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Synthesis, Grafting, and Film Formation of Porphyrins on Silicon Surfaces Using Triazenes

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The ability to attach electroactive molecules to semiconductor surfaces to yield hybrid molecular/semiconductor systems is essential for studies in the field of molecular electronics. We have synthesized a porphyrin bearing an aryltriazene group and its Zn, Cu, and Co complexes. Two methods have been developed for covalently grafting these porphyrins and metalloporphyrins to Si(100) surfaces by the in situ conversion of aryldiethyltriazenes to aryldiazonium salts using an acid, followed by the spontaneous grafting of the aryldiazonium salts to the hydride-passivated silicon surface. These porphyrin and metalloporphyrin films were characterized by X-ray photoelectron spectroscopy, ellipsometry, scanning electron microscopy and electrochemistry. The thicknesses of the molecular films thus formed can be controlled by the grafting conditions.

Introduction

The semiconductor industry is approaching its limitation with the current complementary metal-oxide semiconductor (CMOS) technology. One of the possible strategies to extend the life of the silicon technology is a hybrid molecular/semiconductor design, which involves building functional structures on the surface of semiconductors by the spontaneous surface self-grafting of organic molecules. Indeed, efforts are underway to develop hybrid molecular/semiconductor devices for both logic and memory applications.[1−4] Among the organic molecules that have been introduced into these hybrid structures, electroactive porphyrins and metalloporphyrins have shown great potential as information storage media.[5−8] A number of methods have been examined for the attachment of porphyrins to Si surfaces. These methods include (1) hydrosilylation involving allyl, ethynyl, or triallyl groups on hydride-passivated Si;[8−10] (2) the thermal reactions of alcohols, organo-thiols, and organo-selenols with hydride-passivated Si;[11−14] and (3) attachment to silicon oxide through arylphosphonic acid tethers.[15] Monolayers, multilayers, and polymeric films of porphyrinic molecules have been constructed on Si surfaces using these methods, which were expected to afford significantly higher charge density than the currently used Si/SiO$_2$ capacitors, especially the multilayers and polymeric films. However, these methods of surface attachment usually involve elevated temperature. And, on the basis of the literature, they do not afford good control over the thickness of the multilayers and polymeric films, particularly when relatively thin films (3−10 porphyrins) are desired. The exception was a process using stepwise growth of a multiporphyrin architecture through an imide-forming reaction on the top of a porphyrin monolayer attached to a Si(100) substrate.[16]

Recently, we have developed a new method for directly covalent grafting of molecules onto semiconductor or metal surfaces (Si, GaAs, or Pd) through diazonium chemistry.[17] This spontaneous reaction of organic diazonium salts with H-passivated Si(100) or Si(111) surfaces offered an attractive

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route to highly passivating, robust monolayers and multilayers. Because many organic diazonium species are reactive, difficult to synthesize and isolate, and in some cases, not stable to ambient conditions, we developed a convenient method for in situ film assembly on Si(100) under ambient conditions using organic triazenes.[17b] In this method, a dilute aqueous HF solution was used to convert aryldiethyltriazenes to diazonium salts in situ so that the reactive diazonium salts need not to be isolated. The HF also serves as an in situ etchant for H-passivation of the Si(100) surface, thereby making the surface grafting possible in air. The success of these two methods prompted us to explore the surface grafting of many organic diazonium and triazenes with various functionalities.

We report here the synthesis of triazene-derived porphyrinic molecules and the surface grafting and characterization of their monolayers and multilayers on Si(100).[17,18] Specifically, the synthesis of a porphyrin that bears an aryldiethyltriazene group for surface attachment is described. Three oligo(ethylene glycol) chains were attached to the porphyrin to achieve solubility in aqueous solution so that the porphyrin was compatible with the in situ film assembly in aqueous HF. Furthermore, Cu, Zn, and Co were used to form metalloporphyrin complexes with the porphyrin. We then describe the in situ surface grafting of these porphyrin and metalloporphyrins. The monolayer and multilayer films of porphyrins were examined using techniques including ellipsometry, X-ray photoelectron spectroscopy (XPS) and scanning electron microscopy (SEM). The XPS studies were used to characterize the structures of the molecules on the surface, whereas ellipsometry and SEM were used to measure the thickness and roughness of the monolayers and multilayers. The electrochemical characteristics were obtained by cyclic voltammetry. Collectively, this work introduces a novel approach for preparing Si surface-bound monolayers and multilayers of porphyrinic compounds for applications involving the electrical activities of the porphyrins, particularly for molecular/semiconductor hybrid memory devices.

Experimental Section

General. Unless noted otherwise, reactions were performed under a N_2 atmosphere. Toluene and triethylamine were distilled from CaH_2. Trimethylsilylacetylene (TMSA) was donated by FAR Research, Inc., or Petra Research, Inc. All other commercially available reagents were used as received unless noted otherwise. Reactions were magnetically stirred and monitored by thin-layer chromatography (TLC) using E. Merck silica gel 60 F_{254} precoated plates (0.25 mm) unless stated otherwise. Flash column chromatography was performed with the indicated solvent systems using silica gel grade 60 (230−400 mesh). Preparative TLC was performed with the indicated solvent system using E. Merck silica gel 60 precoated preparative plates (1.0 mm). All ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were collected in $CDCl_3$. Naming of new compounds was done using the Beilstein Autonom software except for the porphyrins, where literature precedent was used.

