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Intramolecular energy transfer in rhodamine–phthalocyanine conjugates

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ABSTRACT

Conjugates of tetrasulphosubstituted zinc phthalocyanine with rhodamine 6G or rhodamine B have been synthesized and characterized to have four rhodamine 6G or average two rhodamine B residues per phthalocyanine molecule. The ionized conjugates (positive charge on the rhodamine part) are non-soluble in water. Photochemical and photophysical measurements, carried out in dimethylsulphoxide, have shown that the main result of conjugation is efficient intramolecular energy transfer from rhodamine to phthalocyanine part of molecular system. The conjugation results in about twofold decrease of quantum yields for photodegradation, fluorescence and singlet oxygen photogeneration.

1. Introduction

Molecular systems combining in one molecule separate chromophores with intramolecular energy/electron transfer received considerable attention in the past two decades. Among them the variety of biomimetic model compounds with covalently linked porphyrin (electron donor) and acceptor such as quinone [1,2], fullerene [3] have been synthesized to investigate the primary reactions of photosynthesis. Other photoactive moieties, which in some cases provide novel or enhanced properties, may be employed in such artificial systems. In this approach a number of light-harvesting materials with improved activity for application under broadband light have been synthesized [4–8], there are few reports on light-harvesting systems for enhanced production of singlet oxygen ($^1O_2$) for use in oxygen sensitizing applications [6,7].

In this paper some rhodamine–phthalocyanine conjugates were prepared to investigate intramolecular energy transfer and efficacy in the production of singlet oxygen. The advantage of these chromophores is their efficient absorption in broad range of visible spectrum. Rhodamines have intense bands at about 540–570 nm with molar extinction coefficients of $10^5\,M^{-1}\,cm^{-1}$ magnitude. Phthalocyanines display extreme intense Q bands at longer wavelengths, in the 650–700 nm range, with molar extinction coefficients even exceeding $10^5\,M^{-1}\,cm^{-1}$. Thus, absorption bands of chromophores in proposed conjugates significantly overlap with the spectrum of the solar radiation, suggesting efficient conversion of sunlight to chemical energy. Other advantages of rhodamines, beneficial for fluorescence energy transfer to phthalocyanine units, are their high, close to unity, quantum yields of fluorescence emission in the 560–600 nm spectral range [9], which is close to Q-band absorption of phthalocyanines. Conjugates of rhodamine B and rhodamine 6G with metal-free and aluminum phthalocyanines were reported recently [10]. In this work we have synthesized conjugates of the rhodamines B and 6G with zinc phthalocyanine. The latter one exhibits a long lifetime and a high quantum yield of triplet excited state to produce efficiently $^1O_2$ [11,12]. In conjugates the rhodamine moieties were linked with phthalocyanine core by ester (rhodamine B) or amide (rhodamine 6G) bonds through ethylene spacers, connected to sulphamide substituents in zinc phthalocyanine molecule.

The proposed photophysical pathway for generation of singlet oxygen within our light-harvesting systems occurs via intramolecular energy transfer from rhodamine donor chromophore to the phthalocyanine, followed by intersystem crossing to the phthalocyanine triplet and sensitization of molecular oxygen to produce singlet oxygen. Experimental results confirm the intramolecular energy transfer in rhodamine–phthalocyanine conjugates.

2. Experimental

2.1. Materials

1,3-Diphenylisobenzofuran (DPBF), 1,4-diazabicyclo[2.2.2] octane (DABCO) and Reinecke salt were used as supplied from Fluka,

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9,10-dimethylanthracene (DMA)—from Aldrich. Dimethylsulphoxide (DMSO, Sigma–Aldrich) was used as received without further purification. Zinc tetra-4(5)-sulphophthalocyanine ($ZnPcS_4$) was synthesized according [13].

2.2. Synthesis of conjugates

2.2.1. Conjugate of zinc sulphophthalocyanine with rhodamine 6G (ZnPcS–Rh6G)

To solution (20 mg, 0.008 mM) of non-metallic sulphophthalocyanine conjugate with rhodamine 6G spirolactame (H_2PcS–Rh6G) [10] in DMSO (1.5 mL) the solution of zinc acetate dihydrate (2 mg, 0.009 mM) in DMSO (0.5 mL) was added. The mixture was stirred during 10 min at room temperature, then the solution was poured on the water, the precipitate was filtered and washed on filter by water and methanol successively. After drying ZnPcS–Rh6G (10 mg, 97%) was obtained. Anal. calcd. for $C_{144}H_{136}N_{24}S_4Zn$: C 65.21; H 4.84; N 12.67. Found: C 64.52; H 4.72; N 12.01.

The prepared conjugate was transformed into salt-like form by dissolution in 1% solution of methanol in chloroform, addition of trifluoroacetic acid (0.2 mL) and heating at 40 °C for 10 min. Then the solvent was evaporated, the residue was rubbed in hexane, filtered and dried.

Conjugate of zinc sulphophthalocyanine with rhodamine B aminoethyl ester (ZnPcS–RhB) was obtained in a similar way, starting from corresponding conjugate H_2PcS–RhB [10].

2.3. Measurements

2.3.1. Spectroscopic and luminescence studies

Absorption spectra were recorded with a Hewlett Packard-8453 spectrophotometer.

Excitation and fluorescence spectra were measured on spectrofluorimeter Hithachi-850. Luminescence spectra of conjugate, corresponding rhodamine, phthalocyanine and mixture of rhodamine and phthalocyanine were measured in DMSO with excitation at $\lambda_{max} = 539$, 565 and 684 nm, respectively.

