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

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Mikhail A. Filatov,*[a,b,] Ernesta Heinrich,[a] Katharina Landfester [a] and Stanislav Baluschev [a,c,d]

Fusion with 9,10-anthraquinone moiety was achieved to extend porphyrin's π-system. Bridged dihydroisoindole derivative was used to prepare corresponding *meso*-tetraphenyltetraanthraquinonoporphyrin (Ph_4TAQP) 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 tetrapyrrolic 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'-tetrasulfolenoporphyrin[13] and an excess of benzoquinone.[10]

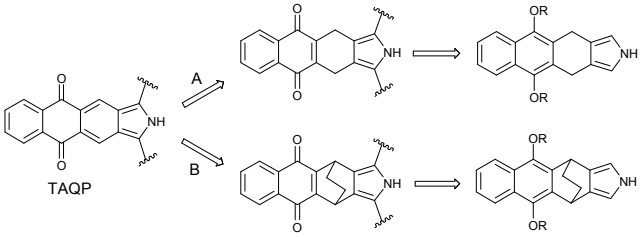
Herein we report a synthetic approach to *meso*-tetraphenyltetraanthraquinonoporphyrin (Ph_4TAQP) based on the bridged dihydroisoindole precursor. In addition we describe basic optical properties of newly synthesized Ph_4TAQP free-base and its metal complexes.

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

porphyrin architecture: oxidative aromatization[15] and thermal retro-Diels–Alder reaction.[16]

As is shown in Scheme 1, use of oxidative aromatization approach for the synthesis of tetraanthraquinonoporphyrin requires 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-annelated porphyrin which can undergo thermal extrusion of ethylene (route B).



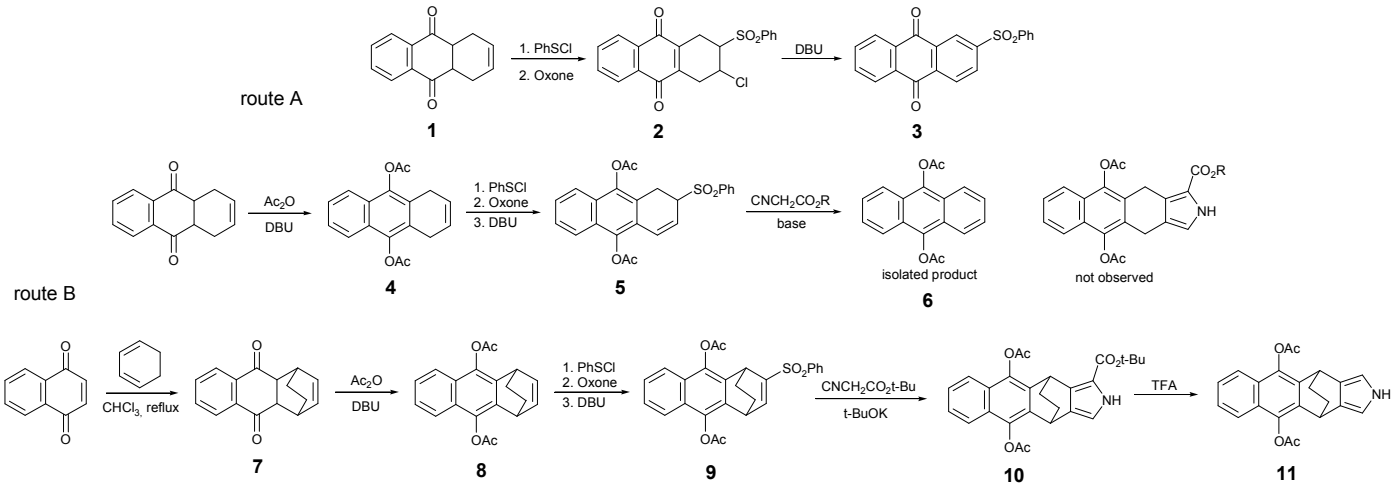
Scheme 1. Retrosynthetical analysis of TAQP system.

