The Unique Structure–Activity Relationship of Porphyrins and Clay Mineral Systems in Modern Applications: A Comprehensive Review

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Review
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Porphyrins are a group of organic heterocyclic macromolecules, composed of four modified pyrrole subunits interconnected at their α carbon atoms via methine bridges. This unique and significant group of compounds has a special relationship with inorganic clay minerals, which are hydrous aluminium phyllosilicates. Clay minerals, known to be typical layered materials, act as unique hosts for porphyrin molecules or their precursor materials. When the porphyrin compound enters between the layers of a clay, it can orient horizontally, diagonally, or perpendicularly. Cation-exchanged clay can provide the acidity required for the formation of porphyrins from its precursor molecules without the need for other auxiliary factors such as heating. Clays are also capable of facilitating the incorporation of various metals into the porphyrin ring to form a metalloporphyrin. The properties of these metalloporphyrin clay complexes have been studied extensively. Modern applications of such clay-porphyrin materials include their use as heterogeneous catalysts for oxidation and polymerization reactions in the synthesis of new materials. These heterogeneous catalysts have a wide range of uses in vital sectors, such as food manufacturing, pharmaceuticals, and the chemical industry. Additionally, clay-porphyrin systems are employed in constructing various types of self-assembling artificial photosynthesis systems.

Keywords
porphyrin-clay systems, structure-activity relationship, heterogeneous catalysts, self-assembling artificial photosynthesis systems

Introduction

Porphyrin molecules are a widely utilized biochemical moiety with applications in materials science, sensing, and pharmaceutical chemistry. These molecules are large aromatic units, approximately flat with a regular and rigid structure[1]. The bare molecule is referred to as porphine, and when the periphery of the ring is substituted, the substituted porphines are called porphyrins[2]. The porphine moiety is capable of bonding with a wide range of substituents by bonding through external carbons in the *β*- and *meso*-positions on the ring (Fig. 1)[3]. Porphyrins containing iron atoms at their centers are vital to life on Earth, playing a variety of roles, including oxygen storage and transport, and are found in numerous enzymes and vitamins[4]. Related macrocycles containing magnesium, known as chlorophylls, are involved in photosynthesis in both the bacterial and plant kingdoms[4]. Synthetic porphyrins and metalloporphyrins exhibit remarkable biological, photophysical, and photochemical capabilities, making them potential candidates for disease treatment[5]. Additionally, they can be used in biological imaging[6], molecular photovoltaics[7], photocatalytic[8], nonlinear optics[9], and many other industrial and analytical applications.

Clay minerals are predominantly fine-grained natural materials with particle sizes of < 2 μm [10]. They essentially consist of two-dimensional arrays of silicon-oxygen tetrahedra and two-dimensional arrays of aluminium- or magnesium-oxygen-hydroxyl octahedra. A unit layer is defined as the combination of one or two tetrahedral sheets with an octahedral sheet, while a unit cell refers to the repeated structural elements contained within one unit layer. Within the unit layers, the two-dimensionally repeating unit cells are aligned parallel to each other. The basal or c-spacing is the distance between a plane in one layer and the corresponding plane in the adjacent layer. The combination of one tetrahedral and one octahedral sheet forms what are known as two-layer minerals or 1:1 type minerals

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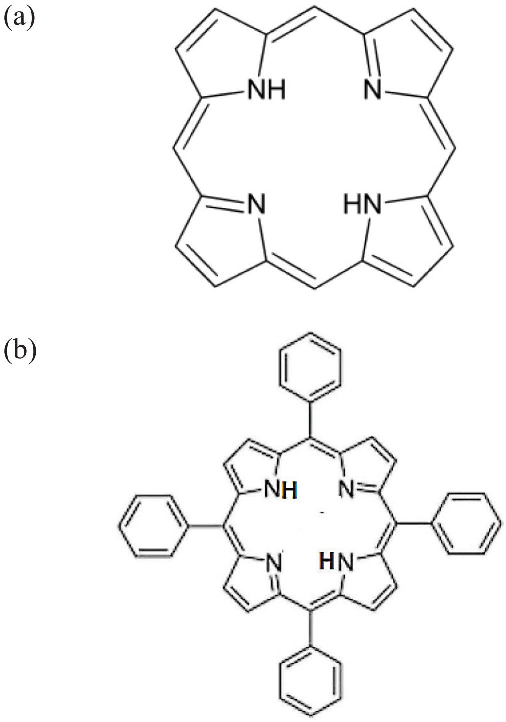

Fig. 1 – *Structure of (a) Porphine, (b) Tetraphenyl porphyrin*

(Fig. 2). In 2:1 type minerals, the octahedral sheet is sandwiched between two tetrahedral sheets, forming what are called three-layer minerals (Fig. 3)[11].

The relationships and interactions between porphyrins and minerals (rocks) have been the subject of ongoing research since the work of Treibs[12]. The debate concerning the origin of porphyrin pigments in petroleum, as well as the origin of petroleum itself, has focused on whether their source is plant or animal. These porphyrins are derived from precursor pigments found in the source material and play an active role in the formation of crude oil from its source, biogenic material[13]. The role of clay minerals in the degradation of chlorophyll to a homologous series of porphyrins, comparable to those found in petroleum, has also been studied[14]. It has been demonstrated that a single porphyrin can generate a sequence of porphyrins by simulating geochemical conditions critical in the production of petroleum[15]. The production of porphyrins from simple environmental molecules in the presence of clay minerals is not well understood, and has been the focus of limited research[16–18]. It was found that the acidity of the clay surface has a substantial impact on its catalytic properties towards organic molecules[19].

This review focuses on the roles of clay in the formation of both porphyrin from its raw materials, and metalloporphyrin through the interaction of porphyrin with various exchangeable cations present in the clay. The modern applications of this process will also be reviewed.

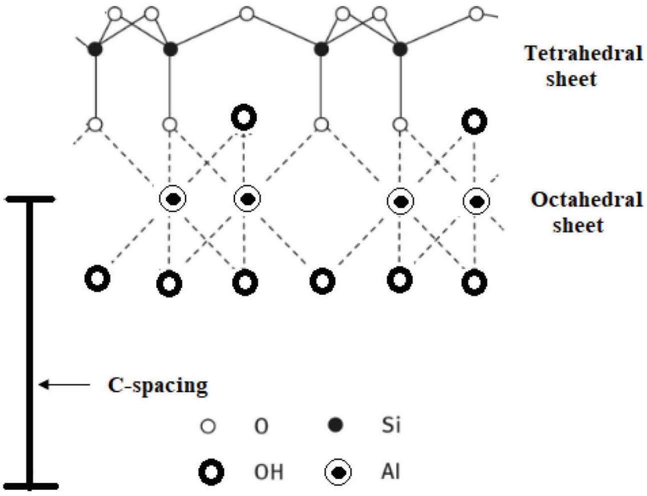

Fig. 2 – *Schematic presentation of a two-layer clay mineral*

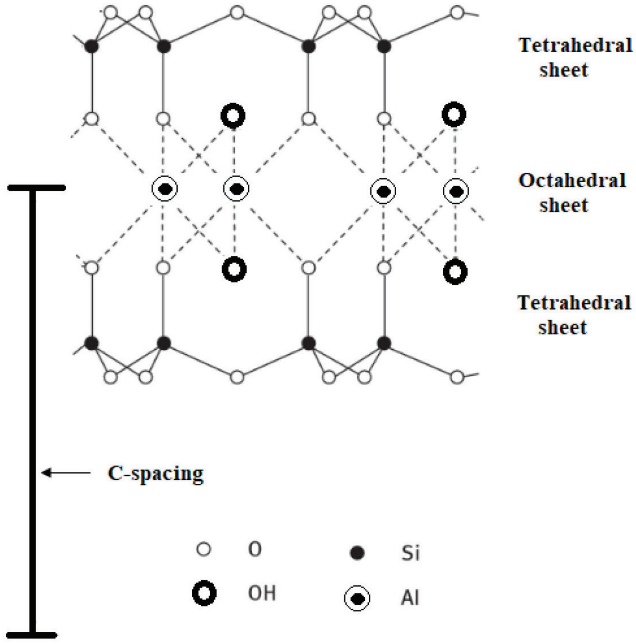

Fig. 3 – *Schematic presentation of a three-layer clay mineral*

Porphyrin synthesis on clays

The first attempt to synthesize porphyrin using a clay surface as a catalyst was reported in 1978 by Cady and Pinnavaia[20]. Later, in 1983, other researchers conducted similar experiments, reacting equimolar amounts of pyrrole and benzaldehyde in the presence of clay samples saturated with various cations. The product from these reactions, porphodimethine, is an intermediate compound on the route to porphyrin formation[21–23]. Using montmorillonite clay K10, *meso*-tetraalkylporphyrins have been synthesized in high yields from aliphatic aldehydes and pyrrole. The nanometer-sized porous structures of K10 montmorillonite were found to be ideal for polymerization-cyclization condensations of aldehyde and pyrrole[18]. Additionally, the synthesis of porphyrins from pyrrole condensed with aldehydes, was facilitated by solid acids such as K10 montmorillonite. The relative amount of the desired mixed porphyrin can be maximized by combining the use of two different aldehydes, A and B, with unequal, statistical quantities of A and B[24]. It was found that K10 montmorillonite is more effective than traditional homogeneous acids like BF_3 etherate at catalyzing the synthesis of alkylporphyrin derivatives from aliphatic aldehydes and pyrroles[25]. A group of porphyrins and pyrromethanes has also been prepared using K10 montmorillonite clay catalyzed with various acids (*p*-TsOH, BF_3 Et_2O). The naturally occurring clay proved to be an effective reagent for such synthesis[26].

Recently, we reported on the reactions of five different aldehydes with pyrrole in the presence of montmorillonite and kaolinite clay samples saturated with Fe(III), Cu(II), Cd(II), Co(II), Zn(II), Ni(II), and Na(I) cations. The aldehydes used were 1-naphthaldehyde, cinnamaldehyde, phenylacetaldehyde, salicylaldehyde, and 4-carboxybenzaldehyde. The initial appearance of a pink color, representing the start of porphyrin generation, was shown to depend on the acidity of the cation in the clay's exchanged sites, as well as on the cation exchange capacity. The intermediate compound, generated in the montmorillonite interlayer as well as on the surface, was oxidized to porphyrin when desorbed from the clay surface by adding chloroform to the solid samples. In contrast, in the presence of kaolinite clay, the intermediate compound formed only on the surface[27].

