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1. Introduction

Macrocyclic porphyrins enjoy much attention, as exemplified by the simulation of proteins in enzyme catalysis [1–3] as well as molecular recognition [4,5] smart materials [6–12], medical treatment [13–17], photo-sensitization and photocatalyst preparation [18–22]. In recent years different heterocycles, metal complexes, as well as porphyrins and their metal derivatives, have been used as photo-sensitizers for polycrystalline TiO₂ in order to enhance the visible light-sensitivity of the TiO₂ matrix and thereby increases its photocatalytic activity [23–28].

It was shown that the central coordinated metal in porphyrins plays a critical role in the photocatalytic processes of the porphyrin– TiO_2 system. In particular, opportunely designed Cu(II) porphyrins– TiO_2 composites were found to be more effective sensitizers in the photodegradation of 4-nitrophenol than other metal–porphyrins (M=Mn, Fe, Zn, Co etc.) [29,30]. The peripherally substituted group within the porphyrins influences the efficiency of

ABSTRACT

Four novel porphyrins, 5-[3-(3-phenoxy)-propoxy]phenyl porphyrin, 5,15-di-[3-(3-phenoxy)-propoxy] phenyl porphyrin, 5,10,15-tri-[3-(3-phenoxy)-propoxy]phenyl porphyrin, 5,10,15,20-tetra-[3-(3-phenoxy)-propoxy]phenyl porphyrin, and their corresponding Cu(II) porphyrins, were synthesized and characterized spectroscopically. The photodegradation of 4-nitrophenol in aq. suspension was used to determine the photocatalytic activity of polycrystalline TiO₂ samples which had been impregnated with the Cu(II) porphyrins, as sensitizers. The photocatalytic activity of the composite depends mainly on the amount of sensitizer on the TiO₂ surface rather than the nature of the substituted porphyrins.

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TiO₂-porphyrin systems, depending on the position of the substituent and spacer length [31,32], strength of the polar group involved (e.g. -OH, $-SO_3$, RCOO-) [33–36] and the electronegativity of the substituent atoms (e.g. O or Cl) combined with the pyrrole units [37,38].

However it remains unclear as to whether the number of peripheral substituents influence the efficiency of TiO₂-porphyrins hybrid systems or whether there exists an optimum ratio of TiO₂:porphyrin. For this reason, this work concerns the synthesis and characterization of four novel porphyrins (H₂Pp; **3a**, **3b**, **3c**, **3d**) each carrying different peripheral substituents, as well as their corresponding copper(II) derivatives (CuPp; **4a**, **4b**, **4c**, **4d**) (Fig. 1). The photocatalytic activity of polycrystalline TiO₂ samples impregnated with CuPp (4a, 4b, 4c, 4d) was investigated via the photodegradation of 4-nitrophenol (4-NP) in aqueous suspension.

2. Experimental section

2.1. Materials and measurements

2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) was obtained from Aldrich, and other reagents were obtained from Beijing Chemical Reagents Company. They were used without further purification with the exception of the pyrrole that was

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Fig. 1. Molecular structures of H₂Pp(3a, 3b, 3c, 3d), and CuPp(4a, 4b, 4c, 4d).

distilled before use. TiO₂ (anatase) was kindly provided by Tioxide Huntsman. The loaded samples used as the photocatalysts for the photoreactivity experiments were prepared by impregnating TiO₂ (Tioxide, anatase phase, BET specific surface area 8 m²/g).

Elemental analyses (C, H and N) were performed by Vario EL-III CHNOS instrument. Diffuse reflectance (DR) spectra were obtained at room temperature in the wavelength range 200-800 nm using a Shimadzu UV-2401PC spectrophotometer with BaSO₄ as the reference material. UV-vis spectra were obtained using a Shimadzu UV-2550 UV-vis-NIR spectrophotometer. ¹H NMR spectra were recorded on a Varian Inova 400 MHz at room temperature; chemicals shifts are reported in ppm with respect to the reference frequency of tetramethylsilane, Me₄Si. Mass spectrometry was carried out on a matrix assisted laser desorption/ionization time of flight mass spectrometer (MALDI-TOF MS, Krato Analytical Company of Shimadzu Biotech, Manchester, Britain). 1 µL of sample solution and of the matrix mixture were spotted into wells of the MALDI sample plate and air-dried. The samples were than analyzed in linear ion mode using CHCA as matrix. External calibration was achieved using a standard peptide and protein mix obtained from Sigma.

