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## Triplet state quenching of phenosafranine dye by indolic compounds studied by transient absorption spectroscopy

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The interaction of the triplet state of the synthetic dye phenosafranine (3,7-diamino-5-phenylphenazinium chloride) with indolic compounds of biological relevance was investigated in water by means of laser flash photolysis. The rate constants for the triplet quenching were determined. The quenching process may be explained by an electron transfer from the indole to the dye in its triplet state. The rate constants present a typical dependence of an electron transfer process with the one-electron oxidation potential of the indole. Indole-3-acetic acid and its homologous indole propionic and indole butyric acids are the most effective quenchers with rate constants reaching the diffusion limit. Rate constants for indole itself, tryptophan and indole-3 carboxylic acid are one order of magnitude lower. The electron transfer nature of the quenching reaction is further confirmed by the detection of the semi-reduced form of the dye by its transient absorption. The absorption coefficients of the transient species were estimated, and the quantum yield of the charge separation process was determined. The efficiency of formation of radical species is between 60 and 90% of the triplets intercepted.

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### 1. Introduction

The photooxidation processes of indolic compounds sensitized by synthetic dyes have been a subject of long standing interest.<sup>1</sup> Thus, the photooxidation of tryptophan (Trp) sensitized by riboflavin (RF) and synthetic dyes was investigated by Yoshimura and Ohno in 1988.<sup>2</sup> Indole carboxylic acids have also attracted the interest of research studies because of their photooxidation reactions<sup>3</sup> mainly in connection with the environmental implication of the compounds, since they form part of an important class of plant growth regulators. In particular indole-3-acetic acid (IAA) is the most common, naturally-occurring plant hormone of the auxin class. The direct and Rose Bengal (RB) sensitized photooxidation of IAA and its derivatives have been investigated by Amat-Guerri *et al.*<sup>4,5</sup> In the RB sensitized reactions, they proposed a competing type I (through direct interaction with the dye excited states) and type II (through singlet oxygen) processes.<sup>5</sup> The detailed mechanism of RF and RB sensitized photooxidation of indole-3-acetic, -propionic (IPA) and -butyric (IBA) acids was examined.<sup>6</sup> The rate constants of the order of  $10^9 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$  were estimated for the quenching of triplet excited RF by the indoles.

The incorporation and photodegradation of indole derivatives in anionic, cationic and neutral micellar dispersions in the presence of RF were studied by Bueno *et al.*<sup>7</sup> The photocatalytic degradation of IAA and IBA in aqueous environments was also reported.<sup>8</sup>

In several of these studies the importance of type I mechanism in the photooxidation process was noticed.<sup>2,5,6</sup> In the type I mechanism the transfer of an electron, or a hydrogen atom, occurs between the excited triplet sensitizer and the substrate, which starts a series of radical reactions. Therefore, it is of interest to have a deeper understanding of the excited state interaction of sensitizers with indolic compounds. The quenching of excited aromatic probes by indolic compounds has been widely investigated. In homogeneous solvents the quenching reaction takes place by electron transfer from the indole to the excited states of the probe.<sup>9,10</sup>

We have previously reported on the excited state quenching of the phenazinium dyes safranine-O (3,7-diamino-2,8-dimethyl-5-phenylphenazinium chloride,  $\text{SH}^+\text{Cl}^-$ ) and phenosafranine (3,7-diamino-5-phenylphenazinium chloride,  $\text{PSH}^+\text{Cl}^-$ ) by several compounds. The kinetics of the electron transfer reaction of the singlet and triplet excited states of the dyes were the subject of detailed studies by our group. In the last few years the photochemistry of both dyes has received great attention because of their photoredox properties.<sup>11,12</sup>  $\text{SF}^+$  and  $\text{PSH}^+$  were used as sensitizers in a large number of applications. In particular the employment of  $\text{SH}^+$  in some areas

