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Tuning photophysical properties of phosphorescent benzoporphyrin complexes via 1-step π -extension



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Keywords: Porphyrin Phosphorescence Platinum Oxygen sensor Upconversion	Complexes of benzoporphyrins are highly promising for application in optical oxygen sensors, as triplet sensi- tizers for generation of singlet oxygen and upconversion based on triplet-triplet annihilation (TTA). Particularly, they benefit from efficient absorption in red part of the spectrum and strong NIR phosphorescence. In this contribution, we investigate different strategies of tuning the photophysical properties of these readily available complexes via 1-step modification. The new π -extended derivatives are obtained via Friedel-Crafts acylation of tetraphenyltetrabenzoporphyrin (TPTBP) complexes and by Suzuki or Sonogashira cross-coupling reaction of the tetrabromo-substituted benzoporphyrins. The Soret and Q absorption bands of the tetra-substituted dyes shift bathochromically by about 15 nm compared to the parent TPTBP compounds. The modified dyes retain their NIR phosphorescent properties and feature slight improvement of the quantum yield. Amplication in optical oxygen

sensing materials and triplet-triplet annihilation-based upconversion systems is demonstrated.

1. Introduction

In the last couple of years, phosphorescent metal complexes excitable in the red part of the spectrum with efficient emission in the NIR-region received much attention due to their broad field of potential applications, for instance in organic light emitting diodes (OLEDs) [1,2] and optical sensors [3-5]. Compared to UV-Vis dyes, these complexes are especially promising for sensing applications due to lower autofluorescence and light scattering, and, because of the compatibility to the NIR optical window (700-950 nm), enable measurements of oxygen (and glucose via an oxygen transducer) in tissues as well as in living organisms [6-9]. Due to efficient generation of singlet oxygen upon quenching, application of such systems in photodynamic therapy is also of high interest [10-12]. Such complexes were also intensively investigated as sensitizers in TTA-based upconversion systems for potential application in photovoltaics [13,14], bioimaging [15] and photocatalysis [16]. Red-light- and NIR-excitable sensitizers are especially attractive for the light conversion applications, since almost 50% of the energy from the sun reaching the earth is NIR radiation [17] with a maximum flux of sunlight at approximately 680 nm [18].

Bathochromic shift of the absorption and the emission bands of various porphyrinoids can be achieved in different ways. However, so

far the most promising way was the extension of the π -conjugated system of the porphyrin core through fusion of various aromatic moieties at the β -pyrrole positions leading to tetrabenzoporphyrins (TBP) [19,20] tetranaphthaloporphyrins (TNP) [2,21-23] or even tetra-anthroporphyrins (TAP) [24]. Significant bathochromic shifts of absorption as well as emission were also achieved via modification of benzoporphyrins in an intramolecular Scholl reaction leading to bridged benzoporphyrin derivatives [9]. All these complexes possess phosphorescence ranging from 770 to 1020 nm but the non-radiative decay rate increases substantially with the decreasing $T_1 - S_0$ energy gap [17]. This indicates a limited potential for the extension of absorption and emission to longer wavelengths. In fact, most NIR absorbing porphyrinoids are non-emissive [25-28]. For many practical applications, it is therefore necessary to find a compromise between the bathochromic shift of absorption and the phosphorescence quantum yield (Φ). Another very important parameter is the photostability of the dyes which can be dramatically reduced by π -extension such as in case of naphthoporphyrins and their molecular hybrids with benzoporphyrins [29]. Although poor photostability and solubility of naphthoporphyrins can be improved, a sophisticated multistep synthesis is necessary [21]. Therefore, investigation of alternative possibilities for adjusting the spectral properties of the phosphorescent porphyrins via π -extension

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remains of much interest.

In this contribution we report the synthesis of new complexes prepared via one step modification of existing benzoporhyrins. Platinum (II) meso-tetra-(4-t-butyl)phenyl-tetra-bromobenzo-porphyrin (Pt-TPTBPtBu₄Br₄) was modified via Suzuki or Sonogashira cross-coupling meso-tetra(4-fluorophenvl)tetrareaction and platinum(II) benzoporphyrin (Pt-TPTBPF) [30] with help of Friedel-Crafts acylation. The resulting platinum(II) benzoporphyrin derivatives show a bathochromic shift of approximately 15 nm in the absorption and therefore become compatible with 632.8 nm line of He-Ne laser as well as 635 nm laser diodes. Furthermore, the new dyes possess similarly good photostability and solubility but higher phosphorescence quantum yields compared to the benzoporphyrin precursors (except Pt-Ph-acetylene).

