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STUDY OF THE FLUORESCENCE-QUENCHING OF Mg-TNP BY ANIONIC ANTHRAQUINONES

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The fluorescence quenching of magnesium 5,10,15,20-tetra-p-naphtyl-porphyrin (Mg-TNP) has been studied in benzene using 9,10-anthraquinone-2-sulfonic acid sodium salt (An 1), 9,10 -anthraquinone-2,6-disulfonic acid sodium salt monohydrate (An 2), 9,10-anthraquinone-1,5-disulfonic disodium salt monohydrate (An 3) as quenchers. The fluorescence quenching rate constants are deduced from the Stern-Volmer curves and it is postulated that the quenching occurs via the formation of a charge transfer complex formation. For all these cases, R_o values are in the 1-10 Å range, which correspond to one singlet quenching processes by diffusion controlled energy transfer. Electron-exchange and/or electron transfer processes are expected to proceed also at these distances. The quenching mechanism is concerted one between static quenching with energy transfer (due to long-range dipole-dipole interaction between excited anthraquinone molecules (donor) and the ground state acceptor molecule Mg-TNP) and electron transfer which should occur from singlet excited state of Mg-TNP to donor anthraquinone molecule, leading to formation of stable radical anion and cations.

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1. Introduction

The catalytic and photosensitization properties of porphyrins for solar energy conversion and storage and biological (photomedicine) applications, involve different interaction processes between photoexcited singlet states of such porphyrins and with many others electron acceptors[1a].

If a molecule Q has an excited state Q* lower than excited state of molecule M*, the excitation energy can be transfered accordind to (1)

$$M^* + Q \text{ ---> } M + Q^* \quad (1)$$

Major energy transfer processes that takes place are either by electron exchange (Dexter) or by dipole-dipole (Förster) mechanisms [1b].

The molecules M* and Q must be in close contact (Van der Waals or hard sphere) for overlaping of orbitals to cause electron transfer. In dipole-dipole interaction the mechanism is via the transition moments of the excitation Q-Q* and deactivation of M-M*. This interaction has a rather shollow distance dependence (< 100A) compared to orbital overlap interaction of electron exchange.

Excited states can be quenched by energy or electron transfer and by photochemical reaction. Energy transfer quenching can also either be dynamic or static. The molecules M* and Q can come

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into contact through their random diffusional motion in dynamic quenching. The rate constant is then diffusion controlled and has an upper limit of 10^{10} M^{-1} s^{-1} for any bimolecular reaction.

Luminescence quantum yield follows the Stern-Volmer equation in dynamic quenching. The molecules M and Q should be in close proximity to each other in static quenching. Each excited molecule is then surrounded be one or several quancher so that quanching occurs instantaneously in Perrin model [1c]. The quenching rates are independent of diffusion control in static quenching and many reach values above 10^{10} M^{-1} s^{-1}.

Electron donor- acceptor molecules, due favorable charge transfer attractions, are expected to quench by electron exchange and by static quenching. Electron acceptors are oriented as quenchers toward donors.

Quinones are known to undergo all these processes; when the triplet state of the quinone lies bellow the triplet state of the molecule being quenched, electronic energy transfer has been shown to occur in many cases. Many evidences indicate that the quenching efficiency is determined by a charge transfer process from an electron-donor to the triplet quinone which may or may not induce a chemical reaction [2].

Knowledge of the photochemical behavior of quinones is important since they are known to act as electron-acceptors in the electron transportation of biological chains [3]. Formation of a triplet charge transfer complex between electron-donors and quinones is well-documented [4] but only a few articles involve an excited singlet state (the quenching of the singlet excited state of the electron-donor by a quinone). It is interesting to note with Harriman and Hosie [5] that the linkage between a porphyrin molecule and a quinone is not necessary to observe fluorescence quenching.

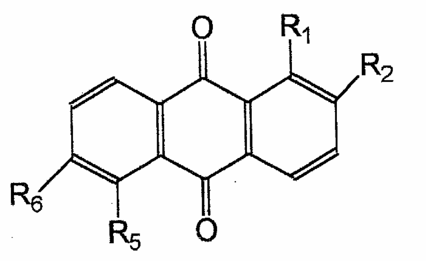
The sulfonate derivatives of anthraquinones have important photochemical and redox applications. They constitute the main chromphoric part of the antitumor drugs. Anthraquinones have been known to be good sensitizers in photooxidation of organic substrates, where a cyclic process involving the semiquinone radical was suggested to play an important role [6]. Reduction-oxidation cycles of quinone are also very important for electron transport in biological membrane [7]. In order to contribute to the understanding of the mechanism of the photochemical processes of anthraquinone and porphyrins we have measured the fluorescence quenching rates between Mg-TNP with π-electron donors molecules of antraquinones differently substituted.

