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Site-Selective Ligand Exchange on a Heteroleptic Ti^{IV} Complex Towards Stepwise Multicomponent Self-Assembly

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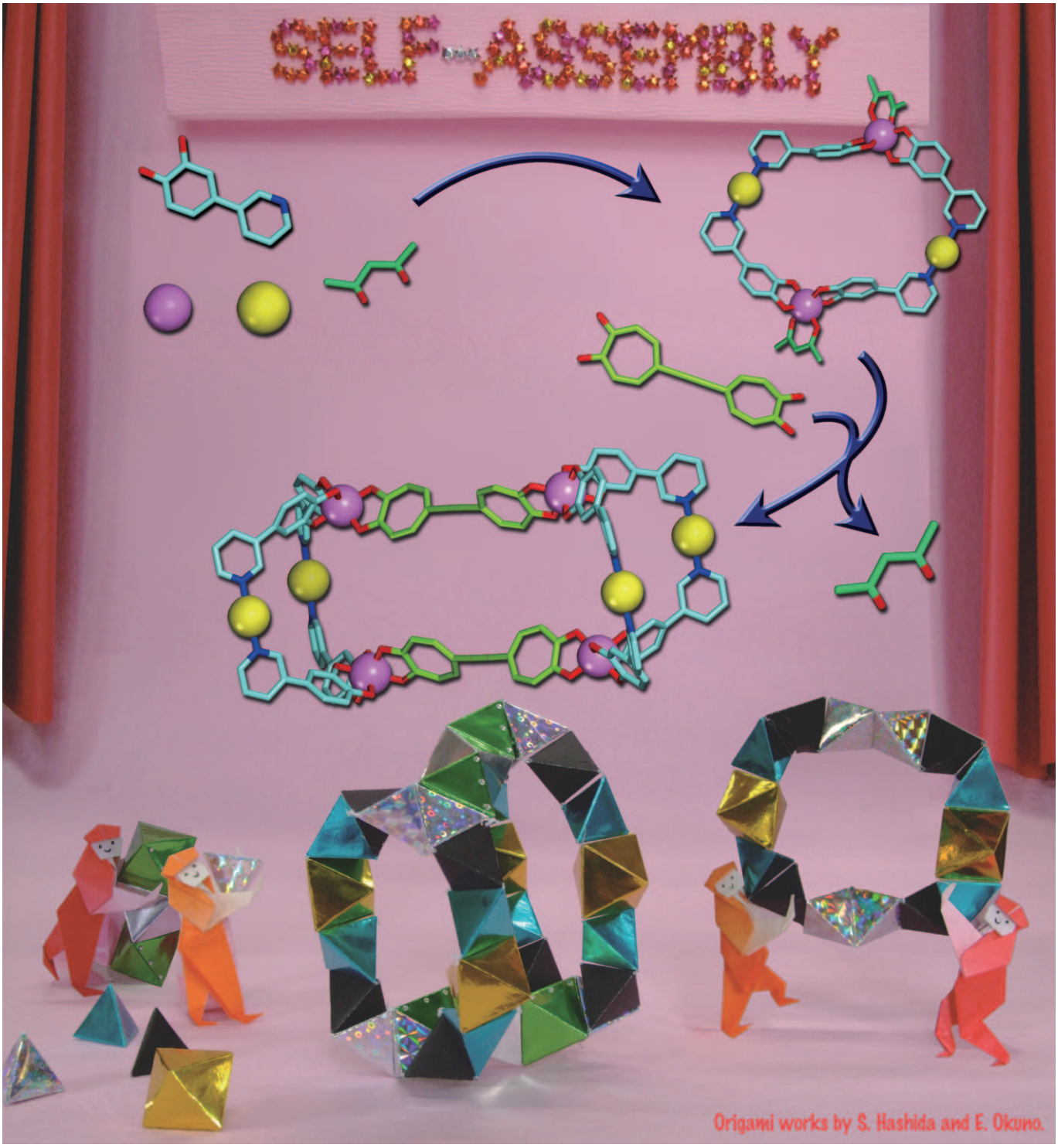

Abstract: A series of heteroleptic $[Ti\mathbf{1}_2X]^-$ complexes have been selectively constructed from a mixture of Ti^{IV} ions, a pyridyl catechol ligand ($H_2\mathbf{1}$; $H_2\mathbf{1}$ = 4-(3-pyridyl)catechol), and various bidentate ligands (HX) in the presence of a weak base, in addition to a previously reported $[Ti\mathbf{1}_2(acac)]^-$ (acac = acetylacetonate) complex. Comparative studies of these Ti^{IV} complexes revealed that $[Ti\mathbf{1}_2(trop)]^-$ (trop = tropolonate) is much more stable than the $[Ti\mathbf{1}_2(acac)]^-$ complex, which allows the replacement of acac with trop on the $[Ti\mathbf{1}_2(acac)]^-$ complex. This Ti^{IV}-centered site-selective ligand exchange reaction also takes place on a heteronuclear Pd^{II}–Ti^{IV} ring complex with the preservation of the Pd^{II}-centered coordination structures. Intra- and intermolecular linking between two Ti^{IV} centers with a flexible or a rigid bis-tropolone bridging ligand provided a tetranuclear and an octanuclear Pd^{II}–Ti^{IV} complex, respectively. These higher-order structures could be efficiently constructed only through a stepwise synthetic route.

Keywords: ligand exchange · palladium · self-assembly · supramolecular chemistry · titanium

Introduction

Metal–ligand exchange is a fundamental characteristic of metal complexes that enables the dynamic transformation of structures and functions of supramolecular coordination compounds.[1] In particular, site-selective reversible exchange of ligands on a certain metal center is an indispensable tool for stepwise construction of higher-order self-assembled structures from metal-centered constructs.[2] In this regard, it is well known that the dynamic behavior of metal–ligand exchange is influenced by the structure and properties of the metal and ligand and its combination (e.g., the hard/soft acid–base rule, HSAB), and external stimuli (e.g., light, acid or base, oxidation or reduction, temperature).[3] However, it is still rather difficult to control the dynamic activities of multiple ligands on a labile metal complex, compared with those on relatively inert metal complexes. If it is possible, the formation of heteronuclear dynamic supramolecules in which the different metal centers work independently would be expected when using the difference of affinities of metal–ligand coordination binding such as the hard and soft nature of metal ions and ligands. In line with the growing strategic importance of more complex, heterogenous self-assembled molecular structures, this study is aimed at developing Ti^{IV}-centered dynamic chemistry, which could provide a platform for heteronuclear higher-order self-assembled architectures.

