Optical Properties of Oxotitanium (IV) Meso-tetrakis(4-sulfonatophenyl)porphyrin Intercalated into the Layered Double Hydroxides (LDH) Studied by Laser Spectroscopy

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Some new nanohybrid materials have been synthesized by intercalating the oxotitanium(IV) meso-tetrakis(4-sulfonatophenyl) porphyrin(O=Ti$^{(IV)}$ TSPP) into the Zn/Al layered double hydroxides (LDHs), and their structures and photophysical properties have been investigated by various laser spectroscopic techniques. According to the XRD pattern of the synthesized nanohybrid materials, the macrocycle plane of O=Ti$^{(IV)}$ TSPP are grafted perpendicular to the LDH layers. The O=Ti$^{(IV)}$ TSPP-intercalated LDH exhibits band broadening of the absorption spectrum and a blue shift of Q-band as compared to that observed in solution. Resonance Raman spectral measurements demonstrate that the positively charged LDHs give rise to a slight decrease of the electronic density of the porphyrin ring accompanying a small change of the electronic distribution of the O=Ti$^{(IV)}$ TSPP. Consequently the LDH environment affects the energies of the two highest occupied molecular orbitals (HOMOs) of the O=Ti$^{(IV)}$ TSPP, a_{1u} and a_{2u}, producing a mixed orbital character. Being consistent with these electronic structural changes of O=Ti$^{(IV)}$ TSPP in LDH, both the fluorescence spectral change and the fs-diffuse reflectance transient measurements imply that the photoexcitation of the O=Ti$^{(IV)}$ TSPP intercalated into LDH undergoes fast relaxation to the O=Ti$^{(IV)}$ TSPP^{+}-LDH^{-} charge transfer (CT) state within a few picoseconds, followed by a photoinduced electron transfer between the O=Ti$^{(IV)}$ TSPP and LDHs with a rate constant greater than 1×10^{10} S^{-1}. No evidence is found for back electron transfer. In conclusion, the O=Ti$^{(IV)}$ TSPP intercalated LDH seems to be a possible candidate for an artificial reaction center for an efficient solar energy conversion system.

Key Words : Layered double hydroxides, O=Ti$^{(IV)}$ TSPP, Optical properties

Introduction

Recently there have been much interests in the nanohybrid materials which often exhibits highly synergetic and complementary functions between two components of the materials.[1,2] The technique for intercalating some guest molecules into the two-dimensional layered materials offers new areas for developing new functional hybrids. Particulary, the layered double hydroxides (LDHs) have received considerable attention due to their technological importance in catalysis, separation technology, optics developement, and nanocomposite material engineering.[3-7] Since LDHs consist of positively charged metal hydroxide layers, various kinds of inorganic or organic anions can be introduced between the hydroxide layers by simple ion-exchange reaction or coprecipitation. The inorganic host materials offer adsorption regions which display open-layered frameworks and higher expansion properties. These major structural differences give us wider possibility for design of new nanoreactors without much consideration for the size of guest molecules. From this view point many efforts have been focused on preparation of new nanohybrid materials having desired functionalities by modification of host-guest arrangements to develop possible photocatalysts to be used for solar energy conversion system.[8,9]

The best photocatalytic system should be highly efficient in the character of natural light harvesting and electron transfer: 1) a high absorption coefficient in visible light region which is the most available on the earth, 2) a highly efficient photoinduced electron transfer which is not generally limited by the occurrence of deactivating back electron transfer, and dominant photoreaction in the exacted state, and 3) feasibility of the catalyst recovery from the product. Usually metalloporphyrins and their derivatives have received considerable attention as photosensitizers in the solar energy photoconversion system because of their structural and functional similarities to chlorophylls having a high absorption coefficient in the visible light region.[10,21-23] The back electron transfer, which is a major problem in most photoredox systems, is generally retarded in heterogeneous systems compared to homogeneous solutions. In this view point, expecting that LDH can provide an appropriate microenvironment for dramatically retarding the back electron

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transfer and lengthening the lifetime of the photogenerated ion pairs, we have attempted to synthesize a LDH nanohybrid material intercalated with oxotitanium(IV) meso-tetrakis(4-sulfonatophenyl)porphyrin (O=Ti$^{(IV)}$ TSPP). In order to confirm the possibility of the nanohybrid materials to be useful as a photocatalyst, their optical properties with respect to their photophysical properties have been studied systematically by using various laser spectroscopic techniques.

Experimental Section

Preparation of Samples: All chemicals were analytical reagent grades and were used as received. O=Ti$^{(IV)}$ TSPP was purchased from Porphyrin Products (Logan, Utah). ZnAl/TiO-TSPP was prepared by coprecipitation under N_2 atmosphere following the conventional route. The mixed solutions of zinc nitrate and aluminum nitrate were prepared with molar ratios of [Zn]/[Al] = 0.75/0.25. In an ambient atmosphere, 100 mL of 0.01 M Zn-Al-nitrate aqueous solution was added into 100 mL of 0.01 M O=Ti$^{(IV)}$ TSPP, respectively, with continuous stirring at room temperature. The pH was kept to be constant at 7.5 ± 0.2 by adding 0.02 M NaOH solution. The precipitates obtained were separated from the reaction solution by centrifugation, and washed with deionized water several times followed by freeze-drying for 1 day.

