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Spin resonance studies of single molecule qubits

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Quantum coherence is an emerging degree of freedom of interest for novel computation and sensing applications. Both electron and nuclear spin as quantum bits (‘qubits’) have been demonstrated in molecular systems, with performance comparable to other leading spin qubit systems but with the added potential of chemical tuning to tailor the coherence properties for particular applications. However, the field has thus far relied on measurements of large ensembles in solution or in powder forms, precluding the study of single-qubit properties and impeding scaling and integration with existing and emerging quantum technologies. In this project, we aimed at extending scanning tunneling microscope-based methods for single-atom coherence measurements to single molecular qubits through a collaborative international research program. Using atomic resolution STM imaging and spectroscopy, we have characterized the adsorption and encapsulation of molecular qubits on the isostructural molecular films. These measurements can then be correlated with single-molecule spin resonance and spin relaxation measurements. In this way, we elucidate how the local environment impacts molecular coherence properties with unprecedented resolution and control. This is an initial step toward integration of molecular qubits into solid-state device architectures for scalable applications.

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Spin resonance studies of single molecule qubits

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Co-PI: Prof., Dr. Jay Gupta (Associate Professor, Department of Physics, The Ohio State University, Columbus, OH, USA); **Dr. Christoph Wolf** (PI, The IBS Center for QNS at Ewha Womans University, Seoul, Republic of Korea);

Key Researchers involved in the Project: William Koll (PhD student, OSU), Kyungju Noh (PhD student, QNS), Ferdous Ara (postdoc, OSU), Corina Urdaniz (postdoc, QNS), Jacob Repicky (PhD student, OSU), Marzieh Kavand (postdoc, OSU)

Period of Performance: 02/Sep/2020 – 03/Sep/2023

Total Cost: $60,000

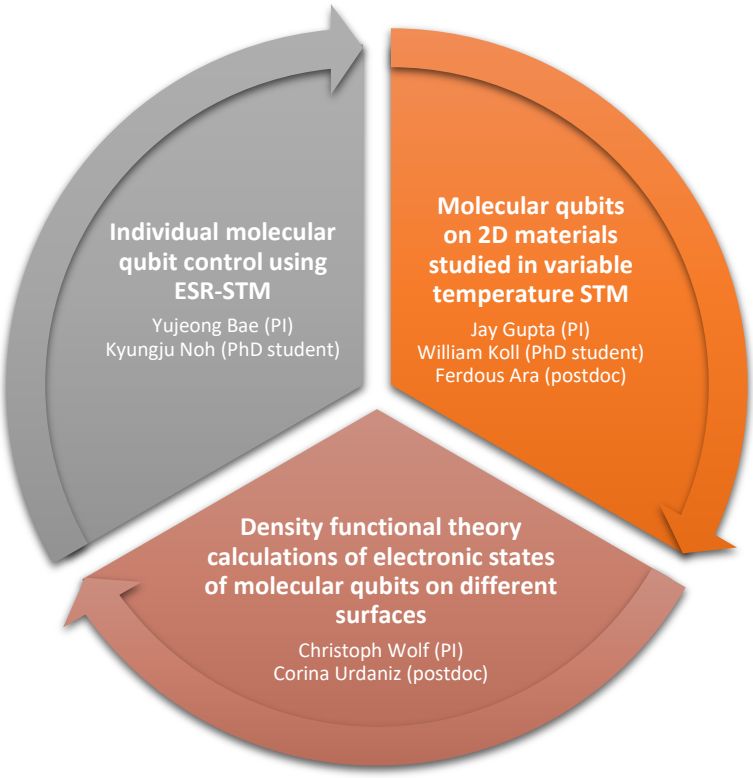
Abstract:
Quantum coherence is an emerging degree of freedom of interest for novel computation and sensing applications. Both electron and nuclear spin as quantum bits ('qubits') have been demonstrated in molecular systems, with performance comparable to other leading spin qubit systems but with the added potential of chemical tuning to tailor the coherence properties for particular applications. However, the field has thus far relied on measurements of large ensembles in solution or in powder forms, precluding the study of single-qubit properties and impeding scaling and integration with existing and emerging quantum technologies. In this project, we aimed at extending scanning tunneling microscope-based methods for single-atom coherence measurements to single molecular qubits through a collaborative international research program. Using atomic resolution STM imaging and spectroscopy, we have characterized the adsorption and encapsulation of molecular qubits on the isostructural molecular films. These measurements can then be correlated with single-molecule spin resonance and spin relaxation measurements. In this way, we elucidate how the local environment impacts molecular coherence properties with unprecedented resolution and control. This is an initial step toward integration of molecular qubits into solid-state device architectures for scalable applications.

Introduction:
Both electron and nuclear spin qubits have been demonstrated in molecular systems. However, the field has thus far relied on measurements of large ensembles in solution, precluding the study of single-qubit properties and impeding scaling and integration with existing and emerging quantum technologies. Molecular materials have previously been integrated into solid-state architectures via the fabrication of molecular tunnel junctions. However, this approach has been limited by difficulties in making non-destructive electrical contacts with minimal leakage currents. Our work will address these challenges by exploiting recent advances in the mechanical transfer of 2D materials such as graphene and boron nitride, to protect molecular qubits from the ambient environment while also providing for electrical interrogation of individual molecules.