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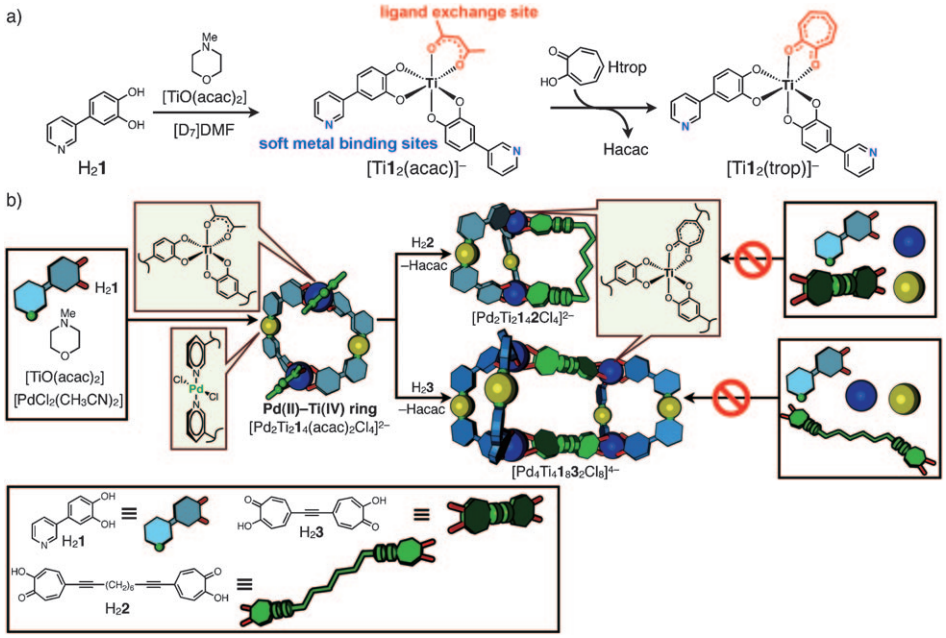
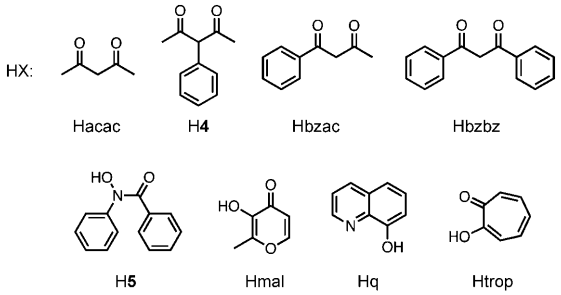
It is well known that the Ti^{IV} ion forms an octahedral complex with three catecholate ligands, $[Ti(cat)_3]^{2-}$ (cat = catecholate), in the presence of a strong base. Because this Ti^{IV} complex is stable in solution and in the solid state, this structural motif has often been used for supramolecular compounds.[4] We recently reported the selective formation of a $[Ti\mathbf{1}_2(acac)]^-$ (acac = acetylacetonate) complex formed from a pyridyl catechol ligand, $H_2\mathbf{1}$ ($H_2\mathbf{1}$ = 4-(3-pyridyl)catechol), and $[TiO(acac)_2]$ in the presence of a weak base.[5] This Ti^{IV} complex contains three bidentate ligands, one monoanionic acac and two dianionic catecholate ligands. Because the acac ligand appears to be more labile compared with the other two catecholate ligands, and the formation of this heteroleptic complex is not affected by the pyridyl ligand in **1** at all, both sites were expected to serve as platforms independently for a site-selective ligand exchange site with various functional ligands and a soft metal binding site,[6] respectively, to construct higher-order heteronuclear coordination molecules in a stepwise manner. In this study, we have examined the reactivity of $[Ti\mathbf{1}_2(acac)]^-$ and have expanded this bifunctional coordination building block into the efficient construction of higher-order structures, tetranuclear $[Pd_2Ti_2\mathbf{1}_4\mathbf{2}Cl_4]^{2-}$ and octanuclear $[Pd_4Ti_4\mathbf{1}_8\mathbf{3}_2Cl_8]^{4-}$, by means of the bis-tropolone bridging ligands $H_2\mathbf{2}$ and $H_2\mathbf{3}$ (Scheme 1).

Results and Discussion

Selective formation of $[Ti\mathbf{1}_2X]^-$ complexes from various bidentate ligands (X^-) and comparison of the stabilities for the resulting $[Ti\mathbf{1}_2X]^-$ complexes: To examine whether the acac moiety of $[Ti\mathbf{1}_2(acac)]^-$ could be substituted for other bidentate ligands, we prepared a diverse array of chelate ligands (HX) for constructing $[Ti\mathbf{1}_2X]^-$ complexes (Hbzac = benzoylacetone, Hbzbz = dibenzoylmethane, H**4** = 3-phenyl-2,4-pentanedione, H**5** = *N*-benzoyl-*N*-phenylhydroxylamine, Hmal = maltol, Hq = quinolinol, and Htrop = tropolone). According to our previous results that $[Ti\mathbf{1}_2(acac)]^-$ can be formed from a mixture of $H_2\mathbf{1}$, *N*-methylmorpholine, Ti(O*i*Pr)$_4$, and Hacac,[5] we performed similar complexation



Scheme 1. a) Site-selective ligand exchange on the heteroleptic $[Ti\mathbf{1}_2(acac)]^-$ complex, b) Schematic representation of the construction of higher-order multicomponent self-assembled complexes through site-selective ligand exchange reactions on a precursory heteronuclear Pd^{II}–Ti^{IV} ring complex.



reactions by using other bidentate ligands (HX) such as β-diketones instead of Hacac. For example, when Htrop (6.0 mM) was added to a mixture of $H_2\mathbf{1}$ (12 mM), *N*-methylmorpholine (12 mM), and $Ti(OiPr)_4$ (9.0 mM) in $[D_7]DMF$, its ^1H NMR spectrum after 12 h showed only one set of signals (Figure 1). The ESI-TOF mass spectrum of the resulting

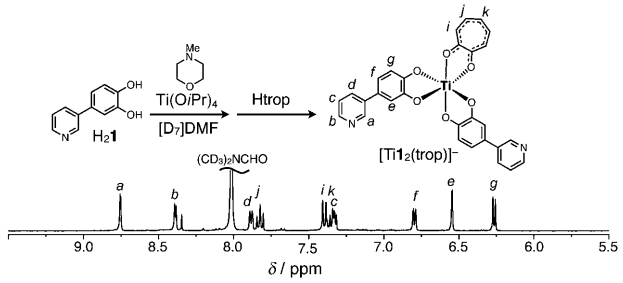


Figure 1. Partial ^1H NMR spectra (500 MHz, $[D_7]DMF$, 293 K, $[H_2\mathbf{1}]$ (12 mM)) of the $[Ti\mathbf{1}_2(trop)]^-$ complex (4:4:3:2 mixture of $H_2\mathbf{1}$, *N*-methylmorpholine, $Ti(OiPr)_4$, and Htrop).

complex exhibited signals that were assignable to $[Ti\mathbf{1}_2(trop)]^-$, $[Ti\mathbf{1}_2(trop)+2H]^+$, and $[\{Ti\mathbf{1}_2(trop)\}_2+3H]^+$ at $m/z = 539.0$, 541.0, and 1081.3, respectively (see Figure S12 in the Supporting Information). These results indicate the selective formation of $[Ti\mathbf{1}_2(trop)]^-$. Under similar reaction conditions, various $[Ti\mathbf{1}_2X]^-$ complexes were exclusively formed not only with a few β-diketone derivatives (HX = Hbzac, Hbzbz, and H**4**) but also with other α-hydroxyketone derivatives (HX = tropolone, maltol, and H**5**) and Hq (see Figures S6–12 in the Supporting Information).

To evaluate the relative stabilities of the $[Ti\mathbf{1}_2X]^-$ complexes, the formation ratio of $[Ti\mathbf{1}A]^-/[Ti\mathbf{1}_2B]^-$ was compared by the ^1H NMR spectra of mixed solutions including two kinds of HXs, HA (6.0 mM) and HB (6.0 mM), in the presence of $H_2\mathbf{1}$ (12 mM), *N*-methylmorpholine (12 mM), and $Ti(OiPr)_4$ (9.0 mM; Table 1 and Figures S13–19 in the Supporting Information). Based on the results of these competitive experiments, the order of the relative stabilities of $[Ti\mathbf{1}_2X]^-$ complexes was determined as follows: $[Ti\mathbf{1}_2(trop)]^- > [Ti\mathbf{1}_2(q)]^- > [Ti\mathbf{1}_2(mal)]^- > [Ti\mathbf{1}_2\mathbf{5}]^- \approx [Ti\mathbf{1}_2(bzbz)]^- > [Ti\mathbf{1}_2(bzac)]^- > [Ti\mathbf{1}_2(acac)]^- > [Ti\mathbf{1}_2\mathbf{4}]^-$. This order has a few features: First, $[Ti\mathbf{1}_2X]^-$ containing a five-membered chelate ring is more stable than that containing a six-membered chelate ring (i.e., $[Ti\mathbf{1}_2(mal)]^-$ vs. $[Ti\mathbf{1}_2(bzbz)]^-$), which is generally known from the relationship between the chelate ring size and the chelate effect. Second, ring-structure-based rigid bidentate ligands provide more stable $[Ti\mathbf{1}_2X]^-$ complexes compared with structurally more flexible ones (e.g., $[Ti\mathbf{1}_2(mal)]^-$ vs. $[Ti\mathbf{1}_2\mathbf{5}]^-$). Third, because the metal complexation is accompanied by deprotonation of the bidentate

Table 1. Comparison of the relative stabilities of the $[Ti\mathbf{1}_2X]^-$ complexes.

