

25 **Propranolol, fulvic acid, aqueous solution, laser flash photolysis, triplet state,**
26 **photodegradation**

27 **1. Introduction**

28 Fulvic (FA) and humic (HA) acids are common products of natural organic matter biodegradation
29 and represent the main organic fraction of natural waters [1]. It is generally assumed that HA and
30 FA can transfer light energy to other components of water solutions strongly affecting the
31 photolysis of dissolved pollutants [2-5]. It is usually assumed that excited triplet states [6] and
32 active oxygen species (AOS) [7, 8] are the main active intermediates formed by UV-light excitation
33 of HA and FA. These intermediates can significantly accelerate the photodegradation of organic
34 pollutants dissolved in natural waters [9, 10]. In general FA are more effective photosensibilizers
35 than HA [11], thereby FA could be promising agent for photochemical water purification.

36 Propranolol ((*RS*)-1-(1-methylethylamino)-3-(1-naphthyloxy)propan-2-ol, further PR) is a beta-
37 blocker widely used in cardiovascular disease treatment [12]. It cannot be totally eliminated in
38 sewage treatment plants and therefore is widely detected in surface waters [13, 14]. It is shown to
39 be toxic to fish, crustaceans and green algae [15-18], which proves the ecological importance of the
40 investigation of PR transformation in environment (including photodegradation). Previous studies
41 have shown that under the sunlight irradiation PR half-life time is 0.6 to 1.9 days in summer and 3.9
42 to 12 days in winter [19], its degradation products are less toxic [20] and loose beta-adrenergic
43 receptor specificity [21]. Direct photolysis of PR is effective only at UV-C and UV-B irradiation (λ
44 < 315 nm) and leads to formation of PR triplet state and hydrated electron - carbon radical cation
45 pair [22]. Observed outcomes of direct photolysis include different products of PR hydroxylation
46 [23], ring oxidation, rearrangement and deoxygenation [19].

47 In natural conditions indirect photodegradation of PR should prevail on direct photolysis. It was
48 shown that PR is readily oxidized by OH radicals produced by nitrate photolysis [11] and that iron
49 ions and hydrogen peroxide accelerate photodegradation of the related beta-blockers atenolol and
50 metoprolol in photo-Fenton reactions [24]. Recently it was shown [11] that PR degradation is also

51 enhanced by the presence of humic substances. Authors proposed mechanism of such enhancement:
52 electron transfer from N-atom of amino group of PR to excited triplet state of FA (³FA, probably
53 ketone-like) followed by a rapid hydrogen transfer to form a carbon-centered radical intermediate.
54 Then, C-O bond is cleaved and naphthalene-1-ol is formed as the main product. It is worth to note
55 that this mechanism was inferred based mainly on results of final product analysis and influence of
56 oxygen content on PR photodegradation rate. We could not find any published direct evidence of
57 ³FA formation and registration of its reaction with PR by time-resolved technique.

58 In our current study we aim to prove the proposed mechanism of FA assisted photodegradation of
59 PR using nanosecond flash photolysis and to estimate the efficiency of photochemical processes
60 involving humic substances in natural waters. We paid special attention to distinguish between two
61 main possibilities: either ³FA directly reacts with PR or triplet state interacts with dissolved oxygen
62 and forms AOS, which then oxidizes the drug.

63 **2. Materials and methods**

64 FA (C, 51.04%; H, 5.22%; O, 39.13%; N, 4.62% [25]) (Henan ChangSheng Corporation),
65 propranolol (hydrochloride salt) (99%, Acros) were used without additional purification.

66 PR concentration in working solutions was varied from 2×10^{-6} M to 2×10^{-4} M: proper volumes of
67 stock PR solution and stock FA solution were mixed and water was added to the desirable volume.

