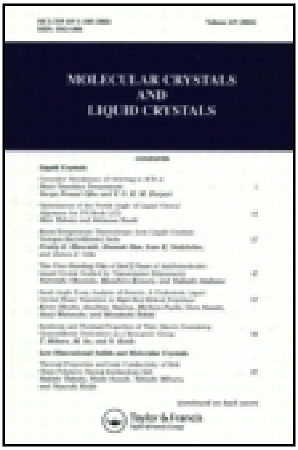

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Enhanced Aggregation of Tin(IV)Porphyrins in a Polyfluorinated Surfactant-Clay Hybrid Environment

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Enhanced Aggregation of Tin(IV)Porphyrins in a Polyfluorinated Surfactant-Clay Hybrid Environment

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Tetra-(4-sulfonatophenyl)porphyrinatotin(IV) aggregated efficiently in a clay (saponite) layer intercalated with a polyfluorinated surfactant, but no aggregation was observed in a hydrocarbon type surfactant-clay hybrid environment. Germanium(IV) porphyrins remained as monomers even in the polyfluorinated environment.

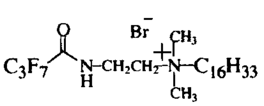
Keywords: clay; saponite; polyfluorinated surfactant; metalloporphyrins

INTRODUCTION

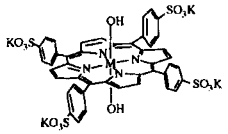
Solid state and solid surfaces as unique photochemical reaction fields have attracted much attention owing to their unique characteristics such as a rigid molecular alignment or a properly restricted molecular motion.[1] Organic-inorganic hybrid layered materials can be tailored by selecting and designing both the guests and hosts.[2] Perfluoroalkane is well characterized to have hydrophobicity, lipophobicity, and very weak intermolecular interactions.[3] Inorganic surfaces modified by polyfluorinated surfactants are, thus, expected to provide novel photochemical reaction fields.[4] We have already reported on intercalation of novel cationic polyfluorinated surfactants into the layered space saponite[5] and aggregation behavior of tetra-(4-sulfonatophenyl) porphyrinatoantimony(V) (Sb(V)TSPP) co-intercalated in those hybrid environments.[6] Among the factors controlling the aggregation phenomena, the effect of net charge of the porphyrin complex might warrant the highest priority for study. We report here on the aggregation behavior of tetravalent metalloporphyrins such as tetra-(4-sulfonatophenyl)porphyrinatotin(IV) (Sn(IV)TSPP) and -germanium(IV) (Ge(IV)TSPP) in a polyfluorinated surfactant-clay hybrid environment.

EXPERIMENTAL

Sodium saponite (Sumecton SA: SA) was kindly offered by Kunimine Industries and was used as received. The cation exchange capacity (CEC) is 99.7 milimol against 100g of the host. The synthesis of the polyfluorinated surfactant (C3F-S) has been reported elsewhere.[4-a] The surfactant-clay hybrid compounds (SCHCs) intercalated with the metalloporphyrins were prepared using the following procedures: An aqueous mixture of SA(1.2mM), C3F-S (3.5mM), and Sn(IV)TSPP or Ge(IV)TSPP (2.4 x 10^{-6}M) was stirred at 65°C for 3 hours. The precipitate was filtered, washed with water, then dried in air at 85°C for 8 hours. The composition of the SCHC was determined by the increased weight of clay and confirmed by elemental analysis. The intercalated amount of metalloporphyrins was calculated from the residual amount of porphyrins in the filtrate solution. The solid SCHC was dispersed in benzene in order to allow measurements of absorption and emission spectra.



C3(F)-S



M=Sn(IV), Ge(IV)

MTSPP

RESULTS AND DISCUSSIONS

Enhanced aggregation of Sn(IV)TSPP in the polyfluorinated SCHC.

The cast film of SCHC (Sn(IV)TSPP:C3F-S:SA = 0.002 : 2.5 : 1.0) had a λmax characteristic of the monomer Sn(IV)TSPP at 427nm with a relatively

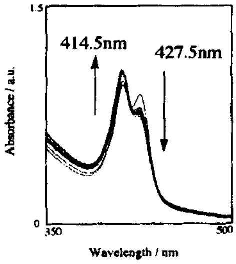


FIGURE 1. Spectral change of Sn(IV)TSPP in the polyfluorinated SCHC upon dispersion in benzene.

