A major bottleneck of computational chemistry in heterogeneous catalysis is found at the difficulty and resultant inaccuracy of molecular models for catalyst surfaces. Here, we review our recent efforts to establish a high-precision molecular model of heterogeneous Ziegler-Natta catalysts for olefin polymerization, which was mainly based on the validation of potential molecular models for a set of experimentally known facts in density functional calculations. The coadsorption of donor molecules with Ti mononuclear species on MgCl₂ surfaces is proposed as an experimentally consistent molecular model, and its successful utilization in a structure-performance relationship study for donors is described.

**Keywords**
Ziegler-Natta catalyst, Propylene polymerization, Density functional calculation, Donor, Structure-performance relationship

1. Introduction

Continuous advances in computational chemistry, parallel computing, and computational resources have enabled more realistic simulation on various materials. It is no longer exaggeration to say that computational chemistry has become a sort of characterization tools for understanding functions of materials at a molecular and electronic precision. Even personal computers allow researchers to access such microscopic information, while large-scale facilities or instruments are essential to experimentally obtain similar information. In this light, computational chemistry offers an opportunity to greatly omit efforts and resources that are required for materials researches. Here, one needs to recognize that computational chemistry tries to approximate a complicated physicochemical system based on a simplified model and that the Shrödinger equation of a multi-body system is not practically solvable without some approximations. Hence, the accuracy of simulation in computational chemistry is fully dependent on the accuracy of the approximations for the molecular model and numerical method that are employed in the simulation. The accuracy shall be determined based on a system or phenomenon of one’s interest within the feasibility of computational resources. For the numerical method, the density functional method is the absolute mainstream in recent years, and the choice of exchange-correlation functionals is greatly aided by historical accumulation of benchmark calculations in literature. On the other hand, the accuracy of a molecular model is not something to be improved in a systematic manner for heterogeneous systems like solid catalysts. This is partly because molecular information that is directly relevant to catalysis is hardly accessed for solid surfaces. The discrepancy of surface states under analytical and operando environment is another reason of the difficulty. Thus, the major bottleneck to employ computational chemistry in heterogeneous catalysis often lies in the accuracy of molecular models that must be determined in the absence of direct experimental clues.

The Ziegler-Natta catalysts are solid catalysts for olefin polymerization, which were originated from the inventions by Karl Ziegler and Giulio Natta\(^1\). They have played the most important role for polyolefin to establish its current status that covers over half of the plastic industry. Specifically for propylene polymerization, the first generation catalyst is TiCl₃, a violet solid, activated with diethylaluminum chloride (DEAC). Attempts to improve the catalyst activity per Ti led to the invention of MgCl₂-supported TiCl₄ catalysts in combination with triethylaluminum (TEA), which were highly active for ethylene polymerization, but not sufficiently stereospecific for propylene polymerization. The prototype of the current Ziegler-Natta catalysts was discovered by cooperation of Montedison and Mitsu: The incorporation and addition of ethylbenzoate (or its derivatives) successfully improved the stereospecificity of the catalyst\(^2\). Since then and to date, the develop-
ment of the Ziegler-Natta catalysts has been mainly driven by the finding of new organic Lewis bases, termed as internal or external donors, depending on whether they are internally incorporated to a solid catalyst or externally added together with an alkylaluminum activator. Representative internal/external donors are phthalate/alkoxysilane for the fourth generation, 1,3-diether/(alkoxysilanes) for the fifth generation, and succinate/alkoxysilane for the sixth generation. It is nowadays well recognized that donors not only improve the stereospecificity of Ti active species supported on MgCl₂, but also affect many other catalytic properties including the activity, the molecular weight or chemical composition distribution of polymer, and hydrogen response. No doubt, the unseen seventh generation will arise from the finding of new donors, that is why a majority of catalyst developers have devoted great efforts to this purpose, and at the same time, met difficulties therein. A major bottleneck in the development of new donors is its heavily demanding aspect in terms of manpower and time. A potential donor can be assessed only through the evaluation of the polymerization performance of a catalyst, where organic synthesis for a desired molecular structure and catalyst preparation using the synthesized donor need to be established prior to the assessment. This demanding cycle needs to be repeated for each molecular structure until a promising donor is identified after dozens of try and error. Under these circumstances, screening of donors based on computational chemistry has been strongly desired, but it has not been realized due to the lack of an “accurate” molecular model of the solid surfaces.

