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The synthesis of new tetrabenzo- and tetranaphthoporphyrins via the addition reactions of 4,7-dihydroisoindole

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ABSTRACT

The double bond in 4,7-dihydroisoindole derivatives was shown to be a useful reaction site to afford new porphyrinogenic pyrrolic precursors bearing substituted annelated rings via various addition reactions. These precursors are further used to afford new extended porphyrins substituted in the annelated rings. The Sharpless osmium-catalyzed dihydroxylation of dihydroisoindole system was shown to be useful in the synthesis of non-ionogenic water-soluble porphyrin, as well as tetrabenzoporphyrin bearing acetoxy-substituents in benzo-rings. The reverse electron-demand Diels–Alder reaction with tetrachlorothiophene-1,1-dioxide afforded new polychlorosubstituted tetranaphthoporphyrin.

1. Introduction

π-Extended porphyrins form a class of porphyrinoids in which pyrrole rings are fused with external aromatic fragments via the β-carbon atoms. The best known and most useful representatives of this class are linearly annelated π-extended porphyrins (LAEP), i.e., tetrabenzoporphyrins (TBP) and tetranaphtho[2,3]porphyrins (TNP) whose optical and other properties attract much interest in materials research,[1] modification of electrodes,[2] organic thin film transistors (OTFT),[3] photovoltaic devices,[4] biomedical imaging and sensing,[5] photodynamic, and boron neutron-capture therapy.[6] A platinum complex of tetraphenyltetranaphthoporhyrin was recently shown to exhibit record efficiency in near-infrared OLED devices.[7] A new interest to LAEP was recently attracted by the discovery that their Pd and Pt complexes are unique light harvesting materials for two-photon up-conversion based on triplet–triplet annihilation, allowing the transformation of low-intensity non-coherent red and near-infrared light into shorter wavelength visible light,[8] spawning applications for all-organic flexible displays,[9] and solar cell efficiency enhancement.[10]

While the problem of synthesis of basic types of LAEP has been adequately resolved, various applications require fine-tuning of photophysical characteristics and other relevant properties, as well as the ability to attach substituents or functional units. Current synthetic approaches however give access generally only to a few of general structures with functionality being limited practically to *meso*-aryl rings, the effect of which on the electronic structure of extended porphyrin systems is negligible, and thus the modification of *meso*-aryls is used mainly to control solubility in different media. Obviously, in order to more profoundly change the properties of extended porphyrin system, substituents should be attached to the annelated rings. To date, there are no good methods of synthesis of such molecules, therefore known extended porphyrins with extra substituents in annelated rings are very scarce.

In the last years we have been developing a general synthetic approach to linearly annelated π-extended porphyrins based on common intermediates of dihydroisoindole type (*the dihydroisoindole approach*[11]), which allowed us to establish effective synthetic protocols to afford fully or partially *meso*-substituted tetrabenzo-, tetranaphtho-, and tetranthraporphyrins.[12] Pivotal for this approach is the chemistry of 4,7-dihydroisoindole **1**. We have described the first synthesis of 4,7-dihydroisoindole using commercially available tosylacetylene as a starting material,[12b] and have shown that in spite of apparent fears that the double bond in this compound is highly reactive, many reactions including those involving strong acids and bases can be used on such compounds to leave the double bond intact. In this way, a good number of compounds containing the 4,7-dihydroisoindole motif bearing a non-conjugated cyclohexene-like double bond including 2-substituted derivatives, dipyrromethanes and porphyrins can be obtained.[12b,c]

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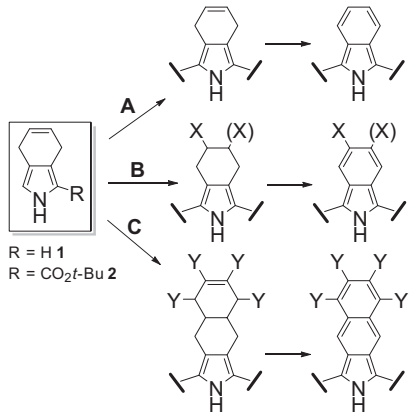
These compounds can be directly used to access tetrabenzoporphyrins unsubstituted in benzo-rings[12b,c] through oxidative aromatization (Scheme 1, path A). The potential of 4,7-dihydroisoindole as a synthon of extended porphyrins is obviously broader, as the isolated double bond in the annelated cyclohexene ring can allow for further modification by addition or cycloaddition reactions. Thus, addition reactions can furnish new intermediates for benzo-substituted tetrabenzoporphyrins (Scheme 1, path B), while the use of cycloaddition reactions can lead to new tetranaphthoporphyrins (Scheme 1, path C).



Scheme 1. 4,7-Dihydroisoindole as a synthon for porphyrin synthesis.

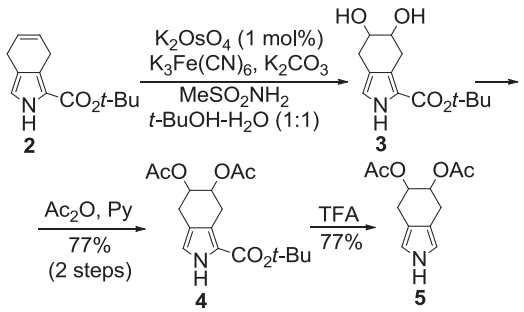
Herein we show that 4,7-dihydroisoindole can be employed as a universal synthon for the synthesis of new interesting porphyrins, both extended and regular, which can not be reasonably accessed by other methods. As examples we have chosen the synthesis of non-ionic water-soluble porphyrin, the first tetrabenzoporphyrin with π-donor substituents in the annelated rings, and a polychlorinated tetranaphthoporphyrin.

