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Photocatalytic Oxidation of Dibutyl Sulfide with Indium(III) Tetraarylporphyrinate

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A new indium(III) 5,10,15,20-tetrakis(4-butoxyphenyl)porphyrinate was synthesized and completely characterized for the evaluation of the effect of indium(III) as a heavy atom in photocatalytic oxidation of organic sulfides. With di-n-butyl sulfide as a model substrate, the applicability of the prepared photosensitizer was evaluated in comparison with parent tetraarylporphyrin. The variation of a light source, catalyst loading and reaction time clearly demonstrated an enhanced efficiency of the prepared porphyrin complex. The application of low-power blue LED lamp with 0.05 mol% catalyst loading allowed complete conversion of the substrate within 1.5 hour of the photoirradiation with nearly quantitative formation of the corresponding sulfoxide.

Keywords: Indium(III) porphyrinate, oxidation of organic sulfides, organic sulfoxide, photocatalysis.

Фотокаталитическое окисление дибутилсульфида в присутствии тетраарилпорфирината индия(III)

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В настоящей работе был получен и полностью охарактеризован новый 5,10,15,20-тетракис(4-бутоксифенил)порфиринат индия(III) для оценки влияния катиона индия(III) как тяжелого атома на фотокаталитическое окисление органических сульфидов. На примере реакции окисления ди-н-бутилсульфида в качестве модельного субстрата была оценена применимость полученного фотосенсибилизатора по сравнению с обычно используемым тетраарилпорфирином. Варьирование источника света, загрузки фотокатализатора и времени реакции ясно продемонстрировало повышенную эффективность полученного порфирината индия(III). Использование фотокатализатора в количестве 0,05 моль% и маломощной светодиодной лампы синего цвета обеспечило полную конверсию субстрата за 1,5 ч облучения с практически количественным образованием соответствующего сульфоксида.

Ключевые слова: Порфиринат индия(III), окисление органических сульфидов, органический сульфоксид, фотокатализ.

Introduction

Oxidation reactions are a key class of chemical transformations widely used in organic synthesis, in particular, in the production of pharmaceutical substances. Application of such reactions is accompanied with a number of challenges, since these transformations usually proceed with low selectivity for the formation of target products and require stoichiometric quantities of toxic or expensive oxidizing agents. In this regard, such processes are among the most polluting reactions in chemistry. These problems could be solved by using photocatalytic oxidation reactions. The implementation of such transformations opens up the possibility of using light energy, eliminating the need for additional chemical activators and reducing the impact on the environment.

Porphyrins, due to their polyaromatic system, demonstrate unique optical and electronic properties, including the ability to transfer energy and electrons to small molecules upon photoexcitation, allowing, for example, the activation of molecular oxygen, which leads to the formation of various reactive oxygen species (ROS).[1–3] The use of photogenerated ROS's allows selective oxidation reactions to be performed under mild conditions and prevents the formation of degradation products of chemical oxidants.[4] In turns, it fulfills the principles of atom-economy and green chemistry. Nevertheless, the known porphyrin-based photocatalysts require significant efforts for the optimization of their photocatalytic characteristics, including activity, photostability, and conditions of photocatalytic reactions.

One of the approaches to tuning of the properties of porphyrin-based photosensitizers consists in an introduction of metal cation into the coordination cavity of macrocycle, which leads to the so-called heavy atom effect.[5] Numerous researches in this area have revealed that metals such as Zn(II), Pd(II), Pt(II), In(III), Mg(II) and others make it possible to successfully implement the heavy atom effect for the enhancement of the photocatalytic outcome of the sensitizers [6–11]. The mentioned effect consist in an increase in the efficiency of intersystem crossing (ISC) from singlet S_1 to long-lived triplet T_1 excited states which in turn leads to an enhancement of quantum yield of singlet oxygen.[6,7,12,13]

Recently we reported a series of investigations, aimed on the enhancement of the photocatalytic performance of porphyrin derivatives by means of structural modification of the porphyrin core [14–18] or variation of the reaction conditions.[19,20] Introduction of a metal ion into the coordination cavity of the macrocycle provides additional degree of freedom in fine tuning of the properties of the photosensitizers. Among the reported applications of metal porphyrinates as photocatalysts, indium(III) porphyrinates are of considerable interest for several reasons. First, In(III) porphyrinates are able to generate active oxygen forms under photoirradiation.[5,21] This metal is also characterized by a stable oxidation state, which provides a constant number of axial ligands and simplifies the process of physicochemical characterization of the synthesized substances. In addition, indium(III) porphyrinates are reported to possess enhanced photocatalytic activity and photostability in oxidation reactions compared to other metal complexes.[5,21] Recently we reported enhanced photocatalytic performance of an indium(III) porphyrinoids.[14,15] These complexes demonstrated significantly higher photocatalytic activity compared to the corresponding free-base porpholactone, as well as compared to other photocatalysts based on tetrapyrrole macrocycles. Thus, in the photooxidation of dibutyl sulfide in MeOH/Tol (2:1 by volume) under irradiation with a blue LED lamp (3 W, 430–505 nm), the reaction rate in the presence of the indium(III) porpholactone exceeded the case of the corresponding free base by over three times. In the presence of In(III) complex, complete conversion of the sulfide was achieved in 3h, while the free base showed only *ca*. 40% substrate conversion over the same time.