Specific surface area was measured using the single point BET method employing a jw-05 apparatus (Beijing China). Total Organic Carbon (TOC) was measured using USA. O. I Analytical TOC.

2.1.1. General procedure for the synthesis of 3-phenoxypropyl bromide (1)

Compound (1) was synthesized as described previously [39]. 28.0 g (0.3 mol) phenol and 37.7 mL (0.37 mol) 1,3-dibromopropane in 150 mL H₂O were heated with stirring at 100 °C on an oil bath and 11.3 g (0.28 mol) NaOH dissolved in 40 mL H₂O were added to the reaction system over 30 min. The mixture was refluxed for 4 h and the water layer was separated and the remaining oil layer distilled under vacuum. The first distillation yielded unreacted 1,3-dibromopropane, whilst 3-phenoxypropyl bromide (1) was obtained from the second distillation. Yield: 85%; Mp: 10–11 °C; Anal. Calcd. for C₉H₁₁BrO, %: C, 50.30; H, 5.09. Found C, 50.26; H, 5.15. n_{20}^{D} : 1.5460.

2.1.2. General procedure for the synthesis

of 3-(3-phenoxy-propoxy)-benzaldehyde (2)

10.0 g (0.082 mol) 3-hydroxybenzaldehyde and 12.5 mL (0.08 mol) 3-phenoxypropyl bromide (1) in 100 mL CH₃CH₂OH were heated with stirring at 80 °C on a water bath and 3.2 g (0.08 mol) of NaOH dissolved in 50 mL CH₃CH₂OH (5 mL distilled water was added to CH₃CH₂OH to completely dissolve the NaOH) were added dropwise over 1 h and the ensuing mixture was refluxed for 30 h. The mixture was cooled to room temperature and filtered to remove NaBr. The filtrate was concentrated under vacuum and the residual brown oil was dissolved in 20 mL CH₂Cl₂, and washed several times with 0.1 M KOH followed by distilled

water. The CH₂Cl₂ was removed and the remaining oil was recrystallized from CH₃CH₂OH to yield colorless crystals of 3-(3-phenoxy) propoxybenzaldehyde (**2**). Yield: 35%; Mp: 34–35 °C; Anal. Calcd. for C₁₉H₁₆O₃, %: C, 75.38; H, 6.28. Found C, 74.98; H, 6.29. ¹H NMR (CDCl₃, 400 MHz): δ , ppm 9.96 (s, 1H), 7.50–7.12 (m, 4H, Ar), 6.93 (t, *J* = 7.73 Hz, 5H, Ar), 4.26 (t, *J* = 5.54 Hz, 2H, OCH₂), 4.16 (t, *J* = 5.75 Hz, 2H, OCH₂), 2.35–2.21 (m, 2H, CH₂).

2.1.3. General procedure for the synthesis of $H_2Pp(\mathbf{3a})$, $H_2Pp(\mathbf{3c})$, and $H_2Pp(\mathbf{3d})$

5,10,15,20-tetra-[3-(3-phenoxy)-propoxy]phenyl porphyrin $H_2Pp(3d)$ was synthesized according to the following steps: 2.13 g (8.3 mmol) 3-(3-phenoxy)propoxybenzaldehyde (**2**) and 0.56 mL (8.3 mmol) pyrrole in 200 mL of chloroform were stirred at room temperature for 10 min under a nitrogen atmosphere. 0.13 mL (2.8 mmol) of BF₃·OEt₂ in 5 mL CHCl₃ were added and the reaction mixture was stirred at room temperature for 40 h and thereafter, for a further 50 h following the addition of 1.4 g (6.16 mmol) of dichloro dicyano quinone(DDQ) in CHCl₃. The solvent was removed under vacuum and the crude product purified by chromatography on a silica gel column using CH₂Cl₂ and hexane (6/4 v/v) as eluant.

 $H_2Pp(3a)$ and $H_2Pp(3c)$ were obtained by statistic synthesis starting from a mixture of benzaldehyde: 3-(3-phenoxy)propoxybenzaldehyde respectively in 3:1 or 1:3 ratio using a procedure similar to that described for the preparation of $H_2Pp(3d)$. The crude products were purified using chromatography on a silica gel column with CH_2Cl_2 and hexane (6/4 v/v) as eluant.