68 FA concentration in working solutions was 15 mg/L (for steady-state photolysis) or 30 mg/L (for
69 laser flash photolysis). Accumulation of 1,4-naphthoquinone (a main final product of PR
70 photodegradation) was monitored by appearance of its characteristic absorption band at 250 nm in
71 differential absorption spectra of photolyzed solutions. Absorption spectra of PR (there is no
72 significant absorbance at $\lambda > 330$ nm), FA and 1,4-naphthoquinone in aqueous solution are shown
73 in Fig. 1.

74 Concentrated solutions of chemically pure sodium hydroxide were used for pH adjustments (natural
75 pH of FA solutions was equal to 4.5). pH measurements were carried out at ANION-4100 pH-meter
76 (Smolensk, Russia) with combined electrode ESK-10614.

77 UV-spectra were recorded on Agilent 8453 spectrophotometer ("Agilent Technologies"). Stationary
78 photolysis was performed using high-pressure mercury lamp (DRSh-500) with water and glass
79 filters for 365 nm mercury line separation. Quantum yield of PR photo-induced degradation was
80 estimated from absorption of 1,4-naphthoquinone at 250 nm taking into account the known
81 difference of absorption coefficient of PR ($\epsilon^{250\text{nm}}_{\text{PR}}$) and 1,4-naphthoquinone ($\epsilon^{250\text{nm}}_{\text{NQ}}$): $\epsilon^{250\text{nm}}_{\text{NQ}} -$
82 $\epsilon^{250\text{nm}}_{\text{PR}} = 21300 \text{ M}^{-1}\text{cm}^{-1}$.

83 A set-up for laser flash photolysis (LFP) which utilizes third harmonic (355 nm) of a Nd:YAG laser
84 (LS-2137U, Solar, Belarus) as an excitation source (pulse duration 6 ns, pulse energy 1-20 mJ, time
85 resolution ca. 50 ns) [26] was used in the experiments. Lamp and laser intensities were measured
86 with SOLO 2 laser power meter (Gentec EO). Absorption of ^3FA in LFP experiments was
87 monitored at characteristic wavelength 620 nm in differential transient absorption spectra.

88 Unless otherwise stated, all photochemical experiments were performed in a 1 cm quartz cell at 298
89 K in air- or argon-saturated aqueous solutions.

90 **3. Results and discussions**

91 **3.1. Laser flash photolysis of FA in the presence of PR**

92 We observed that excitation of FA leads to the triplet state formation ($\lambda_{\text{max}} = 620 \text{ nm}$) with yield
93 maximum in circumneutral solutions [27]. Kinetics of ^3FA decay in argon-saturated solutions has a
94 complex nature and could be adequately fitted by a set of three exponents with characteristic time
95 constants of 4.3, 54 and 830 μs .

96 The excitation of FA solutions at pH 7 in the presence of PR decreases initial amplitude of FA T-T
97 absorption at 620 nm ($\Delta A^{620\text{nm}}$), which occurs due to the static ^3FA quenching by this amine (Fig.
98 2). At PR concentration $\geq 2 \times 10^{-4} \text{ M}$ $\Delta A^{620\text{nm}}$ reaches a stationary value. Thus, there is a fraction of
99 ^3FA , which does not react with PR or is not accessible to PR quenching. It is worth noting that
100 $\Delta A^{620\text{nm}}$ in air-saturated solution is slightly lower than in deoxygenated one, which implies an
101 additional channel of ^3FA static quenching with dissolved oxygen (Fig. 2).

102 Figure 3 exhibits evolving intermediate absorption spectra observed at excitation of argon-saturated
103 FA solution in the presence of 2×10^{-4} M PR. Immediately after excitation, we observe a broad
104 unstructured absorption band with maximum at 670 nm, which corresponds to FA T-T absorption
105 [27]. T-T absorption maximum shifts and spectrum shape changes presumably resulting from
106 selective quenching of FA triplet states (absorbing at 340-650 nm) by the complexed PR. After that
107 T-T absorption intensity decreases, absorption maximum shifts slightly towards shorter
108 wavelengths and the bleaching in UV part of spectrum decays due to partial recovery of FA ground
109 state. It worth to note that addition of PR weakly affects the kinetics of ^3FA decay (Fig. 3b), which
110 indicates that rate constant of dynamic quenching is low. Unfortunately, our LFP data are not
111 definitely conclusive about the role of T-T energy and electron transfer processes (reactions 1 and 2
112 respectively) in ^3FA quenching by PR as absorption bands of cation-radical (max at 380 nm) and
113 triplet state (max at 410 nm) [22] of PR are not registered on the background of FA ground state
114 bleaching at 340-400 nm. It seems that the main channel of ^3FA decay is a physical quenching by
115 PR (reaction 3) and reactions (1) and (2) are not effective. To evaluate their contribution we
116 performed stationary photolysis of the system FA + PR. Below we discuss these experiments in
117 detail.