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.[17] Treatment of **1** with PhSCl, followed by oxidation with Oxone led to chlorosulfone derivative **2**. Further reaction with DBU yielded 2-phenylsulfonylanthraquinone **3**, rather then expected vinyl sulfone. An attempt to introduce **3** into Barton-Zard synthesis was unsuccessful and delivered a mixture of product arising from reduction of quinone moiety. Thus, a protection of the reactive quinonic moiety was necessary to avoid side reactions during the pyrrole synthesis. Convertion of the quinone into corresponding hydroquinone diacetates was preferable over reductive methylation since it requires mild conditions for further deprotection.[18]

Dione **1** is known to form deprotonated dihydronaphthoquinone irreversibly upon treatment with bases.[7] Treatment of **1** with DBU and acetic anhydride provided diacetate **4**. It should be noted that this procedure was found to give higher yields than previously reported aromatization of the dione ring by boiling with acetic anhydride and acetic acid in the presence of p-toluenesulfonic acid as a catalyst.[19]

Diacetate was then used for the preparation of allylsulfone **5**, employing previously established procedure. As expected, compound **5** was formed in good yield. However, under the conditions of Barton-Zard reaction (*t*-BuOK, THF, isocyanacetate), [20] no formation of corresponding pyrrole compound was observed. The only isolated production was found to be 9,10-diacetoxyanthracene **6**. Attemps 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. [21] However, taking into account that similar sulfone derivative containing butoxy-groups instead or acetoxy-groups was previously successfully used in the pyrrole synthesis,[7] it is interesting that sulfone **6** behaves so differently under basic conditions, when the elimination is the predominant pathway.

Thus we focused further efforts on thermal retro-Dield-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 sulfone **9**. As expected, Barton-Zard reaction with isocyanacetate synthesis delivered pyrrole **10**.



Scheme 2. Synthesis of TAQP pyrrole precursor.

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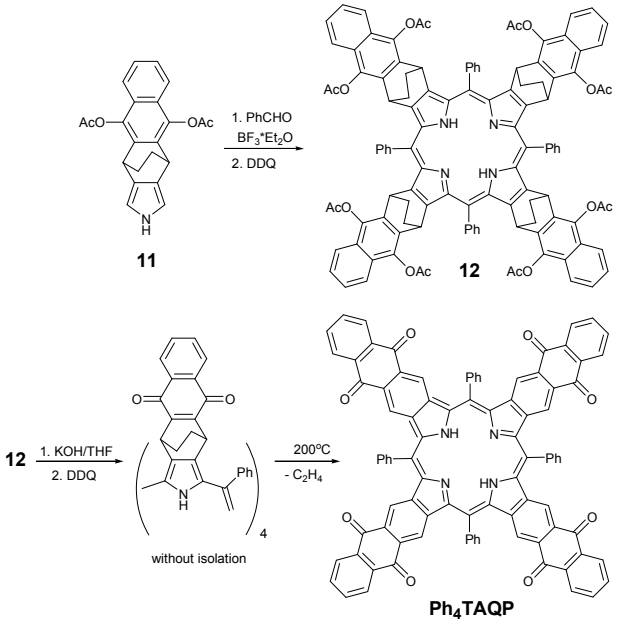
In this case *tert*-butyl isocyanoacetate[24] was used, since for pyrrole *tert*-butyl esters a decarboxylation reaction can be performed via solvolysis in neat trifluoroacetic acid. These conditions were expected to secure hydroquinone moiety from deprotection. Indeeed, treatment with TFA for 30 min delivered pyrrole **11** in good yield (68%).



Scheme 3. Synthesis of Ph_4TAQP.

With pyrrole **11** in hand, we succeeded to prepare intermediate porphyrin **12** according to the conventional Lindsey condensation.[22] As shown in Scheme 3, pyrrole **11** reacted with benzaldehyde in CH_2Cl_2 in the presence of $BF_3{\cdot}OEt_2$, 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 π-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 ^{13}C 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 Ph_4TAQP (ESI†).