2.1.3.1. $5-[3-(3-phenoxy)-propoxy]phenyl porphyrin H_2Pp(3a)$. Yield: 6%. Mp: >200 °C, Anal. Calcd. for C₅₃H₄₀N₄O₂, %: C, 83.69; H, 5.30; N,7.29. Found C, 83.22; H, 5.27; N, 7.32. MS: *m*/*z* 765.9 ([M + H]⁺) amu. ¹H NMR (CDCl₃, 400 MHz): δ , ppm 8.94–8.77 (m, 8H, β position of the pyrrole moiety), 8.21 (d, *J* = 6.3 Hz, 8H, Ar), 7.84–7.70 (m, 12H, Ar), 7.63 (t, *J* = 7.4 Hz, 2H, Ar), 6.96–6.87 (m, 4H, Ar), 4.36 (t, *J* = 6.0 Hz, 2H, OCH₂), 4.23 (t, *J* = 6.0 Hz, 2H, OCH₂), 2.35 (quintuplet, *J* = 6.1 Hz, 2H, CH₂), -2.79 (br s, 2H, NH). UV–vis (CHCl₃): λ_{max} , nm, 418, (Soret band), 515, 550, 590, 645 (Q bands).

2.1.3.2. 5,10,15-tri-[3-(3-phenoxy)-propoxy]phenyl porphyrin H₂Pp(3c). Yield: 5%, Mp: >200 °C Anal. Calcd. for C₇₁H₆₀N₄O₆, %: C, 79.84; H, 5.71; N, 5.32. Found C, 80.05; H, 5.68; N, 5.26. MS: *m*/*z* 1066.1 ($[M + H]^+$) amu. ¹H NMR (CDCl₃, 400 MHz): δ , ppm 8.93–8.77 (q, *J* = 5.13 Hz, 4.76 Hz, 8H, β position of the pyrrole moiety), 8.20 (dd, *J* = 1.62 Hz, 4H, Ar), 7.86–7.74 (m, 10H, Ar), 7.65–7.60 (t, *J* = 7.8 Hz, 8H, Ar), 7.36–7.31 (dd, *J* = 2.4 Hz, 2H, Ar), 7.27–7.20 (m, 6H, Ar), 6.94–6.85 (m, 10H, Ar), 4.35 (t, *J* = 6.0 Hz, 4H, OCH₂), 4.22 (t, *J* = 6.0 Hz, 4H, OCH₂), 2.35 (quintuplet, *J* = 6.0 Hz, 4H, CH₂), -2.81 (br s, 2H, NH). UV-vis (CHCl₃): λ_{max} , nm, 419, (Soret band), 515, 549, 589, 644 (Q bands).

2.1.3.3. 5,10,15,20-tetra-[3-(3-phenoxy)-propoxy]phenyl porphyrin $H_2Pp(3d)$. Yield: 8%, Mp: >200 °C Anal. Calcd. for $C_{80}H_{70}N_4O_8$, %: C,

79.10; H, 5.71; N, 4.68. Found C, 79.05; H, 5.80; N, 4.61. MS: m/z 1216.5 ([M + H]⁺) amu. ¹H NMR (CDCl₃, 400 MHz): δ , ppm 8.87 (s, 8H, β position of the pyrrole moiety), 7.80 (d, J = 8.0 Hz, 8H, Ar), 7.62 (t, J = 7.6 Hz, 4H, Ar), 7.36–7.30 (m, 4H, Ar), 7.21 (t, J = 8.0 Hz, 8H, Ar), 6.92–6.86 (m, 12H, Ar), 4.35 (t, J = 6.0 Hz, 8H, OCH₂), 4.22 (t, J = 6.0 Hz, 8H, OCH₂), 2.34 (quintuplet, J = 6.0 Hz, 8H, CH₂), -2.81 (br s, 2H, NH). UV–vis (CHCl₃): λ_{max} , nm, 420, (Soret band), 516, 550, 589, 644 (Q bands).

