Photochemical Chlorination and Oxygenation Reaction of Cyclohexene Sensitized by Ga(III) Porphyrin–Clay Minerals System with High Durability and Usability

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Photochemical chlorination and oxygenation reaction of cyclohexene sensitized by gallium(III) porphyrin–clay hybrid compound was investigated. Gallium(III) porphyrin did not aggregate on the clay surface, and thus, maintained photoactivity for the photochemical reaction. Gallium(III) porphyrin without clay decomposed immediately in the photochemical reaction. On the other hand, gallium(III) porphyrin adsorbed on clay was more stable than that without clay during the photochemical reaction and the altered porphyrin on clay still had photocatalytic ability along with original porphyrin. It was suggested that gallium(III) porphyrin was protected by clay surface during the photochemical reaction. In addition, the efficiency for the photochemical chlorination and oxygenation reaction was kept even at high porphyrin adsorption densities on clay. These findings are beneficial to construct efficient and durable photochemical reaction systems.

Organic–inorganic hybrid compounds,[1–13] especially dye–clay complexes,[1–8] have been investigated by many researchers with a view to constructing photofunctional materials. Clay minerals used as host materials are multilayered compounds consisting of stacked aluminosilicate nanosheets. Among them, swellable clays such as saponite can disperse completely as single nanosheets in aqueous solution. Saponite has negatively charged structures and the cation-exchange capacity (CEC) is ca. 1.0×10^{-3} equiv g^{-1}.[8] Its structure and stoichiometric formula are shown in Figure S1 (Supporting Information). The aqueous dispersion of saponite whose particle size is small (<ca. 100 nm) is substantially transparent in the UV–visible range.

Cationic dye molecules can adsorb on anionic clay surface and can be intercalated between anionic clay sheets by Coulomb's interaction and form organic–inorganic hybrid compounds.[1–8] However, dye molecules on or in such inorganic host materials are generally likely to lose their photoactivities because of undesirable aggregation behaviors of them.[12] Recently, we have found that tetracationic porphyrin molecules can adsorb on the saponite nanosheet surfaces without aggregation even at high adsorption density. This behavior is observed when the distance of intramolecular cationic points in porphyrin and the average distance of anion points on the clay surface coincide well with each other (size-matching effect or intercharge distance matching effect).[8,14–16] We also have reported that photoactivities of dye molecules such as fluorescence quantum yield or excited lifetime are maintained or enhanced by the complex formation with clay.[17,18] These findings are beneficial to construct photofunctional materials.

On the other hand, photochemical chlorination and oxygenation reactions of alkenes sensitized by metalloporphyrins with water as both electron and oxygen atom donor in homogeneous water–acetonitrile solution have been reported by several groups including us.[19–22] The proposed mechanism of this photochemical reaction is as follows. First, one-electron oxidation of excited triplet state metalloporphyrin takes place by an electron acceptor in aqueous acetonitrile. Subsequently, oxo-complex of metalloporphyrin produced from hydroxo or aquo coordinated porphyrin cation radical is attacked by an alkene. Then, epoxide or alcohol species are produced via carbocationic intermediates of metalloporphyrin. Chlorination of the alkenes is also catalyzed in the presence of chloride anion. The reaction formula using hexachloroplatinate(IV) anion ($[\mathrm{Pt^{IV}Cl_6}]^{2-}$) as an electron acceptor and cyclohexene (C_6H_{10}) as a substrate is shown below. The detailed reaction mechanism is shown in Figure 1. And the proposed chlorination reaction of cyclohexene is shown in Figure S2.

$$\mathrm{C_6H_{10}} + [\mathrm{Pt^{IV}Cl_6}]^{2-} + \mathrm{H_2O} \xrightarrow[\text{Metalloporphyrin}]{h\nu} \mathrm{C_6H_{10}O} + [\mathrm{Pt^{II}Cl_4}]^{2-} + 2\mathrm{HCl} \quad (1)$$

