

Photooxidation of sodium sulfide and sodium thiosulfate under irradiation with visible light catalyzed by water soluble polynuclear phthalocyanine complexes

V. Iliev*, A. Mihaylova

Institute of Catalysis, Bulgarian Academy of Sciences, 1113 Sofia, Bulgaria

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Abstract

The catalytic and photocatalytic activities of polynuclear water soluble phthalocyanine complexes, $[\text{CoPc}(\text{COOH})_n]_{\text{poly}}$, $[\text{ZnPc}(\text{COOH})_n]_{\text{poly}}$, $[\text{AlPc}(\text{COOH})_n]_{\text{poly}}$, and $[\text{Pc}(\text{COOH})_n]_{\text{poly}}$, have been investigated in the oxidation of Na_2S and $\text{Na}_2\text{S}_2\text{O}_3$. The studied complexes represent two-dimensional polymers, formed of condensed phthalocyanine macrocycles. The average number of the phthalocyanine units in them is, respectively: $[\text{CoPc}(\text{COOH})_n]_{\text{poly}} \approx 4$, $[\text{ZnPc}(\text{COOH})_n]_{\text{poly}} \approx 4$, $[\text{AlPc}(\text{COOH})_n]_{\text{poly}} \approx 3$, $[\text{Pc}(\text{COOH})_n]_{\text{poly}} \approx 4$. No visible bathochromic shifting is observed in the Q-band electron transition ($\lambda = 665\text{--}680\text{ nm}$) of the polynuclear complexes with respect to their mononuclear analogues. This fact is an indication of low $\pi\text{--}\pi$ electron delocalization in excited state between the phthalocyanine units of the polynuclear complexes.

The catalytic and photocatalytic activity per mole of the polynuclear complexes is 2–5 times higher than that of the respective mononuclear phthalocyanine complexes. In the dark or upon irradiation with visible light the cobalt(II) phthalocyanine complexes catalyze only the oxidation of Na_2S , which is proceeding incompletely to thiosulfate. The zinc, aluminum and non-metal polynuclear phthalocyanine complexes are active catalysts only in the case of irradiation with visible light. The photooxidation of substrates like Na_2S and $\text{Na}_2\text{S}_2\text{O}_3$ with the previously mentioned photosensitizers is proceeding completely, whereupon the valence state of the sulfur in the final products is S^{6+} . In this case the photooxidation process involves singlet oxygen. The high photocatalytic activity of the polymers might be explained by the proceeding of an intra-molecular triplet–triplet energy transfer between the phthalocyanine macrocycles in accordance with the mechanism of Dexter. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Photocatalysis; Oxidation; Polynuclear phthalocyanine complexes; Sulfides; Thiosulfates

1. Introduction

Sulfur-containing compounds, such as mercaptans, alkali sulfides, alkali sulfites, and alkali thiosulfates are by-products of industrial processes and pollutants of waste and natural waters [1,2]. The presence of sulfide ions in industrial wastewater (oil-processing industry, paper manufacture, synthetic fiber production), communal wastewater, etc. has a mortal effect on the bacterial strains, used for their biological purification [3]. In addition to the toxic properties of these pollutants another problem is the decrease of the dissolved oxygen amount in the waters as a result of the natural oxidation of the compounds. The complete oxidation of sulfur-containing compounds, before discharging them into waterways, has been suggested as a possible solution of the environmental pollution problem [4]. Phthalocyanine

complexes containing metal ions with unfilled d orbitals, like Co^{2+} , are effective catalysts in the dark finding wide practical application for thiol and hydrosulfide oxidation by dioxygen [1,2,5–11]. They are able to coordinate reversibly and to activate dioxygen [12,13], which is the base of the redox mechanism of catalytic oxidation of sulfur-containing compounds [1,2,5–11]. The oxidation of thiols and alkali sulfides, catalyzed by cobalt phthalocyanine complexes (CoPc), is not complete, the end products being disulfides, sulfur and thiosulfates, respectively [5–11]. Some polynuclear cobalt(II) phthalocyanine complexes have also been studied as catalysts for the oxidation of the sulfide ion [10]. It has been shown that they exhibit a much higher specific activity than the mononuclear compound, but the substrate oxidation proceeds incompletely. Recently, it has been established [14–19] that metal-free phthalocyanine complexes and those containing a central metal ion with filled up electron shells or d orbitals exhibit a high photocatalytic activity in the complete oxidation of sulfur-containing compounds.

* Corresponding author. Tel.: +35-92-9792514; fax: +35-92-756116.
E-mail address: iliev@ic.bas.bg (V. Iliev).

During interaction between dioxygen and the long-living triplet state of these complexes, a chemically more reactive singlet dioxygen $^1\text{O}_2$ ($^1\Delta_g$) is formed [14–20] which interacts further with compounds containing sulfur in various oxidation states. The oxidation of mercaptans or hydrosulfides in this case proceeds completely, leading, respectively, to sulfonic acids and sulfates [14–19].

The photooxidation of Na_2S and $\text{Na}_2\text{S}_2\text{O}_3$ are studied in this work catalyzed by mononuclear and polynuclear phthalocyanine complexes. The thiosulfates are the main final products in the case of sulfide ion catalytic oxidation in the presence of cobalt phthalocyanine complexes. The aim of the present work is to juxtapose the photocatalytic properties of the two types of complexes and the effect of polymerization on their activity.