2.1.4. General procedure for the synthesis of H₂Pp(3b)

0.52 g (2 mmol) 3-(3-phenoxy)propoxybenzaldehyde (**2**) and 0.45 g (2 mmol) *meso*-phenyldipyrrole (which was synthesized using the procedure reported in [41]) in chloroform (250 mL) were stirred at room temperature for 10 min under a nitrogen atmosphere. 0.03 mL (0.67 mmol) of BF₃·OEt₂ in 5 mL CHCl₃ were added and the reaction mixture was stirred at room temperature for 20 h; 0.34 g (1.5 mmol) DDQ (in CHCl₃) was added slowly to the solution with vigorous stirring. Subsequently, the reaction mixture was stirred at room temperature was stirred at room temperature for 24 h and then the solvent was removed under vacuum. The reaction mixture was purified through a silica gel-G chromatography column with CH₂Cl₂ and hexane (6/4 v/v) as eluant.

2.1.4.1. 5,15-*di*-[3-(3-*phenoxy*)-*propoxy*]*phenyl porphyrin H*₂*Pp*(3*b*). Yield: 12%, Mp: >200 °C Anal. Calcd. for C₆₂H₅₀N₄O₄, %: C, 81.41; H, 5.63; N, 6.02. Found C, 81.38; H, 5.51; N, 6.12. MS: *m*/*z* 916.6 ([M + H]⁺) amu. ¹H NMR (CDCl₃, 400 MHz): δ , ppm 8.92–8.72 (dd, *J* = 5.12 Hz, 8H, β position of the pyrrole moiety), 8.17 (d, *J* = 6.44 Hz, 4H, Ar), 7.83–7.68 (m, 8H, Ar), 7.62–7.52 (t, *J* = 7.8 Hz, 4H, Ar), 7.33–7.27 (m, 4H, Ar), 6.92–6.86 (m, 8H, Ar), 4.30 (t, *J* = 6.0 Hz, 4H, OCH₂), 4.20 (t, *J* = 6.0 Hz, 4H, OCH₂), 2.31 (quintuplet, *J* = 6.0 Hz, 4H, CH₂), -2.84 (br s, 2H, NH). UV–vis (CHCl₃): λ_{max} , nm, 419, (Soret band), 516, 550, 589, 645 (Q bands).

2.1.5. General procedure for the synthesis of CuPp(4a, 4b, 4c, 4d)

27.0 mg (0.15 mmol) of $CuCl_2$ were added to 60.8 mg (0.05 mmol) of the $H_2Pp(3d)$ dissolved in 20 mL CHCl₃ and 3 mL CH₃CH₂OH. The mixture was stirred for 24 h at room temperature and monitored by TLC until the complete disappearance of the starting material $H_2Pp(3d)$. The unreacted solid salt was filtered and the solvent removed under vacuum. The crude product was purified by chromatography on a silica gel column with CH₂Cl₂ as eluant. CuPp(4d) was obtained in nearly quantitative yield.

The same method was also used to obtain CuPp(4a), CuPp(4b) and CuPp(4c) in almost quantitative yield by using $H_2Pp(3a)$, $H_2Pp(3b)$ or $H_2Pp(3c)$ as the starting material respectively.

2.1.5.1. *Cu*(*II*) 5-[3-(3-*phenoxy*)-*propoxy*]*phenyl porphyrin CuPp*(4*a*). Yield: 95%. Mp: >200 °C, Anal. Calcd. for CuC₅₃H₃₈N₄O₂, %: C, 77.38; H, 4.54; N, 6.53. Found C, 77.03; H, 4.63; N, 6.78. MS: *m*/*z* 827.4 ($[M + H]^+$) amu. UV-vis (CHCl₃): λ_{max} , nm, 416 (Soret band), 539, 572 (Q bands).

2.1.5.2. *Cu*(*II*) 5,10,15,20-*tetra*-[4-(3-*phenoxy*)-*propoxy*]*phenyl porphyrin CuPp*(4*b*). Yield: 96%. Mp >200 °C, Anal. Calcd. for CuC₆₂H₄₈N₄O₄, %: C, 76.49; H, 4.89; N, 5.52. Found C, 76.25; H, 4.95; N, 5.74. MS: *m*/*z* 977.7 ([M + H]⁺) amu. UV-vis (CHCl₃): λ_{max} , nm, 416 (Soret band), 539, 572 (Q bands).

