

Ammonium Imidazoporphyrin – a Newborn in a Family of Porphyrins for Hybrid Materials

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Dedicated to the memory of Prof. G.V. Ponomarev and Prof. A.F. Mironov

The efficient application of the trialkylammonium group as an anchor for grafting of porphyrin to silica is demonstrated. A representative of a new series of functional porphyrins for the development of hybrid materials, namely imidazoporphyrin bearing peripheral triethylammonium unit, is synthesized. The optimal synthetic sequence towards the target type of functional derivatives is revealed. The grafting of the prepared Ni(II) porphyrin to the surface of the commercially available silica is performed and the stability of the obtained hybrid material is investigated. The loading of the porphyrin in the prepared material is evaluated as ca. 13 % by weight. The reported synthetic strategy is expected to form the basis for the development of new type of porphyrin-based hybrid materials.

Keywords: Porphyrins, imidazoporphyrins, hybrid materials, grafting, immobilization, ammonium anchoring groups.

Аммоний–замещенный имидазопорфирин – новорожденный в семействе порфиринов для гибридных материалов

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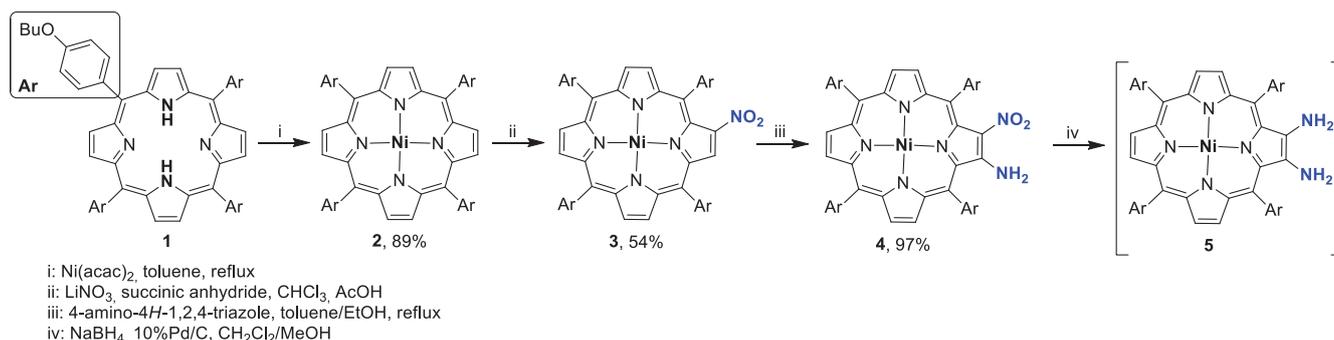
Посвящается памяти проф. Г.В. Пономарева и проф. А.Ф. Миронова

В работе показана возможность эффективного использования триалкиламмонийной группы в качестве якоря для иммобилизации порфирина на поверхности силикагеля. Получен первый представитель такого семейства функционализированных порфиринов – имидазол-аннелированный порфирин, содержащий периферийную триэтиламмонийную группу. Выявлена оптимальная последовательность синтетических стадий для получения производных этого типа. Разработан подход к иммобилизации полученного порфирина никеля(II) на коммерчески-доступный силикагель и изучена стабильность этого гибридного материала. Доля иммобилизованного порфирина никеля(II) в полученном материале составила ~13 масс.%. Ожидается, что разработанная синтетическая стратегия станет основой для получения гибридных материалов нового типа на основе функционализированных порфиринов.

Ключевые слова: Порфирины, имидазопорфирины, гибридные материалы, иммобилизация, аммонийная якорная группа.

Nowadays the development of modern synthetic strategies for further industrial applications is strictly limited by the requirements of green chemistry and sustainable development. In general, green approaches in chemistry are defined as «design of chemical products and processes to reduce or eliminate the use and generation of hazardous substances»^[1] and the well-known so-called “twelve principles” of the green chemistry significantly limit the application of the majority of traditional organic chemistry reactions in the industrial scale.^[2] Such requirements as atom economy, use of renewable sources, prevention of wastes and less hazardous chemical synthesis along with the demand for application of safe solvents and auxiliaries could be fulfilled by the application of catalytic transformations and particularly by means of heterogeneous catalysis. In turn, the industrial use of catalysts requires their cost efficiency and thus the availability of the materials becomes a crucial factor.

