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Influence of electron-withdrawing and electron-donating substituents on photophysical properties of azaphthalocyanines

Zbynek Musil [a], Petr Zimcik [a,*], Miroslav Miletin [a], Kamil Kopecky [a], Pavel Petrik [a], Juraj Lenco [b]

[a] *Department of Pharmaceutical Chemistry and Drug Control, Faculty of Pharmacy, Charles University, Heyrovskeho 1203, Hradec Kralove 50005, Czech Republic*

[b] *Institute of Molecular Pathology, Faculty of Military Health Sciences, University of Defence, Hradec Kralove 50005, Czech Republic*

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Abstract

New zinc azaphthalocyanines (AzaPc) were prepared using a statistical method of synthesis starting from 5,6-bis(*tert*-butylsulfanyl)pyrazine-2,3-dicarbonitrile (A) and 2,3-dicyano-5,6-dibutoxycarbonylpyrazine (B). All the six possible AzaPc derivatives were detected on TLC and isolated using column chromatography on silica, however, the adjacent (AABB) and opposite (ABAB) isomers were not separated. Singlet oxygen quantum yields (Φ_Δ) were measured using the DPBF decomposition method. It was found that presence of carbonyl group bounded directly to the macrocyclic core of AzaPc slightly decreases their Φ_Δ in dependence on the number of the butoxycarbonyl groups in succession 0.67, 0.68, 0.67, 0.59, 0.51 for AAAA, AAAB, ABAB (AABB), ABBB and BBBB type of AzaPc, respectively. Similar dependences were found in the case of fluorescence quantum yield. Conjugation of COOR group with π-macrocyclic system leads to a somewhat bigger red-shift of the Q-band when compared with the red-shift caused by participation of lone pair of sulfur in π-system. In contrast, the former substituents cause less hyperchromic shift at all λ_{max} then the *tert*-butylsulfanyl substituents.

Keywords: Azaphthalocyanines; Tetrapyrazinoporphyrazines; Photodynamic therapy; Singlet oxygen quantum yield; Unsymmetrical substitution; Fluorescence quantum yield

1. Introduction

Phthalocyanine (Pc) derivatives and their analogues are a group of compounds that have very stable physical and chemical properties; they absorb strongly in different regions of the electromagnetic spectrum [1]. They are used in different areas such as chemical sensors [2], industrial dyes, photoreceptors [3,4], liquid crystals [5], Langmuir–Blodgett films [6], electrocatalytic oxidation [7], etc. One of their important application is functioning as photosensitizers for photodynamic therapy (PDT) [8–11]. Due to the intense absorption in the red visible region, high efficiency to generate reactive oxygen species (such as singlet oxygen), and low dark toxicity, phthalocyanines have been used in this kind of treatment for various cancers [12] and photoinactivation of viruses [13].

Due to the large planar π-conjugated systems, unsubstituted Pc tend to aggregate, which results in low solubility, difficulties with purification and characterization. Moreover, aggregation shortens the triplet-state lifetimes and reduces the singlet oxygen quantum yield. This behavior can be suppressed by introduction of bulky substituents to the periphery [14]. Different solvents or various central metals [15] also greatly influence the aggregation.

Although a variety of symmetrical tetra-, octa-, and hexadeca-substituted phthalocyanines have been reported in the literature [16,17], there have been few reports on low-symmetry substituted phthalocyanines, mainly because of the difficulties in preparation and purification [18–20]. There are several methods specifically developed for the preparation of low-symmetry phthalocyanines such as polymer support technique [21], cross-coupling [22], “subphthalocyanine” path [23,24] and statistical condensation, the latter necessarily including separation of congener mixtures [25]. The last path (statistical condensation) is the

* Corresponding author. Tel.: +420 49 5067257; fax: +420 49 5512423.
E-mail address: petr.zimcik@faf.cuni.cz (P. Zimcik).

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most commonly used method in the synthesis of low-symmetry Pc. This method uses two different precursors and generally produces six different products. One or two of the six products can be the dominant ones depending on the differences in structure (e.g. electron-withdrawing or donating substituents, steric hindrance [26]) and ratio of the precursors. The resulting physical and chemical properties of the low-symmetry macrocycles can be controlled by the type and number of electron-donating and electron-withdrawing substituents on the precursors [27–29].