HA	HB	Formation ratios of $[Ti\mathbf{1}A]^-/[Ti\mathbf{1}_2B]^-$[a]	Relative stabilities of $[Ti\mathbf{1}_2X]^-$ complexes
Htrop	Hq	2.0	$[Ti\mathbf{1}_2(trop)]^- > [Ti\mathbf{1}_2(q)]^-$
Hq	Hmal	1.9	$[Ti\mathbf{1}_2(q)]^- > [Ti\mathbf{1}_2(mal)]^-$
Hmal	H**5**	1.3	$[Ti\mathbf{1}_2(mal)]^- > [Ti\mathbf{1}_2\mathbf{5}]^-$
H**5**	Hbzbz	1.0	$[Ti\mathbf{1}_2\mathbf{5}]^- \approx [Ti\mathbf{1}_2(bzbz)]^-$
Hbzbz	Hbzac	1.3	$[Ti\mathbf{1}_2(bzbz)]^- > [Ti\mathbf{1}_2(bzac)]^-$
Hbzac	Hacac	1.4	$[Ti\mathbf{1}_2(bzac)]^- > [Ti\mathbf{1}_2(acac)]^-$
Hacac	H**4**	1.8	$[Ti\mathbf{1}_2(acac)]^- > [Ti\mathbf{1}_2\mathbf{4}]^-$

[a] Determined by integral ratios of the ^1H NMR signals.

ligand, more acidic ligands give more stable complexes under the given condition, for example, Htrop (pK_a = 6.70) > Hmal (pK_a = 8.50).[7]

Site-selective ligand exchange of acac with trop in various Ti^{IV} and Pd^{II}–Ti^{IV} complexes: Subsequently, we investigated the ligand exchange reactivity of the acac group of $[Ti\mathbf{1}_2(acac)]^-$. Because the $[Ti\mathbf{1}_2(trop)]^-$ complex is much more stable than the $[Ti\mathbf{1}_2(acac)]^-$ complex as mentioned above, it was highly expected that ligand exchange of acac with trop would occur efficiently. Upon the addition of an equimolar amount of Htrop to $[Ti\mathbf{1}_2(acac)]^-$ in [D_7]DMF, the signal for coordinating acac, H^h, gradually disappeared whereas that for trop bound to Ti^{IV}, H^{i-k}, appeared within 20 h in the ^{1}H NMR spectrum (Figure 2a and b). This indicated that the acac ligand of $[Ti\mathbf{1}_2(acac)]^-$ was site-selectively replaced by trop to form $[Ti\mathbf{1}_2(trop)]^-$. A 1:1 mixture of Htrop and $[Ti(cat)_2(acac)]^-$ also provided a trop-substituted $[Ti(cat)_2(trop)]^-$ complex (Figure S20 in the Supporting Information). The transformed ratios were fairly high (ca. 70%) in both cases, therefore, both $[Ti\mathbf{1}_2(acac)]^-$ and $[Ti(cat)_2(acac)]^-$ complexes were expected to serve as versatile platforms for higher-order multicomponent self-assembly.

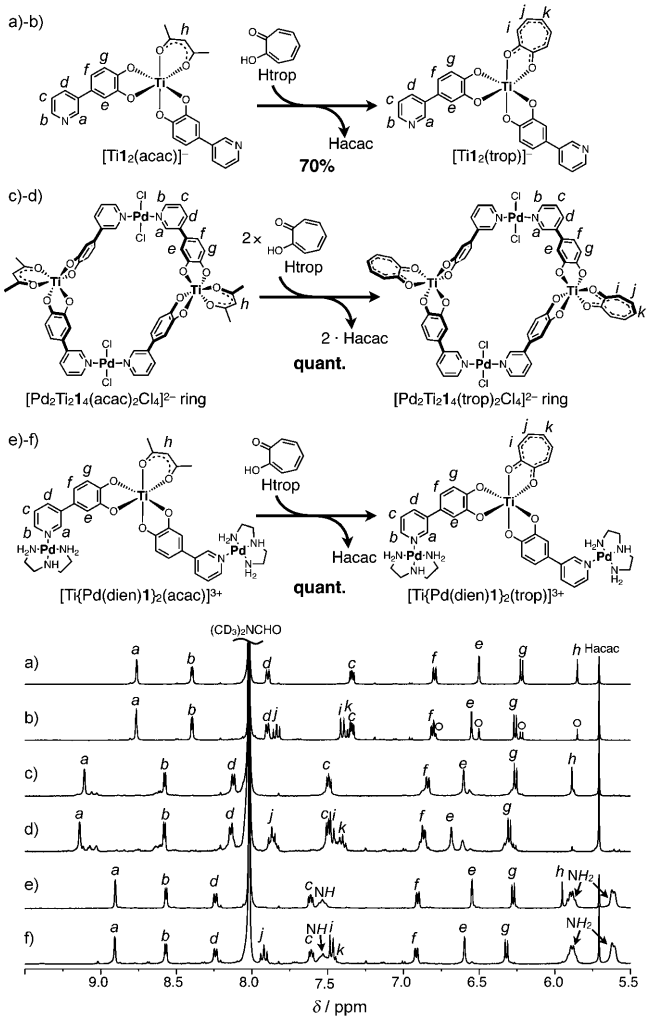


Figure 2. Partial ^{1}H NMR spectra (500 MHz, [D_7]DMF, 293 K, [$H_2\mathbf{1}$] (12 mM)) of site-selective ligand exchange of acac with trop on $[Ti\mathbf{1}_2(acac)]^-$ (a and b), Pd^{II}–Ti^{IV} ring complexes (c and d), and $[Ti\{Pd(dien)\mathbf{1}\}_2(acac)]^{3+}$ (e and f): a) $[Ti\mathbf{1}_2(acac)]^-$, b) 1:1 mixture of $[Ti\mathbf{1}_2(acac)]^-$ and Htrop (20 h; ○ = the signals for $[Ti\mathbf{1}_2(acac)]^-$), c) $[Pd_2Ti_2\mathbf{1}_4(acac)_2Cl_4]^{2-}$ ring, d) 1:2 mixture of the $[Pd_2Ti_2\mathbf{1}_4(acac)_2Cl_4]^{2-}$ ring and Htrop (20 h), e) $[Ti\{Pd(dien)\mathbf{1}\}_2(acac)]^{3+}$, and f) 1:1 mixture of $[Ti\{Pd(dien)\mathbf{1}\}_2(acac)]^{3+}$ and Htrop (20 h).

Furthermore, to confirm whether this Ti^{IV}-centered site-selective ligand exchange takes place in heteronuclear metal complexes with the preservation of the coordination structures of the Pd^{II} centers, ligand exchange properties of the $[Pd_2Ti_2\mathbf{1}_4(acac)_2Cl_4]^{2-}$ ring complex[8] were then investigated. Upon the addition of two equivalents of Htrop to a solution of the ring complex in [D_7]DMF, a new set of the signals appeared in the ^{1}H NMR spectrum, and after 20 h the signal for acac bound to Ti^{IV}, H^h, disappeared but was complemented by the signals for trop bound to Ti^{IV}, H^{i-k}, whereas the signals for the pyridyl catechol ligand $H_2\mathbf{1}$, H^{a-g}, did not exhibit any significant shifts (Figure 2d). The ESI-TOF mass spectrum of the solution showed a signal at m/z = 1399.1 for $[Pd_2Ti_2\mathbf{1}_4(trop)_2Cl_3+2H]^+$ (Figure S24 in the Supporting Information). These results indicate the quantitative formation of the $[Pd_2Ti_2\mathbf{1}_4(trop)_2Cl_4]^{2-}$ ring complex. Notably, this ligand exchange reaction on the Pd^{II}–Ti^{IV} ring complex took place quantitatively, whereas that on the $[Ti\mathbf{1}_2(acac)]^-$ complex did not. To understand what the factors that determine the efficiency of the ligand exchange process are, a control experiment was carried out by using $[Ti\{Pd(dien)\mathbf{1}\}_2(acac)]^{3+}$ (dien = diethylenetriamine)[9] in which a pyridyl group of **1** coordinates to a Pd^{II}–dien complex. The ^{1}H NMR spectrum of a 1:1 mixture of Htrop and $[Ti\{Pd(dien)\mathbf{1}\}_2(acac)]^{3+}$ showed complexation behavior similar to that of a mixture of Htrop and the $[Pd_2Ti_2\mathbf{1}_4(acac)_2Cl_4]^{2-}$ ring complex (Figure 2f). This indicates that the acac ligand of $[Ti\{Pd(dien)\mathbf{1}\}_2(acac)]^{3+}$ was also quantitatively substituted for trop within 2 h. Thus, the coordination of the pyridyl group of $[Ti\mathbf{1}_2(acac)]^-$ to the Pd^{II} ion enhances the ligand exchange from acac to trop to form a thermodynamically stable trop-substituted complex.

