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Tris(3-hydroxypropyl)methyl as a stable linker for porphyrin monolayer on silicate glass

Nao Furuta, Tadashi Mizutani *

Department of Molecular Chemistry and Biochemistry, Faculty of Science and Engineering, Doshisha University, Kyotanabe, Kyoto 610-0321, Japan
Center for Nanoscience Research, Doshisha University, Kyotanabe, Kyoto 610-0321, Japan

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ABSTRACT

To develop a stable organic–inorganic interface, we investigated kinetics of acid hydrolysis of monolayers of various porphyrins prepared by the condensation reaction of hydroxyporphyrin with silanol groups on the surface of silicate glass. The half-lives of the monolayers attached through a 5-hydroxypentyl linker, a tris(hydroxymethyl)methyl linker, and a tris(3-hydroxypropyl)methyl linker in 1 M HCl at 50 °C were 182 min, 27 min and 460 min, respectively, indicating that tris(3-hydroxypropyl)methyl appended porphyrin formed a stable monolayer. To understand the stability of the monolayers, we performed molecular modeling studies. Molecular orbital calculations indicated that the flexible trimethylene spacer facilitates multiple bonding of porphyrin to silicate surface, while the tris(hydroxymethyl)methyl linker was rigid and only one OH group can form silyl ester linkage. The remaining OH groups may function as a catalytic group in acid hydrolysis. Attachment of long alkyl chains to porphyrin also improved the hydrolytic stability of the monolayer, where the hydrolysis rate constant was ten times smaller than that of porphyrin without long alkyl groups.

1. Introduction

Interface between organic active layer and inorganic surface [1–4] plays an important role in essential functions of molecular electronic devices [5–8] and mechanical hybrid materials [9]. Therefore construction of chemically inert interface has been required to obtain stable and durable materials. Self-assembled monolayer formation of semiconductive organic molecules such as porphyrin on metal oxides attracts interest recently [10–12]. There are a number of studies on the use of alkoxysilanes as a coupling reagent to functionalize silicate surface [13,14]. One of the problems of the use of alkoxysilane as a coupling agent is the side reactions such as polymerization of alkoxysilane on the surface of silicate glass [15–18]. Therefore water content during alkoxysilane deposition is crucial for film quality. Another approach is to use the reaction of organophosphonic acid/ester with metal salts and metal oxides [19–21]. PO–metal ionocovalent bonds are stable particularly for metal cations of high oxidation states.

We have been investigating the organic–inorganic interface formation through covalent bonding formed between alcohol and silanol. It is well-known that condensation of alcohol with silanol on the surface of silicate glass occurs at elevated temperatures [22]. The monolayer formed is stable under ambient conditions, while it is hydrolyzed to give the starting alcohol in boiling water [23]. By using the condensation of alcohol and silanol, side reactions such as polymerization of silane coupling reagents can be avoided. Alcohols are ubiquitous and generally stable compounds and a variety of alcohols are available.

Previously we reported that tetrahydroxyporphyrin **1** and its derivative, tetraacetoxyporphyrin **1a**, reacted with silicate glass to form a monolayer of porphyrin on the silicate glass surface [24]. Spin-coated film of **1** on silicate glass was heated at 160 °C to allow the condensation reaction to occur between the hydroxy groups of **1** and silanol groups of silicate glass followed by washing with pyridine to obtain monolayer of **1** on silicate glass. Tetrahydroxyporphyrin **1** reacted with silicate glass faster than tetraacetoxyporphyrin **1a**. In both cases, the reaction occurs across the solid–solid interface because the reaction proceeded well below the melting points of the porphyrins.

We report herein two strategies to improve hydrolytic stability of the monolayer. Firstly, a tris(3-hydroxypropyl)methyl linkage, bishomotris, afforded a hydrolytically stable monolayer against acid hydrolysis. Secondly, hydrophobic alkyl groups on the porphyrin protected the monolayer against acid hydrolysis. We revealed that the number of hydroxy groups, their relative positions, the distance of them, and auxiliary alkyl groups on the porphyrin are controlling factors of the hydrolytic stability of the porphyrin monolayers.

2. Experimental details

2.1. Instrumentation

^{1}H and ^{13}C nuclear magnetic resonance (NMR) spectra were recorded on a JEOL JNM-ECX DELTA spectrometer using tetramethylsilane as an

* Corresponding author. Tel.: +81 774 65 6623; fax: +81 774 65 6794.
E-mail address: tmizutan@mail.doshisha.ac.jp (T. Mizutani).