Azaphthalocyanines (AzaPc) are aza analogues of Pc with some carbons in their macrocyclic system replaced by nitrogens. Although there are some differences between Pc and AzaPc [14] (e.g. tendency to aggregation and bathochromic shift) AzaPc can be potentially used in applications similar to that of Pc. We have synthesized new zinc AzaPc containing two different kinds of substituents. Bulky *tert*-butylsulfanyl substituents ensure very good monomerization of AzaPc in organic solvents, consequently providing good chromatographic properties. The *tert*-butyl group was previously found to inhibit dimerization better than long alkyl chains [14] and alkylsulfanyl derivatives are the best ones from the point of view of $^1O_2$ production [30] possessing thus the highest potential in PDT. This substituent is also electron-donating with positive mesomeric effect (M+). Butoxycarbonyl group represents an alkyl chain substituent with electron-withdrawing properties due to negative mesomeric effect (M−). Further, we have investigated their UV–vis spectroscopic and fluorescence properties, as well as their singlet oxygen production.

2. Experimental

All organic solvents used for synthesis were of analytical grade. 1,3-Diphenylisobenzofuran (DPBF) and dimethylformamide (DMF) (biotech grade, water <0.005%) for singlet oxygen and fluorescence studies was purchased from Aldrich, diaminomaleonitrile and anhydrous DMF for synthesis from Across Organics and carbon tetrachloride from Lachema (Czech Republic). Zinc phthalocyanine (ZnPc) was purchased from Eastman Organic Chemicals (New York, USA). All chemicals and solvents were used as received without further purification except for zinc acetate (Lachema, Czech Republic) that was dried in a drying gun at 78 °C and under a pressure of 13 mbar for 8 h. TLC was performed on Silica gel 60 F_{254} (Merck, Darmstadt). Merck Kieselgel 60 (0.040–0.063 mm) was used for column chromatography. Infrared spectra were measured in KBr pellets or in chloroform on a Nicolet Impact 400 IR-Spectrometer (USA). ^{1}H and ^{13}C NMR spectra were recorded on Varian Mercury, Vx BB 300 (299.95 MHz, ^{1}H and 75.43 MHz, ^{13}C) Bruker Comp. (Karlsruhe, Germany). Chemical shifts are given relative to internal $Si(CH_3)_4$. Elementary analysis was carried out on Automatic Microanalyser EA1110CE (Fisons Instruments S.p.a., Milano, Italy). UV–vis spectra were recorded on a UV-2401PC spectrophotometer from Shimadzu (Shimadzu Europa GmbH, Duisburg, Germany). A slit width of the instrument was set to 0.2 nm. Wavelength accuracy of the instrument at this slit width is ±0.3 nm. Fluorescence data were obtained on AMINCO-Bowman Series 2 luminescence spectrometer (SLM-Aminco, Urbana, IL, USA). MALDI-TOF mass spectra were recorded in negative reflectron mode on a mass spectrometer Voyager-DE STR (Applied Biosystems, Framingham, MA, USA). For each sample, 0.5 μl of the mixture was spotted onto the target plate, air-dried and covered with 0.5 μl of matrix solution consisting of 10 mg of α-cyano-4-hydroxycinnamic acid in 100 μl of 50% ACN in 0.1% TFA. The instrument was calibrated externally with a five-point calibration using Peptide Calibration Mix1 (LaserBio Labs, Sophia-Antipolis, France).

2.1. Synthesis

Compound **1** was prepared by esterification of sodium potassium tartarate in refluxing butanol with addition of *p*-toluenesulphonic acid. Substances **4** [14] and **5** [31] were prepared according to previously published method, in case of **2** [32] analogically to described method. Aromatic ^{13}C NMR signals of all AzaPc were poor, broad and very hard to detect. MALDI-TOF mass spectra showed a mass corresponding to counted values.

