

# Sulphonated phthalocyanines as effective oxidation photocatalysts for visible and UV light regions

P. Kluson<sup>a,\*</sup>, M. Drobek<sup>a</sup>, T. Strasak<sup>a</sup>, J. Krysa<sup>a</sup>, M. Karaskova<sup>b</sup>, J. Rakusan<sup>b</sup>

<sup>a</sup> Institute of Chemical Technology Prague, Technická 5, 166 28 Prague 6, Czech Republic

<sup>b</sup> Research Institute for Organic Syntheses, Pardubice-Rybitví 532 18, Czech Republic

Received 6 February 2007; received in revised form 7 March 2007; accepted 8 March 2007

Available online 15 March 2007

## Abstract

Attention was paid to the synthesis, chemical modification (sulphonation), characterisation and practical catalytic utilisation of metal free phthalocyanine and a series of phthalocyanines (PHCs) with Zn, Al, Si, Co, Ni, Cu and Ti central atoms. These organometallic compounds are referred to as highly active species due to their ability to produce singlet oxygen upon energy absorption. Photocatalytic efficiency of the prepared PHCs was tested in a model oxidation of 4-chlorophenol under illumination with visible and UV light in agreement with location of their distinctive absorption bands in both these regions. It was shown that different types of phthalocyanines revealed very different photocatalytic activities and only those with a long life-time of the excited triplet states (ZnPHC, SiPHC, AlPHC) effectively interacted with molecular oxygen to form the reactive singlet oxygen. The indispensable role of constant pH (~10) was also clarified in separate experiments. Determined values of quantum yields for reactions carried out in the UV region were always higher than for reactions induced by the visible light.

© 2007 Elsevier B.V. All rights reserved.

**Keywords:** Phthalocyanines; 4-Chlorophenol; Photocatalysis; Quantum yield; Singlet oxygen

## 1. Introduction

Synthetic macrocyclic compounds known as phthalocyanines (PHCs) are derived from the basic structure of porphyrine [1] (Fig. 1). They differ in a character of the central atom, which is usually represented by an atom of metal with direct implication in their physical and chemical properties. It must be noted that also various phthalocyanines are synthetically simply available. Because of their characteristic light absorption in the well-defined region of the visible part of the spectrum they have been used as common industrial colorants, such as pigments, direct dyes, reactive dyes, solvent dyes and vat dyes [1,2]. Also, many other applications have appeared recently including the photodynamic therapy, gas sensors, solar cells technology, catalysis and photocatalysis [3–8]. These applications arise from the ability of most of the PHCs to produce highly active oxygen either in the form of singlet  $^1\text{O}_2$  or in the form of various reactive oxygen

species such as a superoxide radical [9]. The former is usually being considered as the prominent active species in a majority of photo-induced reactions with PHCs as photocatalysts [10–16]. However, it is rather correct that the mechanisms are competitive and the appearance of the prevalence form depends upon the photophysical properties of the particular phthalocyanine. Nevertheless, it is generally known [9] that the active singlet oxygen form occurs when porphyrine with longer life-time of the excited triple state is involved. It must be noted that PHCs with a completely occupied valence sphere or d-orbitals are such structures [17–19]. On the other hand, PHCs containing metal ions with not fully occupied d-orbitals (e.g.  $\text{Co}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Ni}^{2+}$ ) tend toward rapid extinction of their excited triple states with consequences in a lower number of formed active species. More details on these aspects are given elsewhere [9,20–29].

Photo-induced reactions involving phthalocyanines and focused on environmental applications may specifically come into account due to negligible toxicity of PHCs and their high activity toward oxidative decomposition of majority of typical organic pollutants appearing in drinking, industrial and waste water [10,11,18,30–35]. However, very low solubility of the PHC molecule in polar and non-polar solvents requires its

\* Corresponding author. Tel.: +420 220 444 158; fax: +420 220 441 968.

E-mail address: [P.Kluson@seznam.cz](mailto:P.Kluson@seznam.cz) (P. Kluson).

URL: [http://www.vscht.cz/kot/en/list/petr\\_kluson.html](http://www.vscht.cz/kot/en/list/petr_kluson.html) (P. Kluson).