2. Experimental

2.1. Materials

1,2-dichlorobenzene, copper(I) iodide, potassium carbonate, phenylacetylene and toluene were ordered from Sigma-Aldrich and acetyl chloride from Fluka. 4-Chlorobenzoyl chloride was purchased from ABCR and Silica-gel 60 and aluminum trichloride from Merck. Polystyrene (PS; $Mw = 260000 \text{ g mol}^{-1}$) was obtained from Acros Organics. Sodium sulfate, potassium carbonate and sodium chloride were from VWR. Tetrakis (triphenylphosphine)palladium (0), 9-phenylcarbazole-3-boronic acid and 9,9-dimethylfluoren-2-boronic acid were purchased from TCI. All the solvents and triethylamine (TEA) were from and Roth. Nitrogen, oxygen (both of 99.999% purity) and test gas (2% O₂ in nitrogen) were acquired from Air Liquide and Linde Gas GmbH. Poly (ethyleneterephthalate) (PET) support Melinex 505 was purchased from Pütz (Taunusstein, Germany). Platinum(II) mesotetra-(4-t-butyl)phenyl-tetra-bromobenzo-porphyrin (Pt-TPTBPtBu₄Br₄) (Fig. S3 and S46, ESI) was prepared via template condensation following the procedure reported earlier [31]. Synthesis of platinum(II) meso-tetra(4-fluoro-phenyl)tetrabenzoporphyrin (Pt-TPTBPF) is described elsewhere [30]. In all cases deionized water was used.

2.2. Synthesis

2.2.1. Pt-fluorene

Pt-TPTBPtBu₄Br₄ (20.0 mg, 12.9 μ mol, 1.00 eq) was dissolved in toluene (6.5 mL) under argon atmosphere. 9,9-Dimethylfluorene-2boronic acid (30.8 mg, 129 μ mol, 10.0 eq) and K₂CO₃ as base (71.4 mg, 517 μ mol, 40.0 eq) were added to the solution. The base was pre-dissolved in H₂O (1.5 mL). Catalyst Pd(PPh₃)₄ (0.89 mg, 0.77 μ mol, 0.06 eq) was added and the reaction mixture was heated to 100 °C and stirred for 4 h. The reaction progress was monitored via absorption spectroscopy (solvent: toluene). The reaction mixture was cooled down to RT. After addition of DCM (dichloromethane), the organic layer was washed with H₂O and dried over Na₂SO₄ and the solvent was removed under reduced pressure. The crude product was purified via column chromatography (silica-gel, cond. cyclohexane (CH), CH:DCM), yielding a dark green solid. Yield: 6 mg, 20%.

¹H NMR (300 MHz, CD₂Cl₂) δ 8.37–8.19 (m, 8H), 8.08–7.94 (m, 8H), 7.84–7.53 (m, 22H), 7.54–7.48 (m, 4H), 7.42–7.27 (m, 14H), 7.21 (d, *J* = 8.9 Hz, 2H), 7.10 (d, *J* = 8.6 Hz, 2H), 1.77–1.62 (m, 36H), 1.50 (s, 28H).

MALDI-TOF m/z [M⁺] C₁₃₆H₁₁₆N₄Pt calcd: 2000.8879, found: 2000.8828.

2.2.2. Pt-carbazole

Pt-carbazole was synthesized analogously to Pt-fluorene but using 25.0 mg (16.2 μ mol, 1.00 eq) of Pt-TPTBPtBu₄Br₄ dissolved in toluene and tetrahydrofuran (THF) (6 + 3 mL) and 9-phenylcarbazole-3-boronic acid (46.4 mg, 162 μ mol, 10.0 eq) instead. The crude product was purified via column chromatography (silica-gel, cond. CH,

CH:DCM, 3:1), yielding a dark green solid. Yield: 11 mg, 31%.

¹H NMR (300 MHz, CD_2Cl_2) δ 8.29–8.01 (m, 16H), 7.97–7.71 (m, 7H), 7.66–7.40 (m, 28H), 7.39–7.27 (m, 13H), 7.26–7.00 (m, 12H), 1.65 (t, J = 4.1 Hz, 9H), 1.53–1.45 (m, 18H), 1.35–1.25 (m, 9H).

MALDI-TOF: m/z [M⁺] C₁₄₈H₁₁₂N₈Pt calcd: 2196.8689, found: 2196.8257.

