

Correlated Magnetism and Electronic Properties in Programmable Molecular Spin Systems

by

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This is to certify that I have examined the above PhD thesis
and have found that it is complete and satisfactory in all respects,
and that any and all revisions required by
the thesis examination committee have been made.

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Abbreviations

1D	One-dimensional
2D	Two-dimensional
3D	Three-dimensional
AFM	Antiferromagnetic
AI	Artificial Intelligence
AI-STM	Artificial Intelligence-Scanning Tunneling Microscopy
AQS	Artificial Quantum Structures
CV	Computer Vision
DC	Direct Current
DFL	Disordered Fermi Liquid
DFT	Density Functional Theory
DMFT	Dynamical Mean-Field Theory
DOS	Density of States
DRL	Deep Reinforcement Learning
FFT	Fast Fourier Transform
FM	Ferromagnetic
HOMO	Highest Occupied Molecular Orbital
HWHM	Half Width at Half Maximum
IGP	Ion Getter Pump
KLM	Kondo Lattice Model

LDOS	Local Density of States
LL	Load Lock
LUMO	Lowest Unoccupied Molecular Orbital
MBPT	Many-Body Perturbation Theory
MOF	Metal-Organic Framework
nc-AFM	Non-contact Atomic Force Microscopy
NRG	Numerical Renormalization Group
PDOS	Projected Density of States
QMC	Quantum Monte Carlo
RKKY	Ruderman-Kittel-Kasuya-Yosida
RL	Reinforcement Learning
RMS	Root Mean Square
SAC	Soft Actor-Critic
SML	Single-Molecule Lithography
SOC	Spin-Orbit Coupling
SOMO	Singly Occupied Molecular Orbital
STM	Scanning Tunneling Microscopy
STS	Scanning Tunneling Spectroscopy
SUMO	Singly Unoccupied Molecular Orbital
TB	Tight Binding
TCP	Transmission Control Protocol

TIAM	Two-Impurity Anderson Model
TMP	Turbomolecular Pump
TSP	Titanium Sublimation Pump
UHV	Ultra-High Vacuum
ZBP	Zero-Bias Peak

Correlated Magnetism and Electronic Properties in Programmable Molecular Spin Systems

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Abstract

Molecular spin systems on surfaces provide atomically precise platforms for exploring correlated magnetism and many-body electronic phenomena. Among them, π -radicals are particularly attractive because their unpaired π -electrons generate localized magnetic moments that can be chemically designed, spatially arranged, and directly probed by scanning tunneling microscopy and spectroscopy. When such radicals are arranged artificially and coupled to metallic substrates, Kondo screening, inter-spin exchange interactions, and finite-size effects can coexist, giving rise to rich low-energy electronic behavior. The ability to construct these spin units into programmable lattices further opens a route to studying Kondo-lattice-related physics and artificial quantum matter at the single-molecule level.

This thesis reports the construction and characterization of programmable molecular spin systems based on tip-induced π -radicals in two-dimensional metal–organic frameworks on Au(111). Low-temperature scanning tunneling microscopy and spectroscopy, together with density functional theory and model Hamiltonian calculations, are used to investigate the structural, electronic, and magnetic properties of these systems. Site-selective dehydrogenation

of tris(4-carbonitrile)-triphenylmethyl (TPM) molecules generates radical molecular spin units, which exhibit low-energy spectroscopic features associated with Kondo correlations. By arranging these radicals into finite one-dimensional chains, systematic changes in the local spectra are observed as a function of chain length and site position, revealing the competition between local Kondo screening and inter-radical magnetic coupling.

The same platform is further extended to finite two-dimensional molecular spin arrays with controlled geometries. Triangular, rhombic, and larger radical lattices show increasingly complex spectral responses near the Fermi level, including peak-like, dip-like, and gap-like features. Their size- and geometry-dependent evolution suggests the development of collective interactions among molecular spins, while also emphasizing the roles of finite-size effects, local coordination, and non-uniform coupling. These results provide a molecular-scale view of how isolated Kondo impurities evolve toward interacting spin arrays and possible finite-size precursors of Kondo-lattice-like behavior.

In addition to probing correlated spin physics, this thesis develops an artificial-intelligence-assisted STM strategy for scalable molecular spin construction. Reinforcement learning is used to optimize tip-manipulation parameters for site-selective dehydrogenation, enabling autonomous fabrication of designed radical patterns and extended molecular lattices with improved efficiency and reproducibility. This approach establishes AI-assisted single-molecule lithography as a powerful route toward programmable artificial quantum structures.

Together, these studies demonstrate a chemically tunable and spatially programmable platform for investigating correlated magnetism in molecular spin systems. By integrating on-surface synthesis, STM tip manipulation, local spectroscopy, theoretical modeling, and AI-assisted fabrication, this work provides a foundation for constructing and studying artificial molecular spin lattices and a metal-organic framework platform with single-molecule precision.

Chapter 1

Introduction

This chapter provides a concise overview of the background and organization of the thesis. I begin with an introduction to two-dimensional metal–organic frameworks (2D-MOFs), a novel member of 2D materials family. I then discuss organic radical spin systems on metallic surfaces, which serve as model platforms for exploring correlation effects. The next section introduces the Kondo effect, a cornerstone phenomenon in many-body physics, followed by a brief review of the Kondo lattice and heavy-fermion materials, where collective interactions give rise to unconventional quantum states. Finally, recent progress in artificial intelligence-assisted scanning tunneling microscopy (STM) study of molecular systems is briefly reviewed. The chapter concludes with an outline of the thesis structure, guiding the reader from the fundamental background to the specific research questions addressed.

1.1 Two-dimensional metal-organic frameworks

Two-dimensional metal–organic frameworks (2D-MOFs) have recently emerged as a new generation of low-dimensional materials distinguished by their exceptional structural and chemical tunability. Unlike conventional inorganic systems such as graphene or transition-metal dichalcogenides, 2D-MOFs offer unprecedented flexibility: their lattice geometry, electronic coupling, and spin states can be precisely engineered through the metal centers and organic ligands, as shown in Figure 1.1(a).¹ This versatility makes them uniquely suited for probing correlated electron phenomena and for the rational design of functional quantum materials.

Beyond the superior chemical performance in catalysis and separation, 2D-MOFs can also host exotic physical states, including superconductivity and magnetic order. For instance, Huang et al. reported a metallic $\text{Cu}_3(\text{C}_6\text{S}_6)$ MOF exhibiting ultrahigh room-temperature conductivity ($\sim 1580 \text{ S cm}^{-1}$) and superconductivity below 0.25 K.^{2,3} Feng et al. demonstrated that Cu-ABDC MOF displays intrinsic room-temperature ferromagnetism.⁴ Most 2D-MOFs synthesized to date are multilayered, yet their monolayers often exhibit distinct properties due to the absence of interlayer π – π interactions. For instance, $\text{Ni}_3(\text{HITP})_2$ has been theoretically predicted to possess nontrivial spin–orbit gaps consistent with topological states.⁵ Similarly, Feng Liu et al.

predicted $\text{Ni}_3\text{C}_{12}\text{S}_{12}$ as a potential organic topological insulator.⁶ These findings highlight the promise of monolayer 2D-MOFs as platforms for exploring topological and quantum phenomena.

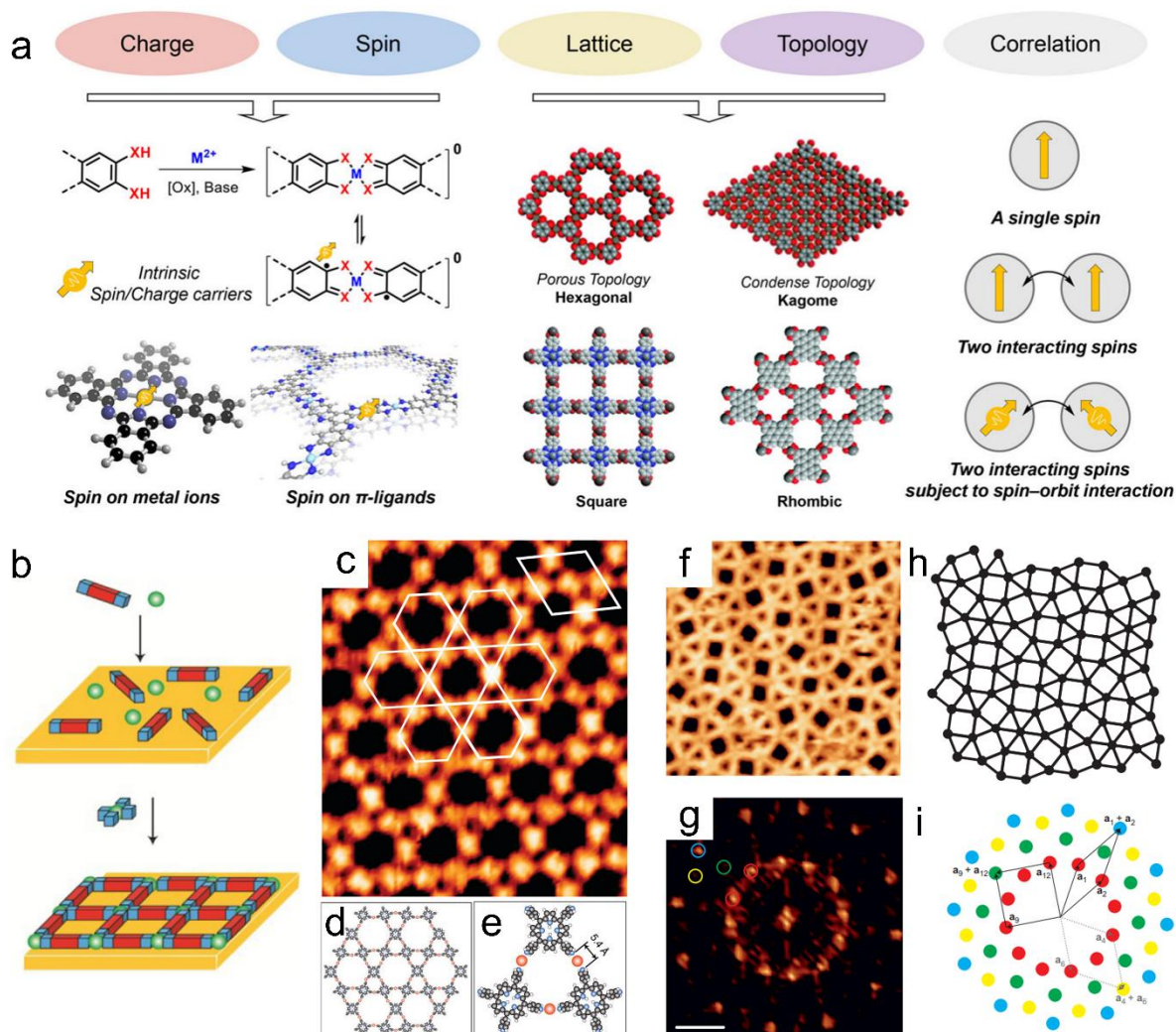


Figure 1.1 (a) The structural flexibility of 2D-MOFs makes them ideal platform for the investigations of electronic and magnetic properties.¹ (b) Schematic illustration of 2D-MOF self-assembly via on-surface synthesis.⁷ (c–e) STM topographies and corresponding structural models of the Au-TPyP MOF on the Au(111) surface.⁸ (f–i) STM image with structural model and the associated FFT pattern of the Eu(*para*-quaterphenyl-dicarbonitrile)_n MOF in the quasicrystalline phase on the Au(111) surface.⁹

Since 2002, Nian LIN and collaborators have pioneered on-surface synthesis as an effective approach to achieving monolayer 2D-MOFs.¹⁰ Unlike conventional hydrothermal or interfacial methods, which typically yield multilayer powders or thick films, on-surface synthesis enables

atomically precise growth directly on crystalline substrates under ultrahigh vacuum conditions (Figure 1.1(b)). This strategy affords direct structural control and compatibility with in-situ characterization techniques. For instance, Ziliang Shi et al. synthesized a Kagome 2D-MOF Au-TpyP on Au(111) surface in 2009 (Figure 1.1(c-e)).⁸ Later in 2016, José I. Urgel et. al reported a quasicrystal 2D-MOF on Au(111) substrate as shown in Figure 1.1(f-i).⁹ These advances establish on-surface synthesis as a powerful platform for both fundamental investigations of correlated electron phenomena and the rational design of functional quantum materials, thereby motivating the research presented in this dissertation.

1.2 π -radicals act as novel spin systems on metal surface

Surface magnetism was traditionally investigated within transition-metal adatoms¹¹⁻¹³ and large π -conjugated macrocyclic molecules such as porphyrins and phthalocyanines adsorbed on metallic substrates.¹⁴⁻¹⁶ These systems provided crucial insights into spin-orbit coupling (SOC), magnetic anisotropy, and substrate-induced quenching of magnetic moments. However, the inherent strong SOC and magnetic anisotropy of d-orbital electrons constrain further exploration of spin phenomena.^{17,18} This makes the flexible control of magnetism at the atomic and molecular scales inherently challenging.

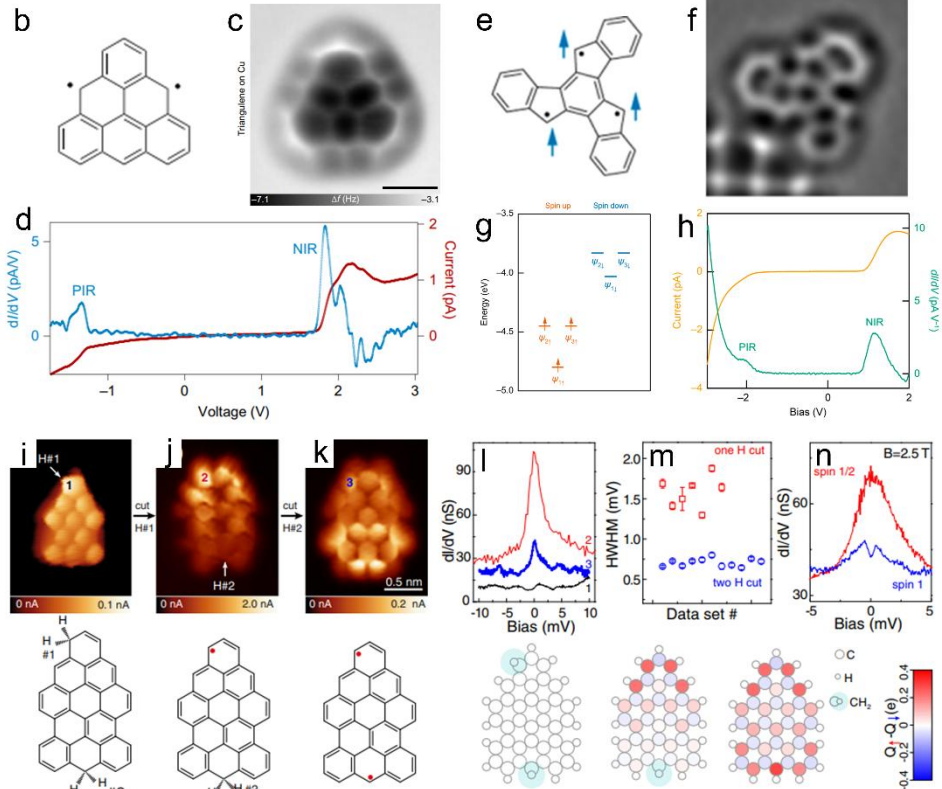
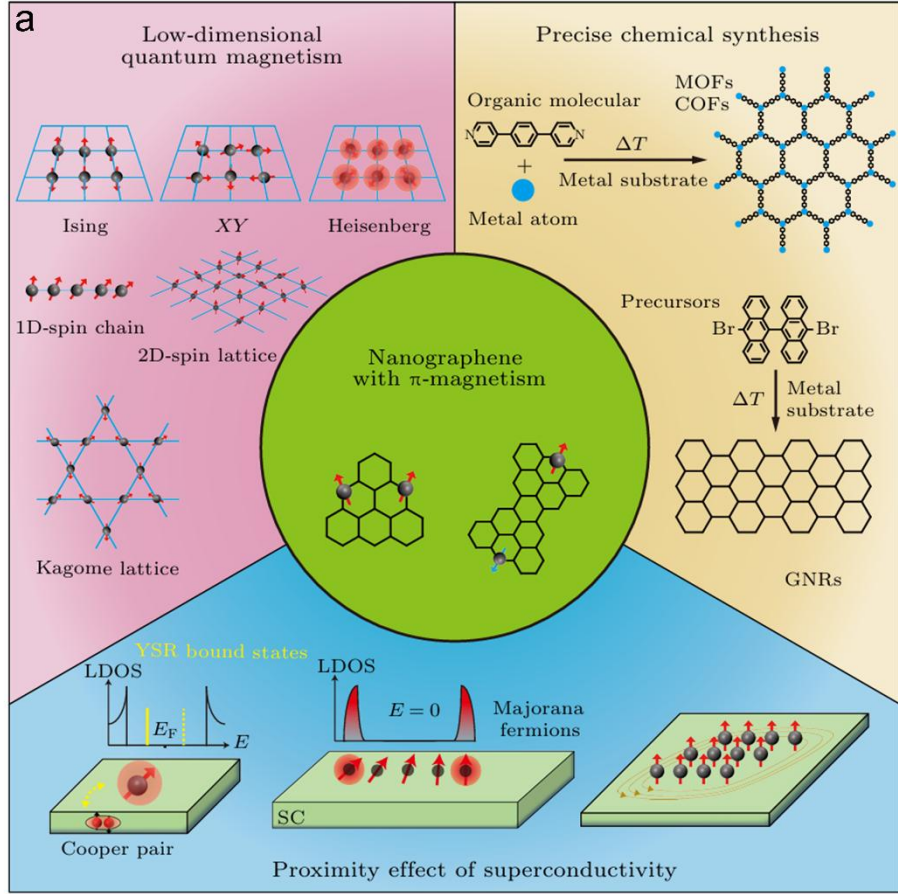


Figure 1.2 (a) Main focus on π -magnetism through precise nanographene synthesis, quantum magnetism, and interaction with superconductivity;¹⁹ (b–d) Triangulene on Xe with AFM and STS results;²⁰ (e–h) Truxene-5,10,15-triyl on NaCl/Cu(111) with DFT-calculated molecular orbitals and dI/dV spectra;²¹ (i–n) Spin-state tuning in ETRI via electron-induced H removal, revealed by STM, STS, and Hubbard simulations.²²

Driven by the need for localized spin control, research has shifted toward π -radicals, whose unpaired p-orbital electrons endow these carbon-based species with intrinsic magnetic moments.^{18,23} Their open-shell electronic configuration directly links electronic structure to magnetism, enabling interactions with external magnetic fields, neighboring spins, or conduction electrons in metallic substrates, and thereby offering unique opportunities for constructing low-dimensional magnetic architectures (Figure 1.2(a)).¹⁹ Compared with conventional metal-centered spin systems, π -radicals combine chemical versatility with the compositional purity of p-orbital magnetism, allowing rational design of spin centers with tailored coupling strengths and spatial arrangements.²⁴ Recent breakthroughs have demonstrated this potential: the precise fabrication of triangulene via atomic manipulation of dihydrotriangulene precursors revealed a robust triplet ground state inaccessible to solution chemistry, as shown in Figure 1.2(b–d).²⁰ Another representative example is that truxene-derived triradicals showcased controllable high-spin ($S = 3/2$) states through tip-induced hydrogen cleavage (Figure 1.2(e–h)).²¹ Furthermore, as demonstrated by Jingcheng Li et al., extended triangulene (ETRI) exhibited tunable Kondo resonances, where sequential hydrogen removal switched spin states from $S = 0$ to $S = 1/2$ and $S = 1$ (Figure 1.2(i–n)).²² In addition, aza-triangulene, a nitrogen-doped variant, highlighted how heteroatom substitution reshapes electronic and magnetic properties, even enabling charge transfer to Au(111).²⁵ Together, these examples illustrate how π -radicals provide a versatile platform for designing atomically precise spin systems and advancing quantum magnetism at the single-molecule level.

Since 2025, Federico Frezza et al. and Can Li et al. report the on-surface synthesis of π -radical-based 2D-MOFs,^{26,27} marking a significant step toward integrating π -magnetism into extended crystalline architectures. As shown in Figure 1.3(a–c), Frezza et al. report the specific coordination modes between cobalt centers and organic ligands dictate the local magnetic exchange interactions.²⁶ STM/nc-AFM characterizations and spin excitation mapping reveal that distinct Co-ligand geometries yield unique spin state transitions. Specifically, a 3–3 coupling configuration exhibits a doublet-to-quartet spin transition at ~ 8 mV, whereas a 1–2

coupling configuration induces a sextet-to-quartet transition at a lower energy of $\sim 3\text{--}4$ mV. Another representative example is the open-shell [2]-triangulene-based MOF(O-MOF) reported by Li et al., which is shown in Figure 1.3(d-l).²⁷ The unique geometry of fractal metal-organic frameworks (O-MOFs) provides a distinct platform for engineering exotic electronic properties. A hallmark of these fractal architectures is the emergence of zero-energy topological corner states. Combined theoretical modeling and high-resolution scanning probe imaging have demonstrated that these topological states are highly spatially selective, with dominant electronic localization occurring specifically at the outermost vertices of the fractal network. These experiments demonstrate that the combination of on-surface synthesis with π -radical chemistry provides an important route to atomically precise 2D quantum materials, where spin states can be engineered through choice of linker, node, and substrate. Such frameworks not only expand the chemical toolbox for quantum magnetism but also open pathways toward scalable spintronic platforms and designer quantum phases.

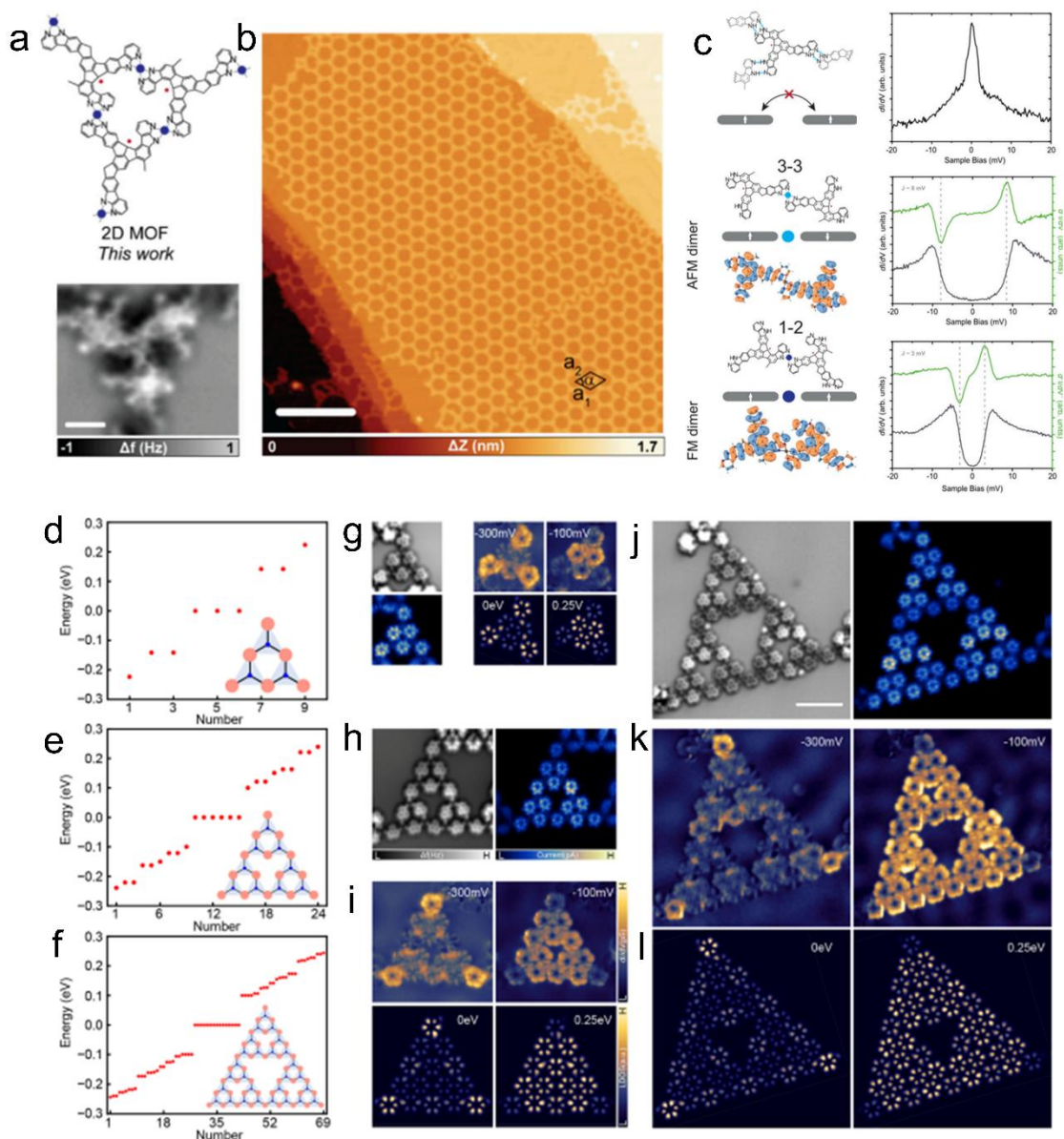


Figure 1.3 Two representative cases of 2D radical-MOFs. (a-c) Structure model, STM/nc-AFM images and dI/dV spectra of 1,3,5-tris(methyl- α -carbolinyl)benzene-based radical MOF.²⁶ (d-l) Fractal O-MOFs exhibit zero-energy topological corner states with electronic localization at the three outermost vertices, confirmed by nc-AFM imaging and tight-binding calculations.²⁷

1.3 Anderson impurity model and Kondo effect

1.3.1 Anderson impurity model

The study of strongly correlated electron systems has been profoundly shaped by the interplay between localized magnetic moments and itinerant conduction electrons. A cornerstone in this field is the Anderson impurity model, introduced by P. W. Anderson in 1961,²⁸ which provides a microscopic framework for understanding the formation of local magnetic moments. The Hamiltonian is conventionally expressed as:²⁹

$$H_{AIM} = \sum_{k,\sigma} \varepsilon_k n_{k\sigma} + \sum_{k,\sigma} V(k) [c_{k\sigma}^\dagger f_\sigma + f_\sigma^\dagger c_{k\sigma}] + E_f n_f + U n_{f\uparrow} n_{f\downarrow}$$

where E_f denotes the localized f states energy, U the Coulomb repulsion, and $V(k)$ the hybridization between localized f -states and conduction electrons. The competition between the Coulomb interaction U and the hybridization term $V(k)$ determines whether a stable local moment emerges. A good perspective for understanding the system Hamiltonian is to decompose it into two parts:

$$H = H_{resonance} + H_{atomic}$$

Where

$$H_{resonance} = \sum_{k,\sigma} \varepsilon_k n_{k\sigma} + \sum_{k,\sigma} V(k) [c_{k\sigma}^\dagger f_\sigma + f_\sigma^\dagger c_{k\sigma}]$$

$$H_{atomic} = E_f n_f + U n_{f\uparrow} n_{f\downarrow} ;$$

From the atomic-limit perspective where $V(k) = 0$, the singly occupied f -state initially forms a magnetic doublet. The system can then be regarded as immersing an f -state atom into an electron sea and gradually turning on the hybridization term. From the complementary adiabatic perspective where $U = 0$, the system begins as a non-interacting resonant ground state, with the Coulomb interaction U subsequently dialed up.

A key parameter to describe the Anderson impurity physics is the resonance width of hybridization between f -state and conduction electrons (Bloch wave):

$$\Delta = \pi \sum_k |V(k)|^2 \delta(\varepsilon_k - \mu) = \pi V^2 \rho$$

with ρ the conduction electron density of states at the Fermi level. This resonance width governs the coupling strength between local spins and conduction electrons and plays a central role in the Kondo effect.

1.3.2 Kondo effect

In 1964, Jun Kondo explained the low-temperature resistivity anomaly in metals with dilute magnetic impurities using the s-d exchange model, showing that antiferromagnetic exchange scattering between localized spins and conduction electrons gives rise to this phenomenon.³⁰ However, Jun Kondo only made such assumptions but neither described the microscopic origin of the antiferromagnetic exchange J nor explained the elimination of valence fluctuations. To overcome these fundamental shortcomings, Schrieffer and Wolff (1966) developed the celebrated Schrieffer–Wolff transformation, starting from the more fundamental Anderson impurity model.³¹ By means of a canonical transformation that systematically projects out high-energy charge fluctuations at the energy scales $\Lambda_I = E_f + U$ and $\Lambda_{II} \approx |E_f|$ in the large- U limit, virtual superexchange processes naturally generate an effective low-energy Hamiltonian—precisely the Kondo s-d model—featuring an antiferromagnetic exchange coupling in the symmetric Anderson model case:

$$J = V^2 \left(\frac{1}{\Delta E_1} + \frac{1}{\Delta E_2} \right) = \frac{4V^2}{U} > 0$$

To clearly describe Kondo model, electron spin-density operator $\vec{\sigma}(0)$ was introduced to treat the effective interaction mediated by virtual charge fluctuations:

$$H_K = J \vec{\sigma}(0) \cdot \vec{S}_f$$

Where S_f is the local moment spin. Therefore, the formal Kondo model that consist of the interaction between local spin and conduction electrons can be written as:

$$H = \sum_{k,\sigma} \varepsilon_k C_{k\sigma}^\dagger C_{k\sigma} + J \vec{\sigma}(0) \cdot \vec{S}_f$$

Physically, the antiferromagnetic exchange coupling ($J > 0$) drives the formation of a many-body Kondo singlet ground state at sufficiently low temperatures. The itinerant conduction

electrons are repeatedly scattered by the local spin, leading to the formation of an antiferromagnetic collective correlation cloud around the magnetic impurity. This cloud gradually screens the local magnetic moment, resulting in a spin-singlet many-body state, Kondo screening, in which the local spin is completely screened by the surrounding conduction-electron cloud (Figure 1.4(a-b)). The characteristic energy scale of this screening is the Kondo temperature T_K , below which the system crosses over from a free local moment to a screened singlet. Schrieffer–Wolff transformation not only supplies a rigorous microscopic foundation for the Kondo model but also establishes a precise correspondence between the Anderson and Kondo Hamiltonians, thereby resolving the limitations of the original phenomenological approach and laying the groundwork for subsequent developments in Kondo physics, heavy-fermion systems, and local Fermi-liquid theory.

To intuitively visualize this cross-scale physical evolution, a renormalization group (RG) flow diagram (Figure 1.4(c)) elegantly illustrates the trajectory of the system across different energy scales Λ . As the energy scale decreases, the high-energy charge degrees of freedom are integrated out, driving the system from the valence fluctuation regime of the full Anderson model ($\Lambda_1 = E_f + U$) into the local moment regime ($\Lambda_1 = -E_f$) governed by the effective Kondo Hamiltonian. Upon further cooling below the characteristic Kondo temperature ($\Lambda \sim T_K$), the flow trajectories universally converge toward a strong-coupling fixed point, characterizing the complete screening of the magnetic impurity and the emergence of a local Fermi-liquid state.

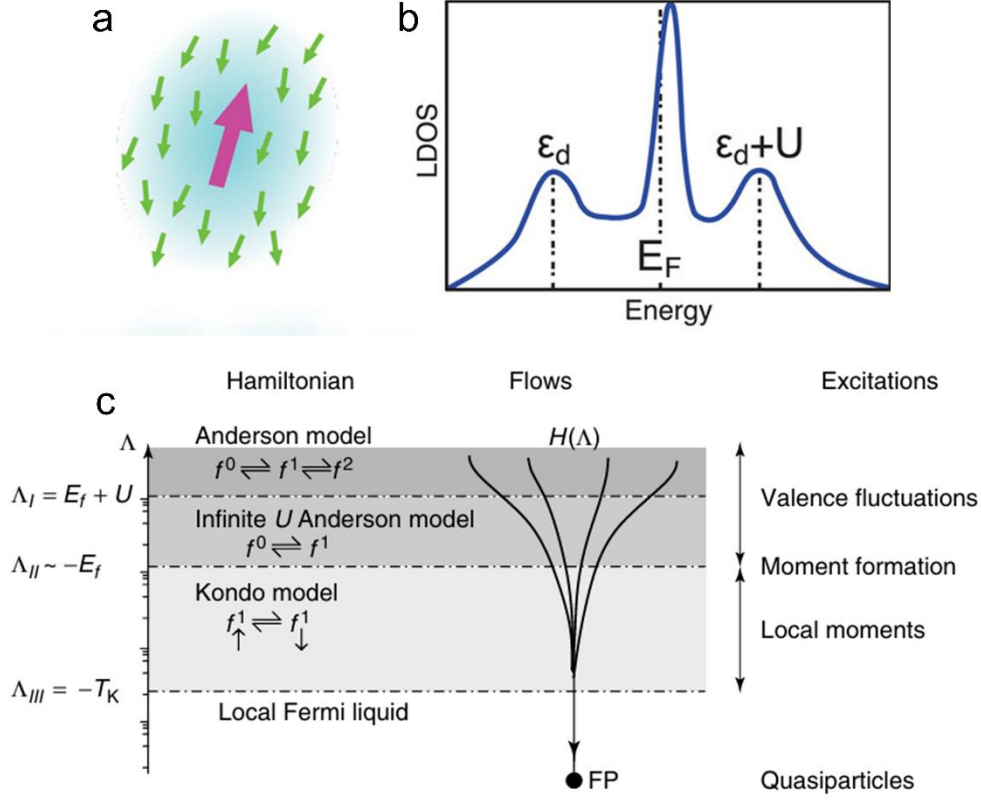


Figure 1.4 (a-b) Scheme of Kondo screening and the LDOS feature at $T < T_K$.³² (c) Crossover energy scales in the Anderson model: below scale I, valence fluctuations into doubly occupied states are suppressed, leaving the infinite- U Anderson model; below scale II, all valence fluctuations vanish and only spin degrees of freedom remain, coupled to conduction electrons via the Kondo interaction; below scale III, the Kondo scale flows to strong coupling, the local moment is screened, and a local Fermi liquid emerges.