Isoselective polymerization of prochiral propylene is mediated via a site-control mechanism, in which the conformational orientation of an incoming monomer and a growing chain is sterically controlled by the symmetry of active sites. This fact dictates that the production of highly isotactic polymer requires the presence of highly isospecific active sites on solid surfaces and that the stereostructure of the polymer is regarded as a sort of a fingerprint of active sites. While a dramatic increment in the stereospecificity of a catalyst by the addition of donors was known in 1970’s, its mechanism, i.e. how the addition of donors creates highly isospecific active sites, had not been clarified until recent years. Historically saying, the first proposal on the mechanism of the stereospecificity improvement by donors was made by Corradini et al. Their proposal was based on an analogy with TiCl₄ crystals of earlier generation, that is, TiCl₄ adsorbs on lateral surfaces of MgCl₂ in an epitactic manner, leading to the creation of intrinsically aspecific TiCl₄ mononuclear species on (110) surfaces and intrinsically isospecific dinuclear species on (100) surfaces (Figs. 1a and 1b). Donors would selectively adsorb on the (110) surfaces due to stronger Lewis acidity, thus blocking the formation of the aspecific mononuclear species. The next hypothesis appeared as a result of experimental updates in 1990’s: A fingerprint of isospecific active sites was found to be sensitive to the molecular structure of a donor added. Hence, the first hypothesis that the same dinuclear species would be formed irrespective of the molecular structure of donors was not anymore reasonable, and researchers nowadays agree with a mechanism that donor molecules coadsorb with TiCl₄ on MgCl₂ surfaces, and this interaction leads to the formation of donor-specific isospecific active sites. An alternative hypothesis was proposed by Busico and his coworkers, in which ligands (L₁,2) at the neighboring cationic sites sterically induce the isospecificity of the Ti center (Fig. 2). This so-called three-site model is the most widely accepted hypothesis for the active sites of MgCl₂-supported Ziegler-Natta catalysts, while the model is yet too general to describe detailed questions like what kinds of interaction donors exert, which surfaces are suitable for creating isospecific active sites, how the coadsorption can explain other effects of donors, and so on.

In this article, our recent efforts are reviewed for establishing an accurate molecular model of Ziegler-Natta catalyst surfaces that can properly reproduce effects of donors on catalysis. The research strategy employed was based on density functional theory (DFT) calculations that were comprehensively validated with experimental facts on donors. We also demonstrate an application of the molecular model in computational screening of donors.
2. Methods

2.1. Numerical

All the density functional calculations assumed the exchange-correlation functional of Perdew-Burke-Emzerhof (PBE) and implemented by DMol3\(^{18,19}\). A double numerical polarized (DNP) basis set was employed together with effective core potentials for core description\(^{19,21}\). Further details are described elsewhere\(^{12-16}\).

As in previous studies, the most stable \(\alpha\)-form was assumed for the \(\text{MgCl}_2\) bulk, and its (110) and (100) lateral surfaces were employed as catalytically representative cuts. These surfaces were expressed by the slab model with 1.5 nm of a vacuum layer. Both the thickness of the unit cells and the density of the k-points were determined in terms of the converged adsorption energies of \(\text{TiCl}_4\) and \(\text{TiCl}_3\) mononuclear species on the \(\text{MgCl}_2\) surfaces\(^{16}\). Also, the widths of the unit cells were decided not to have direct steric interactions between adsorbates in neighboring cells. The \(\text{MgCl}_2\) slabs were fully relaxed except the bottom two atomic layers that were fixed in their bulk positions during geometry optimization and transition state search. An adsorption energy (\(\Delta E_{\text{ad}}\)) was obtained by subtracting the sum of the energies of a bare surface and a free molecule of an adsorbate from the energy of a geometry-optimized surface with an adsorbate. The charge transfer upon the adsorption was evaluated using the Hirshfeld population analysis\(^{22}\).