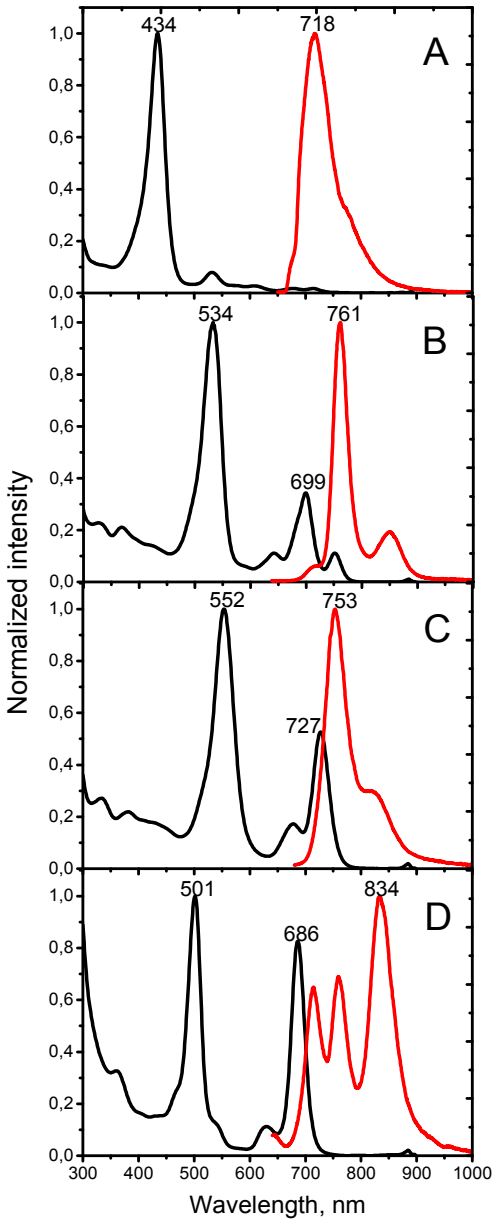


Figure 1. Absorption (black) and emission (red lines) of (A) porphyrin **12**, (B) Ph_4TAQP free base, (C) Ph_4TAQP-Zn, and (D) Ph_4TAQP-Pd. Solvent: toluene.

The absorption and emission spectra of porphyrins **12**, Ph_4TAQP and its metal complexes are compared in Fig. 1. Electronic absorption spectra of **12** are similar to other tetratetraphenyl-β-octaalkylporphyrins, such as the derivatives of octaethylporphyrin (OEP) showing Soret band at 434 nm and Q-bands at 523, 607, 675 nm in CH_2Cl_2 (for comparison, tetraphenyltetracyclohexenoporphyrin free base: Soret band 439 nm, Q-bands 537, 580, 606, 674 nm).[20] Fluorescence spectrum of **12** is also consistent with this type of porphyrin skeleton, showing maximum at 718 nm and low quantum yield of emission ($\varphi_{fl} < 0.01$ in toluene, $\lambda_{exc} = 638$ nm).

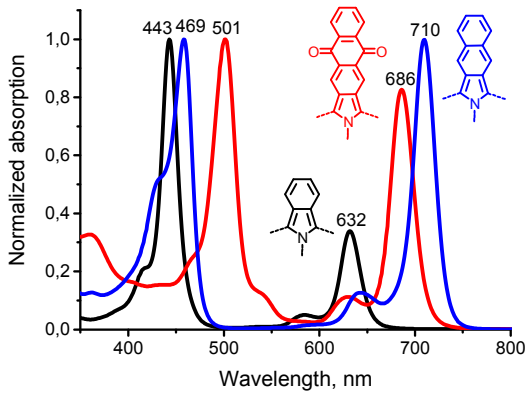


Figure 2. UV-Vis absorption spectra of Ph_4TBPPd (black), $Ph_4TAQPPd$ (red) and Ph_4TNPPd (blue).

Ph_4TAQP 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 (φ_{fl} = 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 (φ_{em} = 0.11 and 0.06 for Zn and Pd-complexes respectively). The emission of Ph_4TAQP shows multiple maxima that may be associated either with excimers formation or formation of charge-transfer excited states. Solutions of Ph_4TAQP and its metal complexes do not decompose noticeably when exposed to daylight for several hours, indication good photostability compared to other π-extended porphyrins.[23]

Comparison of absorption spectra of $Ph_4TAQPPd$ with those of palladium (II) tetraphenyltetrabenzo- and tetraphenyltetranaphthoporphyrins (Ph_4TBPPd and Ph_4TNPPd 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 S_1 and S_2 state of the molecule is manifested by the pronounced red shift of the Soret and Q-band. While in case of Ph_4TBPPd and Ph_4TNPPd the Soret band is shifted only by 20−30 nm with respect to parent tetraphenylporphyrin, fusion of anthracenes causes 100 nm red shift. Nevertheless, a "spectral window" between Soret and Q-bands allows for the application of $Ph_4TAQPPd$ 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 dihydroisoindole. 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 dihydorisoindole precursor failed to deliver target compound due to side reactions in the course of pyrrole synthesis. The optical properties of Ph_4TAQP 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[7] and tert-butyl isocyanacetate [24] 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 tetraphenylporphyrin (φ_{fl} =0.11)[25] in deoxygenated toluene.

