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Boron(III) Subphthalocyanines Axially Modified with Unsaturated and Aromatic Carboxylic Acids: Synthetic Peculiarities and Photochemical Properties

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In this work, the axial modification of boron(III) subphthalocyanine (sPc) with several unsaturated and aromatic carboxylic acids was performed for the first time. Acrylic acid (AA), maleic acid (MA), fumaric acid (FA), and terephthalic acid (TA) were used as precursors. During the substitution reaction of axial bromine in the initial subphthalocyanine with acrylate, the formation of acrylic acid esterification products (sPcAA1-3) was observed. A range of photophysical parameters (quantum yield and fluorescence lifetime) was obtained for all compounds, and the generation of singlet oxygen in DMSO and ethanol was studied. The series of subphthalocyanines examined exhibited high quantum yields of singlet oxygen generation and can be considered as a new type of monomeric photosensitizers with potential for immobilization on the surface of various matrices due to the presence of anchor carboxylic groups. This development could lead to hybrid photoactive materials for oxidative applications in photocatalysis and photodynamic therapy (PDT).

Keywords Subphthalocyanine, axial modification, unsaturated and aromatic carboxylic acids, singlet oxygen, photosensitizers.

Субфталоцианины бора(III), аксиально модифицированные ненасыщенными и ароматическими карбоновыми кислотами: особенности синтеза и фотохимические свойства

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В работе впервые произведена аксиальная модификация субфталоцианина бора(III) (sPc) ненасыщенными и ароматическими карбоновыми кислотами: одноосновной акриловой (AA) и двухосновными малеиновой (MA), фумаровой (FA) и терефталевой кислотой (TA). В ходе проведения реакции замещения аксиального брома в исходном субфталоцианине на акрилат было обнаружено образование продуктов этерификации акриловой кислоты (sPcAA1-3). Для всех соединений получен ряд фотофизических параметров (квантовый выход и время жизни флуоресценции) и исследована генерация синглетного кислорода в ДМСО и этаноле. Изученный ряд субфталоцианинов имеет высокие квантовые выходы генерации синглетного кислорода и может быть рассмотрен в качестве нового типа мономерных фотосенсибилизаторов с последующей возможностью иммобилизации на поверхности различных матриц за счёт якорных карбоксильных групп или полимеризации для разработки гибридных фотоактивных материалов для окислительных приложений фотокатализа.

Ключевые слова: Субфталоцианины, аксиальная модификация, непредельные и ароматические карбоновые кислоты, синглетный кислород, фотосенсибилизаторы.

Introduction

Pyrrole-containing macroheterocyclic compounds, notably porphyrinoids, have been intensively studied for several decades as photosensitizers (PS) for photodynamic therapy[1] and as components of multifunctional materials for organic electronics and catalysis.[2-5] Among them, phthalocyanines (**Pc**)[6,7] and their contracted homologs – subphthalocyanines (***s*Pc**)[8,9] are widely studied in these scopes. The interest in these compounds stems from their ability to generate reactive oxygen species (ROS), particularly singlet oxygen ($^1O_2$), and their capacity to modulate fluorescent properties. sPc exhibit unique advantages, such as resistance to aggregation and retention of fluorescence in solution, including aqueous media, making them valuable for theranostic applications.[10-12]

Numerous strategies exist to modify the physico-chemical and photophysical properties of these macro-cycles. One of such methods is axial modification of ***s*Pc**.[13,14] Previously, our group applied this procedure to develop new p*H*-sensors and cationic receptors based on ***s*Pc** and their azaanalogs,[15,16] as well as photocatalysts for aerobic selective oxidation of sulfides to sulfoxides.[17]

Herein, we describe the synthesis of novel axially modified subphthalocyanines incorporating fragments of monomeric unsaturated (acrylic AA, fumaric FA, and maleic acid MA) and aromatic terephthalic acid TA. TA was used to modify R_8PcSi, serving as precursors for a new class of metal-organic frameworks (MOFs).[18,19] Acrylic acid derivatives were also applied for the functionalization of BODIPY and the preparation of fluorescent polymeric nanoparticles. In our case, we studied a series of monomeric subphthalocyanines with fragments of the above-mentioned carboxylic acids (AA, FA, MA and TA) in the axial position as precursors of photoactive materials. Singlet oxygen generation, fluorescence lifetime and fluorescence quantum yield were studied in toluene, DMSO and ethanol and compared with previously published data for **sPcCl** and **sPcBA** (BA - benzoic acid).

Experimental

General

All chemicals for the syntheses were purchased from certified suppliers (Acros Organics, TCI Europe, Macklin, Sigma Aldrich and Merck) and used as received. In particular, phthalonitrile (PN) was purchased from TCI Europe, acrylic acid from Acros Organics, fumaric, maleic and terephthalic acid from Macklin, boron(III) tribromide from Sigma Aldrich. Commercially available solvents were dried and distilled prior to use. TLC was performed on Merck aluminum sheets coated with silica gel 60 F254. Merck Kieselgel 60 (0.040–0.063 mm) was used for column chromatography.

