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**Статья**
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# Syntheses, Structures and Photosensitizing Properties of New Pt(II) and Pd(II) Porphyrinates

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*Platinum(II) and palladium(II) complexes of coproporphyrin-I tetraisopropyl ester and coproporphyrin-II tetraethyl ester, as well as platinum(II) complexes of mesopyropheophorbide a methyl ester and mesochlorin $e_6$ trimethyl ester were synthesized. Five of them (platinum(II) mesochlorin $e_6$ trimethyl ester is amorphous) were prepared as single crystals and structurally characterized by X-ray diffraction. The porphyrinates were used for sensitization of titania. The photocatalytic activity of the samples was studied in the reactions of methyl orange decomposition under UV irradiation ($\lambda = 250\text{-}400$ nm) or visible light ($\lambda > 450$ nm). The highest photocatalytic activity under UV radiation was found with the use of palladium(II) coproporphyrin-II tetraethyl ester. Under visible light, the best results were achieved for the titania–silica powder modified with platinum(II) coproporphyrin-II tetraethyl ester in the reaction of methyl orange decomposition carried out in the presence of sodium fluoride.*

**Keywords**: Coproporphyrin, chlorophyll *a*, chlorin $e_6$, pyropheophorbide *a*, palladium, platinum, metallocomplexes, photocatalysis, titania.

# Синтез, структуры и фотосенсибилизирующие свойства новых порфиринатов Pt(II) и Pd(II)

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*Синтезированы комплексы Pd(II) и Pt(II) тетраизопропилового эфира копропрфирина-I и тетраэтилового эфира копропорфирина-II, а также Pt(II) комплексы метилового эфира мезопирофеофорбида a и триметилового эфира мезохлорина $e_6$. Пять из них (Pt(II) триметиловый эфир мезохлорина $e_6$ является аморфным) были получены в виде монокристаллов и структурно охарактеризованы рентгеноструктурным анализом. Порфиринаты были использованы для сенсибилизации диоксида титана. Фотокаталитическая активность образцов была исследована в реакциях разложения метилового оранжевого при облучении ультрафиолетовым ($\lambda=250\text{-}400$ нм)*

*или видимым светом (λ>450 нм). При облучении ультрафиолетовым светом наибольшую фотокаталитическую активность проявил образец, для которого в качестве сенсибилизатора был использован Pd$^{II}$ тетраэтиловый эфир копропорфирина-II. При облучении видимым светом лучшие результаты были получены при использовании в качестве фотосенсибилизатора Pd$^{II}$ тетраэтилового эфира копропорфирина-II в присутствии фторида натрия.*

**Ключевые слова**: Копропорфирин, хлорофилл *a*, хлорин *e$_6$*, пирофеофорбид *a*, палладий, платина, металлокомплексы, фотокатализ, диоксид титана.

## Introduction

Porphyrins and related compounds have wide applications in different areas of science, technology and medicine because of unique photophysical and electrochemical properties. Natural porphyrins, chlorins and their metal complexes are of particular interest. Many achievements of supramolecular chemistry such as preparing new materials are associated with porphyrin molecules linked by intermolecular non-covalent bonds.[1-3] Porphyrins and chlorins have applications as versatile sensors for bioassay,[4,5] active entities in pharmacological drugs for diagnostics and therapy of oncologic diseases.[6] The fundamental investigations in searching new analytical sensors are carried out widely in the world.[7] Porphyrin and chlorin complexes with Pd$^{II}$ and Pt$^{II}$ show the highest phosphorescence quantum yields;[8] due to high extinction coefficients, these complexes are suggested as potential compounds for sensitive bioassays, *e.g.* as phosphorescent oxygen-sensitive materials.[9]

Porphyrins, phthalocyanines, and related compounds can be used as components of solar cells, including organic molecular solar cells, polymer cells, and dye-sensitized solar cells. The recent report of a porphyrin dye that achieves 12.3 % power conversion efficiency in a dye-sensitized solar cell indicates that these classes of compounds can be as efficient as the more commonly used ruthenium bipyridyl derivatives.[10] In particular, Cu$^{II}$ and Zn$^{II}$ coproporphyrinates were applied as sensitizers for thin film dye sensitized solar cells.[11]

Photocatalytic degradation of organic dyes, *e.g.* methyl orange,[12] and other organic compounds[13,14] using various (metal)porphyrin/TiO$_2$ complexes activated by visible light was studied. Coproporphyrins (and similar compounds) and their metal complexes seem to be promising sensitizers for titania nanoparticles in the reactions of photodegradation of organic pollutants, since they contain carboxylic groups, which can easily anchor titania surface.

The purpose of the work was to synthesize Pt$^{II}$ and Pd$^{II}$ complexes of coproporphyrins and chlorins and to study their structures and sensitizing properties.

## Experimental

### General Procedures

Syntheses of coproporphyrin I tetraisopropyl ester, coproporphyrin II tetraethyl ester, mesochlorin *e$_6$* trimethyl ester and mesopyropheophorbide *a* methyl ester was carried out as described in literature.[15,16] All other chemicals were used as purchased. Reagent grade solvents were dried by refluxing over P$_2$O$_5$ (chloroform), calcium hydride (acetonitrile, benzonitrile and dicloromethane), sodium (hexane).

