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Photophysical properties of benzoannelated metal-free phthalocyanines

W. Freyer*, S. Mueller, K. Teuchner

Max-Born-Institut für Nichtlineare Optik und Kurzzeitspektroskopie, Max-Born-Str. 2a, D-12489 Berlin, Germany

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Abstract

Symmetrically (**1**–**4**) and unsymmetrically (**5**–**7**) benzoannelated metal-free porphyrazines bearing *tert*-butyl substituents have been investigated in regard to their photophysical properties and their splitting behavior of the *Q*-band. *Q*-band splitting in the series of symmetrical tetraazaporphyrine (**1**), tetrabenzoporphyrazine (**2**), tetranaphthoporphyrazine (**3**), is decreased from ΔQ ∼2000 to ∼0 cm^{-1} while the tetraanthraporphyrazine system (**4**) shows a low splitting of about $\Delta Q = 265\,cm^{-1}$ again. In the unsymmetrically substituted series in going from tribenzomononaphthoporphyrazine (**6**) ($\Delta Q = 903\,cm^{-1}$) to tribenzomonoanthraporphyrazine (**7**) ($\Delta Q = 875\,cm^{-1}$) *Q*-band splitting is very similar while tribenzoporphyrazine (**5**) ($\Delta Q = 2073\,cm^{-1}$) exhibits a drastic increase. In the series **1**–**4**, fluorescence lifetimes 2.6, 5.5, 3.0, 0.5 ns, fluorescence quantum yields 0.17, 0.44, 0.19, 0.01 and singlet oxygen quantum yields 0.53, 0.21, 0.03, $<10^{-4}$ were determined. Fluorescence lifetimes of **5**–**7** are in the range 3.1–4.7 ns. The absorption- and fluorescence spectra as well as the fluorescence lifetimes of the separated isomers of **5** do not differ.

Keywords: Phthalocyanines; Porphyrazines; Isomers; Quantum yields; Fluorescence lifetime; Singlet oxygen

1. Introduction

Metallophthalocyanines (tetrabenzoporphyrazines) have been studied extensively [1] because of their broad application. For example, such compounds are of interest for non-linear optical applications [2,3], as sensitizers for photodynamic therapy [4,5], as gas sensors [6], as supra-molecular materials forming highly organized columnar assemblies for one-dimensional transport of energy and charge [7] as materials for optical data storage [8,9] or in OLEDs (organic light emitting devices) [10,11]. However, spectroscopic and photophysical investigations of higher symmetrically and unsymmetrically acenannelated porphyrazines, specially tetraanthraporphyrazines are rare [12], due mainly to the difficulty of preparing the precursors. We report here a systematic investigation of acenannelation of porphyrazines on absorption and fluorescence behavior and some photophysical properties in the same solvent.

It is known that linear acenannelation causes a dramatic bathochromic shift of the *Q*-band pattern of about 300 nm in going from a simple metalloporphyrazine to a metallotetraanthraporphyrazine (Me = VO or Cu) [13] or Me = Co [14]. It is also well known that the nature of the central metal ion influences the photophysical properties of porphyrazines [15]. For example, phthalocyanines with open shell or paramagnetic metal ions exhibit very fast radiationless deactivation and intersystem crossing processes. Consequently, these porphyrazines do not fluoresce. On the other hand, the photophysical properties are expected to be influenced by the benzoannelation too. However, a comparison of a substituted palladium phthalocyanine with a palladium tetraanthraporphyrazine (metal ion with closed d shell and diamagnetic properties) shows that the fluorescence lifetime is too short for studying the influence of acenannelation [16]. The series of magnesium complexes should be more promising for studying the fluorescence properties, however, aggregation effects and the fact that the corresponding magnesium complex of tetraanthraporphyrazine is not stable in solution makes investigation difficult. To overcome this problem we decided to study a set of metal-free derivatives (**1**–**4**) which are expected to show fluorescence lifetimes in the nanosecond range. In comparison to compounds **1**–**4** we were also interested in studying the fluorescence properties of a set of unsymmetrical tetrabenzoporphyrazines with only one benzo unit modified by linear annelation (compounds **2**, **5**–**7**). Additionally, the splitting behavior in the absorption spectra of these compounds in dependence on benzoannelation was investigated. Furthermore, to determine the influence of *tert*-butyl substituents on photophysical properties the unsubstituted derivatives **1a** and **2a** were involved in the

* Corresponding author. Tel.: +49-30-6392-1343; fax: +49-30-6392-1309.
E-mail address: freyer@mbi-berlin.de (W. Freyer).

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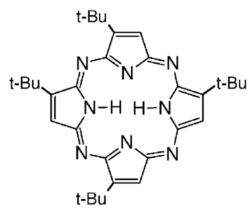
investigations. To compare the results all compounds have to be soluble in the same solvent. We found benzene to be the solvent of our choice where all compounds investigated exist as monomeric species. This solvent is also suitable for determination the singlet oxygen quantum yield because of a relatively long singlet oxygen lifetime (24–32 μs) [17].



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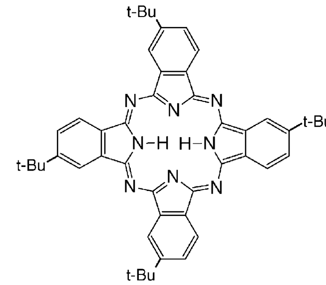

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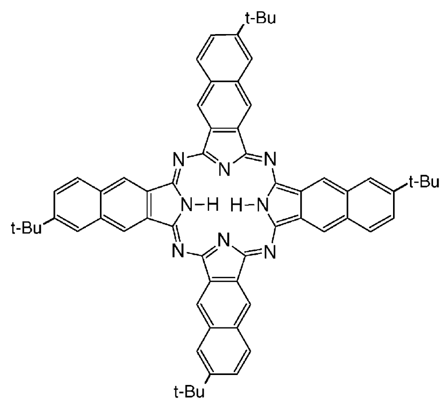