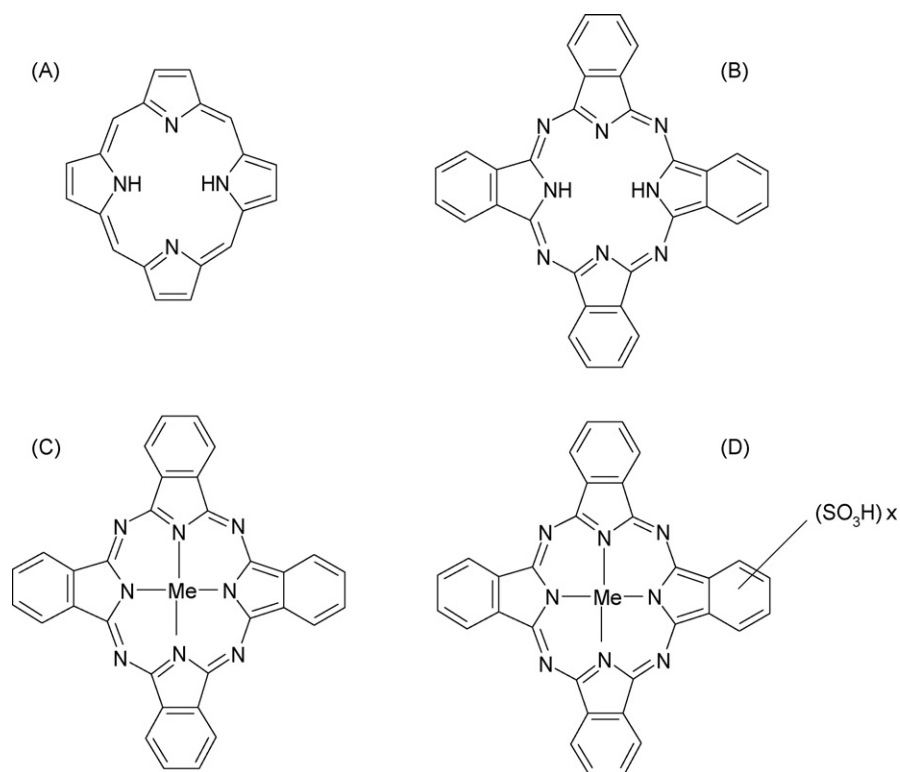


Fig. 1. Basic structure of porphyrin (A), metal free phthalocyanine (B), metal phthalocyanine (C) and sulphonated metal phthalocyanine (D).

chemical modification. For aqueous solutions it is necessary to introduce specific chemical functional groups to benzene rings of the basic PHC skeleton. The most frequent chemical modifications are sulphonated [24,36] or carboxylated [29,37] derivatives already well soluble in water, but, tending to aggregate [25]. For the sulphonated molecules of PHCs it was found that higher the content of more sulphonated individual derivatives, higher the tendency for aggregation [18,36,25]. On the other hand, mixtures of derivatives of PHCs at different sulphonation stages were not seriously affected by aggregation [24]. Also some additives, such as surfactants or certain alcohols may limit this undesired phenomenon [33,38]. Another possibility to prepare active, stable and non-aggregated phthalocyanines could be based on their heterogenisation [39,40].

In this paper, we report on preparation, chemical modification (sulphonation), characterisation and practical catalytic utilisation of metal free phthalocyanine and phthalocyanines with Zn, Al, Si, Co, Ni, Cu and Ti central atoms in 4-chlorophenol oxidation under UV and visible light activation. The role of pH is also discussed. To the best of our knowledge, such a comparison for both distinctive light regions and for such an extended series of PHCs has not been published yet.

## 2. Experimental

### 2.1. Chemicals

*o*-Phthalodinitrile was used for preparation of various PHCs and it was supplied by BASF, all metal ions (Zn<sup>2+</sup>, Si<sup>4+</sup>, Co<sup>2+</sup>, Ni<sup>2+</sup>, Cu<sup>1+</sup>, Ti<sup>4+</sup>) appearing in the PHCs skeletons, with excep-

tion of Al<sup>3+</sup> (aluminium acetate, Aldrich), were of chloride origin (all p.a., Fluka). Other chemicals, such as 4-chlorophenol, quinoline, acetone, methanol, 1,1-dioxithiolan, urea and chlorosulphonic acid were of analytical grades and were received from Aldrich.

### 2.2. Preparation of PHCs

Phthalocyanines used in this work were produced either in a solvent (metal free PHC, SiPHC, ZnPHC, TiPHC) or by means of the solvent free method (AlPHC, CoPHC, NiPHC, CuPHC).

#### 2.2.1. Synthesis in a solvent (batch process)

**Metal free PHC (MeFPHC):** *o*-Phthalodinitrile + quinoline (solvent) mixed for 8 h at 473 K and 10 MPa of hydrogen, then refined from acetone.

**SiPHC:** *o*-Cyanobenzamide (produced from *o*-phthalodinitrile, acetic acid and acetanhydride) + quinoline + *o*-dichlorobenzene, stirred under nitrogen with slow addition of SiCl<sub>4</sub> at 483 K for 2 h, filtered and washed with hot quinoline, pyridine, acetic acid and ethanol.

**ZnPHC:** *o*-Phthalodinitrile + ZnCl<sub>2</sub> + nitrobenzene (solvent), ammonium molybdenate (catalyst), ammonia. This mixture was stirred for 6 h, refluxed and stripped with ammonia, filtered and washed with methanol and finally precipitated from 96% sulphuric acid.

**TiPHC:** *o*-Cyanobenzamide (produced from *o*-phthalodinitrile, acetic acid and acetanhydride) + quinoline + *o*-dichlorobenzene, stirred under nitrogen with slow addition

of  $\text{TiCl}_4$  at 483 K, filtered and washed with hot quinoline, pyridine, acetic acid and ethanol.

### 2.2.2. Solvent free synthesis

**AlPHC:** Phthalanhydride + urea mixed with aluminium acetate, sodium sulphate and ammonium molybdenate, stirred in a batch reactor at 463 K, then precipitated from 96% sulphuric acid.

**CoPHC:** Phthalanhydride + urea mixed with  $\text{CoCl}_2$  dihydrate, sodium sulphate and ammonium molybdenate (catalyst), reaction carried out in continuous stirred tank reactor (CSTR) at 463 K, then it was precipitated from 96% sulphuric acid.

**NiPHC:** Phthalanhydride + urea mixed with  $\text{NiCl}_2$ , sodium sulphate and ammonium molybdenate, carried out in CSTR at 463 K and then precipitated from 96% sulphuric acid.

**CuPHC:** Phthalanhydride + urea mixed with  $\text{Cu}_2\text{Cl}_2$ , sodium sulphate and ammonium molybdenate, carried out in CSTR at 463 K and then precipitated from 96% sulphuric acid.

