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ORIGINAL ARTICLE

Permethylated 6^I-alkenoylamino-6^I-deoxy β-cyclodextrin derivatives as modifiers of photoluminescence sensor response of porous silicon

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Abstract A set of permethylated 6^I-(ω-alkenoyl)-6^I-amino-6^I-deoxy-β-cyclodextrin derivatives with different chain length of the alkenoyl group (used as a spacer) was synthesized. These derivatives were attached by photochemically activated hydrosilylation reaction to the surface of porous silicon. Photoluminescence response of the modified PS to controlled concentrations of various molecules in gas phase revealed strong host-guest interactions between β-cyclodextrin and the detected molecules. The strongest interaction was observed for aromatic molecules, which have the optimal size to fit into the β-cyclodextrin molecular cavity.

Keywords β-cyclodextrin · Photoluminescence · Porous silicon · Chemosensor

Introduction

Cyclodextrins (CDs) are due to their unique complexation properties extensively used as recognition elements of various types of chemosensors. The most frequently studied sensors use fluorescence for detection of organic compounds [1] or metal ions [2]. Porous silicon [3] (PS) is a silicon-based material exhibiting intense visible room temperature photoluminescence (PL). The physico-chemical properties of PS are strongly affected by the state of its surface. Small amounts of various molecules substantially modify PL from PS. Photoluminescence quenching phenomenon can be used for construction of optical sensors of chemical species. In the presence of various amounts of analytes the PL response of PS with covalently bound CD derivatives is expected to be modified due to the host-guest interaction of analyte with CD cavity.

We synthesized β-CD derivatives with spacers of various lengths containing terminal C=C bonds, attached them to the PS surface via photochemically activated hydrosilylation reaction, and measured PL responses to controlled amounts of different types of analytes in gas phase.

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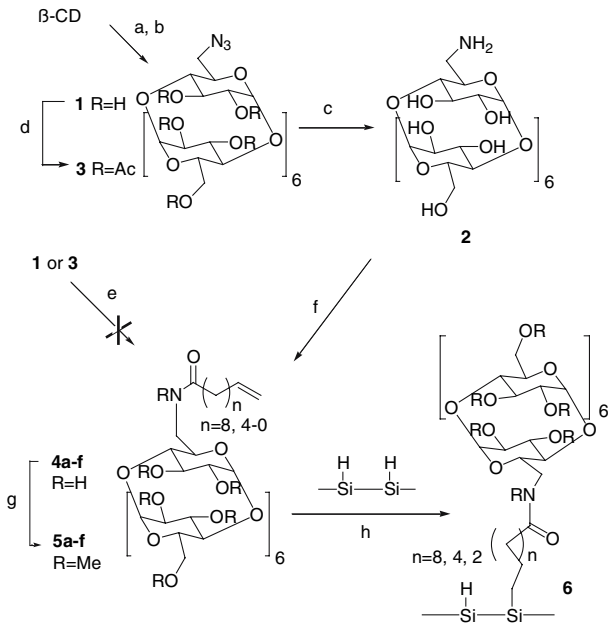
Results and discussion

Synthesis

The synthesis of 6^I-alkenoylamino β-CD derivatives was carried out as described in Scheme 1. The initial attempt to prepare amide bonds by reaction of 6^I-azido-β-CD derivative **1** or its peracetate **3** with corresponding acids in the presence of tributylphosphine or triphenylphosphine was not successful. This type of reaction was described to give good yields for other alkylazides and carboxylic acids [4], but in our case only the intermediate iminophosphoranes can be



Scheme 1 Reagents and conditions: (**a**) 1-(*p*-toluenesulfonyl)-imidazole, NaOH, H_2O (**b**) NaN_3, DMF (**c**) Ph_3P, DMF (**d**) Ac_2O, pyridine (**e**) Ph_3P or Bu_3P, RCO_2H, DMF or toluene (**f**) DIC, HOBt, RCO_2H, DMF (**g**) CH_3I, NaH, DMSO (**h**) CH_2Cl_2, hν

detected. Unusual stability of these intermediates could be explained by steric hindrance caused by bulky CD molecule or by formation of intramolecular inclusion complex of CD with the phosphine substituents.

