

Synthesis and Characterization of *o*-Hydroxybenzophenone Chromophore Bonded to Aminopropyl Silica Gel Microbeads

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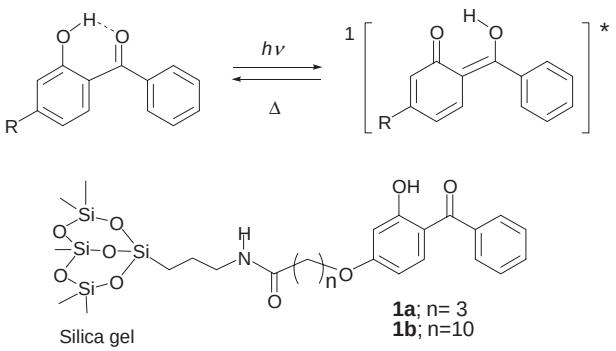
o-Hydroxybenzophenone (Hbp) chromophores were immobilized on 3-aminopropyl silica gel (SiO_2–NH_2) by a reaction of succinimidyl 4-(4-benzoyl-3-hydroxyphenoxy)butanoate (**2a**) and -undecanoate (**2b**) with SiO_2–NH_2 to produce microbeads **1a** and **1b** in 25 and 21% yield, respectively. The bond formation was confirmed by appearance of an absorption at 1550 cm^{-1} due to the N–H bending of the amide bond in the IR spectra of **1a** and **1b**. In order to enhance the thermal and photochemical stabilities, the **1a** and **1b** residual amino group was acetylated by Ac_2O in $CHCl_3$ to produce **7a** and **7b**. Acetylation occurred on the aminopropyl group. However, it did not occur on the phenolic OH group of Hbp from the IR spectra where the absorptions of the bending of the methyl group and the bending of the phenolic OH group appeared at 1375 and 1348 cm^{-1}, respectively. By degradation experiments, it was found that thermal and photochemical stabilities were high in **7a** and **7b** compared with that of **1a** and **1b**.

o-Hydroxybenzophenone (Hbp) chromophores are typical UV absorbents and are normally used in the blending of plastics and UV skin care products.[1–3] Photon energy absorbed by Hbp is effectively converted to thermal energy by an excited-state intramolecular proton transfer (ESIPT) through hydrogen bonding between the *o*-hydroxy and the carbonyl groups.[4,5] Currently Hbp is directly integrated into these materials and causes an undesirable reaction and absorption into the skin. Therefore, it is desirable to isolate Hbp from the other components in the materials. For this purpose, it has been reported that Hbp has been intercalated into layered zinc–aluminum hydroxide.[6–9] Another intercalation of UV absorbents such as triazol and *p*-aminobenzoic acid into anionic clay has been investigated.[10] Silica gel has been widely used as a carrier, because of its large surface area and ability to be immobilized.[11–15] However, few composites of Hbp with silica gel have been reported.[9] Therefore, we intend to immobilize Hbp into porous silica gel in order to avoid direct contact between Hbp and the other components. Here, we have investigated the synthesis and characterization of Hbp **1** immobilized on aminopropyl silica gel microbeads (SiO_2–NH_2) through a covalent bond (Scheme 1).



Scheme 1. Silica gel microbeads **1a** and **1b** having *o*-hydroxybenzophenone chromophores.

Results and Discussion

Immobilization of Hbp on SiO_2–NH_2. Our first efforts were focused on the preparation of succinimidyl ω-(4-benzoyl-3-hydroxyphenoxy)alkanoate **2a** and **2b** in order to immobilize Hbp on SiO_2–NH_2. The reaction of 2,4-dihydroxybenzophenone with alkyl ω-bromoalkanoate produced alkyl (4-benzoyl-3-hydroxyphenoxy)alkanoate **3a** and **3b**, which was converted to **2a** and **2b** by hydrolysis and the subsequent esterification with *N*-hydroxysuccinimide (HOSu) in the presence of dicyclohexylcarbodiimide (DCC) and 4-(dimethylamino)pyridine (DAP) (Scheme 2).

As a model compound to assign the IR spectra of **1** in solid state, *N*-propyl-4-(4-benzoyl-3-hydroxyphenoxy)butanamide (**4a**) was prepared by a reaction of **2a** with propylamine in the presence of imidazole (Im) (Scheme 2). Although SiO_2–NH_2 exhibited strong absorption at 1700–1660, 1300–900, and 800 cm^{-1} in the IR spectra, the characteristic absorptions of **4a** appeared in a region where SiO_2–NH_2 had no absorption (Figure 1). Absorptions (a_1–a_4) at 1544, 1382, 1350, and 701 cm^{-1} can be assigned to an N–H bending of the amide bond (a_1), a C–H bending of methyl group (a_2), a bending mode of OH (a_3), and an out-of-plane bending of aromatic C–H (a_4), respectively (Scheme 3). These characteristic absorptions are listed in Table 1.

The microbeads **1a** and **1b** immobilizing Hbp on SiO_2–NH_2 with intervention of methylene linkage were prepared by a re-