Ellipsometric Measurements. Measurements of surface optical constants and molecular layer thicknesses were taken with a single-wavelength (632.8 nm) laser Gaertner Stokes ellipsometer. The n value for the H-passivated Si(100) surface was 3.83, and k was −0.02. The surface thickness was modeled as a single absorbing layer atop an infinitely thick substrate (fixed n_s). The observed range in repeated measurements of the same spot was typically less than 0.2 nm, and the typical experimental error is ±5%.

XPS Measurements. A Quantera XPS scanning microprobe was used in collecting the XPS data. The takeoff angle was 45°, and a 114.8 W monochromatic Al X-ray source was applied for all the measurements. All XPS peaks were referenced to the C_{1s} major peak at 284.5 eV.

SEM Measurements. The cross-sectional images of porphyrinic films on Si(100) were characterized by a JEOL-6500 field-emission SEM instrument with an accelerating voltage of 15 KV.

Surface Grafting. ***Caution:*** *piranha solution and hydrofluoric acid are hazardous materials that should only be handled by trained personnel using appropriate personal protective measures. Wastes from these procedures should be disposed of only by approved procedures.*[19] Method A: n-Type Si(100) wafers (prime grade, As doped) were cleaned in piranha solution (2:1 H_2SO_4:H_2O_2) followed by rinsing with water (resistivity >18 MΩ cm^{-1}). The wafers were then immersed in the etching solution, a mixture of 2% aqueous HF and CH_3CN (1:1 v:v; 1% HF overall) for 5 min. Porphyrins (**5**, **Co-5**, and **Zn-5**) were dissolved in 1 mL of CH_3CN at various concentration and added to the etching solution containing the Si wafer. The reaction container was then covered with a fitted lid and agitated on a platform shaker at 100 rpm for a certain reaction time. After the reaction, the substrates were rinsed copiously with deionized water and CH_3CN and then dried with a stream of N_2.

Method B: n-Type Si(111) wafers (prime grade, As doped) were cleaned in piranha solution (2:1 H_2SO_4:H_2O_2) followed by rinsing copiously with water (resistivity >18 MΩ cm^{-1}) and drying with a stream of N_2. The wafers were then H-passivated by immersing in N_2-sparged 40% NH_4F for 15 min, rinsed with water, and dried in a stream of N_2. The cleaned and H-passivated wafers were then brought into a N_2-atmosphere glovebox. Inside the glovebox, a solution of the porphyrin (**5**, **Cu-5**, or **Co-5**) was made to various concentrations in CH_3CN, providing enough volume to cover the entire sample inside a reaction container, to which was then added 0.02−0.05 mL HBF_4 (49% aqueous). The substrates were then immersed in the porphyrin solution, sealed to prevent evaporation, and kept for various reaction times. After the reaction, the substrates were brought out of the glovebox, rinsed with CH_3CN, and dried with a stream of N_2.

Electrochemical Characterization. The cyclic voltammetry was performed with a Bioanalytical Systems (BAS CV-50W) analyzer in a self-designed three-electrode cell. The working electrode, porphyrin grafted Si(100), was sealed against an opening in the cell bottom by epoxy resin. An ohmic contact was made on the previously polished rear side of the sample by applying a drop of an In−Ga eutectic. The counter electrode was a platinum wire and 1×10^{-2} M Ag^+/Ag in acetonitrile was used as the reference electrode (+0.29 V vs aqueous SCE). One-tenth molar tetra-*n*-butylammonium perchlorate (Bu_4NClO_4) in acetonitrile was used

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as the electrolytic medium. All electrochemical measurements were carried out at room temperature under a constant flow of N_2.

5,10,15-Tris{4-{2-[2-(2-methoxy-ethoxy)-ethoxy]-ethoxy}}-phenyl-20-(4-diethyltriazene)-phenylporphyrin (5). A solution of pyrrole (1.34 g, 20.0 mmol), 4-trimethylsilanylethynyl-benzaldehyde[20] (1.01 g, 5.0 mmol), and 4-{2-[2-(2-methoxy-ethoxy)-ethoxy]-ethoxy}-benzaldehyde[21,22] (4.02 g, 15.0 mmol) in $CHCl_3$ (275 mL) was treated with boron trifluoride diethyl etherate (0.63 mL, 5.0 mmol) at room temperature. After the solution was stirred for 3 h, 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ, 3.40 g, 15.0 mmol) was added and the mixture was stirred for 1 h. The reaction mixture was then filtered through a silica gel plug (CH_2Cl_2, then 20:1 hexanes:methanol). The porphyrin-containing fractions were collected and concentrated. The residue was further purified by flash chromatography (silica gel, 50:1 hexanes:methanol) to obtain a mixture of porphyrins, one of which, **3**, could not be separated at this stage.

