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Synthesis of Anionic and Cationic Corroles and Study of Their Complexing Ability and Photodynamic Activity towards DNA and Albumin

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Dedicated to the memory of Academician Oskar Iosifovich Koifman

In the work, free base corroles – sulfophenylcorrole (mixture of tri(4-sulfophenyl)corrole and tetrasulfotriphenylcorrole) and tri(N-methylpyridin-4-yl)corrole triiodide were synthesized and associative equilibria in aqueous and organic media were studied. Their binding ability to bovine serum albumin (BSA) and DNA was studied by various physicochemical methods. It has been established that complexes with DNA are formed only by cationic corrole, which binds to DNA by the intercalation method. Both cationic and anionic corroles bind to BSA. It was found that the synthesized corroles are weakly fluorescent fluorophores and practically do not generate singlet oxygen; however, they are capable of generating superoxide anion radicals and can participate in type I photooxidation, which was established on the basis of the processes of photooxidation of nitroblue tetrazolium and BSA. Radical and radical ion reactions underlying the potentiation of BSA oxidation upon photoirradiation with photosensitizer were studied. It was found that the addition of KI significantly accelerates the photooxidation of BSA. It has been proven that the stage of formation of triiodide ions, which trigger a cascade of radical ion reactions, plays an important role in the potentiation processes.

Keywords: DNA, corroles, albumin, BSA.

Синтез анионных и катионных корролов и изучение их комплексообразующей способности и фотодинамической активности по отношению к ДНК и альбумину

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В работе были синтезированы корролы – сульфофенилкоррол (смесь три(4-сульфофенил)коррола и тетрасульфотрифенилкоррола) и три(N-метилпиридин-4-ил)коррол триодид, и изучены ассоциативные равновесия в водных и органических средах. Их способность связываться с бычьим сывороточным альбумином (БСА) и ДНК была изучена различными физико-химическими методами. Установлено, что комплексы с ДНК формируются только с катионным корролом, который связывается с ДНК методом интеркаляции. Как катионные, так и анионные корролы связываются с БСА. Обнаружено, что синтезированные корролы слабо флуоресцируют и практически не генерируют синглетный кислород; однако они способны генерировать радикалы супероксида и могут участвовать в фотоокислении типа I, что было установлено на основе процессов фотоокисления нитросинего тетразолия и БСА. Исследованы радикальные и радикально-ионные реакции, лежащие в основе потенциирования окисления БСА при фотооблучении с фотосенсибилизатором.

Обнаружено, что добавление KI значительно ускоряет фотоокисление БСА. Доказано, что стадия образования трииодид-ионов, инициирующих каскад радикально-ионных реакций, играет важную роль в процессах потенциирования.

Ключевые слова: ДНК, корролы, альбумин, БСА.

Introduction

Corroles are tetrapyrrole macrocycles are similar to porphyrins, but one methine carbon atom is missing between the pyrrole fragments. In addition, corroles, compared to porphyrins, contain one extra proton within the cycle. Protons within the macrocycle of corroles are strongly acidic,[1] while similar protons in porphyrins are weakly basic. The first corrole was obtained in 1965,[2] since then, until 2000, the difficulties of synthesizing these compounds did not allow them to be systematically studied. The situation has changed after the discovery of a simple synthetic methodology.[3,4]

In terms of possible practical applications, corroles are considered as potential catalysts, chemical sensors, solar cells, and anticancer drugs.[5-8] Interaction with DNA and proteins, potential targets for photodynamic therapy (PDT) and photodynamic inactivation (PDI), is currently being actively studied. From the point of view of the interaction of corroles with DNA, a number of studies can be distinguished. The interaction of corroles with DNA through intercalation or interactions at major and minor grooves can cause structural changes in DNA and possible cell destruction through apoptosis or necrosis.[9] Cationic corroles interact more strongly with DNA than analogous porphyrins and form both intercalation and outside binding.[10] Several mechanisms of cationic tris-N-methylpyridyl corrole binding to double-stranded DNA were established.[11] It has been shown that the metal-free cationic corrole is an intercalate for DNA and leads to destabilization of its structure, while the metallocorrole is only capable of outside binding. Uncharged molecules of 5,10,15-tris(4-methoxycarbonylphenyl)corrole and its metal complex with tin(IV) bind to DNA only from the outside.[12] Sulfo derivatives of corroles seem to be promising ligands as DNA, since are more soluble in