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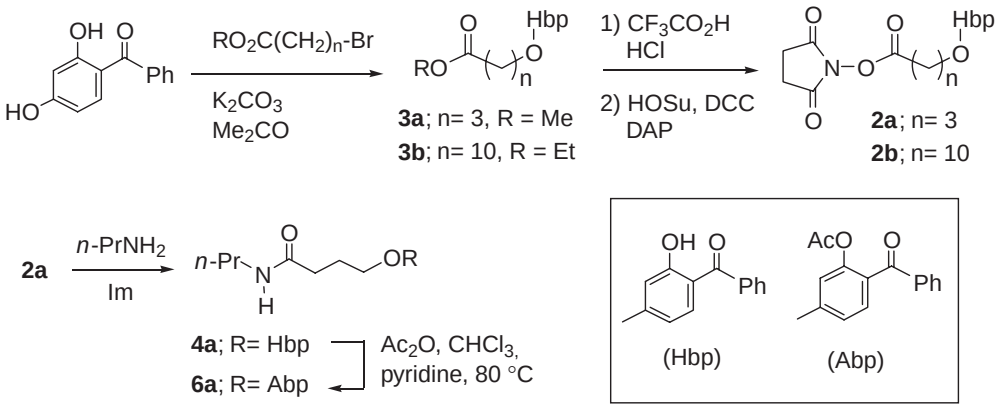
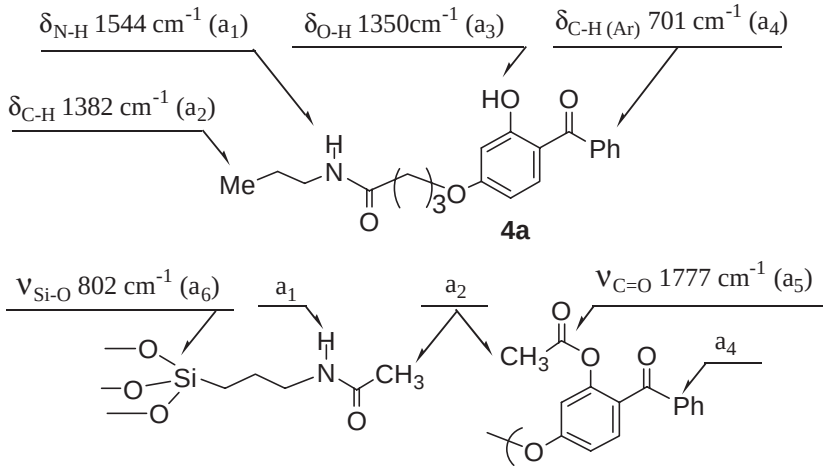


Scheme 2. Preparation of **2a**, **2b** and **4a**: Hbp = 3-hydroxy-4-benzoylphenyl and Abp = 3-acetoxy-4-benzoylphenyl.



Scheme 3. Assignment of IR spectra: a_1 = an N–H bending of amide bond, a_2 = a bending of CH of methyl group, a_3 = a bending of phenolic OH group, a_4 = an out-of-plane bending of aromatic C–H bond, a_5 = a stretching of C=O of acetoxy group, and a_6 = a streching Si–O bond.

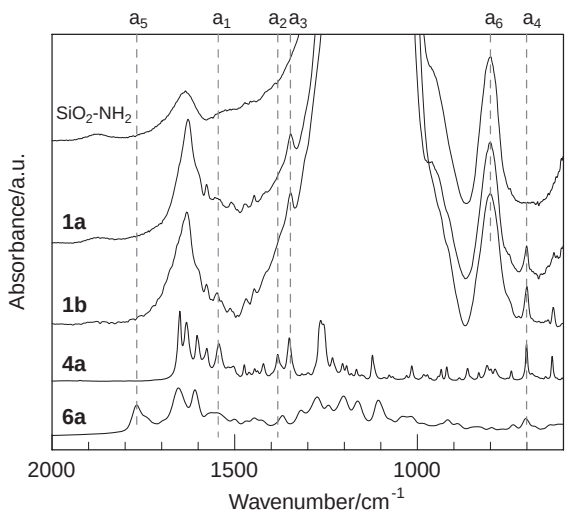


Figure 1. IR spectra of **1a** and **1b** along with those of **4a**, **6a**, and SiO_2–NH_2 in a region 2000–600 cm^{-1}. The N–H bending of amide bond (a_1) appeared at near 1550 cm^{-1}, and the absorptions of the Si–O stretching mode (a_6) and plane bending mode of C–H (a_4) appeared at 802 and 701 cm^{-1}, respectively.

action of **2a** and **2b** with SiO_2–NH_2 (average diameter of beads: 8.3 μm, pore volume: 0.59 $cm^3\,g^{-1}$, the amount of NH_2 (x_a): 1.50 mmol g^{-1}) in the presence of Im for 3 days (Scheme 4). From comparison with a_1 (1544 cm^{-1}) of **4a**, a broad absorption at 1549 cm^{-1} in the IR spectra of **1a** and **1b** (Figure 1) can be assigned to the N–H bending of a newly formed amide bond. Unfortunately, the absorption of amide C=O stretching was not observed because of overlap with the absorptions of SiO_2–NH_2. In order to remove unreacted **2a** and **2b**, the prepared **1a** and **1b** were washed with MeOH to be used for the further experiments after drying under reduced pressure.

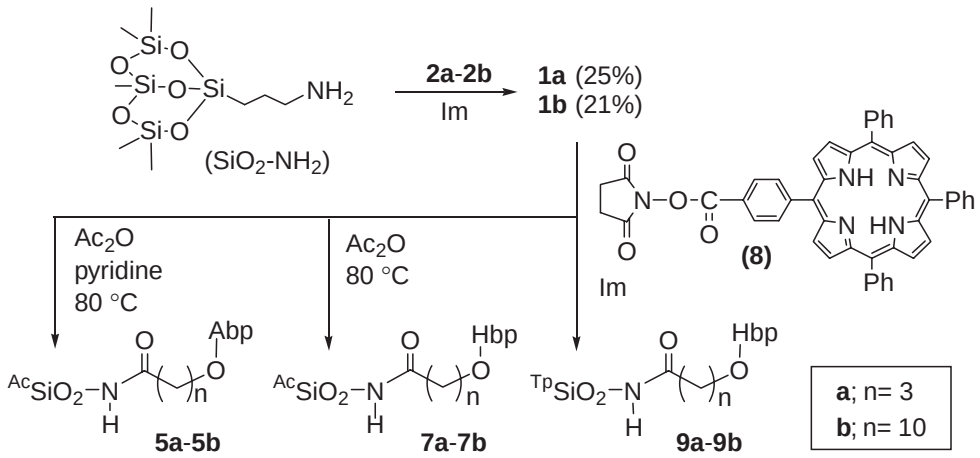
UV absorbents, in general, are required to absorb light from wavelengths shorter than 400 nm.[2,3] The UV spectra of **4a** in MeOH solution showed an absorption maximum (λ_{max}) at 289 and 325 nm with 1.36×10^4 and $8.8 \times 10^3\,M^{-1}\,cm^{-1}$ of molar coefficiency (ε), respectively (Figure 2). The UV spectra of **1a** and **1b** were measured in solid state by a diffuse reflectance method, showing λ_{max} at 289 and 330 nm and 293 and 334 nm, respectively. These showed similar spectra to **4a**, as shown in Table 1. **1a** and **1b** could absorb effectively light wavelengths shorter than 350 nm.