Porphyrins are distinguished molecules with outstanding photophysical properties that determined their multiple practical applications.^[3–6] Photocatalytic oxidation is a type of transformations valuable for industrial applications^[7,8] and also fulfilling the main green principles. In this respect the development of hybrid materials for the application as recyclable heterogeneous photocatalysts is required. In turn, the survey of grafting techniques is unavoidable for the elimination of the problem of leaching of the active molecules from the hybrid materials. Recently we have reported general approaches for the fusion of the porphyrin with functionalized peripheral heterocyclic fragments.^[9–12] Indeed, the first preparation of imidazoporphyrins by condensation of 2,3-dioxochlorins with aromatic aldehydes was reported back in late 90’s,^[13] but that work did not achieve much interest and further efforts were made for the preparation of quinoxalinoporphyrins.^[14,15] Furthermore, the limitations of the application of 2,3-diaminoporphyrins in the synthesis of heterocycle-fused porphyrins were reported,^[16] that hampered the developments in this field. Later the possibility of the application of nickel(II) complexes of 2,3-diaminoporphyrins was demonstrated for the preparation of porphyrins fused with one to four imidazole units,^[17,18] that allowed preparation of the corresponding N-heterocyclic carbene complexes.^[19,20] In turn, our recent developments in this field were aimed on the targeted introduction of various functional units to the heterocyclic fragments with special emphasis to anchoring groups.^[21–23]



Scheme 1. Synthesis of the 2,3-diaminoporphyrin **5**.

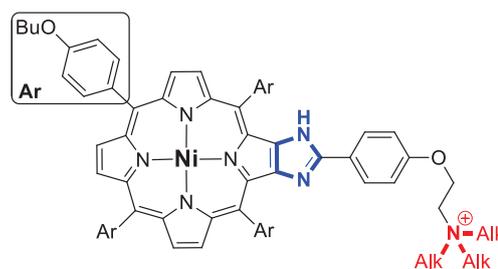
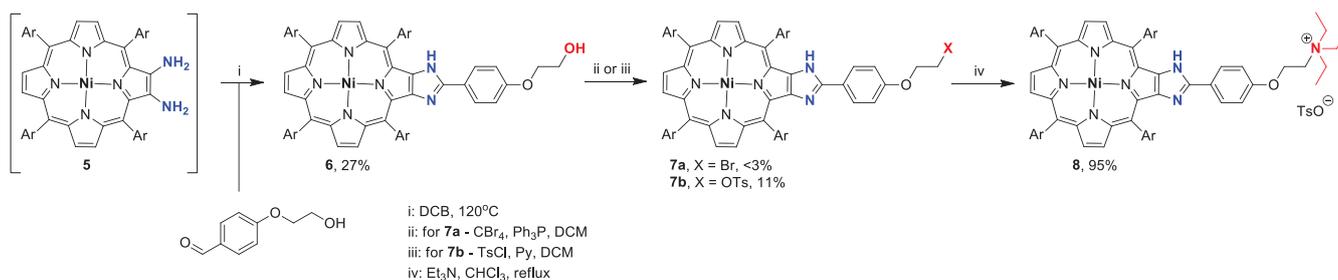


Figure 1. Schematic representation of the target functional porphyrin for grafting to silica support.

Following the idea of development of cost-efficient porphyrin-based hybrid materials we considered commercially available silica as a promising inert solid support and ammonium fragment as a convenient anchoring group. Thus, in the present work we have focused on the synthesis of a new heterocycle-appended porphyrin, bearing peripheral ammonium anchoring unit (Figure 1). The grafting of the prepared functional derivative to the surface of readily available silica as well as the investigation of the stability and composition of the obtained hybrid material were also the aim of the research under discussion.

