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## Kinetics and mechanisms of hydrolysis of tetraphenylporphyrins tethered to silicate glass via a primary or tertiary alcohol linker

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#### 1. Introduction

The interconversion between silanols (hydroxysilanes) and alkoxysilanes (Eq. 1) is a key reaction in a number of practically important processes, such as sol-gel synthesis of ceramics,<sup>1</sup> surface modification of silicate glass or silica gel,<sup>2</sup> and silyl protection/ deprotection of OH groups in organic synthesis.<sup>3</sup>

$$\equiv \mathrm{Si} - \mathrm{OH} + \mathrm{ROH} \rightleftharpoons \equiv \mathrm{Si} - \mathrm{OR} + \mathrm{H}_2\mathrm{O} \tag{1}$$

Surface reactions and adsorption on silicate or other metal oxides are applied to catalysis, separation science, microelectronics and composite materials. Elucidation of the stability of silyl ester bonds and the mechanism of their reactions can extend applicability of the thin film of alcohols on metal oxides to various fields of chemistry and materials science. In this paper, we focus on the reactions between surface silanols on solid silicon oxide and alcohols. In most studies on reactions of silanols on solid surface, primary alcohols have been used, such as methanol, ethanol, and butanol. There are a few reports employing tertiary alcohol.<sup>4</sup> Lambert and Singer<sup>5</sup> reported that chemisorption reactivity of pentanol isomers toward thermally activated silica decreases in the order: normal>iso>secondary>neo>tertiary.

#### ABSTRACT

Tetraphenylporphyrins carrying primary or tertiary alcohols in a phenyl group were bonded to silicate glass by heat treatment. The rate of base catalyzed hydrolysis of tertiary ester was 20 times slower than that of primary ester, while the rate of acid catalyzed hydrolysis of tertiary ester was only 2.5 times slower than that of primary ester. Hydrolysis of tertiary alcohol bonded silica in HCl/H<sub>2</sub><sup>18</sup>O displayed that there is a covalent bond between alcohol oxygen and silicon, and the C-O bond is cleaved under acidic conditions, while the Si-O bond is cleaved under basic conditions.

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Kitahara reported that the forward reaction of Eq. 1 proceeded sluggishly when tert-butyl alcohol was used: the number of alkoxy groups per 100  $Å^2$  of *n*-butyl alcohol bonded silica gel was 3.2 while that of tert-butyl alcohol was 0.7.6 Hasegawa and Sakka reported that transesterification shown in Eq. 2 proceeds in the presence of cation-exchange resin in the proton form for all isomers of butanol, and only tert-butanol unexpectedly gave a reactive silanol species.<sup>7</sup>

$$\equiv \mathrm{Si} - \mathrm{OR} + \mathrm{R'OH} \rightleftharpoons \equiv \mathrm{Si} - \mathrm{OR'} + \mathrm{ROH}$$
(2)

Peculiar reactivities of tertiary alcohols have been reported, while the molecular mechanisms behind the reactivities are not well known.

We report herein comparative studies on the forward and backward reactions of Eqs. 1 and 2 on silicate glass or silica gel employing primary alcohol and tertiary alcohol bearing a porphyrin chromophore. Both primary alcohol and tertiary alcohol reacted with silanol groups on silicate glass to afford alcohol bonded silicate glass. Tertiary alcohol bonded silicate glass was resistant against base catalyzed hydrolysis compared to primary alcohol bonded silicate glass. We found that the acid catalyzed solvolysis (Eqs. 1 and 2) of tertiary alcohol bonded silicate proceeded through C-O bond scission, while the base catalyzed solvolysis reaction of primary and tertiary alcohol bonded silicate as well as the acid catalyzed solvolysis reaction of primary alcohol bonded silicate all proceeded through Si-O bond scission.