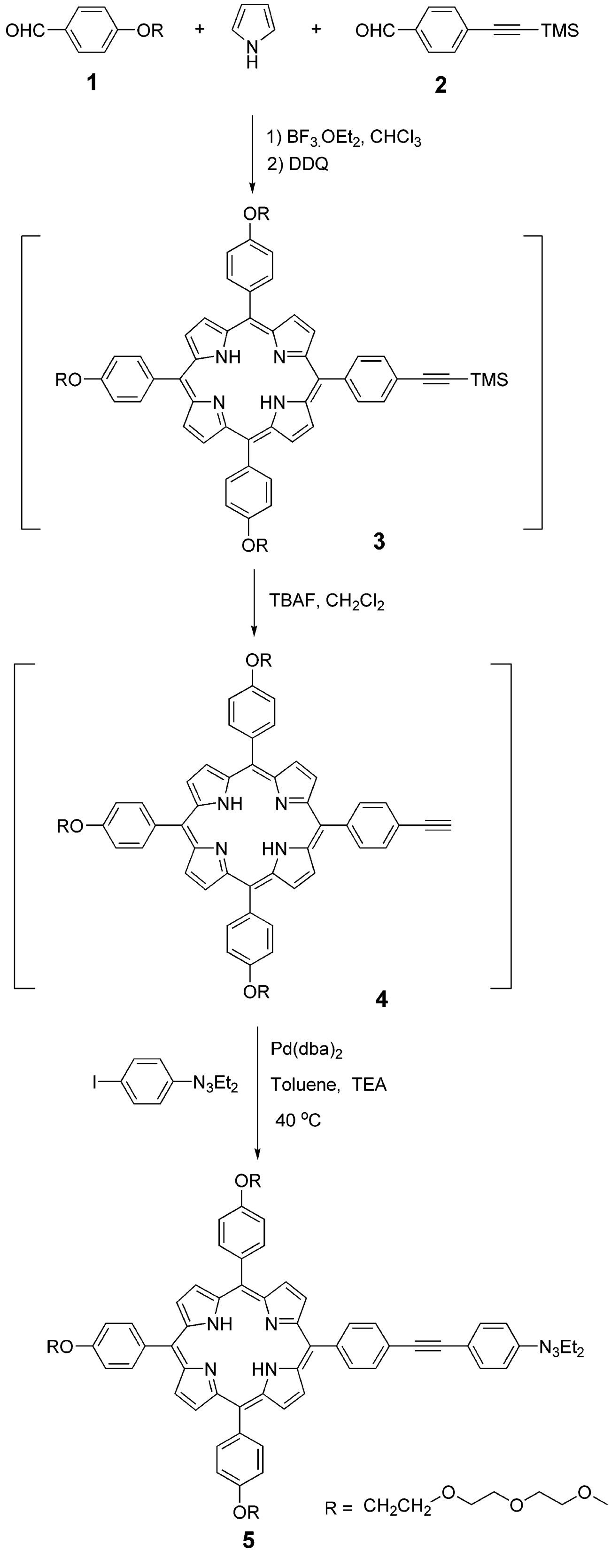
The mixture of porphyrins **3** was dissolved in CH_2Cl_2 (30 mL) and treated with 1 M tetrabutylammonium fluoride (TBAF) solution in THF (5 mL, 5.0 mmol) at room temperature for 15 min. The reaction mixture was then poured into water and the mixture was extracted with CH_2Cl_2 (3×50 mL). The organic layers were combined, dried over $MgSO_4$, and concentrated. The residue was purified by flash chromatography (silica gel, 50:1 hexanes:methanol) to obtain a mixture of porphyrins, one of which, **4**, was used directly in the following Pd-catalyzed coupling reaction.

To an oven dried round-bottom flask containing a magnetic stir bar were added the mixture of porphyrins, 4-iodophenyldiethyltriazene (0.90 g, 3.0 mmol), $Pd(dba)_2$ (26 mg, 0.45 mmol), and tri-*o*-tolylphosphine (0.11 g, 3.6 mmol). The flask was then sealed with a rubber septum, evacuated, and backfilled with N_2 (3×). A cosolvent of toluene (50 mL) and triethylamine (10 mL) was then added. The reaction was heated at 35−40 °C for 18 h. The reaction mixture was concentrated and purified by flash chromatography (silica gel, 50:1 hexanes:methanol) to obtain a mixture of porphyrins. The desired product **5** was isolated by preparative TLC (silica gel, 50:1 hexanes:methanol) as a purple solid (210 mg, 4%). ^1H NMR ($CDCl_3$, 400 MHz): δ 8.87−8.89 (m, Ar−H, 8H), 8.22 (d, $J = 8.2$ Hz, Ar−H, 2H), 8.12 (d, $J = 8.5$ Hz, Ar−H, 6H), 7.94 (d, $J = 8.2$ Hz, Ar−H, 2H), 7.67 (d, $J = 8.5$ Hz, Ar−H, 2H), 7.51 (d, $J = 8.5$ Hz, Ar−H, 2H), 7.30 (d, $J = 8.5$ Hz, Ar−H, 6H), 4.41 (t, $J = 4.8$ Hz, OCH_2CH_2O, 6H), 4.05 (t, $J = 4.8$ Hz, OCH_2CH_2O, 6H), 3.88 (m, OCH_2, 6H), 3.84 (m, NCH_2, 4H), 3.80 (m, OCH_2, 6H), 3.74 (m, OCH_2, 6H), 3.63 (m, OCH_2, 6H), 3.44 (s, OCH_3, 9H), 1.32 (m, NCH_2CH_3, 6H), −2.73 (s, NH, 2H). TOF-ES-MS: ($M + 2H^+$), 651; ($M + H^+$), 1302.

