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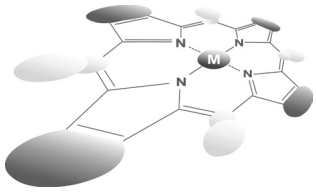

Synthesis and ultrasound mediated antibacterial activity of ferrocene-triazole-porphyrin derivative

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ABSTRACT: The [3 + 2]-cycloaddition reaction of various azides with ferrocenylmethylpropargyl ester in the presence of copper (I) salt lead to the formation of ferrocenyl-containing derivatives, including porphyrin, which exhibit pronounced cytotoxicity against *Escherichia coli* under ultrasound irradiation.

KEYWORDS: ferrocene, porphyrin, sonodynamic therapy, [3 + 2]-cycloaddition, *Escherichia coli*, ultrasound.

INTRODUCTION

Cancer treatment is one of the leading problems in scientific research. Sonodynamic therapy (SDT) is a promising selective treatment method that allows targeting of tumor cells with special drugs (sonosensitizers), the activity of which appears through ultrasound irradiadion [1–7]. Unlike photodynamic therapy (PDT) SDT has the advantage of affecting tumors located deep in organs and tissues. The method of sonodynamic therapy also affects the foci of inflammation, and can be very effective in the treatment of such socially significant diseases as "diabetic foot" (currently, PDT is the only method in use for this) [8–10]. The search for suitable sonosensitizers is a task that must be solved. Porphyrin compounds are now used as sonosensitizers [11, 12]; however, the structures of porphyrin compounds are subjected to various chemical modifications in order to identify and select the best. Interest in ferrocene-containing porphyrins [13] is due primarily to their physicochemical properties. The donor–acceptor nature of such structures and their electrochemical properties are used to study the processes of photoinduced electron transfer in order to simulate the regions responsible for photosynthesis [14, 15]. The redox centers of ferrocenoporphyrins are interesting for modeling molecular machines [16, 17] or molecular electrical sensors [18]. The ability to reversibly accept and give electrons in a different range of potentials can be used in redox catalysis [19], as well as in modeling systems for storing information [20, 21]. Heterocyclic derivatives of ferrocene exhibit a variety of biological activity, including antitumor, while being low toxic compounds [22–29]. Moreover, the membranotrophy of the ferrocene group and the redox properties of ferrocene, manifested in cells, can positively affect the porphyrin system. Ferrocene-modified porphyrins, are hitherto, poorly studied as antitumor and anti-inflammatory agents. Recently, we obtained original ferrocene-containing porphyrins [30–32], which were firstly studied for sonodynamic activity against Staphylococcus aureus [33] (previously such compounds were not studied under the conditions of sonodynamic therapy). Both its own cytotoxic effect and its pronounced amplification under ultrasound were revealed. It appears obvious that further research of such complexes will lead to the creation of new drugs. Existing methods for the synthesis of ferrocene-modified porphyrins are multistage and sometimes difficult to reproduce; others require expensive reagents. In this work we studied CuAAC (copper-catalyzed azide-alkyne cycloaddition) [34, 35] (special case

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of [3 + 2]-cycloaddition) of ferrocenylmethylpropargyl ether with tetraphenylporphyrinazide. Sonodynamic effect of ferrocenyl-1,2,3-triazolylporphyrin using *in vitro* experiments on *Escherichia coli* was studied.