### 2.3. Chemical modification of PHCs

Sulphonations were carried out either in fuming sulphuric acid (AlPHC, CoPHC, NiPHC, CuPHC) or in 1,1-dioxothiolan with chlorosulphonic acid (ZnPHC, MeFPHC, TiPHC). Reactions in fuming sulphuric acid were performed in atmosphere of carbon dioxide. The extent of sulphonation, representation of mono, di, tri and tetra-sulphonated derivatives, was managed in both reaction systems by means of reaction temperature and reaction time. Composition of the prepared mixtures of derivatives was characterised by thin layer chromatography (TLC) together with quantitative elemental (C, N, H, S) analysis (Elementar Vario EL III).

### 2.4. Photocatalytic experiments

These experiments were carried out in a magnetically stirred batch reactor (300 ml, reaction mixture volume 200 ml, saturated with air) illuminated with well-defined sources of light in the UV and visible regions. For the visible light measurements three fluorescent tubes Narva Yellow Special 016 (emission interval 500–700 nm, maximum at 580 nm, verified on spectrofluorometer Fluoromax 2, Jobin Yvon) with nominal output 18 W each were fitted exactly 100 mm above the level of the reaction mixture. The irradiation intensity measured at this level was  $1.52 \text{ mW/cm}^2$  (determined with help of a Si photodiode Hamamatsu S1337-BQ). Experiments in the UV region were carried out with three Narva Blacklight Blue 073 lamps (emission interval 330–400 nm, verified on spectrofluorometer Fluoromax 2, Jobin Yvon) with nominal output 18 W each. The irradiation intensity measured at a level of the reaction mixture was  $1.29 \text{ mW/cm}^2$  (determined with help of UV Light Meters, Mannix Interstate). 4-Chlorophenol solved in high pressure liquid chromatography (HPLC) grade water was employed as a model compound ( $1 \times 10^{-4} \text{ mol/l}$ ). Water solution of PHC in the form of sodium salt of its sulphoacid was introduced as a catalyst ( $7 \times 10^{-6} \text{ mol/l}$ ). Samples of reaction mixtures were analysed

by HPLC (Shimadzu LC 20A Prominence) with LiChrosper 100 RP-18 ( $5 \mu\text{m}$ ) column and methanol/water mobile phase (40/60). Content of PHCs in withdrawn samples of reaction mixtures was verified spectrally (UV–vis spectrometer, Cecil Instruments) within the range 250–800 nm. The same instrumentation was also used for characterisation of absorption intervals of the produced chemically modified mixtures of PHCs derivatives ( $c_{\text{PHC}} = 1.4 \times 10^{-5} \text{ mol/dm}^3$ ). In experiments, constant pH was established and maintained (NaOH solution) by means of the automatic titration equipment Titrator Manager TIM 856 (TitraLab) with a combined pH electrode (Radiometer).

### 2.5. Quantum yields

Values of quantum yields  $\phi$  were evaluated for all studied reactions. The quantum yield (%), Eq. (1) represents a basic kinetic parameter of a photophysical and/or photochemical process reflecting the quantitative relationship between the number of involved (reacting) molecules and the number of involved photons:

$$\phi = \frac{Vc_i k}{J_{h\nu} A} 100 \quad (1)$$

in which  $J_{h\nu}$  is the incident photon flux intensity (Einstein  $\text{s}^{-1} \text{m}^{-2}$ , Eq. (2)),  $V$  represents the reaction volume ( $\text{m}^3$ ),  $c_i$  the initial concentration of 4-chlorophenol ( $\text{mol/m}^3$ ),  $A$  the illuminated area ( $\text{m}^2$ ) and  $k$  is the rate constant ( $\text{s}^{-1}$ ). For determination of rate constants  $k$  the first order kinetics was assumed for all reactions.

$$J_{h\nu} = \frac{\lambda P_f}{h\gamma N_A} \quad (2)$$

where  $P_f$  is the experimentally measured irradiation intensity ( $\text{W/m}^2$ ),  $\lambda$  the maximum wavelength of the used illumination source,  $h$  the Planck constant  $6.626 \times 10^{-34} \text{ Js}$ ,  $\gamma$  the light velocity in vacuum ( $3 \times 10^8 \text{ m/s}$ ) and  $N_A$  denotes the Avogadro number ( $6.022 \times 10^{23} \text{ mol}^{-1}$ ).

## 3. Results and discussion

The principal property of a PHC molecule comprises its ability to absorb photons in two distinctive and well-separated regions. The major absorbance band, which is associated with the visible colour properties of PHCs, is located inside of the interval 500–700 nm and it is usually referred to as the Q band. Significant light absorption below 400 nm denotes then for interactions with highly energetic photons in the UV region. Absorption spectra recorded for a series of eight PHCs used in this work are shown in Fig. 2a–d. The multimodal course (bimodal) of absorption bands in both regions is a characteristic feature revealed by all chemically modified PHCs due to their aggregation tendency. It should be noted that besides monomers mostly dimeric forms appear and their absorption bands are those shifted toward energetically more abundant region. For the modified PHCs it was observed that the higher the content (HPLC) of more sulphonated individual derivatives, the higher was the tendency for their aggregation. On the other hand,

