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Tetraanthra[2,3-*b*,*g*,*l*,*q*]porphyrin

S. E. Aleshchenkov, A. V. Cheprakov, and Academician I. P. Beletskaya

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Porphyrins with extended π systems (containing annelated aromatic systems) are of great interest as possible photosensitizers for photodynamic therapy [1], sensors [2], working materials for optoelectronic devices, and light-harvesting complexes in the long-wavelength visible and near infrared (NIR) regions [3, 4]. Recently, we developed a general and versatile synthetic approach to functionalized tetrabenzoporphyrins (TBPs) and tetranaphthoporphyrins (TNPs) using 4,7-dihydroisoindole (**1**) or 4,9-dihydrobenzo[*f*]isoindole (**2**) and their derivatives substituted at the annelated rings (Fig. 1) as universal synthons (the dihydroisoindole method) [5, 6]. TBPs and TNPs with a different degree of substitution obtained by the dihydroisoindole method and their metal complexes show long-wavelength absorption bands in the range up to 750 nm. A number of science and technology applications require a further shift of the long-wavelength absorption bands of porphyrin chromophores to the NIR region. To solve this task, in this work, we extend the dihydroisoindole method to previously unknown tetraaryltetraanthraporphyrins (tetraanthraporphyrin is denoted for convenience as TAP).

The sole publication on the tetraanthraporphyrin system in the literature deals with the synthesis of a Zn complex of triarylTAP [7] by the high-temperature template condensation of sodium *p*-phenylphenylacetate and anthracene-2,3-dicarboximide. Severe uncontrolled reaction conditions (temperature above 350°C) of this process caused a random distribution of meso substituents, a very poor yield, and a low stability of the product.

Our approach developed for the use of the dihydroisoindole method in the synthesis of TAP requires the following benzo-annelated dihydroisoindole: previously unknown 4,11-dihydronaphtho[2,3-*f*]isoindole **3**. This compound was obtained starting from known 1,4-dihydroanthracene **4** [8], prepared from the adduct of dehydrobenzene and furan by the formation of the third ring via cycloaddition with the use of butadiene resulting in situ from sulfolene (Fig. 2).

By means of the procedure previously developed for similar 1,4-dihydronaphthalene [6], 1,4-dihydroanthracene **4** was converted through allyl sulfone **5** into the *tert*-butoxycarbonyl derivative of dihydroisoindole **6**, using the sulfonyl modification of the Barton–Zard reaction [9]. It should be noted that vinyl sulfones in the described method undergo the Barton–Zard reaction because the first stage of the reaction is a conjugated addition of the isocyanoacetate anion to the double bond of vinyl sulfone. We have shown, however, that allyl sulfones can be involved into the Barton–Zard reaction by the addition of 5% excess of potassium *tert*-butoxide to the reaction mixture because vinyl and allyl sulfones undergo interconversion in the presence of a catalytic amount of a strong base. This modification was found to be extremely convenient because, in the preparation of unsaturated sulfones via chlorosulphenylation–oxidation–elimination [10], as shown previously [6], the double bond migrates quantitatively to the conjugated position to form allyl sulfones similar to **5**.

The hydrolysis and decarboxylation of ester **6** were carried out under mild conditions by treatment with trifluoroacetic acid, and the resultant dihydronaphthoisoindole without purification was subjected to condensation with aromatic aldehyde by the standard procedure of tetraarylporphyrin synthesis.

It is interesting to note that the aromatization of porphyrinogens was not accompanied by the simultaneous aromatization of the partially hydrogenated six-membered rings of the isoindole system when the reaction mixture was treated with dichlorodicyanobenzoquinone (DDQ) to form TBP and TNP from corresponding dihydroisoindoles **1** or **2** [5, 6]. Complete aromatization in these cases should be carried out by the treatment with additional amounts of DDQ, sometimes with solvent replacement and at elevated temperature. On the contrary, it was shown in this work that the aromatization of similar intermediate porphyrin **7** proceeds so fast that the formation of target TAP **8** lasts for 30 min after the addition of the aromatization reagent (Fig. 3) and neither the intermediate porphyrin nor other incompletely aromatized compounds are detected

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Chemistry Department, Moscow State University, Moscow, 119899 Russia

