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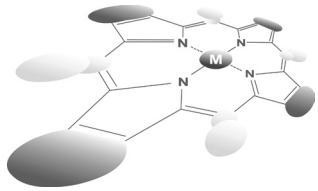

Application of reductive amination reaction for preparation of ferrocene-modified porphyrins

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ABSTRACT: Porphyrin-modified ferrocenes were synthesized *via* the reductive amination reaction of ferrocenylpyrazolecarboxaldehydes and tetraphenylporphyrinamine. The steric hindrance of ferrocene moiety was found to play the key role in this reaction.

KEYWORDS: ferrocene, porphyrin, reductive amination, 5-(*p*-aminophenyl)-10,15,20-triphenylporphyrin, electrochemistry.

INTRODUCTION

For many years, porphyrins have been used in PDT [1, 2]. They can act as radiosensitizers in thick tumors [3], for photodynamic therapy of early esophageal cancer [4]. At the same time, ferrocene-containing bioconjugates are a new class of biomaterials, in which the organometallic ferrocene unit serving on the one hand as a molecular substrate for the construction of an ordered structure via intramolecular hydrogen bonding, on the other hand as a catalytic or redox-active site, *etc*. [5]. Ferrocenylheterocyclic compounds have been found to exhibit biological activities (*e.g.* antitumor [6] and antimicrobial [7]). Noteworthy, pyrazole moiety is the core structure of numerous biologically active compounds [8]. Some pyrazole compounds have affinity for the human CRF-1 receptor [9], exhibit anti-viral/anti-tumor [10], antibacterial [11], anti-parasitic [12], antipyretic [13], anty-flammatory [11, 13, 14], analgesic [14], fungistatic [15], fungicidal [16], and anti-hyperglycemic [17] activity.

Ferrocene and porphyrins have already been associated by means of various synthetic methods. These include direct connection [18, 19, 20–22] particularly *via* Suzuki coupling [23], linkage through conjugated spacers [24], linkage through saturated spacers [25], β-pyrrole-linked ferrocene-porphyrins [26, 27, 28] and ferrocene-porphyrin analogs [29].

The difference of bounding ways in the ferrocene-porphyrin assemblies suggests the variety of application. Their donor–acceptor properties have been employed to study photoinduced electron transfer processes and to simulate photosynthesis active sites [30, 31]. Thus, such structures have been employed as molecular sensors [32] and for an increase of memory density that allowed multibit information storage [33].

Previously, we have studied the reductive amination reaction of ferrocenylpyrazolecarboxaldehydes with primary and secondary aliphatic and aromatic amines [34]. Therefore, we used this reaction to produce ferrocene-porphyrins.

In our work, we synthesized a ferrocene-containing porphyrins, in which the ferrocene linked to porphyrin through the heterocycle (pyrazole, isoxazole). For these compounds, we carried out the reaction of reductive amination of 5-(*p*-aminophenyl)-10,15,20-triphenylporphyrin and ferrocenepyrazolecarboxaldehydes. Such ferrocene-appended porphyrins are of interest for electrochemical studies.

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EXPERIMENTAL

Instrumental

The solvents were dehydrated by conventional methods directly before use. 3-(5-(*p*-Aminophenyl)-10,15,20-triphenylporphyrin)-5-ferrocenyl-1-phenylpyrazole (**4b**), 1,5-diphenyl-4-(5-(p-aminophenyl)-10,15,20-triphenylporphyrin)pyrazole (**8a**) 1,3-diphenyl-4-(5-(p-aminophenyl)-10,15,20-triphenylporphyrin)pyrazole (**8b**) were synthesized according to the method described [35]. Mass spectra (MS) were obtained on a "FINNIGAN POLARIS Q" spectrometer using electron ionization method and on a "LCQ Advantage" spectrometer using electro spray ionization. High resolution mass spectrum was obtained on a Bruker "micro TOF II" spectrometer using electro spray ionization. NMR spectra were registered on an "AVANCE" spectrometer with operational frequency 300 MHz and on a "Bruker DRX-500" spectrometer with operational frequencies 500.13 MHz and 125.76 MHz for ^{1}H and ^{13}C respectivelly, in $CDCl_3$ and DMSO-d_6. Two-dimensional spectra COSY, HSQC and HMBC were registered using the gradient method. The UV-vis spectral measurements were carried out with a "Carl Zeiss Jena" model Specord M40 spectrometer in 200–1000 nm region. Voltammetric experiments were performed with IPC-Win potentiostat, one compartment cell of 10 mL with a platinum wire counter electrode and Ag/AgCl/KCl aq. reference electrode. All potentials below refer to this reference electrode. Working electrode was Pt disk.

Synthesis

General procedure 1. Ferrocenylformylpyrazole 1 mmol and 1.2 mmol of 5-(*p*-aminophenyl)-10,15,20-triphenylporphyrin (or *p*-chloranilin, were mixed in 1,2-dichloroethane (35 mL) for 1 h. at rt and treated with 1.4 mmol of sodium triacetoxyborohydride. The mixture was refluxed for 1 h. The reaction mixture was quenched by adding aqueous saturated $NaHCO_3$, and the product was extracted with 2 × 30 mL dichloromethane. The organic layers combined and washed with brine. After drying over Na_2SO_4 the solvent was evaporated. The residue was purified by means of column chromatography (SiO_2, eluent $CHCl_3$-MeOH 9/1 for *p*-chloranilin derivatives and hexane-ethylacetate 3/1 for ferroceneporphyrins).

