Adsorption of Zinc-Metallated Chlorophyllous Pigments on FSM-Type Mesoporous Silica

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The spectroscopic properties of zinc chlorophyll (Zn-Chl) derivatives within FSM-type mesoporous silica were examined. Visible absorption and resonance Raman spectroscopies suggest that chlorophyllous pigments are successfully incorporated and form hydrogen bonds to silanol groups on silica.

Photosynthesis is a series of physicochemical processes to convert solar energy into chemical free energy available for living organisms. Recently, for the ultimate goal to establish artificial photoredox systems for solar energy conversion and storage, immobilization of chlorophyll (Chl, Figure 1) and porphyrin derivatives on the surface of several porous materials have been studied.[1,2] Ordered mesoporous silicas possessing uniform mesopores, high surface areas and adsorption capacities are expected for useful adsorbents[3,4] because of their high thermal stability and mechanical strength in comparison with organic compounds.

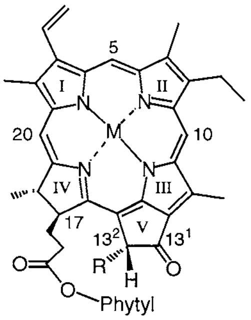

Figure 1. Molecular structure of chlorophyllous pigments. Chl *a*, M = Mg, R = COOMe; Zn-Chl *a*, M = Zn, R = COOMe; Zn-pyroChl *a*, M = Zn, R = H; pheophytin *a*, M = 2H, R = COOMe.

However, these chlorophyllous pigments are easily denatured by heat or solvent treatments such as pheophytinization (demetallation) and allomerization (oxidation of ring V).[5] Almost all of Chls were actually pheophytinized by adsorption on bare mesoporous silicas owing to acidic silanol groups on silica surface.[2] Murata et al. reported that the surface Si–OH groups of FSM-type mesoporous silicas (C_{18}FSM) were esterified with 1,4-butanediol, resulting in the suppression of pheophytinization of Chl *a* during the adsorption on the surface modified C_{18}FSM.[2] However, this way is hampered by difficulties in convenient adsorption of Chls on silica surface because of (i) relatively long reaction time, (ii) possible irregularity of the surface modification and (iii) lowering of the amount of adsorbates owing to the decrease of pore diameter. This has prompted us to improve an efficient adsorption method of chlorophyllous pigments on mesoporous silica. The reason why Zn-Chl *a* and Zn-pyroChl *a* (Zn-C13^2-demethoxycarbonyl-Chl *a*) were selected is as follows. The substitution of the central metal from Mg to Zn increases the chemical (acidic) stability with the similarity of their physicochemical properties,[6] and Zn-Chls have been used for the artificial photosynthesis.[7] Moreover, pyrolyzed Chl does not allomerize under the conditions that lead to extensive allomerization of Chl *a*.[8]

This is the first report dealing with a convenient method for the adsorption of Chl derivatives on C_{18}FSM without any surface modification. The properties of C_{18}FSM/Zn-Chl compounds were characterized by visible absorption, fluorescence emission and resonance Raman (RR) spectroscopies. The integrities of the adsorbed pigments extracted from C_{18}FSMs were also analyzed by normal phase high-performance liquid chromatography (HPLC).[6]

Siliceous C_{18}FSM was synthesized according to the method reported previously.[2] The X-ray diffraction (XRD) pattern (d_{100} = 4.0 nm) and the BET specific surface area (950 m^2 g^{-1}) were similar to those reported in Reference 2. The preparation of Zn-Chl derivatives was described previously.[6] A prescribed amount of Zn-Chls (50–1000 nmol) were dissolved in 2 mL dry CH_2Cl_2, and then 0.1 g of C_{18}FSM was dispersed in the Zn-Chls solutions. The mixtures were stirred at room temperature for 3 h under dark, and the suspensions were centrifuged to remove supernatants and dried under reduced pressure. Supernatants of C_{18}FSM/Zn-Chl mixtures were almost colorless liquid after stirring for 3 h, which suggests that the most part of Zn-Chls were introduced into the pore system of C_{18}FSMs. No alteration of the mesostructure during the adsorption process occurred because the powder XRD patterns of C_{18}FSM/Zn-Chls were quite similar to those of bare C_{18}FSM (d_{100} = 4.0 nm).

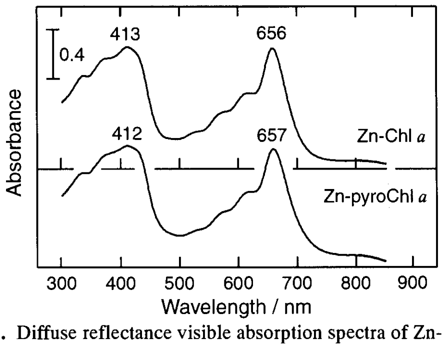

Figure 2. Diffuse reflectance visible absorption spectra of Zn-Chl *a* (top) and Zn-pyroChl *a* (bottom) on C_{18}FSM.