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of research such as analytical,<sup>13,14</sup> biological,<sup>15,16</sup> solar energy<sup>17,18</sup> and initiation of photopolymerization<sup>19–22</sup> was investigated. The electrochemistry of these dyes was investigated long ago by Clark and co-workers<sup>23</sup> and more recently the electrochromic properties of  $\text{PSH}^+$  were reported.<sup>24</sup>  $\text{PSH}^+$  has been extensively employed as a sensitizer in energy and electron transfer reactions in homogeneous media,<sup>25–27</sup> in semiconductors,<sup>28</sup> and in polymers.<sup>29</sup> Since the photophysics of the dye is highly sensitive to polarity of the microenvironment, phenosafranine dye has been used earlier as a probe in micellar and polymeric media.<sup>30</sup> The dye was also employed as a probe in reverse micellar systems<sup>31</sup> and its photostability in polymer-coated semiconductors was investigated.<sup>32</sup> The binding of  $\text{SH}^+$  and  $\text{PSH}^+$  to DNA and polyadenylic acids was recently investigated by Kumar *et al.*<sup>33</sup> The photophysics of the dye in different media was previously reported.<sup>25,34,35</sup> In a pioneering work, Baumgartner *et al.*<sup>36</sup> have studied the triplet state properties of  $\text{SH}^+$  as a function of pH in aqueous media using conventional flash photolysis. Previously we reported on the quenching of  $\text{PSH}^+$  excited states by aromatic electron donors<sup>37</sup> and aliphatic amines in organic solvents.<sup>38</sup> It was found that in organic solvents the quenching by aromatics follows an electron transfer kinetics, while for aliphatic amines the singlet quenching rate constants depend on the one-electron oxidation potential of the amine, but the triplet quenching follows a mechanism with a proton transfer initial step. In view of the interest of sensitization processes involving indolic compounds we undertook the present study in aqueous solution. A detailed study by laser flash photolysis of the interaction of the triplet state of the dye with indolic compounds was undertaken. Rate constants for the electron transfer quenching and quantum yields of radicals were determined. The quenching process may be explained by an electron transfer from the indole to the dye in its triplet state followed by a proton transfer to the semireduced form of the dye.

## 2. Experimental

Phenosafranine was purchased from Aldrich and was used without further purification. It was checked that its photo-physical properties coincided with those reported in the literature. Indole, from Sigma Chem. Co., was purified by recrystallization. The indole-3-carboxylic acids (IAA, IPA, IBA) from Aldrich and Tryptophan (Trp) from Sigma Chem. Co. were used as received.

Laser flash photolysis determination was carried out with a Spectron SL400 Nd:YAG laser generating 532 nm pulses (~18 ns pulse width). The laser beam was defocused in order to cover the entire path length (10 mm) of the analyzing beam from a 150 W Xe lamp. The experiments were performed with rectangular quartz cells with right angle geometry. The temperature of the cell holder was controlled by water circulation. The detection system comprises a PTI (Photon Technology International) monochromator coupled to a Hamamatsu R666 PM tube. The signal was acquired by a digitizing scope where

it was averaged and then transferred to a computer. The solutions were purged with argon for 30 min before use. The results were the same irrespective of argon or nitrogen purging.

Typically, *ca.* 30  $\mu\text{M}$  solutions of the dye were prepared in 1 mM phosphate buffer solutions at the needed pH ( $\pm 0.1$  unit). In non-buffered solutions at neutral pH the latter was adjusted by adding small aliquots of concentrated HCl or NaOH solutions as necessary, after removing the residual  $\text{CO}_2$  by bubbling with Ar. The pH values of the solutions were monitored before and after each experiment, and in all cases they were unchanged. All the determinations of transient absorption spectra in the presence of indole derivatives and quenching experiments were carried out at neutral pH.

## 3. Results and discussion

### 3.1. Photophysics of the dye

In aqueous solution the dye presents a strong absorption with a maximum at 520 nm. The absorption spectrum is independent of pH in the range 2–11. It fluoresces with a maximum at 590 nm, with a quantum yield of 0.04 and a lifetime of 0.87 ns.<sup>39</sup> The triplet quantum yield is 0.19.<sup>39</sup>

Fig. 1 shows the transient absorption spectrum of  $\text{PSH}^+$  in water at pH 7 at 1, 20 and 40  $\mu\text{s}$  after laser flash excitation at 532 nm. It presents three bands at 785, 700 and 420 nm corresponding to the T-T absorption of the monoprotonated triplet state  $^3\text{PSH}^+$ . At lower pH the main absorption corresponding to the diprotonated form of the triplet state,  $^3\text{PSH}_2^{2+}$  is located at 660 nm, while it is at 410 nm for the neutral triplet of the dye,  $^3\text{PS}$ , observed at pH > 9. The structures of the three forms are shown in Scheme 1.