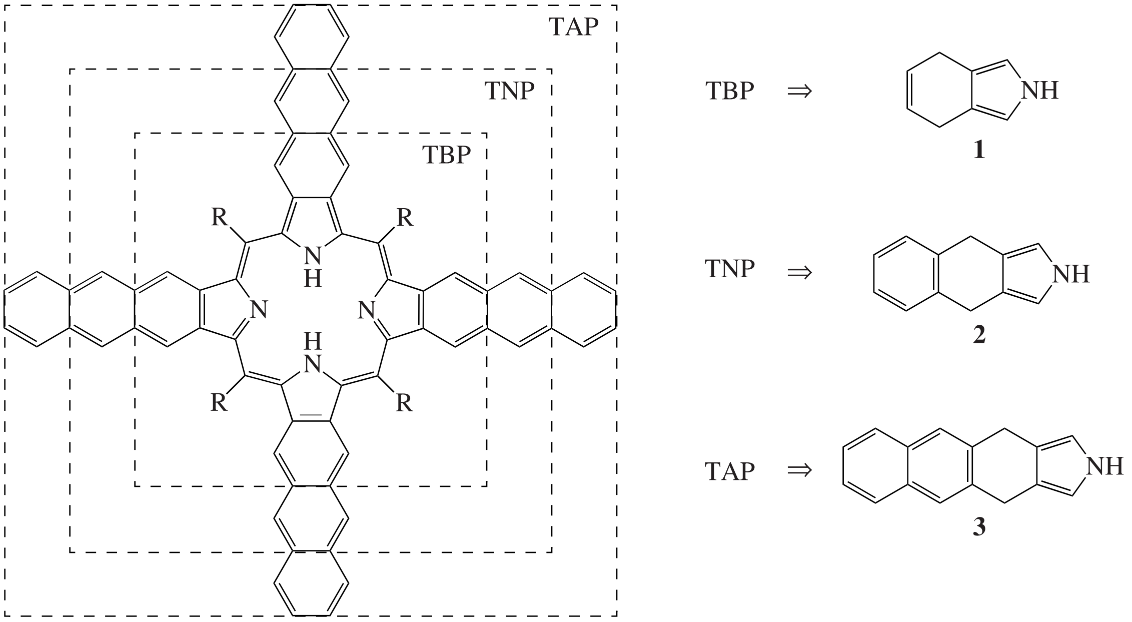


Fig. 1. Porphyrins with extended π systems and their synthetic precursors.

