Immobilization of chlorophyll derivatives possessing ethoxysilyl groups into mesoporous silica and energy transfer between chromophores in mesopores

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Introduction

In the natural photosynthesis, chlorophylls play a key role in converting solar energy to chemical energy. To mimic the highly efficient ET systems, considerable efforts have been directed toward the preparation of donor/acceptor (D/A) systems immobilized in various media (Tweet *et al.* 1964; Colbow 1973). On the other hand, we have recently proposed the use of FSM-type mesoporous silica as an adsorbent of Chls (Furukawa *et al.* 2000; Murata *et al.* 2001), because silica-pigment complexes without solvents are suitable for simple handling. However, our previous studies revealed that the surface silanol groups on FSM denatured incorporated chlorophyllous pigments (Murata *et al.* 2001). Although the surface modification with diols is an effective approach to suppress denaturation of Chls
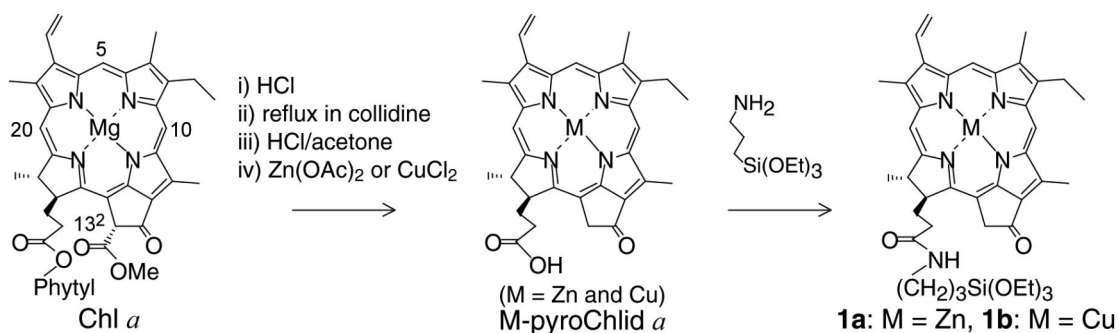

Fig. 1. Synthetic procedure of metallo-substituted pyrochlorophyllide *a* 3-triethoxysilyl propylamide (M = Zn for **1a**; Cu for **1b**).

(Murata *et al.* 2001), the plane of chlorin macrocycles should probably lie down on the organic groups (Furukawa *et al.* 2000). Moreover, the arrangement between neighboring chromophores in mesopores was hardly controlled by simple liquid-phase adsorption (Murata *et al.* 2001), being not suited for the efficient ET. These considerations prompted us to develop an effective immobilization method for the highly efficient ET. In the present study Chl derivatives possessing triethoxysilyl groups (Fig. 1) were synthesized for the first time and grafted on mesoporous silica. We used a pair of Zn-chlorin and Cu-chlorin as the
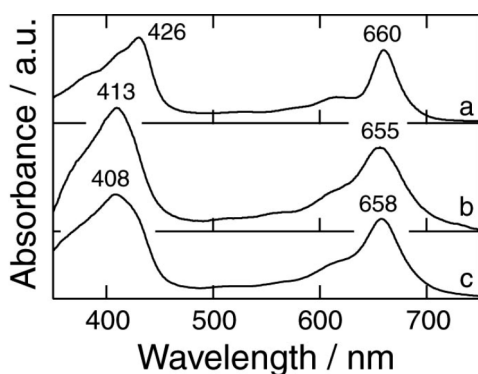
Fig. 2. The diffuse reflectance visible absorption spectra of APTES-FSM/**1a** (a), APTES-FSM/**1b** (b), and APTES-FSM/**1a**–**1b** (c, D/A = 1/2).
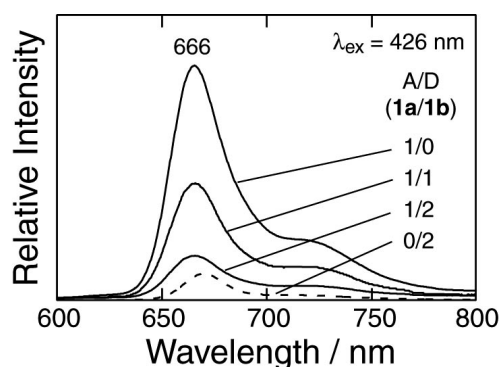
Fig. 3. The fluorescence emission spectra of APTES-FSM/**1** powders.

donor–quencher pair, because the fluorescence of Zn-chlorin should be quenched by Cu-chlorin.

Materials and methods

The synthetic procedure of FSM was reported previously (Murata *et al.* 2001). The X-ray diffraction (XRD) pattern of FSM showed the main peak at a *d*-spacing of 4.0 nm and the sample had the BET surface area of 1000 m^2 g^{-1}. The amidation of Chl is as follows: zinc C13^2-demethoxycarbonyl-chlorophyllide *a* (Zn-pyroChlid *a*, Tamiaki *et al.* 1996) was added to a mixture of APTES, 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide (EDC), dimethylaminopyridinium tosylate in dry CH$_2$Cl$_2$ (Chrisstoffels *et al.* 2000). The mixture was stirred for 12 h under N$_2$ at room temperature. A crude compound was purified by a preparative normal-phase HPLC (eluent: ethyl acetate/hexane/acetone = 6/1/3).

