

論文内容の要旨

Development of Ti(IV)–Centered Dynamic Chemistry for Construction of Multicomponent Self-Assembled Systems

多成分系自己集合型錯体システムの構築を目指した
Ti(IV)イオンを中心とした動的化学の開拓

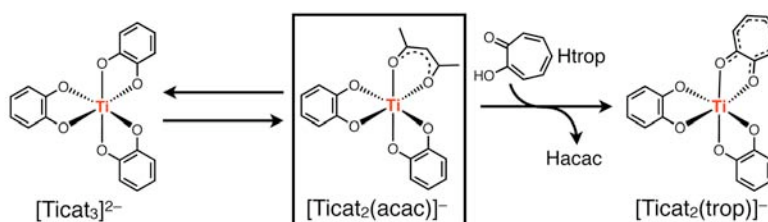
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<Introduction>

Multicomponent self-assembly from a number of different metal ions and ligands has received considerable attention in these years as an excellent strategy to construct higher-order, functionalized molecular architectures. To achieve this, each component is required to contain structural and functional information for self-assembly. Basically, the reversible nature of coordination bonding would allow site-selective metal-ligand exchange on a certain metal center by controlling reaction condition such as acid-base balance. Such dynamic behaviors on metal centers lead to switching functions of the resulting entities. Furthermore, the use of “hard and soft natures of metal ions and ligands” is pretty commonly known for multiple metal-centered self-assembly directed towards multifunctional supermolecules. So far, a number of excellent examples of dynamic supramolecules have been reported mainly using soft metal ions, but the dynamic chemistry on a hard metal ion has only just begun due to its relatively labile nature. Along this line, this work aimed at developing a hard metal-centered dynamic chemistry which would provide a platform for heteronuclear self-assembled systems.

In this study, a novel heteroleptic Ti(IV) complex, $[\text{Ticat}_2(\text{acac})]^-$, (cat = catecholate, acac = acetylacetonate) was synthesized and its dynamic properties have been established. Detailed solution analyses revealed that this Ti(IV) complex is interconvertible with a well-known $[\text{Ticat}_3]^{2-}$ complex by controlling acid-base balance, and that its acac ligand can be site-selectively replaced by a tropolonate (trop) ligand (Scheme 1). Furthermore, a new Pd(II)–Ti(IV) multicomponent self-assembled system has been established using a ditopic pyridyl catechol ligand, **H₂1**, which was designed based on the HSAB principle.

Scheme 1. Ti(IV)-centered dynamic chemistry developed in this study.



<A Novel $[\text{Ti}_2(\text{acac})]^-$ Complex which Allows Ti(V)–Centered Dynamic Interconversion between Pd(II)–Ti(IV) Ring and Cage Complexes>

Based on the Ti(IV)-centered site-selective ligand exchange induced by acid-base control (Scheme 1), a Ti(IV)-centered structural switching system between multinuclear Pd(II)-Ti(IV) ring and cage complexes has been established using a ditopic ligand $\text{H}_2\mathbf{1}$ (Figure 1).

Towards the construction of higher-order heteronuclear complexes, a ditopic ligand $\text{H}_2\mathbf{1}$ bearing a harder catechol and a softer pyridyl moieties has been designed and synthesized, and then its complexation with Ti(IV) in DMF- d_7 solution has been firstly

