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Photophysical and Photochemical Properties of the Pyropheophorbide-Perylene-Pyropheophorbide Triad

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Dedicated to Academician I. P. Beletskaya on the occasion of her Anniversary

A covalently-bonded structure (triad PP-PDI-PP) based on pyropheophorbide dye (PP, chlorin e_6 derivative) and an organic non-fullerene acceptor, perylenediimide derivative (PDI), has been obtained. The triad has a pronounced absorption in the red region of the spectrum. Compared to the native dye, the obtained triad shows partial fluorescence quenching, and its singlet oxygen generation efficiency upon red light irradiation decreases by five times. At the same time, this triad, solubilized in water by polyvinylpyrrolidone, generates superoxide anion-radical three times more efficiently than the native dye. The demonstrated results show the promising potential of such perylene–dye structures as type I photosensitizers for photodynamic therapy.

Keywords: Perylene, chlorin, pheophorbide, dyad, mass spectrometry, fluorescence quantum yield, photochemical activity, superoxide generation.

Фотофизические и фотохимические свойства триады пирофеофорбид-перилен-пирофеофорбид

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Получена ковалентно-связанная структура (триада PP-PDI-PP) на основе красителя пирофеофорбида (производного хлорина e_6) и органического нефуллеренового акцептора – производного перилендиимида (PDI). Триада обладает выраженным поглощением в красной области спектра, по сравнению с исходным красителем в полученной триаде происходит частичное тушение флуоресценции и снижение эффективности генерации синглетного кислорода в 5 раз. Однако в это же время данная триада, инкапсулированная в наночастицы поливинилпирролидона, при облучении красным светом генерировала супероксид анион-радикал в три раза эффективнее, чем исходный краситель, что показывает перспективность дальнейшего исследования структур перилен-краситель в качестве фотосенсибилизаторов I типа для фотодинамической терапии.

Ключевые слова: Перилен, хлорин, феофорбид, диада, масс-спектрометрия, квантовый выход флуоресценции, фотохимическая активность, генерация супероксида.

Introduction

In recent years there has been a rise of interest in medical photonics, which is explained by two factors – the high accuracy of optical technologies and the great success in developing nanoscale photonic materials – metal quantum dots and inorganic semiconductors. Despite the potential toxicity of such materials, they have provided significant progress in such areas as photoacoustic and fluorescent diagnostics, photodynamic and photothermal therapy.[1–4]

From this point of view, replacing such structures with non-toxic organic semiconductors looks extremely promising. For example, the use of fullerenes led to the creation of various fullerene-dye dyads that showed pronounced photodynamic activity.[5–7] Such dyads can generate not only singlet oxygen (type II phototoxicity mechanism) but also different radical oxygen species (type I phototoxicity mechanism) due to photoinduced electron transfer.[8] Noteworthy, photosensitizers of the latter type can maintain photodynamic activity even under conditions of oxygen deficiency (hypoxia) due to the formation of highly active free radicals (including non-oxygen radicals) from various cell substrates.[9]

Another promising semiconductor organic material is the class of the so-called "non-fullerene acceptors" – derivatives of perylenediimides, which have been extensively studied in recent years.[10] These compounds have low cytotoxicity and have already been used for the bioimaging of living cells,[11] as photoacoustic agents for tumor diagnostics,[12] and as nanocontainers for the delivery of chemotherapeutic agents.[13]

Perylene derivatives do not have pronounced absorption in the red and NIR regions of the spectrum, which is the most convenient for biomedical applications since living tissues are highly transparent in this region. As for the fullerene-dye structures mentioned above, this problem could be solved by adding a certain donor molecule (with a high absorbance in the desired spectrum region) to the perylene, which could act as an acceptor. In the current work, we have chosen pyropheophobide *a* as a donor whose analogs are being actively studied for use in various fields of biomedicine.[14,15]

Thus, the present work is devoted to the synthesis and study of the photophysical and photochemical properties of a covalently-linked structure based on a perylene derivative and pyropheophobide, which has pronounced absorption in the red region of the spectrum.

Experimental

Chemicals. Perylenedianhydride (PDA), N,N'-dicyclohexylcarbodiimide (DCC), N,N'-dimethyl-4-aminopyridine (DMAP), DPBF (1,3-diphenylisobenzofuran), NADH (nicotinamide adenine dinucleotide), NBT (nitro blue tetrazolium chloride), EDTA (ethylenediaminetetraacetic acid) was purchased from Sigma-Aldrich. All reagents and solvents were used without additional purification unless otherwise noted.