The applied synthetic strategy for the preparation of imidazoporphyrins implies the generation of labile but highly reactive 2,3-diaminoporphyrin as a key step in the synthesis.^[9,11,17] The proper choice of the *meso*-substituents in the starting porphyrin possess significant influence onto the efficiency of the synthetic steps since allowing to enhance the solubility of the derivatives at all steps. Thus, the introduction of the butoxy-substituents to the *para*-positions of *meso*-aryl groups drastically enhances the solubility of the obtained porphyrins in organic media even in the presence of large appended polyaromatic fragments.^[24]

The interaction of the starting free-base porphyrin **1** with Ni(acac)₂ provided the corresponding complex **2**, which was further introduced to the nitration at β -position (Scheme 1). The application of the metal nitrate in the combination with acid anhydride is a general approach allowing selective β -nitration of various porphyrin metal complexes under mild conditions.^[17,12,11] At the next step the nucleophilic Katritzky-type amination with the application of 4-amino-4H-1,2,4-triazole provided the 2-amino-3-nitroporphyrin **4** with virtually quantitative yield. This derivative



Scheme 2. Synthesis of the target ammonium-substituted imidazoporphyrin **8**.

is a stable direct precursor of the 2,3-diaminoporphyrin **5**. Operation with complex **5** requires inert atmosphere since β -aminoporphyrins are easily oxidized^[16] and may provide a variety of oxidative products, namely dioxochlorins,^[9,25] porpholactones,^[10,25] and secochlorins.^[26] The application of Ni(II) complexes in this sequence allows to enhance their stability by quenching of the photoactivity of porphyrins in comparison with photoactive free-bases or Zn(II) complexes.^[9]

Despite the precautions required during operation with 2,3-diaminoporphyrins, their *in situ* generation and further treatment with the aromatic aldehydes could be performed conveniently from the implementation point of view. In the case of compounds under discussion the presence of the electron-donor group in the applied aromatic aldehyde decreases the electrophilicity of the carbonyl group that in turn determines the relatively low yield of imidazoporphyrin **6** (Scheme 2). Nevertheless, the obtained yield of **6** is in fine consistency with the yield of the related phenoxy substituted imidazoporphyrin.^[21]

The next synthetic step was conducted with the transformation of OH-group of **6** to a good leaving group. We attempted to perform its substitution to bromine atom by means of Appel reaction,^[27] which typically proceeds with high yields.^[28] Unfortunately, the interaction of **6** with excess of CBr₄ and Ph₃P provided **7a** with vanishing yield less than 3 % and we were unable to isolate it in pure form. Such peculiarity could be attributed to the presence of imidazole NH-fragment, which could be competitively deprotonated with CBr₃⁻ anion in the key step of the Appel reaction.

In this respect the tosylation of OH-group was selected as an alternative path. The interaction with TsCl under typical tosylation conditions unexpectedly revealed the significant decrease of the reactivity of the hydroxyl-group. Thus, only 11 % conversion was achieved over 4 days of interaction and the unreacted porphyrin **6** was recovered. Presumably, it also could originate from the acidity of the heterocyclic NH-group, which deprotonation could lead to the anionic state of the molecule and prevent the deprotonation of OH-group. The protection of the imidazole NH could possibly allow to overcome this problem, but the selection of the proper protective group as well as the survey of protection and deprotection methods was out of scope of the present work. At the final step the interaction of **7b** with excess of Et₃N provided the target ammonium-

substituted porphyrin **8**[†] virtually quantitatively. In contrast to other abovementioned porphyrins, the purification of **8** required application of neutral alumina instead of silica. All the discussed derivatives at all stages were isolated in pure form and sufficiently characterized (see *Electronic supporting information*, ESI), except **5** and **7a** (*vide supra*).

UV-Vis data could be used for the determination of the electronic interaction between the porphyrin macrocycle and peripheral fragments.^[24] The introduction of the peripheral electron-acceptor cationic unit could initiate the bathochromic shift of absorption bands in the case of interaction with the porphyrin π -system. The comparison of the UV-Vis spectra of the imidazoporphyrins, bearing terminal hydroxy-, tosyloxy- and ammonium-substituents revealed negligible difference in the positions of the absorption bands (Table 1). In this respect the absence of the influence of the cationic unit onto the electronic structure of the porphyrin could be postulated, that is valuable for the development of porphyrin-based functional hybrid materials.