EXPERIMENTAL

Apparatus and analysis

All chemicals used were reagent grade and used as received without further purification. 5-(*p*-Azidophenyl) -10,15,20-triphenylporphyrin was synthesized accordingly to described method [36]. The solvents purified according to standard procedures and distilled just before use. The mass spectra were obtained by the electron impact method on a Finnigan Polaris Q instrument (USA), the temperature of the ionization chamber was 250 °C, the energy of ionizing electrons was 70 eV, and the electrospray method was used on a Thermo Finnigan instrument under standard conditions (electrospray ionization, acetonitrile, capillary voltage 4.5 kV). The NMR spectra recorded on an Avance spectrometer with operating frequencies of 400 for protons, and 100 MHz for ^{13}C nuclei, in $CDCl_3$ at 30 °C. For calibration, ^{13}C signals and residual protons of deuterium solvents taken. The purity of the isolated compounds was checked by TLC on Silufol UV 254, Sorbfil, 25 DC-Alufolien, and Kieselgel 60 F_{254} plates. Preparative chromatography was performed on neutral alumina (Brockmann activity grade II; from Reanal), Kieselgel 60 F_{254} (Merck), or Kieselgel (0.035–0.070 μm, 90 Å, Acros).

General procedure for CuAAC reaction of ferrocenylmethylpropargyl ether with azides

To a mixture of the ferrocenylmethylpropargyl ether (was synthesized according to the method [37]) (1 mmol) and copper acetate hydrate (3 mg, 1.4 mol%) in toluene (5 ml) was added the corresponding azide (1 mmol) at room temperature. The reaction mixture was stirred at ambient temperature; the reaction progress monitored by TLC. The reaction mixture was cooled to room temperature and then poured into water (20 ml) and ethyl acetate (10 ml). The organic layer was separated and the aqueous phase extracted with ethyl acetate (10 ml). The combined organic fractions were dried ($MgSO_4$) and the solvent was removed. The residue was chromatographed (silica gel, methylene chloride).

Ethyl 4-(4-((*ferrocenylmethoxy*) *methyl*-1*H*-1,2,3-*triazole*-1-*carboxylate* (3*a*)

(110 °C, 24h). Yield 75%. Yellow crystals. mp 65–66 °C ^1H NMR (400 MHz; $CDCl_3$; Me_4Si): δ, ppm 1.31 (t, 3H, CH_2CH_3, J = 8 Hz), 4.15 (s, 5H, C_5H_5), 4.18 (s, 2H, C_5H_4), 4.27 (s, 2H, C_5H_4), 4.28 (m, 2H, CH_2CH_3), 4.40 (s, 2H, -CH_2-), 4.68 (s, 2H, -CH_2-), 7.67 (s, 1H, CH). ^{13}C NMR (100 MHz; $CDCl_3$; Me_4Si): δ, ppm 13.92 (CH_2CH_3), 50.84 (-CH_2-), 62.36 (CH_2CH_3), 63.13 (C_5H_5), 68.47 (C_5H_5), 69.57, 68.61 (-CH_2-), 68.68 (-CH_2-), 82.89 (*ipso*-C_5H_4), 123.98 (Tr), 145.94 (*ipso*-Ctr), 166.2 (C=O). MS (EI): m/z 457 (calc.for $[M]^+$ 457).

4-((*Ferrocenylmethoxy*) *methyl*)-1-(3-(*trifluoromethyl*) *phenyl*)-1*H*-1,2,3-*triazole* (3*b*)

(110 °C, 3h). Yield 90 %. Yellow powder. mp 92–93 °C. ^1H NMR (400 MHz; $CDCl_3$; Me_4Si): δ, ppm 4.16 (s, 5H, C_5H_5), 4.20 (s, 2H, C_5H_4), 4.29 (s, 2H, C_5H_4), 4.46 (s, 2H, -CH_2-), 4.74 (s, 2H, -CH_2-), 7.66–7.72 (m, 2H, C_6H_5), 8.00 (s, 1H, Tr), 8.03 (s, 1H, C_6H_5). ^{13}C NMR (100 MHz; $CDCl_3$; Me_4Si): δ, ppm 63.17 (C_5H_5), 68.50 (C_5H_5), 68.74 (C_5H_5), 69.16 (-CH_2-), 69.67 (-CH_2-), 82.67 (*ipso*-C_5H_4), 117.42 (Ctr), 120.58 (C_6H_5), 121.60 (q, J_1 = 269 Hz, C_1F), 121.97 (*ipso*-C_6H_5), 124.68 (C_6H_5), 125.04 (C_6H_5), 125.33 (C_6H_5), 130.57, 132.30 (q, J_2 = 33 Hz, CF), 137.38 (C_6H_5), 146.90 (*ipso*-Ctr). MS (EI): m/z 441 (calc.for $[M]^+$ 441).