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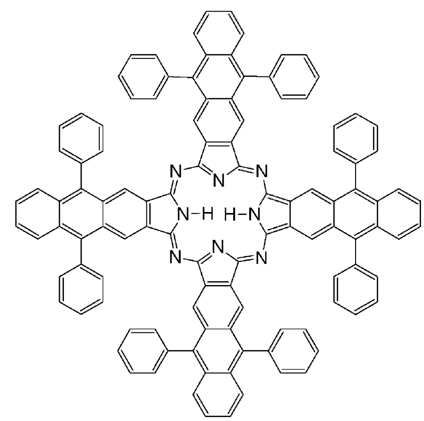

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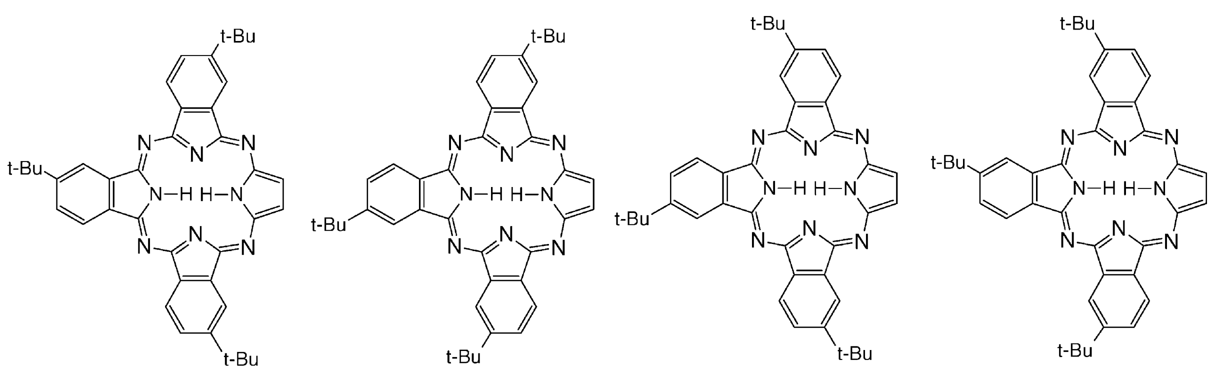

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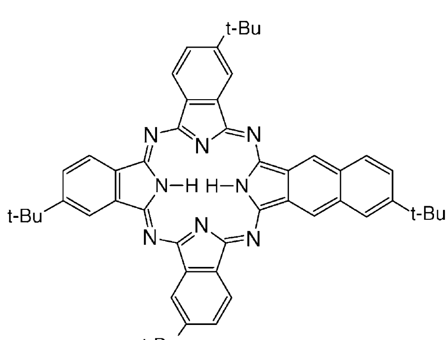

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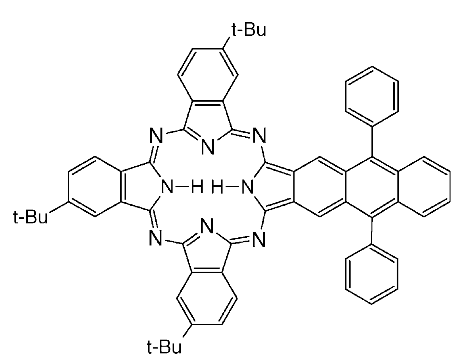

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2. Experimental

2.1. Apparatus and procedures

Absorption spectra in the UV/Visible/NIR region were measured by means of a Perkin Elmer Lamda 900 spectrometer. Fluorescence spectra were recorded with a SPEX industries Fluorolog 2 spectrofluorometer. Fluorescence quantum yields ϕ_{flu} were determined relatively to the fluorescence quantum yields of reference compounds. The following standards were used: (i) cresyl violet in methanol ($\phi_{flu} = 0.54$) [18] for **2**, (ii) rhodamine 101 in ethanol ($\phi_{flu} = 1.0$) [19] for **1**, (iii) bacteriochlorophyll *a* in diethylether ($\phi_{flu} = 0.19$) [20] and (iv) dye IR-132 (Lamda Physics) in methanol ($\phi_{flu} = 0.19$) [21] for **4**. The compounds **3** and **5**–**7** were measured relatively to compound **2**. Each porphyrazine solution was absorbance matched at the excitation wavelength ($OD_{1\,cm} = 0.02$) to the corresponding reference compound and the corrected emission spectra were integrated taking into account the reabsorption and the refractive index of the solutions. The solvents used were spectrograde quality (UVASOL) from Merck and showed no emitting impurities throughout the spectral range used in these experiments.

Time-resolved fluorescence measurements of the compounds **1**–**4** were performed either with the second harmonics (center wavelength: 400 nm) for compounds **1**–**3** or the fundamental wavelength (center: 800 nm) for compound **4** of a Spectra Physics Ti:sapphire femtosecond laser Tsunami (repetition rate 80 MHz, pulse duration <100 fs). The emission was observed at a right angle to the excitation beam and imaged on the entrance slit of a monochromator (type: λ-Scanner, Max-Born-Institute Berlin; aperture 1:3, wavelength range: 300–800 and 600–1100 nm, respectively) fitted with a SPC 300 time-correlated single photon counting module (Becker & Hickl, Berlin) and a high speed photomultiplier tube detector head PMH-100 (Becker & Hickl, Berlin) equipped with a Hamamatsu H5783P-01 photosensor module. Fluorescence decay times measurements of **5**–**7** were carried out with a multidecay spectrometer operating in boxcar mode. Excitation was performed in the range of the *Q*-band by a nitrogen laser (MNL 200; LTB Berlin) pumped dye laser UDL 200 (LTB Berlin; pulse width: 400 ps). The spectrometer is described in detail elsewhere [22]. All time-resolved data were numerically analyzed by deconvolution analysis with a sum of exponentials as model function.

Because of the strong overlap between the long-wavelength absorption and fluorescence bands and a small Stokes' shift reabsorption processes can influence the shape and position of the fluorescence spectrum as well as its fluorescence decay. To suppress this process as far as possible the solutions were diluted for several times until the measured lifetime remains constant (concentrations $<4 \times 10^{-7}$ M).

