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A multiphotochromic tetraanthraporphyrazine based on the involvement of molecular singlet oxygen

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Abstract

A photochromic system working in the red–near IR region is described. The photooxygenation of the palladium complex of octaphenyl-tetraanthra-porphyrazine **1** (λ_{max} = 846 nm in benzene) in the presence of molecular oxygen is studied by absorption spectroscopy. Species with different absorption behaviour are formed and detected in the spectral range 600–850 nm. The final photoproduct is assigned to be a substituted palladium phthalocyanine **2** containing four *trans*-annular endoperoxide bridges in the middle part of the anthracene unit. The formation of this photoproduct involves singlet oxygen. Excitation of the photoproduct **2** into higher excited electronic states by UV-laser light results in the release of molecular oxygen and regeneration of the starting molecule **1**. © 1997 Elsevier Science S.A.

Keywords: Photochromism; Singlet oxygen; Phthalocyanine; Photocycloreversion; Photooxygenation

1. Introduction

A variety of organic photochromic compounds are known and well investigated. Most photochromic systems work in the UV and visible region of the electromagnetic spectrum, e.g., an uncoloured form of the photochromic system can be transformed into a coloured form and vice versa [1]. Photochromic systems working in the near IR region are rare. Up to now only one photochromic system working in the deep red region of the spectrum has been reported [2]. In the following we describe a photochromic system based on the insertion of molecular oxygen and its ejection (Fig. 1). This compound works in the red and near IR region of the spectrum. Aromatic hydrocarbons are known to incorporate molecular oxygen to form *trans*-annular endoperoxides [3,4] which absorb in the UV region. Thermal or photochemical back reaction leads to the starting aromatic hydrocarbons which absorb also in the UV or visible region of the spectrum [5]. The idea was to combine the aromatic hydrocarbon 9,10-diphenylanthracene with the tetraazaporphyrin framework leading to the acenannulated tetraanthraporphyrazine **1** that absorbs in the near IR region.

This compound is expected to insert molecular oxygen. Indeed, we found that four molecules of oxygen can be incorporated in compound **1** which was detected by LSI mass spectrometry [6]. In this work we describe the photochemical formation of **2** and its back reaction to **1** by absorption spectroscopy.

The original motivation for this study was to develop a photosensitizer for photodynamic tumour therapy (PDT) that is able to generate singlet oxygen by common triplet sensitization according to the type II mechanism, as well as from itself, by acting as internal source of singlet oxygen [7] via two photon excitation in the redmost absorption band.

2. Experimental

2.1. Materials

The preparation of octaphenyl-tetra-anthraporphyrazinato palladium (**1**) and its photochemically generated oxygen adduct containing four endoperoxide bridges (**2**) is described in [6]. Photoproduct **2** was purified by TLC (silica gel 60 from Merck) using benzene/chloroform/ethylacetate (30/20/50) as eluent. The blue zone was eluted with benzene. 1,3-Diphenylisobenzofuran (DPBF) was purchased from Aldrich and freshly recrystallised from 95% aqueous ethanol.

Tetra-*tert*-butyltetraazaporphyrinato-palladium and tetra-*tert*-butylphthalocyanato-palladium were synthesized according to [8].

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2.2. Spectroscopy

Absorption spectra were recorded with a Lambda 19 spectrophotometer (Perkin-Elmer) and Beckman UV 5270 spectrophotometer.

2.3. Irradiation procedure

Different light sources were used. For the one photon experiments a Xenon lamp XBO-100 or a He–Ne-laser were used. Formation of the different photoproducts was achieved by using the following cut-off filters from Schott (Mainz): RG 850 ($\lambda_{exc}>820$ nm), RG 780 ($\lambda_{exc}>760$ nm), RG 8 ($\lambda_{exc}>690$ nm), RG 1 ($\lambda_{exc}>590$ nm).

Solutions of **1** or **2** were saturated with oxygen or argon in 1 cm cuvettes (Hellma) for 30 min. Complex concentrations were adjusted in the range 0.5×10^{-5}–5×10^{-5} M.

