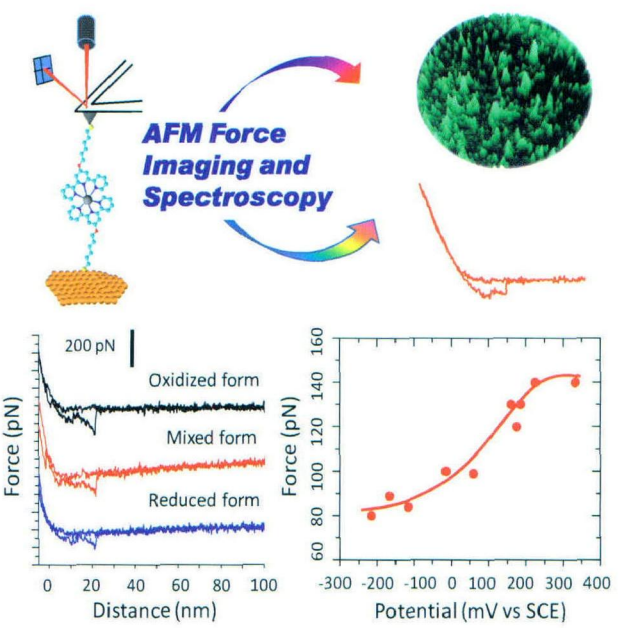
Single-molecule coordinative bonding forces in a transition metal complex

Coordination interaction is itself a very broad area in chemistry, because more than half of the elements in the periodic table are transition metals. Electron transfer and ligand substitution reactions represent the two major classes of reactivity of transition metal complexes for their crucial applications in catalysis, molecular electronics, and medical chemistry. However, most studies in coordination chemistry, including metal-binding free energies and enthalpies, and bond association/disassociation kinetics, are based on average and ensemble level approaches. Funded by the NSFC, Prof. Wang Hongda from Changchun Institute of Applied Chemistry, CAS and co-workers published their research findings in *Nature Communications* (**2013**, 4: 2121).



In this work, single-molecule force analysis has been achieved by combining several interdisciplinary tools, particularly high-resolution electrochemical AFM imaging and force spectroscopy. The proof-of-concept study is a major focus of this work and has been illustrated well by the Os-terpy systems. The Os-terpy bonds are ruptured at 100 ± 30 pN at open circuit potentials, but at 140 ± 60 pN in the oxidized state of the central metal and at the lower value of 80 ± 30 pN in the reduced state. A remarkable effect of the redox state on the coordinative bonding is thus experimentally observed. The different pulling forces in the two oxidation states are rationalized by DFT simulations. The computational procedures are rigorous, though the models used at this stage are relatively crude as the bulk solvation is either disregarded or represented by a single solvation shell only. The emerging pulling forces, however, still disclose clearly the kinematic and electronic nature of the molecular scale pulling events and the subtle interplay between bond stretching and terpy/H_2O ligand substitution that controls the process. The latter is thus an absolute rationale even for the qualitative observations. The quantitative values of the emerging pulling forces are far stronger than those observed (nN rather pN ranges) but the accordance can be expected to change drastically by full scale incorporation of solvent molecular assemblies that incorporate both the dynamics of the accompanying terpy/H_2O ligand substitution and longer range solvation.

The AFM force spectroscopy has shown that a metal-ligand coordinative bonding strength is only equivalent to about 5% of that for a covalent bond. This value appears to be surprisingly smaller than expectation from our traditional understanding of metal-ligand interactions in coordination chemistry. These AFM studies have thus raised several challenging questions such as: (1) how strong a metal-ligand coordination bond should be; (2) how much we have known about the physicochemical nature of metal-ligand bonding; (3) how much external conditions such as solution pH, ionic strength and type of transition metals could affect metal-ligand interactions. These questions would promote ongoing refined researches, for example by systematic design and synthesis of various ligands and by exploring other transition metals as well as introduction of new tools in addition to AFM approaches. The overall approach demonstrated in this work represents a remarkable advancement in studying coordination chemistry at the single-molecule level. The observations should add new insight to our understanding of the physicochemical nature of coordinative bonds. The method is expected to apply generally to other transition metal complexes and to make impacts on coordination chemistry and related areas broadly.