A catalytic scheme for propylene polymerization is summarized in Fig. 3. \(\text{TiCl}_4\) as a precursor is alkylated and reduced with alkylaluminum in a stepwise manner, and the active state is regarded as \(\text{Ti}^{1+}\) rather than coordinatively saturated \(\text{Ti}^{3+}\) or inactive \(\text{Ti}^{2+}\) species\(^{16}\). The resting state of the polymerization is \(\text{TiCl}_2\text{R}\), where \(\text{R}\) expresses the growing polymer and can be approximated by an \(i\)-butyl group\(^{23}\). A propylene monomer coordinates to the vacancy of the resting state and forms a \(\pi\)-complex. An insertion happens through a transition state of a four-membered metallacycle, returning to the resting state. The repetition of the cycle elongates the length of the growing chain, while competition of chain transfer reactions with the insertion regulates the molecular weight of the final polymer. We assumed a chain transfer to propylene monomer as one of the most important pathways, in which \(H_2\) of the growing chain is transferred to incoming monomer, leaving a renewed
resting state of TiCl₂(n-propyl) and vinylidene-terminated polypropylene. In the case of propylene insertion, there are four potential pathways: 1,2- and 2,1-insertion with re and si faces. An ideal active site selectively catalyzes 1,2-insertion with one side of the enantiofaces, while occasional stereo- or regio-misinsertion as well as chain transfer reactions are minimized. Based on the Eyring theory under the assumption of a negligible coverage, the apparent activation energy of a reaction was obtained as a differential energy between the energy of a transition state and that of a resting state\(^{24}\). A transition state was obtained by manually scanning a reaction coordinate, followed by transition state optimization for the imaginary frequency\(^{16}\). After calculating the apparent activation energies for all the potential elemental reactions, the performance of an active site in propylene polymerization was evaluated based on the following measures,

\[
\Delta \Delta E_{\text{stereo}} = |\Delta E_{1,2,\text{re}} - \Delta E_{1,2,\text{si}}| 
\]

\[
\Delta \Delta E_{\text{regio}} = \min(\Delta E_{1,2}) - \min(\Delta E_{2,1}) 
\]

\[
\Delta \Delta E_{\text{CT}} = \min(\Delta E_{1,2}) - \Delta E_{\text{CT}} 
\]

where \(\Delta E_{1,2,\text{re}}\) represents the apparent activation energy for the 1,2-insertion with the re face, \(\min(\Delta E_{2,1})\) is the smaller apparent activation energy for the 2,1-insertion with different enantiomeric faces, \(\Delta E_{\text{CT}}\) is the apparent activation energy for the chain transfer to propylene, and etc. \(\Delta \Delta E_{\text{stereo}}, \Delta \Delta E_{\text{regio}},\) and \(\Delta \Delta E_{\text{CT}}\) measure the stereospecificity, the regiospecificity, and the propensity for chain elongation of an active site, respectively. These measures were utilized in order to validate a molecular model in reproducing experimentally known effects of donors.

2.2. Experimental

In order to utilize the established molecular model for a structure-performance study on donors, a set of experiments were performed using alkoxysilane as external donors. For the simplicity, an internal-donor-free catalyst was prepared by a co-grinding method, in which MgCl₂ powder was mechanically ground with TiCl₄ and subsequently treated with TiCl₄ at an elevated temperature. A series of alkoxysilane compounds, that are, dialkyl dimethoxysilane and alkyl triethoxysilane with different alkyl substituents, were utilized after vacuum distillation (Fig. 4). Stopped-flow-type polymerization was selected, as short-time polymerization can minimize the transient nature of active sites\(^{25,26}\). The polymerization was performed for 0.4 s at 303 K under 1 atm of propylene using dry n-heptane as a solvent and tri-i-butyl aluminum (TiBA) as an activator. For each of the polymerization, an alkoxysilane compound at the Al/Si molar ratio of 6 was added as an external donor. The obtained polypropylene was purified by reprecipitation and weighted to evaluate the activity, while the weight fraction of an insoluble content in o-dichlorobenzene was used as a measure of the stereoregularity of the polymer. Further details are described in our recent paper\(^{17}\).
3. Results and Discussion

3.1. Plausible Surface Structures

Figures 1a)-1c) represents potential structures of TiCl₄ adsorbed on MgCl₂ (110) and (100) surfaces. Their adsorption energies and the charge of a TiCl₄ molecule upon the adsorption are summarized in Table 1. It was found that the TiCl₄ mononuclear species on (110) was absolutely more stable than the other two species on (100). Its adsorption enthalpy, $\Delta H_{ads} = -19.8 \text{ kcal/mol}$, overcomes the entropic loss of ca. $+14 \text{ kcal/mol}$ at 350 K, while the adsorption on (100) was suggested not to be spontaneous. Moreover, the adsorption increased the electron density of TiCl₄ only on the (110) surface. This electron enrichment of TiCl₄ was indeed observed by X-ray photoelectron spectroscopy, and believed as a major reason of a high activity of MgCl₂-supported TiCl₄ toward olefin polymerization.²⁷) Hence, it was considered the TiCl₄ mononuclear species on (110) is not only energetically plausible but also consistent with an experimentally known fact. This conclusion is somewhat surprising that the DFT calculation opposes with the Corradini model, which had been believed for 20 years.