Adsorption of porphyrins on clays

The interactions of porphyrins (and other naturally occurring macrocycles) with clays have been studied extensively to understand both the reactions involved and their potential roles in ancient and modern biospheres[28–63]. The adsorption of commercial K-Cu chlorophyllin by a montmorillonite clay sample saturated with various exchangeable ions was investigated. The organic anions were adsorbed on the surfaces, whilst K^+ cations displaced most of the exchangeable cations. The samples adsorbed the chlorophyllin components selectively and in varying amounts, depending on the exchangeable cations of the clay[28]. Another study showed that the nature of the acidity of the clay changed following adsorption of the chlorophyll molecule, believed to be adsorbed as a protonated species[29]. The adsorption of protoporphyrin IX, and hematoporphyrin by kaolinite and a Ca-montmorillonite in aqueous solutions buffered at pH 4 and 9 was investigated. At pH 9, both kaolinite and montmorillonite showed equivalent saturation of sites by porphyrins in their anionic forms. The largest discrepancies in adsorption isotherms were related to variances in clay exchange capacities[30]. The adsorption of two *meso*-substituted porphyrins, *meso*-tetraphenylporphyrin (TPP) and *meso*-tetra(4-pyridyl)porphyrin (TPyP), on cation-exchanged montmorillonite revealed that TPP was protonated during adsorption, while the behavior of TPyP depended on water content[31]. Studies on the adsorption of TPP with selected cations on the interlamellar surfaces of montmorillonite clay revealed that strongly acidic cations, such as Fe^{3+} and VO^{2+}, react quantitatively with the porphyrin free base TPP to generate the protonated dication $TPPH_4^{2+}$. In contrast, weakly acidic cations like Na^+ and Mg^{2+} on the exchanged sites yield only a trace of the $TPPH_4^{2+}$ species[20]. A similar study revealed that both TPP and TPyP compounds undergo protonation regardless of the exchange cation present on the montmorillonite, but the TPP was adsorbed in smaller amounts than TPyP[32]. The chloride salts of tetrakis(l-methyl-4-pyridiniumyl) porphyrin (TMPyP) and tetrakis(*N,N,N*-trimethyl-4-aniliniumyl)porphyrin were ion-exchanged into the interlayer space of montmorillonite, hectorite, and fluorhectorite. The porphyrins were diprotonated although a portion remained in the form of a free base. The tetrakis(*N,N,N*-trimethyl-4-aniliniumyl)porphyrin was partially metallated during the reaction with Cu-montmorillonite[33]. The Soret band (the strong band at approximately 400 nm) of the compound shifted to longer wavelengths[34]. The TMPyP adsorption on montmorillonite revealed the presence of both protonated and non-protonated species of the compound on the clay[35]. Raman and UV-visible spectroscopies were used to investigate the interaction of the water-soluble 5,10,15,20-tetrakis(l-methyl-4-pyridyl)-21H,23H-porphine with several 2:1 phyllosilicates. Raman results supported the presence of at least two porphyrin species, protonated porphyrin and a more planar non-protonated porphyrin[36]. Smectite clays intercalated with tetrakis(1-methyl-4-pyridinio)porphyrin were found to be thermally stable up to 600 °C [37]. Adsorption of the dicationic porphyrins, cis- and trans-bis(*N*-methylpyridinium-4-yl)diphenyl porphyrins on montmorillonite led to significant changes in their spectra but preserved the photoactivity of the compounds. These changes could be linked to two phenomena: structural changes in the porphyrin molecules (flattening) and molecular aggregation[38]. It was found that the average intermolecular distance between tetrakis(1-methylpyridinium-4-yl)porphyrin molecules on the synthetic saponite surface could be controlled, depending on the charge density of the saponite as indicated by the porphyrin absorption maxima[39]. A study of the spectrum features of *meso*-tetrakis(*N*-methylpyridinium-4-yl)porphyrin adsorbed on clay with various layer charges revealed that the spectral changes could be explained in terms of structural alterations (flattening, protonation), as well as molecular aggregation[40]. The adsorption behavior of protonated species of 5,10-diphenyl-15,20-di(4-pyridyl)porphyrin on the surface of saponite clay was studied in aqueous solution at pH 1. It was found that the compound absorbed on the clay surface without aggregation[41]. Dichroic wave guide spectroscopy was used to examine the relationship between the maximum absorption wavelength (λ_{max}) and the adsorption orientation angle (Q_{ad}) of tetra(*N*-methyl-4-pyridinium)porphyrin derivatives adsorbed on clay nanosheet monolayer film prepared by the Langmuir-Blodgett method. It was found that each porphyrin λ_{max} was red shifted as a result of adsorption on the nanosheets[42]. Using a precise, reproducible, and simple absorption measurement method, 5,10,15,20-tetrakis(1-methylpyridinium-4-yl)porphyrin adsorption on perovskite-type nanosheet can be evaluated even at very low absorbance in the order of 0.001 [43]. The adsorbed 4+ charged cationic porphyrins on an artificially synthesized clay were investigated. It was found that porphyrin molecules adsorbed with high density (without aggregation) on the clay sheet, neutralizing all minus charges on the clay surface. An efficient energy transfer between various porphyrins was induced on the clay surface[44,45].

The orientation of the porphyrin molecule when it is present with clay has attracted special attention. An X-ray diffraction study suggested a flat orientation of the tetramethylpyridylporphyrins TMPyP molecule on the clay[46], with the cationic TMPy groups nearly perpendicular to the plane of the porphine[47]. Cationic porphyrins were intercalated within the interlayer spaces of nano-layered clay by repeated freeze-thaw cycles. The compounds were found to be rigidly packed parallel to the clay layer[48]. The adsorption of the porphyrin compounds tetrakis(1-methylpyridinium-4-yl)porphyrin and tetrakis(1-methylpyridinium-3-yl)porphyrin on clay was studied. The orientation of both compounds on the clay monolayers was found to be parallel and tilted with respect to the clay surface, depending on the solution used[49]. By creating a new technique for sample preparation conditions, cationic porphyrin was successfully intercalated into a transparent clay membrane. When the solvent for the porphyrin penetration process was water:ethanol = 1:2 (v:v), high density intercalation of porphyrin into the clay membrane was accomplished. The porphyrin orientations in the clay layers were nearly parallel to the clay nanosheet as a monolayer[50]. In contrast, it was found that cationic porphyrins with flexible ω-ammonioalkyl side chains could be quantitatively ion-exchanged into the interlamellar spaces of montmorillonite, saponite, and hectorite clay samples without protonation to the porphin ring. The porphin ring was found to be positioned upright rather than parallel to the clay surface[51]. A thermodynamic analysis of the dicationic porphyrin orientation on the clay surface revealed that the entropy component sustained the parallel orientation of the porphyrin primarily, while the enthalpy term stabilized the tilted orientation[52]. It was found that porphyrin molecules could exhibit two forms of orientation, tilted and parallel, toward a surface of silicate nanosheet in a mixture of water and dimethylformamide solvent[53].

Studies on the photochemical energy transfer of cationic porphyrins on an anionic type clay surface indicated that the loading level of porphyrin had a considerable effect on the efficiency of energy transfer and excited-state quenching in the absence of energy transfer. Both energy transfer efficiency and excited-state quenching increased as the loading level increased[54]. According to a PV-ATR study, the multicationic porphyrin molecules on the clay sheets in water were oriented roughly parallel (<5°) to the clay surface[55]. It was found that the structure of porphyrin assembly on the clay can be effectively controlled using the electrostatic host–guest interaction. Almost 100 % efficiency of the energy-transfer reaction was achieved as a typical example for an artificial light-harvesting system[56]. When 4+ charged cationic porphyrins adsorbed on an anionic clay were studied with time-resolved fluorescence and steady-state spectroscopy, the absorption spectra revealed no interaction between the porphyrin transition moments on the clay surface. Even with minimal porphyrin loading, an effective energy transfer pathway from donor to acceptor porphyrin was observed on the clay surface[57].

We have reported that during the adsorption of the free base water-soluble tetra(*p*-sulphophenyl) porphyrin on Fe(II), Fe(III), Cu(II), Co(II), Ni(II), Zn(II), Cd(II), Sn(IV) and UO_2^{2+} metal ion-exchanged montmorillonites, SAT metal-porphyrin complexes of the cations had formed (SAT indicates sitting atop, i.e., the metal is above the porphyrin plane). The incorporation of the metal ion on/into/with the porphyrin ring followed the order: Cu(II) > Zn(II) > Co(II) > Fe(II) > Ni(II) > Cd(II) > Fe(III) > Sn(IV) > UO_2^{2+}. The porphyrin was found to be adsorbed only on the external surface of montmorillonite, but could be intercalated in the presence of sodium ions in solution to open the clay lattice[58].

We also investigated the adsorption of *meso*-tetra-*p*-tolylporphyrin and *meso*-tetra-naphthylporphyrin on montmorillonite, and found that the two compounds tend to be more planar on the clay surface. The metal-exchanged ion in the clay is incorporated into the porphyrin rings when the porphyrin molecules react with montmorillonite saturated with the metal ion of an appropriate size to fit into the porphyrin compound ring, such as Cu(II)[59]. The metallation process occurred in a solvent that was miscible with water, allowing the hydrated sphere of the metal ion to penetrate the montmorillonite interlamellar layers[59]. We suggested that *meso*-tetra-naphthylporphyrin (where the *meso* substituent is less free to rotate) cannot penetrate the interlamellar spacing of the clays[59]. The effects of porphyrin structure on the complex formation behavior with clay have also been studied by others[60,61]. The zwitterionic porphyrin [4-(2-carboxyethyl)pyridinio], when adsorped on the clay surface, formed a three-dimensional structure by electrostatic interactions on the clay surface between porphyrins[61]. The adsorption behavior of *meso*-tetra(4-*N,N,N*-trimethylanilinium)porphyrin onto sodium montmorillonite clay revealed that at low/high pH, the compound adsorbs in a monolayer fashion, but at slightly acidic/neutral pH, the compound may rearrange on the surface and/or form aggregates[62]. Absorption, steady-state, and time-resolved fluorescence spectroscopies were used to investigate the interaction of tetra cationic porphyrin, 5,10,15,20-tetrakis(*N*-methylpyridinium-4-yl)porphyrin, with clays in aqueous dispersions[63]. The adsorption process led to significant changes in the spectral properties of the porphyrins[63].

