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Differently substituted phthalocyanines: Comparison of calculated energy levels, singlet oxygen quantum yields, photo-oxidative stabilities, photocatalytic and catalytic activities

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Abstract

Zinc(II) and cobalt(II) phthalocyanines bearing different electron-donating or -withdrawing substituents were prepared. The following properties of these phthalocyanines were investigated: singlet oxygen quantum yields, photo-oxidative stabilities, photocatalytic activities (photooxidation of (*S*)-(−)-citronellol) and catalytic activities (oxidation of 2-mercaptoethanol). Furthermore, the positions of HOMO/LUMO energy levels of the ground state (S_0), first excited singlet state (S_1) and first excited triplet state (T_1) were calculated. Relationships between HOMO energy levels of S_0 and photodecompositions, photocatalytic activities and photo-decompositions, and catalytic activities and HOMO energy levels of S_0 were found. Singlet oxygen quantum yields of the different metallophthalocyanines are around 0.55 and independent from the calculated triplet energies.

Keywords: Phthalocyanines zinc and cobalt; Photodecomposition; Photooxidation citronellol; Photo-oxidative stability; Oxidation mercaptane

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1. Introduction

Metallophthalocyanines (MPc) are important photocatalysts and catalysts in the industry for the photooxidation and oxidation of different substrates by the reaction with molecular oxygen [1]. Examples of photooxidations for different substrates using phthalocyanines as photocatalysts are toxic sulphur compounds, phenols, chlorinated phenols and citronellol [1,2]. Sulfonated phthalocyanines immobilized on polymers are employed for the cleaning of waste water from toxic pollutants [2e,3]. Structurally related porphyrins in polymer matrices were also investigated for the photooxidation of various substrates [4]. The phototoxicity of Zn and Al phthalocyanines in the photodynamic therapy of cancer is also based on the visible light activation of oxygen [5]. The metal ion in the core of the ligand of a metallophthalocyanine is decisive whether the macrocycle is active as catalyst or photocatalyst. For photocatalytic activities the MPc must contain metal ions with closed p or d electron configuration such as Mg(II), Al(III), Si(IV), Zn(II) which, for example, results in a high excited state life times [6]. In contrast, MPcs with redox active metal ions having a open d shell structure such as Co(II), Fe(II) show catalytic and electrocatalytic properties [1,7]. Well-known for the catalytic activity of MPcs is the catalytic oxidation of sulphur compounds using Co(II) or V(IV)O phthalocyanines as catalysts [8–13]. These MPcs are either used as sulfonated complexes in aqueous alkaline solutions in the mercaptan oxidation process of petroleum gasoline fractions or heterogeneous as unsubstituted complexes on charcoal in the mercaptan sweetening process (MEROX). Another interesting application applying the octacarboxylic acid of Fe(II) phthalocyanine is in odor removing systems [14,15]. MPcs (M = Co(II), Fe(II)) were examined as homogeneous or heterogeneous catalysts in different catalytic oxidations (s for example [1,16]).

In this paper we investigate the influence of electron-donating and -withdrawing substituents at the benzene rings of metallophthalocyanines on catalytic and photocatalytic activities in oxidation reactions. The following MPcs have been selected: unsubstituted MPc **1**, tetra-*tert*-butyl substituted MPc **2**, MPcs **3–5** with butoxy groups as electron-donating substituents at dif-

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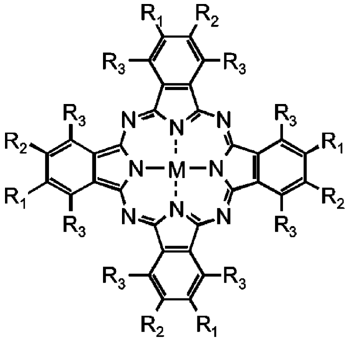


M : a = Zn(II), b = Co(II)

	R1	R2	R3
1a,b	-H	-H	-H
2a	-t-Bu	-H	-H
3a,b	-H	-H	-OBu
4a,b	-OBu	-OBu	-OBu
5a,b	-OBu	-OBu	-H
6a	-COOH	-H	-H
7a,b	-F	-F	-F
8a	-CN	-CN	-H

Fig. 1. Structures and abbreviations of phthalocyanines used in this study.

ferent positions and in different amounts, and MPcs **6–8** with carboxy, fluoro and cyano as electron-withdrawing substituents (Fig. 1). Butoxy groups were chosen because this substituent is long enough to yield good solubilities of MPcs in organic solvents, but not too long to avoid steric hindrance by interaction of reactants with the MPc. The electron-withdrawing substituents fluoro, carboxy and cyano were selected because they exhibit different electron-accepting properties. The MPcs contain the central metal ions zinc(II) or partly cobalt(II). For the investigations of the photocatalytic and catalytic activities the well-known photooxidation of (*S*)-(−)-citronellol and oxidation of 2-mercaptoethanol were selected as test reactions [1]. Measurements were carried out in organic solvents in order to evaluate the influence of substituents at the monomolecular dissolved MPcs. Moreover, the photo-oxidative stabilities and the quantum yields of singlet oxygen formation of the ZnPcs as important parameters for the photocatalytic activities are determined [17,18]. The results of all measurements are accompanied by semi-empirical MO calculations of the differently substituted ZnPcs.