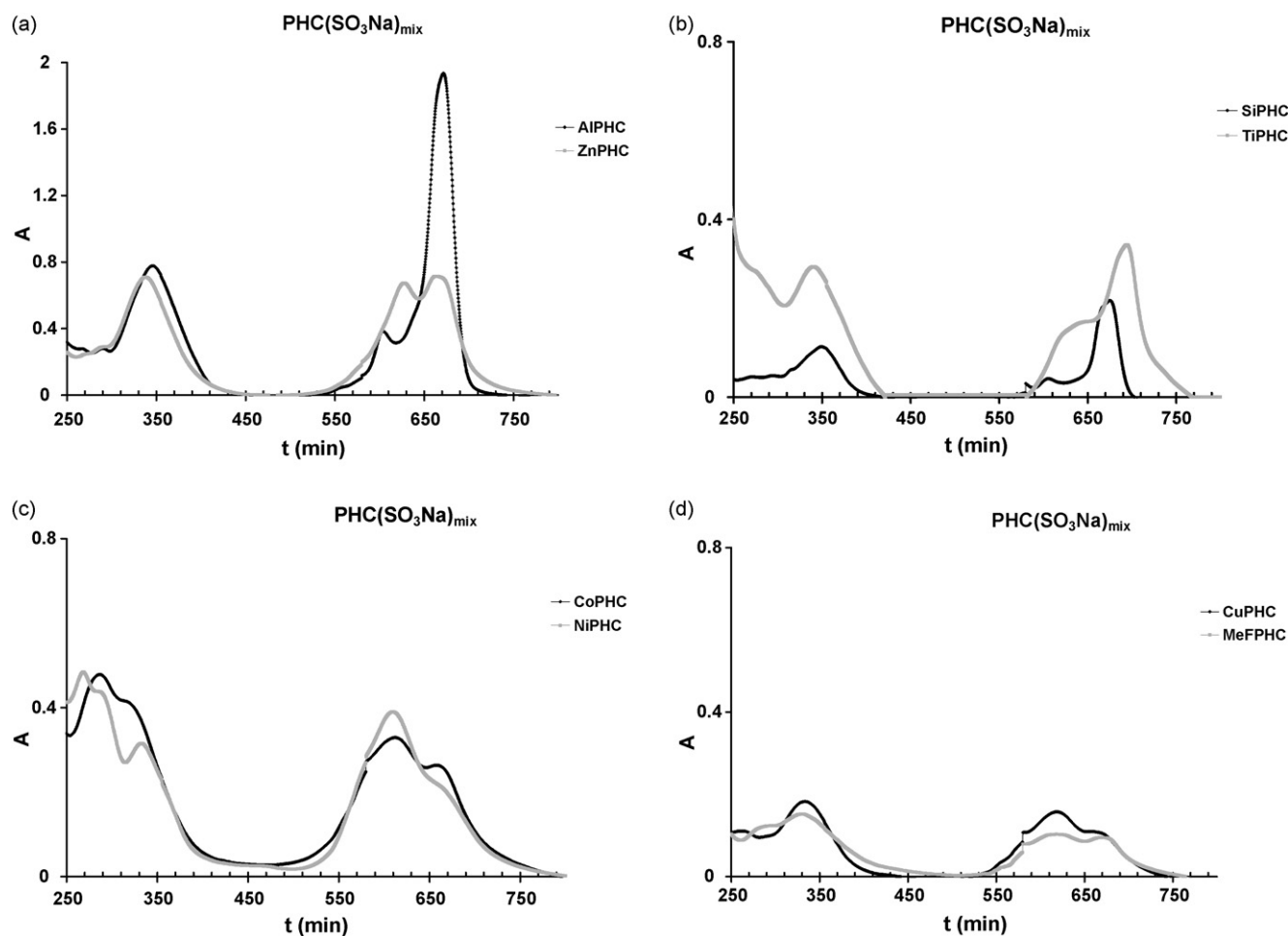


Fig. 2. (a) Absorption spectra of sulphonated Zn and AIPHC,  $c_{\text{PHC}} = 1.4 \times 10^{-5} \text{ mol/dm}^3$ . (b) Absorption spectra of sulphonated Si and TiPHC,  $c_{\text{PHC}} = 1.4 \times 10^{-5} \text{ mol/dm}^3$ . (c) Absorption spectra of sulphonated Co and NiPHC,  $c_{\text{PHC}} = 1.4 \times 10^{-5} \text{ mol/dm}^3$ . (d) Absorption spectra of sulphonated Cu and MeFPHC,  $c_{\text{PHC}} = 1.4 \times 10^{-5} \text{ mol/dm}^3$ .

mixtures of derivatives of PHCs at different sulphonation stages were not seriously affected by this phenomenon and mostly dimers appeared along with the monomeric forms. This finding also described in literature [24] rendered possible to use mixtures of sulphonated derivatives rather than pure individual derivatives obtainable by tedious chromatography separation.

An essential part of this work was focused on activity tests of the prepared and chemically modified PHCs. These tests were accomplished as the homogeneous photocatalytic decomposition of 4-chlorophenol (4CP) in aqueous solution using low intensity visible (500–700 nm) and UV (330–400 nm) light. The model reactant 4-chlorophenol was chosen because of its anticipated simple decomposition mechanism (Fig. 3) and it also represented a characteristic trace pollutant of drinking water

processed by chlorination. Forming intermediates and reaction products were identified by HPLC and LC–MS techniques. However, for the kinetic data treatment only the change of the relative concentration of 4-chlorophenol as a function of time was used and the raw experimental results were plotted as a dependency of natural logarithm of a relative concentration of 4CP on time. Initially, some effort had been spent to describe the progress of the reaction without any catalyst (PHC), only with UV–vis light and 4-chlorophenol. It must be noted that 4-chlorophenol was found completely photo-inactive (under used experimental conditions) and the indispensable role of UV–vis light was also proved by excluding it in reactions involving only PHCs and 4-chlorophenol (no transformation of 4CP). Monitoring of the photocatalytic reaction embodied the periodic sample

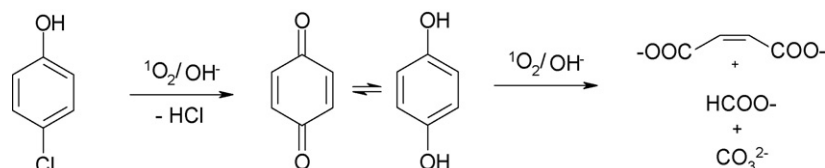


Fig. 3. Oxidation mechanism of 4CP.