2-Benzenesulfonyl-3-chloro-1,2,3,4-tetrahydro-anthra-quinone 2. ^{1}H NMR δ_H (300 MHz, CD_2Cl_2) 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). ^{13}C NMR δ_C (75 MHz, CD_2Cl_2) 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 $C_{20}H_{17}ClO_4S$: C, 61.77; H, 4.41; Found: C, 61.23; H, 4.65.

2-Benzenesulfonyl-anthraquinone 3. ^{1}H NMR δ_H (300 MHz, CD_2Cl_2) 8.76 (1 H, t, J = 1.2 Hz), 8.4 (2 H, t, J = 1.1 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). ^{13}C NMR δ_C (75 MHz, CD_2Cl_2) 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 $C_{20}H_{12}O_4S$: C, 68.95; H, 3.47; Found: C, 68.32; H, 3.72.

9,10-Diacetoxy-1,4-dihydro-anthracene 4. The title compound was prepared following a modified literature procedure. [26] 1,8-Diazabicycloundec-7-ene (10.5 mL, 70 mmol**)** was added to a stirred solution of 1,4,4a,9a-tetrahydroanthraquinone (6.36 g, 30 mmol) and THF (100 mL) at room temperature. The mixture was cooled with ice bath and acetic anhydride (8.5 mL, 90 mmol) was added dropwise over a period of 10 min and the resulting solution was stirred for 2 hours. Then diethyl ether (100 mL) was added to precipitate the product. The solid formed was filtered and washed with ether (50 mL) to give 8.44 g (95%) of the product as a white powder (m.p. 255-257 °C, lit. 256-258 °C). [26] ^{1}H NMR δ_H (300 MHz, CD_2Cl_2) 7.75 (2 H, m), 7.51 (2 H, m), 5.95 (2 H, m), 3.37 (4 H, br. s), 2.49 (6 H, s). ^{13}C NMR δ_C (75 MHz, CD_2Cl_2) 169.57, 142.2, 126.97, 126.52, 125.59, 123.54, 121.62, 25.0, 20.96.

9,10-Diacetoxy-2-benzenesulfonyl-1,2-dihydro-anthracene 5. The title compound was prepared following a modified literature procedure.[27] Thiophenol (2 mL, 2.2 g, 20 mmol) was added dropwise to a suspension of N-chlorosuccinimide (2.67 g, 20 mmol) in CH_2Cl_2 (20 mL) under cooling with ice bath. The mixture was stirred for 1 h at r.t. and the resulting orange solution was added dropwise to a stirred solution of 9,10-diacetoxy-1,4-dihydro-anthracene (5.92 g, 20 mmol) in CH_2Cl_2 (150 mL) at 0 °C. The mixture was stirred at room temperature for 2 h and evaporated in vacuum. The residue was dissolved in methanol (60 mL) and suspension of Oxone (12.3 g, 20 mmol) in water (30 mL) was added under vigorous stirring. The mixture was stirred at room temperature for 2 days, diluted with water (100 mL) and extracted with CH_2Cl_2. The combined organic layers were dried with Na_2SO_4 and evaporated to dryness. Resulting solid was dissolved in CH_2Cl_2 (50 mL), DBU (3 mL, 20 mmol) 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 with Na_2SO_4 and evaporated in vacuum. Solid residue was recrystallized from MeOH to give 6.1 g (70%) of the title compound as a white powder (m.p. 155-157 °C). ^{1}H NMR δ_H (300 MHz, CD_2Cl_2) 7.69 (4 H, m), 7.51 (2 H, m), 7.3 (3H, 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), 2.46 (3 H, s). ^{13}C NMR δ_C (75 MHz, CD_2Cl_2) 169.17, 136.76, 134.33, 129.88, 129.11, 128.06, 128.0, 127.54, 127.43, 127.06, 122.41, 122.09, 121.85, 121.72, 121.51, 23.1, 20.93. Anal. Calcd for $C_{24}H_{20}O_6S$: C, 66.04; H, 4.62; Found: C, 66.32; H, 4.85.

