

Synthesis and photophysicochemical studies of non-metal 2,3,9,10,16,17,23,24-octacarboxyphthalocyanine

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> ABSTRACT: A new method of preparation and the properties (solubility, aggregation, spectralluminescent properties, singlet oxygen and photobleaching quantum yields) of non-metal 2,3,9,10,16,17,23,24-octacarboxyphthalocyanine are reported. The influence of ionization state on photophysicochemical properties of this dye is also presented.

> KEYWORDS: non-metal phthalocyanine, acid-base equilibrium, fluorescence, singlet oxygen, photostability.

INTRODUCTION

Phthalocyanines substituted with carboxylic groups are at present the object of wide investigations [1-3]. They represent interest, especially in form of their watersoluble alkali salts, as photosensitizers for photodynamic therapy [4, 5], dye-sensitized solar cells [6-8], catalysts of different reactions, including of biomedical interest [9], and so on. For example, the water-soluble sodium salt of cobalt 2,3,9,10,16,17,23,24-octacarboxyphthalocyanine is currently under clinical trials for catalytic therapy of cancer [9]. The most known, to date, in this series are 2,9(10),16(17),23(24)-tetra- and especially highly symmetric 2,3,9,10,16,17,23,24-octasubstituted derivatives. The properties of the parent non-metal 2,3,9,10,16,17,23,24-octacarboxyphthalocyanine $(H_2Pc(COOH)_8)$ 1 have not been studied in detail, however. Meanwhile, this compound can be used as luminophor, ligand for different water-soluble phthalocyanine metal complexes, for example in analytical chemistry, for conjugation with metal oxide surfaces, e.g. titanium dioxide, in construction of solar

cells, as starting compound for preparation of various functional derivatives, e.g. conjugates with aminoacids, peptides or carbohydrates and so on. In this paper, we describe new synthetic approach to H₂Pc(COOH)₈ and the photophysicochemical properties of this compound. $H_2Pc(COOH)_8$ possesses two kinds of acidic hydrogen atoms — in carboxylic groups and in the center of macroring. The influence of their ionization upon properties of non-metal octacarboxyphthalocyanine is reported.

RESULTS AND DISCUSSION

It is well-known that the most common way to prepare phthalocyanines is the tetramerization phthalonitriles. According the literature of to $H_2Pc(COOH)_8$ can be prepared with moderate yield by condensation of the 1,2,4,5-tetracyanobenzene in the presence of lithium propylate with subsequent hydrolysis of the cyano groups [10]. It should be noted, however, that the cyclotetramerization reaction of the 1,2,4,5-tetracyanobenzene is accompanied by the formation of oligomeric and polymeric phthalocyaninebased byproducts. In order to avoid their formation, we used as starting phthalogen the compound with one dinitrile group in its molecule — 4,5-bis(ethoxycarbonyl)

⁶SPP full member in good standing

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Scheme 1. Synthetic route to 4,5-bis(ethoxycarbonyl)phthalonitrile 7

0.70

0.65

phthalonitrile 7 [11a, and 11b], which was synthesized by new efficient pathway in several steps from pyromellitic dianhydride 2 (Scheme 1).

Esterification of pyromellitic dianhydride 2 with triethyl orthoformate and subsequent partial hydrolysis were carried out according to the procedure described in [12]. It is wellknown that the esters of ortho-dicarboxylic acids are rather inert, so we decided to apply to the prepared 2,4,5-triethyl pyromellitate 4 common scheme of obtaining а phthalonitriles via phthalimide and phthalamide intermediates. 2,4,5-triethyl pyromellitate 4 was fused with slight excess of urea to form 4,5-bis(ethoxycarbonyl)