Mass-spectrometric measurements were carried out on a MALDI TOF Shimadzu Biotech Axima Confidence spectrometer in the negative and positive modes. Electronic absorption spectra were recorded using a JASCO V-770 spectrophotometer and IR spectra on a Cary 630 FTIR spectrometer using method for KBr disk ATR. NMR spectra (^{1}H, ^{11}B) were measured with a Bruker Avance 500 spectrometer. The chemical shifts are reported as δ values in ppm and are indirectly referenced to $Si(CH_3)_4$ (^{1}H NMR) and $BF_3{\cdot}Et_2O$ *via* the signal from the solvent. *J* values are given in Hz.

Synthesis

***s*PcBr** was synthesized by modifying the procedure[20,21] and reported in our previous work.[17]

*Axial modification **sPc** with acrylic acid.* 0.1 g of ***s*PcBr** (0.2 mmol), acrylic acid (AA) (1.0 mmol, 5-fold excess) was mixed in 10 mL of freshly distilled toluene and refluxed under vigorous stirring for 18 hours. The solvent was then removed under reduced pressure. The residue was chromatographed using column chromatography on silica gel. Primary chromatography was performed by using CH_2Cl_2:EtOH (2%). As a result, 3 fractions were isolated, which were further chromatographed according to the information below.

*Acrylatoboron(III) subphthalocyaninate (**sPc-AA1**).* Crude product was isolated after addition chromatography on SiO_2 using CH_2Cl_2 as eluent (R_f = 0.67, in CH_2Cl_2:EtOAc (5:1)). Yield: 0.023 g, 25 %. Mass LDI TOF (positive ion) *m/z*: 466 Da $[M]^+$ (calculated for $C_{27}H_{15}BN_6O_2$ – 466.14 Da). ^{1}H NMR (500.17 MHz, $CDCl_3$) δ_H ppm: 8.87 (m, 6H, $^{\alpha}$Bz), 7.88 (m, 6H, $^{\beta}$Bz), 5.54 (d, 1H, *J* = 17.0 Hz), 5.21 (d, 1H, *J* = 10.2 Hz), 5.10 (dd, 1H, *J* = = 17.1 Hz, *J* = 10.2 Hz). ^{11}B NMR (160.47 MHz, $CDCl_3$) δ_B ppm: -14.99. IR (KBr) ν cm^{-1}: 3200w, 3060w, 1739vs, 1616w, 1461s, 1396s, 1297s, 1228s, 1139s, 1012m, 867w, 756s, 565vw. UV-Vis (toluene) λ_{max} nm (lgε): 304 (4.33), 564 (4.62).

*Acryloyloxo-propionatoboron(III) subphthalocyaninate (**sPc-AA2**).* Crude product was isolated after addition chromatography on SiO_2 using CH_2Cl_2:EtOH (1%) as eluent (R_f = 0.51, in CH_2Cl_2:EtOAc (5:1)). Yield: 0.020 g, 21 %. Mass LDI TOF (positive ion) *m/z*: 538 Da $[M]^+$ (calculated for $C_{30}H_{19}BN_6O_4$ – 538.16 Da). ^{1}H NMR (500.17 MHz, $CDCl_3$) δ_H ppm: 8.84 (m, 6H, $^{\alpha}$Bz), 7.88 (m, 6H, $^{\beta}$Bz), 6.08 (d, 1H, *J* = 17.1 Hz), 5.80 (dd, 1H, *J* = 17.3 Hz, *J* = 10.4 Hz), 5.61 (d, 1H, *J* = 10.4 Hz), 3.69 (t, 2H, *J* = 6.4 Hz), 1.66 (t, 2H, *J* = 6.4 Hz). ^{11}B NMR (160.47 MHz, $CDCl_3$) δ_B ppm: -15.16. IR (KBr) ν cm^{-1}: 3060vw, 2920vw, 1720vs, 1623w, 1457s, 1394s, 1286s, 1193s, 1140s, 1025m, 865w, 738s, 572vw. UV-Vis (toluene) λ_{max} nm (lgε): 300 nm (3.87), 564 nm (4.17).

*Acryloyloxo-propionyloxo-propionatoboron(III) subphthalocyaninate (**sPc-AA3**).* Crude product was isolated after addition chromatography on SiO_2 using CH_2Cl_2:EtOH (1%) as eluent (R_f = = 0.33, in CH_2Cl_2:EtOAc (5:1)). Yield: 0.004 g, 3 %. Mass LDI TOF (positive ion) *m/z*: 610 Da $[M]^+$ (calculated for $C_{33}H_{23}BN_6O_6$ – 610.18 Da). ^{1}H NMR (500.17 MHz, $CDCl_3$) δ_H ppm: 8.90 (m, 6H, $^{\alpha}$Bz), 7.94 (m 6H, $^{\beta}$Bz), 6.33 (d, 1H, *J* = 17.3 Hz), 6.03 (dd, 1H, *J* = 17.3 Hz, *J* = 10.4 Hz), 5.81 (d, 1H, *J* = 10.4 Hz), 4.21 (t, 2H, *J* = 6.3 Hz), 3.68 (t, 2H, *J* = 6.4 Hz), 2.41 (t, 2H, *J* = 6.3 Hz), 1.64 (t, 2H, *J* = 6.4 Hz). ^{11}B NMR (160.47 MHz, $CDCl_3$) δ_B ppm: -15.15. IR (KBr) ν cm^{-1}: 3068vw, 2924w, 1728vs, 1636m, 1461m, 1394m, 1290m, 1190s, 1021m, 738m. UV-Vis (toluene) λ_{max} nm (lgε): 300 (4.21), 564 (4.43).