X-Ray Diffraction and Spectroscopic Measurements: Powder X-ray diffraction (XRD) patterns were measured by a Philips PW 3710 powder diffractometer equipped with Ni filtered Cu-$K\alpha$ radiation, operated at 40 kV and 20 mA, in the 2θ range of 2-50 with a 0.02 resolution.

CW Raman spectra were obtained using 442 nm He/Cd laser (Omnichrome, series 74) at room temperature, and diffuse reflectance UV-VIS spectra were recorded by using a Shimadzu UV-3101PC spectrometer equipped with an integrating sphere. Absorption spectra of the ground state were evaluated by the Kubelka-Munk function of the diffuse reflectance;

$$\frac{K}{S} = \frac{(1-r)^2}{2r} \qquad (1)$$

where K and S are absorption and scattering coefficients, respectively, and r is diffuse reflectance.

Fluorescence spectra were recorded by a LN_2 cooled CCD (charge coupled device) using a second harmonic (430 nm) of a self-mode-locked Ti : Sapphire laser (Mira 900), 860 nm.

The ps time-resolved transient absorptions were measured by using a femtosecond diffuse reflectance spectroscopic system which has been reported elsewhere.[11,12] Briefly, a light source consists of a CW self-mode-locked Ti : sapphire laser (Mira 900 Basic, Coherent) pumped by an Ar^+ laser (Innova 310, Coherent) and a Ti : sapphire regenerative amplifier system (TR 70, Continuum) pumped with a Q-switched Nd : YAG laser (Sure light I Continuum). The fundamental output from the regenerative amplifier (780 nm, 3-4 mJ/pulse, 170 fs fwhm, 10 Hz) was used to generate a frequency doubled (390 nm) as an excitation light pulse. The energy of the excitation pulse measured with a Joule meter (P25, Scientech) was several tens of μJ and its spot size on the sample was about 2 mm. The shot-to-shot fluctuation of the energy was less than ± 10%. The residual of the fundamental output was focused into quartz cell (1 cm path length) containing H_2O to generate a white-light continuum as a probe pulse. Transient absorption intensity was displayed as percentage absorption.[12]

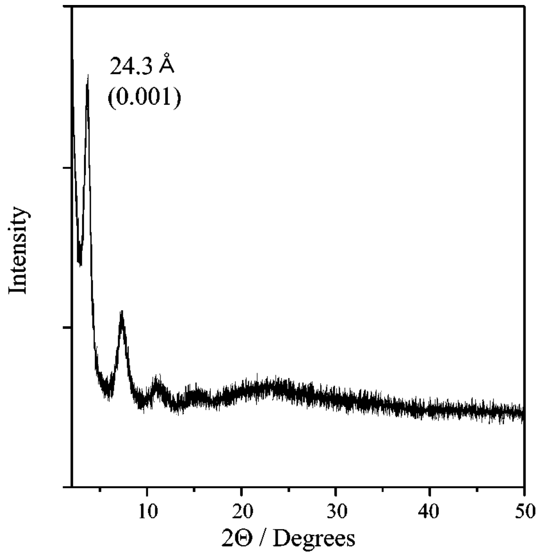

Figure 1. XRD-pattern of the O=Ti^{IV} TSPP intercalated into LDH.

Structural Characterization: The orientation of O=Ti$^{(IV)}$ TSPP intercalated into LDH constructed with the molar ratios Zn/Al = 0.75/0.25 was confirmed by the XRD analysis (Figure 1). The diffractograms of the O=Ti$^{(IV)}$ TSPP/ LDHs consist of a series of (00*l*) diffraction lines, and limited number of (*hkl*) lines. These patterns indicate a structural disorganization which is probably induced by both the highly separated sheets and the weak bonding interactions between the interlayer species and the host lattice. From the LDH $d_{basal\ spacing}$ values and dimensions of the anionic macrocycles of O=Ti$^{(IV)}$ TSPP, it is possible to propose a schematic orientation of the porphyrin between synthetic mineral sheets. The $d_{basal\ spacing}$ value, 24.3 Å, is observed for O=Ti$^{(IV)}$ TSPP/LDH (Figure 1). Subtracting the LDH thickness considered to be 4.8 Å from the basal spacing shows that the gallery height by O=Ti$^{(IV)}$ TSPP is expanding the interlayer by 19.5 Å. It is consistent well with the reported value for the H_2 TSPP being perpendicular to the LDH layers.[13,33-36] Therefore, the observed XRD pattern indicates that the orientation of O=Ti$^{(IV)}$ TSPP is perpendicular to the LDH layers (Figure 2). The perpendicular arrangement of the porphyrin macrocycle in the LDH can give to the advantage for regioselective heterogeneous catalytic reactions as compared to their horizontal orientation on some clay mineral supports.