Fluorescence quantum yields (Φ_F) were determined by the comparative method (Eq. (1)) [14]:

$$\Phi_F = \Phi_F^{ref} \frac{FA^{ref}(n_D)^2}{F^{ref}A(n_D^{ref})^2} \tag{1}$$

where F and F^{ref} are the areas under the fluorescence curves, A and A^{ref} are the respective absorbances at the excitation wavelength (the same in our experiments), n_D and n_D^{ref} are the refractive indexes of solvents for the sample and reference, respectively. Rhodamine 6G and rhodamine B in ethanol ($\Phi_F = 0.94$ and 0.69, correspondingly, [9]) and unsubstituted ZnPc in DMSO ($\Phi_F = 0.20$ [15]) were employed as the references.

Measurements were carried out for dilute solutions to avoid the inner filter effect. Both the sample and reference were excited at right angles and had equal absorbance at the wavelength of excitation. Light flux was sustained equal at each excitation wavelength. Fluorescence spectra were normalized on intensity of a corresponding rhodamine luminescence.

2.3.2. Singlet oxygen and photodegradation quantum yields

The determinations of quantum yields of singlet oxygen (Φ_Δ) and photodegradation (Φ_d) were carried out with two different light sources for excitation either rhodamine or phthalocyanine chromophores. For excitation of rhodamine moieties monochromatic light with λ_{ex} 546 nm (from mercury lamp with a combination of filters) was used. The radiation flux of 546 nm was measured with an actinometer, based on Reinecke salt [16]. Phthalocyanine excitation in the Q absorption band was achieved by using a xenon lamp (150 W). A water filter and glass filter KS-10 were used to cut off infrared radiation and radiation of $\lambda < 600$ nm. An interference filter of 680 ± 25 nm was placed in the light path. The 680 nm light intensity was measured with a power meter Spectra Physics 404 and was found to be 2×10^{15} photons s^{-1} cm^{-2}.

The singlet oxygen quantum yield, Φ_Δ, of the dyes and conjugates in DMSO solution was estimated by using $ZnPcS_4$ as reference and DPBF as $^1O_2$ trap according to the reported procedure [17]. Solution of tested dye (about 5×10^{-6} M) and DPBF (3×10^{-5} M) was irradiated in a 1 cm path length cell. The values of Φ_Δ were calculated using the relationship:

$$\Phi_\Delta = \Phi_\Delta^{ref} \frac{WI_{abs}^{ref}}{W^{ref}I_{abs}} \tag{2}$$

where Φ_Δ^{ref} is the singlet oxygen quantum yield for $ZnPcS_4$ ($\Phi_\Delta^{ref} = 0.68$ [13]), W and W^{ref} are the DPBF photobleaching rates, I_{abs} and I_{abs}^{ref} are the intensities of light absorption for tested dye and reference, respectively. The initial DPBF concentrations are kept the same for reference and the samples. The accuracy of Φ_Δ estimation was about 15%.

Photodegradation quantum yield determinations were performed in DMSO under aerobic conditions. Solutions of dyes (concentration 0.5 to 1×10^{-5} M) were illuminated in the 10 mm path length cell. The decrease of substrate absorbance A (measured in the maximum of the visible absorption band) was followed as a function of irradiation time. Quantum yields of photodegradation Φ_d were calculated from the initial part of the $A(t)$ dependence curves according to the following equation:

$$\Phi_d = \frac{V}{I_{abs} l \varepsilon} \frac{dA}{dt} \tag{3}$$

where V is the reaction volume, I_{abs} is the intensity of light absorption by the sample (Einsteins per second), l is the optical path length, ε is the decimal molar absorption coefficient at the maximum of the absorption band. The term dA/dt was determined graphically.

2.3.3. Photosensitized oxidation of 9,10-dimethylanthracene (DMA)

Experiments were performed under aerobic conditions by using solar irradiation (luminous intensity was about 90,000 luxes) as a photonic source. A 50-mL batch photoreactor was irradiated by solar light from the top through 420 nm cutoff filter. For these runs, solutions of DMA ($\sim 4 \times 10^{-5}$ M) without additives or containing rhodamine (0.8 to 1×10^{-5} M) and/or $ZnPcS_4$ (0.5×10^{-5} M), or conjugates ZnPcS–Rh (0.5×10^{-5} M) in DMSO were used. The samples were withdrawn from the reactor every 30 s, and DMA degradation was followed as decrease of the absorbance at 403 nm maximum.

2.3.4. Photosensitized oxidation of tryptophan

The DMSO solution of the tryptophan (0.4 mM) and sensitizer (50 μM) was introduced into a 1 cm path length spectrophotometric cell and irradiated with a 200 W tungsten lamp under air bubbling conditions. The spectral regions for excitation with light of $\lambda_{ex} > 500$ nm or $\lambda_{ex} > 600$ nm were cut off using glass filters. The optical density in the absorption maximum of dye was adjusted to ~2, to provide full absorption of incident light allowing to compare photosensitizing activity of dyes in about equal irradiation conditions. Rates of tryptophan photooxidation were monitored by the decrease in the absorption maximum at 283 nm.

All the experiments were carried out at ambient temperature.

3. Results and discussion

3.1. Synthesis

The sulphophthalocyanine–rhodamine conjugates have been synthesized by amidation of tetra-4-sulphophthalocyanine sulphochloride with rhodamines Rh6G or RhB having amino group as substituent. Conjugates have four rhodamine 6G or average two rhodamine B residues per phthalocyanine molecule. The sulphochloride was prepared by treatment of corresponding acid with thionyl chloride in the presence of DMF.

Taking into account that zinc sulphophthalocyanines undergo demetallation in acidic solutions, especially at elevated temperatures, leading to formation of corresponding non-metallic phthalocyanines, the synthesis of ZnPcS–RhB and ZnPcS–Rh6G (Scheme 1), was carried out by metallation of corresponding non-metallic analogs – H_2PcS–RhB and H_2PcS–Rh6G [10] – by their treatment with zinc acetate in DMSO at room temperature.