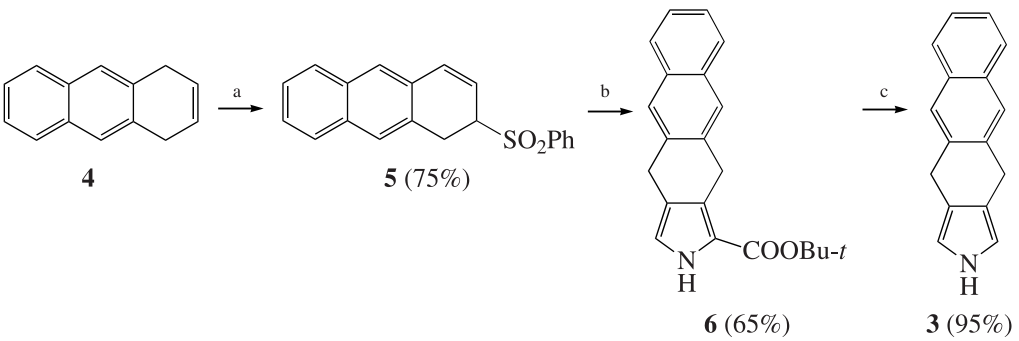


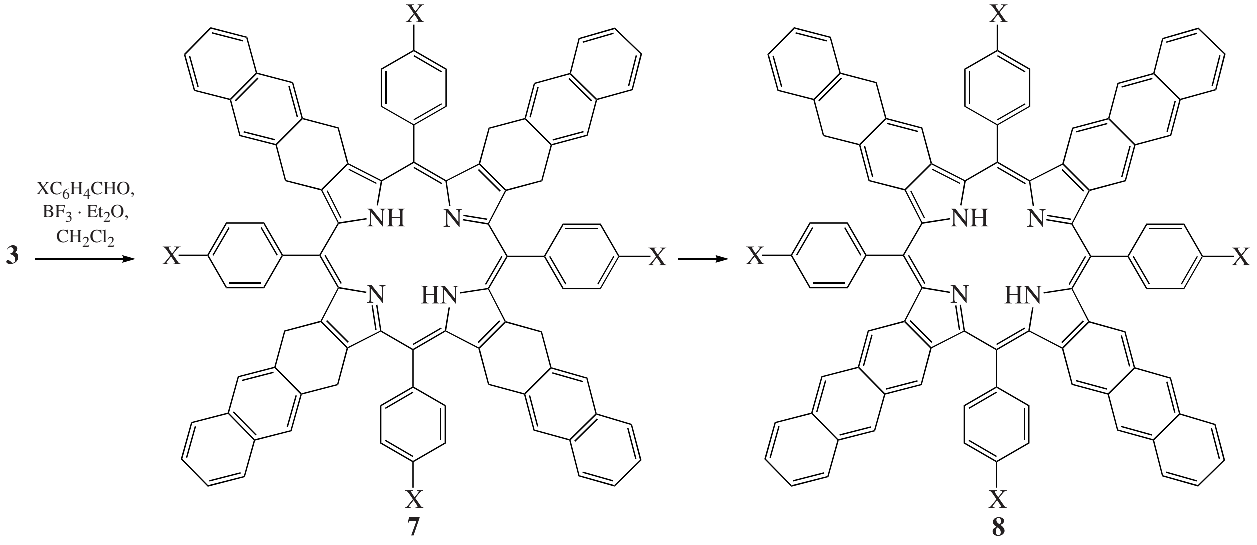
Fig. 2. Synthesis of 4,11-dihydronaphtho[2,3-*f*]isoindole at ambient temperature: (a) (1) PhSCl, CH_2Cl_2, 30 min; (2) Oxone, MeOH–H_2O, 5 h; (3) DBU, CH_2Cl_2, 30 min; (b) $CNCH_2CO_2Bu$-*t*, *t*-BuOK, THF, 12 h; (c) CF_3COOH, 30 min.

when the reaction mixtures are analyzed by MALDI–TOF mass spectroscopy.

The target tetraanthraporphyrin was isolated from the reaction mixture by flash chromatography and crystallization in 32% yield. Similarly to tetraarylTNP, TAP **8** strongly tends to form aggregates in solutions, which leads to broadening of absorption bands, its solubility in common organic solvents being substantially higher than that of similar TNP [6]. The ^1H NMR spectrum of the obtained porphyrin is very similar to the spectrum of the corresponding TNP: the close values of chemical shifts for the analogous groups of protons obviously result from the similar distribution of magnetic anisotropy cones of the aromatic ring system, which, in turn, indicates the resemblance of the structures of these two series.

Figure 4 shows electronic absorption spectra. As compared with similar TNP, the effect of the additional ring appears as a strong shift of the long-wavelength absorption bands; the most intense Q band is shifted by 100 nm (832 nm for TAP and 732 nm for TNP). The short-wavelength B bands are very close (508 nm for TAP and 500 nm for TNP); therefore, the distance between the Q and B bands in TAP is considerably larger. The presence of a wide free range between the long-wavelength and short-wavelength bands (transparency window) is very important for up-conversion systems [3] because it allows one to allocate absorption bands of emitting molecules within this region.

Another important characteristic of porphyrin chromophores with an extended π system is the relative intensity of Q and B bands in the spectrum: the data obtained indicate that the relative intensity of the long-



X = COOMe

Fig. 3. Synthesis of tetrakis(*p*-methoxycarbonylphenyl)tetraanthra[2,3-*b*,*g*,*l*,*q*]porphyrin.

wavelength B band builds up when passing from TBP to TNP and further to TAP, i.e., on extending the conjugated system. This effect is even more pronounced for metal complexes. The metalation of TAP increases the intensity and decreases the width of the bands, the spectrum of the Zn complex shows a slight hypsochromic shift of the Q bands and no marked effect on the position of the B band, whereas all bands for the Pd complex are shifted to the short-wavelength region by 20–30 nm. These trends are quite similar to those observed for TNP. An interesting property of TAP is the extremely high sensitivity to photooxidation: TAP completely decomposes in a dilute solution within 20 min even under a scattered artificial lighting (according to electronic absorption spectra). Let us note for comparison that similar solutions of TBP and TNP are stable under these conditions and display porphyrin decomposition only when exposed to direct sunlight for a long time. Therefore, all manipulations with TAP solutions should be carried out in the dark and under an inert gas atmosphere. TAP crystals are quite stable.