Results and Discussion

Absorption Spectral Properties. The absorption spectral

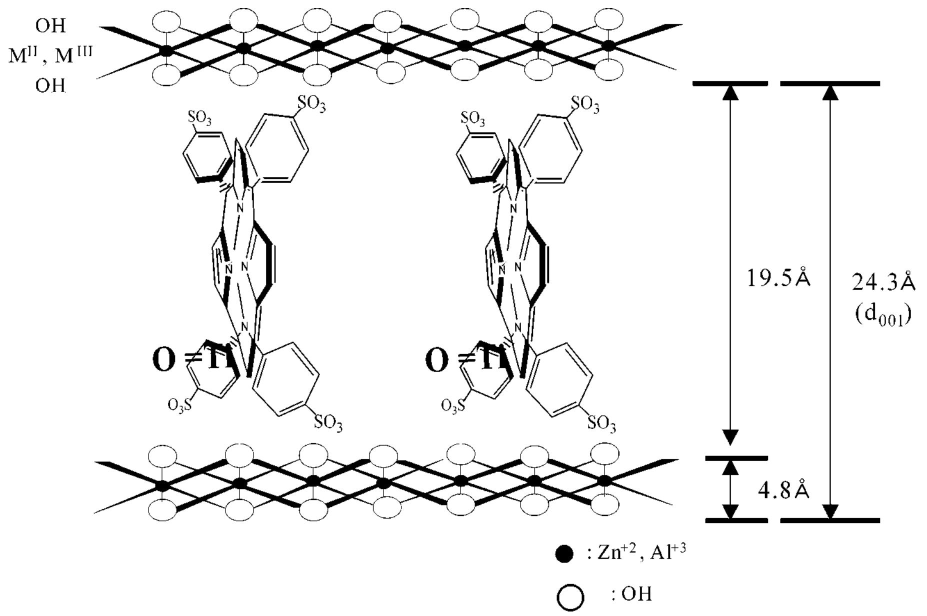

Figure 2. The orientation of the O=Ti^{IV} TSPP intercalated into Zn$_{0.75}$Al$_{0.25}$OH.

feature of the O=Ti$^{(IV)}$ TSPP intercalated into LDH (O=Ti$^{(IV)}$ TSPP/LDH) (b) is compared with those measured in aqueous solution (a) and solid state (c) in Figure 3. In aqueous solution the absorption of the O=Ti$^{(IV)}$ TSPP consists of the strong Soret band at 429 nm and the two weak Q-bands at 565 nm (0-1) and 602 nm (0-0). The absorption spectral feature of the O=Ti$^{(IV)}$ TSPP/LDH exhibits a band broadening and a blue shift of Q-bands by 8-10 nm compared to that in the solution. Furthermore, the ratio of the Soret band/Q band intensities is largely reduced. It has been reported that adsorption of organic molecules on oxide (or hydroxides) supports produces strong perturbation to absorption maxima and the molar absorption coefficient.[16,17] According to the previous papers related to the electronic spectroscopy and surface photochemistry of organic molecules adsorbed on silica gel, the spectral blue shifts are likely originated from a decreased permanent dipole and a reduced polarizability of the excited state O=Ti$^{(IV)}$ TSPP as compared to that of the ground state.[14-17,32] The band broadening of the absorption bands may be due to strong interaction between the sulfonatophenyl group of O=Ti$^{(IV)}$ TSPP and the surface hydroxyl group of LDHs.[16,17,18] Thus, these absorption spectral changes indicate that the intercalated O=Ti$^{(IV)}$ TSPP molecules are forming weak hydrogen bonding with the surface hydroxyl groups of LDHs.

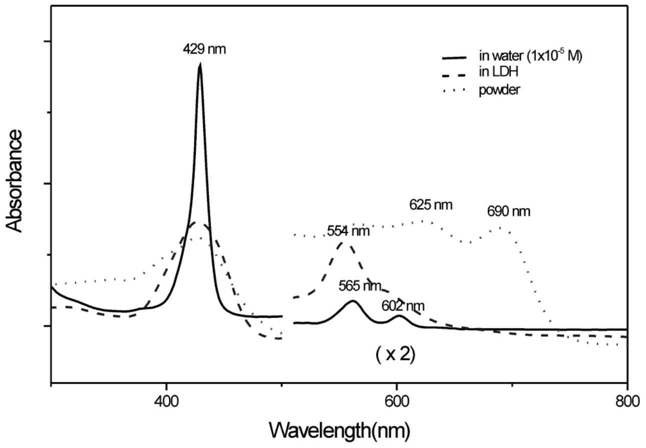

Figure 3. UV-vis absorption spectra of the O=Ti^{IV} TSPP in aqueous solution (—), LDH (---) and powder state (···).

