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CHEMISTRY

Polyphenol Derivatives of Porphyrins Containing Fluorene Units: Synthesis and Positive-Tone Photoresists for 22-Nanometer Lithography

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Abstract—A new strategy was proposed for the synthesis of polyphenol derivatives of fluorene-containing porphyrins to be used as the base for positive-tone photoresists for lithography with exposure at 13.5 nm wavelength, which allow fabrication of microchips with a size of down to 22 nm. Polyphenols based on fluorene-containing porphyrins were synthesized for the first time. It was shown that these polyphenol derivatives can be used to obtain positive-tone photoresists with a resolution of 22 nm.

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The extreme ultraviolet (EUV) nanolithography using the radiation wavelength of 13.5 nm is quite promising for the manufacture of microchips with 22-nanometer standards [1, 2]; however, development of EUV lithography with such characteristics proved to be fairly expensive and is now substantially hampered.

A highly complicated task in the development of this type of lithography on an industrial scale is the design of resists adequately meeting the high requirements to parameters such as light sensitivity, resolution, line edge roughness, and plasma resistance. These properties are balanced in a certain way: improvement of one parameter is accompanied by deterioration of other parameters [1]. The few existing resists for EUV lithography described in the accessible literature [1] do not meet the existing requirements. These systems are usually designed in terms of the concept of molecular resists [1, 2], according to which they are formed from monodisperse low-molecular-weight polyphenol type organic compounds with high film-forming properties, glass transition temperature, and thermal stability.

Our search for aromatic compounds that could be functionalized to give polyphenols promising for the development of new effective photoresists for EUV lithography resulted in selection of aromatic hydrocarbons such as fluorenes and porphyrins possessing unique chemical, light, and thermal stability. Functionalization of these aromatic structures can lead to new compounds with a set of valuable properties for the development of innovative products. In particular, recently reported fluorene-containing porphyrins [3] are of practical interest for the manufacture of light-emitting materials.

Here, we propose a new strategy for the synthesis of polyphenol derivatives of fluorene-containing porphyrins as the base of positive-tone photoresists for lithography with exposure radiation at 13.5 nm, which would allow the manufacture of microchips with sizes of down to 22 nm.

We performed the first synthesis of new polyphenols of the indicated chemical nature via successive chemical transformations of 5,15-bis[4'-(*N*,*N*'-di[9",9"-bis(3",5"-dimethoxybenzyl)fluorenyl-2"]aminophenyl)]-10,20-bis[4'-(*N*,*N*'-di(4"-iodophenyl)aminophenyl)]porphyrin (**I**), which we prepared.

The phenolic hydroxyls in the synthesized fluorene-containing porphyrins were partly protected with various acid-labile groups. We evaluated the lithographic parameters of the positive-tone EUV resists

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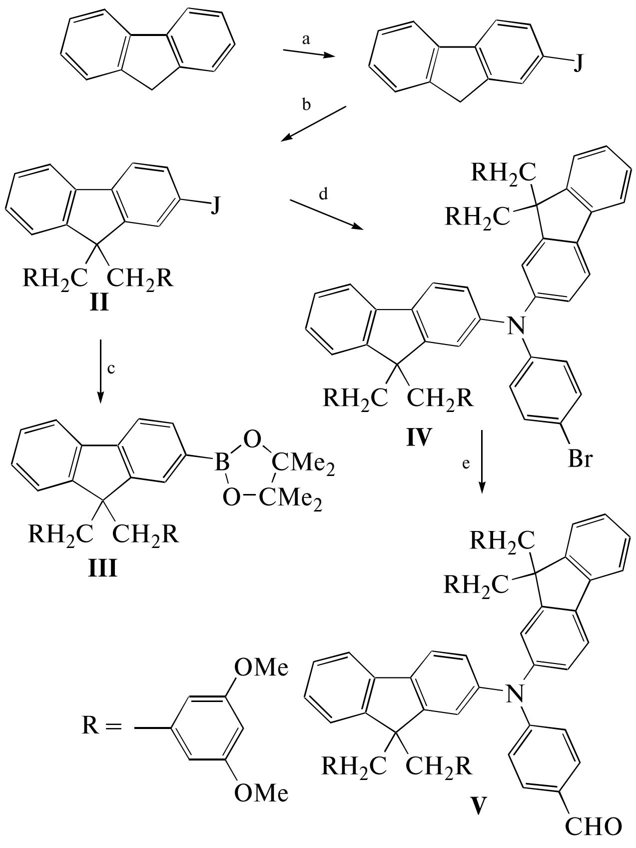
based on the modified porphyrins during the formation of topological structures with a size of down to 22 nm.