The prepared compound **8** possesses high solubility in polar aprotic media such as CHCl₃ and CH₂Cl₂, that significantly simplifies the grafting procedure. The grafting of **8** to silica was performed by the treatment of the solution of the porphyrin in CH₂Cl₂ with commercial silica with

[†] Experimental details on the synthesis of all intermediates are represented in ESI. Compound **8**. Et₃N (1 ml, 7.19 mmol) was added to the solution of **7b** (3 mg, 2 μ mol) in CHCl₃ (3.5 mL) and the mixture was refluxed for 2 d. The solution was evaporated and the residue was purified by column chromatography on neutral alumina (CHCl₃/MeOH, 0 \rightarrow 6 % MeOH) to provide after evaporation 3.2 mg (95 %) of **8** as red solid. ¹H NMR (CDCl₃) δ ppm (*J*, Hz): 8.78 (s, 2H, H _{β}), 8.79–8.77 (d, 1H, H _{β}), 8.76 (d, 1H, ³*J* = 4.9, H _{β}), 8.75–8.72 (2d, 2H, H _{β}), 8.64 (s, 1H, NH), 7.97 (d, 2H, ³*J* = 8.1, o-H_{Ar}), 7.93 (d, 2H, ³*J* = 8.2, o-H_{Ar}), 7.90 (d, 2H, ³*J* = 8.3, o-H_{Ar}), 7.87 (d, 2H, ³*J* = 8.3, o-H_{Ar}), 7.72 (d, 2H, ³*J* = 8.3, o-H_{Ar}), 7.34 (d, 2H, ³*J* = 8.1, m-H_{Ar}), 7.28–7.24 (d, 2H, m-H_{Ar}), 7.19 (d, 2H, ³*J* = 8.4, m-H_{Ar}), 7.17 (d, 2H, ³*J* = 8.3, m-H_{Ar}), 6.98 (d, 2H, ³*J* = 8.3, m-H_{Ar}), 4.58 (t, 2H, CH₂N), 4.27 (t, 2H, ³*J* = 6.6, CH₂O), 4.25 (t, 2H, ³*J* = 6.6, CH₂O), 4.16–4.23 (m, 6H, CH₂O), 3.59 (q, 6H, ³*J* = 7.3, CH₂(NEt₃)), 2.03–1.89 (m, 8H, CH₂), 1.71–1.59 (m, 8H, CH₂), 1.47 (t, 9H, ³*J* = 7.2, CH₃(NEt₃)), 1.13–1.05 (m, 12H, CH₃). UV-Vis (CHCl₃) λ nm (log ϵ): 284 (4.44), 422 (5.31), 534 (4.20), 568 (3.93). MALDI-TOF MS, *m/z*: calcd. for C₇₅H₈₂N₇NiO₅⁺ [*M*⁺] 1218.57, found 1218.50.

Table 1. UV-Vis data for porphyrins 6–8.

Compound	UV-Vis bands (λ_{\max} , nm (log ϵ))
8	284 (4.44), 422 (5.31), 534 (4.20), 568 (3.93)
7	286 (4.61), 422 (5.47), 534 (4.37), 571 (4.10)
6	286 (4.50), 421 (5.37), 534 (4.26), 570 (4.00)