The values for singlet oxygen quantum yields ϕ_{Δ} were determined in benzene by using the oxidation reaction of 1,3-diphenylisobenzofuran (DPBF) [23]. DPBF has the largest rate constant, $8 \times 10^8\,M^{-1}\,s^{-1}$, for quenching O_2 ($^1\Delta_g$) [24]. At this method the consumption of DPBF as a function of irradiation time of the sensitizer is analyzed [25]. The photolysis was carried out at room temperature. Benzene was purged for half-an-hour with oxygen; the oxygen concentration was typically 9.1×10^{-3} M [26]. Irradiation was carried out in 1 cm cells using a total volume of 3 ml. Concentration of DPBF was varied starting with 4×10^{-5} M for each experiment. The absorbance of the sensitizers at the excitation wavelength was OD < 0.05 that corresponds to a concentration $<4 \times 10^{-6}$ M. The solutions were stirred during the photoreaction. For irradiation experiments a 300 W Xenon lamp (LOT-ORIEL) and monochromator or metal interference filters with the center wavelengths 549, 558, 641, 752, and 880 nm were used. The spectral band width of the filters was approximately 20 nm that of the 10 nm monochromator. Additionally, the DPBF method was also evaluated with following standard compounds possessing well-known parameters for ϕ_{Δ}: tetraphenylporphyrin, TPPP ($\phi_{\Delta} = 0.62$, benzene [27]), bis(tri-*n*-hexysiloxy)tetranaphthoporphyrazine, SINP ($\phi_{\Delta} = 0.35$, benzene [28]). The excitation wavelengths were 549 and 558 nm for TPP and **1**, 641 nm for TPP and **2** and 752 nm for SINP and **3**. Compound **4** was excited at 880 nm. Separate test were carried out to establish that neither the compounds **1**–**4** nor DPBF were consumed under excitation conditions. The decreasing DPBF concentration as a function of irradiation time was monitored at the absorption of DPBF $\lambda_{max} = 415$ nm ($\lg \varepsilon = 4.36$). For estimation of the quantum yields according to [25], data obtained at less than 20% conversion of DPBF were used only (first-order kinetics).

Routine mass spectra were obtained on an Auto Spec mass spectrometer (Micromass) using electron impact ionisation (70 eV, 200 °C). HPLC were carried out by using a Bruker System (high-performance pump 2250 and gradient mixer 1155, Bischoff Chromatography Leonberg Germany), diode array detector module (200–1000 nm), interface LC-248M (J & M Analytik Mess- und Regeltechnik GmbH Germany) and chrom scan software (Bruker Franzen). All separations were performed on a Cosmosil Buckyprep column (Promochem GmbH Wesel Germany, 250 mm × 4.6 mm), flow rate of 0.5 ml min^{-1} and room temperature using toluene as a mobile phase.

2.2. Materials

2.2.1. Tetra-(tert-butyl)-porphyrazine (1)

Compound **1** was purchased from Aldrich Chemical Co. The compound was purified by thin layer chromatography (TLC) on silica gel 60 aluminum sheets from Merck using benzene as eluent. UV/Visible/NIR (benzene), λ_{max} [nm] ($\lg \varepsilon$): 622 (4.93), 597 (3.67), 579 sh (3.66), 569 sh (4.16), 553 (4.70), 534 sh (4.12), 370 sh (3.88), 338 (4.88). Fluorescence (benzene), λ_{fluo} [nm]: 628, 650 sh, 689.

*2.2.2. Metal-free tetraazaporphyrin (porphyrazine) (**1a**)*

Compound **1a** was synthesized according to the procedure of Linstead and Whalley [29]. UV/Visible/NIR (benzene), λ_{max} [nm]: 615, 590, 582, 563, 543, 518 sh, 534, 373, 333. Fluorescence (benzene), λ_{fluo} [nm]: 620, 652 sh, 681.

*2.2.3. Tetra-(tert-butyl)-phthalocyanine (**2**)*

Compound **2** was synthesized according to [30] and was chromatographed on silica gel 60 aluminum sheets from Merck using benzene as eluent. UV/Visible/NIR (benzene), λ_{max} [nm] ($\lg \varepsilon$): 700 (5.26), 663 (5.18), 644 (4.72), 632 (4.71), 600 (4.49), 585 sh (3.94), 565 sh (3.67), 400 sh (4.13), 364 sh (4.85), 346 (4.89). Fluorescence (benzene), λ_{fluo} [nm]: 706, 738, 786.

*2.2.4. Metal-free phthalocyanine (**2a**)*

Compound **2a** (from Aldrich Chemical Co.) was purified by high vacuum sublimation at about 10^{-5} mbar. UV/Visible/NIR (benzene), λ_{max} [nm]: 693, 656, 639, 630 sh, 595, 574 sh, 553 sh, 376 sh, 356, 342. Fluorescence (benzene), λ_{fluo} [nm]: 698, 726, 777.

*2.2.5. Tetra-(tert-butyl)-tetranaphthoporphyrazine (**3**)*

Compound **3** was purchased from Aldrich Chemical Co. For purification, compound **3** was chromatographed twice: (1) Al_2O_3/benzene and (2) silica gel/$CHCl_3$. UV/Visible/NIR (benzene), λ_{max} [nm] ($\lg \varepsilon$): 781 (5.27), 742 (4.52), 694 (4.52) 671 sh (4.23), 650 sh (3.82), 435 sh (4.18), 385 sh (4.47), 362 (4.72), 327 (4.75). Fluorescence (benzene), λ_{fluo} [nm]: 786, 833, 887.

*2.2.6. Octaphenyltetraanthraporphyrazine (**4**)*

Lithium powder of 4 mg (0.57 mg atom) was dissolved under argon in 2 ml pentanol. To the solution, 16 mg (0.05 mM) 9,10-diphenylanthracene-2,3-dicarbonitrile were added. The mixture was boiled for 2 h under argon. Pentanol was removed under vacuum. The remaining product was treated with acetic acid for 30 min. The color of the solution turns reddish-brown. After dilution with H_2O and neutralization with Na_2CO_3 the solution was extracted with benzene for several times. The benzene solution was dried over Na_2SO_4. After evaporation of the solvent the crude product was treated for three times with boiling petroleum ether (bp: 30 °C), than extracted with boiling ethanol and treated two times with boiling ethanol containing 2% benzene. The desired porphyrazine (**4**) was obtained as a black solid after vacuum drying at 100 °C. FAB-MS: $m/z = 1523$ ($M^{\bullet+}$), calculated composition: $C_{112}H_{66}N_8$, $m/e = 1523$. UV/Visible/NIR (benzene), λ_{max} [nm] ($\lg \varepsilon$): 901 (4.88), 879 (4.86), 816 (4.24), 782 (4.13), 740 sh (3.76), 581 sh (3.80), 535 (3.96), 507 (4.0), 404 sh (4.43), 352 (4.75). Fluorescence (benzene), λ_{fluo} [nm]: 910, 976, 1019.