aqueous media with a p*H* close to the physiological value. Despite the negative charge of the sulfo group and the possible blocking of the formation of an outside complex with DNA, there are data on the outside binding of anionic carboxy-substituted corroles to DNA.[13]

The binding of corroles to proteins is also being actively studied. There are works devoted to the delivery of corroles by carrier proteins to tumor cells.[14] Based on corroles and proteins, conjugates and nanoparticles are being developed for cancer therapy.[15,16] In a number of works, it is proposed to use albumin as a drug transporter based on corroles.[13,17-19] Based on our own experience for cationic and anionic substituted porphyrins studies on the interaction of albumin and DNA,[20-23] in this study we tried to study the interaction of free-base anionic and cationic corroles with DNA and serum albumin.

Experimental

Bovine serum albumin, fraction V (BSA) was purchased at Acros Organics. 4-Nitro blue tetrazolium chloride (NBT), sodium azide, 5,10,15,20-tetraphenylporphyrin (H_2TPP), 1,3-diphenylisobenzofuran (DPBF) and potassium iodide were purchased in Sigma-Aldrich. Deoxyribonucleic acids, from salmon sperm and ethidium bromide were bought in Acros Organics. DNA concentrations were determined spectrophotometrically using molar extinction coefficient: ε = 6600 $cm^{-1} \cdot M^{-1}$ at 260 nm. A tris-HCl buffer with p*H* 7.4 was used for DNA solutions preparing. A PBS buffer with p*H* 7.4 was used for BSA solutions preparing. For the preparation of solutions, water of the type 1 was used, prepared at UP-2010 water treatment plant (ULAB, China). The studied corroles: sulfophenylcorrole (mixture of tri(4-sulfophenyl)corrole and tetrasulfotriphenylcorrole) (**pSCor**) and tri(N-methylpyridin-4-yl)corrole triiodide (**NMeCor**) have been obtained according to Scheme 1. Synthesized corroles were characterized spectrally; their individuality and purity were confirmed by TLC, ^{1}H NMR, MALDI-TOF. A detailed synthesis procedure is presented in the *Supplementary Materials* available online.

^{1}H NMR spectra were measured on a Bruker Avance-500 instrument (USA). Signals from the solvents were used as internal standards. MALDI-TOF mass spectra of positive ions were detected on a Shimadzu AXIMA Confidence time-of light mass spectrometer with matrix-associated laser desorption (Japan). UV-Vis and fluorescence spectra were registered using AvaSpec-2048 spectrophotometer (Avantes BV, Apeldoorn, Netherlands) at 25 °C in 10 mm quartz cuvettes. The monochromatic LEDs UVTOP-295, λ_{max}=295 nm (Sensor Electronic Technology, Inc. USA) and B5B-433-525, 10 mW, λ_{max}=425 nm (Roitner Lasertechnik Gmbh., Germany) were used as light sources for fluorescence study and irradiation.

The time-resolved fluorescence measurements were carried out by means of a high performance fluorescence lifetime and steady state spectrometer FluoTime 300 (PicoQuant, Germany) with a 460 nm LED PLS 450 (PicoQuant, Germany) as an excitation source. The instrument response function of the system was measured with the stray light signal of a dilute colloidal silica suspension (LUDOX). The fluorescence decay curves were measured at the maximum of the emission peaks and the fluorescence lifetimes were obtained by reconvolution of the decay curves using the EasyTau 2 software package (PicoQuant, Germany).

Quantum yields for singlet oxygen generation were determined by monitoring the sensitized photooxidation of 1,3-diphenylisobenzofuran at 313 nm.[24]

The detection of superoxide anion was carried out by observing the formation of diformazan from NBT.[25,26] Irradiation was carried out for solutions with similar optical densities at irradiation wavelength of 425 nm.

