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meso-Tetraphenylporphyrin with pi-system extended by fusion with anthraquinone

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Fusion with 9,10-anthraquinone moiety was achieved to extend porphyrin’s π-system. Bridged dihydroisoindole derivative was used to prepare corresponding meso-tetraphenyltetraanthraquinonoporphyrin (Ph₄TAQP) via thermal retro-Diels-Alder reaction. Basic optical properties of the prepared new anthraquinonoporphyrin and its complexes with Zn and Pd were studied.

Introduction

Porphyrins with aromatic rings fused to the tetapyrrole core, so-called π-extended porphyrins, have attracted much attention in recent years as materials for numerous applications - from biomedical sensing and imaging to organic optoelectronics.1 Metallated π-extended porphyrins are particularly important for the process of triplet-triplet annihilation photon energy upconversion (TTA-UC).2 A variety of π-extended porphyrins have been synthesized by fusing benzene,3 naphthalene,4 pyrene,5 azulene,6 anthracene,7 corannulene,8 and other aromatic moieties to the meso- and β-positions of the macrocycle. Fusion of aromatic rings to all four pyrrole residues results in particularly strong effects on the π-system, leading to enhanced light absorption and efficient emission in the near-infrared (IR-A) region of the spectrum.9

First reported by Krautler and co-workers, a conjugation of naphthoquinone to a porphyrin has a remarkable effect on its properties. Particularly, resulting materials exhibit optical properties which resemble those of nanoscopic carbon materials with extended π-systems, such as graphene, graphite, and nanotubes.10 Theoretical studies of tetranaphthoquinonoporphyrin (TNQP) revealed that introduction of the carbonyl groups into the π-system results in strong alternations of bonds and a transformation of the conjugation from “benzene-type” to “butadiene-type”. Unidirectional photon-induced current associated with p-π conjugation enables light-harvesting efficiency of this kind of molecular skeleton to reach 90% in the range of 300–800 nm.11 This makes TNQPs attractive materials for panchromatic dye-sensitized solar cells. Moreover, porphyrin fused with quinone moieties are expected to exhibit interesting electrochemical properties, since they are able to accept a load of at least 8 electrons per molecule. Such materials clearly promise to expand the range of multi-electron transfer (MET) catalysts - compounds having ability to accommodate and transfer multiple electrons to reaction substrates at one time.12

Despite promising properties, tetraquinonoporphyrins (TQP) are almost unknown because available synthetic methods in the field of π-extended porphyrins chemistry have been very limited until recently. To the best of our knowledge, the only representative of a porphyrin directly fused with four quinone fragments was obtained by Krautler and co-workers, using [4+2] cycloaddition reaction between β,β’-tetrasulfolenoporphyrin13 and an excess of benzoquinone.10

Herein we report a synthetic approach to meso-tetraphenyltetraanthraquinonoporphyrin (Ph₄TAQP) based on the bridged dihydroisoindole precursor. In addition we describe basic optical properties of newly synthesized Ph₄TAQP free-base and its metal complexes.

Results and discussion

Due to instability of isoindole and its π-expanded analogues,14 the formation of fully conjugated π-system has to be performed after the formation of porphyrin macrocycle. So far, two general synthetic methods have been employed to construct the extended
Barton–Zard synthesis was unsuccessful and delivered a mixture of products arising from reduction of the quinone moiety. Therefore, protection of the reactive quinonic moiety was necessary to avoid side reactions during the pyrrole synthesis. Conversion of the quinone into the corresponding dihydroisoindole derivative (Scheme 1, route A). According to thermal retro-Diels–Alder approach, the target molecule can be prepared from bicyclo[2.2.2]octadiene-annellated porphyrin which can undergo thermal extrusion of ethylene (route B).

Scheme 1. Retrosynthetic analysis of TAQP system.

