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New NIR-emitting complexes of platinum(II) and palladium(II) with fluorinated benzoporphyrins

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ABSTRACT

New platinum(II) and palladium(II) complexes with fluorinated benzoporphyrins are prepared and characterized. The photo-physical and electrochemical properties, as well as quenching by oxygen are investigated. The complexes possess highly efficient room-temperature NIR phosphorescence and are excitable with blue- and red-light. The fluorinated derivatives show improved photo-physical properties and photo-stability. The new dyes are particularly suitable as indicators for the use in optical oxygen sensors.

1. Introduction

Determination of oxygen is of a great importance in various fields of science and technology. Optical sensing and imaging of oxygen is virtually non-invasive and thus it has become extremely popular in the last two decades [1]. UV–vis oxygen indicators are fairly established and are mainly represented by ruthenium(II) polypyridyl complexes (particularly, ruthenium(II)-tris-4,7-diphenyl-1,10-phenanthroline (Ru-dpp)) [2–5], palladium(II) and platinum(II) complexes with porphyrins [6–10], and cyclometallated complexes of platinum(II) and iridium(III) [11–13]. Optical sensors based on UV–vis indicators, however, suffer from some drawbacks. First, a high level of autofluorescence in many biological media is produced upon excitation, since many natural compounds are fluorescent. Typical examples include nucleotides FAD and NAD, which are present in many biological samples and in fermentation media. Many components of an optical set-up (such as long-pass filters or fibers) also can generate background fluorescence; therefore, long-waved excitation allows for purer optical signals. Second, UV–vis indicators are poorly suitable for measurements in scattering media. High scattering is common in bioreactors and in marine sediments, as well as in the case of measurements performed in subcutaneous tissue. Third, UV–vis indicators cannot be used in implantable sensors, since highly scattering blood components efficiently absorb in visible region. Lack of appropriate indicators is thus a serious hindrance for the development of implantable sensors for subcutaneous glucose measurements since this sensor type also relies on oxygen transduction [14].

NIR-excitable probes overcome these drawbacks, but also show much better compatibility with optical components. For example, bright LEDs and laser diodes are available as excitation sources starting from 590 to 630 nm, respectively, while the sensitivity of cheap and compact Si photo-diodes increases at longer wavelengths and reaches maximum at 850–900 nm. A few NIR indicators were reported to be suitable for oxygen sensing. The Pt(II) and Pd(II) complexes of porphyrin lactones [15] and porphyrin ketones [16] possess intense absorption bands in the region 580–600 nm and some of them are excellently compatible with a 590-nm LED. Despite relatively high absorption coefficients the complexes exhibit moderate to low brightnesses (BS, determined as the product of molar absorption coefficient, ε and emission quantum yield, Φ). Moreover, the indicators are practically unsuitable for measurements in subcutaneous tissue or blood since transmittance of the excitation-light is still rather low. The palladium(II) complexes with benzoporphyrins [17] and naphthoporphyrins [17–19] seem to be much more promising for optical sensing [20]. The benzoporphyrin complexes, particularly, possess good brightnesses [17] upon excitation in the red region ($\lambda_{max} > 600$ nm) and are nicely compatible with LEDs and laser diodes. Unfortunately, the luminescence decay time of the palladium(II) complexes often is too long (~400 μs) and the sensitivity to oxygen is too high to provide optimal dynamics in most sensor materials. The respective platinum(II) complexes

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(having shorter decay time) are only sparsely described in the literature and are restrained to unsubstituted benzoporphyrins [21] (that suffer from low solubility and high tendency to aggregation) and water-soluble derivatives [18]. Recently application of a platinum(II) benzoporphyrin in the NIR-OLEDs was demonstrated [22]. Thus, new benzoporphyrin complexes (particularly of platinum(II)) are of much interest for developing advanced optical sensors and biosensors. Fluorinated porphyrins can additionally benefit from improved photo-stability [10]. In this contribution we report the synthesis and photo-physical properties of new platinum(II) and palladium(II) complexes with fluorinated *meso*-tetraphenyltetrabenzoporphyrins.

2. Experimental

2.1. Materials

Ethyl isocyanoacetate, 1-nitro-1-cyclohexene, 2,3-dicyano-5,6-dichlorobenzoquinone (DDQ), poly(octadecyl methacrylate) (average MW, 170,000) and polyvinylpyrrolidone K 30 were purchased from Aldrich (www.sigmaaldrich.com). The fluorinated benzaldehydes (4-fluorobenzaldehyde, 3,5-difluorobenzaldehyde, 3,4,5-trifluorobenzaldehyde and pentafluorobenzaldehyde), palladium(II) chloride, platinum(II) chloride and benzonitrile were from ABCR (www.abcr.de). Dimethylformamide, ethyldiisopropylamine, 1,8-diazabicyclo [5.4.0] undec-7-ene (DBU), benzaldehyde, ethylcellulose (46% ethoxyl content) and poly(vinyl chloride) were obtained from Fluka (www.sigmaaldrich.com). All other solvents were from Roth (www.carl-roth.de). The silica-gel 60 (0.063–0.200 mm) was from Merck (www.merck.de). Polysterene (MW. 250,000) was obtained from Fischer Scientific (www.fishersci.com). Poly(ethylene glycol terephthalate) support (Mylar®) was purchased from Goodfellow (www.goodfellow.com). Platinum(II) octaethylporphyrine (PtOEP) and platinum(II) 5,10,15,20-tetrakis-(2,3,4,5,6-pentafluorophenyl)-porphyrin (PtTFPP) were purchased from Frontier Scientific (www.frontiersci.com). Nitrogen and synthetic-air (all of 99.999% purity) were obtained from Air Liquide (www.airliquide.at). The test gas (1% of oxygen in nitrogen) was purchased from Linde (www.linde-gas.at).