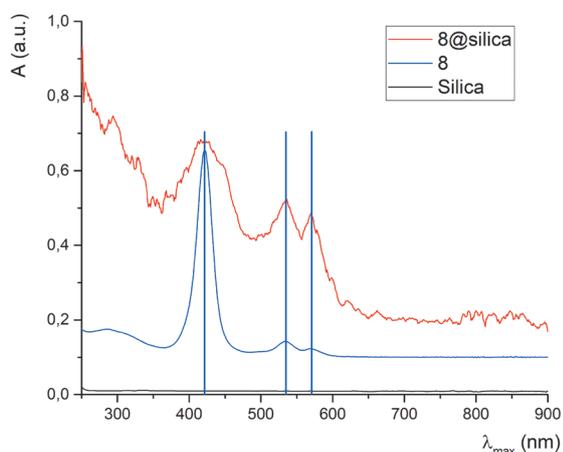
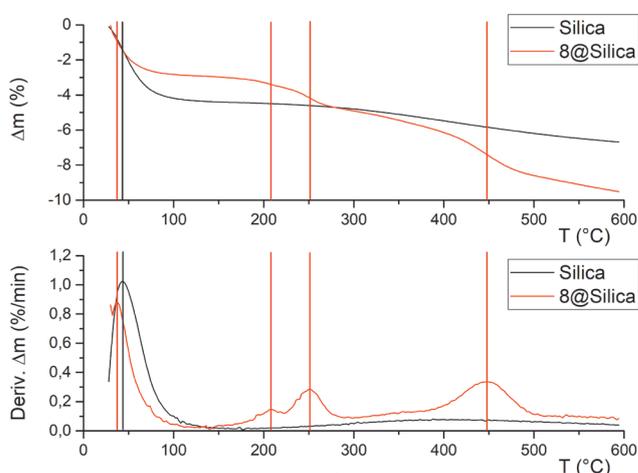
40–63 μm particle size upon intense stirring. Gradual decolourization of the solution was observed upon stepwise addition of the solid material, while the formed solid was deep red in color. The obtained hybrid material **8@silica** was easily separated by centrifugation and the amount of the residual **8** in the solution was quantified by UV-Vis data. The prepared hybrid material after grafting was determined to contain *ca.* 13% of **8** by weight.

The comparison of the UV-vis data of the starting silica, porphyrin **8** and the hybrid material allowed to testify that the porphyrin macrocycle remains unchanged upon grafting (Figure 2). Thus, the starting silica reveals no noticeable bands in the whole investigated UV-vis range of 250–900 nm. In turn, the prepared hybrid material demonstrates a set of broadened bands in the reflectance spectrum which coincide with the absorption bands of the functional porphyrin **8**. The broadening of bands is typical for the reflectance spectra of solid materials, while the preservation of their set and positions allows to assume the absence of the interaction of the porphyrin macrocycle with the support or the intermolecular interactions. Otherwise, the bathochromic shift of the bands should be observed in the spectrum of **8@silica**. The mutual orientation of the porphyrin core, the *meso*-substituents

and the anchoring unit allows to presume the orthogonal orientation of **8** to the surface of silica support.

The stability of the material was estimated by the analysis of its behavior in CH_2Cl_2 . The analysis of washings by UV-vis did not allow determination of leaching of **8**, that reveals the stability of the material in this medium. This is valuable for further catalytic applications of this type of materials, since CH_2Cl_2 is a common solvent in a variety of organic transformations. The thermal stability of the prepared hybrid material **8@silica** was estimated by thermogravimetric analysis (Figure 3). The starting silica demonstrates the main loss of weight below 100 $^\circ\text{C}$ that could be attributed to the removal of the adsorbed water molecules. Further heating of silica to *ca.* 250 $^\circ\text{C}$ does not reveal considerable decrease of the weight, while gradual heating up to 600 $^\circ\text{C}$ reveals slight weight change which could be associated with the slow dehydration of the surface of the material.

In the case of **8@silica** the thermal degradation of the material is different. The loss of weight below 100 $^\circ\text{C}$ also could be attributed to the loss of the adsorbed solvent molecules. Next, in the range of 200–300 $^\circ\text{C}$ two distinct processes could be observed at the derivative of the weight change curve and the decrease of weight is gradually

**Figure 2.** Comparison of UV-Vis data for porphyrin **8** and solid materials.**Figure 3.** Thermogravimetric analysis of **8@silica**.

continued upon further heating in the 300–600 °C range. These processes at temperature above 200 °C could be attributed to the gradual degradation of the porphyrin. Nevertheless, the material is stable up to *ca.* 150 °C that is sufficient for the removal of the majority of typical organic solvents even at ambient pressure. In this respect it could be expected that the related materials of this type could find application in the modern heterogenic catalysis.

Concluding, in the present work we have developed a synthetic pathway towards imidazoporphyrins bearing the cationic ammonium units in the appended heterocyclic fragment. The peculiarities of the steps of the implied synthetic sequence are determined, revealing the possibilities for the optimization of these transformations. The efficient grafting of the prepared Ni(II) complex to the readily available silica is investigated, allowing 13 % loading of the porphyrin by weight in the hybrid material. In general, the reported research outlines the basis for the development of new type of porphyrin-based functional hybrid materials for heterogeneous catalytic applications.

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