   A prescribed amount of compound **1** (50—200 nmol of **1a**, **1b**, or the mixture of **1a** and **1b**) and APTES (4.3 mmol), a modifier to suppress denaturation of Chls, were dissolved in dry CH$_2$Cl$_2$ (2 mL). Then FSM powders (0.1 g), preheated at 150 °C for 3 h under vacuum, were dispersed in the solution of **1** and APTES. The mixtures were stirred at room temperature for 24 h in the dark (*i.e.* under mild conditions) to prevent denaturation of chlorin macrocycles, centrifuged, washed with acetone, and dried under reduced pressure.

Results and Discussion

Triethoxysilyl groups were introduced to M-pyroChlid *a* (M = Zn and Cu) by the amidation reaction, and the NMR peaks of new triethoxysilyl-moieties appeared: *e.g.*, 3.62 and 1.07 ppm (Si(O*Et*)$_3$ for **1a**). The FAB-mass spectra clearly confirmed the formation of the desired compounds **1** (ex. 799.3 for **1a**). Because the triethoxysilyl and C13^2 groups are out of the π-electronic system, the absorption spectral shapes of **1a** (**1b**) and Zn-Chl *a* (Cu-Chl *a*) in acetone were almost identical to each other.

   The formation of new Si–O–Si bondings between APTES and Si–OH groups on FSM was confirmed by solid-state ^{29}Si NMR; the T^1, T^2 and T^3 environments appeared in the region from –50 to –70 ppm. The decrease in the number of Si–OH groups after silylation was also supported by the decrease in the IR absorption in the O–H stretching region (*ca.* 3690 cm^{-1}). The degree of grafting was, however, smaller than that of FSM silylated with APTES by refluxing (Kimura *et al.* 1999), which is ascribed to the milder reaction conditions.

Because the amounts of **1** introduced were much lower than that of APTES molecules, there is no spectroscopic evidence whether the compounds **1** form Si–O–Si bondings with FSM. All APTES-FSM/**1** powders were scarcely bleached by repeated washing with acetone, while Chls incorporated into FSM by simple liquid-phase adsorption were easily desorbed from mesopores by washing with acetone (Furukawa *et al.* 2000; Murata *et al.* 2001), indicating that the

Fig. 4. Schematic representation of ET in the mesopores and TEM image of FSM.

compounds **1** were grafted onto the surface of mesopores as well as APTES-FSM. The mesostructure was also retained after silylation because the XRD patterns of APTES-FSM/**1** were quite similar to that of bare FSM.

Fig. 2 depicts the diffuse reflectance visible absorption spectra of **1a** and **1b** grafted on FSM. The Soret and Q_y absorption peaks of **1a** onto FSM were located at 426 and 660 nm, respectively. The full width at half-maximum of the Q_y band (*ca.* 720 cm^{-1}) was broadened to a lesser extent than that of FSM/Zn-Chl *a* (*ca.* 1100 cm^{-1}, Furukawa *et al.* 2000), indicating that **1a** was well-dispersed in mesopores. Compound **1b** gave the Soret and Q_y absorption peaks at 413 and 655 nm, respectively. In the co-adsorbed state (APTES-FSM/**1a**–**1b**), the absorption band in the Soret region appeared at 408 nm with a small shoulder at 430 nm, which indicates that this absorption spectrum was roughly interpreted as a summation of those of **1a** and **1b**. This also means that the individual chromophores scarcely exhibit the specific interactions in the ground states within the mesopores.

The emission peaks of **1a** and **1b** on APTES-FSM were located at 666 and 670 nm, respectively (Fig. 3). The emission intensity of **1b** was much weaker than that of **1a** in APTES-FSM due to the small quantum yield of Cu-Chl. The spectral overlap between the donor emission and quencher absorption bands is also relatively large, which indicates that the Förster type donor/acceptor (quencher) ET should occur (Förster 1965). In the co-adsorption systems the emission intensity of **1a** was decreased with an increase in the amount of **1b**. The ET efficiency from **1a** to **1b** is approximately estimated by the decrease in the emission area in the Q_y region in comparison with that of APTES-FSM/**1a** complex (90% for D/A = 1/2; 50% for 1/1). Based on the pore volume and pore size of APTES-FSM, the distance between neighboring chromophores (R_0) is calculated to be *ca.* 12 nm. It is of interest that this efficiency is much higher than the ET efficiency between Chl *b* and Chl *a* in diol modified FSM (70% for D/A = 1/10, Murata *et al.* 2001), though the pigment concentration and R_0 in mesopores are basically same. Taking into account the trend that the highly efficient ET is obtained in this grafted systems in comparison to the conventional adsorption methods, the planes of chromophores are probably perpendicular to the silica walls in the mesopores (Fig. 4). This suggests that the interactions between chlorin macrocycle and silica walls are relatively small, and this may be the reason why APTES-FSM/**1a** complexes gave a sharper absorption band in comparison with FSM/Zn-Chl *a*, for which Zn-Chl *a* was incorporated into bare FSM by liquid-phase adsorption (Furukawa *et al.* 2000).
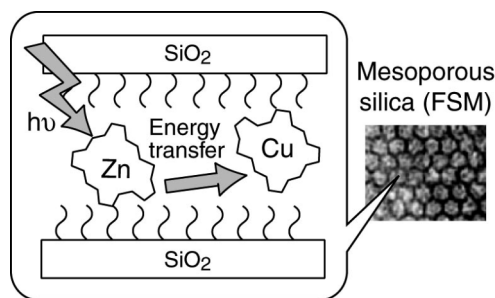
Acknowledgments

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