*General method for axial modification **sPc** with fumaric, maleic and terephthalic acid.* 0.1 g of ***s*PcBr** (0.2 mmol), corresponding acid (FA, MA or TA) (2 mmol, 10-fold excess) was mixed in 2.5 mL of freshly distilled toluene and 2.5 mL of dry pyridine. Mixture was refluxed under vigorous stirring for 3 h. The solvent was then removed under reduced pressure. The reaction mixture was washed with 30% aqueous EtOH solution to remove unreacted corresponding dicarboxylic acid. Primary chromatography was performed by using $CHCl_3$:MeOH (2-5%).

*Hydrofumaratoboron(III) subphthalocyaninate (**sPcFA**).* The third fraction in this case contained crude target product which was isolated by addition column chromatography on SiO_2 using CH_2Cl_2:MeOH (2%) as eluent (R_f = 0.18, in CH_2Cl_2:EtOAc (5:1)). Yield: 0.018 g, 18 %. Mass LDI TOF (positive ion) *m/z*: 511 Da $[M+H]^+$ (calculated for $C_{28}H_{16}BN_6O_4$ – 511.13 Da).

^{1}H NMR (500.17 MHz, $CDCl_3$) δ_H ppm: 8.84 (m, 6H, $^{\alpha}$Bz), 7.87 (m, 6H, $^{\beta}$Bz), 5.90 (d, 1H, J = 15.6 Hz), 5.83 (d, 1H, J = 15.6 Hz). ^{11}B NMR (160.47 MHz, $CDCl_3$) δ_B ppm: -14.94. IR (KBr) ν cm^{-1}: 3068vw, 2924w, 1707s, 1642s, 1454s, 1301vs, 1146s, 1025s, 870w, 753m. UV-Vis (toluene) λ_{max} nm (lgε): 304 (4.30), 564 (4.62).

Hydromaleatoboron(III) subphthalocyaninate ***(sPcMA)***. The second fraction in this case contained crude target product which was isolated by addition column chromatography on SiO_2 using CH_2Cl_2:MeOH (2%) as eluent (R_f = 0.07, in CH_2Cl_2:EtOAc (5:1)). Yield: 0.008 g, 8%. Mass LDI TOF (positive ion) *m/z*: 511 Da $[M+H]^+$ (calculated for $C_{28}H_{16}BN_6O_4$ – 511.13 Da). ^{1}H NMR (500.17 MHz, $CDCl_3$) δ_H ppm: 8.86 (m, 6H, $^{\alpha}$Bz), 7.90 (m, 6H, $^{\beta}$Bz), 5.90 (d, 1H, J = 15.6 Hz), 5.80 (d, 1H, J = 15.6 Hz). ^{11}B NMR (160.47 MHz, $CDCl_3$) δ_B ppm: -14.92. IR (KBr) ν cm^{-1}: 3069vw, 2927w, 1707s, 1642s, 1459s, 1301vs, 1146s, 1025s, 870w, 753m. UV-Vis (toluene) λ_{max} nm (lgε): 303 (4.38), 564 (4.67).

Hydroterephthalatoboron(III) subphthalocyaninate ***(sPcTA)***. The forth fraction in this case contained crude target product which was isolated by addition column chromatography on SiO_2 using $CHCl_3$:MeOH (5%) as eluent (R_f = 0.14, in CH_2Cl_2:EtOAc (5:1)). Yield: 0.047 g, 42%. Mass LDI TOF (positive ion) *m/z*: 561 Da $[M+H]^+$ (calculated for $C_{32}H_{18}BN_6O_4$ – 561.15 Da). ^{1}H NMR (500.17 MHz, DMSO-d_6) δ_H ppm: 13.10 (br.s, 1H, COOH), 8.90 (m, 6H, $^{\alpha}$Bz), 8.04 (m, 6H, m, 6H, $^{\beta}$Bz), 7.62 (d, 2H, J = 8.5 Hz), 7.13 (d, 2H, J = 8.4 Hz). ^{11}B NMR (160.47 MHz, $CDCl_3$) δ_B ppm: -14.45. IR (KBr) ν cm^{-1}: 3062vw, 1700s, 1457s, 1293vs, 1135vs, 1016s, 995s, 893w, 742s, 572m. UV-Vis (EtOH) λ_{max} nm (lgε): 299 (3.74), 563 (3.96).

Fluorescence measurements

Fluorescence emission spectra were measured on a JASCO FP-8350 spectrofluorometer. Fluorescence quantum yields (Φ_F) were determined by a comparative method using the Eq. 1:

$$\Phi_F^S = \Phi_F^R \cdot (F^S/F^R) \cdot (A^R/A^S) \cdot (n^S/n^R)^2, \quad (1)$$

where F is the integrated area under the emission spectrum, A is the absorbance at the excitation wavelength (500 nm), n is the refraction index of the solvent. Superscripts R and S correspond to the reference and the sample, respectively. Rhodamine 6G, which has Φ_F^R=0.94 in ethanol[22] was used as a reference. The emission spectra were corrected for the instrument response. Absorption in the *Q*-band region was kept below 0.1 in order to eliminate an inner filter effect. All measurements were performed three times and presented data represent the mean values of three experiments with the estimated error ±10%.