Equipment for chemical characterization. Mass spectra were recorded using an Axima Confidence mass spectrometer (Shimadzu Biotech) with matrix-assisted laser desorption/ionization (laser wavelength 337 nm) and a time-of-flight detector (MALDI-TOF) operating in the reflectron mode. As a matrix trans-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB) was used. ^{1}H NMR spectra were recorded on a Bruker Avance 500 MHz instrument (Bruker, Switzerland). Absorption spectra were recorded on a Cary-60 spectrophotometer (Agilent Technologies, USA), and stationary fluorescence spectra were recorded on a Varian-Eclipse spectrofluorimeter (Agilent Technologies, USA). For electrochemical measurements – working electrode potential was controlled by an Autolab PGSTAT302N potentiostat (Metrohm, Switzerland).

The synthesis of methylpyropheophorbide *a* and pyropheophorbide *a* was carried out according to previously described procedures[16] from methylpheophorbide *a* (MPP). NMR and mass spectra of these dyes coincide with those given in the work.[17] MPP was obtained by extraction from *Spirulina microalgae* with methanol in the presence of sulfuric acid according to the procedure.[18] The MALDI-TOF, UV-Vis, and IR spectra of the MPP dye coincide with those in the work.[19]

Preparation of the native perylene derivative PDI (***1***) (Figure 1). A mixture of 3,4,9,10-perylenetetracarboxylic acid-3,4:9,10-dianhydride (PDA, Sigma-Aldrich) (2 g, 5.1 mmol), 4-aminophenol freshly recrystallized from ethanol (2.8 g, 20.4 mmol), zinc acetate (0.56 g, 5.1 mmol) and imidazole (40 g) was gradually heated with stirring in an inert atmosphere – first at 100 °C for 2 hours, then at 130 °C for 2 more hours, then at 170 °C for 20 hours. After completion of the process, the resulting mixture was allowed to cool to 80 °C and 50 ml of methanol was added. Then the mixture was filtered and washed on the filter with water, 5% hydrochloric acid solution, 2% potassium chloride solution, water. The product was dried at 120 °C. The product yield was 2.5 g (85%). The ^{1}H NMR and IR spectra coincide with those given in the work.[20]

*Triad **3** synthesis*. DCC (66.7 mg, 0.03 mmol) was added to a solution of pyropheophorbide *a* (144 mg, 0.27 mmol) and DMAP (3.6 mg, 0.03 mmol) in dry acetonitrile and stirred for an hour at room temperature, then derivative ***1*** was added to the reaction mass and left to stir overnight at 70 °C. After completion of the reaction the reaction mass was filtered, and the filtrate was evaporated under a vacuum. The dry residue was dissolved in pyridine and purified by gel permeation chromatography on a cross-linked polystyrene (Bio-Beads SX-1, Bio-Rad) column. The product yield was 83 mg (38%). MS (MALDI-TOF) *m/z*: 1607, calculated for $[C_{102}H_{82}N_{10}O_{10}]^+$ 1607 (triad **3**). ^{1}H NMR (500 MHz, DMSO-d_6/TFA-d) δ_H ppm: 9.99 (s, 2H, 10-PPP), 9.58 (s, 2H, 5-PPP), 9.08 (s, 2H, 20-PPP), 8.94 (d *J*=6.47 Hz, 2H, m-Ph), 8.75…8.49 (br.s, 8H, perylene), 8.43 (d *J*=15.79 Hz, 2H, 3” trans), 8.12 (m, 6H, o-Ph + 13’-PPP), 7.50 (d *J*=15.95 Hz, 2H, 3” cis), 5.25 (dd *J*=19.7 Hz, 4H, 13”-PPP), 4.67 (m, 2H, 18-PPP), 4.41 (m, 2H, 17-PPP), 4.03 (m, 4H, 8’-PPP), 3.83 (s, 6H, 12’-PPP), 3.68 (s, 6H, 2’-PPP), 3.50 (s, 6H, 7’-PPP), 3.36 (m, 4H, 17”-PPP), 3.1 (br.m, 4H, 17’-PPP), 1.80 (d *J*=6.76 Hz, 6H, 18’), 1.66 (t *J*=7.65 Hz, 6H, 8”-PPP). UV-Vis (H_2SO_4) λ_{max} (lgε): 418 nm (4.91), 557 nm (4.33), 602 nm (4.42), 680 nm (4.44).