Stepwise construction of higher-order structures with bridging ligands: In view of the above-mentioned characteristics of the Ti^{IV} precursor complexes in the site-selective ligand exchange, we then performed the construction of higher-order structures by using two types of bridging ligands, $H_2\mathbf{2}$ and $H_2\mathbf{3}$,[10] which have one tropolone moiety on each side and are connected by a structurally flexible alkyl and a rigid ethynylene linker, respectively. These bridging ligands, $H_2\mathbf{2}$ and $H_2\mathbf{3}$, were expected to connect the two Ti^{IV} centers of the $[Pd_2Ti_2\mathbf{1}_4(acac)_2Cl_4]^{2-}$ ring complex intra- or intermolecularly, respectively. ^{1}H NMR titration studies were conducted by using these bridging ligands and the $[Pd_2Ti_2\mathbf{1}_4(acac)_2Cl_4]^{2-}$ ring complex in [D_7]DMF. Upon the addition of an equimolar amount of $H_2\mathbf{2}$ to a solution of the $[Pd_2Ti_2\mathbf{1}_4(acac)_2Cl_4]^{2-}$ ring complex in [D_7]DMF, the signals for the original ring complex gradually disappeared and a

set of new signals appeared with an increase in the intensity of the signals for tropolone groups bound to Ti^{IV}, $H^{l,m}$ (Figure 3b). This result suggests that the acac ligands of the ring

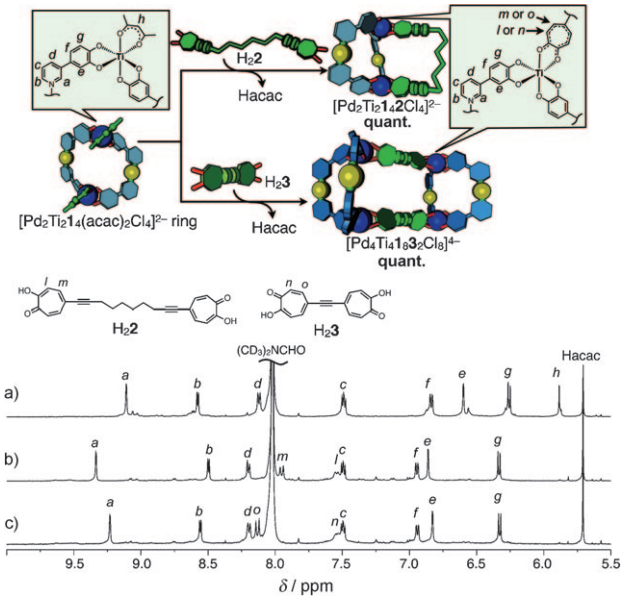


Figure 3. Partial ^{1}H NMR spectra (500 MHz, [D$_7$]DMF, 293 K, [H$_2$**1**] (12 mM)) of site-selective ligand exchange of acac with bridging bistropolone ligands on Pd^{II}–Ti^{IV} ring complexes: a) $[Pd_2Ti_2\mathbf{1}_4(acac)_2Cl_4]^{2-}$ ring, b) 1:1 mixture of the $[Pd_2Ti_2\mathbf{1}_4(acac)_2Cl_4]^{2-}$ ring and H$_2$**2** (20 h), and c) 1:1 mixture of $[Pd_2Ti_2\mathbf{1}_4(acac)_2Cl_4]^{2-}$ ring and H$_2$**3** (20 h).

complex were site-selectively substituted for the tropolone ligands of bridging ligand **2**. ESI-TOF mass spectra of the solution showed a signal at $m/z = 1529.1$, which could be assigned to a 1:1 $[Pd_2Ti_2\mathbf{1}_4\mathbf{2}Cl_3+2H]^+$ complex in which the two Ti^{IV} centers of the ring complex are intramolecularly connected by the structurally flexible ligand **2** (Figure S25 in the Supporting Information). On the other hand, a 1:1 mixture of H$_2$**3** and the $[Pd_2Ti_2\mathbf{1}_4(acac)_2Cl_4]^{2-}$ ring complex resulted in the formation of an intermolecularly connected complex. The ^{1}H NMR spectrum showed the quantitative formation of a single species in which a set of signals for tropolone, $H^{n,o}$, bound to Ti^{IV} was observed (Figure 3c). The ESI-TOF mass spectrum of the mixture showed a signal at $m/z = 2878.8$, which could be assigned to a 2:2 $[Pd_4Ti_4\mathbf{1}_8\mathbf{3}_2Cl_7+4H]^+$ complex, indicating the formation of an octanuclear $[Pd_4Ti_4\mathbf{1}_8\mathbf{3}_2Cl_8]^{4-}$ complex in which the two ring structures were intermolecularly connected by two bridging ligands **3** (Figure S26 in the Supporting Information). The size difference of these two complexes was also supported by diffusion-ordered NMR spectroscopy (DOSY) measurements of a 1:2 mixture of octanuclear $[Pd_4Ti_4\mathbf{1}_8\mathbf{3}_2Cl_8]^{4-}$ and tetranuclear $[Pd_2Ti_2\mathbf{1}_4\mathbf{2}Cl_4]^{2-}$ complexes in [D$_7$]DMF. The spectrum of $[Pd_4Ti_4\mathbf{1}_8\mathbf{3}_2Cl_8]^{4-}$ showed a set of signals with a log D value of -9.78, which is smaller than that of $[Pd_2Ti_2\mathbf{1}_4\mathbf{2}Cl_4]^{2-}$ (-9.63). This indicates that the intermolecularly assembled $[Pd_4Ti_4\mathbf{1}_8\mathbf{3}_2Cl_8]^{4-}$ complex is larger than the intramolecularly assembled $[Pd_2Ti_2\mathbf{1}_4\mathbf{2}Cl_4]^{2-}$ complex (Figure S27 in the Supporting Information) as expected from molecular-modeling studies. In addition, tetranuclear $[Pd_2Ti_2\mathbf{1}_4\mathbf{2}Cl_4]^{2-}$ and octanuclear $[Pd_4Ti_4\mathbf{1}_8\mathbf{3}_2Cl_8]^{4-}$ complexes have two and four possible isomers, respectively, arising from the configurational isomerism of the Ti^{IV} centers. However, both ^{1}H NMR spectra of these two higher-order structures in [D$_7$]DMF showed only one set of signals for the pyridyl catecholate and tropolonate ligands. This may suggest fast isomerization between multiple structures or an existence of only one isomer in each solution. From the molecular-modeling study, the structures shown in Scheme 1 were found to be the most plausible structure for each complex (for the molecular-modeling calculation, see Figure S31 and Table S1 in the Supporting Information).