Analysis of the Amounts of Hbp in Microbeads 1a and 1b. In order to determine the amounts of Hbp (x_{hp}/mmol g^{-1}) immobilized in SiO_2–NH_2 using IR absorption spectrophotom-

Table 1. Properties of Microbeads **1**, **5**, and **7**

MB[a)]	x_{hp}/mmol g^{-1} [b)]	IR spectra/cm^{-1} [c)]					λ_{max}/nm[d)]
		a_1	a_2	a_3	a_4	a_5	
1a	0.37 (24.8)	1549	—	1347	701	—	289, 330
1b	0.31 (20.9)	1549	—	1350	702	—	293, 334
5a	0.28 (18.6)	1544	1376	—	702	1777	287
5b	0.30 (19.7)	1551	1375	—	702	1776	288
7a	0.36 (24.2)	1544	1378	1349	701	—	289, 330
7b	0.29 (19.9)	1552	1373	1350	702	1776	293, 334
4a[e)]	—	1544	1382	1350	701	—	289, 325
6a[e)]	—	1549	1369	—	704	1768	284

a) Using SiO_2–NH_2: the amount of NH_2 (x_a) = 1.50 mmol g^{-1}. b) Amount of Hbp (x_{hp}) in mmol g^{-1} immobilized on SiO_2–NH_2. The values in parenthesis are the immobilizing yields (%) based on x_a. c) Characteristic absorption in IR spectra. The assignments of a_1 to a_5 are shown in Scheme 3. d) Absorption maxima in UV spectra. e) Model compounds to assign the IR spectra of microbeads **1**, **5**, and **7**.



Scheme 4. Synthetic routes to microbeads **1**, **5**, **7**, and **9**. The SiO_2–NH, $^{Ac}SiO_2$–NH, and $^{Tp}SiO_2$–NH denote the untreated, the acetylated, and the Tpp-incorporated aminopropyl silica gel moieties, respectively.

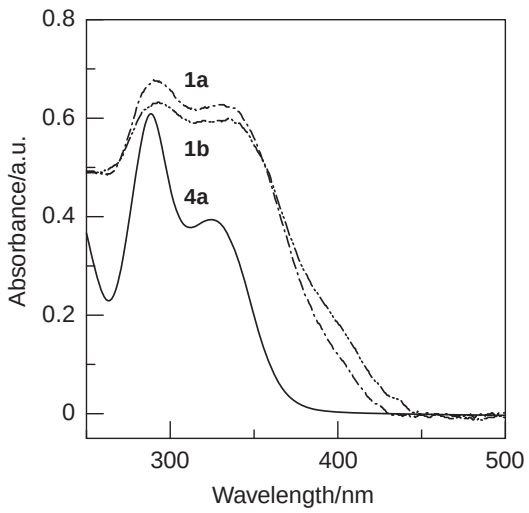


Figure 2. Absorption spectra of the Hbp: **1a** and **1b** measured in solid state by diffuse reflectance along with the absorption spectra **4a** (1.0×10^{-5} mol dm^{-3}) in MeOH solution.

etry, a mixture of **3a** and **3b** with SiO_2–NH_2 was prepared in a given molar ratio (m_3/m_S) where m_3 and m_S denote the molar amounts of **3a**, **3b** and SiO_2–NH_2, respectively. In the IR spectra of the mixed samples, the area ratio of a_4 of the C–H bending at 700 cm^{-1} of **3a** and **3b** to a_6 of the Si–O stretching at 802 cm^{-1} of SiO_2–NH_2 were plotted against m_3/m_S to make calibration lines. Using the calibration line, x_{hp} was determined for **1a** and **1b** which was prepared by reaction of SiO_2–NH_2 with a given amount of **2a** and **2b**. Figure 3 showed that x_{hp} was plotted against the amounts of **2a** added. As the amount of **2a** increased, x_{hp} increased gradually to reach a maximum point at 1.50 mmol g^{-1} of **2a** which was equal to the amount of aminopropyl group (x_a = 1.50 mmol g^{-1}) in untreated SiO_2–NH_2. At the maximum point, 0.37 mmol g^{-1} of x_{hp} was introduced into **1a** (Table 1). This value corresponded to 25% of the immobilization yield ($=100x_{hp}/x_a$) based on x_a. In the case of **2b** with a longer linkage than **2a**, the yield was 21% (x_{hp} = 0.31 mmol g^{-1}). Low yield was probably attributed to the prevention of the OSu group from approaching the aminopropyl group located at a deep level within the SiO_2. This obstruction was caused by an interaction between the phenolic OH group of Hbp and the aminopropyl group in SiO_2. As a consequence, the 1.13

and 1.19 mmol g^{-1} of the amino groups remained in the **1a** and **1b**, respectively.

Acetylation of 1. In general, the amino group is quite damaged under photoirradiation to form colored materials. Therefore, protection of the **1a** and **1b** residual amino group was examined by acetylation. Acetylation was performed with Ac_2O in $CHCl_3$–pyridine at 80 °C to give **5a** and **5b**. Under these conditions it has been confirmed that the amino group of SiO_2–NH_2 was effectively acetylated.[16] Before acetylation, a_3 due to the phenolic OH group apparently appeared at 1350 cm^{-1} in the IR spectra of **1a** and **1b** (Figure 4). In **5a** and **5b**, however, a_3 near 1350 cm^{-1} disappeared. A model compound **4a** was also acetylated under similar conditions to produce *N*-propyl-4-(4-benzoyl-3-acetoxyphenoxy)butanamide (**6a**). From a comparison of **5a** and **5b** with **6a** in IR spectra, the absorptions of **5a** and **5b** were assigned as follows:

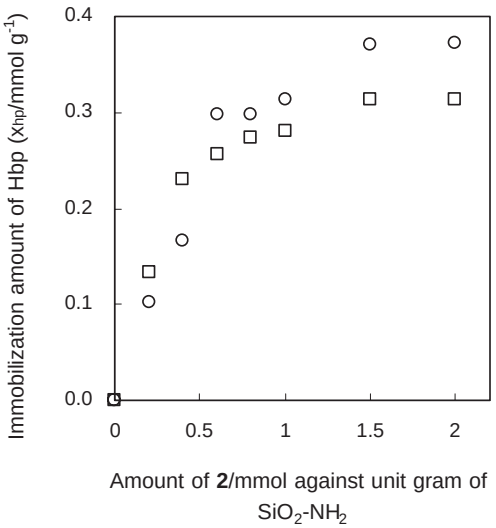


Figure 3. Dependence of the immobilizated amount of Hbp (x_{hp}) in **1** on the amounts of **2a** and **2b** used: **1a** (○) and **1b** (□).

an absorption at 1777 and 1776 cm^{-1} due to C=O stretching of the acetoxy group (a_5), and a C–H bending at 1376 and 1375 cm^{-1} due to the methyl group (a_2). Under the above conditions therefore, acetylation of **1a** and **1b** occurred in both the aminopropyl and the phenolic OH groups.

The presence of a phenolic OH group is requisite for the ESIPT mechanism. Therefore, selective acetylation of only the aminopropyl group was examined. The acetylation of **1a** and **1b** was performed with Ac_2O in $CHCl_3$ at 80 °C to produce acetylated microbeads **7a** and **7b**. In the IR spectra of **7a**, a_2 appeared at 1378 cm^{-1}. Moreover, a_3 of the phenolic OH group at 1349 cm^{-1} remained and a_5 of the acetoxy group near 1780 cm^{-1} hardly appeared (Figure 4). These results showed that the acetylation occurred at mainly the aminopropyl group. In the case of **7b** however, a_5 was considerable (Figure 4B), showing that the phenolic OH group was partially acetylated.

In order to confirm whether the aminopropyl groups were completely acetylated in **7a** and **7b**, they were treated with 5-[4-(succinimidyloxycarbonyl)phenyl]-10,15,20-triphenylporphyrin (**8**) which has been previously used to detect amino groups in SiO_2–NH_2 using fluorescence spectra on a confocal laser-scanning microscope (CLSM).[16] As a reference sample, the microbeads **9a** and **9b** immobilizing 4-(10,15,20-triphenylporphyrinyl)phenyl (Tpp) chromophore on the aminopropyl group was prepared by the reaction of **1a** and **1b** with **8** in the presence of Im (Scheme 4). Similarly **7a** and **7b** was treated by **8** for measurement of the fluorescence spectra by CLSM. The fluorescence of **9a** strongly appeared at 650 nm (Figure 5), but the fluorescence intensity of the **8**-treated **7a** was one twentieth of that of **9a**. This showed that the residual amino groups of **1a** were effectively acetylated by Ac_2O. Similar results were obtained in the case of **7b** (See Supporting Information).

Thermal and Photochemical Stabilities. Prepared Hbp is used in a polymer blend as the UV absorbent.[1,2] During blending, the Hbp is mixed with a melted polymer while being exposed to a softening temperature. Thermal degradations are evaluated using a UV spectrum, since it has been reported that

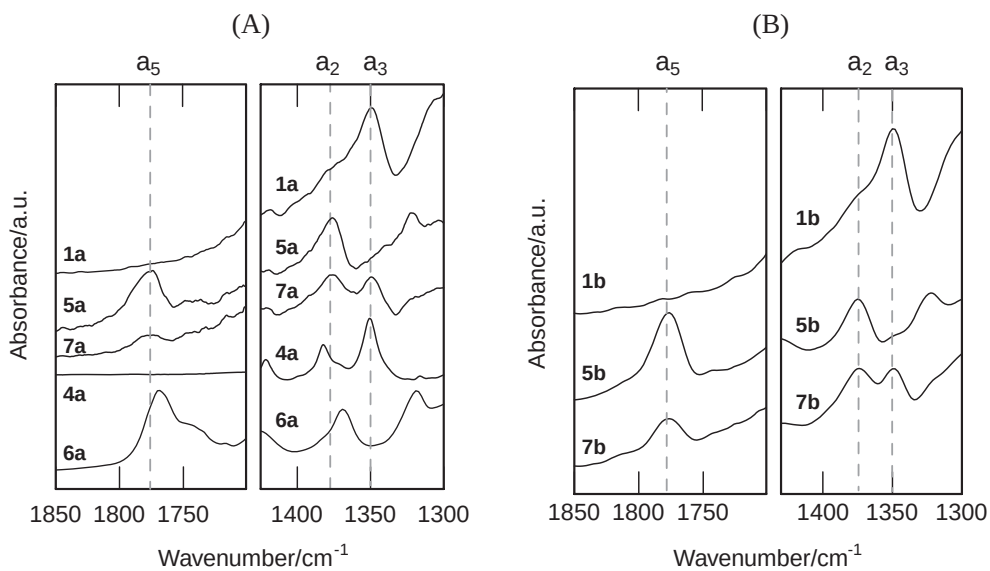


Figure 4. IR spectra in the range of 1850–1700 and 1425–1300 cm^{-1} for (A) **1a**, **5a**, **7a**, **4a**, and **6a**. (B) **1b**, **5b**, and **7b**.

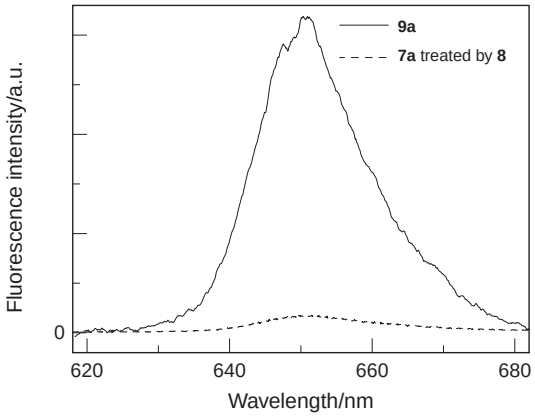


Figure 5. Fluorescence spectra of **7a** treated by **8** (dotted line) in comparison with that of **9a** (solid line).