1-Phenyl-5-ferrocenyl-3-(4-chlorophenylaminomethyl)pyrazole (3a). Yellow-orange powder. Yield 63% mp 150–151 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ, ppm 4.05 (s, 5H, Cp); 4.14 (s, $2H_\alpha$, Cp); 4.19 (s, $2H_\beta$, Cp); 4.38 (s, 2H, CH_2); 6.46 (c, 1H, Pz); 6.67 (d, 2H, *o*-Ph-NH, *J* = 9.0 Hz); 7.15 (d, 2H, *m*-Ph-NH, *J* = 9.0 Hz); 7.34–7.46 (m, 5H, Ph). ^{13}C NMR (75 MHz, $CDCl_3$): δ, ppm 42.3, 68.7, 69.8, 74.6, 105.2, 114.3, 122.2, 126.1, 128.2, 128.9, 140.2, 142.9, 146.7, 150.5. EI/MS: *m/z* (I_{re}, %) 467 (80) $[M]^+$.

1-Phenyl-3-ferrocenyl-4-(4-chlorophenylaminomethyl)pyrazole (3b). Yellow-orange powder. Yield 60%, mp 150–151°C. ^{1}H NMR (300 MHz, $CDCl_3$): δ, ppm 4.13 (s, 5H, Cp); 4.32 (s, $2H_\alpha$, Cp); 4.40 (s, $2H_\beta$, Cp); 4.79 (s, 2H, CH_2); 6.65 (d, 2H, *o*-Ph-NH, *J* = 9.0 Hz); 7.20 (d, 2H, *m*-Ph-NH, *J* = 9.0 Hz); 7.46 (t, 3H, Ph, *J* = 9.0 Hz); 7.69 (d, 2H, *o*-Ph, *J* = 9.0 Hz); 7.87 (s, 1H, Pz). EI/MS: *m/z* (I_{re}, %) 467 (62) $[M]^+$.

1-Phenyl-5-ferrocenyl-4-(4-chlorophenylaminomethyl)pyrazole (3c). Yellow-orange oil. Yield 38%. ^{1}H NMR (300 MHz, $CDCl_3$): δ, ppm 4.06 (s, 5H, Cp); 4.07 (s, $2H_\alpha$, Cp); 4.08 (s, $2H_\beta$, Cp); 4.49 (s, 2H, CH_2); 6.59 (d, 2H, Ph, *J* = 9.0 Hz); 6.70 (d, 2H, Ph, *J* = 9.0 Hz); 7.09 (d, 2H, Ph, *J* = 9.0 Hz); 7.29–7.33 (m, 5H, Ph); 8.31 (s, 1H, Pz). EI/MS: *m/z* (I_{re}, %) 467 (48) $[M]^+$.

1-(Naphtalen-1-yl)-3-ferrocenyl-4-(4-chlorophenylaminomethyl)pyrazole (3d). Yellow-orange powder. Yield 58%, mp 188–189 °C (dec). ^{1}H NMR (300 MHz, $CDCl_3$): δ, ppm 4.15 (s, 5H, Cp); 4.35 (s, $2H_\alpha$, Cp); 4.44 (s, $2H_\beta$, Cp); 4.83 (s, 2H, CH_2); 6.68 (d, 2H, *o*-Ph-NH, *J* = 9.0 Hz); 7.21 (d, 2H, *m*-Ph-NH, *J* = 9.0 Hz); 7.48–7.52 (m, 3H, Nf); 7.88–7.93 (m, 5H, Nf,); 8.01 (s, 1H); 8.11 (s, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ, ppm 39.4, 67.3, 68.9, 69.4, 113.9, 115.6, 118.1, 122.5, 125.7, 126.9, 127.4, 127.8, 129.5, 131.7, 133.7, 146.5. EI/MS: *m/z* (I_{re}, %) 517 (90).

3-(5-(*p*-Aminophenyl)-10,15,20-triphenylporphyrin)-5-ferrocenyl-1-izoxazole (6a). Violet powder. Yield 51%. UV-vis (CH_2Cl_2): λ_{max}, nm 285, 420, 518, 648. ^{1}H NMR (500 MHz, $CDCl_3$): δ, ppm -2.61 (s, 2H, NH), 4.19 (s, 5H, Cp), 4.44 (s, $2H_\beta$, Cp), 4.67 (s, 2H, CH_2), 4.79 (s, $2H_\alpha$, Cp), 6.30 (s, 1H, Izo), 7.07 (d, 2H, *o*-Ph-NH, *J* = 10.0 Hz), 7.75–7.79 (s, 9H, Ph), 8.06 (d, 2H, *m*-Ph, *J* = 10.0 Hz), 8.84–8.85 (m, 6H, 6CH), 8.96 (d, 2H, *J* = 5.0 Hz). ^{13}C NMR (126 MHz, $CDCl_3$): δ, ppm 40.6, 67.2, 69.9, 97.28, 111.5, 119.7, 120.9, 126.7, 127.7, 132.09, 134.6, 135.8, 142.2, 147.1, 162.6. ESI/MS: *m/z* (I_{re} %) 895 (100) $[M + H]^+$.

