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Porphyrin Derivatives of Macrocyclic Tetraindoles: Synthesis and Chemical Transformations

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Abstract—Polyphenols chemically bonded to a molecular platform based on macrocyclic tetraindole porphyrin derivatives were synthesized for the first time. The tetraindole was prepared by two-step tetramerization of 3-(4'-bromophenyl)-4,6-dimetoxyindole. Polyphenols of this type were obtained by the Suzuki—Miyaura reaction between bromo-containing cyclic tetraindole and monoboryl-substituted porphyrin. The subsequent transformations of this molecular construction gave rise to epoxidized polyphenol on a tetraindole support, which served for the development of a new negative resist for electron-beam nanolithography. The resist can form patterns with a 12 nm resolution.

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Numerous indole derivatives form an important class of heterocyclic compounds. Their synthetic accessibility and high electrophysical and thermal properties open up prospects for their use as hole-conducting materials, organic light-emitting diodes, solar batteries, and donor-acceptor dyes [1]. The application of such products for the manufacture of optoelectronic and electronic materials gives rise to interest in the synthesis of new indole derivatives possessing unusual functional properties.

A recent attempt to prepare new porphyrin analogues resulted in the synthesis of macrocyclic tetraindoles [2–4], in which each pyrrole moiety, together with the neighboring meso carbon atom is replaced by an indole group. One more approach used to prepare macrocyclic tetraindoles is the synthesis of saddle—shaped cyclic indole tetramers, in which four indole moieties are chemically bonded to the cyclooctatetraene central core [1, 5, 6]. Both types of macrocyclic tetraindoles with a pseudoporphyrin architecture are considered as promising building blocks for the design of indole-containing optoelectronic and electronic materials.

In recent years, we have been developing a new concept of synthesis of monodisperse polyphenols chemically bonded to a rigid thermally stable molecular platform [7]. In our opinion, in this context, porphyrin derivatives of macrocyclic tetraindoles are of obvious interest for assembling polyphenols suitable as binders of resists for nanolithography. Compounds of this architecture are expected to have high rigidity and thermal stability.

In this study, we demonstrated for the first time the possibility to prepare monodisperse polyphenols chemically bound to a rigid thermally stable molecular platform based on porphyrin derivatives of macrocyclic tetraindole. We prepared these polyphenols by a facile and convenient procedure comprising the Suzuki—Miyaura reaction of bromo-containing cyclic tetraindole and boryl-substituted porphyrin. The subsequent chemical transformations of this molecular construction resulted in the synthesis of epoxidized polyphenol on a tetraindole support with porphyrin side groups, which made it possible to develop new negative resists for electron-beam nanolithography. The corresponding radiation-sensitive systems made it possible to form patterns with a 12 nm resolution.

Unless specified otherwise, Sigma-Aldrich (US) chemicals were used. All experiments were carried out under argon using the standard Schlenk techniques. The synthesis and chemical reactions of the polyphenol derivative of porphyrin tetraindole macrocycle are shown in Scheme 1.

Reagents and conditions: (a) $SnCl_4$, $CH_2Cl_2/MeNO_2$ (3 : 1 v/v), refluxing, 12 h, 48%; (b) HCl, *p*-benzoquinone, CH_2Cl_2, 22°C, 3 h, 47%; (c) **IV**, (([dppf]Fe)$PdCl_2$), KOAc, DMSO, 80°C, 6 h, 66%; (d) **V**, BBr_3, CH_2Cl_2, 22°C, 3 h, 95%; (e) 1-bromomethylcyclohex-3-ene, DBU, HMPA, 60°C, 24 h, 86%; (f) TBHP, DBU, THF, 22°C, 10 h, 93%.