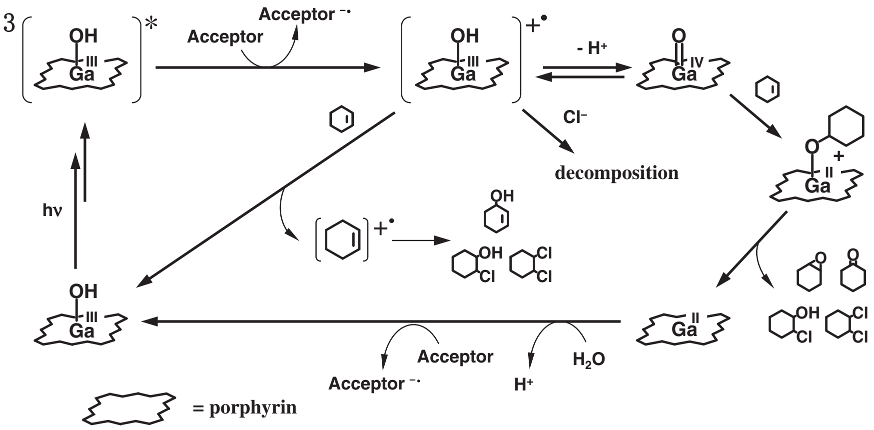
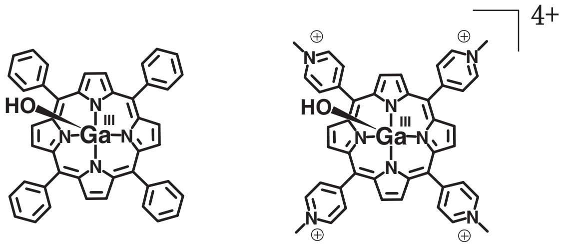


Figure 1. Proposed reaction for the photochemical chlorination and oxygenation of alkene sensitized by Ga^{III} porphyrin.



$[Ga^{III}(TPP)(OH)]$ $[Ga^{III}(TMPyP)(OH)]^{4+}$

Figure 2. Structures of gallium(III) porphyrins.

To extend the utilization and enhance the operability and durability of this photooxygenation reaction, the combination with heterogeneous reaction fields would be beneficial. For example, homogeneous photocatalysts such as metal complexes have been combined with inorganic host materials such as nano scrolls or mesoporous solids.[23–25] However, in such heterogeneous system, photoactivities of catalysts tend to be lowered compared to homogeneous system because the photocatalyst aggregates on the solid surface and loses photoactivity due to the shortened excited lifetime. In addition, typical inorganic materials providing heterogeneous reaction fields are often scattering bodies, and thus, the efficiency of photochemical reaction is lowered. In this sense, clay minerals are beneficial as host material for photochemical reactions, because i) dye molecules adsorb on the clay surface without aggregation and do not lose photoactivity even at high density by choosing appropriate combination of dye and clay and ii) clay nanosheet can disperse into a single nanosheet in solution and can be transparent in the UV–visible range.

In this study, we have investigated photochemical chlorination and oxygenation reaction of cyclohexene sensitized by tetracationic metalloporphyrin–clay complex as a heterogeneous chemical reaction system. Gallium(III) porphyrins are chosen as a metalloporphyrin for the photochemical reaction. Gallium(III) porphyrins are nonionic 5,10,15,20-tetraphenylporphyrinato hydroxo gallium(III) and tetracationic 5,10,15,20-tetrakis(*N*-methyl-4-pyridyl)porphyrinato hydroxo gallium(III) tetrachloride, denoted as $[Ga^{III}(TPP)(OH)]$ and $[Ga^{III}(TMPyP)(OH)]Cl_4$, respectively (Figure 2). $[Ga^{III}(TMPyP)(OH)]Cl_4$ adsorbed on clay nanosheet is used as a heterogeneous photocatalyst. It should be noted that this reaction system is quasi-homogeneous, because the complex can be well swelled in the solution and optically transparent in visible region. $[Ga^{III}(TPP)(OH)]$ is used as a reference photocatalyst without clay, because $[Ga^{III}(TMPyP)(OH)]^{4+}$ forms insoluble salt with an anionic electron acceptor and cannot work as reference photocatalyst in the absence of clay. The photochemical reactions using these photocatalysts with and without clay were examined.