$^1$H NMR spectra were recorded at 298 K on a Bruker Avance III 600 spectrometer operating at 600.13 MHz; $^{195}$Pt NMR spectra were recorded at 298 K on a Bruker Avance III 600 spectrometer operating at 129.01 MHz. $^1$H NMR spectra were referenced to residual protio-solvent resonances, $^{195}$Pt NMR spectra were referenced to 1.2 M Na$_2$PtCl$_6$ in D$_2$O. UV-vis spectra were recorded on a Hitachi U-2900 and Akvilon SF 103. The mass spectra were recorded on MALDI TOF Bruker spectrometer. X-ray powder diffraction patterns of sensitized titania were recorded on a HZG-4A diffractometer, Cu$K_\alpha$ radiation. X-ray monocrystal diffraction experiments were carried out on a Bruker KAPPA APEX II autodiffractometer (Mo$K_\alpha$ radiation, graphite monochromator).

*Platinum(II) coproporphyrin-I tetraisopropyl ester; 2,7,12,17-tetra(isopropiloxycarbonylethyl)-3,8,13,18-tetramethylporphyrinatoplatinum(II) (1).* Coproporphyrin I tetraisopropyl ester (40 mg, 48.6 μmol) was dissolved in benzonitrile (5 ml) and Pt(PhCN)$_2$Cl$_2$ (68.7 mg, 145.8 μmol) was added. The mixture was stirred under argon atmosphere at 165 ºC for 3 h. The solution was cooled and then evaporated to dryness under reduced pressure and purified by silica gel column chromatography (CH$_2$Cl$_2$/MeOH 10:1). The product was precipitated from CH$_2$Cl$_2$ (4 ml) with hexane (2 ml) yielding 37 mg (75 %) of compound **1** as orange solid. $^1$H NMR (CDCl$_3$, 600 MHz) δ$_H$ ppm: 1.16 (24H, d, *J* = 6.3, CH$_3^{i-Pr}$), 3.10 (8H, t, *J* = 8.01, CH$_2$CH$_2$COO), 3.41 (12H, s, β-CH$_3$), 4.14 (8H, t, *J* = 7.8, COOCH$_2$CH$_3$), 5.11 (4H, sept, CH$^{i-Pr}$), 9.55 (4H, s, *meso*-H). $^{195}$Pt NMR (CDCl$_3$, 129.008 MHz) δ$_{Pt}$ ppm: -3206.93. MS (MALDI): *m/z* 1015.2 (calculated for [M+H]$^+$ 1015.2). UV-vis (CHCl$_3$) λ$_{max}$ nm (lgε): 382 (242), 503 (11.1), 536 (44.0).

*Palladium(II) coproporphyrin-I tetraisopropyl ester; 2,7,12,17-tetra(isopropiloxycarbonylethyl)-3,8,13,18-tetramethylporphyrinatopalladium(II) (2).* Coproporphyrin I tetraisopropyl ester (40 mg, 48.6 μmol) was dissolved in acetonitrile (5 ml) and Pd(CH$_3$CN)$_2$Cl$_2$ (12.6 mg, 145.8 μmol) was added. The mixture was refluxed under argon atmosphere for 3 h. The solution was cooled and then evaporated to dryness under reduced pressure and purified by silica gel column chromatography (CH$_2$Cl$_2$/MeOH 10:1). The product was precipitated from CH$_2$Cl$_2$ (4 ml) with hexane (2 ml) yielding 39.5 mg (80 %) of compound **2** as orange solid. $^1$H NMR (CDCl$_3$, 600 MHz) δ$_H$ ppm: 1.07 (24H, d, *J* = 6.3, CH$_3^{i-Pr}$), 3.09 (8H, t, *J* = 8.01, CH$_2$CH$_2$COO), 3.46 (12H, s, β-CH$_3$), 4.18 (8H, t, *J* = 7.8, COOCH$_2$CH$_3$), 4.99 (4H, sept, CH$^{i-Pr}$), 9.76 (4H, s, *meso*-H). MS (MALDI): *m/z* 926.4 (calculated for [M+H]$^+$ 926.4). UV-vis (CHCl$_3$) λ$_{max}$ nm (lgε): 394 (254), 513 (12.4), 547 (45.6).

*Platinum(II) coproporphyrin-II tetraethyl ester; 2,8,12,18-tetra(ethoxycarbonylethyl)-3,7,13,17-tetramethylporphyrinatoplatinum(II) (3).* Coproporphyrin II tetraethyl ester (40 mg, 52.2 μmol) was dissolved in benzonitrile (5 ml) and Pt(PhCN)$_2$Cl$_2$ (73.7 mg, 156.6 μmol) was added. The mixture was stirred under argon atmosphere at 165 ºC for 3h. The solution was cooled and then evaporated to dryness under reduced pressure and purified by silica gel column chromatography (CH$_2$Cl$_2$/MeOH 100:1). The product was precipitated from CH$_2$Cl$_2$ (4 ml) with hexane (2 ml) yielding 35 mg (70 %) of compound **3** as orange solid. $^1$H NMR (CDCl$_3$, 600 MHz) δ$_H$ ppm: 1.12 (12H, t, *J* = 7.8, COOCH$_2$CH$_3$), 3.24 (8H, t, *J*

= 7.8, CH$_2$CH$_2$COO), 3.56 (12H, s, β-CH$_3$), 4.14 (8H, q, $J$ = 7.2, COOCH$_2$CH$_3$), 4.30 (8H, t, $J$ = 7.8, CH$_2$CH$_2$COO), 9.94 (2H, s, *meso*-H), 9.97 (2H, s, *meso*-H). $^{195}$Pt NMR (CDCl$_3$, 129.008 MHz) δ$_{Pt}$ ppm: -3217.10. MS (MALDI): *m/z* 960.3 (calculated for [M+H]$^+$ 960.3). UV-vis (CHCl$_3$) λ$_{max}$ nm (lgε): 381 (242), 501 (11.1), 536 (44.0).