2. Experimental

2.1. Materials

The metallophthalocyanines used for the investigations are shown in Fig. 1. With the exception of **3** and **4** all other MPcs were synthesized according to published procedures and then purified: zinc(II) and cobalt(II) phthalocyanine (**1a**,**b**) purified by zone sublimation at ~400 °C and 10^{-5} mbar (**1a**, $\lambda = 668$ nm in DMF; **1b**, $\lambda = 655$ nm in THF) [19], zinc(II) 2,9,16,23-tetra-*tert*-butylphthalocyanine (**2a**) purified by column chromatography (silica gel, hexane/ether = 1/1) ($\lambda = 675$ nm in DMF) [20], zinc(II) and cobalt(II) 2,3,9.10,16,17,23,24-octabutoxyphthalocyanine (**5a**,**b**) purified at first by treatment with boiling acetone and methanol in a Soxhlet apparatus, and then by column chromatography (silica gel, toluene) (**5a**, $\lambda = 674$ nm in DMF; **5b**, $\lambda = 663$ nm in THF) [21], zinc(II) 2,9,16,23-tetracarboxyphthalocyanine (**6a**) purified by thrice reprecipitation from 0.05 M NaOH with 2 M HCl and then treatment with water and acetone in a Soxhlet apparatus ($\lambda = 685$ nm in DMF) [2a,22], zinc(II) and cobalt(II) hexadecafluorophthalocyanine (**7a**,**b**) purified by zone sublimation at ~420 °C and 10^{-5} mbar (**7a**, $\lambda = 670$ nm in DMF; **7b**, $\lambda = 660$ nm in THF) [23] and zinc(II) 2,3,9,10,16,17,23,24-octacyanophthalocyanine (**8a**) purified by treatment with boiling acetone and methanol in a Soxhlet apparatus, $\lambda = 692$ nm in DMF) [24]. The purity of the Pcs was proven by temperature dependent mass spectra or ionic currents in mass spectra. 3,6-Dibutoxyphthalonitrile [25] and 3,4,5,6-tetrabutoxyphthalonitrile [26] were obtained as described. Solvents used for measurements were of analytical grade or otherwise distillated before use.

2.2. Syntheses

Zinc(II) 1,4,8,11,15,18,22,25-octabutoxyphthalocyanine (***3a***): A mixture of 3,6-dibutoxyphthalonitrile (0.272 g, 1 mmol) and anhydrous zinc chloride (0.092 g, 0.5 mmol) in 1 mL 1-pentanol was refluxed under nitrogen atmosphere. Then 1,8-diazabicyclo-[5.4.0]-undec-7-ene (DBU) (0.15 mL, 1 mmol) was added to the reaction mixture, and the mixture was heated at reflux for further 10 min. Water (50 mL) was poured in to the reaction mixture and the product was extracted by hexane. The solvent was evaporated, and the product was purified by column chromatography (silica gel, hexane/ether = 1:9). Yield: 35 mg (12%); UV/vis $\lambda_{max} = 739$ nm (DMF); ESI-MS (DMF): *m/z* 1153 $[M+H]^+$, 1175 $M+Na]^+$, 1187 $[M+Cl]^-$. Elemental analysis: found C 66.3, H 7.21, N 9.31; calculated C 66.6, H 6.98, N 9.71.

Cobalt(II) 1,4,8,11,15,18,22,25-octabutoxyphthalocyanine (***3b***): The synthesis of this compound was carried out by the same method as used for **3a** with anhydrous cobalt acetate. Yield 10 mg (9%). UV/vis $\lambda_{max} = 718$ nm (THF). ESI-MS (DMF): *m*/z 1148 $[M+H]^+$, 1146 $[M-H]^-$. Elemental analysis: found C 66.5, H 7.32, N 9.39; calculated C 67.0, H 7.03, N 9.77.

Zinc(II) 1,2,3,4,8,9,10,11,15,16,17,18,22,23,24,25-hexadecabutoxyphthalocyanine (***4a***): A mixture of 3,4,5,6-tetrabutoxyphthalonitrile (0.417 g, 1 mmol) and zinc chloride (0.092 g, 0.5 mmol) in 20 mL *n*-pentanol was heated at reflux under nitrogen atmosphere. DBU (0.15 mL, 1 mmol) was added to the reaction mixture, and the reaction mixture is heated to distill off pentanol at first. Then the reaction was continued for 2 h at 180 °C. Water (50 mL) was added to the reaction mixture.