3.2. Ground state properties of rhodamine–phthalocyanine conjugates

The closed lactam form of ZnPcS–Rh6G is readily soluble in organic solvents, such as toluene, chloroform. In neutral or alkaline media it has blue-green color and absorption spectrum characteristic to phthalocyanine. In acidic solutions lactam cycle of rhodamine part opens out giving ionic form, and solution of conjugate acquires violet color. Resulting compound loses solubility in non-polar solvents and gains it in polar ones. Absorption band at about 540 nm (rhodamine part of conjugate) appears in spectrum with intensity, exceeding the band of phthalocyanine part of molecule (Fig. 1). Decrease of acid concentration in solution leads to lowering and disappearance of rhodamine absorption. Such acid–base interconversions between closed and open forms of Rh6G lactam in ZnPcS–Rh6G are characteristic for parent spirolactam of Rh6G and are reversible. Ionized ZnPcS–Rh6G however, having four positively charged fragments of Rh6G, differs from non-conjugated Rh6G being totally insoluble in aqueous media. In acidic DMSO conjugate ZnPcS–Rh6G bleaches with time progressively. In our studies we used only freshly prepared solutions. Hereafter, until otherwise noted, ZnPcS–Rh6G is referred to as ionized form of this conjugate.

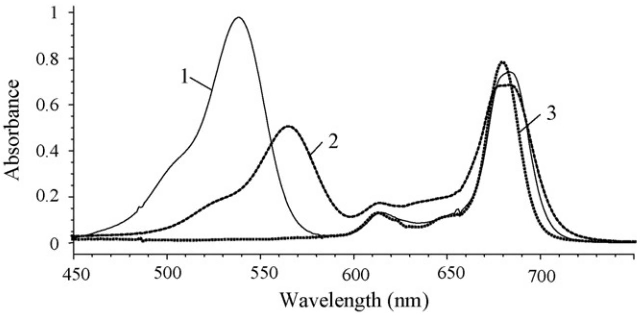
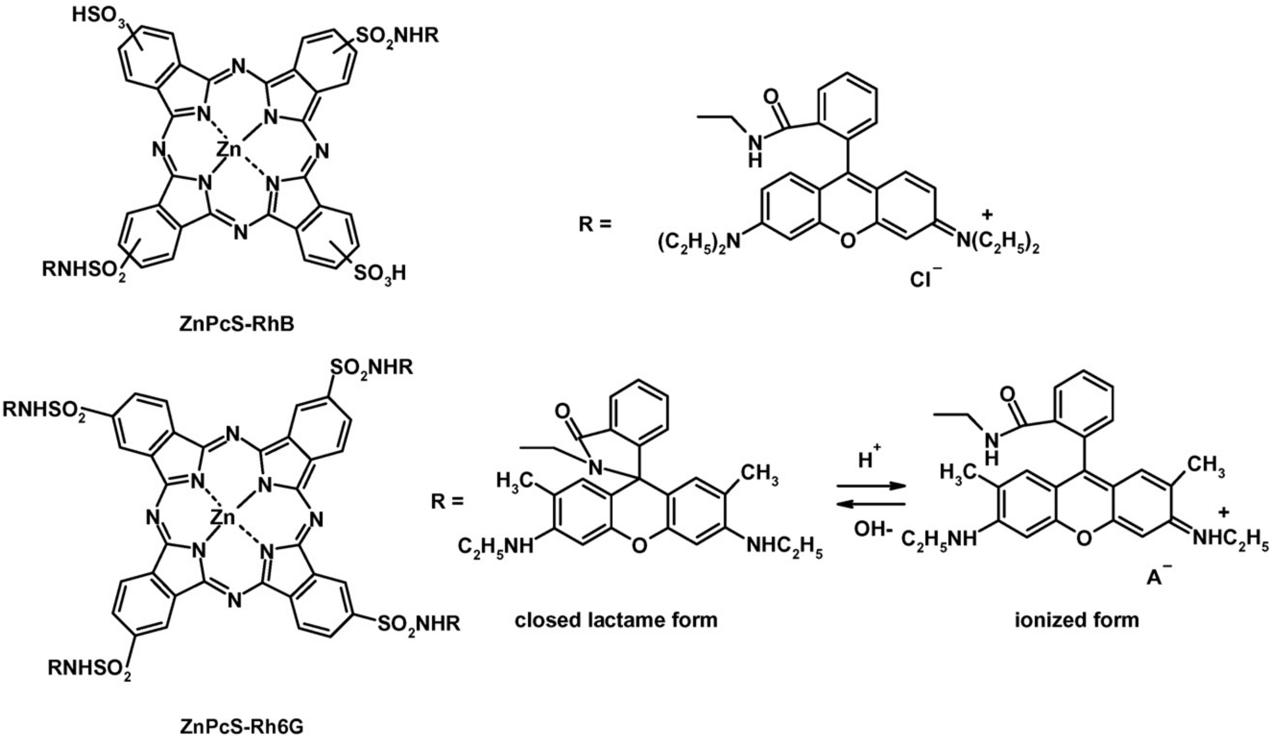


Fig. 1. Visible absorption spectra of ZnPcS–Rh6G (1), ZnPcS–RhB (2) and $ZnPcS_4$ (3) in DMSO.