The influence of different anionic anthraquinone compounds (called here An 1 to 3) on the fluorescence spectra and subsequently on the photodegradation reaction of Mg-TNP, is evaluated in this paper.

2. Experimental parts

2.1. Materials

The following anthraquinones 1-3 have been studied (Fig.1).



1) R_2= SO_3Na ; R_1=R_5=R_6=H
2) R_2=R_6=SO_3Na ; R_1=R_5=H
3) R_1=R_5=SO_3Na ; R_2=R_6=H

Fig. 1. The structure of the studied anthraquinones.

They were purchased from Eastman –Kodak and they were used as provided without any purification. The solvent, benzene, was dried over metallic sodium and subsequently distilled.

The quenching of the fluorescence of anthraquinones 1 to 3 has been carried out at 20 °C in benzene solution. The concentration in anthraquinone is adjusted in order to have an optical density of ca. 0.2 at the excitation wavelength.

The magnesium complex of TNP has been synthesized from TNP free base and the metallic complex of $HClO_4$ after Huennekens method [8]. Its structure is shown in Fig. 2.

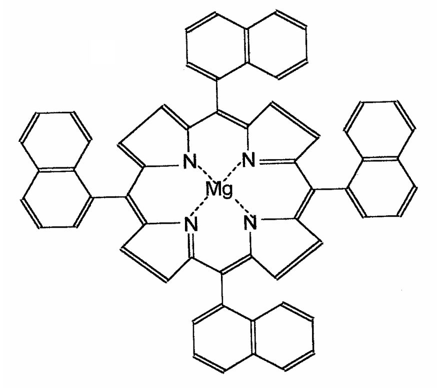


Fig. 2. The structure of Mg-TNP.

2.2. Apparatus

Absorption spectra were recorded by means of a SPECORD M400 Carl Zeiss Jena spectrophotometer equipped with double beam and microprocessor. Quartz cuvettes with 1 cm optical path lengths and containing 2 ml of cell suspension each were used.

Fluorescence measurements were carried out in parallel with the absorption measurements using an Aminco-Bowmann spectrofluorimeter. A 1x1 cm cuvette containing 2 ml solution was used. When recording the excitation spectra of porphyrins, a 580 nm cut-off filter was used to reduce the amount of scattered light, especially in the excitation region 230-350 nm.

In order to evaluate the stabilization effect of anthraquinones over the porphyrins, these samples have been irradiated with a light source was a 375 W mercury lamp (Hg medium pressure).

3. Results and discussion

The absorption spectra of An 1 to 3 are almost identical,in aqueous solution, with a high peak at 208 nm and two another less intense at 256 nm, 328 nm (Fig.3).

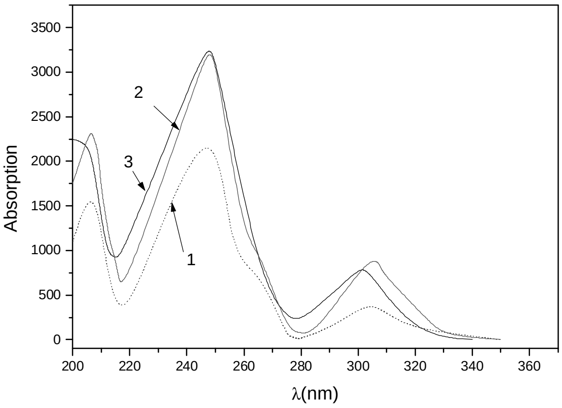


Fig. 3. The absorption spectra of An(1)(1), An(2)(2), An(3)(3).

The porphyrins and the anthraquinone compounds support a less desired photodegradation reaction during light irradiation in oxygenated solutions [9]. But, the anthraquinones have a good photostabilization effect on porphyrins because during the irradiation process, some colored stable products could be obtained, whose major components are hydroxylated anthraquinones with absorption maxima at 475 nm assigned to the corresponding diol derivatives, Fig.4.