On the other hand, the absorption spectral feature of the O=Ti$^{(IV)}$ TSPP observed in solid powder (Figure 3), there is a significant broadening of the absorption in the Soret region with concomitant decrease in the peak intensities. Also the powder sample showed red-shifts in Q bands to 625 and 690 nm. The decrease in the peak intensities in the Soret region is much more pronounced than the Q bands. These types of spectral changes have been reported to be attributed to an aggregation of porphyrin.[19,25,37-40] However these red shift of Q-bands are not observable in the O=Ti$^{(IV)}$ TSPP intercalated LDH, indicating that there is no aggregation of porphyrin in LDH. This is consistent with the structural aspects of O=Ti$^{(IV)}$ TSPP in LDH as shown in Figure 2.

Resonance Raman Spectral Properties. In order to observe the change of polarization and dipole moment of O=Ti$^{(IV)}$ TSPP/LDH, we have measured resonance Raman spectra. Figure 4 shows the Raman spectra of O=Ti$^{(IV)}$ TSPP in aqueous solution, powder state and the O=Ti$^{(IV)}$ TSPP/LDH obtained with 442 nm He/Cd laser excitation which is nearly resonant with the Soret ($S_0 \rightarrow S_2$) electronic transition. The Raman spectrum for O=Ti$^{(IV)}$ TSPP in aqueous solution and solid state were also measured for comparison. All the Raman signals observed for O=Ti$^{(IV)}$ TSPP/LDH were very weak, and the skeletal modes such as υ_1 (C_m-C_{ph}), υ_4 (C-N), and υ_2 (C_β-C_β) were observed with apparent band broadening and frequency shift. The phenyl mode (ϕ_4) near 1600 cm^{-1} was observed to disappear in LDH, while that of the solid state of O=Ti$^{(IV)}$ TSPP was apparently enhanced as

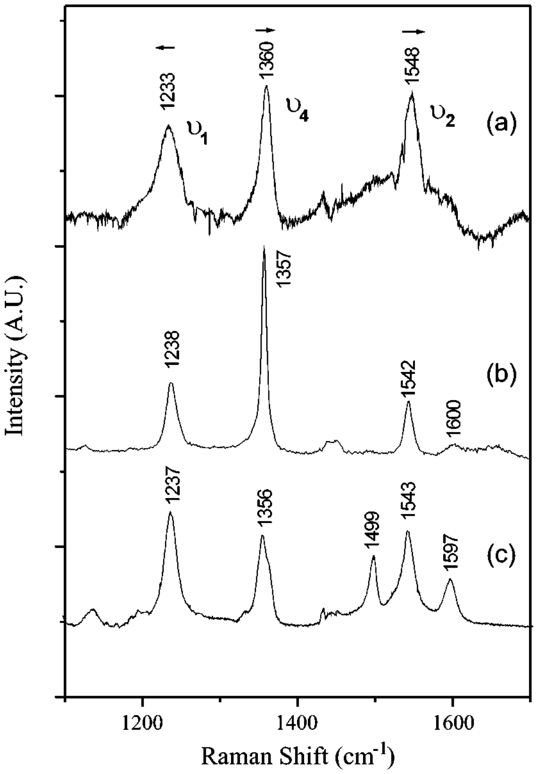

Figure 4. CW Raman spectra of the O=Ti^{IV} TSPP intercalated into LDH (a), in aqueous solution (b) and powder state (c).

compared to that observed in solution. (See Figure 4) The intensity change of the phenyl mode (ϕ_4) at 1600 cm^{-1} is known to be closely related with charge density in phenyl ring.[20] For example, an increased charge density in the phenyl ring generally shows an enhanced phenyl mode (ϕ_4) at 1600 cm^{-1}.[20] Therefore, we consider that the disappearance of phenyl mode of O=Ti$^{(IV)}$ TSPP/LDH is due to decrease of charge density in the phenyl ring. The frequency of the porphyrin skeletal vibrational modes such as υ_4 (C_α-N and C_α-C_β), υ_2 (C_β-C_β and C_α-C_m) are observed to be increased, while that of υ_1 (C_m-C_{ph}) mode is decreased. The υ_2 and υ_4 modes are identified as particularly useful markers because they are strong bands and markedly shifted to higher or lower frequency according to the electronic environmental change of the HOMO's. Shelnutt *et al*.[37,38,41] reported that the shift of υ_2 and υ_4 mode to higher frequency is caused by a decrease in charge of the porphyrin ring. Thus, it is noticed that the υ_2 mode at 1548 cm^{-1} show not only a frequency up shift (6 cm^{-1}), but also an increased intensity compared with υ_4 mode. The υ_2 mode is mixed with $C_\beta C_\beta$ and $C_\alpha C_m$ stretching, and it's frequency shifts can be explained also qualitatively on the basis of the highly occupied molecular orbital patterns.