The product was extracted with hexane, and the solution was dried with anhydrous sodium sulfate. After filtration, the product was purified by column chromatography (silica gel, hexane/ether = 1/1). Yield 0.21 g (49%) UV/vis $\lambda_{max} = 728$ nm (DMF). ESI-MS (DMF): *m/z* 1729 $[M+H]^+$, 1751 $[M+Na]^+$, 1766 $[M+Cl]^-$. Elemental analysis: found C 66.2, H 8.71, N 6.28; calculated C 66.6, H 8.38, N 6.47.

Cobalt(II) 1,2,3,4,8,9,10,11,15,16,17,18,22,23,24,25-hexadecabutoxyphthalocyanine (***4b***): The synthesis of this compound was carried out by the same method as used for **4a** with anhydrous cobalt acetate. Yield 0.12 g (28%). UV/vis $\lambda_{max} = 714$ nm (THF). ESI-MS (DMF): *m/z* 1724 $[M+H]^+$, 1722 $[M-H]^-$. Elemental analysis: found C 66.42, H 8.75, N 6.32; calculated C 66.9, H 8.42, N 6.50.

2.3. Calculations

MO calculations were carried out with the commercially available program Hyperchem, Release 7.0. The method PM3 was used. Neglect of diatomic differential overlap (NDDO) approximation is the basis for MNDO, AM1, and PM3 methods. By Koopmann's theorem the first ionization energy of a closed-shell molecule is approximated to second order by the energy of the highest occupied orbital (HOMO). During ionization, the remaining electrons are recognized, contributing an additional term which is not considered in this theorem. In addition, orbital energies can be approximated in the case of higher ionization potentials. Errors in ionization potentials are typically a few tenth of an electron volt, which are only a small percentage of the total.

For all compounds a full geometry optimization was carried out using PM3 until a gradient of less than 0.001 kcal/(Å mol) was reached. Based on this structure, single point calculations were performed by using the PM3 method (convergence limit less than 0.001; charge on the system: 0). Additional CI calculations were not carried out.

2.4. Measurements

2.4.1. Singlet oxygen quantum yield measurements

Singlet oxygen quantum yields Φ_Δ of ZnPcs were determined with 1,3-diphenylisobenzofurane (DPBF) as chemical quencher in DMF. Details are desribed in [18]. At first the quantum yields Φ_{DBPF} after Eq. (1) (V, reaction volume; t, irradiation; I_{abs}, photon flow) using the extinction coefficients for DPBF in DMF were calculated. The quantum yields Φ_Δ are obtained from Φ_{DBPF} using Eq. (2) (β constant for the DPBF decay in a certain solvent) [27].

$$\Phi_{DPBF} = -\frac{d[DPBF]/dt}{I_{abs}/V} \tag{1}$$

$$\Phi_\Delta = \Phi_{DPBF}(1 + \beta/C_{DPBF}) \tag{2}$$

2.4.2. Photo-oxidative stabilities of zinc phthalocyanines in DMF

The photo-oxidative stabilities of ZnPcs were determined by the decay of the intensity of the Q band in the visible region of light. Details are decribed in Ref. [17]. Measurements were carried out under air and irradiation with visible light in DMF or 1-butanol solutions. The time decay of the absorbance maxima of the Q band for each zinc phthalocyanine obeyed first-order kinetics in the concentration of the complex. Photodecomposition rate constants k were calculated after Eq. (3) (t irradiation time, E_0 absorbance at $t = 0$, E_t absorbance at different times).

$$\ln\frac{E_0}{E_t} = kt \tag{3}$$

2.4.3. Photooxidation of (S)-(−)-citronellol in organic solvents

Measurements for the photocatalytic activities were carried out at 25 °C in a 100 mL reaction vessel connected to a 50 mL gas burette. The vessel was irradiated with a 250 W quartz-halogen lamp of a slide projector, and the light intensity was adjusted to ~180 mW cm^{-2} (for details see [2a,e]). The reaction vessel was filled with 50 mL DMF or 1-butanol solutions containing 1 μmol of a zinc phthalocyanine. Then the apparatus was flushed with pure oxygen for 10 min, and 182 μL (1 mmol) citronellol was added to the vessel (molar ratio substrate to photosensitizer was 1000:1). After closing the apparatus, the reaction vessel was irradiated under intensive magnetic stirring, and the oxygen consumption over time was recorded. The activities are characterized by the turnover number TON (conversion mol oxygen per mol phthalocyanine per min during the first 5 mL oxygen consumption), the initial reaction rate (mL oxygen consumption per min during the first 5 mL) and the oxygen consumption (mL) after 2 h irradiation.