1,2,3,4,4a,9a-Hexahydro-1,4-etheno-anthraquinone 7. A mixture of 1,4-naphthoquinone (10 g, 63 mmol), 1,3-cyclohexadiene (9.5 mL, 100 mmol) and 2,6-di-tert-butylphenol (0.05 g, 0.24 mmol) was dissolved in $CHCl_3$ and refluxed for 24 h under argon. The resulting mixture was evaporated in vacuum and the residue was recrystallized from EtOH to give 12.7 g (85%) of the title compound as a white powder (m.p. 83-85 °C) .^{1}H NMR δ_H (300 MHz, CD_2Cl_2) 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). ^{13}C NMR δ_C (75 MHz, CD_2Cl_2) 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-acetoxy-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. ^{1}H NMR δ_H (300 MHz, CD_2Cl_2) 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). ^{13}C NMR δ_C (75 MHz, CD_2Cl_2) 170.01, 137.63, 135.28, 134.36, 126.61, 126.37, 121.80, 34.95, 24.94, 21.03. Anal. Calcd for $C_{20}H_{18}O_4$: C, 74.52; H, 5.63; Found: C, 74.87; H, 5.85.

9,10-Diacetoxy-12-benzenesulfonyl-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. ^{1}H NMR δ_H (300 MHz, CD_2Cl_2) 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). ^{13}C NMR δ_C (75 MHz, CD_2Cl_2) 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 $C_{26}H_{22}O_6S$: 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.[24] Yield: 78%. White powder with m.p. 186-187 °C. ^{1}H NMR δ_H (300 MHz, CD_2Cl_2) 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),

4.42 (1 H, m), 2.54 (3 H, s), 2.53 (3 H, s), 1.77 (4 H, m), 1.61 (9 H, s). ^{13}C NMR δ_C (75 MHz, CD_2Cl_2) 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 $C_{27}H_{27}NO_6$: C, 70.27; H, 5.90; N, 3.03; Found: C, 69.89; H, 6.14; N, 2.87.

5,10-Diacetoxy-4,11-etheno-2H-naphtho[2,3-f]isoindole 11. 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 CH_2Cl_2 (50 mL), the mixture was washed with water, then with 10% solution of Na_2CO_3, dried with Na_2SO_4 and evaporated in vacuum. The residue was passed through a layer of silica using CH_2Cl_2 as eluent. The solvent was evaporated to give 0.53 g (68%) of the title compound as a gray solid (m.p. 130-132 °C). ^{1}H NMR δ_H (300 MHz, CD_2Cl_2) 7.76 (2 H, m), 7.47 (2 H, m), 6.58 (2 H, d, J = 2.4 Hz), 4.41 (2 H, t, J = 1.3 Hz), 2.53 (6 H, s), 1.75 (4 H, m). ^{13}C NMR δ_C (75 MHz, CD_2Cl_2) 169.96, 137.94, 135.36, 126.91, 126.64, 126.53, 121.82, 109.94, 32.28, 31.05, 27.65, 21.07. Anal. Calcd for $C_{22}H_{19}NO_4$: C, 73.12; H, 5.30; N, 3.88; Found: C, 72.65; H, 5.14; N, 3.47.

Porphyrin 12. 5,10-Diacetoxy-4,11-etheno-2H-naphtho[2,3-f]isoindole (0.3 g, 0.83 mmol) was dissolved in CH_2Cl_2 (83 mL) freshly distilled from CaH_2, and benzaldehyde (0.088 g, 0.83 mmol) was added. The mixture was stirred under nitrogen for 10 min in the dark at room temperature. $BF_3{\cdot}Et_2O$ (10 µL, 0.083 mmol) was added in one portion, and the mixture was stirred for an additional 2 h. DDQ (0.141 g, 0.62 mmol) was added followed by additional stirring for 2 h. Resulting mixture was washed with aqueous Na_2SO_3, dried over Na_2SO_4 and concentrated in vacuum. The residue was purified on a silica gel column (eluent CH_2Cl_2, then CH_2Cl_2-HOAc, green band collected). Additional purification by recrystallization from CH_2Cl_2-Et_2O delivered the title product (67 mg, 18%) as dark-green powder. ^{1}H NMR δ_H (300 MHz, CD_2Cl_2-TFA) 8.96-6.85 (36 H, m), 4.74-4.17 (8 H, m), 3.22-2.74 (24 H, m), 2.15-1.84 (16 H, m). ^{13}C NMR δ_C (75 MHz, CD_2Cl_2-TFA) 170.26, 137.89, 135.43, 134.96, 132.05, 127.12, 126.98, 126.66, 126.27, 121.71, 120.45, 110.42, 32.59, 31.16, 27.34, 21.45. UV/vis (CH_2Cl_2) λ_{max} (log ε): 434 (5.2), 523 (4.21), 607 (3.93), 675 (3.84). MALDI-TOF: m/z found 1791.61, calcd. for [M+] $C_{116}H_{86}N_4O_{16}$ 1791.60. Anal. Calcd for $C_{92}H_{46}N_4O_8$: C, 77.75; H, 4.84, N, 3.13; Found: C, 78.58; H, 5.36; N, 3.41.

