu-3g**, 60
	N, 4	48 h	**Cu-4g**, 37

Table 3. The condensation of **Ni-2a** with dicarbonyl compounds.



α-Diketone	Time	Imd	Product, yield
 2 equiv.	24 h		**Ni-3a**, 77%
 2 equiv.	24 h		**Ni-4a**, 58%
 2 equiv	24 h		**Ni-5a**, 6%*
 2 equiv.	24 h		**Ni-6a**, 3%**
 2 equiv.	24 h		**Ni-7a**, 10%***
 4 equiv.	3 days		**Ni-8a**, 94%

* 77% of **Ni-2a** was recovered;
** 47% of **Ni-2a** was recovered;
*** 82% of **Ni-2a** was recovered.

The stepwise addition of the α-diketone component of the condensation was required in some cases to achieve the complete conversion of the starting material. We have previously reported, that a concurrent process consuming the phenanthrene- and phenanthrolinedione was observed under the reaction conditions.[19] With this consideration 2 equiv. of α-diketone and 20 equiv. of NH_4OAc were added to the reaction mixture each 24 h until complete consumption of the starting formylporphyrin was detected.

We also attempted to evaluate the required reagent ratio in the synthesis of **2H-3a** by slow addition of phenanthrenedione to the reaction mixture. Syringe pump was loaded with a solution of 4 equiv. of phenanthrenedione which was continuously added to refluxed mixture of **2H-2a** and 40 equiv. of NH_4OAc in $CHCl_3$/AcOH. In this case the complete conversion of **2H-2a** was achieved in 42 h and required 3.6 equiv. of phenanthrenedione, thus providing **2H-3a** with 38% yield.

As can be seen, in most cases the substrates were converted to the target β-imidazolyl-derivatives in high yields. Substrates **Cu-2f,g** could be mentioned as an exception in the series, providing lower yields of the condensation products, especially in the case of phenanthroline derivatives. Presumably, it could be attributed to the electron-withdrawing properties of *meso*-substituents, since the sterical effects of *ortho*-substitution in *meso*-fragments did not reveal significant influence on the product yields. Interestingly, in the case of **Cu-2d** and **Cu-2e**, high yields of the condensation products were observed despite the presence of the electron-rich *meso*-substituents which could decrease the electrophilicity of the substrate. We also did not observe any influence of the metal center neither onto the reaction path nor the yields of the condensation products.

The absence of the influence of the *meso*-substituents electronic nature on the reactivity of the porphyrin substrates is not surprising. Previously we attempted to rationalize the influence of the electronic properties of *meso*- and β-substituents on the distribution and energy levels of the porphyrin frontier orbitals for the prediction of their reactivity.[44,45] It was clearly observed that orbital structure of the porphyrin macrocycle is notably less sensitive to β-substitution pattern, compared to *meso*-substitution.

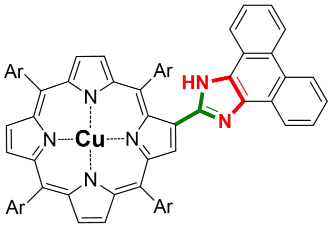
Next, porphyrin **Ni-2a** was chosen as a typical representative for further investigation of the condensation reaction with different α-diketones. The yields of the products as well as the comparison of the reaction conditions are summarized in Table 3..

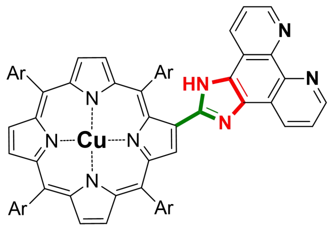
In this case the reaction path as found to be dependent on the nature of the α-diketone component of the condensation. Thus, while the interaction with phenanthrene- and phenanthrolinedione smoothly provided the corresponding areneimidazolyl derivatives **Ni-3a** and **Ni-4a** with moderate to high yields, the application of acenaphthene-quinone, naphthoquinone or 3,5-di-*tert*-butyl-*o*-quinone resulted in the formation of the expected derivatives **Ni-5a** – **Ni-7a** with vanishing yields. The isolation of 47 to 82% of the starting **Ni-2a** in these cases allows to attribute low yield to the instability of the mentioned α-diketones under reaction conditions. Finally, the introduction of benzil into the condensation revealed its decreased reactivity in comparison with polycyclic quinones.

Nevertheless, the interaction over 3 days allowed the preparation of the imidazolyl derivative **Ni-8a** nearly quantitatively.