5,10,15-Tris{4-{2-[2-(2-methoxyethoxy)ethoxy]ethoxy}}phenyl-20-(4-diethyltriazene)-phenylporphinatocobalt(II) (Co-5). A solution of **5** (20 mg, 0.015 mmol) in $CHCl_3$ (20 mL) was treated with a solution of $Co(OAc)_2{\cdot}4H_2O$ (50 mg, 2.0 mmol) in MeOH (5 mL). The reaction mixture was then heated to reflux for 12 h. The mixture was then cooled to room temperature and concentrated. The residue was purified by flash chromatography (silica gel, 50:1 hexanes:methanol) to afford the product as a red solid (19 mg, 94%). TOF-ES-MS: M^{2+}, 678; M^+, 1356.

5,10,15-Tris{4-{2-[2-(2-methoxyethoxy)ethoxy]ethoxy}}phenyl-20-(4-diethyltriazene)-phenylporphinatozinc(II) (Zn-5). A solution of **5** (20 mg, 0.015 mmol) in $CHCl_3$ (20 mL) was treated with a solution of $Zn(OAc)_2{\cdot}2H_2O$ (50 mg, 2.7 mmol) in MeOH (5 mL). The reaction mixture was then heated to reflux for 12 h, cooled to room temperature, and concentrated. The residue was then purified by flash chromatography (silica gel, 50:1 hexanes:methanol) to afford the product as a purple solid (16 mg, 78%). TOF-ES-MS: M^{2+}, 682; M^+, 1364.

Scheme 1. Synthesis of Porphyrin 5 Using a Traditional Statistical Method



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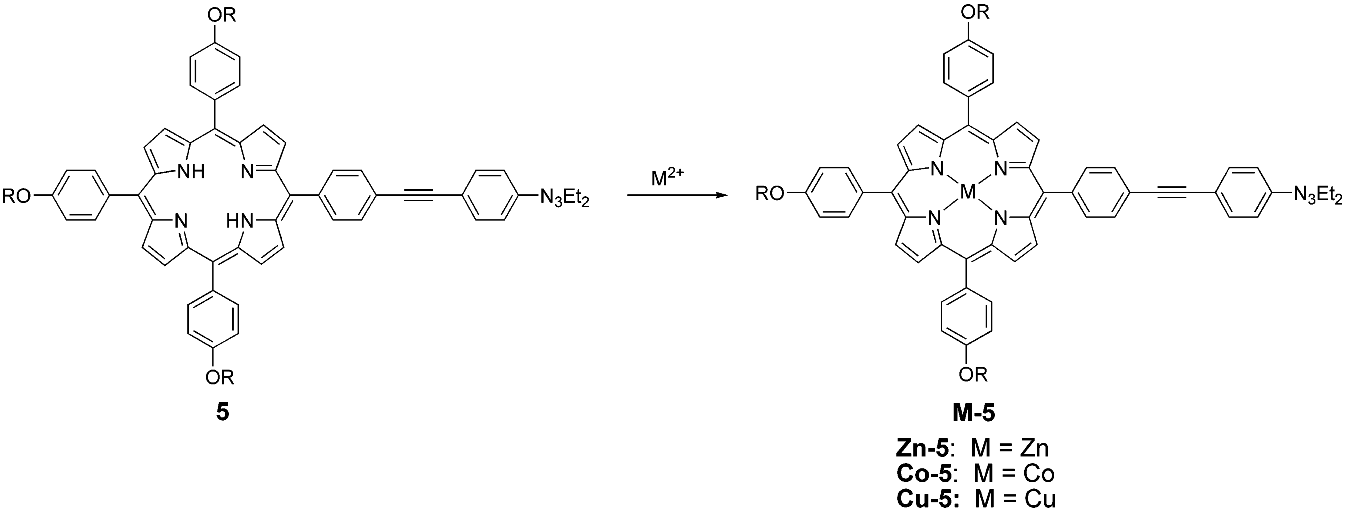
Scheme 2. Formation of Metalloporphyrin Complexes from 5 Where M = Metals Zn, Co, or Cu



5,10,15-Tris{4-{2-[2-(2-methoxyethoxy)ethoxy]ethoxy}}phenyl-20-(4-diethyltriazene)-phenylporphinatocopper(II) (Cu-5). A solution of **5** (20 mg, 0.015 mmol) in $CHCl_3$ (20 mL) was treated with a solution of $Cu(OAc)_2 \cdot H_2O$ (50 mg, 2.5 mmol) in MeOH (5 mL). The reaction mixture was stirred for 12 h and then concentrated. The residue was purified by flash chromatography (silica gel, hexanes/methanol, 50:1) to afford the product as a red solid (20 mg, 98%). TOF-ES-MS: M^{2+}, 681; M^{+}, 1361.

Results and Discussion

Molecular Design and Synthesis. For porphyrins to be grafted onto a Si surface via the diazonium chemistry, their structures need to meet two criteria: (1) there is a triazene or diazonium moiety attached; and (2) there are groups that can greatly increase the solubility of the porphyrins in water and/or in CH_3CN, which are the solvents necessary for the surface grafting of molecules onto Si surfaces. Therefore, we designed a porphyrin (**5**) that has one aryltriazene clip and three oligo(ethylene glycol) chains attached to the porphyrin core as meso substitutes. Three metal chelates of porphyrin **5** (**Zn-5**, **Co-5**, and **Cu-5**) can then be prepared from **5** to provide three cationic states.