2.1.5.3. *Cu*(*II*) 5,10,15,20-*tetra*-[4-(3-*phenoxy*)-*propoxy*]*phenyl porphyrin CuPp*(4*c*). Yield: 95%. Mp >200 °C, Anal. Calcd. for CuC₇₁H₅₈N₄O₆, %: C, 75.41; H, 5.10; N, 4.58. Found C, 75.68; H, 5.19; N, 4.97. MS: *m*/*z* 1128.1 ([M + H]⁺) amu. UV-vis (CHCl₃): λ_{max} , nm, 416 (Soret band), 539, 572 (Q bands).

2.1.5.4. *Cu*(*II*) 5,10,15,20-*tetra*-[2-(3-*phenoxy*)-*propoxy*]*phenyl porphyrin CuPp*(4*d*). Yield: 95%. Mp >200 °C, Anal. Calcd. for CuC₈₀H₆₈N₄O₈, %: C, 75.13; H, 5.64; N, 4.47. Found C, 75.25; H, 5.37; N, 4.39. MS: *m*/*z* 1277.8 ([M + H]⁺) amu. UV-vis (CHCl₃): λ_{max} , nm, 417 (Soret band), 540, 572 (Q bands).

2.1.6. Preparation of the photocatalysts: CuPp(4a)–TiO₂, CuPp(4b)–TiO₂, CuPp(4c)–TiO₂ and CuPp(4d)–TiO₂

An amount $(2,4,6,8,10,12 \text{ and } 14 \mu \text{mol})$ of the sensitizer (CuPp(4a), CuPp(4b), CuPp(4c) or CuPp(4d)) was dissolved in 30 mL of CHCl₃ and 1 g finely ground TiO₂ was added to the solution. The resulting suspension was stirred for 5 h and the solvent was removed under vacuum.

2.2. Photoreactivity experiments

The photodegradation setup consisted of a 200 mL beaker irradiated by a 500 W, 24 V Xenon lamp-house system (instrument: CHF-XM35-500W. Beijing Trusttech Co. Ltd. China) placed in a black box. The distance between the lamp and the solution was 110 cm, and the irradiance measured at the distance of 110 cm was 4.061 mW/cm² (instrument: New Port Dual-Channel Power Meter. Model 2832-C Irvine, CA, USA). The temperature inside the reactor was maintained at ca. 25 °C by means of a continuous circulation of water in a jacket surrounding the reactor.

The reacting suspension consisted of 100 mL 1.0×10^{-4} mol/L 4-NP and 20.0 mg catalyst and it was stirred with a magnetic bar. Air was bubbled into the suspension for 30 min before switching on the lamp and the initial pH value of the suspension was 6.40 units. The photoreactivity runs lasted 400 min and samples of 3 mL were withdrawn from the suspension every 50 min during the irradiation. The photocatalysts were separated from the solution by centrifugation and the quantitative determination of 4-NP was performed by measuring its absorption at 316 nm with a Shimadzu UV2550 UV-vis–NIR spectrophotometer.

3. Results and discussion

3.1. Synthesis of (2), $H_2Pp(3a, 3b, 3c, 3d)$, CuPp(4a, 4b, 4c, 4d) and preparation of the CuPp(4a)– TiO_2 , CuPp(4b)– TiO_2 , CuPp(4c)– TiO_2 and CuPp(4d)– TiO_2 photocatalysts

The synthetic route has been illustrated in Fig. 2. As shown in Fig. 2, the precursors 3-phenoxypropyl bromide (**1**) and 3-(3-phenoxy) propoxybenzaldehyde (**2**) were easily prepared and purified. The four novel porphyrins, $H_2Pp(3a, 3b, 3c, 3d)$, were synthesized by using a procedure inspired the to Lindsey methods [40,41]. 3a and 3c were obtained through statistic synthesis by controlling the ratio of benzaldehyde and 3-(3-phenoxy)propoxybenzaldehyde (**2**) in 3:1 and 1:3, respectively, and provided rather low yields (6 and 5%, respectively), while 3d was in relative a little high yield (8%). 3b was synthesized with 12% yield by the reaction of 3-(3-phenox-y)propoxybenzaldehyde (**2**) and *meso*-phenyldipyrrole, that is, a [2 + 2] approach. The corresponding copper porphyrins, CuP-ps(**4a, 4b, 4c, 4d**) were obtained almost quantitatively.

