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

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ABSTRACT

Complexes of benzoporphyrins are highly promising for application in optical oxygen sensors, as triplet sensitizers 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. Application 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-TPTBPtBu$_4$Br$_4$) was modified via Suzuki or Sonogashira cross-coupling reaction and platinum(II) meso-tetra(4-fluorophenyl)tetrabenzoporphyrin (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 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% O_2 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) meso-tetra-(4-t-butyl)phenyl-tetra-bromobenzo-porphyrin (Pt-TPTBPtBu$_4$Br$_4$) (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-TPTBPtBu$_4$Br$_4$ (20.0 mg, 12.9 μmol, 1.00 eq) was dissolved in toluene (6.5 mL) under argon atmosphere. 9,9-Dimethylfluorene-2-boronic acid (30.8 mg, 129 μmol, 10.0 eq) and K_2CO_3 as base (71.4 mg, 517 μmol, 40.0 eq) were added to the solution. The base was pre-dissolved in H_2O (1.5 mL). Catalyst Pd(PPh$_3$)$_4$ (0.89 mg, 0.77 μmol, 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 H_2O and dried over Na_2SO_4 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%.

^{1}H NMR (300 MHz, CD_2Cl_2) 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$^+$] $C_{136}H_{116}N_4Pt$ 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 μmol, 1.00 eq) of Pt-TPTBPtBu$_4$Br$_4$ dissolved in toluene and tetrahydrofuran (THF) (6 + 3 mL) and 9-phenylcarbazole-3-boronic acid (46.4 mg, 162 μmol, 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%.

^{1}H 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$^+$] $C_{148}H_{112}N_8Pt$ 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 $AlCl_3$ (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 $CHCl_3$ and ethanol (EtOH) 10:1). After complete conversion the reaction mixture was cooled down to RT and treated with EtOH:H_2O (1:1 v/v, 40 mL) and stirred for 10 min to neutralize the excess of $AlCl_3$. After addition of DCM, the organic layer was washed with H_2O and dried over Na_2SO_4 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%.

^{1}H 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$^+$] $C_{88}H_{44}Cl_4F_4N_4O_4Pt$ 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 μL, 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, CD_2Cl_2) 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-TPTBPtBu$_4$Br$_4$ (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(PPh$_3$)$_4$ (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% $CuSO_4$ to remove the excess of TEA. The product was extracted with DCM, the organic layer was dried over Na_2SO_4. 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%.

^{1}H NMR (300 MHz, CD_2Cl_2) 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$^+$] $C_{108}H_{84}N_4Pt$ 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