The T-T transient absorption spectra at pH 3, 7, and 11 are shown in Fig. 2 and the pH dependence of the three maxima are presented in Fig. 3. Under our experimental conditions in the quenching experiments, pH 7–8, the predominant species is the monoprotonated triplet.

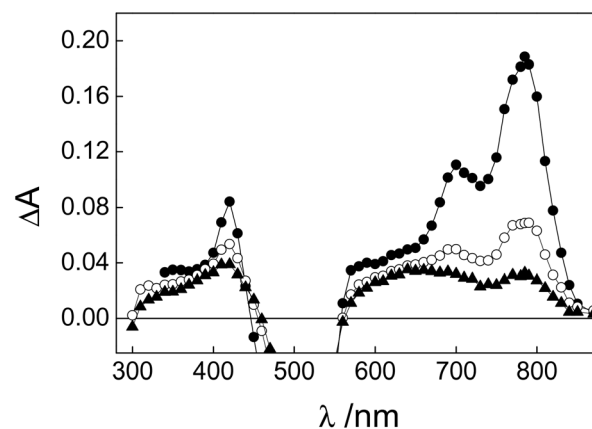


Fig. 1 Transient absorption spectrum of phenosafranine in water at pH 7 at 1 (●), 20 (○) and 40 (▲)  $\mu\text{s}$  after laser flash excitation at 532 nm.

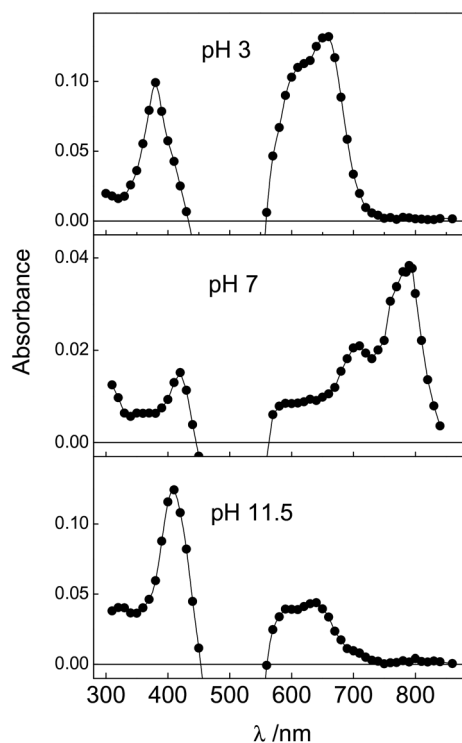
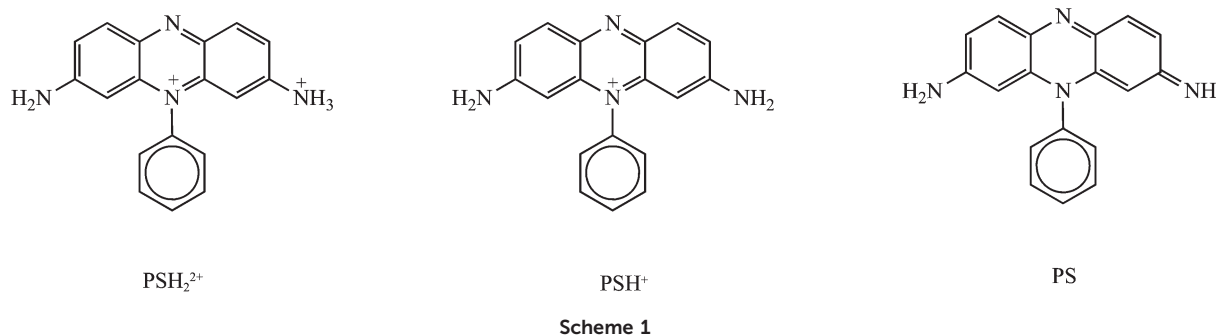


Fig. 2 Transient absorption spectra of phenosafranin in water taken at 1  $\mu$ s after the laser pulse at pH 3, 7 and 11.5.