The a_{2u} orbital has a bonding character of $C_\beta C_\beta$ and $C_\alpha C_m$, whereas the a_{1u} orbital has antibonding character of the $C_\beta C_\beta$.[18,21-24,30] The frequency up shift and the enhanced intensity of υ_2 mode are similar to the changes that are observed in the case of one electron extraction from the a_{1u} orbital or one electron injection to the a_{2u} orbital. Since LDH is a positively charged layer compound, it is considered that such a change observed at υ_2 mode is owing to an electron poor a_{1u} orbital rather than an electron rich a_{2u} orbital.[30,31] It is not generally reasonable because the a_{2u} orbital is higher than a_{1u} orbital for *meso*-substituted porphyrin such as O=Ti$^{(IV)}$ TSPP. However, Holten *et al.* reported that the energy spacing and ordering of the a_{1u} and a_{2u} orbitals are particularly sensitive to the electron withdrawing/releasing effects of the substituent groups that are positioned at the periphery of the macrocycle.[22] In their opinion the strong electron withdrawing groups such as pentafluorophenyl at meso-position stabilize the a_{2u} orbital to such an extent relative to the a_{1u} orbital that the former orbital drops below the latter. In agreement with the suggestion by Holten *et al.*, we suggest that the positively charged LDH affects strongly the HOMO's character of O=Ti$^{(IV)}$ TSPP and the energy spacing between a_{1u} and a_{2u}.[25,27]

Luminescence Spectral Properties. Figure 5 shows luminescence spectra of O=Ti$^{(IV)}$ TSPP/LDH. For comparison, a fluorescence spectrum of O=Ti$^{(IV)}$ TSPP in methanol and that in solid state are shown in the same figure. The emission spectrum of O=Ti$^{(IV)}$ TSPP in solution shows characteristic emission spectral features which originate from two vibrational emissive states at 609 and 664 nm. The emission spectrum of O=Ti$^{(IV)}$ TSPP/LDH exhibited a non-Lorenzian curve type around 654 nm, and this band was analyzed to split into three peaks at 620 nm, 654 nm, 705 nm, respectively (Figure 6). The small band at 705 nm was identical with that of O=Ti$^{(IV)}$ TSPP measured in solid. Thus, the small band can be attributed to the aggregated O=Ti$^{(IV)}$ TSPP. It indicates that although we could not distinguish an absorption peaks of aggregated O=Ti$^{(IV)}$ TSPP from the absorption spectrum of O=Ti$^{(IV)}$ TSPP/LDH, shows O=Ti$^{(IV)}$ TSPP was aggregated somewhat in LDH. Considering the other two emission bands at 620 nm and 654 nm, there are two notable aspects. First, as shown in Figure 7, the spacing (~1240 cm^{-1}) between the peaks in absorption is observed larger than that in emission (~890 cm^{-1}) for the O=Ti$^{(IV)}$ TSPP/LDH, while in solution the spacing (~1088 cm^{-1}) in

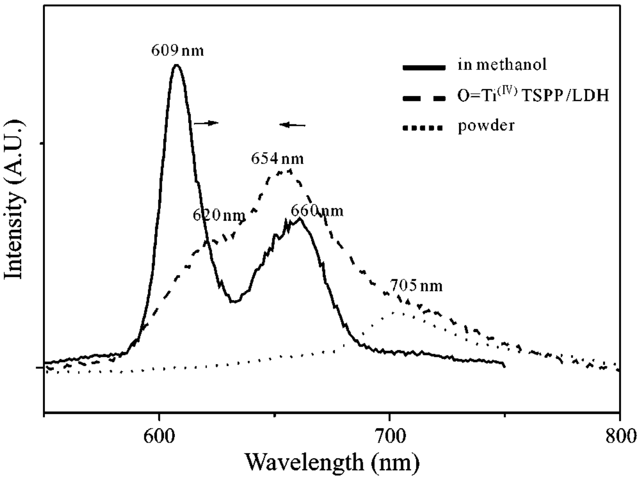

Figure 5. The fluorescence emission spectra of the O=Ti^{IV} TSPP in methanol (—), LDH (---) and powder state (···).

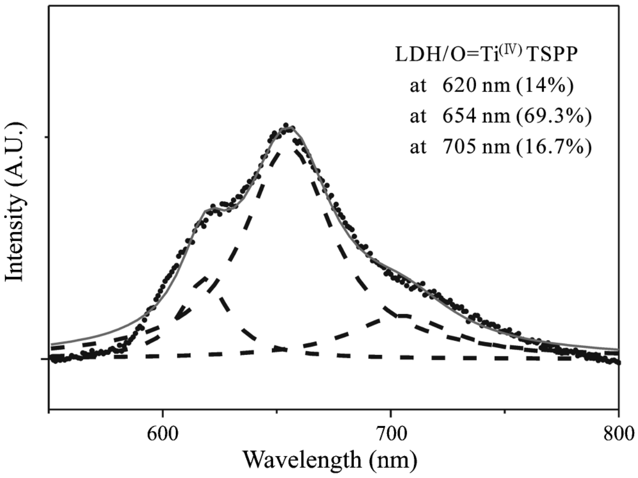

Figure 6. The emission band analysis of the O=Ti^{IV} TSPP in LDH.