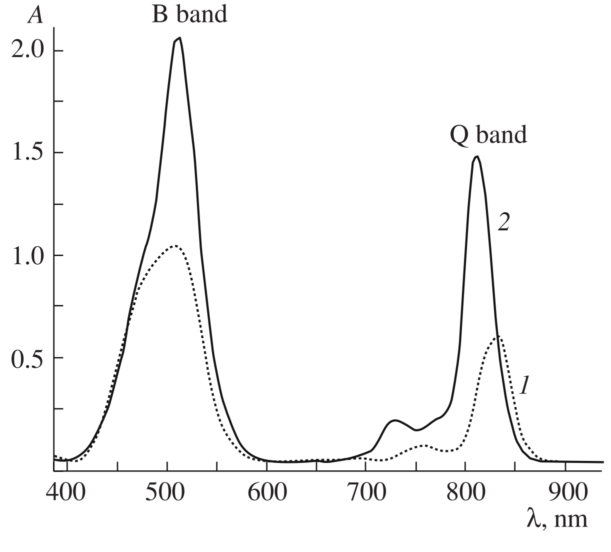


Fig. 4. Electronic absorption spectra of tetranaphthoporphyrin **8** (*1*) and its zinc complex (*2*) in toluene.

Thus, we developed for the first time a convenient synthetic approach to previously unknown tetraaryltetraanthra[2,3-*b*,*g*,*l*,*q*]porphyrins. TAP shows intense narrow absorption bands in the long-wavelength spectral region, the shift of the Q bands being maximal among all known porphyrins with an extended π system. This affords a maximal transparency window between the absorption bands. The unique photophysical properties of this system provide the possibility to use it in up-conversion systems and other optical applications in the near infrared region.

EXPERIMENTAL

Chemicals and solvents were purified by standard procedures. Electronic absorption spectra were recorded on a PerkinElmer Lambda 40 spectrophotometer; LDI–TOF mass spectra were obtained on a Bruker Daltonics Alphaflex II mass spectrometer without use of template. NMR spectra were recorded on a Bruker Avance 400 spectrometer.

Synthesis of tetrakis(*p*-methoxycarbonylphenyl)tetraanthra[2,3-*b*,*g*,*l*,*q*]porphyrin 8. Dihydroisoindole **3** (0.24 g, 1.1 mmol) dissolved in freshly distilled CH$_2$Cl$_2$ (150 mL) was placed into a flask protected from light and equipped with an inert gas inlet and magnetic stirrer, *p*-methoxycarbonylbenzaldehyde

(0.2 g, 1.2 mmol) was added. Then, $BF_3 \cdot Et_2O$ (0.03 mL) was added, the mixture was stirred at ambient temperature for 1 h, a solution of dichlorodicyanobenzoquinone (0.38 g) in 1 mL of toluene was added, and the mixture was stirred for 12 h at ambient temperature. The resultant dark solution was washed with a 10% aqueous solution of Na_2SO_3 (2×100 mL), a 10% aqueous solution of Na_2CO_3 (50 mL), and a saturated solution of NaCl, and dried with Na_2SO_4. The solvent was removed in a vacuum, the residue was purified by recrystallization from a CH_2Cl_2–Et_2O mixture, and the crystals were washed with ether until complete discoloration of the washing liquid. All manipulations were performed in vessels protected with foil in a darkened room.

Small dark brown crystals (a solvate with Et_2O) with a yield of 0.13 g (32%). ^{1}H NMR (400 MHz, $CDCl_3$, TMS δ, ppm): 8.62–8.71 (m, AA'XX', 16H), 8.42 (br s, 8H), 8.02 (m, 8H), 7.94 (br s, 8H), 7.45 (m, 8H), 4.27 (s, 12H), 2.24 (br s, 2H). LDI–TOF MS (*m*/*z*): free base, calculated for ($C_{100}H_{62}N_4O_8$) 1447.46, found: 1447.39; Zn complex, calculated for ($C_{100}H_{60}N_4O_8Zn$) 1509.37, found: 1510.15; Pd complex, calculated for ($C_{100}H_{60}N_4O_8Pd$) 1551.35, found: 1550.27.

For $C_{100}H_{62}N_4O_8 \cdot Et_2O$. Et_2O anal. calcd. (%): C, 82.09; H, 4.77; N, 3.68.

Found (%): C, 81.90; H, 5.09; N, 3.42.

Absorption spectrum, λ_{max}, nm (logε): free base (toluene): 508 (4.65), 758 (3.5), 832 (4.40); dication salts (toluene, CF_3COOH): 544, 800, 914; Zn complex (toluene–pyridine): 510 (4.68), 732 (3.66), 810 (4.54); Pd complex (toluene): 470, 704, 790.

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