Conjugate ZnPcS–RhB is soluble in $CHCl_3$–MeOH (10:1), DMSO, strong HCl and insoluble in water. Its absorption spectrum in DMSO is shown in Fig. 1 over 400–700 nm wavelength range. The spectrum exhibits two main bands in the visible spectral region with higher intensity of phthalocyanine band at 684 nm as compared to band of rhodamine part at 564 (Fig. 1). By using the molar extinction coefficients for RhB and $ZnPcS_4$ in DMSO equal to 115,000 and 210,000 [13], correspondingly, average amount of RhB residues per ZnPc molecule in conjugate ZnPcS–RhB was assessed to be about 2 suggesting the presence of free sulpho groups in molecule. In suspension with 1% aqueous NaOH the progressive hydrolysis of ester bond, accompanied by transition of free dyes into alkaline solution takes place. So, the instability of ZnPcS–RhB in alkaline medium



Scheme 1. Molecular structures of conjugates.

Table 1
Fluorescence quantum yields for rhodamine–phthalocyanine conjugates and relative unconjugated chromophores

Substrate	Absorbance (λ_{max}, nm)	Excitation (λ_{ex}, nm)	Fluorescence	
			λ_{max} (nm)	Quantum yield (Φ_F)
Conjugate of ZnPcS–Rh6G	539, 684	539	565	≈0.02
			695	≈0.02
Conjugate of ZnPcS–Rh6G	539, 684	684	565	0
			695	≈0.02
Mixture of ZnPcS + Rh6G	539, 680	539	565	0.98 ± 0.02
			690	0
Mixture of ZnPcS + Rh6G	539, 680	684	565	0
			690	0.19 ± 0.02
Conjugate of ZnPcS–RhB	564, 684	564	592	≈0.02
			695	≈0.05
Conjugate of ZnPcS–RhB	564, 684	684	592	0
			695	0.12
Mixture of $ZnPcS_4$ + RhB	564, 680	564	592	0.85 ± 0.02
			690	0
Mixture of $ZnPcS_4$ + RhB	564, 680	684	592	0
			690	0.19 ± 0.02
Rh6G	539	539	565	0.98 ± 0.02
RhB	564	564	592	0.85 ± 0.02
$ZnPcS_4$	680	684	690	0.19 ± 0.02

results in low average amount of linked RhB molecules per ZnPc in this conjugate.

Unlike ZnPcS–Rh6G having rhodamine band in absorption spectrum only in acidic media, conjugate ZnPcS–RhB in neutral DMSO is stable and has both rhodamine and phthalocyanine bands in spectrum. Spectra of ZnPcS–RhB as well as spectra of free RhB are independent on solution acidity.

In Table 1, the position of absorption peaks in visible spectral region for ZnPcS–RhB and ZnPcS–Rh6G in DMSO are summarized. For rhodamine subunits the main absorption bands are saving at conjugate formation. However, the Q absorption bands in spectra of both conjugates are broader and 4 nm red shifted in comparison with relative band for unbounded $ZnPcS_4$ (Table 1, Fig. 1) suggesting the loss of ZnPcS molecular symmetry.

3.3. *Photobleaching of conjugates*

Zinc phthalocyanines are known to undergo photodegradation when exposed to visible light [18–20]. Conjugates ZnPcS–RhB and ZnPcS–Rh6G also undergo photobleaching upon irradiation with visible light in DMSO under aerobic conditions. Details of this process were studied for ZnPcS–RhB. Spectral changes of ZnPcS–RhB under excitation into rhodamine ($\lambda_{ex} = 546$ nm) and phthalocyanine ($\lambda_{ex} > 620$ nm) units are shown in Fig. 2 demonstrating the dependence of their pattern on excitation wavelength. Thus, when conjugate is excited into RhB fragment, the absorption of rhodamine and phthalocyanine subunits decreases indicating irreversible degradation of both chromophores. Excitation into phthalocyanine absorption band leads to bleaching of ZnPc unit only. Such behavior is indicative of excitation energy transfer in conjugate from rhodamine B chromophore to zinc phthalocyanine unit, and absence of energy transfer, as expected, in the opposite direction.

In all cases, the photobleaching kinetics follows a first-order law and the time-dependent decrease of absorbance at the absorption maximum is well fitted by a single-exponential decay function (data not shown).

Photodegradation quantum yields (Φ_d) for compounds under investigation are listed in Table 2. It was found that free RhB degrades with $\Phi_d = 1 \times 10^{-5}$ in DMSO in the presence of oxygen. As can be observed in Table 2, conjugation leads to twofold increase of RhB photostability suggesting as much as 50% excitation energy transfer to phthalocyanine part of this bichromophoric system. The Φ_d for unconjugated $ZnPcS_4$ was found to be $2.1 \pm 0.2 \times 10^{-5}$ (Table 2). This value is close to that for other zinc phthalocyanines in DMSO, particularly for unsubstituted ZnPc [20]. Linkage of RhB units results in decrease of Φ_d for zinc phthalocyanine

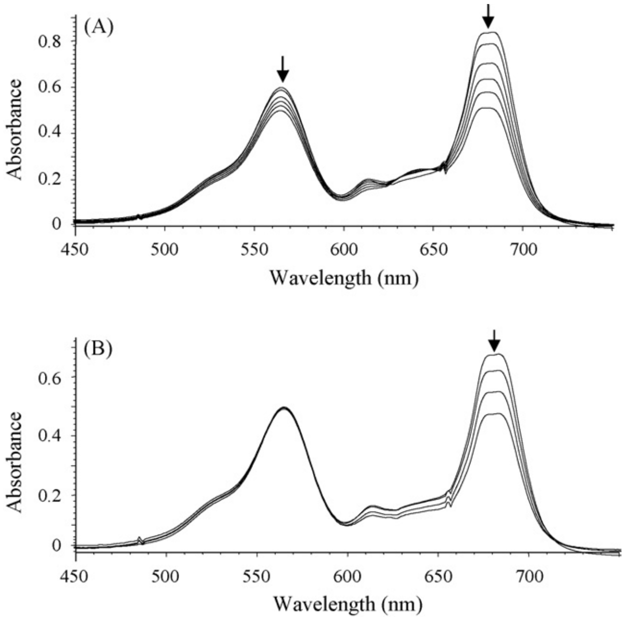


Fig. 2. Spectral change for ZnPcS–RhB in DMSO under excitation into rhodamine (A, $\lambda_{ex} = 546$ nm) or phthalocyanine (B, $\lambda_{ex} = 680 \pm 25$ nm) parts of conjugate.