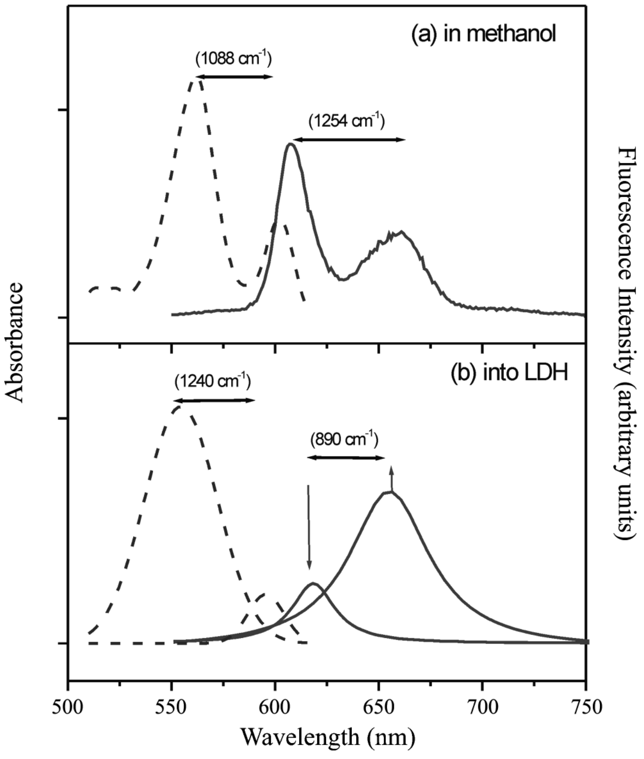

Figure 7. The absorption (---) and emission (—) spectra of the O=Ti^{IV} TSPP in methanol (a) and LDH (b). The excitation wavelength for emission spectra was 430 nm.

the absorption show smaller than that (~1254 cm^{-1}) in emission. It does not correspond to the general observation that the spacing Q(1,0) to Q(0,0) in absorption is smaller than that in emission.[28] As mentioned above, its narrow spacing between emission bands of the O=Ti$^{(IV)}$ TSPP/LDH must be due to a decrease of permanent dipole and a reduced polarization of O=Ti$^{(IV)}$ TSPP in the excited state.[16] Second, it is important to note the difference in aspect of the emission in solution and in LDH. The relative intensity ratio of the Q(0,0)/Q(0,1) emission bands of the O=Ti$^{(IV)}$ TSPP in LDH are observed to be opposite against with that measured in solution. According to the basic principle, the intensity of a vibronic transition is proportional to the square of the overlap integral between the vibrational wavefunctions of the two states that are involved in the transition. In particular, the ratio of the Q(0,0)/Q(0,1) intensities strongly depends on the HOMOs orbitals: the Q(0,0)/Q(0,1) intensity ratio of the *meso*-substituted porphyrin having an a$_{2u}$ HOMO is less than 1, whereas that of *β*-(or non) substituted porphyrin having a$_{1u}$ HOMO is lager than 1. Accordingly, these results reveal the reversal of the a$_{2u}$/a$_{1u}$ orbitals and the change of their ground and excited electronic-state wave functions, indicating the change in the electron-density distribution on the macrocycles. Consequently, these emission spectral changes indicate that the charge transfer takes place from O=Ti$^{(IV)}$ TSPP to LDH, influencing the HOMO's character and the spacing between a$_{1u}$ and a$_{2u}$.[22,25,27]

Unfortunately, the fluorescence quantum yield of O=Ti$^{(IV)}$ TSPP/LDH could not be measured, but visually it was much lower than that in solution. In order to further characterize the emission bands, we measured fluorescence lifetimes of O=Ti$^{(IV)}$ TSPP/LDH, O=Ti$^{(IV)}$ TSPP in methanol and solid state at room temperature. The decay profiles for the emission bands of O=Ti$^{(IV)}$ TSPP in methanol and solid state were observed to be single exponential. The decay time in solution is *ca.* 310 ± 10 ps, whereas that was observed to be relatively shorter (27 ± 2 ps) in LDH than in solution (Table 1). In general, a fast fluorescence decay of the O=Ti$^{(IV)}$ TSPP solid state is attributed to a sequence of strong intermolecular interactions, resulting in an energy transfer and exciton migration within the aggregates.[29] The fast fluorescence decay of the O=Ti$^{(IV)}$ TSPP was also observed in LDH, and thus it must be due to a strong intermolecular interaction of porphyrins, being consistent with the interpretation of the O=Ti$^{(IV)}$ TSPP solid state.