2. Experimental

Merck Na_2S and $\text{Na}_2\text{S}_2\text{O}_3$ were used without any further purification. Cobalt(II) 2,9,16,23-phthalocyanine tetracarboxylic acid [$\text{CoPc}(\text{COOH})_4$], zinc(II) 2,9,16,23-phthalocyanine tetracarboxylic acid [$\text{ZnPc}(\text{COOH})_4$], aluminum(III) 2,9,16,23-phthalocyanine tetracarboxylic acid [$\text{AlPc}(\text{COOH})_4$] and non-metallic 2,9,16,23-phthalocyanine tetracarboxylic acid [$\text{Pc}(\text{COOH})_4$] were prepared by the interaction of trimellitic anhydride with urea and purified according to the methods described in the literature [21,22]. Zinc(II) 2,3,9,10,16,17,22,23-phthalocyanine octacarboxylic acid [$\text{ZnPc}(\text{COOH})_8$], aluminum(III) 2,3,9,10,16,17,22,23-phthalocyanine octacarboxylic acid [$\text{AlPc}(\text{COOH})_8$] and non-metallic 2,3,9,10,16,17,22,23-phthalocyanine octacarboxylic acid [$\text{Pc}(\text{COOH})_8$] were synthesized according to the methods described in the literature [23]. The 33 mmol of the metal salt, 18 mmol pyromellitic anhydride, 0.33 mmol urea and 0.2 mmol ammonium molybdate were mixed and heated for 3 h at 240°C in a flask, immersed in a silicone oil bath. The reaction product was washed consecutively with water and acetone. The dried product was stirred with 500 ml of 6 M hydrochloric acid for 12 h at room temperature. The acid was removed and the solid product was washed with hot water until $\text{pH} = 7$ was reached. The transformation of the end imide groups into carboxylic groups in the polynuclear complexes was carried out by heating the mixture for 5 h at 90°C , using 200 ml of solution, containing 2 M sodium hydroxide and 80 g sodium chloride [24]. After filtration the product was acidified with 2 M hydrochloric acid, washed with water up to $\text{pH} = 7$ and the solid residual was isolated. The solid product was heated three times for 30 min at 90°C , with 100 ml dimethylformamide (DMF)–water solution at a ratio of 5:1. The prepared solutions were vaporized at a lowered pressure. Dark green metal phthalocyanine complexes were prepared with a yield of 15–25%. The metal-free phthalocyanine complex, $\text{Pc}(\text{COOH})_8$, was prepared on the basis of the same method by demetallizing $\text{MgPc}(\text{COOH})_8$

upon dissolving it in concentrated sulfuric acid. The complexes $\text{MPc}(\text{COOH})_8$ and $\text{Pc}(\text{COOH})_8$ were characterized by elemental analysis and titration of the carboxylic groups in peripheral position. Carboxylic end groups ($\nu(\text{CO})$ at 1700 cm^{-1}) were registered by IR spectroscopy.

The polynuclear phthalocyanine complexes [$\text{AlPc}(\text{COOH})_n$]_{poly}, [$\text{ZnPc}(\text{COOH})_n$]_{poly}, [$\text{CoPc}(\text{COOH})_n$]_{poly}, [$\text{Pc}(\text{COOH})_n$]_{poly} has been obtained following the procedure described in [10,23–25]. A flask, immersed in a silicone oil bath, containing 30 mmol of the respective metal salt, 24 mmol pyromellitic acid, 1.6 mol urea and 0.5 mmol ammonium molybdate was heated for 3 h at 240°C . The reaction product was washed consecutively with water and acetone. The dried product was stirred with 500 ml of 6 M hydrochloric acid for 12 h at room temperature. The acid was removed and the solid product was washed with hot water up to $\text{pH} = 7$. The end imide groups in the polynuclear complexes were transformed into carboxylic groups upon heating the mixture for 5 h at 90°C using 250 ml of solution containing 2 M sodium hydroxide and 80 g sodium chloride [24]. After filtration the product was acidified with 2 M hydrochloric acid, washed with water until $\text{pH} = 7$ was reached and the solid residual was isolated. The separation of the polynuclear phthalocyanine complexes from the mononuclear ones was carried out by multiple dissolving of the reaction product in DMF and precipitation with chloroform. Dark green products were isolated with an yield of 20–40%, containing a mixture of metal polynuclear phthalocyanine complexes. The metal-free polynuclear phthalocyanine complex, [$\text{Pc}(\text{COOH})_n$]_{poly}, was obtained on the basis of the same method by demetallizing the [$\text{MgPc}(\text{COOH})_n$]_{poly} upon dissolving it in concentrated sulfuric acid.

The average number of phthalocyanine structural units in the polynuclear complexes was estimated on the basis of the data from the elemental analysis, titration of the carboxylic groups in peripheral position and determination of the viscosity of the complexes in a DMF solution [10,23–25]. The viscosity of solutions containing 0.0108 g of phthalocyanine in 100 ml of DMF was determined at 298 K by means of an Ostwald viscosimeter. Moreover, the relative viscosity, η_{rel} , was estimated on the basis of the ratio between the time interval of flowing out of the solution and that of the solvent. The absorption spectra of the phthalocyanine complexes were registered on a Hewlett-Packard 89500 UV–Vis spectrophotometer.