One-pot syntheses of higher-order structures: As mentioned above, tetranuclear $[Pd_2Ti_2\mathbf{1}_4\mathbf{2}Cl_4]^{2-}$ and octanuclear $[Pd_4Ti_4\mathbf{1}_8\mathbf{3}_2Cl_8]^{4-}$ complexes can be quantitatively constructed through a preassembled $[Pd_2Ti_2\mathbf{1}_4(acac)_2Cl_4]^{2-}$ ring complex in a stepwise manner. To establish the efficacy of such a stepwise procedure, the one-pot syntheses were conducted in a way such that all components were mixed at once. Upon mixing H$_2$**1**, H$_2$**3**, $[TiO(acac)_2]$, $[PdCl_2(CH_3CN)_2]$, and *N*-methylmorpholine at the same time in [D$_7$]DMF, a precipitate was immediately formed. The ^{1}H NMR spectrum of the mixture showed broadened and complicated signals (Figure 4c). After 15 h, the spectrum showed two sets of signals that could be assigned to $[Pd(H_2\mathbf{1})_2Cl_2]$ and the desired

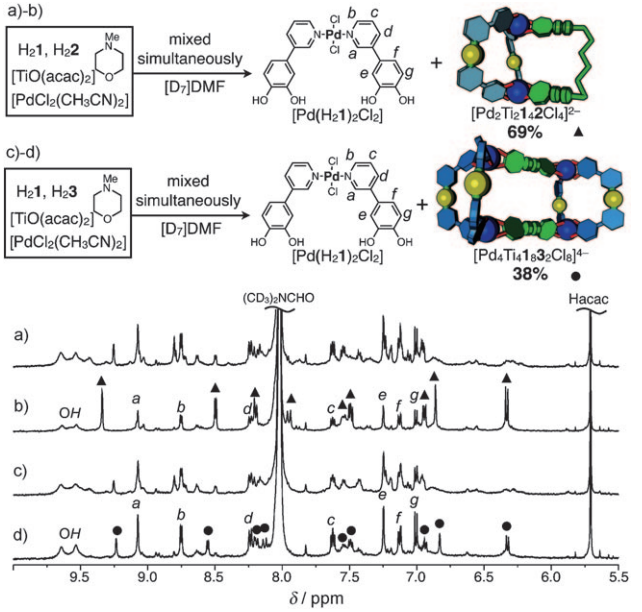


Figure 4. Partial ^{1}H NMR spectra (500 MHz, [D$_7$]DMF, 293 K, [H$_2$**1**] (12 mM)) of the one-pot syntheses of tetranuclear $[Pd_2Ti_2\mathbf{1}_4\mathbf{2}Cl_4]^{2-}$ and octanuclear $[Pd_4Ti_4\mathbf{1}_8\mathbf{3}_2Cl_8]^{4-}$complexes: a and b) 4:4:3:2:1 mixtures of H$_2$**1**, *N*-methylmorpholine, $[TiO(acac)_2]$, $[PdCl_2(CH_3CN)_2]$, and H$_2$**2** after 5 min (a) and 15 h (b; ▲ = the signals for $[Pd_2Ti_2\mathbf{1}_4\mathbf{2}Cl_4]^{2-}$); c and d) 4:4:3:2:1 mixtures of H$_2$**1**, *N*-methylmorpholine, $[TiO(acac)_2]$, $[PdCl_2(CH_3CN)_2]$, and H$_2$**3** after 5 min (c) and 15 h (d; ● = the signals for $[Pd_4Ti_4\mathbf{1}_8\mathbf{3}_2Cl_8]^{4-}$).

octanuclear $[Pd_4Ti_4\mathbf{1}_8\mathbf{3}_2Cl_8]^{4-}$ complexes, although the precipitate still remained (Figure 4d). The yield of the octanuclear complex was estimated to be 38% from the integral ratio of ^{1}H NMR spectrum. Moreover, the one-pot synthesis of the tetranuclear $[Pd_2Ti_2\mathbf{1}_4\mathbf{2}Cl_4]^{2-}$ complex resulted in only 69% yield of the desired complex (Figure 4a and b). Thus, the one-pot syntheses of the tetranuclear $[Pd_2Ti_2\mathbf{1}_4\mathbf{2}Cl_4]^{2-}$ and octanuclear $[Pd_4Ti_4\mathbf{1}_8\mathbf{3}_2Cl_8]^{4-}$ complexes were not quantitative under the given conditions.[11]

Because $[Pd(H_2\mathbf{1})_2Cl_2]$ was observed in the solution of the mixture in both cases, it is likely that the insoluble material contains Ti^{IV} and bridging ligand **2** or **3** at an early stage of the reaction process. In a model study, upon mixing $H_2\mathbf{3}$ and $[TiO(acac)_2]$ in the presence of *N*-methylmorpholine in $[D_7]$DMF, a precipitate was immediately formed and the signals of the aromatic region completely disappeared in the ^{1}H NMR spectrum (Figure 5b), implying that a polymeric

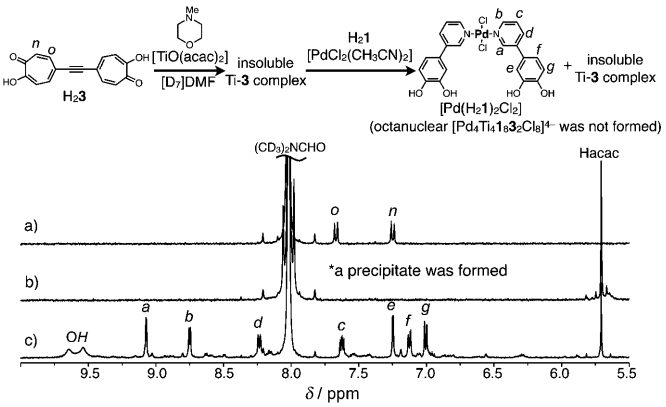


Figure 5. ^{1}H NMR spectra (500 MHz, $[D_7]$DMF, 293 K, $[H_2\mathbf{3}]$ (3.0 mM)) of a) $H_2\mathbf{3}$; b) 1:4:3 mixture of $H_2\mathbf{3}$, *N*-methylmorpholine, and $[TiO(acac)_2]$ (a precipitate appeared immediately after mixing); and c) after addition of $H_2\mathbf{1}$ and $[PdCl_2(CH_3CN)_2]$ to the solution from (b) (the spectrum of a 1:4:3:4:2 mixture of $H_2\mathbf{3}$, *N*-methylmorpholine, $[TiO(acac)_2]$, $H_2\mathbf{1}$, and $[PdCl_2(CH_3CN)_2]$ showed signals that could be assigned to $[Pd(H_2\mathbf{1})_2Cl_2]$).

insoluble material was formed. Even when $H_2\mathbf{1}$ and $[PdCl_2(CH_3CN)_2]$ were further added to the mixture, the ^{1}H NMR spectrum showed only one set of signals, which could be assigned to $[Pd(H_2\mathbf{1})_2Cl_2]$ (Figure 5c). These results indicate that once insoluble material arising from Ti^{IV} with **3** is formed, the formation of the octanuclear complex is partially inhibited, even in the presence of $H_2\mathbf{1}$ and $[PdCl_2(CH_3CN)_2]$.[12] To understand the ligand exchange processes on the Ti^{IV} centers further, a simple model synthesis was conducted by using $[Ti\mathbf{1}_2(trop)]^-$ in both a one-pot and a stepwise manner. When $H_2\mathbf{1}$, $[TiO(acac)_2]$, and Htrop were mixed at once in the presence of *N*-methylmorpholine, $[Ti\mathbf{1}_2(trop)]^-$ was formed relatively slowly, which was confirmed by time-course ^{1}H NMR analysis over five days (Figure S29 in the Supporting Information). In contrast, when Htrop was added to $[Ti\mathbf{1}_2(acac)]^-$, $[Ti\mathbf{1}_2(trop)]^-$ was formed within two hours (Figure S30 in the Supporting Information). From these results, in the case of the one-pot synthesis, the formation of $[Ti\mathbf{1}_2(trop)]^-$ was partially inhibited by some kinetically controlled products containing Ti^{IV} and trop. Overall, in all the one-pot syntheses, the formation of the desired product was inhibited to some extent owing to the formation of kinetically controlled insoluble products (Figure 6).[13] Thus, we demonstrated that the stepwise synthesis employed here is an efficient tool for constructing the higher-order tetranuclear $[Pd_2Ti_2\mathbf{1}_4\mathbf{2}Cl_4]^{2-}$ and octanuclear $[Pd_4Ti_4\mathbf{1}_8\mathbf{3}_2Cl_8]^{4-}$ complexes.