2. Results and discussion

2.1. Dihydroxylation reaction

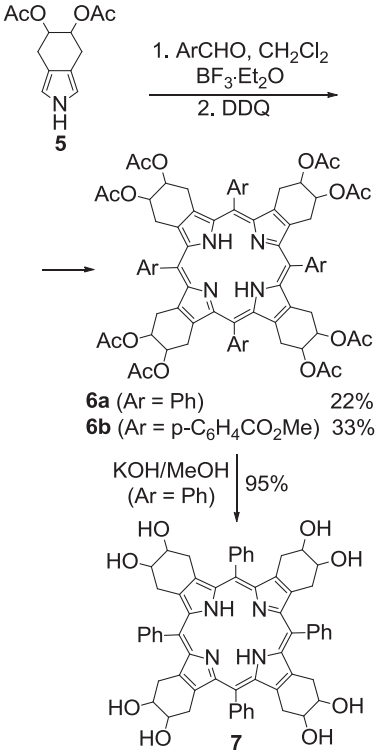
The dihydroxylation reaction was chosen as a typical double bond addition reaction. This reaction is well known to be smooth and tolerant of sensitive functionality. Hydroxylic groups are very valuable substituents for porphyrins, as they deliver multiple functions by providing convenient anchor points for further modification, enhancing the hydrophilicity, and modulating spectral parameters.

Indeed, dihydroisoindole-2-carboxylate **2** was smoothly dihydroxylated using the Sharpless dihydroxylation method (Scheme 2) with a catalytic amount of potassium osmate(VI)[13] to give the respective diol **3**, which was transformed into diacetate **4** prior to



Scheme 2. Dihydroxylation of 4,7-dihydroisoindole.

entering the porphyrin synthesis, because the *vic*-diol moiety was expected to interfere with the aldehyde condensation. As enantioselectivity in this case is irrelevant, we have excluded the chiral ligands normally used in the Sharpless dihydroxylation, while keeping all components of the standard Sharpless system. Further, the removal of the *tert*-butoxycarbonyl group was performed by the regular TFA solvolysis method without any complications, and the resulting tetrahydroisoindole diacetate **5** was used in Lindsey's porphyrin synthesis (Scheme 3).

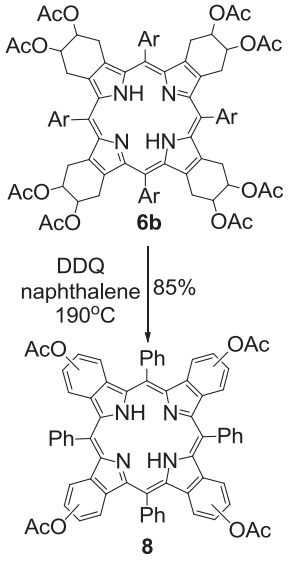


Scheme 3. Synthesis of octahydroxyporphyrin.

The resulting octaacetoxysubstituted porphyrins **6a**,**b** were formed in good yields without the loss of acetate groups. As the dihydroxylation is a *syn*-addition reaction and starting pyrrole **5** is a *cis*-isomer, porphyrins **6** are formed as random diastereomeric mixtures, which is evident from NMR spectra of these porphyrins showing the inequivalence of several groups of protons attributable to cyclohexano-rings, and similar inequivalence of carbon resonances. Tetraphenylporphyrin **6a** was hydrolyzed to obtain octahydroxyporphyrin **7**. Due to the high hydrophilicity of this porphyrin the work-up after neutralization was performed by extraction with butanol, as common solvents ($CHCl_3$, CH_2Cl_2, ether, etc.) failed to extract it from the aqueous phase. Porphyrin **7** was isolated after evaporation of solvent as a green microcrystalline material.

In addition we have attempted the aromatization of octaacetoxyporphyrin **6b**. This porphyrin belongs not to the dihydroisoindolic series of porphyrins, which are very easily aromatized,[11] but to the tetrahydroisoindolic series,[23] the aromatization of which is less facile, having been shown to require metalation prior to the treatment by DDQ. In this case the task is complicated by the presence of hydroxy or acyloxy-groups in the ring to be aromatized, which are prone to be eliminated during the aromatization. Indeed, the aromatization of a zinc complex of porphyrin **6b**, using the method described previously,[23] resulted in random loss of AcO-groups leading to inseparable mixtures of partially acetoxylated tetrabenzoporphyrins. It was evident that all eight substituents could not be retained in any case, but we

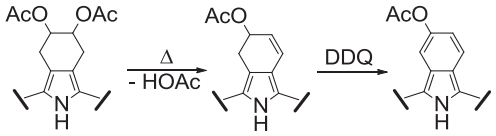
succeeded to find conditions under which one acetoxy-group is eliminated selectively from each ring. This was accomplished using a new procedure recently developed by us for aromatization of annelated rings in tetracyclohexenoporphyrins[12c] by heating porphyrin free base with DDQ in naphthalene melt. This procedure afforded tetraacetoxytetrabenzoporphyrin **8** as the major product (Scheme 4), which was confirmed by registering MALDI mass-spectrum of crude reaction mixture showing the only intense cluster of ions with mass distribution conforming to the molecular ion of porphyrin **8**.



Scheme 4. Aromatization of octaacetoxyporphyrin.

Porphyrin **8** has been isolated, and indeed showed to be tetrabenzoporphyrin with one AcO group per benzo ring attached to 2 (3)-positions, as is evident from ^{1}H NMR spectrum showing the signals of benzo-rings with ABX type of splitting.

An interesting question why the reaction at high temperature in the naphthalene melt (190 °C) is more selective than the aromatization by DDQ at lower temperatures in conventional solvents? In our opinion, this can be tentatively rationalized by a pathway involving thermal elimination of the first acetoxy-group followed by facile dehydrogenation of unsaturated ring (Scheme 5).