2.1.1. Dioxo-succinic acid dibutyl ester (2)

A suspension of 8.5 g (33 mmol) of **1** and 17.8 g (100 mmol) of *N*-bromosuccinimide was refluxed in 400 ml of anhydrous CCl_4 for 2 h. The mixture was cooled down, filtered and the precipitate washed with diethyl ether. The solvents were evaporated and the residue was dissolved in cold diethyl ether (−20 °C). The precipitate was filtered off and washed with cold diethyl ether. The solvent was evaporated to yield 7.4 g (86.3%) of yellow oil. IR ($CHCl_3$) 2964, 2936, 2876, 1746 (CO), 1466. ^{13}C NMR ($CDCl_3$) δ 13.6, 18.9, 30.4, 66.2, 72.0, 171.6. ^{1}H NMR ($CDCl_3$) δ 4.25 (t, 4H, J = 6.9 Hz, O–CH_2), 1.60–1.72 (m, 4H, CH_2), 1.31–1.46 (m, 4H, CH_2), 0.93 (t, 6H, J = 7.4 Hz, CH_3). Anal. found C 55.81, H 7.02, Calc. ($C_{12}H_{18}O_6$) C 55.27, H 6.70.

2.1.2. 2,3-Dicyano-5,6-dibutoxycarbonylpyrazine (3)

A mixture of 2.58 g (10.0 mmol) of **2** and 1.1 g (10.0 mmol) of diaminomaleonitrile was refluxed in glacial acetic acid for 2 h. The solvent was evaporated and the product was purified by chromatography on silica with chloroform as eluent to yield 3.0 g (91.0%) of yellowish oil. IR ($CHCl_3$) 2964, 2936, 2876, 2245 (CN), 1739 (CO), 1465, 1411. ^{13}C NMR ($CDCl_3$) δ 13.5, 18.9, 30.2, 67.9, 111.7, 133.3, 146.5, 161.5. ^{1}H NMR ($CDCl_3$) δ 4.45 (t, 4H, J = 6.7 Hz, O–CH_2), 1.70–1.85 (m, 4H, CH_2), 1.35–1.53 (m, 4H, CH_2), 0.98 (t, 6H, J = 7.4 Hz, CH_3). Anal. found C 58.17, H 5.49, N 16.96, Calc. ($C_{16}H_{18}N_4O_4$) C 58.29, H 5.31, N 16.68.

2.1.3. General procedure of synthesis of unsymmetrical AzaPc

A mixture of 2.0 g (6.54 mmol) of **4** and 3.5 g (16.0 mmol) of anhydrous zinc acetate in 30 ml of anhydrous DMF was immersed into oil bath preheated to 160 °C and stirred at this temperature until the solution started to turn green (approximately 15 min). Then a solution of 3.0 g (9.1 mmol) of **3** in 20 ml of DMF was added dropwise during 1 h. After the addition was completed, the heating was maintained for an additional 90 min. The mixture was cooled and poured into distilled water (400 ml).

The fine suspension was filtered, washed with water and air-dried. The blue-green solid was then extracted with chloroform and solvent evaporated to yield about 3 g of crude product. This mixture of the six different AzaPc and some side products was separated using column chromatography on silica. The different AzaPc were obtained as green fractions (the last fractions were rather blue) using mobile phase chloroform/THF 30:1. The first band eluted corresponds to compound **5**, the second to compound **6** and the third to compound **7**. When the band corresponding to **7** was eluted from the column, the mobile phase was changed to chloroform/THF 14:1 to obtain compound **8**. Each such isolated crude AzaPc was chromatographically purified further (usually twice).

*2.1.4. 2,3,9,10,16,17-Hexakis(tert-butylsulfanyl)-23,24-bis(butoxycarbonyl)-1,4,8,11,15,18,22,25-octaazaphthalocyaninato zinc(II) (**6**)*

This compound was synthesized according to the general procedure. The title compound isolated from the mixture was then purified on silica gel column using mobile phase chloroform/THF 30:1 and then once more with toluene/THF 14:1. Yield 57 mg (2.0%). IR (KBr) 2960, 2919, 2873, 1735 (CO), 1517, 1456, 1363, 1252. ^{13}C NMR ($CDCl_3$) δ 13.9, 19.3, 29.7, 30.6, 51.4, 66.4. ^{1}H NMR ($CDCl_3$) δ 4.37–4.54 (m, 4H, O–CH_2), 1.90–2.62 (bs, 4H, CH_2), 1.56–1.73 (m, 54H, CH_2), 1.34–1.44 (m, 4H, CH_2), 0.93–1.00 (t, 6H, J = 7.3 Hz CH_3). UV–vis (DMF) λ_{max}, nm (ε) 656 (174,500), 597 (21,100), 394 (92,000). MALDI-TOF MS m/z 1312 ($M - H^+$).