Unless otherwise specified, Sigma-Aldrich (United States) chemicals were used. The successive chemical transformations for the synthesis of polyphenol fluorene porphyrin derivative **I** are shown in Schemes 1 and 2.



Scheme 1.

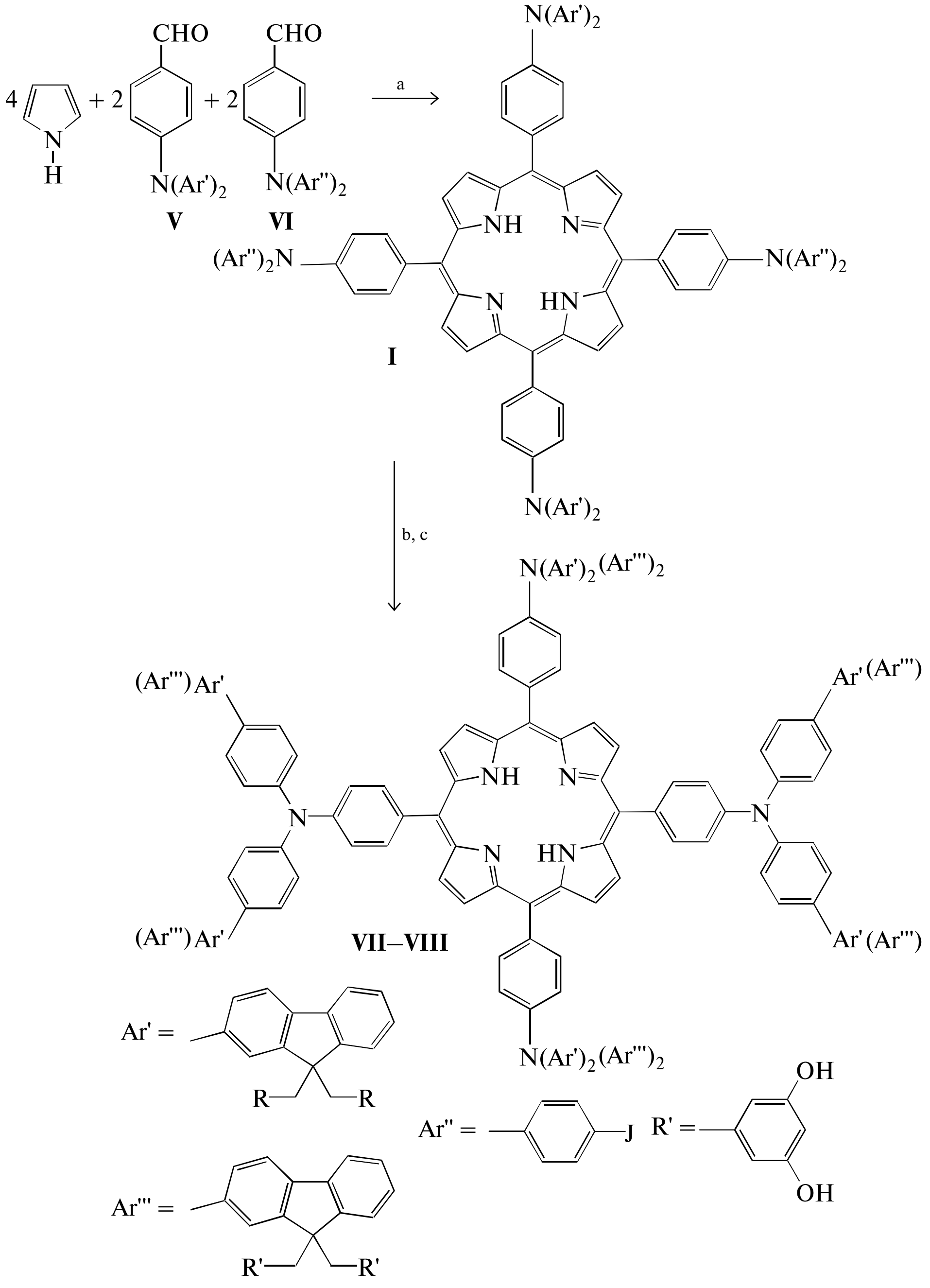
Scheme 1 presents the synthesis of intermediate fluorene derivatives needed for the subsequent transformations. The initial 2-iodofluorene was prepared by the procedure reported in [4]. This compound was treated with 3,5-dimethoxybenzyl bromide (Tokyo Kasei Kogyo Co. Ltd., Japan) in dimethyl sulfoxide (DMSO) [4] to give 2-iodo-9,9'-bis(3',5'-dimethoxybenzyl)fluorene (**II**). The latter product was converted to 2-(4',4',5',5'-tetramethyl-1',3',2'-dioxaborolan-2'-yl)-9,9'-bis(3',5'-dimethoxybenzyl)fluorene (**III**) in tetrahydrofuran (THF) according to procedure [5]. 4-Bromo-[*N*,*N*'-di(9,9'-bis(3',5'-dimethoxybenzyl)fluoren-2'-yl)]aniline (**IV**) was synthesized by procedure [6]. The fluorene-containing aniline obtained in this way by procedure [3] was converted to benzaldehyde (**V**).