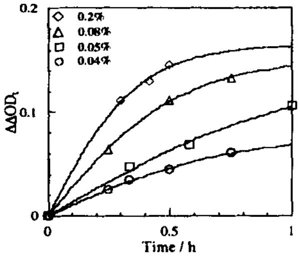


FIGURE 2. Effect of concentration of Sn(IV)TSPP on the spectral change. (λ_1=480nm, λ_2=427.5nm)

large red shift from that in aqueous solution (418nm), while the SCHC exhibited a λmax at 427.5nm upon dispersion in benzene during the first hour. The large red shift indicates that the microenvironment surrounding Sn(IV)TSPP in the SCHC is inherently sufficiently non-polar and benzene molecules should be able to penetrate into the interlayer space. Upon dispersion in benzene, the Soret band of Sn(IV)TSPP drastically shifted to the blue in three steps. During the initial 60 min the monomer band at 427.5nm decreased and a new band appeared at 414.5nm with sharp isosbestic points at 422, 439nm. (Fig. 1) In the second step up to 30 hours, the 414.5nm band shifted to 404nm with different isosbestic points at 408nm. On prolonged standing for ca. 200 hours, the band further shifted to 399nm. Excitation of the starting 427.5nm species gave the monomer fluorescence spectrum (600, 655nm) in good agreement with that observed in aqueous solution, while the spectral shape of the fluorescence from the 414 and 404nm species with much lower intensities were very similar to each other but completely different (605, 639, 659nm) from the monomer emission. Obviously the starting monomeric Sn(IV)TSPP is converted into other species within 60min during the first step and the resulting species suffered small blue shifts during the subsequent second and third steps without change in their inherent character. In order to get more information about the spectral change, the effect of concentration of Sn(IV)TSPP was further studied. The difference in absorption, $\Delta\Delta OD_t$ at two fixed wavelength λ_1, λ_2 defined as Eq.(1) was plotted against time as shown in Fig.2.

$$\Delta\Delta OD_t = (OD_{\lambda 1} - OD_{\lambda 2})_{t=0} - (OD_{\lambda 1} - OD_{\lambda 2})_{t=t} \qquad (1)$$

, where $(OD_{\lambda i})t=0$ or t denotes the observed absorbance for the wavelength λi at t=0 or t. The $\Delta\Delta OD_t$ term effectively removes the scattering effect of the incident light by the subtraction procedure in Eq.(1). As indicated in Fig. 2, the spectral change during the first step was evidently accelerated by an increase of [Sn(IV)TSPP], while no concentration effect was observed during the second step. These results strongly suggest that during the initial 60min the starting monomeric Sn(IV)TSPP dimerizes upon penetration of a benzene molecule into the interlayer space of the clay. Assuming the dimer formation, the following kinetic expressions in Eqs. (2)-(4) can be deduced.

$$\mathrm{Monomer} + \mathrm{Monomer} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{Dimer} \qquad (2)$$

$$\frac{d[D]}{dt} = k_1[M]^2 - k_{-1}[D] = \frac{d(C_0 X)}{dt} = k_1 C_0{}^2 (1-2X)^2 - C_0 k_{-1} X \qquad (3)$$

$$X = \frac{1-e^{-pt}}{(1/n)-(1/m)e^{-pt}}, \quad \left(p = \frac{4k_1C_0}{\sqrt{\eta^2-16}} \quad m = \frac{\eta-\sqrt{\eta^2-16}}{8} \quad \eta = 4+\frac{k_{-1}}{k_1C_0} \quad n = \frac{\eta+\sqrt{\eta^2-16}}{8}\right) \qquad (4)$$

, where k_1, k_{-1}, [M], [D], C_0, X are the rate constants of formation and dissociation of the dimer porphyrin, concentrations of the monomer and dimer, the initial concentration of porphyrin, and the molar ratio of the dimer at t = t, respectively. The $\Delta\Delta OD_t$ term in Eq. (1) can be further expressed as Eq. (5), assuming the dimer formation.[6]

$$\Delta\Delta OD_t = C_0 (2\,\Delta\varepsilon_M - \Delta\varepsilon_D)\, X \qquad (5)$$

, where $\Delta\varepsilon_M$ and $\Delta\varepsilon_D$ denote differences in the extinction coefficients of the monomer and dimer at λ_1 and λ_2. Using the relationships in Eqs.(4) and (5), computer simulated curve fitting for the plots were carried out by varying the three parameters k_1, k_{-1} and $\Delta\varepsilon_D$. The curves fit well to the experimental data as shown in Fig. 2. Among the parameters obtained the rate constants k_1 ($2.58 - 2.52 \times 10^{-2}\ s^{-1}\,mol^{-1}$) and $\Delta\varepsilon_D$ ($9.00 - 9.41 \times 10^5\ M^{-1}\,cm^{-1}$)showed pretty good agreement with each other when making independent simulations at different