Nevertheless, the carbodiimide way of amide synthesis using diisopropyl carbodiimide (DIC) and hydroxybenzotrizole (HOBt), which we decided to use later, worked with moderate to good yields. Crude products obtained this way are difficult to purify due to their low solubility, so we purified them in the form of peracetates. Peracetates are soluble in chlorinated solvents and can be easily purified by chromatography on silica gel. During the subsequent deacetylation a small portion of the amine **2** is also formed, but it can be removed by repeated crystallization of the product from water. Permethylation was performed using standard conditions (sodium hydride/methyl iodide in DMSO) in high yields. Permethylated derivatives are more suitable for the surface modification of porous silicon due to their higher stability and solubility.

The permethylated 6^I-alkenoylamino β-CD derivatives were attached to the PS surface via photochemically activated addition of the terminal double bond to the Si–H bonds which are present on the surface of freshly prepared PS. The relative decrease of the band at about 2100 cm^{-1} characteristic for Si–H stretching modes serves for the estimation of the extent of hydrosilylation reaction. As follows from the increase of oxygen backboned Si–H vibration modes at about 2200 cm^{-1}, partial oxidation of PS surface took place as well.

The extent of hydrosilylation reaction was estimated from transmission infrared spectra (not shown, see [5]). From the relative decrease of the band at about 2100 cm^{-1} characteristic for Si–H stretching modes we estimated the relative substitution of the Si–H bonds on the PS surface for the β-CD derivatives with the spacer lengths C_4, C_7 and C_{11} as 4%, 22% and 31%, respectively. These values of surface substitution extent correspond to those found in literature (10–30%) [6], lower extent of substitution for C_4-β-CD can be ascribed to steric effects due to short spacer length.

The strength of host-guest interaction of various analytes with β-CD modified PS is revealed by modification of PL behavior in the presence of precisely controlled amounts of these analytes. In Fig. 1 there are plots of concentration dependence of relative PL quenching for as prepared (Fig. 1a) and functionalized PS (Fig. 1b). For as prepared PS we observed only PL quenching. For β-CD functionalized PS the PL

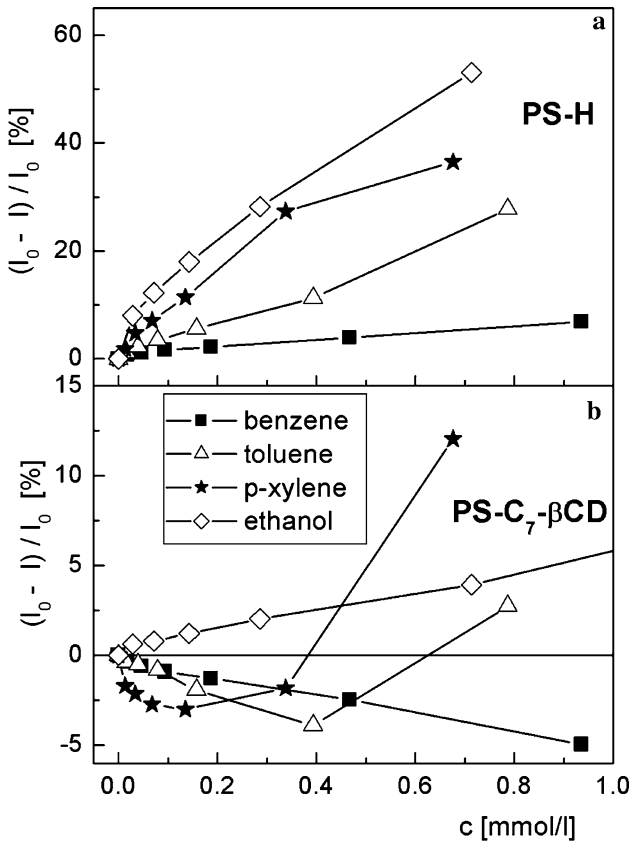


Fig. 1 Concentration dependence of relative photoluminescence quenching $\Delta I/I_0$ for as prepared porous silicon (**a**) and permethyl 6^I-heptanoylamino-6^I-deoxy-β-CD functionalized porous silicon (**b**) of selected analytes in gas phase

response depended on analyte concentration and its complexation strength with β-CD cavity. Quenching responses for aromatic compounds differ substantially from those of aliphatic compounds.

We can see that all aromatic molecules exhibited PL enhancement in low concentration range followed by PL quenching for higher concentrations. The observed behavior can be explained by size-depended interaction of analyte with β-CD cavity. The aromatic molecules strongly interact with β-CD on the PS surface and could not enter into PS matrix. PL enhancement is most probably caused by electron transfer from analyte/β-CD complex to the PS matrix.