examined. Upon addition of $\text{TiO}(\text{acac})_2$ to a mixture of $\text{H}_2\mathbf{1}$ and $n\text{-Bu}_4\text{NOH}$ in DMF- d_7 , the ^1H NMR spectrum immediately after mixing showed the formation of two distinct species (Figure 2b). However, after 20 h, a set of signals for one species completely disappeared (Figure 2d). From a time-course analysis of ESI-TOF mass spectra of the mixture, it appears that the final product and an intermediate firstly formed can be assigned to $[\text{Ti}_3]^{2-}$ and $[\text{Ti}_2(\text{acac})]^-$, respectively. Since the intermediate species was also detected as $[\text{Ti}_2(\text{acac}) + 2\text{H}]^+$ in its ESI-TOF mass measurement, the intermediate species was thought to be stable under a weakly basic condition. To confirm this, the effect of a weaker base, N -methylmorpholine, instead of $n\text{-Bu}_4\text{NOH}$, was examined. As a result, the ^1H NMR spectrum of the mixture was identical with that of the intermediate $[\text{Ti}_2(\text{acac})]^-$ (Figure 2e). A series of amine bases were then examined to clarify the relationship between their degree of basicity and the molar fraction of the two species, $[\text{Ti}_3]^{2-}$ and $[\text{Ti}_2(\text{acac})]^-$. As shown in Figure 3, the molar fraction of generated kinetic intermediate is potentially correlated with the $\text{p}K_a$ values of the conjugated acids. Moreover, from various ^1H NMR titration studies, it was also found that $[\text{Ti}_2(\text{acac})]^-$ is partially protonated as $\text{TiH}_2(\text{acac})$ whereas the remaining complex $[\text{Ti}_2(\text{acac})]^-$ pairs with protonated N -methylmorpholine in solution. Thus,

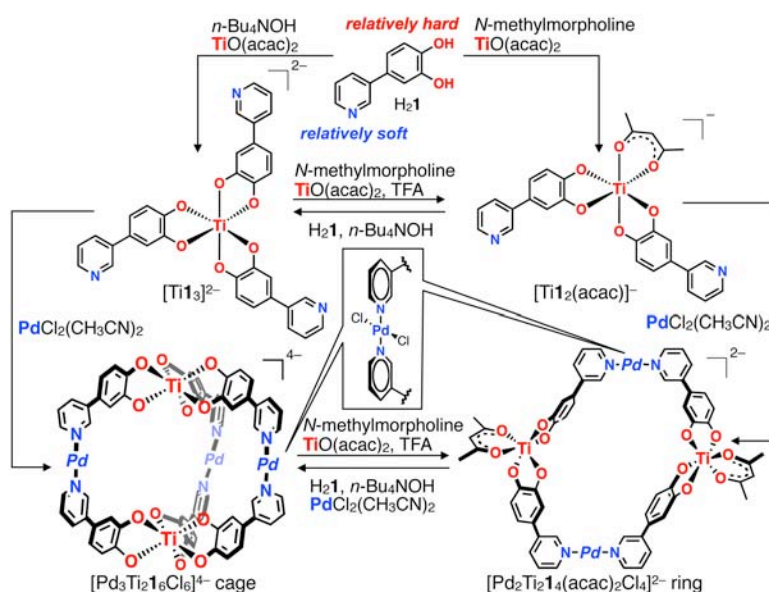


Figure 1. Formation of Ti(IV) and heterologous multinuclear Pd(II)–Ti(IV) complexes.