1.4 Kondo physics and heavy fermion system

Beyond the physics of Kondo singlets, Doniach proposed an interesting model—Kondo lattice model (KLM, by Kasuya, 1956)³³—to describe the heavy-electron materials:

$$H = \sum_{k\sigma} \epsilon_k c_{k\sigma}^\dagger c_{k\sigma} + J \sum_j \vec{S}_j \cdot c_{k\alpha}^\dagger \vec{\sigma}_{\alpha\beta} c_{k,\beta} e^{i(k'-k) \cdot R_j}$$

The Kondo lattice model describes conduction-electron dispersion and their exchange interaction with localized magnetic moments. Start from Kondo singlet picture, when a second local spin is introduced into the system, the scattered conduction electrons will form a Friedel

oscillation to affect the first spin,³⁴ which is the famous Ruderman-Kittel-Kasuya-Yosida (RKKY) interaction:

$$J_{RKKY}(r) \approx -J_\rho \frac{\cos 2k_F r}{k_F r}$$

Doniach introduced two important scales in Kondo lattice, the Kondo temperature T_K for single magnetic moment and the RKKY temperature T_{RKKY} for the RKKY interaction:

$$T_K = D e^{-1/(2J_\rho)}$$

$$T_{RKKY} = J_\rho^2$$

A key perspective to understand the KLM is the competition between spin localization (Kondo screening) and itinerant nature of conduction electrons (RKKY interaction), which is described by the Doniach phase diagram (Figure 1.5(a)). When $T_K > T_{RKKY}$, the Kondo lattice forms a coherent heavy-fermion liquid: local moments are fully screened, producing quasiparticles with enormously enhanced effective mass ($\frac{m^*}{m} \sim \frac{qD}{T_K}$), an enlarged Fermi surface including f-electron contributions, and a Kondo resonance near the Fermi level. As Kondo coherence enhances, this resonance may further induce the opening of a hybridized gap. This picture explains the anomalously large specific heat, transport anomalies, and unconventional superconductivity in heavy-fermion metals. In contrast, when $T_K < T_{RKKY}$, magnetic order emerges, with the quantum critical point between these regimes ($T_K \approx T_{RKKY}$) central to modern unconventional heavy-fermion research. Microscopically, the Kondo lattice model arises from the Anderson lattice via the Schrieffer–Wolff transformation, which generates an antiferromagnetic exchange coupling between local moments and conduction electrons. Large-N mean-field theory and dynamical mean-field theory further reveal how hybridization drives the evolution from localized spins to coherent heavy quasiparticles, and how filled heavy bands lead to insulating behavior in Kondo insulators.

A more profound view of the Kondo lattice goes beyond a simple collection of independent Kondo singlets. To intuitively visualize this spatial and thermodynamic evolution, Figure 1.5(b-d) illustrates the progression from isolated magnetic impurities to a macroscopic quantum state. The system begins with individual Kondo singlets, where conduction electrons screen isolated local spins (Figure 1.5(b)), accompanied by the RKKY interaction mediating non-local spin-

spin coupling (Figure 1.5(c)). In a periodic array—the Kondo lattice (Figure 1.5(d))—screening becomes a collective process. This coherent hybridization between localized moments and itinerant electrons gives rise to heavy quasiparticles, an enlarged Fermi surface and, in certain cases, a hybridization gap near the Fermi level. At the same time, the same conduction-electron bath mediates indirect magnetic exchange between local moments, giving rise to RKKY interactions. The essence of the Kondo lattice is therefore the competition and coexistence between local screening, magnetic exchange and electronic coherence. Within this framework, the Kondo lattice provides a unified description of how localized spins acquire itinerant character, how heavy-fermion bands emerge, and how magnetic order, quantum criticality and unconventional superconductivity can arise from the same microscopic ingredients.

A representative experimental realization of this heavy-fermion physics is found in artificial van der Waals heterostructures by Peter Liljeroth’s group, such as the 1T-TaS₂/1H-TaS₂ system (Figure 1.5(e)). 1T-TaS₂ layer acts as a Mott insulator hosting localized magnetic moments, while the metallic 1H-TaS₂ layer provides the itinerant conduction electron bath. The interlayer Kondo exchange coupling J_K and spin-spin interaction J_H entangle these two subsystems. As schematically illustrated in Figure 1.5(f–i), the interaction generates a strongly correlated, flat Kondo resonance band from the 1T layer. When this narrow flat band hybridizes with the dispersive conduction band of the 1H layer, it avoids band crossing and opens a heavy-fermion gap near the Fermi level. This platform captures the microscopic essence of the Kondo lattice model, providing direct momentum-space and real-space evidence for the emergence of heavy quasiparticles.

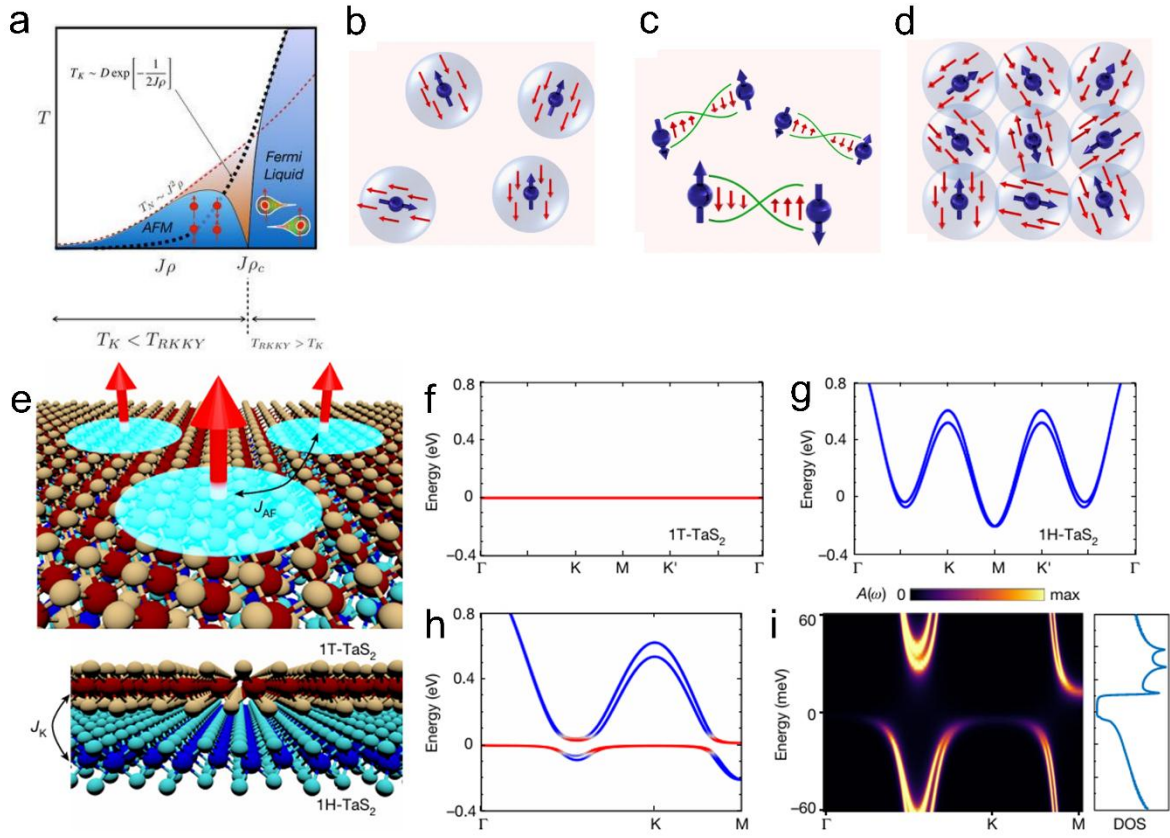


Figure 1.5 (a) Doniach phase diagram.³⁵ (b-d) Scheme of Kondo singlets, RKKY interaction and Kondo lattice.³⁶ (e) 1T-TaS₂/1H-TaS₂ heterostructure with 1T-localized moments and 1H-itinerant electrons, linked by Kondo exchange coupling J_K and spin-spin interaction J_{AF} .³⁷ (f-i) Schematic illustration of heavy-fermion gap formation: the flat Kondo band of 1T-TaS₂ hybridizes with the conduction band of 1H-TaS₂, opening a strongly correlated gap near the Fermi level.³⁷

1.5 Artificial intelligence-assisted STM study of molecular systems

The ability to manipulate matter at the atomic scale has long been a central aspiration in condensed matter physics and materials science. Since the pioneering demonstration of atomic manipulation by STM in 1990,³⁸ researchers have constructed artificial quantum structures (AQS) with unprecedented precision, enabling explorations of quantum simulation,^{39,40} memory storage,^{41,42} quantum information,^{24,43} and magnetism.^{44,45} However, conventional STM manipulation remains heavily dependent on human operators, requiring extensive time and effort to assemble even modest structures. This reliance on manual operation has limited

scalability and hindered systematic investigation of collective quantum phenomena in larger molecular architectures.

Recent advances in artificial intelligence (AI) provide a transformative pathway to overcome these limitations. By integrating machine learning and reinforcement learning algorithms, STM can autonomously recognize molecular configurations, optimize operational parameters, and execute site-specific manipulations with adaptive precision.⁴⁶ As shown in Figure 1.6(a-b), CARP framework conceptualizes an "AI-chemist" system that elevates single-molecule manipulation from simple automation to intelligent synthesis. By integrating expert-trained deep neural networks with scanning probe microscopy, the system effectively executes autonomous, site-selective molecular reactions (e.g., cyclodehydrogenation) to construct specific quantum π -magnets. Furthermore, analyzing these trained models extracts underlying physical and chemical parameters, complementing theoretical calculations and guiding the discovery of novel reaction mechanisms at the single-molecule level.⁴⁶ Deep learning approaches have already demonstrated expert-level image recognition and automated tip conditioning, while reinforcement learning enables self-optimization and autonomous reaction control.⁴⁷⁻⁵¹ A representative example is shown in Figure 1.6(c-d), the autonomous manipulation system operates through a seamless integration of automated structural recognition and reinforcement learning (RL).⁵² Computer vision techniques first identify the molecule's precise location, orientation, and local chemical state. This digitized structural information is fed into an advanced SAC policy network, which strategically navigates a multi-dimensional action space to determine the optimal STM tip position, voltage, and current for site-specific manipulation. By analyzing real-time electronic feedback (current and voltage traces) during the tip-induced processes, the AI agent can autonomously classify reaction outcomes and guide subsequent synthetic steps with single-bond precision. These developments mark the emergence of AI-assisted STM as a powerful tool for studying molecular systems, offering the potential to construct complex nanostructures with reproducibility, efficiency, and scalability.

Extending AI-driven STM beyond isolated molecules or small clusters toward large-scale molecular assemblies opens new opportunities to probe emergent quantum phenomena. In particular, molecular systems with tailored spin states and charge⁵³⁻⁵⁵ provide fertile ground for exploring the interplay between magnetism, superconductivity, and quantum coherence. AI-assisted STM thus represents not only a technical advance in nanoscale fabrication but also a

conceptual leap toward realizing atomically precise architectures for next-generation quantum matter.

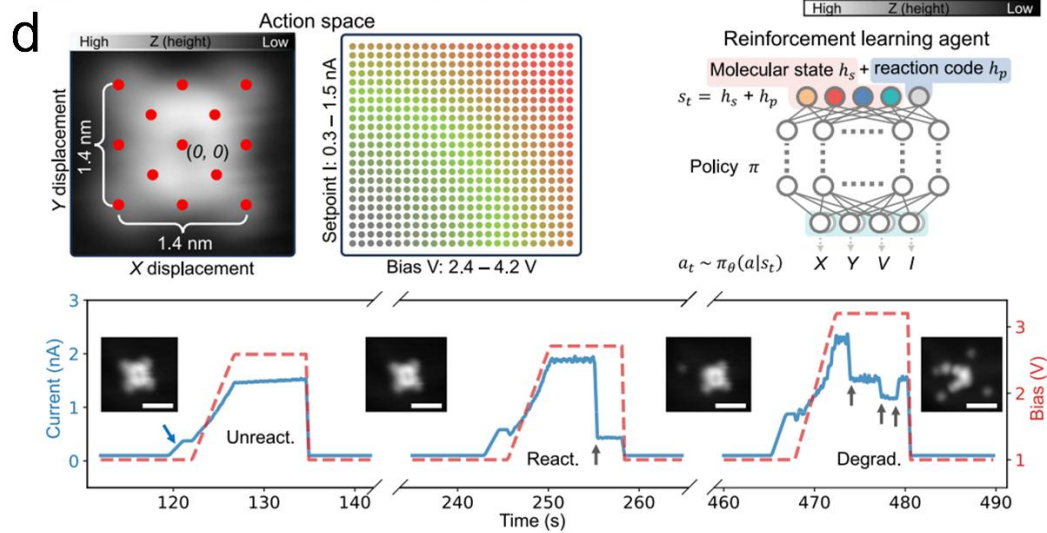
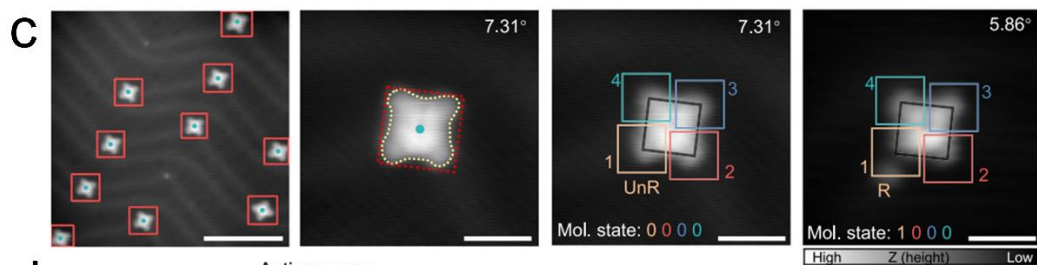
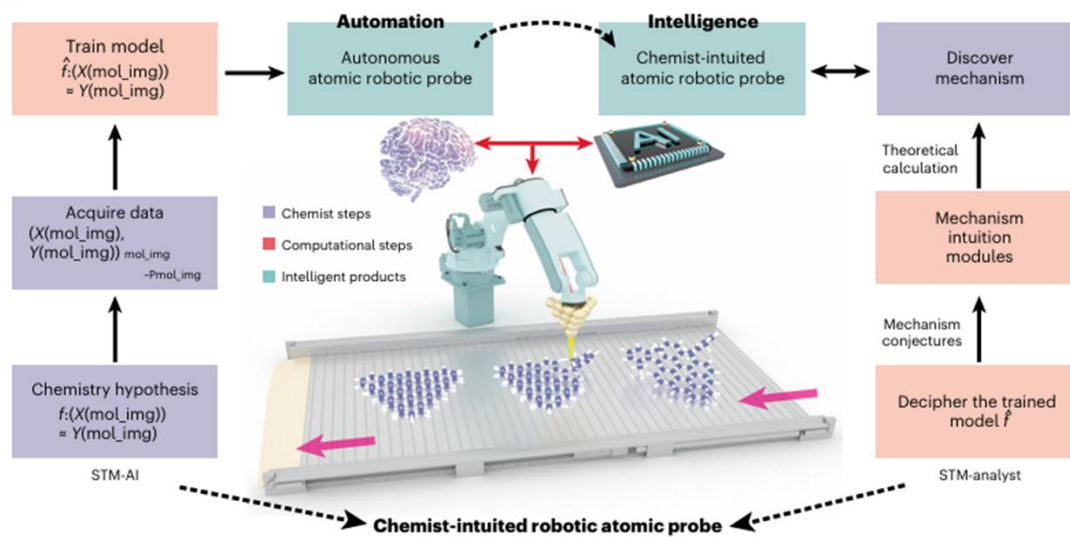
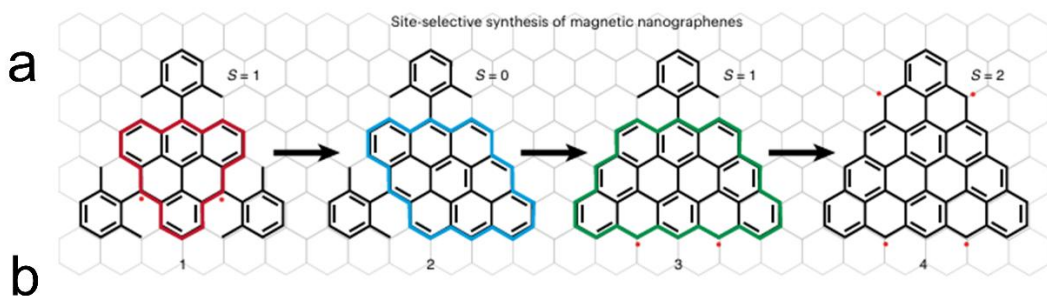


Figure 1.6 (a) The routine of site-selective probe-induced synthesis of nanographene π -magnet. (b) Workflow of AI-STM for precise chemical synthesis.⁴⁶ (c-d) Workflow of reinforcement learning-guided STM molecular search, recognition, and manipulation for 5,10,15,20-tetra(4-bromophenyl) porphine molecules.⁴⁹

1.6 Organization of the thesis

Chapter 2 presents the experimental techniques together with their theoretical foundations, covering scanning tunneling microscopy (STM), scanning tunneling spectroscopy (STS), and additional methods such as ultra-high vacuum (UHV), low-temperature systems, and sample preparation.

Chapter 3 investigates finite one-dimensional (1D) π -radical chains constructed by site-selective tip-induced dehydrogenation of TPM molecules in a Ni-TPM MOF on Au(111). By combining site-resolved STS with mean-field modeling, this chapter analyzes the evolution from isolated Kondo-active radicals to finite exchange-coupled radical chains governed by competing Kondo screening and inter-radical exchange.

Chapter 4 extends the programmable radical platform to finite two-dimensional molecular spin lattices. Triangular clusters with different sizes are constructed and characterized by site-resolved STS, revealing a size-dependent evolution from local Kondo-like resonances to gap-like spectral suppression near the Fermi level.

Chapter 5 investigates how substitution of the metal centers modifies the electronic and magnetic properties of the radical MOF platform. After replacing Ni with Fe, d-TPM forms a SOMO-Fe-*d* hybridized state that can be locally gated toward E_F , where it develops a soft-gap-like LDOS suppression. This chapter highlights metal-center substitution as a chemical strategy for tuning orbital hybridization and correlation-driven electronic behavior in radical MOFs.

Chapter 6 develops an AI-assisted STM strategy for scalable single-molecule lithography. Reinforcement-learning-optimized manipulation parameters are used to autonomously construct large and programmable radical lattices with high yield.

Finally, Chapter 7 concludes the thesis with a summary and outlook for future research.

The thesis progresses from physical understanding to scalable fabrication. Chapter 3 first establishes the Ni-TPM platform as a programmable radical spin system in one-dimensional chains. Chapter 4 extends this platform to finite two-dimensional lattices and examines the emergence of collective spectral features. Chapter 5 shows the electronic properties tunability of TPM-MOF platform by substituting metal centers with Fe atoms. Chapter 6 then addresses the fabrication bottleneck by introducing AI-assisted single-molecule lithography for autonomous construction of large-scale radical lattices.

Chapter 2

Experimental Techniques and Theoretical Background

Scanning tunneling microscopy (STM) and scanning tunneling spectroscopy (STS) are among the most powerful tools for probing surfaces, adsorbates, and low-dimensional nanostructures with atomic-scale spatial resolution. STM provides real-space topographic information and, under appropriate conditions, information about the local electronic structure. STS extends this capability by measuring the energy dependence of the tunneling current, thereby enabling spatially resolved characterization of the local density of states (LDOS). Because the tunneling process is localized and sensitive to the tip-sample distance, STM/STS can be used not only for imaging and spectroscopy, but also for atomic- and molecular-scale manipulation. This section summarizes the fundamental theory, instrumentation, imaging modes, spectroscopic principles, and tip-manipulation mechanisms of STM/STS.

2.1 Scanning tunneling microscopy (STM)

2.1.1 Theory of STM

The physical foundation of STM is quantum-mechanical tunneling.⁵⁶ In classical mechanics, an electron with energy lower than a potential barrier cannot pass through that barrier. In quantum mechanics, however, the electronic wave function penetrates into the classically forbidden region and decays exponentially rather than vanishing abruptly. If the barrier is sufficiently thin, the wave function has a finite amplitude on the other side of the barrier, giving a finite probability for electron transmission.

For a one-dimensional barrier in the vacuum gap between tip and sample, the time-independent Schrodinger equation can be written as

$$\left[-\frac{\hbar^2}{2m} \frac{d^2}{dz^2} + U(z) \right] \psi(z) = E\psi(z)$$

where m is the electron mass, $U(z)$ is the potential energy barrier, and E is the electron energy. In the classically forbidden region, where $E < U$, the equation becomes

$$\frac{d^2\psi(z)}{dz^2} = \kappa^2\psi(z)$$

with the decay constant

$$\kappa = \sqrt{\frac{2m(U - E)}{\hbar^2}}$$

The wave function in the vacuum barrier therefore has the form

$$\psi(z) \propto e^{-\kappa z}$$

Because the transmission probability is proportional to $|\psi|^2$, the tunneling probability decreases exponentially with barrier width:

$$T \propto e^{-2\kappa z}$$

The tunneling current follows the same exponential dependence:

$$I \propto e^{-2\kappa z}$$

For a typical work function of a few electronvolts, κ is of the order of $1 \text{ \AA}^{-1}$. As a result, a change in tip-sample distance of only 1 Å can change the tunneling current by approximately one order of magnitude. This extreme distance sensitivity is the key reason STM can achieve atomic-scale vertical resolution.

A more rigorous treatment of the tunneling current was developed by Bardeen.^{57,58} In this approach, the tip and sample are treated as two weakly coupled electrodes, and the tunneling current is obtained from the transition rate between tip states and sample states. In a general form, the current can be expressed as

$$I = \frac{2\pi e}{\hbar} \sum_{\mu, \nu} [f(E_\mu) - f(E_\nu + eV)] |M_{\mu\nu}|^2 \delta(E_\mu - E_\nu)$$

where $f(E)$ is the Fermi-Dirac distribution function, V is the sample bias, E_μ and E_ν are the energies of the tip and sample states, and $M_{\mu\nu}$ is the tunneling matrix element. The matrix element describes the overlap between the unperturbed wave functions of the tip and sample across the vacuum barrier.

The difficulty in applying Bardeen's formula directly is that the atomic structure and electronic wave function of the tip apex are usually unknown. The most commonly used approximation in STM is therefore the Tersoff-Hamann approximation.⁵⁹⁻⁶¹ In this model, the tip apex is approximated as a locally spherical s -wave emitter, the tip density of states is assumed to be nearly constant over the relevant energy range, and the tunneling matrix element is treated as weakly energy dependent. Under low-temperature and low-bias conditions, the tunneling current becomes approximately proportional to the sample LDOS at the position of the tip:

$$I(\mathbf{r}_0, V) \propto V \rho_s(\mathbf{r}_0, E_F)$$

where $\rho_s(\mathbf{r}_0, E_F)$ is the sample LDOS at the Fermi energy evaluated at the tip position $\mathbf{r}_0$. More generally, at finite bias,

$$I(\mathbf{r}_0, V) \propto \int_{E_F}^{E_F+eV} \rho_s(\mathbf{r}_0, E) T(E, V) dE$$

where $T(E, V)$ is the energy- and bias-dependent transmission coefficient. This expression is central to the interpretation of STM images: an STM image is not a purely geometric height map, but a convolution of surface morphology and local electronic structure.

2.1.2 General setup of STM

A typical STM system contains three essential components: an atomically sharp metallic tip, a conductive or semiconductive sample, and an electronic feedback controller coupled to piezoelectric scanners (See Figure 2.1). Together, the probe and target sample configure a metal–vacuum–metal barrier. Upon the application of an external bias potential across this junction, electrons undergo quantum mechanical tunneling through the classically forbidden vacuum gap, thereby generating a measurable tunnel current that typically scales within the picoampere-to-nanoampere regime.

Tungsten and platinum–iridium (PtIr) alloys serve as the primary source materials for fabricating the microscopic tips. A strict requirement is imposed on the tip topology: the apex radius must be refined until electron tunneling becomes highly localized, occurring predominantly via the outermost single atom. The sample must be electrically conductive, or at least sufficiently coupled to a conducting substrate, so that tunneling current can flow. The relative position between the tip and sample is controlled by piezoelectric elements, which

allow sub-angstrom displacement in the vertical direction and precise raster scanning in the lateral directions.

The feedback controller plays a central role in conventional STM imaging. It compares the measured tunneling current with a user-defined setpoint current. If the measured current is higher than the setpoint, the feedback retracts the tip; if the current is lower, the feedback brings the tip closer to the sample. In this way, the system maintains a nearly constant tunneling current while the tip scans across the surface.

High-resolution STM generally requires ultrahigh-vacuum and low-temperature conditions. UHV minimizes contamination of the tip and sample surface, while low temperature suppresses thermal diffusion, thermal drift, and vibrational noise. In a low-temperature UHV STM system, the STM chamber is commonly connected to a preparation chamber and a load-lock chamber. Ion getter pumps, titanium sublimation pumps, turbomolecular pumps, and backing pumps are used to maintain pressures down to approximately 10^{-10} mbar. A cryostat using liquid nitrogen and liquid helium provides thermal shielding and cooling, allowing operation near the liquid helium temperature.

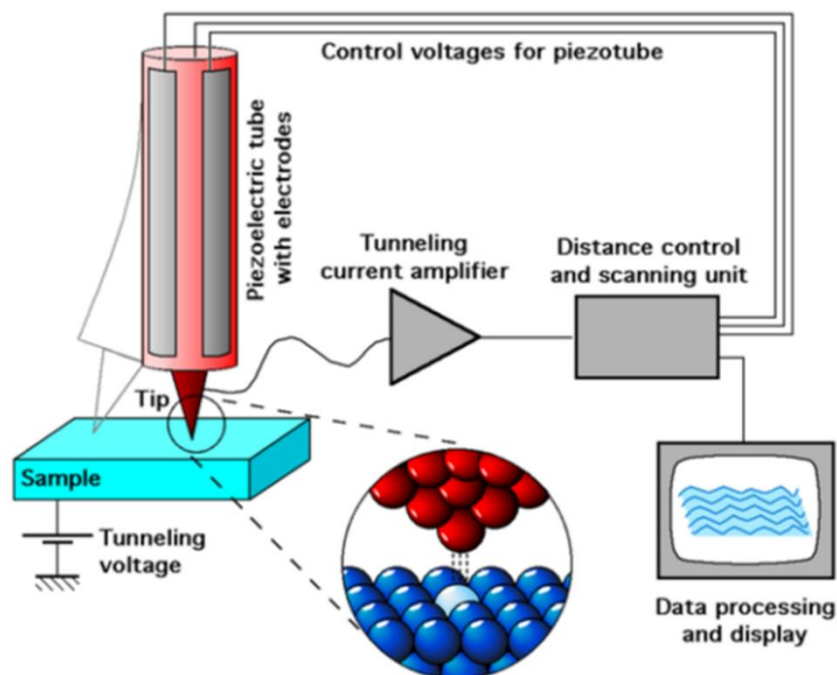


Figure 2.1 Schematic of a scanning tunneling microscope. Reproduced from Wikimedia Commons, created by Michael Schmid, TU Wien (Licensed under CC BY-SA 2.0).

2.1.3 Imaging with STM

STM imaging is based on recording how the tunneling current changes as the tip is scanned over a surface. The current depends exponentially on the tip-sample distance and also on the local electronic states available for tunneling. A simplified expression for the tunneling current at position (x, y) is:⁵⁹

$$I(x, y, z, V) \propto \rho_s(x, y, E_F + eV)e^{-2\kappa z}$$

This equation illustrates the two main contributions to STM contrast. First, a geometrically higher part of the surface reduces the tip-sample distance and increases the current. Second, a region with larger LDOS at the tunneling energy also increases the current. Therefore, apparent height in STM must be interpreted carefully: bright contrast may correspond to true topographic protrusion, enhanced LDOS, or both.

The most common imaging mode is constant-current mode.⁶² In this mode, the feedback loop adjusts the vertical tip position to maintain a constant current. The recorded height signal $z(x, y)$ is used to form the STM topograph. If the current is fixed at a setpoint value I_0 , the approximate relation can be rearranged as:

$$I_0 \propto \rho_s(x, y, E)e^{-2\kappa z(x, y)}$$

which gives:

$$z(x, y) \approx \frac{1}{2\kappa} \ln \rho_s(x, y, E) + \text{constant}$$

This expression shows that a constant-current STM image is effectively a contour map of constant integrated LDOS, rather than a direct map of nuclear positions. For unknown surfaces, constant-current imaging is safe and robust because the feedback protects the tip from crashing into surface protrusions.

A second imaging mode is constant-height mode.⁶² Here, the feedback loop is disabled and the tip is scanned at a fixed height while the tunneling current is recorded. Because the tip height is fixed, the current signal is more directly sensitive to lateral variations in LDOS and surface corrugation. Constant-height mode can provide very high spatial resolution and faster imaging, but it is normally used only on sufficiently flat surfaces because the risk of tip crash is higher.

In molecular systems, conventional STM images often reflect the LDOS near the applied bias and may not directly reveal the chemical skeleton. To obtain bond-resolved contrast, the tip can be functionalized with a small molecule such as CO.⁶³ In this regime, the probe particle at the tip apex responds to short-range Pauli repulsion from the molecule. The lateral relaxation of the probe particle modifies the tunneling conductance and produces apparent intramolecular contrast. This approach is particularly powerful for identifying molecular structures, although electronic states near the Fermi level can still contribute to the contrast and must be considered in the interpretation.

2.2 Scanning tunneling spectroscopy (STS)

2.2.1 Theory of STS

Scanning tunneling spectroscopy (STS) uses the same tunnel junction as STM, but instead of measuring current only at one bias during lateral scanning, STS measures the current as a function of bias voltage at a selected position. The resulting $I(V)$ curve contains information about the energy-dependent tunneling channels between tip and sample. The most important quantity in STS is differential conductance,

$$\frac{dI}{dV}$$

which, under suitable approximations, is proportional to the sample LDOS at the energy selected by the applied bias.^{62,64}

Starting from the finite-bias tunneling current,

$$I(V) \propto \int_0^{eV} \rho_s(E) T(E, eV) dE$$

where the tip density of states has been assumed constant, differentiating with respect to bias gives:

$$\frac{dI}{dV} \propto e \rho_s(eV) T(eV, eV) + \int_0^{eV} \rho_s(E) \frac{\partial T(E, eV)}{\partial (eV)} dE$$

The first term is directly related to the sample LDOS at energy $E_F + eV$. The second term is a background contribution from the energy dependence of the transmission coefficient. If $T(E, V)$

varies smoothly with energy, then the sharp spectral structures in dI/dV mainly reflect the sample LDOS:

$$\frac{dI}{dV}(\mathbf{r}, V) \propto \rho_s(\mathbf{r}, E_F + eV)$$

This relationship is the theoretical basis for using STS to identify molecular orbitals, band edges, surface states, Kondo resonances, superconducting gaps, and other electronic features.

In practice, dI/dV is usually measured using a lock-in amplifier. A small sinusoidal modulation is added to the DC sample bias:

$$V(t) = V_{dc} + V_{ac}\sin(\omega t)$$

The current response can be expanded as a Taylor series:

$$I(V + V_{ac}\sin\omega t) = I(V) + \frac{dI}{dV}V_{ac}\sin\omega t + \frac{1}{2}\frac{d^2I}{dV^2}V_{ac}^2\sin^2\omega t + \dots$$

The component of the current oscillating at the modulation frequency ω is proportional to dI/dV . The lock-in amplifier selectively detects this component, strongly improving the signal-to-noise ratio. The energy resolution of STS is limited by both thermal broadening and modulation broadening. This is one reason low-temperature operation is essential for high-resolution STS.

2.2.2 Electronic properties characterized by STS

STS is widely used to characterize the local electronic structure of atoms, molecules, and nanostructures on surfaces. Since dI/dV approximately follows the LDOS, peaks and dips in the spectrum can be assigned to local electronic states or many-body resonances. For molecular adsorbates, occupied molecular states usually appear at negative sample bias and unoccupied states at positive sample bias, depending on the bias convention. The energy separation between frontier orbital resonances can provide an experimental estimate of the transport gap or quasiparticle gap.

For a molecular orbital $\psi_n(\mathbf{r})$ with energy E_n , the LDOS can be written as:

$$\rho_s(\mathbf{r}, E) = \sum_n |\psi_n(\mathbf{r})|^2 \delta(E - E_n)$$

Therefore, the spatial intensity of a dI/dV signal at a particular resonance energy reflects the spatial distribution of the corresponding electronic state. This is the basis of orbital imaging using STS.