Experimental

General information

β-CD was purchased from Wacker-Chemie, cinnamyl bromide and other special chemicals were purchased from Aldrich, silica gel for column chromatography (40–60 μm) from Fluka, TLC plates (DC-Alufolien Kieselgel 60 F_{254}) from Merck and solvents and common reagents from Lachema (Neratovice, Czech Republic). ESI-MS spectral data were collected using the Esquire 3000 mass spectrometer (Bruker Daltonik GmbH, Germany). All NMR experiments were performed on a Varian ^{UNITY}*INOVA* 400 FT spectrometer (^{1}H at 400 MHz, ^{13}C at 100.58 MHz) in deuteriochloroform at 25 °C with tetramethylsilane as the internal standard (in ^{13}C NMR, δ ($CDCl_3$) 77.00 ppm) or in dimethylsulfoxide-d_6 with a few drops of acetic acid-d_4 at 35 °C (in ^{1}H NMR, δ (DMSO-d_6) 2.50 ppm; in ^{13}C NMR, δ (DMSO-d_6) 39.50 ppm). Chemical shift values (δ-scale, ppm) and coupling constants (Hz) in the ^{1}H NMR spectra were obtained by first-order analysis.

6^I-Azido-6^I-deoxy-β-CD **1** and 6^I-amino-6^I-deoxy-β-CD **2** were prepared from 6^I-*O*-*p*-toluenesulfonyl-β-CD [7] using the published procedure [8]. The following chromatography elution mixtures were used: for monosubstituted CD derivatives—*n*-propanol/water/ethyl acetate/conc. aq. ammonia (6/3/1/1); for persubstituted derivatives—chloroform/methanol (50/1–10/1).

Photoluminescence sensor response of porous silicon samples was measured with an adapted luminescence set-up [9]. PL from PS sample was excited with a UV LED (λ = 375 nm, *P*~1 mW cm^{-2}), collected by means of a glass fibre, analyzed in a 20 cm monochromator and detected by a photomultiplier. Signal was processed by a Lock-In amplifier. PS sample was placed in an optode where precisely controlled amounts of analytes were introduced. The injection system operated with nitrogen as a carrier gas.

Per-O-acetyl-6^I-azido-6^I-deoxy-β-CD **3**

Compound **1** (0.5 g, 0.43 mmol) was dissolved in mixture of pyridine (5 mL) and acetic anhydride (2 ml, 21.17 mmol). The reaction mixture was stirred at 110 °C for 4 h. The solvents and reagents were evaporated and the solid 4 × codistilled with toluene (6 mL). The product was purified by chromatography on silica gel (5 g, eluent $CHCl_3$/MeOH 50/1). Yield 0.85 g (98%). M.p. 151–152 °C. ^{1}H-NMR corresponds to lit. [10]. MS(ESI): *m/z* 2022.5 $[M + Na]^+$. Anal. Calc. For $C_{82}H_{109}N_3O_{54}$: C 49.23; H 5.49; N 2.10, Found: C 48.91; H 5.53; N 1.96.

General method for preparation of 6^I-(ω-alkenoylamino)-6^I-deoxy-β-CD 4a-f

Compound **5** (700 mg, 0.62 mmol) was dissolved in dimethyl formamide (DMF) (14 mL). The corresponding alkenecarboxylic acid (0.74 mmol) was added and the reaction mixture cooled down to 0 °C. Then 1-hydroxybenzotriazol (HOBt) (167.0 mg, 1.24 mmol) and *N,N′*-diisopropyl carbodiimide (DIC) (94.9 mg, 1.24 mmol) were added. After 1.5 h at 0 °C the mixture was stirred at rt for 12 h. Reaction mixture was then poured into acetone (500 mL), the formed precipitate isolated by centrifugation and dried at 8.5 Pa, 25 °C for 3 h. The obtained solid was peracetylated and the peracetate purified as described for cmpd. **3** and deacetylated using 4 molar excess of 0.1 M NaOMe v MeOH for 2 h at rt. The mixture was then neutralized using DOWEX 50Wx2 in H^+ cycle (1 g of swelled catex for 1 mL 0.1 M NaOMe). The final product **4** was obtained by repeated (4×) crystallization from hot (90 °C) water (30 mL) followed by drying at 8.5 Pa, 90 °C for 4 h. The product is white crystalline solid.