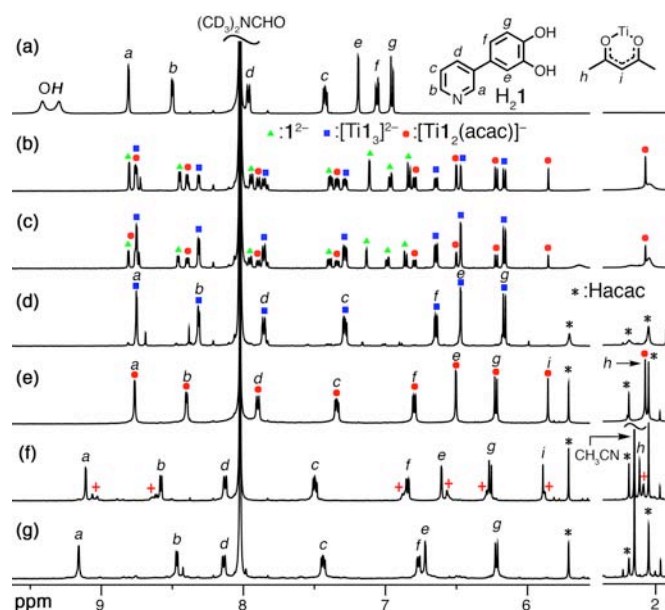


Figure 2. Partial ^1H NMR spectra (500 MHz, DMF- d_7 , 293 K, $[\text{H}_2\mathbf{1}] = 15$ mM); (a) $\text{H}_2\mathbf{1}$; (b)–(d) a 1:0.43:0.67 mixture of $\text{H}_2\mathbf{1}$, $\text{TiO}(\text{acac})_2$, and $n\text{-Bu}_4\text{NOH}$. (b) 5 min; (c) 1 h; (d) 20 h ($[\text{Ti}_3]^{2-}$); (e) a 4:4:3 mixture of $\text{H}_2\mathbf{1}$, $\text{TiO}(\text{acac})_2$, and N -methylmorpholine ($[\text{Ti}_2(\text{acac})]^-$); (f) Pd(II)-Ti(IV) ring ($[\text{Pd}_2\text{Ti}_2\mathbf{1}_4(\text{acac})_2\text{Cl}_4]^{2-}$); (g) Pd(II)-Ti(IV) cage ($[\text{Pd}_3\text{Ti}_2\mathbf{1}_6\text{Cl}_6]^{4-}$). Signals with a + mark in (f) are assigned to those of a cyclic 3:3 complex $[\text{Pd}_3\text{Ti}_3\mathbf{1}_6(\text{acac})_3\text{Cl}_6]^{3-}$.

examined to clarify the relationship between their degree of basicity and the molar fraction of the two species, $[\text{Ti}_3]^{2-}$ and $[\text{Ti}_2(\text{acac})]^-$. As shown in Figure 3, the molar fraction of generated kinetic intermediate is potentially correlated with the $\text{p}K_a$ values of the conjugated acids. Moreover, from various ^1H NMR titration studies, it was also found that $[\text{Ti}_2(\text{acac})]^-$ is partially protonated as $\text{TiH}_2(\text{acac})$ whereas the remaining complex $[\text{Ti}_2(\text{acac})]^-$ pairs with protonated N -methylmorpholine in solution. Thus,

the stability of $[\text{Ti}1_2(\text{acac})]^-$ depends on the degree of the protonation (hereafter referred to as $[\text{Ti}1_2(\text{acac})]^-$ for clarify). In addition, the binding of acac to $[\text{Ti}1_2(\text{acac})]^-$ was also confirmed by IR spectra of a solid sample. Its UV-vis absorption spectrum in DMF showed a characteristic LMCT band which is red-shifted from that of $[\text{Ti}1_3]^{2-}$.

These two distinct Ti(IV) complexes were found to be interconvertible, and the component fraction depends on the acid-base balance. When $\text{TiO}(\text{acac})_2$ and TFA were added to a solution of $[\text{Ti}1_3]^{2-}$, $[\text{Ti}1_2(\text{acac})]^-$ was produced. On the other hand, when $\text{H}_2\mathbf{1}$ and *n*-Bu₄NOH were added to the solution of $[\text{Ti}1_2(\text{acac})]^-$, $[\text{Ti}1_3]^{2-}$ was quantitatively regenerated. In this reversible process, the pyridyl group of ligand **1** was coordinatively free.