To obtain spatially resolved electronic information, one can perform grid-mode spectroscopy. In the grid-mode, the microscope measures a dI/dV spectrum at every point in a predefined two-dimensional area. From this dataset, conductance maps can be extracted at selected bias voltages. Such maps reveal how the LDOS is distributed at a given energy. In many cases, experimental dI/dV maps can be compared with calculated LDOS maps from density functional theory or tight-binding models, allowing assignment of spectral features to specific molecular orbitals, band states, or surface states.

Because the measured conductance can be influenced by the setpoint condition and by the exponential distance dependence of tunneling, normalized conductance is often used. A common normalization is:

$$\frac{dI/dV}{I/V}$$

which partially compensates for the slowly varying tunneling background and improves comparison between different spatial positions.⁶⁵ Thus, this normalization must be executed with strict constraints, as the low-current conditions prevalent near zero bias are highly susceptible to division-by-zero artifacts.

More complex electronic and magnetic configurations are accessible via STS. For spin networks and open-shell systems, characteristic features such as spin-split orbitals, Kondo resonances at zero bias, and inelastic spin transitions can be resolved. As a case in point, the screening of a localized spin by conduction electrons yields a Kondo screening cloud, leading to a sharp resonance state near the Fermi edge. Due to quantum interference between the discrete orbital state and the continuum channel, the resulting dI/dV line shape can be described by the simplified Fano equation:

$$\frac{dI}{dV} \propto A \cdot \frac{(q + \epsilon)^2}{1 + \epsilon^2}, \quad \epsilon = \frac{eV - E_0}{\Gamma}$$

Here, the spectral magnitude is scaled by the resonance peak amplitude A as a function of the bias voltage V . E_0 denotes the energy center of the Kondo resonance relative to the Fermi level.

The dimensionless parameter q is the Fano asymmetry factor, which describes the spectral line shape and reflects the quantum interference between the direct tunneling channel (into the substrate's conduction continuum) and the resonant tunneling channel (into the localized Kondo state). Most importantly, Γ represents the intrinsic HWHM of the resonance. The physical significance of Γ is fundamentally tied to the energy scale of the Kondo screening. If the thermal broadening was excluded, the intrinsic Γ is directly proportional to the Kondo temperature, T_K , governed by the relation $\Gamma \sim k_B T_K$, where k_B is the Boltzmann constant. However, under experimental conditions, the measured spectra are subject to both thermal and electronic broadening:

$$\Gamma = \sqrt{(\alpha k_B T_{eff})^2 + (2k_B T_K)^2}$$

$$T_{eff} = \frac{1}{5.4k_B} \sqrt{(5.4k_B T)^2 + (1.7V_{rms})^2}$$

Here, the effective temperature T_{eff} accounts for the combined broadening effects of the lock-in modulation and the Fermi-Dirac distribution.⁶⁶ The expression for Γ originates from approximations based on Fermi liquid theory and NRG calculations, where the dimensionless constant α is typically set to π in specific models or treated as a free parameter for spectral fitting in varied-temperature experiments.⁶⁶⁻⁶⁸ The extracted Γ provides an experimental estimate of the Kondo energy scale and reflects the effective coupling between the localized molecular spin and the substrate conduction electrons.¹³

The instrumental basis of STS is the same as STM, but the measurement procedure is different. A typical point STS measurement proceeds through the following steps. First, the tip is positioned over a selected site of interest. Second, the junction is stabilized at a chosen setpoint current and bias voltage. Third, the feedback loop is disabled to hold the tip-sample distance fixed. Fourth, the bias voltage is swept over the desired range while the current $I(V)$ and the lock-in signal dI/dV are recorded.

STS measurement relies on a stable tunnel junction paired with low-noise electronics and lock-in detection. Setting the lock-in modulation involves a direct physical trade-off. While applying a larger modulation significantly boosts the signal clarity, it inherently smears the spectral line shapes. Conversely, achieving high energy resolution requires keeping this amplitude to a

minimum—a strict condition that places extreme demands on the overall mechanical and electrical quietness of the instrument.

The overall energy resolution reflects the combined contributions from three dominant broadening mechanisms: thermal fluctuations, instrumental modulation, and intrinsic lifetime effects. Qualitatively, this limit can be parameterized as:⁶⁹

$$\Delta E_{\text{eff}} \sim \sqrt{(3.3k_B T)^2 + (\alpha e V_{\text{mod}})^2}$$

where V_{mod} is the modulation amplitude and α is a numerical factor that depends on the convention used for peak or RMS modulation amplitude. This expression emphasizes that both low temperature and small voltage modulation are required for resolving narrow spectral features.

For grid-mode STS, the same measurement is repeated over a grid. At each pixel (x_i, y_j) , a spectrum is recorded:

$$G(x_i, y_j, V) = \left. \frac{dI}{dV} \right|_{(x_i, y_j)}$$

The resulting three-dimensional dataset $G(x, y, V)$ can be expressed either as spectra at selected points or as conductance maps at selected energies. This makes STS a powerful tool to obtain local spectra and real-space electronic-state images.

2.3 Tip manipulation of STM

STM can also be used as an atomically precise manipulation tool. The sharp tip that detects tunneling current can locally modify the adsorbate or surface by applying mechanical force, electric field, or tunneling-electron excitation. This makes STM a unique platform for constructing and modifying matter at the single-atom or single-molecule level.

Several physical mechanisms can contribute to tip manipulation. In lateral manipulation, the tip is brought close enough to an atom or molecule that the tip-adsorbate interaction changes the adsorption potential, allowing the adsorbate to be moved across the surface. This precise control was spectacularly demonstrated by the construction of the famous "IBM" pattern using individual Xenon atoms on a Nickel surface (Figure 2.2a),³⁸ and later utilized to assemble Iron atoms into "quantum corrals" on Cu(111) to confine surface state electrons (Figure 2.2b).⁷⁰ In

vertical manipulation, the adsorbate can be transferred between the surface and the tip. In electron-induced manipulation, tunneling electrons excite vibrational, electronic, or spin states, driving bond cleavage, bond formation, conformational switching, or desorption. In field-induced manipulation, the intense electric field in the tunnel junction lowers an activation barrier or polarizes the adsorbate, making a reaction more likely.

For tip-induced reactions such as dehydrogenation, a simplified energetic criterion is:

$$E_{\text{local}} \gtrsim E_a$$

where E_a is the activation barrier for the reaction and E_{local} represents the local energy supplied through tunneling electrons, electric field, or mechanical interaction. In practice, tip-induced dehydrogenation often proceeds by positioning the tip over a chemically active site, stabilizing the junction at a chosen setpoint, and then applying a voltage pulse. A sudden change in current or tip height can indicate that the reaction has occurred.

The reaction rate under tunneling-electron excitation can be described phenomenologically as:

$$R \propto I^N$$

where I is the tunneling current and N is the number of electrons involved in exciting the reaction pathway. For a one-electron process, $N \approx 1$; for a multi-electron vibrational ladder-climbing process, $N > 1$ may be observed.

In molecular surface science, STM tip manipulation provides a route to deterministic on-surface chemistry. It allows individual molecules to be converted, removed, repositioned, or connected with atomic-level selectivity. A compelling example of this is the tip-induced cross-coupling between 2-iodotriphenylene (IT) and 2,7-dibromopyrene (DBP) on a NaCl/Cu(111) surface, where single-molecule covalent bonds are forged on demand (Figure 2.2c).⁷¹ In the context of

programmable molecular lattices, tip manipulation can therefore function not only as a probe, but also as a lithographic tool for building artificial structures with single-molecule precision.

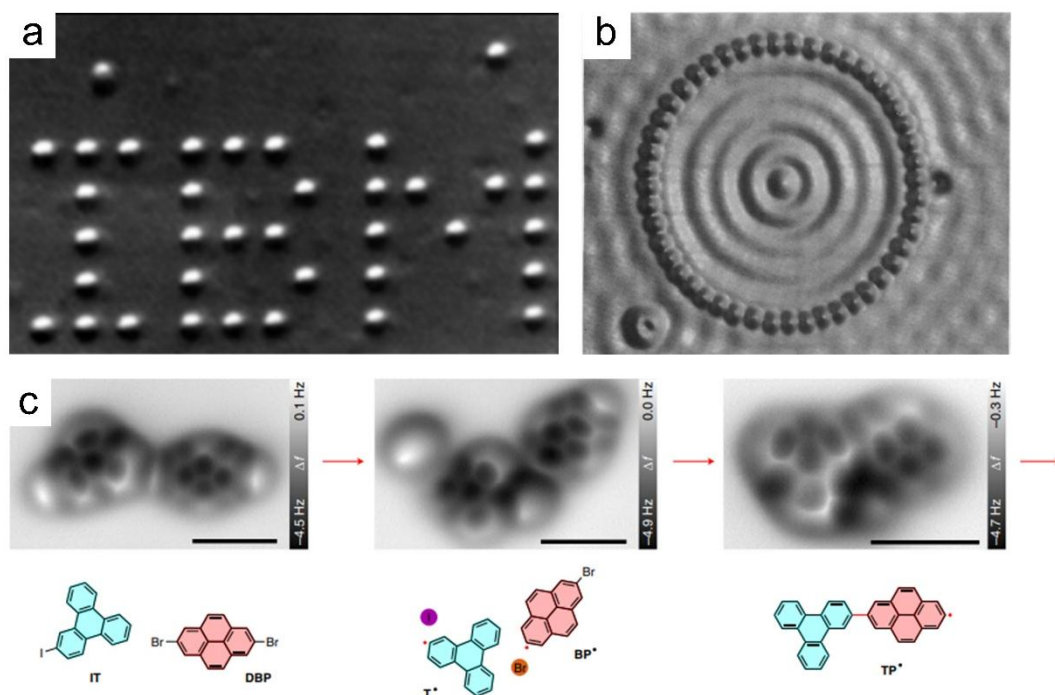


Figure 2.2 Classical examples of atoms/molecules manipulation via STM. (a) Famous “IBM” pattern constructed by Xenon atoms on Nickel surface via STM probe manipulation.³⁸ (b) Quantum corrals of Fe atoms on Cu(111) surface.⁷⁰ (c) Tip-induced cross-coupling between 2-iodotriphenylene (IT) and 2,7-dibromopyrene (DBP) on 2ML NaCl/Cu(111).⁷¹

2.4 Experimental Approaches and Methods

2.4.1 STM instrumentation

Surface characterization was performed utilizing a commercial Createc low-temperature scanning tunneling microscope (LT-STM) operated under ultra-high vacuum (UHV) conditions at a base temperature of 5 K, ensuring both high resolution and stability, and also minimizing thermal drift for both topography and spectroscopy. The experimental setup, schematized in Figure 2.3, comprises distinct functional modules: an STM analysis chamber and a sample preparation chamber, isolated from one another via an integrated gate valve. A specialized ultra-high vacuum pumping network maintains the pressure integrity across these zones. Specifically, the STM main chamber is continuously evacuated by an ion getter pump (IGP) assisted by a

titanium sublimation pump (TSP), sustaining a base pressure of approximately $5\text{E-}10$ mbar and directly housing the cryogenic cryostat. A matching IGP-TSP assembly evacuates the preparation chamber, which is equipped with a dedicated sample manipulator. Rapid sample introduction is facilitated by a fast-entry load lock (LL) chamber, which is backed by a turbomolecular pump (TMP) capable of drawing the pressure down from 1 mbar to a base of roughly $1\text{E-}8$ mbar. All TMPs in the system are supported by a dry scroll roughing pump, which manages the initial exhaust stage from atmospheric levels down to $1\text{E-}1$ mbar.

Low-temperature environments within the setup are established via cryostats filled with liquid helium and liquid nitrogen. A multi-layered shielding architecture is implemented to suppress the boil-off rate of the volatile cryo-liquids. The central element of this architecture is the main 4 K liquid-helium vessel. The mitigation of external radiation and thermal gradients is achieved through successive cryogenic barriers. A 30 K helium exhaust shield serves as the primary barrier, which is subsequently jacketed by a 77 K liquid nitrogen reservoir and its associated

evaporation shroud. Global thermal isolation of the instrument is guaranteed by the surrounding ultra-high vacuum enclosure.

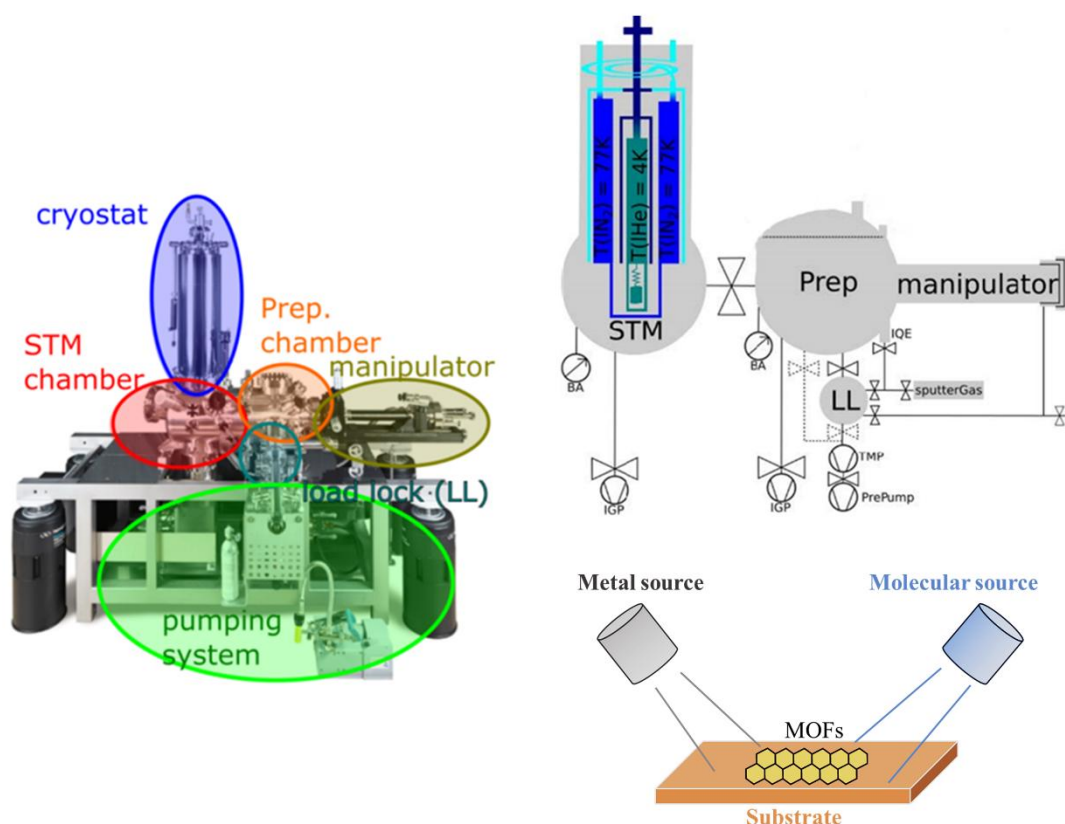


Figure 2.3 Left: The system's primary components; Right: The schematic arrangement of the vacuum unit, cooling system, and the on-surface synthesis setup.

2.4.2 Sample preparation

In-situ sample fabrication and characterization were conducted in a custom ultrahigh vacuum (UHV) system (base pressure $< 5.0 \times 10^{-10}$ mbar) equipped with a CreaTec low-temperature scanning tunneling microscope (STM). Sample preparation consists of two primary stages: substrate cleaning and molecular deposition. All experiments were performed on atomically clean Au(111) substrates, which were prepared through repeated Ar^+ sputtering and annealing cycles. During the sputtering phase, argon gas was introduced into the preparation chamber via a leak valve until the pressure reached $1\text{E-}5$ mbar. The surface was then bombarded with Ar^+ ions for approximately 10 min using an ion gun operated at an acceleration voltage of 0.7 keV and an ion current of 2–3 μA . After recovering the UHV condition, the sample was subsequently annealed at ~ 650 K for 15 min using a filament mounted on the manipulator. This procedure

effectively removes residual contaminants and restores the substrate's crystalline order, yielding large, atomically flat terraces.

For the molecular assembly, 4-[bis(4-cyanophenyl)methyl]benzene-1 carbonitrile (TPM) were thermally evaporated from a Knudsen cell maintained at ~ 428 K onto the metallic substrate. The specific organic molecule used in this study is detailed in Figure 2.4. Subsequently, nickel (Ni) atoms were dosed onto the sample by resistively heating a high-purity Ni source via a direct current power supply (3.2 V, 3.9 A). Iron was deposited on the substrate using an e-beam evaporator. Annealing process was conducted at 135°C for 15 minutes to facilitate the on-surface reaction between TPM molecules and Ni atoms. After the sample preparation, it was transferred directly into the cryogenic STM chamber for topographic and spectroscopic characterizations. All topographic images were acquired in constant-current mode. STS measurements of dI/dV spectra were recorded utilizing a standard lock-in amplifier technique with a modulation voltage of 0.5 mV. Furthermore, dehydrogenation of TPM molecules was achieved via precise tip-induced voltage pulses. Specifically, the STM apex was positioned directly above the center of a target molecule with the feedback loop stabilized at a bias of -0.5 V and a tunneling current of 100 pA. A constant voltage pulse of -4 V was then applied until an abrupt reduction in the tip-sample distance ($\Delta Z > 20$ pm) appeared, indicating successful molecular manipulation.

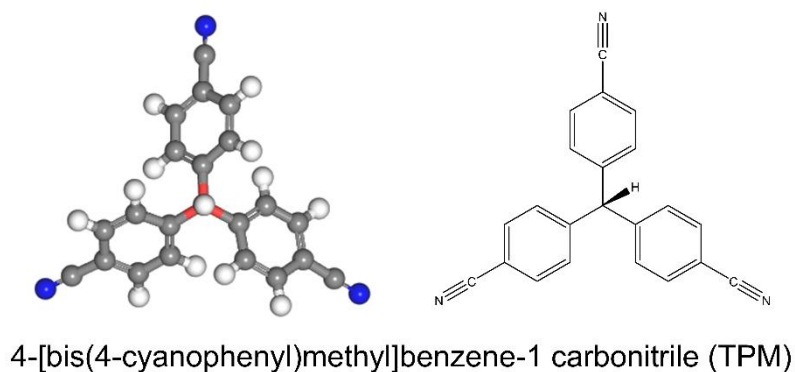


Figure 2.4 Details of the molecules employed in this thesis, including their names and structural models. Sublimation temperature is ~ 428 K.

Chapter 3

Coexistence of Kondo screening and inter-spin coupling in finite-size π -radical chains

3.1 Introduction

Many-body physics, as a central field studying collective behavior in systems with multiple interacting particles, reveals the profound connection between single-particle quantum mechanics and macroscopic quantum phenomena. Within this framework, quantum spin chains stand out as a fundamental model of many-body physics. Despite being composed only of spins arranged in one dimension, spin chains exhibit a wealth of quantum phase transitions and collective excitations, such as antiferromagnetic order in the Heisenberg model and topologically protected states in the Haldane phase.^{72,73} Serving as an ideal testbed for both theory and experiment, quantum spin chains not only provide a foundation for understanding strongly correlated systems but also open pathways to exploring frontier topics including quantum criticality, topological phases, and Kondo physics.

Beyond conventional spin chains constructed from magnetic metal atoms, π -magnetism arising from unpaired π -electrons in organic systems introduces a novel dimension to many-body physics (see Chapter 1.2). π -magnetism offers unique advantages: the chemical tunability of organic molecules enables the design of programmable multi-spin systems. The intrinsically weak spin-orbit coupling of light carbon atoms and the low nuclear spin environment endow carbon-based π -electron systems with long spin coherence times. Together with the delocalized magnetism associated with π -electrons, these features provide an ideal platform for investigating spin-spin interactions and advancing quantum information studies. In 2021, Roman Fasel and co-workers first demonstrated the on-surface synthesis of an $S = 1$ spin chain on the Au(111) surface.⁷⁴ As illustrated in Figure 3.1(a–c), each triangulene monomer, hosting two radical sites, can be regarded as an effective $S = 1$ unit within the organic spin chain. For an open-ended chain with $n = 16$ units, STS data revealed a pronounced zero-bias peak at the Fermi level localized at the edge spins, while the bulk states remained gapped—hallmarks of the Haldane phase in an $S = 1$ chain (See Figure 3.1(c)). In contrast, the zero-bias edge states disappear in a closed-ended chain or loop of the same length, further confirming the topological nature of the Haldane phase under periodic boundary conditions. The spectral weight distribution shown in Figure 3.1(c) highlights the edge-localized character of the excitations, in

excellent agreement with the STS measurements. Later in 2025, Fasel's team successfully realized the $S=1/2$ antiferromagnetic Heisenberg spin chain via a π -magnetism system.⁴⁴ As shown in Figure 3.1(d), each Olympicene monomers contain $S=1/2$ and interact with neighbor spins with antiferromagnetic exchange coupling $J \approx 38$ meV. The experimental results are well described by the antiferromagnetic $S = 1/2$ Heisenberg chain model, whose intrinsic ground state in the thermodynamic limit is gapless. For finite chains, inelastic tunnelling spectroscopy reveals length-dependent spin excitations: even-numbered chains exhibit gapped singlet ground states, whereas odd-numbered chains host a zero-bias resonance associated with an unpaired spin-1/2. As shown in Figure 3.1(e-g), in long chains, the excitation spectrum evolves into a nearly V-shaped continuum, consistent with the gapless behavior predicted by Bethe ansatz.⁷² Furthermore, spatially resolved dI/dV maps display a standing-wave modulation of the zero-bias conductance, in excellent agreement with the calculated spin spectral weight, thereby providing direct evidence for the existence of spinons in one-dimensional nanographene chains (See Figure 3.1(h-i)). These studies have established π -magnetism spin systems as an ideal platform for exploring many-body physics.

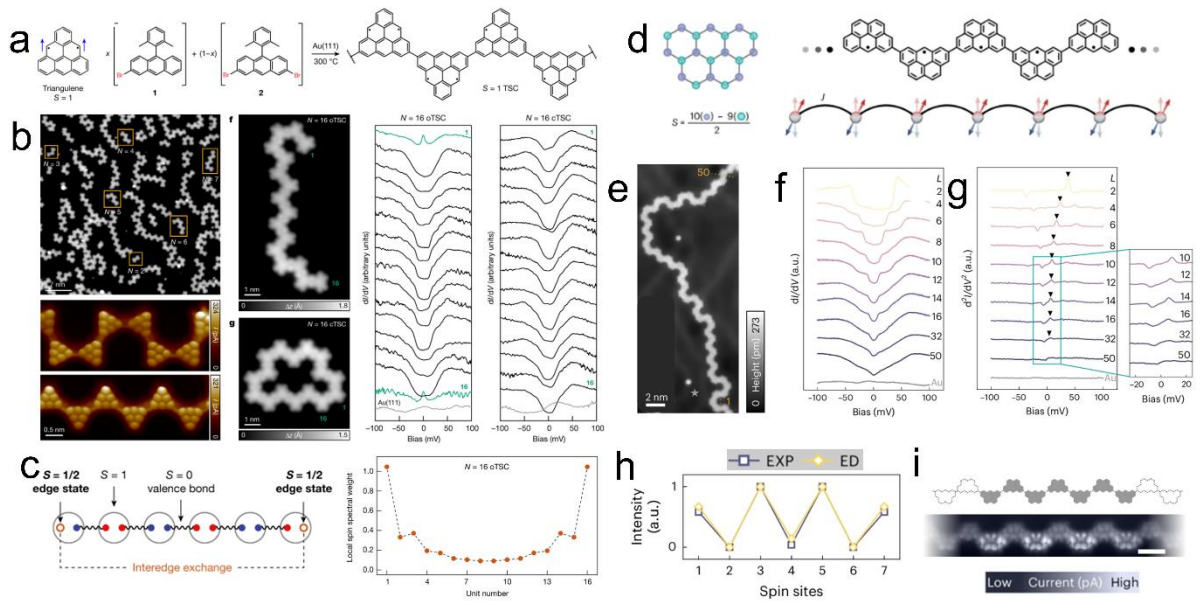


Figure 3.1 (a–c) Triangulene-based $S = 1$ chains show edge-localized zero-bias states and gapped bulk excitations, characteristic of the Haldane phase.⁷⁴ (d) Olympicene-based $S = 1/2$ chains realize the antiferromagnetic Heisenberg model with strong exchange coupling. (e–g) Length-dependent spectra reveal gapped singlets in even chains, while long chains evolve into a gapless continuum. (h–i) Spatially resolved conductance maps display a standing-wave modulation of the zero-bias conductance.

standing-wave modulation, evidencing spinon excitations in one-dimensional nanographene systems.⁴⁴

Benefiting from the chemical tunability of organic molecules, π -magnetism provides a versatile platform where spin–spin exchange interactions and spin–substrate couplings can be engineered by molecular design. Building upon this concept, Nian Lin and collaborators realized a tetraphenylethylene (TPE)-based radical chain on Au(111), in which each π -radical carries an $S = 1/2$ Kramers doublet. The local spins are strongly coupled to conduction electrons of the substrate, giving rise to enhanced Kondo screening with a characteristic Kondo temperature of ~ 60 K. At the same time, antiferromagnetic exchange interactions of the order of 10–20 meV exist between neighboring radicals. The competition between Kondo screening and magnetic ordering drives the system into a regime that can be described by a one-dimensional Kondo lattice model, thereby establishing organic radical chains as a promising platform to explore heavy-fermion physics and quantum criticality.

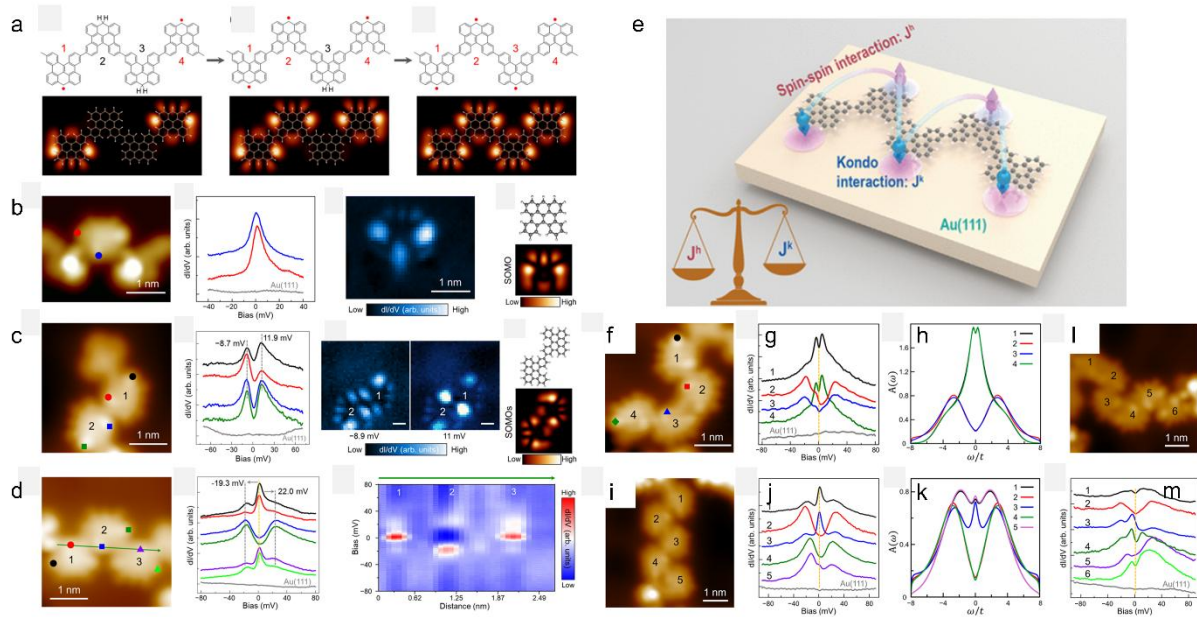


Figure 3.2 (a) On-surface synthesis of TPE chains on Au(111), where controllable tip-induced dehydrogenation generates localized $S = 1/2$ spins with characteristic spin-density distributions. (b–d) STM images, differential conductance spectra, spatial dI/dV maps, and simulated SOMOs for radical monomer, dimer, and trimer. The zero-bias resonance observed in the monomer evolves into a pair of split peaks in the dimer, while the trimer recovers edge-localized zero-bias peaks accompanied by a central dip near the Fermi level. (e) Schematic of the Kondo–Heisenberg chain model, illustrating the competition between

spin–substrate Kondo coupling J_k and inter-radical antiferromagnetic exchange J_h . (f–h) Experimental dI/dV spectra and simulated LDOS for tetramers reveal gapped states across all sites. (i–k) In pentamers, odd sites exhibit gapless zero-bias resonances, whereas even sites display gapped excitations. (l–m) Hexamer spectra show the absence of zero-bias peaks and the emergence of multi-peak structures, highlighting the systematic even–odd chain-length dependence of low-energy electronic states.

In this chapter, we present our study of 1D π -radical chains realized on a 2D metal-organic framework (2D-MOF) platform that constructed by 4-[bis(4 cyanophenyl)methyl]benzene-1-carbonitrile (TPM) molecules and Nickel (Ni) atoms on Au(111) surface. Using tip-induce dehydrogenation, we bottom-up realized radical chains and systematically analyzed the spin behaviors via STS measurement with mean-field theory. Unlike covalently fused nanographene spin chains, the present d-TPM radical chains are embedded in a MOF on Au(111), where inter-radical coupling may involve a combination of π –d– π exchange, substrate-mediated RKKY interaction and Kondo screening.

3.2 Results and Discussions

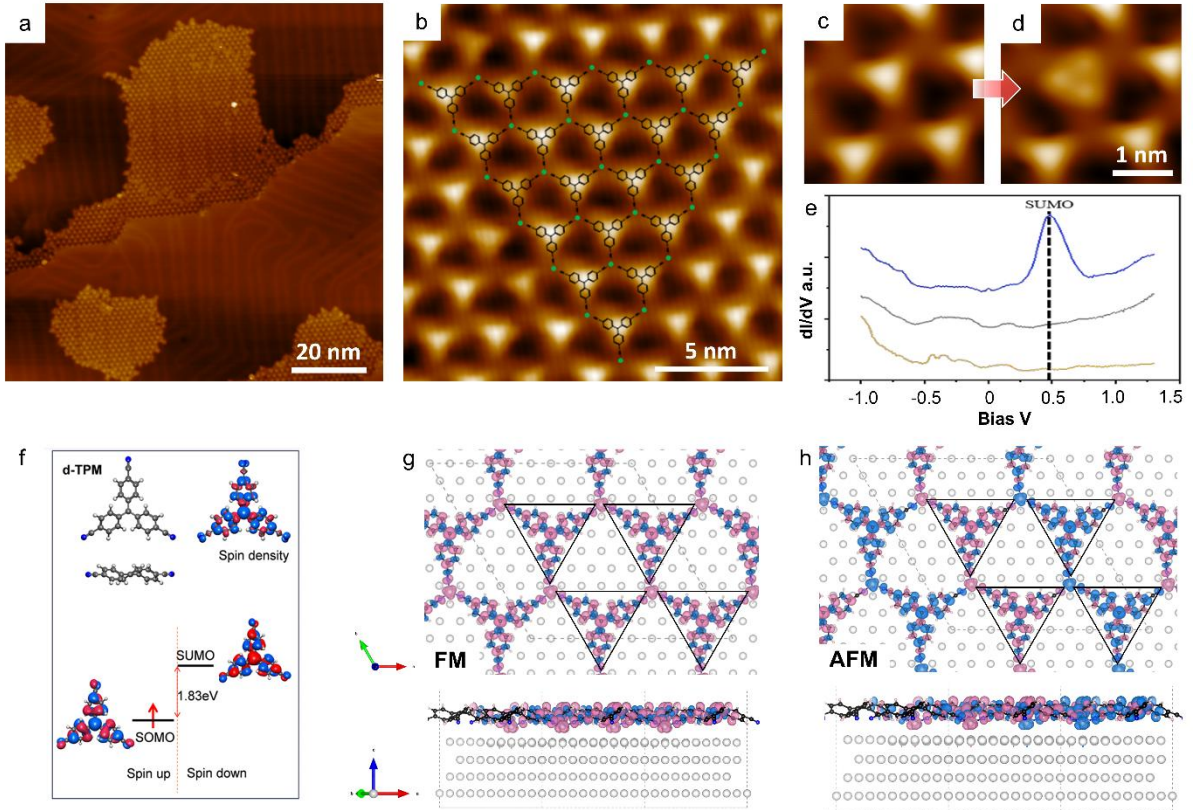


Figure 3.3 Topography and electronic structure of Ni-TPM on Au(111). (a) Large-scale STM image of Ni-TPM. (-1 V, 20 pA, scale bar: 20 nm) (b) Zoom-in STM image of Ni-TPM with structure model overlaid. (-0.1 V, 100 pA, scale bar: 5 nm) (c-d) STM image of the formation of d-TPM monomer. (-0.1 V, 100 pA, scale bar: 1 nm) (e) large-range dI/dV spectra taken at Au(111) substrate (yellow), intact TPM (grey) and d-TPM (blue). (f) DFT-calculation of frontier molecular orbitals and spin density of gas-phase d-TPM. (g-h) DFT-predicted spin density distribution in the periodic Ni-d-TPM lattices, showing the ferromagnetic (FM, g) and antiferromagnetic (AFM, h) cases. $E_{\text{AFM}} - E_{\text{FM}} = 44.4$ meV/super cell reveals the collinear FM ground states of Ni-d-TPM lattice (Pink: spin up; Blue: spin down).