For the laser flash photolysis of **2** the following lasers were used: nitrogen laser NIL 1000 $\lambda_{em}=337$ nm, 1 mJ, pulse duration: 6 ns, nitrogen laser MSG 800 LTB (Laser Technik, Berlin), 400 μJ, pulse duration: 400 ps, excimer laser (XeCl) (Lambda Physics) $\lambda_{em}=308$ nm, 100 mJ, pulse duration: 14 ns, excimer laser (KrF) (Lambda Physics) $\lambda_{em}=248$ nm, 200 mJ, pulse duration: 20 ns.

2.4. Singlet oxygen detection

Quantitative quenching experiments have been performed with DPBF. The concentration was adjusted to about 1×10^{-4}–1.6×10^{-4} M. The oxygen adduct formation of DPBF was monitored by a decrease of its absorption maximum at 415 nm. Careful control experiments with DPBF alone have found to be necessary, because DPBF is light sensitive. Only freshly recrystallized samples have been used.

3. Results

A solution of **1** in benzene shows its Q(0,0) absorption band maximum at 846 nm (Fig. 2). The long wavelength absorption is due to the extension of the π-system by linear acenannulation compared to the corresponding palladium tetra-*tert*-butyl-tetraazaporphyrin which has its Q(0,0) absorption maximum at 575 nm. The molar extinction coefficient of **1** at 846 nm is 2.3×10^5 M^{-1} cm^{-1}.

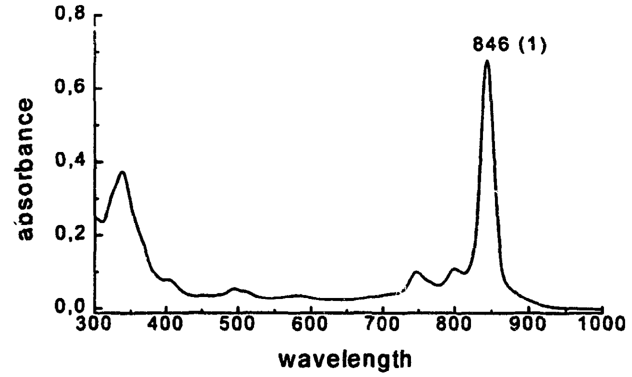
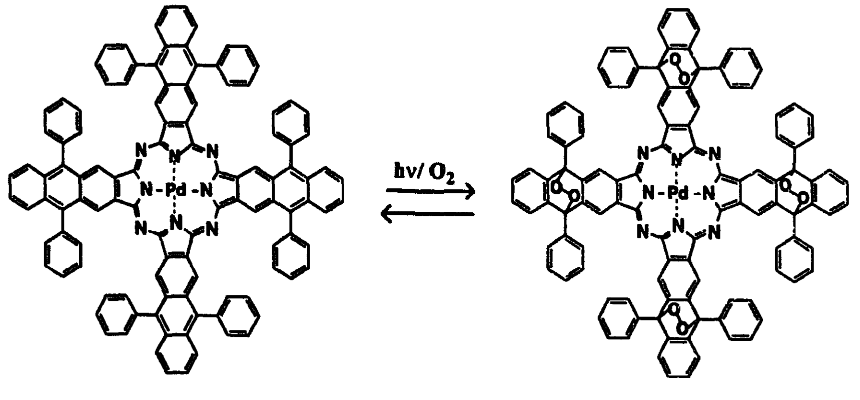


Fig. 2. Absorption spectrum of **1** dissolved in benzene. ($c=2.9\times10^{-6}$ M).