In the next step, the complexation behavior of the pyridyl groups of the Ti(IV) complexes was examined using softer Pd(II) ions. From a 1:1 mixture of $\text{PdCl}_2(\text{CH}_3\text{CN})_2$ and $[\text{Ti}1_2(\text{acac})]^-$, $[\text{Pd}_2\text{Ti}_21_4(\text{acac})_2\text{Cl}_4]^{2-}$ ring complex was formed selectively, and similarly the complexation of $[\text{Ti}1_3]^{2-}$ with $\text{PdCl}_2(\text{CH}_3\text{CN})_2$ provided $[\text{Pd}_3\text{Ti}_21_6\text{Cl}_6]^{4-}$ cage complex. The formation of these complexes was characterized by ¹H NMR (Figure 2), ESI-TOF mass, and UV-vis absorption measurements. The interconversion between the $[\text{Pd}_2\text{Ti}_21_4(\text{acac})_2\text{Cl}_4]^{2-}$ ring and $[\text{Pd}_3\text{Ti}_21_6\text{Cl}_6]^{4-}$ cage was also achieved by the Ti(IV)-centered ligand exchange similarly to the interconversion between $[\text{Ti}1_2(\text{acac})]^-$ and $[\text{Ti}1_3]^{2-}$ complexes.

<Efficient Construction of Self-Assembled Pd(II)-Ti(IV) Complexes with a Ditopic Tropolonate Bridging Ligand Based on Site-Selective Ligand Exchange Reactions on the Heteroleptic $[\text{Ti}1_2(\text{acac})]^-$ Complex >

Site-selective ligand exchange on a heteroleptic complex is an effective tool for introducing additional functionality and thereby constructing higher-order self-assembled structures with greater functions. In this regard, a heteroleptic $[\text{Ti}1_2(\text{acac})]^-$ complex appeared to show promise for site-selective ligand exchange because it contains both relatively labile acac and relatively inert catechol ligands.

As a result of exploring bidentate ligands which can replace acac in $[\text{Ti}1_2(\text{acac})]^-$, it was found that a mixture of $\text{H}_2\mathbf{1}$, $\text{Ti}(\text{O}^i\text{Pr})_4$, *N*-methylmorpholine, and various bidentate ligands in DMF provide $[\text{Ti}1_2\mathbf{X}]^-$

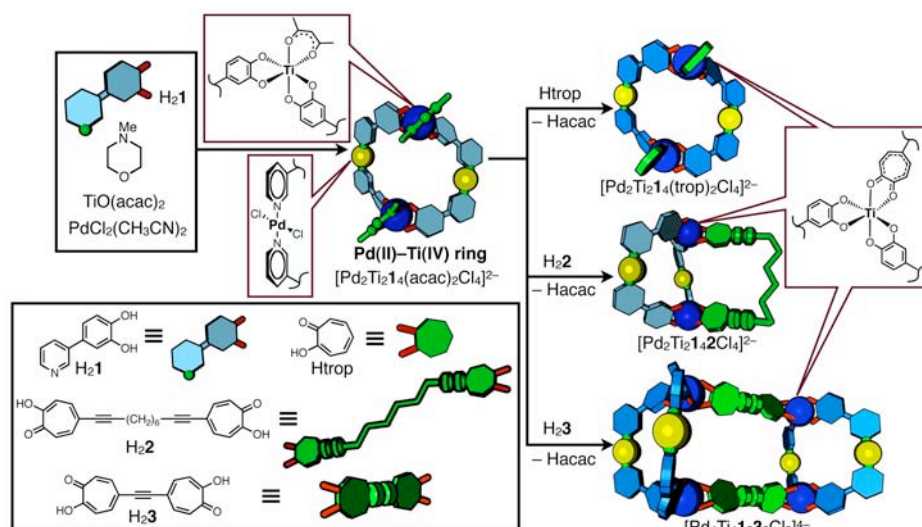


Figure 4. Schematic representation of construction of higher-order multicomponent assembled complexes by site-selective ligand exchange reactions on the Pd(II)-Ti(IV) ring complex.