The synthesis of porphyrin **5** was achieved from a traditional statistical method as shown in Scheme 1. The reaction of pyrrole with benzaldehydes **1** and **2** afforded a mixture of porphyrins containing the desired product **3**, which was not isolated because the porphyrins in the mixture all have similar polarity due to the oligo(ethylene glycol) side chains. This mixture was then used directly in the deprotection reaction to remove the TMS groups by using TBAF. A mixture of porphyrins that contained porphyrin **4**, which had only one free alkyne attached, was then collected and used in the following Pd-catalyzed coupling reaction[22] with the 4-iodophenyldiethyltriazene to afford the final product **5**, which could be isolated by preparative TLC. The overall yield of **5** was low because of the low yields of the statistical porphyrin formation reaction and the Cu-free Pd-catalyzed coupling reaction. The Cu-free Pd-coupling conditions were essential to obtaining **5** in the Cu-free form.

Three metalloporphyrin complexes, **Zn-5**, **Co-5**, and **Cu-5**, were then prepared from reactions of porphyrin **5** with the respective divalent salts under different conditions (Scheme 2).

Table 1. Film Thicknesses Resulting from Grafting of Porphyrin 5, Zn-5, and Co-5 on Hydrogen Passivated Si(100) Using Aqueous HF/CH_3CN Conditions

entry	compd	conc (mM)	time (min)	measured thickness (nm)[a]
1	**5**	0.1	10	3.5 ± 0.1
2	**5**	0.1	30	35.9 ± 2.1
3	**5**	0.1	60	52.5 ± 1.8
4	**5**	0.1	90	76.0 ± 1.4
5	**5**	0.2	30	56.6 ± 1.4
6	**5**	0.2	60	61.0 ± 0.4
8	**Zn-5**	0.2	30	1.2 ± 0.1
9	**Zn-5**	0.2	60	2.0 ± 0.1
10	**Zn-5**	0.2	120	3.2 ± 0.2
11	**Co-5**	0.1	30	1.5 ± 0.1
12	**Co-5**	0.1	60	13.7 ± 0.7
13	**Co-5**	0.1	120	19.8 ± 0.5

[a] The measured values are the average of five different spots on the same film with the ± values indicating the range of measurements.

Table 2. Film Thickness of In situ Grafting of Porphyrin 5, Cu-5, and Co-5 on H-passivated Si(100) in Acetonitrile Using HBF_4 Instead of Aqueous HF

entry	compd	conc (mM)	time (min)	measured thickness (nm)[a]
1	**5**	0.5	20	8.0 ± 0.3
2	**5**	0.5	40	11.7 ± 0.3
3	**5**	0.5	60	14.4 ± 0.3
4	**Cu-5**	0.2	30	2.5 ± 0.1
5	**Cu-5**	0.2	60	3.2 ± 0.1
6	**Cu-5**	0.2	120	5.7 ± 0.2
7	**Co-5**	0.2	20	2.9 ± 0.6
8	**Co-5**	0.2	40	2.8 ± 0.1
9	**Co-5**	0.2	60	3.3 ± 0.1

[a] The measured values are the average of five different spots on the same film with the ± values indicating the range of measurements.

Surface Grafting. Following our previously reported procedure for in situ surface grafting of organic triazenes on Si(100),[17b] porphyrin **5**, **Zn-5**, and **Co-5** can be readily grafted to form near-monolayers or multilayers on H-passivated Si(100) surfaces. All the grafting was done in a 1% aqueous HF solution (1:1 2% HF:CH_3CN). Different film thicknesses were achieved by varying the concentrations of the porphyrins or reaction times. The thicknesses of these films were characterized by ellipsometry and the results are summarized in Table 1.

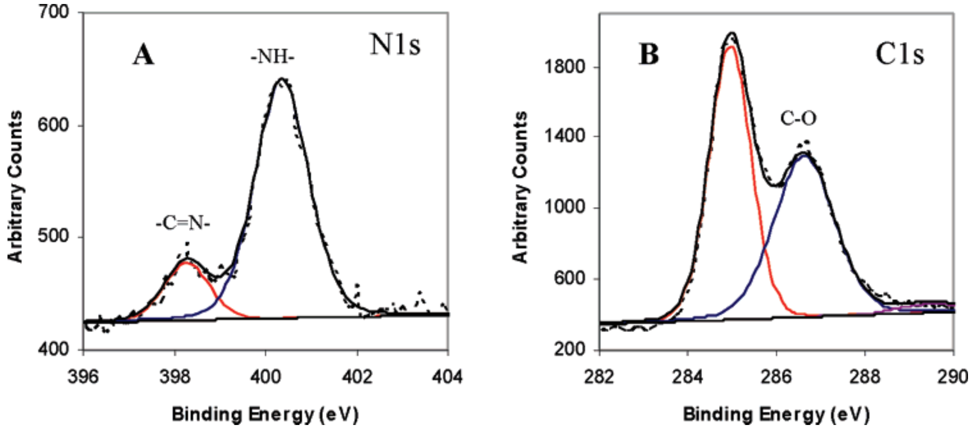


Figure 1. XPS spectra of a multilayer film (35.9 nm thickness, entry 2 in Table 1) of porphyrin **5** on Si(100): (A) N1s region, (B) C1s region.