The fluorescence quantum yield of corroles was determined as follows.[27] H_2TPP was used as a standard ($\Phi(f)$=0.12, $\Phi(^1O_2)$=0.64[28]). For solution with optical density more than 0.1 the fluorescence correction for compensation of inner filter effect was made in terms of the Equation (1):

$$F_{corr(\lambda)} = F_{obs(\lambda)} \cdot 10^{\left(\frac{A_{ex(\lambda)}+A_{em(\lambda)}}{2}\right)}, \quad (1)$$

where $F_{corr(\lambda)}$ and $F_{obs(\lambda)}$ – corrected and observed fluorescence at the corresponding wavelengths, $A_{ex(\lambda)}$ and $A_{em(\lambda)}$ – the optical densities of the solution at the excitation and emission wavelengths.[29]

The Scatchard constants were calculated as published earlier. [30]

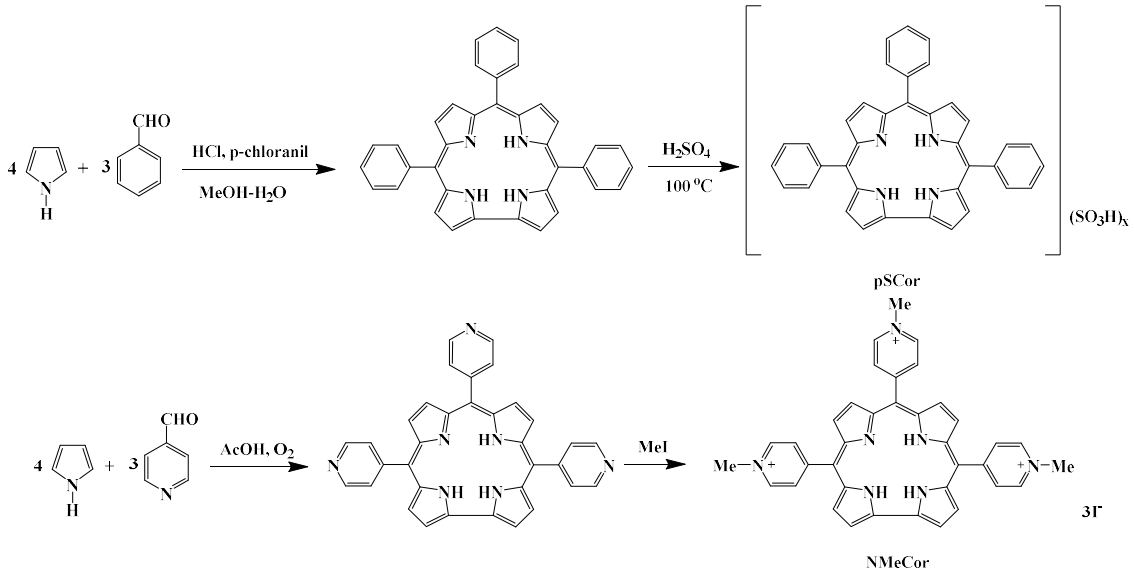
Results and Discussion

Association of Corroles

Cationic and anionic free-base corroles are prone to association; therefore, the initial stage of this work was the establishment of associative equilibria in solutions of **NMeCor** and **pSCor**.

The UV-Vis spectra of corroles are similar to porphyrins, corroles have a Soret band with an extinction coefficient of more than 100,000 $M^{-1}cm^{-1}$ and Q-bands in the region of 500–650 nm with extinction coefficients of 10,000–20,000. **pSCor** is incapable of participating in deprotonation processes, since the nature of the UV-visible spectrum practically does not change with an increase in p*H* from 7.4 to 9. With a decrease in p*H* (Figure 1), protonation of the fourth nitrogen atom in the macroring probably occurs, which is confirmed by the red shift of the Soret band by 20 nm, the disappearance of the band in the region of 514 nm and the appearance of absorption in the long-wave region of the spectrum at 588 and 646 nm (Figure 1).