3-(5-(*p*-Aminophenyl)-10,15,20-triphenylporphyrin)-5-ferrocenyl-1-(4-methylphenyl)pyrazole (6b). Violet powder. Yield 53%. UV-vis (CH_2Cl_2): λ_{max}, nm 263, 420, 518, 649. ^{1}H NMR (500 MHz, $CDCl_3$): δ, ppm -2.61 (s, 2H, NH), 4.13 (c, 5H, Cp), 4.25 (s, $2H_\alpha$, Cp), 4.27 (c, $2H_\beta$, Cp), 4.70 (s, 2H, CH_2), 6.62 (s, 1H, Pz), 7.14 (d, 2H, *o*-Ph-NH, *J* = 10.0 Hz), 7.38 (d, 2H, Ph, *J* = 5.0 Hz), 7.48 (d, 2H, Ph, *J* = 5.0 Hz), 7.75–7.80 (m, 9H, Ph), 8.08 (d, 6H, Ph, *J* = 10.0 Hz), 8.82–8.86 (m, 6H), 9.00 (d, 2H, *J* = 10.0 Hz). ESI/MS: *m/z* (I_{re} %) 984 (100) $[M + H]^+$.

3-(5-(*p*-Aminophenyl)-10,15,20-triphenylporphyrin)-5-ferrocenyl-1-(4-tert-butylphenyl)pyrazole (6c). Violet powder. Yield 55%. UV-vis (CH_2Cl_2): λ_{max}, nm 276, 420, 516, 557, 649. ^{1}H NMR (500 MHz, $CDCl_3$): δ, ppm -2.61 (s, 2H), 4.13 (s, 5H, Cp), 4.25 (s, $2H_\alpha$, Cp), 4.25 (s, $2H_\beta$, Cp), 4.70 (s, 2H, CH_2), 6.62 (s, 1H, CH, Pz), 7.14 (d, 2H, *o*-Ph-NH, *J* = 10.0 Hz), 7.38 (d, 2H, Ph, *J* = 5.0 Hz) 7.48 (d, 2H, Ph, *J* = 10.0 Hz), 7.75–7.80

(m, 9H, Ph), 8.08 (d, 6H, Ph, J = 5.0 Hz), 8.24 (d, 6H, Ph, J = 5.0 Hz), 8.82–8.87 (m, 6H, 6CH), 9.00 (d, 2H, 2CH, J = 5.0 Hz). ^{13}C NMR (126 MHz, $CDCl_3$): δ, ppm 31.4, 42.5, 68.7, 69.9, 74.3, 105.1, 115.5, 125.7, 125.8, 126.7, 127.6, 134.6, 135.8, 142.4, 151.4. ESI/MS: *m/z* (I_{re} %) 1025 (100) $[M + H]^+$.

3-(5-(*p*-Aminophenyl)-10,15,20-triphenylporphyrin)-5-ferrocenyl-1-(2-chlorophenyl)pyrazole (6d). Violet powder. Yield 42%. UV-vis (CH_2Cl_2): λ_{max}, nm 285, 420, 518, 557, 648. ^{1}H NMR (500 MHz, $CDCl_3$): δ, ppm -2.61 (s, 2H, NH), 4.16 (s, 5H, Cp), 4.26 (s, $2H_\alpha$, Cp), 4.28 (s, $2H_\beta$, Cp), 4.70 (s, 2H, CH_2), 6.70 (s, 1H, Pz), 7.14 (d, 2H, *o*-Ph-NH, J = 10.0 Hz), 7.34–7.39 (m, 4H, Ph), 7.72–7.80 (m, 9H, Ph), 8.07 (d, 2H, *m*-Ph-NH, J = 10.0 Hz), 8.23 (d, 6H, Ph, J = 5.0 Hz), 8.85 (s, 6H, 6CH), 8.99 (d, 2H, J = 5.0 Hz). ^{13}C NMR (126 MHz, $CDCl_3$): δ, ppm 42.5, 68.9, 69.9, 74.6, 106.3, 111.5, 116.7, 119.6, 119.9, 121.2, 124.0, 126.1, 126.7, 127.6, 128.0, 129.7, 131.6, 134.5, 135.8, 141.2, 142.3, 147.7, 151.4. ESI/MS: *m/z* (I_{re} %) 1021(80) $[M + H]^+$.

3-(5-(*p*-Aminophenyl)-10,15,20-triphenylporphyrin)-5-ferrocenyl-1-(3-chlorophenyl)pyrazole (6e). Violet powder. Yield 45%. UV-vis (CH_2Cl_2): λ_{max}, nm 279, 421, 517, 556, 649. ^{1}H NMR (500 MHz, $CDCl_3$): δ, ppm -2.61 (s, 2H, NH), 4.13 (s, 5H, Cp), 4.24 (s, $4H_{\alpha,\beta}$, Cp), 4.71 (s, 2H, CH_2), 6.69 (s, 1H, Pz), 7.15–7.16 (d, 2H, *o*-Ph-NH, J = 5.0 Hz), 7.75–7.79 (m, 9H, Ph), 8.08 (d, 2H, *m*-Ph-NH, J = 5.0 Hz), 8.24 (d, 6H, Ph, J = 5.0 Hz), 8.85 (s, 6H, 6CH), 8.99 (d, 2H, J = 5.0 Hz). ^{13}C NMR (126 MHz, $CDCl_3$): δ, ppm 42.5, 68.7, 69.9, 105.5, 111.6, 126.2, 126.6, 127.6, 128.2, 128.8, 134.6, 135.8, 142.4, 147.8, 150.9. ESI/MS: *m/z* (I_{re} %) 1003 (100) $[M + H]^+$.