We first synthesize monolayer Ni-TPM MOF on Au(111) substrate as shown in Figure 3.3(a). A zoomed-in STM image (Figure 3.3(b)) reveals that the TPM molecules adopt a triangular lattice arrangement with a lattice constant of 1.43 ± 0.03 nm. A structural model overlaid on the image highlights the triangular geometry of the TPM molecules. The bright protrusion at the center of each triangle is attributed to the central sp^3 C–H bond. Through tip-induced manipulation, a TPM molecule can be converted into its dehydrogenated form (d-TPM), as illustrated in Figure 3.3(c–d). The d-TPM species exhibits a characteristic three-lobed protrusion corresponding to the three benzene rings, while the central carbon appears darker due to the transition from sp^3 to sp^2 hybridization. To confirm the formation of d-TPM, dI/dV spectroscopy was performed. As shown in Figure 3.3(e), the d-TPM molecule displays a weak resonance near the Fermi level and a pronounced peak at 490 mV, which can be assigned to the Kondo resonance and the single unoccupied molecular orbital (SUMO), respectively, consistent with previous reports.⁷⁵

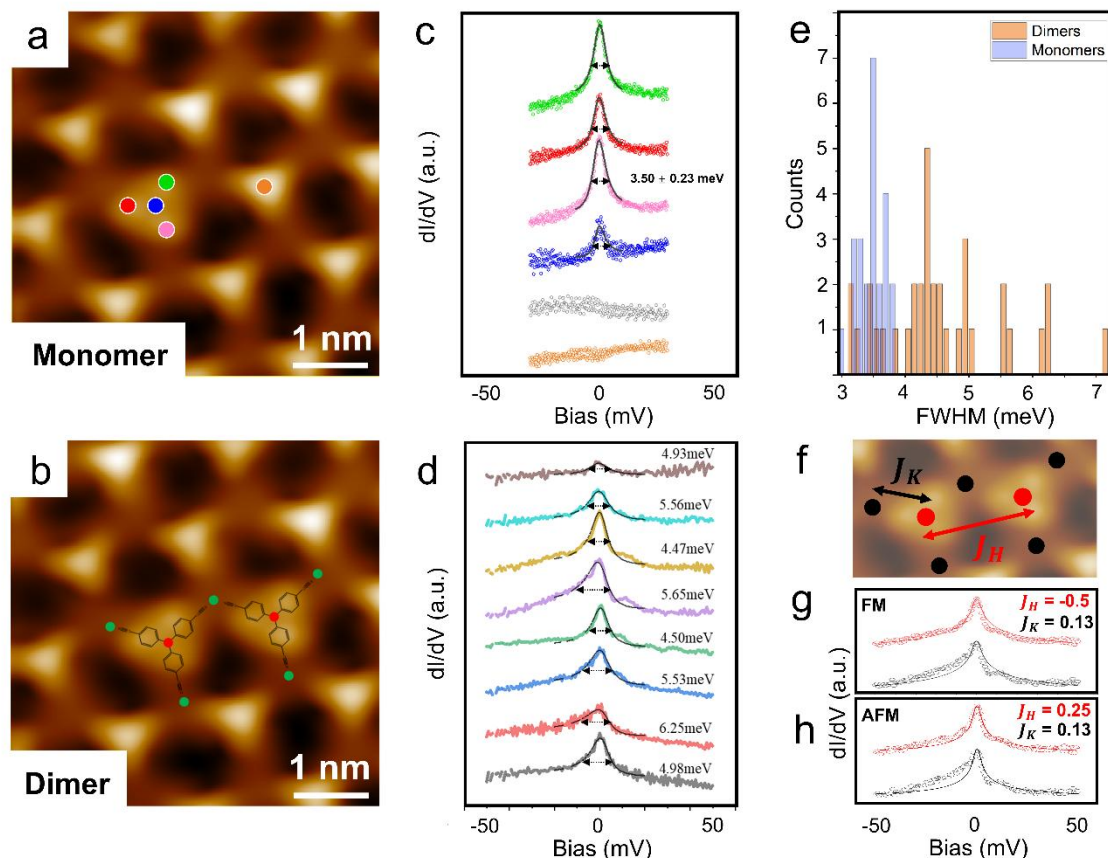


Figure 3.4 Kondo resonance of d-TPM monomer and dimer. (a-b) STM image of a d-TPM monomer and dimer, respectively. (c) dI/dV spectra taken at a monomer (Red, green, pink for benzenes, blue for carbon center) and an intact TPM (yellow). The spectra on Au(111) is shown in grey.⁷⁵ (condition: ± 50 mV, 3 nA) (d) 8 typical dI/dV spectra taken at benzene lobes of 4 different dimers. The width of peaks are broader than that of monomers. (e) Distribution of the Fano fitting HWHM of monomers and dimers, showing the broadening of dimer's dI/dV peaks. (f-h) Theoretical model, experimental (dots) and simulated dI/dV spectra (lines) of a representative d-TPM spin dimer in FM (g) and AFM (h) cases, respectively. For the theoretical model, π -spins are marked in red while Ni atoms marked in black. Using Ternes model, we define the interaction between π -spins and Ni atoms/Au(111) as J_K , while the inter-spin exchange coupling is J_H . The simulated dI/dV shows two broader peaks around Fermi level, with a HWHM of ~ 6.2 meV in Fano fitting.

Based on our previous work, density functional theory (DFT) provides the frontier molecular orbital of gas phase single d-TPM molecule (as shown in Figure 3.3(f)), exhibiting the isolated spin occupies the single occupied molecular orbital (SOMO). Furthermore, the spin density distribution among Ni-d-TPM lattices in ferromagnetic and antiferromagnetic states are

presented in Figure 3.3(g-h), where $E_{\text{AFM}} - E_{\text{FM}} = 44.4$ meV/super cell reveals the collinear FM ground states of Ni-d-TPM lattice. Since the d-TPM molecules not only form a triangular lattice but also are non-planar, where the geometric frustration and non-collinear magnetic ground state may also exist, this calculation only provide a reference for the collinear magnetism configuration and determine neither FM nor AFM exchange among radicals in the experiments. Previous work also indicate that the DFT-calculated spin density of the d-TPM monomer is distributed across the three phenyl rings and the central carbon atom, with a stronger localization at the center. The π -electrons of the d-TPM molecule form hybridized states with the itinerant electrons of the Au(111) surface mediated by the d-orbitals of the Ni atom, thereby triggering the Kondo screening effect. dI/dV measurements corroborate that the Kondo resonance peak is uniformly distributed across the three phenyl rings, while the central carbon atom exhibits a weaker Kondo resonance intensity. This further indicates a distinctive Kondo screening mechanism mediated by the Ni atom.

We dehydrogenated 20 different monomers in the present work (See Figure 3.4(a, c) for a representative monomer), and the resonance line shapes were fitted using the Fano line-shape formula to extract the half-width at half-maximum (HWHM), as plotted in Figure 3.4 (g). The spectral shape of the Kondo resonance is fitted using the following Fano line shape formula:

$$\frac{dI}{dV}(V) \propto A \cdot \frac{q + \epsilon^2}{1 + \epsilon^2}$$

where $\epsilon = \frac{eV - \epsilon_0}{\Gamma}$ (For details of Fano line-shape fitting, see chapter 2.2.2). As can be seen from Figure 3.4(f), the HWHM distribution of the monomers is primarily concentrated in the range of 3.0–3.8 meV. The Gaussian-fitted peak value for monomers' HWHM distribution is located at ~ 3.5 meV, corresponding to a Kondo temperature of approximately 40.6 K. Subsequently, we constructed 17 dimers using the same approach, from which 4 independent dimers were selected for detailed plotting, as shown in Figure 3.4 (d). The dI/dV spectra in Figure 3.4(d) reveals that the line shapes of certain peaks undergo noticeable modifications. The Fano fitting HWHM results are presented beside the spectra. We also performed single-peak Fano line shape fitting on a dataset of 15 dimers (total 30 spectra). The resulting HWHM distribution for the dimers is substantially broader, spanning from 3.2 to 7.2 meV, with the Gaussian-fitted median positioned at ~ 4.3 meV. This corresponds to a higher Kondo temperature of ~ 49.9 K. From the HWHM statistical distribution in Figure 3.4(g), the Gaussian-fitted center of the dimer distribution is approximately 0.8 meV higher than that of the monomer distribution. The

broadening, and shifting of the Kondo temperature, together with the frequent appearance of asymmetric line shapes, indicates that the two neighboring d-TPM radicals no longer behave as independent Kondo impurities. Generally, in a system characterized by multiple Kondo impurities, two types of coupling interactions may be considered: (1) Substrate-mediated RKKY interaction; (2) spin-spin direct exchange coupling. The data do not allow us to rule out any of the possibilities. According to the literature, a FM dimer leads to Kondo underscreening, resulting in a narrower Kondo resonance and a reduced Kondo temperature, whereas an AFM dimer broadens the Kondo resonance and enhances the Kondo temperature. Therefore, based on the experimental results shown in Figure 3.4(d–g), we infer that the exchange coupling between radicals is more likely to be antiferromagnetic.

For the multiple Kondo impurities case, we constructed a theoretical model to simulate the spectroscopic behavior observed in our experimental system. Here we introduced the Hamiltonian of Ternes model:⁷⁶

$$\hat{H} = \hat{H}_t + \hat{H}_s + \hat{H}_a + \hat{H}'$$

Where H_t and H_s describe the tip and sample electron reservoirs, H_a describes the localized spin system, and H' describes the scattering interaction. For better understanding of the parameters related to our experiments, the Ternes model can be rewritten as:

$$\begin{aligned}\hat{H} &= \hat{H}_t + \hat{H}_s + \hat{H}_{\text{spin}} + \hat{H}_{\text{Kondo}} + \hat{H}_{\text{Coulomb}} \\ \hat{H}_{\text{spin}} &= \sum_i g_i \mu_B \mathbf{B} \cdot \hat{\mathbf{S}}_i + \sum_i \left[D_i (\hat{S}_z^i)^2 + E_i \left((\hat{S}_x^i)^2 - (\hat{S}_y^i)^2 \right) \right] + \sum_{i,j} J_{ij} \hat{\mathbf{S}}_i \cdot \hat{\mathbf{S}}_j \\ \hat{H}_{\text{Kondo}} &= \sum_i J_{K,i} \mathbf{s} \cdot \hat{\mathbf{S}}_i \\ \hat{H}_{\text{Coulomb}} &= \sum_i U_i \hat{I}\end{aligned}$$

In this compact notation, J_{ij} is the Heisenberg exchange between localized spins, whereas $J_{K,i}$ is the Kondo exchange between a localized spin and conduction electrons, and U_i is the potential scattering term.

Figures 3.4(c–h) display a representative dimer. We simulated the corresponding dI/dV spectra using the aforementioned Hamiltonian. To establish the simulation parameters, we first fitted the spectra of seven isolated monomers to determine the distribution of the Kondo exchange

coupling, J_K . This yielded an effective J_K parameter centered around 0.1 meV, with a fitting range of 0.05–0.13 meV, which was then used as a reference range in subsequent simulations. Because J_K in the Ternes model depends on the model normalization and the assumed tunneling/scattering channels, these values should be regarded as effective fitting parameters rather than directly measured microscopic exchange constants. We consider both AFM ($J_H > 0$) and FM ($J_H < 0$) Heisenberg exchange interaction and the AFM Kondo screening ($J_K > 0$) in the Ternes model fitting. For the FM dimer (Figure 3.4(g)), at the condition $J_K = 0.13$ meV, it requires $J_H = -0.5$ meV to produce two Lorenz peaks, while for the AFM cases, the $J_H = 0.25$ meV is enough to reproduce similar features. However, we cannot determine either FM or AFM for inter-radicals exchange coupling so far since such parameters both work. Because the Ternes model relies on a third-order perturbation approximation of the Kondo scattering process, it neglects the higher-order, low-energy expansion terms that emerge when applying the Schrieffer-Wolff transformation to the Anderson impurity model. Consequently, the model provides only a qualitative description of the Kondo resonance and heavily relies on Heisenberg exchange term, which cannot fully reproduce the Fano-like dI/dV spectra observed experimentally. Specifically, as shown in Figure 3.4(g-h), the simulated line shapes fail to reproduce the experimentally observed dI/dV asymmetry between positive and negative sample bias.

Furthermore, as illustrated in Figure 3.4(d-e), the two spin sites within each dimer frequently display asymmetric spectroscopic behaviors (e.g., manifesting as one broad peak and one narrow peak). The statistical distribution of the half-width at half-maximum (HWHM) of the Kondo peaks for the dimers is notably broad, ranging from ~3.2 meV to ~7.2 meV. We propose that a plausible reason for this phenomenon is the spatial inhomogeneity of the interactions between the two spins within a given dimer. Indeed, the Kondo peak width of the monomers already exhibits a statistical fluctuation of ~20%. In the Ternes model, the fitting AFM J_H ranges from 0.1-0.4 meV. We speculate that such fluctuations may originate from differences in the specific adsorption sites of the molecules on the Au(111) substrate. Alternatively, it could be attributed to variations in the chemisorption configurations of the molecules themselves, such as the rotation angle of the phenyl rings or orbital misalignment during the coordination between the cyano groups and the Ni atoms. These observations support the presence of inter-radical coupling in the dimer, although the present STS data cannot uniquely distinguish direct exchange, substrate-mediated RKKY interaction or the Kondo cloud-mediated coherence.

Given the limitations of the Ternes model in simulating Kondo many-body interactions, a more rigorous approach is to employ specific methods for handling many-body problem such as the Numerical Renormalization Group (NRG),⁷⁷⁻⁸⁰ Quantum Monte Carlo (QMC),⁸¹⁻⁸⁴ or Many-Body Perturbation Theory (MBPT) to solve the Kondo/Anderson impurities model.⁸⁵⁻⁸⁷ For instance, Taner Esat et al. utilized a comprehensive theoretical framework combining DFT, MBPT, and NRG in study of the Kondo interactions between two Au-PTCDA molecules and the magnetic exchange coupling induced by wavefunction overlap.⁸⁷ The theoretical treatment consists of two main steps: first, *ab initio* calculations (using DFT and MBPT) are performed to evaluate the essential physical parameters (such as hybridization functions and Coulomb repulsion) required to construct the Two-Impurity Anderson Model (TIAM). Second, the NRG method is applied to solve this model, yielding spectral functions that can be directly compared with experimental dI/dV spectra. As shown in Figure 3.5 (a-c), AFM exchange coupling will gradually open a dip in the Kondo resonance peak at the Fermi level as the absorption configuration changes. Furthermore, the asymmetric lineshape observed in the experimental spectra can be accurately described by the quantum interference effects arising from the odd and even orbitals. Another representative example is shown in Figures (d-f), the experimental dI/dV spectra and NRG simulations together elucidate the spectral evolution of the Fe dimers.⁸⁸ Compared to the monomer, moderate AFM coupling leads to a pronounced broadening of the zero-bias resonance in the dimer, whereas FM coupling reduces the peak width as a consequence of Kondo underscreening. In light of these findings, we anticipate that the inter-radical exchange coupling in our Ni-d-TPM system is antiferromagnetic.

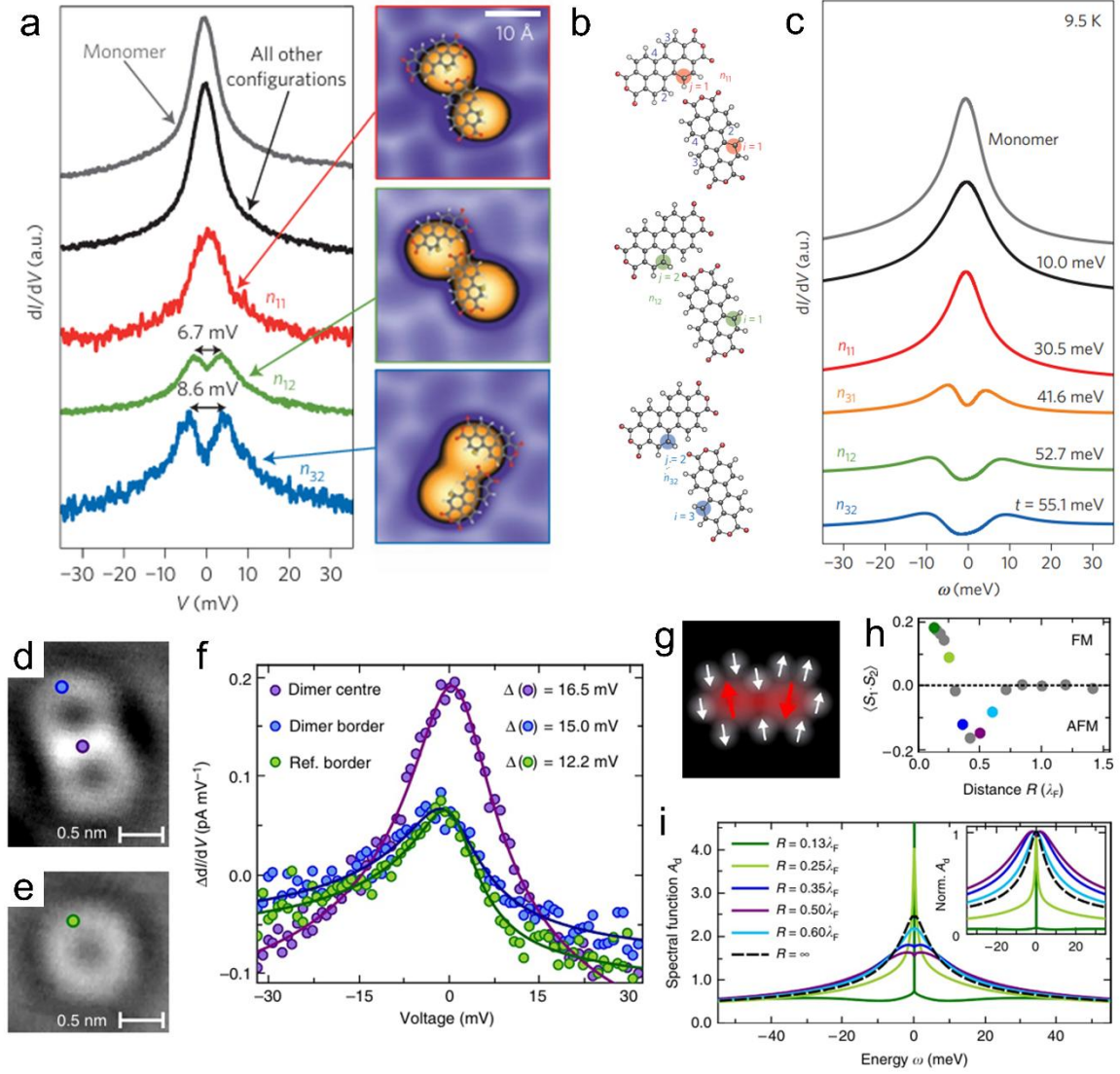


Figure 3.5 (a-b) dI/dV spectra of various Au-PTCDA dimers on Au(111).⁸⁷ Depending on the adsorption configuration, the spectral lineshape transitions from a sharp resonance for the monomer to broadened and eventually split double peaks for the dimers. (c) The corresponding NRG simulations for dimers' spectra exhibit excellent agreement with the experimental spectra. (d-f) Experimental and NRG-simulated dI/dV spectra of Fe monomers and dimers on Cu(110), demonstrating that moderate AFM coupling leads to a pronounced broadening of the zero-bias resonance in the dimers.⁸⁸

To further examine how the interaction evolves beyond dimers, we constructed finite one-dimensional radical chains. As a first step, short chains with length $L=3$ were assembled and characterized by site-resolved STS, as shown in Figure 3.6(a–h). In contrast to isolated monomers, where the dominant low-energy feature is a Kondo-like resonance peak, selected

sites in the $L=3$ chains show a pronounced suppression of conductance near the Fermi level. The coexistence of peak-like and dip-like line shapes within the same finite chain indicates that the local Kondo response is strongly modified by coupling to neighboring radicals. We used Fano lineshape to determine the HWHM of peaks and dips in dI/dV spectra. As shown in Figure 3.6 (b), the three radicals within $L=3$ chain #1 show peaks in width of 3.95, 7.29 and 11.55 meV, respectively, while the chain #2 exhibits two dips in width of 3.33, 3.48 meV and a peak of 6.95 meV. This observation supports the presence of inter-radical interactions in the short chains, but the STS line shape alone does not uniquely determine whether the dominant coupling is direct exchange, substrate-mediated RKKY interaction, framework-mediated exchange, or a combination of these effects.

As depicted in Figure 3.6(e-j), we employed the Ternes model to fit the dI/dV spectra of two $L=3$ radical chains, with the corresponding results displayed in Figures 3.6(e-i). First we consider a FM case for inter-radical coupling. For chain #1, simulated dI/dV spectra in Figure 3.6(e) was achieved by introducing symmetric FM Heisenberg exchange couplings ($J_{H1-2} = J_{H2-3} = -0.5$ meV) alongside asymmetric Kondo screening parameters ($J_{K1} = J_{K2} = 0.12$ meV, $J_{K3} = 0.1$ meV). While the narrow peak with a HWHM of 3.95 meV is well-reproduced, the simulated curve significantly deviates from the two broader peaks. Such an asymmetric fitting result is physically plausible in the presence of non-uniform chemisorption configurations. The d-TPM molecules can adopt slightly different adsorption geometries on the substrate; such structural variations may rearrange the local spin density and modify the effective inter-radical coupling. For chain #2, an approximate fitting of two dips and a peak near Fermi level required highly asymmetric exchange interactions ($J_{H1-2} = -2$ meV, $J_{H2-3} = -0.3$ meV) combined with uniform Kondo screening ($J_{K1} = J_{K2} = J_{K3} = 0.08$ meV). In the STM images, no distinct structural differences are observed between the radical molecules, and thus such a pronounced variation in FM Heisenberg exchange interactions among spins within the same chain appears implausible. Therefore, we exclude the assumption of FM coupling in our experimental system.

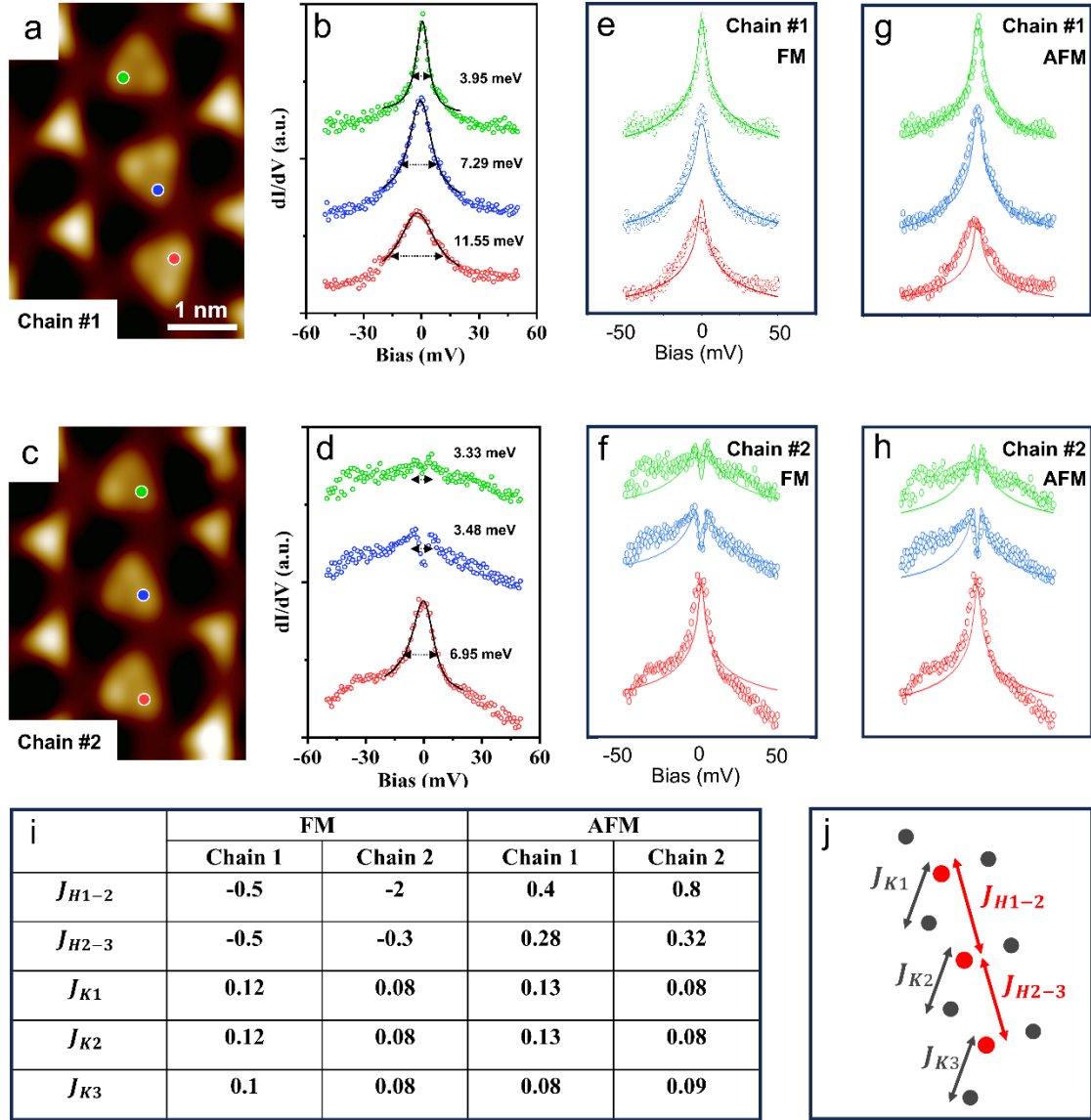


Figure 3.6 Short radical chains in length of $L=3$. (a-d) STM images and corresponding dI/dV spectra taken at 2 different $L=3$ radical chain, where the dip features near Fermi level sometimes appear. The Fano fitting HWHM is marked beside spectra. (e-h) The simulated dI/dV curves from Ternes model for fitting experimental data. (i) The fitting parameters of chain 1 and chain 2 in the FM (e-f)/AFM (g-h) cases are listed in the table. (j) Scheme of Ternes model with Heisenberg exchange coupling J_{H1-j} and Kondo interaction J_{Ki} .

In contrast, for chain #1, assuming AFM coupling with disordered Heisenberg interactions ($J_{H1-2} = 0.4$ meV, $J_{H2-3} = 0.28$ meV) and non-uniform Kondo screening ($J_{K1} = J_{K2} = 0.13$ meV, $J_{K3} = 0.08$ meV), the narrow blue and green peaks are successfully reproduced (Figure 3.6(g)).

However, the broad red peak remains poorly fitted. For chain #2, a qualitative fit is achieved using $J_{H1-2} = 0.8$ meV, $J_{H2-3} = 0.32$ meV, $J_{K1} = J_{K2} = 0.08$ meV and $J_{K3} = 0.09$ meV, a qualitative fitting is presented in Figure 3.6(h). Although both FM and AFM models only partially capture the broad peak/dip features in the experimental spectra for both chains, the non-uniform Heisenberg exchange J_H values are physically more reasonable in the AFM scenario. As previously discussed, underscreening often occurs in FM-coupled spin systems, which suppresses the Kondo resonance in the LDOS. The significantly broader dI/dV features observed in the $L = 3$ chains are more naturally explained by an AFM exchange scenario than by a FM underscreened scenario. Therefore, the combined experimental trends and Ternes-model analysis suggest that AFM inter-radical coupling is likely dominant in these short chains.

Nevertheless, because different combinations of Heisenberg coupling, Kondo exchange, and potential scattering can yield similar low-energy lineshapes, these fitted parameters should be interpreted merely as evidence of coupling inhomogeneity rather than as uniquely determined microscopic constants. Fundamentally, the Ternes model fails to fully capture the exact experimental dI/dV lineshapes—such as the characteristic Fano-like asymmetry—due to its inherent limitations in describing complex many-body Kondo physics. Consequently, our simulations serve primarily as a qualitative validation of the underlying exchange interactions, rather than a tool for extracting precise quantitative parameters from this experimental system.

Next, we fabricated longer spin chains, including lengths of $L=5, 10$, and 15 , and collected their corresponding STS data (as shown in Figure 3.7). All peaks are fitted by Fano lineshape while all dips are fitted by 2nd order differential to extract the HWHM, which are plotted beside the dI/dV spectra. In our experimentally fabricated finite chains (Figure 3.7(a-c)), we observe that as the chain length increases, although the spectral behavior along the entire spin chain lacks strict geometric symmetry, the characteristic dip and peak features occasionally alternate at specific sites (e.g., red spectra in Figure 3.7(a-c)). They should therefore be regarded as finite interacting Kondo-radical chains rather than ideal 1D Kondo lattices. Considering the relatively weak and spatially inhomogeneous Kondo and inter-spin exchange interactions in our system, compounded by the non-negligible finite-size effects of the short chains, it is currently difficult for the entire system to fully transition into an ideal 1D Kondo lattice ground state.

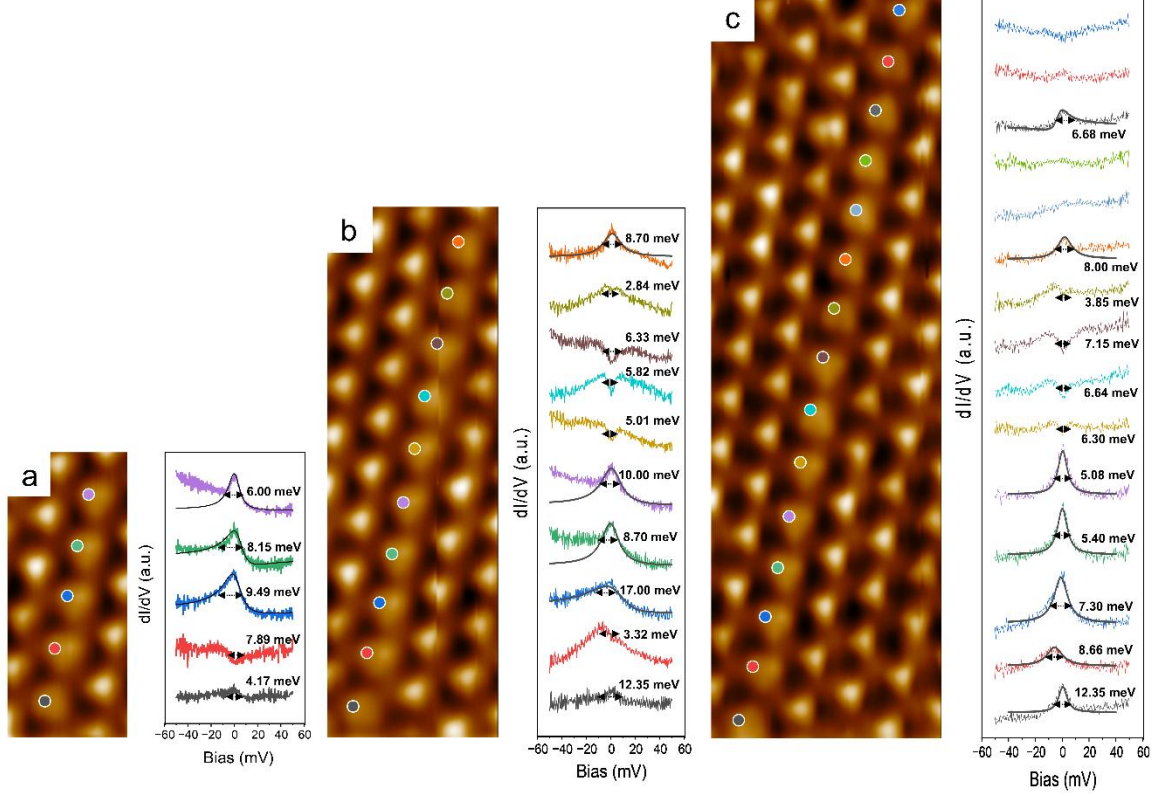


Figure 3.7 Length-dependent dI/dV spectra in radical chains. (a–f) STM images and dI/dV spectra of radical chains with $L = 5$ (a), 10 (b), and 15 (c). The Fano fitting HWHM is presented beside the spectra. Weak dI/dV features that cannot be reliably classified as peak-like or dip-like are excluded from the Fano-type line-shape analysis.

With increasing chain length, the Hilbert space dimension of the Ternes model grows exponentially, resulting in unattainable computational costs and a loss of accuracy. Therefore, we formulated the Hamiltonian using mean-field theory:

$$H^{eff} = \sum_{ijss'} t_{ij}^{ss'} c_{i,s}^{\dagger} c_{i,s'} + \gamma_K \sum_{\langle i\mu \rangle s} c_{i,s}^{\dagger} f_{\mu,s} + \gamma_J \sum_{\mu\nu} f_{\mu,s}^{\dagger} f_{\nu,s} + \mu_J \sum_{\mu s} f_{\mu,s}^{\dagger} f_{\mu,s} + h.c.$$

where the first term describes the kinetic energy of the conduction electrons c , with $t_{i,j}^{ss'}$ being the hopping integral between sites i and j . The second term represents the Kondo hybridization between the conduction electrons and localized magnetic moments (denoted by pseudo-fermions f), parameterized by the hybridization strength γ_K . The third term accounts for the exchange interaction between adjacent localized spin sites (capturing the RKKY interaction or direct spin-spin exchange coupling), with γ_J as the exchange coupling strength. The fourth term

introduces the chemical potential μ_J to enforce the single-occupancy constraint of the localized fermions, and *h. c.* denotes the Hermitian conjugate.