The spectra of **NMeCor** in water, DMF and borate buffer with p*H*=7.4 are poorly resolved (Figure 2), which also indicates the presence of associates in solution. The addition of hydrochloric acid to aqueous solutions of **NMeCor** leads to an increase in the absorption intensity in the region of 481 nm and causes the appearance of new bands in the region of 317 nm and 689 nm (Figure 2). In this case, fluorescence is quenched (Figure 2).



Scheme 1. Scheme of synthesis of water soluble corroles.

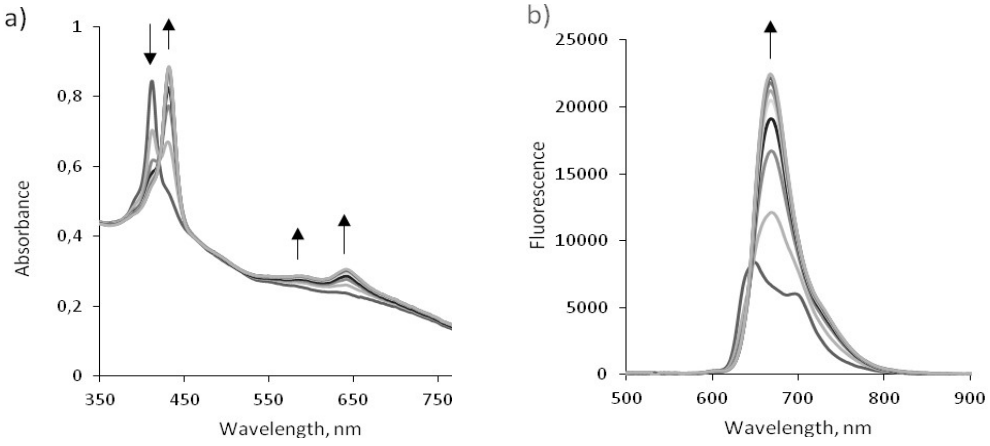


Figure 1. UV-Vis (a) and fluorescence spectra (b) of **pSCor** upon titration with HCl in H_2O. Titration was performed by adding hydrochloric acid (0.1 M, 2 μL by 8 steps) to 2 mL of corrole solution in H_2O in a cuvette with stirring at 25 °C.

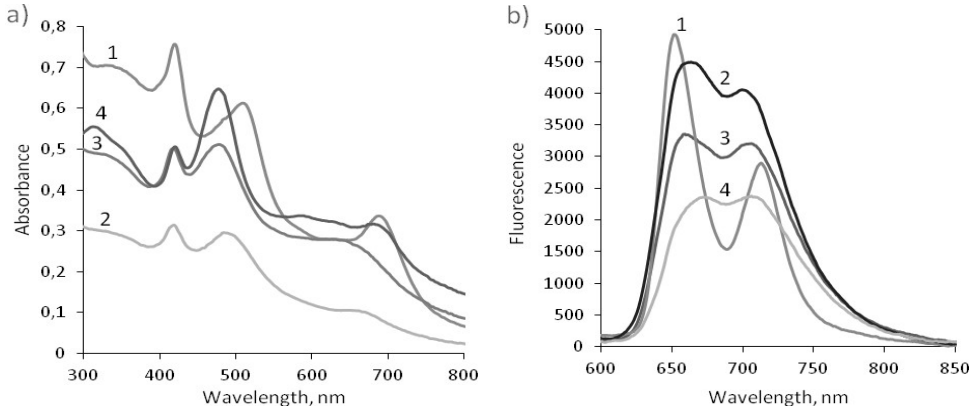


Figure 2. UV-Vis (a) and fluorescence (λ_{ex}=425 nm) spectrum (b) **NMeCor**: 1 – DMF; 2 – p*H*=7.4 (TRIS); 3 – H_2O; 4 – H_2O + 1N HCl (2 mL + 6 μL).