2.2.3. Pt-benzoyl-Cl

Pt-TPTBPF (20.0 mg, 18.5 µmol, 1.00 eq) was dissolved in 1,2-dichlorobenzene (8 mL) under argon atmosphere. 4-Chlorobenzoyl chloride (0.12 mL, 0.93 mmol, 50.0 eq) and AlCl₃ (40.0 mg, 0.30 mmol, 16.2 eq) were added to the solution. The reaction mixture was heated to 130 °C and stirred for 30 min. The reaction progress was monitored via absorption spectroscopy (solvent mixture of CHCl₃ and ethanol (EtOH) 10:1). After complete conversion the reaction mixture was cooled down to RT and treated with EtOH:H₂O (1:1 v/v, 40 mL) and stirred for 10 min to neutralize the excess of AlCl₃. After addition of DCM, the organic layer was washed with H₂O and dried over Na₂SO₄ and the solvent was removed under reduced pressure. The crude product was purified via column chromatography (silica-gel, cond. toluene, DCM:Tol, 7:1), yielding a dark green solid. Yield: 26.0 mg, 33%.

¹H NMR (300 MHz, CD_2Cl_2) 8.33–8.18 (m, 2H), 8.18–8.07 (m, 3H), 8.06–7.92 (m, 2H), 7.80 (dt, J = 13.5, 7.5 Hz, 4H), 7.66 (d, J = 7.4 Hz, 2H), 7.53 (dd, J = 11.8, 5.4 Hz, 16H), 7.44–7.32 (m, 5H), 7.31–7.19 (m, 2H), 7.19–7.02 (m, 4H).

MALDI-TOF: m/z [M⁺] C₈₈H₄₄Cl₄F₄N₄O₄Pt calcd: 1634.1699, found: 1634.1671.

2.2.4. Pt-acetyl

This acylation was performed analogously to Pt-TPTBPF-benzoyl-Cl but with acetyl chloride ($66 \,\mu$ L, 0.93 mmol, 50.0 eq) instead of 4-chlorobenzoyl chloride. The crude product was purified via column chromatography (silica-gel, cond. toluene, DCM:Tol, 8:1), yielding a dark green solid. Yield: 18.3 mg, 77%.

 ^{1}H NMR (300 MHz, CD₂Cl₂) δ 8.37–8.09 (m, 8H), 8.07–7.43 (m, 16H), 7.28–7.03 (m, 4H), 2.43–2.17 (m, 12H).

MALDI-TOF: $m/z \ [M^+] \ C_{68}H_{40}F_4N_4O_4Pt$ calcd: 1248.2655, found: 1248.2158.

2.2.5. Pt-Ph-acetylene

This synthesis was performed analogously to literature [32,33]. Pt-TPTBPtBu₄Br₄ (50.0 mg, 32.3 µmol, 1.00 eq) and catalytic amount of CuI (1.23 mg, 6.50 µmol, 0.20 eq) was dissolved in 1.5 mL abs. THF and 0.7 mL abs. triethylamine (TEA) in a Schlenk flask under Ar atmosphere. Pd(PPh₃)₄ (3.73 mg, 3.23 µmol, 0.10 eq) and phenylacetylene (33.0 mg, 323 µmol, 10.00 eq) were added to the solution. The solution was stirred for 18 h at 75 °C. Conversion control of the reaction was performed via TLC (silica-gel, CH:DCM 3:1). The green solution was first washed 4 times with 10% CuSO₄ to remove the excess of TEA. The product was extracted with DCM, the organic layer was dried over Na₂SO₄. The solvent was removed under reduced pressure. Further purification was conducted via column chromatography (silica-gel, cond. CH, CH:DCM 7:1) yielding fractions with different number of substituents. The product containing fractions were determined via absorption spectra. Yield: 2.0 mg, 4%.

¹H NMR (300 MHz, CD₂Cl₂) δ 8.16 (m, 8H), 7.98 (td, J = 20.4, 5.7 Hz, 8H), 7.49 (m, 5H), 7.37 (m, 10H), 7.32 (s, 1H), 7.29 (d, J = 5.4 Hz, 2H), 7.25 (m, 5H), 7.22–7.19 (m, 1H), 7.16 (m, 7H), 7.10–7.03 (m, 2H), 1.68 (d, J = 8.1 Hz, 36H).

MALDI-TOF: m/z [M⁺] C₁₀₈H₈₄N₄Pt calcd: 1632.6372, found: 1632.6532.

2.3. Preparation of sensor films

The "cocktails" were prepared by dissolving the respective indicator (0.5-1 wt% in respect to the polymer) and polystyrene (10 wt% in)



Scheme 1. Synthesis of the new platinum(II) benzoporphyrin derivatives via one step modification of porphyrin complexes available via template condensation.

respect to the solvent) in chloroform. Then the "cocktails" were knifecoated on a dust-free PET support using a 25 mm-wide Gardner coating knife (Pompano Beach, United States) with a wet thickness of 25 μ m. Finally, the sensor films were dried for 24 h at 60 °C to ensure complete removal of solvent.