To simplify the calculation and obtain an idealized reference limit, we first set the explicit inter-spin exchange term J_H to zero, so that the calculated spectra mainly reflect Kondo hybridization and partial RKKY interaction within a translationally invariant model. This simplification means that the calculation should be regarded as a theoretical reference rather than a quantitative model of the experimentally observed finite chains. The simplified Hamiltonian becomes:

$$H^{eff} = \sum_{ijss'} t_{ij}^{ss'} c_{i,s}^\dagger c_{i,s'} + \gamma_K \sum_{\langle i\mu \rangle s} c_{i,s}^\dagger f_{\mu,s} + \mu_J \sum_{\mu s} f_{\mu,s}^\dagger f_{\mu,s} + h. c.$$

As shown in Figure 3.8(a-c), we utilized these parameters (employing $\frac{\gamma_K}{t}$ as the energy scales for hybridization) to simulate a scenario where Kondo screening and RKKY interaction coexist, assuming an abundant density of states of conduction electrons near the Fermi level. In Figure 3.8(d), we calculated the average LDOS of an idealized infinite 1D Kondo-lattice model performed by the Large-N formulation and Mean-field theory. Under the chosen parameter of $\frac{\gamma_K}{t} = 0.5$, the calculation shows a hybridization-gap near the Fermi level and flat-band-like features, providing a useful theoretical reference for the coherent Kondo-lattice limit. Although the experimental data shown in Figure 3.7 do not fully exhibit the theoretically predicted hybridized gap, this discrepancy may arise from both finite-size effect and the inhomogeneous exchange interactions between radicals and Kondo screening, which are induced by variations in molecular adsorption configurations (as detailed in the table in Figure 3.6(f)).

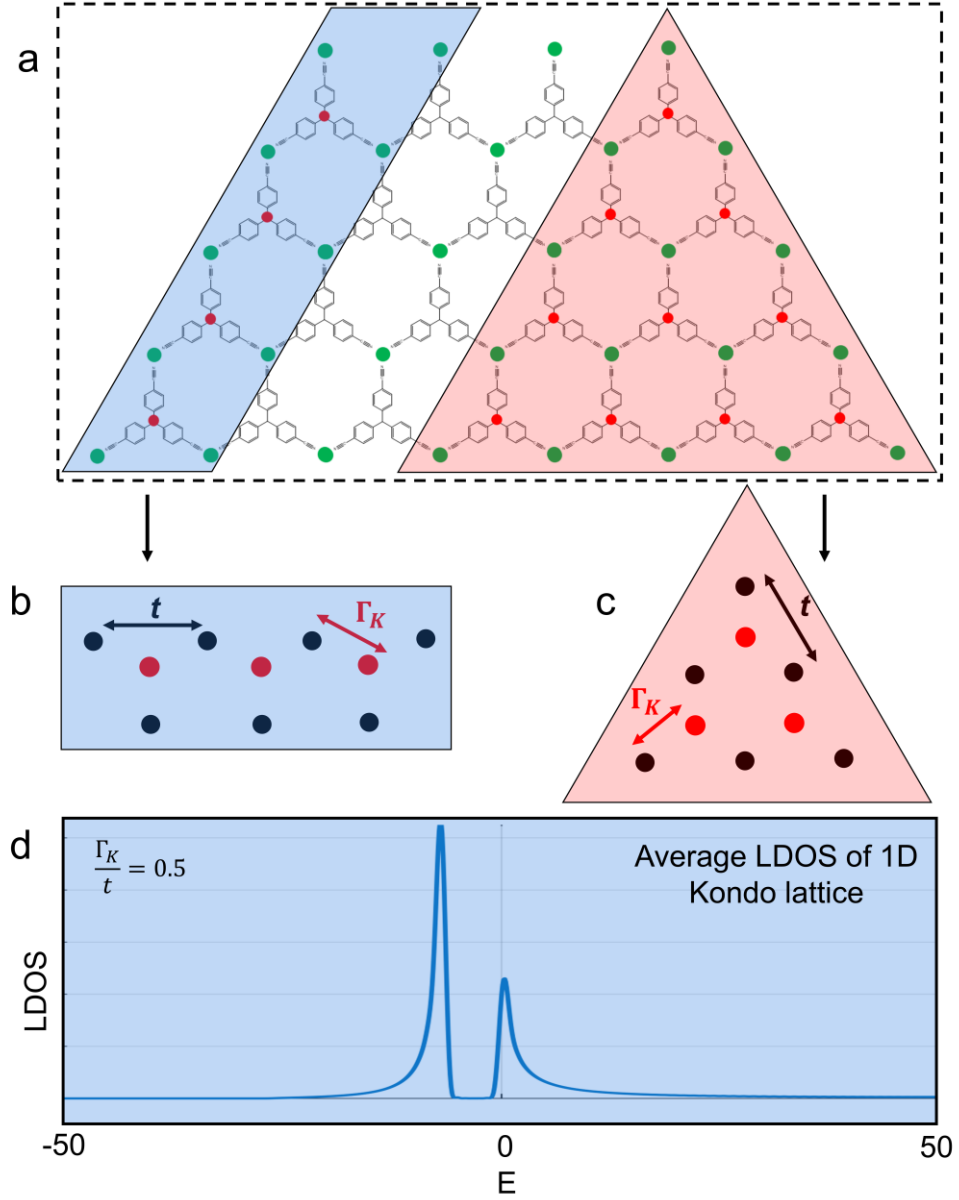


Figure 3.8 (a) Chemical structure model of Ni-TPM lattice. Blue area highlights a radical chain while red area shows the 2D radical lattice. The spin interaction models are shown in (b) for spin chain and (c) for spin lattice, respectively. (d) Average LDOS of the 1D Kondo lattice, exhibiting a hybridization gap and two flat bands attributed to the interplay between the RKKY interaction and the Kondo effect. It provides a theoretical reference for the coherent lattice limit.

Figure 3.9(a–c) presents the simulated LDOS of finite-size 1D Kondo chains by using effective Kondo lattice model. To account for finite-size effects and the spatial inhomogeneity observed in our experimental dI/dV spectra, a random disorder term, $\frac{\delta\Gamma_K}{t}$ in $[-0.5, 0.5]$, is incorporated into the Hamiltonian. The simulated spectra reveal that for the $N=5$ and $N=10$ chains, the

spectral features evolve to exhibit split peaks and gap-like features near the Fermi level, indicating that the LDOS line shapes are strongly modulated by both size effects and disorder. As the chain length increases to $N=15$, a gap-like feature becomes markedly more pronounced, accompanied by a significant broadening of the peak structures. Furthermore, the inclusion of the random disorder term explicitly breaks the spatial geometric symmetry of LDOS along whole chain. Because large- N expansion and mean-field theories inherently struggle to capture the granular details of finite-size 1D spin systems, this effective model cannot exactly reproduce the site-specific peak/dip configurations of the experimental data. Nevertheless, the simulated LDOS of these disordered spin chains provides a robust qualitative framework that is highly consistent with our measured dI/dV spectra.

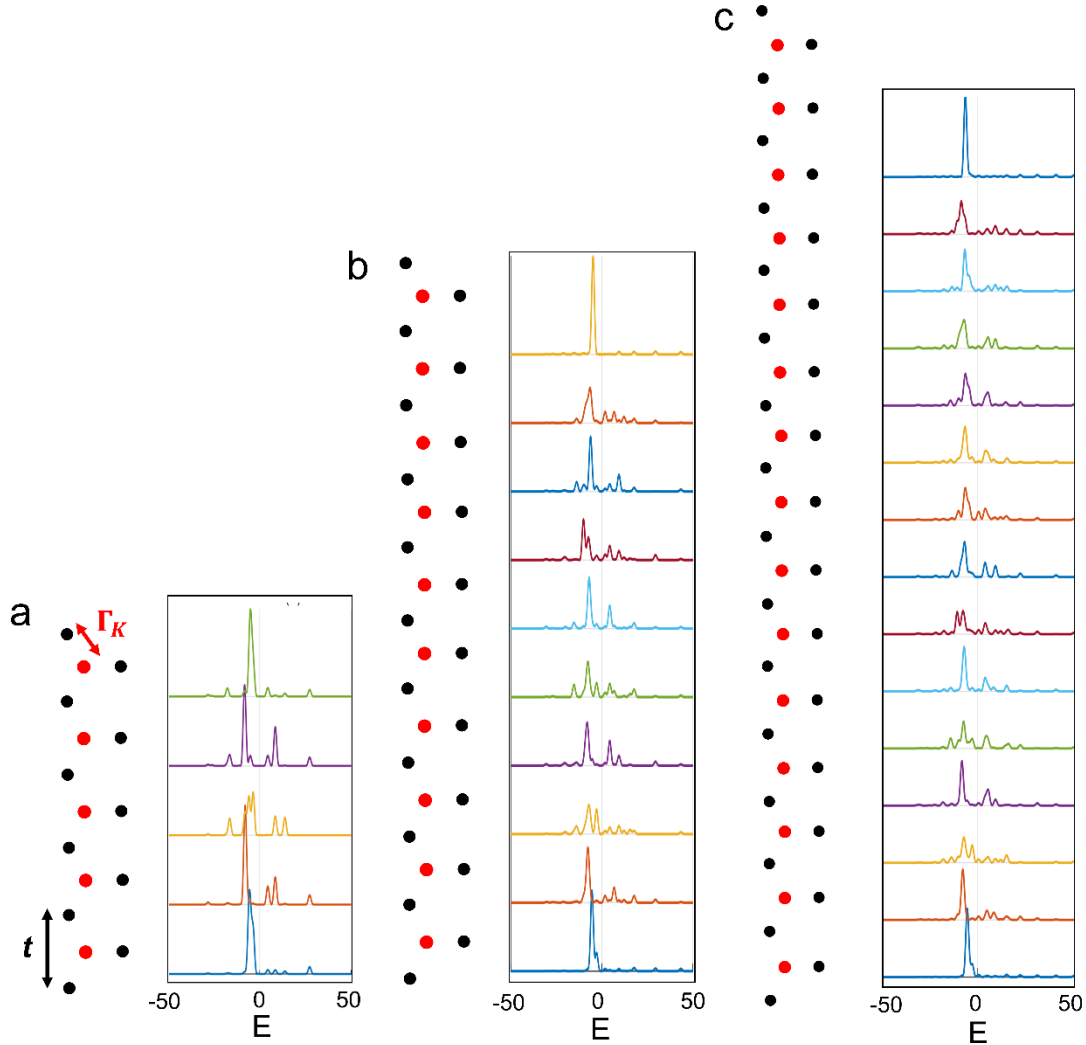


Figure 3.9 Scheme of effective Kondo lattice model and simulated LDOS for the $N=5$ (a), $N=10$ (b) and $N=15$ (c) Kondo chain, with $\frac{\Gamma_K}{t} \sim 0.5$ and a 30% disorder in $\frac{\Gamma_K}{t}$ term. With

disorder in Kondo screening Γ_K and hopping between itinerant electrons t , the spectra exhibits various dips and peaks feature in the chains. As the chain becomes longer, simulated spectra shows more clear dip/gap feature in the bulk. The results illustrates how finite size and disorder can reconstruct the local spectra of coupled Kondo-radical chains.

3.3 Conclusions

In conclusion, we constructed a series of 1D finite π -radical chains on the Ni-TPM/Au(111) platform by combining on-surface synthesis with site-selective STM tip-induced dehydrogenation. Isolated d-TPM radicals exhibit Kondo resonances with $T_K \sim 40$ K, establishing d-TPM as spin units embedded in the Ni-TPM framework. When radical dimers are formed, the low-energy resonances in dI/dV become statistically broader and more spatially asymmetric than those of isolated monomers. This spectral modification indicates that adjacent radicals no longer behave as independent Kondo impurities. Ternes-model simulations provide a qualitative description of the AFM coupled-spin spectra, but the fitted parameters should be regarded as effective indicators of non-uniform coupling rather than uniquely determined microscopic exchange constants. Extending the system to finite chains with $L = 3$ to 15 further reveals site-dependent peak-like, dip-like and asymmetric spectral features near the Fermi level. These observations show that the dI/dV spectra of finite radical chains are progressively reconstructed by inter-radical coupling, finite-size effects and the non-uniform MOF/substrate environment. The idealized 1D infinite Kondo lattice calculation provides a useful theoretical reference for the coherent lattice limit, but the experimental chains remain finite and inhomogeneous and should not be interpreted as fully developed one-dimensional Kondo lattices.

Overall, this chapter establishes the Ni-TPM system as a programmable molecular platform for studying finite exchange-coupled spin chains. The results provide spectroscopic evidence for the evolution from isolated radicals to interacting one-dimensional spin chains, while leaving the precise microscopic coupling mechanism to future temperature-dependent, magnetic-field-dependent and more quantitative theoretical studies.

Chapter 4

Collective quantum magnetism in finite-size π -radical lattices

4.1 Introduction

Strongly correlated electron systems have long been at the forefront of condensed matter physics. Their rich physical phenomena—including Mott insulating states, quantum spin liquids, non-Fermi liquid behavior, heavy fermions and unconventional superconductivity—provide unique experimental platforms for understanding quantum many-body effects. Among these systems, heavy-fermion materials are typically composed of rare-earth or actinide elements with partially filled f -electron shells. At low temperatures, the exchange interaction between localized magnetic moments and conduction electrons triggers the Kondo effect: a single magnetic impurity is antiferromagnetically screened by the surrounding conduction electrons, forming a Kondo singlet. As schematically illustrated in Figure 4.1(a), the local density of states (LDOS) of such a Kondo singlet typically shows a resonance peak near the Fermi level. When such local moments are arranged periodically, a Kondo lattice emerges. In this configuration (Figure 4.1(b)), coherent scattering modifies the LDOS to exhibit a hybridized gap around the Fermi level. In this lattice system, in addition to the single-impurity Kondo temperature T_K , a lower coherence temperature T^* arises, marking the onset of a coherent heavy-fermion state in which the Fermi surface expands and the effective electron mass is strongly enhanced.

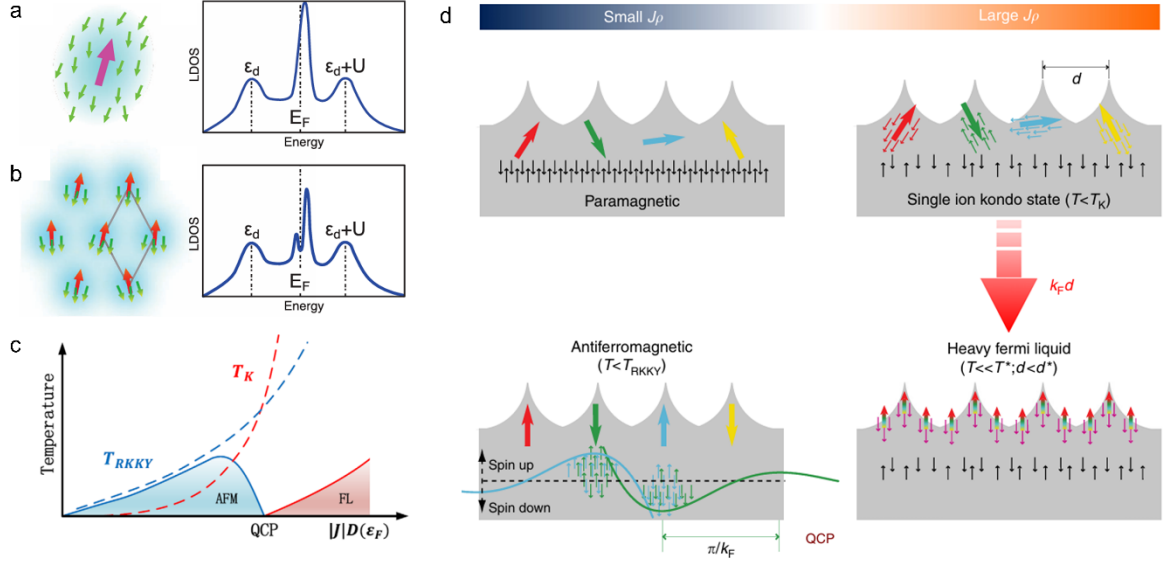


Figure 4.1 (a-b) Schematic of Kondo singlets, whose local density of states (LDOS) shows a resonance peak near the Fermi level (a), and of a Kondo lattice, where the LDOS exhibits a hybridized gap around the Fermi level. (c) Doniach phase diagram illustrates the competition between RKKY interaction and Kondo screening: when $J_{RKKY} > J_K$, the system develops an antiferromagnetic (AFM) ground state at low temperature; when $J_{RKKY} < J_K$, it evolves into the heavy Fermi liquid phase. (d) The Kondo lattice phase diagram shows four regimes: paramagnetic (local spins decoupled), single-ion Kondo state (each spin individually screened), antiferromagnetic order (via RKKY coupling), and the heavy Fermi liquid (all spins coherently screened into a large Fermi surface). The balance between exchange coupling J_ρ , inter-impurity spacing d , and temperature determines which phase emerges, with a quantum critical point separating AFM and heavy Fermi liquid states.

However, the physics of the Kondo lattice is not governed solely by Kondo screening. Local moments also interact via conduction electrons through the Ruderman–Kittel–Kasuya–Yosida (RKKY) interaction, which favors long-range magnetic order and competes with Kondo screening. Within this framework, Doniach proposed a famous phase diagram (Figure 4.1(c)) illustrating the competition between the RKKY interaction and Kondo screening: at zero temperature, when the Kondo exchange coupling J_K is weak, the RKKY interaction J_{RKKY} dominates and the system tends toward antiferromagnetic order; when J_K is strong, Kondo screening overwhelms RKKY, evolving into the heavy Fermi liquid phase. Expanding on this, the comprehensive Kondo lattice phase diagram (Figure 4.1(d)) maps out four distinct regimes

governed by the delicate balance of exchange coupling J_ρ , inter-impurity spacing d , and temperature T : a paramagnetic state where local spins are decoupled, a single-ion Kondo state where each spin is individually screened, an antiferromagnetic order driven by RKKY coupling, and the heavy Fermi liquid where all spins are coherently screened into a large Fermi surface. Near the critical regime separating the AFM and heavy Fermi liquid states, a quantum critical point may emerge, accompanied by non-Fermi liquid behavior and unconventional superconductivity. This competition and balance form the central problem of heavy-fermion physics and are key to understanding many-body effects in strongly correlated electron systems.

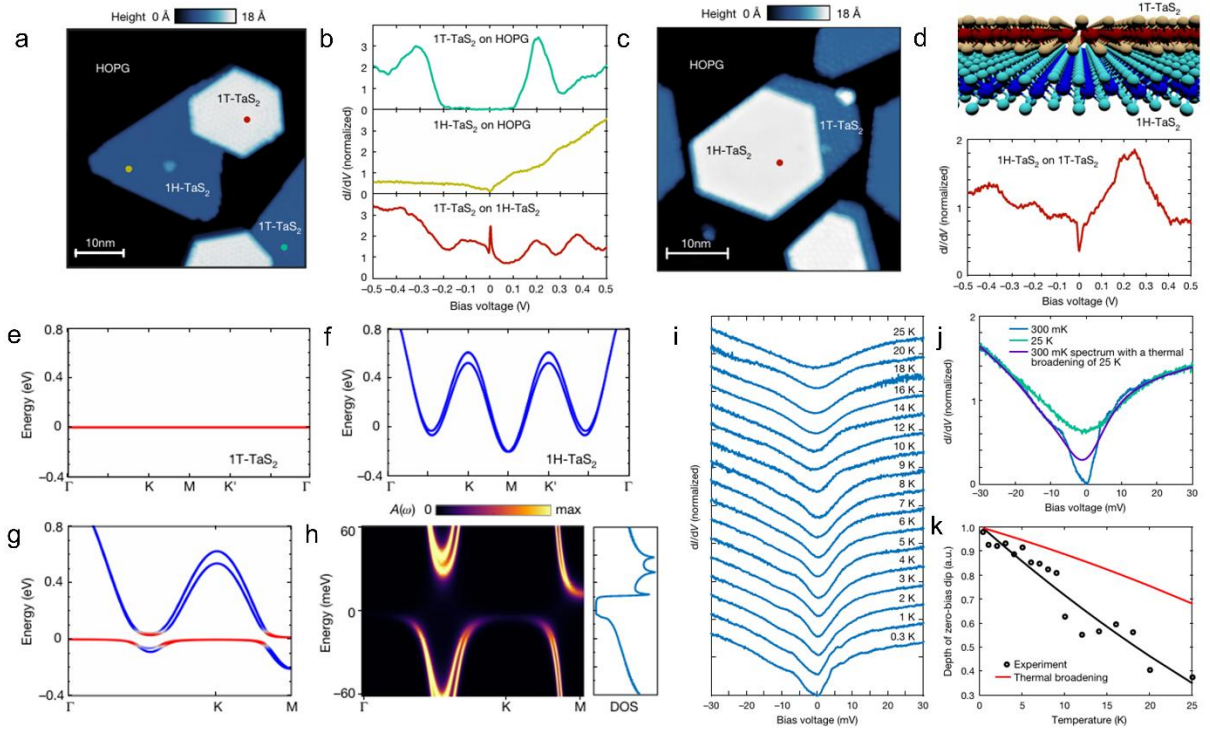


Figure 4.2 (a-b) STM image and corresponding dI/dV spectra taken on different materials, showing Mott gap of 1T-TaS₂, Metallic behavior of 1H-TaS₂ and Kondo resonance of 1T/1H TaS₂ heterostructure.³⁷ (c-d) STM image, structure model and corresponding dI/dV feature of 1H/1T TaS₂ heterostructure. (e-h) Mean-field theory simulation of LDOS for 1T/1H TaS₂. (i-k) Temperature-dependent STS measurements of the hybridized gap reveal that it decays faster than thermal broadening, demonstrating the hybridization between the zero-bias flat band and the dispersive conduction band across the Fermi level.

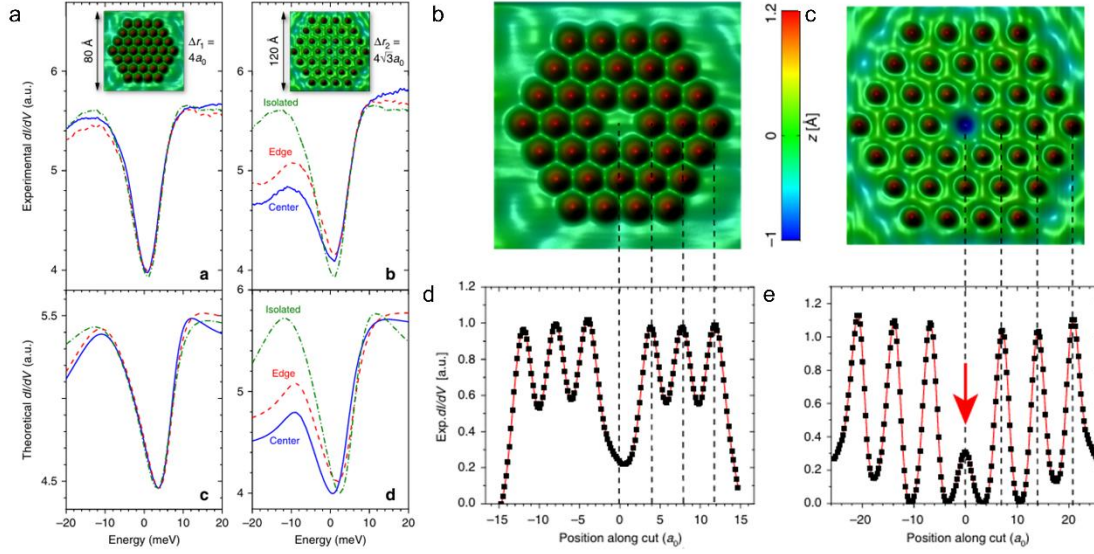


Figure 4.3 (a) Two Co atom droplets built on Cu(111) with different lattice constants, showing a constructive/deconstructive interference of Kondo clouds. (b-e) Observation of Kondo echo in the constructively coherent finite-size Kondo lattice. ⁸⁹

In recent years, the rapid development of two-dimensional materials and artificial structures has enabled the exploration of Kondo lattice physics in simpler and more tunable platforms. For example, in 1T/1H heterobilayers of transition metal dichalcogenides such as TaS₂, charge-density-wave-induced local moments couple to conduction electrons in the metallic layer, and experiments have demonstrated the emergence of heavy-fermion hybridized gap.³⁷ As shown in Figures 4.2(a) and (b), the 1T-TaS₂ phase exhibits an intrinsic Mott gap and displays a Kondo resonance when placed on the metallic 1H-TaS₂ phase. Conversely, when the 1H-phase is stacked on top of the 1T-phase, the dI/dV spectra reveal a hybridized gap around the Fermi level, signifying the emergence of heavy-fermion states (Figures 4.2(c-d)). This is consistent with the local density of states (LDOS) simulated via mean-field theory (Figures 4.2(e-h)). Furthermore, the temperature-dependent suppression of the gap highlights the heavy-fermion-like nature of these states in the heterostructure (Figures 4.2(d-k)). These van der Waals heterostructures preserve the essential ingredients of strong correlations while offering unprecedented controllability, such as tuning through stacking order, twist angle, or electrostatic gating. In parallel, atomically engineered Kondo droplets have revealed the evolution from single-impurity physics to coherent lattice behavior, even exhibiting nonlocal phenomena such as the Kondo echo.⁸⁹ Through the deliberate design of strongly correlated systems, bottom-up construction and investigation of the underlying physics of Kondo lattices provide significant insights into the mechanisms of heavy-fermion materials. As a representative case, Figure 4.3(a)

illustrates Co atoms arranged on a Cu(111) surface via tip manipulation with varying lattice constants, which modulates the RKKY interaction to track the evolution of Kondo lattice coherence. Furthermore, an artificial vacancy introduced into a specific Co atomic lattice exhibits a Kondo echo, revealing the coherent state of the emerging Kondo lattice (Figures 4.3(b–e)).

In this chapter, we fabricated a series of triangular radical lattices of different sizes through tip-manipulation techniques. To probe their electronic properties, we employed STS to characterize the DOS features associated with these radical patterns. We also applied large-N expansion and mean-field theory to simulate the strongly correlated behavior emerging within the spin lattices. Rather than treating these finite structures as fully developed bulk Kondo lattices, we use them as molecular-scale model systems to examine how local Kondo-like resonances evolve when multiple radical spins are arranged into designed two-dimensional geometries.

4.2 Results and Discussions

4.2.1 Trimers

First, we fabricated a series of d-TPM trimers via tip-induced dehydrogenation, as illustrated in Figure 4.4. According to the chemical structure of the Ni-TPM MOF, the Ni atoms and TPM molecules occupy two distinct sublattices, resulting in two distinct local linkage geometries for the d-TPM trimers (Figure 4.4(a, i)). For systematic analysis, the configuration in which three d-TPM molecules are connected via a single shared Ni atom is denoted as a single nickel-connected trimer (1NcT), whereas the configuration linked by three separate Ni atoms is termed a triple nickel-connected trimer (3NcT). We have constructed 7 1NcTs and 6 3NcTs and characterized them using STS (Figure 4.4(b–h) and (j–o)). The results reveal that both types of trimers primarily exhibit three distinct spectroscopic behaviors: (1) All-peaks: all d-TPM molecules within a trimer display a zero-bias resonance peak in their dI/dV spectra; (2) Co-existed: a fraction of the molecules exhibit a resonance peak, while the remainder show a zero-bias dip; and (3) All-dips: all molecules within the trimer display a zero-bias dip.

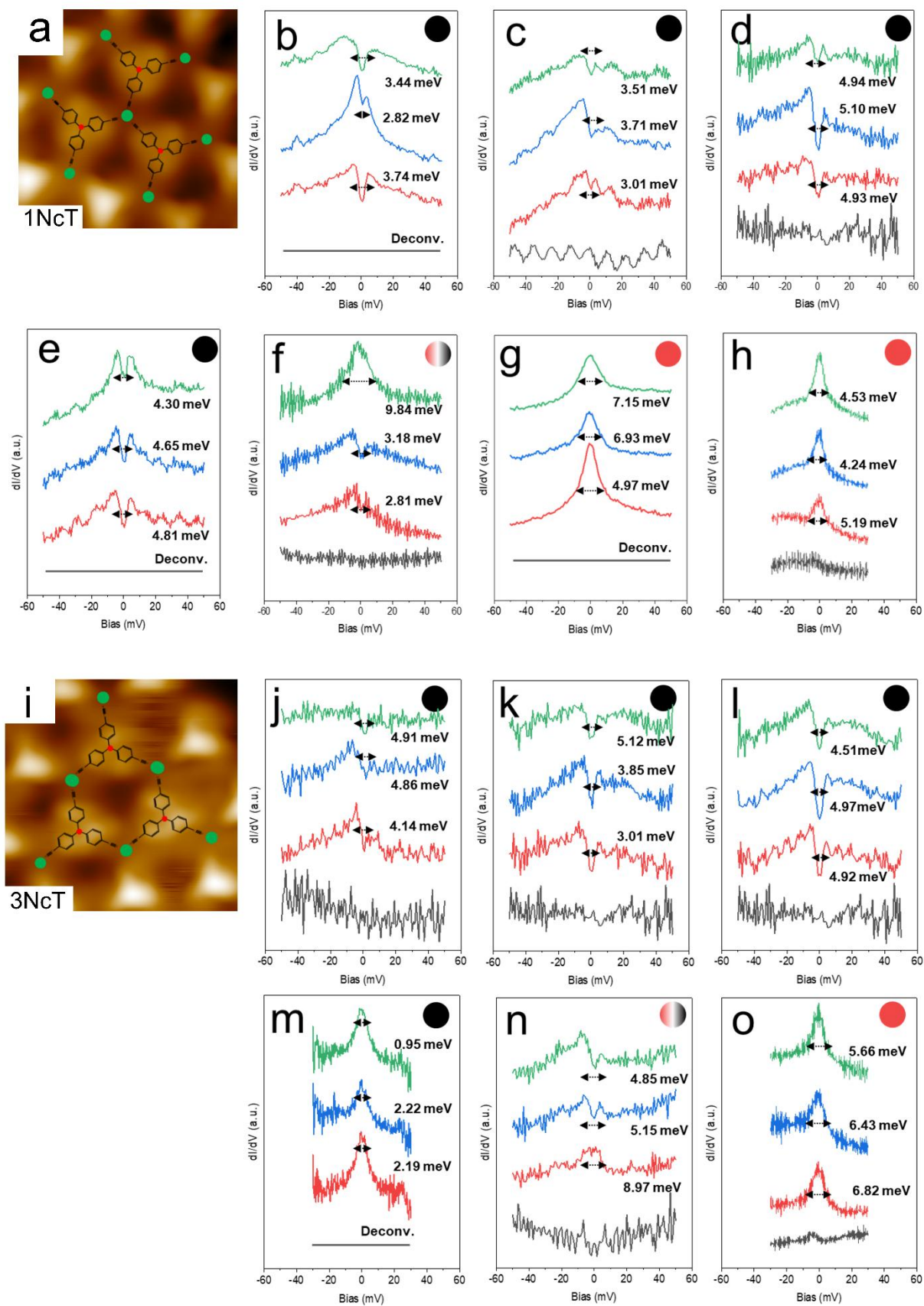


Figure 4.4 STM images and dI/dV spectra of two types of trimers. (a-h) Structure model and low-energy STS measurement for 7 different 1NcTs. (Spectra in grey: Au(111), green/blue/red: individual radical sites in a trimer) The colored circles on the dI/dV spectra shows the main features. (Black: dip; Red: peak; Half-filled: co-existed) Tip deconvolution is applied to (b), (e), (g) and (m) for excluding the asymmetric tip influence. Fano/2nd order differential fitting results for peaks/dips are listed beside spectra. (i-o) Structure model and low-energy STS measurement for 7 different 3NcTs.

Statistical analysis of the dI/dV spectral behaviors was performed for both trimer configurations (Figure 4.4(p)). For the 1NcTs, the "All-peaks" and "Co-existed" cases account for only ~28% and ~15%, respectively, while the "All-dips" state dominates at 57%. This indicates that the local Kondo-like response of the three d-TPM radicals is strongly modified once they are assembled into a trimer, suggesting that the radicals no longer behave as independent Kondo impurities. We used Fano line-shape fitting to estimate the characteristic widths of peak-like features, while the widths of dip-like suppressions were estimated from the second derivative of the spectra; the results are shown in Figure 4.4(b–h). Most peak-like features have widths of ~4.24–9.34 meV, whereas the dip-like features have characteristic widths of ~2.81–5.10 meV. Compared with isolated monomers and dimers, the broader peak-like resonances and the frequent emergence of dip-like line shapes provide spectroscopic evidence for enhanced inter-radical coupling in the trimers. However, these features should not be assigned uniquely to π -d- π antiferromagnetic exchange, because Fano interference, substrate-mediated interactions, site-dependent hybridization and many-body Kondo-related correlations may also contribute to the observed spectral reconstruction. Similarly, analysis of the 3NcTs shows that the "All-peaks" and "Co-existed" cases each account for ~17%, whereas the "All-dips" case reaches ~66%, further supporting the presence of strong inter-radical spectral reconstruction among the π -radicals. Most of peaks are in width of ~5.66-8.97 meV, while dips are in width of ~0.95-5.15 meV. Comparing the dI/dV spectral trends of the 1NcTs and 3NcTs, we observed no fundamental differences in the spectroscopic signatures between the two chemical configurations. Thus, the observed spectral reconstruction cannot be solely attributed to a simple AFM π -d- π exchange interaction. Drawing on the analysis of the 1D radical chains presented in Chapter 3, we tentatively suggest that multiple coupling channels may coexist in the Ni-TPM system, including framework-mediated exchange, substrate-mediated RKKY-type interactions, site-dependent molecule–substrate hybridization, and Kondo-related many-body

correlations mediated by the conduction-electron bath. At the present stage, the STS data do not provide sufficient evidence to isolate a unique microscopic mechanism.