6^I-Deoxy-6^I-(undec-10-enoylamino)-β-CD **4a**

Yield 179.1 mg (58.4%). M.p. 255–260 °C (decomp.), $[\alpha]_D$ + 117° (c 0.50, DMSO). ^{1}H NMR (400 MHz, d_6-DMSO): δ 7.59 (t, J = 5.2, 1H, NH), 5.83–5.69 (m, 15H), 5.00 (m, 1H), 4.94 (m, 1H), 4.85–4.80 (m, 7H), 4.51–4.44 (m, 6H), 3.69–3.50 (m, 21H), 3.40–3.10 (m, 21H), 2.08–2.05 (m, 2H), 2.03–1.97 (q, J = 6.8, 2H), 1.48–1.41 (m, 2H), 1.35–1.28 (m, 2H), 1.26–1.18 (m, 8H). IR (KBr): 3321 (OH), 1654 (HNC=O), 1155, 1030

(C–O). MS(ESI): *m/z* 1322.3 $[M + Na]^+$. Anal. Calc. For $C_{53}H_{89}NO_{35}\cdot 6H_2O$: C 45.20; H 7.23; N 0.99, Found: C 45.3; H 7.00; N 0.89.

6^I-Deoxy-6^I-(hept-6-enoylamino)-β-CD **4b**

Yield 383.3 mg (70.2%). M.p. 250–253 °C (decomp.), $[\alpha]_D$ + 129° (c 0.50, DMSO). ^{1}H NMR (400 MHz, d_6-DMSO): δ 7.62 (t, J = 5.2, 1H, NH), 5.83–5.69 (m, 15H), 5.00 (m, 1H), 4.93 (m, 1H), 4.85–4.80 (m, 7H), 4.51–4.44 (m, 6H), 3.69–3.50 (m, 21H), 3.40–3.10 (m, 21H), 2.12–2.07 (m, 2H), 2.02–1.96 (q, J = 6.8, 2H), 1.49–1.41 (m, 2H), 1.35–1.27 (m, 2H). IR (KBr): 3339 (OH), 1646 (HNC=O), 1155, 1030 (C–O). MS(ESI): *m/z* 1266.5 $[M + Na]^+$. Anal. Calc. For $C_{49}H_{81}NO_{35}\cdot 6H_2O$: C 43.5; H 6.93; N 1.04, Found: C 43.88; H 6.55; N 1.00.

6^I-Deoxy-6^I-(hex-5-enoylamino)-β-CD **4c**

Yield 291.2 mg (60.6%). M.p. 266–269 °C (decomp.), $[\alpha]_D$ + 140° (c 0.50, DMSO). ^{1}H NMR (400 MHz, d_6-DMSO): δ 7.64 (t, J = 5.2, 1H, NH), 5.83–5.66 (m, 15H), 4.99 (m, 1H), 4.95 (m, 1H), 4.85–4.80 (m, 7H), 4.51–4.44 (m, 6H), 3.69–3.50 (m, 21H), 3.40–3.10 (m, 21H), 2.11–2.07 (t, J = 6.8, 2H), 2.00–1.95 (q, J = 7.2, 2H), 1.58–1.50 (m, 2H). IR (KBr): 3314 (OH), 1651 (HNC=O), 1155, 1032 (C–O). MS(ESI): *m/z* 1252.6 $[M + Na]^+$. Anal. Calc. For $C_{48}H_{79}NO_{35}\cdot 3H_2O$: C 44.89; H 6.69; N 1.09, Found: C 44.81; H 6.53; N 1.02.

6^I-Deoxy-6^I-(pent-4-enoylamino)-β-CD **4d**

Yield 186.5 mg (49.7%). M.p. 239–242 °C (decomp.), $[\alpha]_D$ + 124° (c 0.50, DMSO). ^{1}H NMR (400 MHz, d_6-DMSO): δ 7.69 (t, J = 5.2, 1H, NH), 5.81–5.69 (m, 15H), 5.00 (dd, J = 17.2, 1.6, 1H), 4.92 (dd, J = 10.4, 1.6, 1H), 4.86–4.82 (m, 7H), 4.52–4.44 (m, 6H), 3.69–3.52 (m, 21H), 3.39–3.1 (m, 21H), 2.22–2.16 (m, 4H). IR (KBr): 3281 (OH), 1651 (HNC=O), 1155, 1032 (C–O). MS(ESI): *m/z* 1238.4 $[M + Na]^+$. Anal. Calc. For $C_{47}H_{77}NO_{35}\cdot 6H_2O$: C 42.63; H 6.77; N 1.06, Found: C 42.92; H 6.36; N 1.07.