[Sn(IV)TSPP], while the very small value for k_{-1} showed some fluctuation ($1.80 - 3.58 \times 10^{-17}\ s^{-1}$). The rate of dimerization was much faster than that observed for Sb(V)TSPP. These results and analyses clearly indicate that the monomer Sn(IV)TSPP effectively dimerizes in the polyfluorinated micro-environment of the interlayer of the clay. The blue-shifted λmax strongly suggests that the dimer should be an H type aggregate. Very interestingly, the monomer Sn(IV)TSPP remained unchanged in the SCHC containing the hydrocarbon type surfactant C3H-S (Sn(IV)TSPP:C3H-S:SA=0.002 : 1.9 : 1.0). This indicates that the dimerization is obviously enhanced in the polyfluorinated microenvironment. The lipophobic character of the perfluorinated alkyl chain might expel the surrounding lipophilic porphyrin rings causing aggregation. The benzene solvent assists their migration within the interlayer of clay. Another interesting point is the tilt angle of the porphyrin plane; how do the metalloporphyrins orient themselves in the interlayer of the clay among the polyfluorinated surfactant? Dichroic absorption spectra of a cast film of SCHC on a quartz glass plate were observed. The film was prepared by casting a mixture of SCHC and benzene onto a quartz glass plate. The parallel orientation of the SCHC against the glass plate was confirmed by observing XRD and SEM images. Detailed analyses of the dichroic absorption spectra reveal that the the tilt angle of the monomer Sn(IV)TSPP is 11° relative to the clay layer and the dipole moment of the dimer is tilted in 5° relative to the clay layer. The tilt angle of the monomer (11°) is quite different from that for the polyfluorinated surfactant C3F-S (30°), suggesting that Sn(IV)TSPP is located outside of the oriented surfactant forest. The benzene solvent, thus, could easily transport Sn(IV) TSPP molecules for aggregation.

Ge(IV)TSPP in a polyfluorinated SCHC.

Another type of SCHC containing Ge(IV)TSPP was prepared. When this SCHC (Ge(IV)TSPP:C3F-S:SA=0.002 : 2.5 : 1.0) was dispersed in benzene, the Soret band of Ge(IV)TSPP was observed at 422 nm noticeably red shifted from that in aqueous solution (416.5nm). The Soret band width (22.0nm) was broader than that in aqueous solution (8.5nm) and a shoulder band was observed at 412.5nm. Very interestingly, the Soret band of Ge(IV)TSPP in the SCHC dispersed in benzene remained unchanged even for prolonged standing in excess of 50 hours. Fluorescence spectra upon excitation at 422nm and

412.5 nm exhibited only the monomer emission. Measurement of dichroic absorption spectra indicated that Ge(IV)TSPP is tilted 30° relative to the clay layer which is at the same tilt angle as that for the polyfluorinated surfactant C3F-S. Ge(IV)TSPP is thus fully incorporated and deeply trapped within the surfactant forest in the interlayer of the clay, unable to migrate upon penetration of the benzene solvent. The sharp contrast between enhanced aggregation in the case of Sn(IV)TSPP and no dimer formation for Ge(IV) TSPP could be ascribed to the differences involving how and where the porphyrins are located in the interlayer space of the clay. Though it is not yet clear why the location of the porphyrins within the interlayer of clay are different between the tetravalent porphyrins Sn(IV)TSPP and Ge(IV)TSPP, systematic examination of other metalloporphyrins with different valences and formal charges should reveal the mechanism.

References

[1] (a) J. K. Thomas, *Chem. Rev.*, **80,** 283 (1980). (b) K. B. Yoon, *Chem. Rev.*, **93,** 321 (1993). (c) K. Kalyanasundaram, *Photochemistry in Micro Heterogeneous Systems* (Academic Press, Inc., Orlando, FL, 1987). (d) V. Ramamurthy, *Tetrahedron,* **42,** 5753 (1986).

[2] M. Ogawa, and K. Kuroda, *Chem. Rev.*, **95,** 399 (1995), and references therein.

[3] (a) R. E. Banks, *Organfluorine Chemicals and their industrial Application* (Ellis Horwood Ltd., Chichester, 1979). (b) A. Negishi, *Chemistry of Fluorine* (Maruzen, Tokyo, 1988). (c) T. Kitazume, T. Ishihara, and T. Taguchi, *Chemistry of Fluorine* (Kodansha Scientific, Tokyo, 1993).

[4] (a) Y. Kameo, S. Takahashi, M. K. Kowald, T. Ohmachi, S. Takagi, and H. Inoue, *J. Phys. Chem. B,* in press. (b) H. Kusaka, M. Uno, M. K. Kowald, T. Ohmachi, S. Kidokoro, T. Yui, S. Takagi, and H. Inoue, *Phys. Chem. Chem. Phys.*, in press.

[5] T. Yui, and H. Inoue, *Langmuir* in contribution.

[6] L. A. Lucia, T. Yui, R. Sasai, K. Takagi, D. G. Whitten, and H. Inoue *Langmuir* in contribution.