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#### 2. Results and discussion

#### 2.1. Preparation of porphyrin alcohols

Three alcohols bearing a porphyrin chromophore 1, 2, and 3 were prepared to compare influence of the alcohol structures on the forward and backward reactions of Eq. 1. Monolavers of porphyrin on silicate glass can be easily detected with electronic absorption spectroscopy owing to the large molar absorptivity of porphyrin in the visible region, so that kinetic studies were feasible. Alcohol **1** was prepared by the Williamson ether synthesis reaction of 5-(4-hydroxyphenyl)-10,15,20-triphenylporphyrin with 5bromopentyl acetate followed by alkaline hydrolysis of the ester.<sup>8</sup> Alcohol 2 was obtained by the Williamson ether synthesis reaction of the same porphyrin with methyl 5-bromopentanoate, followed by the reaction with the methyl Grignard reagent. Alcohol **3** was prepared by the ether synthesis reaction of the same porphyrin with methyl 5-bromo-2-ethylpentanoate, followed by reduction with LiAlH<sub>4</sub>. Alcohols **1**, **2**, and **3** were characterized with <sup>1</sup>H NMR and MALDI-TOF mass spectroscopy (Supplementary data) (Chart 1).



Fig. 2. Plots of absorbances at the Soret band of UV–visible spectra of 2 bonded silicate glass against time.

absorbances increased as the reaction time was longer and saturated when the temperature was high. The absorbances of 1 or 2 bonded glass were saturated at 0.07 and 0.06, respectively. The amounts of porphyrins bonded to silicate glass was determined by immersing the silicate glass in 0.1 M NaOH at 50 °C for 30 min, and



#### 2.2. Reaction of alcohols with silicate glass

Alcohols **1** and **2** were spin-coated on silicate glass and heated at 80-240 °C for up to 5 h. Washing with chloroform to remove unreacted alcohols afforded the alcohol bonded silicate glass. Figs. 1 and 2 show plots of absorbance at the Soret band of the glass against reaction time for various reaction temperatures. The



**Fig. 1.** Plots of absorbances at the Soret band of UV–visible spectra of **1** bonded silicate glass against time.

the amounts of desorbed porphyrin was spectrophotometrically determined.<sup>8</sup> The amounts of porphyrins **1** and **2** adsorbed on silicate glass were  $1.8 \times 10^{14}$  and  $1.4 \times 10^{14}$  molecules/cm<sup>2</sup>, respectively. Therefore, tertiary alcohol reacted slower than primary alcohol, while the adsorbed amount of tertiary alcohol was not much smaller than that of primary alcohol. The Langmuir rate constant<sup>9</sup> at 180 °C for formation of **1** bonded silicate glass was 0.012 min<sup>-1</sup> while that for **2** was 0.0058 min<sup>-1</sup>, indicating that tertiary alcohol **2** reacted ca. two times slower than primary alcohol **1**. The amount of bonded **2** was much smaller than **1** at temperatures below 160 °C, consistent with reported low reactivity of *tert*-alcohol at 55 °C toward thermally activated silica gel.<sup>5</sup>

#### 2.3. Kinetic studies on hydrolysis of alcohol-bonded silica

Alcohol **1** and **2** bonded silicate glass was immersed in 1 M aq HCl at 50 °C or in 1 M aq NH<sub>3</sub> at 30 °C and progress of hydrolysis was monitored by recording UV–visible spectra of the glass after washing it with CHCl<sub>3</sub>. The progress of hydrolysis under acidic conditions is shown in Fig. 3. Comparison of the half-life of the reaction showed that hydrolysis of **2** in HCl was ca. 2.5 times slower than that of **1**. It is interesting to note that the progress of acid-catalyzed hydrolysis did not follow a simple first-order kinetic model. There seem to be fast and slow fractions owing to

inhomogeneous solid surface. Incomplete acid hydrolysis of alcohols on silicate glass was also observed for other hydroxyporphyrins.<sup>8</sup> The progress of hydrolysis can be fit to the double exponential function:



Fig. 3. Absorbance changes at the Soret band during the reactions of 1, 2, and 3 on silicate glass with 1 M aq HCl at 50 °C. UV–visible spectra were recorded after washing with CHCl<sub>3</sub>.

$$A = p e^{-k_1 t} + (1 - p) e^{-k_2 t}$$
(3)

where *A* represents the normalized absorbance at time *t*,  $k_1$  and  $k_2$  are the rate constants of hydrolysis of labile and inert silicate ester, respectively, and *p* is the fraction of the labile silicate ester. Table 1 lists the kinetic parameters. The labile fraction *p* of tertiary alcohol **2** bonded silicate glass was much smaller than that of primary alcohol **1** bonded silicate glass. Branched primary alcohol with steric hindrance **3** also showed a smaller *p* value. Therefore steric hindrance seems to increase the inert fraction of silicate ester on silicate glass.