*Palladium(II) coproporphyrin-II tetraethyl ester; 2,8,12,18-tetra(ethoxycarbonylethyl)-3,7,13,17-tetramethylporphyrinato-palladium(II) (4).* Coproporphyrin II tetraethyl ester (40 mg, 52.2 μmol) was dissolved in acetonitrile (5 ml) and Pd(CH$_3$CN)$_2$Cl$_2$ (13.5 mg, 156.6 μmol) was added. The mixture was refluxed under argon atmosphere for 3 h. The solution was cooled and then evaporated to dryness under reduced pressure and purified by silica gel column chromatography (CH$_2$Cl$_2$/MeOH 100:1). The product was precipitated from CH$_2$Cl$_2$ (4 ml) with hexane (2 ml) yielding 36.3 mg (80 %) of compound **4** as orange solid. $^1$H NMR (CDCl$_3$, 600 MHz) δ$_H$ ppm: 1.14 (12H, t, $J$ = 7.8, COOCH$_2$CH$_3$), 3.28 (8H, t, $J$ = 7.8, CH$_2$CH$_2$COO), 3.58 (12H, s, β-CH$_3$), 4.16 (8H, q, $J$ = 7.2, COOCH$_2$CH$_3$), 4.39 (8H, t, $J$ = 7.8, CH$_2$CH$_2$COO), 10.10 (2H, s, *meso*-H), 10.12 (2H, s, *meso*-H). MS (MALDI): *m/z* 871.28 (calculated for [M+H]$^+$ 871.28). UV-vis (CHCl$_3$) λ$_{max}$ nm (lgε): 393 (258), 511 (13.2), 546(48.0).

*Platinum(II) mesopyropheophorbide a methyl ester; (17S, 18S)-7,12-diethyl-2',2²,17,18-tetrahydro-3,8,13,17-tetramethyl-2¹-oxo-18-(methoxycarbonylethyl)cyclopenta[at]porphyrinato platinum(II) (5).* Mesopyropheophorbide *a* methyl ester (50 mg, 90.8 μmol) was dissolved in propionic acid (10 ml) and Pt(PhCN)$_2$Cl$_2$ (214 mg, 45.4 μmol) was added. The mixture was refluxed under argon atmosphere for 30 minutes. Sodium acetate (38.2 mg, 45.4 μmol) was added gradually by small portions for 30 minutes. The solution was cooled and then evaporated to dryness under reduced

pressure and purified by silica gel column chromatography (CH$_2$Cl$_2$/MeOH 96:4). The product was precipitated from CH$_2$Cl$_2$ (4 ml) with hexane (2 ml) yielding 39.5 mg (80 %) of compound **5** as blue solid. $^1$H NMR (CDCl$_3$, 600 MHz) δ$_H$ ppm: 1.67 (3H, t, $J$ = 7.6, 8²-CH$_3$), 1.72 (3H, t, $J$ = 7.8, 3²- CH$_3$), 1.78 (3H, d, $J$ = 7.3, 18-CH$_3$), 2.22 (1H, m, 17¹- CH$_2$$^a$), 2.28 (1H, m, 17²- CH$_2$$^a$), 2.51 (1H, m, 17¹- CH$_2$$^b$), 2.54 (1H, m,17²-CH$_2$$^b$), 3.17 (3H, s, 7-CH$_3$), 3.20 (3H, s, 2-CH$_3$), 3.60 (3H, s, 12-CH$_3$), 3.63 (2H, q, $J$ = 7.8, 8¹-CH$_2$), 3.65 (3H, s, 17⁴-COOCH$_3$), 3.72 (2H, q, $J$ = 7.8, 3¹-CH$_2$), 4.30 (1H, m, 17H), 4.57 (1H, q, $J$ = 7.3, 18H), 4.99 (1H, d, $J$ = 19.0, 15-CH$_2$$^a$), 5.06 (1H, d, $J$ = 19.0, 15-CH$_2$$^b$), 8.54 (1H, s, 20H), 9.22 (1H, s, 5H), 9.44 (1H, s, 10H). $^{195}$Pt NMR (CDCl$_3$, 129.008 MHz) δ$_{Pt}$ ppm: -2903.75. MS (MALDI): *m/z* 743.4 (calculated for [M+H]$^+$ 743.4). UV-vis (CHCl$_3$) λ$_{max}$ nm (lgε): 388.5 (268), 403.5 (302), 480 (10.7), 521.5 (15.4), 584 (46.2), 625 (273.6).