Singlet oxygen quantum yield

The generation of the singlet oxygen in EtOH (absolute) solution was used to assess the singlet oxygen quantum yields (Φ_Δ). The technique relies on the measurements of kinetics of decomposition of 1,3-diphenylisobenzofuran (DPBF) using a bengal rose (BR) as a reference (Φ_Δ = 0.68[23] in EtOH and 0.16 in DMSO[24]). A solution of DPBF (absorbance at 410 nm *ca*. 1.16–1.27) was transferred into a 1×1 cm quartz optical cuvette and bubbled with oxygen for 30 s. Then, a portion of EtOH solution of the studied compound was added to keep the absorbance at the Q-band about 0.1. The solution was stirred and irradiated for a given time with a 100 W ozone free Xe arc lamp (Newport) equipped with focusing lens. Incident light was filtered through a water filter (6 cm) and through a longpass FSQ-GG 455 nm (Newport) to exclude the direct heating and the irradiation with wavelengths shorter than 455 nm, respectively.

The decrease in the DPBF content in solution with irradiation time was monitored at 417 nm. The Φ_Δ value was calculated using the Eq. 2:

$$\Phi_\Delta^S = \Phi_\Delta^R \frac{k^S \cdot I_{aT}^R}{k^R \cdot I_{aT}^S}, \quad (2)$$

where k is a slope of the plot of the dependence of $\ln(A_0/A_t)$ on the irradiation time t, and A_0 and A_t are the absorbance of DPBF at 410 nm before irradiation and after irradiation with time t, respectively. I_{aT} is the total intensity of light absorbed by the compound. Superscripts R and S indicate the reference and the sample, respectively.

Fluorescence lifetime

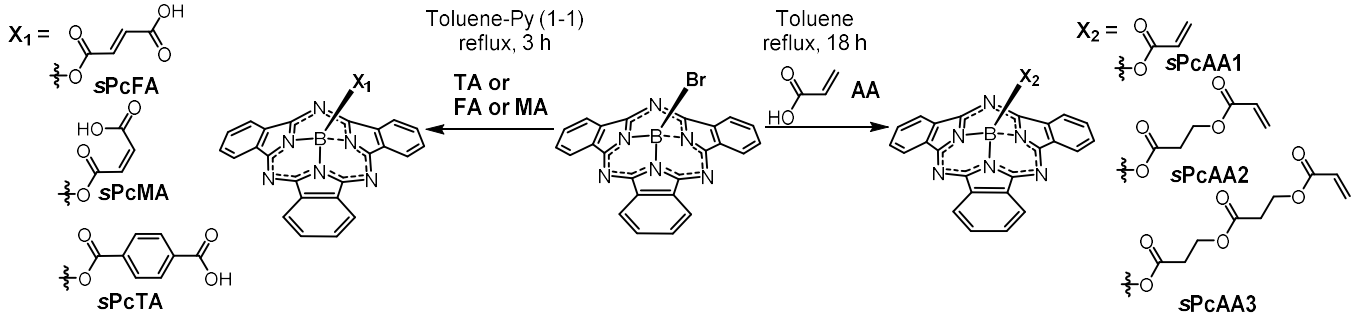
The time-resolved fluorescence measurements were performed on a FluoTime 300 spectrometer (PicoQuant) with Sub-nanosecond Pulsed LEDs excitation at 480±25nm (PLS 500, pulse width ~800 ps) by time correlated single photon counting method (TCSPC). The decay curves were fitted to exponential functions with EasyTau software.

Radiative and nonradiative decay constants

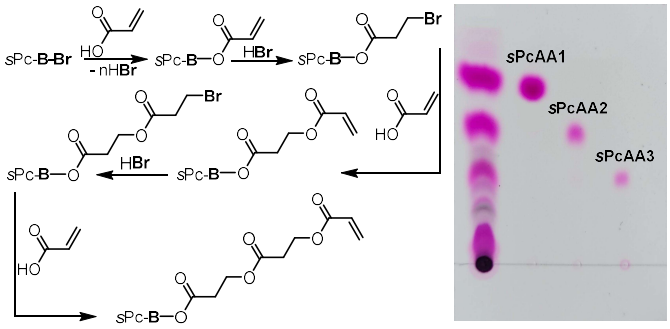
Since the fluorescence decays were monoexponential, the rate constants of radiative (k_r) and nonradiative (k_{nr}) decay were calculated from the value of fluorescence quantum yield (Φ_F) and fluorescence lifetime (τ_F) according to Eqs. 3 and 4:

$$k_r = \Phi_F/\tau_F, \quad (3)$$

$$k_{nr} = (1 - \Phi_F)/\tau_F \quad (4)$$



Scheme 1.