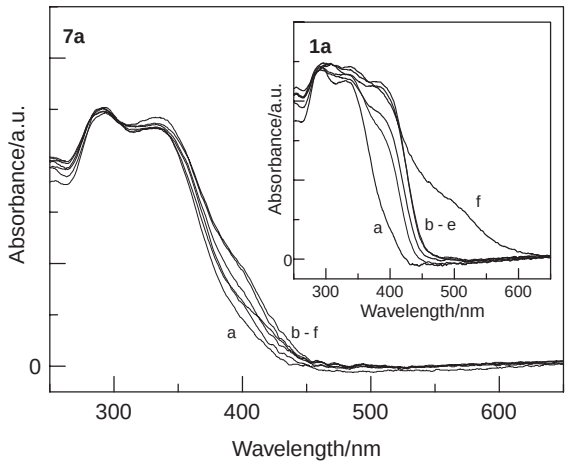


Figure 6. Thermal degradation of **1a** and **7a**. Spectral changes in UV spectra of **7a** after thermal treatment at (b) 50, (c) 100, (d) 150, (e) 200, and (f) 250 °C for 30 min along with (a) the spectra before heating. Inset: the results of the thermal treatment of **1a** were shown.

degradation species of Hbp derivatives appear at a wavelength longer than 400 nm.[8] Therefore, the thermal and photochemical stabilities of **1a**, **1b** and **7a**, **7b** themselves were evaluated using diffuse reflectance UV–visible spectra. Thermal degradations of **1a**, **1b** and **7a**, **7b** were performed in solid state by heating for 30 min under aerated conditions at given temperatures in a range of 50–250 °C.

Figure 6 showed the UV spectra of samples obtained from the thermal treatment of **1a** and **1b**. As the temperature of the thermal treatment increased, the peaks around 400 nm in the UV spectra also gradually increased as a consequence of thermal degradation. In the IR spectra of thermally treated **1a** and **1b**, a new absorption appeared at 1655 cm^{-1} probably due to formation of an imino bond between the carbonyl group of Hbp and the aminopropyl group (See Supporting Information). On the other hand, remarkable spectral change was not observed at all in the UV spectra in the thermal treatment of **7a** and **7b**. Also, the IR spectra were not changed. These results demonstrated that **7a** and **7b** was thermally stable compared with **1a** and **1b**.

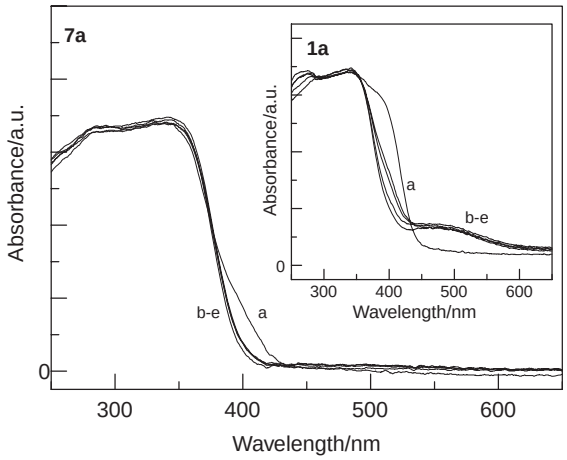


Figure 7. Photochemical degradation of **1a** and **7a**. Spectral change in UV spectra of **7a** after irradiation for a given time: t = (a) 0, (b) 12, (c) 24, (d) 36, and (e) 48 h. Inset: the spectral changes in the photochemical degradation of **1a** are shown.

Photochemical degradations of the Hbp derivatives of **7a** and **1a** in solid state were examined under irradiation >280 nm using a high-pressure mercury lamp through a Pyrex filter for 0–48 h. With increase of irradiation time, new absorption at longer than 500 nm increased in the UV spectra of **1a**, while negligible spectral changes were observed in **7a** and **7b** (Figure 7). Similar results were obtained in the thermal and photochemical degradations of **1b** and **7b** (See Supporting Information).

Also, thermal degradation of **5a** and **5b** was checked by IR spectra. While heating at >200 °C, a_5 due to AcO at 1777 cm^{-1} disappeared and a_3 due to the phenolic OH appeared at 1350 cm^{-1}. Thus, thermal treatment of **5a** and **5b** converted Abp to Hbp to produce **7a** and **7b** (Figure 8).

In conclusion, **7** was the most stable thermally and photochemically among the microbeads tested. Thus, Hbp was successfully immobilized in porous SiO_2 through a covalent bond in order to prevent elution.

Experimental

Instruments. ^1H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were aquired on a Bruker AV 400M spectrometer in $CDCl_3$ solution using $SiMe_4$ as an internal standard. MS was aquired on a Hitachi M2000A. Matrix-assisted laser desorption/ionization mass spectra (MALDI-TOFMS) were measured on a Bruker Daltonics Autoflex II TOF/TOF in the positive ion mode at the Miyazaki Prefectural Industrial Support Foundation. FTIR was measured on a JASCO Herscel FT/IR-300 with a Micro-20 spectrometer. UV–vis spectra of the solutions were obtained on a JASCO V-550 spectrophotometer. Absorption spectra of the solid state were measured by diffuse reflectance on an Ocean Optics HR-2000. Microscopic spectroscopy in the micro-regions was performed using an Olympus FV-300 CLSM equipped with a spectrophotometer (STFL 250, Seki Technotron) linked to the CLSM by an optical fiber.