To obtain preliminary qualitative insights, we performed physical modeling on two representative cases of 1NcTs and 3NcTs. The simulations employed the Ternes model with parameter ranges fitted in Chapter 3, where an effective AFM Heisenberg exchange scenario between radicals is described by J_H and the Kondo interaction between radicals and itinerant electrons as J_K , as illustrated in Figures 4.5(a–b) and (d–e). Here, J_K and J_H should be regarded as effective fitting parameters within the perturbative Ternes framework, rather than uniquely determined microscopic exchange constants. The resulting simulated dI/dV spectra were qualitatively compared with the experimental data shown in Figs. 4.5(c) and (f). For the selected 1NcT, we fixed the Kondo screening strength at 0.08 meV while setting the AFM Heisenberg exchange between spins 1–2 and 1–3 to 0.9 meV, and between spins 2–3 to 0.99 meV. The corresponding fits consistently revealed spin-excitation steps superimposed on a Kondo-modified line shape. For the 3NcT, we adopted a uniform Heisenberg exchange of $J_H = 0.9$ meV across all three spins, together with the same Kondo screening magnitude of 0.08 meV. However, the dimer fitting results show $J_H = 0.4$ meV as the upper limit of inter-radical exchange in Ternes model. The J_H used in trimer is approximately 2 times larger than that used for dimer, revealing that the exchange coupling among radicals may be the superposition of π -d- π coupling and other interaction like RKKY interaction, geometric frustration and Kondo cloud-mediated coherence. The use of similar effective parameters for 1NcT and 3NcT is consistent with the experimental observation that the two trimer geometries do not show fundamentally different spectral statistics, further supporting the co-existence of multiple interactions in Ni-d-TPM system. It should be emphasized that, due to the inherent limitations of the Ternes model, these fittings provide only qualitative indications of spin exchange. At this stage, what is evident is that these finite triangular three-radical clusters already show clear collective spectral reconstruction compared with isolated Kondo-active monomers and dimers, although the precise microscopic origin of the coupling remains to be clarified.

We refer some theoretical work to further elucidate the interplay between the Kondo effect and inter-radical exchange coupling.^{90–93} Figure (h) presents Quantum Monte Carlo (QMC) simulations of the Kondo trimer motifs.⁹⁰ In the FM scenario, the magnetic moments act synergistically, maintaining a robust Kondo resonance centered at the Fermi level. Conversely, the AFM equilateral triangle (ET) introduces geometric frustration and manifesting as a distinct

spectral dip near zero energy. Breaking this spatial symmetry to form an isosceles triangle (IT) lifts the degeneracy, driving the trimer to separate into a binding singlet dimer and a monomer. Consequently, the spatially distant, isolated spin recovers a sharp Kondo peak, whereas the dimerized spin pair exhibits a dip near Fermi level. Beside, Chudnovskiy et. al. use a static mean-field approach to demonstrate these phenomena in Figures (i–k).⁹¹ The calculations underscore that the frustrated ground state is highly sensitive to the exact spatial configuration. Even weak symmetry breaking in the RKKY interactions can induce large changes in the LDOS at different atomic sites (Figure 4.5(i–j)). Specifically, the closely spaced spins within the IT geometry yield broadened and shifted spectral features, reflecting strong localized hybridization and the abrupt redistribution of the low-energy spectral weight (See Figure 4.5(k)).

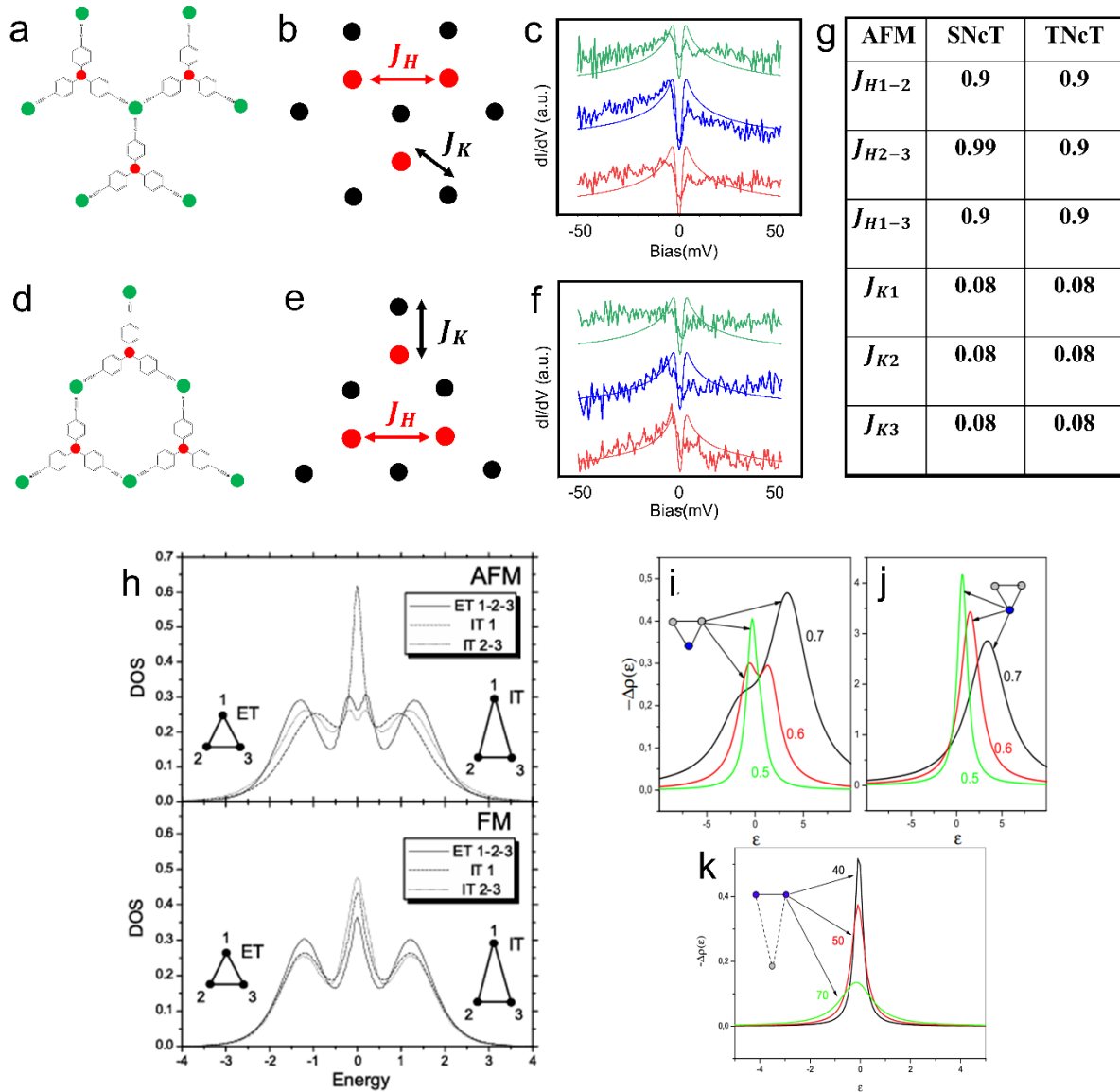


Figure 4.5 Chemical structure, Ternes model and experimental/simulated dI/dV spectra of 1NcTs (a-c) and 3NcTs (d-f). (g) The fitting parameters from Ternes model. (h) QMC study of AFM (top) and FM (bottom) Kondo triangular trimers.⁹⁰ The LDOS of the equilateral triangle (ET) AFM trimer exhibits a dip near the Fermi level, whereas the isosceles triangle (IT) configurations show a peak for the distant spin and dips for the others. The FM cases exhibit only peak features around the Fermi level. (i-j) LDOS of the Kondo trimer calculated using a static mean-field ansatz, revealing drastic variations in the low-energy LDOS even under subtle variations in the RKKY interactions.⁹¹ (k) LDOS of the IT Kondo trimer, showing broad peaks at the closer spin sites.

4.2.2 Triangular lattices with increasing size

We constructed triangular lattices of varying dimensions and measured their LDOS. Herein, we constructed bottom-up radical triangular clusters with sizes of $N = 3, 6$, and 10 . As shown in Figure 4.6(a, d), in the $N = 3$ triangle, the dI/dV spectra at all three radical sites exhibit resonance peaks, accompanied by a dip (broadened by ~ 2 meV) at the Fermi level. The fitting HWHM of the small dips are presented beside spectra. As the lattice expands to an $N = 6$ cluster (Figure 4.6(b, e)), the spectral signatures of the original trimer sites undergo transformations. The red site evolves from a narrow peak to a broad resonance in width of ~ 7.99 meV, with its peak position shifting toward deeper energy level by ~ 3 meV. Concurrently, the yellow and green sites develop deeper gaps in width of ~ 2.93 and 3.16 meV, respectively, manifesting as a double-peak feature with a peak-to-peak separation of ~ 7.40 meV. Notably, despite variations in peak position and width, all three corner radical sites (red, blue, pink) retain peak-like features near the Fermi level; conversely, the three radical sites located on the edges of the $N = 6$ triangle (yellow, green, magenta) display dip features accompanied by double-peak structures at the Fermi level.

Subsequently, we further expanded the finite-size lattice to $N = 10$ (Figure 4.6(c, f)). At this stage, the spectra of the initial six radical sites are reconstructed once again: the red peak broaden from ~ 7.99 to ~ 11.18 meV in width, and the yellow site exhibit relatively minor changes, while the double-peak feature of the green site gradually weakens, transitioning into a step-like profile. The blue, pink, and magenta sites experience drastic alterations; specifically, the blue and pink sites transform directly from broad peaks to step-like behaviors with the HWHM of ~ 5.11 and 5.63 meV respectively, while the deepening of the dip at the magenta site

renders its step-like feature more pronounced (with an inter-step distance of ~ 11 meV). This dramatic and site-dependent spectral evolution further substantiates the existence of significant magnetic exchange coupling among the radicals, although the specific coupling types and underlying mechanisms remain to be fully elucidated. In the $N = 10$ lattice, apart from the red corner site (which presents an energy-shifted broad peak), all other edge and bulk sites (including the brown and greyish-blue corner sites) exhibit dip or step-like spectral signatures. Given that the spectra of different sites still display discrepancies, we deduce that the inter-spin interactions possess intrinsic disorder.

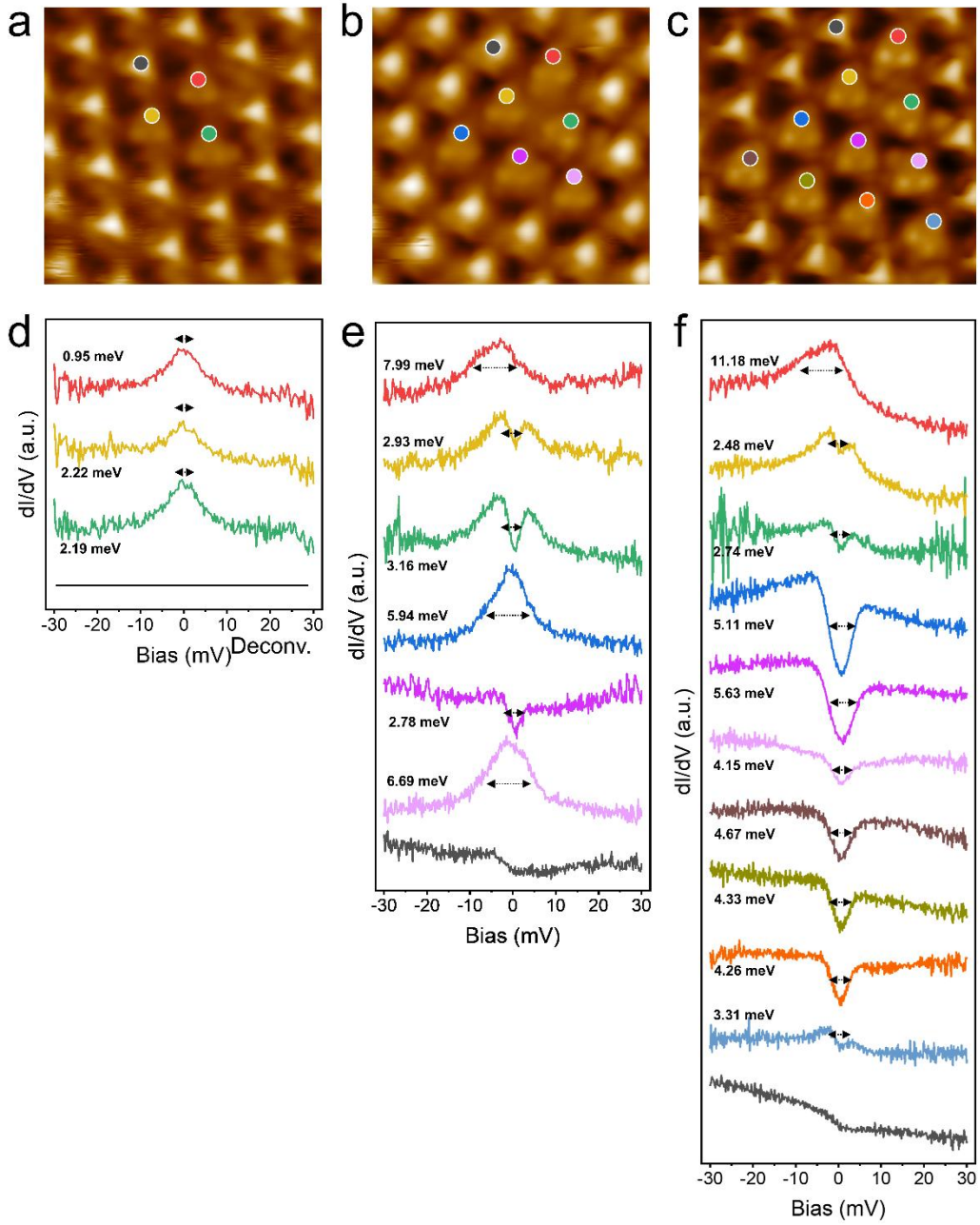


Figure 4.6 STM images and dI/dV spectra of triangular patterns in size of $N=3$ (a-b), $N=6$ (c-d) and $N=10$ (e-f). The specific sites for STS measurements are marked by colored dots. For the spectra in (d), a tip-substrate deconvolution is applied to clearly resolve the dip features near the Fermi level. As the size increases from $N = 3$ to $N = 10$, the proportion of these dips increases.

As shown in Figure 4.7, we successfully constructed a 2D radical triangular lattice of $N = 45$ with a defect rate below 7%. The STS measurements reveal that, except for the first spin site which exhibits a peak, all other measured sites present a dip at the Fermi level. For intuitive analysis, we overlaid the spectra featuring peaks with red background and those featuring dips with grey background. All Fano/ 2^{nd} order differential fitting results for peak/dips are presented beside the spectra, showing the domination of dip feature among $N=45$ d-TPM lattice. As shown in Figure 4.7, the peaks fitted with a Fano lineshape exhibit a linewidth of approximately 8 meV. Conversely, the full width at half maximum (HWHM) of the dips, determined via second-order differentiation, ranges from 2.88 to 14.39 meV, with the majority falling within the 4.32 to 5.04 meV interval.

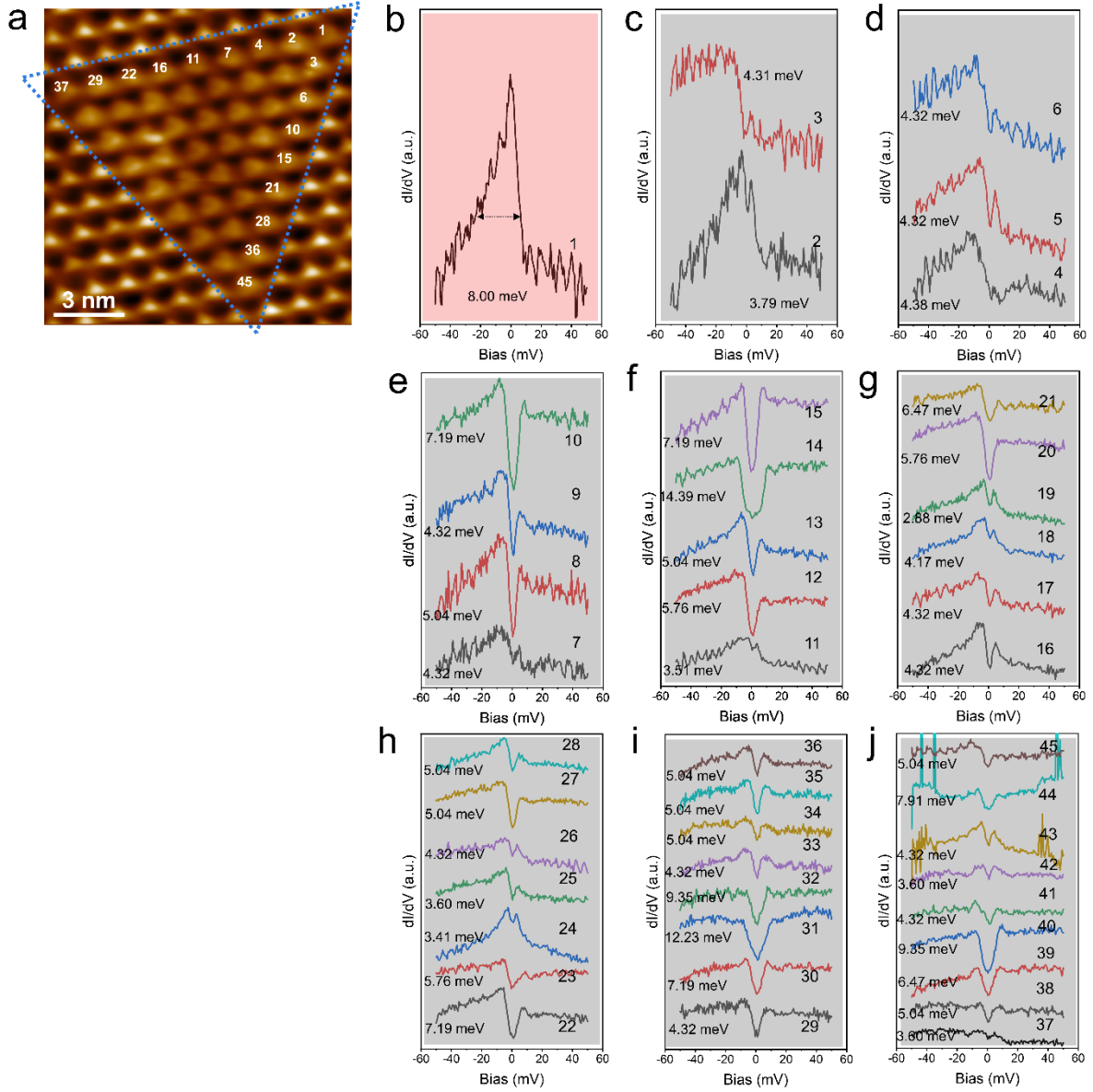


Figure 4.7 STM images (a) and dI/dV spectra (b-j) of triangular patterns in size of $N=45$. The radical sites are labelled and related STS measurements are presented, showing the domination of dips around Fermi level in the finite-size 2D radical lattice.

We attempted to use the effective Kondo lattice model introduced in Chapter 3 to qualitatively fit the spectral features observed in the experiment. Similarly, the LDOS is simulated by applying large- N expansion and mean-field theory with $\frac{\Gamma_K}{t} = 0.5$. We first calculate the LDOS for $N = 6$ finite-size Kondo lattice and the results are shown in Figure 4.8(d-f). The corner sites (1, 3, 6) exhibit peaks feature while the edge sites (2, 4, 5) show dips feature, in consistence with the dI/dV spectra of $N = 6$ d-TPM lattice shown in Figure 4.6(e). As the Kondo lattice model size is scaled up to $N = 36$ (Figure 4.8(c)), a universal spatial evolution pattern emerges

in the simulated LDOS: every corner spin site of the triangle presents a sharp peak near the Fermi level, the edge sites exhibit a weak hybridization gap, and the bulk sites display a pronounced and clear hybridization gap (Figure 4.8(h-o)). The physical origin of this phenomenon lies in the imbalance of the spin coordination numbers (nearest neighbors are 2, 4, and 6 for corner, edge, and bulk sites, respectively). The spectral variations, specifically the magnitude of the gap, directly reflect the enhancement of exchange interactions and quantum coherence driven by the increased coordination number. The overall spectral behavior of the $N = 45$ radical lattice closely aligns with the simulated results for $N = 36$ (i.e., the extensive formation of a hybridization gap). However, we failed to observe the predicted peak behaviors (corner states) at all geometric corners. We speculate that an unknown inhomogeneous magnetic exchange mechanism still exists within the system, which perturbs the finite-size boundary effects of the 2D Kondo lattice and leads to the quenching of the corner states. Despite of this, such results illustrate a qualitative feature expected for an idealized finite 2D Kondo-lattice model—the competition between the Kondo effect and the RKKY interaction leads to the opening of a hybridization gap, which is the core mechanism underlying the evolution of heavy fermion bands. We further calculated an infinite 2D Kondo lattice. The results show that translational symmetry is restored, and the spectra of all sites become identical, exhibiting a clear heavy fermion hybridization gap and two branches of heavy fermion bands (the band dispersion and averaged LDOS are presented for clarity in Figure 4.6(c)).

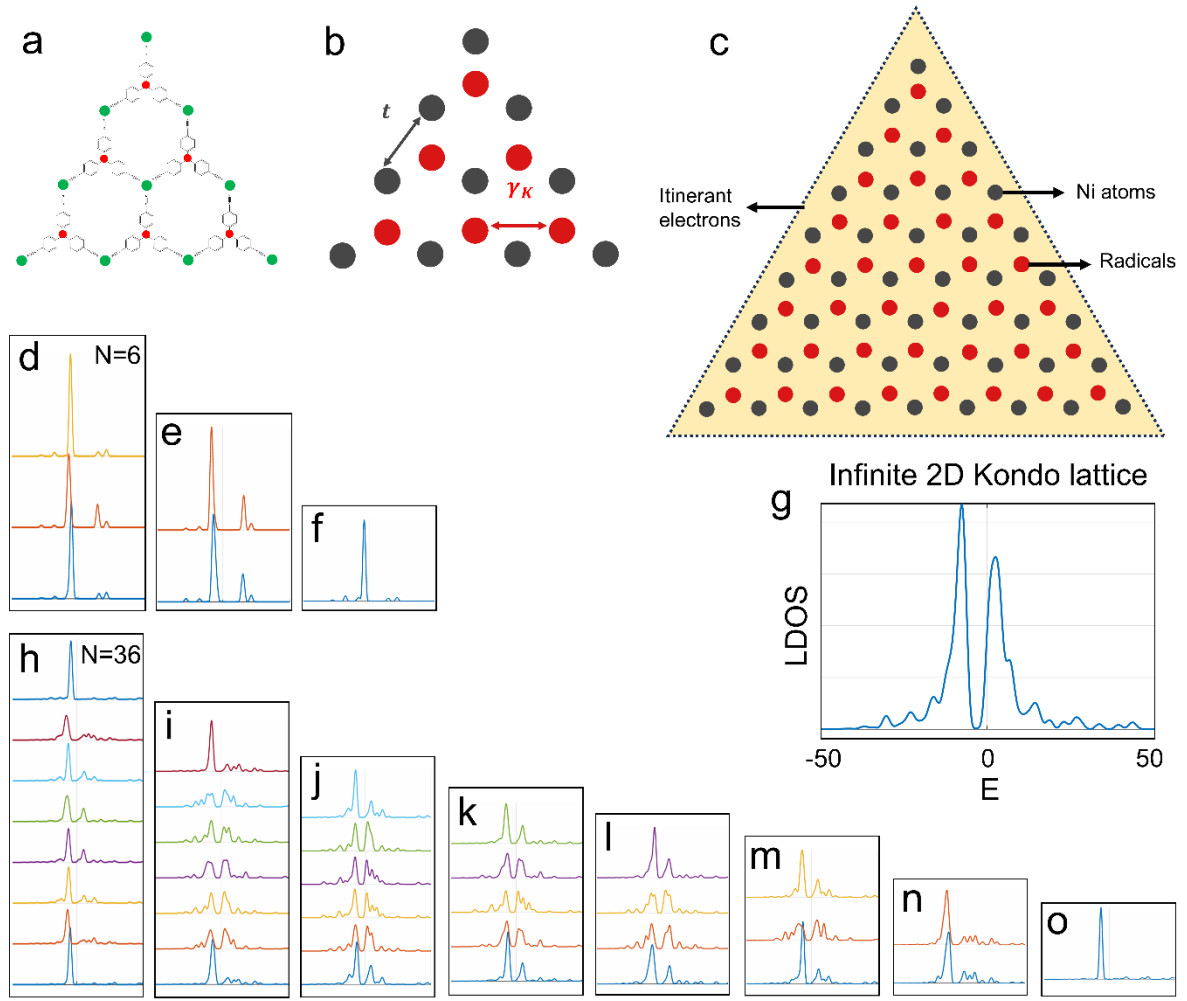


Figure 4.8 Theoretical model for finite and infinite-size 2D Kondo lattice. (a) Scheme of $N = 6$ finite-size 2D d-TPM lattice. (b) Theoretical model of the effective Kondo lattice, where red dots and black dots represent radicals and Ni/Au(111) itinerant electrons, respectively. Two key parameters are adjusted in the model: Kondo screening Γ_K and itinerant electrons hopping t between Ni atoms. (c) Model of $N=36$ finite-size 2D Kondo lattice, including itinerant electrons (yellow background), Ni atoms (black dots) and radicals (red dots). (d-f) LDOS of an $N=6$ 2D Kondo lattice with $\frac{\gamma_K}{t} = 0.5$, where the three corners show peaks feature while edge sites exhibit a dip feature around Fermi level. (g) Average LDOS of an infinite-size 2D Kondo lattice with $\frac{\gamma_K}{t} = 0.5$, showing a clear hybridized gap and heavy fermion flat bands. (h-o) The LDOS of $N=36$ Kondo lattice is simulated by the effective Kondo lattice model, exhibiting the corner states (peaks), edge states (weak gaps) and bulk states (intensive gaps).

Despite the remaining complex physical mechanisms yet to be fully understood, this work has taken a critical step forward: by combining the on-surface synthesis of MOFs with single-molecule tip manipulation, we have successfully realized the bottom-up construction of size-tunable 2D artificial spin lattices. This provides an unprecedented experimental platform for the profound exploration of Kondo physics, heavy fermion systems, and related many-body phenomena at the atomic scale.

4.3 Conclusions

In this chapter, finite 2D d-TPM radical lattices were constructed on the Ni-TPM/Au(111) platform by site-selective STM tip-induced dehydrogenation and characterized by site-resolved STS. Radical trimers with different chemical configurations both show dominant dip-like spectral features near the Fermi level at parts of radical sites, indicating that the radicals are electronically coupled and do not behave as isolated Kondo impurities. By increasing the lattice size from $N = 3$ to larger triangular arrays, the low-energy spectra evolve from mainly peak-like Kondo resonances to dip- or gap-like LDOS suppression. This size- and site-dependent evolution suggests collective spectral reconstruction driven by inter-radical coupling, local coordination and finite-size effects. Effective Kondo-lattice-type simulations qualitatively reproduce the tendency toward coordination-dependent gap-like suppression, supporting the interpretation that larger radical arrays approach finite-size Kondo-lattice-like behavior.

Overall, these results establish finite d-TPM radical lattices as a programmable molecular platform for exploring the evolution from isolated Kondo-active spins to interacting two-dimensional spin arrays, while leaving the precise microscopic mechanism to future temperature-, field-dependent and more quantitative theoretical studies.

Chapter 5

Opening Coulomb gap in the frontier molecular orbital

5.1 Introduction

Tuning the energy alignment of molecular frontier orbitals with respect to the Fermi level is an important route to regulating correlated electronic states in molecular materials. In molecular systems, small changes in charge state, coordination environment, or electrostatic potential can modify the spatial distribution, energy alignment, and many-body response of frontier orbitals. Open-shell π -radical molecules, which contain a singly occupied molecular orbital (SOMO) and a singly unoccupied molecular orbital (SUMO), can host localized spins and are sensitive to their local charge environment. They therefore provide useful platforms for studying molecular spintronics, molecular magnetism, and correlated electronic behavior. Among them, triphenylmethyl-derived frameworks are representative π -radical systems. Their central carbon radical or anionic electronic configuration can be stabilized by resonance over the three conjugated phenyl rings, leading to π -electron delocalization. Recent work by Yufeng Zhang and co-workers showed that, in a trigonal triphenylmethyl CPh_3^- -type carbanion, suitable electronic-structure modulation can delocalize the central negative charge over the three aryl branches and generate a quinoidal electronic structure, in which the excess charge is not confined to the central carbon but extends over the molecular π framework.⁹⁴ As illustrated in Figure 5.1(a), this charge-delocalized carbanion model provides an important conceptual reference for TPM-derived systems: once the electronic occupation of the central carbon is modified, the frontier molecular state can reorganize over the three phenyl branches rather than remaining localized at a single atomic site.

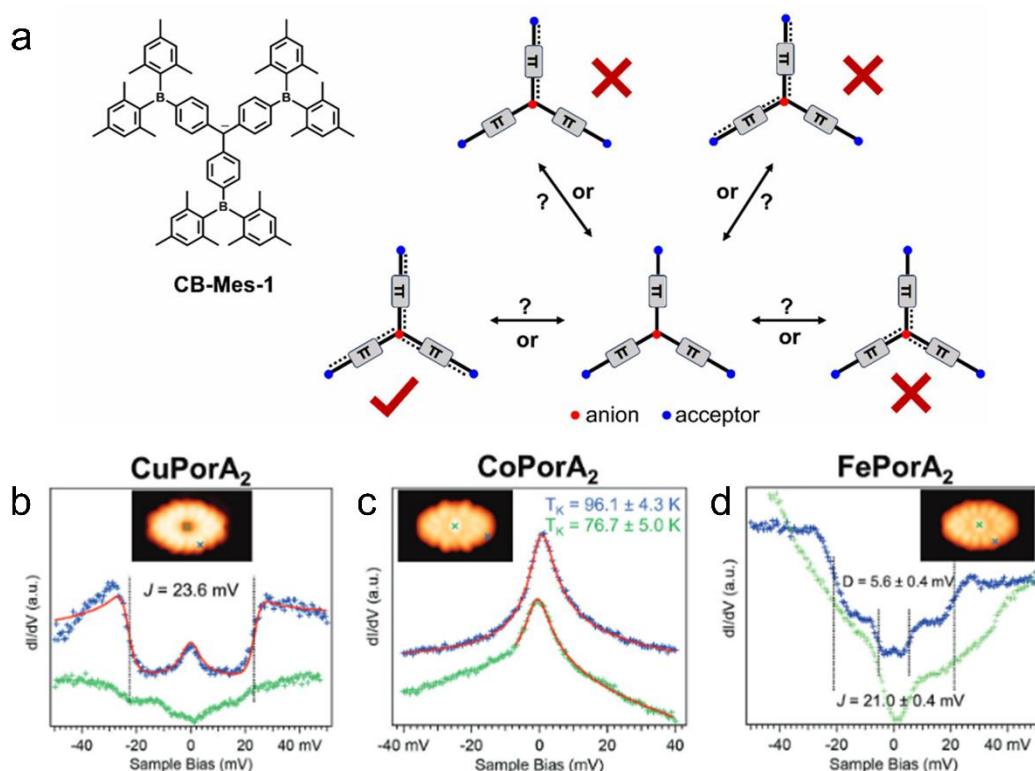


Figure 5.1 (a) Schematic illustration of the electron delocalization profile in CB-Mes-1, depicting alternative localized models versus the uniform triple quinoidal resonance structure.⁹⁴ (b-d) Site-dependent dI/dV spectra highlighting the states of Open-shell porphyrin with three different metal centers: (b) CuPorA₂, showing a ferromagnetic exchange coupling of 23.6 mV captured by a dynamic scattering model; (c) CoPorA₂, exhibiting a localized Kondo screening behavior with site-specific T_K values determined by Frota functions; and (d) FePorA₂, displaying clear spin-flip steps symmetric around the Fermi level.⁹⁵

On surfaces, chemical design and surface-assisted reactions allow charge-delocalized open-shell π molecules to coordinate with transition-metal atoms, forming molecule–metal hybrid electronic structures. Metal nodes can act not only as structural linkers, but also as active components that participate in charge transfer, tune orbital occupation, and hybridize their (d) orbitals with molecular π frontier orbitals. For example, Qiang Sun and co-workers investigated open-shell π -extended metallocporphyrins containing Cu, Co, and Fe centers using STM/STS and DFT.⁹⁵ Their results showed metal-dependent magnetic interactions between central metal (d) electrons and ligand π electrons. The Cu and Fe derivatives mainly exhibit ligand-based π -spin coupling, whereas the low-energy spectra of the Co derivative are dominated by a Kondo

resonance associated with the Co d_{z^2} orbital. These examples, summarized in Figure 5.1(b–d), demonstrate that the same open-shell ligand framework can display distinct low-energy many-body responses depending on the metal center. Therefore, metal substitution provides a chemically controlled route to tune orbital hybridization, charge transfer and spin-related electronic behavior in surface-supported molecular systems. Our previous work on a Ni–TPM coordination network on Au(111) also showed that tip-induced dehydrogenation can convert TPM into a carbon-centered radical, d-TPM, producing near-Fermi level molecular states and a zero-bias Kondo resonance.⁷⁵ DFT calculations further showed that the SOMO/SUMO orbitals of d-TPM hybridize with Ni (d) orbitals and Au(111) substrate states, forming d-TPM–Ni–Au molecule–metal–substrate hybrid states. This hybridization enables conduction electrons from Au to screen the localized π spin of d-TPM indirectly through the Ni atomic contacts. The high-resolution STM image, site-specific dI/dV spectra and zero-bias conductance map in Figure 3.4(a, c) show that the Ni–d-TPM system behaves as a Kondo-active radical platform. This motivates a central question of the present chapter: how does replacing Ni with Fe modify the electronic structure and many-body response of the dehydrogenated TPM unit?