Experimental

Materials and Measurements. Clay minerals (saponite): Sumecton SA was received from Kunimine Industries Co., Ltd. Hydroxo(5,10,15,20-tetraphenylporphyrinato)gallium(III) ($[Ga^{III}(TPP)(OH)]$, denoted as Ga^{III}TPP) was synthesized according to A. Coutsolelos and K. M. Kadish's methods[26,27] and characterized by ^{1}H NMR. Hydroxo[5,10,15,20-tetrakis-(*N*-methyl-4-pyridyl)porphyrinato]gallium(III) tetrachloride ($[Ga^{III}(TMPyP)(OH)]Cl_4$, denoted as Ga^{III}TMPyP) was purchased from Mid-Century Chemicals (Chicago, IL). Hexachloroplatinate(IV) disodium salt (denoted as $Na_2[Pt^{IV}Cl_6]$) was purchased from Aldrich. Cyclohexene was purchased from Nacalai Tesque and purified by short alumina column just before use.

UV–visible absorption spectra were obtained on Shimadzu UV-3150 spectrophotometer. Monochromatic light through filters (Edmund Optics Inc.) from a 500W Xe arc lamp (USHIO 500-DKO) was used for photochemical reactions. Interference filters were used for ca. 10 mW monochromatic lights ($\lambda_{max} = 550$ and 610 nm). Long pass filters of 630 nm and IR short path filters were used for monochromatic light ($\lambda_{max} = 640$ nm). Irradiation photon intensity was measured with an ADCMT 8230 optical power meter (ADC Corporation). The reaction products were analyzed by Shimadzu QP-2010 GC-MS spectrometer.

Photochemical Reaction Using Ga^{III}TPP without Clay. The concentrations of Ga^{III}TPP as a sensitizer, cyclohexene as a substrate and $Na_2[Pt^{IV}Cl_6]$ as an electron acceptor were 1.0×10^{-5}, 1.0×10^{-1}, and 5.0×10^{-4} M ($M = mol\,L^{-1}$), respectively. The solvent was 5 mL water–acetonitrile (30/70 (v/v)). The sample solution was added to a $1 \times 1 \times 4$ cm quartz cell sealed with a septum cap. The oxygen in sample solution was removed by nitrogen bubbling for 30 min in the dark at room temperature. Monochromatic light ($\lambda_{max} = 550$ nm) was irradiated to the stirred sample through a 4 cm light path. The photochemical reaction was monitored with a UV–visible spectrometer through a 1 cm light path. The reaction mixture after the photochemical reaction was vacuum-distilled, and the products were analyzed by GC-MS spectrometer. Monochromatic light ($\lambda_{max} = 640$ nm) was used for the subsequent photochemical reaction sensitized by altered Ga^{III}TPP.

Preparation and Identification of Ga^{III}TMPyP/Clay Complex. Ga^{III}TMPyP/clay complex was prepared by mixing porphyrin and clay in solution. Adsorption of porphyrin on clay was identified judging from an absorption spectral shift of porphyrin on the clay.[28] The concentration of porphyrin was 1.0×10^{-5} M. The adsorption densities of porphyrin on the clay surface were controlled by the clay concentrations. The loading levels of porphyrin were 20, 40, and 60% vs. CEC of clay in 2.0×10^{-4}, 1.0×10^{-4}, and 6.7×10^{-5} equiv L^{-1} clay dispersion, respectively. At all loading levels, Ga^{III}TMPyP was adsorbed on the clay without aggregation according to absorption spectra.

Photochemical Reaction Using Ga^{III}TMPyP/Clay Complex. The concentrations of porphyrin, substrate, and electron acceptor, the volumes of solvent and optical cell, and the methods of optical measurement and product analysis were same as those in the investigation without clay. Monochromatic light ($\lambda_{max} = 550$ nm) was irradiated to the sample. Monochromatic light ($\lambda_{max} = 610$ nm) was used for the subsequent photochemical reaction sensitized by altered Ga^{III}TMPyP.