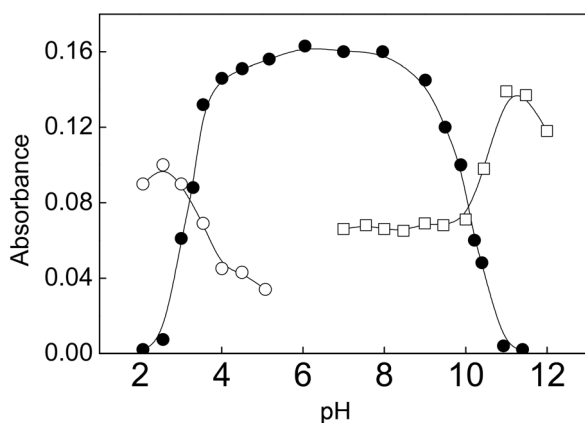


Fig. 3 Initial absorbance at the maximum of the T-T transient absorption spectrum of phenosafranin as a function of pH. Absorption at 785 nm (●); absorption at 660 nm (○); absorption at 410 nm (□).

Apparent pKs are at 3.5 and 9.5 for the acid and mono-protonated triplets, respectively. These values reflect the effect of the methyl substitution on the heterocyclic ring of the related dye safranin with pKs of 7.5 and 9.2.<sup>36</sup> In water at pH 7 the triplet state decays by a first order process with a lifetime in the range of 20–100  $\mu$ s depending on the dye concentration. It can be seen in Fig. 1 that after the triplet decay a long lived absorption remains in the regions 640–670 and 400–430 nm. This can be assigned to the combined absorption of the semi-reduced and semioxidized forms of the dye originated in a self-quenching reaction of the triplet by the ground state of the dye.

### 3.2. Triplet quenching by indolic compounds

The triplet is efficiently quenched by the indolic compounds. The triplet quenching rate constants ( $k_q$ ) were obtained from the triplet lifetime (measured by the T-T absorption at 785 nm) as a function of the indole concentration according to

$$\tau^{-1} = k_o + k_q[\text{In}] \quad (1)$$

where  $\tau$  is the triplet lifetime,  $k_o$  is the first order rate constant for the triplet decay in the absence of the indole and [In] is the analytical concentration of the quencher.

It should be noted that at the indolic compound concentration in the range 0–3 mM used in the triplet quenching experiments, singlet quenching was not observed due to the short singlet lifetime of the dye. A representative plot of the triplet quenching according to eqn (1) is shown in Fig. 4. Triplet quenching rate constants are given in Table 1.

The values in Table 1 follow the expectation for an electron transfer reaction from the indole derivative to the triplet state of the dye. In effect, it is well known that the oxidation potential of indoles decreases with substitution by electron donating groups on position 3 of the heterocyclic ring and increases with electron accepting groups.<sup>40</sup> The oxidation potential of indole derivatives is 1.24 V for indole and tryptophan and 1.07 V vs. SCE for 3-methyl indole.<sup>10,41</sup> The reduction potential of phenosafranin is 0.55 V in MeCN<sup>42</sup> and 0.34 V in water at pH 7 vs. NHE.<sup>44</sup> Using the triplet energy of the dye, 1.77 eV,<sup>42,43</sup> the reduction potential vs. SCE for the triplet state of the dye may be estimated as  $-1.20$  V in water. Accordingly, the electron transfer quenching for 3-substituted indoles should be exothermic by ca.  $-0.12$  eV, while for indole and Trp it should