Method of square-wave voltammetry. Cross-sections of glassy carbon (GC) rod (geometric area of 0.95 mm^2) was used as a working electrode. Ag wire immersed into 10 mM Ag^+ + 0.1 M $TBAPF_6$ solution in acetonitrile served as a reference electrode. An auxiliary electrode was Pt foil; its surface area was several tens as large as that of the working electrode. Insertion of the solution's components and electrodes into the cell as well as the implementation of electrochemical measurements were performed with the use of Schlenk line under a slightly excessive argon pressure (~ 20 mbar) over the solution. To record voltammograms, DMSO was used as a solvent; the supporting electrolyte was 0.1 M $TBAPF_6$. The initial potential of the square wave voltammogram for each sample was 0 V.

Photochemical activity tests. The *formation of singlet oxygen* $^1O_2$ was detected by the standard method using a 1,3-diphenylisobenzofuran (DPBF) probe.[21,22] A cuvette with a solution of the test compound and DPBF (50 μM) in pyridine was illuminated on a setup based on a Specord M-40 spectrophotometer equipped with an interface for computer recording of spectra, a temperature-controlled cell compartment with integrated LEDs (λ = 660 nm, the light flux power = 5 mW/cm^2), and an Arduino-based control unit. Each sample was irradiated for 2 seconds, after which the absorption spectrum was recorded (350–700 nm); in total, there were 12 irradiation cycles for each sample. The effectiveness of $^1O_2$ generation was estimated from the decrease in the absorption peak of the DPBF probe at 420 nm; for the relative $^1O_2$ quantum yield calculation, zinc phthalocyanine was used as a reference (Φ_Δ = 40% in DMSO).[23]

The detection of the *superoxide anion-radical formation* was performed by the standard formazan method[24] based on the reaction of a nitro blue tetrazolium probe (NBT) with superoxide in an aqueous solution. For the sample irradiation, the setup described above was used with the modified parameters (λ = 660 nm, light flux power = 70 mW/cm^2, 8 irradiation cycles of 30 s each). The studied compounds were encapsulated in the polyvinylpyrrolidone (PVP) nanoparticles according to the method.[17] The compound under study was dissolved in pyridine, and a solution of polyvinylpyrrolidone (PVP, Mr = 45000–55000) in pyridine was added in a dye/PVP molar ratio of 1/10. The solvent was removed on a rotary evaporator until a dry film was formed. Next, the resulting film was dissolved in 3–5 mL of water using an ultrasonic bath, and then the water was also removed on a rotary evaporator to completely remove traces of pyridine and dissolved in a pre-calculated volume of water to obtain a final concentration of the compound under study of 0.2 mM. The size of the obtained NPs was estimated by the dynamic light scattering method on a Photocor Compact device (Photocor LTD., Moscow, Russia). The intensity of superoxide generation was estimated from the formazan absorption peak increase at 560 nm. All results of photochemical activity measurements are presented in the form of "mean value ± standard error" based on the results of at least three different experiments.

Results and Discussion

Triad **3** was synthesized by standard ester formation method using DCC according to the scheme shown in Figure 1.

Derivatives of perylenetetracarboxylic acid diimide are dyes with absorption maxima in the region of 490 and 530 nm with extinction coefficients of about 44000 M^{-1}cm^{-1} and 71000 M^{-1}cm^{-1}, respectively (log $\varepsilon \approx$ 4.6 and 4.8).[25] The native dye methylpheophorbide (MPP) has absorption maxima typical of chlorin e_6 derivatives – the Soret peak in the region of 412 nm (log $\varepsilon \approx$ 4.6) and the Q band peak at 666 nm (log $\varepsilon \approx$ 4.55) (Figure 2 and Table 1).

For the obtained triad, the extinction coefficient decrease is observed with a significant broadening of the absorption peaks of the Soret and Q bands compared to the native MPP dye. A similar pattern is observed for the absorption bands of the perylene moiety of the triad (Figure 2 and Table 1). Bathochromic shifts are also observed for both the Soret and Q bands peaks of the MPP moiety (Figure 2 and Table 1). We believe that the observed pattern is associated with a high degree of aggregation of triad molecules in pyridine solution.

