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First Principles Calculations on Atomistic Mechanisms of Surface/Interface-Induced Properties and Database Construction

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Abstract: Surfaces and interfaces play a critical role in exploring novel chemical and physical properties because the interactions between surface and adsorbents, as well as interfacial interactions, can be finely tuned by the interface configurations at the atomic level across a wide range, from strong covalent and ionic bonds to weak hydrogen bonds and van der Waals interactions. These interactions enable precise control over molecular adsorption, self-assembly, and activation, facilitating the design of nanostructures and modulation of novel properties. Recent developments in computational technologies, including high-throughput screening and machine learning, have significantly accelerated the discovery of functional materials. This review highlights theoretical progress in manipulating the physical and chemical properties of organic molecules at surfaces and interfaces, with a focus on controlling molecular configuration and magnetism, selective activation, on-surface synthesis, and interfacial engineering of 2D materials. Our goal is to understand the key factors influencing the physical and chemical properties at surfaces and interfaces, with a particular focus on theoretical insights and computational approaches.

Key words: surface chemistry, interface chemistry, computational simulation, 2D materials, molecular adsorption.

1. Introduction

Surfaces and interfaces serve as critical platforms for exploring novel chemical and physical properties due to their ability to provide unique and tunable interactions across a wide energy range [1,2]. For instance, the strength of covalent bonds typically ranges from 1 to 10 eV, while ionic bonds have strengths between 2 and 4 eV. In contrast, hydrogen bonds and van der Waals (vdWs) interactions are much weaker, with energies ranging from 0.01 to 0.4 eV for hydrogen bonds and 0.001 to 0.01 eV for vdWs interactions. Furthermore, the symmetry of surface structures, along with variations in potential energy surfaces at different sites, enables the adsorption [3], assembly [4], and activation processes [5] on surfaces to be finely tuned. For example, exchange interactions in magnetic

materials, which typically occur at the meV level, are comparable in magnitude to vdWs interactions. It enables the modulation of magnetic properties through weak adsorption at surfaces or interfaces [6]. Moreover, thermal excitation of molecules on surfaces at elevated temperatures involves energies between 0.1 and 1 eV, which can drive the breaking or reforming of chemical bonds. This provides a pathway for atomic-level design and engineering of novel nanostructures [7]. The rapid development of two-dimensional (2D) materials over the past decade has not only enabled the modification using thermal [5], optical [8-10], magnetic [11] and electric field [12] approaches, but also allows for tuning through mechanical methods such as stretching and folding [13]. These advantages result in significant increases in the potential applications of nanomaterial-based devices [14], including nanorecording [15-19], asymmetric
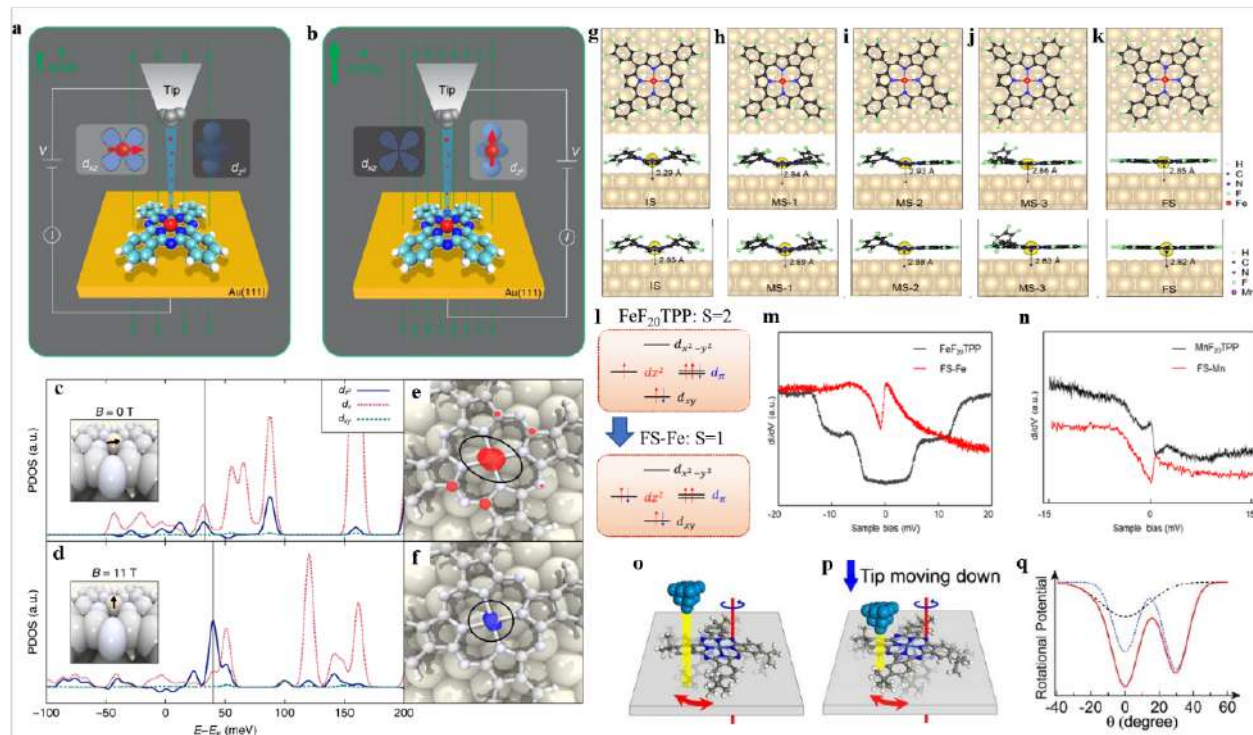
Figure 1. Magnetic, intramolecular cyclization and mechanical regulation of M-Pc molecules. **a**, **b** Schematics of the electron transport process through an FePc molecule adsorbed on a Au(111) surface at different magnetic fields. **c**, **d** Calculated lm-decomposed partial density of states (PDOS) of the Fe atom (d_π represents d_{xz} or d_{yz}). **e**, **f** Band-decomposed charge density plots for the molecular orbitals close to E_F, showing the spatial distribution of the Kondo resonance. **g-k** DFT calculated the adsorption configurations and spin density distributions of IS, MS1, MS2, MS3 and FS on Au(111). **l**, Schematic representations of the transition from the $S = 2$ electronic state of FeF$_{20}$TPP to the $S = 1$ electronic state of the final state (FS). **m** The differential conductance dI/dV spectra acquired upon the center of the FeF$_{20}$TPP and FS-Fe molecules. The dip-like feature around zero bias voltage and symmetric steps represents Kondo resonance (red curve) and IETS (black curve). **n** The differential conductance dI/dV spectra acquired upon the center of the MnF$_{20}$TPP and FS-Mn molecules. The conductance dip (or peak) near zero energy represents Kondo resonance (red line and black line) (V_s=-20 mV, I_t=300 pA, lock-in modulation: V_{rms}=0.5 mV). **o** Sketch of the dominant adsorption configuration of (t-Bu)$_4$-NiPc on Au(111) when the tip is far away. **p** Sketch of adsorption configuration of (t-Bu)$_4$-NiPc after the tip approaches the sample surface. **q** Schematic representation of the rotational potential energy around two configurations consisting of the native potential well without tip molecule interaction (blue dotted line); the tip-induced potential well (black dashed line); the potential landscape with added contributions of the native and tip-induced potentials (red solid line). $V_{Sample} = -1$ V and the feedback loop is open.

