Usage Report for Fiscal Year 2019

Project Title:

Computational Studies on the Electronic Structures and the Reaction Mechanisms of Rare-Earth- and Transition-Metal Complexes

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1. Background and purpose of the project, relationship of the project with other projects

The rare-earth- and transition-metal complexes catalyzed chemical transformations are important procedures in both industrial and academia fields, thus, the development of more efficient and reactive rare-earth- and transition-metal catalysts is one of the important topics in modern chemistry. To date, a diverse of rare-earth- and transition-metal catalysts have been successfully developed, and numerous valuable chemical products have been produced by using these organometallic complexes. The reactivity and selectivity of organometallic catalysts could be mainly ascribed to its unique physical and chemical properties, which could be modulated by the cooperation effect between metal center and auxiliary ligand. Although much effort has been made to intensively develop the new catalyst by modification of the ligand sphere, the rational design of new catalyst, especially the computational guided catalyst design, is the state-of-the-art approach.

To develop new catalysts more efficiently, the fully understanding of the catalytic mechanism is of fundamental importance, in which the key factors controlling the catalytic reactivity and selectivity could be found. However, it is difficult for traditional experimental to investigate the detailed reaction mechanism, because the intermediates and transition states during reaction are highly reactive and rarely detected, which hinders the rational catalyst design. Instead, the computational chemistry, as a powerful tool for studying chemical process at the molecular and atomic level, could help to elucidate the detailed reaction mechanisms, the electronic structures of catalysts, the key factors controlling the reactivity and selectivity, and *etc.* These mechanistic insights would help improve the performance of existing catalysts and further provide instructive information for rational catalyst design. Therefore, based on the experiment results, a series of computational jobs were carried out for better understanding of the related mechanisms which could contribute to the development of new catalysts and reactions.

2. Specific usage status of the system and calculation method

During the FY2019, a large number of specified computational resources were used for the theoretical calculations. In general, the geometry structures were optimized by DFT method using Gaussian 09 and Gaussian 16 software. The electronic structures of key active species and transition states were characterized by utilizing the ADF software. In addition, high level *ab-initio* calculations such as DLPNO-CCSD(T), and NEVPT2/CASSCF have been carried out to obtain the accurate energies. Natural Bond Orbital (NBO) analyses were also performed using some programs such as Gaussian 09, Gaussian 16 and so on.

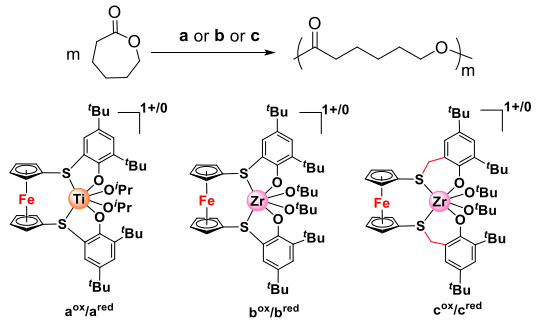
The B3LYP, B3PW91, TPSS, PBE, PBE0 and M06 functionals were utilized for DFT calculations. Dispersion corrections were treated with the D3 version of Grimme's dispersion with Becke–Johnson damping (GD3BJ) as well. For calculation of the relatively large catalytic system, such as multinuclear clusters, large polymerization systems, and the bioactive systems, the QM/MM method (ONIOM) was also adopted for accelerating the

calculations and analyses.

3. Results

(a) DFT study on the Redox-switchable Ring-Opening Polymerization of ε-Caprolactone catalyzed by Group 4 Metal Complexes.

Redox-switchable polymerization has drawn increasing attention, in particular for the ring-opening polymerization (ROP) of biomass-derived monomers. However, an understanding of how the switch determines the observed changes is still limited. In this study, DFT calculations were employed to understand the redox-switchable ROP mechanism of ε-caprolactone catalyzed by group 4 metal complexes bearing [OSSO]-type bis(phenolato) ferrocene ligands (Scheme 1).