Figure 2 (top) depicts the diffuse reflectance visible absorption spectrum of C_{18}FSM/Zn-Chl *a* (1000 nmol of Zn-Chl *a* was initially adsorbed). The Soret and Q_y absorption peaks of Zn-Chl *a* on C_{18}FSM were located at 413 and 656 nm, respectively. The spectral shape of Zn-Chl *a* was reminiscent of the absorption spectrum of Chl *a* on C_{18}FSM modified with 1,4-butanediol.[2] The spectral shape of C_{18}FSM/Zn-Chl *a* was also independent of the amounts of encapsulated pigments. The fluorescence emission peak in the Q_y region appeared at 660 nm (λ_{ex} = 430 nm), indicating that the absorption of green-colored C_{18}FSM was attributed to incorporated pigments. The number of Zn-Chl in the unit surface area is roughly estimated to be 3×10^{-4}—5×10^{-3} molecules nm^{-2}, based on the adsorbed amounts of Zn-Chls and the BET surface area. It should be noted that the Soret peak of C_{18}FSM/Zn-Chl *a* was located at a shorter wavelength by 14 nm than that of Zn-Chl *a* in benzene, while the Q_y peaks were roughly identical (658 nm in benzene).[6] The absorption spectrum of C_{18}FSM containing pure pheophytin *a* showed a Soret absorption band at 406 nm (data not shown), which indicates Zn-Chl *a* was partially pheophytinized during the adsorption process. The Q_y peak of Zn-Chl *a* on C_{18}FSM was broadened in comparison with that of Zn-Chl *a* in benzene (full width at half maximum at the Q_y band; *ca.* 1100 cm^{-1} in C_{18}FSM and 420 cm^{-1} in benzene). This finding suggests the presence of intermolecular interactions between Zn-Chls and C_{18}FSM surfaces, being in line with a previous report for a clay/Chl system.[9,10]

Similar tendency was observed in the absorption spectrum of Zn-pyroChl *a* (Figure 2) because the C13^2 moiety was out of the π-conjugated system. Zn-pyroChl *a* into C_{18}FSM gave the absorption at 412 and 657 nm in the Soret and Q_y regions, respectively, and gave the emission peak at 660 nm.

The purities of Zn-Chls extracted from C_{18}FSMs were determined by analytical HPLC after 1 week from the adsorption of Zn-Chls. The HPLC trace of extracted pigments revealed that less than 5% of Zn-Chl *a* was pheophytinized during the adsorption on C_{18}FSM (data not shown). Similar trend was observed in the case of Zn-pyroChl *a*. The difference in pH between Zn-Chl *a* and Mg-Chl *a* is about 2.5 at a common half-time of pheophytinization of Chls.[11] It is reasonable to assume that the acid property of C_{18}FSM is not so high, being consistent with previous observations.[12] On the other hand, allomerization behavior of these Zn-Chls was drastically different. Approximately 90% of Zn-Chl *a* was allomerized by the adsorption on C_{18}FSM, while 80% of Zn-pyroChl *a* was extracted without degradation, in spite of the substantially identical absorption spectra (Figure 2). The stability of Zn-pyroChl *a* in C_{18}FSM should be suited for the material design of biomimetic solar energy system.

The RR spectrum of C_{18}FSM/Zn-pyroChl *a* (Figure 3) shows relatively small pigment degradation. Though 3000 nmol of Zn-pyroChl *a* was adsorbed for the RR measurement, its absorption spectral feature was quite similar to that of C_{18}FSM/Zn-pyroChl *a* (1000 nmol). This observation denies the possibilities of both the aggregation of Zn-pyroChl *a* in C_{18}FSM and the multilayer adsorption of pigments on the external surface of C_{18}FSM. Raman lines in the wavenumber region of 1100—1400 cm^{-1} mainly originated from the C–H and C–N bonds in the macrocycle and the peripheral substituents.[13,14] Scattering bands at 1533—1540, 1563, and 1618 cm^{-1} are assigned to C=C stretching modes of the chlorin macrocycle.[13] The location of these bands reveals that central Zn atom of Zn-pyroChl *a* is in the five-coordinate state.[13] The relative intensities of the 1533—1540 cm^{-1} band and the 1563 cm^{-1} band were reminiscent of the RR spectra of monomeric Zn-Chls.[13,14] The C13^1=O band at around 1680 cm^{-1} was slightly downshifted than the C13^1 keto band of Zn-Chl *a* recorded in the monomeric state (1691 cm^{-1}).[15] These findings indicate that silanol groups on C_{18}FSM probably formed hydrogen bondings to not only central Zn atom but C13^1=O moiety. This leads that the amount of adsorbed Zn-Chls is correlated with the affinity between Zn-Chl molecules and the solvents on the adsorption of Zn-Chls. That is, strong coordination interactions between Zn-Chls and solvents (acetone, methanol, and ether, for example) interfere with the formation of hydrogen bondings between Zn-Chls with silanol groups in C_{18}FSM. In contrast, Zn-Chls were well adsorbed into mesoporous silica in CH_2Cl_2 and toluene due to weak interactions, as in the case of this study. This is also in line with the poor adsorption capacity of trimethysilylated C_{18}FSM owing to the lower possibility for the formation of intermolecular hydrogen bondings.[2]

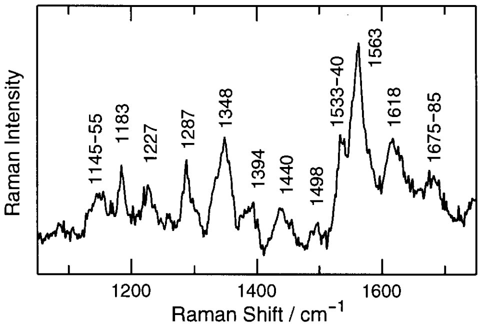

Figure 3. RR spectrum of Zn-pyroChl *a* on C_{18}FSM, using the 457.9-nm line of an Ar$^+$ laser for excitation.

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10 There is no evidence that the spectral broadening depends simply on the interactions between Zn-Chl and C_{18}FSM. However, it is reasonable to suppose that silanol groups on the silica surface are in contact with not only the central Zn atoms but also the chlorin macrocycles. This probably leads to the disturbance of π-conjugate system on the macrocycle, resulting in the spectral change as in this case (Figure 2).
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