2.4. Measurements

 1 H and 13 C NMR were recorded on a 300 MHz instrument (Bruker AVANCE III). In all spectra, the residual signal of the deuterated solvent was used as an internal standard to reference the chemical shifts δ . Data analysis was performed with the MestreNova NMR software. High resolution mass spectra were recorded using a Micromass TofSpec 2 E as positive reflector on a Bruker Ultraflex Extreme MALDI-TOF/TOF spectrometer. The mass spectra were analyzed with the FlexAnalysis 3.0 software (Bruker Daltonics).

The absorption spectra of the dyes were recorded on a CARY 50 conc UV-Vis spectrophotometer from Varian (Palo Alto, United States). Molar absorption coefficients were determined in three independent measurements. The luminescence spectra were recorded on a FluoroLog[®] 3 spectrofluorometer from Horiba Scientific equipped with a NIR-sensitive R2658 photomultiplier from Hamamatsu. Quantum yields were determined according to Crosby and Demas [34] using a solution of dibutoxy-aza-BODIPY (BF2 chelate of [5-(4-buthoxyphenyl)-3-phenyl-1Hpyrrol-2-yl][5-(4-buthoxyphenyl)-3-phenylpyrrol-2-ylidene]-amine) in chloroform as a reference ($\Phi = 36\%$) [35,36]. All dye solutions were deoxygenated in a screw-cap cuvette (Hellma; Müllheim, Germany) by bubbling argon through the solution for 10 min. Photophysical studies in solutions were performed for the dye concentrations of between 2 and 4 \times 10⁻⁶ mol*L⁻¹. The phosphorescence decay times of the complexes in solution and in sensing foils were obtained in frequency domain using a Firesting oxygen meter from PyroScience (Aachen, Germany) at a modulation frequency of 4 kHz.

2.5. Photostability tests

The dye solutions in toluene (HPLC-grade) were filled in a screw-cap cuvette and illuminated with a high-power LED array (λ_{max} 635 nm, www.LED-TECH.de) using a constant current LED driver from Dehner (Model: LED-350MA35W-IP67; Oestrich-Winkel, Germany) at the 35 W and 350 mA. The light of the LED-array was focused onto the glass cuvette utilizing a lens from Edmund optics. The photon flux was > 20.000 µmol s⁻¹ m⁻² µA (irradiance 377 mW*cm⁻²) as determined with a Li-250 A light meter from Li-COR (Nebraska, USA). For measurements at air saturation the cuvette was unsealed and shaken after each irradiation interval to ensure air saturation in the sample.

2.6. Oxygen response in solution and polystyrene

The composition of the gas was adjusted utilizing a custom-build gas-mixing device based on mass-flow controllers from MKS (Munich, Germany) and Voegtlin (Aesch, Switzerland) by mixing nitrogen and the test gas ($2\% O_2$ in nitrogen) for the solution studies and by mixing compressed air, nitrogen and oxygen for the sensor characterization. The temperatures during the characterization were controlled and kept constant using a cryostat ThermoHaake DC50 (www.thermoscientific. de/home).

2.7. Upconversion experiments

The upconversion experiments were conducted on FluoroLog^{*} 3 spectrofluorometer from Horiba. For excitation of the sensitizer-annihilator solutions in toluene a 450 W xenon lamp from the fluorometer or a laser diode (635 nm, from www.roithner-laser.com.) were used. Due to the high concentration of the sensitizer-annihilator solutions all spectra were recorded in the front-face mode. The solutions were deoxygenated in a screw-cap cuvette by bubbling argon through the

solution for 10 min. Neutral density filters (50%, 25%, 10%, 5% of transmission) were used to modulate the intensity of the excitation light. The exact transmissions at the excitation wavelength were calculated from absorption spectra of the filters. The quantum yields of the upconverted fluorescence were roughly estimated by comparing the emission of the annihilator and the emission of the sensitizer without the annihilator. The photographic images of the upconverted fluorescence were acquired using 635, 650 and 675 nm laser diodes (Roithner) with Canon 5D camera.

3. Results and discussion

3.1. Synthesis

The new complexes are prepared via one step modification of Pt(II) meso-tetraaryltetrabenzoporphyrins conveniently accessible via a 3step synthesis. The template condensation of either phthalimides or dicyanobenzenes with phenylacetic acid (Scheme 1) results in Zn(II) benzoporphyrins with moderate yields (5-10%) which however can be obtained on multi-gram scale from inexpensive chemicals. The Zn(II) complexes are demetalated in acidic conditions and the Pt(II) dyes are prepared via platination of the free-base porphyrin. It should be mentioned that only condensation using dicyanobenzenes results in analytically pure benzoporphyrins, whereas synthesis of the dyes in the "classical" template condensation is accompanied by formation of benzyl-fused adducts and other by-products (porphyrins without 1 Br atom; Fig. S46, ESI) which are virtually impossible to separate. These by-products significantly diminish the yields of the aimed complexes in subsequent π -extension reactions. Since 4-bromodicyanobenzene was not commercially available and optimization of the yield was not the aim of the current study, we used the route starting from 4-bromophthalimide to obtain tetrabromo-substituted benzoporphyrins.