Adsorption of metalloporphyrins on clays

An early attempt to study the adsorption of a metalloporphyrin complex (hemin) on clays dates back to the early seventies[30]. Since then, there has been ongoing interest to study the behavior of metalloporphyrins and their complexes when they are adsorbed on the surface of clay or between its layers. Additionally, the behavior of the metal within the porphyrin ring and the extent of its stability inside the ring during the reaction with clays has aroused much interest[64–77]. Studies using UV/visible and luminescence spectroscopy on the adsorption of Sn(IV)TPyP (*meso*-tetrapyridylporphyrin) on sodium hectorite revealed that the complex demetallates to the dication TPyP upon dehydration of the clay. The process was found to be reversible[64]. It was found that stable metalloporphyrins like Sn(IV)TPP can be adsorbed without demetallation while in the presence of sufficient water. In contrast, complexes like Fe(III)TPP are demetallated during adsorption[31]. On the other hand, water-soluble porphyrin complexes of Cu(II) and Fe(III), tetrakis(*N*-methylpyridyl)porphyrin, and tetrakis(*N,N,N*-trimethylanilinium)porphyrin were intercalated in the Ca(II) montmorillonite interlayer without demetallation upon adsorption[65]. A study on the stability of metal-porphyrins on clays found that vanadyl and nickel porphyrin complexes were the most stable, while Mg porphyrin was unstable in contact with the clay[66]. When the Co(II) *meso* tetrakis(1-methyl-4-pyridyl)porphyrin complex reacted with montmorillonite, it intercalated into the interlayer without demetallation[67], adopting a flat orientation relative to the host layers[39]. Other researchers have reported that Fe(III) and Co(II) porphyrin complexes are stable when reacting with montmorillonite and fluorhectorite clays[33]. The transition probabilities and fluorescence quantum yields of mono-, tri-, and penta-cationic antimony(V) porphyrin derivatives showed a tendency to increase upon complex formation with clay[68]. The flattening of the *meso* substituent with respect to the plane of the porphyrin ring was experimentally verified as the mechanism causing the distinctive absorption spectral shifts of porphyrin complexes upon adsorption on the clay surface[69]. On anionic saponite, 3+ charged subporphyrin derivatives with *m*- and *p*-methylpyridinium as *meso* aryl substituents were adsorbed. Despite the dense introduction of dye molecules onto the solid surface, their fluorescence properties on the saponite surface were not only maintained but also significantly improved[70]. The porphyrin complexes Fe(III)tetraphenylporphyrin chloride, Fe(III)tetranaphthylporphyrin, μ-oxo-bis[tetraphenylporphyriniron(III)], μ-oxo-bis[tetranaphthylporphyriniron(III)], Sn(IV)tetraphenylporphyrin chloride, and Sn(IV) tetra-naphthylporphyrin were adsorbed onto montmorillonite clay[71], with all the complexes absorbed onto the clay without demetallation. The only process that occurred is that the dimeric form of iron complexes transformed to the monomeric form[71]. In a saponite clay layer intercalated with a polyfluorinated surfactant, tetra-(4-sulfonatophenyl)porphyrinatotin(IV) aggregated efficiently, while no aggregation was found in a hydrocarbon-type surfactant-clay hybrid environment[72]. Even in a polyfluorinated environment, germanium(IV) porphyrins remained monomers[72]. A red shift of the Soret band was observed after the adsorption and intercalation of 1+ charged cationic dihydroxo(tetraphenylporphyrinato)antimony(V) bromide into an artificially synthesized smectite clay. The hydroxo group as an axial ligand resulted in successful intercalation[73]. The same result was observed during the adsorption of 2+ charged cationic [3-(trimethylammonio)propoxo(methoxo)(tetraphenylporphyrinato) antimony(V)]. The ammonium cationic part on the axial ligand led to the effective non-aggregated intercalation into the clay[74]. The water-soluble porphyrin (tetra(4-sulfonatophenyl)porphyrinatoantimony(V) co-intercalated with polyfluorinated surfactant/clay hybrid microstructures, demonstrating distinct spectrum alterations[75]. A synthetic clay and cationic tetraphenylporphyrinatoantimony(V) bromide with varied axial ligands were used to synthesize novel metalloporphyrin-clay composites. It was found that the axial ligand structure might control not only crystal structure formation but also adsorption behaviors with aggregation or non-aggregation onto clay sheets[76]. Using a glass plate modified with ammonium cation, tetraphenylporphyrinatoantimony(V) complex (SbTPP) adsorbed cation-exchangeable smectite nano clay sheets films were prepared. The surface state of the glass plate substantially influenced the dispersibility of SbTPP-adsorbed smectite sheets. The fluorescence images emitted from the films revealed that the porphyrin had adsorbed onto clay sheets without aggregation[77].

Applications of clay-porphyrin system

The growing interest in intercalation compounds is driven by the host-guest interactions that alter the chemical, catalytic, electrical, and optical properties of guest components. Porphyrins and metalloporphyrin complexes can perform redox catalysis under ambient conditions[78]. Intercalation of cationic metalloporphyrins into clay results in metalloporphyrin-loaded clay catalysts with higher selectivity and enhanced catalytic activity[79]. These heterogeneous catalysts offer a wide range of applications in vital sectors like food manufacturing, pharmaceuticals, and the chemical industry.

Much research has been devoted to developing technologies for producing chemicals through oxidation processes. A significant challenge in catalysis is finding novel heterogeneous catalysts and/or alternative oxidants to improve reaction selectivity toward targeted products[80]. It has been shown that using a clay-porphyrin combination is a novel way to control the photochemical characteristics of porphyrins[81], providing a unique environment for photochemical reactions[82]. Photochemical electron transfer reactions were observed during the reaction of cationic porphyrins and anionic clay[83–85]. Studies on the behavior of complex formation between synthetic saponite clay and cationic porphyrin have shown that the average intermolecular distance between the porphyrin molecules on the clay surface can be controlled. This finding is crucial for developing photochemical reaction systems, such as energy transfer in complexes[39]. Studies using photochemical energy transfer reactions on anionic clays onto which two different porphyrin molecules had been adsorped, showed moderate energy transfer reactions, concluding that strongly fixed dye assemblies on the clay mineral surfaces suppress dye aggregation and segregation. Such surfaces are particularly promising for constructing effective photochemical reaction systems[86]. It has been established that an excited guest molecule densely adsorbed on a solid surface is quenched by unfavorable interactions between the guest molecules, making photochemical reactions such as electron and energy transfers less efficient compared to those in homogeneous systems. The mechanism of the unfavorable quenching process of dye molecules on a clay surface for photochemical energy transfer was systematically investigated using a series of porphyrin derivatives. It was found that the quenching rate constants of excited guest dye molecules, determined by time-resolved fluorescence measurements, correlated well with the strengths of Coulombic interaction between host and guest[87]. A strong Coulombic interaction is expected to suppress the mobility and collision frequency of guest molecules on the clay surface, suggesting that guest molecule collisions are the origin of unfavorable quenching for photochemical reactions on the clay surface[87]. Working with this principle, the authors suggested it should be possible to construct efficient photochemical reaction systems without a quenching process, such as efficient energy transfers toward an artificial light-harvesting system[87]. In fact, the authors had already achieved almost 100 % energy transfer by suppressing the quenching process on the clay surface in an earlier paper[88] reporting that the porphyrin compounds tetrakis(1-methylpyridinium-3-yl)porphyrin and tetrakis(1-methylpyridinium-4-yl)porphyrin were the more suitable porphyrins for achieving a quantitative energy transfer reaction[88]. On an anionic clay surface, the same group of researchers studied an excited energy transfer process from tetrakis(1-methylpyridinium-2-yl) porphyrin to tetrakis(1-methylpyridinium-4-yl) porphyrin[89]. They reported that both the energy transfer efficiency and quenching efficiency increased as the compound loadings increased. The major factor lowering the energy transfer efficiency was the self-quenching of the donor porphyrin on the clay surface[89].