2.4.4. Oxidation of 2-mercaptoethanol

Measurements for the catalytic oxidations were carried out in the same equipment at 25 °C as used for the photocatalytic oxidations. THF solutions (50 mL) containing 0.5 μmol of a cobalt phthalocyanine were used. After filling the reaction flask with 50 mL of the solution, the apparatus was flushed with oxygen for 10 min. Then 500 μl (7.1 mmol) 2-mercaptoethanol (molar ratio substrate to catalyst was 14,200:1) and 1 mL of a 0.25 wt% aqueous sodium hydroxide solution were added, and the reaction system was closed. The oxygen consumption over time was recorded. The activities are characterized as mentioned before for the photooxidation.

3. Results and discussions

3.1. Syntheses and characterization of phthalocyanines

To increase the solubility in organic solvents, phthalocyanines with butoxy groups were synthesized. Zinc and cobalt phthalocyanines **3a**,**b** and **4a**,**b** were prepared from 3,6-dibutoxyphthalonitrile or 3,4,5,6-tetrabutoxyphthalonitrile, respectively, and the corresponding anhydrous metal salts in the presence of DBU in 1-pentanol. Important are not too long reaction times (10 min for **3a**,**b**, 2 h for **4a**,**b**) because longer reaction times result in byproducts. Metallophthalocyanines **1a**,**b**, **2a**, **5a**,**b**, **6a**, **7a**,**b**, **8a** were obtained after known procedures.

Table 1
Energy levels of zinc phthalocyanines used in this study

Compound	S_0		S_1			T_1		
	HOMO (eV)	LUMO (eV)	HOMO (eV)	LUMO (eV)	Orbital gap (eV)	HOMO (eV)	LUMO (eV)	Orbital gap (eV)
1a	−7.37	−2.28	−5.71	−3.91	1.80	−5.62	−4.25	1.37
2a	−7.27	−2.19	−5.60	−3.82	1.78	−5.52	−4.16	1.36
3a	−7.07	−2.02	−5.39	−3.64	1.75	−5.30	−3.97	1.33
4a	−7.40	−2.36	−5.73	−3.96	1.77	−5.65	−4.31	1.34
5a	−7.47	−2.40	−5.81	−4.02	1.79	−5.72	−4.37	1.35
6a	−7.88	−2.79	−6.21	−4.40	1.81	−6.12	−4.75	1.37
7a	−8.44	−3.42	−6.79	−5.01	1.78	−6.69	−5.35	1.34
8a	−8.63	−3.57	−6.97	−5.18	1.79	−6.88	−5.51	1.37

MPcs were purified by zone sublimation, column chromatography or reprecipitation. The metal complexes **2a**–**5a** exhibit good solubilities in DMF, THF and 1-butanol. For the zinc(II) complexes **1a**, **6a**–**8a** the solubilities in DMF are moderate but high enough to get 1 µmol solutions with monomolecular dissolved metal complexes (proven by UV/vis spectra) which is a prerequisite for good photocatalytic activities. The solubilities of **1b**, **3b**–**5b**, **7b** in THF are high enough to get 0.5 µmol solutions for the measurements of the catalytic activities. The Q band absorptions of **1**, **2**, **5**–**8** are seen between $\lambda \sim 665$ and 690 nm. Only **3** and **4** containing the electron-donating groups at the positions 1, 4, 8, 11, 15, 18, 22, 25 show the Q band at $\lambda > 700$ nm.

3.2. Calculation of energy levels

The positions of HOMO/LUMO energy levels of the ground state (S_0), first excited singlet state (S_1), and first excited triplet state (T_1) of the zinc(II) phthalocyanines **1a**–**8a** were calculated by the PM3 method (Table 1) in order to find correlations to different investigated properties of the MPcs. It is assumed that the HOMO values of the ground state S_0 correlate with the photodecomposition rate constants k (Eq. (3); reaction of singlet oxygen with the Pc ligand in the ground state—see below) and the catalytic activities (reaction of triplet oxygen with the metal of a Pc in the ground state—see below). The energy difference between the HOMO and LUMO of S_1 should correspond to the position of the Q band (1.8 eV = 690 nm), and the triplet energy (difference between the HOMO and LUMO of T_1 with ~1.35 eV) shows if energy transfer from the excited triplet state of MPc to triplet oxygen to get singlet oxygen necessary for photooxidations is energetically possible (see below).

The positions of HOMO/LUMO energies of S_0, S_1 and T_1 shift to lower energy (more negative values) with increasing electron-withdrawing properties of substituents and to higher energy (less negative values) with increasing electron-donating properties of substituents at the phthalocyanines ligand (Table 1) [7,17]. The arrangement of increasing negative values of HOMO/LUMO (lower energy) is as follows: **3a** < **2a** < **1a** < **4a** < **5a** < **6a** < **7a** < **8a**. The redox potentials of cobalt phthalocyanines bearing different substituents were compared with the positions of calculated HOMO/LUMO energy levels [7]. Linear correlations exist between the oxidation potential and the position of the HOMO level, and the reduction potential and the position of the LUMO level. Electron-withdrawing substituents stabilize the HOMO, and electron-donating substituents stabilize the LUMO.