Friedel-Crafts acylation of Pt-TPTBPF with either 4-chlorobenzoyl chloride or acetyl chloride in 1,2-dichlorobenzene in presence of $AlCl_3$ results in formation of Pt-benzoyl-Cl or Pt-acetyl, respectively, in good yields (30–70%) obtained as a mixture of isomers (Scheme 1).

Suzuki coupling reaction of Pt-TPTBPtBu₄Br₄ with the respective boronic acids (9,9-dimethylfluorene-2-boronic acid and 9-phenylcarbazole-3-boronic acid) led to formation of Pt-fluorene and Ptcarbazole derivatives, respectively (Scheme 1). Sonogashira coupling of the same porphyrin with phenylacetylene resulted in the formation of Pt-Ph-acetylene (Scheme 1). Due to above-mentioned impurities in Pt-TPTBPtBu₄Br₄ and incomplete substitution during the Suzuki and Sonogashira reactions, the yields of the tetra-substituted products are very low and chromatographic purification is laborious.

3.2. Photophysical properties

Fig. 1 shows absorption and emission spectra of the new platinum (II) benzoporphyrins in toluene in comparison with their respective benzoporphyrin precursors. π -extension via Suzuki and Sonogashira coupling results in bathochromic shift of the Soret and Q bands by about 15 nm (Table 1). Interestingly, the π -extended complexes of fluorene, carbazole and Ph-acetylene have higher ratio of the molar absorption coefficients for the Q to Soret bands compared to the precursor.

Very similar bathochromic shift is observed upon introduction of acetyl and chlorobenzoyl groups in the same position. Interestingly, the Q-bands for these dyes are broader than for the Pt-TPTBPF precursor (FWHM of Pt-TPTBPF: 460 cm^{-1} at 615 nm; Pt-benzoyl-Cl: 666 cm^{-1} at 631 nm and Pt-acetyl: 634 cm^{-1} at 629 nm).

These subtle effects, however, have pronounced impact on potential applications of the dyes in sensing and imaging. In fact, the newly synthesized dyes are much better compatible with a number of light sources used in compact instruments and in microscopy such as bright blue 455-nm LED, 635-nm red laser diode, 455 nm line of the Ar laser



Fig. 1. Absorption (solid lines) and emission (dashed lines) spectra of new Pt(II) complexes and precursors in toluene at 25 °C; anoxic conditions for emission measurements.

and 632.8 nm line of the He-Ne laser. Importantly, all these sources almost perfectly fit the maxima of the Soret and the Q-bands, which together with very high molar absorption coefficients (exceeding 210.000 and $110.000 \, \text{M}^{-1} \text{cm}^{-1}$ for the Soret and the Q-band respectively) and high phosphorescence quantum yield (QY), Table 1, ensures excellent brightness. This can be of high interest if the dyes are used for imaging in cells and tissues. Notably, the position of the absorption bands of the new Pt(II) porphyrins is very similar to that of the Pd(II) complex with TPTBPF, which phosphorescence quantum yield is, however, significantly lower than for the Pt(II) complexes.

The new benzoporphyrin derivatives possess strong room-temperature phosphorescence in the NIR region in deoxygenated organic solvents such as toluene. The bathochromic shift of the emission spectra is smaller than the changes observed in the absorption spectrum, i.e. the new dyes possess smaller S_1 - T_1 energy gap compared to the parent benzoporphyrins. This effect is particularly pronounced for the Ptbenzoyl-Cl and Pt-acetyl complexes, which show the behaviour similar to that for the previously reported benzoporphyrins bearing highly electron-withdrawing sulfone groups in the same position [36]. Interestingly, all substitutions, except for the introduction of a triple bond in Pt-Ph-acetylene, favourably affect the phosphorescence quantum yields, which increase by about 25% compared to Pt-TPTBPF. This is again in good correlation to the properties of the sulfone-substituted complexes [36]. On the other hand, bulky phenylcarbazole and

Table 1

Photo	ohysica	l prop	erties (of the	new	platinum(II)	com	plexes	and	their	precursors	in	anoxic	toluene	at 2	25 °C	з.