3-(5-(*p*-Aminophenyl)-10,15,20-triphenylporphyrin)-5-ferrocenyl-1-(4-fluorophenyl) pyrazole (6f). Violet powder. Yield 66%. UV-vis (CH_2Cl_2): λ_{max}, nm 280 (12000), 421 (103500), 518 (16000), 558 (3000), 649 (1500). ^{1}H NMR (500 MHz, $CDCl_3$): δ, ppm -2.61 (s, 2H), 4.14 (s, 5H, Cp), 4.22 (s, $2H_\alpha$, Cp), 4.25 (s, $2H_\beta$, Cp), 4.69 (s, 2H, CH_2), 6.67 (s, 1H, Pz), 7.14–7.17 (m, 4H, Ph, J = 15.0 Hz), 7.41–7.44 (m, 2H, Ph), 7.74–7.79 (m, 9H, Ph), 8.07 (d, 2H, m-Ph-NH, J = 10.0 Hz), 8.23 (d, 6H, Ph, J = 5.0 Hz), 8.85 (s, 6H, 6CH), 8.99 (d, 2H, 2CH, J = 5). ^{13}C NMR (126 MHz, $CDCl_3$): δ, ppm 42.5, 68.7, 69.9, 74.6, 105.6, 111.5, 115.7, 119.6, 119.9, 121.2, 126.6, 127.6, 127.9, 131.5, 134.6, 135.8, 136.4, 142.3, 143.1, 147.8, 151.0. ESI/MS: *m/z* (I_{re} %) 988 (100) $[M + H]^+$.

General procedure 2. To the solution of 1 mmol of ferrocenylporphyrin **4b** in $CHCl_3$ the saturated methanolic solution of 10 fold excess of corresponding metal acetate was added. The resulted mixture was refluxed with TLC monitoring. After reaction was complete the mixture was cooled to the room temperature and washed with water. After drying over Na_2SO_4 solvents were removed under reduced pressure.

Zn^{II}[3-(5-(*p*-aminophenyl)-10,15,20-triphenylporphyrin)-5-ferrocenyl-1-phenylpyrazole] 9a. Violet powder. Yield 95%. UV-vis (CH_2Cl_2): λ_{max}, nm 297 (12000), 424 (112500), 552 (6000), 598 (3000). ^{1}H NMR (500 MHz, $CDCl_3$): δ, ppm 4.16 (s, 5H, Cp); 4.25 (s, $4H_{\alpha,\beta}$, Cp); 4.55 (s, 2H); 6.60 (s, 1H, Pz); 6.97–6.98 (d, 2H, *o*-Ph-NH, J = 10.0 Hz), 7.74–7.78 (m, 9H, Ph), 8.02–8.05 (d, 2H, *m*-Ph-NH, J = 10.0 Hz), 8.25–8.24 (d, 6H, Ph, J = 5.0 Hz), 8.93 (s, 6H), 9.07 (d, 2H, J = 5.0 Hz). ^{13}C NMR (126 MHz, $CDCl_3$): δ, ppm 68.7, 69.9, 75.0, 105.4, 111.5, 119.6, 119.9, 121.3, 126.6, 127.6, 128.1, 128.9, 131.5, 134.6, 135.8, 140.4, 142.3, 142.4, 142.9, 147.8, 150.9. ESI/MS: *m/z* 1032 $[M]^+$. Anal. found % C, 74.11; H, 4.28; Fe, 5.47; N, 9.60. Calcd. for $C_{63}H_{43}FeN_7Zn$%: C, 74.24; H, 4.25; Fe, 5.48; N, 9.62.

Cu^{II}[3-(5-(*p*-Aminophenyl)-10,15,20-triphenylporphyrin)-5-ferrocenyl-1-phenylpyrazole] 9b. Crimson powder. Yield 97%. UV-vis (CH_2Cl_2): λ_{max}, nm 289 (12000), 417 (112500), 542 (9000), 589 (6000). ESI/MS: *m/z* 1031 $[M]^+$. Anal. found % C, 73.97; H, 4.28; Fe, 5.46; N, 9.59. Calcd. for $C_{63}H_{44}CuFeN_7$%: C, 74.37; H, 4.26; Fe, 5.49; N, 9.64.