catalysis [20], giant magnetoresistive devices [6], molecular machines [21-24], and spintronics [12,25,26].

In recent years, the development of computational technologies has enabled data-driven paradigms in materials science, including high-throughput screening and machine learning, accelerating the design of functional materials. Within these paradigms, high-quality databases are recognized as the foundations, because one can both efficiently identify high-performance functional materials and use those databases as extensive data resources for training machine learning model.

In this review, we present the recent progress from a theoretical perspective on manipulating physical and chemical properties at surfaces and interfaces, and constructing databases based on the deep insights into the structure-property relations. First, we discuss various methods for controlling the molecular configuration and magnetism of organic molecules utilizing magnetic fields, electric fields, and intramolecular cyclization. Next, we focus on the selective activation of organic molecules and highlight strategies for the bottom-up synthesis of graphene nanoribbons through surface activation. Finally, we explore interfacial engineering of 2D materials, from weak van der Waals stacking to strong interlayer

interactions via covalent and ionic bonds.

2. Surface-induced physicochemical properties

2.1. Novel properties of single molecule on surface

Metal-phthalocyanines (M-Pc) and metal-porphyrins (M-PP) are versatile functional molecules widely used in catalysis and organic electronics due to their unique optical and electrochemical properties [27,28]. Their ability to form stable complexes with metal ions and exhibit strong light absorption makes them ideal for applications in solar cells, sensors, and molecular devices [29,30]. For example, Yang *et al.* used scanning tunneling microscopy (STM) to investigate the transport of a single FePc molecule, demonstrating how an external magnetic field can control the spin states and conductance [6]. Notably, the Fe ion in FePc is located at bridge site with a magnetic moment of 2μB. At weak fields (as shown in **Figure 1a**), the spin is in-plane, and electrons flow via the d_{xz}/d_{yz} orbitals. At stronger fields (as shown in **Figure 1b**), the spin aligns with the field, and tunneling occurs through the d_{z2} orbital. **Figure 1(c-f)** show that increasing magnetic field intensity alters the transmission path from