Research Summary

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The research interests of mine till now are mainly focused on (i) the synthesis of novel main group element and transition metal corrole and porphyrin complexes, and their reactivity together with corresponding mechanism study toward small molecules and (ii) developing simpler and more environmentally friendly rare earth separation methods with high single step efficiency. Thus as below, I would like to introduce the summary of my research in three sections, i.e., the main group chemistry based part, the transition metal compounds based part and the rare earth separation based part:

1 Researches on Main Group Element Chemistry

The chemistry of heavier group 14 elements, including silicon, germanium, tin and lead, are usually considered to only resemble the behavior of their light congener carbon in textbooks and literatures for decades. However, the first decade of 21st century has witnessed the revival of group 14 chemistry. With the introduction of specially designed ligand, collections of group 14 element complexes have been reported to have applicable frontier orbitals which are able to interact with substrates in the similar manners as those found for the transition metal complexes, thus have extremely interesting structures and reactivities. Although a variety of active group 14 element complexes has been prepared in recent years, in most cases the metal centers are in low oxidation states (oxidation states of 0, +1 and +2). The group 14 element complexes with a center oxidation state of +3, which can be viewed as the congeners of the active carbon radical, are far less encountered. To date, only examples of persistent and stable “Gomberg” type group 14 element radicals are represented. And the heavier group 14 element complexes with a center oxidation state of +4, which can be regarded as a typical Lewis acid, are also barely explored. Synthetic difficulties for these high valent group 14 complexes pose a significant challenge and impede further structural and reactivity investigations of these active species. Therefore, the majority of my research interests was focused on synthesis and characterizations of high valent heavier group 14 complexes with novel coordination geometries and electron configurations, and on their reactivities toward small molecules. Some interesting reactivities about the low valent group 14 complexes are also included in my research. The detailed contents of my research are listed as below:

1.1 Synthesis of [(TPFC)Ge(II)] anion and its reactivity toward small molecules

The tris(pentafluorophenyl)corrole (TPFC) germanium hydride complex (TPFC)Ge–H is prepared by the reduction of (TPFC)Ge-OCH$_3$ with NaBH$_4$. The Ge–H bond in (TPFC)Ge–H is acidic due to the electron withdrawing property of the TPFC ligand. In the presence of base such as KOH, the (TPFC)Ge–H can be deprotonated producing the [(TPFC)Ge(II)]$^-$ anion. [(TPFC)Ge(II)]$^-$ is a strong nucleophile and can react with series of small molecules such as aldehydes, olefins and alkyl halides to produce α-hydroxy alkyl and alkyl complexes as shown in figure 1.

1.2 Synthesis of [(TPFC)Ge(III)]$^0$ radical and its reactivity toward E–H (E = N,O) bonds

(TPFC)Ge(TEMPO) (TEMPO = (2,2,6,6-tetramethylpiperidin-1-yl)oxyl) is synthesized by oxidation of (TPFC)Ge–H with TEMPO$^*$ radical and characterized by X-ray diffraction and spectroscopic studies. EPR studies indicated that the weak Ge–O bond in (TPFC)Ge(TEMPO) could be smoothly photo-cleaved under ambient condition to form a tetra-coordinated germanium(III)
radical [(TPFC)Ge(III)]0 together with TEMPO•. The active [(TPFC)Ge(III)]0/TEMPO• radical pair is capable of N–H bond activation in a series of amines. Under visible-light irradiation, (TPFC)Ge(TEMPO) reacts rapidly with ammonia, primary/secondary aliphatic amines and aniline at room temperature to produce (TPFC)Ge–NR1R2 (R1R2 = HPr, HPr, H’Bu, HPh, Et2, iPr2) complexes in high yields (65% - 95%) (Figure 2). (TPFC)Ge(TEMPO) is also capable of O–H bond activation in water and methanol both in dark and under visible light irradiation at room temperature. EPR analysis and computation studies showed the entire process for the E–H bond (E = N, O) activation by (TPFC)Ge(TEMPO) after formation of [(TPFC)Ge(III)]0/TEMPO• radical pair consisted of two sequential steps: (i) the coordination of substrates to the germanium center in [(TPFC)Ge(III)]0 leading to the formation of radical adduct [(TPFC)Ge(EHLn)]0 (EHLn = amine substrates, water or methanol; E = N,O) and (ii) cleavage of E–H bond in the newly formed radical adduct via a PCET process during the following reaction with TEMPO• (Figure 3). Metal-ligand cooperation plays a pivotal role in the observed E–H bond activation by (TPFC)Ge(TEMPO).