*Platinum(II) mesochlorin e$_6$ trimethyl ester; (7S,8S)-2,8,12,17-tetramethyl-7,8-dihydro-13,18-diethyl-5-(carboxymethyl)-3-carboxy, 7-propionic acid-21H,23H-porphinatoplatinum(II) (6).* Mesochlorin e$_6$ trimethyl ester (100 mg, 156.2 μmol) was dissolved in benzonitrile (5 ml) and Pt(PhCN)$_2$Cl$_2$ (221 mg, 469.0 μmol) was added. The mixture was stirred at 160 ºC under argon atmosphere for 4 h. Sodium acetate (39.4 mg, 469.0 μmol) was added gradually by small portions for 3 h. The solution was cooled and then evaporated to dryness under reduced pressure and purified by silica gel column chromatography (CH$_2$Cl$_2$/MeOH 96:4). The product was precipitated from CH$_2$Cl$_2$ (4 ml) with hexane (2 ml) yielding 39.5 mg (80 %) of compound **6** as blue solid. $^1$H NMR (CDCl$_3$, 600 MHz) δ$_H$ ppm: 1.68 (3H, t, $J$=7.8, 8²-CH$_3$), 1.72 (3H, t, $J$ = 7.7, 3²- CH$_3$), 1.77 (3H, d, $J$ = 7.3, 18-CH$_3$), 2.03 (1H, m, 17¹-CH$_2$$^a$), 2.17 (1H, m, 17²- CH$_2$$^a$), 2.21 (1H, m, 17¹- CH$_2$$^b$), 2.54 (1H, m,17²-CH$_2$$^b$), 3.18 (3H, s, 7-CH$_3$), 3.25 (3H, s, 2-CH$_3$), 3.51 (3H, s,
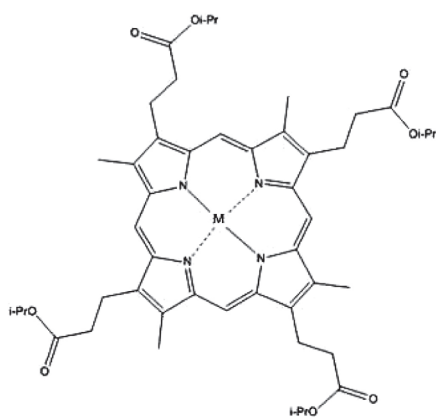


M = Pt (**1**), Pd (**2**)
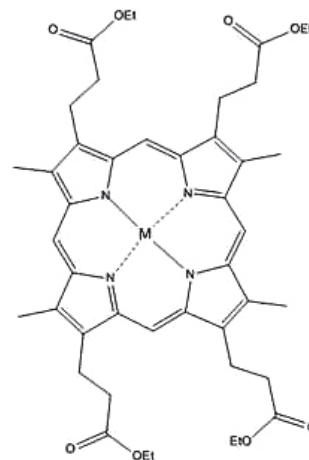


M = Pt (**3**), Pd (**4**)
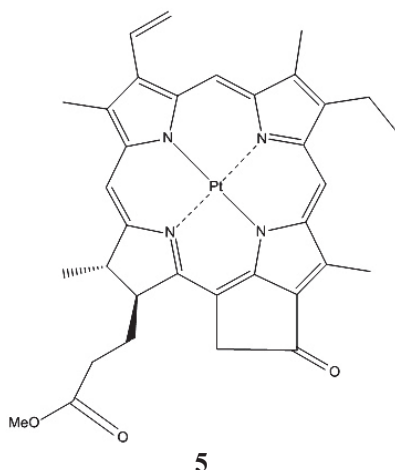


**5**
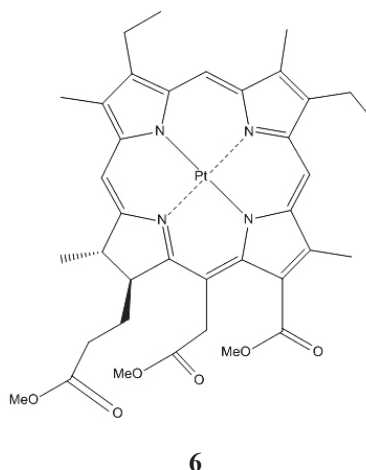


**6**

12-CH$_3$), 3.64 (3H, s, 17$^4$-COOCH$_3$), 3.70 (2H, q, *J* = 7.8, 8$^1$-CH$_2$), 3.75 (2H, q, *J* = 7.7, 3$^1$-CH$_2$), 3.89 (3H, s, 15$^3$-COOCH$_3$), 4.21 (3H, s, 13$^2$-COOCH$_3$), 4.38 (1H, dd, *J* = 10.3, *J* = 2.8, 17H), 4.42 (1H, q, *J* = 7.3, 18H), 4.94 (1H, d, *J* = 19.7, 15-CH$_2$$^a$), 5.13 (1H, d, *J* = 19.7, 15-CH$_2$$^b$), 8.64 (1H, s, 20H), 9.38 (1H, s, 5H), 9.50 (1H, s, 10-H). $^{195}$Pt NMR (CDCl$_3$, 129.008 MHz) δ$_{Pt}$ ppm: -2903.75. MS (MALDI): *m/z* 833.2 (calculated for [M+H]$^+$ 833.2). UV-vis (CHCl$_3$) λ$_{max}$ nm (lgε): 388 (242), 475(12.5), 563 (11.1), 602(72.0).