Next, the coadsorption of ethylbenzoate (EB) with TiCl₄ was examined on the (110) surface, as EB adsorbs similarly strongly on the (110) and (100) surfaces. Figure 5 displays typical coadsorption states and Table 2 summarizes the coadsorption energy of EB with TiCl₄ at each state. As can be seen, the formation of a TiCl₄·EB complex was far inferior to the other states. This is consistent with the absence of the complex in the IR spectra of catalysts.²⁸) As long as EB adsorbs on the MgCl₂ surface, the energy required for the coadsorption was small enough compared with the magnitudes of the adsorption energy (i.e. the coadsorption energies were not greatly different from that of the adsorption in the absence of TiCl₄). It means that the coadsorption of EB does not possess any positional preference, so that the occurrence of the coadsorption simply depends on the surface coverage. Considering an experimental fact that a higher donor/TiCl₄ molar ratio leads to a higher catalyst stereospecificity, it is logical that the coadsorption at the nearest position is the most preferable. This idea also suffices the three-site model in a sense that an EB molecule occupies the L₉₂ position. Moreover, the coadsorption of EB on the (110) surface further enriched the electron density of TiCl₄, because the adsorption of EB as a Lewis base reinforces the electron donation ability of MgCl₂. This fact is consistent with an experimental observation, and a similar phenomenon never happened for the coadsorption on (100).¹⁴),¹⁵),²⁹)

As described above, TiCl₄ mononuclear species and its coadsorption with a donor molecule on the (110) surface were considered to be plausible in terms of

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Table 1 Adsorption Energy and Charge Density of TiCl₄ on MgCl₂ Surfaces

| Species            | Adsorption energy [kcal/mol] | Charge density of TiCl₄ [e]| |
|--------------------|-----------------------------|----------------------------|
| Mononuclear species on (110) | $-19.8$                      | $-0.122$                   |
| Mononuclear species on (100) | $-13.0$                      | $+0.085$                   |
| Dinuclear species on (100) | $-11.1$                      | $+0.018$                   |

a) Defined as $(E(TiCl₄/MgCl₂) - E(MgCl₂) - E(TiCl₄))/n$. Stronger adsorption accompanies a negatively large value.
b) Based on a Hirshfeld analysis.²²) A negative sign indicates electron transfer from MgCl₂ to enrich the electron density of TiCl₄.

c) The coadsorption states are shown in Fig. 4.
d) The energy for EB to coadsorb with TiCl₄, which is defined as $(E(TiCl₄/MgCl₂) - E(MgCl₂) - E(TiCl₄) - E(EB))/n$.
e) The adsorption of EB on the MgCl₂ surface in the absence of TiCl₄ nearby.

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energy and consistency with experimental characterizations. Consequently, the validity of this molecular model was investigated based on the catalytic performance of active sites. The interests were whether the coadsorption of a donor molecule can reproduce known effects of the addition of donors or not, and if yes, the mechanisms for donors to modulate the performance of an active site. The known effects include improvements in the stereospecificity, the regiospecificity, and the propensity for chain elongation of an active site in a way sensitive to the molecular structure of donors\(^9,10,30,31\).

As was explained above, the action of alkylaluminum converts TiCl\(_4\) into an active state, TiCl\(_2\)R, where R was approximated by \(i\)-butyl. Figure 6 displays major pathways for propylene to react at the active site. For the insertion, eight different pathways are considered, depending on the orientations of the growing chain and propylene. As shown in Figs. 6a and 6b, the growing chain in an \(\alpha\)-agostic conformation (\(H_\alpha\) is interacted with the Ti center) can adopt two different orientations, depending on the orientation of \(C_\beta\). In the present case, the left-oriented growing chain may sterically interfere with the coadsorbed EB molecule (Fig. 6b), while the rightward orientation looks less hindered. The 1,2-insertion requests the placement of the methyl group at either of \(R_{1,2}\), while the 2,1-insertion at either of \(R_{3,4}\). In the case of chain transfer, the growing chain needs to adopt a \(\beta\)-agostic conformation, and the \(H_\beta\) atom is transferred to the incoming propylene through a six-membered transition state (Fig. 6c)).