Coordination of indium(III) is also reported to enhance the activity of PDT agents. Thus, In(III) complexes of chlorin e_6 and related compounds are under intense investigation.[22–28] It is reported that In(III) porphyrinates demonstrate higher photoactivity compared to the commercial PDT agent Photofrin©,[13] as well as compared to PDT agents based on Zn(II) porphyrinates.[22]

Despite all the described advantages of tetrapyrrole indium(III) complexes, only a limited number of reports describe their use in photocatalytic oxidation reactions. In the present study we aimed to investigate the influence of introduction of indium(III) cation into the porphyrin cavity onto the photocatalytic activity in oxidation reactions. The oxidation of organic sulfides to corresponding sulfoxides was chosen as a model photoreaction since the sulfoxides found application in various fields of science and technology, for example, in the extraction of noble metals.[29] The sulfoxidation also possess great industrial importance, allowing a decrease of the environmental impact and an improvement in the quality of raw materials in the production of petroleum products.[30,31] The sulfoxide group is also present in many natural biologically active compounds, as well as pharmaceuticals[32–35] and products of agricultural industries,[36,37] which has led to a large number of studies of efficient sulfoxide synthesis. Thus, the purpose of this work was to study the applicability of the indium(III) porphyrinate and identify the optimal conditions for photocatalytic oxidation of organic sulfides.

Experimental

Materials and methods

All used reagent-grade chemicals were purchased from commercial suppliers, unless otherwise stated. The solvents have been purified according to conventional methods.[38] MALDI TOF mass spectra were recorded using a Ultraflex spectrometer (Bruker Daltonics, Switzerland) in positive ions mode without matrix. UV-Vis spectra were recorded using an Evolution 200 spectrophotometer (Thermo Scientific, MA USA) in rectangular quartz cells with a 10 mm optical path. NMR spectra were recorded using a Avance III (Bruker, Fällanden, Switzerland) spectrometer with 600.13 MHz proton frequency in $CDCl_3$ at ambient temperature with the use of the residual solvent signal as an internal reference. Chromatographic purification was performed at Macherey-Nagel Silica 60 (0.063–0.2 mm). Size-exclusion chromatography was performed at Bio-Beads SX-1 sorbent (Bio-Rad) in $CHCl_3$/MeOH (98:2) mixture. Merck aluminum plates (TLC Silica 60 F254) were used for TLC analysis which was performed with dichloromethane as an eluent.

Photocatalytic experiments were carried out with a low-power LED lamp of blue (410–510 nm, 3 W), white (400–770 nm, 3 W) or red (590–665 nm, 3 W) light. The results of the photocatalytic experiments were analyzed by ^{1}H NMR in mixture of $CDCl_3/CCl_4$ 1/1 (v/v) with *o*-DCB as an internal standard (0.5 equiv.).

Synthesis

*4-Butoxybenzaldehyde **2**.* 4-Hydroxybenzaldehyde **1** (10g, 8.2 mmol) was dissolved in freshly distilled acetone (150 mL). *n*-Butyl bromide (13.3 mL, 12.3 mmol), KI (13.6 g, 8.2 mmol) and K_2CO_3 (11.3 g, 8.2 mmol) were added to the solution. The reaction mass was refluxed for 6 h. Then the mixture was extracted with EtOAc / NaOH (0.1 M) once and with EtOAc/H_2O twice. The organic fraction was dried under Na_2SO_4 and evaporated under reduced pressure to provide **2** quantitatively (14 g). ^{1}H NMR δ_H ppm: 9.87 (s, 1H, CHO), 7.82 (d, ^3J = 8.7 Hz, 2H, CH), 6.98 (d, ^3J = 8.5 Hz, 2H, CH), 4.04 (t, ^3J = 6.5 Hz, 2H, OC*H*$_2$CH$_2$CH$_2$CH$_3$), 1.83–1.76 (m, 2H, OCH$_2$C*H*$_2$CH$_2$CH$_3$), 1.54–1.46 (m, 2H, OCH$_2$CH$_2$C*H*$_2$CH$_3$), 0.98 (t, 3H, ^3J = 7.4 Hz, OCH$_2$CH$_2$CH$_2$C*H*$_3$). ^{13}C NMR δ_C ppm: 190.98, 132.13, 129.90, 114.91, 68.25, 31.21, 19.29, 13.89.