When an oxygen saturated benzene solution of **1** is irradiated with $\lambda_{exc}>820$ nm, using a cut-off filter RG 850, dramatic changes of the absorption spectrum occur. While the main band at 846 nm decreases, new absorption bands appear at 820 and 783 nm. Prolonged irradiation with the same filter leads to a decrease of the 820 nm band and to an further increase at the 783 nm band. An isosbestic point is observed at 825 nm although it is not well-defined. Changing the irradiation wavelengths now by using a cut-off filter RG 780 ($\lambda_{exc}>760$ nm) results in a decrease of the 783 nm band and appearance of a new band at 754 nm. An isosbestic point seems to be present at 760 nm. Further irradiation with $\lambda_{exc}\geq690$ nm (cut-off filter RG 8) results in a new band system with absorption maxima at 700 and 662 nm which later completely changes to the 662 nm band. On prolonged irradiation with $\lambda_{exc}\geq590$ nm using a cut-off Filter RG1 no further changes of the absorption spectrum are observed. The same changes in the absorption spectra were obtained when irradiation experiments of **1** were performed with an He–Ne-laser or by using a cut-off filter RG 8 ($\lambda_{exc}>690$ nm) instead of the step by step excitation experiments with different cut-off filters. Fig. 3 illustrates the absorbance profile produced



1 **2**

Fig. 1.

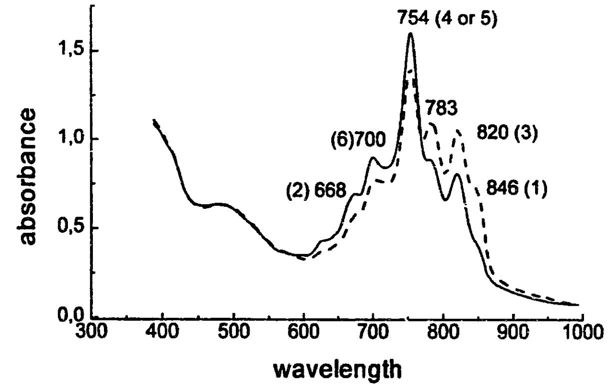


Fig. 3. Absorption spectra of intermediate stages of the possible photoproducts 2–6 generated by xenon lamp irradiation of 1 in the presence of molecular oxygen (cut-off filter RG 8 (λ_{exc} > 690 nm), solvent benzene, concentration of 1: $c = 5 \times 10^{-5}$ M. The starting compound 1 (shoulder at λ_{max} = 846 nm) has already been transformed for the most part. The formation of the final photoproduct 2 is seen in the spectrum as shoulder at 668 nm. It is formed by further irradiation and has its absorption maximum at λ_{max} = 662 nm (see Fig. 4). Irradiation time: - - - after 2 h, —— after 2.5 h.

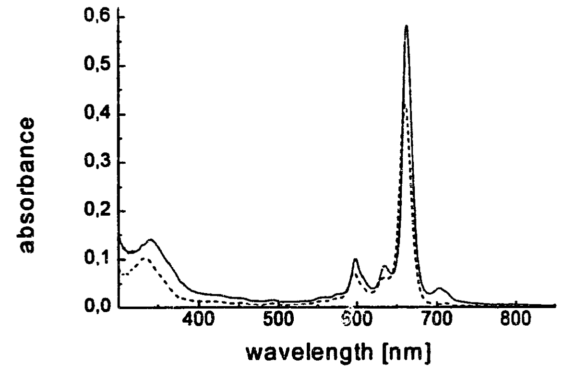


Fig. 4. Absorption spectra of 2 λ_{max} = 662 nm ($c = 3.2 \times 10^{-6}$ M) (——) and of palladium tetra-*tert*-butylphthalocyanine λ_{max} = 661 nm ($c = 1.6 \times 10^{-6}$ M) (- - -) dissolved in benzene. The small satellite-absorption band at 700 nm is assigned to the metal-free compound of 2 which could not be separated from 2 yet [10].

by irradiation of 1 in benzene under conditions that several species are formed using a cut-off filter RG 8 (λ_{exc} > 690 nm).

A total of four different species could be detected by pursuing the absorption spectra in dependence of the irradiation time. However, the exclusive formation of each of the species is more difficult to observe. Because the absorption of at least two species strongly overlaps, excitation at a certain wavelength results in a transformation of both forms. The following main maxima are assumed to be associated with the following photoproducts: starting compound (1): 846 nm, (3): 820, 783 nm, (4 or 5): 754 nm, (6): 700 nm, (2): 662 nm.