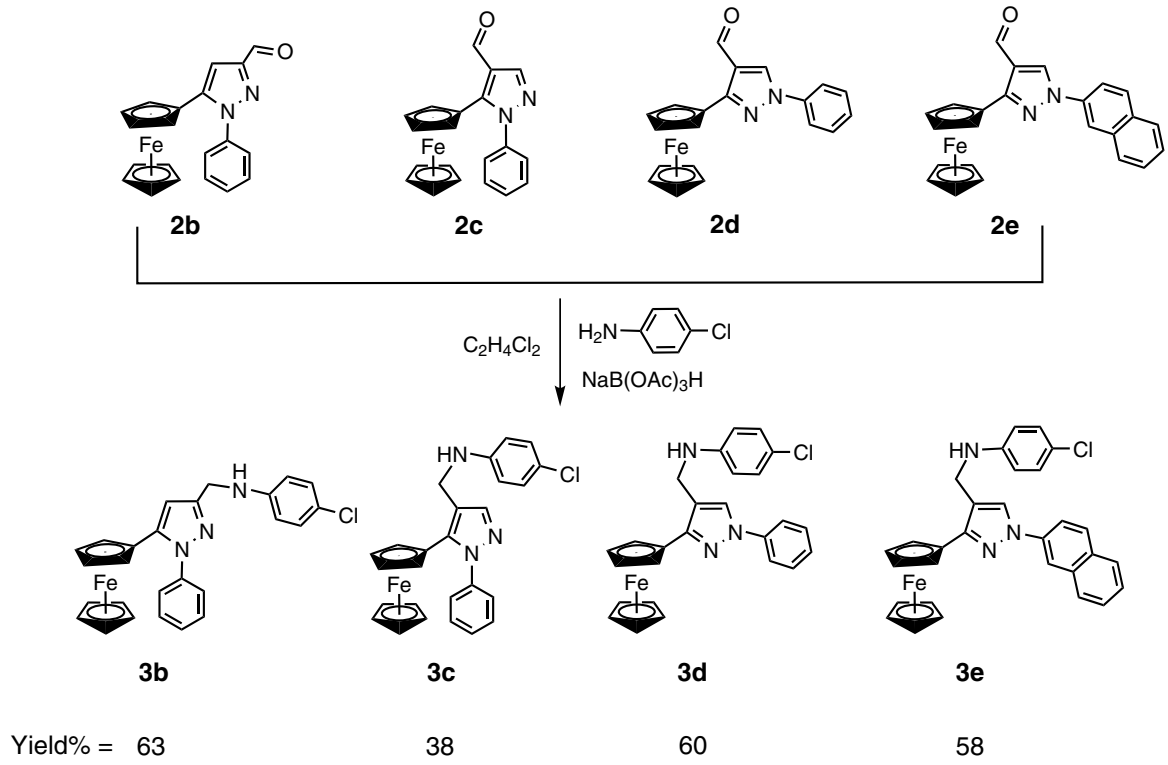
Mn^{II}[3-(5-(*p*-Aminophenyl)-10,15,20-triphenylporphyrin)-5-ferrocenyl-1-phenylpyrazole] 9c. Green powder. Yield 98%. UV-vis (CH_2Cl_2): λ_{max}, nm 287 (12000), 419 (112500), 548 (8000), 590 (6000). ESI/MS: *m/z* 1022 $[M]^+$. Anal. found % C, 74.74; H, 4.32; Fe, 5.52; N, 9.68. Calcd. for $C_{63}H_{43}FeMnN_7$ %: C, 75.00; H, 4.30; Fe, 5.54; N, 9.72.

RESULTS AND DISCUSSION

The synthesis of these ferrocenyl porphyrins involved the reductive amination reaction, using 5-(*p*-aminophenyl)-10,15,20-triphenylporphyrin and ferrocenyl formyl pyrazoles as starting materials. The porphyrin precursor **1** could be prepared by well-known method derived from 5,10,15,20-tetraphenylporphyrin [36]. Formyl ferrocene [37] **2a,** ferrocenyl formyl heterocyclic compounds (1-phenyl-5-ferrocenyl-3-formylpyrazole [38] **2b**, 1-phenyl-5-ferrocenyl-4-formylpyrazole [39] **2c**, 1-aryl-3-ferrocenyl-4-formylpyrazoles [35, 40] **2d**) and phenylformylpyrazoles (1-phenyl-5-ferrocenyl-4-pyrazolecarboxaldehyde [41] **8a**, and 1-phenyl-3-ferrocenyl-4-pyrazolecarbaldehyde [42] **8b**) were obtained by methods described in literature.

To predict the reaction of ferrocenylheterocycles with 5-(*p*-aminophenyl)-10,15,20-triphenylporphyrin, we at first carried out the model reduction amination reaction with ferrocenylpyrazolecarbaldehydes where *p*-chloraniline was taken as amino component. Thus, ferrocene derivatives of *p*-chloroaniline **3b-e** were synthesized with yields up to 63% (Scheme 1). The maximal yield was reached in the case with 1-phenyl-5-ferrocenyl-3-formylpyrazole in which the minimal steric hindrance between ferrocene and formyl group took place.

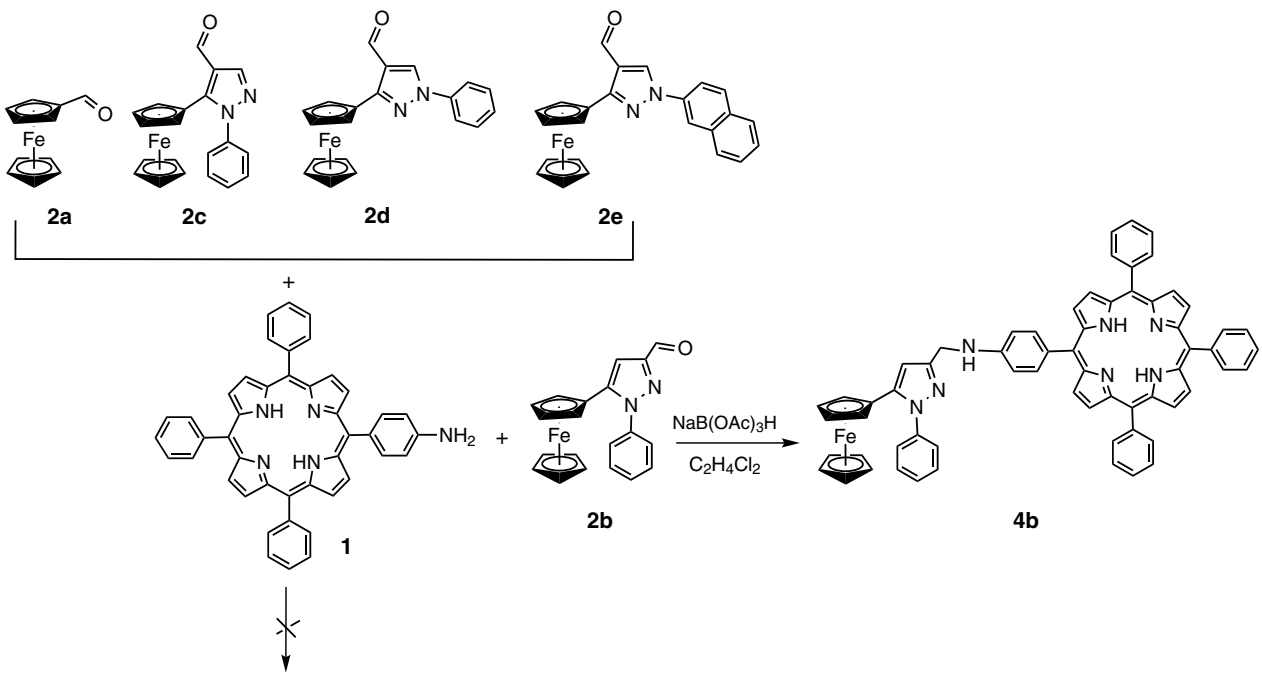
As we can see the different substituents at the heterocyclic fragment does not affect the yield of the