The rates of Na_2S or sodium thiosulfate catalytic and photocatalytic oxidation were evaluated by the consumption of dioxygen, which was measured by a gas burette. The oxidation and photooxidation process was performed at 293 K, $\text{pH} = 9$ and atmospheric pressure in a static reactor by exposure to a halogen lamp (12 V, 50 W), the illumination being 38 mW/cm^2 . The oxidation of sulfide ion into thiosulfate has been confirmed semi-quantitatively by means of UV spectroscopy ($\lambda = 205\text{--}240\text{ nm}$) [6,19]. The amount of sulfate ions formed upon photooxidation

of $\text{Na}_2\text{S}_2\text{O}_3$ is determined gravimetrically by precipitation with BaCl_2 . The accuracy of the analysis was ± 7 wt.%. The photodestruction of the phthalocyanine complexes was determined spectrophotometrically based on the decrease in the intensity of their Q-bands at $\lambda \approx 680$ nm.

In order to show the participation of $^1\text{O}_2$ for the photooxidation process, measurements with 1,3-diphenylisobenzofuran (1,3-DPBF) as chemical quencher were carried out. The measurements were performed in a quartz cell (1×1 cm²) at 19 °C by the method described in the literature [26]. A DMF solution (2.5 ml) containing 4 μM sensitizer and 65 μM DPBF was used. Kinetic data were analyzed by calculating the initial rate of the photooxidation of DPBF. The reactions show zero-order kinetics within the first 90 s. Quantum yields (Φ) for the photooxidation of DPBF were calculated by $\Phi = d[\text{DPBF}]/dt$ per J_{abs}/V (J_{abs} is the absorbed photons, V the volume of the solution in the quartz cell) as described [26].

3. Results and discussion

The studied polynuclear phthalocyanine complexes represent two-dimensional polymers, formed of condensed phthalocyanine macrocycles (Fig. 1). The delocalization of

the π -electrons over the entire macromolecule is hampered in them by the units, connecting the phthalocyanine nuclei [24,27,28]. The Q-band electron transitions in the studied mononuclear and polynuclear phthalocyanine complexes are almost identical (Fig. 2). This fact, however, does not exclude the possibility that weak π - π exchange interactions are occurring between the neighboring phthalocyanine units [24,27,28]. Some changes are observed in the molar extinction coefficients. They have quite lower values for the polynuclear phthalocyanine complexes in comparison to those for the mononuclear ones. It is considered [24,27,28] that the absorbance of light is associated with a single electron transition ($S_{\text{Pc unit}}^0 \rightarrow S_{\text{Pc unit}}^*$) whereupon it is only one phthalocyanine unit of the polynuclear complex that is participating in the elementary act.

The separation of the polynuclear phthalocyanine complexes from their mononuclear analogues $\text{MPc}(\text{COOH})_8$ has been carried out by their extraction with DMFA [25]. The average number of phthalocyanine units in the polynuclear complexes may be estimated on the basis of their elemental analysis, the acid–base titration of the carboxylic groups in peripheral position and the determination of the complex solution viscosity.

The C/N ratios of the elemental analysis of the complexes, which are the most sensitive to changes in the