 Table 1

 Kinetic parameters of acid hydrolysis of 1–3 bonded silicate glass

	$k_1/\min^{-1}$	$k_2/\min^{-1}$	p (fraction of labile component)
<b>1</b> <sup>a</sup>	$(7.6\pm1.5)\times10^{-2}$	$(8.1\pm1.4)\times10^{-4}$	0.42±0.02
2	$(7.7\pm1.7)\times10^{-2}$	$(1.6\pm0.05)\times10^{-3}$	0.16±0.02
3	$(7.5\pm0.02) imes10^{-2}$	$(8.6\pm0.9) imes10^{-4}$	$0.26 {\pm} 0.02$

<sup>a</sup> Taken from literature.<sup>8</sup>

Fig. 4 shows the progress of hydrolysis in 1 M aq NH<sub>3</sub> of 1, 2, and 3 bonded silicate glass at 30 °C. Decrease in absorbance was fit to the first-order kinetic decay: Abs/Abs<sub>0</sub>= $e^{-kt}$ . The rate constant for **2** was determined with the data up to 6 h, since decrease in absorbance after 6 h was faster than expected from the first order kinetics. The first-order rate constants are listed in Table 2. Hydrolysis of **2** in 1 M aq NH<sub>3</sub> was 20 times slower than **1**. Sterically hindered primary alcohol **3** showed ca. two times slower hydrolysis than primary alcohol 1. Steric effects seem to be important in hydrolysis, particularly under basic conditions. Interestingly, the primary alcohol with a branched chain 3 showed relatively fast hydrolysis, indicating that the tertiary structure of **2** is significant. Similar retardation of hydrolysis due to steric effects has been reported for tetraalkoxysilane<sup>10</sup> and trialkylsiloxane<sup>11</sup> in homogeneous solutions and for alkoxylated silica<sup>12</sup> in a heterogeneous system. Enhanced steric effects in alkaline hydrolysis compared to acid



**Fig. 4.** Absorbance changes at the Soret band during the reactions of **1**, **2**, and **3** bonded silicate glass with 1 M aq NH<sub>3</sub> at 30 °C. Curves represent the simulated absorbance changes due to the first-order kinetics with  $k_{obs}$ =3.4±0.2 h<sup>-1</sup> for **1**, 0.17±0.007 h<sup>-1</sup> for **2** and, 1.89±0.05 h<sup>-1</sup> for **3**. UV–visible spectra were recorded after washing with CHCl<sub>3</sub>.

# Table 2 The first-order rate constants of hydrolysis of 1, 2, and 3 bonded silicate glass in 1 M aq NH<sub>3</sub> at 30 $^\circ\text{C}$

	$k/h^{-1}$
1	3.4±0.2
2	0.17±0.007
3	1.85±0.05

hydrolysis were reported by Shirai et al.:<sup>11</sup> they found that hydrolysis of *tert*-butoxytrimethylsilane in acidic aq acetone at 37 °C proceeded seven times slower than benzyloxytrimethylsilane, while hydrolysis in basic media proceeded 9600 times slower.

#### 2.4. Mechanism of solvolysis of alcohol-bonded silica

In order to gain more insights into the mechanism of hydrolysis, we performed the acid or base catalyzed ethanolysis of 1 and 2 bonded silica gel and the products were characterized by MALDI-TOF mass spectroscopy. We used silica gel instead of silicate glass to obtain enough amounts of products for mass spectroscopic analysis. The reaction of 2 bonded silica gel in 0.1 M HCl in ethanol at 50 °C yielded several products. They were separated with silica gel chromatography and the molar ratios of each product were determined with UV-visible spectroscopy. The products were ethyl ether 4, alkene 5, and alcohol 2 in a molar ratio of 44:44:12 (for the structures of the products, see Scheme 1). We confirmed that neither ether **4** nor alkene **5** was detected with mass spectroscopy after heating a solution of 2 in 0.1 M HCl in ethanol at 50 °C in the presence of silica gel or in the absence of silica gel. Therefore, formation of 4 and 5 was not due to the aging of a solution of 2 under acidic conditions. We also carried out hydrolysis of 2 bonded silica gel in 0.1 M HCl in H<sub>2</sub><sup>18</sup>O at 30 °C for 24 h. The MALDI-TOF mass spectrum of the product showed that the recovered 2 was almost exclusively labeled with <sup>18</sup>O (Fig. 5). Hydrolysis of 2 bonded silica gel in 1 M HCl at 50 °C for 24 h yielded not only alcohol 2 but also alkene 5. As a control experiment, a mixture of 2 and silica gel was heated under the same conditions. The mass spectrum showed that no <sup>18</sup>O was introduced in 2 (dotted line, Fig. 5). These results demonstrated that (1) tert-alcohol 2 was bonded to silica gel via a covalent bond, and (2) acid solvolysis of tert-alcohol 2 bonded silica gel proceeded through C-O bond scission. The solvolysis of primary alcohol 1 bonded silica gel in 0.1 M HCl in ethanol afforded