*2.1.5. 2,3,16,17-Tetrakis(tert-butylsulfanyl)-9,10,23,24-tetrakis(butoxycarbonyl)-1,4,8,11,15,18,22,25-octaazaphthalocyaninato zinc(II) and 2,3,9,10-tetrakis(tert-butylsulfanyl)-16,17,23,24-tetrakis(butoxycarbonyl)-1,4,8,11,15,18,22,25-octaazaphthalocyaninato zinc(II) (**7**)*

These two compounds were synthesized according to the general procedure and isolated as a mixture of two isomers (due to similar Rf). The title compounds isolated from the mixture were then purified on silica gel column using mobile phase chloroform/THF 14:1 and then once more with toluene/THF 5:1. Yield 42 mg (1.0%). IR (KBr) 2960, 2930, 2873, 1733 (CO), 1457, 1363, 1248. ^{13}C NMR ($CDCl_3$) δ 13.8, 19.2, 30.5, 51.8, 66.9. ^{1}H NMR ($CDCl_3$) δ 4.17–4.95 (bs, 8H, O–CH_2), 0.34–2.66 (bs, 66H).

UV–vis (DMF) λ_{max}, nm (ε) 660 (194,300), 599 (23,100), 391 (83,000). MALDI-TOF MS m/z 1336 ($M - H^+$).

*2.1.6. 2,3,9,10-Bis(tert-butylsulfanyl)-16,17,23,24-hexakis(butoxycarbonyl)-1,4,8,11,15,18,22,25-octaazaphthalocyaninato zinc(II) (**8**)*

This compound was synthesized according to the general procedure. The title compound isolated from the mixture was then purified on silica gel column using mobile phase chloroform/acetone 2:1. Yield 258 mg (6.3%). IR (KBr) 2960, 2933, 2873, 1732 (CO), 1465, 1401, 1246. ^{13}C NMR ($CDCl_3$) δ 13.6, 19.4, 30.5, 51.9, 67.1. ^{1}H NMR ($CDCl_3$) δ 4.14–4.91 (bs, 12H, O–CH_2), 1.27–2.44 (bs, 42H), 0.72–1.24 (bs, 18H). UV–vis (DMF) λ_{max}, nm (ε) 660 (159,500), 602 (20,700), 394 (55,500). MALDI-TOF MS m/z 1360 ($M - H^+$).

*2.1.7. 2,3,9,10,16,17,23,24-Octakis(butoxycarbonyl)-1,4,8,11,15,18,22,25-octaazaphthalocyaninato zinc(II) (**9**)*

A mixture of 600 mg (1.82 mmol) of **3**, 800 mg (3.65 mmol) of anhydrous zinc acetate and 10 ml of anhydrous dimethylformamide (DMF) was immersed into oil bath preheated to 160 °C and stirred at this temperature for 90 min. The dark blue solution was poured into cold water (200 ml), left for half an hour and crude **6** was filtered off. The solid was then dried and purified by chromatography on silica with chloroform/acetone 2:1 as eluent to yield 80 mg (12.7%) of dark blue solid. IR (KBr) 2961, 2873, 1732 (CO), 1496, 1467, 1250. ^{13}C NMR ($CDCl_3$) δ 13.8, 19.1, 30.4, 67.4, 145.8, 148.8, 150.8, 164.3. ^{1}H NMR ($CDCl_3$) δ 4.32–4.83 (bs, 16H, O–CH_2), 1.72–2.11 (bs, 16H, CH_2), 1.35–1.70 (bs, 16H, CH_2), 0.75–1.20 (bs, 24H, CH_3). UV–vis (DMF) λ_{max}, nm (ε) 659 (136,000), 598 (18,900), 393 (35,100). MALDI-TOF MS m/z 1384 ($M - H^+$).