121 **3.2. Stationary photolysis (365 nm) of FA aqueous solutions in the presence of PR**

122 Fig. 4b shows the evolution of differential absorption spectra in the FA + PR system (air-saturated
123 solution, dissolved oxygen concentration is 2.8×10^{-4} M [28]) observed during stationary photolysis.
124 Absorption bands corresponding to PR (maxima at 210 and 290 nm) disappear and new band
125 appears at about 250 nm indicating the accumulation of 1,4-naphthoquinone (Fig. 1) as a main final
126 photoproduct [22].

127 We performed experiments with different initial PR concentrations: 4×10^{-5} M (60% of static
128 quenching) and 2×10^{-4} M (80% of static quenching) in air-saturated solutions. The results indicate
129 that with increase of amine concentration from 4×10^{-5} M to 2×10^{-4} M formation rate of final
130 photoproduct absorption at 250 nm increases from 0.01 per hour to 0.032 per hour (Fig. 5).
131 Assuming that 1,4-naphthoquinone is a main photodegradation product one can estimate the
132 quantum yield of PR photo-induced degradation as 1.1×10^{-5} and 3.5×10^{-5} , accordingly. These
133 values are in fair agreement with ones published in [11]. Correlation of PR degradation quantum
134 yield with amine concentration allowed us to propose that the main channel of PR photodegradation
135 is connected with direct electron transfer from N-atom of amino group in complexed PR to excited
136 triplet state of FA [11] rather than with AOS generation.

137 To support this suggestion we performed stationary photolysis of FA + PR system in argon –
138 saturated solution (Fig. 4a). Observed spectral changes indicate that presence of oxygen is not
139 necessary for photo-induced PR degradation. However, absorption spectra and nature of final
140 photoproducts in argon-saturated solution differ from ones in air-saturated solution (Fig. 4a, b).
141 Thus, dissolved oxygen takes part in reactions with active intermediates of PR degradation or in
142 oxidation of primary photochemical products. Detailed study of this question is beyond of the scope
143 of current article.

144 3.3. Modeling of triplet state quenching process with PR

145 Let us suggest that ^3FA static quenching by PR is connected with FA-PR complexation. In the first
146 approximation, we can assume that all binding constants are equal and each molecule of FA can
147 form a number of independent 1:1 complexes with PR. In this approximation we can express
148 concentrations of occupied (Complex) and free (FA) binding sites as:

$$149 \frac{[\text{Complex}]}{[\text{FA}][\text{Pr op}]} = K_{\text{st}} = \frac{[\text{X}]}{[\text{C}_{\text{FA}} - \text{X}][\text{C}_{\text{Pr op}} - \text{X}]} \quad (4)$$

150 where C_{FA} is effective concentration of PR binding sites. X can be found by formula (5):

151 $[X] = \frac{(C_{FA} + C_{Prop} + K_{st}^{-1}) - \sqrt{(C_{FA} + C_{Prop} + K_{st}^{-1})^2 - 4C_{FA}C_{Prop}}}{2}$ (5)