Preparation of Alkyl *ω*-(4-Benzoyl-3-hydroxyphenoxy)alkanoate (3). As starting materials for the preparation of ethyl 11-(4-benzoyl-3-hydroxyphenoxy)undecanoate (**3b**), ethyl 11-bromoundecanoate was prepared. Ethanol solution (300 mL) containing 11-bromoundecanoic acid (7.96 g, 30.0 mmol), and *p*-toluenesulfonic acid monohydrate (0.50 g) was refluxed with a Dean–Stark trap

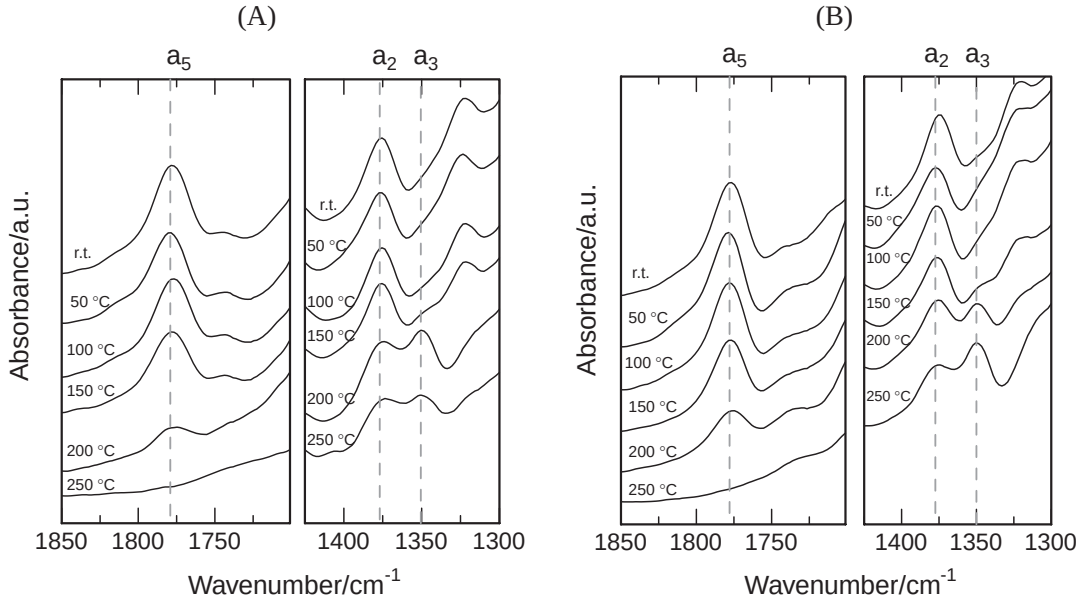


Figure 8. IR spectra in a range of 1850–1700 and 1450–1300 cm^{-1} for the thermal treatment of (A) **5a** and (B) **5b** at a given temperature.

for 8 h. After evaporation, the reaction mixture was washed three times with 100 mL of water and then dried over $MgSO_4$. Purification was performed by silica gel column chromatography using CH_2Cl_2 as eluent to produce ethyl 11-bromoundecanoate as colorless oil (8.48 g). K_2CO_3 (6.22 g, 45.0 mmol) and alkyl ω-bromoalkanoate (15.0 mmol) were added to an acetone solution (100 mL) of 2,4-dihydroxybenzophenone (2.72 g, 15.0 mmol). Then the reaction mixture was stirred at ambient temperature for 3 d in the preparation of **3a** and at 60 °C for 2 d in the preparation of **3b**. The reaction was monitored by TLC. The mixture was filtered and concentrated. Purification was performed using silica gel column chromatography using MeOH–$CHCl_3$ (1:100) as eluent to give **3** as white solid.

Ethyl 11-Bromoundecanoate: Yield 96%. ^{1}H NMR: δ 1.24–1.29 (m, 13H), 1.41 (m, 2H), 1.62 (m, 2H), 1.85 (quint, $J = 7.1$ Hz, 2H), 2.29 (t, $J = 7.6$ Hz, 2H), 3.40 (t, $J = 7.2$ Hz, 2H), 4.12 (q, $J = 7.2$ Hz, 2H); ^{13}C NMR: δ 14.2, 24.9, 28.1, 28.7, 29.0, 29.1, 29.2, 29.3, 32.8, 33.8, 34.3, 60.0, 173.7; IR (neat) 2929, 2854, 1736, 1464, 1371, 1246, 1178, 1036, 723, 563, 420 cm^{-1}.

Methyl 4-(4-Benzoyl-3-hydroxyphenoxy)butanoate (3a): Yield 81%. Mp 72–73 °C. ^{1}H NMR: δ 2.14 (q, $J = 6.73$ Hz, 2H), 2.53 (t, $J = 7.2$ Hz, 2H), 3.70 (s, 3H), 4.08 (t, $J = 6.2$ Hz, 2H), 6.39 (dd, $J_{ortho} = 9.0$ Hz, $J_{meta} = 2.5$ Hz, 1H), 6.50 (d, $J_{meta} = 2.4$ Hz, 1H), 6.59–7.54 (m, 1H), 7.47–7.53 (m, 2H), 7.51 (d, $J_{ortho} = 9.0$ Hz, 1H), 7.46–7.65 (m, 2H), 12.65 (s, 1H); ^{13}C NMR: δ 24.3, 30.4, 51.7, 67.1, 101.7, 107.6, 113.2, 128.3, 128.8, 131.4, 135.3, 138.3, 165.4, 166.3, 173.4, 200.0; IR (KBr) 3506, 3081, 3028, 2958, 1765, 1629, 1578, 1371, 1348, 1267, 1233, 1200, 1117, 1079 cm^{-1}; HRMS Found: 314.1148. Calcd for $C_{18}H_{18}O_5$: 314.1154 [M^+].

Ethyl 11-(4-Benzoyl-3-hydroxyphenoxy)undecanoate (3b): Yield 95%. Mp 54–55 °C. ^{1}H NMR: δ 1.24–1.48 (m, 15H), 1.59–1.65 (m, 2H), 1.80 (quint, $J = 6.8$ Hz, 2H), 2.29 (t, $J = 7.2$ Hz, 2H), 4.01 (t, $J = 6.8$ Hz, 2H), 4.12 (q, $J = 7.2$ Hz, 2H), 6.40 (dd, $J_{ortho} = 8.8$ Hz, $J_{meta} = 2.4$ Hz, 1H), 6.50 (d, $J_{meta} = 2.4$ Hz, 1H), 7.48–7.51 (m, 3H), 7.54–7.56 (m, 1H), 7.62–7.64 (m, 2H), 12.68 (s, 1H); ^{13}C NMR: δ 14.3, 25.0, 25.9, 28.9, 29.1, 29.2, 29.3, 29.3, 29.4, 34.5, 60.1, 68.5, 101.5, 107.8, 113.0, 128.3, 128.8, 131.4, 135.2, 138.3, 165.9, 166.3, 173.9, 198.7; IR (KBr) 2920, 2850, 1726, 1622, 1595, 1574, 1381, 1344, 1263, 1240, 1225, 1203, 1178, 1113, 698, 629 cm^{-1}; HRMS Found: 426.2370. Calcd for $C_{26}H_{34}O_5$: 426.2406 [M^+].