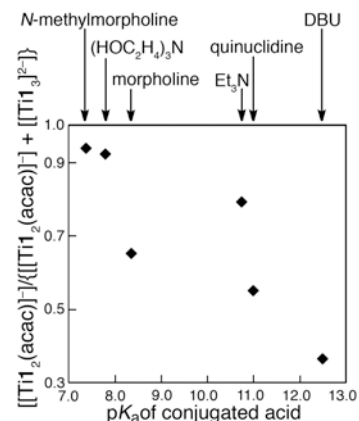


Figure 3. Plot of the molar fraction of $[\text{Ti}1_2(\text{acac})]^-$ in the mixture against pK_a value of the conjugated acids.

(HX = benzoylacetone, dibenzoylmethane, 3-phenyl-2,4-pentanedione, *N*-benzoyl-*N*-phenylhydroxylamine, quinolinol, maltol, and tropolone). Furthermore, from competitive experiments to evaluate the relative stability of a series of these complexes it was proven that $[\text{Ti}1_2(\text{trop})]^-$ complex is much more stable than $[\text{Ti}1_2(\text{acac})]^-$

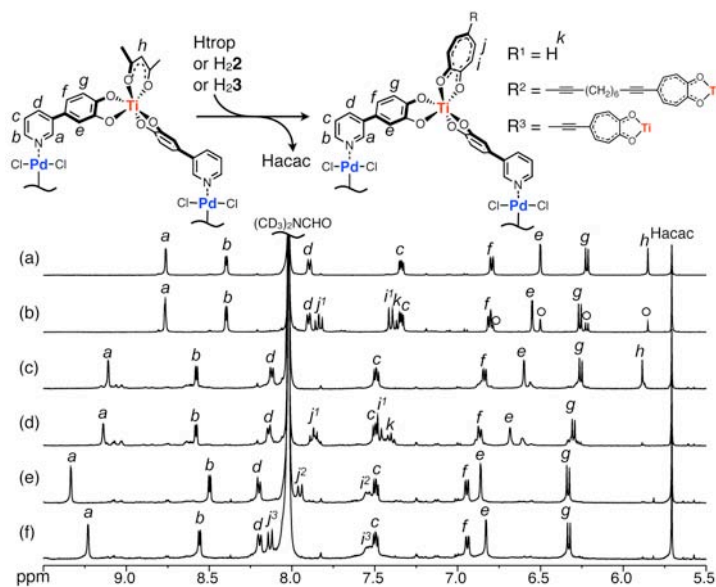


Figure 5. Partial ^1H NMR spectra (500 MHz, $\text{DMF-}d_7$, 293 K, $[\text{H}_2\mathbf{1}] = 12$ mM) of site-selective ligand exchange of acac with tropolone on $[\text{Ti}_{12}(\text{acac})]^-$ (a-b) and $[\text{Pd}_2\text{Ti}_2\mathbf{1}_4(\text{acac})_2\text{Cl}_4]^{2-}$ ring complex (c-f). a) $[\text{Ti}_{12}(\text{acac})]^-$ and Htrop (20 h). The signals for $[\text{Ti}_{12}(\text{acac})]^-$ complex are marked by open circles. c) Pd(II)–Ti(IV) ring, d) a 1:2 mixture of Pd(II)–Ti(IV) ring and $\text{H}_2\mathbf{2}$ (20 h), e) a 1:1 mixture of Pd(II)–Ti(IV) ring and $\text{H}_2\mathbf{2}$ (20 h), f) a 1:1 mixture of Pd(II)–Ti(IV) ring and $\text{H}_2\mathbf{3}$ (20 h).