### Sensitization of Titania

*Method 1.* Titanium(IV) oxysulfate sulfuric acid hydrate (7.35 g) was mixed with 40 ml of distilled water, heated till clearing and aged at 90-95 °C for 4 min. Then a corresponding porphyrinate **1-6** (*ca.* 15 mg) pre-dissolved in acetic acid (20 ml) was added. The suspension was stirred at 65-70 °C for 15 min. The resulting solid was filtered off, washed with water and acetone and annealed at 90-110 °C for 1 h.

For studying the process of titania coating with complex **6**, the commercial solution of TiOSO$_4$ in sulfuric acid (15 %, 21 ml) was heated to 80 °C under stirring, stirred at this temperature for 3 min, cooled to room temperature, and mixed with the solution of complex **6** (15 mg) in acetic acid (20 ml). The reaction mixture was allowed to stay at room temperature for 3 h and then at 90-94 °C for 12 min. The process was monitored by UV-vis spectrometry.

*Method 2.* Titanium(IV) oxysulfate sulfuric acid hydrate (7.35 g) was mixed with 100 ml of distilled water, heated up to boiling and aged at 95-98 °C for 10 min. Then the reaction mixture was cooled down to 75-80 °C, and porphyrinate **5** (*ca.* 15 mg) pre-dissolved in acetic acid (20 ml) was added. The suspension was stirred at 70±0.5 °C for 7 h. The resulting solid was filtered off, washed with water and acetone and annealed at 90-110 °C for 1 h.

*Method 3.* Titanium(IV) oxysulfate sulfuric acid hydrate (7.35 g) was mixed with 40 ml of distilled water, heated till clearing and aged at 90-95 °C for 4 min. Then ultra-dispersed SiO$_2$ (Aeroxide, specific surface area 400 m$^2$/g) (*ca.* 2 g) suspended in the solution of a corresponding porphyrinate **3** or **6** (*ca.* 15 mg) in acetic acid (20 ml) was added. The suspension was stirred at 60-65 °C under UV irradiation for 1 h. The resulting solid was filtered off, washed with water and acetone and annealed at 90-110 °C for 1 h.

### Structure Determination and Refinements

X-ray diffraction experiments were carried out on a Bruker KAPPA APEX II automated diffractometer (MoK$_α$ radiation, graphite monochromator).[17] Data reduction was made using the SAINT-Plus program.[18] Absorption correction was made using the SADABS program.[19] The structures were solved by the direct method (SHELXS97) and refined on *F*$^2$ with the full-matrix least-squares procedure (SHELXL97)[20] using all reflections. All non-hydrogen atoms were refined with anisotropic displacement factors.

The H atoms were placed in geometrically calculated positions with isotropic displacement factors equal to 1.2 (for CH and CH$_2$ groups) and 1.5 (for CH$_3$ groups) multiplied *U*$_{eq}$ of adjacent C atoms. Orientation of several CH$_3$ groups was refined.

The Flack parameter *x*[21] for **5** shows the correctness of the determination of the chemical absolute configuration.[22,23]

Data collection and structure refinement details are listed in Table 1.

### Photocatalysis

The photocatalytic activity of the samples was studied in the reactions of methyl orange decomposition at a dye concentration of 1.04 mmol/l and a catalyst content of 0.1 g/l under UV irradiation (λ = 250-400 nm) or visible light (λ > 450 nm). In some cases, NaF (0.1 M) was added. The dye concentration was monitored by recording the intensity of the absorption band of the chromophore group at λ = 490-510 nm.

## Results and Discussion

Palladium(II) coproporphyrinates were prepared by a new method based on the reaction of Pd(CH$_3$CN)$_2$Cl$_2$

**Table 1**. Crystal data and structure refinement for the complexes.

| Parameter | 1 | 2 | 3 | 4 | 5 |
|---|---|---|---|---|---|
| Empirical formula | C$_{48}$H$_{60}$N$_4$O$_8$Pt | C$_{48}$H$_{60}$N$_4$O$_8$Pd | C$_{44}$H$_{52}$N$_4$O$_8$Pt | C$_{44}$H$_{52}$N$_4$O$_8$Pd | C$_{34}$H$_{36}$N$_4$O$_3$Pt |
| Molecular weight | 1015.14 | 926.34 | 959.34 | 870.28 | 743.24 |
| Crystal system | monoclinic | monoclinic | monoclinic | monoclinic | orthorhombic |
| Space group | *P*2$_1$/*c* | *P*2$_1$/*c* | *C*2/*c* | *C*2/*c* | *P*2$_1$2$_1$2$_1$ |
| *a*, Å | 5.3661(3) | 5.3701(10) | 38.354(3) | 38.376(8) | 8.1711(5) |
| *b*, Å | 14.9404(11) | 14.940(4) | 5.0214(4) | 5.0050(9) | 14.3884(10) |
| *c*, Å | 29.201(2) | 29.105(8) | 21.6175(14) | 20.872(4) | 24.6378(18) |
| α,deg | 90.00 | 90.00 | 90.00 | 90.00 | 90.00 |
| β, deg | 90.8910(10) | 91.048(5) | 90.951(4) | 92.472(4) | 90.00 |
| γ, deg | 90.00 | 90.00 | 90.00 | 90.00 | 90.00 |
| *V*, Å$^3$ | 2340.8(3) | 2334.7(10) | 4162.8(5) | 4005.1(13) | 2896.6(3) |
| Z | 2 | 2 | 4 | 4 | 4 |
| *T*, K | 293(2) | 293(2) | 293(2) | 100(2) | 293(2) |
| μ, mm$^{-1}$ | 3.053 | 0.453 | 3.428 | 0.523 | 4.887 |
| Unique reflections | 5310 | 5208 | 4765 | 3472 | 6638 |
| Observed reflections | 3516 | 2403 | 3065 | 2127 | 5475 |
| *R* [I$_0$≥2σI$_0$] | 0.0355 | 0.0735 | 0.0325 | 0.0601 | 0.0391 |
| *R$_w$* [I$_0$≥2σI$_0$] | 0.0793 | 0.1466 | 0.0646 | 0.1137 | 0.0607 |
| Goodness of fit | 1.062 | 0.942 | 1.000 | 0.964 | 1.009 |