Scheme 1. The reductive amination of ferrocene compounds with *p*-chloroaniline

reaction. The main idea is in the difference between the relative position of formyl and ferrocenyl groups in heterocycle (pyrazole). Thus we assumed that the reaction with bulky aminoporphyrin would proceed more readily in the case of 1-phenyl-5-ferrocenyl-3-formylpyrazole.

In the reaction of ferrocenylpyrazolecarbaldehydes with 5-(*p*-aminophenyl)-10,15,20-triphenylporphyrin the target product was obtained only from 1-phenyl-5-ferrocenyl-3-formylpyrazole, with the 62% yield (Scheme 2). The verifying of reaction time and



Scheme 2. The reductive amination of ferrocene compounds with TPP-NH_2

conditions for another aldehydes led only to traces of the target products. We assume that in contrast to the reaction of ferrocenylcarboxaldehydes with *p*-chloroaniline, in the case of bulky aminoporphyrin fragment the presence namely of ferrocene near the CO group in pyrazole prevents the interaction with amine.

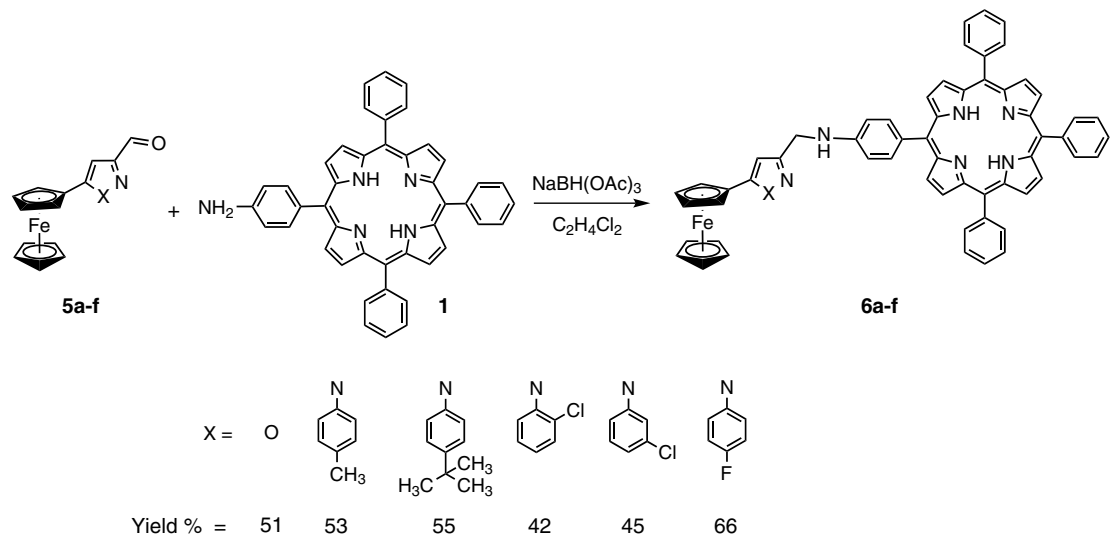
To confirm our prepositions that the reductive amination reaction proceeds with only 1-aryl-5-ferrocenyl-3-formylazoles **5a**–**5f** and aryl moieties didn't affect the reaction we carried the one with various aromatic substituents at nitrogen in pyrazole ring along with ferrocenylformylisoxazole (Scheme 3).

As result we got a number of ferrocene derivatives where porphyrin moety connects to heterocycle *via* amino spacer.