Ph_4TAQP free base. Porphyrin **12** (50 mg) was dissolved in THF (10 mL) and a solution of KOH (0.25 g) in EtOH (5 mL) was added. The mixture was stirred at room temperature for 12 h, then concentrated HCl (1 ml) was added and the solution was evaporated in vacuum. The residue was washed several time with CH_2Cl_2 to separate soluble porphyrin from inorganic solid, resulting solution was dried with Na_2SO_4 and filtered. DDQ (0.188 g, 0.83 mmol) was then added and the mixture was stirred for 6 h. Resulting mixture was washed with aqueous Na_2SO_3, dried over Na_2SO_4 and concentrated in vacuum. The residual solid was heated in vacuum oven at 200 °C for 4 h. Then it was dissolved in CH_2Cl_2 and purified on a silica gel column (eluent CH_2Cl_2, then CH_2Cl_2-THF, purple band collected). Additional purification by repetitive precipitation from CH_2Cl_2-Et_2O delivered the title product (24 mg, 65%) as purple powder. ^{1}H NMR δ_H (500 MHz, $C_2D_2Cl_4$ – TFA) 8.69 (8 H, m), 8.44 (8 H, s), 8.38 (4 H, m), 8.29-8.17 (16 H, m), 7.83 (8H, m), 4.05 (4 H, br. S). ^{13}C NMR δ_C (125 MHz, $C_2D_2Cl_4$ – TFA) 181.73, 142.53, 138.04, 135.86, 135.52, 134.56, 133.53, 133.12, 133.11, 130.39, 127.33, 124.70, 117.37. UV/vis (CH_2Cl_2) λ_{max} (log ε): 534 (5.18), 642 (4.22), 699 (4.72), 752 (4.22). MALDI-TOF: m/z found 1355.33, calcd. for [M+] $C_{92}H_{46}N_4O_8$ 1355.33. Anal. Calcd for $C_{92}H_{46}N_4O_8$: C, 82.75; H, 3.47, N, 4.20; Found: C, 83.57; H, 3.98; N, 4.74.

Ph_4TAQP-Pd was obtained in 75% yield after heating of a mixture of the free-base porphyrin, excess $PdCl_2(PhCN)_2$ (2 Eq) and Et_3N (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 CH_2Cl_2) and evaporation of filtrate. UV/vis (CH_2Cl_2) λ_{max} (log ε): 501 (5.05), 629 (4.11), 686 (4.97). MALDI-TOF: m/z found 1439.2361, calcd. for [M+] $C_{92}H_{44}N_4O_8Pd$ 1439.22.

Ph_4TAQP-Zn was obtained in 90% yield after treatment of a free-base in THF with an excess of $Zn(OAc)_2{\cdot}2H_2O$, followed by subsequent precipitation with MeOH, filtration and drying in vacuum. UV/vis (CH_2Cl_2) λ_{max} (log ε): 552 (5.12), 677 (4.35), 727 (4.84). MALDI-TOF: m/z found 1397.24, calcd. for [M+] $C_{92}H_{44}N_4O_8Zn$ 1397.24.

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Notes and references

[a] *Max Planck Institute for Polymer Research, Ackermannweg 10, D-55128 Mainz, Germany, Fax: +496131379100*
[b] *Institute of Polymers, Bulgarian Academy of Sciences, Acad. G. Bonchev Str., block 103-A, BG - 1113 Sofia, Bulgaria e-mail: filatov@polymer.bas.bg*
[c] *Optics and Spectroscopy Department, Faculty of Physics, Sofia University ''St. Kliment Ochridski'', 5 James Bourchier, 1164 Sofia, Bulgaria*
[d] *Freiburg Institute for Advanced Studies (FRIAS), Albert-Ludwigs-Universität Freiburg, Albertstraße 19, D-79104 Freiburg, Germany.*

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