3.3. Singlet oxygen quantum yields

Excitation in the absorption region of a phthalocyanine yields the excited singlet state ($^1PS^*$) and then by intersystem crossing (ISC) the excited triplet state ($^3PS^*$) [6]. Then the spin allowed triplet–singlet energy transfer from $^3PS^*$ to triplet oxygen ($^3O_2$, $^3\Sigma_g^-$) gives singlet oxygen ($^1O_2$, $^1\Delta_g$). Singlet oxygen plays a key role in photooxidation reactions [1,18,28,29,30]. Thermodynamically the energy transfer from $^3PS^*$ to $^3O_2$ is possible with phthalocyanines: $E(^1O_2–^3O_2) = 0.98$ eV, $E_T(Pc) \sim 1.2$ eV (calculated values in Table 1 for the energy difference between HOMO and LUMO of $T_1 \sim 1.35$ eV) [31]. For phthalocyanines in dependence of the central metal ion with closed electron configuration quantum yields of $^1O_2$ formation (Φ_Δ) between 0.2 and 0.6 were found [18].

Singlet oxygen quantum yields (Φ_Δ) of the prepared ZnPcs were determined in DMF using 1,3-diphenylisobenzofurane (DPBF) as the chemical singlet oxygen quencher [18]. At first Φ_{DPBF} was calculated from the Eq. (1). Because the constant for the DPBF decay β in DMF is known, Φ_Δ can be calculated (Eq. (2)) [27]. Singlet oxygen quantum yields of ZnPcs are in the range of 0.47 and 0.63 (Table 2). The unsubstituted ZnPc **1a** and the substituted ZnPcs **2a**–**5a** bearing electron-donating

Table 2
Singlet oxygen quantum yields and photodecomposition rate constants of zinc phthalocyanines in organic solvents

Compound	Φ_{DPBF}	Φ_Δ	k (min^{-1})
1a	0.39	0.58	2.0×10^{-2}
2a	0.42	0.61	3.1×10^{-2}
3a	0.38	0.58	4.5×10^{-2}
4a	0.40	0.63	1.1×10^{-1}
5a	0.39[a]	0.58	4.1×10^{-2}[b]
6a	0.34	0.51	1.3×10^{-2}
7a	0.39	0.58	2.0×10^{-3}
8a	0.32	0.47	4.0×10^{-3}

[a] 0.25 in 1-butanol.

[b] 1.5×10^{-3} min^{-1} in 1-butanol.

substituents exhibit Φ_Δ values between 0.63 and 0.58, whereas compounds **6a**–**8a** bearing electron-withdrawing substituents have slightly lower values between 0.58 and 0.47. The influence of substituents at the ZnPcs on the magnitude of Φ_Δ is relatively small. One reason may be that the triplet energies (orbital gap between HOMO and LUMO of T_1) of the ZnPcs are not so different and exceed $E(^1O_2–^3O_2)$. An approximate tendency can be seen that shift of HOMO/LUMO energies of T_1 to lower energy (more negative values) reduces the singlet oxygen quantum yields slightly. Exemplarily it is shown for **5a** in Table 2 that Φ_{DPBF} in 1-butanol, which is also used as solvent for photooxidation experiments, is much lower than in DMF. Because the β value in 1-butanol is not known, it is not possible to calculate Φ_Δ after Eq. (2).

3.4. Photo-oxidative stabilities

The photo-oxidative stabilities of the zinc phthalocyanines were determined in DMF by measuring the decrease of the intensity of the Q band over time by irradiation with visible light under air. Under irradiation in the presence of oxygen the formed singlet oxygen is responsible for the decomposition of phthalocyanines [17]. The mechanism for the decomposition is explained by combining wavefunction structures of the HOMO of the tetraazaporphyrin derivative and LUMO of singlet oxygen [17a]. Finally, phthalimide was found as oxidation product. The decay of the Q band was calculated as pseudo first-order kinetics (excess of oxygen) in the concentration of the complex according to Eq. (3). The pseudo first-order constants k for the decomposition of the ZnPcs are shown in Table 2. Smaller values of k correspond to a higher photo-oxidative stability. In DMF the stabilities of ZnPcs decrease as follows: **7a**, **8a** > **6a** > **1a** > **2a** > **3a**, **5a** > **4a**. ZnPcs containing electron-withdrawing substituents exhibit a higher photo-oxidative stability than those containing electron-donating groups. A correlation of the HOMO position of S_0 with the rate constant k was found before by us (Eq. (4)), and α and β values of −6.49 and −0.65 eV, respectively, were determined [17a]. Lower energy of the HOMO level results in a higher photo-oxidative stability. Fig. 2 shows that this relation is also valid for the investigated compounds **1a**–**8a**. Calculated values of α -6.19 ± 0.3 and β -0.86 ± 0.19 eV are in good agreement with the before mentioned ones. Therefore Eq. (4) with α of around −6.3 eV and β of around −0.75 eV characterizes for ZnPcs under the chosen condition the dependence of the photodecomposition from the HOMO position of S_0.