*2.2.7. Tri-(tert-butylbenzo)-porphyrazine (**5**)*

Activated magnesium powder of 720 mg (0.03 g atom) and 15 ml dried pentanol were refluxed for 7 h. To the alcoholate, 553 mg (3 mM) 4-*tert*-butyl-phthalodinitrile and 24 mg (0.3 mM) maleic dinitrile were added and the mixture was refluxed for 1 h. The pentanol was evaporated in vacuum. For separation from the symmetrical magnesium tetra-(*tert*-butyl)-phthalocyanine a part of the residue was dissolved in $CHCl_3$/acetone (9:1) containing 5% EtOH and chromatographed on silica thick layer plates from MERCK. The magnesium complexes of **5** were eluated with ethyl acetate. After evaporation of the solvent the residue was stirred in acetic acid for 1.5 h. The mixture was diluted with water and treated with bicarbonate solution. The product was extracted with $CHCl_3$ and washed with water. After drying with sodium sulfate and evaporation of $CHCl_3$ the mixture of **5** containing different isomers was prepurified by thick layer chromatography on Al_2O_3 using benzene as eluent. The different isomers were than separated by HPLC using a Cosmosil Buckyprep column and toluene as eluent.

*2.2.8. Mixture of all isomers (**5**)*

MS: $m/z = 632.3$ ($M^{\bullet+}$), calculated composition: $C_{40}H_{40}N_8$, $m/e = 632.4$ UV/Visible/NIR (benzene), λ_{max} [nm] ($\lg \varepsilon$): 680 (4.58), 650 sh (3.98), 619 sh (4.12), 596 (4.54), 572 sh (4.16), 565 sh (4.12), 532 sh (3.11), 354 (4.52). Fluorescence (benzene), λ_{fluo} [nm]: 686, 726, 760. Separated isomers were denoted as:

- Compound **5a**—MS: $m/z = 632.3$, calculated composition: $C_{40}H_{40}N_8$, $m/e = 632.4$. UV/Visible/NIR (benzene), λ_{max} [nm] ($\lg \varepsilon$): 677 (4.56), 646 (3.95), 620 sh (4.12), 594 (4.53), 568 (4.14), 554 sh (4.10), 531 sh (3.10), 353 (4.49). Fluorescence (benzene), λ_{fluo} [nm]: 686, 726, 760.
- Compound **5b**—MS: $m/z = 632.2$, calculated composition: $C_{40}H_{40}N_8$, $m/e = 632.4$. UV/Visible/NIR (benzene), λ_{max} [nm] ($\lg \varepsilon$): 678 (4.57), 648 (3.96), 620 sh (4.11), 595 (4.52), 568 (4.16), 554 sh (4.12), 531 sh (3.10), 351 (4.50). Fluorescence (benzene), λ_{fluo} [nm]: 687, 726, 760.
- Compound **5c**—MS: $m/z = 632.2$ calculated composition: $C_{40}H_{40}N_8$, $m/e = 632.4$. UV/Visible/NIR (benzene), λ_{max} [nm]: 681, 653 sh, 619 sh, 597, 572 sh, 561, 537 sh, 352. Fluorescence (benzene), λ_{fluo} [nm]: 687, 727, 761.

*2.2.9. Tri-(tert-butylbenzo)naphthoporphyrazine (**6**)*

Lithium powder of 140 mg (20.2 mg atom) was dissolved in 15 ml pentanol under argon. To the solution a mixture of 368 mg (2 mM) 4-*tert*-butylphthalodinitrile and 47 mg (0.2 mM) 6-*tert*-butyl-naphthalene-2,3-dicarbodinitrile were added. The solution was refluxed for 3 h. After cooling to room temperature pentanol was evaporated and the residue was stirred in 10 ml acetic acid for 2.5 h. After neutralization the product was extracted with $CHCl_3$ and the solvent evaporated. The crude product was treated with petroleum ether to yield 61 mg of a green powder. For purification and separation from the symmetrical compound **3** a part of the crude

product was chromatographed using thick layer chromatography on Al_2O_3 60 plates (eluent: benzene(6)/*n*-hexane (4)). MS: $m/z = 788.5$, calculated composition: $C_{52}H_{52}N_8$, $m/e = 788.5$. UV/Visible/NIR (benzene), λ_{max} [nm] ($\lg \varepsilon$): 729 (4.93), 684 (4.91), 664 (4.72), 634 (4.34), 616 (4.41), 569 sh (3.69), 404 sh (4.19.), 347 (4.79). Fluorescence (benzene), λ_{fluo} [nm]: 736, 770 sh, 822.

2.2.10. Tri-(tert-butylbenzo)anthraporphyrazine (7)

In the same manner, 14 mg (2.02 mg atom) lithium powder, 2 ml pentanol, 18.4 mg (0.1 mM) 4-*tert*-butylphthalodinitrile and 4.8 mg (0.01 mM) 9,10-diphenylanthracene-2,3-dicarbonitrile were allowed to react. For purification and separation from the symmetrical compound **4** a part of the crude product was chromatographed using thick layer chromatography on Al_2O_3 60 plates (eluent: benzene (6)/*n*-hexane (4)/$CHCl_3$). MS: $m/z = 934.5$, calculated composition: $C_{64}H_{54}N_8$, $m/e = 934.6$. UV/Visible/NIR (benzene), λ_{max} [nm] ($\lg \varepsilon$): 757 (4.59), 710 (4.62), 687 (4.39), 636 (4.12), 600 sh (3.50), 464 (3.25), 348 (4.47). Fluorescence (benzene), λ_{fluo} [nm]: 764, 803, 855.