Pyrrole derivative containing naphthoquinone moiety represents a direct precursor for the synthesis of TAQP through route A. We first examined the possibility to apply directly 1,4,4a,9a-tetrahydro-anthraquinone 1 (Scheme 2) for the synthesis of corresponding pyrrole from vinyl or allyl sulfones via Barton–Zard reaction. Treatment of 1 with PhSCI, followed by oxidation with Oxone led to chlorosulfone derivative 2. Further reaction with DBU yielded 2-phenylsulfanylanthraquinone 3, rather then expected vinyl sulfone. An attempt to introduce an isocyanacetate synthesis delivered pyrrole 10, rather than into the pyrrole precursor. As expected, compound 5 was formed in good yield. However, under the conditions of Barton–Zard reaction (t-BuOK, THF, isocyanacetate), no formation of the corresponding pyrrole compound was observed. The only isolated production was found to be 9,10-diacetoxyanthracene 6. Attempts to optimize the reaction conditions: change of base (DBU, potassium and sodium tert-butoxides, HMDS), solvents and temperature regimes failed to deliver target product. It is known that aromatization of cyclohexadienes can be incurred by strong bases. However, taking into account that similar sulfone groups was previously successfully used in the pyrrole synthesis, it is interesting that sulphone 6 behaves so differently under basic conditions, when the elimination is the predominant pathway.

Thus we focused further efforts on thermal retro-Diels-Alder approach. 1,4-Naphthoquinone was reacted with 1,3-cyclohexadiene to obtain dione precursor 7. Its acetylation gave 8, which was used for the preparation of corresponding sulphone 9. As expected, Barton–Zard reaction with isocyanacetate synthesis delivered pyrrole 10.

Scheme 2. Synthesis of TAQP pyrrole precursor.
In this case tert-butyl isocynoacetate was used, since for pyrrole tert-butyl esters a decarboxylation reaction can be performed via solvolysis in neat trifluoroacetic acid. These conditions were expected to secure hydroquinone moiety from deprotection. Indeed, treatment with TFA for 30 min delivered pyrrole 11 in good yield (68%).

**Scheme 3.** Synthesis of Ph₄TAQP.

With pyrrole 11 in hand, we succeeded to prepare intermediate porphyrin 12 according to the conventional Lindsey condensation. As shown in Scheme 3, pyrrole 11 reacted with benzaldehyde in CH₂Cl₂ in the presence of BF₃·OEt₂, followed by oxidation with 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ) at room temperature for additional 3 hours to afford porphyrin 12 in 18% yield after purification. After further treatment of the obtained porphyrin 12 with KOH and oxidation by DDQ resulting crude intermediate was heated at 200 °C in vacuum during 4 h. Target tetraanthraquinonoporphyrin was isolated in 65% yield after chromatographic purification and recrystallization. To our surprise, instead of the expected problems with poor solubility due to ππ-stacking, we observed rather good solubility (as compared to tetranaphtho- or tetraanthraporphyrins) of the obtained product in common organic solvents (chlorohydrocarbons, aromatics, THF).

The aromatization was clearly observed by disappearance of methylene groups and appearance of a new singlet peak in the aromatic region corresponding to eight protons on the anthraquinone rings in ¹H NMR spectrum. It is noteworthy that well-resolved ¹H and ¹³C NMR spectra were obtained after addition of a trace of trifluoroacetic acid (TFA) which converted the porphyrin into dication form. MALDI-TOF mass spectra gave the additional evidence for the formation of Ph₄TAQP (ESI†).

**Figure 1.** Absorption (black) and emission (red lines) of (A) porphyrin 12, (B) Ph₄TAQP free base, (C) Ph₄TAQP-Zn, and (D) Ph₄TAQP-Pd. Solvent: toluene.
The absorption and emission spectra of porphyrins 12, Ph₄TAQP and its metal complexes are compared in Fig. 1. Electronic absorption spectra of 12 are similar to other tetratetraphenyl-β-octaalkyloporphyrins, such as the derivatives of octaethylporphyrin (OEP) showing Soret band at 434 nm and Q-bands at 523, 607, 675 nm in CH₂Cl₂ (for comparison, tetraphenylethacyclohexenoporphyrin free base: Soret band 439 nm, Q-bands 537, 580, 606, 674 nm). Fluorescence spectrum of 12 is also consistent with this type of porphyrin skeleton, showing maximum at 718 nm and low quantum yield of emission (φₑ < 0.01 in toluene, λₑ×c = 638 nm).