Table 3 summarizes the apparent activation energies of the propylene insertion and chain transfer to propylene at the TiCl\(_2\)R mononuclear species on the MgCl\(_2\) (110) surface in the absence or presence of a coadsorbed EB molecule. Representative methyl placements are selected for the brevity. For example, the 1,2-insertion absolutely favors an \(anti\) relation between the \(Me-C_2\) and \(C_\alpha-C_\beta\) bonds due to a steric reason. Therefore, the methyl group of propylene is placed at \(R_2\) (\(si\)) when the growing chain is right-oriented, while \(R_1\) (\(re\)) for the left orientation. In contrast, a \(syn\) relation tends to be preferred in the 2,1-insertion, and so on. In Table 3, it can be seen that the TiCl\(_2\)R mononuclear

| Orientation of growing chain | Methyl placement\(^a\) | Activation energy in the absence of EB [kcal/mol] | Activation energy in the presence of EB [kcal/mol] |
|-----------------------------|------------------------|-----------------------------------------------|-----------------------------------------------|
| 1,2-insertion                | Right \(R_2\) (\(si\)) | 7.36                                          | 7.90                                          |
|                             | Left \(R_1\) (\(re\))  | 7.52                                          | 10.2                                          |
| 2,1-insertion                | Right \(R_1\) (\(re\)) | 8.82                                          | 9.99                                          |
|                             | Left \(R_4\) (\(si\))  | 8.90                                          | 11.0                                          |
| Chain transfer              | n.a. \(R_{1,2}\)       | 8.42                                          | 12.6                                          |

\(\Delta\Delta E_{stereo}^{b}\) [kcal/mol] 0.16 2.27
\(\Delta\Delta E_{regio}^{b}\) [kcal/mol] 1.46 2.09
\(\Delta\Delta E_{CT}^{b}\) [kcal/mol] 1.06 4.66

\(\Delta\Delta E_{stereo}^{b}\) Defined by Eqs. (1)-(3).

Potential placements (and their enantiofaces) of the methyl group of propylene are denoted.

Fig. 6 Major Pathways for Propylene to React at an Active site: a) insertion with the growing chain oriented rightward, b) insertion with the growing chain oriented leftward, and c) chain transfer to propylene.
species catalyzes the 1,2-insertion with the opposite enantiofaces at similar activation energies in the absence of EB, i.e. almost completely aspecific. This is because the TiCl₂R mononuclear species itself cannot sterically distinguish the right and left orientations of the growing chain. The coadsorption of an EB molecule at the nearest position imposes the steric hindrance selectively to the left-oriented growing chain, and thereby penalizes the insertion with the \( \text{re} \) enantioface. This selective steric hindrance introduced the stereospecificity of 2.3 kcal/mol to the TiCl₂R mononuclear species. The 2,1-insertion of propylene was found to be energetically inferior to the 1,2-insertion even in the absence of EB, affording a moderate regiospecificity of 1.5 kcal/mol. It is well known that at the transition state of olefin insertion, the Ti-C\(_\alpha\) bond gets polarized like Ti\( ^\delta^- \)C\(_\alpha\)\( ^\delta^- \), and the placement of the electron-donating methyl group at R\(_{3,4}\) for the 2,1-insertion causes electrostatic repulsion\(^{32}\). As shown in Table 2, the coadsorption of a donor molecule adds up electron transfer from MgCl₂ to the Ti mononuclear species, which further destabilizes the 2,1-insertion. Indeed, the coadsorption of EB improved the regiospecificity of the active site to 2.1 kcal/mol. As for the chain transfer to propylene, the steric hindrance and electron enrichment brought by EB penalize the bulky six-membered transition state of the chain transfer and weaken the \( \beta \)-agostic interaction, respectively. As a result, the coadsorption of EB raised the \( \Delta \Delta E_{\text{CT}} \) value of the active site by 3.6 kcal/mol. Likewise, we firstly found that the TiCl₂R mononuclear species coadsorbed with a donor molecule on the MgCl₂ (110) surface can reproduce experimentally known consequences of the addition of donors, that are, improvements in the stereospecificity, the regiospecificity, the propensity for the chain elongation. It was clear that these improvements happen in a way to be sensitive to the molecular structure of donors, as the bulkiness and the electron donating ability of a donor molecule depend on it.