152 We may disunite PR binding sites and triplet state formation sites and differ their total number.
 153 However, for the sake of simplicity, we will further assume that one complex formed can quench β
 154 FA triplet states. Parameter β accounts for the fact that one binding center can quench several 3FA
 155 as well as for the presence of 3FA not accessible for quenching by PR due to energy and/or steric
 156 reasons. As the absorption coefficient at excitation wavelength (365 nm) is equal for complexed and
 157 free FA, the amount of absorbed light does not change on varying PR concentration. Thus, changes
 158 of 3FA yield are connected only with the process of static quenching of these states by complexed
 159 PR. The amount of quenched triplet centers will be equal to βX , and concentration ($C_T(X)$) and the
 160 absorption at 620 nm ($\Delta A(X)$) of 3FA escaped quenching will be respectively:

161 $C_T(x) = C_T - \beta X; \quad \Delta A(X) = \Delta A_0 - \varepsilon_T^{620nm} l \beta X$ (6)

162 where ΔA_0 – initial amplitude of T-T absorption in the absence of PR, ε_T^{620nm} – coefficient of T-T
 163 absorption at 620 nm, l – optical path length. Using formulae (5) and (6) we get the final expression
 164 (7):

165 $\frac{\Delta A_0}{\Delta A(X)} = \frac{\Delta A_0}{\Delta A_0 - \varepsilon_T^{620nm} l \beta X} = \frac{2}{2 - \gamma \left[\left(1 + \frac{C_{Prop}}{C_{FA}} + \frac{K_{st}^{-1}}{C_{FA}} \right) - \sqrt{\left(1 + \frac{C_{Prop}}{C_{FA}} + \frac{K_{st}^{-1}}{C_{FA}} \right)^2 - 4 \frac{C_{Prop}}{C_{FA}}} \right]}$ (7)

166 Thus, $\Delta A_0/\Delta A(X)$ is determined by three parameters – ratio of PR and FA binding center
 167 concentrations, reverse product of stability constant to binding center concentrations and
 168 $\gamma = \varepsilon_T^{620nm} l C_{FA} \beta / \Delta A_0$. The latter parameter accounts for relative decrease of T-T absorption
 169 yield when all binding centers are occupied. Inset for Fig. 2 shows a smooth curve representing the
 170 best fit of data for argon-saturated solutions according to formula (7) with parameters $\gamma = 0.83$, C_{FA}
 171 $= 10^{-6}$ M и $K_{st} = 1.5 \times 10^5$ M⁻¹. Same parameters fit well the dependence of T-T absorption amplitude

172 on PR concentration (formula (6), Fig. 2). So one can assume that this simple model is adequate
173 enough for description of observed experimental data.

174 Knowing γ , the initial amplitude of T-T absorption signal, binding sites concentration and assuming
175 $\beta = 1$ one can estimate effective coefficient of T-T absorption, which is equal to $\varepsilon_T^{620\text{nm}} \approx 5 \times 10^4 \text{ M}^{-1}\text{cm}^{-1}$.
176 The latter value and the product $\phi_T \varepsilon_T^{620\text{nm}} \approx 3.3 \times 10^2 \text{ M}^{-1}\text{cm}^{-1}$, determined in [28], allows one
177 to estimate the ^3FA quantum yield as $\phi_T = 0.6 \%$. Comparing the quantum yield of PR degradation
178 (3.5×10^{-5}) and ϕ_T one can conclude that less than 1% of ^3FA takes part in processes (1) and (2)
179 leading to PR degradation. This finding can explain why it is impossible to detect cation-radical or
180 triplet of PR in LFP experiments.

181 We should note that literature data on molar absorption coefficients and quantum yields for triplet
182 states of humic substances is scarce. There are only few papers where quantum yield values were
183 estimated as 0.3-1% depending on excitation wavelength [29]. This estimate is very important to
184 understand the efficiency of photochemical processes involving humic substances in natural waters.

