Selective adsorption of biladien-*ab*-one and zinc biladien-*ab*-one to mesoporous silica

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ABSTRACT

The adsorption of linear tetrapyrroles and porphyrins to mesoporous silicas with pore diameters of 2.3, 2.7, 4.0, and 7.0 nm from a benzene solution was investigated. As linear tetrapyrroles, 1,15,21,22-tetrahydro-19-benzoyl-5,10,15-triphenyl-15-hydroxybilin-1-one (biladien-*ab*-one, **1a**), its zinc complexes (**2** and **3**), 1,15,21,22-tetrahydro-19-(4-hexyloxybenzoyl)-5,10,15-tri(4-hexyloxy)phenyl-15-hydroxybilin-1-one (C6-biladienone, **1b**), 1,15,21,22-tetrahydro-19-(4-nonyloxybenzoyl)-5,10,15-tri(4-nonyloxy)phenyl-15-hydroxybilin-1-one (C9-biladienone, **1c**), 1,15, 21,22-tetrahydro-19-(4-dodecyloxybenzoyl)-5,10,15-tri(4-dodecyloxy)phenyl-15-hydroxybilin-1-one (C12-biladienone, **1d**), and 1,15,21,22-tetrahydro-19-(3,5-didodecyloxybenzoyl)-5,10,15-tri(3, 5-di-dodecyloxy)phenyl-15-hydroxybilin-1-one (**1e**) were employed. As porphyrins, 5,10,15,20-tetraphenylporphyrin (**4a**) and 5,10,15,20-tetra(4-methoxyphenyl)porphyrin (**4b**) were used. The isothermal adsorption curves were determined, showing that the amount of adsorption decreases in the order, **1a** > **1b** > **1c** > **1d** > **2**, while neither **1e**, **4a**, nor **4b** were adsorbed to mesoporous silicas. Mesoporous silica with the diameter of 4.0 nm adsorbed the largest amounts of biladienones. The adsorption was not observed in THF, acetone or ethanol. Neither **1c** nor **1d** was adsorbed to mesoporous silica with the pore diameter of 2.3 nm. These results indicate that the absorption is driven by polar interactions such as hydrogen bonding, and size exclusion effects are observed even for a molecule with flexible alkyl chains. The amount of adsorbed biladienone increased as the temperature was raised from 25 to 35 °C. The adsorption of biladien-*ab*-ones at 80 °C caused dehydration of biladien-*ab*-one to bilatrien-*abc*-one due to the acidity of the mesoporous silica.

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1. Introduction

Functionalization of inorganic surface by organic molecules is an area of intense investigations [1–6]. Self-assemblying of π-conjugated molecules displays unique photochemical [7] and electrochemical properties [8]. The adsorption of chlorophyll *a* to mesoporous silica has been investigated for construction of artificial photosynthetic systems [9]. The adsorption of various molecules such as organic compounds [10], coordination complexes [11] and proteins [12] to mesoporous silica has been studied. For the adsorption of proteins, electrostatic interactions play important roles [13]. The study of adsorption of organic molecules is relatively rare, with representative investigations employing ionic dyes [14] and alkylphenols [15] in aqueous solutions. To elucidate the interactions between the adsorbent and the molecule for the liquid-phase adsorption, use of organic solvent is preferred since the detailed investigations into the solvent effects will give useful information. Kuroda et al. reported that Taxol was adsorbed to FSM® in dichloromethane and toluene while not adsorbed in methanol and acetone [16]. Devoisselle et al. reported that the amounts of adsorption of ibuprofen (p-$(CH_3)_2CHCH_2C_6H_4CH(CH_3)COOH$) to MCM 41 depend on the solvents and increase with decreasing solvent polarity in the order: DMA < DMSO < DMF < ethanol < hexane [17]. These studies indicate that the solvent plays an important role in the thermodynamics of adsorption, and polar interactions such as hydrogen bonding is one of the driving forces of adsorption. Due to the limited data, however, we do not deduce any structural requirement of the adsorbed molecule for incorporation into the nanospace of mesoporous silicas. Understanding of adsorption mechanism would help prepare functional materials with mesoporous silica and also help use it for chromatographic applications.