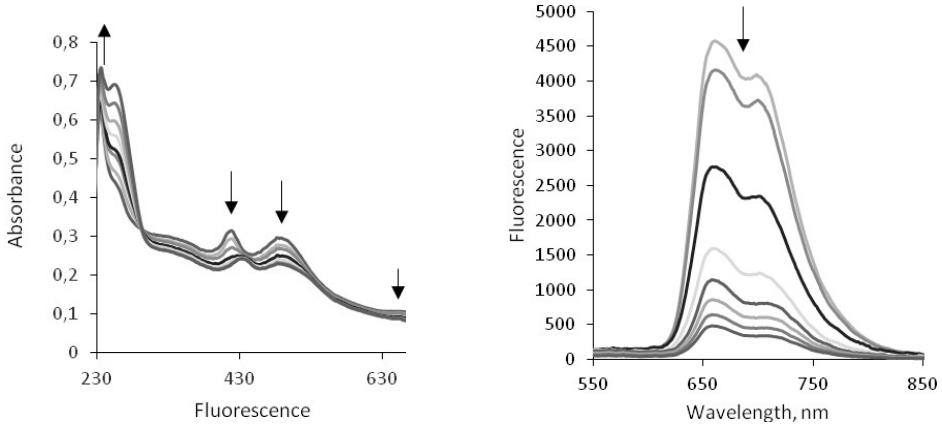


Figure 3. UV-Vis and fluorescence (λ_{ex}=425 nm) spectra of **NMeCor** (12 μM) while titration with DNA. Titration was performed by adding DNA (1.6 mM, 10 μL by 7 steps) to 2 mL of corrole solution in Tris-buffer in a cuvette with stirring at a temperature of 25 °C.

The obtained spectral data suggest that in aqueous solutions **NMeCor** is in an associated state, the main role in stabilization of which is played by H-bonds between corrole molecules in the associate. An increase in p*H* due to the introduction of ammonia into solutions of **NMeCor** in water causes a red shift of the band at 480 nm by 16 nm and a decrease in absorption in the region of 480 nm, which is logical and is associated with the processes of destruction of H-bonded associates in the presence of a strong base NH_4OH. A decrease in the optical density of solutions in the entire analyzed spectral range and a decrease in fluorescence indicates the processes of self-aggregation of cationic corrole. Probably, the partial neutralization (+) of the charge of the peripheral cationic groups during the introduction of alkali is the reason for this.

The above spectral studies allow us to conclude that in neutral and acidic solutions, cationic corrole forms solvate-separated H-associates, in the formation of which the protons of the reaction center and the hydrating medium participate. In the UV-Vis spectra, these associates are manifested by the presence of absorption in the region of 317, 480, 591, and 689 nm. In alkaline solutions and DMF, cationic corrole forms π-π associates, the formation of which causes an increase in absorption in the region of 496 nm. In DMF, in π-π associates, probably, multicenter H-bonding occurs between the atoms of corrole molecules in the associate, which is explained by the appearance of a peak in the region of 689 nm.

Binding of corroles with DNA

The next stage was to study the interaction of the synthesized corroles with DNA and albumin. The UV-Vis spectrum of **pSCor** during titration with DNA does not undergo significant changes (Figure S1), 5% hypochromism is recorded with the Soret band position preserved. Such changes are usually interpreted as corresponding to outside binding of corrole with DNA.[13] For our objects, the proposed interaction option is unlikely. The negative charge of the phosphate backbone and the negative charge of corrole's sulfo substituents can prevent corrole to outside binding with DNA.