A supported Mn-porphyrin catalyst was prepared by immobilizing Mn[*meso*-tetra (4-*N*-methylpyridiniumyl)porphyrin]Cl^{4+} on montmorillonite. This catalyst demonstrated efficiency for alkene epoxidation and alkane hydroxylation by PhIO, with a higher ability to oxidize alkanes, particularly short linear alkanes[90]. Fe(III) and Mn(III) cationic porphyrins were adsorbed on the surface of montmorillonite clay platelet crystals. The concentration of the porphyrin immobilized in the clay, as well as variables like the metal ion species in the porphyrins, the choice of solvent, and the concentration of the iodosyl benzene oxidant, all had an impact on the catalytic activity of the intercalated complexes for the oxidation of alkane. The catalytic oxidation of cyclohexane by iodosylbenzene showed good selectivity for cyclohexanol rather than cyclohexanone[91]. Manganese *meso*-tetrakis(tetramethylpyridinio)porphyrin pentaacetate has been shown to be an effective immobilized catalyst for the oxidation of monomeric and dimeric lignin model compounds by hydrogen peroxide. It can oxidize both phenolic and non-phenolic models, producing side-chain oxidation and cleavage products[92]. A clay-Mn porphyrin complex proved to be a stable, recyclable, and efficient catalyst for the H_2O_2 catalyzed oxidation of various lignins and representative lignin model compounds in an environmentally acceptable manner[93]. The anionic iron(III) porphyrin: 5,10,15,20-tetrakis(2,6-difluoro-3-sulfonatophenyl)porphyrinatoiron(III) chloride, was immobilized using silanized kaolinite as a novel inorganic support. After one hour, this system proved to be an efficient and highly selective catalyst for cyclooctene epoxidation (97 % cyclooctene oxide) and cyclohexane hydroxylation (90 % cyclohexanol)[94]. Kaolinite clay has been functionalized with a *meso*-tetrakis(pentafluorophenyl)porphinatoiron(III) complex through purifying the natural clay by dispersion−sedimentation, expanded by insertion of dimethyl sulfoxide, and functionalized with amino groups by substitution of dimethyl sulfoxide with ethanolamine. These preceding steps allowed clay functionalization with the porphyrin complex, leading to a layered material. The functionalized clay's catalytic activity was assessed in the epoxidation of cyclooctene, with perfect selectivity for the epoxide (100 % epoxide yield), and the ketonization of cyclohexane, with cyclohexanone as the primary product[95]. In photocatalytic aerobic oxidation of cyclohexene catalyzed by 5,10,15,20-tetrakis(pentafluorophenyl)porphyriniron(III) chloride under visible light irradiation, the coexistence of hydrotalcite clay was found to enhance the selectivity for cyclohexene oxide dramatically[96]. An anionic iron(III) porphyrin was immobilized on a sol-gel synthesized aluminosilicate, and employed as a catalyst in the oxidation of organic substrates. The catalytic activity of the immobilized iron(III) porphyrin in the oxidation of cyclooctene, cyclohexane, and *n*-heptane was investigated using iodosylbenzene as the oxygen donor. This system showed promise for effective and selective oxidation processes[97]. The immobilization of two different cationic manganese porphyrins [Mn(T4MPyP)]Ac5 and [Mn(BrT3MPyP)]Cl_4 on magnetite Fe_3O_4 coated with silica and on nanotubes of raw halloysiteis, were utilized in the 30 % hydrogen peroxide bleaching reaction of the dye "brilliant green". The systems exhibited distinctive catalytic activity[98]. Intercalating cationic *meso*-tetrakis(1-ethyl-3-pyridinio)porphyrinato cobalt complex with the substituents of the quaternary ammonium salt of heterocyclic amine into a montmorillonite interlayer enabled the formation of a composite material. This composite demonstrated maximum catalytic activity, preferentially producing 1,2-epoxycyclohexane when isobutyraldehyde was present. Montmorillonite contributed to the stabilization of the porphyrin cobalt complex and played a role in accelerating oxidation by activating oxygen molecules by constructing a three-dimensional reaction field regulated by electrostatic interaction with guest molecules[99]. A cationic iron(III) porphyrin was immobilized into the nanotubes/nanoscrolls of natural halloysite. The catalytic activity of iodosylbenzene as an oxygen donor was tested in the oxidation of cyclooctene, cyclohexane, and *n*-heptane. These unique immobilized catalysts have proven promising for selective oxidation processes[100]. Using a simple cation exchange method, three types of Co porphyrin complexes with different porphyrin ring substituents and nonionic or cationic structures were intercalated into lithium taeniolite. The intercalated catalysts were used in the oxidative cleavage of isoeugenol to vanillin using molecular oxygen as the only oxidant, and the reaction proceeded efficiently at mild reaction conditions[101]. Catalyzed by cationic cobalt *meso*-tetrakis (1-methyl-4-pyridyl) metalloporphyrins immobilized in montmorillonite interlayers, a very efficient aerobic oxidation of alcohols to carbonyl compounds was achieved[102]. Manganese *meso*-tetrakis-(1-methyl-4-pyridyl) immobilized into montmorillonite also showed good activity and selectivity for the aerobic epoxidation of olefins under ambient conditions, yielding more than 90 % epoxides[103]. *Meso*-tetra-(2,6-dichloro-3-sulfonatophenyl)porphyrinateMn(III) chloride immobilized on kaolinite and montmorillonite exhibited catalytic activity several times greater than the free catalyst in solution toward the oxidative coupling reaction of a phenolic monomer, (the latter is commonly found in the humified natural organic matter that is ubiquitous in the environment)[104].

Metakaolinite and metahalloysite were formed by calcining raw clay minerals kaolinite and halloysite at specified temperatures and times. The resultant materials were used as supports for anionic Fe(III) porphyrin, and it was found that only metahalloysite was adequate for Fe(III) porphyrin immobilization. The catalytic activity of metahalloysite-supported Fe(III) porphyrin was tested in heterogeneous oxidation processes using iodosylbenzene as the oxidant and cyclooctene, cyclohexane, or *n*-heptane as the substrate, yielding high product yields for all substrates[105]. The effective adsorption of a 5,10,15,20-tetrakis(4-carboxyphenyl) porphyrin from acidic solution in methanol by Cloisite 30B monotallow bis(hydroxyethyl)ammonium-modified montmorillonite clay yielded a new form of hybrid photosensitizer. The obtained material has been found to be an excellent photosensitizer for the oxidation of phenol in aqueous solution when exposed to visible light[106]. Fe(III) *meso*-tetrakis(tetracarboxyphenyl)porphinato has been used to functionalize kaolinite. In the epoxidation of *cis* cyclooctene, the catalyst exhibited full selectivity for the epoxide. The recovered catalysts were used as antibacterial agents against diverse bacteria, with activity comparable to commercial drugs such as streptomycin[107]. Biomimetic iron porphyrin heterogeneous catalysts have been developed by grafting Fe(III) 5,10,15,20-tetrakis(4-hydroxyphenyl) porphyrin onto 3-chloropropyltrimethoxysilane functionalized kaolinite, and tested for the epoxidation of (Z)-cyclooctene and oxidation of cyclohexane using iodosylbenzene as an oxygen donor. The system showed good catalytic activity[80]. Kaolinite modified with tris(hydroxymethyl)aminomethane and reacted with 5,10,15,20-tetrakis(4-sulfonatophenyl)manganese(III) porphyrinate was synthesized as a material for application in caprolactone (ε-Cl) polymerization. The study demonstrated that chemical modification of kaolinite followed by metalloporphyrin adsorption is an essential approach for producing initiator catalysts for polymerization processes in the synthesis of new materials[108]. An artificial photosynthesis system model consisting of a photochemical reaction system with a light harvesting function was constructed on a clay nanosheet using a metalloporphyrin as a photocatalyst and a subporphyrin as a photoantenna. The metalloporphyrin photocatalyst catalyzed the photochemical conversion of cyclohexene by exciting both the subporphyrin photoantenna and itself. The results could be useful in the development of various types of artificial photosynthesis systems based on self-assembly of the subcomponents[109]. Saponite and a cationic porphyrin were employed as an anionic inorganic nanosheet and an adsorbing dye (an energy acceptor) on the clay surface. Through silane coupling, the edge of saponite was modified by pyrene, an energy donor. The adsorption distribution of the cationic porphyrin dye on the nanosheet surface was studied using Förster resonance energy transfer (FRET). As the efficiency of FRET depends on the distance between the energy donor and the acceptor, it was demonstrated that FRET can be used as a molecular ruler to estimate the distribution of dye molecules on the clay surface[110].

Adsorption of 5,10,15-triphenyl-20-mono(*N*-methyl-4-pyridyl)porphyrin on clay revealed that the compound adsorbed with the porphyrin ring parallel to the clay surface. The compound's fluorescence was severely quenched as its adsorption density increased[111]. A smectite clay and a metal-free *meso*-tetra(4-carboxyl phenyl)porphyrin were used to modify carbon paste electrodes and then employed for the simultaneous electrochemical detection of tyrosine, dopamine, and acetaminophen. The developed sensors were used to determine the concentration of acetaminophen in a pharmaceutical preparation and simultaneously dopamine, acetaminophen, and tyrosine in human urine[112]. Tetra(*p*-sulfonatophenyl)porphinatomanganese(III) anions were intercalated perpendicularly into the interlayer spaces of Mg-Al-layered double hydroxide clay, and employed as a catalyst for the oxidation of 2,4,6-trichlorophenol[78]. Iron(III)-tetrakis(*N*-methylpyridinium-4-yl)porphyrin, a biomimetic catalyst, was intercalated into montmorillonite and pillared clay. Its catalytic activity for the decolorization of Acid Orange 7 in the absence and presence of humic acid, a major component of wastewater, were compared. These results indicated that the pillared clay is a more suitable support for the Fe(III)porphyrin catalyst than montmorillonite[79].

The adsorption of four porphyrin compounds on flat clay surfaces was used to investigate photochemical energy transfer. It was found that the relative orientation change between dyes could regulate energy transfer efficiency. The key element influencing energy transfer efficiency was the change in orientation factor and spectral overlap factor. This approach could be used to make photo-functional materials like chromic and light-harvesting systems[113]. A porphyrin/viologen monolayer on an anionic synthetic saponite showed fluorescent behavior when studied using steady-state and time-resolved fluorescence spectroscopy. It was shown that the structure of the dye had a strong influence on segregation behavior, and that an efficient electron transfer system may be built on the clay surface[114]. The cationic porphyrin complex μ-*meso*-tetra(4-pyridyl) porphyrinatecobalt(II) tetrakis[bis(bipyridine)(chlorido)ruthenium(II) was intercalated into smectite clay. The intercalated porphyrin was used to modify glassy carbon electrodes, which were successfully used to determine acetaminophen and tyrosine simultaneously. The composite displayed good compatibility and stability, high selectivity and sensitivity[115]. Studies on the adsorption and photochemical behavior of Pt(II) *meso*-tetra(*N*-methyl-4-pyridinium)porphyrin on saponite clay revealed that adsorption on the clay surface increased complex phosphorescence compared to that in water[116]. New hybrid nanomaterials composed of 5,10,15,20-tetrakis(3,4-dimethoxyphenyl)porphyrin encapsulated in silica matrices were prepared. This system was found to be of scientific interest due to the prospect of its use in high-density optical data storage[117]. Sumecton clay as a host material was reacted with Pt(II) and Pd(II) porphyrins as guest materials. These materials displayed unique oxygen sensing properties[118]. It has been found that an anionic clay nanosheet, along with Zn-porphyrin, and a neutral aromatic molecule contained within a cationic organic cavitand, undergoes an effective energy transfer reaction[119]. From a study on the reaction of tetra cationic porphyrazine with clay, a novel strategy to create efficient photochemical reaction systems and photodevices was proposed[120]. A photochemical oxygenation reaction was conducted on cyclohexane using a clay surface sensitized by two types of Ru(II) porphyrin complexes[121]. A transparent hybrid film composed of cationic magnesium porphyrin and clay was developed via intercalation of magnesium porphyrin into clay film without aggregation. It was found that the chromic behavior of the film depended on relative humidity[122]. Steady-state and time-resolved fluorescence studies have been used to reveal that the adsorption distribution of a di-cationic porphyrin on a clay surface is not uniform[123].