3. Results and discussion

3.1. Synthesis

Porphyrazines **1**–**3** were prepared by using a base-catalyzed cyclization of the appropriate carbodinitriles. A convenient method for preparing the hitherto unknown tetraanthraporphyrazine (**4**) is the treatment of 9,10-diphenyl-anthra-2,3-dicarbonitrile with lithium pentanolate in pentanol. Using lithium alkoxides of hexanol, heptanol and octanol do not improve the yield of **4**. For demetallation of the lithium complex acetic acid was used. Displacement of lithium metal ion can also be achieved by short treatment with sulfuric acid.

Generally, for synthesis of unsymmetrical porphyrazines both the subphthalocyanine route and statistical method can be used [31,32]. To obtain the unsymmetrical 3:1 porphyrazines (**5**–**7**), the statistical condensation method including the separation of the different isomers by chromatography and HPLC technique was applied. For preparation of **6** and **7** the corresponding carbodinitriles in the ratio 10:1 were allowed to react with lithiumpentanolate in pentanol under reflux. Use of the 10:1 ratio of the two different carbodinitrile precursors minimizes the formation of other cross-tetramerisation products. The lithium complexes were then demetalled with acetic acid. The residue that mainly contains **2** was separated from the other metalloporphyrazines by chromatography. Pure **6** and **7** were collected by repeated thin layer chromatography on silica gel.

Compound **5** was prepared by reaction of magnesium pentyloxide with the two dinitrile precursors. The magnesium complexes of **5** are than separated from magnesium tetra-(*tert*-butyl)-phthalocyanine by thick layer chromatography and than treated with acetic acid. Separation of a mixture of the different isomers is achieved by chromatography on Al_2O_3. Porphyrazines **1**–**3** and **5**–**7** consist of a mixture of different structural isomers refer to the position of the *tert*-butyl group. The separation of structural isomers of phthalocyanines bearing *tert*-butyl substituents (D_2, C_2, and C_4 symmetry) is a problem which is difficult to solve [33,34]. However, in case of the four possible structural isomers of **5** separation of the isomers was achieved for the first time. Three isomers (denoted as **5a**–**5c**) could be separated by HPLC using a Cosmosil Buckyprep column and toluene as eluent. A careful investigation of the HPLC data shows the fourth isomer missing. That could mean either that the missing isomer is not formed or only as a very minor component. A reason could be a strong steric interaction that disfavors the formation of such an isomer. Characterization of the structural isomers separated was achieved by mass spectrometry, comparison of the retention times in HPLC, and their UV/Visible/NIR absorption. All spectroscopic data for **1**–**3**; **5**–**7** were taken from the mixture of isomers of these compounds. Especially for **5**, three isomers isolated by HPLC (see above) were investigated separately.

3.2. The Q-absorption band

Two aspects are of interest: (i) the position of the *Q*-band in the absorption spectra and (ii) the magnitude of the splitting in dependence on the nature of the macrocycle.

The absorption spectra of the monomeric porphyrazines **1**–**4** are characterized by strong *Q*-absorption bands spanning the range 550–900 nm (Fig. 1). The position of the *Q*-band maxima strongly depends on the number of the benzo-fused moieties. The shift of the redmost *Q*-band absorption maxima in going from **1** (622 nm) to **4** (901 nm) is 279 nm. *tert*-Butyl substitution has a little effect on the absorption spectra of a few nanometers (Q_x (**1**–**1**a) = 7 nm, Q_x (**2**–**2**a) = 7 nm). *Q*-band absorption data are given in Table 1. Theoretical calculations by Orti et al. [39] explain this effect by a decrease of the HOMO–LUMO energy gap along the series of annelated compounds.

Another remarkable feature of the metal-free compounds **1**, **2** and **4** is their different splitting of the *Q*-band into Q_x- and Q_y-components, whereas Q_x is more intensive than Q_y. The two main absorption maxima with similar oscillator strengths can be assigned to the 0–0 vibrations of the Q_x- and Q_y-transitions. The shoulders at shorter wavelengths in the absorption spectra can be assigned to sub-levels within the Q_x- and Q_y-states. The splitting effect of peripherically unsubstituted **1a** and **2a** is well known and theoretically investigated in detail [40,41]. *Q*-band splitting is correlated with the $a_u \rightarrow b_{2g}$ and $a_u \rightarrow b_{3g}$ transitions. The quasi-degeneracy of the $a_u \rightarrow b^*_{2g}$ and $a_u \rightarrow b^*_{3g}$ orbitals (only $\Delta E \sim 0.17$ eV) is explained by the quasi-identical geometry of all the isoindole moieties. From calculations using the valence effective Hamiltonian (VEH) quantum-chemical method and using D_{2h} symmetry constraints can be concluded that the carbon–nitrogen

Table 1
Absorption and fluorescence characteristics of metal-free porphyrazines (**1**–**7**) in benzene at room temperature

Compound	λ_{abs}^{max} ± 0.5 nm		ΔQ (cm^{-1})	λ_{fluo}^{max} ± 0.5 nm	Stokes' shift (cm^{-1})	τ (ns)	ϕ_{flu} ± 15%	ϕ_{Δ} ± 20%
	Q_x	Q_y						
1	622	553	2006	628	147	2.6[a]	0.17	0.53
1a	615	543	2183	620	131	2.3[a]	0.16	0.46
2	700	663	797	706	122	5.5[a] (7.1[b])	0.44	0.21,(0.16[b])
2a	693	656	814	698	111	5.0[a] (6.5[c], 6.3[d])	0.43	0.19
2a[e]	686	623	1474	–	–	–	–	–
3	781[f]		–	786	81	3.0[a] (4.6[b])	0.19	0.03
4	901	879	265	910	110	0.5[g]	0.01	$<10^{-4}$
5[h]	680	596	2073	686	202	3.4[i]		
5a	677	594	2064	686	194	3.9[i]		
5b	678	595	2058	687	193	4.0[i]		
5c	681	597	2066	687	128	3.1[i]		
2	700	663	797	706	122	5.7[i]		
6	729	684	903	736	130	4.7[i]		
7	757	710	875	764	121	4.0[i]		

[a] ±0.1 ns.
[b] In CCl_4 [36].
[c] In $CHCl_3$ [37].
[d] In 1-chloronaphthalene [38].
[e] Gas phase [35].
[f] Only one maximum.
[g] ±0.05 ns.
[h] Mixture of isomers.
[i] ±0.3 ns.