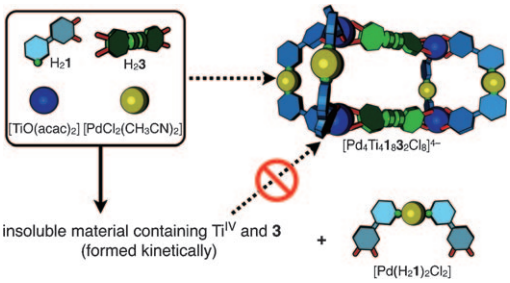


Figure 6. Schematic representation of the one-pot synthesis of the octanuclear $[Pd_4Ti_4\mathbf{1}_8\mathbf{3}_2Cl_8]^{4-}$ complex. A mixture of $H_2\mathbf{1}$, $H_2\mathbf{3}$, $[TiO(acac)_2]$, and $[PdCl_2(CH_3CN)_2]$ gave $[Pd(H_2\mathbf{1})_2Cl_2]$ and insoluble material containing Ti^{IV} and **3** as the kinetically controlled products in addition to $[Pd_4Ti_4\mathbf{1}_8\mathbf{3}_2Cl_8]^{4-}$.

Conclusion

In conclusion, we have developed Ti^{IV}-centered dynamic chemistry on heteroleptic $[Ti(cat)_2(acac)]^-$ and $[Ti\mathbf{1}_2(acac)]^-$ complexes that are stabilized by an acid–base balance. A series of $[Ti\mathbf{1}_2X]^-$ complexes were selectively formed by using other bidentate chelate ligands, HX, such as β-diketone derivatives, Hmal, and Htrop. Comparative studies of the thermodynamic stabilities among these $[Ti\mathbf{1}_2X]^-$ complexes revealed that $[Ti\mathbf{1}_2(trop)]^-$ is more stable than the $[Ti\mathbf{1}_2(acac)]^-$ complex. On the basis of these results, we demonstrated that the acac ligand can be site-selectively replaced by tropolonate on the $[Ti\mathbf{1}_2(acac)]^-$ complex. Because the binding of the pyridyl group of **1** to Pd^{II} takes place almost independently of the ligand exchange on the Ti^{IV} center, the $[Pd_2Ti_2\mathbf{1}_4(acac)_2Cl_4]^{2-}$ ring complex prepared from the $[Ti\mathbf{1}_2(acac)]^-$ complex provides a platform for stepwise construction of higher-order multicomponent Pd^{II}–Ti^{IV} complexes, tetranuclear $[Pd_2Ti_2\mathbf{1}_4\mathbf{2}Cl_4]^{2-}$ and octanuclear $[Pd_4Ti_4\mathbf{1}_8\mathbf{3}_2Cl_8]^{4-}$, by using bis-tropolone bridging ligands. Notably, the one-pot syntheses of these complexes were not highly efficient. Thus, the present stepwise synthesis through a heteroleptic metal complex has great potential for multicomponent self-assembly by site-selective ligand exchange. Higher-order multinuclear constructs formed as a result would provide excellent platforms for multipoint molecular recognition and multitopic catalysis.

Experimental Section

General: All ambient ^{1}H NMR spectra were recorded on a Bruker DRX 500 (500 MHz) by using TMS ($CDCl_3$), DMSO ([D_6]DMSO), and DMF ([D_7]DMF) as the internal references. ESI-TOF mass spectra were recorded on a Micromass LCT mass spectrometer KB 201.

General procedures for the syntheses of $[Ti\mathbf{1}_2X]^-$ complexes: *N*-Methylmorpholine (0.54 mg, 5.3 mmol, 1.0 equiv) and $Ti(OiPr)_4$ (1.2 μL, 4.0 mmol, 0.75 equiv) were added to a solution of $H_2\mathbf{1}$ (1.0 mg, 5.3 mmol) in [D_7]DMF (0.45 mL), and the reaction mixture was allowed to stand at room temperature for 12 h. A bidentate ligand HX (2.7 mmol, 0.50 equiv) was then added to the solution, which was allowed to stand for an additional 12 h. The respective ^{1}H NMR studies showed the selective formation of each $[Ti\mathbf{1}_2X]^-$ complex.

$[Ti\mathbf{1}_2(bzac)]^-$: ^{1}H NMR (500 MHz, [D_7]DMF, 293 K): $\delta=8.75$ (d, $J=1.8$ Hz, 2H), 8.39 (dd, $J=4.7$, 1.8 Hz, 2H), 8.09 (d, $J=7.4$ Hz, 2H), 7.88 (ddd, $J=7.9$, 1.8, 1.8 Hz, 2H), 7.57 (t, $J=7.4$ Hz, 1H), 7.49 (dd, $J=7.4$, 7.4 Hz, 2H), 7.33 (dd, $J=7.9$, 4.7 Hz, 2H), 6.79 (dd, $J=8.0$, 2.1 Hz, 2H), 6.71 (s, 1H), 6.52 (d, $J=2.1$ Hz, 2H), 6.24 (d, $J=8.0$ Hz, 2H), 2.25 ppm (s, 3H); ESI-TOF (DMF): *m/z*: 579.0 $[Ti\mathbf{1}_2(bzac)]^-$, 581.4 $[Ti\mathbf{1}_2(bzac)+2H]^+$, 1161.3 $[\{Ti\mathbf{1}_2(bzac)\}_2+3H]^+$.

$[Ti\mathbf{1}_2(bzbz)]^-$: ^{1}H NMR (500 MHz, [D_7]DMF, 293 K): $\delta=8.75$ (d, $J=1.8$ Hz, 2H), 8.38 (dd, $J=4.7$, 1.8 Hz, 2H), 8.30 (d, $J=7.4$ H, 4H), 7.88 (ddd, $J=7.9$, 1.8, 1.8 Hz, 2H), 7.61 (t, $J=7.4$ Hz, 2H), 7.53 (dd, $J=7.4$, 7.4 Hz, 4H), 7.49 (s, 1H), 7.32 (dd, $J=7.9$, 4.7 Hz, 2H), 6.79 (dd, $J=8.0$, 2.2 Hz, 2H), 6.54 (d, $J=2.2$ Hz, 2H), 6.26 ppm (d, $J=8.0$ Hz, 2H); ESI-TOF (DMF): *m/z*: 641.1 $[Ti\mathbf{1}_2(bzbz)]^-$, 643.2 $[Ti\mathbf{1}_2(bzbz)+2H]^+$, 1285.3 $[\{Ti\mathbf{1}_2(bzbz)\}_2+3H]^+$.

$[Ti\mathbf{1}_2\mathbf{4}]^-$: ^{1}H NMR (500 MHz, [$D_7$]DMF, 293 K): $\delta=8.77$ (d, $J=1.8$ Hz, 2H), 8.39 (dd, $J=4.7$, 1.8 Hz, 2H), 7.89 (ddd, $J=7.9$, 1.8, 1.8 Hz, 2H), 7.45 (t, $J=7.5$ Hz, 2H), 7.39–7.29 (m, 5H), 6.80 (dd, $J=8.0$, 2.1 Hz, 2H), 6.53 (d, $J=2.1$ Hz, 2H), 6.26 (d, $J=8.0$ Hz, 2H), 1.88 ppm (s, 6H); ESI-TOF (DMF): *m/z*: 593.1 $[Ti\mathbf{1}_2\mathbf{4}]^-$, 595.2 $[Ti\mathbf{1}_2\mathbf{4}+2H]^+$, 1189.3 $[(Ti\mathbf{1}_2\mathbf{4})_2+3H]^+$.

$[Ti\mathbf{1}_2\mathbf{5}]^-$: ^{1}H NMR (500 MHz, [$D_7$]DMF, 293 K): $\delta=8.76$ (d, $J=1.7$ Hz, 2H), 8.38 (dd, $J=4.5$, 1.7 Hz, 2H), 7.89 (ddd, $J=8.0$, 1.7, 1.7 Hz, 2H), 7.48–7.32 (m, 12H), 6.80 (dd, $J=8.0$, 2.1 Hz, 2H), 6.57 (d, $J=2.1$ Hz, 2H), 6.30 ppm (d, $J=8.0$ Hz, 2H); ESI-TOF (DMF): *m/z*: 630.1 $[Ti\mathbf{1}_2\mathbf{5}]^-$, 632.2 $[Ti\mathbf{1}_2\mathbf{5}+2H]^+$, 1263.3 $[(Ti\mathbf{1}_2\mathbf{5})_2+3H]^+$.