*5,10,15,20-Tetra(4-butoxyphenyl)porphyrin **2H TBPP**.* 4-Butoxybenzaldehyde **2** (14.5 g, 80 mmol) and pyrrole (5.7 mL, 80 mmol) were dissolved in propionic acid (600 mL). The resulting mixture was heated to reflux upon vigorous stirring for 3.5 h. Afterwards the reaction mass was cooled and kept at *ca*. 5 °C overnight. The formed purple precipitate was filtered washed with cold EtOH. Then the mother liquor was partially evaporated, cooled to 5 °C and filtered again to provide additional portion of the reaction product. The porphyrin **2H TBPP** was obtained with 19% yield (3.46 g). ^{1}H NMR δ_H ppm: 8.86 (s, 8H, H$_\beta$), 8.11 (d, ^3J = 8.3 Hz, 8H, o-CH), 7.28 (d, ^3J = 8.5 Hz, 8H, m-CH), 4.27 (t, ^3J = 6.5 Hz, 8H, OC*H*$_2$CH$_2$CH$_2$CH$_3$), 2.01–1.95 (m, 8H, OCH$_2$C*H*$_2$CH$_2$CH$_3$), 1.68 (h, ^3J = 7.4 Hz, 8H, OCH$_2$CH$_2$C*H*$_2$CH$_3$), 1.11 (t, ^3J = 7.4 Hz, 12H, OCH$_2$CH$_2$CH$_2$C*H*$_3$), –2.73 (s, 2H, NH). ^{13}C NMR δ_C ppm: 59.16, 135.76, 134.65, 119.97, 112.88, 68.19, 31.75, 19.60, 14.15. MALDI-TOF MS *m/z*: $[M+H]^+$ calcd. for $C_{60}H_{63}N_4O_4$: 903.48, found 903.282. UV-Vis ($CHCl_3$) λ nm (lgε): 420 (5.78), 521 (4.33), 556 (4.20), 594 (3.85), 651 (3.87).

*5,10,15,20-Tetra-(4-butoxyphenyl)-porphyrinatoindium(III) chloride **In TBPP**.* **2H TBPP** (154 mg, 0.171 mmol) was dissolved in acetic acid (40 mL). $InCl_3$ (113 mg, 0.5139 mmol) and CH_3COONa (183 mg, 2.23 mmol) were added to the solution. The mixture was refluxed for about 10 h. upon stirring with TLC control. After complete consumption of the starting material, the mixture was cooled to ambient temperature and diluted with $CHCl_3$ (100 mL) and water (100 mL). The organic layer was separated, dried with Na_2SO_4 and evaporated to dryness. The solid product was applied in DCM to column packed with silica in DCM/MeOH and eluted with DCM/MeOH mixtures (0%→20% of MeOH). The fractions containing the target product were evaporated and purified by size-exclusion chromatography providing 73% (131 mg) of **In TBPP**. ^{1}H NMR δ_H ppm: 9.13 (s, 8H, H$_\beta$), 8.17 (dd, ^3J = 152.0, ^5J = 7.5 Hz, 8H, o-CH), 7.34 (dd, ^3J = 35.7, ^5J = 7.9 Hz, 8H, p-CH), 4.31 (s, 8H, OC*H*$_2$CH$_2$CH$_2$CH$_3$), 2.11–1.86 (m, 8H, OCH$_2$C*H*$_2$CH$_2$CH$_3$), 1.72 (h, ^3J = 7.4 Hz, 8H, OCH$_2$CH$_2$C*H*$_2$CH$_3$), 1.15 (t, ^3J = 7.4, 12H, OCH$_2$CH$_2$CH$_2$C*H*$_3$). ^{13}C NMR δ_C ppm: 159.39, 149.93, 136.35, 135.49, 134.18, 132.83, 121.67, 113.13, 112.90, 68.21, 31.73, 19.59, 14.14. MALDI-TOF MS *m/z*: $[M+H]^+$ calcd. for $C_{60}H_{61}ClInN_4O_4$: 1051.34, found 1051.13, $[M-Cl]^+$ calcd. for $C_{60}H_{60}InN_4O_4$: 1016.36, found 1016.11. UV-Vis ($CHCl_3$) λ nm (lgε): 409 (4.73), 429 (5.85), 564 (4.43), 607 (4.31).

Photocatalysis

Photosensitizer **2H TBPP** or **In TBPP** was dissolved in mixture of freshly distilled toluene to obtain porphyrin solution ($3.11\cdot10^{-3}$ M). Then an aliquot, containing required amount of photosensitizer (from 0.001 to 0.1 mol%), was added to a photocatalytic vial and dried. Then the photosensitizer was dissolved in mixture of freshly distilled toluene and ethanol (1/2 v/v, 1.5 mL). Dibutyl sulfide (0.5 mmol, 87 μL) and *o*-DCB (0.5 equiv., 28 μL) were added to the solution. Photocatalytic experiments were carried out in open vials, in a 12-position photoreactor, under vigorous stirring and under irradiation of a low-power LED lamp of blue (410–510 nm, 3 W), white (400–770 nm, 3 W) or red light (590–665 nm, 3 W) for 15–120 min without additional enrichment of the solution with oxygen. Then the reaction mass (200 μL) was evaporated for 5 min at 400 torr, 200 μL of CCl_4 and 200 μL of $CDCl_3$ were added. The results of the photocatalytic experiments were analyzed by ^{1}H NMR.