$$E_{\mathrm{HOMO}} = \alpha + \beta \cdot \log(k) \qquad (4)$$

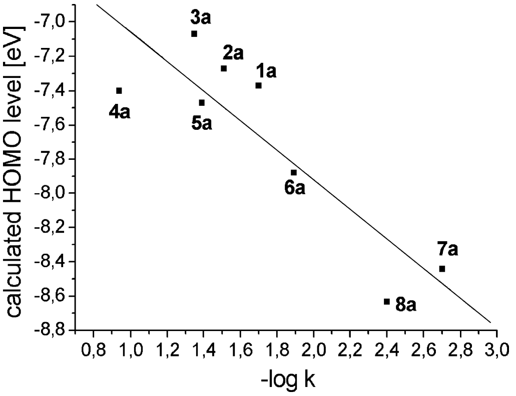
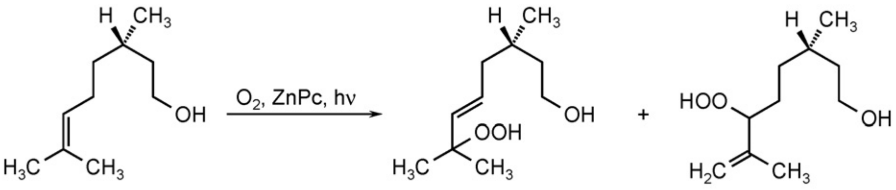


Fig. 2. Calculated HOMO energies of S_0 in relation to the logarithm of the determined photodecomposition rate constants k of zinc phthalocyanines.

The photo-oxidative stability may also depend on the singlet oxygen quantum yield. For example, **1a**, **3a**, **5a** and **7a** exhibit the same singlet oxygen quantum yield of 0.58 but different stabilities. Therefore no dependence of the photo-oxidative stability from the amount of formed singlet oxygen can be seen. The photodecomposition constant k of **5a** was also determined in 1-butanol (Table 2). The stability of **5a** in this solvent is higher than in DMF. One explanation is that in 1-butanol Φ_{DBPF} is much lower compared to Φ_{DBPF} in DMF.

3.5. Photocatalytic oxidation of (S)-(−)-citronellol

As mentioned before, singlet oxygen obtained by excitation of a sensitizer followed by energy transfer to triplet oxygen is responsible for photooxidations. One example is the well-known photooxidation of (*S*)-(−)-citronellol (**9**) which results in the two peroxides **10**,**11** as ene-products (Eq. (5)). The peroxides can be converted to rose oxide [1,2e,28,29]. The photooxidation of **9** finally to rose oxide is an industrial process in annual multi-ton quantities employing Rose Bengal as photosensitizer. Also phthalocyanines were investigated as photosensitizer for the photooxidation of citronellol, and therefore this is a suitable photoreaction to test the photocatalytic activities of the synthesized ZnPcs [1,2e].



9 **10** **11** (5)

The photoactivities of the prepared ZnPcs dissolved in DMF are compared by measuring the oxygen consumption over time for the oxidation of citronellol (molar ratio citronellol to ZnPc = 1000:1) (Fig. 3; Table 3). The oxygen consumption in the dark is negligible. Also under irradiation without addition of a ZnPc no oxygen was consumed. Longer light irradiation time of 1 mmol citronellol in the presence of a ZnPc can result in the consumption of 24 mL oxygen, which corresponds to the

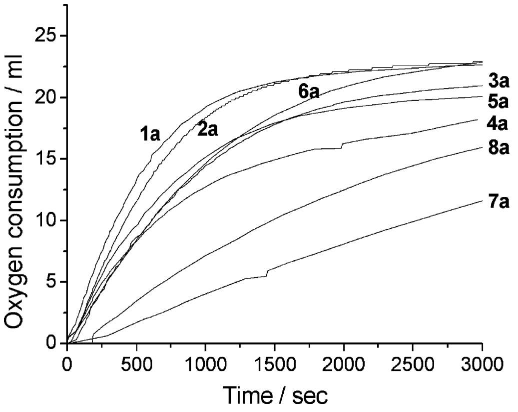


Fig. 3. Photooxidation of (*S*)-(−)-citronellol by zinc phthalocyanines as photocatalysts in DMF.