6^I-Deoxy-6^I-(but-3-enoylamino)-β-CD **4e**

Yield 130.4 mg (59.9%). M.p. 240–243 °C (decomp.), $[\alpha]_D$ + 133° (c 0.50, DMSO). ^{1}H NMR (400 MHz, d_6-DMSO): δ 7.71 (t, J = 5.6, 1H, NH), 5.83–5.68 (m, 15H), 5.07 (m, 1H), 5.02 (m, 1H), 4.86–4.80 (m, 7H), 4.53–4.40 (m, 6H), 3.68–3.50 (m, 21H), 3.40–3.14 (m, 21H), 2.92–2.89 (d, J = 4.8, 2H). IR (KBr): 3291 (OH), 1659 (HNC=O), 1154, 1031 (C–O). MS(ESI): *m/z* 1224.5 $[M + Na]^+$. Anal. Calc. For $C_{46}H_{75}NO_{35}\cdot 3H_2O$: C 43.98; H 6.50; N 1.12, Found: C 43.92; H 6.39; N 1.11.

6^I-Deoxy-6^I-(prop-2-enoylamino)-β-CD **4f**

Yield 80.5mg (65.5%). M.p. 236–239 °C (decomp.), $[\alpha]_D$ + 135° (c 0.50, DMSO). ^{1}H NMR corresponds to lit. [11]. MS(ESI): *m/z* 1210.5 $[M + Na]^+$. Anal. Calc. For $C_{45}H_{73}NO_{35}\cdot 6H_2O$: C 41.70; H 6.61; N 1.08, Found: C 41.32; H 6.21; N 1.06.

General method for preparation of *N*-methyl-per-*O*-methyl-6^I-(ω-alkenoylamino)-6^I-deoxy-β-CDs **5a-f**

Compound **4** (0.08 mmol) was dissolved in dry DMSO (3.5 mL) and to the solution cooled to 10–15 °C sodium hydride (60% dispersion in oil) (257.20 mg, 6.43 mmol) and methyl iodide (913.2 mg, 0.4 mL, 6.43 mmol) were added. After 2 h of cooling the mixture was stirred for another 18 h at rt. Reaction was poured to water (40 mL), acetic acid (1.5 mL) added and the water solution was extracted with toluene (5 × 20 mL). Collected toluene extracts were washed with water (3 × 30 ml), dried $MgSO_4$, filtered through Celite, evaporated, dried for 2 h at 8.5 Pa, 85 °C, purified by chromatography on silica gel (100 g) using elution mixture $CHCl_3$/MeOH 50/1, freeze dried from benzene and then dried for 3 h at 40 °C to yield white powder.

N-Methyl-per-*O*-methyl-6^I-deoxy-6^I-(undec-10-enoylamino)-β-CD **5a**

Yield 93.7 mg (76.4%). M.p. 77–79 °C, $[\alpha]_D$ + 126° (c 0.50, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.80 (m, 1H), 5.19–4.90 (m, 9H), 3.90–3.10 (bm, 105H), 2.40 (m, 2H), 2.03 (m, 2H), 1.60 (m, 2H), 1.36–1.25 (m, 10H). IR ($CHCl_3$): 3006 (=C–H), 1638 (C=O), 1037 (C–O). MS(ESI): *m/z* 1616.9 $[M + Na]^+$. Anal. Calc. For $C_{74}H_{131}NO_{35}$: C 55.73; H 8.26; N 0.88, Found: C 55.95%; H 8.42%; N 0.86%.

N-Methyl-per-*O*-methyl-6^I-deoxy-6^I-(hept-6-enoylamino)-β-CD **5b**

Yield 107.2 mg (86.7%). M.p. 85–86 °C, $[\alpha]_D$ + 144° (c 0.50, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.80 (m, 1H), 5.19–4.92 (m, 9H), 3.90–3.10 (bm, 105H), 2.40 (m, 2H), 2.08 (m, 2H), 1.22 (m, 2H), 1.44 (m, 2H). IR ($CHCl_3$): 3006 (=C–H), 1639 (C=O), 1037 (C–O). MS(ESI): *m/z* 1560.9 $[M + Na]^+$. Anal. Calc. For

$C_{70}H_{123}NO_{35}$: C 54.64; H 8.06; N 0.91, Found: C 54.42; H 8.14; N 0.98.