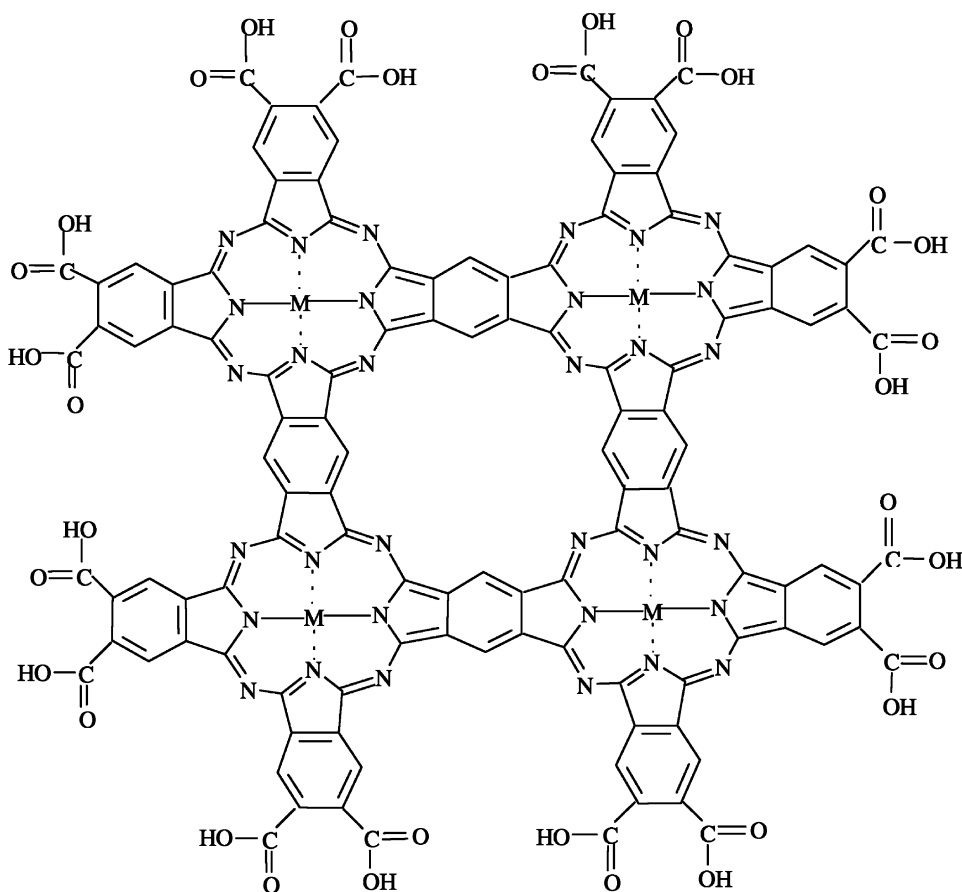


Fig. 1. Two-dimensional polynuclear phthalocyanine complex.

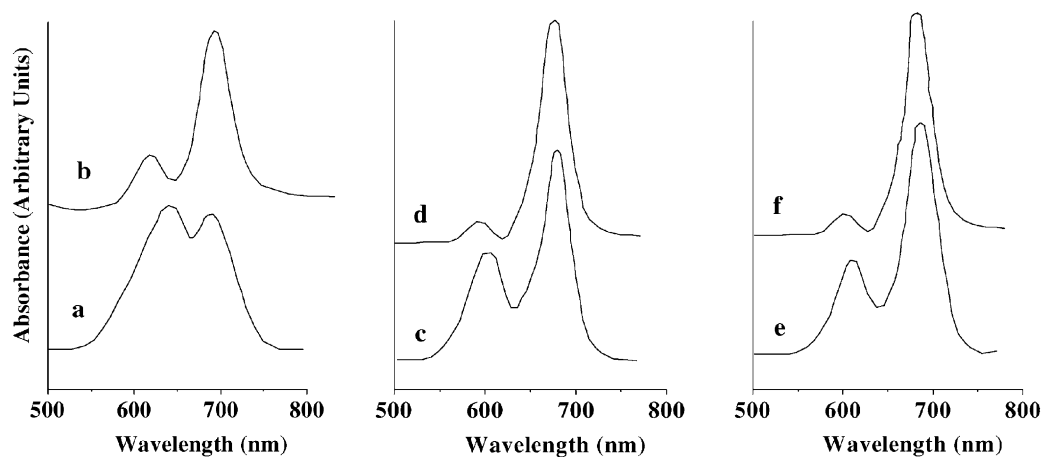


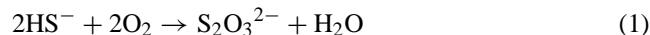
Fig. 2. UV-Vis spectra of: (a) $\text{ZnPc}(\text{COONa})_4$; (c) $\text{ZnPc}(\text{COONa})_8$; (e) $[\text{ZnPc}(\text{COOH})_n]_{\text{poly}}$ dissolved in H_2O ; and (b) $\text{ZnPc}(\text{COONa})_4$; (d) $\text{ZnPc}(\text{COONa})_8$; (f) $[\text{ZnPc}(\text{COOH})_n]_{\text{poly}}$ dissolved in H_2O -TBAC.

number of phthalocyanine units in the polynuclear complex [24] are, respectively: $[\text{AlPc}(\text{COOH})_n]_{\text{poly}} = 3.65$, $[\text{ZnPc}(\text{COOH})_n]_{\text{poly}} = 3.52$, $[\text{CoPc}(\text{COOH})_n]_{\text{poly}} = 3.54$ and $[\text{Pc}(\text{COOH})_n]_{\text{poly}} = 3.56$. The ratio in all the four mononuclear analogues ($\text{MPc}(\text{COOH})_8$) of the polymers is ≈ 4.5 . Having in mind the previous detailed studies focused on the analysis of the polynuclear phthalocyanine complexes [10,24,27,28], the obtained results may be interpreted to the effect that the average number of phthalocyanine units in the studied polymers is the following: $[\text{AlPc}(\text{COOH})_n]_{\text{poly}} \approx 3$, $[\text{ZnPc}(\text{COOH})_n]_{\text{poly}} \approx 4$, $[\text{CoPc}(\text{COOH})_n]_{\text{poly}} \approx 4$ and $[\text{Pc}(\text{COOH})_n]_{\text{poly}} \approx 4$. This result is confirmed also by the data of the titration of carboxylic groups in peripheral position in the polymers, which lie within the interval 7.0–7.6 mmol COOH/g of the respective complex. In the case of the mononuclear analogues ($\text{MPc}(\text{COOH})_8$) the number of the carboxylic in peripheral position amounts to 8.4 mmol/g. The relative viscosities, η_{rel} , of MPc and $(\text{MPc})_{\text{poly}}$ are, respectively, 1.02 and 1.13–1.17, which serves as an evidence for the formation of polynuclear complexes of different molecular weight.

The results of the catalytic and photocatalytic oxidation of Na_2S and $\text{Na}_2\text{S}_2\text{O}_3$ are represented in Table 1. The standard calculation methods were applied to determine the initial rates of the sulfide and thiosulfate conversions. They are denoted by r and expressed in (mol O_2 /min g of catalyst) and, respectively, r in (mol O_2 /min mol of catalyst).