π-system nearly possesses D_{4h} symmetry [42]. So the magnitude of the quasi-degeneracy of the $a_u \rightarrow b_{2g}^*$ and $a_u \rightarrow b_{3g}^*$ orbitals can be considered as a measure of the departure of the system from D_{4h} symmetry. A comparison of the absorption spectra of **1**–**4** shows that the magnitude of splitting of the *Q*-band strongly depends on the number of the linearly fused benzo units (Fig. 1). *Q*-band splitting of **1** is 2006 cm^{-1}, of **2** is 797 cm^{-1} (but 1474 cm^{-1} in the gas phase [35]). In the case of the naphthoporphyrazine (**3**) no splitting is observed. Surprisingly, further benzoannelation causes a small splitting of 265 cm^{-1} again as can be seen in the case of the tetraanthraporphyrazine (**4**). A small splitting is also observed by alkoxy substituents neighboring to the inner porphyrazine ring in octa(isopentoxy)anthralocyanine (980 nm, 954 nm ($\Delta Q = 278\ cm^{-1}$), solvent: toluene) [43]. This very small *Q*-band splitting effect is in agreement with calculations which predict a splitting of 0.01 eV for unsubstituted anthralocyanine [39]. The splitting values of unsubstituted **1a** and **2a** compared with those of *tert*-butyl-substituted **1** and **2** only slightly differ indicating that additional splitting contribution caused by *tert*-butyl groups which decrease the symmetry (D_2, C_2, and C_4 symmetry) of the molecules can be neglected.

Q-band splitting decreasing in going from **1** to **3** is due to a perturbation of the D_{2h} symmetry which results in a nearly complete degeneration of the b_{2g} and b_{3g} states. However, in case of **4** the large dimension of the molecule could be responsible for the small splitting of the *Q*-band. It is interesting to compare the splitting effect on other metal-free phthalocyanines and naphthalocyanines caused by substituents. Different metal-free octaalkoxy-substituted phthalocyanines exhibit same *Q*-band splitting values as compared to **2** [44]. The values slightly depend on the position of the alkoxy substituent at the benzo unit of the phthalocyanine ring [45]. In accordance with **3** also in the case of octaalkoxy-naphthalocyanines no splitting was found [45]. That means, the splitting behavior of the *Q*-band absorption is strongly influenced by symmetrical benzoannelation of porphyrazines while a common substituent effect at fixed symmetrical porphyrazine structure plays only a subordinate part (compare **1**, **1a**, and **2**, **2a** in Table 1). On the other hand, solvation of the porphyrazine ring seems also to have a strong influence on the splitting behavior as can be seen by comparing the absorption maxima of **2a** in solution and in the gas phase. However, the influence of solvent polarity on $\Delta(Q_x - Q_y)$, for example, of **2** is small [46].

In the set **2**, **5**–**7** the influence of unsymmetrical extension of the π-system on the absorption behavior was investigated. The series **5**–**7** was classified to the lower C_{2v} point group of symmetry compared to **2** for which D_{2h} was assumed. As can be seen from Table 1 and Fig. 2, the Q_x-band absorption maximum in going from **5** to **7** is shifted from 680 to 757 nm due to the narrowing of the HOMO–LUMO gap in this series. That means benzoannelation of a single benzo unit in **2** even results in a bathochromic shift of 76 nm. It is noteworthy that although the different separated isomers of **5** have different symmetry properties, all of them show the same absorption maxima. The values for the splitting of the *Q*-band of compounds **5**–**7** are higher than those for compounds **1**–**4** reflecting the lower symmetry of the un-

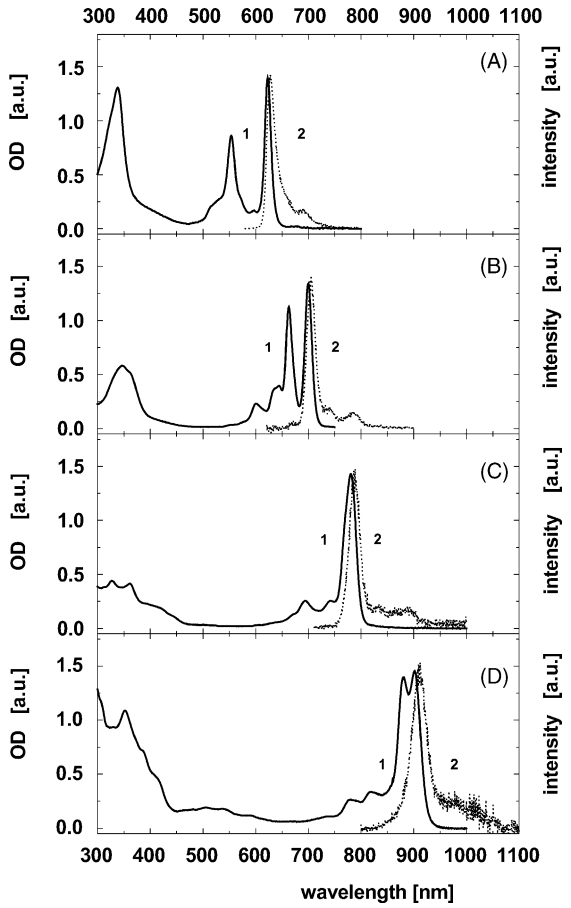

Fig. 1. Absorption and fluorescence behavior of compounds **1**–**4** in benzene: (A) compound **1**, (B) compound **2**, (C) compound **3**, (D) compound **4**; (1) absorption spectra, (2) fluorescence spectra (optical density at the maximum of the long-wavelength absorption band $OD_{1\,cm} < 0.03$).