The final product of the photochemical reaction has an intense absorption maximum at 662 nm and an extinction coefficient of 1.8×10^5 M^{-1} cm^{-1}. Fig. 4 shows the absorption spectra of 2 and of palladium tetra-*tert*-butylphthalocyanine.

The photoproduct 2 is relatively stable toward one photon excitation at 660 nm and generates singlet oxygen.

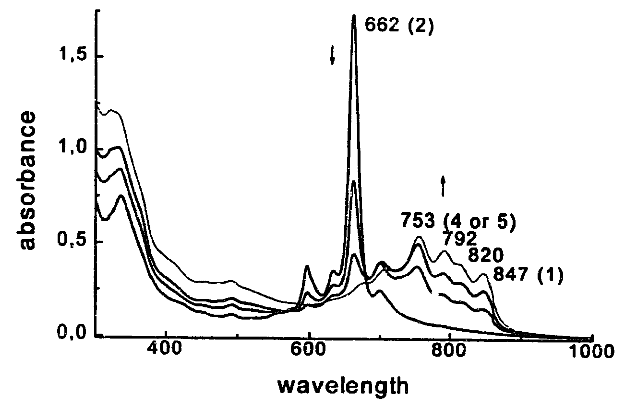


Fig. 5. Photocycloreversion of 2 (λ_{max} = 662 nm; $c = 9.7 \times 10^{-6}$ M) by nitrogen laser excitation (λ_{exc} = 337 nm) into higher excited electronic states (solvent: tetrahydrofuran). Absorption maxima are assigned to photoproducts in brackets.

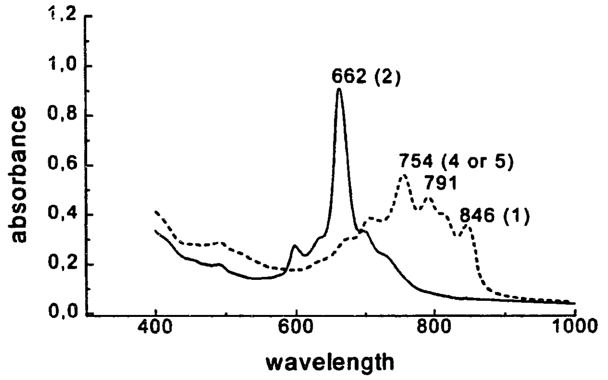


Fig. 6. Proof of photochromism of the photoproduct obtained by the cycloreversion of 2 following nitrogen laser irradiation (λ_{exc} = 337 nm). (- - -) spectrum obtained by nitrogen laser irradiation of 2 (compare Fig. 5), (——) one photon irradiation into the S_0–S_1 region of the different photoproducts reverts 2 completely (Xenon lamp XBO-100; cut-off filter RG 8; solvent: tetrahydrofuran).

However, irradiation at 337 nm (nitrogen laser), at 308 or 248 nm (excimer laser) as well as with the UV lines of a Hg arc lamp into higher excited states of the photoproduct 2 dissolved in argon saturated tetrahydrofuran or benzene results in dramatic changes of the absorption spectrum. A pattern of absorption bands with maxima at 700, 753, 792 (cp. below), 820 and 847 nm has been measured at continuing irradiation (Fig. 5).

The pattern of the absorption spectrum closely resembles to that obtained at one photon irradiation experiments with 1. A comparison of both spectra shows that the positions of the absorption maxima are almost identical.

In addition to the absorption band of the starting molecule 1 three of the above mentioned species seem to be indicated in the absorption spectrum. To test this, the following experiment was performed. The UV laser photolysed solution of 2 is irradiated again under one photon excitation conditions using a cut-off filter RG 8 (λ_{exc} > 690 nm). The absorption spectrum almost completely reverts into that of 2 (Fig. 6). This result indicates the reversibility of the phototransformation.