3.2. Structure-performance Relationship

The successful establishment of a highly consistent molecular model of catalyst surfaces has enabled us to study a structure-performance relationship for donors. Here, our recent results for alkoxyisilane external donors are described. Figure 7 summarizes the results of the stopped-flow propylene polymerization using a variety of commercially available alkoxyisilane donors.

![Fig. 7 Stereoregularity of Polypropylene Obtained by Stopped-flow Polymerization in the Presence of Different External Donors: a) dimethoxysilane and b) triethoxysilane](image)

These “good” donors all possess branches at the \( \alpha \)-position, while the order among them was hardly explained in a systematic manner\(^{17}\). Meanwhile, the order of the ability among triethoxysilane compounds followed cyclohexyl > ethyl > allyl or vinyl, and so on (Fig. 7b). Obviously, it was almost impossible to find a correlation between the molecular structure and the obtained results, and to be surprising, the cyclopentyl substituent, which was the best for dimethoxysilane, was found to be poor for triethoxysilane. This lack of a clear relationship between the molecular structure and resultant performance has been a major reason why researchers have been forced to adopt a demanding try-and-error approach in finding new donors.

Figure 8 summarizes the stereospecificity of an active site, which was calculated assuming the coadsorption of alkoxyisilane compounds. The obtained results clearly reflected the sensitivity of the stereospecificity to the molecular structure of donors, in agreement with the experimental results. Specifically, the calculated stereospecificity well reproduced the explained order of dicyclopentyl > di-i-propyl > dicyclohexyl for dimethoxysilane, the order of cyclohexyl > ethyl > vinyl for triethoxysilane (inconsistency for
allyl was unclear), and the inverse relationship of cyclopentyl and cyclohexyl between dimethoxysilane and triethoxysilane. The difference of the performance among the donors was hardly understandable by seeing the structure of isolated molecules, but the molecular structure upon the coadsorption successfully clarified this point. As shown in the bottom of Fig. 8, a cyclopentyl ring orients its face toward the active site, while a cyclohexyl ring faces vertical to the active site direction for dimethoxysilane. Inversely, the cyclohexyl ring orients its face toward the active site, and the cyclopentyl ring faces away from the active site. Likewise, a structure-performance relationship of donors is never realized without reproducing the exact interaction of donors with the active site. To the end, the capability of the molecular model is exemplified in Fig. 9, where a quantitatively reasonable one-to-one correlation was obtained between the calculated stereospecificity and experimentally acquired stereoregularity of polypropylene.

4. Conclusion

In the present contribution, our recent efforts are summarized on establishing an accurate molecular model for Ziegler-Natta propylene polymerization catalysts. Based on DFT calculations, the Ti mononuclear species and its coadsorption on the MgCl₂ (110) surface was found to be plausible in terms of energy and experimental consistency. Successful utilization of the established molecular model was demonstrated for a structure-performance relationship study of alkoxysilane external donors, which illustrates how critical the existence of an accurate molecular model is in describing solid catalysts based on computational chemistry.

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要  旨

Ziegler-Natta触媒に関する高精度分子モデリング

谷池 俊明，寺野 稔

北陸先端科学技術大学院大学，923-1292 石川県能美市旭台1-1

固体触媒研究における計算化学の最大の難関は、触媒表面の分子モデル構築における低精度である。本稿では、不均一系 Ziegler-Natta オレフィン重合触媒の高精度分子モデリングに関する近年の我々の研究成果を総括する。密度汎関数計算において、様々な分子モデル候補を実験事実に基づき多面的に検証する方法論によって、MgCl₂表面上でTt 単核種とドナー分子が共吸着した「共吸着モデル」を提案した。共吸着モデルは、歴史的に知られたドナーの添加効果（立体・位置特異性の向上や分子量の増大等）を系的に説明可能な初めての高精度分子モデルであり、ドナーの構造性能相関研究やインシリコ設計において極めて有用である。

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