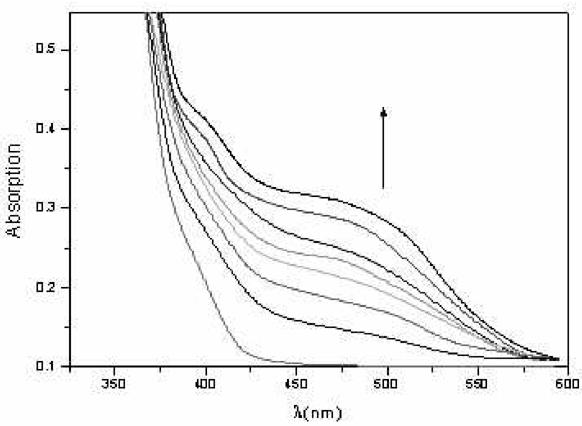


Fig. 4. The spectral changes of An 2 during the photodegradation process (Δt=2min).

In the presence of any of the anthraquinones studied here, Mg-TNP is more photostable than in their absence.

The possible interactions between Mg-TNP and any of the studied anthraquinones could be analysed by fluorescence spectroscopy. Mg-TNP has a specific and strong fluorescence emission at 610 nm with a shoulder at 575 nm.

The fluorescence of anthraquinones 1 to 3 is comprised of a large and structureless band, the maximum position of which depends on the substituents on the aromatic ring (Tab.1).

Table 1. Position of the maximum of fluorescence band for An 1 to 3 (λ_{exc}= 325 nm) and the fluorescence quenching rate of MgTNP ($\tau_{Mg\text{-}TNP}$ from ref.1a) with An 1 to 3.

Compound	1	2	3
λ_{em}^{max}	575	585	590
k_q (M^{-1} s^{-1})	$2.6\text{x}10^{11}$	$0.92\text{x}10^{12}$	$5.4\text{x}10^{11}$

A striking observation (Table 1) is that the fluorescence quenching rates increase due to π - electron donor capacities of An 1 to 3. An 2 is known to be one of the strongest aromatic π-electron systems.

Another unusual result of Table 1 is that fluorescence quenching rates of 10^{11}-10^{12} M^{-1} s^{-1} are greater than the diffusion-controlled rates of quenching 10^{10} M^{-1} s^{-1}. A static quenching of Perrin model appears to be applicable rather than the dynamic quenching of Stern-Volmer model.

The fluorescence quenching of Mg-TNP does not obey a simple Stern-Volmer linear relatioship, i.e., the inversed fluorescence intensities of Mg - TNP at (Io/I) vs. the quencher concentrations [Q] deviated upward from a stright line (Fig.5).

This should be ascribed to static quenching due to the formation of an electrostatic association complex between Mg-TNP and An 1 to 3.

On the other hand, it is expected that the sulfonated anthraquinones cannot associate with Mg-TNP in the ground state due to the electrostatic repulsion, under these circumstances, a dynamic quenching is able to takes place at this process simultaneously with a static process one. Because, the

Stern-Volmer plots do not intersect 1 value of I_o/I plot it can be concluded that a chemical quenching (a chemical reaction occur) during the process.

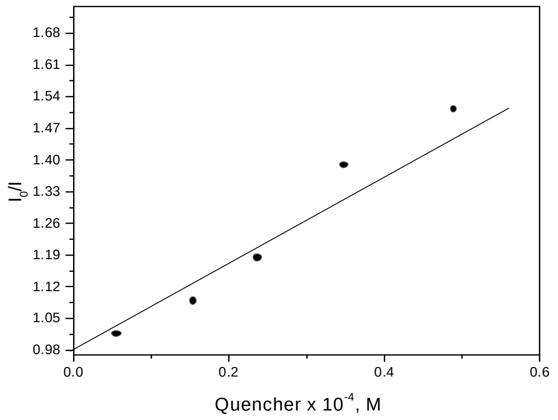


Fig. 5. The Stern-Volmer plot for Mg TNP fluorescence quenching by An 2.