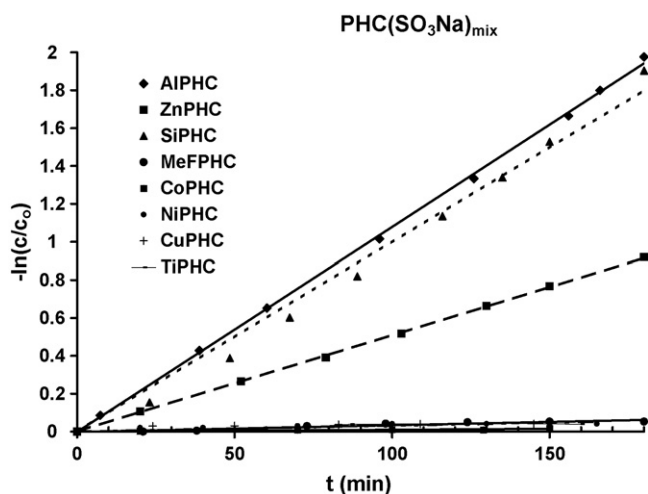


Fig. 4. Photooxidation of 4CP catalysed by sulphonated phthalocyanines with different central metal atoms in the visible light region ( $c_{4CP(\text{initial})} = 1 \times 10^{-4} \text{ mol/dm}^3$ ,  $c_{\text{PHC}} = 7 \times 10^{-6} \text{ mol/dm}^3$ , pH 10).

withdrawal, the HPLC analysis and the verification spectral analysis on the content of PHC. With the used concentrations and sources of photon flux a typical reaction run took about 200 min.

The first set of experiments was carried out at pH 10 and with photons emitted in the visible region. It was evident (Fig. 4) that sulphonated phthalocyanines of Si and Al significantly surpassed the remaining members of the series. ZnPHC revealed moderate photocatalytic activity and the other used PHCs could be referred to as not active. These findings were in compliance with the prominent concept of the singlet oxygen generation only by certain PHCs with a specific electronic molecular structure. The excited triplet states with longer life-time are characteristic for porphyrins involving metal ions with completely occupied d-orbitals (e.g. AIPHC, SiPHC, ZnPHC). In such cases, probability of interactions of the lower active triplet oxygen with molecular oxygen yielding the active singlet oxygen was much higher. On the other hand, CoPHC, NiPHC, CuPHC and TiPHC contained ions with not fully occupied d-orbitals. Thus, these molecules upon photon flux absorption tended toward rapid extinction of their excited triple states with consequences in a lower number of formed active species (singlet oxygen) and thus also in much lower observed photocatalytic activity. Negligible photocatalytic activity observed for metal free phthalocyanine (MefreePHC) could be ascribed to a similar phenomenon despite no metal ion was present in its molecule (incompletely occupied valence sphere).

As expected, experiments with variable load of PHC (variable initial concentration of PHC in water) revealed more rapid decomposition of 4CP with increased initial concentration of PHC as shown in Fig. 5 for AIPHC. However, this trend was not linear, especially at higher concentrations of AIPHC. The interpretation might be sought both in terms of the “light transport” effects causing that the activating photons still available in high abundance were, however, absorbed by only some of the PHC molecules despite vigorous mixing and potentially also by their increased tendency to aggregate (typical at high concentrations). Another possible reason might be seen in a deficiency

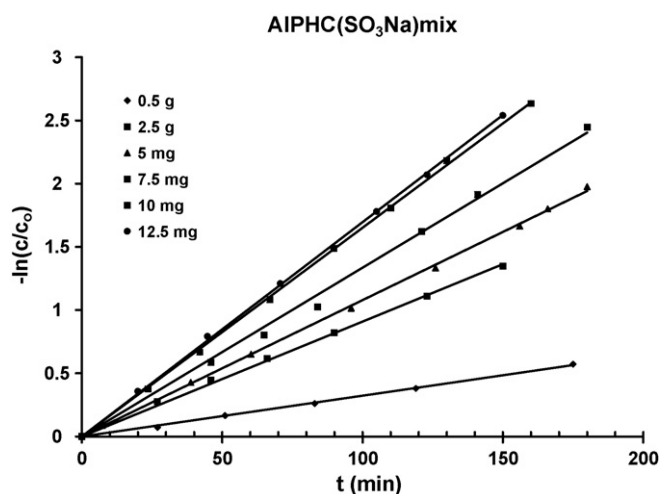


Fig. 5. Photooxidation of 4CP catalysed by sulphonated AIPHC in the visible light region ( $c_{4CP(\text{initial})} = 1 \times 10^{-4} \text{ mol/dm}^3$ , pH 10), variable conc. of AIPHC—different amount of the catalyst.

of dissolved oxygen molecules in the reaction mixture at high PHC concentrations.