Scheme 2. Possible esterification way of **sPcAA1** to formation of **sPcAA2** and **sPcAA3**, respectively. Photograph of TLC-plate on SiO_2 (eluent CH_2Cl_2:EtOAc (5:1))

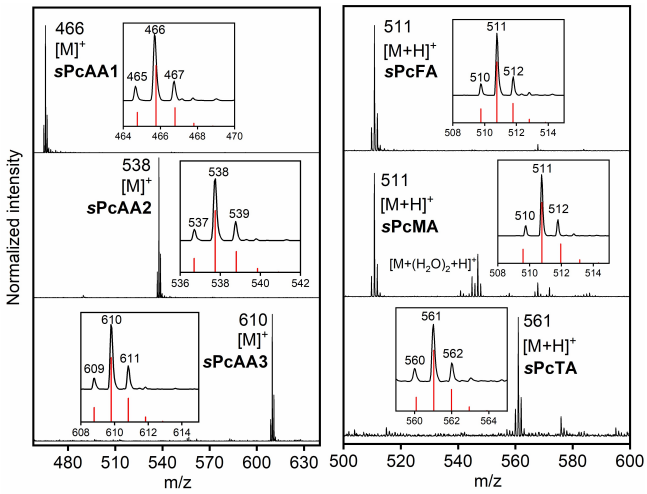


Figure 1. LDI-TOF spectra of obtained subphthalocyanines recorded in the positive region. Theoretical isotope distribution is shown in the red insets.

Results and Discussion

Synthesis

Homborg's method[21] as standard procedure was used for the axial modification of subphthalocyanine boron(III) bromide in case of synthesis of acrylate derivatives (***s*PcAA**). Brominated subphthalocyanine did not require extensive chromatographic purification before axial modification and had highest yields with respect to chlorinated *s*Pc. The synthesis was conducted in boiling dry toluene for 18 h (Scheme 1). Preliminary analysis using thin-layer chromatography (TLC) in CH_2Cl_2:EtOAc (5:1) on silica gel revealed three main fractions, in addition to the fraction of ***s*PcBr** (Scheme 2, see fraction on the start on TLC plate). Each fraction was isolated through column chromatography and further purified by additional chromatography. The structures of the isolated fractions were determined based on LDI TOF mass spectrometry and ^{1}H NMR spectroscopy (see further description below). The first fraction was identified as the target product and contained acrylato-*s*Pc (***s*PcAA1**).

The interesting products were isolated from the second and third fractions. We found that during the axial modification the released HBr promotes the formation of acryloyloxy-propionato- (***s*PcAA2**) and acryloyloxy-propionyloxy-propionato (***s*PcAA3**) derivatives *via* hydrobromination stages against Markovnikov's rule according to the Scheme 2. Fumarato-, maleato-, and terephthalato-*s*Pc (***s*PcFA**, ***s*PcMA** and ***s*PcTA**, respectively) could only be obtained in a boiling pyridine-toluene mixture (1:1) for 3 h. The target axially modified sPcs could not be synthesized in pure toluene. Pyridine was used to dissolve the corresponding dicarboxylic acids, since FA, MA, and TA exhibited poor solubility in toluene.

Characterization

The LDI mass spectra of ***s*PcX** confirm the formation of the target subphthalocyanine macrocycles (Figure 1). In the positive region the intense molecular ion peaks $[M]^+$ with characteristic isotopic distribution patterns are observed at *m/z* = 466, 538 and 610 Da for ***s*PcAA1**, ***s*PcAA2** and ***s*PcAA1**, respectively (see Figure 1, left side). Mass spectra of ***s*PcFA**, ***s*PcMA** and ***s*PcTA**, demonstrate the clusters of molecular ions $[M+H]^+$ (*m/z* = 511 and 561 Da, respectively), which are characteristic of compounds with anchor carboxylic groups (Figure 1, right side). Protonation of the COOH-group is a common feature of these compounds and was previously identified by us for the 4-carboxy-phenoxy derivative ***s*PcPHBA**[17]. Theoretical calculated isotope distribution is in good agreement with the experimental pattern in all cases (Figure 1, red line in the insets).

The presence of carbonyl fragments in the axial ligands of the obtained subphthalocyanines is confirmed by the FTIR spectra. The valence vibrations of C=O bond of the ***s*PcAA1-3** series appear in the range of 1720–1740 cm^{-1} (Figure 2, left side). Whereas $\nu_{C=O}$ appear at 1700–1707 cm^{-1} for ***s*PcFA**, ***s*PcMA** and ***s*PcTA** (Figure 2, right side). This shift in the vibration frequency to lower values by ~40 cm^{-1} should be associated with the presence of intermolecular hydrogen bonds between the anchor carboxylic groups. The broadened band in the region of ~2500 cm^{-1} indicates the *H*-bond (see the spectra of ***s*PcFA**, ***s*PcMA** and ***s*PcTA**, Figure 2), which was not found in the case of the ***s*PcAA** series. The stretching vibration of the $\nu_{B\text{-}O}$ bond is a characteristic frequency for such axially modified subphthalocyanines and appears in the range of 1010–1025 cm^{-1}. These values are consistent with the literature data on the IR spectroscopy of benzoato- and acetato-*s*Pc derivatives, described in the work of H. Homborg *et al.*[21]

The FTIR spectra of ***s*PcFA** and ***s*PcMA** are identical in contrast to the spectra of the starting carboxylic acids (see Supporting Information, Figure S1). In particular, maleic acid has a carboxylate anion band at 1567–1587 cm^{-1} due to the formation of an intramolecular *H*-bond, which is absent in fumaric acid. This intense band is also absent in the case of ***s*PcMA** due to the coordination with the electrophilic boron center.