Preparation of ω-(4-Benzoyl-3-hydroxyphenoxy)alkanoic Acid (10). **3** (7.0 mmol) was dissolved into concd HCl (130 mL) and trifluoroacetic acid (130 mL). After 20 h, the mixture was extracted with $CHCl_3$ (350 mL). The organic layer was separated and washed again with water until the pH was approximately 6–7 and then dried over $MgSO_4$. After evaporation, the crude precipitate was purified by repeated recrystallization from EtOH–hexane (10:1) to create **10** as a white solid.

4-(4-Benzoyl-3-hydroxyphenoxy)butanoic Acid (10a): Yield 94%. Mp 111–113 °C. ^{1}H NMR (DMSO-d_6): δ 1.96 (q, $J = 6.9$ Hz, 2H), 2.39 (t, $J = 7.3$ Hz, 2H), 4.08 (t, $J = 6.4$ Hz, 2H), 6.55 (dd, $J_{ortho} = 8.8$ Hz, $J_{meta} = 2.5$ Hz, 1H), 6.56 (d, $J_{meta} = 2.3$ Hz, 1H), 7.43 (d, $J_{ortho} = 8.8$ Hz, 2H), 7.52–7.58 (m, 2H), 7.61–7.67 (m, 2H), 12.00 (s, 1H), 12.17 (s, 1H); ^{13}C NMR (DMSO-d_6): δ 24.2, 30.1, 67.4, 101.9, 107.5, 114.1, 128.6, 128.9, 132.0, 134.7, 138.0, 163.9, 164.8, 174.2, 198.8; IR (KBr) 3609, 3059, 2925, 1747, 1628, 1598, 1576, 1504, 1348, 1284, 1253, 1226, 1194, 1171, 1119, 695 cm^{-1}; HRMS Found: 300.1009. Calcd for $C_{17}H_{16}O_5$: 300.0998 [M^+].

11-(4-Benzoyl-3-hydroxyphenoxy)undecanoic Acid (10b): Yield 99%. Mp 79–81 °C. ^{1}H NMR (DMSO-d_6): δ 1.29–1.54 (m, 14H), 1.75 (quint, $J = 6.9$ Hz, 2H), 2.22 (t, $J = 7.6$ Hz, 2H), 4.08 (t, $J = 6.4$ Hz, 2H), 6.56 (dd, $J_{ortho} = 8.8$ Hz, $J_{meta} = 2.4$ Hz, 1H), 6.59 (d, $J_{meta} = 2.4$ Hz, 1H), 7.46 (d, $J_{ortho} = 8.8$ Hz, 1H), 7.58–7.61 (m, 2H), 7.66–7.69 (m, 3H), 11.99 (s, 1H), 12.09 (s, 1H); ^{13}C NMR (DMSO-d_6): δ 24.4, 25.4, 28.4, 28.5, 28.6, 28.7, 28.8, 28.9, 33.6, 68.1, 101.6, 107.4, 113.7, 128.4, 128.7, 131.8, 134.6, 137.8, 163.9, 164.9, 174.4, 198.7; IR (KBr) 2918, 2852, 1714, 1639, 1576, 1512, 1354, 1286, 1192, 1167, 1132, 1014, 850, 789, 698, 650 cm^{-1}; HRMS Found: 398.2075. Calcd for $C_{24}H_{30}O_5$: 398.2093 [M^+].

Preparation of Succinimidyl ω-(4-Benzoyl-3-hydroxyphenoxy)alkanoate (2). CH_2Cl_2 (20 mL) containing **10** (0.5 mmol), HOSu (0.07 g, 0.6 mmol), DCC (0.12 g, 0.6 mmol), and DAP

(0.06 g, 0.5 mmol) was stirred for 12 h at ambient temperature. The reaction was monitored by TLC. The urea derived from DCC was removed by filtration and the solution was concentrated. The mixture was washed with acetic acid and then dried over $MgSO_4$. After evaporation, the crude product was purified by silica gel column chromatography using MeOH–$CHCl_3$ (1:100) as eluents and repeated recrystallization from EtOH–hexane (1:10) to produce **2** as a white solid.

Succinimidyl 4-(4-Benzoyl-3-hydroxyphenoxy)butanoate (2a): Yield 86%. Mp 124–127 °C. ^{1}H NMR: δ 2.26 (q, $J = 6.6$ Hz, 2H), 2.85 (s, 4H), 2.86 (t, $J = 7.2$ Hz, 2H), 4.14 (t, $J = 6.0$ Hz, 2H), 6.43 (dd, $J_{ortho} = 9.0$ Hz, $J_{meta} = 2.5$ Hz, 1H), 6.52 (d, $J_{meta} = 2.4$ Hz, 1H), 7.51 (d, $J_{ortho} = 9.0$ Hz, 1H), 7.46–7.53 (m, 2H), 7.54–7.59 (m, 1H), 7.61–7.66 (m, 2H), 12.65 (s, 1H); ^{13}C NMR: δ 24.3, 25.8, 27.8, 66.5, 101.9, 107.8, 113.5, 128.5, 129.0, 131.6, 135.5, 138.4, 165.3, 166.4, 168.3, 169.2, 200.2; IR (KBr) 3059, 2947, 1819, 1786, 1743, 1639, 1373, 1350, 1265, 1217, 1117, 1076, 1043, 700, 650, 629 cm^{-1}; MALDI-TOFMS Found: 398.3. Calcd for $C_{21}H_{18}NO_7$: 397.1 [$M - H^+$].