4-((*Ferrocenylmethoxy*) *methyl*)-1-*phenyl*-1*H*-1,2,3-*triazole* (3*c*)

(60 °C, 12h). Yield 85 %. Yellow powder. mp 98–99 °C. ^1H NMR (400 MHz; $CDCl_3$; Me_4Si): δ, ppm 4.18 (s, 5H, C_5H_5), 4.21 (s, 2H, C_5H_4), 4.31 (s, 2H, C_5H_4), 4.45 (s, 2H, -CH_2-), 4.74 (s, 2H, -CH_2-), 7.46 (t, 1H, C_6H_5, J = 8Hz), 7.55 (t, 2H, C_6H_5, J = 8Hz), 7.74 (d, 2H, C_6H_5), 7.96 (s, 1H, CH). ^{13}C NMR (100 MHz; $CDCl_3$; Me_4Si): δ, ppm 63.24 (C_5H_4), 68.49 (C_5H_5), 68.69 (C_5H_4), 68.96 (-CH_2-), 69.64 (-CH_2-), 82.81 (*ipso*-C_5H_4), 120.53 (C_6H_5), 120.72 (C_6H_5), 128.73 (C_6H_5), 129.76 (C_6H_5), 137.08 (C_6H_5), 146.29 (*ipso*-Ctr). MS (EI): m/z 373 (calc.for $[M]^+$ 373).

4-((*Ferrocenylmethoxy*) *methyl*)-1-(4-*methoxyphenyl*)-1*H*-1,2,3-*triazole* (3*d*)

(20 °C, 5h) Yield 95%. Yellow powder. mp 98–99 °C. ^1H NMR (400 MHz; $CDCl_3$; Me_4Si): δ, ppm 3.88 (s, 3H, CH_3), 4.16 (s, 5H, C_5H_5), 4.19 (s, 2H, C_5H_4), 4.29 (s, 2H, C_5H_4), 4.45 (s, 2H, CH_2), 4.72 (s, 2H, CH_2), 7.01 (d, 2H, C_6H_4 J = 12 Hz), 7.61 (d, 2H, C_6H_4 J = 12 Hz), 7.87 (s, 1H, CH). ^{13}C NMR (100 MHz; $CDCl_3$; Me_4Si): δ, ppm 55.64 (O-CH_3), 63.27 (C_5H_4), 68.48 (C_5H_5), 68.69 (C_5H_4), 69.93 (-CH_2-), 69.65 (-CH_2-), 82.81 (*ipso*-C_5H_4), 114.77 (Ctr), 120.91, 122.18, 130.6, 146.05 (*ipso*-Ctr), 159.93 (-C-OCH_3). MS (EI): m/z 403 (calc.for $[M]^+$ 403).

Zinc 4-((*ferrocenylmethoxy*) *methyl*)-1-(5-(*p*-*aminophenyl*)-10,15,20-*triphenylporphyrin*)-1*H*-1,2,3-*triazole* (5)

Yield 75%. Purple powder. mp >250 °C. ^1H NMR (400 MHz; $CDCl_3$; Me_4Si): δ, ppm 4.16 (s, 5H, C_5H_5), 4.21 (s, 2H, C_5H_4), 4.30 (s, 2H, C_5H_4), 4.43 (s, 2H, -CH_2-), 4.74 (s, 2H, -CH_2-), 7.74–7.83 (m, 9H, Ph); 8.05–8.07 (d, 2H, Ph, J = 8 Hz), 8.23–8.25 (d, 6H, Ph, J = 8 Hz),