3-(4'-Bromophenyl)-4,6-dimetoxyindole (**I**) obtained by procedure [8] was subjected to dimerization as

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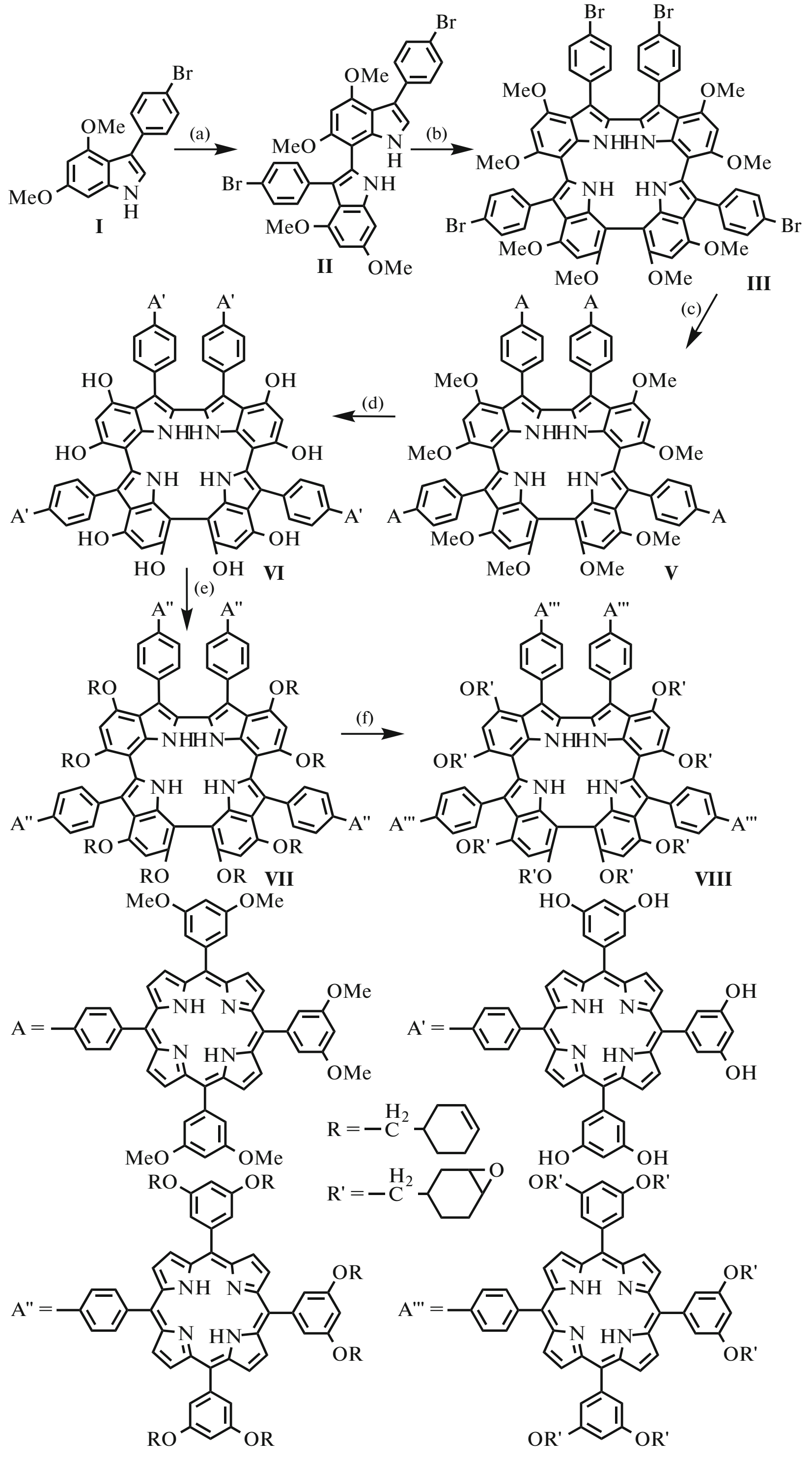