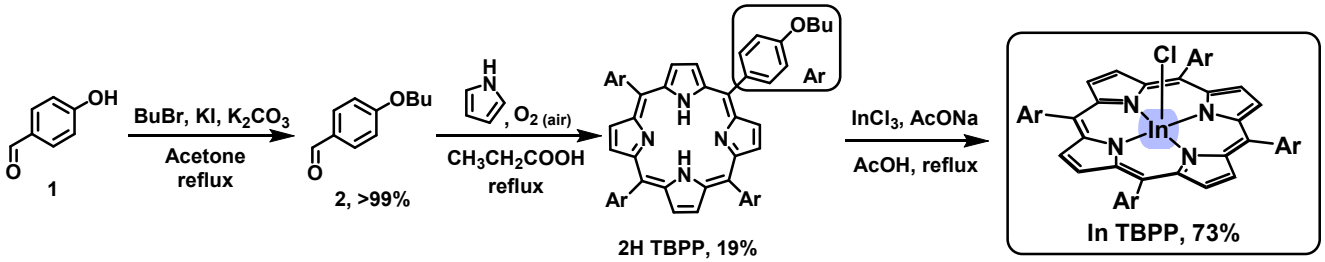
Photostability investigations

Photosensitizer **In TBPP** was dissolved in mixture of freshly distilled toluene and EtOH 1/2 (v/v) to obtain porphyrin solution (C_{start} = ~$5\cdot10^{-6}$ M). The solution was irradiated with a low-power LED lamp of blue (410–510 nm, 3 W) while stirring in a closed quartz cuvette (optical path of 10 mm) at room temperature. The photostability of the photosensitizer was analyzed for 1 h through the decrease of the Soret absorption band intensity.

Results and Discussion

At the first stage, symmetrical 5,10,15,20-tetra(4-butoxyphenyl)porphyrin **2H TBPP** was obtained. The choice of aromatic substituents in the *meso*-positions of the tetrapyrrole macrocycle was determined by the need of sufficient solubility of the macrocycle in various organic solvents including dichloromethane, chloroform, toluene, *etc*. Tetraarylporphyrin was synthesized by condensation of the 4-substituted benzaldehyde and pyrrole in refluxing propionic acid in accordance with the Adler procedure[39] (Scheme 1). In turn, the corresponding 4-butoxybenzaldehyde **2** was prepared by alkylation of 4-hydroxybenzaldehyde **1**. Metallation of **2H TBPP** was performed using indium chloride and sodium acetate upon reflux in acetic acid with 73% yield. The firstly obtained 5,10,15,20-tetra(4-butoxyphenyl)porphyrinato indium(III) chloride **In TBPP** was isolated in individual form and fully characterized by a set of physicochemical methods.

The structure of **In TBPP** was confirmed by NMR spectroscopy. The comparison of ^{1}H NMR spectra of the initial **2H TBPP** and **In TBPP** showed considerable complications of a set of resonances in the latter case (Figure 1). The presence of an axial ligand on the metal center of the complex led to a decrease in the symmetry of the molecule relatively to the mean plane of the macrocycle, which in turn determined magnetic non-equivalence of the protons of *meso*-substituents, oriented towards the ligand or *vice versa*.



Scheme 1. Synthesis of 5,10,15,20-tetra(4-butoxyphenyl)porphyrinatoindium(III) chloride **In TBPP**.