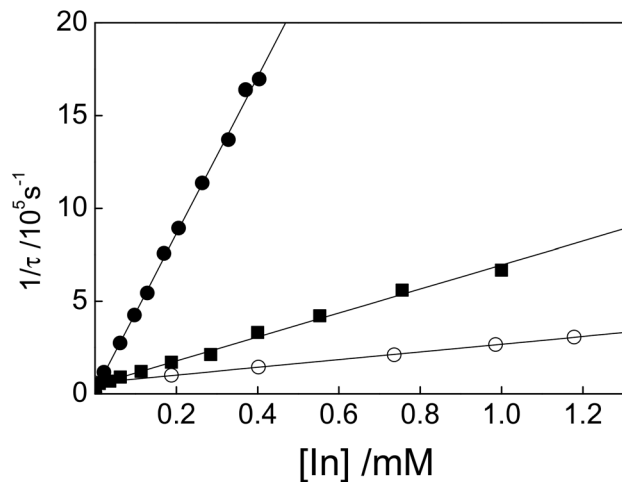


Fig. 4 First order triplet decay rate constant as a function of quencher concentration, measured at 785 nm at neutral pH. Indole (○); Trp (■); IAA (●).

Table 1 Rate constants for the triplet quenching of phenosafranine by indolic compounds

	$k_q/10^9 \text{ M}^{-1} \text{ s}^{-1}$
Indole	0.21
Indole-3-acetic acid	4.3
Indole-3-propionic acid	5.8
Indole-3-butyric acid	6.0
Indole-3-carboxylic acid	0.18
Tryptophan	0.68

be near thermoneutral. Therefore, it is expected that for the carboxylic acids with a methylene substitution at position 3 of the indole ring the rate constants reach the diffusion limit, while for tryptophan and indole they have lower values. To our knowledge the oxidation potential of indole-3-carboxylic acid is not available in the literature, but due to the deactivating effect on the heterocyclic ring of the carboxylic group, a lower value of the quenching rate constant is expected, as it is found.

The transient absorption spectra in the presence of indole and IAA are shown in Fig. 5 and 6, respectively. In the presence of the indoles the long time transient absorption spectrum differs from that in the absence of the quenchers. After the decay of the absorption of the triplet at 785 nm, a new long lived species remains, with absorption maxima at 650 and 410 nm. This new species can be attributed to the semireduced dye. An enlargement of the absorption in the region 350–450 nm can be seen in the inset of Fig. 5 and in Fig. 6 for IAA. A band at 425 nm is present at short times and it undergoes a blue shift to 410 nm at longer times. The band at 425 nm can be ascribed to the T-T absorption while that at 410 nm corresponds to the semireduced form of the dye.<sup>44</sup>

However, the formation of the semireduced form of the dye does not follow simple kinetics. This can be concluded from the time profile of the absorption at different wavelengths as illustrated in Fig. 7.

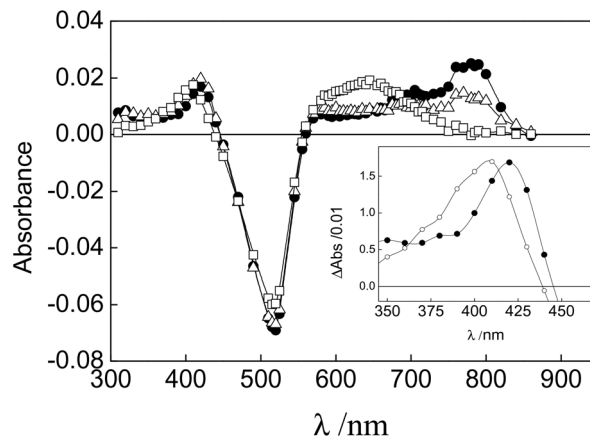


Fig. 5 Transient absorption spectrum of phenosafranine in the presence of indole 3 mM at neutral pH taken at 1 (●), 2 (Δ) and 30 (□) μs after the laser pulse. Inset: enlargement of the region 350–450 nm at 1 μs (●) and 44 μs (○) after the laser pulse.

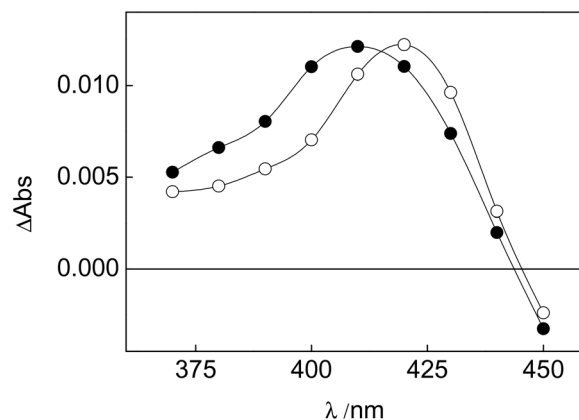


Fig. 6 Transient absorption spectrum in the presence of IAA 0.37 mM at 0.7 μs (○) and 30 μs (●) after the laser pulse.