Furthermore, it is interesting to note that the fluorescence decay of the O=Ti$^{(IV)}$ TSPP in LDH is biexponential with an additional longer decay time (~150 ps). This new decay component may be attributed to a formation of an excited state CT between O=Ti$^{(IV)}$ TSPP and LDH frame.[21]

ps-Diffuse Reflectance Spectral Properties. Figure 8 shows time-resolved diffuse reflectance spectra of O=Ti$^{(IV)}$ TSPP intercalated into LDH (bottom), and decay profiles at 480 nm and 650 nm (top). The dips observed at 550 and 580 nm are due to the ground state bleaching of Q bands. Decay profiles observed at 480 and 650 nm were fitted as bi-

Table 1. Fluorescence decay times for the O=Ti^{IV} TSPP/LDH, O=Ti^{IV} TSPP in methanol and solid

	Wavelength	τ_1	a$_1$	τ_2	a$_2$
O=Ti$^{(IV)}$ TSPP **in methanol**	610 nm	303 ps			
	660 nm	310 ps			
O=Ti$^{(IV)}$ TSPP **in LDH**	610 nm	26.9 ps	0.81	195 ps	0.19
	650 nm	23.9 ps	0.76	100.5 ps	0.24
	700 nm	29.8 ps	0.73	168.3 ps	0.27
O=Ti$^{(IV)}$ TSPP **powder**	705 nm	26.0 ps			

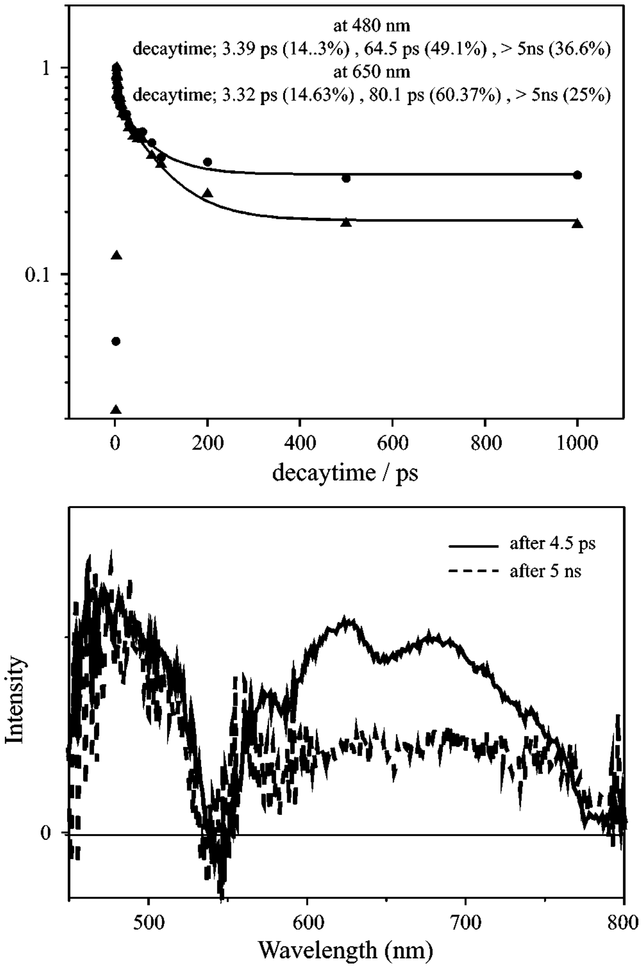

Figure 8. The transient diffuse reflectance spectra of the O=Ti^{IV} TSPP intercalated into LDH at 4.5 ps and 5 ns after laser pulse and the decay profiles at 480 nm and 650 nm.

exponential function with a longer lived component than 5 ns. The transient absorption spectrum of O=Ti$^{(IV)}$ TSPP/LDH observed at 4.5 ps after pulse excitation is quite different from S-S and T-T transient absorption spectral feature of the O=Ti$^{(IV)}$ TSPP in aqueous solvent (Fig. 9). Again the transient absorption spectrum observed at 4.5 ps indicates the O=Ti$^{(IV)}$ TSPP^{+}-LDH^{-} intermolecular charge transfer (CT) state, arising from O=Ti$^{(IV)}$ TSPP singlet state within a few picoseconds.[21]

The transient absorption spectral feature of long-lived O=Ti$^{(IV)}$ TSPP-LDH observed at 5 ns after the pulse excitation is apparently different from any transient absorption spectra of O=Ti$^{(IV)}$ TSPP^{+}-LDH^{-} CT state and O=Ti$^{(IV)}$ TSPP triplet or singlet state (Fig. 9), although any clear change in the absorption wavelength were not observed. It is rather similar to the transient absorption spectral feature of O=Ti$^{(IV)}$ TSPP cation radical (not shown). Therefore, we attribute the long lived species observed at 5 ns to O=Ti$^{(IV)}$ TSPP cation radical, indicating the photoinduced electron transfer from O=Ti$^{(IV)}$ TSPP to LDH. It leads us to conclude that the photoinduced electron transfer between O=Ti$^{(IV)}$ TSPP and LDH occurs with a rate constant larger than 10^{10} S^{-1} from CT state of porphyrin to the LDH frame. Their lifetimes could not be observed because of a time-resolution limit of our instruments. However, we confirmed this cation radical by measuring ESR spectrum at room temp. (not shown).