The structures of all the obtained compounds were confirmed by ^{1}H and ^{11}B NMR spectra (Figures 3, 4 and S2-12). The integrated intensities of the characteristic multiplets of the peripheral and non-peripheral protons of the benzene annulated rings (Figure 3, blue and red circles at 8.9 and 7.9 ppm, respectively) have a 1:1 ratio in all cases. The diastereotopic protons of the axial ligands of the

acrylate fragment in ***s*PcAA1** and the acryloyl group in ***s*PcAA2-3** (Figure **3**, purple and green circles) have resonances in the form of doublets with the characteristic spin-spin coupling constants of 17.0-17.3 and 10.2–10.4 Hz, respectively. The low-field shift of the resonances of vinyl protons (Figure 3, purple, green and yellow circles) by 0.6–0.8 ppm as the number of propionyloxy groups of the axial ligand increases in the ***s*PcAA1- AA3** series is due to the influence of the macrocyclic current of the *s*Pc. The presence of the propionate group in ***s*PcAA2** and the propionyloxy-propionate fragment in ***s*PcAA3** is confirmed by the characteristic triplets in the high field region (Figure 3, pink, brown, gray and light blue circles). These signals have the identical ratio of integrated intensities and typical J = 6.3–6.4 Hz.

The vicinal protons of the fumarate and maleate groups for ***s*PcFA** and ***s*PcMA** have characteristic signals in the form of two doublets in the region of 5.9–5.8 ppm (Figure 4). The signals of the fumarate fragment are slightly shifted to the low-field region compared to the maleate protons, which is typical for the monoesters of FA and MA.[21] The first spin-spin coupling constant does not differ for ***s*PcFA** and ***s*PcMA** (J_{ab} = 15.6 Hz). Whereas, J_{ac} for ***s*PcMA** is 1.3 times higher than for ***s*PcFA**.

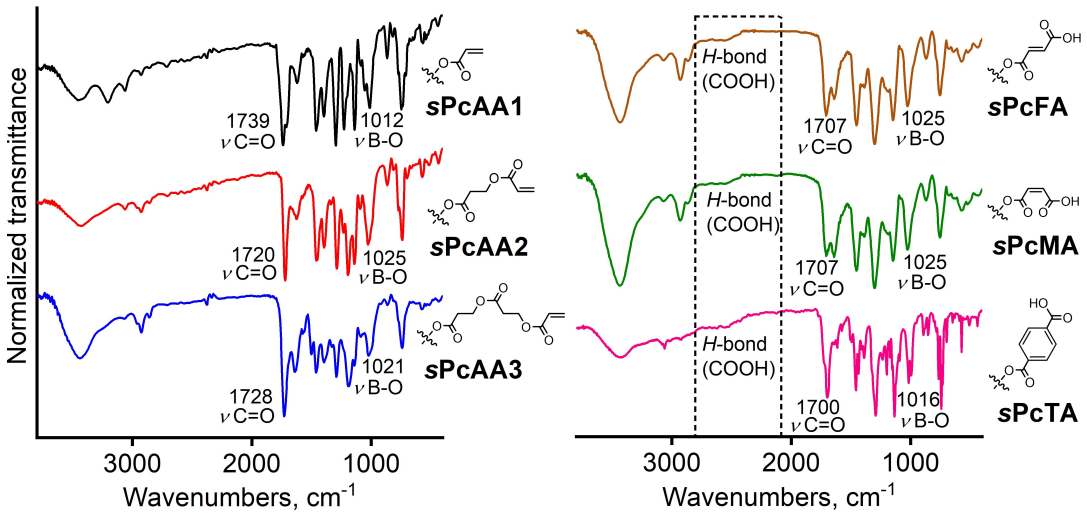


Figure 2. FTIR-spectra of obtained subphthalocyanines in KBr disk.