phthalimide 5 with yield up to 90%. Then phthalimide 5 was converted to 4,5-bis(ethoxycarbonyl)phthalamide 6 by the reaction with concentrated ammonia also with very high yield. It is noteworthy, that opening of the imide ring with ammonia takes only one or two minutes. During this time phthalimide 5 completely dissolves in concentrated ammonia and in a few seconds the precipitate of phthalamide 6 quickly forms. Phthalamide 6 was dehydrated with phosphorus oxychloride in DMF to form 4,5-bis(ethoxycarbonyl) phthalonitrile 7 with yield from 75% to 85%. Also some amount of phthalimide 5 was isolated as a by-product. Phthalonitrile 7 readily gave non-metal phthalocyanine in standard conditions (hexyl alcohol, DBU), however, the elemental analysis showed that it was not expected individual 2,3,9,10,16,17,23,24-octa (ethoxycarbonyl)phthalocyanine but the mixture of esters with both ethoxycarbonyl- and hexoxycarbonyl - H₂Pc(COOEt)_{8-x}(COOHx)_x 8. So, the groups partial transesterification proceeds along with the tetramerization reaction. The resulting mixture of esters 8 was hydrolyzed according to the procedure for 2,3,9,10,16,17,23,24-octacyanophthalocyanine [10] in 15% solution of KOH in triethylene glycol at 135 °C with the exception of reaction time, which in our case was 3 hours instead of 4 days. Prepared $H_2Pc(COOH)_8$



was characterized by elemental analysis, IR spectroscopy (Fig. 1) and MALDI-TOF analysis.

400

 $H_2Pc(COOH)_8$ is soluble in DMSO and displays in this solvent absorption spectrum with a splitting in the Q-band which is consistent with D_{2h} symmetry. Distinct splitting and vibrational structure of Q-band evidence monomer form of $H_2Pc(COOH)_8$ in DMSO (Fig. 2). Upon excitation at 670 nm, $H_2Pc(COOH)_8$ in DMSO exhibits fluorescence with a single maximum at 712 nm (Fig. 2) and quantum yield of 0.16. The emission spectrum for $H_2Pc(COOH)_8$ is not splitted, since metal free Pcs are known to fluoresce with only one main peak which has been assigned as the 0–0 transition of the fluorescence [13, 14].

The influence of pH upon $H_2Pc(COOH)_8$ spectra and aggregation in aqueous solutions was described in [15] and confirmed in the present study. In water, unionized $H_2Pc(COOH)_8$ has limited solubility and aggregation behavior. For many phthalocyanines, aggregation occurs readily in aqueous solutions. Two main aggregate species have been identified as J and H aggregates with J-aggregates marked by a red-shift in the monomer peak due to head-to-tail aggregation, while H-aggregates are marked by a blue shift caused by face-to-face aggregation [16, 17]. The absorption spectrum for $H_2Pc(COOH)_8$ in



Fig. 2. Normalized absorption spectrum in distilled water (1) and absorption (2) and emission (3) spectra in DMSO for $H_2Pc(COOH)_8$

aqueous solution exhibits unresolved broad band with a blue shift (Fig. 2) indicative of H-aggregate formation. It is assumed that in H₂Pc(COOH)₈ association besides the van der Waals (π - π) interactions between Pc macrocycles the hydrogen bonding between carboxyl groups of the adjacent molecules ought to be taken into account [15]. Aqueous solutions of H₂Pc(COOH)₈ aggregates possess negligible fluorescence.

Titration of $H_2Pc(COOH)_8$ aggregates in H_2O by NaOH gives reversible two-step spectral change — in 5–7 and 10–11.5 pH intervals, with isosbestic points as shown in Figs 3a and 4a, accordingly. As in [15], the first step of spectral changes upon NaOH addition (Fig. 3a) was assigned to shift from $H_2Pc(COOH)_8$ aggregates to monomeric octacarboxylate species $H_2Pc(COO^-)_8Na^+_8$. Splitting of Q-band confirms the freebase $H_2Pc(COO^-)_8Na^+_8$ structure at pH 6–10.

The pH dependence of the $H_2Pc(COO^{-})_8Na^{+}_8$ absorbance at wavelength 707 nm is shown on Fig. 3a (insert). It is obvious that pH increase leads to progressive ionization of carboxyl groups in H₂Pc(COOH)₈ and dye disaggregation due to the electrostatic repulsion between molecules and better solubility of a carboxylate form. The effect of number of ionized groups on macrocycle periphery upon aggregation of non-metal phthalocyanines in water has not been studied. However, it is known that for cationic zinc phthalocyanines above six charged groups per molecule are needed for dye monomerization [18]. Thus, it may be assumed that about up to four carboxyl groups deprotonation will not result in H₂Pc(COOH)₈ disaggregation, and the apparent pKa value of 6.1, derived from the plot in Fig. 3a insert, may be assigned to ionization of above six to seven carboxyl groups per molecule.