$[Ti\mathbf{1}_2(q)]^-$: ^{1}H NMR (500 MHz, [D_7]DMF, 293 K): $\delta=9.01$ (dd, $J=4.7$, 1.0 Hz, 1H), 8.75 (d, $J=1.7$ Hz, 2H), 8.53 (dd, $J=8.3$, 1.0 Hz, 1H), 8.38 (dd, $J=4.7$, 1.7 Hz, 2H), 7.87 (ddd, $J=7.9$, 1.7, 1.7 Hz, 2H), 7.71 (dd, $J=8.3$, 4.7 Hz, 1H), 7.50 (dd, $J=8.0$, 8.0 Hz, 1H), 7.32 (dd, $J=7.9$, 4.7 Hz, 2H), 7.28 (d, $J=8.0$ Hz, 1H), 6.81–6.79 (m, 3H), 6.57 (br, 2H), 6.29 ppm (d, $J=7.9$ Hz, 2H); ESI-TOF (DMF): *m/z*: 561.9 $[Ti\mathbf{1}_2(q)]^-$, 564.0 $[Ti\mathbf{1}_2(q)+2H]^+$, 1125.0 $[\{Ti\mathbf{1}_2(q)\}_2+H]^-$, 1127.1 $[\{Ti\mathbf{1}_2(q)\}_2+3H]^+$.

$[Ti\mathbf{1}_2(mal)]^-$: ^{1}H NMR (500 MHz, [D_7]DMF, 293 K): $\delta=8.75$ (d, $J=1.8$ Hz, 2H), 8.44 (d, $J=5.1$ Hz, 1H), 8.38 (dd, $J=4.7$, 1.8 Hz, 2H), 7.88 (ddd, $J=7.9$, 1.8, 1.8 Hz, 2H), 7.32 (dd, $J=7.9$, 4.7 Hz, 2H), 6.78 (d, $J=5.1$ Hz, 1H), 6.78 (dd, $J=8.0$, 2.1 Hz, 2H), 6.52 (d, $J=2.1$ Hz, 2H), 6.25 (d, $J=8.0$ Hz, 2H), 2.38 ppm (s, 3H); ESI-TOF (DMF): *m/z*: 543.0 $[Ti\mathbf{1}_2(mal)]^-$, 545.0 $[Ti\mathbf{1}_2(mal)+2H]^+$, 1089.0 $[\{Ti\mathbf{1}_2(mal)\}_2+3H]^+$.

$[Ti\mathbf{1}_2(trop)]^-$: ^{1}H NMR (500 MHz, [D_7]DMF, 293 K): $\delta=8.76$ (d, $J=1.8$ Hz, 2H), 8.39 (dd, $J=4.7$, 1.8 Hz, 2H), 7.89 (ddd, $J=7.9$, 1.8, 1.8 Hz, 2H), 7.83 (dd, $J=10.4$, 10.4 Hz, 2H), 7.40 (d, $J=10.4$ Hz, 2H), 7.36 (t, $J=10.4$ Hz, 1H), 7.33 (dd, $J=7.9$, 4.7 Hz, 2H), 6.80 (dd, $J=8.0$, 2.1 Hz, 2H), 6.55 (d, $J=2.1$ Hz, 2H), 6.27 ppm (d, $J=8.0$ Hz, 2H); ESI-TOF (DMF): *m/z*: 539.0 $[Ti\mathbf{1}_2(trop)]^-$, 541.0 $[Ti\mathbf{1}_2(trop)+2H]^+$, 1081.3 $[\{Ti\mathbf{1}_2(trop)\}_2+3H]^+$.

General procedure for the competitive experiments: *N*-Methylmorpholine (0.54 mg, 5.3 mmol, 1.0 equiv), and $Ti(OiPr)_4$ (1.2 mL, 4.0 mmol, 0.75 equiv) were added to a solution of $H_2\mathbf{1}$ (1.0 mg, 5.3 mmol) in [D_7]DMF (0.45 mL), and the reaction mixture was allowed to stand at room temperature for 12 h. Then, HA (2.7 mmol, 0.50 equiv) and HB (2.7 mmol, 0.50 equiv) were added to the solution, and the reaction mixture was allowed to stand for additional 12 h. The formation ratio of $[Ti\mathbf{1}A]^-/[Ti\mathbf{1}_2B]^-$ was determined by the integral ratio of ^{1}H NMR signals.

Ligand exchange of acac by trop in various Ti^{IV} complexes: Tropolone (0.33 mg, 2.7 μmol, 1.0 equiv based on acac) was added to a solution of each Ti^{IV} complex (2.7 μmol for $[Ti\mathbf{1}_2(acac)]$ and $[Ti\{Pd(dien)\mathbf{1}\}_2(acac)]^{3+}$ (dien = diethylenetriamine), and 1.3 μmol for the $[Pd_2Ti_2\mathbf{1}_4(acac)_2Cl_4]^{2-}$ ring complex; all of the Ti^{IV} complexes were prepared from $H_2\mathbf{1}$ (1.0 mg, 5.3 μmol)) in [D_7]DMF (0.45 mL), and the reaction mixture was then allowed to stand for 2–20 h at room temperature. ^{1}H NMR titration studies demonstrated highly selective ligand exchange reactions of acac with trop in Ti^{IV} complexes as shown in Figure 2.

$[Ti\{Pd(dien)\mathbf{1}\}_2(trop)]^{3+}$ ring: ^{1}H NMR (500 MHz, [D_7]DMF, 293 K): $\delta=8.91$ (s, 2H), 8.57 (d, $J=5.5$ Hz, 2H), 8.24 (d, $J=8.0$ Hz, 2H), 7.92 (dd, $J=8.1$, 8.1 Hz, 2H), 7.61 (dd, $J=8.0$, 5.5 Hz, 2H), 7.56–7.51 (m, 2H), 7.51–7.45 (m, 3H), 6.92 (dd, $J=8.1$, 2.0 Hz, 2H), 6.60 (d, $J=2.0$ Hz, 2H), 6.32 (d, $J=8.1$ Hz, 2H), 5.91–5.86 (m, 4H), 5.63–5.60 (m, 4H), 3.36–3.28 (m, 2H), 3.24–3.20 ppm (m, 4H; one signal that could be assigned to the methylene protons was behind the water peak); ESI-TOF (positive, DMF): *m/z*: 854.1 $[M-2H-dien]^+$, 957.3 $[M-2H]^+$, 1020.3 $[M-H+NO_3]^+$ ($M=[Ti\{Pd(dien)\mathbf{1}\}_2(trop)]^{3+}$).

$[Pd_2Ti_2\mathbf{1}_4(trop)_2Cl_4]^{2-}$ ring: ^{1}H NMR (500 MHz, [D_7]DMF, 293 K): $\delta=9.14$ (s, 4H), 8.58 (d, $J=5.4$ Hz, 4H), 8.14 (d, $J=8.0$ Hz, 4H), 7.87 (dd, $J=10.3$, 10.3 Hz, 4H), 7.50 (dd, $J=8.0$, 5.4 Hz, 4H), 7.47 (d, $J=10.3$ Hz, 4H), 7.40 (t, $J=10.3$ Hz, 2H), 6.87 (dd, $J=8.1$, 2.0 Hz, 4H), 6.68 (br, 4H), 6.30 ppm (d, $J=8.1$ Hz, 4H); ESI-TOF (positive, DMF): *m/z*: 1399.1 $[Pd_2Ti_2\mathbf{1}_4(trop)_2Cl_3+2H]^+$.