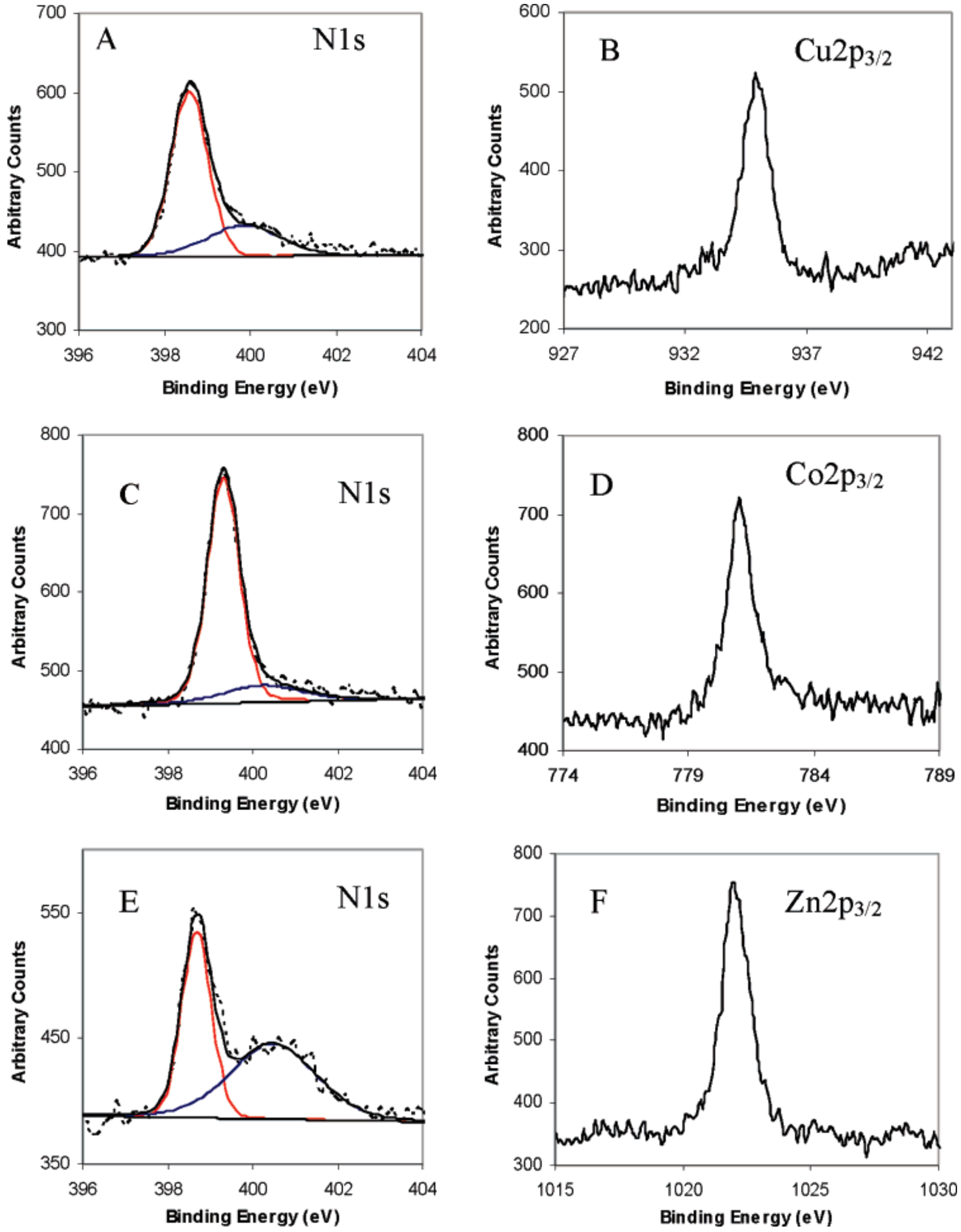


Figure 2. XPS spectra for **Cu-5** (A) N1s region and (B) $Cu2p_{2/3}$ region; **Co-5** (C) N1s region and (D) $Co2p_{2/3}$ region; **Zn-5** (E) N1s region and (F) $Zn2p_{2/3}$ region.

A thin film of porphyrin **5** with thickness of 3.5 nm was obtained at low concentration (0.1 mM) and very short reaction time (10 min) (entry 1 in Table 1). This thickness is close to that of a monolayer considering the calculated molecular length (3.75 nm) of molecule **5** with the tilt angle of Si−C bond on the Si(100) surface being 60°. With longer reaction times and higher concentrations, multilayers of **5** grew from a few tens of nanometers to hundreds of nanometers. As shown in entry 5, a multilayer of about 61 nm thick was grown on Si(100) using a 0.2 mM solution of **5** for 60 min. The growth of films of the metalloporphyrins **Zn-5** and **Co-5** was considerably slower compared to that obtained in the growth of **5**. For **Zn-5**, with relatively high concentration (0.2 mM) and long reaction time (2 h) (entry 10), a film of nearly a monolayer thickness was formed. For **Co-5**, the thickness of the films was in the range of that of submonolayers (1.5 nm, entry 11) to multilayers (19.8 nm, entry 13) by controlling the reaction time. One possible reason for the slow film growth of metalloporphyrins is the low stability of the metalloporphyrin radical species that formed from the corresponding triazenes. According to our proposed mechanism for the reaction of the aryl diazonium salts with H-passivated Si surfaces, the formation of the radical species from the diazonium salts is a crucial step.[17] With the low stability of the metalloporphyrin radicals, the concentration of the active species is relatively low, leading to the slow film growth of metalloporphyrins on Si(100).