Titration of the **NMeCor** with DNA leads to significant spectral changes (Figure 3). The optical density of the Soret band decreases and undergoes a red shift, and the absorption intensity also decreases in the region of 488 nm and 660 nm. The resulting spectral changes (Figure 3), with the exception of changes in the Soret region, are very simi-

lar to the changes caused by the action of alkali. This allows us to speak about the partial neutralization of the charges of cationic substituents upon binding to DNA. The changes in the Soret band of corroles in DNA solutions and in alkaline solutions differ significantly. As mentioned above, titration of a **NMeCor** with a strong base does not cause any shift of the Soret band and only slightly decreases its intensity. When titrating **NMeCor** with DNA, both hypochromism and a redshift of 20 nm are recorded. It is noteworthy that already at the 4th step of the titration, the corrole fluorescence practically disappears. The average fluorescence lifetime of NMeCor in TRIS buffer is 1.88 ns, in the complex with DNA – 0.1 ns (Figures S3, S4). All these data suggest that the cationic corrole intercalates between pairs of nitrogenous bases in DNA. In this case, the π-π-interaction between the π-system of corrole and nitrogenous bases and the electrostatic interaction between the phosphate backbone and the cationic substituents of corrole are probably realized.

The results of competitive titration of the complex of ethidium bromide with DNA triiodide tri(N-methylpyridin-4-yl)corrole confirm the intercalation mechanism of the interaction of corrole with DNA (Figure S2).

The parameters of DNA binding to cationic corrole indicate a high DNA affinity for tri(N-methylpyridin-4-yl) corrole trioidide ($4\cdot10^{-7}$ M), which is close to DNA affinity for tetra(N-methylpyridin-4-yl)porphyrin tetraiodide ($3.64\cdot10^{-7}$ M).[31] Another specific feature of DNA complexes with corrole is the established ratio of nitrogenous base pairs to corrole equals to 1. This indicates a low selectivity of corrole binding without a preference for AT or CG-enriched regions of DNA. Unlike, for example, tetra(N-methylpyridin-4-yl)porphyrin tetraiodide, which predominantly intercalates in DNA CG-enriched regions.[32]

The binding of corroles with albumin

Titration of BSA with both cationic and anionic corroles leads to fluorescence quenching of tryptophan amino acid residues (Figure 4.) For BSA complexes with corroles, the Scatchard plot is well match by a straight line equation (Figure 4), which indicates that the synthesized corroles are bound by the protein in a unique way. The affinity of the protein for cationic corrole ($2.5\cdot10^{-5}$ M) is slightly higher than for sulfo derivatives of corrole ($1.8\cdot10^{-5}$ M) and significantly lower than the similar characteristic obtained for BSA-porphyrin systems.[29]

Photochemical properties of corroles

In the context of the main task of the study – the search for promising photosensitizer (PS) capable of photoinactivation of pathogens, it was important to evaluate the photochemical properties of the synthesized corroles. It is believed, that corroles have higher fluorescence quantum yields than porphyrins, along with a lifetime on the order of several nanoseconds.[25,26] Our data showed the fluorescence quantum yields Φ(f) (λ_{ex}=525 nm) of **NMeCor**, **pSCor** in DMF to be 0.003 and 0.02, respectively; the quantum yields of singlet oxygen for both corroles are 0.01. The fluorescence lifetime in TRIS buffer was 3.08 ns for **NMeCor** and 1.88 ns for **pSCor** (Figures S3, S5). It should be noted that the obtained values should be related not with individual compounds, but with associates of corroles, as evidenced by their analysed UV-Vis spectra. Another possible explanation for the low quantum yield of singlet oxygen is the high rate of physical $^1O_2$ quenching by corrole.[33]

Due to the fact that corroles practically do not generate singlet oxygen, we evaluated their ability to photooxidize substrates according to type I[34] by the reaction of destruction of NBT to diformazan (Figure 5). In the case of cationic corrole, with an increase in the duration of irradiation, an increase in the optical density of the absorption band in the region of 500–600 nm, corresponding to the absorption of diformazan, is recorded (Figure 5). Therefore, cationic corrole, even in a partially associated form, is capable of generating superoxide anion radicals and can participate in type I photooxidation processes. In the case of anionic corrole, changes in UV-Vis spectrum in the region of 570 nm are practically the same as upon irradiation of a solution of individual NBT, which indicates the absence of the ability of **pSCor** to type I photoreactions.