The practical use of a photochromic system depends on the number of photocycles. We repeated the photocycle twice and have observed under our not optimized irradiation conditions no complete reversibility, although the different photoproducts are thermally stable. Whether photodegradation is responsible or not has to be studied yet.

4. Discussion

These results clearly demonstrate that the system $1 \rightleftarrows 2$ is photochromic and that molecular oxygen plays an important part in it. The transformation of **1** into **2** requires oxygen and can be described as a self-sensitized photoreaction involving singlet oxygen. This conclusion can be drawn from the following facts. Firstly, the triplet state of **1** is populated leading to energy transfer and singlet oxygen generation. This is confirmed by using DPBF as singlet oxygen scavenger. Secondly, in an additional sensitization experiment we used the external sensitizer tetra-*tert*-bytyl- tetraazaporphyrinato palladium with $\lambda_{max} = 575$ nm (a region where the absorption of **1** is very low). The experiments were carried out in oxygen-saturated benzene containing about 9×10^{-3} M oxygen [9]. The concentration of the external sensitizer was adjusted so that about 95% of the incident dye laser light at 575 nm is absorbed. The rate of the photooxygenation of **1** in the presence of the sensitizer is about two times faster then without external sensitizer.

In the presence of the singlet oxygen scavenger DPBF and **1** almost no photoreaction of **1** was observed. The same result is observed when a benzene solution of **1** is bubbled with oxygen-free argon. These experiments clearly indicate the participation of singlet oxygen in the photochemical reaction of $1 \rightarrow 2$.

We reported the photoproduct **2** to be an endoperoxide [6]. The mass spectrum indicates the insertion of eight oxygen atoms as four endoperoxide bridges. The absorption spectrum of the photoproduct **2** ($\lambda_{max} = 662$ nm) resembles that of palladium tetra-*tert*-butylphthalocyanine ($\lambda_{max} = 661$ nm) (cf. Fig. 4). So it is reasonable to assume the endoperoxide bridges to be attached in the middle ring of the anthracene unit.

The other species absorbing in the range 695–820 nm are assumed to contain one, two or three endoperoxide bridges as illustrated in Fig. 7. Because of the difficulty to separate the photoproducts by HPLC, the assignment of the absorption maxima of the photoproducts is still uncertain in part. But the compound with a main absorption maximum at 754 nm definitely corresponds to the insertion of two endoperoxide bridges (isomers **4** and **5**), as was found by LIS mass spectrometry [10].

It is noteworthy to make some remarks on the symmetry properties of the generated photoproducts. Only in the case of **1** and its photoproduct **2** containing four endoperoxide bridges the molecules are considered to have D_{4h} symmetry. Reduction of symmetry from D_{4h} for instance by unsymmetrical benzoannulation of the tetraazaporphyrin framework or deviation from planar structure of the tetraazaporphyrin ring results in a splitting of the Q-band. Both, metal-free phthalocyanine and unsymmetrically substituted benzonaphthoporphyrazines exhibit a double maximum of the absorption band [11,12].