Cyclic tetrapyrroles and linear tetrapyrroles are important compounds as light-absorbing dyes in photosynthesis and light-sensor systems of plants [18]. These tetrapyrrolic dyes have analogous electronic structures to chlorophyll and phycocyanobilin which are major components of the photosynthetic dye assembly. Control of supramolecular structures of these dyes is still the subjects of active investigations [7a]. We report in this paper systematic studies on the liquid-phase adsorption of tetrapyrrolic dyes, such as porphyrins, biladien-*ab*-ones, and zinc biladien-*ab*-ones. Biladienoes were prepared from tetraarylporphyrins using a coupled oxidation reaction [19]. Zinc biladienones were prepared from the free base biladienones by the reaction with zinc acetate [20]. We prepared biladienones bearing hexyloxy, nonyloxy, and decyloxy groups in the para position of the phenyl groups, and two decyloxyl groups in the meta position of the phenyl groups to explore any effects of alkyl chains on adsorption and self-assembly of the dyes.

2. Experimental

Nitrogen adsorption/desorption isotherms were measured using Autosorb-1 (Quantachrome) at the temperature of liquid nitrogen (77 K). Sample preparation included degassing at 90 °C for 1 h. Specific surface areas and pore size distributions were calculated using Brunauer–Emmett–Teller (BET) and Barrett–Joyner–Halenda (BJH) method [21], respectively.

Porphyrins **4a** and **4b** were prepared according to the published procedures [22]. Biladienones **1b** and **1c** were prepared using a similar route to **1d** [20]. Mesoporous silicas FSM®-14, FSM®-16, TMPS-4, and TMPS-7, were prepared according to the literature using cationic surfactants as a template [23].

2.1. 3,5-Didodecyloxybenzaldehyde

A solution of 3,5-dihydroxybenzaldehyde (5 g), dodecyl bromide (90 mL), 18-crown-6 (9.5 g) and K_2CO_3 (50 g) in DMF (400 mL) was heated at 60 °C for 3 h. After cooled to room temperature, K_2CO_3 was removed by filtration, and the filtrate was evaporated. The residue was taken up in CH_2Cl_2-water and the organic layer was dried over Na_2SO_4. The product was purified by column chromatography (SiO$_2$, hexane:ethyl acetate = 9:1). Yield 6.8 g (40%). ^{1}H NMR δ 9.88 (s, 1H), 6.97 (s, 2H), 6.69 (s, 1H), 3.97 (t, 4H), 1.78 (m, 4H), 1.25 (m, 36H), 0.87 (t, 6H). FAB-MS *m/z* 475 (MH).

2.2. 5,10,15,20-Tetrakis(3,5-didodecyloxyphenyl)porphyrin

To a refluxed propionic acid (300 mL) was added pyrrole (5 mL) and 3,5-didodecylbenzaldehyde (6.8 g) and the reaction mixture was refluxed for 30 min. The solvent was evaporated *in vacuo* and the residue was dissolved in a small amount of CHCl$_3$. Reprecipitation with methanol and further purification by SiO$_2$ column chromatography (hexane:CH$_2$Cl$_2$ = 7:3) afforded 0.40 g (5.7%) of the porphyrin. ^{1}H NMR δ 8.93 (s, 8H), 7.35 (d, 8H), 6.87 (t, 8H), 4.10 (t, 8H), 1.85 (m, 8H), 1.21–1.47 (m, 8H), 0.83 (t, 64H), −2.87 (s, 2H). FAB-MS *m/z* 2089 (MH).

2.3. [5,10,15,20-Tetrakis(3,5-didodecyloxyphenyl)porphyrinato]iron(III) chloride

A solution of the porphyrin (0.405 g), FeCl$_2$ · 4H$_2$O (0.83 g) in DMF (50 mL) was heated at 160 °C for 5 h. After cooled to room temperature, CHCl$_3$ was added, and washed with water and with 0.1 M HCl. The organic layer was dried over Na$_2$SO$_4$ and the CHCl$_3$ was evaporated to obtain violet crystals, 0.39 g (94%).