2.2. Singlet oxygen quantum yield

Singlet oxygen measurements were performed as DPBF decomposition reactions. In all cases, 2.5 ml of a stock solution of DPBF in DMF (5×10^{-5} M) was transfered into a 10 mm × 10 mm quartz optical cell and bubbled with oxygen for 1 min. DMF stock solution of the tested dye (usually 30 μl) was then added. Absorbance of the dye solution in Q-band maximum was always about 0.1. The solution was then stirred and irradiated for defined times using a halogen lamp (Tip, 200 W). Incident light was filtered through a water filter (6 cm) and an orange HOYA G filter to remove infrared light and light under 506 nm, respectively. A decrease of a DPBF amount in the solution (maximum 15%) was measured as the decrease in its absorbance at 415 nm. Singlet oxygen quantum yield (Φ_Δ) of the dye was calculated using Eq. (1):

$$\Phi_\Delta^S = \Phi_\Delta^R \frac{k^S I_{aT}^R}{k^R I_{aT}^S} \quad (1)$$

where k is a slope of a plot of the dependence of $\ln(A_0/A_t)$ on irradiation time t, with A_0 and A_t being the absorbances of the DPBF at 415 nm before irradiation and after irradiation time t, respectively. I_{aT} is a total amount of light absorbed by the dye. Superscripts R and S indicate reference and sample, respectively. AzaPc **5** in DMF was used as the reference ($\Phi_\Delta = 0.67$) [31]. I_{aT} is calculated as a sum of intensities of the absorbed light I_a at wavelengths from 506 to 800 nm (step 0.5 nm). Light under 506 nm is completely filtered off by HOYA G filter and light above 800 nm is not absorbed by the dyes. I_a at given wavelength is calculated using Beer's law (Eq. (2)):

$$I_a = I_0(1 - e^{-2.3A}) \quad (2)$$

where transmittance of the filter at given wavelength stays for I_0 and absorbance of the dye at this wavelength stays for A.

2.3. Fluorescence quantum yield

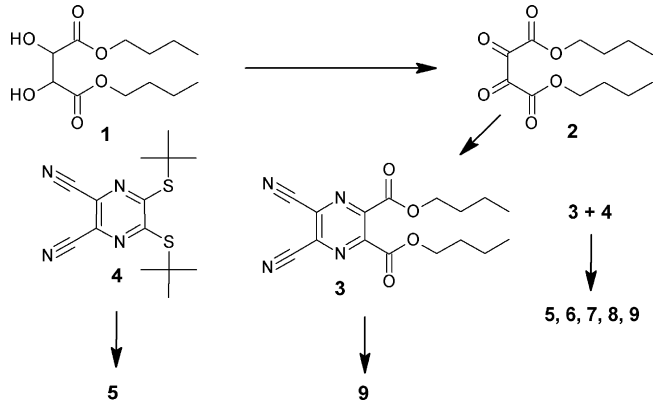
Fluorescence quantum yields of the dyes were determined relative to that of ZnPc ($\Phi_F = 0.17$ in DMF [33]) and calculated using integrated areas under the fluorescence emission spectrum of the sample and Ref. [34]. Fluorescence emission spectra were recorded after excitation at 390 nm. Fluorescence excitation spectra were recorded observing the fluorescence signal at 710 nm. In all cases the absorbance at λ_{max} of the Q-band was below 0.04.

3. Results and discussion

3.1. Synthesis

The synthetic route for preparation of all compounds in this work is shown in Scheme 1. Compound **2** was prepared with some impurities (mainly *N*-bromosuccinimide), which were very difficult to remove (distillation, extraction to various solvents). Only extraction to diethyl ether was relatively successful. On the other side, these impurities did not negatively influence the following step. Compound **3** was synthesized chemically pure from **2** by simple condensation of this diketone with diaminomaleonitrile in very good yields (91%).

Unsymmetrical AzaPc were prepared by a statistical method based on the mixed condensation of two different precursors (**3** and **4**). Such an approach lead to a mixture of six compounds (Fig. 1) and chromatographic separation was required. For simplification, the symmetrical substances **5** and **9** were not separated from the mixture but prepared in a separate reaction.



Scheme 1. Scheme of synthesis.