The cobalt phthalocyanine complexes catalyze only the oxidation of Na_2S . The oxidation of $\text{Na}_2\text{S}_2\text{O}_3$ is not catalyzed by $\text{CoPc}(\text{COOH})_4$ [16–19] and $[\text{CoPc}(\text{COOH})_n]_{\text{poly}}$ complexes (Table 1). The rate of oxidation of the substrate per mole of catalyst (Table 1) is higher in the case of $[\text{CoPc}(\text{COOH})_n]_{\text{poly}}$ than that registered with the $\text{CoPc}(\text{COOH})_4$ complex. This could be explained with the possibility to coordinate the hydrosulfide anion and oxygen on two adjacent cobalt atoms in the polynuclear phthalocyanine complex [10].

The oxidation of Na_2S does not proceed completely in the presence of the studied cobalt phthalocyanine complexes (Table 1). The main oxidation product is the thiosulfate formed by the following reaction:



This is proved by the fact that no further catalytic oxidation of $\text{Na}_2\text{S}_2\text{O}_3$ is occurring in the presence of the cobalt phthalocyanine complexes (Table 1), the semi-quantitative estimation of the final products by means of UV spectroscopy [6,19] and the consumed quantity of O_2 (≈ 12 mmol) (Fig. 3), corresponding to the stoichiometry of reaction (1). The final products contain also about 25% sulfate ions, formed via the mechanism, described in a previous investigation [19].

The cobalt phthalocyanine complexes show no increase in the oxidation rate of Na_2S under irradiation [14,16–19] (Table 1). The lack of photocatalytic activity of the cobalt complexes is due to a very short lifetime of the excited triplet electronic state (${}^1\sigma_{\text{CoPc}} \approx 0.065$ μs) [29] and for this reason they are unable to convert the triplet dioxygen, ${}^3\text{O}_2$ (${}^3\Sigma_g^-$), into singlet dioxygen, ${}^1\text{O}_2$ (${}^1\Delta_g$).

In a similar way the mononuclear [14,16–19] and polynuclear zinc, aluminum and non-metal phthalocyanine complexes show no catalytic activity for oxidation of Na_2S and $\text{Na}_2\text{S}_2\text{O}_3$ in the dark. These complexes are unable to coordinate and activate molecular dioxygen [13]. They demonstrate a high catalytic activity only in the case of irradiation with visible light. Upon irradiation these complexes (Sens) manifest long lifetimes of the excited triplet electron state (${}^1\sigma_{\text{ZnPc}} \approx 245$ μs ; ${}^1\sigma_{\text{AlPc}} \approx 500$ μs) [29]. The dioxygen, ${}^3\text{O}_2$ (${}^3\Sigma_g^-$), interacts with the excited triplet electronic state of the complexes and, as a result of an energy transfer, it is converted to a more reactive singlet dioxygen, ${}^1\text{O}_2$ (${}^1\Delta_g$), according to the following scheme:

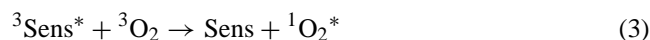


Table 1

Oxidation and photooxidation of Na_2S (10 mmol) and $\text{Na}_2\text{S}_2\text{O}_3$ (10 mmol) in aqueous solution at pH = 9.24, catalyzed by water soluble phthalocyanine complexes (6.3 mg)

| Number | Complex | [C] _{comp} (μmol) | Medium | Na_2S oxidation | | $\text{Na}_2\text{S}_2\text{O}_3$ oxidation | | Degradation of catalysts (%) ^a at 60 min |
|--------|---|--|---|---|--|---|--|---|
| | | | | r_{O_2} ($\times 10^2$ mol/g min) | r_{O_2} (min^{-1}) | r_{O_2} ($\times 10^2$ mol/g min) | r_{O_2} (min^{-1}) | |
| 1 | $\text{CoPc}(\text{COOH})_4^{\text{b,c}}$ | 8.4 | H_2O | 5.7 | 42.75 | 0 | 0 | – |
| 2 | $\text{ZnPc}(\text{COOH})_4^{\text{c}}$ | 8.4 | H_2O | 0.46 | 3.46 | 0.08 | 0.62 | 38 |
| | | 8.4 | H_2O -TBAC ^d | 1.32 | 10.02 | 0.19 | 1.42 | – |
| 3 | $\text{ZnPc}(\text{COOH})_8^{\text{c}}$ | 6.7 | H_2O | 1.26 | 11.90 | 0.16 | 1.44 | 44 |
| | | 6.7 | H_2O -TBAC ^d | 2.28 | 21.42 | 0.17 | 1.58 | – |
| 4 | $\text{ZnPc}(\text{SO}_3\text{H})_4^{\text{c}}$ | 7.0 | H_2O | 1.42 | 12.60 | 0.18 | 1.61 | – |
| | | 7.0 | H_2O -TBAC ^d | 3.36 | 29.89 | 0.22 | 1.98 | – |
| 5 | $\text{AlPc}(\text{COOH})_8^{\text{c}}$ | 6.8 | H_2O | 1.02 | 9.49 | 0.21 | 2.00 | 41 |
| | | 6.8 | H_2O -TBAC ^d | 1.83 | 17.00 | 0.24 | 2.27 | – |
| 6 | $\text{Pc}(\text{COOH})_8^{\text{c}}$ | 7.8 | H_2O | 0.51 | 4.45 | 0.22 | 1.87 | 48 |
| | | 7.8 | H_2O -TBAC ^d | 0.72 | 6.29 | 0.24 | 2.13 | – |
| 7 | $[\text{CoPc}(\text{COOH})_n]_{\text{poly}}^{\text{b,c}}$ | 2.1 | H_2O | 3.84 | 114.52 | 0 | 0 | – |
| 8 | $[\text{ZnPc}(\text{COOH})_n]_{\text{poly}}^{\text{c}}$ | 2.1 | H_2O | 1.86 | 55.45 | 0.20 | 6.06 | 9 |
| | | 2.1 | D_2O | 2.27 | 67.76 | 0.24 | 7.39 | 9 |
| | | 2.1 | NaN_3^{e} | 1.36 | 40.47 | 0.15 | 4.42 | 5 |
| | | 2.1 | H_2O -TBAC ^d | 3.66 | 108.48 | 0.24 | 6.96 | – |
| 9 | $[\text{AlPc}(\text{COOH})_n]_{\text{poly}}^{\text{c}}$ | 2.8 | H_2O | 1.08 | 24.60 | 0.24 | 5.52 | 8 |
| | | 2.8 | H_2O -TBAC ^d | 2.28 | 52.30 | 0.28 | 6.32 | – |
| 10 | $[\text{Pc}(\text{COOH})_n]_{\text{poly}}^{\text{c}}$ | 2.3 | H_2O | 0.51 | 13.84 | 0.06 | 1.60 | 18 |
| | | 2.3 | H_2O -TBAC ^d | 1.32 | 35.74 | 0.13 | 3.52 | – |