Table 2
Photodegradation quantum yields (Φ_d) for free and conjugated dyes $ZnPcS_4$ and RhB in DMSO under aerobic conditions

Substrate	λ_{ex} (nm)	Φ_d ($\times 10^5$)	
		RhB	ZnPcS
ZnPcS–RhB	546	0.55 ± 0.05	1.2 ± 0.1
ZnPcS–RhB	680	≤0.1	0.7 ± 0.1
RhB	546	1.0 ± 0.1	–
$ZnPcS_4$	680	–	2.1 ± 0.2

chromophore to $0.7 \pm 0.1 \times 10^{-5}$. Interestingly, Φ_d for $ZnPcS_4$, induced by excitation energy transfer from RhB part (under 546 nm excitation), is equal to 1.2×10^{-5} (Table 2).

In this work we have not studied the mechanism of conjugate photodegradation besides the test on singlet oxygen contribution. For this purpose the reaction was studied in the presence of DABCO. This compound is known to act as a singlet oxygen quencher [21]. It was found that yield of rhodamine part photobleaching is not significantly affected by the presence of 0.005 M DABCO, thus eliminating any major contribution of $^1O_2$ to the process. As to the photodegradation of phthalocyanine part, the twofold inhibition of the process by DABCO at the same concentration was observed. This result indicates partial photodegradation of phthalocyanine fragment with participation of $^1O_2$. Hence, two chromophores linked in conjugate behave themselves independently from each other.

3.4. Fluorescence energy transfer study

Fluorescence resonance energy transfer (FRET) was also monitored. FRET involves non-radiative energy transfer from a photoexcited donor fluorophore to an acceptor. The degree of spectral overlap of the donor fluorescence and the acceptor absorption spectra and a highly fluorescent donor are important [22].

In bichromophoric systems, synthesized in this work, Rh6G and RhB were employed as excitation energy donors. They have high fluorescence quantum yields (Φ_F): in ethanol $\Phi_F = 0.94$ and 0.69 for Rh6G and RhB, respectively [9]. However, no data on Φ_F for rhodamines in DMSO were reported. In this work we have found that efficacy of Rh6G and RhB fluorescence in DMSO is even higher than in ethanol, corresponding quantum yields are equal to 0.98 and 0.85 (Table 1). Maxima of absorption and fluorescence bands of rhodamines are 10–14 nm red shifted in DMSO relatively to ethanol solutions.

In Fig. 3 the normalized emission spectra of Rh6G and RhB are overlaid with the absorption spectrum of $ZnPcS_4$. It may be seen (Fig. 3) that there is a little overlap between the fluorescence spectra of rhodamines and the absorption spectrum of $ZnPcS_4$ (shaded in Fig. 3), however, it suggests the possibility of FRET from rhodamine moieties to $ZnPcS_4$ in conjugates. The donor–acceptor centre-to-centre distance (16–17 Å) is favorable for singlet–singlet excitation energy transfer as evidenced by the following results on fluorescent properties of conjugates.

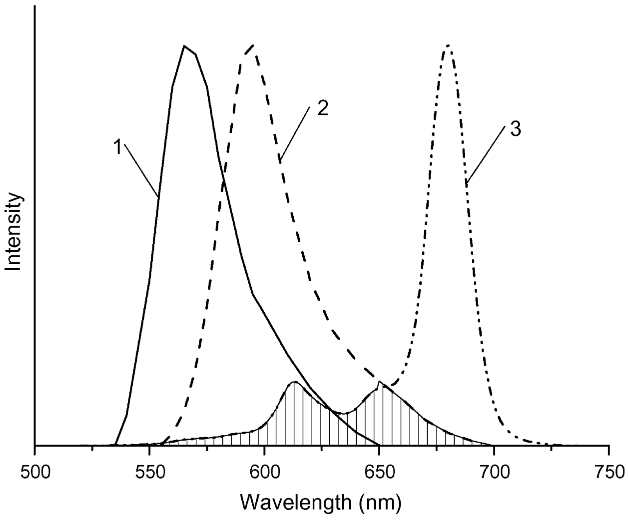


Fig. 3. Normalized fluorescence spectra for Rh6G (1), RhB (2) and absorption spectrum of $ZnPcS_4$ (3) in DMSO.

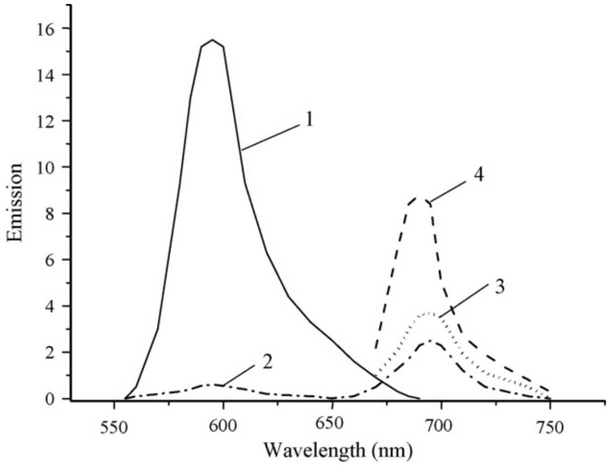


Fig. 4. Fluorescence spectra in DMSO for RhB (**1**, $\lambda_{ex} = 564$ nm); ZnPcS–RhB (**2**, $\lambda_{ex} = 564_{HM}$); ZnPcS–RhB (**3**, $\lambda_{ex} = 684_{HM}$); $ZnPcS_4$ (**4**, $\lambda_{ex} = 684_{HM}$).