To elucidate the photostability of AIPHC, ZnPHC and SiPHC constrained to the duration of a typical reaction run these photocatalysts were exposed to standard experimental conditions (without 4CP) and the mixtures were analysed on their content periodically. Decomposition of the three active phthalocyanines induced by photons emitted inside of the Q-band was insignificant as indicated in Fig. 6 (diminution of the relative absorbance as a function of time). After an initial decline down the level of  $\sim 90\%$  (25 min) the parameter of relative absorbance ( $A/A_0$ ) remained already constant.

The pH value as one of the most important parameters affecting rate of the studied photocatalytic reaction was optimised separately for AIPHC and SiPHC. The positive role of the more basic reaction environment is shown in Fig. 7 for the pH interval 7.5–10. By increasing the pH value of the reaction mixture the tendency of the Lewis type acids Al(III) or Si(IV) to coordinate  $\text{OH}^-$  ions also increased. Due to this coordination the discussed phenomenon of aggregation was significantly limited

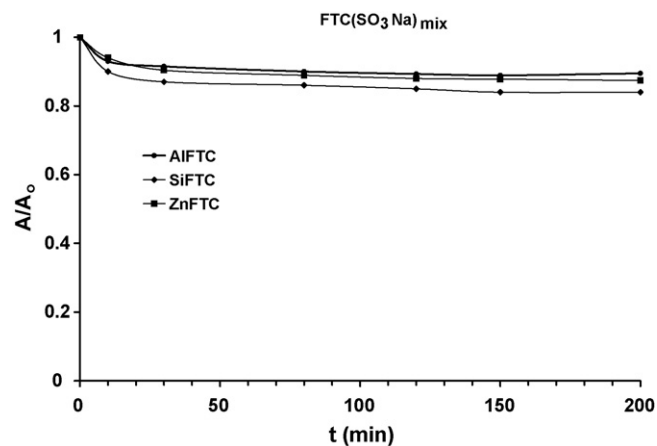


Fig. 6. Diminution of the relative absorbance of phthalocyanine in time ( $c_{\text{PHC}(\text{initial})} = 7 \times 10^{-5} \text{ mol/dm}^3$ ).



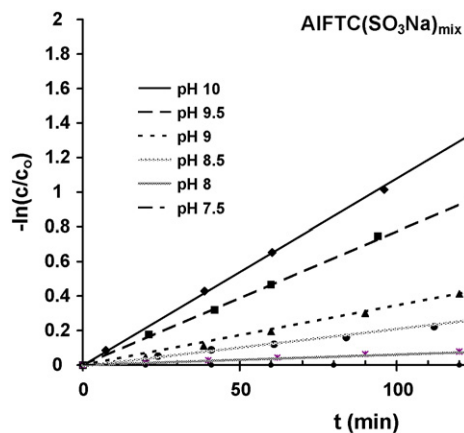


Fig. 7. Photooxidation of 4CP catalysed by sulphonated AIPHC in the visible light region ( $c_{4CP(\text{initial})} = 1 \times 10^{-4} \text{ mol/dm}^3$ ,  $c_{\text{PHC}} = 7 \times 10^{-6} \text{ mol/dm}^3$ ), different values of pH.

and only sulphonated PHC monomers and dimers were spectrally detected. Larger aggregates appearing at pH values closer to the neutral region were found much less active. It must also be noted that, specifically for 4CP, in basic reaction environment more molecules of 4-chlorophenol were transformed to phenolates with lower redox potential and thus it was easier to oxidise them. At higher pH values 4-chlorophenol was oxidised stepwise with formation of various intermediates. Among them *p*-benzoquinone (in equilibrium with hydroquinone) dominated. Due to high pH of the solution further oxidation lead especially to formation of sodium salts of maleic and fumaric acids. Such reaction products and intermediates caused rapid decline of pH, consequent aggregation of PHC and then a drop of its photoactivity. To avoid these unfavourable effects constant pH was established and maintained (NaOH solution) by means of the automatic titration equipment combined with a pH electrode.

Similar experimental setup (pH 10) with exception of the source of the photon flux was used to inspect the photocatalytic properties of the series of sulphonated PHCs in the UV region. As clearly evidenced in Fig. 8 again only AIPHC, SiPHC and ZnPHC might be referred to as photoactive species. This finding was not very surprising because the same mechanism as previously was being considered responsible for their enhanced photocatalytic activity. Despite presence of energetically more abundant photons the three active PHCs were again found very stable under experimental conditions.

The first order kinetics of the 4CP decomposition is explicit from the previously discussed graphs and thus the slopes of the lines could be identified with the rate constants  $k$ . These values are listed in Table 1 for the UV and visible regions together with quantum yields and corresponding pH values for AIPHC, SiPHC and ZnPHC. The parameter of quantum yield  $\phi$  reflected the quantitative relationship between the number of reacting molecules of 4CP and the total number of involved photons in the particular region of the lamp emission. Irradiation intensities in the UV and visible regions were very similar,  $1.29 \times 10^{-2}$  and  $1.52 \times 10^{-2} \text{ W/cm}^2$ , respectively. However, when photon flux intensities were inferred values differing significantly were