185 **Conclusions**

186 We performed mechanistic study of propranolol photodegradation in the presence of fulvic acid in
187 aqueous solution using both flash (355 nm) and steady-state photolysis (365 nm) techniques. We
188 obtained direct evidence that FA-assisted photodegradation is due to static quenching of ^3FA by
189 propranolol via electron transfer mechanism. We found that less than 1% of ^3FA total quantity takes
190 part in PR degradation and the quantum yield of this process is 3.5×10^{-5} . For the first time we
191 obtained the estimates of the ^3FA quantum yield ($\phi_T \approx 0.6 \%$) and the T-T absorption coefficient
192 ($\varepsilon_T^{620\text{nm}} \approx 5 \times 10^4 \text{ M}^{-1}\text{cm}^{-1}$) from modeling of yields of ^3FA in the presence of propranolol. Humic
193 substances could be important factor for acceleration of propranolol photodegradation in natural
194 waters under UV-A light irradiation.

195 **Acknowledgments**

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275 **Figures**

276 **Fig. 1.** Ultraviolet/visible absorption spectra of PR ($C = 1 \times 10^{-4}$ M) (1), FA ($C = 15$ mg/L) (2) and
277 1,4-naphthoquinone ($C = 4 \times 10^{-5}$ M) (3); structural formulae of PR (1) and 1,4-naphthoquinone (3).

278 **Fig. 2.** The dependence of the T-T absorption yield at 620 nm on PR concentration in argon-
279 (circles) and in air-saturated (points) solutions. FA concentration is 30 mg/L, pH 7. Inset - the ratio
280 of amplitudes of T-T absorption signal at a zero and current PR concentration depending on [PR] in
281 argon- (circles) and in air-saturated (points) solutions. Smooth curves are modeling by formulas (5)
282 and (6) with the parameters specified in paragraph 3.3.

283 **Fig. 3.** Laser flash photolysis of FA (30 mg/L) with PR (2×10^{-4} M) in argon-saturated aqueous
284 solution at pH 7. (a) – Transient absorption spectra recorded at 0.4 (1), 1.2 (2), 4 (3) and 48 (4) μ s
285 after excitation. (b) – Kinetic curves at 380 (1), 520 (2) and 660 (3) nm.

286 **Fig. 4.** Differential optical spectra, registered at 1 (1), 2 (2), 4 (3), 7 (4) and 9 (5) hours of
287 irradiation at 365 nm (8.1 mW) during stationary photolysis of FA ($C = 15$ mg/L) with PR (4×10^{-5}
288 M) in argon- (a) and in air-saturated (b) solutions at pH 7.

289 **Fig. 5.** The dependence of optical density at 250 nm during stationary photolysis of FA (15 mg/L)
290 with different initial PR concentrations: (circles) - 4×10^{-5} M and (squares) - 2×10^{-4} M in air-
291 saturated solutions at pH 7.

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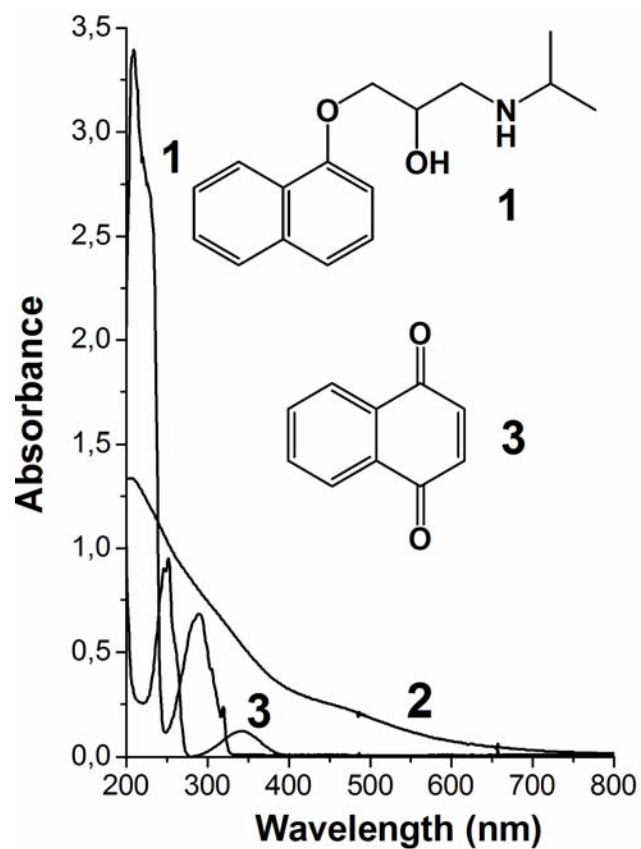


Fig. 1.