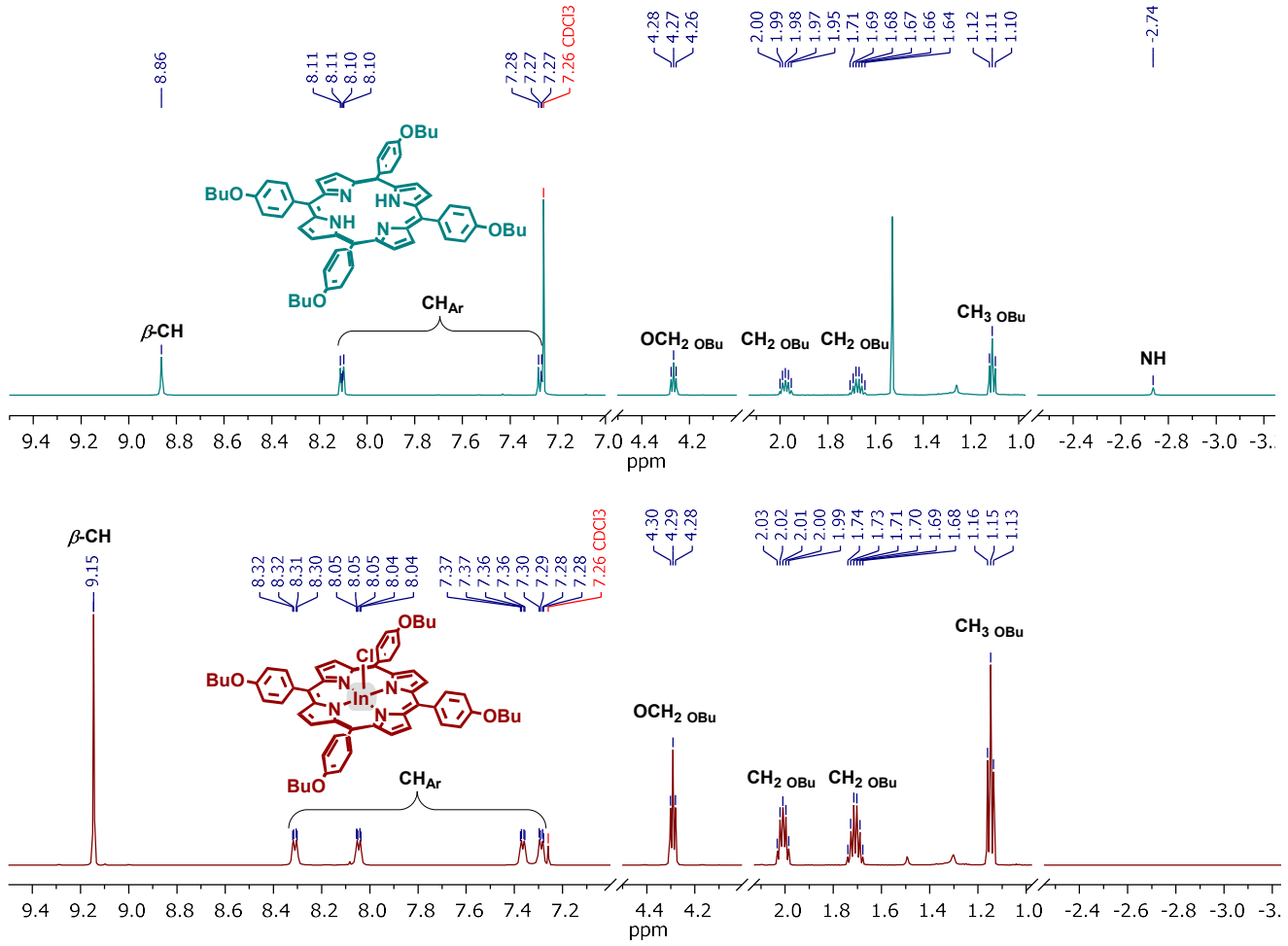
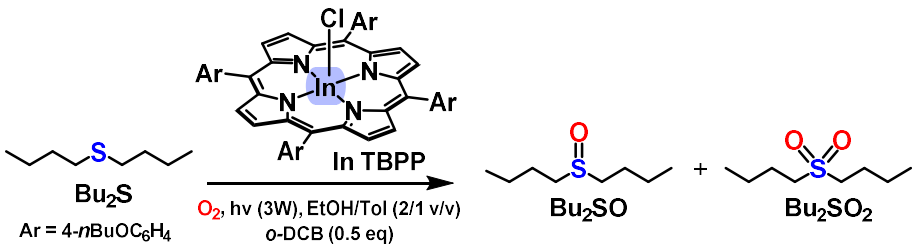


Figure 1. ^{1}H NMR of **2H TBPP** and **In TBPP** ($CDCl_3$).



Scheme 2. Model photocatalytic reaction of dibutyl sulfide oxidation.

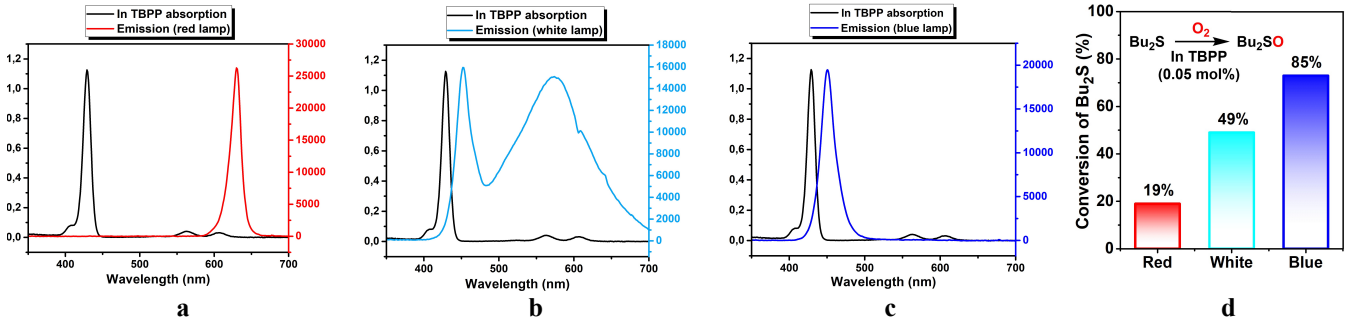


Figure 2. Normalized absorption spectra of **In TBPP** and emission spectra of red (a), white (b) and blue (c) LED lamps (3 W); photocatalytic performance in the presence of **In TBPP** under different lights (d).