Approach:
The central tool for this effort is the scanning tunneling microscope (STM), with its capabilities for atomic resolution imaging, single atom/molecule manipulation, and tunneling spectroscopy. While these capabilities allow for detailed study of the static molecular properties, they do not provide insight into the dynamical properties such as spin coherence time. Toward this end, we will extend the STM-electron spin resonance (STM-ESR) methods to molecular qubit systems.

The goal of this project is to develop a general framework for the integration of molecular spin-based qubits into solid state architectures, harnessing the ability to tune quantum states in molecular systems via synthetic control of ligand fields and electron-nuclear spin coupling to demonstrate a uniquely powerful approach to generating qubits-by-design.

Our main target material system is Vanadyl-Phthalocyanine (VOPc) molecular qubits on surfaces. VOPc molecules are known to have long spin coherence time, which stems from the limited overlap between the electron spin at the V *d*-orbital and the ligand's molecular orbitals. However, the coherent control of VOPc molecules on surfaces has not been realized at the single molecular level with individual addressability. Using the electron spin resonance (ESR) combined with scanning tunneling microscopy (STM), we aim to demonstrate coherent control of spins carried by VOPc molecules with well-defined spin-spin interactions and decoupling from substrate electrons. In 2022, QNS team has investigated the electronic states of VOPc molecules on one monolayer of Titanyl-Phthalocyanine (TiOPc) on Ag(100), where the isostructural TiOPc molecular layer induces the creation of highly-ordered VOPc molecular patterns. In 2023, the team also prepared individual VOPc molecules on two monolayers of MgO on Ag(100) and characterized their electronic and magnetic states. In parallel, OSU team prepared multi-layer VOPc and individual VOPc molecules on h-BN. We are currently preparing a joint publication reporting these initial studies of VOPc self-assembly, from isolated molecules to multilayer thin films, with theoretical input from the theory team led by Dr. Christopher Wolf at QNS.



Research Performance*

	QSN	OSU
1st year	Generalizing the integration of ESR in STM *Rev. Sci. Instrum. 93, 093703 (2022)*	Modification of an existing low-temperature STM for ESR integration
2nd year	Template-directed 2D nanopatterning of S=1/2 molecular spins: VOPc molecules on TiOPc molecular layer on Ag(100) *Nanoscale Horiz. 8, 624 (2023)*	Preparing atomically-clean substrates (Ag(111) and HOPG) for VOPc deposition Characterizing rf transmission of STM system
3rd year (& *on-going)*	Characterization of VOPc and TiOPc molecules' spin states on a different insulating layer (two monolayers of MgO on Ag(100)) and modification of their adsorption and chemical configuration	Characterization of the electronic states of VOPc molecules on Ag(111) and VOPc islands Preparing hBN substrates for ESR-STM measurements

*Each subject in table is described in detail below.

1. Generalizing integration of ESR in STM (QNS)

While the STM has been commonly employed in surface science studies for several decades, the STM combined with ESR is pretty unique. To our knowledge, around 10 groups in the world have STM with ESR capability. ESR-STM allows the phase-sensitive control and detection of individual spins on a surface, which is necessary to utilize the spin states of surface spins for quantum information processing. ESR measurement in STM requires cables for high frequency electric fields transmission. To modify the low-temperature STM for ESR measurement, adding high-frequency cables or replacing the existing cables by high-frequency cables is not trivial since most of STM are already compactly wired and the semi-rigid cables for high frequency powers might cause vibration and heat transmissions to the STM junction.

Furthermore, to obtain enough ESR signals of a single atom/molecule to be measured, it is important to polarize the spin state to the ground state. Considering many of STM operate at 2–4 Kelvin temperature, around 2 T of external magnetic field is required for the polarization of surface spins, which requires enough RF transmission to the STM junction in the frequency range of 30–40 GHz.

To overcome these limitations, QNS team explores several different approaches to apply RF signals to the STM junction without requiring extensive modification of the existing STM systems. Figure 1 shows the STM head QNS team made. Here, the high frequency cable (denoted as 'antenna') passes near the STM junction (the junction between the sample and STM tip) without a direct contact with any part of the STM. The end of antenna is terminated by 50 Ohm and thermally anchored to the coldest area in STM. We found this integration of high-frequency cables enables us to apply the RF signals with frequency of around 40 GHz, which will allow many STM groups to modify the existing system more easily and apply high frequency signals to the STM junction. The QNS team has shared this experience with the OSU team in regular videoconference meetings as part of this project to accelerate the translation of ESR-STM techniques to OSU.