The equilibrium shift from $H_2Pc(COOH)_8$ aggregates to monomeric H₂Pc(COO⁻)₈Na⁺₈ results in appearance of fluorescence with a maximum at 717 nm. The fluorescence appearance along with dye disaggregation is consistent with only the monomeric species being fluorescent. The maximum of fluorescence for $H_2Pc(COO^{-})_8Na^{+}_8$ in $H_2O:DMSO = 1:9 v/v$ mixture is about 10 nm red-shifted in comparison to that for H₂Pc(COOH)₈ (fluorescence maxima for carboxylate and carboxy forms are 724 and 713 nm, correspondingly). The measured fluorescence quantum yield, $\Phi_{\rm F}$, for H₂Pc(COO⁻)₈Na⁺₈ form at pH 7–10 is 0.06 (Table 1). This value is less than $\Phi_{\rm F} = 0.16$ for $H_2Pc(COOH)_8$ in DMSO. The measured fluorescence intensity at 717 nm maximum as a function of pH yields a pKa 0.61 (Fig. 3b, insert), which coincides with the apparent pKa value obtained from the spectral data so far as both spectral and fluorescent pH-changes are due to the same process — phthalocyanine disaggregation. The influence of pH on absorbance intensity of $H_2Pc(COOH)_8$ on this step is close to that, observed for



Fig. 3. Absorption (a) and fluorescence (b) spectral changes in the course of titration of $H_2Pc(COOH)_8$ in water with HCl and NaOH in pH range 3–9. Insert: (a) absorbance change at 707 nm; (b) fluorescence intensity change at 717 nm

Form	Medium	Absorption λ_{max} , nm (log ϵ)	Fluorescence		$\Phi_{\scriptscriptstyle{\Delta}}$	$\Phi_{ m p}$
			λ_{max} , nm	$\Phi_{\rm F}$	_	
H ₂ Pc(COOH) ₈	DMSO	674 (5.09); 703 (5.14)	712	0.16	0.12 ± 0.01	1.6×10^{-5}
H ₂ Pc(COO ⁻) ₈ Na ⁺ ₈	pH 7.4 (Buffer)	675 (5.06); 707 (5.1)	717	0.06	0.1 ± 0.02	0.7×10^{-4}
H ₂ Pc(COO ⁻) ₈ Na ⁺ ₈	pH 9.18 (Buffer)	675 (5.04); 707 (5.08)	717	0.06	0.1 ± 0.03	1.2×10^{-4}
Pc ²⁻ (COO ⁻) ₈ Na ⁺ ₁₀	pH 12 (NaOH)	690 (5.3)	703	0.10	~ 0.4	2.5×10^{-3}

Table 1. Spectral and photochemical properties of metal-free octacarboxyphthalocyanine in differently ionized forms



Fig. 4. Absorption (a) and fluorescence (b) spectral changes in the course of titration of $H_2Pc(COOH)_8$ in water with NaOH in 9–12 pH range. Insert: (a) absorbance changes at 690 nm; (b) fluorescence intensity changes at 703 nm

zinc octacarboxyphthalocyanine [19], which confirms its assignment to carboxy-groups ionization.

The presence of isosbestic points on the second step of spectral changes (Fig. 4a) is taken to indicate the existence of equilibrium between H₂Pc(COO⁻)₈Na⁺₈ and inner deprotonated species, also assumed for this spectra transformation in [15]. The splitted Q-band of H₂Pc(COO⁻)₈Na⁺₈ upon pH increase from 9.18 to 11.8 transforms to single band with 690 nm maximum. A plot of absorbance at 690 nm maximum vs pH (Fig. 4a, insert) gives single wave and apparent pK = 10.83. This value perfectly falls in the range 9.6-11.23 of known experimental and calculated values of pK for the deprotonation of internal N-H groups in metal-free phthalocyanines [20 and references therein]. Under further pH increase up to 13.5 the spectrum remains unchanged. Hence, it may be assumed that in pH interval from 9.18 to 11.8, H₂Pc(COO⁻)₈Na⁺₈ loses two inner protons to give Pc²⁻(COO⁻)₈Na⁺₁₀ species. Properties of $Pc^{2-}(COO^{-})_8Na^{+}_{10}$ were investigated at pH 12.