Complex	λ_{max} abs (ϵ), nm (M ⁻¹ cm ⁻¹)	λ_{max} em, nm	Stokes shift, cm^{-1}	QΥ, Φ	τ, μs	K_{sv} , kPa^{-1}	k_q , $Pa^{-1}s^{-1}$
Pt-TPTBPF	430 (212.000); 565 (16.300); 615 (146.000)	769	3260	0.24	53.0	4.58	87
Pt-TBrTtBuPP	436 (238.000); 564 (16.100); 615 (137.500)	760	3100	0.17	32.6	3.78	116
Pt-fluorene	443 (274.000); 575 (22.000); 627 (171.000)	777	3080	0.28	45.5	2.68	59
Pt-carbazole	444 (240.000); 578 (21.400); 630 (171.700)	777	3000	0.29	44.0	2.56	58
Pt-benzoyl-Cl	448 (218.000); 579 (17.400); 631 (121.000)	773	2910	0.29	47.4	2.75	58
Pt-acetyl	445 (216.000); 577 (16.000); 629 (114.000)	773	2960	0.31	49.8	3.19	64
Pt-Ph-acetylene	446 (285.000), 577 (22.500) 630 (169.000)	772	2920	0.13	45.0	2.34	52

dimethylfluorene substituents may reduce radiativeless deactivation via molecular vibrations. Obviously, binding of phenyl-acetylene groups via triple bond, as it is the case for Pt-Ph-acetylene, results in similar absorption characteristics compared to the other Pt(II) complexes, but to a less pronounced bathochromic shift of the emission band and decreased quantum yields.

Apart from platinum(II) porphyrins, the respective palladium(II) analogues are also known for their fairly strong fluorescence. Compared to the Pt(II) porphyrins, the Pd(II) complexes generally feature bath-ochromically shifted absorption and emission, significantly longer phosphorescence decay times but lower quantum yields. Pd-benzoyl-Cl was obtained analogously to Pt-benzoyl-Cl from palladium(II) tetra(4-fluorophenyl)tetrabenzoporphyrin with good yields (Fig S1, ESI). Its photophysical properties (Table S1, Fig. S4, ESI) follow the above expectations with absorption maxima at 461, 595 and 645 nm (molar absorption coefficients 283.000, 16.000 and 108.000 M^{-1} cm⁻¹, respectively), emission maximum at 799 nm, phosphorescence decay time of 313 µs and quantum yield of 0.13 (all for anoxic toluene at 25 °C).

3.3. Photostability

This property is of great importance especially if the dye-based materials are exposed to high light densities or/and irradiated over a longer period of time, conditions which are typical for many applications such as upconversion or microscopy. Photodecomposition in air-saturated conditions might be particularly critical due to formation of singlet oxygen. Moreover, Pt-benzoyl-Cl possesses the benzophenone motive, which is a well-known photoinitiator. Photodegradation of the new platinum(II) complexes dissolved in air saturated toluene was tested upon continuous irradiation with a high power 635 nm LED array (35 W, 350 mA, photon flux: > 20.000 μ mol s⁻¹ m⁻²; irradiance



Fig. 2. Photodegradation profiles for the new Pt(II) complexes and Pd-TPTBP as reference in air-saturated toluene solution at 25 $^\circ$ C upon irradiation with a high power 635 nm LED.

 377 mW cm^{-2}). Fig. 2 shows that the photostability of the new porphyrins is rather similar to that of palladium(II) tetraphenyltetrabenzoporphyrin (Pd-TPTBP), which was chosen as a reference due to almost identical position of the Q-band corresponding to the excitation wavelength. Electron-withdrawing acetyl and chlorobenzoyl substituents improve the photostability whereas electron-donating phenylcarbazole and phenyl-acetylene slightly decrease it. Thus, photooxidation appears to be the most likely photodegradation mechanism. Despite faster photobleaching of Pt-carbazole and Pt-Phacetylene, even in this case the photostability is adequate for most applications. For instance, in sensing applications not only the intensities of the excitation light are much lower but also interrogation times of 10–20 ms are sufficient for acquisition of a measurement point.

3.4. Luminescence quenching in solution and in polymeric matrix

Because of the favorable photophysical properties the new dyes can be promising as indicators for application in optical oxygen sensors. First, phosphorescence quenching in solution was investigated (Fig. 3). The quenching constants K_{SV} obtained from the linear fit of the Stern-Volmer plots are reported in Table 1. Interestingly, the bimolecular quenching constants $k_{q} = K_{SV}/\tau_{0}$ were found to be lower than for the parent compounds Pt-TPTBPF and Pt-TBrTtBuPP. According to Smoluchovski equation [37,38], the rate constant for the diffusion-limited reaction k_d is proportional to the sum of the diffusion coefficients of the reactants and to the reaction distance which is approximated as the sum of the radii for the reacting molecules. Since the diffusion coefficient for oxygen is about 1 order of magnitude higher than for the metalloporphyrin [30], the k_d is expected to be very similar for all the dyes. Therefore, it can be speculated that the bulky substituents on periphery of the dye protect the porphyrin core from collision with molecular oxygen similar to porphyrin-based dendrimers. This results in smaller k_a values than can be expected from the radii and diffusion coefficients



Fig. 3. Phosphorescence quenching by molecular oxygen for the Pt(II) complexes dissolved in toluene (at 25 °C).