^a Na_2S oxidation.

^b In the absence of irradiation.

^c Upon irradiation.

^d 0.3 mmol TBAC.

^e 0.3 mmol NaN_3 .

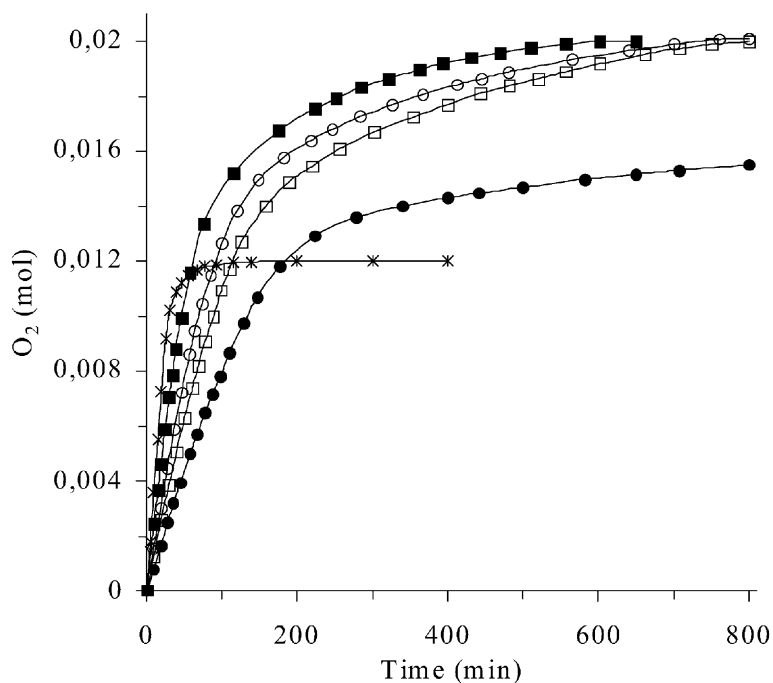
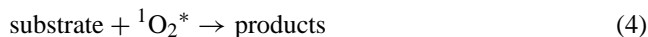


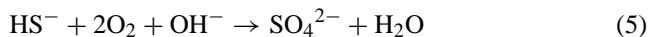
Fig. 3. Typical curves of O_2 consumption during Na_2S oxidation. Photocatalysts: (■) $[\text{ZnPc}(\text{COOH})_n]_{\text{poly}}$ dissolved in H_2O -TBAC; (○) $[\text{ZnPc}(\text{COOH})_n]_{\text{poly}}$ dissolved in H_2O ; (□) $\text{ZnPc}(\text{COONa})_8$ dissolved in H_2O -TBAC; (●) $\text{ZnPc}(\text{COONa})_8$ dissolved in H_2O . Catalysts: (*) $\text{CoPc}(\text{COOH})_8$ dissolved in H_2O .

The singlet oxygen reacts with the substrates whereupon some compounds are obtained displaying the highest oxidation state of the sulfur in them (S^{6+}):



There are several possibilities for the qualitative demonstration whether singlet oxygen is involved or not in the photooxidation. First, it is possible to quench singlet oxygen in the presence of physical (sodium azide) or chemical (1,3-DPBF) quenchers and, second, singlet oxygen has a longer lifetime in D_2O [14,26,30]. During photooxidation of sulfur-containing compounds catalyzed by mononuclear phthalocyanine complexes, it was established that the singlet oxygen, obtained via photoinduced energy transfer from the excited photosensitizer, is involved in the photooxidation process of sulfur-containing compounds [14,30]. In order to gain insight if singlet oxygen is involved in the photooxidative process catalyzed by polynuclear phthalocyanine complexes, different experiments have been carried out. The photooxidation of Na_2S and $Na_2S_2O_3$ in the presence of $ZnPc(COOH)_{poly}$ has been carried out in H_2O , D_2O and in water containing sodium azide. The initial rates r (min^{-1}) increased in D_2O , but decreased in NaN_3 solution (Table 1), which fact confirms the participation of singlet oxygen in the redox process.