The fluorescence change, respective to step two, is shown on Fig. 4b. The observed pH-dependence of

fluorescence evidences the decrease of $H_2Pc(COO^-)_8Na^+_8$ emission at 717 nm and concomitant emergence of fluorescence at 703 nm. Again, we assume $Pc^{2-}(COO^-)_8Na^+_{10}$ is responsible for 703 nm fluorescence, which has 0.1 quantum yield and is 14 nm blue-shifted relative to fluorescence of $H_2Pc(COO^-)_8Na^+_8$. The pH-dependence of fluorescence intensity at 703 nm gives wave at pH 11.15. This pH is higher than observed for absorption spectra changes (wave at pH 10.83) and implies that $H_2Pc(COO^-)_8Na^+_8$ in singlet excited state is weaker acid than in ground state.

The absorption and fluorescence emission parameters for three forms (Scheme 2) — $H_2Pc(COOH)_8$ in DMSO, $H_2Pc(COO^{-})_8Na_8^{+}$ in two phosphate buffer solutions (with pH 7.4 and 9.18, for comparison) and $Pc^{2-}(COO^{-})_8Na_{10}^{+}$ in water at pH 12 — are summerized in Table 1. It may be seen that absorption characteristics of $H_2Pc(COOH)_8$ in DMSO and $H_2Pc(COO^{-})_8Na_8^{+}$ in phosphate buffer are similar. However, it was found that in the $H_2O:DMSO =$ 1:9 v/v mixture the ionization of carboxy groups results in about 13 nm bathochromic shift of Q-band (λ_{max} 678 and 704 nm for $H_2Pc(COOH)_8$, 693 and 715 nm for



Scheme 2. Ionization of metal-free octacarboxyphthalocyanine

 $H_2Pc(COO^-)_8Na^+_8)$. Fluorescence quantum yields for three forms of non-metal octacarboxyphthalocyanine under consideration are in 0.06–0.16 range, values typical of non-metalated phthalocyanines [21]. Stokes shifts are 10–20 nm.

The important photophysical parameter that determines the photosensitizing ability of a compound is the singlet oxygen quantum yield (Φ_{Λ}) . Φ_{Λ} for H₂Pc(COOH)₈ was obtained in DMSO using the DPBF chemical trapping method. The measured value of Φ_{Λ} for acid H₂Pc(COOH)₈ is 0.12. Determination of Φ_{Δ} for deprotonated $H_2Pc(COO^-)_8Na^+_8$ and Pc²⁻(COO⁻)₈Na⁺₁₀ species was carried out in aqueous basic media with water-soluble tetrasodium anthracene-9,10-bis-methylmalonate (ADMA) as singlet oxygen trap. Increased photodegradation of compound under investigation in basic conditions resulted in decrease of precision of measurements, so Φ_{Δ} were found to be 0.1 ± 0.02 and 0.1 ± 0.03 for H₂Pc(COO⁻)₈Na⁺₈ in phosphate buffer solutions with pH 7.4 and 9.18, correspondingly, and estimated value about 0.4 was obtained for $Pc^{2}(COO)_{8}Na_{10}^{+}$. So, inner deprotonation results in significant Φ_{Λ} increase, most probably due to decrease of intermolecular interactions between dye molecules. In general, $H_2Pc(COOH)_8$ has moderate singlet oxygen yields, typical of non-metalated Pcs.

Photostability of the sensitizers is of utmost importance for their application. The collapse of the absorption spectra without any distortion of the shape was found for H₂Pc(COOH)₈ under irradiation in all media employed. Since no distinctive new absorption bands appear in the 330-750 nm region, it is logical to assume photodegradation of the phthalocyanine chromophore. The photobleaching quantum yield $\Phi_{\rm p}$ for $H_2Pc(COOH)_8$ is 1.6×10^{-5} in aerated DMSO (Table 1), demonstrating relatively high photostability. Species $H_2Pc(COO^{-})_8Na^{+}_8$ showed about one order of magnitude less photostability, with $\Phi_p 0.7 \times 10^{-4}$ and 1.2×10^{-4} at pH 7.4 and 9.18, respectively. These data exhibit a trend to Φ_{p} increase along with solution alkalinity. Further ionization to $Pc^{2-}(COO^{-})_8Na^{+}_{10}$ gives sequential increase of photodegradation with Φ_p of 2.5 × 10⁻³ at pH 12. Obtained results are in agreement with augmentation

of phthalocyanine derivatives photodegradation by the negatively charged groups, noted in our previous investigations [22].