The UV–vis spectra of **3a**, **3b**, **3c**, **3d**, show almost the same Soret and Q bands. The corresponding copper porphyrin **4a**, **4b**, **4c**, **4d**, leads to a decrease of the number of Q band peaks from four to two (540 and 572 nm). Moreover, the position of the peaks of the compounds displayed a weak violet shift (2–3 nm for Soret and 10– 17 nm for Q band, respectively) depending on the porphyrin ligand. The mass spectra of the porphyrins **3a**, **3b**, **3c**, **3d** and the copper(II) porphyrins **4a**, **4b**, **4c**, **4d** showed the positively charged $[M + H]^+$ *m/z* adducts.



Fig. 2. Synthesis of the metal-free porphyrins H₂Pp(3a, 3b, 3c, 3d) and copper(II) porphyrins CuPp(4a, 4b, 4c, 4d).

The ¹H NMR spectra were also consistent with the structure of the isolated **3a**, **3b**, **3c**, **3d**, and one was shown in Fig. 3. Different symmetry of porphyrin molecules 3a, 3b, 3c, 3d, leads to different resonance of the β -H of the pyrrole moiety due to the different number of substituents as shown in Fig. 4. The eight β -H of pyrrole moiety in **3a** and **3c** show the unsymmetrical spin-splitting pattern because two or six β -H are close to the long *meso*-substituents (which appear in the high field, 8.89 and 8.88 respectively) and the other six or two β -H are close to the phenyls (which appear in the low field, 8.83 and

8.82 respectively), and the ratios of two group spin-splitting peaks area are 2:6 and 6:2 for 3a, 3c, respectively. Similarly, the eight β -H of pyrrole moiety in **3b** show the ratio of two groups symmetrical spin-splitting peaks area is 4:4. **4b** shows one simple peak in 8.87 because its eight β -H locate in the same surrounding.

The DR spectra of CuPp(4a)-TiO₂ having impregnation ratio in the range 6–14 µmol/1 g of TiO₂ together with the bare TiO₂ used as photocatalysts are reported in Fig. 5. It is worth noting that no shift of the band gap edge of TiO₂ can be observed in all loaded samples.



Fig. 3. The ¹H NMR spectrum of H₂Pp(3b).



Fig. 4. The spin-splitting patterns of H-pyrrole peaks in ¹H NMR spectra of H₂Pp(3a, 3b, 3c, 3d).

Nevertheless they reflect light less significantly than the bare support and their absorption increases by increasing the loading, showing characteristic strong absorption bands centered at 416–422 nm (Soret band) and at 540 nm (Q band). The maximum absorption values of the bands are similar to those observed for CuPp(4a) in CHCl₃ solution (Fig. 5, inset).

3.2. Photoreactivity experiments

The photocatalytic activities for the degradation of 4-nitrophenol (4-NP) in water were tested using prepared CuPp(4a)-TiO₂-CuPp(4d)-TiO₂ photocatalysts.

The most efficient photocatalysts require an appropriate amount of sensitizer in order to achieve an optimum coverage of the TiO₂ surface. In fact, a deficient coverage of the TiO₂ surface could not efficiently induce an extension of light absorption in the visible range, whereas an over coverage could give rise to formation of multi-layered aggregates with a detrimental effect for the photocatalytic activity. Consequently different photocatalysts were prepared by impregnating TiO₂ with various amounts (2, 4, 6, 8, 10, 12 and 14 μ mol/1 g TiO₂) of the sensitizer CuPp(**4a**, **4b**, **4c**, **4d**) for the sake of comparison. Fig. 6 shows results of 4-NP degradation in aqueous suspension (after 200 min of irradiation) in the presence of TiO_2 -porphyrin systems impregnated with different amounts of sensitizers.

The photoreactivity results indicated that the most effective amount of sensitizer is 10, 8, 8 and 6 μ mol/1 g TiO₂ for CuPp(4a)–CuPp(4d), respectively. This can produce an optimal situation of monolayer having, presumably, just a minimal extent of aggregation of the porphyrin molecules impregnated onto TiO₂ surface.

Data of CuPp(4a)–TiO₂, CuPp(4b)–TiO₂, CuPp(4c)–TiO₂, CuPp(4d)–TiO₂ samples impregnated with the practical optimal values of sensitizer and their photocatalytic activities are reported in Table 1.