N-Methyl-per-*O*-methyl-6^{I}-deoxy-6^{I}-(hex-5-enoylamino)-β-CD **5c**

Yield 114.4 mg (92.3%). M.p. 87–89 °C, $[\alpha]_D$ + 140° (c 0.50, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.80 (m, 1H), 5.18–4.85 (m, 9H), 3.90–3.10 (bm, 105H), 2.40 (m, 2H), 2.10 (m, 2H), 1.72 (m, 2H). IR ($CHCl_3$): 3006 (=C–H), 1639 (C=O), 1037 (C–O). MS(ESI): *m/z* 1546.7 $[M + Na]^+$. Anal. Calc. For $C_{69}H_{121}NO_{35}$: C 54.35; H 8.00; N 0.92, Found: C .54.36; H 7.97; N 0.85.

N-Methyl-per-*O*-methyl-6^{I}-deoxy-6^{I}-(pent-4-enoylamino)-β-CD **5d**

Yield 106.0 mg (85.3%). M.p. 87–89 °C, $[\alpha]_D$ + 144° (c 0.50, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.86 (m, 1H), 5.18–4.98 (m, 9H), 3.95–3.15 (bm, 105H), 2.50–2.46 (t, J = 7.6, 2H), 2.40–2.33 (m, 2H). IR ($CHCl_3$): 3006 (=C–H), 1640 (C=O), 1037 (C–O). MS(ESI): *m/z* 1532.8 $[M + Na]^+$. Anal. Calc. For $C_{68}H_{119}NO_{35}$: C 54.06; H 7.94; N 0.93, Found: C 54.07; H 8.04; N 0.84.

N-Methyl-per-*O*-methyl-6^{I}-deoxy-6^{I}-(but-3-enoylamino)-β-CD **5e**

Yield 107.6 mg (86.4%). M.p. 90–93 °C, $[\alpha]_D$ + 146° (c 0.50, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.85 (m, 1H), 5.19–5.01 (m, 9H), 4.05–3.00 (bm, 107H). IR ($CHCl_3$): 3006 (=C–H), 1643 (C=O), 1037 (C–O). MS(ESI): *m/z* 1518.7 $[M + Na]^+$. Anal. Calc. For $C_{67}H_{117}NO_{35}$: C 53.77; H 7.88; N 0.94, Found: C 54.28; H 7.93; N 0.87.

N-Methyl-per-*O*-methyl-6^{I}-deoxy-6^{I}-(prop-2-enoylamino)-β-CD **5f**

Yield 103.8 mg (82.6%). M.p. 90–92 °C, $[\alpha]_D$ + 130° (c 0.50, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.70 (dd, J = 16.8, 10.6, 1H), 6.30 (dd, J = 16.8, 1.9, 1H), 5.64 (dd, J = 10.6, 1.9, 1H), 5.20–5.01 (m, 7H), 4.05–3.01 (bm, 105H). IR ($CHCl_3$): 3006 (=C–H), 1648 (C=O), 1037 (C–O). MS(ESI): *m/z* 1504.8 $[M + Na]^+$. Anal. Calc. For $C_{66}H_{115}NO_{35}$: C 53.47; H 7.82; N 0.94, Found: C 54.01; H 7.92; N 0.93.

Attachment of permethylated 6^{I}-alkenoylamino-6^{I}-deoxy-β-CDs to PS

Macroporous silicon samples were prepared by electrochemical etching of crystalline silicon ((100), boron doped, ρ~10 Ωcm) in a HF(50%): ethanol (96%) = 1:2.5 mixture at current density of 10 mA cm^{-2} for 60 min. After fabrication PS samples were rinsed with ethanol, CH_2Cl_2 and immediately derivatized with permethyl-6^{I}-alkenoylamino-6^{I}-deoxy-β-CD in a 5 wt.% solution in CH_2Cl_2 via photochemically induced hydrosilylation reaction for 1.5 h. For excitation the 365 nm line of 500 W mercury lamp was used.

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