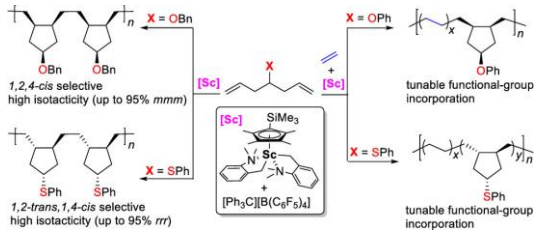
Scheme 1. Group 4 metal catalysts bearing [OSSO]-type bis(phenolato) ferrocene-based ligands for ε-caprolactone (CL) polymerization.

Having achieved an agreement between calculation and experiment, it was found that the higher activity of the oxidized forms **a**^{ox} and **c**^{ox} compared to that of their corresponding reduced forms stems from the higher Lewis acidity of the catalytic metal center in the oxidized species. In contrast, the lower activity of the oxidized species **b**^{ox} compared to that of bred is due to an increased stability of the intermediate following the monomer coordination that results in a high energy barrier. The current results also indicate that the stronger Lewis acidity of the catalytic metal center generally increases the activity of the catalyst. However, it could also increase the energy barrier of a reaction when the Lewis acidity of metal center is strong enough to overstabilize the coordination complex.

In the series of [OSSO]-type bis(phenolato) ferrocene-based group 4 metal complexes, our computational modelling indicates that a Hf analogue may possess better redox-switchable property for the ROP of CL compared to its corresponding Zr complex. Furthermore, the redox-switchable activity of the Zr complexes with different bridging-heteroatoms in their ancillary ligands follows the order of O < S < Se. These findings are expected to provide useful information on developing new redox-switchable polymerization catalysts for the synthesis of biodegradable polymers from biomass-derived monomers. (published in *Inorg. Chem. Front.* , accepted.)

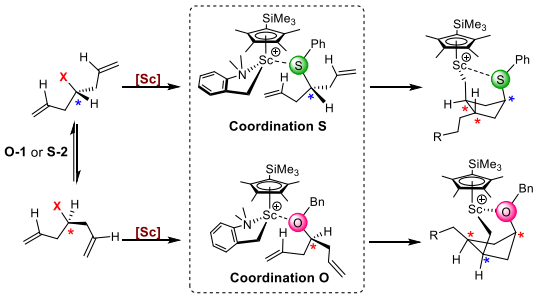
(b) DFT study on Scandium-Catalyzed Regio- and Stereoselective Cyclopolymerization of Functionalized α,ω-Dienes and Copolymerization with Ethylene.

The precise control of regio- and stereochemistry in the cyclopolymerization of heteroatom-functionalized α,ω-dienes is of much interest and importance, but has remained a challenge to date. We have achieved for the first time the regio-, diastereoselective and stereoregular cyclopolymerization of ether- and thioether-functionalized 1,6-heptadienes by a half-sandwich scandium catalyst (Scheme 2). The polymerization of 4-benzyloxy-1,6-heptadiene selectively afforded the corresponding benzyloxy-functionalized cyclic polymer composed of 1,2,4-cis-substituted-ethylenecyclopentane (ECP) microstructures in a isospecific fashion (95% *mmm*). In contrast, the polymerization of 4-phenylthio-1,6-heptadiene exclusively yielded 1,2-trans-1,4-cis-ECP units with high isotacticity (95% rrr).



Scheme 2. Sc-Catalyzed cyclopolymerization of heteroatom-functionalized 1,6-Heptadienes and copolymerization with ethylene.

The DFT calculations revealed that the unprecedented diastereoselectivity and stereoregularity could be ascribed to the unique interaction between the catalyst metal center and the heteroatom in a diene monomer (Scheme 3). This protocol has afforded a new family of heteroatom-functionalized cyclic polyolefins which were difficult to prepare previously. Our findings may also help design and synthesize new catalysts for efficient and regio-, stereoselective cyclopolymerization and related transformations of various functional dienes. (published in *Journal of the American Chemical Society* **2019**, *141*, 12624–12633.)



Scheme 3. Interaction between the catalyst metal center and the heteroatom in the diene monomer.

(c) DFT study and multidimensional quantitative analysis of ligand effects on yttrium catalyzed stereoselective polymerization of 2-vinylpyridine.