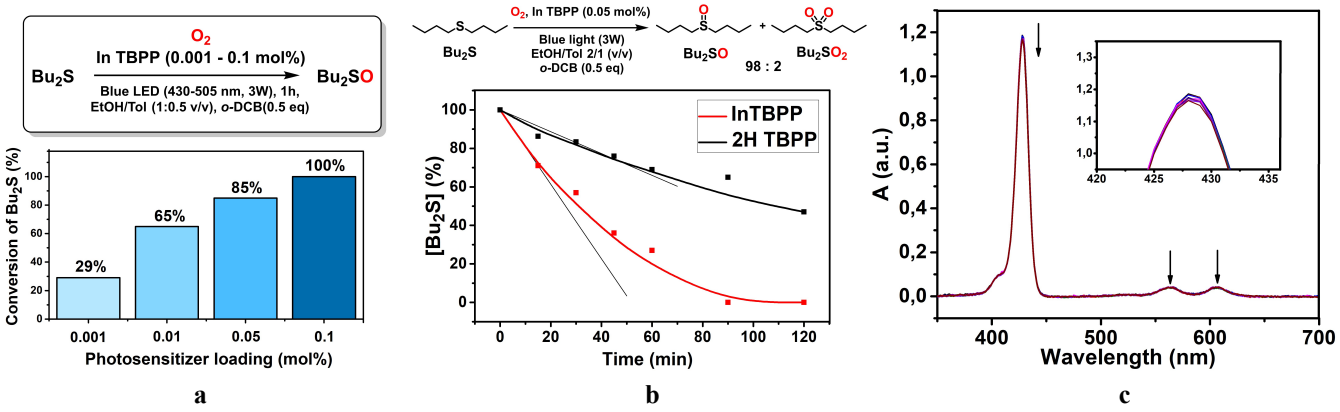


Figure 3. Dependence of dibutyl sulfide conversion on the catalyst loading of **In TBPP** (a); kinetics of photocatalytic oxidation of dibutyl sulfide in the presence of 0.05 mol% of **In TBPP** or **2H TBPP** (b); photostability investigation of **In TBPP** under blue light in Tol/EtOH 1/2 (v/v) for 1.5 h (c).

The photocatalytic activity of **In TBPP** was investigated using selective photooxidation of organic sulfide to corresponding sulfoxide. As mentioned before the oxidation of sulfur-containing organic compounds is of considerable interest, since the sulfoxide group is a constituent unit of various organic synthesis products.[40] In the present study the oxidation of dibutyl sulfide (**Bu_2S**) to dibutyl sulfoxide (**Bu_2SO**) was chosen as a model reaction (Scheme 2).

The photooxidation of organic sulfides requires additional stabilization of the intermediate persulfoxide, formed in course of the reaction.[41] This can be achieved by protonation of the persulfoxide, with a proton donor being a protic polar solvent, an acid added in catalytic amounts, or the sulfide itself containing protons in the α-position.[41] In the present study, toluene and ethanol as a polar protic co-solvent were used. This solvent system ensures sufficient solubility and high photostability of the porphyrinate in photocatalysis. A 12-position photoreactor was used to carry out the photocatalytic tests, where the reaction mass was irradiated using a low-power LED lamp (3 W).

At the first stage, the effect of the light source on the photocatalytic activity of **In TBPP** was studied. The experiments were carried out for one hour under irradiation with a low-power LED lamp (3 W) of red (590–665 nm), white (400–770 nm) and blue (410–510 nm) light (Figure 2,a-c). It was found that using **In TBPP** (0.05 mol%) after 1 h, the highest conversion of **Bu_2S** (85%) was observed when using the blue light source (Figure 2,d). The lowest conversion of **Bu_2S** was observed in this case of use of red light. Thus, the blue light source was chosen for the further experiments.

Interestingly, the photocatalytic activity of the porphyrin is considerably enhanced under the blue light irradiation, despite the fact that the emission of the white lamp overlaps not only with Soret band and also with both Q-bands. It is worth noting that the absorptions of Q-bands of porphyrin are 2 orders of magnitude decreased in comparison with Soret band. Therefore, their contribution to the photosensitization could be neglected. The maximum emission of the blue lamp is close to the Soret band, which provides the main absorption. Nevertheless, the observed photoactivity of porphyrin under white light opened up prospects for photocatalytic reactions under the ambient light.

Then the effect of photocatalyst loading on sulfide conversion was investigated. Photocatalytic experiments were carried out under blue light (410–510 nm, 3 W), ranging the loadings from 0.001 mol% to 0.1 mol%. After 1h the complete conversion of dibutyl sulfide **Bu_2S** was observed at 0.1 mol% of **In TBPP** (Figure 3,a). The selectivity of **Bu_2SO** formation under the conditions was more than 98%, which favorably affects this catalyst among the published similar photocatalysts for this reaction.[42,43] Further decrease of the photocatalyst loading rationally led to a decrease of the sulfide conversion. The loading of 0.05 mol% also showed a high degree of the substrate transformation (85%), and then we suggested that increasing the reaction time could allow achieving complete conversion.