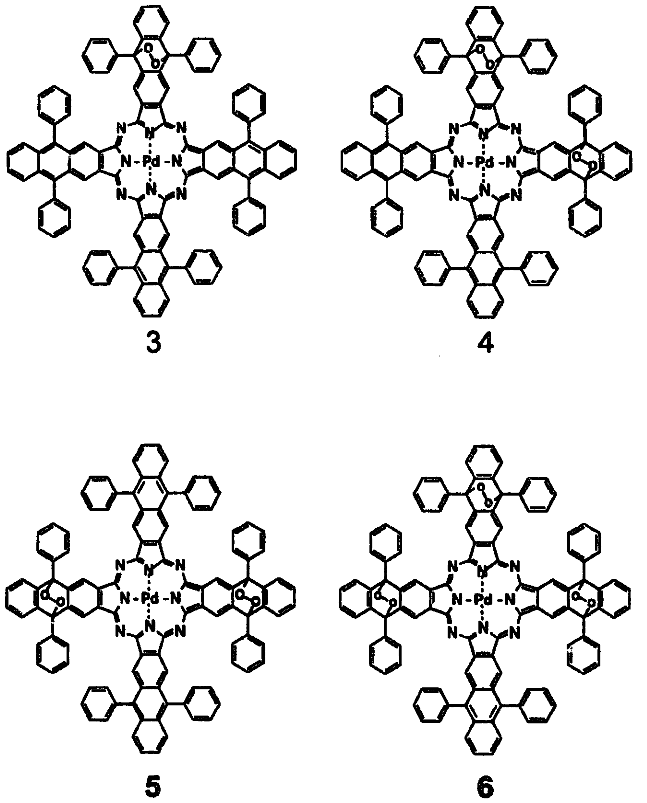


Fig. 7. Possible photoproducts generated by one photon excitation in the Q-band region of **1** in the presence of oxygen.

Consequently, the photoproducts **3**, **4**, **5** and **6** are considered to be unsymmetrically substituted benzoanthraporphyrazines with a lower symmetry than **2**. As a consequence the absorption pattern of **3–6** should differ from that obtained for **1** and **2**.

9,10-Diphenylanthracene is known to form photochemically the corresponding 9,10-peroxy-9,10-diphenylanthracene in the presence of oxygen [13] but it is not very stable [14]. Such a system is known to be highly photochromic [15]. By analogy with the behaviour of 9,10-diphenylanthracene endoperoxide we also observe photocycloreversion by exciting **2** in the region of the B band at 337 nm. Under these conditions the absorption spectrum of the products exhibits a pattern that is superimposed to the spectra of compounds **3–6**. This behaviour reflects the release of oxygen resulting in the formation of compounds bearing a different number of endoperoxide bridges. The mechanism can be understood on the basis of Fig. 8. Some years ago we showed linear benzoannulation of an tetraazaporphyrin to cause a strong shift of the Q-band to longer wavelengths while the position of the B band is only slightly shifted [8]. Because the compounds **3–6** represent mixed substituted benzoan-

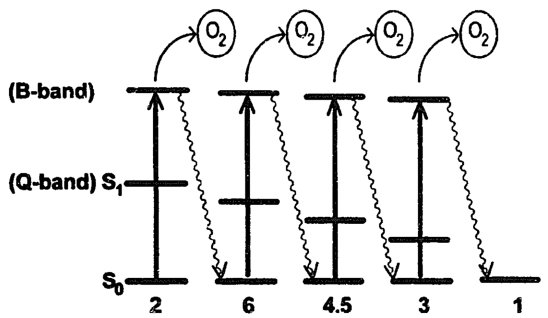


Fig. 8. Postulated step by step ejection of molecular (singlet) oxygen as a result of several one photon excitations in the B band (330 nm) of the photoproducts.

thraporphyrazines the observations made in [8] can be applied to **3–6**. As can be seen from Fig. 8 the stepwise release of oxygen is associated with a strong bathochromic shift of the Q-band while the position of the B-band remains almost constant (splitting of the Q-band due to deviation from D_{4h} symmetry of **3–6** is not considered). This means all compounds have an absorption band in the region of the laser excitation wavelength (cf. above). Because one UV photon can eject only one oxygen molecule it is reasonable to admit that the ejection of oxygen from **2–6** is a step by step process. The difference between the absorption maximum at 791 nm obtained upon the photocycloreversion of **2** in tetrahydrofuran and the maximum at 783 nm resulting from one photon irradiation of **1**, might reflect the appearance of the different isomers depicted in Fig. 7. However, one photon excitation of the photoproducts following the photocycloreversion of **2** is found to regenerate **2** reversibly (Fig. 6).