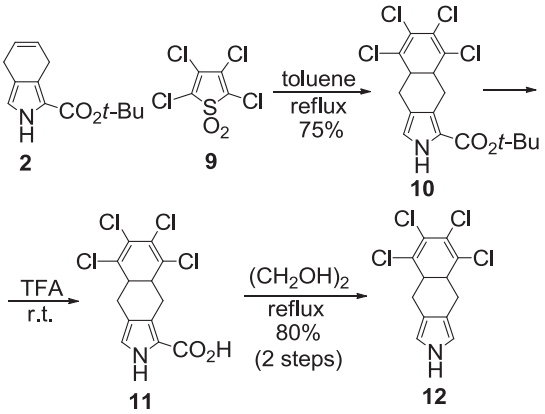


Scheme 5. A probable pathway of the aromatization.

2.2. Inverse electron-demand Diels–Alder reaction

As the double bond in 4,7-dihydroisoindole and its derivatives is dialkylsubstituted, it can be used in the inverse electron-demand Diels–Alder reactions[14] using electron-deficient dienes. The choice of the electron-deficient diene was 2,3,4,5-tetrachlorothiophene-1,1-dioxide **9** known to effect cycloadditions followed by loss of SO_2 with non-activated isolated double bonds under mild conditions.[15] We have obtained this diene in high yield by oxidation of tetrachlorothiophene according to the published method,[16] but using an in situ prepared solution of CF_3CO_3H in $CHCl_3$ in place of the dangerous 100% peroxoacid used in the original reference.

The reaction with dihydroisoindole-1-carboxylate **2** gave the expected product, *tert*-butyl 5,6,7,8-tetrachloro-4,4a,8a,9-tetrahydro-2*H*-benzo[*f*]isoindole-1-carboxylate **10**, formed via extrusion of SO_2 from initially formed adduct, in high yield. *tert*-Butyl ester **10** in neat trifluoroacetic acid failed to give the respective 2,5-unsubstituted pyrrole, but underwent the solvolysis giving the acid **11**, practically insoluble in this media, which prevented further decarboxylation. The decarboxylation should be performed separately by heating the crude acid **11** in refluxing ethylene glycol (Scheme 6). Thus, the desired pyrrole **12** was obtained in good overall yield (58%) and high purity confirmed by ^{1}H and ^{13}C NMR spectra. It should be noted that ^{1}H and ^{13}C NMR spectra of pyrrole **12** show unusually large downfield shifts of bridgehead protons and carbons and the diene residue carbons, which is very well seen in comparison with the similar parent molecule **10**.

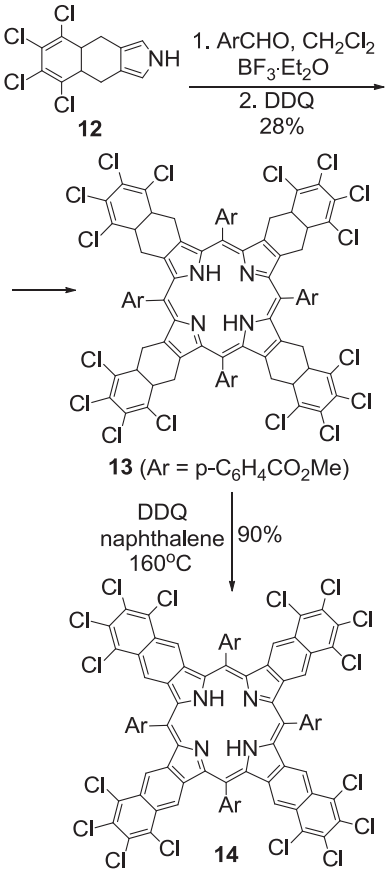


Scheme 6. Cycloaddition to 4,7-dihydroisoindole.

The condensation of pyrrole **12** with *p*-methoxycarbonylbenzaldehyde under the standard Lindsey's conditions gave the expected porphyrin **13** (Scheme 7). Quite unusually, in this case the aromatization of intermediate porphyrinogen was very slow to take 12 h for completion (as monitored by absorption spectroscopy), while normally this process is almost instantaneous. The reason why this porphyrinogen is so inert in the reaction with DDQ is not clear, as the influence of remote tetrachlorodiene residues on the dehydrogenation of *meso*-methylene bridges is unlikely to be significant. After stirring overnight with DDQ the formation of porphyrin **13** was complete, but no traces of further aromatization of annelated rings could be revealed, even the terminal rings bearing chlorine atoms remained in the diene form, which was unambiguously established by NMR spectra. The aromatization of annelated rings in porphyrin **13** took place only under forced conditions using DDQ treatment in naphthalene melt. In this case the respective tetranaphthoporphyrin (5,10,15,20-*tetrakis*(*p*-methoxycarbonylphenyl)hexadecachloro-tetranaphthoporphyrin **14**) was formed in high yield (90%) and high purity, achieved after a single recrystallization.

2.3. Properties

2.3.1. Octahydroxyporphyrin. Hydrophilic (water-soluble and water-dispersible) porphyrins draw a lot of interest and research efforts due to their wide applicability in biomedical and other areas.[17] Hydrophilicity is usually imparted to porphyrins by attaching ionic (cationic ammonium or anionic sulfonate, carboxylate etc.) groups, which, besides clear advantages, bring in clear drawbacks—dependence on pH and ionic strength, strong interaction with biomolecules, etc. On the other hand, non-ionogenic



Scheme 7. Synthesis of tetranaphthoporphyrin **14**.

hydrophilic porphyrins are much rarer. Such porphyrins can be formed by attaching long polyethyleneglycol tails to carboxylic or hydroxylic groups on *meso*-aryls.[18] Hydrophilization can also be achieved through growing dendrimeric shells over porphyrin cores,[19] additionally modified by PEG layer.[5k] Such heavy protection layers are essential for specific applications, but in many cases smaller molecules are required. Therefore a small hydrophilic porphyrin seems a useful addition to the arsenal of these important pigments. The simplest and smallest hydrophilizing group is the hydroxyl, but the influence of this group is strongly dependent on where it is attached. Introducing a number of hydroxy groups is known to render hydrophilicity to porphyrins, chlorines,[20] and even phthalocyanines,[21] in the majority of the known cases hydroxy groups are attached to *meso*-aryls or similar relatively remote pendants, where their influence is subdued, and not a true water-solubility but rather a limited hydrophilicity allowing for the use of aqueous organic solvents, is achieved.