Conclusion

Clay minerals, due to their layered structures, serve as useful and special hosts for porphyrins or the substances that synthesize them. When porphyrin complexes enter between the layers of clay, they can orient horizontally, diagonally, or perpendicularly. Cation-exchanged clays can provide the necessary acidity for porphyrin synthesis from raw materials, without the need for auxiliary factors such as heating. They also facilitate the incorporation of various metals into the porphyrin ring, forming complexes. The process is straightforward if the metal ion is the appropriate size to fit in the center of the porphyrin ring, such as Cu(II). Porphyrin intercalation in clays results in a wide range of porphyrin-loaded clay catalysts with enhanced selectivity and catalytic activity. These heterogeneous catalysts have diverse applications in vital sectors, such as food processing, pharmaceuticals, and the chemical industry.

References

1. *Kingsbury, C. J., Senge, M. O.,* The shape of porphyrins, Coord. Chem. Rev. **431** (2021) 213760.
doi: https://doi.org/10.1016/j.ccr.2020.213760
2. *Pushpan, S. K., Venkatraman, S., Anand, V. G., Sankar, J., Rath, H., Chandrashekar, T. K.,* Inverted porphyrins and expanded porphyrins: An overview, J. Chem. Sci. **114** (2002) 311.
doi: https://doi.org/10.1007/BF02703823
3. *Cook, L. P., Brewer, G., Wong-Ng, W.,* Structural aspects of porphyrins for functional materials applications, Crystals **7** (2017) 223.
doi: https://doi.org/10.3390/cryst7070223
4. *Valicsek, Z., Eller, G., Horváth, O.,* Equilibrium, photophysical and photochemical examination of anionic lanthanum (III) mono-and bisporphyrins: The effects of the out-of-plane structure, Dalton Trans. **41** (2012) 13120.
doi: https://doi.org/10.1039/C2DT31189E
5. *Ptaszyńska, A. A., Trytek, M., Borsuk, G., Buczek, K., Rybicka-Jasińska, K., Gryko, D.,* Porphyrins inactivate Nosema spp. Microsporidia, Sci. Rep. **8** (2018) 5523.
doi: https://doi.org/10.1038/s41598-018-23678-8
6. *Varchi, G., Foglietta, F., Canaparo, R., Ballestri, M., Arena, F., Sotgiu, G., Guerrini, A., Nanni, C., Cicoria, G., Cravotto, G., Fanti, S.,* Engineered porphyrin loaded core-shell nanoparticles for selective sonodynamic anticancer treatment, Nanomedicine **10** (2015) 3483.
doi: https://doi.org/10.2217/nnm.15.150
7. *Saito, S., Osuka, A.,* Expanded porphyrins: Intriguing structures, electronic properties, and reactivities, Angew. Chem. Int. Ed. **50** (2011) 4342.
doi: https://doi.org/10.1002/anie.201003909
8. *Leng, F., Liu, H., Ding, M., Lin, Q. P., Jiang, H. L.,* Boosting photocatalytic hydrogen production of porphyrinic MOFs: the metal location in metalloporphyrin matters, ACS Catal. **8** (2018) 4583.
doi: https://doi.org/10.1021/acscatal.8b00764
9. *Dini, D., Calvete, M. J., Hanack, M.,* Nonlinear optical materials for the smart filtering of optical radiation, Chem. Rev. **116** (2016) 13043.
doi: https://doi.org/10.1021/acs.chemrev.6b00033
10. *Guggenheim, S., Adams, J. M., Bain, D. C., Bergaya, F., Brigatti, M. F., Drits, V. A., Formoso, M. L., Galán, E., Kogure, T., Stanjek, H.,* Summary of recommendations of nomenclature committees relevant to clay mineralogy: Report of the Association Internationale pour l'Etude des Argiles (AIPEA) Nomenclature Committee for 2006. Clays Clay Miner. **54** (2006) 761.
doi: https://doi.org/10.1346/CCMN.2006.0540610
11. *Van Olphen, H.,* An Introduction to Clay Colloid Chemistry: For Clay Technologists, Geologists, and Soil Scientists, Krieger Pub. Co., Malabar, 1991, 301 p.
12. *Treibs, A.,* Chlorophyll and hemin derivates in bituminous rocks, petroleum, coals, and phosphate rocks, Justus Liebigs Annal. Chem. **517** (1935) 172.
doi: https://doi.org/10.1002/jlac.19355170113
13. *Hodgson, G. W., Baker, B. L., Peake E.,* Geochemistry of Porphyrins, in Nagy, B. and Colombo, U. (Eds.), Fundamental Aspects of Petroleum Geochemistry, Elsevier, Amsterdam, 1967, pp 177-260.
14. *Hodgson, G. W., Hitchon, B.,* Primary degradation of chlorophyll under simulated petroleum source rock sedimentation conditions, Am. Assoc. Pet. Geol. Bull. **43** (1959) 2481.
doi: https://doi.org/10.1306/0BDA5EC7-16BD-11D7-8645000102C1865D
15. *Casagrande, D. J., Hodgson, G. W.,* Geochemical simulation evidence for the generation of homologous decarboxylated porphyrins, Nat. Phys. Sci. **233** (1974) 123.
doi: https://doi.org/10.1038/physci233123a0
16. *Jackson, A. H., Pandey, R. K., Rao, K. R. N., Roberts, E.,* Reactions on solid supports part II: A convenient method for synthesis of pyrromethanes using a montmorillonite clay as catalyst, Tetrahedron Lett. **26** (1985) 793.
doi: https://doi.org/10.1016/S0040-4039(00)89139-X