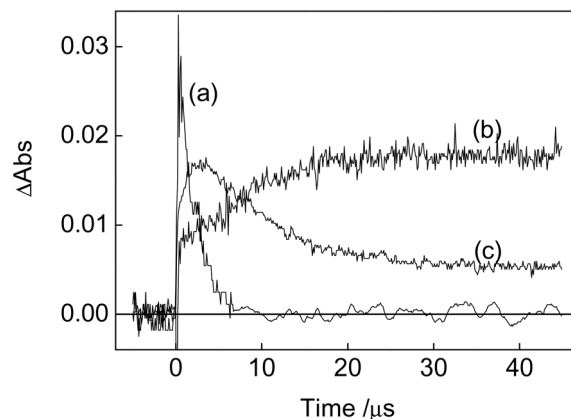
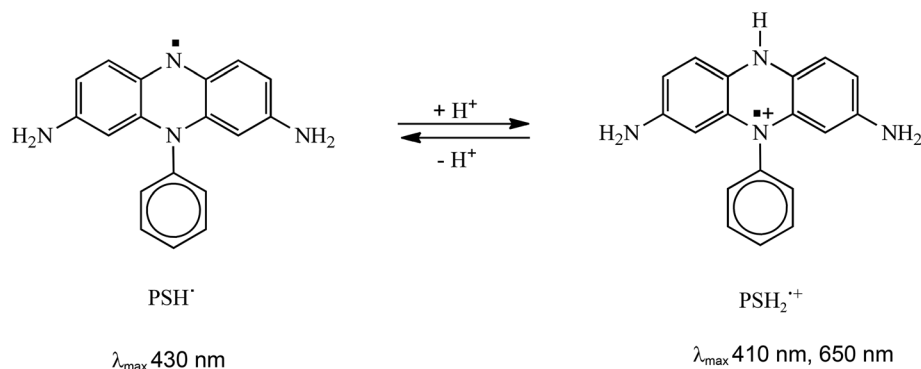


Fig. 7 Time profile of the absorption at 785 nm (a), 650 nm (b) and 430 nm (c) of phenosafranine in the presence of indole 3 mM.



Scheme 2

At the same time the absorption at 785 nm of the monoprotonated triplet  $\text{PSH}^+$  decays, a new species absorbing at 430 nm is formed. Afterwards, the absorption at 430 nm decays and a new absorption at 650 nm develops with the same kinetics. According to Guha and Mittal<sup>45</sup> assignment of the bands for the semireduced forms of the related dye safranine, the species absorbing at 430 nm corresponds to the neutral radical  $\text{PSH}^{\bullet}$ . The absorption at 410 and 650 nm may be ascribed to the diprotonated radical of the dye  $\text{PSH}_2^{\bullet+}$ . In the ground state the dye molecule is in the monocationic form  $\text{PSH}^+$  in the pH range 2–11. On the other hand the one-electron reduced species,  $\text{PSH}^{\bullet}$  has a higher affinity for protons and it is protonated in a fast process taking place in the few microseconds following the initial electron transfer step. The structure of the semireduced species and the absorption bands are shown in Scheme 2.

The rate of formation of the radical  $\text{PSH}_2^{\bullet+}$  is practically the same as in the cases of indole and IAA, in spite of the diverse electron transfer rate constants. Therefore it can be inferred that the proton donor is the aqueous medium and not the radical cation of the indolic compound as was the case in the reaction of singlet excited anthracene with indoles.<sup>9</sup> This mechanism should be compared to the quenching of the dye by aliphatic amines in a protic organic solvent. In that case the initial step was a proton transfer interaction of the amine with the dye in its excited triplet state. With indolic compounds, due to its low basicity and better electron donor capability, the initial step is an electron transfer reaction.