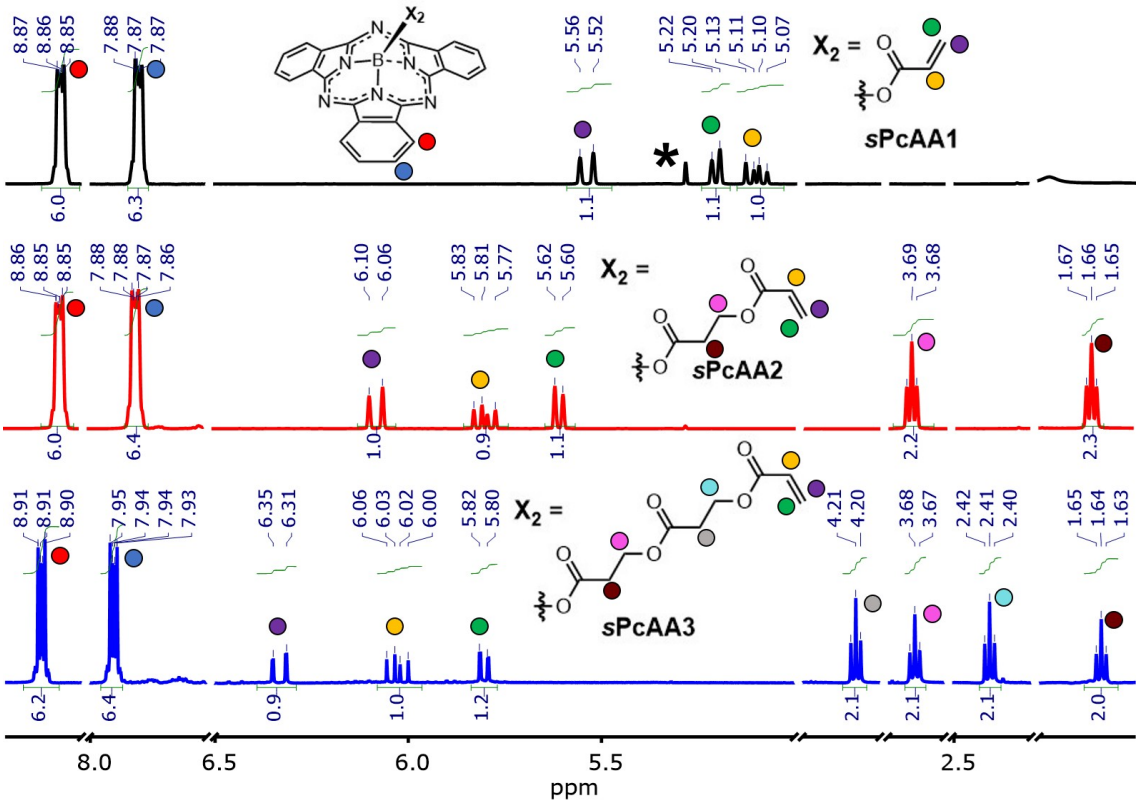


Figure 3. ^{1}H NMR spectra of **sPcAA1-3** recorded in $CDCl_3$.

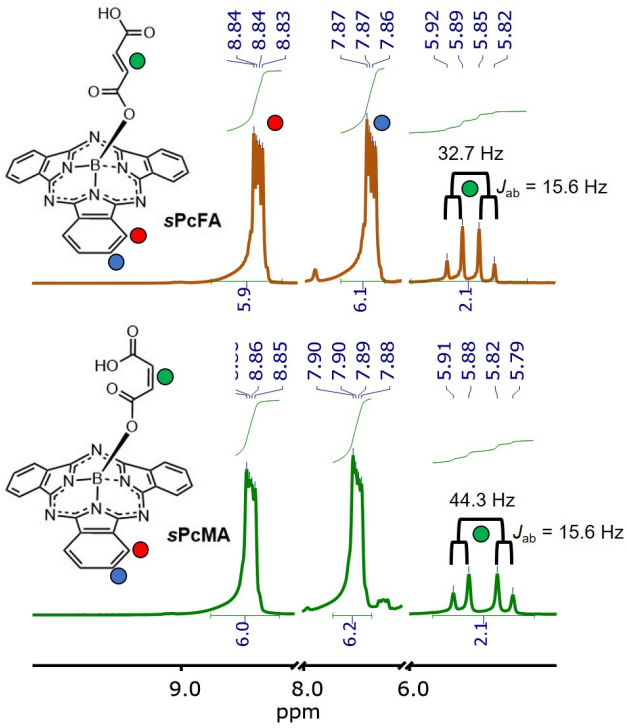


Figure 4. ^{1}H NMR spectra of **sPcFA** and **sPcMA** recorded in $CDCl_3$.

Photophysical properties

Electronic absorption and fluorescence emission spectra of all *s*Pcs were recorded in toluene, DMSO and ethanol. The emission bands in all cases have mirror symmetry with the *Q* band in the corresponding excitation spectra in accordance with Levshin's law (Figures S13-18). The Stokes shift between the maxima in the absorption and emission spectrum is 7–14 nm which indicates only small geometrical rearrangements occur in the excited states. The excitation spectra perfectly matched the absorption spectra, confirming that the compounds were in all solvents in monomeric form during the measurements and that aggregation did not affect the photophysical data.

The axial ligand of the obtained compounds in all cases has a strong effect on the photophysical characteristics (primarily, the lifetime of fluorescence) compared to axially chlorinated ***s*Pc**. The fluorescence lifetime of ***s*PcCl** increases in toluene compared to an ethanol solution. The carboxylate-derivatives (including ***s*PcBA** – benzoateboron subpthalocyanine) have the opposite trend (Figure 5a) and τ_F decreases in the series EtOH-Toluene-DMSO. Value of τ_F does not correlate with the fluorescence quantum yield (Φ_F), which may indirectly indicate the occurrence of nonradiative processes in the excited state with the participation of the proton-acceptor solvent (DMSO) and the acidic center of the axial ligand of *s*Pc. This is indicated by the values of the nonradiative decay constants (k_{nr}), which have a maximum value of ~ $(4.5–4.8)\cdot10^8$ s^{-1} in DMSO compared to other solvents.

The obtained subphthalocyanines demonstrate high values of quantum yield (Φ_Δ) of $^1O_2$ generation (0.50–0.75) in ethanol (see Table 1). These values are higher than for ***s*PcCl** (Φ_Δ= 0.40) and are comparable with previously obtained data on benzoato-*s*Pc (Φ_Δ = 0.59). Among the studied *s*Pc in this work, the most effective photosensitizers were ***s*PcAA3** (Φ_Δ = 0.75) and ***s*PcFA** (Φ_Δ = 0.73). In DMSO, the values were lower (0.27–0.31), but were higher than for Rose Bengal standard by ~2 times.