![Figure 1. Reactivity of [(TPFC)Ge(II)]− anion.](image1)

![Figure 2. Reactivity of [(TPFC)Ge(III)]0 radical.](image2)

![Figure 3. Mechanism for E–H bond cleavage by (TPFC)Ge(TEMPO).](image3)

![Figure 4. Reactivity of [(TPFC)Ge(IV)]+ cation.](image4)

1.3 Synthesis of [(TPFC)Ge(IV)]+ cation and its reactivity toward small molecules

[(TPFC)Ge]+, a planar tetra-coordinated germanium(IV) cation, was synthesized by the
reaction of (TPFC)Ge–H with [Ph₃C][B(C₆F₅)₄] quantitatively. The highly active [(TPFC)Ge]+ was found to be capable for the activations of small molecules such as benzene, ethylene and cyclopropane producing a series of aryl or alkyl germanium corroles. The σ-type germlyium-benzene adduct [(TPFC)Ge(C₆H₆)]+, which was the key intermediate in the electrophilic addition of [(TPFC)Ge]+ to benzene, was isolated and characterized by single crystal X-ray diffraction. The strong Lewis acidity and corresponding reactivities might mainly originate from the well exposed cationic germanium center lacking conjugation to π-system and the three electron-withdrawing pentafluorophenyl groups in the presented germlyium cation.

1.4 Synthesis of [(TPFC)Sn(II)]− anion and its reactivity toward small molecules

A series of corrole Sn(IV) and Sn(II) complexes are prepared and studied by various characterization techniques. The unusual tetra-coordinate [(TPFC)Sn(II)]− shows interesting reactivity toward alkenes and alkyl halides via a nucleophilic addition pathway leading to the quantitative formation of alkyl stannyl corrole complexes like the [(TPFC)Ge(II)]−.

2 Researches on Transition Metal Compounds

2.1 Copper corrole catalyst for hydrogen evolution from water

The increasing energy demand and environmental concerns about the use of fossil fuels have made energy related researches the paramount task for our world. Hydrogen gas is one of the ideal energy sources due to it is carbon-free, renewable and produces only water as the combustion product. Thus, hydrogen gas production from water using electrochemical method has attracted much attention recently. Our group collaborates with Professor Cao’s group in Shaanxi Normal University in developing a robust and efficient (with a TOF of ~ 30,000 s⁻¹) molecular copper corrole based hydrogen evolution catalyst (HEC) (Figure 5). The two mechanistic insights accorded with each other very well and indicated a most plausible catalytic pathway as: (i) double reduction of [(cor)Cu] to [(cor)Cu]²⁻ on the electrode; (ii) protonation of [(cor)Cu]²⁻ to [(cor)CuH]− and (iii) reaction of [(cor)CuH]− with H⁺ leading to the formation of H₂ and the regeneration of the [(cor)Cu] catalyst.

2.2 Nickel porphyrin catalyst for hydrogen evolution from water

Our group collaborates with Professor Cao’s group in Shaanxi Normal University in investigating different hydrogen-evolution-reaction (HER) mechanisms using a nickel(II) porphyrin (por⁵⁷⁷)Ni (por⁵⁷⁷ = 5,10,15,20-tetrakis(pentafluorophenyl)porphyrin) compound (Figure 6). Doubly reduced (por⁵⁷⁷)Ni ([(por⁵⁷⁷)Ni]²−) was involved in H₂ production from acetic acid, whereas a singly reduced species ([(por⁵⁷⁷)Ni]−) initiated HER with stronger trifluoroacetic acid (TFA). High activity and stability of (por⁵⁷⁷)Ni were observed in catalysis, with a remarkable i/iₚ value of 77 with TFA at a scan rate of 100 mV s⁻¹ and 20 °C. Electrochemical, stopped-flow, and theoretical studies indicated that a hydride species (por⁵⁷⁷)NiH is formed by oxidative protonation of [(por⁵⁷⁷)Ni]−. Subsequent rapid bimetallic homolysis to give H₂ and (por⁵⁷⁷)Ni is probably involved in the catalytic cycle. HER cycling through this one-electron-reduction and homolysis mechanism has been proposed previously but rarely validated. The present results could thus have broad implications for the design of new exquisite cycles for H₂ generation.
Figure 5. Hydrogen evolution from water catalyzed by molecular copper corrole and mechanism study using stopped-flow and UV-Visible spectroelectrochemistry measurements.

Figure 6. Hydrogen evolution from water catalyzed by nickel(II) porphyrin and mechanism study using stopped-flow measurements.