The Φ_F value for unbounded $ZnPcS_4$ in DMSO was determined to be 0.19. It is worthy to note that fluorescence spectra both for acceptor ($ZnPcS_4$) and donor (Rh6G or RhB) are unchanged in their mixture (Table 1). Hence, without conjugation no excitation energy transfer between rhodamine and phthalocyanine occurs.

Fig. 4 presents fluorescence emission spectra of ZnPcS–RhB, obtained under conjugate excitation into rhodamine or phthalocyanine parts of molecular system. These spectra are compared with emission spectra of unconjugated dyes under the same excitation conditions. It was observed that fluorescence spectrum of ZnPcS–RhB conjugate under excitation into phthalocyanine fragment has only one band, which coincides well with band in fluorescence emission spectrum of unbounded $ZnPcS_4$ (Fig. 4, curve 3). Quantum yield of phthalocyanine fluorescence in this conjugate is 0.12, smaller than for free dye (for $ZnPcS_4$ $\Phi_F = 0.19$, Table 1). The excitation energy transfer results in appearance of the acceptor (phthalocyanine) fluorescence at irradiation of the donor (rhodamine) part. As shown in Fig. 4 (curve 2), when RhB fragment of conjugate is excited, the rhodamine emission almost disappears and emission corresponding to phthalocyanine chromophore appears. This observation shows that there is energy transfer between the linked subunits. Linkage to the $ZnPcS_4$ results in drastic (about 50 times) quenching of the RhB fluorescence (Table 1). From the results summarized in Table 1, it can be noticed also that the phthalocyanine fluorescence quantum yield in ZnPcS–RhB under excitation into RhB fragment is ≈0.05, which is about twofold smaller than may be expected with FRET close to 1 considering high efficiency of Φ_F for RhB and its almost complete quenching during conjugation.

Compound ZnPcS–Rh6G has shown similar behavior but, as it is clear from the spectra shown in Fig. 5, the emission band of donor chromophore in this case is quenched not so effectively compared to conjugate with RhB. It is due to the fact that the emission band of RhB has larger overlap with the Q absorption band of $ZnPcS_4$, and singlet excitation energy can be transferred to phthalocyanine unit more effectively in ZnPcS–RhB than in ZnPcS–Rh6G. Accordingly, for ZnPcS–Rh6G we have found smaller efficiency for phthalocyanine fluorescence, induced by the energy transfer from the Rh6G fragment ($\Phi_F \approx 0.02$, Table 1). Interestingly, the $ZnPcS_4$ fluorescence in ZnPcS–Rh6G at 680 nm excitation is also quenched ($\Phi_F \approx 0.02$).

Hence, conjugation leads to the fluorescence quenching for both rhodamine and phthalocyanine subunits suggesting appearance of another competitive process of excitation energy dissipation.

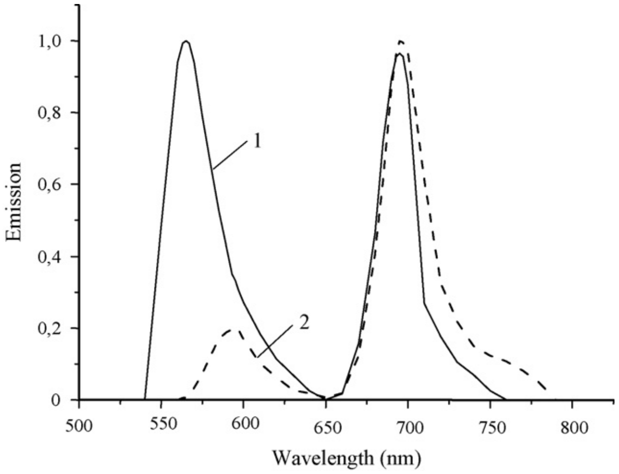


Fig. 5. Normalized fluorescence emission spectra of ZnPcS–Rh6G (**1**) and ZnPcS–RhB (**2**) in DMSO. Excitation into rhodamine fragment.

3.5. *Singlet oxygen generation*

The aerobic excitation of conjugate ZnPcS–Rh6G or ZnPcS–RhB in DMSO was performed in the presence of 1,3-diphenylisobenzofuran (DPBF) as a singlet oxygen trap. Example in Fig. 6 with conjugate ZnPcS–RhB and 546 nm excitation into rhodamine fragment shows typical photolysate spectra change with the DPBF band (λ_{max} = 418 nm) decrease. Kinetic of the DPBF photooxidation follows a pseudo-first-order law (data not shown).

To reveal the mediation of $^1O_2$ in the photooxidation of DPBF sensitized by conjugates, the test reactions were used. Thus, it was confirmed that no degradation of DPBF was observed under excitation in an argon-saturated oxygen-free DMSO, containing conjugate ZnPcS–Rh6G or ZnPcS–RhB. This observation shows that oxygen is necessary for the photooxidation of the DPBF and excludes direct electron or energy transfer between conjugate and DPBF is responsible for the degradation of the singlet oxygen trap. Under conjugate aerobic irradiation in the DMSO the decay of DPBF was almost completely inhibited by DABCO at concentration 5×10^{-3} M. This result is indicative that $^1O_2$ is the main species responsible for DPBF photooxidation in employed conditions.