17. *Cornelis, A., Laszlo, P., Pennetreau, P.,* Some organic syntheses with clay-supported reagents, Clay Miner. **18** (1983) 437.
doi: https://doi.org/10.1180/claymin.1983.018.4.09
18. *Onaka, M., Shinoda, T., Izumi, Y., Nolan, E.*, Porphyrin synthesis in clay nanospaces, Chem. Lett. **22** (1993) 117.
doi: https://doi.org/10.1246/cl.1993.117
19. *Reddy, C. R., Bhat, Y. S., Nagendrappa, G., Jai Prakash, B. S.,* Bronsted and Lewis acidity of modified montmorillonite clay catalysts determined by FT-IR spectroscopy, Catal. Today **141** (2009) 157.
doi: https://doi.org/10.1016/j.cattod.2008.04.004
20. *Cady, S. S., Pinnavaia, T. J.,* Porphyrin intercalation in mica-type silicates, Inorg. Chem. **17** (1978) 1501.
doi: https://doi.org/10.1021/ic50184a022
21. *Lindsey, J.,* The synthesis of *meso*-substituted porphyrins. ChemInform. **34** (2023) 1.
doi: https://doi.org/10.1002/chin.200317269
22. *Wnuk, M.,* The probable ways of the synthesis of porphyrin compounds during chemical evolution, Rocz. Filoz. **31** (1983) 185.
https://www.jstor.org/stable/43410523
23. *Onaka, M., Shinoda, T., Izumi, Y., Nolen, E.,* Clay-mediated meso-tetraarylporphyrin synthesis, Tetrahedron lett. **34** (1993) 2625.
doi: https://doi.org/10.1016/S0040-4039(00)77641-6
24. *Laszlo, P., Luchetti, J.,* Porphyrin synthesis using clays. Taking advantage of statistical product distributions, Chem. Lett. **22** (1993) 449.
doi: https://doi.org/10.1246/cl.1993.449
25. *Izumi, Y., Urabe, K., Onaka, M.,* Recent advances in liquid-phase organic reactions using heteropolyacid and clay, Catal. Surv. from Asia **1** (1997) 17.
doi: https://doi.org/10.1023/A:1019056425569
26. *Freeman, B. A., Smith, K. M.,* Alternate syntheses of pyrromethanes and porphyrins using acid-modified montmorillonite K-10 clay, Synth. Commun. **1** (1999) 1843.
doi: https://doi.org/10.1080/00397919908086174
27. *Hassen, J. H., Silver, J.,* Chemisorption role of clay surfaces in the synthesis of porphyrins from its raw materials via room temperature reactions, Chem. Biochem. Eng. Q. **36** (2022) 17.
doi: https://doi.org/10.15255/CABEQ.2021.2001
28. *Kaufherr, N., Yariv, S., Heller, L.*, The effect of exchangeable cations on the sorption of chlorophyllin by montmorillonite, Clays Clay Miner. **19** (1971) 193.
doi: https://doi.org/10.1346/CCMN.1971.0190308
29. *Mokaya, R., Jones, W., Davies, M. E., Whittle, M. E.,* The mechanism of chlorophyll adsorption on acid-activated clays, J. Solid State Chem. **111** (1994) 157.
doi: https://doi.org/10.1006/jssc.1994.1212
30. *Kosiur, D. R.,* Porphyrin adsorption by clay minerals, Clays Clay Miner. **25** (1977) 365.
31. *Van Damme, H., Crespin, M., Obrecht, F., Cruz, M. I., Fripiat, J. J.,* Acid-base and complexation behavior of porphyrins on the intracrystal surface of swelling clays: *Meso*-tetraphenylporphyrin and meso-tetra (4-pyridyl) porphyrin on montmorillonites, J. Colloid Interface Sci. **66** (1978) 43.
doi: https://doi.org/10.1016/0021-9797(78)90182-0
32. *Canesson, P., Cruz, M. I., Van Damme, H. X.,* XPS study of the interaction of some porphyrins and metalloporphyrins with montmorillonite, Dev. Sedimentol. **27** (1979) 217.
doi: https://doi.org/10.1016/S0070-4571(08)70717-9
33. *Carrado, K. A., Winans, R. E.,* Interactions of water-soluble porphyrins and metalloporphyrins with smectite clay surfaces, Chem. Mate. **2** (1990) 328.
doi: https://doi.org/10.1021/cm00009a027
34. *Takagi, S., Shimada, T., Eguchi, M., Yui, T., Yoshida, H., Tryk, D. A., Inoue, H.,* High-density adsorption of cationic porphyrins on clay layer surfaces without aggregation: The size-matching effect, Langmuir **18** (2002) 2265.
doi: https://doi.org/10.1021/la011524v
35. *Dias, P. M., De Faria, D. L. A., Constantino, V. R. L.,* Spectroscopic studies on the interaction of tetramethylpyridylporphyrins and cationic clays, J. Incl. Phenom. **38** (2000) 251.
doi: https://doi.org/10.1023/A:1008173315471
36. *Dias, P. M., de Faria, D. L. A., Constantino, V. R. L.,* Clay-porphyrin systems: Spectroscopic evidence of TMPyP protonation, non-planar distortion and Meso substituent rotation, Clays Clay Miner. **53** (2005) 361.
doi: https://doi.org/10.1346/CCMN.2005.0530404
37. *Píšková, A., Bezdička, P., Hradil, D., Káfuňková, E., Lang, K., Večerníková, E., Kovanda, F., Grygar, T.,* High-temperature X-ray powder diffraction as a tool for characterization of smectites, layered double hydroxides, and their intercalates with porphyrins, Appl. Clay Sci. **49** (2010) 363.
doi: https://doi.org/10.1016/j.clay.2009.09.004
38. *Čeklovský, A., Takagi, S., Bujdák, J.,* Study of spectral behaviour and optical properties of cis/trans-bis (*N*-methylpyridinium-4-yl) diphenyl porphyrin adsorbed on layered silicates, J. Colloid Interface Sci. **360** (2011) 26.
doi: https://doi.org/10.1016/j.jcis.2011.04.010
39. *Egawa, T., Watanabe, H., Fujimura, T., Ishida, Y., Yamato, M., Masui, D., Shimada, T., Tachibana, H., Yoshida, H., Inoue, H., Takagi, S.,* Novel methodology to control the adsorption structure of cationic porphyrins on the clay surface using the "size-matching rule", Langmuir **27** (2011) 10722.
doi: https://doi.org/10.1021/la202231k
40. *Čeklovský, A., Boháč, P., Czímerová, A.,* Spectral behaviour of TMPyP/layered silicate hybrid nanomaterials in aqueous dispersions of reduced-charge montmorillonites, Appl. Clay Sci. **126** (2016) 68.
doi: https://doi.org/10.1016/j.clay.2016.03.004
41. *Eguchi, M., Tsukamoto, T., Ohtani, Y., Shimada, T., Takagi, S.,* The adsorption behavior of protonated cationic porphyrin on the clay surface, Clay Sci. **17** (2013) 31.
doi: https://doi.org/10.11362/jcssjclayscience.17.2_31
42. *Hirade, Y., Ishida, T., Shimada, T., Takagi, S.,* Adsorption and absorption behavior of cationic porphyrin on titania and clay nanosheets, Colloids Surf. A: Physicochem. Eng. **624** (2021) 126747.
doi: https://doi.org/10.1016/j.colsurfa.2021.126747
43. *Oshima, M., Sano, K., Hirade, Y., Nakazato, R., Ishida, T., Shimada, T., Takagi, S.,* Precise evaluation of adsorption behavior of cationic porphyrin on monolayer of perovskite-type niobia nanosheet by absorption spectroscopy, J. Phys. Chem. Solids. **161** (2022) 110423.
doi: https://doi.org/10.1016/j.jpcs.2021.110423
44. *Takagi, S., Shimada, T., Yui, T., Inoue, H.,* High density adsorption of porphyrins onto clay layer without aggregation: Characterization of smectite-cationic porphyrin complex, Chem. Lett. **30** (2001) 128.
doi: https://doi.org/10.1246/cl.2001.128
45. *Eguchi, M., Takagi, S., Tachibana, H., Inoue, H.,* The 'size matching rule'in di-, tri-, and tetra-cationic charged porphyrin/synthetic clay complexes: Effect of the inter-charge distance and the number of charged sites, J. Phys. Chem. Solids. **65** (2004) 403.
doi: https://doi.org/10.1016/j.jpcs.2003.10.029
46. *Constantino, V. R., Barbosa, C. A., Bizeto, M. A., Dias, P. M.,* Intercalation compounds involving inorganic layered structures, An. Acad. Bras. Cienc. **72** (2000) 45.
doi: https://doi.org/110.1590/s0001-37652000000100006

47. *Chernia, Z., Gill, D.,* Flattening of TMPyP adsorbed on laponite. Evidence in observed and calculated UV− Vis spectra, Langmuir **15** (1999) 1625.
doi: https://doi.org/10.1021/la9803676
48. *Eguchi, M., Tachibana, H., Takagi, S. Inoue, H.,* Microscopic structures of adsorbed cationic porphyrins on clay surfaces: Molecular alignment in artificial light-harvesting systems, Res. Chem. Intermed. **33** (2007) 191.
doi: https://doi.org/10.1163/156856707779160753
49. *Nishina, H., Hoshino, S., Ohtani, Y., Ishida, T., Shimada, T., Takagi, S.,* Anisotropic energy transfer in a clay–porphyrin layered system with environment-responsiveness, Phys. Chem. Chem. Phys. **22** (2020) 14261.
doi: https://doi.org/10.1039/D0CP02263B
50. *Fujimura, T., Shimada, T., Hamatani, S., Onodera, S., Sasai, R., Inoue, H., Takagi, S.,* High density intercalation of porphyrin into transparent clay membrane without aggregation, Langmuir **29** (2013) 5060.
doi: https://doi.org/10.1021/la4003737
51. *Onaka, M., Shinoda, T., Aichi, K., Suzuki, K., Yusukeizumi,* Intercalation of cationic porphyrin bearing four ω-ammonioalkyl substituents at meso-positions into clay montmorillonite, saponite, and hectorite, Mol. Cryst. Liq. Cryst. Sci. Technol., Sect. A. **277** (1996) 149.
doi: https://doi.org/10.1080/10587259608046017
52. *Eguchi, M., Shimada, T., Tryk, D. A., Inoue, H., Takagi, S.,* Role of hydrophobic interaction in controlling the orientation of dicationic porphyrins on solid surfaces, J. Phys. Chem. C. **117** (2013) 9245.
doi: https://doi.org/10.1021/jp400645d
53. *Eguchi, M., Shimada, T., Inoue, H., Takagi, S.,* Kinetic analysis by laser flash photolysis of porphyrin molecules' orientation change at the surface of silicate nanosheet, J. Phys. Chem. C. **120** (2016) 7428.
doi: https://doi.org/10.1021/acs.jpcc.6b01211
54. *Takagi, S., Eguchi, M., Shimada, T., Hamatani, S., Inoue, H.,* Energy transfer reaction of cationic porphyrin complexes on the clay surface: Effect of sample preparation method, Res. Chem. Intermed. **33** (2007) 177.
doi: https://doi.org/10.1163/156856707779160889
55. *Eguchi, M., Tachibana, H., Takagi, S., Tryk, D. A., Inoue, H.,* Dichroic measurements on dicationic and tetracationic porphyrins on clay surfaces with visible-light-attenuated total reflectance, Bull. Chem. Soc. Jpn. **80** (2007) 1350.
doi: https://doi.org/10.1246/bcsj.80.1350
56. *Shinsuke, T., Tetsuya, S., Yohei, I., Takuya, F., Dai, M., Hiroshi, T., Miharu, E., Haruo, I.,* Size-matching effect on inorganic nanosheets: Control of distance, alignment, and orientation of molecular adsorption as a bottom-up methodology for nanomaterials, Langmuir **29** (2013) 2108.
doi: https://doi.org/10.1021/la3034808
57. *Shimada, T., Hamatani, S., Onodera, S., Ishida, Y., Inoue, H., Takagi, S.,* Investigation of adsorption behavior and energy transfer of cationic porphyrins on clay surface at low loading levels by picosecond time-resolved fluorescence measurement, Res. Chem. Intermed. **39** (2013) 269.
doi: https://doi.org/10.1007/s11164-012-0647-1
58. *Hassen, J. H., Silver, J.,* Montmorillonite surface as a catalyst for the formation of SAT metal tetra (*p*-sulphophenyl) porphyrins, J. Teknol. **82** (2020) 1.
doi: https://doi.org/10.11113/jurnalteknologi.v82.14564
59. *Hassen, J. H., Silver, J.,* Adsorption of the meso-tetra-p-tolylporphyrin (TTPH$_2$) and meso-tetra-naphthylporphyrin (TNPH$_2$) onto montmorillonite, J. Turk. Chem. Soc. A: Chem. **10** (2023) 641.
doi: https://doi.org/10.18596/jotcsa.1224193
60. *Takagi, S., Aratake, Y., Konno, S., Masui, D., Shimada, T., Tachibana, H., Inoue, H.,* Effects of porphyrin structure on the complex formation behavior with clay, Microporous Mesoporous Mater. **141** (2011) 38.
doi: https://doi.org/10.1016/j.micromeso.2009.11.011
61. *Eyama, T., Yogo, Y., Fujimura, T., Tsukamoto, T., Masui, D., Shimada, T., Tachibana, H., Inoue, H., Takagi, S.,* Adsorption and stacking behaviour of zwitterionic porphyrin on the clay surface, Clay Miner. **47** (2012) 243.
doi: https://doi.org/10.1180/claymin.2012.047.2.07
62. *Rice, Z., Bergkvist, M.,* Adsorption characteristics of a cationic porphyrin on nanoclay at various pH, J. Colloid Interface Sci. **335** (2009) 189.
doi: https://doi.org/10.1016/j.jcis.2009.02.070
63. *Čeklovský, A., Czímerová, A., Lang, K., Bujdák, J.,* Effect of the layer charge on the interaction of porphyrin dyes in layered silicates dispersions, J. Lumin. **129** (2009) 912.
doi: https://doi.org/10.1016/j.jlumin.2009.03.032
64. *Abdo, S., Cruz, M. I., Fripiat, J. J.,* Metallation-demetallation reaction of tin tetra(4-pyridyl) porphyrin in Na-hectorite, Clays Clay Miner. **28** (1980) 125.
doi: https://doi.org/10.1346/CCMN.1980.0280208
65. *Carrado, K. A., Wasserman, S. R.,* Stability of Cu(II)− and Fe(III)−porphyrins on montmorillonite clay: An x-ray absorption study, Chem. Mater. **8** (1996) 219.
doi: https://doi.org/10.1021/cm950330w
66. *Bergaya, F., Van Damme, H.,* Stability of metalloporphyrins adsorbed on clays: A comparative study, Geochim. Cosmochim. Acta. **46** (1982) 349.
doi: https://doi.org/10.1016/0016-7037(82)90226-5
67. *Kameyama, H., Suzuki, H., Amano, A.,* Intercalation of Co(II) *meso*-tetrakis (1-methyl-4-pyridyl) porphyrin into montmorillonite, Chem. Lett. **17** (1988) 1117.
doi: https://doi.org/10.1246/cl.1988.1117
68. *Tsukamoto, T., Shimada, T., Takagi, S.,* Photochemical properties of mono-, tri-, and penta-cationic antimony (V) metalloporphyrin derivatives on a clay layer surface, J. Phys. Chem. A. **117** (2013) 7823.
doi: https://doi.org/10.1021/jp405767s
69. *Ishida, Y., Masui, D., Shimada, T., Tachibana, H., Inoue, H., Takagi, S.,* The mechanism of the porphyrin spectral shift on inorganic nanosheets: The molecular flattening induced by the strong host–guest interaction due to the "size-matching rule", J. Phys. Chem. C. **116** (2012) 7879.
doi: https://doi.org/10.1021/jp300842f
70. *Tsukamoto, T., Shimada, T., Takagi, S.,* Photophysical properties and adsorption behaviors of novel tri-cationic boron (III) subporphyrin on anionic clay surface, ACS Appl. Mater. Interfaces. **8** (2016) 7522.
doi: https://doi.org/10.1021/acsami.5b11988
71. *Hassen, J., Silver, J.,* Stability of Fe(III) and Sn(IV) metalloporphyrins adsorbed on cation-exchanged montmorillonite, Trends Sci. **19** (2022) 3426.
doi: https://doi.org/10.48048/tis.2022.3426
72. *Matsuoka, R., Yui, T., Sasai, R., Takagi, K., Inoue, H.,* Enhanced aggregation of tin (IV) porphyrins in a polyfluorinated surfactant-clay hybrid environment, Mol. Cryst. Liq. Cryst. Sci. Technol. Sect. A. Mol. Crys. Liq. Cryst. **341** (2000) 333.
doi: https://doi.org/10.1080/10587250008026162
73. *Shiragami, T., Nabeshima, K., Yasuda, M., Inoue, H.,* Roles of axial ligands on intercalation of cationic metalloporphyrin into smectite clay layers, Chem. Lett. **32** (2003) 148.
doi: https://doi.org/10.1246/cl.2003.148
74. *Shiragami, T., Nabeshima, K., Matsumoto, J., Yasuda, M., Inoue, H.,* Non-aggregated intercalation of dicationic tetraphenylporphyrinatoantimony (V) complexes into smectite clay layers, Chem. Let. **32** (2003) 484.
doi: https://doi.org/10.1246/cl.2003.484