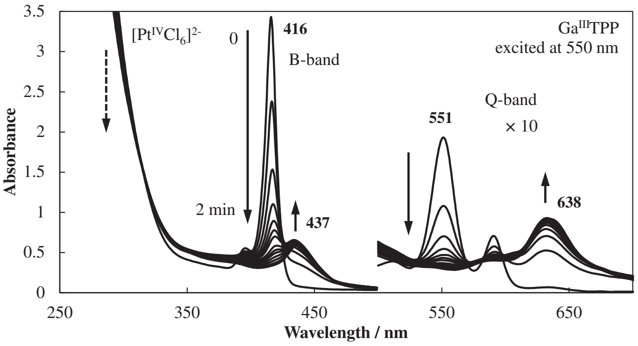


Figure 3. The absorption spectral change of the photoreaction mixture sensitized by Ga^{III}TPP. [Ga^{III}TPP] $= 1.0 \times 10^{-5}$ M. [cyclohexene] $= 1.0 \times 10^{-1}$ M. [Na$_2$Pt^{IV}Cl$_6$] $= 5.0 \times 10^{-4}$ M. The solvent was water–acetonitrile (30/70 (v/v)). Irradiation time ($\lambda_{max} = 550$ nm) was 0, 0.33, 0.67, 1, 1.33, 1.67, 2, 3, 4, 5, 7, 10, 15, and 20 min.

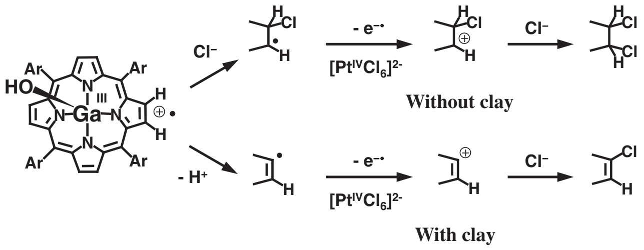


Figure 4. Proposed decomposition reaction for porphyrin cation radical with and without clay.

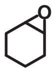
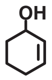
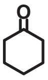
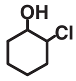
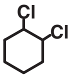
Results and Discussion

Photocatalytic Reaction Sensitized by Ga^{III}TPP without Clay. Photochemical chlorination and oxygenation reaction of cyclohexene sensitized by Ga^{III}TPP without clay was examined by irradiating visible light ($\lambda_{max} = 550$ nm). As a result, the photochemical reaction proceeded according to the change of absorption spectra of Ga^{III}TPP and [Pt^{IV}Cl$_6$]$^{2-}$. The electron-transfer reaction to [Pt^{IV}Cl$_6$]$^{2-}$ would be from not excited singlet state Ga^{III}TPP but excited triplet state judging from the fact that porphyrin could react with a small amount of electron acceptor. During the photoirradiation, B-band at 416 nm and Q-band at 551 nm of Ga^{III}TPP decreased and disappeared after 2 min irradiation (Figure 3). And, the quantum yield (Φ_{eT}) for the electron transfer from excited Ga^{III}TPP to [Pt^{IV}Cl$_6$]$^{2-}$ was estimated to be 4×10^{-2} from the irradiation photon intensity and the decreased amount of [Pt^{IV}Cl$_6$]$^{2-}$ absorption at 2 min irradiation. The Φ_{eT} value is rough and it is difficult to estimate an exact value because the absorption spectra of photolyte of porphyrin were superimposed some what on those of [Pt^{IV}Cl$_6$]$^{2-}$. The absorption spectra of reaction mixture did not change by air exposure after irradiation. Judging from its absorption spectra ($\lambda_{max} = 437$ and 638 nm), the photolyte of Ga^{III}TPP was supposed to be chlorin derivative in which one β-pyrrole position of porphine macrocycle becomes a single bond.[29–32] The decomposition of porphyrin would be due to an addition of chloride anion (Cl$^-$) to a β-pyrrole position of its cation radical ([Ga^{III}TPP]$^{\bullet+}$). This speculation is supported by the fact that the decomposition of Ga^{III}TPP was suppressed by the addition of AgNO$_3$ as quencher of Cl$^-$ (not shown). The proposed producing scheme of Cl-adducts of porphyrin without clay is shown in Figure 4. On the other hand, [Pt^{IV}Cl$_6$]$^{2-}$ was consumed slightly with the decomposition of Ga^{III}TPP (shown as dotted arrow in Figure 3). The oxidative products of cyclohexene in the photoreaction mixture were almost not observed by GC-MS; the total concentration of photoproduct was 0.5×10^{-5} M at 7 min irradiation (Table 1). The product was not formed by a catalytic process with Ga^{III}TPP because the turnover number (TON), that is molar number of oxidative products of cyclohexene until 1 mol photocatalyst is decomposed, was about 0.6. These results suggest that most porphyrin cation radical [Ga^{III}TPP]$^{\bullet+}$ produced by photoinduced electron-transfer reaction was decomposed without participating in a catalytic cycle.