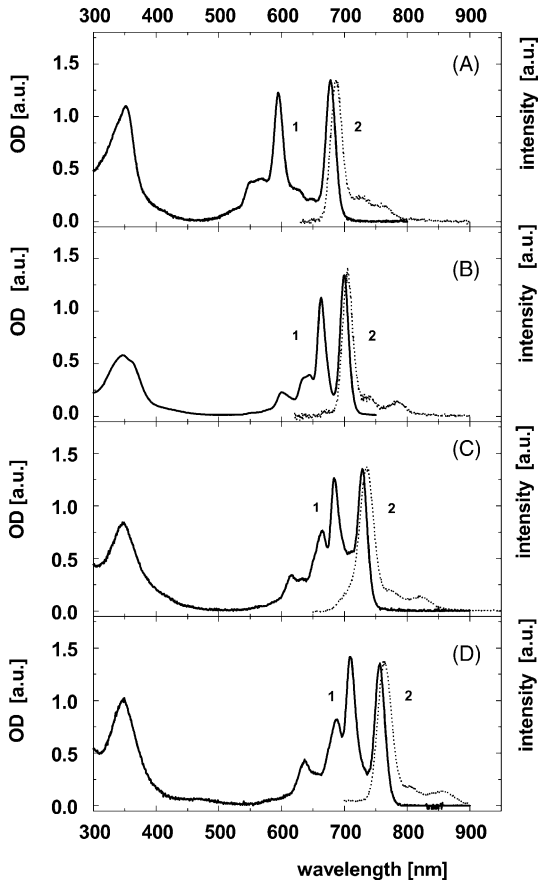

Fig. 2. Absorption and fluorescence behavior of compounds **5**–**7** in benzene (additionally compound **2** in benzene is included): (A) compound **5**, (B) compound **2**, (C) compound **6**, (D) compound **7**; (1) absorption spectra, (2) fluorescence spectra (optical density at the maximum of the long-wavelength absorption band $OD_{1\,cm} < 0.02$).

symmetrical set. A comparison of our experimentally determined transition energies for the *Q* bands with theoretical calculations by Orti et al. [47] using the VEH method shows considerable deviations from the calculated values.

3.3. Fluorescence properties and singlet oxygen production

Fluorescence is observed from all compounds in benzene solution for excitation in the *Q*-band region (Figs. 1 and 2). The emission spectra at room temperature of the symmetrical set of porphyrazines are characterized by a main maximum at 628 nm (**1**), 620 nm (**1a**), 706 nm (**2**), 698 nm (**2a**), 786 nm (**3**), 910 nm (**4**) and subordinate maxima at longer wavelengths (Fig. 1 and Table 1). In the unsymmetrically substituted set the main fluorescence maxima are found at 686 nm (**5a**), 687 nm (**5b**), 687 nm (**5c**), 736 nm (**6**), 764 nm (**7**). The position of the maxima is independent on the excitation wavelength. The main emission band for all compounds is assigned to the 0–0 transition of the fluorescence. The fluorescence excitation spectra of these compounds coincide with the corresponding absorption spectra. The emission spectra are mirror images of the *Q*-band absorption spectra (compare for instance, fluorescence of **2** in [48]). The Stokes' shift of all porphyrazines compared to the maximum of the Q_x-transition in the absorption spectra is small. Benzoannelation changes Stokes' shift non-essentially only even for the large molecule **4**. That suggests that only a minor geometric relaxation occurs in the first excited state. However, quantum yield of the fluorescence ϕ_{flu} originating from the singlet S_1 strongly depends on the degree of benzoannelation and is found to be 0.17, 0.16, 0.44, 0.43 and 0.19 for **1**, **1a**, **2**, **2a** and **3**. The lowest value was found for the tetraanthraporphyrazine (**4**) (0.01). The corresponding fluorescence lifetimes τ, measured by excitation into the range of the *Q*-band are listed in Table 1.

Without exception all fluorescence decays can be described by a monoexponential decay function. As can be seen from Table 1 the fluorescence lifetimes τ decrease in the order **2**, **2a** > **3** > **4** while τ of **1**, **1a** is lower compared with **2**, **2a**. This phenomenon of τ has also been observed for the set **2** > **6** > **7**, while τ of **5** and their isomers **5a**–**5c**

Table 2
Triplet-state properties and singlet oxygen quantum yields ϕ_Δ of tetraazaporphyrines (TAP), phthalocyanines (Pc), naphthalocyanines (NC), and anthralocyanines (AnC) in benzene

Compound	S_1 (eV)	T_1 (eV)	τ_{T_1} (μs)	τ_T	ϕ_Δ
(*t*-Butyl)$_4$PcH$_2$ (**2**)	1.77	0.99 [49]	83 [50]	0.1 [50]	0.20 [50], 0.21 (this work)
(Hexadecyl)$_8$PcH$_2$	–	0.99 [49]	143 [49]	0.19 [49]	–
(*t*-Butyl)$_4$PcZn	1.85 (in dioxane)	1.13 [50]	41 [50]	0.24 [50]	0.25
(*t*-Butyl)$_4$PcPd	1.88	1.22 [16]	10.4 [50]	0.49 [50]	0.86 [16], 0.52 [49]
(Butoxy)$_8$PcH$_2$	1.63	–	17 [51]	0.095 [51]	<0.05 [52]
(Butoxy)$_8$PcZn	1.68	1.04 [51]	63 [51]	0.46 [51]	0.45 [51]
(Butoxy)$_8$PcPd	1.71	1.13 [52]	3.5 [52]	0.77 [52]	0.64 [52]
(Butoxy)$_8$PcRu	1.80	–	0.53 [52]	0.88 [52]	0.42 [52]
(Butoxy)$_8$NCPd	1.44	0.93 [55]	0.95 [55]	0.76 [55]	Singlet oxygen generation observed [55]
(tri-*n*-Hexylsiloxy)$_2$NCSi	1.60	0.93 [53,54]	459 [53], 330 [54]	0.2 [54]	0.19 [54]
(Phenyl)$_8$AnCPd	1.47	0.93 [16]	1.3 [16]	–	0.14 [16]

show a special behavior again. Fluorescence lifetimes of **2**, **2a**, **3** have also been determined by other authors, but in different solvents (see footnote in Table 1), they are of same magnitude as in benzene.

We also determined singlet oxygen quantum yields of the symmetrical set **1**–**4** in benzene. The values of ϕ_Δ decrease drastically in the order **1** > **1a** > **2** > **2a** > **3** > **4**. No singlet oxygen generation could be observed for **4**. To understand this behavior we collected data for different porphyrazines from the literature which are presented in Table 2.