The photocycloreversion of 9,10-diphenylanthracene endoperoxide occurs from an higher excited π,π^* singlet state to give the singlet ground state of 9,10-diphenylanthracene and singlet oxygen. [16]. Excitation of the lower lying S_1 (π^*,σ^*) state of the endoperoxide chromophore results in a cleavage of the endoperoxide bridge. The resulting biradical is the precursor of several reaction products [17]. However, differently from the S_1 (π^*,σ^*) state of 9,10-diphenyl anthracene endoperoxide, the S_1 state of the photoproduct **2** being this latter a substituted phthalocyanine has π,π^* character. Transitions of phthalocyanines in the UV region are classified in a less intense broad B band (ca. 330 nm) and N, L, and C bands below 280 nm. They are assumed to have also π,π^* character, but transitions in the region of the B-band resulting from the involvement of the bridge nitrogen atoms cannot be ruled out completely [18,19]. Additionally, metal-related transitions were predicted in the whole spectral range [18].

However, the photocycloreversion seems not to be exclusively relevant to higher excited π,π^* transitions of an aromatic system. Recently photocycloreversion has been found of anorganic complexes such as oxodiperoxomolybdenum VI [20] or bis(triphenylphosphine) dioxygenplatinum [21]. The nature of the excited states involved seems strongly to influence whether oxygen is produced in its excited singlet state $^1\Delta_g$ or in the triplet ground state. For the mentioned molybdenum and platinum complexes the release of oxygen in its $^1\Delta_g$ state is observed whereas irradiation of bis (triphenylphosphine) dioxygeniridium leads also to the release of oxygen but in triplet ground state.

Experiments with **2** have been performed to determine whether the photocycloreversion produces oxygen in its excited singlet state or in the triplet state. Complex **2** was irradiated with a nitrogen laser at 337 nm in degassed benzene solutions using DPBF as scavenger of singlet oxygen. Control experiments have been carried out with DPBF alone. A comparison of the decrease of the absorption maximum intensity of DPBF at 415 nm shows that the decrease in the solution containing **2** is more pronounced. From this result the preliminary conclusion is drawn that excitation of **2** with light absorbed by the B-band may produce singlet oxygen.

5. Conclusions

The palladium complex of octaphenyltetraanthraporphyrazine was found to be a multiphotochromic system working in the red–near IR region. The photochromic effect is due to the insertion of singlet oxygen to form a substituted phthalocyanine containing four endoperoxide bridges and its ejection as molecular oxygen (likely in its $^1\Delta_g$ state). Both, the

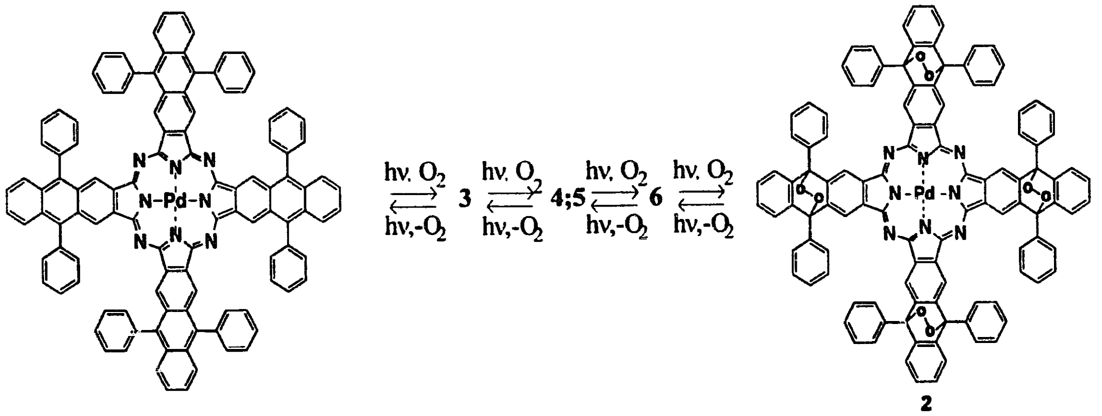


Fig. 9. Reversible multistep processes involving molecular oxygen in its $^1\Delta_g$ state.

insertion of oxygen and the ejection are assumed to be multistep processes as illustrated in Figs. 8 and 9.

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