The further photochemical reaction sensitized by the chlorin-like photolyte of Ga^{III}TPP was also examined by irradiating visible light ($\lambda_{max} = 640$ nm). [Pt^{IV}Cl$_6$]$^{2-}$ was slightly consumed and chlorin-like porphyrin decomposed gradually by 180 minutes irradiation as shown in Figure 5. And, the quantum yield (Φ'_{eT}) for the electron transfer from the excited photolyte of Ga^{III}TPP to [Pt^{IV}Cl$_6$]$^{2-}$ judging from the decrease of [Pt^{IV}Cl$_6$]$^{2-}$ absorption was estimated to be 1×10^{-2} at 10 min irradiation. The additional total photochemical oxygenated product in subsequent irradiation was 0.7×10^{-5} M ($= (1.2 - 0.5) \times 10^{-5}$ M) (Table 1). The TON value was about 3. These results indicate that the chlorin-like porphyrin also acts as a sensitizer for the photochemical chlorination and oxygenation.

Photocatalytic Reaction Sensitized by Ga^{III}TMPyP^{4+}/Clay Complex. Photochemical chlorination and oxygenation reaction of cyclohexene sensitized by Ga^{III}TMPyP–clay com-

Table 1. Products of Photochemical Chlorination and Oxygenation Reaction of Cyclohexene Sensitized by $Ga^{III}TPP$ and $[Ga^{III}TMPyP]$–Clay Complex[a)]

Sensitizer	Products/10^{-5} M							Irradiation	
							Total yield	Power/mW (λ_{max}/nm)	Time /min
				cis	*trans*	*trans*			
$Ga^{III}TPP$	0	0	0	0.2	0.1	0.2	0.5	8.3 (550)	7
$Ga^{III}TPP$ (photolyte)	0	0	0	0.1	0.1	1.0	1.2	4.1 (640)	+180
$[Ga^{III}TMPyP]$–clay	0.1	0.1	0.5	0.2	0.4	2.7	4.0	8.1 (550)	40
$[Ga^{III}TMPyP]$–clay (photolyte)	0.5	0.3	1.5	1.2	3.2	27.0	33.7	8.5 (610)	+220

a) [Ga^{III} porphyrin] = 1.0×10^{-5} M, [$Na_2Pt^{IV}Cl_6$] = 5.0×10^{-4} M, [cyclohexene] = 1.0×10^{-1} M, [clay] = 2.0×10^{-4} equiv L^{-1}. Visible light for porphyrins (550 nm) was irradiated first. Subsequently, other visible lights for the photolytes of $Ga^{III}TPP$ and $Ga^{III}TMPyP$ were irradiated at 640 and 610 nm, respectively. The solvent was 5 mL water–acetonitrile (30/70 (v/v)). The product values of porphyrin photolyte are the sum of products obtained in first and subsequent irradiation.