To test this assumption, we compared the absorption spectra of the triad in different solvents. Thus, in pyridine and chloroform, the absorption spectrum of the triad has a pronounced pattern of strong aggregation; however, the addition of a small amount of trifluoroacetic acid to a solution of the triad in chloroform leads to a significant increase in absorption in the characteristic maxima of all peaks (curves 1 and 3 in Figure 3). These data are also confirmed by ^{1}H NMR spectra, which also show significant aggregation. However, the solubility of the triad in all solvents used (DMSO, chloroform, pyridine) is relatively high ($C_{PP\text{-}PDI\text{-}PP}$ >2 mM). It should also be noted that the triad showed the highest solubility in sulfuric acid (Figures 2 and 3). We attribute these effects to a decrease in the degree of triad aggregation due to the protonation of intracyclic nitrogen atoms in the MPP macrocycle moiety.

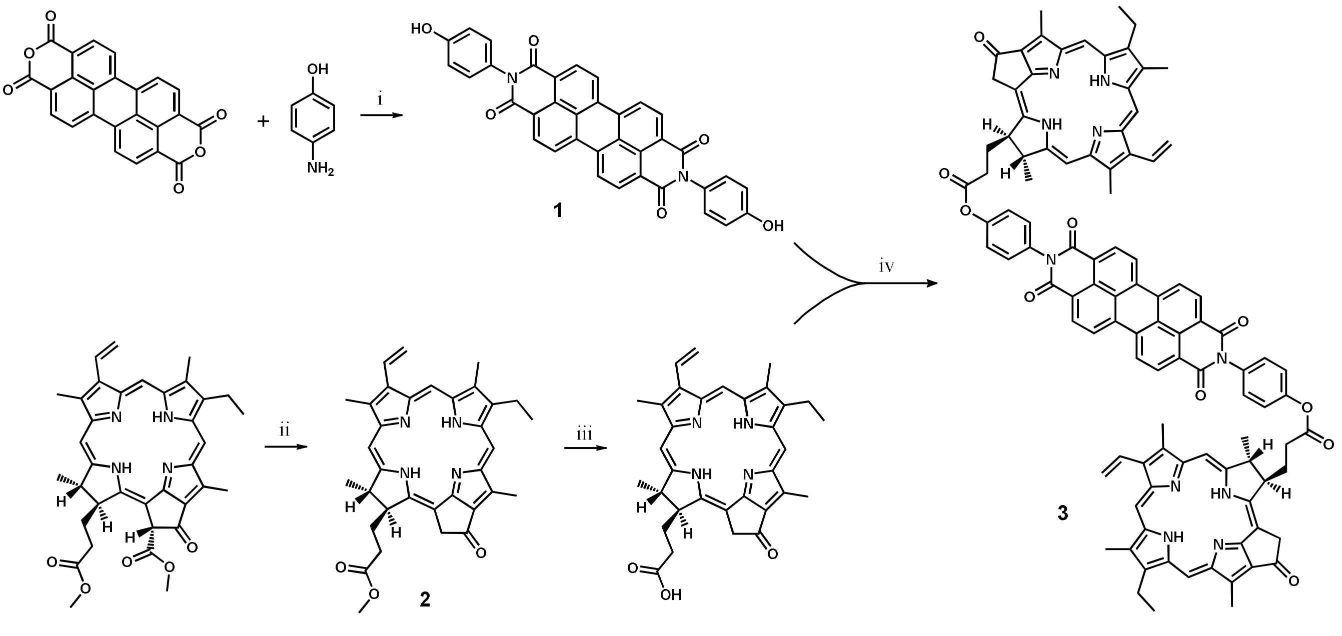

Figure 1. Structural formulas of the native compounds – perylene derivative PDI (**1**), dye MPP (**2**) and the scheme of triad PP-PDI-PP (**3**) synthesis, where: i – molten imidazole, 150 °C; ii – collidine, boiling; iii – 1: acetone, aqueous NaOH solution, boiling, 2: AcOH; iv – DCC, DMAP, acetonitrile, room temperature.