Tuning of such hybrid states by electrostatic or local electric fields may drive the system into a regime where electron–electron interactions become important. Studies of highly doped IDT-BT polymer semiconductors have shown that, when a molecular-derived density of states is gated toward the Fermi level, localization, disorder, and long-range Coulomb interactions can suppress the density of states near E_F , giving rise to a soft Coulomb gap.⁹⁶ As shown in Figure 5.2(a,b), the IDT-BT polymer semiconductor provides a representative molecular system in which the electronic DOS can be tuned relative to E_F . The schematic in Figure 5.2(c) summarizes the key gating behavior: the soft Coulomb gap opens when the relevant DOS is brought to E_F and vanishes when it is moved away from E_F . This highlights a general principle: when a narrow, localized or weakly dispersive electronic state is brought close to the Fermi level, its spectrum may be reshaped not only by single-particle level alignment but also by electron–electron interactions.

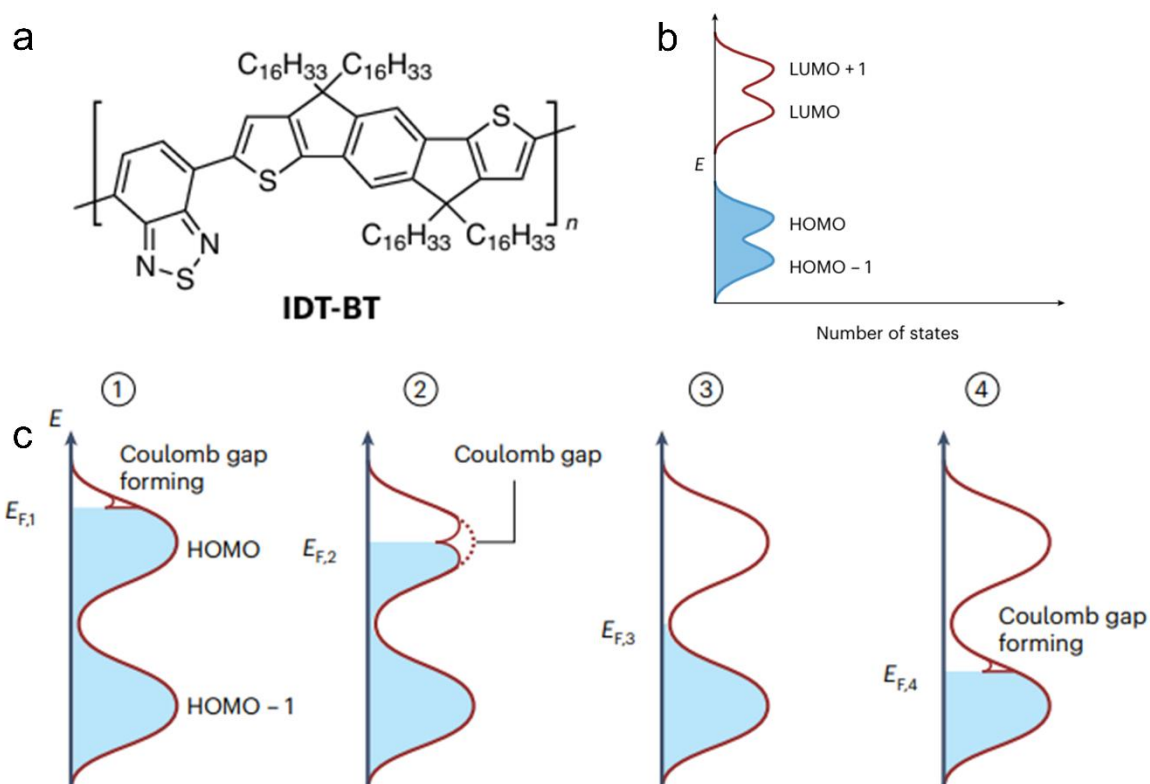


Figure 5.2 Emergence of a Coulomb gap. (a-b) Chemical structure and corresponding electronic DOS schematic for the IDT-BT polymer semiconductor. The variable E represents energy. (c) The soft Coulomb gap opens when the DOS gating to E_F and vanishes when it move away from E_F .⁹⁶

Here, we synthesized a Fe-TPM MOF on Au(111), in which individual TPM units can be converted into dehydrogenated TPM (d-TPM) by tip manipulation. We propose that dehydrogenation of the central carbon first creates an open-shell d-TPM molecular unit. This unit then coordinates with Fe nodes, where metal–ligand charge transfer stabilizes a carbanion-like electronic configuration and promotes hybridization between the molecular SOMO and Fe d orbitals. STS measurements reveal a molecular resonance near the Fermi level, with a spatial distribution consistent with a SOMO–d hybridized state. Under tip-induced gating, this resonance can be shifted reversibly towards or away from E_F . When it approaches the Fermi level, a soft-gap-like suppression appears in the low-energy density of states. Combining STM/STS measurements with electronic-structure calculations, we attribute this behavior to a gate-tuned, correlation-driven suppression of the density of states in a localized SOMO–d hybrid state, namely a Coulomb-gap-like many-body response. This system provides a molecular-scale platform for studying Coulomb-correlated electronic states in programmable metal–organic lattices.

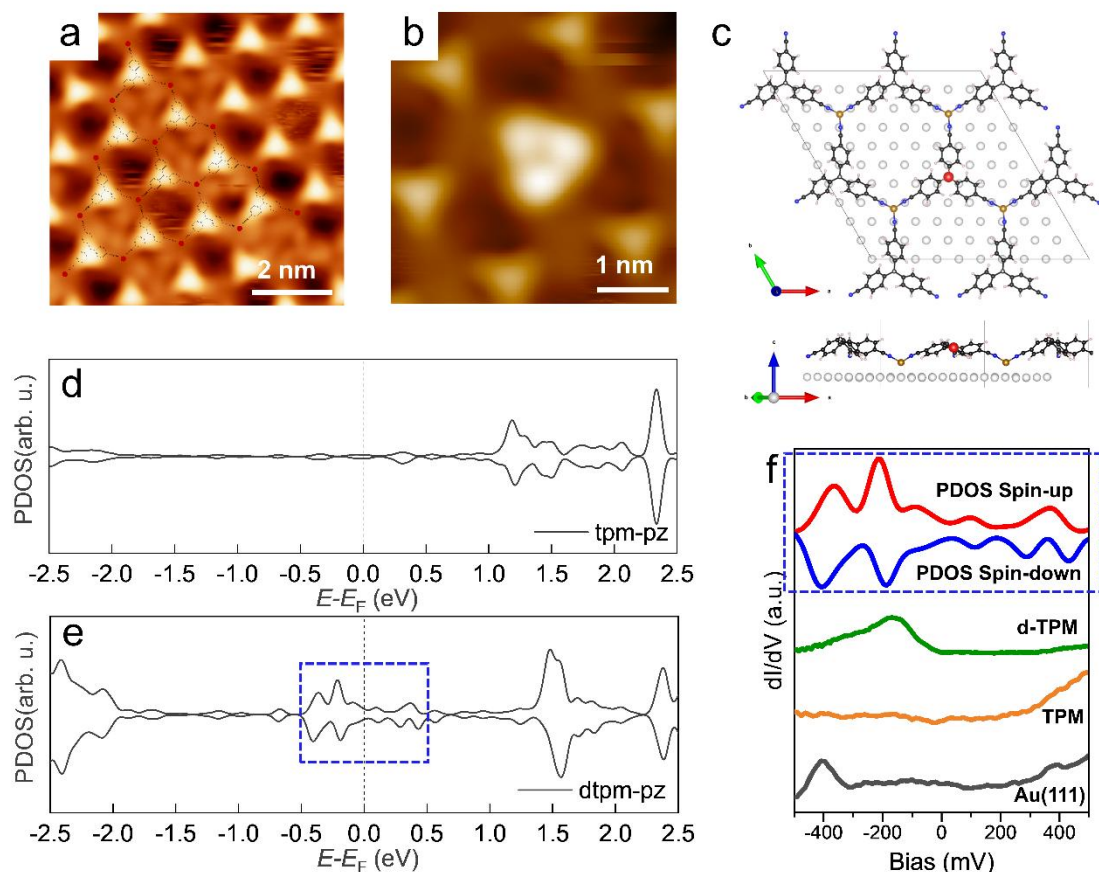


Figure 5.3 STM topography of the Fe-TPM MOF on Au(111). Both the TPM molecules and Fe atoms form a triangular lattice with a lattice constant of $14.76 \pm 0.1 \text{ \AA}$ ($V = -500 \text{ mV}$, $I = 100 \text{ pA}$, scale bar: 2 nm). (b) High-resolution STM image of an individual d-TPM molecule, resolving a characteristic three-lobed protrusion ($V = -500 \text{ mV}$, $I = 100 \text{ pA}$, scale bar: 1 nm). (c) Structural model of the Fe-TPM MOF on the Au(111) substrate. Each unit cell contains a single d-TPM molecule, with the radical center indicated by a red sphere. Top and bottom panel show the top-view and side-view of Fe-TPM structure, respectively. (d-e) DFT-calculated spin-polarized PDOS for the TPM (d) and d-TPM (e) p_z orbitals, revealing SOMO-d hybridized states located at -400 meV and -200 meV . (f) Comparison of the calculated spin-polarized PDOS (red and blue curves) with the experimental dI/dV spectra of d-TPM (green). The reference spectra acquired on an intact TPM molecule (orange) and Au(111) substrate (black) is also shown.

5.2 Results and Discussions

The monolayer Fe-TPM MOF was synthesized on Au(111) surface using the same method that introduced in chapter 2. Figure 5.3(a) shows the STM image of Fe-TPM MOF with lattice

constant of $\sim 14.76 \pm 0.1 \text{ \AA}$, which is similar to Ni-TPM. Both TPM molecules and Fe atoms form into triangular lattice. d-TPM molecules can be constructed via tip-induced dehydrogenation as shown in Figure 5.3(b). After dehydrogenation, the molecule displays a characteristic three-lobed protrusion in high-resolution STM images, consistent with the formation of a triphenylmethyl-derived dehydrogenated unit. This structural transformation provides the basis for modifying the frontier electronic state of the TPM molecule through local chemical conversion. We performed DFT calculations for a structural model of Fe-TPM on Au(111), in which one d-TPM molecule was included in the unit cell, as shown in Figure 5.3(c–e). In the structural model shown in Figure 5.3(c), both the top-view and side-view configurations demonstrate the arrangement of the Fe-TPM structure, with the radical center explicitly indicated by a red sphere in the middle of the d-TPM molecule. The spin-polarized PDOS of the d-TPM p_z orbitals forms hybridized states mainly located around -400 meV and -200 meV. These calculated states are consistent with the broad experimental peak observed at approximately -190 mV in the dI/dV spectrum of d-TPM (green curve in Figure 5.3(f)). This panel provides a direct comparison of the calculated spin-up and spin-down PDOS (red and blue curves) with the experimental d-TPM spectra, while also establishing a baseline with reference spectra acquired on an intact TPM molecule and the pristine Au(111) substrate. The overlap between the calculated d-TPM p_z states and Fe d -orbital contributions indicates that this resonance is not a purely molecular orbital, but a SOMO–Fe- d hybridized state. The absence of such a -190 mV resonance on intact TPM further supports that this state is generated by the dehydrogenation-induced change in the electronic configuration of the TPM. DFT calculations reveal that before dehydrogenation, the Fe atoms carry a magnetic moment of $2.95 \mu_B$. After dehydrogenation, the Fe moment changes slightly to $3.00 \mu_B$, while the d-TPM molecule obtains only a small moment of $0.05 \mu_B$. This result suggests that the Fe–d-TPM monomer does not host a robust localized spin in the calculated ground state. Instead, dehydrogenation and metal–ligand charge transfer likely stabilize a carbanion-like, charge-delocalized configuration in which the SOMO-derived molecular state is strongly hybridized with Fe d orbitals. Therefore, the broad resonance at approximately -190 mV is assigned to a SOMO– d hybridized molecular state.

Interestingly, the dI/dV spectra of d-TPM molecules show the SOMO-derived states can be shifted by actions of applying voltage pulses or performing Z-ramp operations on the tip. Figure 5.4(a–b) summarizes the dI/dV spectra collected from 13 d-TPM molecules after multiple tip-actions, including Z-ramp operations of 700 pm–1 nm and voltage pulses of -3 to -5 V. For

comparison, the spectra are numbered from 1 to 13 according to the position of the main peak relative to the Fermi level, and the peak positions are indicated by colored arrows. As shown in Figure 5.4(a), when the SOMO–d hybridized state shifts from approximately -190 mV towards the Fermi level, the initially single peak begins to split around state 9, accompanied by a suppression of the spectral intensity near the Fermi level. This spectral evolution suggests that tip modification acts as a local gating process, most likely by changing the electrostatic environment of the junction or inducing partial charge transfer between the molecule, metal nodes and substrate. In this way, the SOMO–d hybridized state can be reversibly shifted toward or away from the Fermi level without destroying the molecular structure. The narrow-range spectra in Figure 5.4(b) further show that this suppression is not an intrinsic gap associated with a complete depletion of the density of states, but rather a soft gap feature in which the DOS near the Fermi level is partially reduced. We further analyzed the energy positions of the two split peaks in states 9–13 and found that they are not symmetric with respect to the Fermi level (Figure 5.4(c)). The d^2I/dV^2 fitting results indicate that the soft-gap sizes range from 8.35 to 16.76 meV. This behavior differs from the approximately bias-symmetric features expected for typical inelastic spin excitations. In addition, DFT calculations indicate that the system has a non-magnetic ground state in the considered charge state, which does not support a stable intramolecular two-spin configuration. Therefore, an assignment of the double-peak structure to intramolecular magnetic excitations or a Kondo resonance is unlikely. Because the SOMO–d hybridized state can be reversibly shifted towards or away from the Fermi level by changing the tip state, we infer that tip modification may alter the local electrostatic environment to effectively gate the d-TPM, thereby shifting the SOMO–d hybridized state of d-TPM. When this molecular state approaches the Fermi level, intra-molecular electron–electron interactions may become more relevant, leading to a redistribution of spectral weight across the Fermi level and producing a soft gap near E_F . This behavior is more appropriately described as a correlation-induced reconstruction of the spectral function involving Coulomb interactions, rather than a simple single-particle level splitting or an intrinsic band gap.^{96,97}

To further examine this picture, we performed dI/dV mapping at the energies of the two split peaks located just below and above the Fermi level. As shown in Figure 5.5(a-d), the electronic states measured at -18.1 mV and +14.1 mV exhibit nearly identical spatial distributions. In both cases, the spectral weight is delocalized over the Fe–d-TPM molecule, with higher DOS on the three phenyl rings than at the central carbon atom. This similarity suggests that the two split peaks do not originate from two independent molecular orbitals, but more likely arise from

a redistribution of spectral weight within the same parent SOMO–d hybridized state near the Fermi level. As a comparison, we also performed dI/dV mapping on another d-TPM molecule in Figure 5.5(e-g) that remains in a single-peak state, with the main peak located at approximately -126 mV. This state is also assigned to the SOMO–d hybridized state and is delocalized over the whole molecule, in consistent with the PDOS distribution of states at -200 meV calculated by DFT (Figure 5.5(h)). This comparison suggests that, when the SOMO–d hybridized state is shifted close to the Fermi level, intra-molecular Coulomb interactions gives rise to the observed soft gap spectroscopic response.

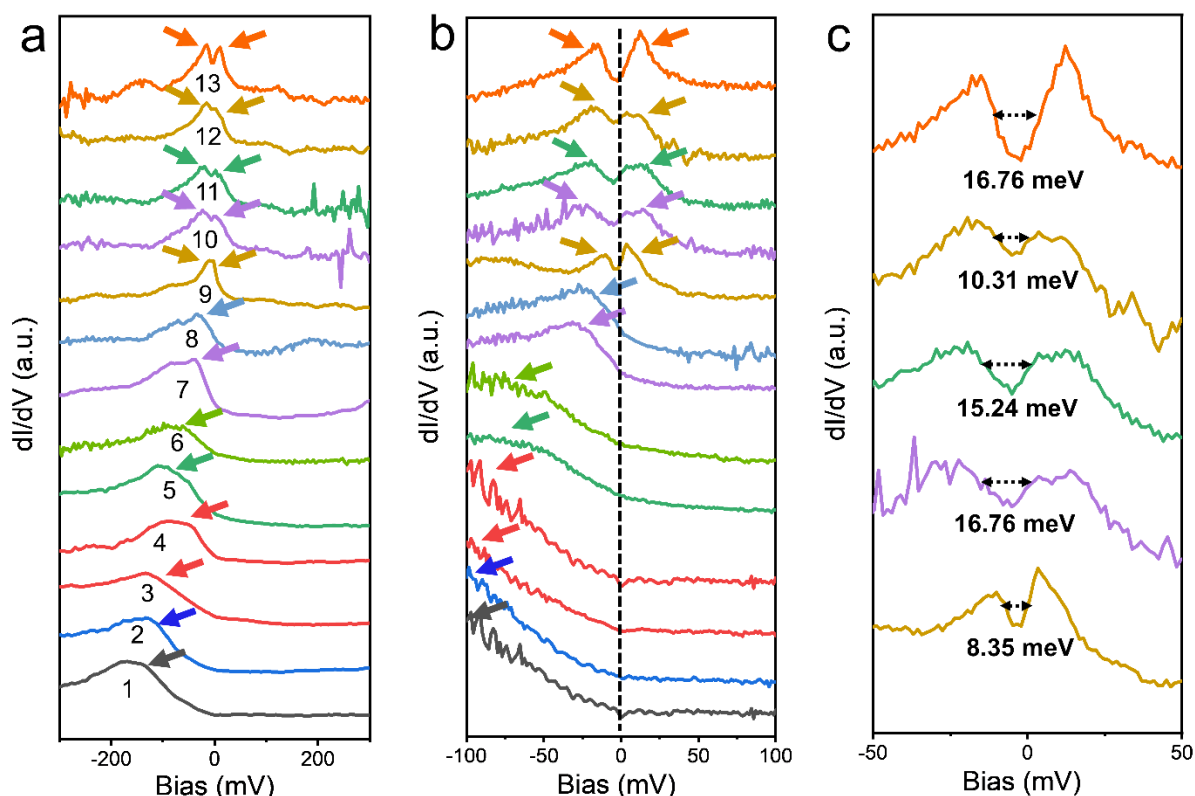


Figure 5.4 (a-c) Wide-range (a) and low-energy (b) dI/dV spectra acquired on 13 individual d-TPM monomers. Main spectral peaks are indicated by colored arrows. The spectral evolution demonstrates that as the SOMO-d state approaches the Fermi level, it splits into two peaks, opening a soft gap at the Fermi energy. (c) Five representative dI/dV spectra exhibiting a soft-gap feature, with the corresponding d^2I/dV^2 fitting results of gap sizes listed alongside each spectra (in range from 8.35 to 16.76 meV), highlighting the asymmetry around E_F .

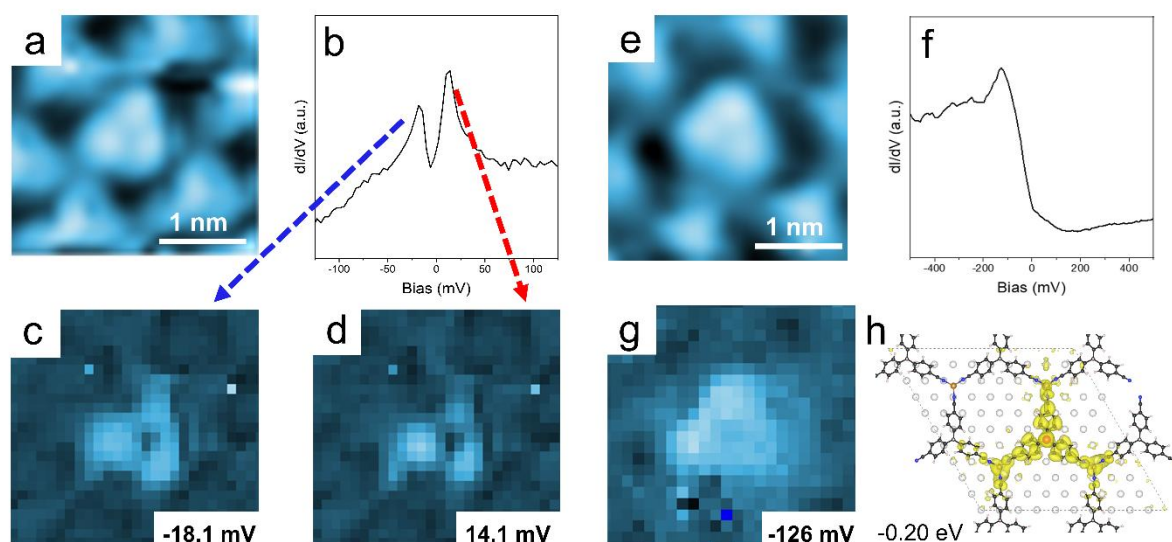


Figure 5.5 (a) High-resolution STM image of a d-TPM molecule exhibiting a soft gap around the Fermi level in its dI/dV spectra, shown in (b) ($V = -100$ mV, $I = 100$ pA, scale bar: 1 nm). (c, d) dI/dV mappings of the d-TPM monomer in (a) acquired at biases of (c) -18.1 mV and (d) $+14.1$ mV. The identical spatial distribution of states indicates they originate from the same molecular orbital. (e) High-resolution STM image of another d-TPM molecule whose corresponding dI/dV spectra, shown in (f), displays prominent SOMO-d hybridized states centered around -126 mV. (g) dI/dV mapping recorded at -126 mV, revealing a delocalized state distribution across the entire molecule, likely originating from the same molecular orbital observed in (c, d). (h) Spatial distribution of PDOS of SOMO-d states at -200 meV.

5.3 Conclusions

In this chapter, we demonstrate that metal-center substitution provides an effective route to tuning the electronic properties of radical TPM-based MOFs on Au(111). Replacing Ni with Fe produces a Fe-TPM framework in which individual TPM units can be converted into d-TPM by STM tip-induced dehydrogenation. STM images confirm the formation of an ordered triangular Fe-TPM network and a characteristic three-lobed d-TPM species. DFT calculations and STS measurements together show that dehydrogenation generates a SOMO-d hybridized molecular state, observed experimentally as a broad resonance around -190 mV. The small calculated magnetic moment on d-TPM suggests that the Fe-d-TPM monomer is better described as a carbanion-like, charge-delocalized hybrid state rather than a robust localized radical spin.

Tip actions by voltage pulses or Z-ramp operations can reversibly shift the SOMO-d hybridized resonance towards or away from the Fermi level. When this state approaches E_F , the single resonance evolves into a two-peak structure accompanied by a soft-gap-like suppression near the Fermi level. The asymmetric positions of the split peaks, together with the non-magnetic DFT ground state, rule out spin excitations. Energy-resolved dI/dV maps reveal that the two split peaks at -16.0 mV and +12.6 mV exhibit nearly identical spatial distributions, indicating that they originate from the same parent molecular orbital rather than from two independent states. A comparison with a single-peak d-TPM molecule at -126.0 mV shows that the soft gap appears only when the SOMO-d hybridized state is shifted close to E_F . These results support a physical picture in which local tip-induced gating shifts the SOMO-d hybridized state close to the Fermi level, enhancing intra-molecular Coulomb interactions and producing a Coulomb-gap-like suppression. The Fe-TPM platform therefore provides a molecular-scale system for studying gate-tunable, correlation-driven orbital reconstruction.

Chapter 6

Integrating AI into STM for the construction of large-scale radical lattices

6.1 Introduction

As Richard Feynman envisioned back in the fifths last century, “What would the properties of materials be if we could really arrange the atoms the way we want them?”⁹⁸. The vision of constructing atomic- and molecular-precision architectures that harness emergent phenomena has long been a central goal in nanomaterial science and technology. The realization of this vision materialized with the first demonstration of atomic manipulation by STM in 1990³⁸. Over the past decades, STM’s capabilities of imaging and manipulating down to sub-nanometer precision has enabled the fabrication of different artificial quantum structure (AQS) with potential in quantum simulations^{39,40,99}, memory storage^{41,42}, quantum information^{24,43}, and quantum magnetisms^{44,45,74,100,101}. However, current practices of STM manipulation heavily rely on human operators, which are labor-intensive and prone to human errors. Typically, a human operator often spends long hours constructing structures made of few tenths of molecules or atoms. This limitation has hindered scalable AQS fabrication and thus restricts the exploration of collective quantum phenomena manifested at larger scales.

Recent advances in AI offer a promising route to overcome these limitations. By integrating machine learning and decision-making algorithms, STM can autonomously recognize, analyze, and manipulate at the atomic scale¹⁰²⁻¹⁰⁴. A representative example is shown in Figure 6.1(a-c). Through continuous interactions with the STM environment, a trained DRL agent learns to manipulate individual Ag atoms with atomic precision, ultimately enabling the automated construction of a complex 42-atom kagome lattice when combined with path-planning algorithms.¹⁰⁴ Parallel to the advance in manipulation, deep learning models have also achieved expert-level image recognition, enabling automatically identifying molecular configuration^{47,48,105} and automated tip conditioning with minimum human intervention but high stability^{49-51,106}. In addition, reinforcement-learning algorithms allow STM to self-optimize operational parameters, perform autonomous manipulation of single molecules, and execute site-specific reactions with adaptive precision^{46,103,104,107}. Nevertheless, most existing AI-STM demonstrations remain limited to isolated molecules or small clusters. Extending the AI-driven STM to effectively construct large-scale molecular structures has not been reported.

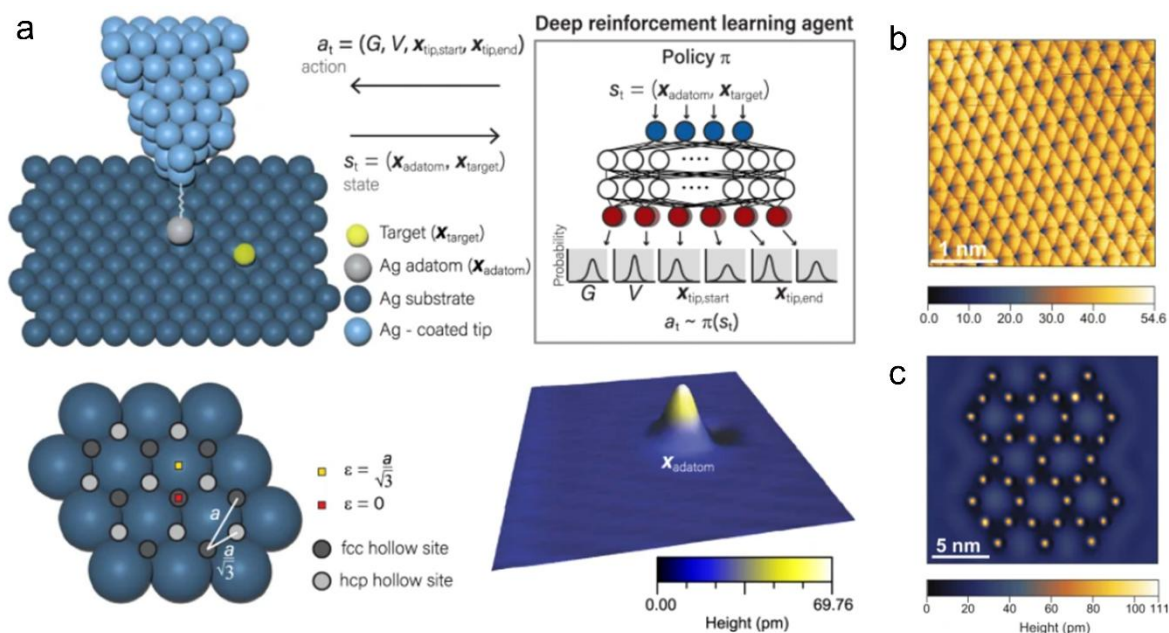


Figure 6.1 (a) DRL agent interacts with the STM environment to manipulate Ag adatoms with atomic precision. The policy network outputs conductance, bias, and tip trajectory to move atoms toward target adsorption sites. (b-c) STM imaging of manipulated Ag atoms confirms lattice orientation, while a trained DRL agent, combined with assignment and path-planning algorithms, enables the atomically precise construction of a 42-atom Kagome lattice.¹⁰⁴

Here, we combine AI-driven STM with on-surface reactions for autonomous construction of programmable lattices of molecular radicals. STM tip-induced on-surface reactions has been used for realizing single-molecule radicals^{22,44,54,108}. Here we used a platform of tris(4-carbonitrile)-triphenylmethyl (termed TPM thereafter) metal–organic frameworks self-assembled on a Au(111) substrate. Our prior work showed that dehydrogenated TPM (d-TPM) retains localized spin⁷⁵, making it an ideal building block for spin AQS. By employing a soft actor–critic (SAC) reinforcement-learning algorithm, we have optimized the parameter of dehydrogenation to achieve a successful rate of $\sim 93\%$ (an experienced human operator normally can achieve $\sim 67\%$). Using the optimized parameters, we constructed triangular, Kagome and honeycomb lattices of molecular radicals in Fe-TPM and Ni-TPM platforms. We also employed the fully autonomous SML to construct (1) a large triangular lattice containing 632 molecular radicals, and (2) programmable structures of specific shape and size. Our work demonstrates that SML is a transferable strategy for bottom-up construction of scalable AQS.

6.2 Results and discussion

6.2.1 Workflow of SML

The SML is built on a closed-loop workflow that integrates molecular recognition, autonomous decision-making and STM-based reaction execution. A deep-learning model is first trained to identify target molecules with high accuracy. As shown in Figure 6.2, each autonomous cycle starts from STM imaging, followed by deep-learning-based analysis of molecular positions and states, which identifies the sites of the target molecules, after which the system applies tip-induced manipulation to dehydrogenate the target molecules. For each manipulation operation, the control policy determines the dehydrogenation parameters, including the lateral position of the tip (X , Y), the bias voltage (V) and the tunnelling current (I). The outcome is subsequently verified by STM imaging to classify the molecules as intact, dehydrogenated or degraded. The verified outcome is then fed back into the next cycle, enabling progressive refinement of the manipulation conditions through repeated rounds of scanning, analysis, execution and verification. This loop operation laid the foundation autonomous SML with high fidelity and high efficiency, thereby establishing the feasibility of scalable fabrication of AQS.

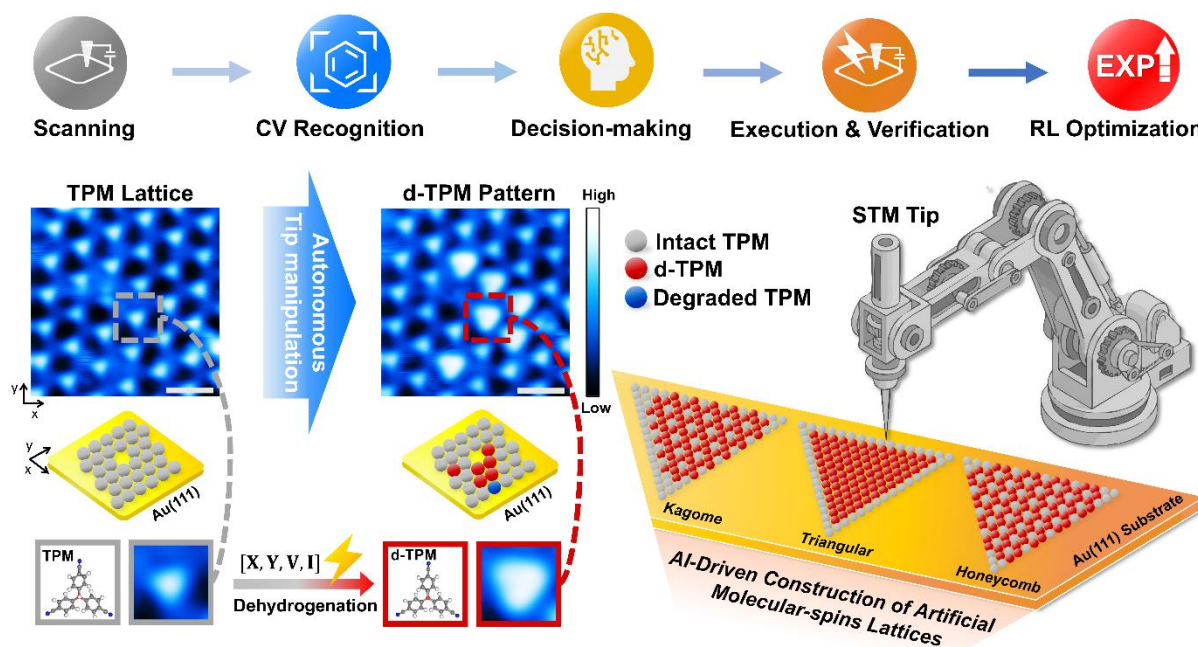


Figure 6.2 Overview of the AI-driven single-molecule lithography for constructing artificial lattices of molecular radicals. Top panel: Schematic of a single training cycle. Each cycle consists of five steps: scanning, computer-vision (CV) recognition, decision-

making, execution and verification, and reinforcement-learning (RL) optimization. Left panel: The AI agent autonomously performs site-specific TPM dehydrogenation via optimized tip pulses, then rescan and classify molecules as intact TPM (grey), d-TPM (red), or degraded (blue). Right panel: The optimized SML workflow enables programmable fabrication of Kagome, triangular, and honeycomb d-TPM lattices on TPM/Au(111).