2.2. Synthesis

The synthesis of 4,5,6,7-tetrahydroisoindole and *meso*-tetraphenyltetracyclohexenoporphyrin (H_2TPTHP, Fig. 1) were performed according to a literature procedure [23]. The platinum(II) complex with *meso*-tetraphenyltetrabenzoporphyrin (PtTPTBP) was further prepared according to Borek et al. [22]. The modification includes addition of 500 μL of ethyldiisopropylamine per 700 mg of *meso*-tetraphenyltetracyclohexenoporphyrin to promote the platination. The reaction was completed within 1 h. The complexes of platinum(II) with *meso*-tetra(4-fluorophenyl) tetrabenzoporphyrin (PtTPTBPF), *meso*-tetra(3,5-difluorophenyl) tetrabenzoporphyrin (PtTPTBPF_2) and *meso*-tetra(3,4,5-trifluorophenyl)tetrabenzoporphyrin (PtTPTBPF_3) were prepared in a similar manner. Oxidation of platinum(II) complex with *meso*-tetra(3,4,5-trifluorophenyl)tetracyclohexaneporphyrin (PtTPTHPF_3) was performed in chloroform (150 mL per 500 mg of the complex) at 60 °C for 4 h. Ten equivalents (923 mg) of DDQ were used. The excess of DDQ was quenched with aqueous solution of sodium sulphate and the organic phase was purified on a silica-gel column using toluene as an eluent. Then, silica-gel was soaked with the solution of the dye and dried overnight at 60 °C. The platinum(II) complex with *meso*-tetra(3,5-difluorophenyl)tetrabenzoporphyrin also was not isolated but absorbed on silica-gel after purification by chromatography.

The respective palladium(II) benzoporphyrin complexes were prepared analogously except for the metallation step. The palladium(II) complexes with *meso*-substituted tetracyclohexenoporphyrins were obtained by boiling the respective ligand with 2 equiv. of $PdCl_2$ in tetrahydrofuran (~100 mL per 1 mmol of the ligand). The reaction was completed in 5 min after addition of 1 mL of triethylamine. The solvent was removed under reduced pressure, and the product was purified by column chromatography on silica-gel using CH_2Cl_2 as an eluent. In the last step, the palladium(II) complex with *meso*-tetra(3,5-difluorophenyl)tetrabenzoporphyrin was not isolated from the solution but absorbed on silica-gel.

2.2.1. *meso*-Tetraphenyltetracyclohexenoporphyrin (H_2TPTHP)

MS (MALDI): *m*/*z* $[MH]^+$ calc. 831.4427, found 831.4415. UV–vis: (CH_2Cl_2), λ/nm (relative intensity): neutral—440 (1.00), 535 (0.089), 575 (0.043), 614 (0.036), 677 (0.018); dication—466 (1.00), 620 (0.045), 676 (0.095).

2.2.2. *meso*-Tetra(4-fluorophenyl)tetracyclohexenoporphyrin (H_2TPTHPF)

MS (MALDI): *m*/*z* $[MH]^+$ calc. 903.4050, found 903.4077. UV–vis: (CH_2Cl_2), λ/nm (relative intensity): neutral—440 (1.00), 535 (0.077), 575 (sh), 615 (0.019), 677 (0.013); dication—467 (1.00), 618 (0.044), 677 (0.081).

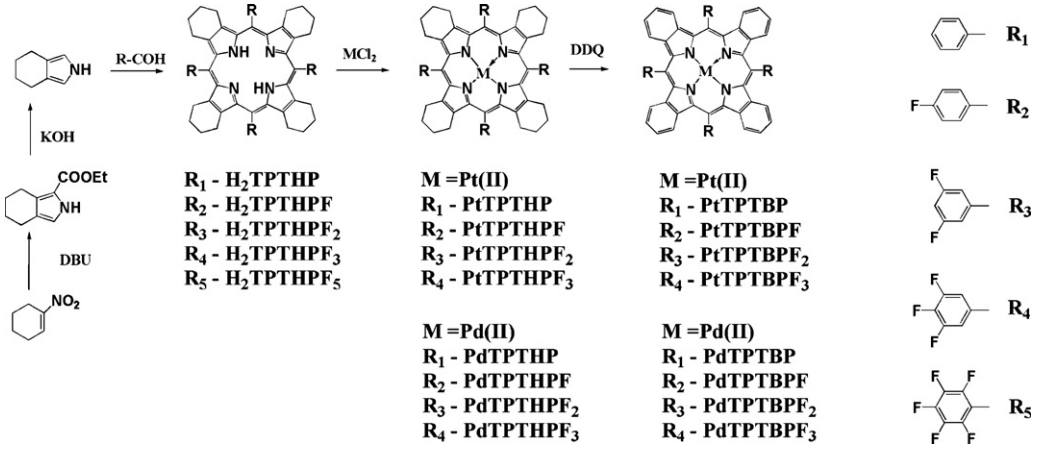

Fig. 1. Schema of synthesis and chemical structures of the benzoporphyrin complexes.