We have tried to prepare the AzaPc using various cyclization methods, via magnesium butanolate or refluxing in high-boiling solvents (dimethylaminoethanol, quinoline, DMF) with zinc salt. Finally, we found DMF to be the best cyclization medium for both precursors. In parallel, we had to solve the problem of different reactivity of both precursors. The electron withdrawing effect of carbonyl groups increases the reactivity of carbonitrile groups and supports fast self-condensation of precursors **3**. The yields of mixed AzaPc were therefore very low as detected on TLC and the main products were only compounds **5** and **9**. That is why we have modified the reaction conditions: we added **3** dropwise to the solution of **4** in refluxing DMF. This approach was found to be optimal giving reasonable yields of all AzaPc and all unsymmetrical compounds **6–8** could be separated from one reaction. The bulkiness of side chains ensures

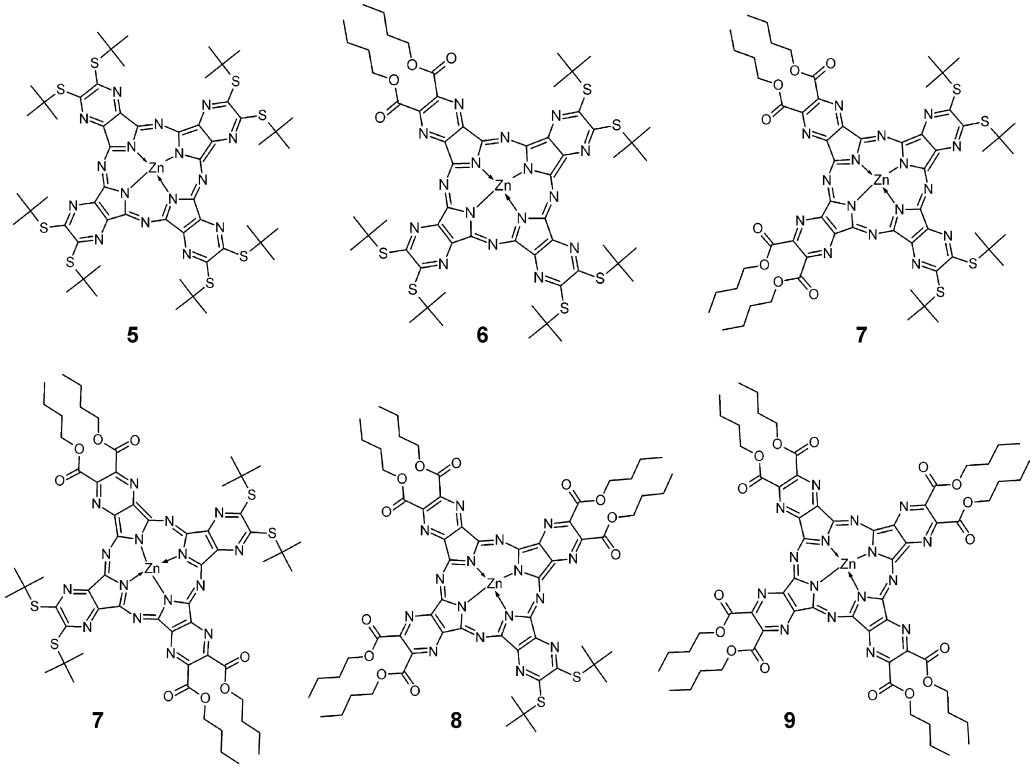


Fig. 1. Structures of AzaPc in mixture.

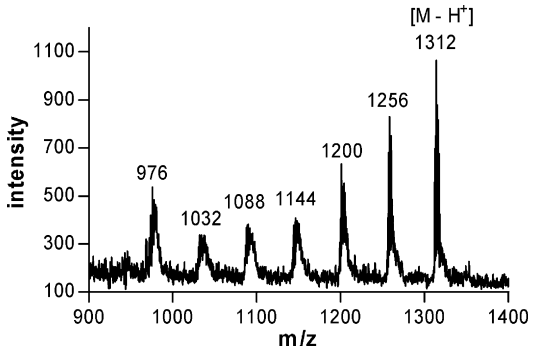


Fig. 2. MALDI-TOF fragmentation spectra of compound **6**.