with coproporphyrins (3:1) in acetonitrile. In contrast to the earlier reported method of synthesizing palladium(II) coproporphyrinates in more rigid conditions (PdCl$_2$ in DMF at 153 °C[24] or Pd(PhCN)$_2$Cl$_2$ in benzonitrile at 160 °C[25]) this method allows to carry out the reactions in milder conditions with higher yields. Platinum(II) complexes were prepared under heating in water-free benzonitrile in Ar atmosphere; in other conditions, the yield was low due to porphyrin degradation.

Five porphyrinate structures **1-5** were refined from single crystal data. Single crystals of the compounds were grown at the phase boundary in the CH$_2$Cl$_2$:EtOAc mixtures under isothermal conditions. Complex **6** is amorphous. As shown in Figures 1-5, the porphyrin core in all five structures has standard square-plane configuration. In structure **5**, it is less symmetric than in structures **1-4**, the C–N distances varying in the 1.335-1.402 and 1.355-1.384 Å ranges, respectively. The Pd-N bond lengths in **2**, **4** fall within the 2.005-2.21 Å range, while the Pt-N distances are 2.024-2.025, 2.17-2.018, and 1.991-2.069 Å in **1**, **3**, and **5**, respectively. The N–M–N angles are close to 90°, excepting one angle in **5** (87.44°).
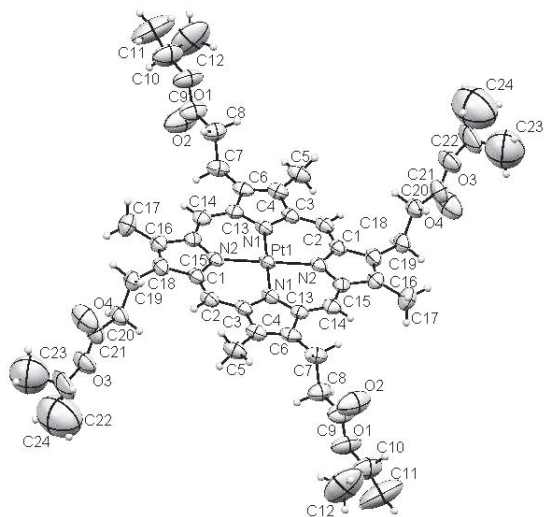
For sensitization of titania with the synthesized porphyrinates, **1-6** were pre-dissolved in acetic acid by stirring at 75-80 °C for 0.5-1 h. Solubility of complexes **1-6** in acetic acid is caused by hydrolysis of ether groups and formation of carboxylic groups on the porphyrinate periphery. Carboxylic groups can anchor the titania surface fixing complex molecules. The process of titania sensitization with complex **6** was monitored step by step by recording UV-vis spectra (Figure 6). Dissolution of **6** in acetic acid causes significant changes in its UV-vis spectrum (Figure 6) reflecting hydrolysis of the ether group. Addition of the equal volume of the TiOSO$_4$ solution results in the two-fold reduction of intensity of the band at 476 nm. The band at 443 nm shifts to lower wavelength and approaches to the edge of titania absorption which, in turn, is shifted to higher
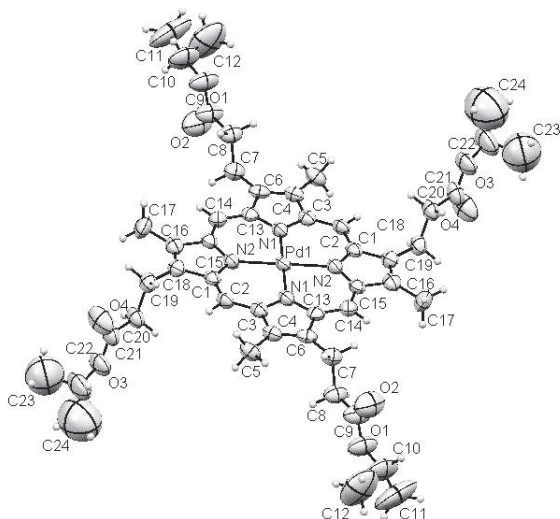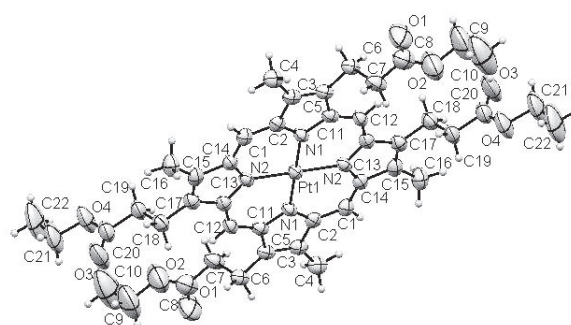