The quantum yields of $^1O_2$ production (Φ_Δ) were calculated comparing the rates of DPBF photooxidation, sensitized by conjugate and reference, ZnPcS$_4$. For both conjugates the Φ_Δ values were found to be about 0.40 under excitation in *Q* absorption band of ZnPc fragment (Table 3). The parameter Φ_Δ under excitation with 546 nm light in a rhodamine part of conjugate was assessed to be $\Phi_\Delta = 0.43 \pm 0.05$ for conjugate ZnPcS–RhB and 0.45 ± 0.05 for ZnPcS–Rh6G. It is known that intact rhodamines have low yields of excited triplet states ($\Phi_T < 0.1$) [23] and near-zero yields of singlet oxygen [23,24]. In full accordance with this was our finding that DPBF does not degrade significantly in DMSO solution of RhB or Rh6G and irradiation with 546 nm light. The values of Φ_Δ for these compounds in DMSO were estimated to be <0.01 (Table 3). It is obvious that efficient formation of singlet oxygen under excitation of conjugates with 546 nm light indicates energy transfer from rhodamine pendants to singlet oxygen generating phthalocyanine part of conjugate.

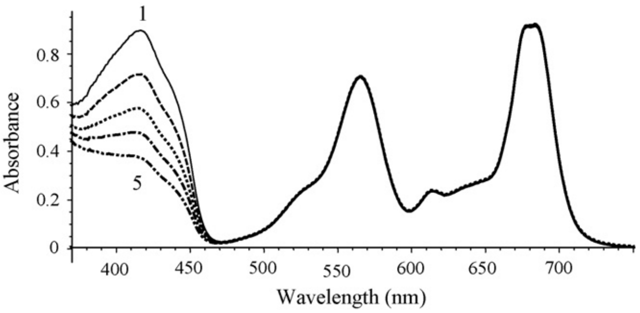


Fig. 6. Spectral changes in the DPBF absorption band during 546 nm-irradiation of its solution in DMSO, containing conjugate ZnPcS–RhB. DPBF: 3×10^{-5} M; ZnPcS–RhB: 5×10^{-6} M.

Table 3
Singlet oxygen quantum yields for zinc phthalocyanine conjugates with rhodamine B and rhodamine 6G (in DMSO)

Sensitizer	Φ_Δ	
	λ_{ex} = 546 nm	λ_{ex} = 680 nm
ZnPcS–RhB	0.43 ± 0.05	0.40 ± 0.05
ZnPcS–Rh6G	0.45 ± 0.05	0.40 ± 0.05
ZnPcS$_4$	–	0.68 [13]
RhB	<0.01	–
Rh6G	<0.01	–
Mixture of ZnPcS$_4$ + Rh6G	<0.01	0.64 ± 0.08

It can be noticed that Φ_Δ values for investigated conjugates both under excitation of rhodamine or phthalocyanine chromophores are lower than Φ_Δ = 0.68 for unbounded ZnPcS$_4$.

3.6. *Photosensitizing properties of conjugates under broadband light excitation*

Fig. 1 shows that absorption of rhodamine–phthalocyanine conjugates covers the visible range fairly well suggesting light-harvesting properties. Efficacy of conjugates under broadband light excitation was tested in the model reactions of sensitized oxidation of 9,10-dimethylanthracene (DMA) and tryptophan.

It is well known that DMA is oxidized by singlet oxygen into endoperoxide, and this process is accompanied by the loss of DMA absorption in the near UV–visible region of spectrum [25]. The increase of this process efficacy may be expected under broadband light excitation and conjugate as sensitizer due to the fact that yields of singlet oxygen formation upon excitation into rhodamine and phthalocyanine parts are summarized.

In our experiments the absorption of DMA in DMSO was found to decline readily under sunlight illumination even without sensitizer because of substrate self-sensitized oxidation. To avoid direct DMA excitation the 420 nm cutoff filter was used. Under these conditions no DMA photodegradation was observed in the absence of sensitizers. In the presence of ZnPcS–Rh6G, ZnPcS$_4$ or mixture of ZnPcS$_4$ with Rh6G the sensitized oxidation of DMA occurred, and respective decrease of DMA absorption at 403 nm maximum is plotted in Fig. 7. It can be noticed that the substrate degradation followed pseudo-first-order kinetics. Sharp decline of the reaction rate after addition of DABCO to the solution is indicative of singlet oxygen participation in the oxidation of DMA. The data on DMA photolysis under sunlight with unconjugated Rh6G are plotted in Fig. 7 also, showing no Rh6G effect on DMA oxidation rate. Photooxidation of DMA in the presence of ZnPcS$_4$ or mixture of ZnPcS$_4$ with Rh6G occurred with negligible difference indicating absence of rhodamine input in singlet oxygen photogeneration by ZnPcS$_4$.

Data in Fig. 7 demonstrate that performance with sensitizer ZnPcS–Rh6G is slightly better than with ZnPcS$_4$. Testing of ZnPcS–RhB have shown no beneficial effect on DMA sensitized oxidation at all. One would therefore conclude that under broadband light excitation the additional energy, received by phthalocyanine part of conjugate from rhodamine fragment, only compensates the decrease of Φ_Δ, found for conjugated zinc phthalocyanine. Hence,