Porphyrin **7** has an unusual solubility profile, being insoluble or sparingly soluble in common 'good' solvents for regular porphyrins, such as aromatic hydrocarbons or chlorohydrocarbons, but is well soluble in 'bad' (for regular porphyrins) solvents (e.g., ethers or lower alcohols). It is well soluble in water; aqueous solutions can be easily obtained not only by dilution of solutions in MeOH or DMF by water, but directly—upon the addition of water to solid material a deeply green colored solution being obtained immediately on gentle stirring. Such behavior is indicative of true solubility, and not just the formation of a dispersion.

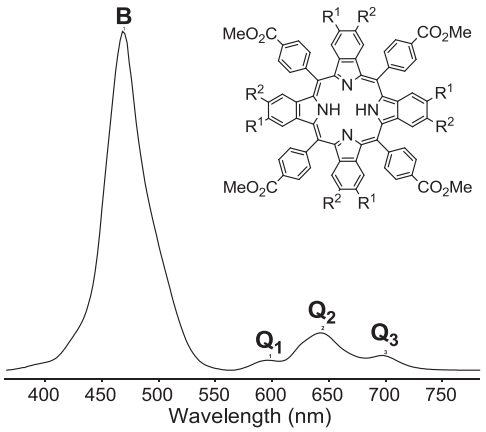
Electronic absorption spectra of porphyrin **7** are similar to other tetratetraphenyl-β-octaalkylporphyrins, such as the derivatives of classical octaethylporphyrin (OEP) system showing Soret band at 438 nm and Q-bands at 536, 628, 690 nm in polar organic solvent (DMF) (for comparison, tetraphenylOEP (OETPP) free base **15**: Soret band 446 nm, Q-bands 548, 588, 634, 686 nm;[22] tetraphenyltetracyclohexenoporphyrin free base **16**: Soret band 439 nm, Q-bands 537, 580, 606, 674 nm[23]). Thus porphyrin **7** can be regarded as a water-soluble analogue of the classical and thoroughly studied OEP and OETPP systems. It should be noted that the spectra taken in aqueous solutions (cf. Supplementary data) feature sharp and well-resolved absorption bands obeying the Bouguer–Lambert–Beer law with spectral parameters (*fwhh*, asymmetry) close or better than those for the spectra of the same porphyrin in polar organic solvents, or parent (like **16**), which shows that true solutions without appreciable aggregation are formed.

High hydrophilicity of porphyrin **7** is delivered by eight vicinal hydroxy groups attached to the annelated cyclohexane rings. The strong influence of vicinal diol residues on water-solubility is not surprising, as a high hydrophilicity of this motif is well known to account, for e.g., the anti-freezing effect of lower polyols, and high water-solubility of sugars. Recent theoretical studies have revealed that *vic*-diols in aqueous environments are incapable of intramolecular hydrogen bonding, instead being involved in the hydrogen-bonded network of water molecules, as the geometry of *vic*-diol fragment fits in the system of intermolecular hydrogen bonds formed in bulk water. Thus, *vic*-diol fragments do not disrupt the structure of liquid water, but function as water structuring centers.[24] Therefore, it is not surprising that *vic*-diol motif is probably the most effective non-ionic hydrophilizing element, making porphyrin **7** one of the most compact water-soluble porphyrins known. Moreover, such tight hydration shell is likely to suppress aggregation through intermolecular interaction of porphyrin molecules more effectively than other types of hydrophilizing modifiers.

2.3.2. Tetraacetoxytetrabenzoporphyrin. Porphyrin **8** is the first example of TBP bearing mesomeric donor substituents in benzo-rings. So far, benzo-substituted TBP have been altogether quite rare. Practically all tetrabenzoporphyrins known belong to *meso*-unsubstituted class and were obtained as metal complexes by unreliable high temperature template condensation methods or similar approaches, which rarely afford pure materials with unambiguously proven structures.[25] Thus, a series of 1,3-dimethylisoindoles bearing alkyl or phenyl substituents in benzo-rings were shown by Bender et al. and later Ichimura et al. to afford benzo-substituted tetrabenzoporphyrins in reasonable yields upon heating at 220 °C with metal carboxylates (metals Zn, Ni, Mg, Cu etc.) via multistep transformations of uncertain stoichiometry and unknown mechanism.[26] *tert*-Butyl substituted TBP was obtained by Luk'yanetz et al. from *tert*-butylphthalimide.[27] This method has been further used for obtaining TBP bearing other substituents, such as Ph, Br or OMe, though the yields were low and the target products were obtained as mixtures of porphyrins with varied number of substituents.[28]

The absorption spectrum of the obtained porphyrin **8** is compared with absorption spectra of known tetrabenzoporphyrins with the same *meso*-substituents in Fig. 1—benzo-unsubstituted tetrabenzoporphyrin **17** and tetrabenzoporphyrin bearing eight methoxycarbonyl substituents **18**.[23] All three spectra are similar featuring the same pattern of intense Soret (B) band and three Q-bands. Interestingly, the spectra of benzo-unsubstituted TBP **17** and tetraacetoxyTBP **8** are almost identical, with all maxima coinciding within 1–2 nm. On the other hand, the π-acceptor substituents (COOMe) cause a substantial red shift of all maxima by ca. 12 nm, likely to be associated with the stabilization of LUMO. Acetoxy-groups can be readily saponified, and the resulting tetrahydroxyTBP used for further derivatization which will be disclosed elsewhere.