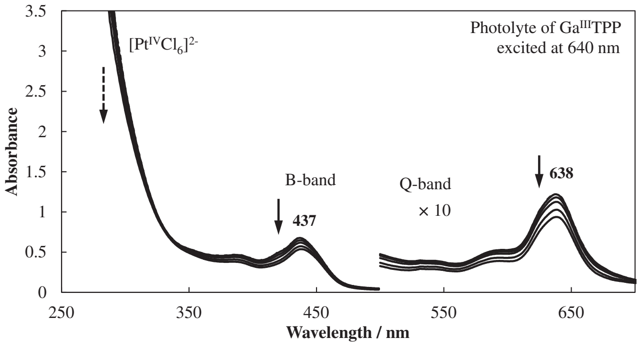


Figure 5. The absorption spectral change of the photoreaction mixture sensitized by the photolyte of $Ga^{III}TPP$ that would be Cl-adducts of porphyrin. [$Ga^{III}TPP$] = 1.0×10^{-5} M. [cyclohexene] = 1.0×10^{-1} M. [$Na_2Pt^{IV}Cl_6$] = 5.0×10^{-4} M. The solvent was water–acetonitrile (30/70 (v/v)). Irradiation time (λ_{max} = 640 nm) was 0, 1, 10, 30, 90, and 180 min.

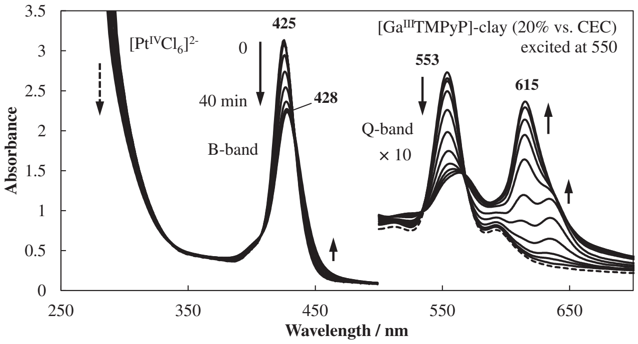


Figure 6. The absorption spectral change of the photoreaction mixture sensitized by $Ga^{III}TMPyP$–clay complex. The loading level was 20% vs. CEC of clay. [$Ga^{III}TMPyP$] = 1.0×10^{-5} M. [cyclohexene] = 1.0×10^{-1} M. [$Na_2Pt^{IV}Cl_6$] = 5.0×10^{-4} M. [clay] = 2.0×10^{-4} equiv L^{-1}. The solvent was water–acetonitrile (30/70 (v/v)). Irradiation time (λ_{max} = 550 nm) was 0, 1, 2, 5, 10, 15, 20, 25, 30, 35, and 40 min.

plex was examined by irradiating visible light (λ_{max} = 550 nm). Although the photochemical reaction proceeded along with $Ga^{III}TPP$, some differences from $Ga^{III}TPP$ were observed. Under the condition of 20% dye loading versus CEC of clay, during the photoirradiation, the absorption of $Ga^{III}TMPyP$ decreased more slowly than that of $Ga^{III}TPP$ as shown in Figure 6. And, most of the B-band of $Ga^{III}TMPyP$ was preserved even after 40 min irradiation in contrast to complete decomposition of $Ga^{III}TPP$ after 2 min irradiation. The quantum yield (Φ_{eT}) for the electron transfer from the excited $Ga^{III}TMPyP$ to $[Pt^{IV}Cl_6]^{2-}$ was estimated to be 3×10^{-2} at 2 min irradiation. From these results, it was suggested that $Ga^{III}TMPyP$–clay complex was more stable in the photochemical reaction than $Ga^{III}TPP$ without clay. During the 40 min photoirradiation, the B-band at 425 nm and Q-band at 553 nm of $Ga^{III}TMPyP$ decreased and new B-band at 428 nm and Q-band at 615 nm were superimposed on the spectra (Figure 6). The absorption wavelength and spectral shape of the new species were different from those of the photolyte of $Ga^{III}TPP$. These results indicate that the observed species maintained most of its own porphyrin π-conjugated system. Judging from absorption wavelength and spectral shape, the species on clay was expected to be not chlorin derivatives but Cl-substitutions of porphyrin.[33,34] This result suggests the attack of Cl^- to porphyrin cation radical should be suppressed or controlled by anionic clay surface sterically and electrically and the proton dissociation from porphyrin cation radical might proceed, leading to Cl-substitutes of porphyrin (Figure 4). On the other hand, $[Pt^{IV}Cl_6]^{2-}$ was consumed somewhat on its absorption. And the total concentration of photochemical oxygenated product was 4.0×10^{-5} M at 40 min irradiation (Table 1). The TON value was about 30. These results indicate that the $Ga^{III}TMPyP$–clay complex has a higher catalytic ability compared to $Ga^{III}TPP$.