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described in [2] to give 3,3'-bis(4'-bromophenyl)-4,4',6,6'-tetramethoxy-1H, 1'H-2,7'-bis-indole (**II**). Then dimer **II** was oxidized with *p*-benzoquinone in a CH_2Cl_2–nitromethane ($MeNO_2$) mixture to give macrocyclic tetraindole (**III**). The reaction was carried out by a reported procedure [2]. Tetramer **III** was treated with 5-[4'-(4'',4'',5'',5''-tetramethyl-1'',3'',2''-dioxaborolan-2''-yl)phenyl]-10,15,20-tris(3',5'-dimethoxyphenyl)porphyrin (**IV**) under Suzuki–Miyaura reaction conditions. Compound **IV** was synthesized by the procedure reported in our paper [9] by condensation of pyrrole, 3,5-dimethoxybenzaldehyde, and 4-(4',4',5',5'-tetramethyl-1',3',2'-dioxaborolan-2'-yl)benzaldehyde. The cross-coupling was conducted by a reported procedure [10] in dimethyl sulfoxide (DMSO) in the presence of the dichloro[1,1-bis(diphenylphosphino)ferrocene]palladium ([dppf]Fe]$PdCl_2$) as the catalyst (Strem Chemical Co., USA). The product of this reaction (**V**) was subjected to exhaustive demethylation by a known procedure [11] to give polyphenol derivative of indole tetramer (**VI**).

Indole-containing polyphenol **VI** was then treated with 1-bromomethylcyclohexen-3-one [12], as recommended in [13], to give unsaturated tetraindole macrocycle (**VII**) with cyclohexene side moieties. The reaction was conducted in a hexamethylphosphoramide (HMPA) in the presence of 1,8-diazabicyclo[5,4,0]-7-undecene (DBU). Finally, the target tetramer with epoxide side groups (**VIII**) was synthesized by treatment of cyclohexene-containing macrocycle **VII** with a solution of *tert*-butyl hydroperoxide (TBHP) in tetrahydrofuran (THF) under the action of DBU according to a procedure we described earlier [14].

The newly synthesized compounds **II**–**VIII** were purified by preparative high performance liquid chromatography (HPLC). Their structures were established by MALDI-TOF mass spectrometry and ^{1}H NMR, ^{13}C NMR, and IR spectroscopy and confirmed by analytical HPLC and elemental analysis data. Table 1 summarizes the molecular weights of the obtained compounds.

Table 1. Molecular weights of the products

Compound	Molecular formula	Molecular weight, g/mol	
		found*	calculated
II	$C_{32}H_{26}Br_2N_2O_4$	662.3927	662.3930
III	$C_{64}H_{48}Br_4N_4O_8$	1320.7536	1320.7542
IV	$C_{56}H_{53}BN_4O_8$	920.8794	920.8798
V	$C_{264}H_{212}N_{20}O_{32}$	4176.7467	4176.7480
VI	$C_{232}H_{148}N_{20}O_{32}$	3727.8806	3727.8812
VII	$C_{456}H_{468}N_{20}O_{32}$	6740.9291	6740.9292
VIII	$C_{456}H_{468}N_{20}O_{64}$	7252.9091	7252.9100

*According to MALDI-TOF mass spectrometry.

According to IR and NMR spectroscopy data, the above conditions of epoxidation of unsaturated macrocycle **VII** were sufficient for complete conversion of cyclohexene moieties to epoxycyclohexane ones. After completion of this reaction, the IR spectrum of modified indole-containing tetramer no longer exhibits the absorption bands for the cyclohexene double bonds (3025, 1620 m, and 660 cm^{-1}), but shows new bands for the oxirane ring vibrations. In particular, low-frequency bands at 816 and 885 cm^{-1} are of analytical value.

The ^{1}H NMR spectrum of epoxidized macrocycle **VIII** exhibits a signal for the methine proton in the oxirane rings (multiplet at δ 3.15 ppm). Also, the ^{13}C NMR spectrum of this compound contains a signal for methine carbon atoms in the oxirane rings at 50.4–52.2 ppm. Meanwhile, no carbon signal for cyclohexene double bonds is present at 124.7–126.7 ppm.

The obtained analytical data were considered in more detail in relation to epoxidized tetraindole macrocycle **VIII**; only those absorption bands and signals are indicated that are analytically significant for structure assignment. The IR spectrum of this compound shows 3311 and 1469 cm^{-1} absorption bands (pyrrole NH groups) and a band at 1440 cm^{-1} (pyrrole C=N groups). Also, the bands at 3406 cm^{-1} (pyrrole NH groups) and 1593, 1519, 1463, 1090, 830, and 545 cm^{-1} were assigned to the tetraindole cyclic core of compound **VIII**. In the spectrum of compound **VI**, attention is attracted by a band at 3526 cm^{-1}, which can be assigned to phenolic hydroxyl groups. This band completely disappears for compounds **VII** and **VIII**.