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internal reference (0 ppm). Matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectra were obtained with a Brucker Autoflex Speed mass spectrometer. UV–visible spectra were obtained with a Perkin-Elmer Lambda 950 spectrophotometer. Spin-coating on a silicate glass was performed using a Mikasa MS-A 100 spin-coater. A hot stage Mettler-Toledo FP82HT was used for heat treatment of the spin-coated film. A silicate glass was prepared by splitting Matunami 76 × 26 mm borosilicate slide glass almost evenly into three pieces.

2.2. Syntheses of porphyrins 1–7

Porphyrin **1** was prepared by a reported procedure [24] and porphyrins **2**–**7** were synthesized according to Schemes 1–5. Porphyrins **2**, **3**, **6** and **7** were soluble in $CHCl_3$ and toluene, while porphyrins **1**, **4** and **5** were sparingly soluble in them. They were, however, well soluble in pyridine.

2.2.1. General experimental methods

CH_2Cl_2 was dried over CaH_2 and distilled. NaOMe was prepared by adding Na metal to MeOH, and the solution was transferred to a reaction mixture.

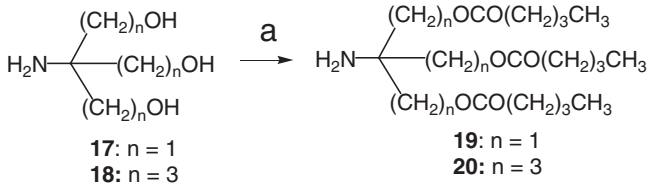
2.2.2. Synthesis of porphyrin 2

*2.2.2.1. 5,10-Bis(4-acetoxyphenyl)-15,20-diphenylporphyrin (**8**), 5-(4-acetoxyphenyl)-10,15,20-triphenylporphyrin (**9**), and 5,15-bis(4-acetoxyphenyl)-10,20-diphenylporphyrin (**10**).* 4-Acetoxybenzaldehyde (3.72 mL, 0.027 mol) and benzaldehyde (2.72 mL, 0.027 mol) were dissolved in propionic acid (225 mL) in a 500 mL three-necked flask and the solution was refluxed. Pyrrole (3.72 mL, 0.054 mol) was slowly added to the refluxed solution and the mixture was refluxed for 30 min in dark. After the reaction mixture was cooled to room temperature, the solvent was evaporated under reduced pressure. **8**, **9** and **10** were separated by silica gel column chromatography eluted with CH_2Cl_2:hexane (3:1). Further purification by silica gel column chromatography using CH_2Cl_2:hexane (2:1) yielded 487 mg (5.4%) of **9** followed by silica gel chromatography using CH_2Cl_2:hexane (3:1) gave 350 mg (3.6%) of **8** and 293 mg (3.0%) of **10**.

8: ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = −2.80 (s, 2H; NH), 2.49 (s, 6H; $-OCOCH_3$), 7.50 (d, J = 8.25 Hz, 4H; 5,10-phenylene H-3′), 7.73–7.80 (m, 6H; 15,20-phenyl H-3′, H-4′), 8.20–8.23 (m, 8H; 5,10-phenylene H-2′ and 15,20-phenyl H-2′), 8.85 (overlapped two singlets and two doublets, 8H; pyrrole-βH); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 21.4, 118.9, 119.8, 120.4, 126.7, 127.8, 131.0 (br), 134.5, 135.3, 139.7, 142.1, 150.6, 169.5 ppm; MS (MALDI-TOF): m/z = 730 $[M]^+$ (calcd. for $C_{48}H_{34}N_4O_4$ m/z = 730).

9: ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = −2.78 (s, 2H; NH), 2.49 (s, 3H; $-OCOCH_3$), 7.50 (d, J = 7.95 Hz, 2H; 5-phenylene H-3′), 7.73–7.80 (m, 9H; 10,15,20-phenyl H-3′, H-4′), 8.20–8.23 (m, 8H; 5-phenylene H-2′ and 10,15,20-phenyl H-2′), 8.84–8.86 (m, 8H; pyrrole-βH); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 21.4, 118.9, 119.8, 120.2, 120.3, 126.7, 127.7, 130.9 (br), 134.5, 135.3, 139.7, 142.1, 150.6, 169.5 ppm; MS (MALDI-TOF): m/z = 672 $[M]^+$ (calcd. for $C_{46}H_{32}N_4O_2$ m/z = 672).