Ph₄TAQP exhibits strongly red-shifted Soret and Q-bands (Fig. 1B). The vibronic structure in the Q-band region is well-resolved. The lowest energy Q-band (752 nm) is red-shifted by 77 nm relative to the corresponding transition of the porphyrin 12 due to the effect of extended π-conjugation. At the same time, intensification of Q-bands is taking place – the maximum absorption ratio of Q-band to Soret band is enhanced from 0.09 (in 12) to 0.35. The free-base shows much stronger emission (φₑ = 0.08) than the parent compound 12, with a small Stokes shift (9 nm). Metal insertion has a profound effect on optical properties. The absorption spectra of Zn and Pd complexes, are shown in Figure 1C-D. Very strong red-shift by about 90 nm upon zinc insertion and blue-shift by 20–40 nm upon palladium insertion are observed. Both complexes show relatively strong emission (φₑ × c = 0.11 and 0.06 for Zn and Pd-complexes respectively). The emission of Ph₄TAQP shows multiple maxima that may be associated either with excimers formation or formation of charge-transfer excited states. Solutions of Ph₄TAQP and its metal complexes do not decompose noticeably when exposed to daylight for several hours, indication good photostability compared to other π-extended porphyrins.

Comparison of absorption spectra of Ph₄TAQPPd with those of palladium (II) tetratetraphenylbenzono- and tetratetraphylanaphthophorphyrins (Ph₄TBPPd and Ph₄TNPPd respectively, Figure 2) demonstrates the effect of anthraquinone fusion to the porphyrin core with respect to annelation of extra benzo-rings. Strong effect on the energies of S₁ and S₂ state of the molecule is manifested by the pronounced red shift of the Soret and Q-band. While in case of Ph₄TBPPd and Ph₄TNPPd the Soret band is shifted only by 20–30 nm with respect to parent tetratetraphenylporphyrin, fusion of anthracenes causes 100 nm red shift. Nevertheless, a “spectral window” between Soret and Q-bands allows for the application of Ph₄TAQPPd as sensitizer for TTA-UC process, that will be reported as a separate study.

Conclusions

Two approaches towards the synthesis of TAQP were explored: the one based on hydroisoindole precursor and bridged dihydrosoindole. The latter was found to be suitable for the synthesis of target compound using the Barton-Zard reaction. The strategy based on oxidative aromatization of dihydrosoindole precursor failed to deliver target compound due to side reactions in the course of pyrrole synthesis. The optical properties of Ph₄TAQP indicate electronic features that call for theoretical studies, as well as for better characterization using photophysical and electrochemical experiments. Indeed, new quinonoporphyrins are expected to exhibit interesting electrochemical properties as a result of the directly conjugated porphyrin and quinone moieties. Such materials appear to be of interest in photon energy conversion systems and in other applications. We relay a detailed discussion of the photophysical properties of variously substituted TAQP for a separate study.