2.3.3. Octadechloronaphthoporphyrinc. Porphyrin **14** is, as far as we know, the first example of a polychlorinated π-extended porphyrin.

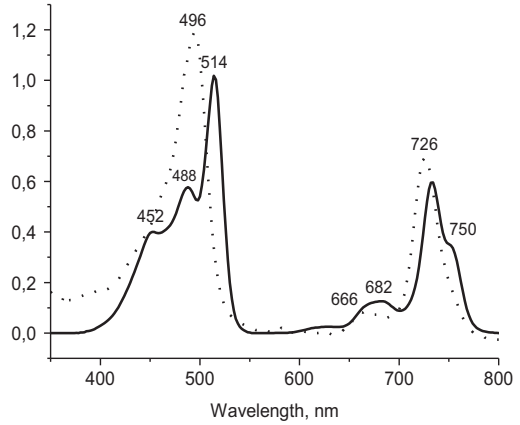


	7	17	18
Band	R^1 = OAc, R^2 = H	R^1 = R^2 = H	R^1 = R^2 = COOMe
B	468 (5.30)	467 (5.48)	480 (5.54)
Q_1	596 (3.68)	595 (4.32)	598 (4.39)
Q_2	642 (4.28)	644 (4.65)	647 (4.66)
Q_3	698 (3.86)	701 (4.26)	708 (4.24)

Fig. 1. Absorption spectra of benzo-substituted and benzo-unsubstituted tetrabenzoporphyrins.

The addition of multiple chlorine atoms to regular porphyrinic or phthalocyaninic pigments is a well known approach widely used to render higher stability toward photo- or chemical oxidation.[29] Recently, the polychlorination of highly conjugated systems including acenes and phthalocyanines was shown to serve as effective tool for the design of air-stable organic semiconductors because chlorine substituents favorably modulate HOMO–LUMO gaps and other relevant electronic parameters of such systems.[30]

The absorption spectrum of hexadecachlorotetranaphthoporphyrin **14** in general conforms to that of the parent non-chlorinated tetranaphthoporphyrin **19** obtained earlier (Fig. 2),[12a]—but with an essential difference. Superposition of two spectra reveals that chlorinated TNP exhibits better resolved bands both in B- and Q-parts of spectra, while parent porphyrin **19** displays



	14	19	20
Band	X = Y = Cl	X = Y = H	X = OMe, Y = H
B	514 (5.32)	496 (5.32)	508 (5.34)
Q_1	682 (4.40)	666 (4.42)	685 (4.42)
Q_2	732 (5.07)	726 (5.04)	754 (5.13)

Fig. 2. The comparison of absorption spectra of differently substituted tetranaphthoporphyrins (in the graph: porphyrin **25** (solid line)), porphyrin **26** (dotted line).

a spectrum looking like a roughly smoothened version of the former spectrum, in which all of the resolved evident in the spectrum of chlorinated porphyrin are seen as weak shoulders on main bands. Though we relay a detailed discussion of the photophysical properties of variously substituted tetranaphthoporphyrins to a separate study, we suppose that the most probable source of better resolution in electronic absorption spectra is the suppression of aggregation in solution. The same factor probably accounts for better solubility of chlorinated TNP **14** in common organic solvents as compared to parent porphyrin **19**. In what concerns the positions of the absorption bands, chlorination results in red shifts of all bands, with the effect being more pronounced on Soret band, which appears at 514 nm—the farthest red shift so far noted in tetranaphthoporphyrin family. The effect on Q-bands is much smaller. The comparison with tetranaphthoporphyrin **20** bearing methoxy substituents in the terminal rings of naphtho-system, obtained by us earlier[12a] shows an opposite trend, as the Soret band in less strongly red-shifted relative to unsubstituted porphyrin, while Q-bands experience a strong shift by 28 nm.

The other notable feature of chlorinated porphyrin **14** is a markedly enhanced stability. One of the major drawbacks of tetranaphthoporphyrins known so far is a fast bleaching if exposed in solutions to sunlight in the presence of air; usually the characteristic color of such solutions disappears within 1–2 h, with total disappearance of absorption bands in spectra. On the other hand, the solutions of porphyrin **14** turned out to be markedly more stable, and retained at least half of the initial concentration after 8 h exposure to the sunlight in aerated solutions with full retention of band shape (cf. Supplementary data). In view of projected applications of such porphyrins as optical materials outlined in the introduction, both suppress aggregation, better solubility, and increased photostability are welcome features.

3. Conclusions

Thus, 4,7-dihydroisoindole derivatives, readily available by a reliable short synthesis from commercial precursors, and earlier demonstrated to serve as convenient precursors for benzo-unsubstituted benzoporphyrins, were shown to afford an efficient approach to benzo- and naphthoporphyrins bearing substituents in the annelated aromatic rings. The isolated olefinic double bond in dihydroisoindole derivatives is stable toward undesirable shifts under the reaction conditions used in porphyrin synthesis. Thus, the isolated double bond in 4,7-dihydroisoindole derivatives can be used in various addition reactions to provide an easy access to new pyrrolic compounds useful for the synthesis of new benzo- and naphthoporhyrins. The Sharpless osmium-catalyzed dihydroxylation of dihydroisoindole-1-carboxylate gives dihydroxytetrahydroisoindole derivative, which was used for the synthesis of new porphyrins bearing hydroxyl- and acetoxy-groups in annelated cyclohexano or benzo-rings. The porphyrin bearing *vic*-diol motif was found to be water-soluble, thus being one of the most compact hydrophilic porphyrins known solubilized via non-ionogenic groups. On the other hand, the double bond of dihydroisoindole was used in reverse electron-demand Diels–Alder reaction, which gave access to tetranaphthoporphyrin with perchlorinated outer rings. Polychlorination of tetranaphthoporphyrin system has a profound favorable influence on the properties, such as solubility in organic solvents, suppressed aggregation and enhanced photostability.