8.43–8.45 (d, 2H, Ph, J = 8 Hz), 8.80–8.92 (m, 8H$_{\alpha\beta}$, Py). ^{13}C NMR (100 MHz; $CDCl_3$; Me_4Si): δ, ppm 63.17 (C_5H_5), 68.50 (C_5H_5), 68.74 (C_5H_5), 69.16 (-CH_2-), 69.67 (-CH_2-), 82.67 (*ipso*-C_5H_4), 117.42 (Ctr), 118.97, 120.40, 126.81, 127.85, 128.38, 134.67, 135.82, 139.03, 139.92, 142.20. MS (ESI): m/z 973 (calc.for $[M + H]^+$ 973).

Zinc 5-(*p-azidophenyl*)-10,15,20-*triphenylporphyrin* (4)

A solution containing 1 mol of zinc acetate in ethanol was added to a solution of 0.001 mol of 5-(*p*-azidophenyl)-10,15,20-triphenylporphyrin porphyrin in methylene chloride. The reaction mass was stirred at room temperature for 15 minutes. Next, the organic layer was washed with water, dried over $MgSO_4$. The solvent was removed *in vacuo*.

Yield 98%. Purple powder. mp >250 °C. ^{1}H NMR ($CDCl_3$, 400δ, ppm): 7.48 (d, 2H, 2CH, Ph-NH, J = 6 Hz), 7.80–7.85 (m, 9H, 9CH, Ph), 8.28–8.33 (m, 8H, 2CH, Ph-NH), 8.72 (br s, 1H, 2CH, Ph), 7.81 (m, 8H, Py). ^{13}C NMR ($CDCl_3$, 126 MHz, δ, ppm): 117.53, 118.97, 120.40, 126.81, 127.85, 128.38, 134.67, 135.82, 139.03, 139.92, 142.20. MS (ESI): m/z 717 (calc.for $[M + H]^+$ 717).

The bacterial model

Viability and effects were evaluated on *Escherichia coli* bacteria. The bacterial culture was grown on Endo gel medium, prepared with the addition of agarose, at a temperature of 37 °C. For the experiment, a suspension of bacterial cells was prepared in a sterile isotonic sodium chloride solution, washing off the bacterial cells from the gel substrate into the solution. To assess cell viability, preparations were introduced into the culture medium at a concentration of 0.002 g/ml suspension of microorganisms, the preparations were dissolved in DMSO.

Assessment of the impact of ultrasound on bacterial suspension

Viability assessment was performed minus the effect of exposure to DMSO. 10 ml of a suspension of bacterial cells and the experimental substance was introduced into a vessel with a soundproof bottom. The vessel was placed in a thermostatic bath with water at a temperature of 37 °C above an ultrasonic emitter (0.88 MHz) and the suspension was subjected to ultrasonic treatment for 5 min at ultrasound intensities of 1.5 W/cm^2. Then 1 ml of the suspension was transferred onto a sterile medium in a Petri dish with the culture medium. The Petri dishes were then placed in an air thermostat. The temperature in the thermostat for culturing bacteria was 37 °C. The result of bacterial growth was evaluated after 24 h, counting the number of colony forming units in the experimental and control samples. The experiments were performed in duplicate. The final result was evaluated as a percentage of control/experience.

RESULTS AND DISCUSSION

CuAAC reaction of ferrocenylmethyl propargyl ether with azides

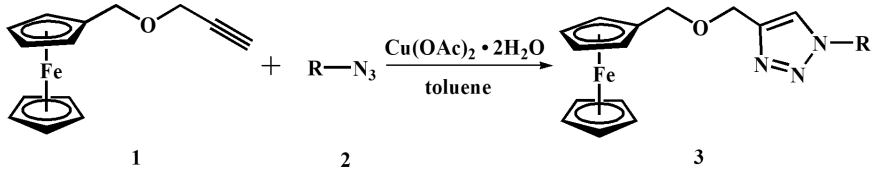
In order to develop and optimize the CuAAC reaction for the synthesis of ferrocene-containing porphyrin, reactions of ferrocenylmethyl propargyl ether with aromatic azides and azidoacetic ester were carried out in toluene using copper acetate. (Scheme 1)

The fastest reaction occured with the participation of electron-donor substituents at phenyl ring, at 20 °C for 5 h. With phenylazide the reaction proceeds for 12h at 60 °C, and under boiling temperature for a day with a trifluoromethyl substituent. When using aliphatic azides the reaction time increased.