Molecular weights of the synthesized products

Compound	Formula	Molecular weight, g/mol	
		found*	calculated
I	$C_{192}H_{158}N_8J_4O_{16}$	3341.0704	3341.0617
II	$C_{31}H_{29}JO_4$	592.4756	592.4788
III	$C_{37}H_{41}BO_6$	592.5476	592.5468
IV	$C_{68}H_{62}BrNO_8$	1101.1598	1101.1632
V	$C_{69}H_{63}NO_9$	1050.2744	1050.2728
VII	$C_{316}H_{274}N_8O_{32}$	4695.7438	4695.7416
VIII	$C_{284}H_{210}N_8O_{32}$	4246.8753	4246.8747

* MALDI-TOF.

Reagents and conditions: (a) J_2, H_5JO_6, AcOH, H_2SO_4, H_2O, 110°C, 4 h, 78%; (b) 3,5-dimethoxybenzyl bromide, triethylbenzylammonium chloride, 50% aq. NaOH, DMSO, 22°C, 6 h, 67%; (c) n-BuLi, THF, 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane, –78°C, 12 h, 72%; (d) 4-bromoaniline, CuCl, 1,10-phenanthroline, KOH, toluene, 125°C, 12 h, 72%; (e) n-BuLi, –78°C to+22°C, 4 h, DMF, –78°C...+22 °C, 8 h, 58%.



Scheme 2.

We synthesized (Scheme 2) porphyrin **I** for the first time and used it as a new building block for the preparation of polyphenol fluorene porphyrin derivatives. Compound **I** was prepared by a procedure reported in [7] by condensation of pyrrole (Janssen Chimics, Belgium), benzaldehyde (**V**), and 4-[*N*,*N*'-di(4'-iodophenyl)amino]benzaldehyde (**VI**), which was prepared by procedure [8]. The reaction was carried out in CH_2Cl_2 under argon using standard Schlenk technique. After formation of the intermediate porphyrinogen was completed, *p*-chloranil (2,3,5,6-tetrachloro-1,4-benzoquinone) was added to the reaction mixture. Then, substituted fluorene moieties were introduced into porphyrin **I** via the reaction of **I** with dioxaborolanyl-containing fluorene **III** by procedure [9] using dichloro[1,1-bis(diphenylphosphino)ferrocene]palladium ([dppf]Fe]$PdCl_2$) (Strem Chemical, United State) as the catalyst. Porphyrin **VII** thus formed was subjected to exhaustive demethylation by procedure [2] to give polyphenol fluorene porphyrin derivative **VIII**.

Reagents and conditions: (a) **V**, **VI**, pyrrole, BF_3–OEt_2, CH_2Cl_2, 22°C, 8 h, then 45°C, 1 h, 3.5%; (b) **III**, ([(dppf)Fe]$PdCl_2$), KOAc, DMSO, 80°C, 6 h, 71%; (c) BBr_3, CH_2Cl_2, 22°C, 3 h, 94%.

The newly synthesized compounds were purified by preparative high performance liquid chromatography (HPLC). The product structures were established by MALDI-TOF mass spectrometry and ^1H and ^{13}C NMR and IR spectroscopy and confirmed by analytical HPLC and elemental analysis data. The table gives the molecular weights of the products.