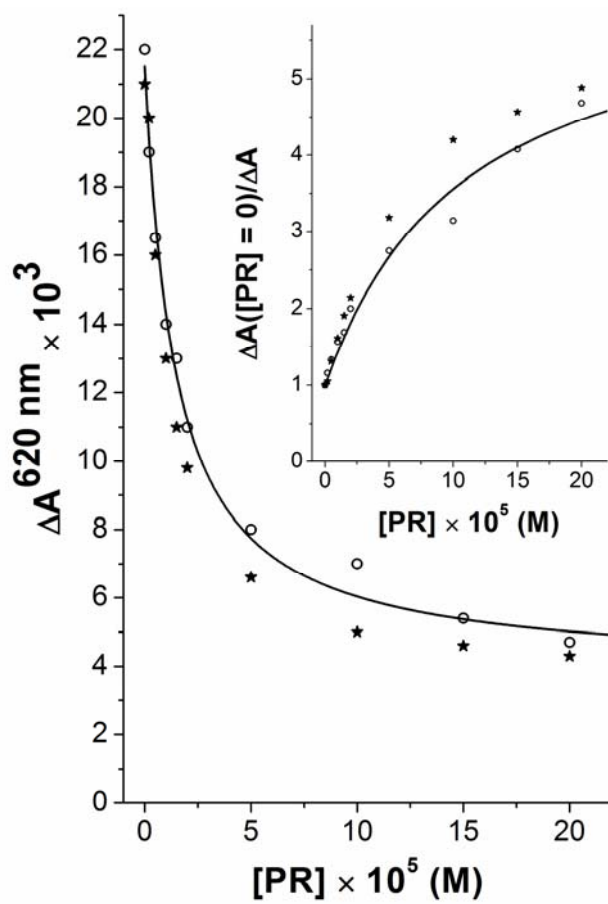


Fig. 2.