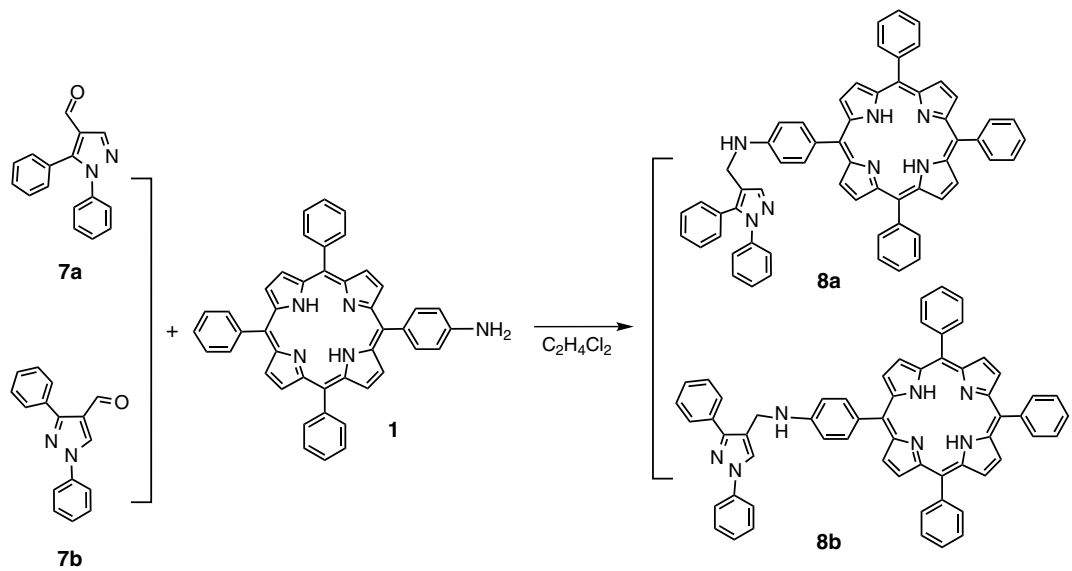
According to these results one may conclude that yields little depend on electronic effects of substituents in phenyl ring due to at first the remoteness of the phenyl substituent from carbonyl group and at the second noncoplanarity of the phenyl and pyrazole prohibiting the conjugation between carbonyl group and the substituent in phenyl radical. UV-visible spectroscopy data have familiar values confirming the fact about no investigations of substituents in phenyl ring in general molecular behavior.

To confirm our suggestion about the steric hindrance caused by the ferrocenyl group, we carried out the reaction of aminoporphyrin with 1,5-diphenyl-4-pyrazolecarbaldehyde **7a**, and 1,3-diphenyl-4-pyrazolecarbaldehyde **7b**.

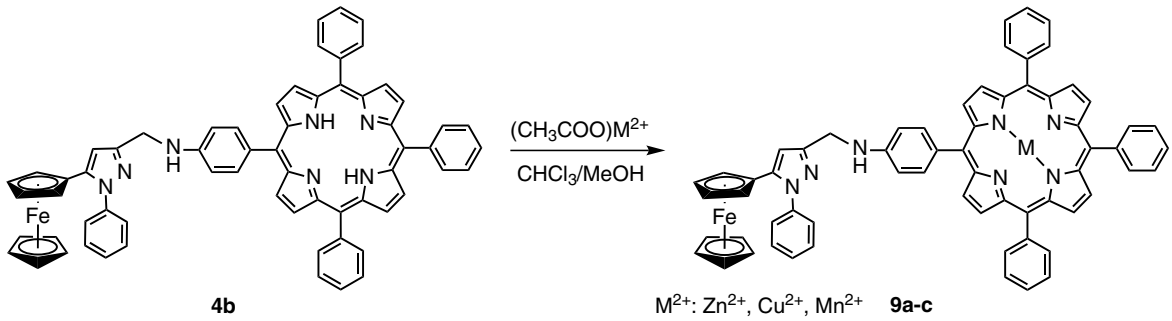
In contrast to the ferrocene analogs, diphenylaldehydes **7a** and **7b** entered into in this reaction. Diphenylpyrazoleporphyrins were synthesised with yields up to 45% (Scheme 4).



Scheme 3. The reductive amination of 5-ferrocenylazole-4-carboxaldehyds with TPP-NH_2



Scheme 4. The synthesis of diphenylpyrazoleporphyrins by the reductive amination of diphenylpyrozoles with TPP-NH_2



Scheme 5. The metalation reaction of 3-(5-(*p*-aminophenyl)-10,15,20-triphenylporphyrin)-5-ferrocenyl-1-phenylpyrazole

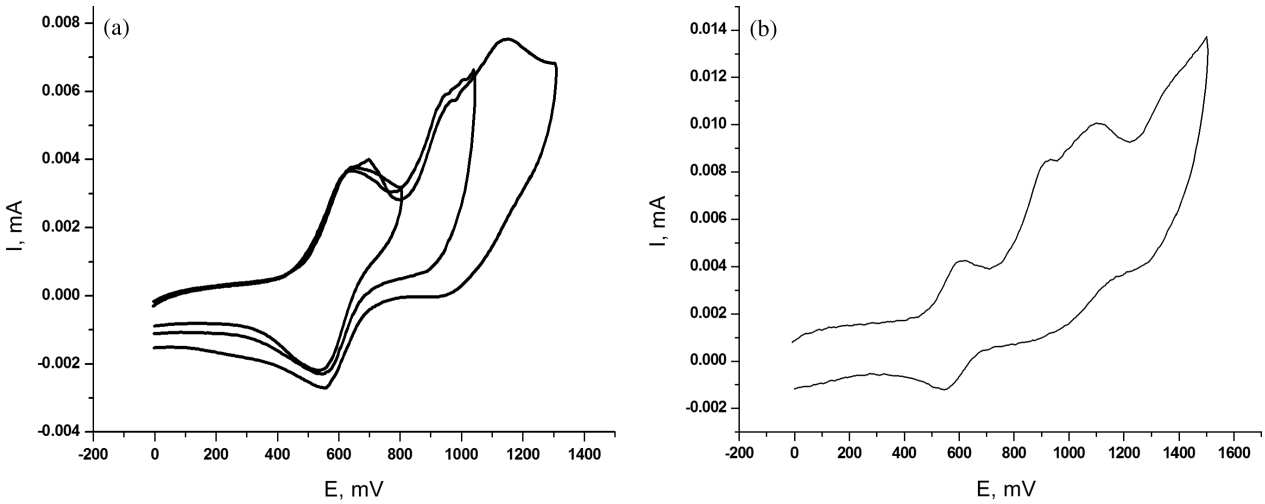


Fig. 1. CVA curves of Fc-TPP (a) and Fc-TPP-Cu (b) (1 mM, CH_3CN, 0.05 M Bu_4NBF_4, Pt, 100 mV/s)