75. *Lucia, L. A., Yui, T., Sasai, R., Takagi, S., Takagi, K., Yoshida, H., Whitten, D. G., Inoue, H.,* Enhanced aggregation behavior of antimony (V) porphyrins in polyfluorinated surfactant/clay hybrid microenvironment, J. Phys. Chem. B. **107** (2003) 3789.
doi: https://doi.org/10.1021/jp026648a
76. *Shiragami, T., Nabeshima, K., Nakashima, S., Matsumoto, J., Takagi, S., Inoue, H., Yasuda, M.,* Effects of axial ligands on the formation of a layered structure in mono-and di-cationic charged tetraphenylporphyrinatoantimony (V)/synthetic clay composites, Bull. Chem. Soc. Jpn. **78** (2005) 2251.
doi: https://doi.org/10.1246/bcsj.78.2251
77. *Shiragami, T., Mori, Y., Matsumoto, J., Takagi, S., Inoue, H., Yasuda, M.,* Non-aggregated adsorption of cationic metalloporphyrin dyes onto nano-clay sheets films, Colloids Surf. A: Physicochem. Eng. Asp. **284** (2006) 284.
doi: https://doi.org/10.1016/j.colsurfa.2005.11.102
78. *Tong, Z., Shichi, T., Takagi, K.,* Oxidation catalysis of a manganese (III) porphyrin intercalated in layered double hydroxide clays, Mater. lett. **57** (2003) 2258.
doi: https://doi.org/10.1016/S0167-577X(02)01206-5
79. *Nishimoto, R., Zhu, Q., Miyamoto, T., Sato, T., Tu, X., Aneksampant, A., Fukushima, M.,* Monopersulfate oxidation of Acid Orange 7 with an iron (III)-tetrakis (N-methylpyridinium-4-yl) porphyrin intercalated into the layers of montmorillonite and pillared clay, J. Mol. Catal. A: Chem. **396** (2015) 84.
doi: https://doi.org/10.1016/j.molcata.2014.09.035
80. *Cintra, T. E., Saltarelli, M., Salmazo, R. M. D. F., da Silva, T. H., Nassar, E. J., Trujillano, R., Rives, V., Vicente, M. A., de Faria, E. H., Ciuffi, K. J.,* Catalytic activity of porphyrin-catalyts immobilized on kaolinite, Appl. Clay Sci. **168** (2019) 469.
doi: https://doi.org/10.1016/j.clay.2018.12.012
81. *Takagi, S., Konno, S., Ishida, Y., Ceklovsky, A., Masui, D., Shimada, T., Tachibana, H., Inoue, H.,* A unique “Flattening effect” of clay on the photochemical properties of metalloporphyrins (2010 TMC Special Paper), Clay Sci. **14** (2010) 235.
doi: https://doi.org/10.11362/jcssjclayscience.14.6_235
82. *Takagi, S., Eguchi, M., Tryk, D. A., Inoue, H.,* Porphyrin photochemistry in inorganic/organic hybrid materials: Clays, layered semiconductors, nanotubes, and mesoporous materials, J. Photochem. Photobiol. C: Photochem. **7** (2006) 104.
doi: https://doi.org/10.1016/j.jphotochemrev.2006.04.002
83. *Tatsumi, D., Tsukamoto, T., Honna, R., Hoshino, S., Shimada, T., Takagi, S.,* Highly selective photochemical epoxidation of cyclohexene sensitized by Ru(II) porphyrin–clay hybrid catalyst, Chem. Lett. **46** (2017) 1311.
doi: https://doi.org/10.1246/cl.170521
84. *Takagi, S., Eguchi, M., Tryk, D. A., Inoue, H.,* Light-harvesting energy transfer and subsequent electron transfer of cationic porphyrin complexes on clay surfaces, Langmuir **22** (2006) 1406.
doi: https://doi.org/10.1021/la052911y
85. *Takagi, S., Tryk, D. A., Inoue, H.,* Photochemical energy transfer of cationic porphyrin complexes on clay surface, J. Phys. Chem. B. **106** (2002) 5455.
doi: https://doi.org/10.1021/jp0200977
86. *Ishida, Y., Masui, D., Tachibana, H., Inoue, H., Shimada, T., Takagi, S.,* Controlling the microadsorption structure of porphyrin dye assembly on clay surfaces using the “size-matching rule” for constructing an efficient energy transfer system, ACS Appl. Mater. Interfaces **4** (2012) 811.
doi: https://doi.org/10.1021/am201465a
87. *Ishida, Y., Shimada, T., Tachibana, H., Inoue, H., Takagi, S.,* Regulation of the collisional self-quenching of fluorescence in clay/porphyrin complex by strong host–guest interaction, J. Phys. Chem. A. **116** (2012) 12065.
doi: https://doi.org/10.1021/jp309502j
88. *Ishida, Y., Shimada, T., Masui, D., Tachibana, H., Inoue, H., Takagi, S.,* Efficient excited energy transfer reaction in clay/porphyrin complex toward an artificial light-harvesting system, J. Am. Chem. Soc. **133** (2011) 14280.
doi: https://doi.org/10.1021/ja204425u
89. *Ishida, Y., Fujimura, T., Masui, D., Shimada, T., Tachibana, H., Inoue, H., Takagi, S.,* What lowers the efficiency of an energy transfer reaction between porphyrin dyes on clay surface? (TMC2010). Clay Sci. **15** (2011) 169.
doi: https://doi.org/10.11362/jcssjclayscience.15.4_169
90. *Barloy, L., Battioni, P., Mansuy, D.,* Manganese porphyrins supported on montmorillonite as hydrocarbon mono-oxygenation catalysts: Particular efficacy for linear alkane hydroxylation, J. Chem. Soc., Chem. Commun. **19** (1990) 1365.
doi: https://doi.org/10.1039/C39900001365
91. *Machado, A. M., Wypych, F., Drechsel, S. M., Nakagaki, S.,* Study of the catalytic behavior of montmorillonite/iron (III) and Mn (III) cationic porphyrins, J. Colloid Interface Sci. **254** (2002) 158.
doi: https://doi.org/10.1006/jcis.2002.8488
92. *Crestini, C., Pastorini, A., Tagliatesta, P.,* Metalloporphyrins immobilized on montmorillonite as biomimetic catalysts in the oxidation of lignin model compounds, J. Mol. Catal. A: Chem. **208** (2004) 195.
doi: https://doi.org/10.1016/j.molcata.2003.07.015
93. *Crestini, C., Pastorini, A., Tagliatesta, P.,* The immobilized porphyrin-mediator system Mn (TMePyP)/clay/HBT (clay-PMS): A lignin peroxidase biomimetic catalyst in the oxidation of lignin and lignin model compounds, Eur. J. Inorg. Chem. **2004** (2004) 4477.
doi: https://doi.org/10.1002/ejic.200400351
94. *Nakagaki, S., Benedito, F. L., Wypych, F.,* Anionic iron (III) porphyrin immobilized on silanized kaolinite as catalyst for oxidation reactions, J. Mol. Catal. A: Chem. **217** (2004) 121.
doi: https://doi.org/10.1016/j.molcata.2004.03.004
95. *Bizaia, N., de Faria, E. H., Ricci, G. P., Calefi, P. S., Nassar, E. J., Castro, K. A., Nakagaki, S., Ciuffi, K. J., Trujillano, R., Vicente, M. A., Gil, A., Korili, S. A.,* Porphyrin–kaolinite as efficient catalyst for oxidation reactions, Appl. Mater. Interfaces **1** (2009) 2667.
doi: https://doi.org/10.1021/am900556b
96. *Teramura, K., Ogura, K., Sugimoto, T., Tsuneoka, H., Shishido, T., Tanaka, T.,* Photocatalytic aerobic epoxidation of alkenes under visible light irradiation by an iron (III) porphyrin with Mg–Al hydrotalcite anionic clay, Chem. lett. **38** (2009) 1098.
doi: https://doi.org/10.1246/cl.2009.1098
97. *Machado, G. S., de Freitas Castro, K. A. D., de Lima, O. J., Nassar, E. J., Ciuffi, K. J., Nakagaki, S.,* Aluminosilicate obtained by sol–gel process as support for an anionic iron porphyrin: Development of a selective and reusable catalyst for oxidation reactions, Colloids Surf. A: Physicochem. Eng. Asp. **349** (2009) 162.
doi: https://doi.org/10.1016/j.colsurfa.2009.08.013
98. *Ucoski, G. M., Machado, G. S., de Freitas Silva, G., Nunes, F. S., Wypych, F., Nakagaki, S.,* Heterogeneous oxidation of the dye Brilliant Green with H_2O_2 catalyzed by supported manganese porphyrins, J. Mol. Catal. A: Chem. **408** (2015) 123.
doi: https://doi.org/10.1016/j.molcata.2015.07.020