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Scheme 1. Reaction scheme of acid or base catalyzed solvolysis of primary or tertiary alkyl silicate glass.



**Fig. 5.** MALDI-TOF MS of the product of acid hydrolysis of **2** bonded silica gel in 0.1 M HCl in  $H_2^{18}O$  at 30 °C for 24 h (solid line), and **2** deposited on silica gel in 0.1 M HCl in  $H_2^{18}O$  at 30 °C for 24 h (dotted line).

only alcohol **1** as a sole product. Solvolysis under basic conditions gave completely different results. For the reaction of both **1** and **2** bonded silica gel in 0.1 M EtONa in ethanol afforded only the corresponding alcohols. Thus, solvolysis of **1** under acidic conditions and solvolysis of **1** and **2** under basic conditions all proceeded through Si–O bond scission. Suggested reaction mechanisms of acid-catalyzed and base-catalyzed solvolysis are summarized in Scheme 2.

It has been demonstrated that hydrolysis of silicate esters in homogeneous solutions proceeds through Si-O bond scission instead of C-O bond scission by several lines of evidence, such as isotope labeling studies using H<sub>2</sub><sup>18</sup>O.<sup>13</sup> Silicon can form a pentacoordinated intermediate so that the Si-O bond is more labile than the C–O bond.<sup>14,15</sup> Utsugi et al. demonstrated that hydrolysis of the chiral alcohol bonded silica proceeds through Si–O bond scission based on the optical activity of the hydrolyzed alcohol.<sup>16</sup> We demonstrated that acid solvolysis of tert-alcohol bonded silica proceeded through C-O bond scission, indicating that the reactivity of the tertiary C–O bond can be competitive with that of the Si-O bond under acidic conditions. The C-O bond scission of tertalcohol is consistent with the observation of (EtO)<sub>3</sub>SiOH formation during acid-catalyzed transesterification of Si(OEt)<sub>4</sub> and tert-butyl alcohol.<sup>7</sup> The slower rate of base hydrolysis of tertiary alcohol **2** bonded silica than that of primary alcohol 1 bonded silica can be ascribed to the steric hindrance of the neighboring methyl groups of **2** for nucleophilic attack of the OH<sup>-</sup> ion to Si.

#### 2.5. Mechanism of reaction of alcohol with silicate glass

The reaction mechanism of condensation of alcohols with silanol on silica gel is not well understood, and previous studies focused on the effects of preheating of silica on the reaction with alcohols.<sup>17</sup> We prepared (<sup>18</sup>O)-**2** bonded silica gel and subsequent

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primary alkyl





Scheme 2. Suggested reaction mechanisms of acid or base catalyzed solvolysis of primary or tertiary alkyl silicate glass.

solvolysis with NaOEt/EtOH yielded (<sup>18</sup>O)-**2**, as determined by MALDI-TOF mass spectroscopy (Scheme 3). Therefore, condensation of **2** with silanol proceeded with attack of the alcohol oxygen to Si. Formation of a carbenium ion intermediate was excluded even for sterically crowded *tert*-alcohol. In conclusion, we demonstrated that *tert*-alcohol was bonded to silicate glass and silica gel by heating the spin-coated film of *tert*-alcohol on silica. Alkaline hydrolysis of *tert*-alcohol bonded silica was 20 times slower than primary alcohol, while acid hydrolysis of *tert*-alcohol bonded silica was only 2.5 times slower than primary



Scheme 3. Reactions of condensation of (18O)-labeled tertiary alcohol with silanol groups on silicate glass followed by solvolysis in NaOEt/EtOH.

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alcohol bonded silica. Solvolysis in  $H_2^{18}O$  or in ethanol demonstrated that acid catalyzed solvolysis of *tert*-alcohol bonded silica proceeded through the C–O bond scission, contrary to generally accepted mechanism of Si–O bond scission.