The mechanism of singlet oxygen formed by photoexcitation can be described by the following scheme:

$$\mathrm{Pz(S_0)} \xrightarrow{h\nu} \mathrm{Pz(S_1)}$$

$$\mathrm{Pz(S_1)} \rightarrow \mathrm{Pz(T_1)}$$

$$\mathrm{Pz(T_1) + O_2(^3\Sigma_g^-) \rightarrow Pz(S_0) + O_2(^1\Delta_g)}$$

$$\mathrm{O_2(^1\Delta_g) \rightarrow O_2(^3\Sigma_g^-) + h\nu\,(1268\,nm\,(0.97\,eV))}$$

or

$$\mathrm{O_2(^1\Delta_g) + diene \rightarrow Diels\text{–}Alder\ product}$$

where Pz are the porphyrazine molecules in the ground and excited singlet and triplet states. The generated singlet oxygen can be detected either by its photoluminescence at 1268 nm or as a photoproduct formed by Diels–Alder reaction with a suitable diene (1,3-diphenyl-isobenzofurane (DPBF)) which can be monitored by absorption spectroscopy or HPLC. DPBF is particularly suitable as it has the largest rate constant, $8 \times 10^8\,M^{-1}\,s^{-1}$, for quenching $O_2(^1\Delta_g)$ [48,56]. The singlet oxygen quantum yield ϕ_Δ depends not only on the triplet quantum yield or the triplet lifetime of the compound but also on the energy gap between the lowest excited triplet state $Pz(T_1)$ and the $O_2(^1\Delta_g)$ level (at 0.98 eV).

Because metal-free phthalocyanines do not phosphoresce their triplet energy was determined from transient absorption measurements [49]. For **2** as well as for other alkyl-substituted metal-free phthalocyanines a value of 0.99 eV for the triplet energy could be found. This value is significantly lower than that of metallophthalocyanines (Table 2). From Table 2 can be seen that the triplet energy of naphthalocyanines and anthralocyanines is lower than the activation energy of singlet oxygen. Careful investigation of the quenching of the T_1 state of metallophthalocyanines by oxygen showed an exponential decay behavior. However, in the case of (*t*-butyl)$_4$PcH$_2$, (butoxy)$_8$PcH$_2$, (tri-*n*-hexylsiloxy)$_2$NCSi, (butoxy)$_8$NCPd, a biphasic decay kinetics was found. This behavior was interpreted as a reversible energy transfer between the porphyrazine and oxygen according the following equilibrium [51,54]:

$$\mathrm{Pz(T_1) + O_2(^3\Sigma_g^-) \underset{k_2}{\overset{k_1}{\Leftrightarrow}} Pz(S_0) + O_2(^1\Delta_g)}$$

From Table 2 further can be seen that ϕ_Δ is mainly influenced by the energy of T_1 and partly by the triplet quantum yield too. The triplet lifetime τ_{T_1} seems to be not so important for τ_{T_1} values >1 μs. When the $S_0 \rightarrow T_1$ energy gaps are above the $^3\Sigma_g^- \rightarrow {}^1\Delta_g$ energy gap (0.97 eV) singlet oxygen is produced in high quantum yield (see (*t*-butyl)$_4$PcZn, (*t*-butyl)$_4$PcPd, (butoxy)$_8$PcZn, (butoxy)$_8$PcPd). However, if T_1 is similar to 0.97 eV or smaller, ϕ_Δ strongly decreases. Table 2 also shows that the $S_1 \rightarrow T_1$ energy gap of palladium complexes (*t*-butyl)$_4$PcPd, (butoxy)$_8$PcPd, (butoxy)$_8$NCPd, and (phenyl)$_8$AnCPd are similar (0.54–0.66 eV). For metal-free **2** a $S_1 \rightarrow T_1$ gap of 0.78 eV can be estimated using $T_1 = 0.99$ eV from Table 2. Assuming that also the metal-free porphyrazines in the series **2**, (butoxy)$_8$PcH$_2$, **3**, and **4** have similar $S_1 \rightarrow T_1$ energy gaps we roughly estimate T_1 energies of **3** and **4** to be approximately 0.9 and 0.7 eV, respectively. Both values are remarkable less energetic than that of the $^1\Delta_g$ state of oxygen. Although the triplet energy of **3** seems to be significant lower than that of (tri-*n*-hexylsiloxy)$_2$NCSi, (butoxy)$_8$NCPd, and (phenyl)$_8$AnCPd formation of singlet oxygen of **3** in this endogenic process is evident. The reasons why **4** does not produce singlet oxygen might be due to a extremely low-lying triplet state, a very low triplet quantum yield or a ground state quenching as it has been observed for carotenoids [57].

4. Conclusions

Sets of metal-free symmetrically benzoannelated porphyrazines (**1**–**4**) and unsymmetrically benzoannelated tribenzoporphyrazines (**5**–**7**) have been synthesized and characterized by various spectroscopic methods, including MS, HPLC, electronic absorption and fluorescence emission.

Linear benzoannelation of both sets give rise to a strong bathochromic shift of the Q_x- and Q_y-band in the absorption spectrum. This shift is stronger on the symmetrically benzoannelated porphyrazines. Both sets of molecules show a strongly split *Q*-band absorption. The degree of splitting $\Delta(Q_x{-}Q_y)$ is dependent of the total numbers of benzo-moieties fused with the porphyrazine ring. The split becomes smaller with extension of the π-electron system reflecting a decrease of the quasi-degeneration of the two lowest unoccupied b_g orbitals. In the lower symmetrical set of benzoannelated tribenzoporphyrazines, $\Delta(Q_x - Q_y)$ is larger due to an decrease of symmetry. An additional influence of peripheral substituents on both absorption maxima and splitting behavior is small.

The ring expansion also evidently influences the photophysical properties. In the symmetrical set **1**–**4**, fluorescence quantum yields, fluorescence lifetimes, and singlet oxygen quantum yields decrease distinctly with increasing number of benzo-moieties. On the other hand, the influence of *tert*-butyl substituents in dependence of their position at the benzo-moiety on absorption and fluorescence spectra as well as their fluorescence lifetimes is insignificant as found for three isomers of tri-(*tert*-butylbenzo)-porphyrazine (**5**).

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