For **Cu-5**, no complete film was formed on the surface of Si(100) using the in situ grafting method in aqueous HF solutions due to the low solubility of the **Cu-5** in aqueous solutions. To solve this problem, a second surface grafting method for aryltriazenes on Si(100) was developed. In this method, the Si(100) surfaces were H-passivated by 2% HF first and then immersed into an acetonitrile solution of the aryltriazene and a small amount of HBF_4. The aryltriazenes were converted in situ to the diazonium species by the HBF_4. Because **Cu-5** had relatively good solubility in CH_3CN, its surface grafting was successful under this new grafting method. As shown in Table 2, films of **Cu-5** with thickness from 2.5 to 5.7 nm were formed using different reaction times with 0.2 mM concentration of **Cu-5** (entries 4−6). This grafting method was also applied to porphyrin **5** (entries 1−3, Table 2) and **Co-5** (entries 7−9, Table 2). Both of these compounds formed good films on Si(100) using this new method, even though higher concentrations and longer reaction times were required to form monolayer and multilayer films when compared to that using the in situ method in HF aqueous solutions. For **Zn-5**, no film was formed on the Si(100) surface using this new grafting method because of the demetallation of **Zn-5** in the presence of the strong acid HBF_4.

XPS Studies. The XPS spectra of the porphyrin films were obtained. All elements of the porphyrins, including C, N, O, and different metals for the metalloporphyrins, were found in the XPS spectra of their grafted films on Si(100). The XPS spectra of N1s region for a film of porphyrin **5** on Si(100) is shown in Figure 1A. There are two peaks in the N1s region at 398.3 and 400.3 eV that can be assigned to two different types of N atom in the porphyrin: imine (−C=N−) nitrogen and pyrrole (−NH−) nitrogen.[23−24] Pyrrole nitrogen usually has higher N1s binding energy than imine nitrogen.[25] Therefore, the peak at 398.3 eV represents imine nitrogen, whereas the peak at 400.3 is from pyrrole nitrogen. The peak area ratio of the pyrrole nitrogen to the imine nitrogen is considerably higher than 1:1, which is expected for the ideal porphyrin structure because of the protonation of the imine nitrogens, which decreases the intensity of the N1s peak at the lower binding energy. As stated in the former section, the grafting of porphyrin **5** was done in 1% HF in H_2O/CH_3CN or in a mixture of one drop of HBF_4 and CH_3CN. In both cases, the imine nitrogens in the porphyrin cores would be protonated. Another possible factor is that the surface adsorbed N_2[26] increases the intensity of the N1s peak at the higher binding energy, because dinitrogen's binding energy is also at about 400 eV.

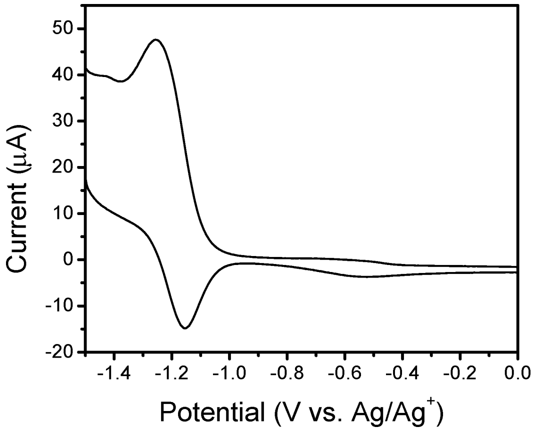


Figure 3. Representative voltammogram (1 V s^{-1}) of a **Co-5** film on Si(100) (average thickness 6.6 nm).

The grafting of the porphyrins on the Si(100) surface is also indicated by the C1s signal, as shown in Figure 1B. The two peaks at 285.0 and 286.6 eV represent the nonoxygenated carbon and oxygenated carbon, respectively, in these porphyrins.

The N1s and corresponding metal ion region of the XPS spectra of the films of metalloporphyrins **Cu-5**, **Co-5**, and **Zn-5** on the Si(100) surface are shown in Figure 2. The N1s signals of these metalloporphyrins usually have two peaks at about 399 and 400 eV as shown in Figure 2A, C, and E. The peak with the lower binding energy can be assigned to the metal-binding nitrogens. Both of the films of **Cu-5** and **Co-5** showed a small peak at the higher binding energy, which could be assigned to surface-adsorbed N_2[26] or a small portion of metal-free porphyrins on the surface introduced to the film as an impurity in the metalloporphyrins **Cu-5** and **Co-5**. The film of **Zn-5**, however, showed a relatively large peak at the higher binding energy. Because the surface grafting proceeded under acidic conditions and Zn−porphyrin complexes are usually not stable in acidic conditions, a large portion of the **Zn-5** would have been converted to protonated metal-free porphyrins during surface grafting. Therefore, the large peak at ~400 eV in the XPS spectra of **Zn-5** films can be assigned to the nitrogens in the metal-