EXPERIMENTAL

Materials and equipment

The reagents and solvents of HPLC grade were purchased from Sigma-Aldrich, Merck, Fluka or Alfa Aesar and used as received, unless otherwise stated. Zinc phthalocyanine (PcZn) was from the Organic Intermediates and Dyes Institute, Russian Federation as trade reagent. Tetrasodium anthracene-9,10-bismethylmalonate (ADMA) was prepared according to [23]. Basic aqueous and phosphate buffer solutions of H₂Pc(COOH)₈ were prepared in deionized water.

¹H NMR spectra were run on Inova 500 MHz NMR (Varian) spectrometer. Mass spectra were obtained under GC/MS conditions on Varian 3800 GC with Varian 2200 ion trap mass spectrometer (EI 70 eV). The MALDI-TOF MS spectrum was measured with a Bruker Ultraflex instrument. IR spectra were recorded with Monitoring 1201 FT-IR spectrometer (KBr pellets). Elemental analyses were carried out on a Vario Micro Cube CHN Analyzer. Electronic absorption spectra were recorded with Hewlett Packard 8453 spectrophotometer, fluorescence excitation and emission spectra were recorded with Cary Eclipse spectrofluorimeter. The monochromatic light intensity was measured with a calibrated Si photodiode (Thorlabs).

Synthesis

2,4,5-triethyl pyromellitate 4 was synthesized according to the reported procedure [12].

4,5-bis(ethoxycarbonyl)phthalimide 5. 2,4,5-triethyl pyromellitate **4** (1.0 g, 2.96 mmol) and urea (0.21 g, 3.55 mmol) were heated with stirring to 175–180 °C and kept at that temperature for 20 min. Then the temperature was raised up to 200–205 °C for 5 mins. After this, the reaction mixture was cooled, refluxed with chloroform and filtered. The precipitate was washed with hot

chloroform. The filtrates were collected and the solvent was evaporated in vacuum. The resulting residue was recrystallized from toluene to yield 0.77 g (90%) of phthalimide **5** as white crystals with mp 155–156 °C. IR (KBr): v, cm⁻¹ 3465, 3275, 2987, 1790, 1730, 1600. ¹H NMR (CDCl₃; Me₄Si): $\delta_{\rm H}$, ppm 8.20 (2H, s, Ar*H*), 8.14 (1H, s, N*H*), 4.44 (4H, q, *J* = 7.0 Hz, C*H*₂), 1.41 (6H, t, *J* = 7.5 Hz, C*H*₃). GC/MS: *m/z* 292.20 [M + H]⁺. Calcd. for C₁₄H₁₃NO₆ 291.26. Anal. calcd. for C₁₄H₁₃NO₆: C, 57.73; H, 4.50; N, 4.81. Found: C, 57.57; H, 4.56; N, 4.71.

4,5-bis(ethoxycarbonyl)phthalamide 6. Powdered 4,5-bis(ethoxycarbonyl)phthalimide **5** (1.0 g, 3.44 mmol) was added with stirring to 10 mL of 25% ammonia. Within one minute phthalimide **5** completely dissolved and white precipitate formed, which was filtered, washed with a small amount of water and dried in the air to yield 0.94 g (89%) of phthalamide **6** with mp 197–198 °C . IR (KBr): v, cm⁻¹ 3401, 3355, 3187, 2983, 1729, 1663, 1618. ¹H NMR (DMSO-d₆; Me₄Si): $\delta_{\rm H}$, ppm 7.95 (2H, s, NH₂), 7.76 (2H, s, ArH), 7.56 (2H, s, NH₂), 4.30 (4H, q, *J* = 7.0 Hz, CH₂), 1.29 (6H, t, *J* = 7.0 Hz, CH₃). Anal. calcd. for C₁₄H₁₆N₂O₆: C, 54.55; H, 5.23; N, 9.09. Found: C, 54.32; H, 5.27; N, 8.81.