#### 3. Experimental section

#### 3.1. Materials

Micro glass slide (76 mm×26 mm) was purchased from Matsunami Glass Ind., Ltd. The glass slides were immersed in a solution of  $H_2SO_4/30\%$   $H_2O_2$  (70:30, v/v) at 80 °C for 1 h, washed with water, bath-sonicated in water, and dried under N<sub>2</sub> gas. H<sub>2</sub><sup>18</sup>O ( $\geq$ 98 atom% <sup>18</sup>O) was purchased from Taiyo Nippon Sanso Corp. 0.1 M and 1 M HCl in  $H_2^{18}$ O was prepared by addition 12 M HCl in  $H_2^{16}$ O to  $H_2^{18}$ O. Melting points were determined by Shimadzu Differential Calorimeter DSC-60. Silica gel, CARiACT Q-6, was purchased from Fuji Silysia Chemical Ltd. It had a specific surface area of 451 m<sup>2</sup> g<sup>-1</sup>. A hot stage Mettler-Toledo FP82HT was used for heat treatment of the spin-coated films. UV-visible spectra were obtained with a Perkin–Elmer Lambda 950 spectrophotometer. <sup>1</sup>H NMR spectra were recorded with a JEOL JNM-ECA500 spectrometer. Tetramethylsilane was used as an internal standard. Matrix-assisted laser desorption-ionization time-of-flight mass (MALDI-TOF MS) spectra were recorded on a Bruker Daltonics Autoflex Speed spectrometer.

## 3.2. Preparation of porphyrin 1–3 monolayers on silicate glass

A silicate glass was cleaned by immersion in a '*piranha*' solution ( $H_2SO_4$ :30%  $H_2O_2$ =70:30 (v/v)) for 1 h at 80 °C. After being cooled to room temperature, it was rinsed with ultrapure water, filtered with a MilliQ system from Millipore and then sonicated in ultrapure water. Then it was dried in a N<sub>2</sub> stream. A CHCl<sub>3</sub> solution of **1–3** (60 µL, 4.2 mM) was spin-coated on the silicate glass at 3000 rpm for 60 s. The spin-coated film was then heated on a hot stage at 80–240 °C for 5 min to 5 h to allow a condensation reaction to proceed. The silicate glass was washed with CHCl<sub>3</sub> to remove unreacted porphyrins. The resultant glass adsorbing porphyrin was analyzed by UV–visible spectroscopy.

#### 3.3. Preparation of porphyrins 1 or 2 bonded silica gel

Porphyrin (1: 3.59 mg or 2: 3.72 mg) was dissolved in CHCl<sub>3</sub> (5 mL) and silica gel (50 mg) dried at 100 °C for 1 h in vacuo was added to the CHCl<sub>3</sub> solution. After evaporation of the CHCl<sub>3</sub>, the silica gel was heated at 160 °C (for 1) or 200 °C (for 2) for 4 h. The silica gel was cooled to room temperature and then washed in CHCl<sub>3</sub> in a bath sonicator to remove unreacted porphyrins. The red silica gel was collected by suction filtration and dried in vacuo. The resultant silica gel was subjected to the studies of hydrolysis and ethanolysis.

#### 3.4. Acid catalyzed ethanolysis of porphyrin bonded silica gel

Porphyrin bonded silica gel dried at 50 °C for 1 h in vacuo was stirred in 0.1 M HCl in EtOH (50 mL) at 50 °C for 18 h under Ar. After cooling the suspension to room temperature, it was filtered and the silica gel was washed with CHCl<sub>3</sub>, acetone, and saturated NaHCO<sub>3</sub> aq. To the filtrate was added CHCl<sub>3</sub>, and the organic layer was separated and washed with saturated NaHCO<sub>3</sub> aq three times and with H<sub>2</sub>O three times. The organic layer was dried over Na<sub>2</sub>SO<sub>4</sub> and evaporated in vacuo and the products were characterized by MALDI-TOF mass spectroscopy.

#### 3.5. Base catalyzed ethanolysis of porphyrin bonded silica gel

Porphyrin bonded silica gel dried at 50 °C for 1 h in vacuo was stirred in 0.1 M EtONa in EtOH (50 mL) at 50 °C for 18 h under Ar. The suspension was cooled to room temperature, followed by filtration. The silica gel was washed with CHCl<sub>3</sub> and acetone. The filtrate was neutralized with 0.1 M HCl and CHCl<sub>3</sub> was added. The organic layer was separated and washed with saturated NaHCO<sub>3</sub> aq three times and H<sub>2</sub>O three times. The organic layer was characterized by MALDI-TOF mass spectroscopy.