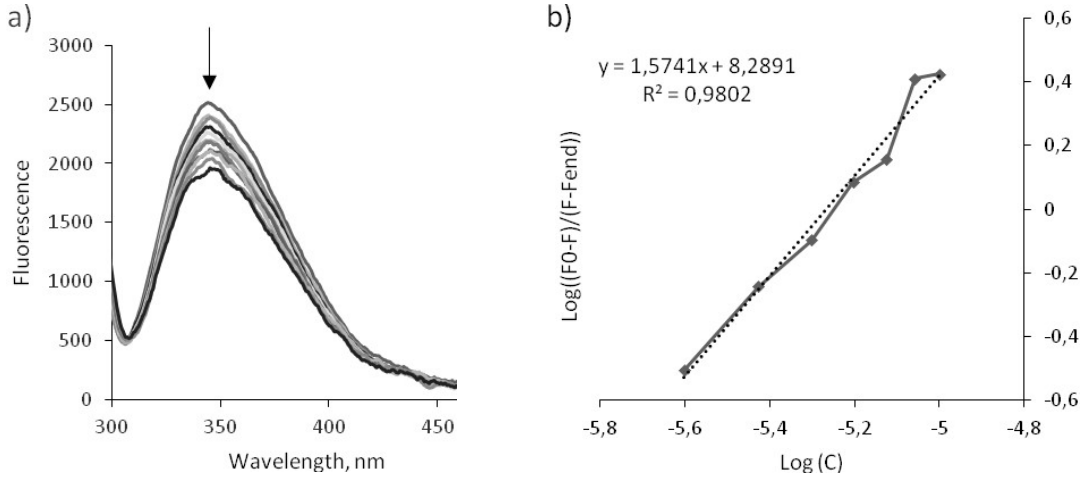


Figure 4. Corrected fluorescence spectra, λ_{ex}=295 nm (a), Scatchard plot (b) of BSA (12 μM) during titration with sulfo-substituted corrole (0-12 μM) in TRIS.

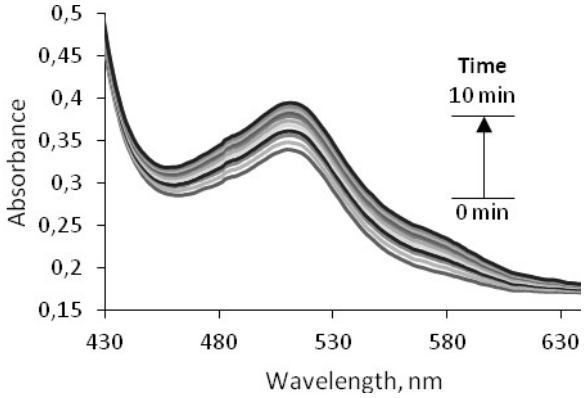


Figure 5. UV-Vis spectra of NBT and NMeCor upon irradiation with light (λ=525 nm, 10 mW) in DMF.

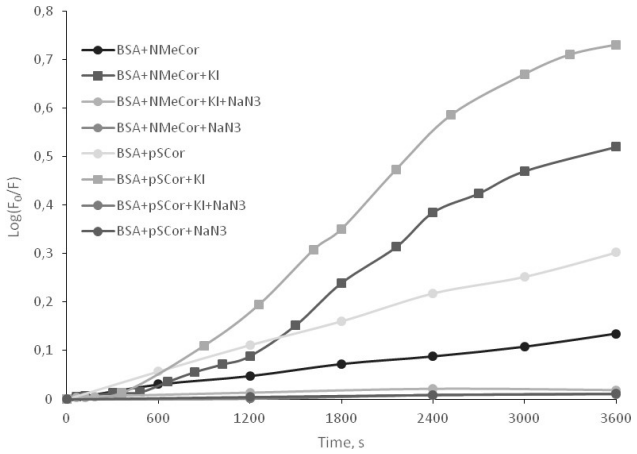


Figure 6. Dependences $\log(F_0/F)=f(\text{time})$ during irradiation of corrole solutions with BSA depending on the addition of a quencher (NaN_3) and potentiation with potassium iodide.