The main parameters for the quenching of the fluorescence are deduced from the slope of the Stern-Volmer plot for various electron-donor molecules, ec.(2)

$$\Phi_f{}^o / \Phi_f = 1 + K_q \tau_s [\text{ quencher }] \quad (2)$$

where:

$\Phi_f{}^o$ and Φ_f are the fluorescence quantum yield of Mg-TNP in aerated and deoxygenated solutions;

K_q is is the bimolecular rate constant for Mg-TNP quenching;

τ_s is the fluorescence lifetime of Mg-TNP;

[quencher] is the quencher (anthraquinone) concentration.

The evidence for quenching occuring by means of a chemical reaction between Mg-TNP and the sulphonated anthraquinone is the following:

-the absorption maxima of the complex TNP-Mg-An show bathochromic shifts with respect to TNP-Mg alone (Fig. 6);

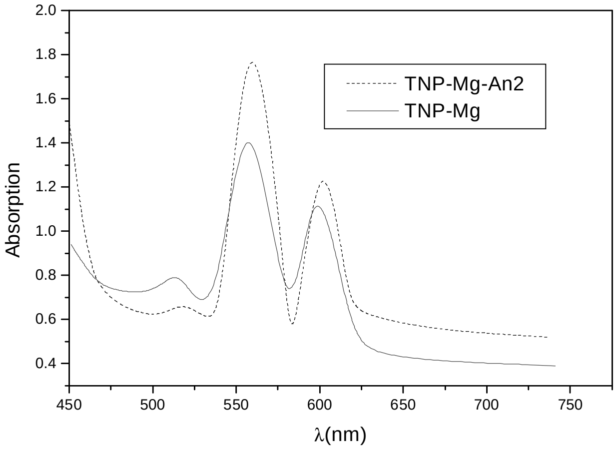


Fig. 6. The absorption spectra of Mg-TNP in the absence (-) and in the presence of An(2)(…).

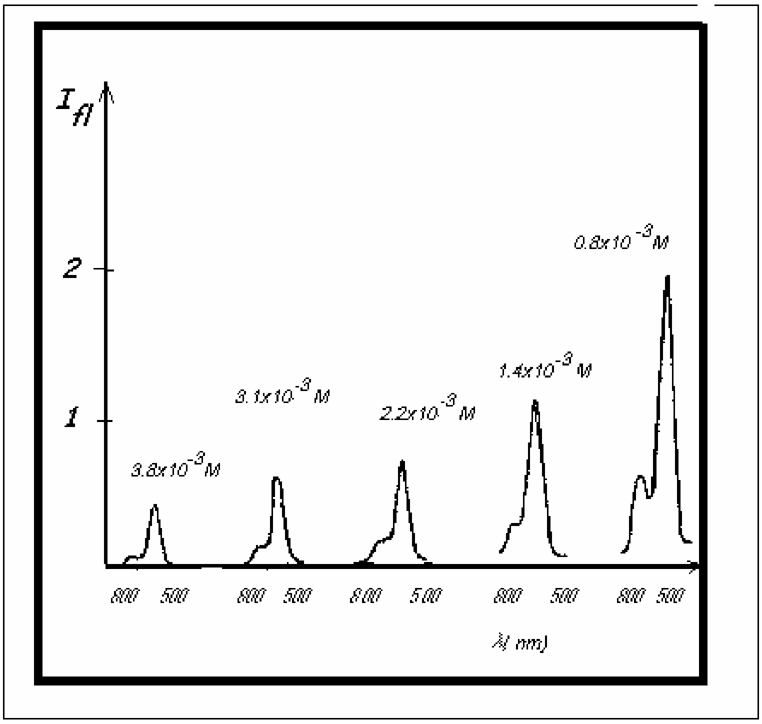


Fig. 7. The fluorescence spectrum of Mg-TNP 1×10^{-4}M in the presence of different concentration of An 2 (2×10^{-5} M).

-the fluorescence spectrum of the complex Mg - TNP-An shows different emission bands (650 nm) with respect to Mg - TNP alone (612 nm);

-the coupling reaction between TNP-Mg –ground state and any of the used anthraquinones occurs with a higher rate than the triplet excited state generation by the porphyrin. In the presence of An 1 to 3 the well-known photodegradation reaction of Mg - TNP- occur with a lower rate (Fig. 8).