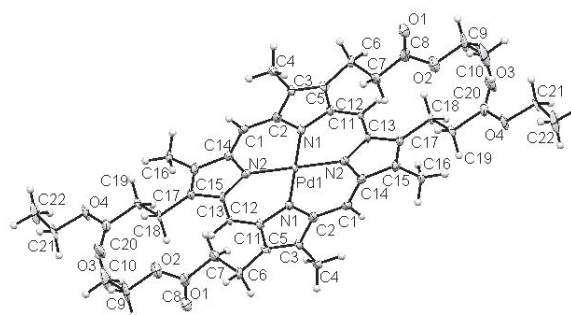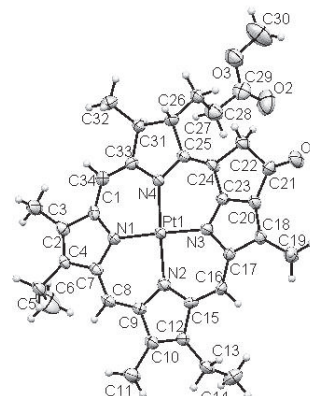**Figure 3.** Crystal structure of **3**.



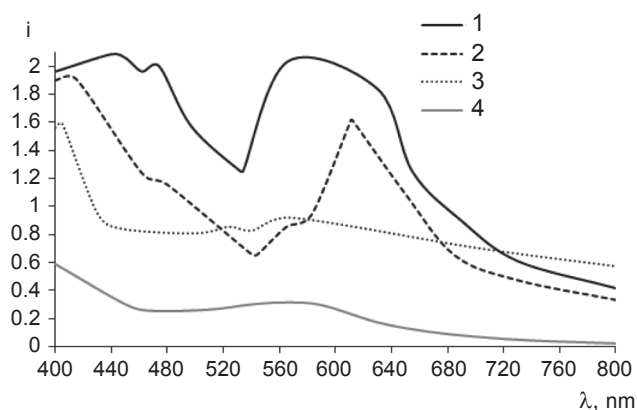**Figure 4.** Crystal structure of **4**.



**Figure 1.** Crystal structure of **1**.



**Figure 2.** Crystal structure of **2**.



**Figure 5.** Crystal structure of **5**.

**Figure 6.** UV-vis spectra of complex **6** after dissolving in acetic acid (*1*), mixing with $TiOSO_4$ solution (*2*), and heating for 17 min (*3*) and 3 h (*4*).

wavelength as compared to a pure titania sol (398 nm). The band at *ca*. 580 nm shifts to 612 nm, its intensity reduces slightly. Heating the reaction mixture decreases intensities of the bands; this may be caused by removal of the porphyrinate from the solution.

The samples of sensitized titania show noticeable photocatalytic activity under UV radiation (Table 2), which is comparable to pure titania. However, the current area of interest in this field has been the modification of $TiO_2$ sensitive to visible light.[26] Sensitization of titania with **1-6** by method 1 results in weak photocatalytic activity under visible light
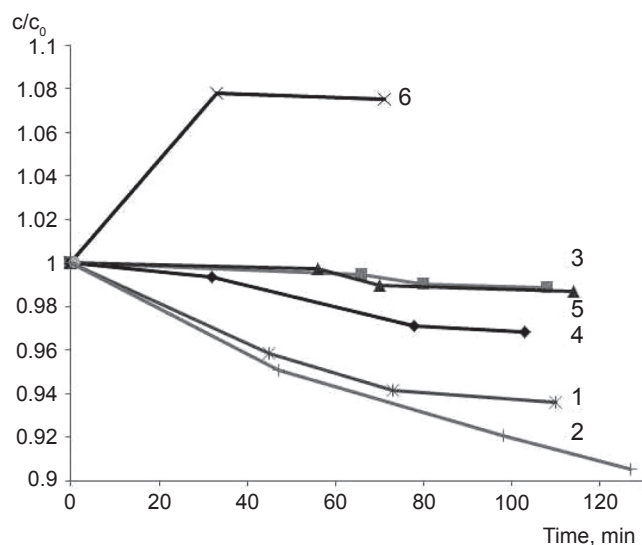


**Figure 7.** Kinetic curves for decolorization of methyl orange, $c_0 = 1.04$ mmol/l, p*H* 5, OSRAM halogen lamp (*P* = 60 W, $\lambda$ = 450-700 nm), in the presence of $TiO_2$ modified by method 1 with **1-6** (*1-6*, respectively).

(Figure 7, Table 2). It does not exceed the photocatalytic activity of the samples with tetraphenylporphyrinates reported in [12]. The best results are achieved for **2**. The apparent increase of dye concentration in the case of **6** is caused by the remove of the colored complex from the titania surface into the reaction mixture. Probably, the presence of only one carboxylic group prevents strong bonding of the compound to the titania surface.