Several experiments were carried out to evaluate the reaction rate using 0.05 mol% of the photocatalyst **In TBPP**. The reaction time was varied from 15 minutes to 2 h. It was shown that 100% conversion of **Bu_2S** was achieved in 1.5 h, while the selectivity for the formation of sulfoxide **Bu_2SO** was maintained at a level of 98–99% (Figure 3,b). With irradiation of the reaction mass for more than 1.5 h, no further overoxidation of **Bu_2S** to dibutyl sulfone **Bu_2SO_2** was observed. The turnover frequency of the photocatalyst (TOF) reached 1333 h^{-1}. When comparing the indium(III) complex as photocatalyst with the initial free base **2H TBPP**, the photooxidation rate in the presence of **In TBPP** (0.05 mol%) was shown to be significantly higher than in case of **2H TBPP** (Figure 3,b). The indium(III) porphyrinate provided 100% transformation after 2 h, while the free base **2H TBPP** provides only 53% conversion over the same time that could prove the implementation of the heavy atom effect.

Photostability seemed to be one of the key characteristics of the photosensitizers. The obtained indium(III) porphyrinate **In TBPP** remained photostable for 1.5 h under photoirradiation of blue light in mixture Tol/EtOH 1/2 (v/v). Its photobleaching did not exceed 0.5% (Figure 3,c), which allows us to consider this photosensitizer as quite robust among reported porphyrin and metalloporphyrin photocatalysts.[3,14,44]

Conclusions

In the present work, 5,10,15,20-tetrabutoxyphenylporphyrinato indium(III) chloride was prepared for the first time and fully characterized by a set of physicochemical analytical methods. The applicability of the indium(III) complex as a photocatalyst for the oxidation of organic sulfides was studied with dibutyl sulfide as example. The variation of the photooxidation conditions, namely the photocatalyst loading, the light irradiation source and the reaction time, it was found that this photosensitizer exhibits the highest photocatalytic activity under irradiation of blue light lamp. Complete conversion of dibutyl sulfide at an extremely low photocatalyst loading (0.05 mol%) is achieved in only 1.5 h. In all cases, the reaction proceeded with a high selectivity for the formation of dibutyl sulfoxide (98–99%). The prolonged irradiation didn't lead to the further overoxidation of the sulfide to corresponding sulfone. Also, the indium(III) porphyrinate turned out to be photostable under irradiation of with blue light and its photobleaching did not exceed 1%. Altogether, it makes this photosensitizer an efficient photocatalyst for sulfoxidation among those described earlier.