## 3.6. Acid catalyzed hydrolysis of porphyrin 2 bonded silica gel in ${\rm H_2}^{18}{\rm O}$

After (<sup>16</sup>O)-**2** bonded silica gel was dried at 50 °C for 1 h in vacuo, it was stirred in 0.1 M HCl in  $H_2^{18}O(8 \text{ mL})$  at 30 °C for 24 h under Ar. The suspension was cooled to room temperature and then it was filtered. The silica gel was washed by CHCl<sub>3</sub>, acetone, and saturated NaHCO<sub>3</sub> aq. To the filtrate was added CHCl<sub>3</sub> and washed with saturated NaHCO<sub>3</sub> aq three times and  $H_2O$  three times. The organic layer was dried over Na<sub>2</sub>SO<sub>4</sub> and evaporated in vacuo. The product was characterized by MALDI-TOF mass spectroscopy.

#### 3.7. Preparation of <sup>18</sup>O-labeled porphyrin 2 ((<sup>18</sup>O)-2)

After ( ${}^{16}$ O)-**2** bonded silica gel was dried at 50 °C for 1 h in vacuo, it was stirred in 1 M HCl in H<sub>2</sub>  ${}^{18}$ O (8 mL) at 50 °C for 72 h under Ar. The suspension was cooled to room temperature and then it was filtered. The silica gel was washed by CHCl<sub>3</sub>, acetone, and saturated NaHCO<sub>3</sub> aq. To the filtrate was added CHCl<sub>3</sub> and washed with saturated NaHCO<sub>3</sub> aq three times and H<sub>2</sub>O three times. The organic layer was dried over Na<sub>2</sub>SO<sub>4</sub> and evaporated in vacuo. The product was analyzed by MALDI-TOF mass spectroscopy to confirm that <sup>18</sup>O-labeled porphyrin **2** was obtained.

## 3.8. Acid catalyzed reaction of porphyrin 2 in the presence of SiO<sub>2</sub> gel in EtOH or ${\rm H_2}^{18}{\rm O}$

Porphyrin **2** (3.72 mg) was dissolved in CHCl<sub>3</sub> (5 mL), and silica gel (50 mg), which had been dried at 100 °C for 1 h in vacuo, was added to the CHCl<sub>3</sub> solution. Evaporation of the CHCl<sub>3</sub> gave silica gel with porphyrin **2** deposited on the surface. Under Ar, the **2** physisorbed on SiO<sub>2</sub> gel was stirred in 0.1 M HCl in EtOH (50 mL) at 50 °C for 18 h or in 0.1 M H<sub>2</sub><sup>18</sup>O (8 mL) at 30 °C for 24 h. After the suspension was cooled to room temperature, it was filtered. The silica gel was washed with CHCl<sub>3</sub> and washed with saturated NaHCO<sub>3</sub> aq. To the filtrate was added CHCl<sub>3</sub> and washed with saturated NaHCO<sub>3</sub> aq three times and H<sub>2</sub>O three times. The organic layer was dried over Na<sub>2</sub>SO<sub>4</sub> and evaporated in vacuo. The product was characterized by MALDI-TOF mass spectroscopy.

## 3.9. Acid catalyzed reaction of porphyrin 2 in the absence of $SiO_2$ gel in EtOH

Porphyrin **2** (3.72 mg) was dissolved in 0.1 M HCl in EtOH (50 mL) and the solution was stirred at 50 °C for 18 h under Ar. It was cooled to room temperature, followed by adding CHCl<sub>3</sub> (50 mL). The organic layer was washed with saturated NaHCO<sub>3</sub> aq three times and H<sub>2</sub>O three times. The organic layer was dried over Na<sub>2</sub>SO<sub>4</sub> and the solvents were evaporated in vacuo. The product was characterized by MALDI-TOF mass spectroscopy.

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#### 3.10. Synthesis of porphyrins 1–3

#### See Supplementary data.

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#### Supplementary data

Synthesis of porphyrins 1-3 and spectroscopic data for 1-3 are available. Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.tet.2014.05.007.

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