CuAAC reaction for the synthesis of ferrocenyl-1,2,3-triazole-porphyrin

Successful testing of the CuAAC reaction of ferrocenylmethylpropargyl ether with aromatic azides allowed the reaction with tetraphenylporphyrinazide (Scheme 2).

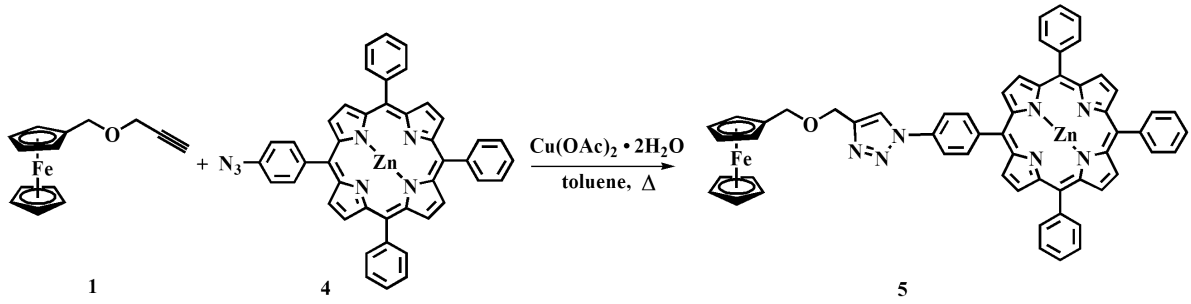
It should be noted that when using catalytic amounts of copper acetate the terminal triple bond was not activated, and only the incorporation of the copper ion into porphyrin was observed. When an equivalent amount of copper acetate added, the target product formed in which copper is embedded in the porphyrin ring. In order to avoid the incorporation of copper into porphyrin we conducted a metallation reaction of azidoporphyrin with zinc acetate in a mixture of ethanol/methylene chloride solvents. Afterwards, a similar CuAAC reaction of ferrocenylmethylpropargyl ether with tetraphenylporphyrinazide was carried out (Scheme 2).



1 2 3

R: -$CH_2OOC_2H_5$ (a), -C_6H_4-*m*CF_3 (b), -C_6H_5 (c), -C_6H_4-*o*CH_3 (d)

Scheme 1. CuAAC reaction of ferrocenylmethyl propargyl ether with azides.



Scheme 2. CuAAC reaction of ferrocenylmethyl propargyl ether with porphyrinazide.