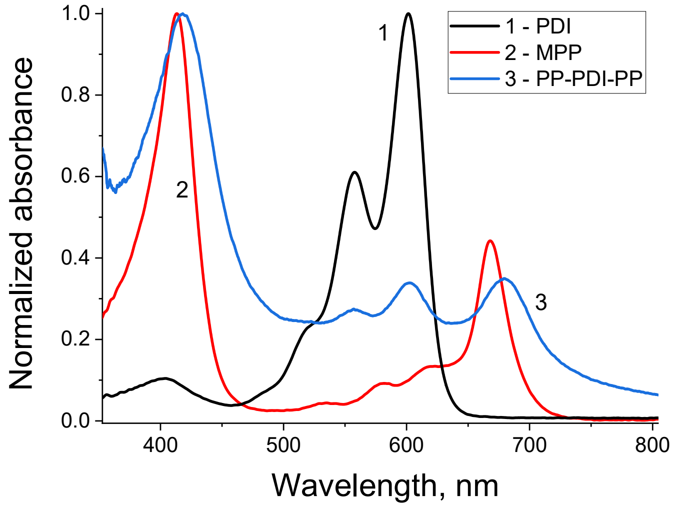

Figure 2. Normalized absorbance spectra of PDI (1), MPP (2), PP-PDI-PP (3) in sulfuric acid.

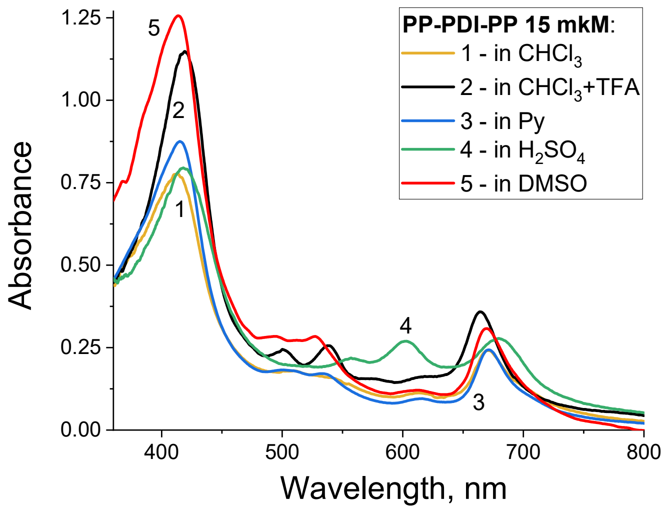

Figure 3. Absorbance spectra of triad **3** PP-PDI-PP (15 μM) in chloroform (1) and in a mixture of chloroform with trifluoroacetic acid (2), in pyridine (3), in sulfuric acid (4), in DMSO (5).

Table 1. Photophysical and photochemical properties of triad **3** and native compounds.

		PDI (**1**)	MPP (**2**)	PP-PDI-PP (**3**)
1	Absorbance maximum (λ, nm) and the decimal logarithm of the extinction coefficient ε at λ_{max} (lg [ε $M^{-1}cm^{-1}$]) in H_2SO_4	558 (4.98) 601 (3.99)	413 (5.09) 668 (4.73)	418 (4.91) 557 (4.33) 602 (4.42) 680 (4.44)
2	Absorbance maximum (λ, nm) and the decimal logarithm of the extinction coefficient ε at λ_{max} (lg [ε $M^{-1}cm^{-1}$]) in pyridine	494 (4.58), 530 (4.79)	412 (4.86) 666 (4.55)	415 (4.93) 501 (4.25) 532 (4.22) 671 (4.38)
3	Fluorescence λ_{max}, nm	540, 580	672	540, 580, 675
4	Fluorescence quantum yield* $\Phi^{(\lambda ex,\ nm)}$, %	1.0^{490}	42^{630}	0.5^{490} (λ_{max} 540, 580 nm) 25.4^{630} (λ_{max} 675 nm)
5	Singlet oxygen quantum yield Φ_{Δ}^{**}, %	<0.3	20.7	4.1
6	Hydrodynamic radius (R_h) of nanoparticles with PVP, nm	67±30	103±71	65±56
7	Relative superoxide radical-anion generation efficiency in water	0.2	1	3.1
8	First reduction potential *vs* Fc/Fc$^+$, V	-0.90	-1.25	--
9	LUMO energy, eV	-4.2	-3.85	--
10	First oxidation potential *vs* Fc/Fc$^+$, V	--	0.47	--
11	HOMO energy, eV	-6.55***	-5.57	--

*The fluorescence quantum yield of triad **3** PP-PDI-PP was calculated relative to MPP (Φ_{fl} = 42% in dichloromethane).[29] The fluorescence quantum yield of the perylene derivative PDI **1** was calculated relative to eosin Y (Φ_{fl} = 67% in ethanol).[30]

**Singlet oxygen quantum yield was calculated relative to zinc phthalocyanine (Φ_{Δ} = 40% in DMSO).[23]

***The HOMO energy for the PDI derivative (**1**) was determined from the phosphorescence spectra.[28]

Absorption and fluorescence spectra of compounds under study were measured in pyridine unless otherwise indicated. Redox potentials (lines 8 and 10) were measured in DMSO.