4. Experimental

4.1. General

NMR spectra were recorded with Bruker Avance-400 spectrometer. Electronic absorption spectra were recorded on

Perkin–Elmer Lambda 40 instrument. MALDI-TOF spectra were obtained on Brucker Daltonics Alphaflex II instrument using anthracene or cinnamic acid matrices. Generally, fully aromatized π-extended porphyrins can be registered as $[M^+]$ ions, while other porphyrins require protonating matrix and are registered as $[(M+H)^+]$ ions. Melting points are uncorrected.

1-*tert*-Butoxycarbonyl-4,7-dihydro[2*H*]isoindole (**2**) was obtained according to published method.[1] Other reagents and solvents were received from the respective commercial suppliers and used as received, solvents were purified according to standard procedures.

*4.1.1. 1-tert-Butoxycarbonyl-5,6-diacetoxy-4,5,6,7-tetrahydro-[2H] isoindole (**4**).* A mixture of 1-*tert*-butoxycarbonyl-4,7-dihydro[2*H*] isoindole (**2**) (1.09 g, 5 mmol), potassium osmate (0.02 g, 0.054 mmol), potassium hexacyanoferrate (4.92 g, 15 mmol), potassium carbonate (2.07 g, 15 mmol), methanesulfonamide (0.471 g, 5 mmol), *tert*-butanol (60 mL), and water (60 mL) was stirred at room temperature for 12 h. After the addition of sodium sulfite (0.88 g, 7 mmol) the mixture was stirred for 2 h. Organic layer was separated, aqueous layer was extracted with ethyl acetate (3×20 mL). The united organic phase was evaporated in vacuum, the residue was dissolved in dry pyridine (20 mL), treated by acetic anhydride (2.04 mL, 20 mmol), stirred at room temperature for 12 h, diluted by dichloromethane (50 mL), washed by 5% HCl (5×100 mL), brine, dried over Na_2SO_4, and evaporated in vacuum. The solid was recrystallized from petroleum ether to give white powder (1.30 g, 77%). Mp 146–148 °C [found: C, 60.8; H, 6.6; N, 4.0. $C_{17}H_{23}NO_6$ requires C, 60.5; H, 6.9; N, 4.15%]; ν_{max}(KBr) 3280, 1735, 1730, 1700 cm^{-1}; (400 MHz, $CDCl_3$) 9.29 (1H, br s, NH), 6.64 (1H, s, C*H*=NH), 5.34 (1H, m, C*H*OAc), 5.27 (1H, m, C*H*OAc), 3.15 (1H, dd, *J*=5.18, 17.43 Hz, CH_2), 3.02 (1H, ABX, *J*=6.44, 17.43 Hz, CH_2), 2.86 (2H, m, CH_2), 2.06 (3H, s, Ac), 2.04 (3H, s, Ac), 1.54 (9H, s, *t*-Bu); δ_C (100 MHz, $CDCl_3$) 170.7, 170.6, 161.0, 122.4, 119.5, 118.4, 117.4, 80.9, 70.0, 69.8, 28.5, 26.5, 24.7, 21.2.

*4.1.2. 5,6-Diacetoxy-4,5,6,7-tetrahydro[2H]isoindole (**5**).* A mixture of ester **4** (1.01 g, 3 mmol) and 20 mL of trifluoroacetic acid was stirred for 30 min at room temperature under argon, diluted with 50 mL of dichloromethane, and thoroughly washed by water (2×100 mL), 10% sodium bicarbonate (2×100 mL), brine, dried over Na_2SO_4, and evaporated in vacuum. The residue was purified by flash-chromatography on silica using dichloromethane as eluent. Colorless oil (0.55 g, 77%). The material gives satisfactory NMR spectrum, but due to instability on storage pyrrole **5** was immediately used in porphyrin synthesis, and further purification to analytical standards was not attempted.

*4.1.3. 5,10,15,20-Tetraaryl-2^2,2^3,7^2,7^3,12^2,12^3,17^2,17^3-octaacetoxyhexadecahydrotetrabenzoporphyrin (**6**), mixture of diastereomers.* To the solution of pyrrole **5** (0.47 g, 2 mmol) and respective benzaldehyde (2 mmol) in 200 mL of freshly distilled dichloromethane, $BF_3 \cdot Et_2O$ (0.06 mL, 0.1 mmol) was added. The solution was stirred at room temperature for 1 h in the dark, quenched by the solution of DDQ (0.34 g, 1.5 mmol) in toluene (10 mL) and stirred overnight. The solution was then washed by 10% Na_2SO_3 solution (1×100 mL), brine, dried over Na_2SO_4, and evaporated in vacuum. The dark residue was chromatographed on a silica column using dichloromethane–acetic acid (100:1 v/v) as eluent. Porphyrin bands were identified by UV–vis spectra. Porphyrin was additionally purified by recrystallization from DCM–petroleum ether, and drying in vacuum. Compound **6a** deep green crystalline powder (0.14 g, 22%); δ_H (400 MHz, $CDCl_3$–CF_3COOH, 40:1 v/v) 8.38 (m, 8H, Ph), 7.96 (12H, m, Ph), 4.74–5.32 (m, 8H, C*H*OAc), 2.80–2.90 (m, 8H, CH_2), 2.20–2.40 (8H, m, CH_2), 1.53 (s, 12H, AcO), 1.51 (s, 12H, AcO), 0.30–0.80 (br s, 4H, NH); δ_C (100 MHz, $CDCl_3$–CF_3COOH, 40:1 v/v) 170.4, 170.0, 143.2, 137.3, 135.9, 131.0, 129.4, 129.1, 119.0, 68.4, 67.8, 26.9, 21.0, 20.3; *m*/*z* (MALDI TOF) 1295.28 (MH^+). Compound **6b** deep green crystalline powder (0.25 g, 33%); δ_H (400 MHz, $CDCl_3$–CF_3COOH, 40:1 v/v) δ 8.63 (AA′BB′, 8H, *meso*-C_6H_4), 8.48 (AA′BB′, 8H, *meso*-C_6H_4), 5.29–4.72 (m, 8H, C*H*OAc), 4.18 (s, 12H, COOMe), 2.80 (m, 8H, CH_2), 2.24 (m, 8H, CH_2), 1.54 (s, 24H, OAc), 0.10–0.60 (br s., 4H, NH); δ_C (100 MHz, $CDCl_3$–CF_3COOH, 40:1 v/v) δ 170.3, 170.1, 166.4, 142.5, 140.3, 135.8, 132.4, 130.6, 130.2, 118.6, 68.0, 67.3, 52.9, 27.1, 21.0, 20.2; HRMS (ESI): MH^+, found: 1527.5026. $C_{84}H_{79}N_4O_{24}$ requires 1527.5079; UV–vis (THF): λ_{max} (ϵ, L mol^{-1} cm^{-1}) 266 (26,000), 301 (21,000), 333 (28,000), 449 (885) nm.