7. 4,5-bis(ethoxycarbonyl)phthalonitrile Phthalamide 6 (1.0 g, 3.24 mmol) was added with stirring to 5 mL of fresh-distilled DMF and the mixture was stirred for 15 min until a homogeneous suspension formed. Then the reaction mass was cooled to 0 °C and phosphorus oxychloride (0.6 mL, 6.50 mmol) was added dropwise with stirring within 2 h. After that the reaction mixture was allowed to warm to room temperature and stirring was continued for 30 min. Then the reaction mixture was poured on ice, the precipitate was filtered, washed with cold water and dried to yield 0.72 g (82%) phthalonitrile 7 as white crystals with mp 121-122 °C. IR (KBr): v, cm⁻¹ 2959, 2239, 1732. ¹H NMR (CDCl₃; Me₄Si): $\delta_{\rm H}$, ppm 8.15 (2H, s, ArH), 4.44 (4H, q, J = 7.0 Hz, CH_2), 1.41 (6H, t, J = 7.5 Hz, CH_3). GC/MS: m/z273.30 [M + H]⁺. Calcd. for $C_{14}H_{12}N_2O_4$ 272.2. Anal. calcd. for C₁₄H₁₂N₂O₄: C, 61.76; H, 4.44; N, 10.29. Found: C, 61.82; H, 4.29; N, 10.38.

2,3,9,10,16,17,23,24-octacarboxyphthalocyanine **1.** A mixture of 4,5-bis(ethoxycarbonyl)phthalonitrile **7** (2.0 g, 7.35 mmol) and 1,8-diazabicyclo[5.4.0]undec-7-ene (0.55 mL, 3.68 mmol) in n-hexanol (40 mL) was heated to reflux for 4 h under inert atmosphere. After being cooled to room temperature, the mixture was evaporated under reduced pressure, and the residue was chromatographed on a silica gel column using CHCl₃/ EtOH (30:1) as the eluent. The dark blue fraction was collected. After evaporation of the solvent, the solid was treated with ethanol, filtered off, washed repeatedly with ethanol until the filtrate was colourless and dried in the air to yield 1.44 g of mixed octaesters 8. IR (KBr): v, cm^{-1} 2959, 2825, 1728. Anal. calcd. for $C_{56}H_{50}N_8O_{16}$ (H₂Pc(COOEt)₈): C, 61.65; H, 4.62; N, 10.27. Anal. calcd. for $C_{64}H_{66}N_8O_{16}$ (H₂Pc(COOEt)₆(COOHx)₂): C, 63.84; H, 5.53; N, 9.31. Found: C, 63.98; H, 5.47; N, 9.40.

A mass of 1.44 g of mixed octaesters 8 was added to a warm (80 °C) solution of KOH (3.2 g) in triethylene glycol (16 mL) and heated at 135 °C for 4 h under inert atmosphere (argon). After being cooled to room temperature, the mixture was poured into 7% hydrochloric acid solution (300 mL). A dark blue precipitate was formed, filtered off and washed with warm 1% hydrochloric acid solution. Because of the high solubility of phthalocyanine 1 in water at neutral pH it is impossible to remove the HCl by washing with water without the loss of significant amount of substance. So we washed off the HCl by 10% acetic acid solution and the precipitate was allowed to dry in the air. The resulting dark blue solid was powdered, treated with toluene to remove the traces of acetic acid, filtered off and dried in the air to yield 0.83 g (52%) of phthalocyanine 1 as a dark blue powder. IR (KBr): v, cm⁻¹ 3440, 1704. MS (MALDI-TOF): *m*/*z* 867.67 (calcd. for [M + H]⁺ 867.62). Anal. calcd. for $C_{40}H_{18}N_8O_{16} \times 2 H_2O$: C, 53.22; H, 2.46; N, 12.41. Found: C, 53.18; H, 2.94; N, 12.63.

Methods

Fluorescence quantum yields (Φ_F) were determined by the comparative method according to Eq. 1:

$$\Phi_F = \Phi_F^{ref} \frac{FA^{ref} (n_D)^2}{F^{ref} A (n_D^{ref})^2}$$
(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 \mathbf{n}_D^{ref} are the refractive indices of solvents for the sample and reference, respectively. PcZn in DMSO was used as a reference ($\Phi_F^{ref} = 0.20$ [24]). Excitation wavelength of 670 nm was employed.