Stereoregular polymers generally exhibit particular and valuable properties and have attracted much attention in both academic and industrial fields. In the context of stereospecific synthesis of polymers, organometallic catalysis is an effective strategy to enable polymer microstructures to be precisely controlled. However, it is still challenging partly due to the difficulties in appropriate modifications of ancillary ligands to regulate the selectivity, especially for the stereoselective polymerization of polar monomers.

In this work, through a combination of density functional theory (DFT) calculations and multivariate regression analysis, the origin of the stereoselectivity of yttrium-catalysed polymerization of 2-vinylpyridine (2VP) has been investigated (Figure 1, left). Having achieved an agreement between theory and experiment, the detailed polymerization mechanism of 2VP mediated by such complexes has been computationally studied. It is found that the steric effect of ligand substituents of such catalysts mainly accounts for the experimentally observed isoselectivity. More interestingly, the application of Sterimol descriptors and multivariate linear regression models to the analysis of twenty-one catalysts (six experimentally treated and fifteen computationally designed ones) disclosed that the stereoselectivity quantitatively correlates the ligand substituent descriptors (Figure 1, right). The analysis results indicate that the larger difference in the substituent minimum-width between the two ortho-substituents near the metal center is more apt to produce higher stereoselectivity. Such a difference in the minimum-width of ortho-substituents therefore plays an important role in stereoselectivity regulation, arising from the coordination-space induced enantioface selectivity of monomer insertion. The results reported here shed new light on the design of highly stereoselective catalysts for 2VP polymerization. Such a combination of DFT-derived energy-barrier and multidimensional quantitative analysis is expected to be effective in assessing the selectivity of catalysts for both macro- and small-molecular systems. (published in *Catalysis Science & Technology* **2019**, *9*, 6227–6233.)

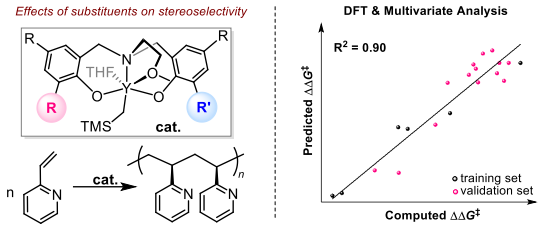
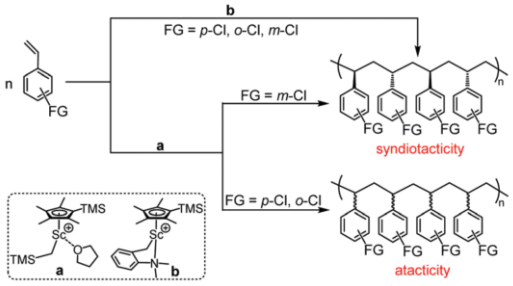


Figure 1. Yttrium catalyzed stereoselective polymerization of 2-vinylpyridine (left), and Plot of computed vs predicted $\Delta\Delta G^{\ddagger}_{si\text{-}re}$ (kcal/mol) using the multivariate linear regression model (right).

(d) DFT study on the stereoselective olefin polymerization regulated by "C–H…π Interaction".

The precise control of stereoselectivity in olefin polymerization is of great importance but challenging for the synthesis of polymers with desired properties. Generally, the stereoselectivity of polymerization catalysts can be mainly regulated by their ancillary ligands or metal centers. In this work, the origin of syndiotactic and atactic selectivity in the polymerization of various halogenated styrenes catalyzed by $(C_5Me_4SiMe_3)Sc(CH_2SiMe_3)(THF)^+$ (**a**) and $(C_5Me_4SiMe_3)Sc(CH_2\text{-}C_6H_4NMe_2\text{-}o)^+$ (**b**) has been comparatively revealed through DFT calculations (Scheme 4).



Scheme 4. Polymerization of various ClSt by cationic species **a** and **b**.

It is found that the coordinating THF participates in regulating the stereoselectivity via C–H…π interaction between the THF and the phenyl ring of monomer units. Such a noncovalent interaction is capable of altering the interaction strength between the inserting monomer and the metal center in transition states (Figure 2). Further theoretical investigations into a series of proposed polymerization reactions of various analogous monomers confirm the role of such C–H…π interactions in stereoselectivity regulation. This is achieved through the electron-withdrawing substituent(s) and the substitution position to alter the electron density of the phenyl ring of the monomer. More interestingly, it is found that the stereoselectivity could shift from syndiotacticity to isotacticity by an appropriate substitution. The results presented here suggest that a noncovalent interaction such as C–H…π could serve as a promising strategy to regulate the stereoselectivity in olefin polymerization and probably in small-molecule activations. (published in *Chem. Commun.* **2019**, *55*, 6689–6692.)