Stepwise construction of tetranuclear $[Pd_2Ti_2\mathbf{1}_4\mathbf{2}Cl_4]^{2-}$: Ligand $H_2\mathbf{2}$ (0.50 mg, 1.3 μmol, 1.0 equiv) was added to a solution of the $[Pd_2Ti_2\mathbf{1}_4(acac)_2Cl_4]^{2-}$ ring complex (1.3 μmol, prepared from 1.0 mg of $H_2\mathbf{1}$) in [D_7]DMF (0.45 mL), and the reaction mixture was then allowed to stand for 12 h at room temperature. The ^{1}H NMR spectrum showed the quantitative formation of the $[Pd_2Ti_2\mathbf{1}_4\mathbf{2}Cl_4]^{2-}$ complex as shown in Figure 3b.

$[Pd_2Ti_2\mathbf{1}_4\mathbf{2}Cl_4]^{2-}$: ^{1}H NMR (500 MHz, [$D_7$]DMF, 293 K): $\delta=9.33$ (s, 4H), 8.50 (d, $J=5.4$ Hz, 4H), 8.20 (d, $J=8.1$ Hz, 4H), 7.95 (d, $J=10.9$ Hz, 4H), 7.54 (d, $J=10.9$ Hz, 4H), 7.49 (dd, $J=8.1$, 5.4 Hz, 4H), 6.95 (dd, $J=8.1$, 2.1 Hz, 4H), 6.86 (d, $J=2.1$ Hz, 4H), 6.33 (d, $J=8.1$ Hz, 4H), 2.51 (t, $J=6.0$ Hz, 4H), 1.67–1.63 (m, 4H), 1.61–1.57 ppm (m, 4H); ^{13}C NMR (125 MHz, [D_7]DMF, 293 K): $\delta=181.11$, 172.62, 162.06, 151.54, 149.97, 139.10, 135.69, 125.98, 125.65, 125.35, 118.29, 118.19, 111.96, 109.19, 94.54, 83.86, 28.80, 28.53, 19.39 ppm; ESI-TOF (positive, DMF): *m/z*: 1529.1 $[Pd_2Ti_2\mathbf{1}_4\mathbf{3}Cl_3+2H]^+$.

Stepwise construction of octanuclear $[Pd_4Ti_4\mathbf{1}_8\mathbf{3}_2Cl_8]^{4-}$: Ligand $H_2\mathbf{3}$ (0.36 mg, 1.3 μmol, 1.0 equiv) was added to a solution of the $[Pd_2Ti_2\mathbf{1}_4(acac)_2Cl_4]^{2-}$ ring complex (1.3 μmol, prepared from 1.0 mg of $H_2\mathbf{1}$) in [D_7]DMF (0.45 mL), and the reaction mixture was then allowed to stand for 12 h at room temperature. The ^{1}H NMR spectrum showed the quantitative formation of $[Pd_4Ti_4\mathbf{1}_8\mathbf{3}_2Cl_8]^{4-}$ as shown in Figure 3c.

$[Pd_4Ti_4\mathbf{1}_8\mathbf{3}_2Cl_8]^{4-}$: ^{1}H NMR (500 MHz, [$D_7$]DMF, 293 K): $\delta=9.23$ (s, 8H), 8.56 (d, $J=5.5$ Hz, 8H), 8.19 (d, $J=8.1$ Hz, 8H), 8.13 (d, $J=12.0$ Hz, 8H), 7.54 (br, 8H), 7.49 (dd, $J=8.1$, 5.5 Hz, 8H), 6.94 (dd, $J=8.1$, 2.0 Hz, 8H), 6.83 (d, $J=2.0$ Hz, 8H), 6.33 ppm (d, $J=8.1$ Hz, 8H); ^{13}C NMR (125 MHz, [D_7]DMF, 293 K): $\delta=181.49$, 172.59, 161.92, 151.17, 150.19, 143.81, 139.22, 136.02, 125.64, 125.50, 118.43, 118.29, 112.07, 109.05, 94.72 ppm; ESI-TOF (positive, DMF): *m/z*: 2878.8 $[Pd_4Ti_4\mathbf{1}_8\mathbf{3}_2Cl_7+4H]^+$.

One-pot synthesis of tetranuclear $[Pd_2Ti_2\mathbf{1}_4\mathbf{2}Cl_4]^{2-}$: *N*-Methylmorpholine (0.54 mg, 5.3 μmol, 1.0 equiv), $[TiO(acac)_2]$ (1.1 mg, 4.0 μmol, 0.75 equiv), and $[PdCl_2(CH_3CN)_2]$ (0.69 mg, 2.7 μmol, 0.50 equiv) were added to a solution of a mixture of $H_2\mathbf{1}$ (1.0 mg, 5.3 μmol) and $H_2\mathbf{2}$ (0.50 mg, 1.3 μmol, 0.25 equiv) in [D_7]DMF (0.45 mL), and the reaction mixture was then allowed to stand for 15 h at room temperature. A precipitate was generated and the ^{1}H NMR spectrum of the resulting suspension showed the formation of $[Pd_2Ti_2\mathbf{1}_4\mathbf{2}Cl_4]^{2-}$ (69% yield) and $[Pd(H_2\mathbf{1})_2Cl_2]$ complexes as shown in Figure 4b.

One-pot synthesis of octanuclear $[Pd_4Ti_4\mathbf{1}_8\mathbf{3}_2Cl_8]^{4-}$: *N*-Methylmorpholine (0.54 mg, 5.3 μmol, 1.0 equiv), $[TiO(acac)_2]$ (1.1 mg, 4.0 μmol, 0.75 equiv), and $[PdCl_2(CH_3CN)_2]$ (0.69 mg, 2.7 μmol, 0.50 equiv) were added to a solution of a mixture of $H_2\mathbf{1}$ (1.0 mg, 5.3 μmol) and $H_2\mathbf{3}$ (0.36 mg, 1.3 μmol,

0.25 equiv) in [D_7]DMF (0.45 mL), and the reaction mixture was then allowed to stand for 15 h at room temperature. A precipitate was formed and the ^{1}H NMR spectrum of the resulting suspension showed the formation of octanuclear $[Pd_4Ti_4\mathbf{1}_8\mathbf{3}_2Cl_8]^{4-}$ (38% yield) and $[Pd(H_2\mathbf{1})_2Cl_2]$ as shown in Figure 4d.

Complexation studies of bridging ligands with [TiO(acac)$_2$]: *N*-Methylmorpholine (0.54 mg, 5.3 μmol, 4.0 equiv), and $[TiO(acac)_2]$ (1.1 mg, 4.0 μmol, 3.0 equiv) were added to a solution of bridging ligand (1.3 μmol; 0.50 mg for $H_2\mathbf{2}$, 0.36 mg for $H_2\mathbf{3}$) in [D_7]DMF (0.45 mL). A precipitate was immediately formed after mixing, and no signals were observed in the aromatic regions of the ^{1}H NMR spectra as shown in Figure S28 in the Supporting Information and Figure 5 for $H_2\mathbf{2}$ and $H_2\mathbf{3}$, respectively. Ligand $H_2\mathbf{1}$ (1.0 mg, 5.3 μmol, 4.0 equiv) and $[PdCl_2(CH_3CN)_2]$ (0.69 mg, 2.7 μmol, 2.0 equiv) were also added to the suspension, and the reaction mixture was then allowed to stand for 21 h at room temperature. These ^{1}H NMR spectra showed the formation of $[Pd(H_2\mathbf{1})_2Cl_2]$ in solution although the precipitate still remained.

Acknowledgements

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[9] The selective formation of $[Ti\{Pd(dien)\mathbf{1}_2\}(acac)]^{3+}$ complex was confirmed by the ^{1}H NMR titration study and ESI-TOF mass spectrometry (for further details, see Figures S21 and 22 in the Supporting Information).

[10] For the syntheses, see the Supporting Information.

[11] These higher-order structures were neither quantitatively formed, even after one month, nor accelerated at elevated temperatures.

[12] Complexation of $H_2\mathbf{2}$ and $[TiO(acac)_2]$ in the presence of *N*-methylmorpholine produced a similar result (see Figure S28 in the Supporting Information).

[13] Elemental analysis of the insoluble material from a mixture of $H_2\mathbf{3}$, $[TiO(acac)_2]$, and *N*-methylmorpholine revealed that the material contains a nonstoichiometric mixture of Ti^{IV}-bound tropolonate and TiO_2 arising from hydrolysis of the Ti^{IV} species.

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