In an alkaline aqueous solution Na_2S and $Na_2S_2O_3$ are photooxidized completely according to the following equations:



The kinetics of photocatalytic complete oxidation of Na_2S is somewhat more complex because the process is accomplished by a series of parallel reactions. Polysulfides, sulfur, sulfite and thiosulfate are formed as intermediate species in the process of complete oxidation of the sulfide ion to sulfate [6,8]. The analysis of the final products and the total amount of oxygen consumed (Fig. 3), which is close to the stoichiometrical value, allows the estimation of the completeness of the substrate oxidation in accordance with Eqs. (5) and (6).

The photocatalytic activity per mole of the polynuclear phthalocyanine complexes, r (min^{-1}), in the complete oxidation of sulfur-containing compounds (see Table 1 and Fig. 4), is 2–5 times higher than that of the respective mononuclear phthalocyanine complexes ($MPc(COOH)_8$). The quantum yields of 1O_2 generation using polynuclear phthalocyanine complexes in the presence of DPBF as quencher is much higher than that of the respective mononuclear complexes. The quantum yields, calculated for DPBF photooxidation in the presence of $ZnPc(COOH)_8$ and $[ZnPc(COOH)_n]_{poly}$, are $\Phi = 0.28$ and 0.39 , respectively. The high photocatalytic activity of the polynuclear phthalocyanine complexes is to be explained with the option of intercomponent energy transfer realized by means of exchange interactions between the phthalocyanine units in the polynuclear complexes via

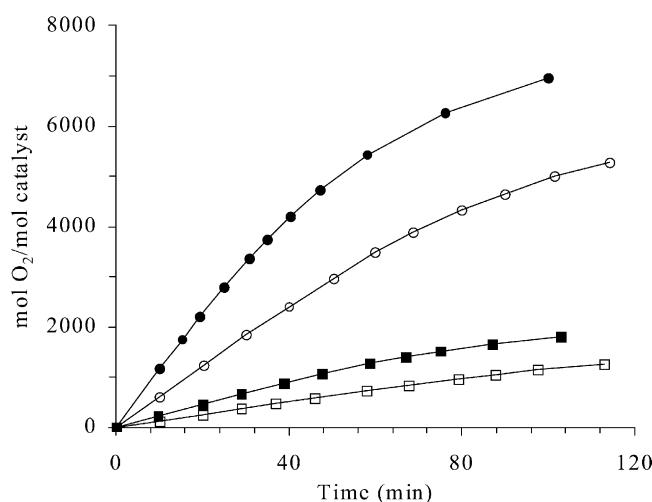


Fig. 4. Initial rates of Na_2S catalytic oxidation. Photocatalysts: (●) $[ZnPc(COOH)_n]_{poly}$ dissolved in H_2O -TBAC; (○) $[ZnPc(COOH)_n]_{poly}$ dissolved in H_2O ; (■) $ZnPc(COONa)_8$ dissolved in H_2O -TBAC; (□) $ZnPc(COONa)_8$ dissolved in H_2O .

the mechanism of Dexter [31]. The necessary conditions are available to realize the intercomponent energy transfer [31–33] in the studied supramolecular complexes, and namely, the absence of effective conjugation in the polynuclear phthalocyanine complexes [24,27,28], whereupon the electron transition $S_{Pc\ unit}^0 \rightarrow S_{Pc\ unit}^*$ is registered due to excitation of a structural unit in the polymer and the small distance 0.5–0.7 nm (Fig. 1) between the π -electron systems of the neighboring phthalocyanine units. The supposition of weak charge-transfer interactions between the π -electron systems of the phthalocyanine units has been put forward in earlier studies [24,27,28]. In addition metal-free phthalocyanine complexes and those containing a central metal ion with filled electron shells or d orbitals manifest long lifetimes of the excited triplet electron state, which is due to the absence of exchange interactions arising from mixing the π and d electronic states of the ligand and the metal [20]. The intercomponent triplet–triplet energy transfer in polynuclear phthalocyanine complexes, described by the mechanism of Dexter, is represented schematically in Fig. 5. The probability of realizing an energy transfer from the triplet state of one of the excited phthalocyanine units, $T_{1Pc\ unit}$, to the triplet state of neighboring phthalocyanine units of the polymer, $T_{1Pc\ poly}$ is higher, taking into account the structure of polynuclear phthalocyanine complexes and the small distance between the structural units in them. The oxygen 3O_2 may interact with the triplet $T_{1Pc\ unit}$ and $T_{1Pc\ poly}$ states of the polynuclear molecule in accordance with Eq. (3), as a result of which the quantum yield of singlet oxygen (${}^1O_2^*$) is increased. The higher rate of oxidation of the substrates according to Eq. (4) is connected with the increased concentration of the singlet oxygen, generated by the polynuclear complexes. The complete oxidation of the substrates gives the reason to conclude that the