First, we used the Fe-TPM MOF platform to train the agent. We implemented an AI-STM framework organized into three functional components: (i) image analysis, (ii) decision-making, and (iii) execution with verification. The three components operate in a closed loop through a TCP communication interface connected to the STM control system^{46,52}. Each cycle begins with STM imaging, then the states and positions of all TPM molecules in the STM image are analyzed and identified based on the characteristic STM topographies: Intact TPM molecules appear as triangular features with a bright center attributed to the sp^3 C-H out-plane protrusion (marked in grey), whereas the molecules subjected to tip-induced dehydrogenation (d-TPM) exhibit a threefold clover leaf appearance (marked in red)⁷⁵. Molecules that lose their intrinsic three-fold symmetry are classified as degraded species, as illustrated in Figure 6.3 (b-c) and marked in blue.

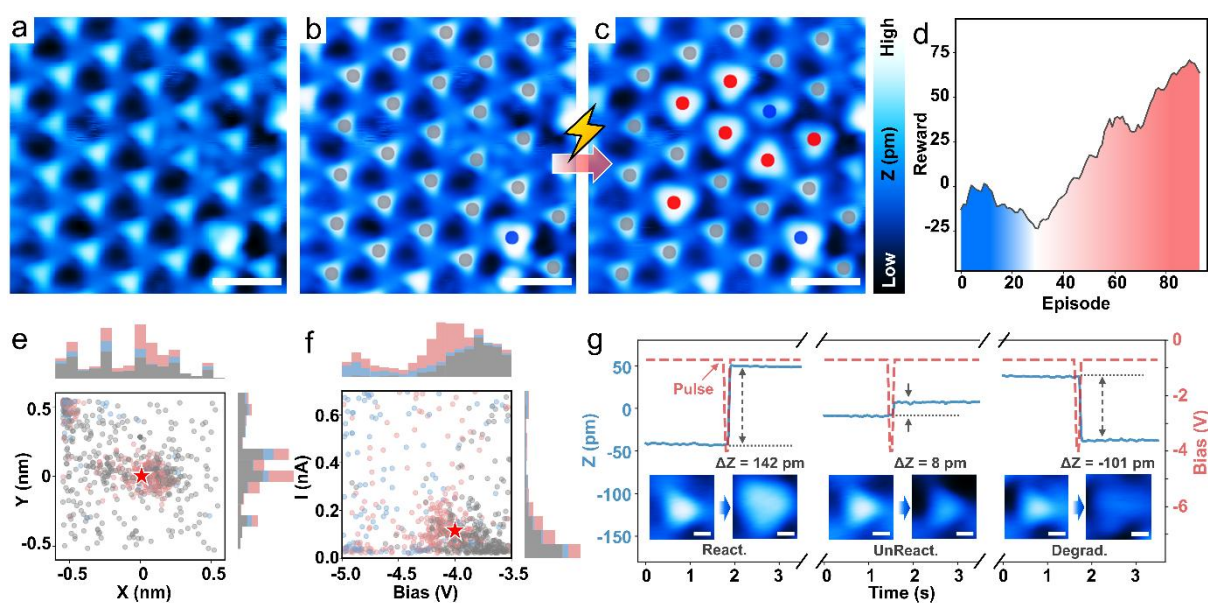


Figure 6.3 AI-driven molecular reaction and model training. a, Initial STM image before tip manipulation (100 pA, -500 mV). b, AI-based image recognition of a, identifying intact TPM (grey) and defects (blue). c, Representative agent verification during training, where

molecular states are: success (red), failure (blue), and no reaction (grey). d, Evolution of the rolling average episode reward (10-episode window). The blue-to-red transition indicates the agent's convergence toward a high-reward regime via accumulated successful reactions. e, f, Statistical dependence of reaction outcomes on tip spatial offsets (bin width 0.05 nm) and manipulation parameters. Colors denote outcomes as in c. Red stars mark optimal conditions for success: the TPM center (0, 0) and (−4.0 V, 100 pA), respectively. Axis histograms display corresponding outcome probabilities. g, Representative tip-height (ΔZ) trace during manipulation in constant-current mode ($\Delta Z > 0$ indicates height increase). Insets: STM images of corresponding outcomes. Scale bars, 2 nm (a–c) and 0.5 nm (g insets).

The acquired STM images are subsequently processed by a machine-vision module based on a YOLOv7 key-point detection algorithm^{47,109}, which outputs the centroid coordinates and molecular states of all molecules within the current scan frame, presented by colored dots for visualization as shown in Figure 6.3 (b). To ensure robust performance, this visual model is trained independently prior to closed-loop operation. The training dataset consists of 28 STM images that are further expanded through data augmentation to generate a dataset of more than 1500 images, which is used to train the visual-recognition model. Once the molecular positions and states are established, we adopt a reinforcement learning-based strategy to autonomously optimize the manipulation process. Successful dehydrogenation occurs only within a narrow region in a high-dimensional parameter space. The parameters are optimized as a sequential decision-making problem based on experimental feedback by the reinforcement-learning agent within a continuous four-dimensional action space. A parameter vector $[X, Y, V, I]$ defines the experimentally accessible STM control variables, where X and Y specify the lateral tip position relative to the molecular centre, and V and I denote the sample bias and tunnelling current, respectively. The bias was applied for 100 ms in each manipulation event at a constant current. The parameters generated by the SAC agent are executed through a standardized STM manipulation protocol. Guided by the parameters proposed by the decision module, the system executes tip-induced manipulations within a closed-loop framework that continuously evaluates outcomes and refines the control policy. The state observed by the agent encodes the molecular configuration before and after manipulation, as identified by the vision module. To ensure data efficiency and stability under real experimental conditions, parameter optimization is performed using a batch-update scheme. The resulting state–action–reward tuples are accumulated in a replay buffer and repeatedly sampled to update the policy.

In total, 1040 molecular manipulation events were collected over 104 episodes. As shown in Figure 6.3(d), the evolution of episode-level rewards reveals a clear learning trajectory: During the early episodes, the rewards are predominantly negative and strongly fluctuating (blue region in Figure 6.3(d)), reflecting exploratory behavior associated with a low reaction success rate. As training proceeds, the cumulative reward increases steadily and converges to a stable positive plateau after approximately 60–70 episodes (red region in Figure 6.3(d)), indicating the emergence of a consistent and effective manipulation policy. Further analysis of the converged action outputs reveals statistically structured distributions across all four parameters. As shown in Figure 6.3(e), the lateral displacement parameters (X, Y) converge to near-zero values, indicating a strong preference for tip placement directly above the molecular center, where the tip is nearest to the central C–H bond. The bias-voltage distribution centers at -4.0 V (Figure 6.3(f)) and is concentrated within ± 0.3 V, indicating that the agent consistently identifies a well-defined voltage regime for successful dehydrogenation. The tunneling current (I) outputs centers near 100 pA (Figure 6.3(f)). The agent's outputs stabilized near the optimized dehydrogenation parameters $[X, Y, V, I] = [0 \text{ nm}, 0 \text{ nm}, -4.0 \text{ V}, 100 \text{ pA}]$ (See Figure 6.3(e-f)), which reached a success rate 72% along with 8% degradation and 20% non-reaction events. Figure 6.3(g) shows representative changes in the tip-height signal recorded during the manipulation of the three kinds of events, showing $\Delta Z > 100 \text{ pm}$ for successful dehydrogenation, $-20 < \Delta Z < 20 \text{ pm}$ for no reaction, and $\Delta Z < -100 \text{ pm}$ for degradation.

6.2.2 AI-assisted construction of artificial lattices

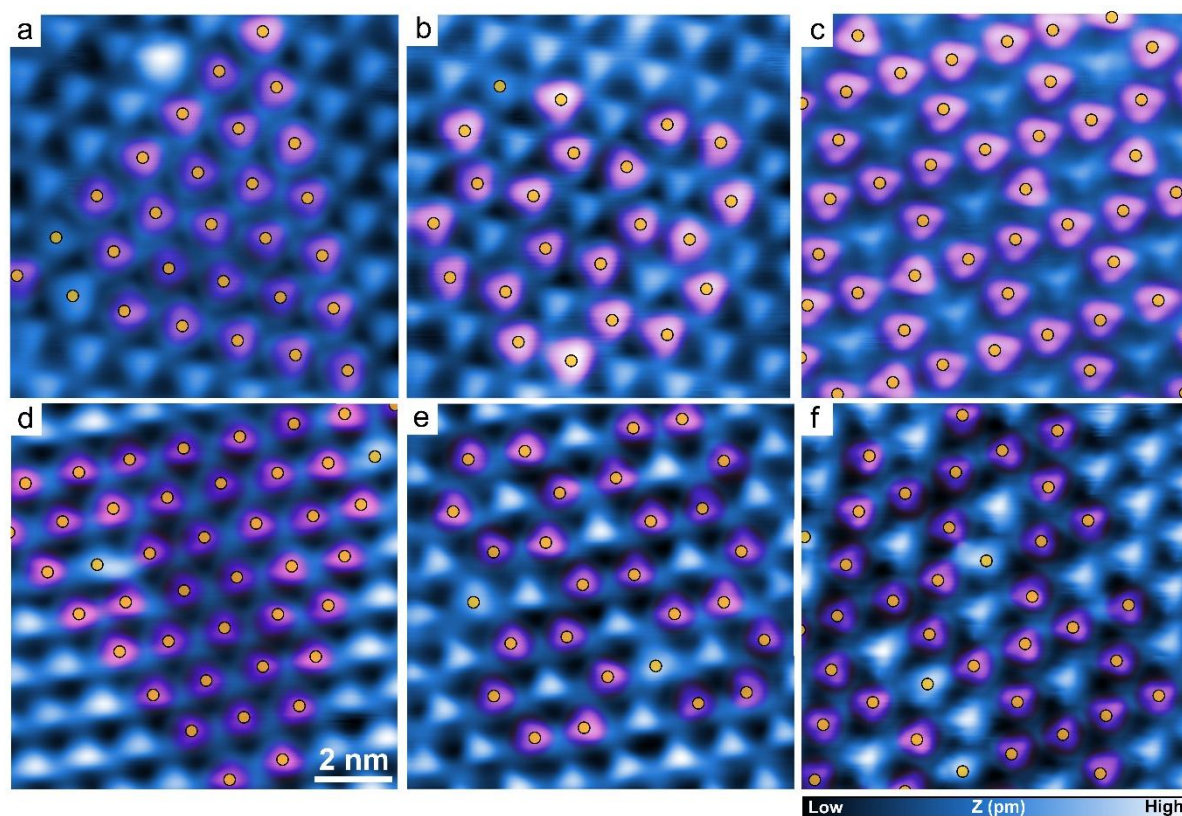


Figure 6.4 AI-guided artificial fabrication of d-TPM lattices. Construction of triangular, honeycomb, and Kagome lattices using Fe-TPM (a–c) and Ni-TPM (d–f). The visual-selected positions for tip-manipulation are marked by yellow circles. The d-TPM molecules are marked in purple to enable rapid distinction among intact TPM and degraded TPM. Under identical imaging conditions (constant current, -500 mV, 100 pA), Fe–d-TPM appears as bright protrusions while Ni–d-TPM shows darker contrast, reflecting their distinct electronic structures. (Scale bars, 5 nm).

Using the AI-optimized dehydrogenation parameters, we fabricated a series of artificial d-TPM lattices on the Fe–TPM platform (Figure 6.4(a–c)). The operator-guided protocol involved an initial 20×20 nm scan to identify target molecules for dehydrogenation (indicated by yellow dots in Figure 6.4). The field of view was then narrowed to an 8×8 nm region (-500 mV, 100 pA), where the probe was precisely positioned over the selected targets to apply a -4.0 V pulse. This sequence was performed iteratively: after each pulse, the area was rescanned, and the process was repeated until all target molecules were either fully dehydrogenated or partially degraded. Ultimately, 93% of the targeted molecules were successfully converted to d-TPM,

with the remaining 7% comprising degraded molecules, defects, or vacancies. This high success rate confirms the robustness and practical stability of the learned operating regime.

We applied the same protocol to fabricate artificial lattices on the Ni-TPM platform. Figs. 6.4(d–f) show the artificial spin structures exhibiting triangular, Kagome, and honeycomb lattices, respectively. Note that Ni-d-TPM and Fe-d-TPM exhibit markedly different STM contrast under identical imaging conditions due to the different electronic states. This cross-platform transferability highlights the robustness of the SML protocol. Given the chemical tunability of two-dimensional MOFs, substituting the coordinated metal center provides an effective means of modulating the exchange interaction between organic radicals and transition-metal d electrons. In this context, SML offers a programmable nanofabrication strategy for constructing artificial molecular structures on chemically variable platforms. The spin characteristics of these artificial structures were investigated using tunneling spectroscopy, revealing systematic changes in the low-energy spectral lineshape with increasing lattice size. Although the microscopic origin of this size-dependent spectral evolution is beyond the scope of the present work, these observations indicate that the autonomously fabricated lattices provide access to study emerging quantum phases, which will be systematically studied in future.

6.2.3 Fully autonomous fabrication of large-scale triangular lattice

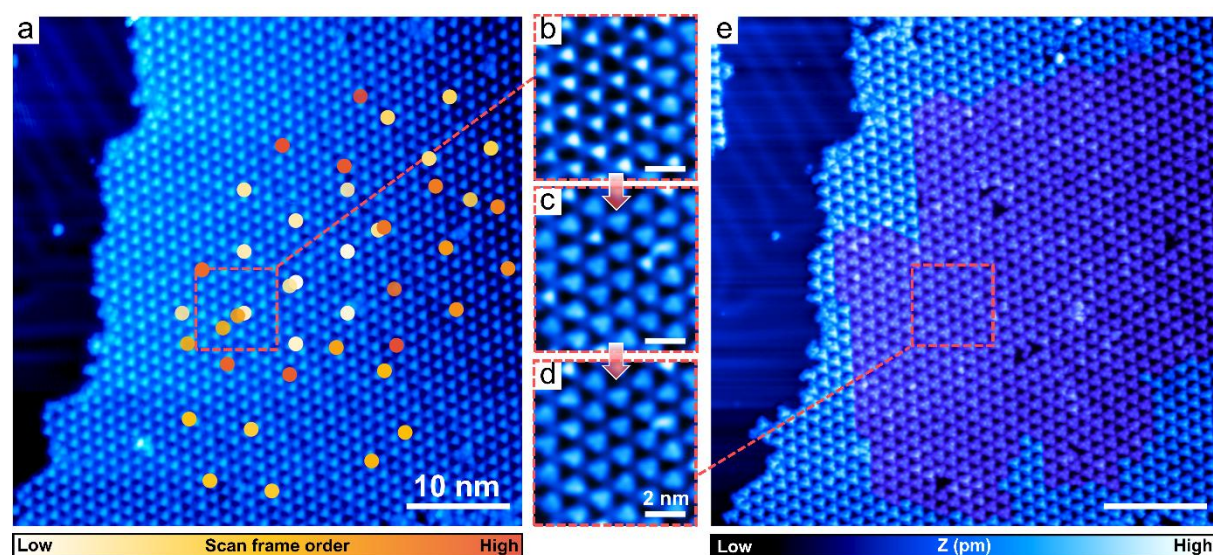


Figure 6.5 SML for autonomous construction of a large-scale d-TPM lattice. **a**, Initial STM image ($50 \times 50 \text{ nm}^2$; -1 V , 20 pA) prior to AI manipulation via localized $8 \times 8 \text{ nm}^2$

windows. The order of scan frames' center are marked by colored dots. b-d, Lattice expansion via iterative scan-manipulate-rescan cycles (-0.5 V, 100 pA). The scan window shifts automatically upon full conversion of local intact TPM. e, A 632-site triangular d-TPM lattice (highlighted in purple) constructed autonomously in 4 h (-1 V, 20 pA). The 86.7% yield is derived from 938 tip-pulse attempts on 729 identified molecules. Scale bars, 10 nm (a, e) and 2 nm (b-d).

We integrated the AI-optimized dehydrogenation parameters with path-planning to achieve fully autonomous fabrication of large-size lattices. The workflow of this fully autonomous experiment is illustrated in Figure 6.5. The AI agent first acquires an overview STM image of a 50×50 nm² region and then zooms into a series of 8×8 nm² windows. All TPM molecules identified within a given window were autonomously dehydrogenated. The tip-height signal is used as a rapid auxiliary indicator of the reaction outcome. If the measured height change suggests that no reaction has occurred, the agent repeated the dehydrogenation operation on the same molecule until a significant change in the tip-height signal is observed. This imaging-manipulation-verification loop is repeated until all TPM molecules within the current window were successfully dehydrogenated. Afterward, the agent automatically shifted to an adjacent region and repeats the same procedure.

As depicted in Figure 6.5(a), the colored markers denote the center coordinates of the localized zoom-in scan frames. The sequential execution of these scans—spanning from the 1st to the 105th frame—is mapped by the color gradient. The subsequent panels (Figure 6.5(b-d)) capture the representative step-by-step evolution of fabricating large-scale d-TPM artificial lattices guided by the AI-driven SML workflow. As shown in Figure 6.5, the fully autonomous SML enables the construction of extended molecular structures over a large area. In this experiment, the agent identified 729 molecules, executed 938 dehydrogenation attempts and successfully fabricated a triangular lattice comprising 632 spin units. The total fabrication time was 9 h, and the overall success rate reached 86.7%. These results highlight the practical viability of fully autonomous SML for the fabrication of large-area artificial quantum structures.

6.2.4 Programmed fabrication of structures with pre-designed shape and size

Finally, we used the SML to construct triangular structures with specific sizes. To realize this goal, we developed an agent to extract the local lattice geometry. In Fig 6.6., the molecular centroids identified by the vision model are treated as lattice nodes, and nearest-neighbor

centroids are connected to generate a set of line segments from which the intermolecular spacing is obtained statistically. In parallel, the segment orientations are analyzed by Mean Shift clustering to determine the principal lattice directions. Because the nearest-neighbor vectors in a triangular lattice exhibit a 60° angular periodicity (reflecting sixfold rotational symmetry), we define the lattice orientation angle (measured counterclockwise relative to the X-axis) within the strictly periodic interval of 0° to 60° . Since the period of such orientation angle is 60° , for clarity in statistical analysis, we define the lattice orientation angle $\theta = \min(|angle - n * 60|), n = 0, 1, 2 \dots$, and plot it together with the lattice constant d in the polar coordinate system of Figure 6.6(b). For the representative assembly shown in Figure 6.6(a), this analysis yields a lattice constant d of 1.45 nm and a lattice orientation angle θ of 11.4° ¹¹⁰. These parameters establish a unified geometric reference frame that enables the agent to assign target sites and generate precise coordinates for subsequent tip-induced reactions.

Next, the agent is commanded to fabricate a user-specified structure within the $8 \times 8 \text{ nm}^2$ window. As illustrated in Figure 6.6(c), the machine-vision module first labels the molecules belonging to a selected 10-site equilateral triangular pattern, after which the SML system iteratively performs scan-manipulate-validate cycles until the prescribed motif is completed. The corresponding STM image acquired after task completion (Figure 6.6(d)) confirms that the pre-designed structure is produced successfully. In this workflow, lattice recognition is therefore not merely an auxiliary image-analysis step, but the key bridge between molecular identification and autonomous structure fabrication. We employed this strategy to construct triangular motifs with various sizes. As shown in Figure 6.6(d–g), the agent successfully fabricated 3-site, 6-site, 10-site and 15-site triangular structures of molecular radicals. This strategy provides a practical route for constructing programmable structures on this platform.

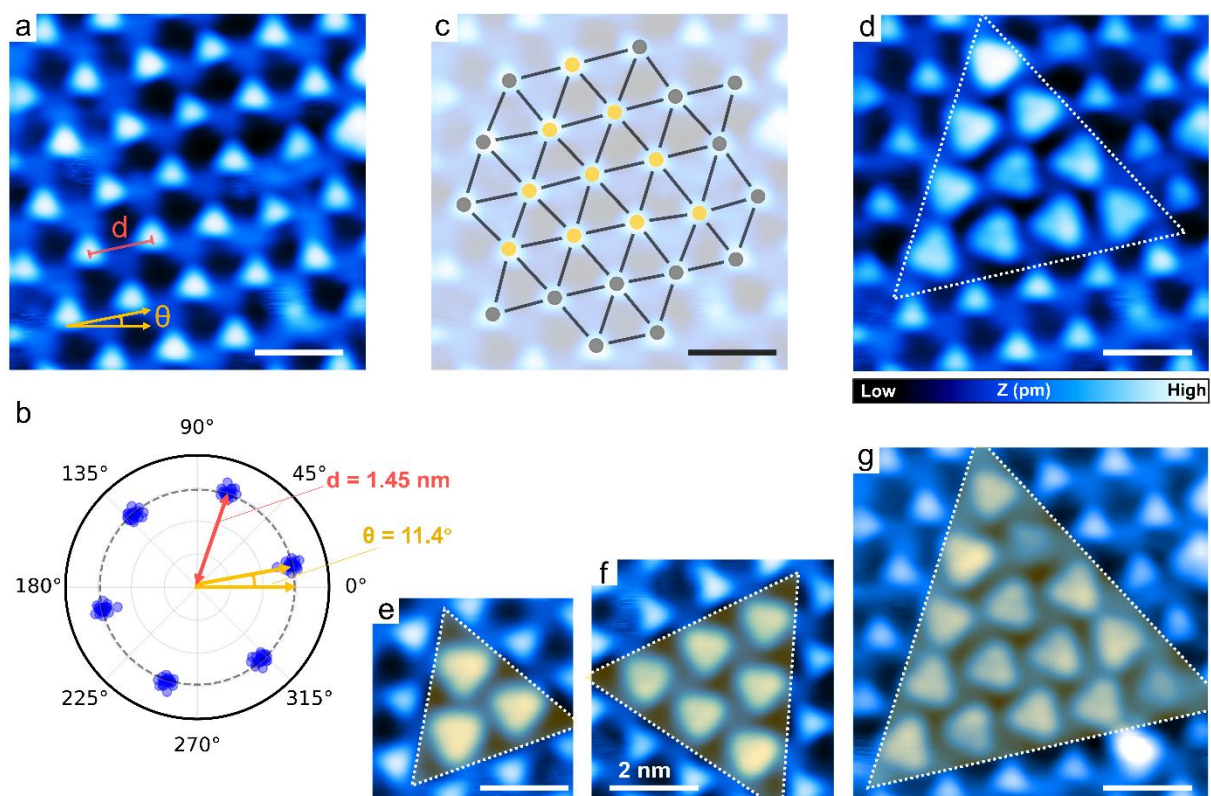


Figure 6.6 Autonomous AI-guided construction of triangular molecular patterns. a, Initial STM image prior to SML. b, Structural parameters (bond angles θ and intermolecular distances d) extracted via mean-shift clustering, plotted as blue dots in polar coordinates, where the converged results are: $\theta = 11.4^\circ$, $d = 1.45 \text{ nm}$. c-d, Machine-vision labelling of target molecules (c) for a programmed 10-site equilateral triangular d-TPM motif (targets: yellow; intact-TPM background: grey), and the resulting STM image (d) of the constructed lattice (white dashed outline). d–g, Autonomous construction of triangular patterns of varying sizes. Yellow masks are overlaid to enhance the contrast of d-TPM lattices.

6.3 Conclusions

We have developed an AI-driven single-molecule lithography strategy for the autonomous fabrication of programmable molecular lattices. By integrating reinforcement-learning-based control with scanning tunnelling microscopy and on-surface reactions, this strategy overcomes the scalability bottleneck of conventional manual manipulation and enables the reliable construction of extended lattices with designed geometries across distinct MOF platforms. The resulting capability transforms scanning probe manipulation from a labor-intensive operation

into a scalable nanofabrication framework for designer molecular architectures. The AI-driven single-molecule lithography therefore provides a practical route toward extended artificial molecular nanostructures. Specifically, the TPM platform offers programmable lattices of open-shell molecular radicals, which may exhibit interesting quantum phenomena for future studies.

Chapter 7

Summary and perspectives

7.1 Summary

This thesis investigates correlated magnetism and electronic properties in programmable artificial molecular spin systems constructed on metal surfaces. The central platform is based on 2D TPM-based MOF on Au(111), in which selected TPM molecules can be converted into dehydrogenated TPM (d-TPM) units by STM tip-induced manipulation. Low-temperature scanning tunneling microscopy and spectroscopy were used to characterize the structural and local electronic properties of these systems with single-molecule precision. Density functional theory, Ternes-model analysis, large-N and mean-field theory simulations were further employed to interpret the observed spectroscopic features and to establish possible physical mechanisms underlying the experimental observations.

A TPM-based radical MOF is established as programmable platforms for studying finite-size Kondo physics. In the Ni-TPM framework, isolated d-TPM molecules behave as Kondo impurities, while dimers and finite radical chains exhibit broadened, asymmetric and site-dependent spectra, revealing the coexistence and competition between local Kondo screening and inter-radical coupling. Extending the system to finite 2D radical lattices further shows a size- and geometry-dependent evolution from peak-like Kondo resonances to dip- or gap-like LDOS suppression near the Fermi level. These results suggest that programmable radical MOFs provide a molecular-scale route to explore the evolution from isolated Kondo impurities to interacting spin arrays and possible finite-size precursors of Kondo lattice.

TPM-based radical MOFs are not only platforms for studying spin correlations, but also chemically tunable and scalable artificial quantum architectures. By replacing Ni with Fe, the electronic structure of d-TPM changes from a Kondo impurity to a SOMO-d hybridized molecular state that can be locally gated toward the Fermi level, where it develops a soft gap associated with correlation-driven spectral reconstruction. In parallel, AI-assisted STM was developed to overcome the scalability limitation of artificial tip manipulation. Reinforcement-learning-optimized single-molecule lithography enables autonomous construction of large and programmable radical lattices, providing a practical route toward high-quality molecular spin

architectures with designed geometry, tunable electronic properties and single-molecule precision.

7.2 Future Outlook

Looking forward, programmable radical MOFs provide a versatile platform for exploring correlated molecular spin systems beyond the current finite-size regime. A key next step is to perform systematic ultra-low-temperature and magnetic-field-dependent STM/STS measurements. As illustrated in Fig. 7.1(a–c), magnetic-field-dependent spectra of single atoms, ferromagnetic (FM) dimers and antiferromagnetic (AFM) dimers provide a direct benchmark for distinguishing different spin-coupling regimes.¹¹¹ Similar measurements on d-TPM dimers, trimers and finite chains would help clarify whether the observed peak-like, dip-like and spin-excitation-like features originate from antiferromagnetic inter-radical exchange, Kondo screening or substrate-mediated interactions.

With the development of AI-assisted STM, this platform can be further extended from small spin clusters to large, high-quality molecular spin lattices. Candidate geometries such as honeycomb, triangular and Kagome lattices are shown in Fig. 7.1(d). Such artificial lattices provide a molecular realization of the Kondo-lattice concept, where periodic local spins interact with itinerant substrate electrons, as schematically shown in Fig. 7.1(e). In this context, the Doniach phase diagram in Fig. 7.1(f) provides a useful framework for understanding the competition between RKKY interaction and Kondo screening. Large and ordered radical arrays would allow systematic examination of whether finite-size Kondo-lattice-like spectral features develop into long-range collective behavior, including coherent Kondo screening and heavy-fermion-like quasiparticle formation.¹¹²

More broadly, these molecular lattices may provide access to many-body phenomena known from correlated-electron materials. The heavy-fermion band structure and dI/dV spectra of CeCoIn_3 shown in Fig. 7.1(g) serve as a reference for identifying hybridization-gap-like spectral features in extended radical lattices.¹¹² At lower temperatures, randomly overlapping Kondo clouds may develop coherence, leading to Kondo-condensation-related behavior, as schematically illustrated in Fig. 7.1(h). The field-tuned phase diagram of Si:P in Fig. 7.1(i) further highlights how zero-bias conductance can be used to track the evolution between magnetic Kondo-condensed and paramagnetic phases. These examples motivate future

STM/STS studies of AI-fabricated radical MOFs as artificial platforms for exploring heavy-fermion physics, Kondo coherence and correlation-driven quantum phases.³⁶

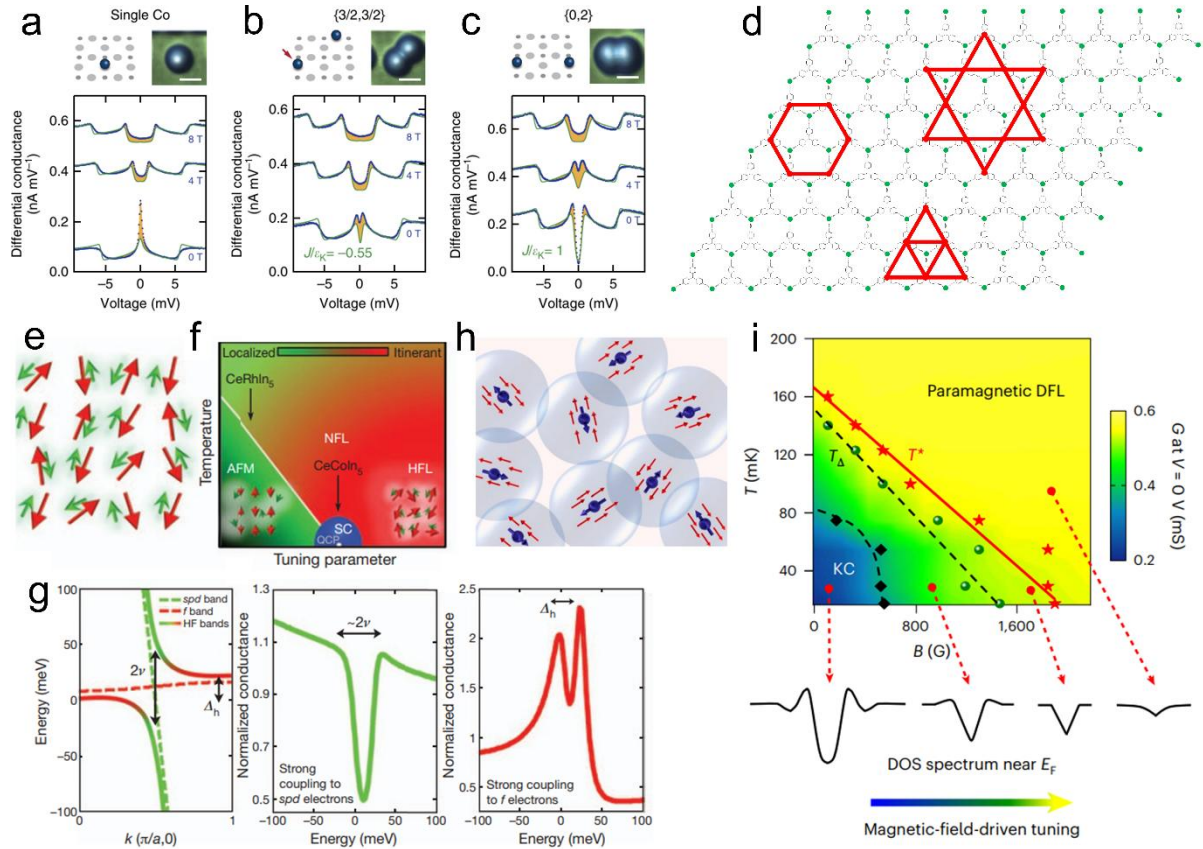


Figure 7.1 (a-c) Experimental measurements (blue) alongside simulated dI/dV spectra (green). These results were acquired from a single Co atom (a), FM dimer (b) and AFM dimer (c) structures showing distinct coupling in increasing magnetic field.¹¹¹ (d) Candidate lattices in TPM-based radical MOFs platform, including honeycomb, triangular and Kagome lattices. (e) Scheme of Kondo lattice containing periodic local spins (red) and itinerant electrons (green). (f) Simplified Doniach phase diagram shows the competition between RKKY and Kondo screening, where a non-fermi liquid phase lies at the quantum critical point. (g) Low-energy band structure and dI/dV spectra of heavy fermion material CeCoIn₃.¹¹² (h) Schematic representation of Kondo condensation, where the randomly overlapped Kondo clouds coherent at ultralow temperature. (i) Phase diagram of Si:P derived from zero-bias conductance (DOS at E_F). The map illustrates the magnetic field-tuned evolution from the magnetic Kondo condensation phase to the paramagnetic DFL phase. Key phase boundaries, including the transition temperature T^* and relevant spectral markers, are overlaid. The lower panels display the representative DOS spectra for each specific phase.³⁶

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