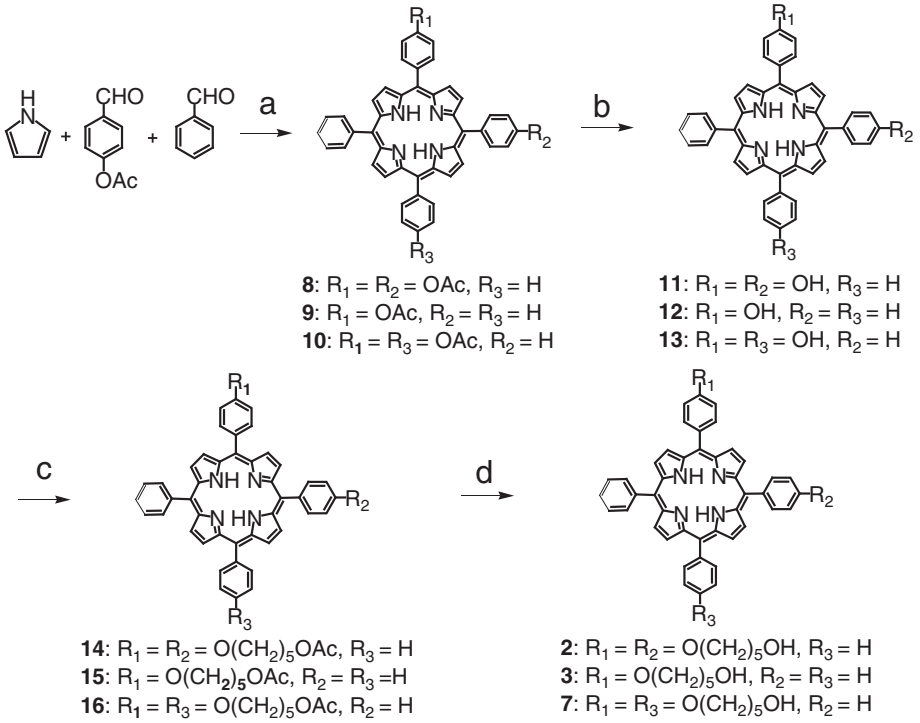
10: ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = −2.80 (s, 2H; NH), 2.49 (s, 6H; $-OCOCH_3$), 7.50 (d, J = 8.00 Hz, 4H; 5,15-phenylene H-3′), 7.73–7.80 (m, 6H; 10,20-phenyl H-3′, H-4′), 8.20–8.22 (m, 8H; 5,15-phenylene H-2′and 10,20-phenyl H-2′), 8.85 (d, J = 4.70 Hz, 4H; pyrrole-βH), 8.86 (d, J = 4.70 Hz, 4H; pyrrole-βH); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 21.4, 118.9, 119.8, 120.3, 126.7, 127.8, 131.3 (br), 134.6, 135.3, 139.7, 142.0, 150.6, 169.6 ppm; MS (MALDI-TOF): m/z = 730 $[M]^+$ (calcd. for $C_{48}H_{34}N_4O_4$ m/z = 730).



17: n = 1
18: n = 3

19: n = 1
20: n = 3

Scheme 2. Syntheses of **19** and **20**. Reagents and conditions: (*a*) valeric acid, *p*-toluenesulfonic acid, toluene, reflux.



8: $R_1 = R_2 = OAc$, $R_3 = H$
9: $R_1 = OAc$, $R_2 = R_3 = H$
10: $R_1 = R_3 = OAc$, $R_2 = H$

11: $R_1 = R_2 = OH$, $R_3 = H$
12: $R_1 = OH$, $R_2 = R_3 = H$
13: $R_1 = R_3 = OH$, $R_2 = H$

14: $R_1 = R_2 = O(CH_2)_5OAc$, $R_3 = H$
15: $R_1 = O(CH_2)_5OAc$, $R_2 = R_3 = H$
16: $R_1 = R_3 = O(CH_2)_5OAc$, $R_2 = H$

2: $R_1 = R_2 = O(CH_2)_5OH$, $R_3 = H$
3: $R_1 = O(CH_2)_5OH$, $R_2 = R_3 = H$
7: $R_1 = R_3 = O(CH_2)_5OH$, $R_2 = H$

Scheme 1. Syntheses of porphyrins **2**, **3** and **7**. Reagents and conditions: (*a*) propionic acid, reflux; (*b*) NaOMe, THF, reflux; (*c*) $Br(CH_2)_5OAc$, K_2CO_3, 18-crown-6, DMF, 60 °C; (*d*) NaOMe, pyridine, reflux.