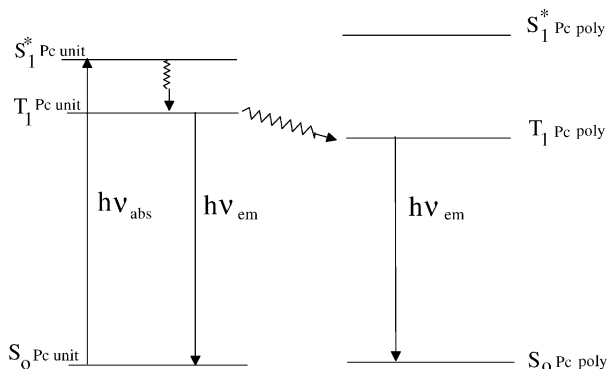


Fig. 5. A schematic representation of intercomponent energy transfer in polynuclear phthalocyanine complexes.

photocatalytic redox process occurs with the participation of singlet oxygen according to Eqs. (2)–(4).

The increased probability of interaction of $^1\text{O}_2^*$ with the substrates in the solvent cage may also influence the higher photocatalytic activity of metal polynuclear phthalocyanine complexes. It is known that $^1\text{O}_2^*$ is a short-living species with a lifetime of 4.4 μs in aqueous medium [34] and a diffusion pathway of around 780 nm [35,36]. In case of adduct formation as a result of reversible coordination of the substrates to the central metal atom of the phthalocyanine complexes their local concentration around the photosensitizer is growing up. In comparison to the mononuclear metal phthalocyanine complexes [37] the possibility of axial adduct formation in the case of polynuclear complexes is higher due to the larger number of phthalocyanine macrocycles (Fig. 1). This results in increase of the quantum yield of the photocatalytic processes, occurring in the presence of polynuclear phthalocyanine complexes. One of the explanations of the lower photocatalytic activity of the metal-free polynuclear phthalocyanine complex $[\text{Pc}(\text{COOH})_n]_{\text{poly}}$ (Table 1) is the impossibility to form axial adducts with the hydrosulfide anion. As the inorganic thiosulfate anion is a harder base in comparison with the hydrosulfide anion [38], the adduct formation of the former with the phthalocyanine complex is weakly expressed.

The effectiveness of phthalocyanine complexes as catalysts and photocatalysts for oxidation of sulfur-containing compounds is decreased in the case of self-association [7,9,14–19,39]. In photoinitiated processes, upon formation of dimers as a result of bimolecular triplet–triplet annihilation, the excited triplet electron state of the complexes is quenched, the quantum yield of $^1\text{O}_2$ ($^1\Delta_g$) being decreased [14–19]. Thus, the quantum yield of $^1\text{O}_2^*$, formed from the monomeric $\text{ZnPc}(\text{COOH})_4$ species, was 0.7, whereas that of the dimeric species was 0.1 [39]. The presence of monomer–dimer equilibrium of the phthalocyanine complexes in solution is confirmed by the existence of specific electron transitions in the Q-band ($\lambda = 600\text{--}800\text{ nm}$) [14,16,40]. In agreement with previous assignment [18,40,41], the specific electron transitions in

the Q-band absorption transitions at 670–680 and 630 nm (Fig. 2) are attributed to monomeric and dimeric species, respectively. The growth of the rate of photocatalytic oxidation of Na_2S or $\text{Na}_2\text{S}_2\text{O}_3$ in the presence of bulky cations like tetrabutylammonium chloride (TBAC) (Table 1) is due to a decrease in the aggregation degree of the mononuclear and polynuclear complexes (Fig. 2) and the increase of the quantum yield of $^1\text{O}_2^*$ generation [14–19].

Upon irradiation in solution the metal phthalocyanine complexes are decomposed by photogenerated $^1\text{O}_2^*$ [14–18]. The mechanism of phthalocyanines oxidation by $^1\text{O}_2^*$ has already been studied in detail [14]. During photocatalytic oxidation of Na_2S the polynuclear phthalocyanine complexes are more stable than the mononuclear ones (Table 1). The lower degree of photodestruction of the polynuclear phthalocyanine complexes could be explained with the higher probability for interaction of $^1\text{O}_2^*$ with the substrate in the solvent cage. The local concentration of the substrate around the investigated photocatalysts is increased as a result of the adduct formation.

4. Conclusions

In the oxidation of Na_2S and $\text{Na}_2\text{S}_2\text{O}_3$ the photocatalytic activity per mole of the polynuclear phthalocyanine complexes: $[\text{ZnPc}(\text{COOH})_n]_{\text{poly}}$, $[\text{AlPc}(\text{COOH})_n]_{\text{poly}}$ and $[\text{Pc}(\text{COOH})_n]_{\text{poly}}$ is 2–5 times higher than that of the respective mononuclear complexes. There are two factors influencing the activity of the polynuclear complexes: the first one is the increase of the quantum yield of singlet oxygen as a result of exchange interactions between phthalocyanine units, proceeding in accordance with the mechanism of Dexter. The second one is the higher probability for interaction of $^1\text{O}_2^*$ with the substrates in the solvent cage, due to their increased local concentration, caused by the adduct formation.

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