on the Pd(II)–Ti(IV) ring complex, synthetic bridging ligands with two terminal tropolone ligands, flexible $\text{H}_2\mathbf{2}$ and rigid $\text{H}_2\mathbf{3}$, have been examined to exploit higher-order self-assembled constructs. Upon the addition of an equimolar amount of $\text{H}_2\mathbf{2}$ to a solution of $[\text{Pd}_2\text{Ti}_2\mathbf{1}_4(\text{acac})_2\text{Cl}_4]^{2-}$ ring in $\text{DMF-}d_7$, two acac moieties were intramolecularly replaced by ligand $\mathbf{2}$ and quantitatively formed a tetranuclear $[\text{Pd}_2\text{Ti}_2\mathbf{1}_4\mathbf{2}\text{Cl}_4]^{2-}$ cage-shaped complex as determined by ^1H NMR (Figure 5e) and ESI-TOF mass measurements. On the other hand, a 1:1 mixture of $\text{H}_2\mathbf{3}$ and $[\text{Pd}_2\text{Ti}_2\mathbf{1}_4(\text{acac})_2\text{Cl}_4]^{2-}$ ring resulted in the quantitative formation of an intermolecularly connected complex, an octanuclear $[\text{Pd}_4\text{Ti}_4\mathbf{1}_8\mathbf{3}_2\text{Cl}_8]^{4-}$ complex (Figure 5f).

To firmly establish the efficacy of such a stepwise procedure, one-pot synthesis was conducted in a way that all components were mixed at a time. In the result, tetranuclear $[\text{Pd}_2\text{Ti}_2\mathbf{1}_4\mathbf{2}\text{Cl}_4]^{2-}$ and octanuclear $[\text{Pd}_4\text{Ti}_4\mathbf{1}_8\mathbf{3}_2\text{Cl}_8]^{4-}$ were generated in 69% and 38% yields, respectively. This lower efficiency is due to the formation of an insoluble material kinetically formed from Ti(IV) and bridging ligands as revealed by various NMR titration studies. Thus, the stepwise procedure employed is an excellent tool for constructing the higher-order heteronuclear self-assembled complexes.

<Conclusion>

In this study, a synthetic method of a novel heteroleptic Ti(IV) complex has been established, and it was further extended to a structural switching system ($[\text{Ticat}_2(\text{acac})]^-$ and $[\text{Ticat}_3]^{2-}$) which is controllable by acid-base balance. The heteroleptic $[\text{Ticat}_2(\text{acac})]^-$ complex also serves as a platform for constructing higher-order constructs through site-selective ligand exchange reactions on more labile acac sites. By using a ditopic pyridyl catechol ligand instead of catechol, a stepwise synthetic method was accomplished for constructing heteronuclear Pd(II)–Ti(IV) complexes. Such a synthetic strategy would be useful in supramolecular approaches to heterogeneous, multicomponent self-assembled systems which possess molecular functions depending on metal-centered dynamic chemistry.

complex. Actually, when an equimolar amount of Htrop (= tropolone) was added to a solution of $[\text{Ti}_{12}(\text{acac})]^-$ in DMF, 70% of $[\text{Ti}_{12}(\text{trop})]^-$ was formed as a result of site-selective ligand exchange of acac with trop as monitored by ^1H NMR spectroscopy (Figures 5a-b). This reaction took place similarly in the $[\text{Pd}_2\text{Ti}_2\mathbf{1}_4(\text{acac})_2\text{Cl}_4]^{2-}$ ring complex. ^1H NMR spectrum of a 2:1 mixture of Htrop and $[\text{Pd}_2\text{Ti}_2\mathbf{1}_4(\text{acac})_2\text{Cl}_4]^{2-}$ ring complex showed that $[\text{Pd}_2\text{Ti}_2\mathbf{1}_4(\text{trop})_2\text{Cl}_4]^{2-}$ ring complex was quantitatively formed in a way that the precursory ring framework was preserved (Figures 5c-d). A model study with $[\text{Ti}\{\text{Pd}(\text{dien})\mathbf{1}\}_2(\text{acac})]^-$ (dien = diethylenetriamine) suggested that this ligand exchange reaction could be promoted by the binding of the pyridyl groups of $[\text{Ti}_{12}(\text{acac})]^-$ to Pd(II) ions.

Based on the above-mentioned site-selective ligand exchange reaction