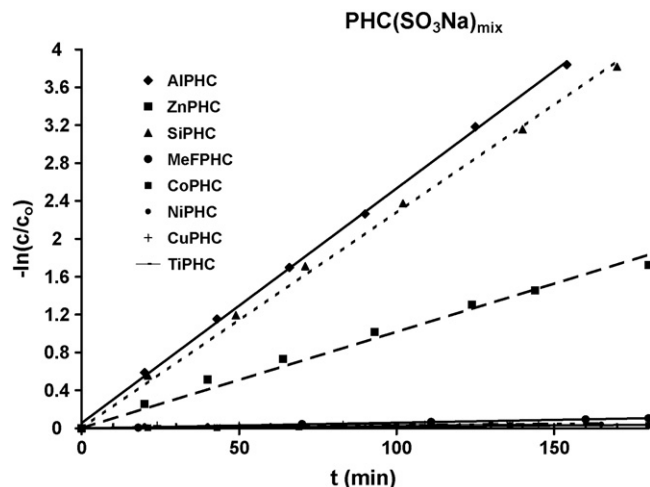


Fig. 8. Photooxidation of 4CP catalysed by sulphonated phthalocyanines with different central metal atoms in the UV light region ( $c_{4CP(\text{initial})} = 1 \times 10^{-4} \text{ mol/dm}^3$ ,  $c_{\text{PHC}} = 7 \times 10^{-6} \text{ mol/dm}^3$ , pH 10).

obtained ( $3.93 \times 10^{-9} \text{ Einstein s}^{-1} \text{ cm}^{-2}/\text{UV}$  and  $7.39 \times 10^{-9} \text{ Einstein s}^{-1} \text{ cm}^{-2}/\text{VIS}$ ). Such a distinction might be theoretically attributed to the fact that the light source in the visible region emitted more photons than that emitting in UV. In the UV region photons were, on the other hand, more abundant in energy. Regarding the studied photocatalytic transformation of 4CP the key parameter was represented rather by the number of photons than their energies because of the accepted theoretical stoichiometry, one incident photon = one transformed molecule. Accordingly, the reactions in the visible regions should be favoured, however, as it is evident from Table 1 that rate constants and calculated quantum yields were much higher for reactions carried out with UV light. Emission spectrum of the lamp in the UV region covered perfectly the very strong absorbance band of the three active PHCs (AIPHC, SiPHC, ZnPHC). It might be expected that most of the incident photons were effectively absorbed. On the other hand maximum of the emission spectrum of the visible light source was shifted slightly toward the yellow colour comparing with the maximum of absorption bands of PHCs. In this case, it might be expected that only a certain proportion of incident photons was effectively absorbed with direct implications in the values of the rate con-

Table 1  
Rate constants and quantum yields for reactions with AIPHC, SiPHC and ZnPHC

	pH	Visible region		UV region	
		$k \text{ (min}^{-1}\text{)}$	$\Phi_{4CP} \text{ (%)}$	$k \text{ (min}^{-1}\text{)}$	$\Phi_{4CP} \text{ (%)}$
AIPHC(SO <sub>3</sub> Na) <sub>mix</sub>	10	$1.1 \times 10^{-2}$	0.53	$2.5 \times 10^{-2}$	2.25
	9	$3.4 \times 10^{-3}$	0.16		
	8	$3.3 \times 10^{-3}$	0.16		
SiPHC(SO <sub>3</sub> Na) <sub>mix</sub>	10	$9.5 \times 10^{-3}$	0.45	$2.3 \times 10^{-2}$	2.03
	9	$3.9 \times 10^{-3}$	0.19		
	8	$5.4 \times 10^{-4}$	0.02		
ZnPHC(SO <sub>3</sub> Na) <sub>mix</sub>	10	$5.0 \times 10^{-3}$	0.24	$1.0 \times 10^{-2}$	0.91
	9	$1.9 \times 10^{-3}$	0.09		
	8	$5.0 \times 10^{-4}$	0.02		

stants and quantum yields. Thus, the evaluated quantum yields in the visible region must be referred to only as apparent due to a limited number of absorbed photons and their comparison with formally similar values for the UV region must be carried out with precaution.

The indispensable role of constant pH value carefully optimised ( $\sim 10$ ) in the experiments with visible light is also evident from Table 1. Only a fractional decline below the optimised level was immediately reflected in lower values of rate constants and apparent quantum yields.

#### 4. Conclusion

A series of phthalocyanines with different central atoms including the metal free phthalocyanine were successfully synthesised. These structures were chemically modified by means of sulphonation with fuming sulphuric acid or chlorosulphonic acid in the organic solvent sulpholane. The prepared derivatives, mostly in monomeric and dimeric forms, were characterised spectrally and then used in photochemical reactions. Due to their significant absorption in visible and UV regions the experiments were also carried out in two well-separated regions with two distinctive sources of photons. The singlet oxygen  $^1O_2$ , which was generally accepted as the active species in such reaction, was identified sufficiently abundant only for phthalocyanines with completely occupied d-orbitals. AlPHC, SiPHC, ZnPHC revealed much longer life-time of the excited triple-states in comparison with CoPHC, NiPHC, CuPHC, TiPHC, MefreePHC and yielding effectively upon their contact with molecular oxygen its active singlet form. Determined values of quantum yield for reactions carried out in the UV region were always higher than for reactions induced by the visible light. The effectiveness of the studied photoreaction was also strongly dependent on the pH value. It was optimised in a set of experiments in the visible region and then kept constant ( $\sim 10$ ). In neutral or less basic reaction environment molecules of PHCs tend to aggregate with consequences in diminishing their photocatalytic activity.

#### Acknowledgements

Authors wish to thank to Ministry of Education of the Czech Republic, project NanoPin No. 1M4531433201 and to Grant Agency of Academy of Sciences of the Czech Republic, project HNPM No. KAN400720701, for funding this research. M.D. also thanks to Grant Agency of the Czech Republic for funding partly his Ph.D. (Doctoral Grant No. 203/03/H140).