Fig. 4. Stern-Volmer plots for the Pt(II) complexes embedded in polystyrene (at 25 °C).

of the reactants. On the other hand, the k_q value for Pt-acetyl is closer to the values obtained for the other π -extended dyes rather than to k_q of Pt-TPTBPF (Table 1). As was discussed previously [30], the bimolecular quenching constant may also correlate to the energy of the triplet state of the dye due to its proximity to the $^{1}\Sigma_{g}^{+}$ level of oxygen (E = 13121 cm $^{-1}$) [39]: i.e. the lower the triplet energy the lower the k_q . In fact, the triplet energy of the new π -extended dyes is lower than for Pt-TPTBPF. Pt-TBrTtBuPP emits even at shorter wavelength

compared to Pt-TPTBPF (Table 1) and shows about 30% higher kq.

In order to evaluate their sensing behaviour, the dyes were embedded in polystyrene (0.5 % wt. of the indicator) serving as a model matrix. Not surprisingly, the phosphorescence of all dyes is efficiently quenched by oxygen in this polymer (Fig. 4).

The non-linear Stern-Volmer plots are typical for the oxygen sensors based on polystyrene-immobilized (benzo)porphyrins. The plots can be described by the so called "two-site model" [40] which assumes

Table	2
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Fit parameters for the oxygen sensors based on the new benzoporphyrins embedded in polystyrene.

Complex	f	m	τ_0/K_{SV1} at 5 °C, $\mu s/kPa^{-1}$	τ_0/K_{SV1} at 25 °C, $\mu s/kPa^{-1}$	τ_0/K_{SV1} at 45 °C, $\mu s/kPa^{-1}$	dτ/dt, %/K at 25 $^\circ\text{C}$
Pt-TPTBPF [41]	0.85	0	-	52.6/0.218	-	0.07
Pt-fluorene	0.81	0.107	48.7/0.208	48.1/0.246	47.5/0.271	0.065
Pt-carbazole	0.78	0.103	47.0/0.160	46.4/0.182	45.6/0.201	0.074
Pt-benzoyl-Cl	0.80	0.075	51.3/0.184	50.6/0.220	49.5/0.255	0.089
Pt-acetyl	0.84	0.072	52.1/0.206	51.21/0.245	50.23/0.292	0.092
Pt-Ph-acetylene	0.83	0.147	45.9/0.235	45.0/0.281	44.0/0.309	0.105

location of the indicator in two different microenvironments. The equation also adequately fits the decay time plots for the average decay times obtained in frequency domain:

$$\frac{\tau_0}{\tau} = \frac{1}{\frac{f}{1+K_{SV1}*p_{O_2}} + \frac{1-f}{1+(K_{SV1}*m)*p_{O_2}}}$$
(1)

where τ_0 and τ represent the lifetimes of the indicator under anoxic conditions and in presence of oxygen, while K_{SV1} and K_{SV1} *m are the Stern-Volmer constants for the two microenvironments, and f is the fraction of the overall emission for the first site. The fit parameters at different temperatures are summarized in Table 2.

It is evident that all the complexes have very similar behaviour in respect to the quenching efficiency and the linearity of the Stern-Volmer plots. In contrast to the solution, no evident correlation between the size of the substituent or energy of the triplet state and the quenching efficiency is observed. However, because of much higher complexity of the polymeric matrix compared to the solution some minor trends may not be visible. In fact, due to different size and polarity of the substituents, the localization of the dyes in the polymer may be not fully identical. Since different polymeric domains are characterised by different oxygen permeabilities, the linearity of the Stern-Volmer plots and the calculated quenching constants may be indirectly influenced by the substituents.

In respect to thermal quenching of phosphorescence (determined from the temperature dependency of the decay time under anoxic conditions) all the dyes are again rather similar with slightly higher temperature coefficients for Pt-benzoyl-Cl, Pt-acetyl and Pt-Ph-acetylene. Moreover, these properties match very well those of polystyreneimmobilized Pt-TPTBPF which was used as a reference material. Although the dynamic range of the new sensors is from about 0.1 to 100 kPa, and thus is the same as for the parent compounds, it can be extended into significantly lower concentration range by using polymers with higher oxygen permeability (ethyl cellulose, organicallymodified silica etc.). Also, the sensitivity of the oxygen sensor based on Pd-benzoyl-Cl embedded in polystyrene (Table S2, Fig. S5, ESI) is about 5-fold higher than for the sensor based on Pt-benzoyl-Cl (K_{sv1} at 25 °C is 1.03 and 0.22 kPa⁻¹, respectively) which is explained by significantly longer phosphorescence decay time of the Pd(II) complex (346 µs at 25 °C).