### 3.3. Determination of radical quantum yields

The fraction of triplets intercepted by the quencher Q may be written as

$$f = \frac{k_q[Q]}{k_0 + k_q[Q]} \quad (2)$$

The values of  $f$  are given in Table 2. In the spectra shown in Fig. 4 and 5  $f$  was higher than 0.9. Radical quantum yields were obtained according to the following equation:

$$\Phi_R = \frac{\Delta A_R \varepsilon_T}{\Delta A_T \varepsilon_R} \Phi_T \quad (3)$$

Here  $\Delta A_R$  is the long-time absorption remaining after the triplet decay in the presence of the indole measured at

Table 2 Radical quantum yields

	Concentration/mM	$f$	$\Phi_R$
Indole	3	0.93	$0.17 \pm 0.03$
Tryptophan	1	0.96	$0.14 \pm 0.02$
Indole-3-acetic acid	0.37	0.97	$0.11 \pm 0.02$

410 nm,  $\Delta A_T$  is the prompt T–T transient absorption measured at 785 nm immediately after the laser pulse,  $\varepsilon_R$  and  $\varepsilon_T$  are the respective molar absorption coefficients and  $\Phi_T$  is the triplet quantum yield in the absence of the indole derivative. The T–T extinction coefficient at 785 nm,  $\varepsilon_T$ , equals  $15\,800 \text{ l mol}^{-1} \text{ cm}^{-1}$  from ref. 39.

In order to determine  $\Phi_R$  by means of eqn (3) the absorption coefficients of the radical are necessary. It was determined by the ground state depletion (GSD) method.<sup>46</sup> The transient negative absorbance difference at the maximum wavelength of the ground absorption,  $\Delta A_G$ , was compared with the absorption at the maximum of the spectrum of the semireduced dye,  $\Delta A_R$ , with the aid of eqn (4).

$$\varepsilon_R = \left( \frac{\Delta A_R}{\Delta A_G} \right) \varepsilon_G \quad (4)$$

In eqn (4)  $\varepsilon_R$  and  $\varepsilon_G$  are the molar absorption coefficients of the radical and the ground state respectively, at the wavelengths of their absorbance maxima. The quantum yields obtained in this way are given in Table 2.

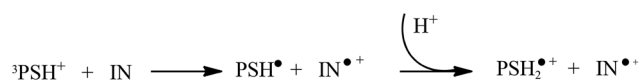
We checked the values of the absorption coefficients using *N,N'*-dimethylaniline as a quencher of  $^3\text{PSH}^+$ . Using the GSD method a lower limit of  $7500 \text{ M}^{-1} \text{ cm}^{-1}$  and  $8200 \text{ M}^{-1} \text{ cm}^{-1}$  at 650 and 410 nm, respectively, was obtained. In a pulse radiolysis study Mittal *et al.*<sup>44</sup> reported  $\varepsilon_R = 12\,600 \text{ M}^{-1} \text{ cm}^{-1}$  at 410 nm and  $11\,300 \text{ M}^{-1} \text{ cm}^{-1}$  at 650 nm. The errors quoted in Table 2 reflect this difference in absorption coefficients.

From the values in Table 2 it can be seen that the indolic compounds are particularly efficient in generating active radicals in the triplet quenching of the dye. From the triplet quantum yield of the dye (0.19) and the radical quantum yields in Table 2 it can be concluded that, at the concentrations employed in our experiments, nearly 60% of the

triplets intercepted by the IAA undergo complete radical separation. This amounts to more than 90% in the case of indole. It is interesting to note that the more effective quencher, IAA, is the less efficacious in generating radicals.

## 4. Conclusions

The triplet state of phenosafranin was efficiently quenched by indolic compounds in water solution. For the indoles substituted by an aliphatic chain in position 3 the quenching rate constants are diffusion controlled, while for indole and tryptophan they are one order of magnitude lower, in agreement with their higher reduction potentials. An electron transfer from the indole to the excited triplet of the dye was established as the quenching mechanism. The protonated semireduced form of the dye was the final species resulting in the quenching reaction, according to:



where the proton donor is the aqueous medium.

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