#### References

[1] F.H. Moser, A.L. Thomas, Phthalocyanine Compounds, Reinhold Publ., New York, 1963.

[2] F.H. Moser, A.L. Thomas, The Phthalocyanines I and II, CRC Press, Boca Raton, 1983.

[3] J.D. Spikes, Photochem. Photobiol. 43 (1986) 691.

[4] I. Rosenthal, Photochem. Photobiol. 53 (1991) 859.

[5] P.S. Vakusic, J.R. Sambles, Thin Solid Films 221 (1992) 311.

[6] J. Griffiths, J. Schofield, M. Wainwright, S.B. Brown, Dyes Pigments 33 (1997) 65.

[7] A. Visona, A. Angelini, S. Gobbo, A. Bonamone, G. Thiene, A. Pagnan, D. Tonello, E. Bonandini, G. Jori, J. Photochem. Photobiol. B 57 (2000) 94.

[8] J.J. He, G. Benko, F. Korodi, T. Polivka, R. Lomoth, B. Akermark, L.C. Sun, A. Hagfeldt, V. Sundstrom, J. Am. Chem. Soc. 124 (2002) 4922.

[9] K. Lang, J. Mosinger, D. Wagnerova, Chem. Listy 99 (2005) 211.

[10] R. Gerdes, D. Wohrle, W. Spiller, G. Schneider, G. Schnurpfeil, G. Schultz-Ekloff, J. Photochem. Photobiol. A 111 (1997) 65.

[11] N. Nensala, T. Nyokong, J. Mol. Catal. A 164 (2000) 69.

[12] N. Nensala, T. Nyokong, Polyhedron 17 (1998) 3467.

[13] N. Nensala, A. Nzimande, T. Nyokong, J. Photochem. Photobiol. A 98 (1996) 129.

[14] J.H. Zagal, Coord. Chem. Rev. 119 (1992) 89.

[15] K. Ozoemena, N. Kuznetsova, T. Nyokong, J. Photochem. Photobiol. A 139 (2001) 217.

[16] K. Ozoemena, N. Kuznetsova, T. Nyokong, J. Mol. Catal. A 179 (2001) 29.

[17] K. Lang, M. Wagnerova, J. Brodilova, J. Photochem. Photobiol. A 72 (1993) 9.

[18] V. Iliev, V. Alexiev, L. Bilyarska, J. Mol. Catal. A 137 (1999) 15.

[19] E.A. Lukyanets, J. Porphyrins Phthalocyanines 3 (1999) 424.

[20] A. Sorokin, J.-L. Séris, B. Meunier, Science 268 (1995) 1163.

[21] J.R. Darwent, P. Douglas, A. Harriman, G. Porter, M.C. Richoux, Coord. Chem. Rev. 44 (1982) 83.

[22] M.E. Dario, P.F. Aramendia, E.A. San Roman, S.E. Braslavsky, Photochem. Photobiol. 54 (1991) 367.

[23] A.K. Sobbi, D. Wohrle, D. Slettwein, J. Chem. Soc., Perkin Trans. 2 (1993) 481.

[24] R. Edrei, V. Gottfried, J.E. van Lier, S. Kimel, J. Porphyrins Phthalocyanines 2 (1998) 191.

[25] P.C. Martin, M. Gouterman, B.V. Pepich, G.E. Renzoni, D.C. Schindele, Inorg. Chem. 30 (1991) 3305.

[26] F.M. Braun, M.T. Maurette, E. Oliveras, Photochemical Technology, Wiley, Chichester, 1991.

[27] X.-F. Zhang, H.J. Xu, J. Photochem. Photobiol. B 22 (1994) 235.

[28] C.S. Fotte, Photochem. Photobiol. 54 (1991) 659.

[29] V. Iliev, A. Mihaylova, L. Bilyarska, J. Mol. Catal. A 184 (2002) 121.

[30] A.M. Volodin, Catal. Today 58 (2000) 103.

[31] V. Iliev, L. Prahov, L. Bilyarska, H. Fischer, G. Schultz-Ekloff, D. Wohrle, L. Petrov, J. Mol. Catal. A 151 (2000) 161.

[32] V. Iliev, A. Ileva, L. Bilyarska, J. Mol. Catal. A 126 (1997) 99.

[33] G. Schneider, D. Wohrle, W. Spiller, J. Stark, R. Gerdes, G. Schultz-Ekloff, J. Photochem. Photobiol. A 60 (1994) 333.

[34] V. Iliev, A. Ileva, J. Mol. Catal. A 103 (1995) 147.

[35] M.J. Tomas, C.S. Foote, Photochem. Photobiol. 27 (1978) 683.

[36] D. Dhami, D. Philips, J. Photochem. Photobiol. A 100 (1996) 77.

[37] N.A. Kuznetsova, N.S. Gretsova, E.A. Kalmykova, E.A. Makarova, S.N. Dashkevich, V.M. Negrimovskii, O.L. Kaliya, E.A. Lukyanets, Zh. Obsch. Khim. 70 (2000) 133.

[38] W. Spiller, D. Wohrle, R. Gerdes, G. Schultz-Ekloff, W.T. Ford, G. Schneider, J. Stark, J. Photochem. Photobiol. A 95 (1996) 161.

[39] A. Zsigmond, F. Notheisz, M. Bartók, J.E. Bäckvall, Stud. Surf. Sci. Catal. 78 (1993) 417.

[40] A. Zsigmond, F. Notheisz, J.E. Bäckvall, Catal. Lett. 65 (2000) 135.