Metalloporphyrins

Porphyrin-modified ferrocene **4b** was entered in the reaction with three metal salts of Zn(II), Cu(II), Mn(II) (Scheme 5). The resulted products were obtained with quantitative yields. ^{1}H NMR spectrum was obtained only for diamagnetic complex of zinc. Copper and manganese complexes were characterized by ESI MS.

Electrochemistry

The measurements were carried out in acetonitrile solution in the presence of 0.05 M Bu_4NBF_4 at a platinum working electrode. All investigated compounds demonstrate of redox activity in the cathodic and anodic potential area.

Electrochemical oxidation of Fc-TPP revealed three peaks at the potentials of 640/560, 920 and 1130 mV (Fig. 1). The first peak is one-electron and reversible. It likely corresponds to the oxidation of the ferrocene fragment. The second and third peaks are also one-electron and are attributed to the oxidation of the porphyrin ring. The oxidation potentials of Fc-TPP are in good agreement with literature data for unsubstituted TPP [43] (Table 1). The similarity of the oxidation potentials observed for the complex with the oxidation potentials of its individual fragments indicates a weak electronic interaction between porphyrin and ferrocene parts.

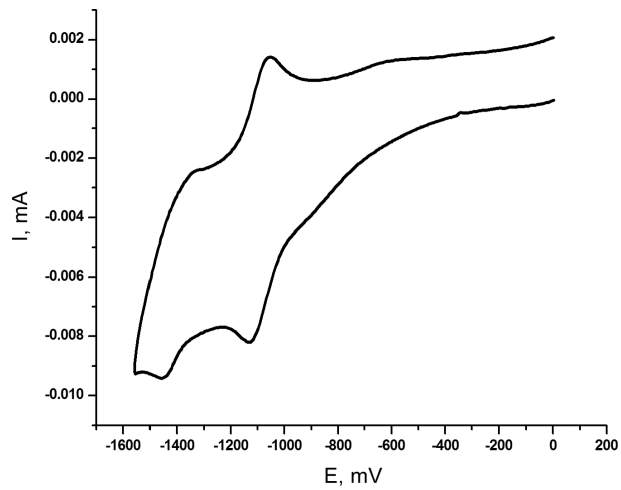


Fig. 2. CVA curves of Fc-TPP and Fc-TPP-Met (Met = Cu, Mn, Zn) (1 mM, CH_3CN, 0.05 M Bu_4NBF_4, Pt, 100 mV/s)

Two one-electron reversible peaks (-1120/-1050 and -1450/-1350 mV) (Fig. 2) corresponding to the reduction of the porphyrin ring can be observed in CV curve of

Table 1. The oxidation potentials of the complexes of Fc-TPP-X (X = Cu^{2+}, Mn^{2+}, 2H) (CH_3CN, 0.05 M Bu_4NBF_4, Pt, 100 mV/s)

Substance	E_1^{Ox}, mV	E_2^{Ox}, mV	E_3^{Ox}, mV	E_4^{Ox}, mV	$-E_1^{Red}$, mV	$-E_2^{Red}$, mV
Fc-TPP	640/560	920	1130	—	1120/1050	1450/1350
Fc-TPP-Cu	630/550	960	1160	1420	1190/1130	1530/1450
Fc-TPP-Mn	650/550	920	1120	1380	1100/1020	1430/1320
p-CH_3-C_6H_4-Fc-TPP	610/520	930	1140	—	1110/1020	1460/1350
H_2TPP		920[44]	1130[44]		1780 /1650*	2120/2010*

* In solution 0.2 M Bu_4NPF_6 in CH_2Cl_2. Platinum electrode, referred to Fc/Fc^+ [45].

Fc-TPP in the anodic potentials area. Reduction potentials as one similar to the literature data [43] for the TPP.

The introduction of metals (Cu^{2+} or Mn^{2+}) in the porphyrin ring confirms the argument of the weak electronic interaction of the ferrocene and the porphyrin unit of the complex, namely the oxidation potentials of Fc-TPP-Cu **9b** (640/560 mV) and Fc-TPP-Mn **9c** (630/550 mV) are very close to the potential of Fc-TPP (650/ 550 mV). (Table 1).

The introduction of electron-donating fragment in the ferrocene unit of the complex has no effect on the oxidation and reduction potentials of the porphyrin fragment and the oxidation potential of ferrocene are slightly shifted in the cathode area.

CONCLUSION

We first obtained the ferrocenylheterocyclic porphyrin by means of the reductive amination reaction and optimized the reaction conditions. It was revealed that the reaction proceeded only with those ferrocenylformaldehydes, that lacked steric hindrances between substituents in the pyrazole unit. Biological tests of obtained ferrocene-porphyrin **3a** are carrying out.

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