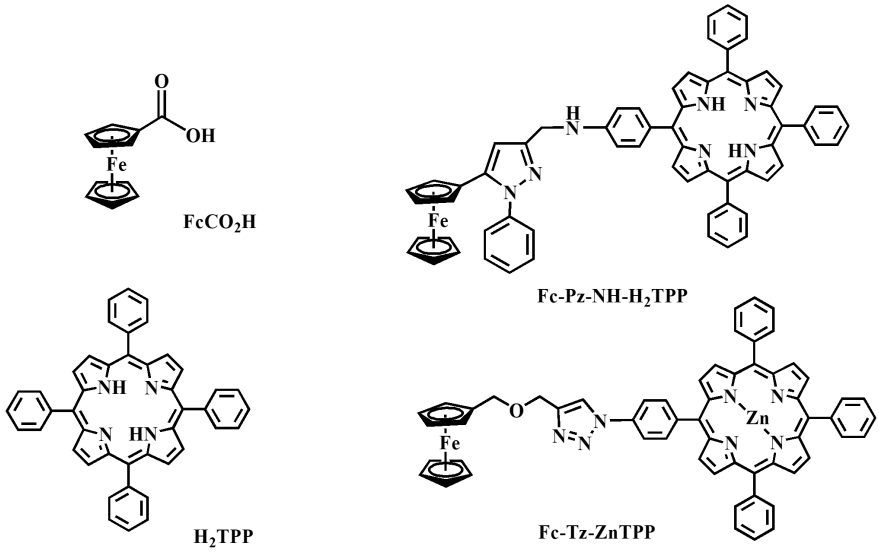


Fig. 1. Sonosensitisers for SDT experiment.

Table 1. The results of SDT experiment on *Escherichia coli* cells.

Sonosensitiser*	DMSO mkl/10 ml**	US control, % death	US + sample, % death	Effect %	Stand. deviation
$FcCO_2H$	300	20	28	8	0.41
H_2TPP	300	20	38	18	0.72
Fc-Pz-NH-H_2TPP [33]	300	20	29	9	0.47
Fc-Tz-H_2TPP	300	20	41	21	0.71

*Sonosensitiser molar concentration 10^{-5} M (0.001 g/ml).
**DMSO concentration in 10 ml of bacterial medium.

Sonodynamic experiment

In vitro tests using ultrasound irradiation to study the biocidal action of several porphyrin and ferrocene compounds against *Escherichia coli* were carried out. Effects of ferrocenylporphyrin with results for tetraphenylporphyrin, ferrocenecarboxilic acid and the previously synthesized ferrocene-modified porphyrin [33] were first compared. In a DMSO solution, a pronounced cytotoxic effect of all injected samples, led to the death of *Escherichia coli*. Under the ultrasound action, as expected, there was an increase in biocidal action of all samples. It is noteworthy that, in its activity, ferrocene carboxylic acid ($FcCO_2H$) is not inferior in activity to ferrocene-modified substrates. Concerning tetraphenylporphyrin, its activity is lower than that of ferrocenemodifiedporhyrin (Fc-Tz-ZnTPP), and higher than that of Fc-Pz-NH-H_2TPP; however, the effect of H_2TPP cannot be denied. Unfortunately, the effect of Fc-Pz-NH-H_2TPP under ultrasound is lower than was

hoped. The most effective compound was Fc-Tz-ZnTPP (Fig. 1). Table 1 shows the number of dead cells in the experiment on *Escherichia coli*.

This was a screening study for the sono-activity presence or absence where the primary effect of different "classes" (types) of compounds obtained were investigated. Since some activity had been identified, all of these compounds will be tested on cancer cells.

CONCLUSION

Reactions of ferrocenylmethyl propargyl, both with aliphatic and aromatic azides, were carried out in toluene using copper acetate. The reaction rate depends on the electronic effect of substituent. For the CuAAC reaction new ferrocene-modified porphyrins were obtained. The results obtained are one of the test steps being carried out at present and will continue to be carried out in the future with other samples from a large amount of self-obtained ferrocenemodified porphyrins and ferrocene derivatives. Sonodynamic effect of ferrocene-modified porphyrin was studied on *Escherichia coli* cells and compared with synthesized previously ferrocene-porphyrin, tetraphenylporphyrin and ferrocene carboxylic acid. The insolubility of most compounds in water makes experiments with them difficult. Alternative use of oils or DMSO sometimes have negative affects on the state of experimental cell cultures which are already extremely sensitive to external factors. The need for water-soluble preparations led these investigations to a new stage in the development of appropriate synthetic methods, which is planned as the next large-scale project. The main achievement lies in the fact that ferrocene-containing porphyrins are promising compounds for consideration of new drugs to treat sonodynamic cancer therapy diseases and inflammatory processes.

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