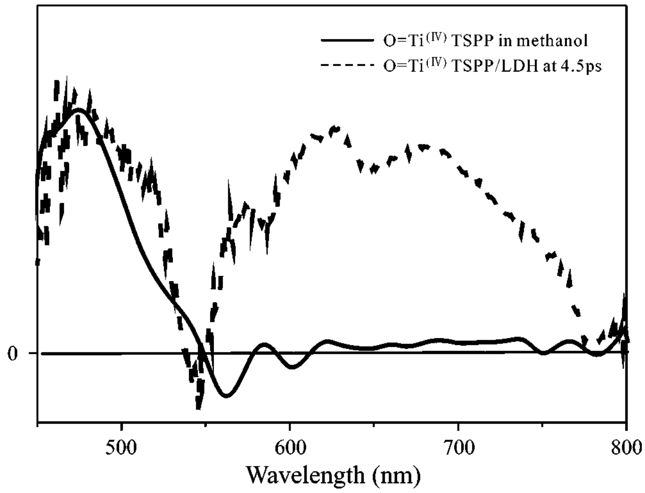

Figure 9. The transient diffuse reflectance spectra of the O=Ti^{IV} TSPP intercalated into LDH and in aqueous solution at 4.5 ps after laser pulse.

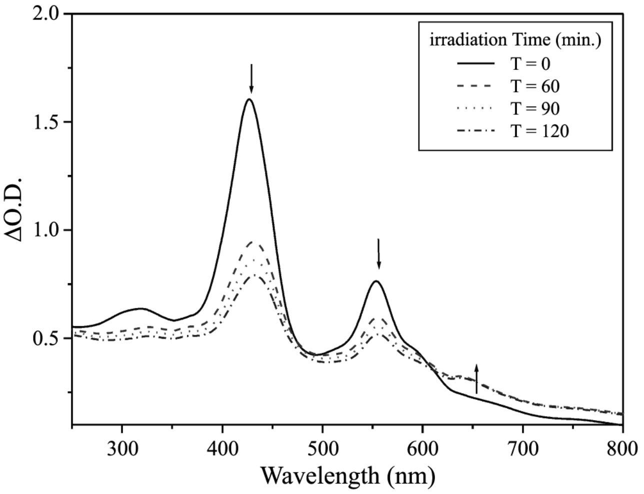

Figure 10. Absorption spectra of O=Ti^{IV} TSPP intercalated into LDH as a function of various irradiation time.

In order to further confirm the long lived species we measured ground-state absorption spectra after and before irradiation (≥ 380 nm). As shown in Figure 10, upon irradiation the ground-state absorption spectrum of O=Ti$^{(IV)}$ TSPP/LDH was significantly changed, and the resulting spectral change corresponds well to the previous reported absorption-spectral features of Zn TPP and Mg TPP cation radicals, possessing a rather diffuse structure from 500-700 nm. Furthermore, as mentioned above, this cation radical did not decay, indicating that no back electron transfer takes place from LDHs framework. These results imply that the synthesized nanohybrid material, O=Ti$^{(IV)}$ TSPP/LDH, is useful as asymmetric charge carrier to a certain substrate, and consequently possible candidate of the reaction center for developing solar energy conversion system.

Conclusion

LDH nanohybrid material intercalated O=Ti$^{(IV)}$ TSPP have been found to be useful for developing solar energy conversion system. After irradiation, O=Ti$^{(IV)}$ TSPP cation radicals were detected, and furthermore any evidence for back electron transfer was not observed.

About the photophysical and photochemical properties of O=Ti$^{(IV)}$ TSPP/LDH, intercalation of anion charged O=Ti$^{(IV)}$ TSPP into positively charged LDH induces an intermolecular charge transfer from O=Ti$^{(IV)}$ TSPP to LDH. It influences the HOMO's character and the spacing between two highest occupied molecular orbitals, a_{1u} and a_{2u}. As known well, the a_{1u} is HOMO for unsubstituted porphyrin, whereas the a_{2u} is HOMO for meso-substituted porphyrins. Unlike the general metallo-TPP where a_{2u} is classified as HOMO, the HOMOs of the O=Ti$^{(IV)}$ TSPP intercalated into LDH have a mixed orbital character of both a_{1u} and a_{2u}. The photoexcitation of the O=Ti$^{(IV)}$ TSPP intercalated into LDH undergoes fast relaxation to the O=Ti$^{(IV)}$ TSPP$^+$-LDH$^-$ charge transfer (CT) state within a few picoseconds, followed by photoinduced electron transfer from O=Ti$^{(IV)}$ TSPP$^+$-LDH$^-$ CT state to LDH with a rate constant larger than 1×10^{10} S^{-1}.

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