99. *Kameyama, H., Narumi, F., Hattori, T., Kameyama, H.,* Oxidation of cyclohexene with molecular oxygen catalyzed by cobalt porphyrin complexes immobilized on montmorillonite, J. Mol. Catal. A: Chem. **258** (2006) 172. doi: https://doi.org/10.1016/j.molcata.2006.05.022
100. *Machado, G. S., de Freitas Castro, K. A. D., Wypych, F., Nakagaki, S.,* Immobilization of metalloporphyrins into nanotubes of natural halloysite toward selective catalysts for oxidation reactions, J. Mol. Catal. A: Chem. **283** (2008) 99. doi: https://doi.org/10.1016/j.molcata.2007.12.009
101. *Adilina, I. B., Hara, T., Ichikuni, N., Shimazu, S.,* Oxidative cleavage of isoeugenol to vanillin under molecular oxygen catalysed by cobalt porphyrin intercalated into lithium taeniolite clay, J. Mol. Catal. A: Chem. **361** (2012) 72. doi: https://doi.org/10.1016/j.molcata.2012.05.005
102. *Xiantai, Z. H. O. U., Hongbing, J. I.,* Cobalt porphyrin immobilized on montmorillonite: A highly efficient and reusable catalyst for aerobic oxidation of alcohols to carbonyl compounds, Chinese J. Catal. **33** (2012) 1906. doi: https://doi.org/10.1016/S1872-2067(11)60461-0
103. *Zhou, X., Ji, H.,* Manganese porphyrin immobilized on montmorillonite: A highly efficient and reusable catalyst for the aerobic epoxidation of olefins under ambient conditions, J. Porphyr. Phthalocyanines **16** (2012) 1032. doi: https://doi.org/10.1142/S1088424612500721
104. *Nuzzo, A., Piccolo, A.,* Enhanced catechol oxidation by heterogeneous biomimetic catalysts immobilized on clay minerals, J. Mol. Catal. A: Chem. **371** (2013) 8. doi: https://doi.org/10.1016/j.molcata.2013.01.021
105. *Machado, G. S., de Lima, O. J., Ciuffi, K. J., Wypych, F., Nakagaki, S.,* Iron (III) porphyrin supported on metahalloysite: An efficient and reusable catalyst for oxidation reactions, Catal. Sci. Technol. **3** (2013) 1094. doi: https://doi.org/10.1039/C2CY20736B
106. *Drozd, D., Szczubiałka, K., Skiba, M., Kepczynski, M., Nowakowska, M.,* Porphyrin–nanoclay photosensitizers for visible light induced oxidation of phenol in aqueous media, J. Phys. Chem. C. **118** (2014) 9196. doi: https://doi.org/10.1021/jp500024h
107. *Lovo de Carvalho, A., Ferreira, B. F., Martins, C. H., Nassar, E. J., Nakagaki, S., Machado, G. S., Rives, V., Trujillano, R., Vicente, M. A., Gil, A., Korili, S. A.,* Tetracarboxyphenylporphyrin–kaolinite hybrid materials as efficient catalysts and antibacterial agents, J. Phys. Chem. C. **118** (2014) 24562. doi: https://doi.org/10.1021/jp5077356
108. *Ferreira, B. F., do Prado, M. V., Marçal, L., Ciuffi, K. J., Vicente, M. A., Gil, A., de Faria, E. H.,* Manganese-sulfonato porphyrin adsorbed on amino kaolinite as heterogeneous catalyst for oxidation and polymerization reactions, Appl. Clay Sci. **235** (2023) 106871. doi: https://doi.org/10.1016/j.clay.2023.106871
109. *Tsukamoto, T., Shimada, T., Takagi, S.,* Artificial photosynthesis model: Photochemical reaction system with efficient light-harvesting function on inorganic nanosheets, ACS Omega **3** (2018) 18563. doi: https://doi.org/10.1021/acsomega.8b02594
110. *Nakayama, A., Mizuno, J., Ohtani, Y., Shimada, T., Takagi, S.,* Elucidation of the adsorption distribution of cationic porphyrin on the inorganic surface by energy transfer as a molecular ruler, J. Phys. Chem. C. **122** (2018) 4365. doi: https://doi.org/10.1021/acs.jpcc.7b12104
111. *Wakayama, S., Takagi, S., Shimada, T.,* Adsorption and photochemical behavior of mono-cationic porphyrin onto synthetic saponite, Clay Sci. **20** (2017) 39. doi: https://doi.org/10.11362/jcssjclayscience.20.3-4_39
112. *Kemmegne-Mbouguen, J. C., Ngameni, E.,* Simultaneous quantification of dopamine, acetaminophen and tyrosine at carbon paste electrodes modified with porphyrin and clay, Anal. Methods **9** (2017) 4157. doi: https://doi.org/10.1039/C7AY01173C
113. *Eguchi, M., Watanabe, Y., Ohtani, Y., Shimada, T., Takagi, S.,* Switching of energy transfer reaction by the control of orientation factor between porphyrin derivatives on the clay surface, Tetrahedron Lett. **55** (2014) 2662. doi: https://doi.org/10.1016/j.tetlet.2014.03.027
114. *Konno, S., Fujimura, T., Otani, Y., Shimada, T., Inoue, H., Takagi, S.,* Microstructures of the porphyrin/viologen monolayer on the clay surface: Segregation or integration, J. Phys. Chem. C. **118** (2014) 20504. doi: https://doi.org/10.1021/jp5076274
115. *Kemmegne-Mbouguen, J. C., Toma, H. E., Araki, K., Constantino, V. R. L., Ngameni, E., Angnes, L.,* Simultaneous determination of acetaminophen and tyrosine using a glassy carbon electrode modified with a tetraruthenated cobalt (II) porphyrin intercalated into a smectite clay, Microchim. Acta. **183** (2016) 3243. doi: https://doi.org/10.1007/s00604-016-1985-2
116. *Arakawa, K., Suzuki, K., Nakazato, R., Hirade, Y., Shimada, T., Ishida, T., Yui, T., Takagi, S.,* Unique non self-luminescence quenching behavior of cationic Pt(IV)porphyrin on clay surface, Clay Sci. **25** (2021) 27. doi: https://doi.org/10.11362/jcssjclayscience.MS-21-6
117. *Fagadar-Cosma, E., Enache, C., Vlascici, D., Fagadar-Cosma, G., Vasile, M., Bazylak, G.,* Novel nanomaterials based on 5,10,15,20-tetrakis(3,4-dimethoxyphenyl)-21H,23H-porphyrin entrapped in silica matrices, Mater. Res. Bull. **44** (2009) 2186. doi: https://doi.org/10.1016/j.materresbull.2009.08.010
118. *Čeklovský, A., Takagi, S.,* Oxygen sensing materials based on clay/metalloporphyrin hybrid systems, Cent. Eur. J. Chem. **11** (2013) 1132. doi: https://doi.org/10.2478/s11532-013-0238-z
119. *Ishida, Y., Kulasekharan, R., Shimada, T., Ramamurthy, V., Takagi, S.,* Supramolecular-surface photochemistry: Supramolecular assembly organized on a clay surface facilitates energy transfer between an encapsulated donor and a free acceptor, J. Phys. Chem. C. **118** (2014) 10198. doi: https://doi.org/10.1021/jp502816j
120. *Ishida, Y., Shimada, T., Takagi, S.,* "Surface-fixation induced emission" of porphyrazine dye by a complexation with inorganic nanosheets, J. Phys. Chem. C. **118** (2014) 20466. doi: https://doi.org/10.1021/jp506766t
121. *Tatsumi, D., Tsukamoto, T., Honna, R., Hoshino, S., Shimada, T., Takagi, S.,* Highly selective photochemical epoxidation of cyclohexene sensitized by Ru(II) porphyrin–clay hybrid catalyst, Chem. Lett. **46** (2017) 1311. doi: https://doi.org/10.1246/cl.170521
122. *Fujimura, T., Shimada, T., Sasai, R., Takagi, S.,* Optical humidity sensing using transparent hybrid film composed of cationic magnesium porphyrin and clay mineral, Langmuir **34** (2018) 3572. doi: https://doi.org/10.1021/acs.langmuir.7b04006
123. *Ohsaki, Y., Shibatani, R., Shimada, T., Ishida, T., Takagi, S.,* Estimation of adsorption distribution of di-cationic porphyrin on anionic nanosheet surface using self-fluorescence quenching as a probe, Chem. Lett. **50** (2021) 1983. doi: https://doi.org/10.1246/cl.210506