The triad has a pronounced fluorescence signal from both moieties – the perylene (signal in the region of 540–580 nm) and pyropheophorbide (signal in the ~670 nm region, Figure 4 and Table 1). It is interesting to note that for the perylene moiety, there is no shift of the fluorescence maxima, while for the pyropheophorbide moiety, a weak bathochromic shift of its maximum from 672 to 675 nm is observed (Figure 4 and Table 1). These effects indicate a weak influence of dye moieties in the triad on each other.

At the same time, the fluorescence of the MPP moieties in the triad is weakly quenched – their quantum yield is reduced by a factor of 1.7 compared to the native MPP dye (Table 1). The observed quenching can be associated both with the effect of the perylene moiety on the MPP fragments linked with it and with the aggregation of the molecules of the triad itself in the solution. In the first case, this quenching can occur due to the mechanism of photoinduced electron transfer from the photoexcited

MPP dye to the perylene moiety of the triad. To evaluate the possibility of this transfer, we analyzed the energies of the HOMO and LUMO levels of the native derivatives by the electrochemical method.

The MPP voltammogram shows an oxidation peak at 0.47 V relative to Fc/Fc$^+$, and three reduction peaks at –1.25, –1.44, and –1.72 V relative to Fc/Fc$^+$ (Figure 5 and Table 1). Perylene derivative **1** exhibits two reduction peaks at –0.90 and –1.12 V relative to Fc/Fc$^+$ (Figure 5 and Table 1). Taking into account the work function of the Fc/Fc$^+$ pair of 5.1 eV[26] relative to the vacuum, we calculated the HOMO and LUMO energy levels (Table 1). As can be seen from the obtained values, the energy gap between the LUMO orbitals of MPP and perylene derivative **1** is 0.35 eV, and the energy of the charge transfer state (CTS) can be estimated ~1.37 eV relative to the ground state, which is close to the CTS energy calculated in[27] for a porphyrin-fullerene dyad, and also close to the energy of the triplet level of the pheophorbide *a* (structurally similar to pyropheophorbide), determined from the phosphorescence spectra (~1.33 eV).[28] Thus, the formation of CTS in triad **3** seems to be energetically possible, and in polar media it may be able to compete with the population of the excited triplet level of pyropheophorbide.

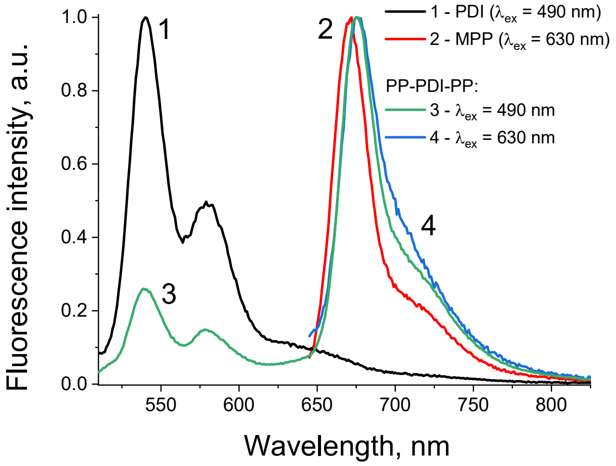

Figure 4. Fluorescence spectra of the native perylene derivative PDI (**1**), MPP (**2**), and triad ***3*** in pyridine upon excitation at 490 nm (3) and 630 nm (4).