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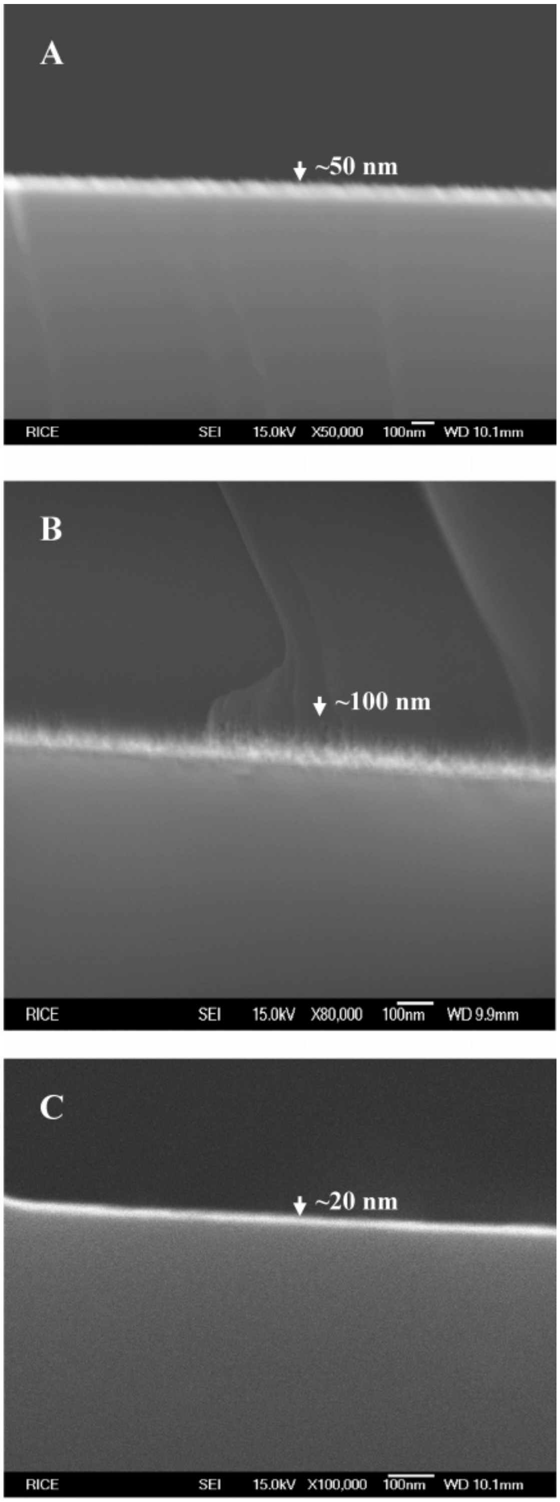

Figure 4. (A) SEM image of film of **5** with an ellipsometric thickness of about 50 nm. (B) SEM image of film of **5** with an ellipsometric thickness of about 100 nm. (C) SEM image of film of **Co-5** with an ellipsometric thickness of about 20 nm.

free protonated porphyrin cores. In addition, as shown in Figure 2B, D, and F, the XPS spectra of the metalloporphyrin films also exhibit the strong $2p_{2/3}$ signal of the corresponding metal ions.

Electrochemical Studies. A representative cyclic voltammogram for a multilayer film of **Co-5** on a Si(100) electrode (~0.5 cm^2) is shown in Figure 3. At reducing potentials, the **Co-5** film exhibited two resolved redox couples at −0.55 and −1.80 V vs Ag/Ag^+. As this was a typical pattern for the cobalt porphyrin complex,[27] these redox couples were attributed to the redox of the cobalt, Co(III)/(II) and Co(II)/(I), respectively. The surface coverage Γ obtained by integrating the voltammetric waves is about 1×10^{-9} mol cm^{-2},[28] which supports the conclusion of the multilayer formation of the **Co-5** on Si(100) (with an ellipsometric film thickness of 6.6 nm) because a monolayer would be expected to have about 1×10^{-10} mol cm^{-2}.[9] These results also indicate that the mutilayers of the porphyrins formed on Si(100) by diazonium chemistry could have a considerably high charge density despite the presence of the bulky oligo(ethylene glycol) side chains.

SEM measurements. The cross-sectional SEM images of films of porphyrin **5** and **Co-5** with different thicknesses are shown in Figure 4. The thickness of these films ranged from ~20 to ~100 nm. All of these films showed relatively uniform bulk material characteristics, especially for the film of **Co-5** with a thickness of about 20 nm (Figure 4C). These thick layers might prove useful in memory systems that require high levels of charge storage or for low-k dielectric layers in fabricated structures.

Conclusion

A porphyrin and its metal complexes bearing aryltriazene groups have been synthesized for attachment to Si(100) surface via diazonium chemistry. For the porphyrins with relatively good solubility in aqueous solution, they have been grafted onto H-passivated Si(100) surfaces through a convenient in situ method using aqueous HF. Conversely, a new grafting method has been developed for those porphyrins with relatively poor solubility in aqueous solution, where Si(100) wafers were pretreated to produce H-passivated surfaces and HBF_4 served as the reagent for conversion of the triazene into the diazonium species in an acetonitrile solution.

In both grafting methods, the thicknesses of the porphyrin films could be readily controlled in the range from a few nanometers to about 100 nm by varying the concentration and reaction time. The results from ellipsometry and SEM showed that all of the films had uniform texture and relatively smooth surfaces except when the films were relatively thick (~100 nm). Collectively, the preparation and surface grafting of porphyrins bearing aryltriazenes might be useful in future generation molecule/semiconductor devices.

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