reaction shown in Eq. (5). The turnover numbers (TON) and initial reaction rates calculated from the initial linear slope of the oxygen consumption are given in Table 3. The turnover numbers decrease as follows: **1a** > **2a** > **5a**, **3a** > **4a**, **6a** > **8a** > **7a**. No correlation of the photocatalytic activities with the quantum yields of singlet oxygen exists (Tables 2 and 3). For example, **1a** and **7a** exhibit the same Φ_Δ of 0.58 but very different TON of 73 and 11 min^{-1}, respectively. Another point must be considered. In Fig. 4 turnover numbers of the photooxidation are plotted against the photodecomposition rate constants *k*. Surprisingly, the most stable compounds **7a** and **8a** have low activity. On the other side **4a** with low stability exhibits medium activity. Compounds **1a** and **2a** show the highest activities but moderate photo-oxidative stability. Compound **6a** combines good activity, singlet oxygen quantum yield and photo-oxidative stability, and is therefore the most interesting photosensitizers for the photooxidation. The photoactivity in 1-butanol is lower, as exemplarily shown for **5a** in Table 3 which is due to the much lower amount of formed singlet oxygen under irradiation in butanol compared to DMF.

3.6. Catalytic oxidation of 2-mercaptoethanol

Well known for the catalytic activity of MPcs is the catalytic oxidation of sulphur compounds using Co(II) or V(IV)O phthalocyanines as catalysts [1,8–13,16]. Different mechanisms are discussed for the oxidation of sulphur compounds. Monomolecular dissolved CoPcs as used in this work coordinate the thiolate anion RS^- and O_2 at the two free axial sides of the central Co(II) in CoPc. Then electron transfer from the thiolate to oxygen via the Co(II) occurs under formation of the disulfide and hydrogen peroxide. In a second uncatalyzed step thiolate is oxidized to the disulfide by hydrogen peroxide under formation of water. The overall reaction for the catalytic oxidation is shown in Eq. (6). The oxidation of 2-mercaptoethanol is a suitable test reaction to prove the catalytic activities of the prepared CoPcs [1].

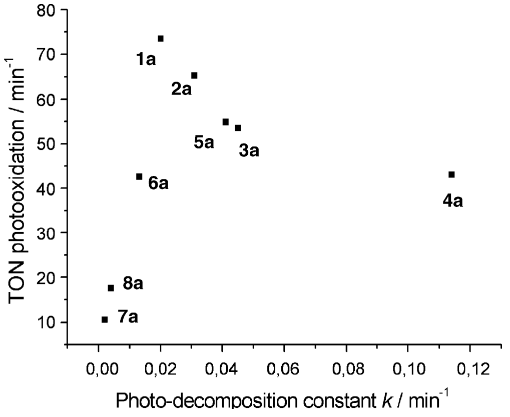


Fig. 4. TON of the photooxidation of citronellol in relation to the photodecomposition rate constants *k* of zinc phthalocyanines.

Table 3
Photooxidation of (*S*)-(−)-citronellol by zinc phthalocyanines as photocatalysts in DMF

Compound	TON (min^{-1})	Initial reaction rate (mL min^{-1})	Oxygen consumption after 2 h (mL)
1a	73	1.8	23
2a	65	1,7	23
3a	54	1.4	22
4a	43	1.2	18
5a	55	1.3	20
5a[a]	14	0.35	20
6a	43	1.0	23
7a	11	0.27	23
8a	18	0.50	21

[a] In 1-butanol.

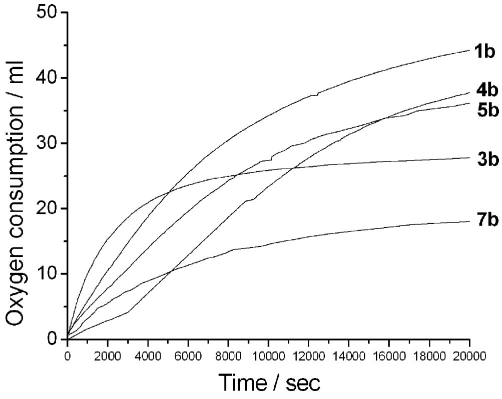


Fig. 5. Oxidation of 2-mercaptoethanol by cobalt phthalocyanines as catalysts in THF.

$$2\text{R-S}^- + 0.5\text{O}_2 + \text{H}_2\text{O} \rightarrow \text{R-S-S-R} + 2\text{HO}^- \qquad (6)$$

The catalytic activities of the CoPcs dissolved in THF are compared by the measuring the oxygen consumption over time (Fig. 5) for the oxidation of 2-mercaptoethanol (molar

Table 4
Oxidation of 2-mercaptoethanol by cobalt phthalocyanines as catalysts in THF

Compound	TON (min^{-1})	Initial reaction rate (mL min^{-1})	Oxygen consumption after 2 h (mL)
1b	25	0.31	29
3b	55	0.66	25
4b	14	0.18	12
5b	18	0.22	22
7b	9.4	0.12	12