*4.1.4. 5,10,15,20-Tetraphenyl-2^2,2^3,7^2,7^3,12^2,12^3,17^2,17^3-octahydroxyhexadecahydrotetrabenzoporphyrin (**7**), mixture of diastereomers.* Porphyrin **6a** (0.065 g, 0.05 mmol) was dissolved in methanol (20 mL), to which KOH (0.056 g, 1 mmol) was added, and the mixture was stirred for 12 h at room temperature. The reaction mixture was diluted with water and extracted by *n*-butanol (3×30 mL). The combined extracts were washed by brine, dried over Na_2SO_4 and evaporated to dryness in vacuum. Dark-green powder (0.045 g, 95%); δ_H (400 MHz, acetone-d_6) 8.03 (m, 8H, Ph), 7.55 (m, 12H, Ph), 7.0 (br s, 8H, OH), 3.43 (m, 8H, C*H*OH), 2.25 (m, 8H, CH_2), 1.53 (m, 8H, CH_2); HRMS (ESI): MH^+, found 959.3991. $C_{84}H_{79}N_4O_{24}$ requires 959.4014.

*4.1.5. 5,10,15,20-Tetrakis(p-methoxycarbonylphenyl)tetra-(acetoxybenzo)porphyrin 2(3) randomers (**8**).* The mixture of porphyrin **6b** (0.030 g, 0.02 mmol), DDQ (0.06 g, 0.26 mmol), and naphthalene (3 g) was heated at stirring in a closed thick-wall tube for 2 h at 190 °C. After cooling to room temperature the mixture was dissolved in CH_2Cl_2 (10 mL), transferred to round-bottom flask and evaporated in vacuum until all naphthalene was removed. The residue was dissolved in CH_2Cl_2 (20 mL), washed by 10% aqueous Na_2SO_3, brine, dried over Na_2SO_4, evaporated in vacuum, and chromatographed on silica (CH_2Cl_2 as eluent). The green fraction was collected and recrystallized from CH_2Cl_2–ether to give green solid with golden metallic shine (0.022 g, 85%); free base δ_H (400 MHz, CD_2Cl_2) 8.53–8.55 (8H, m, *meso*-aryl CH), 8.43–8.45 (8H, m, *meso*-aryl CH), 6.65–7.20 (12H, m, benzo-CH), 4.15 (12H, CH_3O), 2.23 (12H, s, CH_3CO), −1.22 (2H, br s, NH); dication δ_H (400 MHz, CD_2Cl_2–CF_3COOH 40:1 v/v) 8.60–8.75 (16H, m, *meso*-aryl CH), 7.35 (4H, dd, *J*=8, 19.5 Hz, benzo-CH), 7.22 (4H, m, benzo-CH), 7.13 (4H, br d, *J*=19.5 Hz, benzo-CH), 4.20 (12H, s, CH_3O), 2.26 (12H, s, CH_3CO), 1.28 (4H, br s, NH); HRMS (ESI): MH^+, found 1279.3566. $C_{76}H_{55}N_4O_{16}$ requires 1279.3608; UV–vis (CH_2Cl_2): λ_{max} (log ϵ) 468 (5.30), 596 (3.68), 642 (4.28), 698 (3.86) nm; dication λ_{max} (log ϵ) 508 (5.40), 652 (4.18), 704 (4.05) nm.

*4.1.6. tert-Butyl 5,6,7,8-tetrachloro-4,4a,8a,9-tetrahydro-2H-benzo[f] isoindole-1-carboxylate (**10**).* A mixture of 1-*tert*-butoxycarbonyl-4,7-dihydro[2*H*]isoindole **2** (0.44 g, 2 mmol) and 2,3,4,5-tetrachlorothiophene-1,1-dioxide (0.51 g, 2 mmol) was dissolved in 5 mL of toluene and refluxed for 1 h. After cooling the precipitate formed was filtered off, washed by 5 mL of toluene, and dried to give white powder (0.61 g, 75%). Mp 238–240 °C (decomp.) [Found: C, 49.64; H, 3.95; N, 3.19. $C_{17}H_{17}Cl_4NO_2$ requires C, 49.91; H, 4.19; N, 3.42%]; ν_{max}(KBr) 3340 cm^{-1}; δ_H (400 MHz, THF-d_8) 10.63 (br s, 1H, NH), 6.64 (d, 1H, *J*=2.78 Hz, CH pyrrolic), 3.28 (m, 1H, CH), 3.21 (m, 1H, CH), 3.02–3.17 (overlapp. m., 2H, CH_2), 2.98 (ABX, 1H, CH_2), 2.83 (ABX, 1H, CH_2), 1.53 (s, 9H, *t*-Bu); δ_C (100 MHz, THF-d_8) 161.1, 136.4, 135.8, 124.9, 124.5, 124.0, 120.0, 119.1, 118.3, 80.15, 42.4, 41.7, 28.7, 24.4, 23.2.