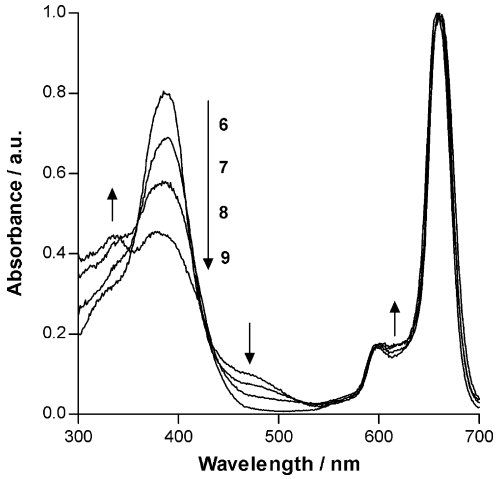


Fig. 3. Changes in UV–vis spectra of **6–9** in DMF. Spectra are normalized to the same absorption at Q-band.

very good monomerization of AzaPc molecules and therefore they could be purely separated on a silica gel column by step gradient chromatography. Compound **5** was eluted first, followed by other AzaPc in the following order: **6–9**. Unfortunately, we have not succeeded in the separation of two positional isomers of compound **7**—adjacent (AABB) and opposite (ABAB). The presence of both isomers was detected on TLC as two overlapping products in the fraction of compound **7** but column chromatography isolation was not successful.

NMR signals of the dyes showed strong broadening. The ^{1}H NMR signals even fused together in the case of unsymmetrical AzaPc (**6–8**) and it was impossible to unequivocally confirm the structure from NMR studies. That is why we had to use MALDI-TOF mass spectrometry that unambiguously confirmed the mass corresponding to the counted values. A cluster typical for the presence of Zn in the structure was found at corresponding masses in all cases for compounds **6–9** and their fragments. Fragmentation of the mass $[M - H^+]$ showed loosening of the fragment of molecular weight of 56 in several steps according to the number of *tert*-butylsulfanyl substituents in the molecule. A proposed mechanism of such fragmentation of AzaPc containing *tert*-butylsulfanyl group has been already reported by us earlier [35]. No lower fragments were found after loosening all possible isobutenes from the *tert*-butylsulfanyl substituent. This behavior confirmed the expected structure further. An example of such mass spectra for compound **6** is presented in Fig. 2.

3.2. UV–vis absorption

UV–vis spectra showed typical monomeric character and a typical Q-band shape in different solvents (DMF, tetrahydrofuran and chloroform) that is characteristic for metal Pc and AzaPc. A considerable decrease in extinction coefficients at all λ_{max} was observed with increasing number of butoxycarbonyl groups in the molecule (Table 1). Such decrease is more pronounced in the area of the B-band. This can be well observed when the absorption spectra are normalized to the same absorption at Q-band (Fig. 3). The intensity of absorption is often influenced by electron-donating (M+) and withdrawing (M−) effects. The positive effect on extinction coefficients is much higher for substituents with M+ effect (in our case alkylsulfanyl substituents) than in the case of M− effect even if this substituent is conjugated with π-system. That is why we have observed the important decrease in intensity of absorption by compounds **6–9**.

At the same time, a shoulder around 480 nm slowly fades away with decreasing number of *tert*-butylsulfanyl substituents completely disappearing by compound **9** with only butoxycarbonyl substituents (Fig. 3). This shoulder arises from the n–π* transition of lone pair electron of sulfur. Relatively weak bands in this area were also observed in the case of similar compounds with ether oxygen bound to Pc macrocycle [36]. Very strong bands in this area were found by alkylamino AzaPc with a lone pair on nitrogen [30].

The Q band of all prepared AzaPc is red-shifted for approximately 25 nm against unsubstituted tetrapyrazinoporphyrazines (TPP) (635 nm in DMSO [37]) or TPP with peripheral chains bound through carbon (636 nm in acetone [38]). If we consider

Table 1
Photophysical and photochemical data of prepared compounds

	Absorbance (DMF)				Fluorescence (DMF)		
	Q-band λ_{max} (nm)	Q-band ε (M^{-1} cm^{-1})	B-band λ_{max} (nm)	B-band ε (M^{-1} cm^{-1})	λ_{max} (nm)	Φ_F[a]	Φ_Δ (DMF)[a]
5	654	281,000	390	137,000	661	0.224	0.670
6	656	174,000	394	92,000	671	0.145	0.676
7	660	194,000	391	83,000	673	0.118	0.668
8	660	160,000	394	56,000	674	0.102	0.592
9	660	136,000	393	35,000	672	0.107	0.515

[a] Mean of three independent measurements. Experimental error was maximum ±8% and ±5% for Φ_F and Φ_Δ, respectively.