Next, the photoreaction sensitized by the photolyte of $Ga^{III}TMPyP$ on clay was also examined irradiating visible light (λ_{max} = 610 nm). Interestingly, $[Pt^{IV}Cl_6]^{2-}$ was completely consumed by 220 min irradiation on the absorption spectra (Figure 7). And, the quantum yield (Φ'_{eT}) for the electron transfer from the excited photolyte of $Ga^{III}TMPyP$ to $[Pt^{IV}Cl_6]^{2-}$ was estimated to be 1×10^{-2} at 10 min irradiation. The additional total photochemical oxygenated product in subsequent irradiation was 29.7×10^{-5} M (= $(33.7 - 4.0) \times 10^{-5}$ M) (Table 1). Considering both the first and subsequent irradiations, total products by $Ga^{III}TMPyP$–clay complex were 28 times those by

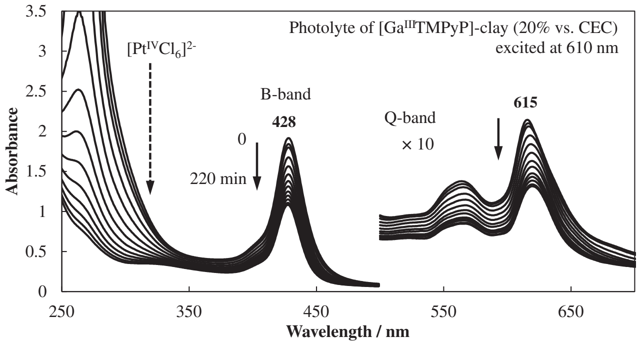


Figure 7. The absorption spectral change of the photoreaction mixture sensitized by the photlyte of Ga^{III}TMPyP that would be Cl-substitutes of porphyrin. The loading level was 20% vs. CEC of clay. [Ga^{III}TMPyP] $= 1.0 \times 10^{-5}$ M. [cyclohexene] $= 1.0 \times 10^{-1}$ M. [Na$_2$Pt^{IV}Cl$_6$] $= 5.0 \times 10^{-4}$ M. [clay] $= 2.0 \times 10^{-4}$ equiv L^{-1}. The solvent was water–acetonitrile (30/70 (v/v)). Irradiation time ($\lambda_{max} = 610$ nm) was 0, 10, 20, 40, 60, 80, 100, 120, 120, 140, 160, 180, 200, and 220 min.

Ga^{III}TPP. The TON value reached about 80. Moreover, the photolyte of Ga^{III}TMPyP was stable and not completely decomposed by subsequent irradiation as shown in Figure 7. These results indicate that the photolyte of Ga^{III}TMPyP–clay complex also has a higher catalytic ability than that of Ga^{III}TPP. It is suggested that there are some types of Cl-substitutions of Ga^{III}TMPyP and that the substitution of Cl into porphyrin macrocycle occurred continuously with proceeding of photoreaction because some changes of the absorption spectra of Q-band were observed (Figures 6 and 7).

As a result, it is accomplished to improve the efficiency of the photochemical reaction due to steric and electric protection effect of photocatalyst by clay nanosheet surface.