*4.1.7. 5,6,7,8-Tetrachloro-4,4a,8a,9-tetrahydro-2H-benzo[f]-isoindole (**12**).* A mixture of ester **10** (0.41 g, 1 mmol) and trifluoroacetic acid (20 mL) was stirred at room temperature for 30 min,

diluted with 50 mL of CH_2Cl_2, washed with water, 10% solution of Na_2CO_3, brine, dried over Na_2SO_4, and evaporated in vacuum to dryness. Solid residue was added to ethylene glycol (30 mL), and the mixture was refluxed under Ar for 30 min. After cooling to room temperature, the mixture was diluted with 50 mL of CH_2Cl_2, thoroughly washed with water (5×200 mL), brine, dried over Na_2SO_4, and evaporated in vacuum to dryness. The residue was purified by flash-chromatography on silica (CH_2Cl_2 as eluent) to give colorless oil solidified on standing (0.25 g, 80%); δ_H (400 MHz, $CDCl_3$) 8.15 (br s, 1H, NH), 6.55 (d, 2H, J=2.40 Hz, CH pyrrolic), 5.35 (m, 2H, CH), 2.96 (m, 4H, CH_2); δ_C (100 MHz, $CDCl_3$) 170.8, 115.2, 113.7, 70.7, 25.0, 21.2.

*4.1.8. 5,10,15,20-Tetrakis(p-methoxycarbonylphenyl)hexadeca-chlorohexadecahydrotetranaphthoporphyrin (**13**).* To a solution of pyrrole **12** (0.15 g, 0.50 mmol) and *p*-methoxycarbonylbenzaldehyde (0.082 g, 0.50 mmol) in 50 mL of freshly distilled CH_2Cl_2 boron trifluoride etherate (0.015 mL, 0.1 mmol) was added, and the mixture was stirred in a vessel protected from light for 1 h under Ar atmosphere. After that a solution of DDQ (0.085 g, 0.37 mmol) in toluene (5 mL) was added, and the mixture was left stirring for 12 h (control by UV–vis spectroscopy by appearance of Soret band). The resulting mixture was washed by 10% solution of Na_2SO_3, brine, dried over Na_2SO_4, and evaporated in vacuum to dryness. The residue was chromatographed on silica column, using gradient elution by CH_2Cl_2–AcOH mixture (content of AcOH was gradually increased to 5 vol %) with first washing off and discarding all fractions moved by neat CH_2Cl_2. The residue was recrystallized by slow diffusion of MTB into CH_2Cl_2 solution of crude porphyrin to give brownish-green crystals (0.063 g, 28%); δ_H (400 MHz, $CDCl_3$–CF_3COOH 40:1 v/v) 8.63 (m, 16H, *meso*-C_6H_4), 4.17 (s, 12H, COOMe), 3.21 (m, 4H), 2.86 (m, 8H), 2.48 (m, 4H), 2.19 (br s, 4H, NH), 1.81 (m, 8H). MS (MALDI TOF) MH^+, found: 1815.13. $C_{84}H_{55}Cl_{16}N_4O_8$ requires 1815.90.

*4.1.9. 5,10,15,20-Tetrakis(p-methoxycarbonylphenyl)hexadeca-chlorotetranaphthoporphyrin (**14**).* A mixture of porphyrin **13** (0.036 g, 0.02 mmol), DDQ (0.054 g, 0.24 mmol), and 2 g of naphthalene was heated at stirring in a thick-wall closed tube at 160 °C for 1 h. On cooling the mixture was dissolved in CH_2Cl_2 (10 mL), transferred to a round-bottom flask and distilled in vacuum until full removal of naphthalene. The residue was dissolved in CH_2Cl_2 (20 mL), washed by 10% solution of Na_2SO_3, brine, dried over Na_2SO_4, and evaporated in vacuum to dryness. The resulting solid was recrystallized by slow diffusion of ether into a solution of crude porphyrin in CH_2Cl_2 to give deep bluish-green shiny crystals (0.032 g, 90%); δ_H (400 MHz, $CDCl_3$–CF_3COOH, 40:1 v/v) 8.75 (AA′BB′, 16H, *meso*-C_6H_4), 8.56 (s, 8H, CH), 4.23 (s, 12H, COOMe), 2.69 (br s, 4H, NH); δ_C (100 MHz, $CDCl_3$–CF_3COOH) 166.5, 157.9, 157.6, 142.3, 140.6, 134.8, 132.9, 132.1, 131.7, 131.2, 130.6, 129.4, 123.6, 113.6, 53.0; UV–vis free base (CH_2Cl_2): λ_{max} (log ϵ) 452 (4.90), 488 (5.06), 514 (5.32), 628 (3.73), 682 (4.40), 732 (5.07) nm; UV–vis dication (CH_2Cl_2–CF_3COOH): λ_{max} (log ϵ) 452 (4.43), 540 (5.45), 704 (4.23), 776 (4.99) nm; MS (MALDI TOF) M^+, found: 1797.81. $C_{84}H_{38}Cl_{16}N_4O_8$ requires 1797.76.

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Supplementary data

The spectra of all new compounds can be found in the Supplementary data. Supplementary data associated with this article can be found in online version at doi:10.1016/j.tet.2011.01.052. These data include MOL files and InChIKeys of the most important compounds described in this article.

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