Potentiation of photooxidation reactions of BSA by potassium iodide

Potentiation of photooxidation reactions opens up broad prospects for the creation of preparations with a low content of a photosensitizer, but at the same time effectively destroying pathogens. Potentiation with potassium iodide is based on the ability of macroheterocyclic compounds to generate reactive oxygen species during photoirradiation, which trigger a chain of radical reactions (Equations E1-E11, *Supplementary materials*).[35-39] Singlet oxygen or $O_2^{\bullet-}$, $HO^{\bullet}$, $RO^{\bullet}$, $ROO^{\bullet}$ radicals are reactive forms of oxygen. Of these, the superoxide radical anion has the longest lifetime (1 μs), a sufficiently large diffusion radius of 0.3 μm in biological substrates, and is relatively easily and reliably detected using NBT.

The study of the effect of potassium iodide on the efficiency of albumin photodegradation by corroles was evaluated by studying a series of solutions:[39] 1) BSA + Cor + *hv*; 2) BSA + Cor + *hv* + NaN_3; 3) BSA + Cor + *hv* + KI (50 mM); 4) BSA + Cor + *hv* + KI (50 mM) + NaN_3 (Figure 6, S6). Solutions were irradiated with 425 nm light in a cuvette at a constant temperature (25 °C) with stirring. The optical density of the solutions at the **NMeCor** and **pSCor** irradiation wavelengths was approximately the same. Sodium azide was added to the analyzed solutions to deactivate singlet oxygen and remove the contribution of type II photooxidation to protein photodegradation. Irradiation of solutions of BSA complexes with synthesized corroles with light at a wavelength of 425 nm leads to quenching of the fluorescence of tryptophan amino acid residues (Figure S6). The addition of sodium azide (50 mM) to solutions of analyzed protein-PS complexes leads to blocking of BSA photodegradation.

The addition of KI leads to an acceleration of protein photooxidation (Figures 6 and S6), while the electronic absorption spectra of the analyzed solutions change, namely, an increase in optical density in the 360 nm region is recorded (Figures S7, S8), which corresponds to the formation of triiodide ions that trigger the ion cascade - radical reactions (Schemes E4-E11, *Supplementary materials*).

Conclusions

The physicochemical properties and complexing ability of the synthesized corroles have been studied. It has been established, that sulfo-substituted corroles tend to participate in autoprotonation processes. In aqueous media and in DMF, cationic corrole is associated. In neutral and acidic solutions, cationic corrole forms solvate-separated H-associates, the formation of which involves the protons of the reaction center and the hydrating medium. In alkaline solutions and DMF, cationic corrole forms π-π associates, in which multicenter H-bonding occurs between the atoms of the reaction center of neighbouring corrole molecules in the associate.

It has been established that complexes with DNA are formed only by cationic corrole, which binds to DNA by the intercalation method. The parameters of DNA binding to cationic corrole indicate a high DNA affinity for cationic corrole, which is close to the DNA affinity for the related cationic porphyrin (TMPyP4). The low selectivity of corrole binding to DNA has been proven, with no preference for AT or CG enriched DNA regions.

The synthesized corroles form complexes with BSA. The affinity of BSA for the cationic corrole is higher than for the sulfo derivative. The synthesized corroles are weakly fluorescent fluorophores and practically do not generate singlet oxygen; however, they are capable of generating superoxide anion radicals and can participate in type I photooxidation.

Studies of protein photooxidation and potentiation with potassium iodide have been carried out. Photoirradiation of BSA complexes with corroles leads to fluorescence quenching of tryptophan amino acid residues. The addition of NaN_3 to solutions of protein complexes with PS leads to almost complete blocking of BSA photodegradation.

Radical and radical ion reactions underlying the potentiation of BSA oxidation upon photoirradiation with PS were studied. It was found that the introduction of KI leads to a 5–10-fold acceleration of BSA photooxidation. It has been proven that the stage of formation of triiodide ions, which trigger a cascade of radical ion reactions, plays an important role in the potentiation processes.

Declaration of Competing Interest. The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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