Experimental

1,4,4a,9a-tetrahydroanthraquinone and tert-butyl isocyanacetate were prepare according to published synthetic protocols. DBU, thiophenol, bis(benzonitrile)palladium(II) chloride, DDQ, N-chlorosuccinimide, Oxone, 1,4-naphthoquinone, trifluoroacetic acid, benzaldehyde, boron trifluoride etherate and extra dry THF were purchased from Sigma-Aldrich. The handling of all air/water sensitive materials was carried out using standard high vacuum techniques. All solvents and reagents were obtained from commercial sources and used as received. Where mixtures of solvents were used, ratios are reported by volume. Column chromatography was carried out on silica gel 60 at normal pressure. NMR spectra were recorded on a Bruker DPX 250, Bruker AC300 NMR and Bruker Avance 500 spectrometers, with the solvent proton or carbon signal as an internal standard. Elemental analysis was carried out using a Foss Heraeus Vario EL. Electronic absorption spectra were recorded on Perkin Elmer Lambda 25 instrument. MALDI-TOF spectra were obtained on Bruker Reflex spectrometer III instrument using dithranol as a matrix. Melting points were determined on a Büchi hot stage apparatus and are uncorrected. Emission spectra were measured using Fluoromax-2 instrument. Emission quantum yields of the compounds were measured relative to the fluorescence of free-base tetratetraphenylporphyrin (φₑ =0.11) in deoxygenated toluene.
bath and acetic anhydride (8.5 mL, 90 mmol) was added to a stirred solution of quinone 2 at r.t. and the resulting orange solution was added dropwise over a period of 10 min at 0 °C. The mixture was stirred for 1 h at room temperature, washed with water, dried and evaporated to dryness. Resulting solid was recrystallized from MeOH to give 6.1 g (70%) of the title compound as a white powder (m.p. 155-157 °C). 1H NMR δH (300 MHz, CDCl3) 7.69 (4 H, m), 7.51 (2 H, m), 7.3 (3 H, d, J = 6.9 Hz), 6.84 (1 H, dd, J = 9.9 Hz), 6.18 (1 H, dd, J = 9.9 Hz), 4.09 (1H, m), 3.48 (1 H, m), 3.11 (1H, m), 2.49 (3 H, s). 13C NMR δC (75 MHz, CDCl3) 169.17, 136.76, 134.33, 129.88, 129.11, 128.06, 128.0, 127.54, 127.06, 122.41, 122.09, 121.85, 121.72, 121.51, 23.1, 20.93. Anal. Calcd for C24H12O6S: C, 66.04; H, 4.62; Found: C, 66.32; H, 4.85.

2-Benzensulfonyl-1,3-dichloro-2,3,4-tetrahydro-anthraquinone 2. 1H NMR δH (300 MHz, CDCl3) 8.06 (2 H, m), 7.97 (2 H, m), 7.79-7.59 (5 H, m), 5.03 (1 H, q, J = 3.3 Hz), 4.05 (1 H, m), 3.42-2.92 (4 H, m). 13C NMR δC (75 MHz, CDCl3) 184.04, 140.57, 140.45, 139.49, 135.24, 134.59, 134.56, 133.21, 130.52, 129.97, 127.01, 126.94, 62.80, 51.53, 30.72, 20.30. Anal. Calcd for C20H12ClO4S: C, 61.77; H, 4.41; Found: C, 61.23; H, 4.65.

2-Benzensulfonyl-anthraquinone 3. 1H NMR δH (300 MHz, CDCl3) 8.76 (1 H, t, J = 1.2 Hz), 8.4 (2 H, t, J = 1 Hz), 8.28 (2 H, m), 8.09-8.03 (2 H, m), 7.90-7.82 (2 H, m), 7.64-7.53 (2 H, m). 13C NMR δC (75 MHz, CDCl3) 182.06, 148.44, 142.38, 137.36, 135.57, 135.41, 135.37, 134.94, 134.73, 134.61, 134.57, 133.18, 130.62, 129.26, 129.16, 128.02, 127.05. Anal. Calcd for C20H12O4S: C, 68.95; H, 3.47; Found: C, 68.32; H, 3.72.

9,10-Diaconty-1,4-dihydro-anthracene 4. The title compound was prepared following a modified literature procedure. 1H NMR δH (300 MHz, CDCl3) 7.98 (2 H, m), 7.69 (2 H, m), 6.13 (2 H, m), 3.3 (2 H, m), 3.21 (2 H, t, J = 1.3 Hz), 1.78 (2 H, m), 1.38 (2 H, m). 13C NMR δC (75 MHz, CDCl3) 198.12, 181.74, 151.07, 136.28, 134.47, 134.33, 134.24, 133.83, 133.0, 127.14, 126.59, 50.99, 36.26, 34.72, 25.44, 25.11. Anal. Calcd C, 80.65; H, 5.92; O, 13.43; Found: C, 80.12; H, 6.04.

9,10-Diacetoxy-1,2,3,4-tetrahydro-1,4-etheno-anthracene 8. The title compound was obtained according to the procedure described for 4. Yield: 90%. White powder with m.p. 232-233 °C. 1H NMR δH (300 MHz, CDCl3) 7.8 (2 H, m), 7.5 (2 H, m), 6.55 (2 H, m), 4.08 (2 H, m), 2.52 (2 H, m), 1.58 (4 H, s). 13C NMR δC (75 MHz, CDCl3) 170.01, 137.63, 135.28, 134.36, 126.61, 126.37, 121.80, 34.95, 24.94, 21.03. Anal. Calcd for C20H14O4: C, 74.52; H, 5.63; Found: C, 74.87; H, 5.85.