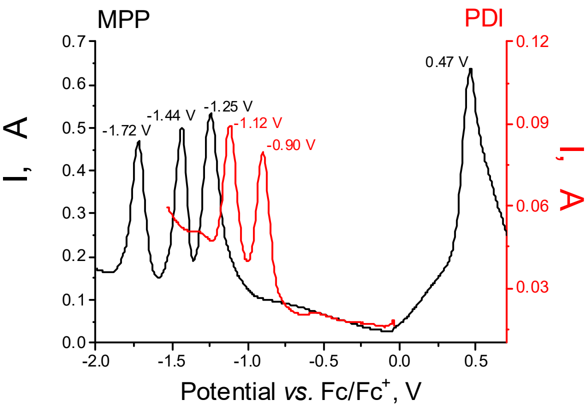

Figure 5. Square wave voltammogram of the native compounds MPP **2** and PDI **1** in DMSO.

The analysis of the reactive oxygen species generation showed that the perylene derivative **1** practically does not generate singlet oxygen in a pyridine solution, while the native dye MPP generates it rather efficiently – the value of Φ_Δ for MPP is 20.7% (Figure 6A and Table 1). The quantum yield of singlet oxygen for triad **3** is reduced by more than 5 times compared to MPP (Figure 6A and Table 1). As in the case of fluorescence quenching, the observed effect can be associated with two factors: the aggregation of triad molecules in solution, which can reduce the efficiency of $^1O_2$ photogeneration, and the interaction of MPP and perylene moieties of the triad and activation of photoinduced electron transfer.

To evaluate the efficiency of the superoxide anion-radical generation in water, we created water-soluble forms of the compounds under study by encapsulating them into nanoparticles (NP) with polyvinylpyrrolidone according to the procedure previously used for hydrophobic fullerene-chlorine dyads.[17] The obtained NPs had a characteristic size of 130–200 nm (R_h = 65–100 nm, Table 1). NPs of the native dye MPP showed a pronounced ability to generate superoxide when irradiated with red light, but the activity of triad **3** exceeds the activity of MPP by 3.1 times (Figure 6B and Table 1). We believe that this enhancement could be explained by the activation of the photoinduced electron transfer mechanism, which shows the promising potential of such structures as type I photosensitizers for photodynamic therapy.

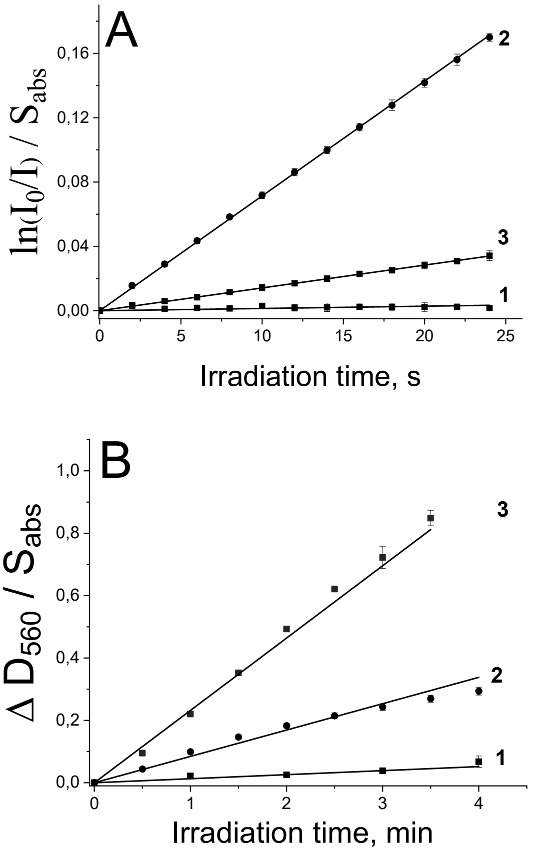

Figure 6. Generation of singlet oxygen in pyridine (A) and superoxide anion-radical in water (B) under red light irradiation (λ = 660 nm): native compounds PDI (1), MPP (2) and triad PP-PDI-PP (3).

Conclusions

We have obtained a covalently-bonded structure based on pyropheophorbide dye and an organic non-fullerene acceptor, a perylenediimide derivative. Compared to the native pyropheophorbide dye, the resulting triad exhibits partial quenching of fluorescence and a significant decrease in the ability to generate singlet oxygen. At the same time, this triad showed a threefold increase in the superoxide anion-radical generation ability compared to the native dye. The obtained results indicate activation of the photoinduced electron transfer from the excited pyropheophorbide moiety to the perylene in the triad. This makes the obtained triad worthy of attention in further developing compounds based on donor-acceptor pairs as type I photosensitizers for photodynamic therapy.

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