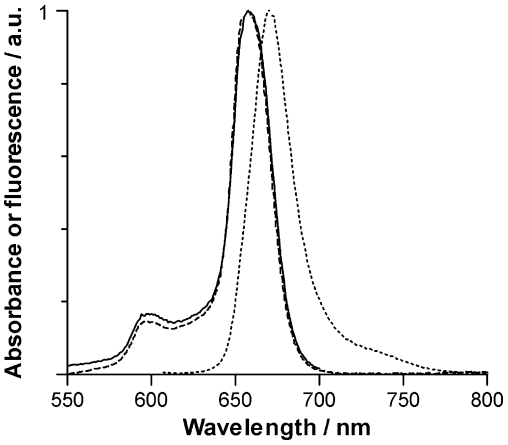


Fig. 4. Normalized fluorescence emission (dotted line), fluorescence excitation (full line) and UV–vis absorption spectra (dashed line) of **6** in DMF.

compound **5** with only *tert*-butylsulfanyl substituents, this shift is caused by the participation of lone pair electrons of sulfur on the π-system. If we consider compound **9**, which lies on the second end of our line of different substitution, conjugation of butoxycarbonyl groups with π-system also shifts the Q-band maximum to higher wavelengths. As we can see from the Q-band λ_{max} values (Table 1), the effect of both substitutions is very similar in this case (the difference between **5** and **9** is only 6 nm) and therefore we observe the λ_{max} values of unsymmetrical compounds to be in the same area too.

3.3. Fluorescence

Fluorescence quantum yields (Φ_F) were determined in the DMF (Table 1). The fluorescence excitation spectra of all compounds correspond to their absorption spectra (Fig. 4). This confirms that tested AzaPc are present in solution almost exclusively in a monomeric form. The presence of dimers in solution influences the shape of absorption spectra but not the excitation spectra because dimers do not fluoresce. A perfect accordance of absorption and fluorescence excitation spectra is therefore a warranty of no aggregation.

The fluorescence emission spectra are of typical shape for AzaPc. The maxima of compounds with butoxycarbonyl substituents are considerably red-shifted against compound **5**. The fluorescence quantum yields (Φ_F) increases with the number of *tert*-butylsulfanyl substituents showing negative influence of butoxycarbonyl groups on the Φ_F (Fig. 5).

3.4. Singlet oxygen measurements

Singlet oxygen tests were performed in DMF as the solvent that ensures monomerization of AzaPc in solution. Light less than 506 nm was filtered off to eliminate the self-decomposition of DPBF. No changes in DPBF concentration were observed upon irradiation of its solution without the dye; therefore the use of the filter was efficient. Quantum yields of singlet oxygen were calculated using AzaPc **5** as the Ref. [31]. Results obtained from these measurements are presented in Table 1. From the Φ_Δ values of the compounds, it is apparent that similar dependences can be formulated as in the case of Φ_F but the decrease of Φ_Δ is less and slower (Fig. 5).

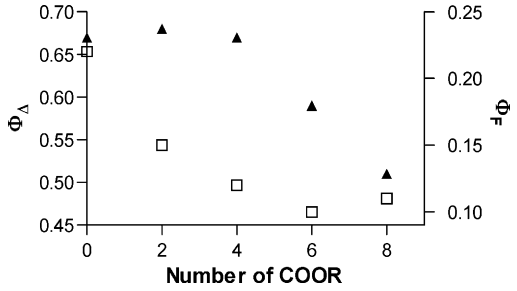


Fig. 5. The dependence of Φ_Δ (▲) and Φ_F (□) values on amount of butoxycarbonyl groups in molecule of AzaPc.

4. Conclusion

Using bulky substituents on periphery of AzaPc causes very good monomerization of this kind of planar dyes and therefore enables efficient purification of a statistical mixture arising from condensation of two different precursors. In the case when two kinds of substituents with different properties (with M+ and M− effects) are present, the differences in photophysical properties can be observed. The electron-donating effect of *tert*-butylsulfanyl substituents shifts the Q-band bathochromically and strongly hyperchromically. The electron-withdrawing effect of butoxycarbonyl has only a small effect on the intensity of absorption but conjugation of carbonyl group causes a slightly stronger red-shift of the Q-band than simple participation of sulfur free electron pair in π-system. Butoxycarbonyl substituents attached directly to π-system also negatively influence the Φ_Δ and Φ_F values.

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