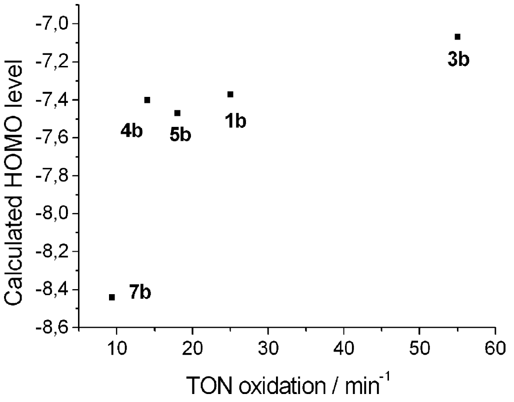


Fig. 6. Calculated HOMO energies of S_0 in relation to TON of the catalytic oxidation of 2-mercaptoethanol by cobalt phthalocyanines.

ratio thiol:catalyst = 14,200:1). A small amount of aqueous NaOH solution was added to obtain the thiolate anion of 2-mercaptoethanol. Some CoPcs consume after longer reaction times ~40 mL oxygen which is in agreement with the amount of employed thiol and its oxidation to the disulfide (Eq. (6)). Turnover numbers and initial reaction rates are shown in Table 4. The order of both, TON and initial reaction rate, increases as follows: **7b** < **4b** < **5b** < **1b** < **3b**. Oxygen consumption without a CoPc or without addition of sodium hydroxide is negligible. The activities correlate comparatively well with the position of the HOMO energies of the S_0 state (Fig. 6). Increasing HOMO energies lead to higher TON and initial rates. Therefore it is assumed that electron-donating substituents increase the electron density at the Co(II) of the phthalocyanines. This favours the interaction with the electron acceptor oxygen and its reduction accompanied by the oxidation of Co(II) to Co(III) which is then followed again by reduction to Co(II) through the oxidation of thiolate. This is in agreement with the fact that CoPcs bearing electron-donating substituents with less negative values of the HOMO S_0 energy level (see Table 1) are easier to oxidize from Co(II)Pc to Co(III)Pc [7]. The same authors found for different substituted CoPcs on graphite a relation between calculated Hammett parameters [32] and electrocatalytic activities [7]. Hammett constants for **1b**, **3b**, **4b**, **5b** and **7b** were calculated, but no correlation between the catalytic activities in the oxidation of 2-mercaptoethanol and the Hammett parameters was found.

4. Conclusions

Zinc(II) and cobalt(II) phthalocyanines **1–8** were prepared in order to compare the influence of their substituents on different properties:

- The positions of HOMO/LUMO energy levels at the ground state (S_0), first excited singlet state (S_1), and first excited triplet state (T_1) of zinc(II) phthalocyanines **1a**–**8a** were calculated by the PM3 method. The energy levels of HOMO/LUMO shift to lower energy (more negative values) with increasing electron-withdrawing properties of substituents and to higher energy (less negative values) with increasing electron-donating properties of substituents at the phthalocyanines.
- Singlet oxygen quantum yield determinations showed that the influence of the substituents at the ZnPcs on the magnitude of Φ_Δ (values around 0.55) is relatively small. One reason may be that the triplet energies of all ZnPcs exceed E($^1O_2$–$^3O_2$) by around 0.3 eV. A tendency was seen that shift of HOMO/LUMO energies of T_1 to lower energy (more negative values) reduces the singlet oxygen quantum yields slightly.
- ZnPcs bearing electron-withdrawing substituents exhibit a higher photo-oxidative stability than those containing electron-donating groups. A correlation of the HOMO S_0 position with the photodecomposition rate constant *k* was found. Decreasing energy of the HOMO level results in a better photo-oxidative stability. Eq. (4) describes the dependence of the photodecomposition rate constant *k* from the HOMO S_0 positions of substituted ZnPcs.
- The photooxidation of (*S*)-(−)-citronellol was selected to evaluate the photocatalytic activities of the ZnPcs. No dependence of the photocatalytic activities from the singlet oxygen quantum yields exits. Some correlation between the photocatalytic activities (for example expressed in turnover numbers) and the photodecomposition rate constant *k* were found. The most stable compounds **7a** and **8a** have low activities. Compounds **1a** and **2a** showed the highest activities but moderate photo-oxidative stabilities. Compound **6a** combines good activity, singlet oxygen quantum yield and photo-oxidative stability, and is therefore the most interesting photosensitizers for the photooxidation.
- The catalytic activities of CoPcs in the oxidation of 2-mercaptoethanol correlate relatively well with the position of the HOMO energies of the S_0 state. Increasing HOMO energies led to higher turnover numbers and initial rates. Therefore it is assumed that electron-donating substituents increase the electron density at the Co(II) of the phthalocyanines and lead to better interaction with the electron acceptor oxygen.

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