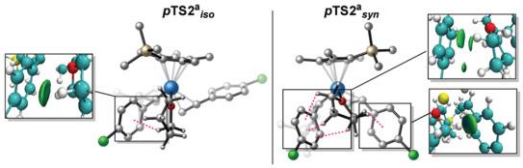
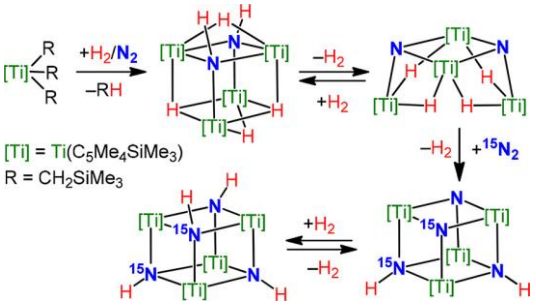


Figure 2. Interaction analyses for pTS2$^{a}_{iso}$ and pTS2$^{a}_{syn}$. The green cloud represents the existence of weak interaction.

(e) DFT Study on Dinitrogen Activation and Hydrogenation at a Tetranuclear Titanium Imide/Hydride Framework.

In nature, N_2 can be transformed to ammonia (NH_3) by nitrogenase enzymes under ambient conditions. The biological transformation of one molecule of N_2 to two molecules of NH_3 consumes eight electrons and eight protons, which is accompanied by release of one molecule of H_2. However, the biological ammonia synthesis is not yet well understood, and it is difficult to mimic artificially.



Scheme 5. Activation and transformation of dinitrogen at a tetranuclear titanium framework.

In this work, the activation of N_2 by a tetranuclear titanium(III) diimide/tetrahydride complex $[(Cp'Ti)_4(\mu_3\text{-}NH)_2(\mu\text{-}H)_4]$ ($Cp'= C_5Me_4SiMe_3$) (**1**), which was obtained by the reaction of the Cp′-ligated titanium trialkyl complex $Cp'Ti(CH_2SiMe_3)_3$ with H_2 and N_2, was investigated in detail by experimental and density functional theory studies (Scheme 5). We have examined the activation of N_2 by a tetranuclear titanium(III) diimide/tetrahydride complex **1**. It has been revealed that the reaction is initiated by cleavage of an imide N–H bond to give a mononitride/monoimide/pentahydride intermediate, which subsequently releases one molecule of H_2 by deprotonation of the other imide (NH) species with a hydride ligand and yields the dinitride/tetrahydride complex $[(Cp'Ti)_4(\mu_3\text{-}N)_2(\mu\text{-}H)_4]$ (**3**). The migration of a hydride ligand to a nitride ligand in **3** (or its isomer) may take place to generate a monoimide/mononitride/trihydride species. The coordination of N_2 to a titanium atom could then take place, followed by release of one molecule of H_2 through the reductive elimination of two hydride ligands. The N–N bond cleavage subsequently proceeds to give a monoimide/trinitride/monohydride species. Finally, the migration of the hydride ligand to a nitride ligand affords the diimide/dinitride product $[(Cp'Ti)_4(\mu_3\text{-}N)_2(\mu_3\text{-}NH)_2]$ (**2**). Under a high pressure of H_2, the hydrogenation of **2** occurs to give a tetraimide complex $[(Cp'Ti)_4(\mu_3\text{-}NH)_4]$ (**4**). This reaction was initiated byσ-bond metathesis between H_2 and atitanium–nitride bond, followed by migration of the resulting hydride ligand to the remaining nitride ligand. In all of thesetransformations, the interplay among the hydride, imide, and nitride ligands, including the reversible dehydrogenation/hydrogenation of imide and nitride species, at the multimetallic titanium framework has a critically important role. (published in *Journal of the American Chemical Society* **2019**, *141*, 2713–2720.)