It can be noticed that the photocatalytic activity decreased in the following order when using the most efficient photocatalysts:

8-CuPp(4c)-TiO₂ > 8-CuPp(4b)-TiO₂ > 6-CuPp(4d)-TiO₂ > 10-CuPp(4a)-TiO₂ > TiO₂ (bare).

Fig. 7 shows some experiments carried out by using 6-CuPp(4a)– TiO₂–6-CuPp(4d)–TiO₂ samples impregnated with the same amount of sensitizer (6 μ mol/1 g TiO₂) to compare the influence of the number of the peripheral substitutions on the efficiency of TiO₂– porphyrins systems. All these composites showed a photocatalytic efficiency for the degradation of 4-NP in aqueous suspension, and the photocatalytic activity decreased in the following order:



Fig. 5. Diffuse reflectance spectra of bare TiO_2 and differently loaded samples obtained by impregnation of TiO_2 with CuPp(4a). Inset: spectrum of CuPp(4a) in CHCl₃.



Fig. 6. Comparison of the photocatalytic activities in terms of 4-NP concentration vs. different impregnation ratio CuPp(4a)–TiO₂–CuPp(4d)–TiO₂ after 200 min of irradiation time.

Table 1

Some relative data and comparison of the photocatalytic activities in terms of degradation of 4-NP vs. optimal impregnation ratio $CuPp(4a)-TiO_2-CuPp(4d)-TiO_2$ after 200 min irradiation.

Samples	Size of the sensitizer molecule $(\times 10^{-18} \text{ m}^2)$	Calculated optimal value (µmol/1 g TiO ₂) ^a	Practical optimal value (µmol/1 g TiO ₂)	4-NP (%) converted after 200 min irradiation
CuPp(4a)-TiO ₂	1.53	8.7	10	60.76
CuPp(4b)-TiO ₂	1.86	7.1	8	63.26
$CuPp(4c)-TiO_2$	2.37	5.6	8	64.95
CuPp(4d)-TiO ₂	2.88	4.6	6	61.59

 $^{\rm a}\,$ The calculated optimal value refer to 1 g TiO_2 flatly covered by porphyrins onto the surface.



Fig. 7. 4-NP concentration vs. irradiation time using the same amounts of 6-CuPp(4a-4d)/TiO_2.

 $6\text{-}CuPp(4d)\text{-}TiO_2>6\text{-}CuPp(4c)\text{-}TiO_2>6\text{-}CuPp(4b)\text{-}TiO_2>6\text{-}CuPp(4a)\text{-}TiO_2>TiO_2$ (bare).

Total organic carbon (TOC) was measured during the photodegradation runs and it was reduced by 29% and 68% after 200 and 400 min, respectively, when $6-CuPp(4d)-TiO_2$ was used as the photocatalyst.

For the 6-CuPp(4a)–TiO₂–6-CuPp(4d)–TiO₂ composites the number of the substitutions influences the photocatalytic efficiency up to a certain extent although it is not very obvious, especially for the 6-CuPp(4b)–TiO₂ and 6-CuPp(4c)–TiO₂. It can be presumed that the different number of the substituents cannot influence the redox potential of the sensitizers [30], but it can influence the porphyrin–porphyrin and porphyrin–surface interactions as well as the electrons transfer involving the sensitizer onto the substitutions from CuPp(4a) to CuPp(4d) provokes the increasing of photocatalytic efficiency of the system.

4. Conclusions

The synthesis and the spectroscopic characterization of four new porphyrins with different numbers of substituents and their Cu(II) complexes have been described. Various CuPp(4a)–TiO₂– CuPp(4d)–TiO₂ composites exhibited relatively high photoactivities – compared with the bare TiO₂ – when they were used for the photodegradation of 4-nitrophenol under irradiation. The different amount of CuPp influences the photocatalytic activity and the optimal amount depends on the size of the CuPp molecule. The different number of substitutions in the porphyrin ring can affect the efficiency of the photodegradation to a certain extent with the following decreasing photocatalytic activity order:

 $6\text{-}CuPp(4d)\text{-}TiO_2>6\text{-}CuPp(4c)\text{-}TiO_2>6\text{-}CuPp(4b)\text{-}TiO_2>6\text{-}CuPp(4a)\text{-}TiO_2>TiO_2$

The photocatalytic activity of the studied composites depends mainly on the amount of sensitizer impregnated onto the TiO_2 surface and only in lesser extent on the peripheral substitutions of the porphyrins.

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