Conclusions

Acrylic, fumaric, maleic and terephthalic acids were successfully applied for the axial modification of boron(III) bromide of subphthalocyanine for the first time. The reaction of sPc with acrylic acid resulted in stepwise esterification with the formation of the corresponding acryloyloxy-propionato-sPc and acryloyloxy-propionyloxy-propionato-sPc. The composition and structure of all obtained compounds were proved using a set of spectral

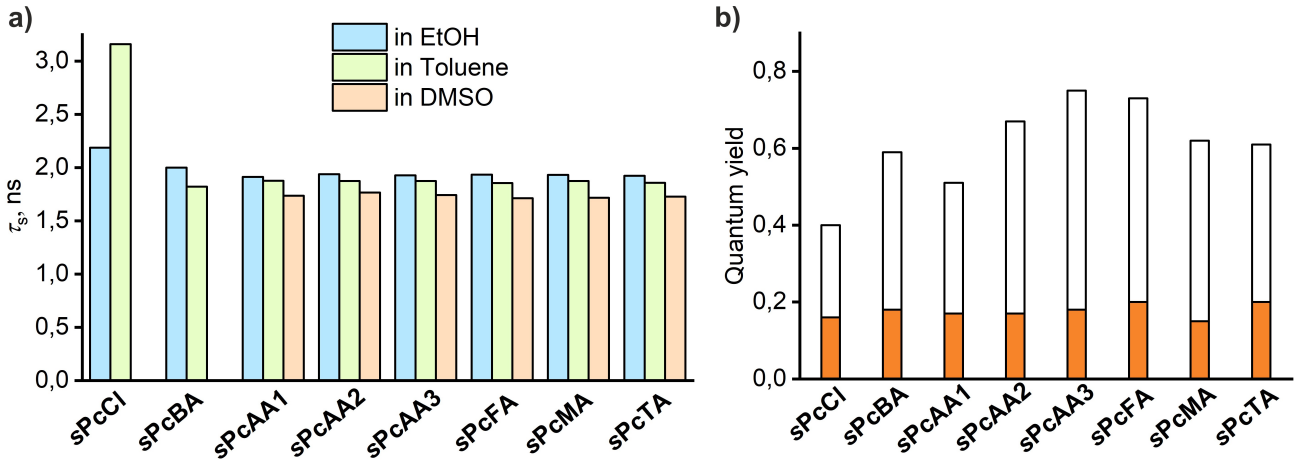


Figure 5. a) – Fluorescence lifetime for investigated subphthalocyanines determined in different solvents; b) – Fluorescence quantum yields (Φ_F, full orange columns) and singlet oxygen quantum yields (Φ_Δ, blank columns) for investigated subphthalocyanines.

Table 1. Photophysical data of investigated subphthalocyanines.

Compound	λ_{abs}, nm (lg ε)	λ_{em}, nm	$\Delta\lambda$, nm	Φ_F	τ_F, ns[a]	$k_r\times10^8$, s^{-1}	$k_{nr}\times10^8$, s^{-1}	Φ_Δ	$\Phi_F+\Phi_\Delta$	Solvent	Ref.
***s*PcCl**	560	574	14	0.16	2.187	0.73	3.84	0.40	0.56	EtOH	[17]
	564	573	9	0.39	3.160	1.23	1.93			Toluene	[17]
***s*PcBA**	562	576	14	0.18	2.001	0.90	4.10	0.59	0.77	EtOH	[17]
	565	572	7	0.22	1.822	1.21	4.28			Toluene	[17]
***s*PcAA1**	562	573	11	0.17	1.913	0.88	4.34	0.51	0.67	EtOH	tw
	564 (4.62)	573	9	0.24	1.877	1.28	4.05			Toluene	tw
	567	577	10	0.18	1.737	1.04	4.72	0.30	0.48	DMSO	tw
***s*PcAA2**	562	573	11	0.17	1.939	0.88	4.28	0.67	0.84	EtOH	tw
	564 (4.17)	572	8	0.18	1.874	0.96	4.38			Toluene	tw
	567	577	10	0.20	1.767	1.13	4.53	0.31	0.51	DMSO	tw
***s*PcAA3**	562	574	12	0.18	1.929	0.93	4.25	0.75	0.93	EtOH	tw
	564 (4.43)	572	8	0.22	1.876	1.17	4.16			Toluene	tw
	566	577	11	0.18	1.744	1.03	4.70	0.29	0.47	DMSO	tw
***s*PcFA**	562	573	11	0.20	1.934	1.03	4.14	0.73	0.93	EtOH	tw
	564 (4.62)	573	9	0.17	1.856	0.92	4.47			Toluene	tw
	567	578	11	0.18	1.714	1.05	4.78	0.28	0.46	DMSO	tw
***s*PcMA**	562	574	12	0.15	1.932	0.78	4.40	0.62	0.77	EtOH	tw
	564 (4.67)	573	9	0.23	1.876	1.23	4.10			Toluene	tw
	567	578	11	0.19	1.717	1.11	4.72	0.27	0.46	DMSO	tw
***s*PcTA**	563 (3.96)	574	11	0.20	1.923	1.04	4.16	0.61	0.81	EtOH	tw
	565	573	8	0.20	1.857	1.08	4.31			Toluene	tw
	567	578	11	0.19	1.729	1.10	4.68	0.27	0.46	DMSO	tw

[a] – The error was less than 0.009 ns.

methods (NMR, FTIR spectroscopy and mass spectrometry). All obtained compounds demonstrated high values of the quantum yield of singlet oxygen in ethanol up to 0.75. The obtained sPcs can be used for the development of new hybrid photoactive materials (including copolymers) for oxidative applications in photocatalysis.

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