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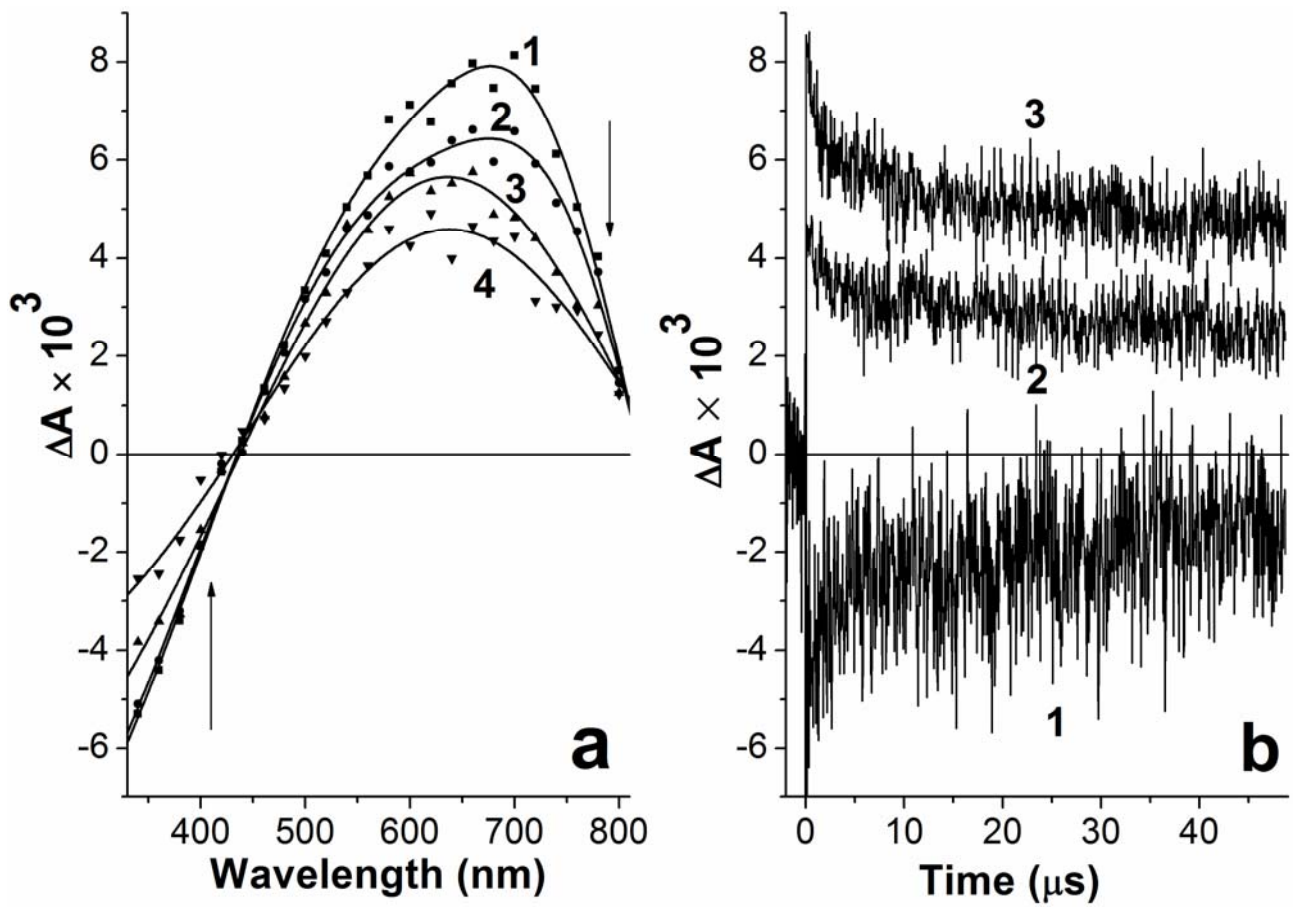


Fig. 3.