3.5. Dyes as sensitizers in TTA-based upconversion systems

As mentioned above, benzoporphyrins have already been successfully used as synthesizers in triplet-triplet-annihilation (TTA) based upconversion systems. Briefly, after absorption of light by the sensitizer and inter-system crossing, an annihilator in triplet excited state is formed via triplet-triplet energy transfer from sensitizer to annihilator (Scheme S1). Collision of two excited annihilator molecules results in formation of one of them in the singlet excited state following by fluorescence which is located at shorter wavelength compared to the excitation light. The annihilator should feature very high fluorescence quantum yields (close to unity), good solubility in organic solvents and outstanding photostability [42,43]. In order to be useful for energy



Fig. 5. Left: Emission spectrum (λ exc 635 nm) of the TTA system based on $5 \cdot 10^{-5}$ M of Pt-benzoyl-Cl and $2.5 \cdot 10^{-4}$ M of Solvent green 5 (structure shown) in anoxic toluene. The insert shows the photographic image of the upconverted fluorescence for the same system upon excitation of the solution with two laser diodes.

conversion applications, the sensitizer should efficiently absorb light in the red part of the electromagnetic spectrum due to the considerable solar power and low photovoltaics efficiency in this region [44-47] and transfer its energy to the annihilator. Not only benzoporphyrins [36] but also their molecular hybrids with naphthalooporphyrins proved to be viable sensitizers for TTA upconversion systems [44,45,47,48], but the photostability of the latter compounds is poor [29]. Since new benzoporphyrin derivatives benefit from higher quantum yields, bathochromically shifted absorption as well as emission and photostability similar to that of the parent benzoporphyrins, they are expected to be promising sensitizers for upconversion of red light. As a proof of concept, ability of the new dyes to act as sensitizers in TTA upconversion was investigated. As can be seen (Fig. 5, Fig. S12-S15 ESI), bright upconversion from perylene dye Solvent Green 5 (2.5 \times 10⁻⁴ M) is observed upon excitation of the new Pt(II) complexes (5 \times 10 $^{-5}$ M) with a 635 laser diode. A quadratic dependence of upconverted fluorescence on the intensity of excitation light was observed upon excitation of the dyes with a Xenon lamp (slope of the logarithmic plot approximately 2), Fig. S6-S11 ESI. On the contrary, excitation with the 635 nm laser diode revealed a linear region with a slope of unity demonstrating saturation conditions (Fig. S12-17, ESI) [49]. This phenomenon is typical for nonlinear processes like TTA based upconversion [42-44,50]. Since the Q-bands of the Pd-benzoyl-Cl located at even longer wavelength compared to the corresponding Pt(II) complex, this dye may even be more promising sensitizer for the red part of the spectrum. Indeed (Fig. S10, S11, S16-S18, Table S3 ESI), bright upconversion was observed with two perylene dyes, Solvent Green 5 and Lumogen Orange even at comparably long excitation wavelengths.

Considering scientific progress in developing of nanoparticles featuring TTA [15,51], the combination of the red-light-excitable sensitizers with different annihilators may result in a new generation of imaging agents for *in vivo* measurements which possess much higher brightness than the lanthanide nanoparticles [52,53].

4. Conclusions

We have demonstrated several different strategies for modification of known benzoporphyrins complexes within one reaction step. Modification via Friedel-Crafts acylation is particularly efficient and can be performed with good yields both for Pt(II) and Pd(II) complexes. The new platinum(II) complexes show a bathochromic shift in the absorption spectra, now enabling efficient excitation with 635 nm laser diode/632.8 nm line of He-Ne laser (O band) and with blue LEDs/ 455 nm line of the Ar laser (O-band). Modification with the respective groups also results in increased quantum yields with the exception of phenylacetylene-modified dye, whereas the decay time and photostability are similar to those of the parent compounds. The new dyes represent promising indicators for oxygen sensors particularly in respect to in vivo applications, due to better light penetration and lower light scattering at longer wavelengths. They may also be useful for application in enzymatic glucose sensors relying on oxygen transducers. The new complexes are also valuable sensitizers for TTA upconversion systems and allow more efficient harvesting of red light than the parent benzoporphyrin dyes. Even longer sensitization wavelengths can be achieved if the central atom is substituted to palladium(II).

Associated content

Synthesis, photophysical properties, optical oxygen sensor, TTA upconversion, ¹H and ¹³C NMR and mass spectra (PDF).

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Appendix A. Supplementary data

Supplementary data related to this article can be found at https://doi.org/10.1016/j.dyepig.2018.07.017.

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