2.4. 1,15,21,22-Tetrahydro-19-(3,5-didodecyloxybenzoyl)-5,10,15-tri(3,5-didodecyloxy)phenyl-15-hydroxybilin-1-one (*1e*)

A solution of iron porphyrin (0.394 g), pyridine (24 mL), ascorbic acid (2 g) in CHCl$_3$ (200 mL) was stirred with O$_2$ bubbling for 30 min at room temperature. Ascorbic acid was removed by filtration and the filtrate was washed with water several times. To the CHCl$_3$ solution was added 150 mL of 1 M HCl and the solution was stirred at room temperature for 1 h. The organic layer was washed with 1 M HCl and with water. Purification with SiO$_2$ column chromatography (CH$_2$Cl$_2$) afforded **1e** (0.11 g, 29%). ^{1}H NMR (CDCl$_3$) δ 12.46 (br s, 1H, N$_{24}$–H), 10.76 (br s, 1H, N$_{21}$-H), 9.89 (br s, 1H, N$_{23}$–H), 6.97 (s, 2H, 2′-H of 20-phenyl), 6.96 (d, 2H, H-3), 6.87 (d, 1H), 6.86 (d, 1H, H-17), 6.85 (d, 1H), 6.66 (s, 2H, H-2′ of 15-phenyl), 6.65 (d, 1H), 6.61 (s, 1H, H-4′ of 20-phenyl), 6.58 (s, 1H, H-4′ of 15-phenyl), 6.55 (s, 1H, H-4′ of 5-phenyl), 6.50 (s, 1H, H-4′ of 10-phenyl), 6.48 (s, 2H, H-2′ of 10-phenyl), 6.42 (d, 2H), 6.37 (d, 1H, H-18), 6.34 (s, 1H, OH), 6.19–6.16 (m, 3H, H-2, H-2′ of 5-phenyl), 3.96–3.93 (m, 16H), 1.77–1.75 (m, 16H), 1.29–1.25 (m, 144H), 0.87 (t, 24H). FAB-MS *m/z* 2120 (M-OH).

2.5. Adsorption isotherm

Biladien-*ab*-ones, zinc biladien-*ab*-ones or tetraphenylporphyrin was dissolved in 3 mL of benzene (0.3–5 mM), and mesoporous silica (10 mg) was added. After the suspension was stirred for 3 h at 25 °C or 35 °C, the concentration of dyes in supernatant was determined by UV–visible spectroscopy. The amounts of dyes adsorbed to mesoporous silica were calculated from the decrease in concentration of the dye before and after the mesoporous silica addition. The adsorption isotherm was analyzed on the basis of the Langmuir adsorption model

$$x = \frac{x_{max}ac}{1 + ac} \tag{1}$$

where x is the amount of adsorbed biladien-*ab*-one at equilibrium (mg/10 mg of silica), a is the adsorption constant (mM^{-1}), x_{max} is the maximum adsorption capacity (mg/10 mg of silica), and c is the equilibrium biladien-*ab*-one concentration (mM).

2.6. Rate of adsorption

The rate of adsorption was determined by following the UV–visible spectral changes of a solution of 4×10^{-5} M of biladien-*ab*-one in benzene and mesoporous silica at every five minutes. The kinetic parameters were obtained using the Langmuir adsorption model [24]. The rate of adsorption of biladienone to the mesoporous silica was analyzed based on the following first order rate equation

$$-\frac{dc}{dt} = kc \tag{2}$$

where c is the concentration of biladienone at time t and k is the rate constant.

2.7. Characterization of biladienone-mesoporous silica hybrid

Diffuse-reflection UV–visible spectra of FSM®-16 adsorbing **1a**, **2** and **3** were recorded.

3. Results and discussion

3.1. Synthesis

Chart 1 shows the structure of the dyes employed in the adsorption experiments to mesoporous silica. Biladienones **1a**–**e** were prepared by the coupled oxidation of the corresponding iron por-