UV-Vis absorption spectral data allow evaluation of the mutual influence of the parts of the functionalized porphyrin derivatives (Table 4). First, it should be noted, that the introduction of the β-imidazolyl substituent results in the bathochromic shift of Soret and Q-bands by *ca*. 5 nm that reveals the orbital perturbation. Nevertheless, such slight shift does not allow to expect the expansion of the porphyrin π-system. It could be attributed to skewed conformation of the molecule as a result of steric repulsion between areneimidazolyl substituent and the neighboring *meso*-aryl group. As can be seen, the positions of the absorption bands in the spectra of related phenanthrene- and phenanthroline-appended derivatives virtually coincide with *ca*. 1-3 nm deviations, that reveals the absence of notable influence of the appended polycyclic fragment onto the electronic structure of the macroheterocycle. Moreover, this variation of the electronic nature of the *meso*-substituents also results in nearly negligible variation of the maxima of the bands. The nature of the metal center possesses virtually negligible influence on the position of Soret band, while Q-bands are shifted hypsochromically by *ca*. 10 nm. Altogether, these observations allow to conclude, that the aromatic fragments of the prepared β-areneimidazolyl-porphyrins could be considered as independent units, that is valuable for the design of supramolecular tectons with predictable reactivity.[23,46]

Table 4. UV-Vis data of the series of copper(II) complexes **Cu-3a-g** and **Cu-4a-g** ($CHCl_3$).





Cu-3a*	422 (5.49)	546 (4.30)	582 (3.76)	**Cu-4a***	422 (5.46)	545 (4.28)	581 (3.75)
Ni-3a	422 (5.17)	535 (4.16)	570 (3.82)	**Ni-4a**	423 (5.26)	535 (4.20)	569 (3.86)
Cu-3b	423 (5.47)	546 (4.34)	585 (3.83)	**Cu-4b**	424 (5.45)	546 (4.28)	581 (3.80)
Cu-3c	424 (5.37)	548 (4.22)	584 (3.78)	**Cu-4c**	425 (5.47)	547 (4.24)	584 (3.82)
Cu-3d	425 (5.46)	548 (4.34)	583 (3.86)	**Cu-4d**	428 (5.40)	548 (4.24)	584 (3.78)
Cu-3e	426 (5.08)	549 (4.53)	584 (4.07)	**Cu-4e**	427 (5.54)	548 (4.41)	585 (3.98)
Cu-3f**	421 (5.49)	545 (4.28)	579 (3.76)	**Cu-4f****	424 (5.55)	546 (4.26)	582 (3.84)
Cu-3g	419 (5.03)	546 (4.25)	584 (3.91)	**Cu-4g**	422 (5.44)	547 (4.25)	587 (3.98)

* The reported UV-Vis data for **Cu-1a**, λ_{max} nm: 416, 540, 574 (CH_2Cl_2).[31,43]

** The reported UV-Vis data for **Cu-1f**, λ_{max} nm (log ε): 417 (5.31), 540 (3.96).[47,48]

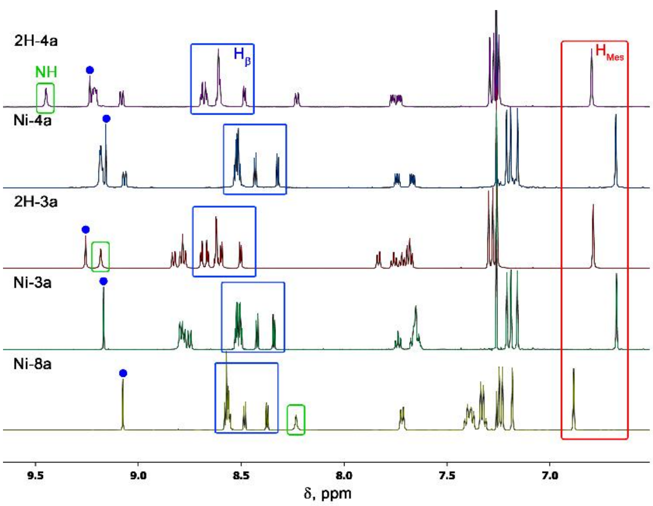
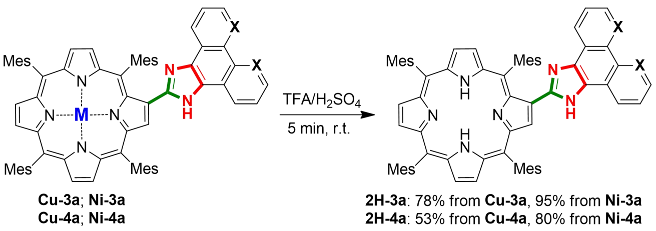


Figure 1. Selected ^{1}H NMR spectra of synthesized compounds in $CDCl_3$ (aromatic region).