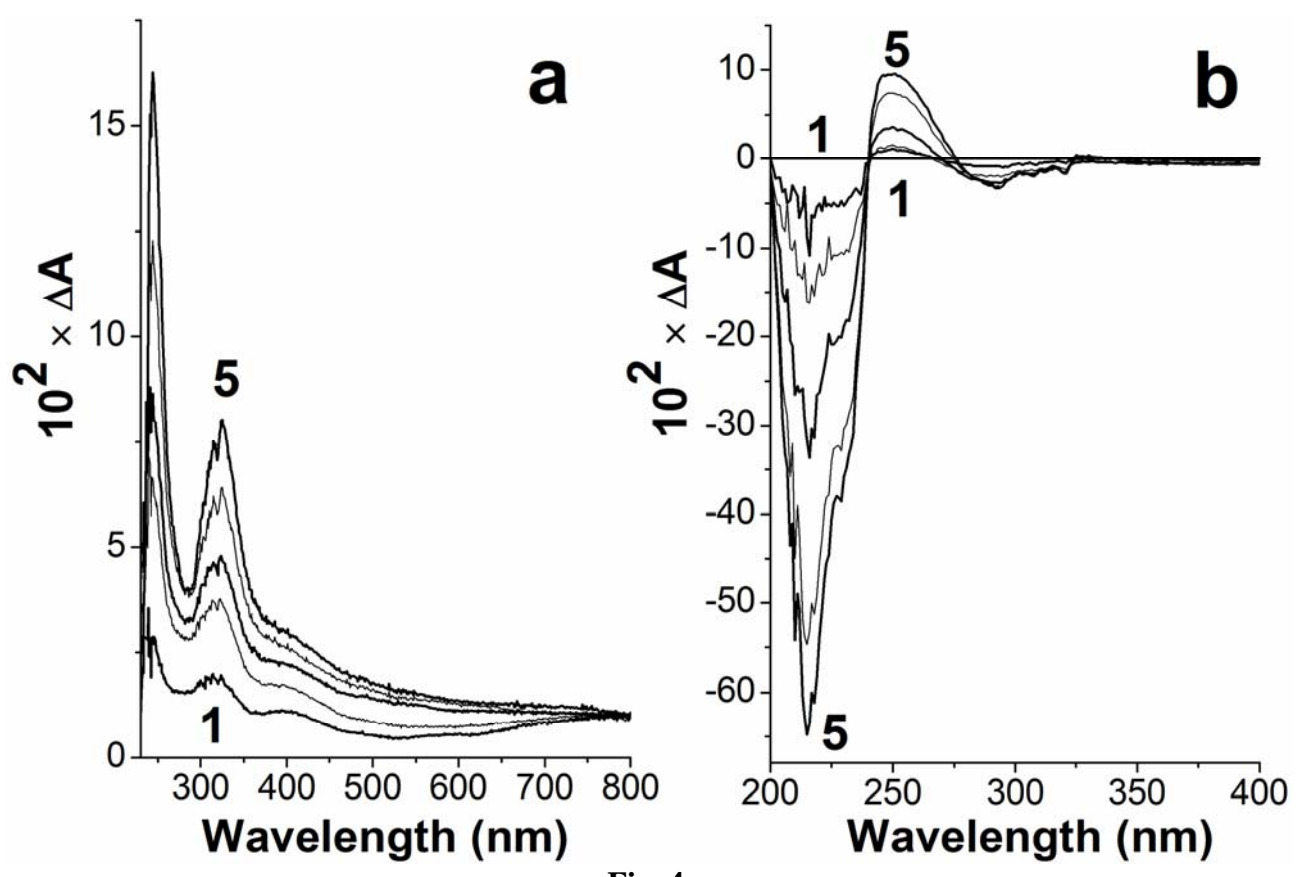
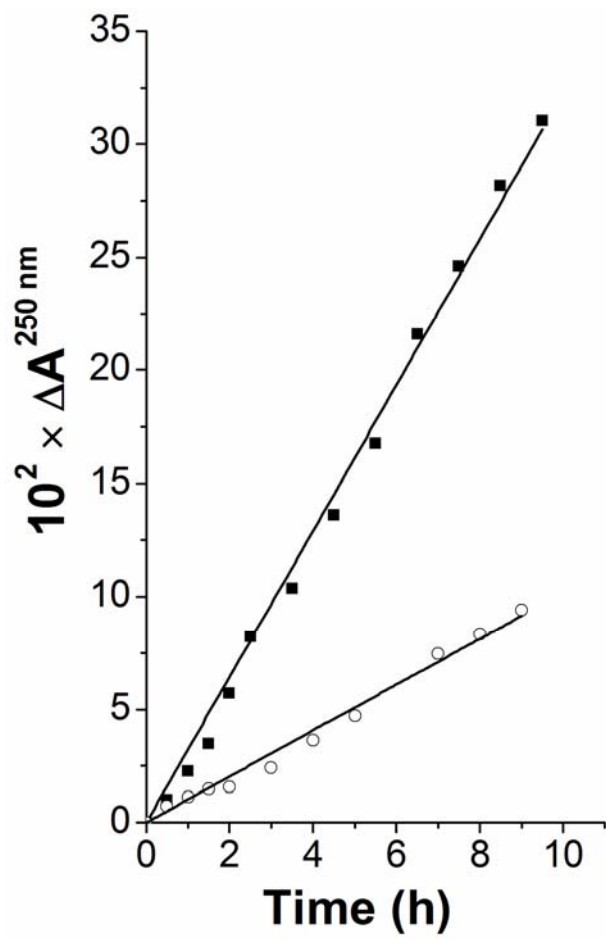


Fig. 4.

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Fig. 5.