4. Conclusion

With the help of HOKUSAI system, (1) the mechanistic aspect redox-switchable ring-opening polymerization of ε-Caprolactone catalyzed by Group 4 Metal Complexes has been studied, offering the mechanistic information of Redox-switchable ring-opening polymerization of ε-Caprolactone; (2) we have computationally studied scandium-catalyzed regio- and stereoselective cyclopolymerization of functionalized α,ω-Dienes and copolymerization with ethylene the obtained mechanistic insight could guide designing new catalysts; (3) DFT study and multidimensional quantitative analysis of ligand effects on yttrium catalyzed stereoselective polymerization of 2-vinylpyridine have been mechanistically investigated, such a combination of DFT-derived energy-barrier and multidimensional quantitative analysis is expected to be effective in assessing the selectivity of catalysts for both macro- and small-molecular systems; (4) DFT study on the stereoselective olefin polymerization have been studied. The results presented here suggest that a noncovalent interaction such as C–H…π could serve as a promising strategy to regulate the stereoselectivity in olefin polymerization and probably in small-molecule activations; (5) DFT study on dinitrogen activation and hydrogenation at a tetranuclear titanium imide/hydride framework has been intensively studied. It is computationally found that the interplay among the hydride, imide, and nitride ligands, including the reversible dehydrogenation/hydrogenation of imide and nitride

species, at the multimetallic titanium framework has a critically important role during dinitrogen activation process. These studies were successful in unveiling the key role of rare-earth- and transition-metal complexes in chemical reactions.

5. Schedule and prospect for the future

In the future, the reaction mechanism of inert molecule activation (such as H_2, N_2, NH_3) catalyzed by multinuclear cluster will be studied continuously. Besides, we will focus on the copolymerization of ethylene and polar monomer mediated by rare-earth- and transition-metal complexes. Furthermore, date analysis of the polymerization will be carried out.

We wish to continue to use HOKUSAI system for the current long-term project. Although some primary results have been obtained, more systematic studies on the mechanism of newly discovered reactions mediated by rare-earth- and transition-metal complexes are obviously necessary

Fiscal Year 2019 List of Publications Resulting from the Use of the supercomputer

[Paper accepted by a journal]

(1) Haobing Wang, Yanan Zhao, Masayoshi Nishiura, Yang Yang, Gen Luo, Yi Luo*, Zhaomin Hou* "Scandium-Catalyzed Regio- and Stereoselective Cyclopolymerization of Functionalized α,ω-Dienes and Copolymerization with Ethylene" *Journal of the American Chemical Society* **2019**, *141*, 12624–12633. (SCI, Impact Factor: 14.695)

(2) Yanan Zhao, Han Lu, Gen Luo,* Xiaohui Kang,* Zhaomin Hou, and Yi Luo,*"Origin of Stereoselectivity and Multidimensional Quantitative Analysis of Ligand Effects on Yttrium-Catalysed Polymerization of 2-Vinylpyridine" *Catalysis Science & Technology* **2019**, *9*, 6227−6233. (SCI, Impact Factor: 5.726)

(3) Yanan Zhao, Gen Luo,* Xiaohui Kang, Fang Guo, Xuefeng Zhu, Rencheng Zheng, Zhaomin Hou and Yi Luo* "C−H···π Interaction Regulates Stereoselectivity in Olefin Polymerization" *Chem. Commun.* **2019**, *55*, 6689–6692. (SCI, Impact Factor: 6.164)

(4) Takanori Shima, Gen Luo, Shaowei Hu, Yi Luo,* and Zhaomin Hou* "Experimental and Computational Studies of Dinitrogen Activation and Hydrogenation at a Tetranuclear Titanium Imide/Hydride Framework" *Journal of the American Chemical Society* **2019**, *141*, 2713–2720. (SCI, Impact Factor: 14.695)

(5) Gen Luo, Fan Liu, Yi Luo,* Guangli Zhou, Xiaohui Kang, Zhaomin Hou, and Lun Luo* "Computational Investigation of Scandium-Based Catalysts for Olefin Hydroaminoalkylation and C–H Addition" *Organometallics* **2019**, *38*, 1887−1896.