The analytical data were illustrated in more detail in relation to the polyphenol fluorene porphyrin derivative **VIII**. We indicated only those bands and signals that have diagnostic value. For example, the IR spectrum of compound **VIII** exhibits absorption bands at 3311 and 1469 cm^{-1} (NH in the pyrrole moieties) and a band at 1440 cm^{-1} (C=N in the same moieties).

In the ^1H NMR spectrum of **VIII**, the porphyrin moieties are responsible for the signals at –2.89 ppm (2H, NH) and in the 8.75–8.92 ppm range (β–H in the pyrrole rings). The phenyl groups in the fluorene side groups account for the proton signals at δ 7.79–7.77, 7.68–7.66, 7.47–7.45, 6.85, 6.73–6.72, 6.69–6.67, and 6.62–6.60 ppm. The ^1H NMR spectrum exhibits an intense signal at 10.24 ppm corresponding to the phenolic hydroxyl protons, while the singlet at δ 3.89 ppm, corresponding to methoxy group protons is missing.

The ^{13}C NMR spectrum of modified porphyrin **VIII** contains carbon signals at 151.7, 139.35, 127.65, 127.22, 125.95, 120.32, and 63.56 ppm for the fluorene moieties. The porphyrin macrocycles account for a number of signals in this spectrum. In particular, the *meso*-carbon atoms are responsible for 119.1, 123.1, and 123.7 ppm signals. The signal at 117.3 ppm refers to C-2 and C-5 pyrrole carbon atoms, while the signal at 107.6 ppm is due to the C-3 and C-4 pyrrole atoms.

Considering the development of positive-tone EUV resists based on the polyphenol fluorene porphyrin derivative **VIII**, we partly protected the phenolic hydroxyls by successive introduction of two protective groups—pentaspiran and *tert*-butyl butyrate ones. The degrees of protection of phenolic hydroxyls in **VIII** by these groups were 11 and 25 mol %, respectively; the desired degree of protection was attained by varying the amounts of the chloromethyl ether of pentaspiro[3.0.2.0.3.0.2.0.3.1]nonadecan-19-ol [10] and *tert*-butyl 2-bromobutyrate (Alfa Aesar, China), respectively, added to the reaction mixture. The modification was accomplished by procedure [10]. The degree of substitution of phenolic hydroxyls in the modified **VIII** was determined from the intensity change of the proton signals of these groups at δ 10.24 ppm.

The positive-tone photoresist film based on modified porphyrin derivative **VIII** and triphenylsulfonium perfluorobutanesulfonate as the acid photogenerator (5% relative to the porphyrin weight) formed on a silicon substrate from a solution in 1-methoxypropan-2-ol was exposed to EUV light (extreme ultraviolet region) at 13.5 nm. The irradiation was performed on a small exposure field pilot setup (Canon, USA) with a numerical aperture of 0.3. The resist film was dried at 130°C for 90 s and the post-exposure drying was performed at 110°C (90 s). The resist was developed by a standard 2.38% aqueous solution of tetramethylamminium hydroxide (NMD-3 developer, Tokyo Ohka Co., Japan).

This resist has an extremely high resolution: topological structures with line and gap widths of 22 nm were formed in a 50-nm thick resist film. The line edge roughness was 3.2 nm, which is quite acceptable for the fabrication of microchips with topological standards of 20 nm [1, 2]. Attention is attracted by the rather high light sensitivity of the developed EUV resist (7.9 mJ/cm^2). The photoresist has plasma resistance adequate to the modern nanolithography and comparable with that attained in the plasma etching of industrial positive-tone novolac-based photoresists.

Thus, we synthesized for the first time a polyphenol derivative of fluorene-containing porphyrin via several successive transformations of the initial porphyrin. The phenolic hydroxyls in the resulting derivative were partially protected by introducing two different types of protective groups, pentaspiran and *tert*-butyl butyrate ones. The degrees of substitution of the phenolic hydroxyls in the porphyrin derivative by these groups were 11 and 25 mol %, respectively. The modified compound was shown to be suitable for the design of promising positive-tone photoresists exhibiting high characteristics for EUV-nanolithography on exposure to light at 13.5 nm in the manufacture of 20-nanometer generation microchips. The analytical procedures were described in previous papers [2, 7].

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