Photocatalytic Reaction Using Ga^{III}TMPyP^{4+}/Clay Complex at Various Loading Levels. Additionally, the photocatalytic reactions using Ga^{III}TMPyP–clay complex at various loading levels of Ga^{III}TMPyP were investigated by controlling concentrations of clay. Even in increasing adsorption densities of Ga^{III}TMPyP on the clay surface, their behavior for the photoreaction were not different. Both of the amounts of products and the behaviors of decomposition of Ga^{III}TMPyP were almost the same at 20, 40, and 60% vs. CEC loadings (Figures S3, S4, S5, and S6). As a result, the quantum yields for electron transfer from excited Ga^{III}TMPyP (Φ_{eT}) and its excited photolyte (Φ'_{eT}) to [Pt^{IV}Cl$_6$]$^{2-}$ were almost constant at all dye loadings. The Φ_{eT} and Φ'_{eT} values were 3×10^{-2} at 2 min irradiation and 1×10^{-2} at 10 min irradiation, respectively. The amounts of the oxidative products of cyclohexene were also the same regardless of dye loadings (Table S1). These results indicated that its catalytic ability can be maintained and the protection effect of photocatalyst by clay can be working uneventfully even under high density adsorption conditions due to nonaggregate array of dye molecules on the clay surface (Size-matching Effect).[8,14–16]

Reusability of Ga^{III}TMPyP^{4+}/Clay Complex. Ga^{III}TMPyP–clay complex works like homogeneous photocatalyst in stirred reaction mixture due to dispersion of clay nanosheet and the photoreaction could proceed well along with Ga^{III}TPP without clay. This mixture of dye–clay complex is useful for photoreaction because the clay dispersion is transparent in UV–visible range. And, they behaved as heterogeneous and the product mixture and precipitated catalyst could be separated when the reaction mixture was stored without stirring (Figure 8). The separation of product mixture and photocatalyst is useful for systemization of the photoreaction because it is possible to extract products and add reactants over again.

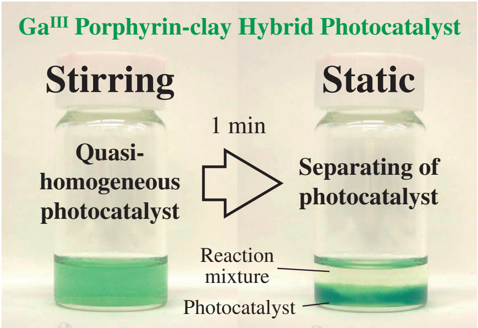


Figure 8. The appearance of photoreaction mixture sensitized by the altered Ga^{III}TMPyP–clay complex with and without stirring.

Conclusion

Photochemical chlorination and oxygenation reactions of cyclohexene sensitized by gallium(III) porphyrin without clay and cationic gallium(III) porphyrin–anionic clay complex were investigated. In a homogeneous system without clay, porphyrin as photocatalyst decomposed immediately in the photoreaction and the altered porphyrin did not have photocatalytic ability. On the other hand, porphyrin molecule complexed with clay was more stable than that without clay. Additionally, the altered porphyrin with clay maintained its own π-conjugation system and also had catalytic ability along with original porphyrin. These results were expected to be due to steric and electric protection of porphyrin cation radical from chloride anion by clay surface. Moreover, the protection of porphyrin and photochemical reaction efficiency did not change even under high porphyrin adsorption conditions on clay. These results were expected to be due to adsorption behavior of porphyrin molecules on the clay surface without aggregation. The porphyrin–clay complex could catalyze the photochemical reaction well like homogeneous photocatalyst in stirred reaction mixture and could be separated from product mixture like heterogeneous one without stirring. This behavior allows both efficient photoreaction and convenient extraction of product. These findings are beneficial to construct and develop artificial photochemical systems using the porphyrin–clay hybrid compounds as quasi-homogeneous photocatalysts.

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Supporting Information

The structure of synthetic saponite (Figure S1), the proposed reaction scheme for the chlorination reactions of cyclohexene

(Figure S2), the absorption spectral change of the photoreaction mixture sensitized by Ga^{III}TMPyP–clay and its photolyte–clay complexes at 40 and 60% vs. CEC (Figures S3, S4, S5, and S6), and the products of photochemical oxygenation reaction of cyclohexene sensitized by Ga^{III}TMPyP and its photolyte on the clay surface at various dye loadings (Table S1) are available electronically on J-STAGE.

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