Succinimidyl 11-(4-Benzoyl-3-hydroxyphenoxy)undecanoate (2b): Yield 66%. Mp 72–76 °C. ^{1}H NMR: δ 1.32–1.50 (m, 12H), 1.73–1.79 (m, 4H), 2.60 (t, $J = 7.6$ Hz, 2H), 2.83 (s, 4H), 4.02 (t, $J = 6.8$ Hz, 2H), 6.40 (dd, $J_{ortho} = 9.0$ Hz, $J_{meta} = 2.5$ Hz, 1H), 6.51 (d, $J_{meta} = 2.4$ Hz, 1H), 7.48–7.51 (m, 3H), 7.54–7.58 (m, 1H), 7.62–7.64 (m, 2H), 12.69 (s, 1H); ^{13}C NMR: δ 24.3, 25.8, 27.8, 66.5, 101.9, 107.8, 113.5, 128.5, 129.0, 131.6, 135.5, 138.4, 165.3, 166.4, 168.3, 169.2, 200.2; IR (KBr) 2922, 2852, 1809, 1784, 1736, 1630, 1599, 1576, 1377, 1350, 1265, 1204, 1122, 1070, 810, 700, 629 cm^{-1}; MALDI-TOFMS Found: 495.3. Calcd for $C_{28}H_{33}NO_7$: 495.3 [M^+].

Preparation of *N*-Propyl-4-(4-benzoyl-3-hydroxyphenoxy)-butanamide Derivatives 4a and 6a. **2a** (0.20 g, 0.50 mmol) was dissolved in dichloromethane (30 mL). Then propylamine (0.03 g, 0.50 mmol) and Im (0.03 g, 0.50 mmol) were added. The reaction mixture was stirred for 10 min at ambient temperature. The reaction was monitored by TLC. After evaporation, the reaction mixture was purified by silica gel column chromatography using MeOH–$CHCl_3$ (1:20) as eluents and recrystallization from EtOH–hexane (1:10) to give **4a** as white solid (0.14 g, 0.45 mmol). The acetylation was performed by the reaction of **4a** (0.27 mmol) with Ac_2O (1 mL) in $CHCl_3$–pyridine (2:1; 1.5 mL) at 80 °C for 6 h to give **6a**.

***N*-Propyl-4-(4-benzoyl-3-hydroxyphenoxy)butanamide (4a):** Yield 90%. Mp 93 °C. ^{1}H NMR: δ 0.91 (t, $J = 7.4$ Hz, 3H), 1.52 (sext, $J = 7.2$ Hz, 2H), 2.16 (quint, $J = 6.6$ Hz, 2H), 2.37 (t, $J = 7.1$ Hz, 2H), 3.23 (q, $J = 7.1$ Hz, 2H), 4.08 (t, $J = 6.0$ Hz, 2H), 5.45 (brs, 1H), 6.40 (dd, $J_{ortho} = 9.0$ Hz, $J_{meta} = 2.5$ Hz, 1H), 6.50 (d, $J = 2.5$ Hz, 1H), 7.47–7.52 (m, 2H), 7.50 (d, $J = 8.8$ Hz, 2H), 7.54–7.59 (m, 1H), 7.62–7.64 (m, 2H), 12.64 (s, 1H); ^{13}C NMR: δ 13.3, 22.9, 24.9, 32.8, 41.3, 67.4, 101.8, 107.4, 113.2, 128.3, 128.8, 131.5, 135.3, 138.3, 165.5, 166.2, 171.8, 200.0; IR (KBr) 3337, 3083, 2967, 2931, 1650, 1632, 1603, 1576, 1544, 1474, 1445, 1421, 1382, 1350, 1265, 1232, 1205, 1194, 1123, 701, 631, 539 cm^{-1}.

***N*-Propyl-4-(4-benzoyl-3-acetoxyphenoxy)butanamide (6a):** Yield 75%. Oil. ^{1}H NMR: δ 0.91 (t, $J = 7.4$ Hz, 3H), 1.52 (sext, $J = 7.2$ Hz, 2H), 1.97 (s, 3H), 2.16 (q, $J = 6.4$ Hz, 2H), 2.40 (t, $J = 7.0$ Hz, 2H), 3.23 (q, $J = 6.8$ Hz, 2H), 4.08 (t, $J = 5.9$ Hz, 2H), 5.81 (brs, 1H), 6.69 (d, $J = 2.3$ Hz, 1H), 6.81 (dd, $J_{ortho} = 8.6$ Hz, $J_{meta} = 2.3$ Hz, 1H), 7.42–7.46 (m, 2H), 7.52 (d, $J = 8.6$ Hz, 2H), 7.54–7.58 (m, 1H), 7.70–7.73 (m, 2H); ^{13}C NMR: δ 11.3, 20.5, 22.9, 25.0, 32.7, 41.3, 67.5, 109.5, 111.6, 123.7, 128.3, 129.6, 132.5, 132.9, 138.4, 150.9, 162.4, 169.2, 172.0, 194.2; IR (neat) 3298, 2964, 2935, 2875, 1770, 1651, 1612, 1566, 1549, 1200, 1163, 1109, 702, 638 cm^{-1}.

General Procedure for the Preparation of 1a and 1b. SiO_2–NH_2 (average diameter of beads: 8.3 μm, pore volume: 0.59 cm^3 g^{-1}, x_a: 1.50 mmol g^{-1}) was purchased from Fuji Sylisia Chemical. SiO_2–NH_2 (1.0 g) and Im (0.10 g, 1.5 mmol) were added to a **2a** and **2b** (1.5 mmol) dichloromethane solution (2.0 mL). The reaction mixture was gently agitated for 3 d at ambient temperature. Then **1a** and **1b** was separated by filtration and washed thoroughly with $CHCl_3$ and MeOH.

The Degradation of 1 and 7. **1** and **7** were set in a thin layer between two Pyrex glass plates. The photodegradation test was performed in solid state >280 nm with irradiation from a high-pressure mercury lamp under aerated conditions. Thermal degradation of **1** and **7** were performed in an oven set at a given temperature under aerated conditions.

Supporting Information

The following data are included: the fluorescence spectra of **7b** treated by **8**, the UV spectra in the thermal and photochemical degradations of **1b** and **7b**, and IR spectra in a range of 1800–1500 cm^{-1} for the thermal treatment of **1a** and **1b** at a given temperature. This material is available free of charge on the web at http://www.csj.jp/journals/bcsj/.

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