The photodegradation quantum yield (Φ_p) estimations were carried out with concentration of the H₂Pc(COOH)₈ about 3 μ M. Xenon lamp (150 W) was used as a light source. The excitation light first passed through a yellow glass filter GS-18 and water filter to cut off ultraviolet and infrared radiation and then through an interference filter with the transmission maximum at 680 and \pm 25 nm bandpass. The light intensity at the sample surface was 2.4 × 10¹⁵ photons.s⁻¹.cm⁻². The decrease of the phthalocyanine absorbance (A) was measured in the longwavelength maximum as a function of irradiation time. The quantum yields Φ_p were calculated from the initial part of the A(t) dependence curves according to Eq. 2:

$$\Phi_{P} = \frac{V}{I_{abs} l\varepsilon} \frac{dA}{dt}$$
(2)

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 — decimal molar absorption coefficient at the maximum of the absorption band. The term *dA/dt* was determined graphically.

The quantum yields of photodegradation were estimated with about 15% accuracy.

The singlet oxygen quantum yield, Φ_{Δ} , of the $H_2Pc(COOH)_8$ in DMSO solution was estimated by using PcZn as reference ($\Phi_{\Delta}^{ref} = 0.67$ in DMSO [25]), and DPBF as hydrophobic ${}^{1}O_2$ trap according to the reported procedure [26]. To avoid chain reactions induced by DPBF in the presence of singlet oxygen [26] the concentration of DPBF was lowered to ~ 3×10^{-5} M. In basic aqueous solutions Φ_{Δ} values were determined relatively to the sulfonated aluminum phthalocyanine (in water at pH 7.4 $\Phi_{\Delta} = 0.38$ [27]) using ADMA as water-soluble singlet oxygen trap. Equation 3 was employed for the calculations of Φ_{Λ} :

$$\Phi_{\Delta} = \Phi_{\Delta}^{ref} \frac{WI_{abs}^{ref}}{W^{ref} I_{abs}}$$
(3)

where Φ_{Δ}^{ref} is the singlet oxygen quantum yield for reference; W and W^{ref} are the trap photobleaching rates in the presence of sensitizer of singlet oxygen generation under investigation and reference, respectively. I_{abs} and I_{abs}^{ref} are the intensities of light absorption by sensitizer under investigation and reference, respectively. The initial trap concentrations are kept the same for reference and the samples. The accuracy of Φ_{Δ} estimation was about 10%.

All the experiments were carried out at ambient temperature.

CONCLUSION

Non-metal 2,3,9,10,16,17,23,24-octacarboxyphthalocyanine was synthesized with good yield by tetramerization reaction of 4,5-bis(ethoxycarbonyl)phthalonitrile 7 followed by the hydrolysis of ester groups in alkaline media. The usage of phthalonitrile 7 as the starting material allows to avoid the formation of oligomeric species and to obtain a product of high purity. Phthalonitrile 7 was prepared with high yield by new synthetic pathway in several steps from pyromellitic dianhydride.

In DMSO, $H_2Pc(COOH)_8$ shows monomeric behavior. In water, unionized $H_2Pc(COOH)_8$ is aggregated and possesses no fluorescence. At pH about 6, $H_2Pc(COOH)_8$ aggregates transform into monomeric octacarboxylated form. On further pH increase, in pH interval from 10 to 11.5, inner deprotonation (loss of two protons) takes place.

Fluorescence quantum yields for three forms of nonmetal octacarboxyphthalocyanine ionization are in 0.06– 0.16 range. The significant increase of quantum yield of singlet oxygen generation, from 0.1 for $H_2Pc(COO^-)_8Na^+_8$ up to 0.4 for $Pc^{2-}(COO^-)_8Na^+_{10}$, was found upon inner deprotonation. In aerated DMSO, $H_2Pc(COOH)_8$ has relatively high photostability (photobleaching quantum yield 1.6×10^{-5}). Obtained results exhibit a trend to increase of phthalocyanine photodegradation by the negatively charged groups. Thus, species H₂Pc(COO⁻)₈Na⁺₈ showed about one order of magnitude less photostability, further ionization to Pc²⁻(COO⁻)₈ Na⁺₁₀ gives sequential increase of photodegradation ($\Phi_p = 2.5 \times 10^{-3}$ at pH 12).

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