9,10-Diacetoxy-12-benzensulfonyl-1,2,3,4-tetrahydro-1,4-etheno-anthracene 9. The title compound was obtained according to the procedure described for 5. Yield: 65%. White powder with m.p. 213-214 °C. 1H NMR δH (300 MHz, CDCl3) 7.81 (3 H, m), 7.69 (1 H, m), 7.62 (1 H, m), 7.51 (5 H, m), 4.34 (2 H, m), 2.52 (3 H, s), 2.42 (3 H, s), 1.65 (4 H, m). 13C NMR δC (75 MHz, CDCl3) 169.80, 169.50, 147.74, 144.23, 139.86, 138.46, 138.14, 134.08, 131.21, 131.18, 129.84, 128.32, 127.23, 127.15, 126.75, 126.56, 122.06, 121.93, 36.5, 35.59, 25.60, 24.81, 21.0, 20.86. Anal. Calcd for C24H12O6S: C, 67.52; H, 4.79; Found: C, 67.89; H, 5.04.

5,10-Diacetoxy-4,11-etheno-2H-naphtho[2,3-f]isoindole-1-carboxylic acid tert-butyl ester 10. The title compound was obtained according to previously published general procedure. Yield: 78%. White powder with m.p. 186-187 °C. 1H NMR δH (300 MHz, CDCl3) 8.62 (1 H, br. s), 7.78 (2 H, m), 7.5 (2 H, m), 6.7 (1 H, d, J = 2.7 Hz), 4.93 (1 H, m), 3.89 (2 H, m), 3.73 (2 H, m), 2.66 (3 H, s).
Na NMR δ C (75 MHz, CD2Cl2) 169.93, 169.87, 161.40, 138.45, 137.96, 134.75, 134.21, 132.88, 129.02, 126.83, 126.56, 126.55, 121.86, 117.12, 114.22, 81.06, 32.54, 32.29, 28.84, 28.51, 27.20, 26.59, 21.14, 21.06. Anal. Calcd for C27H27NO4C: C, 70.27; H, 5.90; N, 3.03; Found: C, 69.89; H, 6.14; N, 4.27.

Porphyrin 12. 5,10-Diacetoxy-4,11-etheno-12H-naphtho[2,3-f]-jisoindole

Compound 10 (1 g, 2.2 mmol) was dissolved in TFA (30 mL), and the solution was stirred for 30 min under Ar at room temperature. After the addition of CH2Cl2 (50 mL), the mixture was stirred for 2 h. Resulting mixture was washed with aqueous Na2SO3, dried over Na2SO4 and concentrated in vacuum. The residue was purified by repetitive precipitation from CH2Cl2-THF delivered the title product (67 mg, 18%) as dark green powder.

Ph2TAQP-Pd was obtained in 90% yield after heating of a mixture of the free-base porphyrin, excess PdCl2(PhCN)2 (2 Eq) and Et3N (10 Eq) in benzonitrile at 160 °C for 0.5-3 h (control by UV-Vis spectroscopy), with subsequent filtration through a layer of silica (eluent CH2Cl2) and evaporation of filtrate. UV/vis (CH2Cl2) λmax (log ε): 501 (5.05), 629 (4.11), 686 (4.97). MALDI-TOF: m/z found 1439.2361, calcd. for [M+] C29H46N4O4Pd 1439.22.

Ph2TAQP-Zn was obtained in 90% yield after treatment of a free-base in THF with an excess of Zn(OAc)2·2H2O, followed by subsequent precipitation with MeOH, filtration and drying in vacuum. UV/vis (CH2Cl2) λmax (log ε): 552 (5.12), 677 (4.35), 727 (4.84). MALDI-TOF: m/z found 1397.24, calcd. for [M+] C29H44N4O4Zn 1397.24.

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