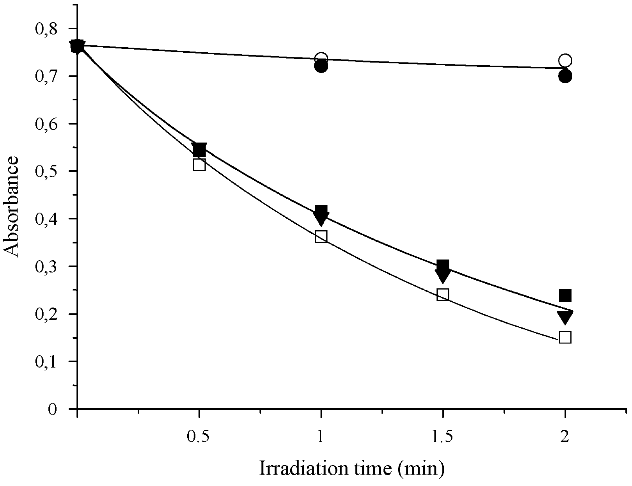


Fig. 7. Photobleaching of DMA (4×10^{-5} M) in DMSO, monitored at 403 nm maximum (○) and in the presence of Rh6G (●), ZnPcS$_4$ (■), ZnPcS–Rh6G (□) and mixture of ZnPcS$_4$ with Rh6G (▼) (under sunlight, $\lambda_{ex} \ge 420$ nm).

substantial increase of DMA photooxydation rate under sunlight excitation with conjugates of phthalocyanines with rhodamines as singlet oxygen sensitizers was not achieved. Experiments with tryptophan gave the same results.

Tryptophan represents a suitable substrate for testing the efficiency of photosensitizing agents since it is efficiently photooxidized by both type I (radical) and type II (singlet oxygen) reaction mechanisms [26,27]. In this section we have tested relative activities of ZnPcS–RhB and unconjugated ZnPcS$_4$ in photosensitization of tryptophan oxidation under broadband artificial light.

As can be observed in Fig. 8, the destruction of tryptophan, photosensitized by ZnPcS–RhB or ZnPcS$_4$, followed zero-order kinetics, and this is consistent with high substrate concentration. We have found that under light with $\lambda_{ex} \ge 600$ nm (excitation of phthalocyanine part only) the tryptophan photooxidation rate is about 50% higher with ZnPcS$_4$ sensitizer than with conjugate ZnPcS–RhB. This finding is in agreement with relative activities of conjugated and unconjugated ZnPcS$_4$ in sensitization of singlet oxygen (Table 3). When the RhB part of conjugate is included into excitation also ($\lambda_{ex} \ge 500$ nm), activity of conjugate is almost as good as that of free ZnPcS$_4$ (Fig. 8).

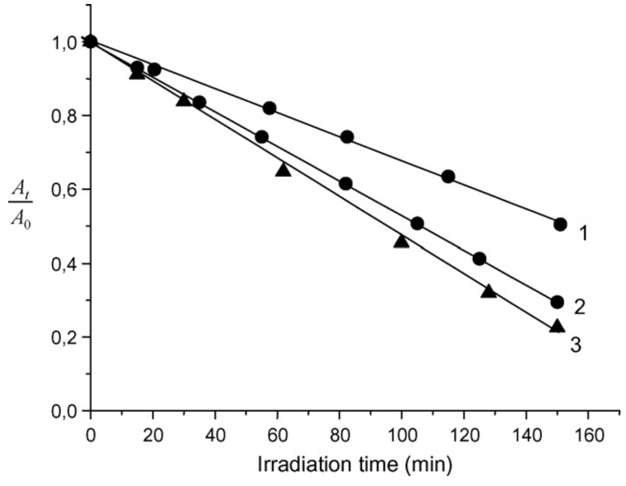


Fig. 8. Change of absorbance at 283 nm maximum for tryptophane in DMSO with irradiation time in the presence of ZnPcS–RhB: $\lambda_{ex} \ge 600_{HM}$ (1), $\lambda_{ex} \ge 500_{HM}$ (2), and in the presence of unconjugated ZnPcS$_4$ ($\lambda_{ex} \ge 500_{HM}$, $\lambda_{ex} \ge 600_{HM}$) (3).

4. Conclusions

New conjugates of Rh6G or RhB with ZnPcS$_4$ were synthesized with aim to evaluate their light-harvesting properties and ability to sensitize singlet oxygen formation. In these conjugates, the rhodamine chromophore is isolated from phthalocyanine macrocycle by amide (Rh6G) or ester (RhB) bonds through ethylene spacers. Notwithstanding 2–4 positive charges in molecule, conjugates are insoluble in aqueous media, so their properties were tested in DMSO.

Photochemical and photophysical measurements have shown that the main result of conjugation is efficient intramolecular energy transfer from rhodamine to phthalocyanine part of molecular system. Though, it would be mentioned that the twofold decrease of photodegradation, fluorescence, singlet oxygen photogeneration quantum yields, reducing so light-harvesting properties of conjugates, has been observed. In this connection it is important to recall that in polychromophoric molecular systems the high probability of intramolecular charge-transfer-mediated radiationless process, that deactivate the excited-state sensitizer, generally arises [4,5,28]. Taking this into account we may conclude that the photoinduced charge transfer between rhodamine and phthalocyanine subunits in conjugate is most likely responsible for quantum yields of photochemical and photophysical processes decrease under conjugation. Obtained herein data are consistent with about 50% of conjugate excitation energy expense in the charge-transfer-mediated deactivation channel; however, this conclusion requires further investigation.

Despite to the fact that spectra of ZnPcS–Rh6G and ZnPcS–RhB cover visible spectral range fairy well, activities of conjugates in sensitization of both DMA and tryptophan oxidation under broadband light excitation appeared to be as large as those of unconjugated ZnPcS$_4$. Hence, additional energy of excitation, received by phthalocyanine part of conjugate from rhodamine one in FRET process, only compensates the decrease of Φ_Δ for conjugated zinc phthalocyanine.

In conclusion, it should be mentioned that phthalocyanine conjugates with donors, having better than rhodamines emission spectra overlap with phthalocyanine absorption, are of interest for improvement of light-harvesting properties of such type conjugates.

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