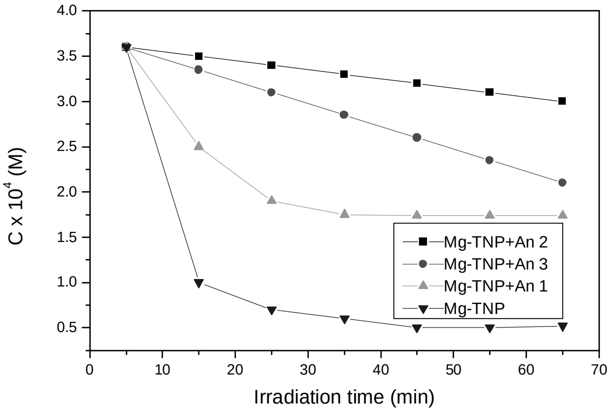


Fig. 8. The concentration decrease of Mg-TNP in the absence and in the presence of different anthraquinones.

The best photostabilizer for Mg-TNP could be An 2 due to its more planar structure without any steric hindrance and due to its high capacity to be very close to the porphyrinic structure [10].

The critical distances (R_o) which means the optimal distance for occuring energy transfer yielding to the quenching of singlet excited state (the distance at which energy transfer and singlet emission processes are equally probably), after the reference [11]:

$$R_o = (3000 / 4\pi N\,[A]^{1/2})^{1/3} \qquad (3)$$

$$R_o = (7.35 / [A]^{1/2})^{1/3} \qquad (4)$$

Where:

R_o is the critical distance acceptor (Mg-TNP)-donor (anthraquinone);
N is Avogadro's number;
A is the acceptor concentration (Mg-TNP);
For the studied system Mg- TNP-An 1 to 3, R_o values are:
An 1 $R_o = 6$ Å; An 2 $R_o = 10$ Å; An 3 $R_o = 8$ Å

For all these cases, R_o values are in the 1-10 Å range, which correspond to one singlet quenching processes by diffusion controlled energy transfer. The final conclusion is the following: increased the value R_o, will yield to an increased stability of the porphyrin, which is known having a low photostability, in spite of their important application.

These anthraquinones and the porphyrin, as we can see are in close proximity to each other at critical transfer distances of less than 10 Å. Electron-exchange and/or electron transfer processes are expected to proceed dominantly at these distances. The electron transfer should occur from singlet excited state of Mg-TNP to donor anthraquinone molecule, leading to formation of stable radical anion and cations (5)

$$\text{Mg-TNP} \xrightarrow{h\nu} {}^{1}\text{Mg-TNP}^{*} + \text{donor} \xrightarrow{\text{electron transfer}} \text{Mg-TNP}^{-\cdot} + \text{donor}^{+\cdot} \qquad (5)$$

Dominant back electron transfer (2) is expected to decay the radical species, preventing the electron escape from the cage (40 ps)

$$\text{Mg-TNP}^{-\cdot} + \text{donor}^{+\cdot} \xrightarrow{\text{electron transfer}} \text{Mg-TNP} + \text{Donor} \qquad (6)$$

Strong π -electron donors evidently transfers electrons to Mg-TNP. Favored back electron transfer from Mg-TNP. Outputs an overall electron exchange interaction as in Dexter process, and additional static quenching causes the observation of high fluorescence quenching between Mg-TNP and aromatic π-electron donors.

4. Conclusion

The fluorescence quenching rate constants, as deduced from the Stern-Volmer curves, once the singlet lifetime has been measured by independent method is postulated to go through a charge transfer complex formation. The quenching occurs via an energy transfer mechanism. The calculated critical transfer distances (R_o) are as high as that for collisional energy transfer (R_o= 1-10 Å). The quenching mechanism is that of resonance energy transfer, due to long-range dipole-dipole interaction between excited anthraquinone molecules (donor) and the ground state acceptor molecule Mg-TNP.

The coupling reaction between Mg – TNP - ground state and any of the used anthraquinones occurs with a higher rate than the triplet excited state generation by the porphyrin. In the presence of An 1 to 3 the well-known photodegradation reaction of Mg - TNP occur with a lower rate, the best photostabilizer being the 2, 6-sulfonated anthraquinone .

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Strong **π** -electron donors (An2) evidently transfers electrons to Mg-TNP . Favored back electron transfer from Mg-TNP. Outputs an overall electron exchange interaction as in Dexter process, and additional static quenching causes the observation of high fluorescence quenching between Mg-TNP and aromatic **π**-electron donors.

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