^{1}H NMR data of typical representatives of the prepared set of porphyrin derivatives allows to get insight into the mutual influence of the molecular fragments of β-imidazolylporphyrins (Figure 1). First of all, the dissymmetrization of the porphyrin core is testified by the magnetic inequivalence of all β-protons of the macrocycle. It could be also noted, that the resonance of the proton, occupying the vicinal position to the imidazolyl unit, is shifted downfield by *ca*. 0.5 ppm, that could be attributed to the influence of the magnetic anisotropy of the introduced aromatic heterocyclic fragment. In contrast, the respective orientation of the *meso*-substituent and the imidazole or areneimidazole group results in upfield shift of the signal, corresponding to aromatic proton of the neighboring mesityl fragment. Interestingly, the resonance of the proton of the NH-group is observed only in the case of **2H-3a**, **2H-4a** and **Ni-8a**. In these cases, the signal of this proton demonstrates the significant difference in the position on the scale. Thus, in the case of **2H-3a** and **2H-4a** the titled resonance is observed in the typical 9.0-9.5 ppm region, that is determined by its in-plane orientation with respect to the polycyclic fragment and the corresponding influence of the magnetic anisotropy of the aromatic system. In contrast, in the case of **Ni-8a** the resonance of the imidazole NH fragment is shifted upfield by *ca*. 1 ppm. Such shift may originate from the shielding effect of the phenyl groups, which occupy nearly orthogonal position with respect to the imidazole fragment.

The preparation of free-base β-areneimidazolyl-substituted porphyrins upon demetalation in highly acidic conditions was performed for complexes **Cu-3a**, **Cu-4a**, **Ni-3a** and **Ni-4b** (Scheme 1). The selected set of metal(II) porphyrins allowed evaluation of the stability of areneimidazolyl-moiety under these conditions.



Scheme 1. The preparation of free-base β-areneimidazolyl-substituted porphyrins.

In all cases complete conversion of the metal complexes was achieved within 5 min at ambient temperature. Surprisingly, it was observed, that demetalation of nickel(II) complexes **Ni-3a** and **Ni-4a** provides higher yields of the free-base porphyrins **2H-3a** and **2H-4a**, compared to Cu^{II} precursors. Moreover, in both cases phenanthroline-substituted derivatives demonstrated decreased yields of the demetalation compared to phenanthrene analogues. The latter observation could be reasonably attributed to instability of the peripheral heterocycle under acidic conditions. Thus, the β-areneimidazolyl group is found to tolerate the highly acidic demetalation conditions and a variety of free-base β-imidazolyl derivatives could also be prepared for further synthesis of desired metal complexes.

Conclusions

Thus, in the present work we have investigated the applicability of the Debus-Radziszewski condensation of 2-formylporphyrins with aromatic α-diketones for the preparation of 2-imidazolyl-substituted derivatives. The efficiency of this approach was found to be virtually independent from the electronic effects of *meso*-substituents and the nature of metal center of the starting formylporphyrin. In all cases the condensation with polycyclic quinones, namely phenanthrene- and phenanthrolinedione, successfully provided the expected derivatives with moderate to nearly quantitative yields. The steric effects of *ortho*-groups of *meso*-substituents also did not suppress the condensation. In contrast, such α-diketones as acenaphthene-quinone, naphthoquinone or 3,5-di-*tert*-butyl-*o*-quinone revealed low stability under reaction conditions that resulted in low conversion of the starting formylporphyrin. In the case of benzyl, complete conversion of the formylporphyrin substrate could be achieved providing the corresponding diaryl-substituted imidazolyl-derivative virtually quantitatively, while the reactivity of this α-diketone was found to be considerably decreased in comparison with polycyclic ones. Hence, the condensation of 2-formylporphyrins with aromatic α-diketones could be considered as a convenient straightforward pathway for the introduction of the functional fragments to the porphyrin β-positions by means of the imidazole heterocyclic bridge.

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