Increase of duration of the sensitization process from 15 min to 7 h (method 2) leads to the three-fold increase photocatalytic activity of titania (Figure 8, Table 2), however, it is still lower than for the samples reported in [12].
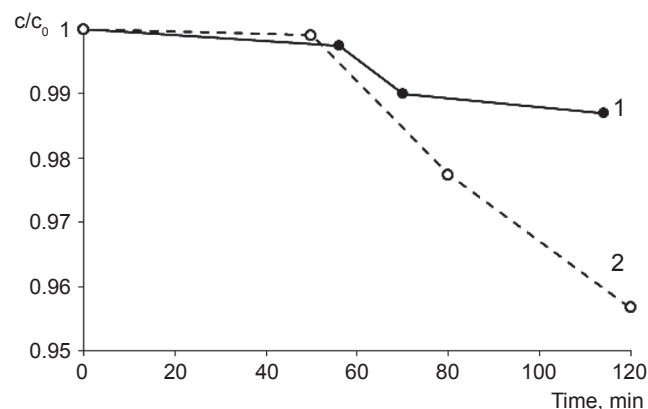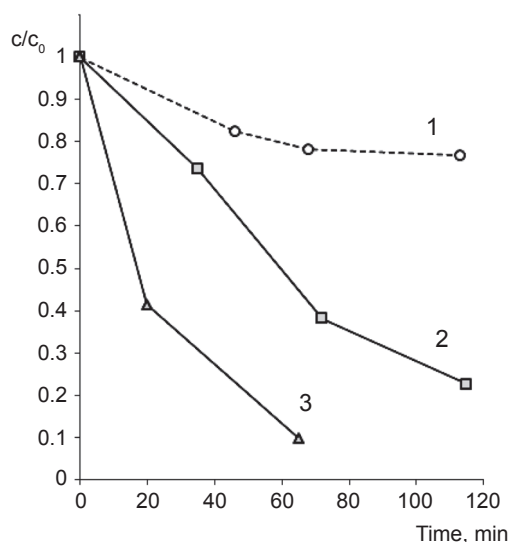


**Figure 8.** Kinetic curves for decolorization of methyl orange, $c_0 = 1.04$ mmol/l, p*H* 5, OSRAM halogen lamp (*P* = 60 W, $\lambda$ = 450-700 nm), in the presence of $TiO_2$ modified with **5** by methods 1 (*1*) and 2 (*2*).

Taking into account high affinity of carboxylic groups to silica and information of visible-light photocatalytic activity of porphyrin-sensitized silica–titania composites,[27] we applied method 3 for better coating the titania surface with porphyrinates. Sensitization of titania with method 3 by complex **6** resulted in drastic increase of the photocatalytic activity as compared to method 1 (Figure 9, curve *1*; Table 2). However, application of method 3 to complex **3** gave a colorless product, which should show no photocatalytic activity under visible light.

Fluorinated $TiO_2$ particles are known to cause photocatalytic degradation of dyes under visible irradiation.[28] Therefore, we proposed that addition of NaF into the reaction mixture should affect the photocatalytic reaction. The result was the noticeable increase of photocatalytic activity of the samples (Figure 9, curves *2* and *3*; Table 2). Application of method 3 to complex **3** (containing 4 carboxylic groups) combined with addition of NaF gave the photocatalytic

**Table 2.** Rate constants (min⁻¹) of methyl orange decolorization for the samples of titania sensitized with **1-6** by various methods.

| Method | 1 | 2 | 3 | | 4 | | 5 | | 6 | |
|---|---|---|---|---|---|---|---|---|---|---|
| | visible | visible | UV | visible | UV | visible | UV | visible | UV | visible |
| 1 | 0.00062 | 0.00077 | 0.0316 | 0.00010 | 0.0490 | 0.00033 | 0.0188 | 0.00011 | | |
| 2 | | | | | | | 0.0215 | 0.00038 | | |
| 3 | | | 0.0573 | 0.00236 | | | | | 0.0467 | |
| 3 (+NaF) | | | | 0.0351 | | | | | | 0.0134 |

**Figure 9.** Kinetic curves for decolorization of methyl orange, $c_0$ = 1.04 mmol/l, p$H$ 5, OSRAM halogen lamp ($P$ = 60 W, $\lambda$ = 450–700 nm), in the presence of TiO$_2$ modified by method 3 with **3** (*1*); with **6** (*2*) and **3** (*3*) on addition of NaF (0.1 M).

activity much higher than reported in [12]. It approaches to the best earlier reported visible-light photocatalyst, N,Ag-doped titania; with its use, complete decomposition of methyl orange took 1.5 h.[29]

The detailed mechanism of methyl orange dye catalyzed degradation states that conduction band electrons (e•) and valence band holes (h+) are generated when aqueous TiO$_2$ suspension is irradiated with light energy greater than its band gap energy.[30] Sensitization of titania with colored porphyrinates moves the band gap of pure titania (3.2 eV for anatase) to lower values corresponding to visible light range.

In this work, the highest photocatalytic activity of porphyrinate-modified titania under UV radiation was found with the use of palladium(II) coproporphyrin-II tetraethyl. Under visible light, the best results were achieved for the titania–silica powder sensitized with platinum(II) coproporphyrin-II tetraethyl ester in the reaction of methyl orange decomposition carried out in the presence of sodium fluoride.

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