2.3 Electron configuration study for the (TMP)Rh(II)(CO)₂ complex

The electron configuration for the metalloporphyrins are always very tricky due to the low-laying $4e(\pi^*)$ of the porphyrin ligands referred to the $d$-orbitals of the center metals. For (TMP)Rh(II) and its single CO adduct (TMP)Rh(II)CO (TMP = tetramesitylporphyrin), for decades both the experimental observation and the computational results have confirmed the unpaired electron is mainly localized on the $d_{z^2}$ orbital of the rhodium center. Although the unpaired electron in (TMP)Rh(II)(CO)₂, which has a formal 19-electron metal center, is proposed to be delocalized over the porphyrin ligand, no direct experimental observation has been reported yet. We have successfully synthesized the (TMP)Rh(II)(CO)₂ by light irradiation of (TMP)Rh–CH₃ under about 1 atm of CO. The EPR measurement of (TMP)Rh(II)(CO)₂ shows the feature of the porphyrin anion radical (Figure 7). Further research about the spectroscopy and computational study of this odd-electron complex is still on the way.
Figure 7. EPR spectra of (TMP)Rh(II)(12CO)2 (a) and (TMP)Rh(II)(13CO)2 (b) in benzene at 123K.

Figure 8. Mechanism for (por)Rh(II) catalyzed photo production of formamides from CO and amines.

2.4 Mechanism Study for Metalloradical Porphyrin Rhodium (II) Promoted Photo Production of Formamides from CO and Amines

The photo production of formamides exclusively from CO and amines could be catalyzed by (por)Rh(II) (por = tetramesitylporphyrin, tetraphenylporphyrin) under mild conditions. The EPR measurement together with computational study shows the entire 100% atom efficiency catalytic cycle contains 5 steps (Figure 8): (a) coordination of CO to the rhodium metal center in (por)Rh(II) producing (por)Rh(II)CO; (b) N–H bond cleavage by two molecules of (por)Rh(II)CO metalloradical leading to the formation of (por)RhCHO and (por)RhCONR1R2; (c) amine substrates could then react with (por)RhCHO which lead to the formation of the formamides and (por)RhH; (d) the weak Rh–C bond could be easily photocleaved thus leading to the regeneration of catalyst and the formation of R1R2NCO• radical; (e) the newly formed active R1R2NCO• radical could abstract the hydrogen atom from the Rh–H bond in (por)RhH which results in the regeneration of catalyst and the production of the formamides.

2.5 Resonance Raman Characterization of Nonheme Cobalt-Hydorperoxo/Superoxo Compounds

Bubbling O2 into a THF solution of Co(II)(BDPP) (H2BDPP = 2,6-bis((2-(S)-diphenyldihydroxy)methyl-1-pyridinyl)methyl)-pyridine) at -90 °C generates an O2 adduct, Co(III)(BDPP)(O2). The resonance Raman and EPR investigations reveal that Co(BDPP)(O2)
contains a low spin cobalt(III) ion bound to a superoxo ligand. Significantly, at \(-90 \degree C\), Co(BDPP)(O\textsubscript{2}) can react with TEMPOH (2,2,6,6-tetramethyl-1-hydroxypiperidine) to form a structurally characterized cobalt(III)-hydroperoxo complex, Co(III)(BDPP)(OOH) and TEMPO• radical (Figure 9).

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\nu^{(16O-16O)} = 1135 \text{ cm}^{-1} \\
\nu^{(18O-18O)} = 1070 \text{ cm}^{-1} \\
\nu^{(16O-16O)} = 795 \text{ cm}^{-1} \\
\nu^{(18O-18O)} = 748 \text{ cm}^{-1}
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**Figure 9.** Synthesis and resonance Raman characterization of Co(III)(BDPP)(O\textsubscript{2}) and Co(III)(BDPP)(OOH).

### 3 Researches on Developing Simpler and Environmentally Friendly Rare Earth Elements Separation Methods with High Single Step Efficiency\textsuperscript{11}

Rare earth elements are key components in crucial materials extensively used in modern-day technologies. Efforts have been made in pursuing simpler and more efficient separation of these elements during the past decades. However, most of the developed strategies rely on the thermodynamic properties of rare earth element complexes, such as ligand coordination/dissociation equilibrium and distribution equilibrium in liquid-liquid extraction, while their kinetic properties remain unexploited. Here, we demonstrate a new and simple approach for rare earth separation by using kinetic differences of the oxidation rates of a series of rare earth compounds containing the redox non-innocent TriNOx\textsuperscript{3-} ([(2-\text{BuNO})(C\textsubscript{6}H\textsubscript{4}CH\textsubscript{2})\textsubscript{3}N]\textsuperscript{3-}) ligand. A single-step separation factor up to 261 was obtained for the separation of a 50:50 yttrium-lutetium mixture (Figure 10).

**Figure 10.** Kinetic separation of Y/Eu, Y/Yb and Y/Lu mixtures.

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