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References

1. Jin L., Lv S., Miao Y., Liu D., Song F. *ChemCatChem* **2021**, *13*, 140–152.
2. Li A., Pan B., Mu C., Wang N., Li Y.-L., Ouyang Q. *Synlett* **2021**, *32*, 679–684.
3. Shremzer E.S., Polivanovskaia D.A., Birin K.P., Gorbunova Y.G., Tsivadze A.Y. *Dyes Pigm.* **2023**, *210*, 110935.
4. Skolia E., Gkizis P.L., Kokotos C.G. *ChemPlusChem* **2022**, *87*, 1–16.
5. Johnson J.A., Zhang X., Reeson T.C., Chen Y.-S., Zhang J. *J. Am. Chem. Soc.* **2014**, *136*, 15881–15884.
6. Harriman A. *J. Chem. Soc., Faraday Trans. 2* **1981**, *77*, 1281–1291.
7. Solov'ev K.N., Borisevich E.A. *Physics-Uspekhi* **2005**, *48*, 231–253.
8. Da Silva A.R., Pelegrino A.C., Tedesco A.C., Jorge R.A. *J. Braz. Chem. Soc.* **2008**, *19*, 491–501.
9. Hajimohammadi M., Mofakham H., Safari N., Manesh A.M. *J. Porphyrins Phthalocyanines* **2012**, *16*, 93–100.
10. Pandey V., Jain D., Pareek N., Gupta I. *Inorg. Chim. Acta* **2020**, *502*, 119339.
11. Guo H., Xia H., Ma X., Chen K., Dang C., Zhao J., Dick B. *ACS Omega* **2020**, *5*, 10586–10595.
12. Azenha E.G., Serra A.C., Pineiro M., Pereira M.M., Seixas de Melo J., Arnaut L.G., Formosinho S.J., d'A Rocha Gonsalves A.M.. *Chem. Phys.* **2002**, *280*, 177–190.
13. da Silva A.R., Pelegrino A.C., Tedesco A.C., Jorge R.A. *J. Braz. Chem. Soc.* **2008**, *19*, 491–501.
14. Oparina A.D., Shremzer E.S., Polivanovskaia D.A., Birin K.P., Tsivadze A.Y. *J. Photochem. Photobiol. A Chem.* **2025**, 116389.
15. Shremzer E.S., Polivanovskaia D.A., Birin K.P., Tsivadze A.Y. *J. Catal.* **2025**, *450*, 116327.
16. Korobkov S.M., Birin K.P., Gorbunova Y.G., Tsivadze A.Y. *Dyes Pigm.* **2022**, *207*, 110696.
17. Polivanovskaia D.A., Abdulaeva I.A., Birin K.P., Gorbunova Y.G., Tsivadze A.Y. *ChemPlusChem* **2025**, *90*, e202400469.
18. Polivanovskaia D.A., Abdulaeva I.A., Birin K.P., Gorbunova Y.G., Tsivadze A.Y. *J. Catal.* **2022**, *413*, 342–352.
19. Korobkov S.M., Birin K.P., Tsivadze A.Y. *J. Catal.* **2025**, *445*, 116008.
20. Korobkov S.M., Birin K.P., Tsivadze A.Y. *Dyes Pigm.* **2023**, *220*, 111749.
21. Abdulaeva I.A., Filatov M.A., Kechiche A., Bessmertnykh-Lemeune A. *Molecules* **2025**, *30*, 864.
22. Isaac-Lam M.F., Hammonds D.M. *Pharmaceuticals* **2017**, *10*(2), 41.
23. Soy R.C., Babu B., Oluwole D.O., Nwaji N., Oyim J., Amuhaya E., Prinsloo E., Mack J., Nyokong T. *J. Porphyrins Phthalocyanines* **2019**, *23*, 34–45.
24. Makola L.C., Managa M., Nyokong T. *Photodiagn. Photodyn. Ther.* **2020**, *30*, 101736.
25. da Silva A.R., Inada N.M., Rettori D., Baratti M.O., Vercesi A.E., Jorge R.A. *J. Photochem. Photobiol. B Biol.* **2009**, *94*, 101–112.
26. Parthiban V., Yen P.Y.M., Uruma Y., Lai P.-S. *Bull. Chem. Soc. Jpn.* **2020**, *93*, 978–984.
27. Krylova L.V., Otvagin V.F., Gribova G.P., Kuzmina N.S., Fedotova E.A., Zelepukin I.V., Nyuchev A.V., Kustov A.V., Morshnev P.K., Berezin D.B., Koifman M.O., Vatsadze S.Z., Balalaeva I.V., Fedorov A.Y. *J. Med. Chem.* **2025**, *68*, 1901–1923.
28. Atmaca G.Y., Sabbagh N.K., Celep K., Şen P., Şahin F., Erdoğmuş A. *J. Mol. Struct.* **2025**, *1340*, 142583.
29. Afzaletdinova N.G., Ibatova E.R., Murinov Y.I. *Russ. J. Inorg. Chem.* **2006**, *51*, 971–976.
30. Mjalli F.S., Ahmed O.U., Al-Wahaibi T., Al-Wahaibi Y., AlNashef I.M. *Rev. Chem. Eng.* **2014**, *30*, 337–378.
31. Krivtsov E.B., Merzhigot M.I., Sviridenko Y.A. *ChemChemTech* **2025**, *68*(8), 101–111. doi: 10.6060/ivkkt.20256808.6t
32. Legros J., Dehli J.R., Bolm C. *Adv. Synth. Catal.* **2005**, *347*, 19–31.
33. Matsugi M., Hashimoto K., Inai M., Fukuda N., Furuta T., Minamikawa J., Otsuka S. *Tetrahedron: Asymmetry* **1995**, *6*, 2991–3000.

34. Fernández I., Khiar N. *Chem. Rev.* **2003**, *103*, 3651–3705.
35. Ognibene M., Pezzolo A. *Sci. Rep.* **2020**, *10*, 12902.
36. Formentini E.A., Mestorino O.N., Marino E.L., Errecalde J.O. *J. Vet. Pharmacol. Ther.* **2001**, *24*, 199–202.
37. Hainzl D., Cole L.M., Casida J.E. *Chem. Res. Toxicol.* **1998**, *11*, 1529–1535.
38. Armarego W.L.F. In: *Purification of Laboratory Chemicals*, Elsevier, **2017**. pp. 95–634.
39. Adler A.D., Longo F.R., Finarelli J.D., Goldmacher J., Assour J., Korsakoff L. *J. Org. Chem.* **1967**, *32*, 476–476.
40. Gittins D.I., Caruso F. *Angew. Chem., Int. Ed.* **2001**, *40*, 3001–3004.
41. Skolia E., Gkizis P.L., Nikitas N.F., Kokotos C.G. *Green Chem.* **2022**, *24*, 4108–4118.
42. Dang C., Zhu L., Guo H., Xia H., Zhao J., Dick B. *ACS Sustain. Chem. Eng.* **2018**, *6*, 15254–15263.
43. Guo Q., Ma Z., Zhou C., Ren Z., Yang X. *Chem. Rev.* **2019**, *119*, 11020–11041.
44. Kechiche A., Al Shehimy S., Khrouz L., Monnereau C., Bucher C., Parola S., Bessmertnykh-Lemeune A., Rousselin Y., Cheprakov A.V., Nasri H. *Dalton Trans.* **2024**, *53*, 7498–7516.

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