In the ^{1}H NMR spectrum of **VIII** (799.809 MHz, $CDCl_3$), the porphyrin moieties are responsible for the proton signals at δ 2.89 ppm (NH) and in the range δ 8.75–8.92 ppm (β-H in the porphyrin rings). The tetraindole core of **VIII** gives rise to proton signals at δ 9.76 and 8.64 ppm (NH) and δ 6.02 ppm. The last-mentioned signal corresponds to protons at the indole C-5 atom. This ^{1}H NMR spectrum contains no signals at about 10.24 ppm (phenolic hydroxyl protons) or δ 3.89 ppm (methoxy group protons).

In the ^{13}C NMR spectra (200.13 MHz, $CDCl_3$) of compound **VIII**, several signals were assigned to the porphyrin macrocycle. In particular, the signals for meso carbon atoms occur at δ 119.1, 123.14, and 123.7 ppm. The δ 117.3 ppm signal corresponds to the C-2 and C-5 carbon atoms of the pyrrole rings. The signal at 107.6 ppm also belongs to the pyrrole rings (C-3 and C-4). The indole core of compound **VIII** gives rise to signals at δ 146.8, 143.7, 140.2, 137.5, 132.5, 129.8, 123.8, 117.5, 115.8, and 107.5 ppm.

The epoxidized tetraindole macrocycle **VIII** was used for the development of a new chemically amplified negative electron-beam resist suitable for the fabrication of microchips with cell size of 12 nm. The negative resist film based on compound **VIII** and triphenylsulfonium perfluorobutanesulfonate as the radiation-sensitive acid generator (5% relative to the weight of **VIII**) was formed on a silicon substrate (Rockwood Electronic Materials) from a solution in 2-acetoxy-1-methoxypropane and was dried at 95°C for 2 min. The post-exposure drying was performed at 125°C (2 min). The resist was developed with a 3 : 1 v/v cyclohexanone/butanol mixture.

The resolution of the negative electron beam resist was determined by irradiating the resist film in a JEOL JBX-6300FS electron beam system with exposure energy of 100 keV. The resist had a very high resolution: patterns with 12 nm-wide isolated lines were formed in a 30 nm-thick resist film. The line edge roughness was 2.8 nm, which is quite acceptable for the fabrication of some microchips for the 12 nm node [15]. The resolution and line edge roughness were estimated using a Hitachi S-5500 scanning electron microscope.

The sensitivity of the resist based on compound **VIII** was determined using a JEOL FEI XL30 SFEG electron beam system equipped with a Raith ELPHY Plus image generator at an exposure energy of 20 keV. The resist sensitivity under these conditions was 3×10^{-6} C/cm^2, which complies with the Roadmap requirements [15]. It is noteworthy that the developed negative electron beam resist has a plasma resistance adequate to the modern nanolithography and comparable with that attained in the plasma etching of commercial novolac-based photoresists such as SAL601 (manufactured by Rohm and Haas).

Thus, we proposed a new strategy for the synthesis of polyphenols chemically bonded to a rigid thermally stable molecular platform based on porphyrin derivatives of macrocyclic tetraindole. The starting macrocycle was synthesized by two-step tetramerization of 3-(4'-bromophenyl)-4,6-dimetoxyindole. We accomplished a facile and convenient synthesis of polyphenols of this type by the Suzuki–Miyaura reaction between brominated cyclic tetraindole and monoboryl-substituted porphyrin. The latter was obtained by condensation of 4-(4',4',5',5'-tetramethyl-1',3',2'-dioxaborolan-2'-yl)benzaldehyde, 3,5-dimethoxybenzaldehyde, and pyrrole. Then several successive chemical transformations of porphyrin-containing tetraindole macrocycle were carried out. In particular, this compound was demethylated, the product was etherified with 1-bromomethylcyclohexen-3-one, and the unsaturated derivative was epoxidized by reaction with *tert*-butyl hydroperoxide. The tetraindole-supported epoxidized polyphenol was used to develop a new negative resist for electron beam nanolithography capable of forming 12 nm node patterns.

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