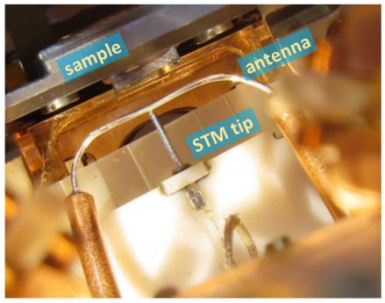


Figure 1. STM head integrated with high frequency cables for ESR measurement. Photograph of the RF antenna used to apply RF voltages to the STM junction.

2. RF integration with STM (OSU)

Following methods developed by QNS, we have measured the rf transmission of our STM system up to 25 GHz (Figure 2). The Cu(111) surface has an electronic state that appears as ripples in STM images (Fig. 2a), and as a step in tunneling spectroscopy (black curve in Fig. 2b)). RF excitation modulates the bias volage and produces broadening in spectroscopy, shown in the blue curve in Fig. 2b. To estimate the rf amplitude at the junction, we analytically broaden the black curve due to the RF modulation. The amplitude of modulation is adjusted until the broadened curve (red) matches the measured curve (blue). This gives V_{rf} at the junction, which can then be used to calculate the system transmission as a function of rf frequency (Fig. 2c). This is the critical characterization measurement that must be done in order to look for ESR-STM signals.

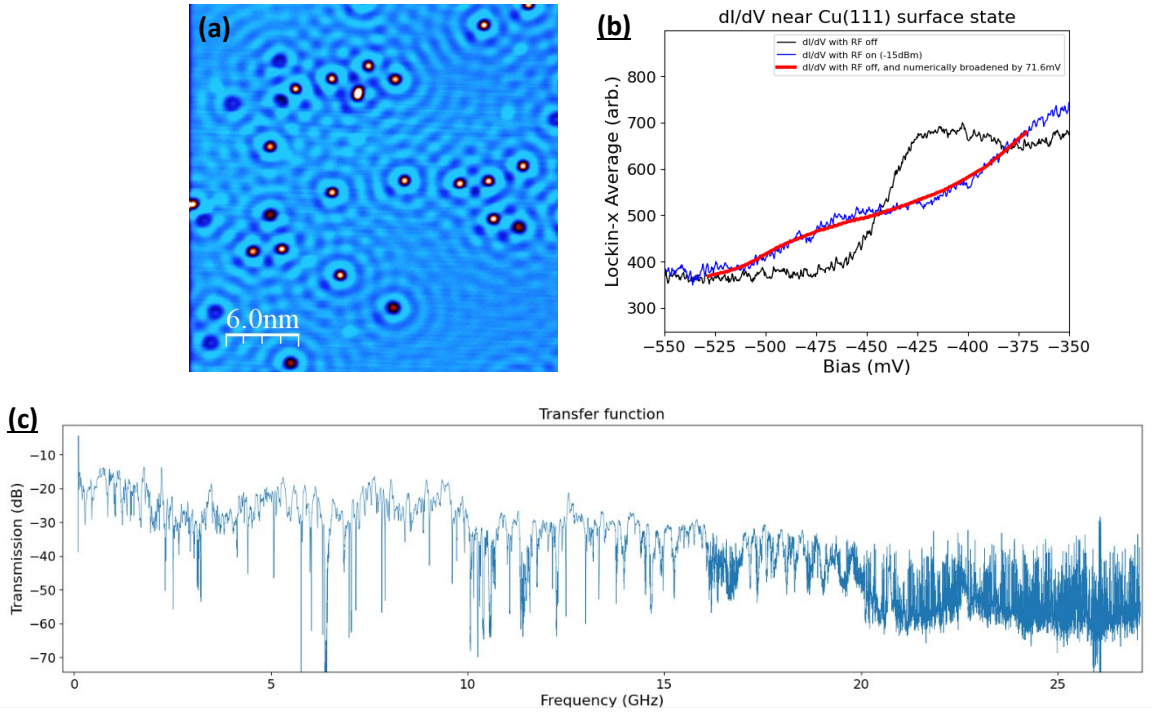


Figure 2. RF-coupled STM measurements at OSU. (a) STM image of a Cu(111) surface, showing spherical ripples of the surface state electrons scattering off surface adsorbates. (b) Tunneling spectroscopy with rf excitation (blue) and without (black). (c) Transfer function for the OSU STM system using the data in (b). T=5K

3. Preliminary measurements of molecular qubits: VOPc on Ag(100) (OSU)

In addition to RF characterization of the system, ESR-STM requires high quality preparation of clean surfaces with spin qubit candidates. The OSU team has identified model molecular qubits that can be cleanly deposited onto surfaces in ultrahigh vacuum. These molecules are synthesized by our collaborator, Prof. Danna Freedman, who is a leading quantum synthetic chemist at M.I.T. We have deposited VOPc prepared by the Freedman group onto a variety of 2D substrates (HOPG, Ag(111), Cu(111)) via sublimation from an alumina ceramic crucible in UHV. Figure 3 confirms successful deposition of VOPc molecules on Ag(111) at room temperature. STM measurements at 77 K show well-resolved molecular orbitals of the VOPc. Individual VOPc molecules within a single image can exhibit two distinct contrast levels, which we attribute to distinct adsorption geometries with respect to the surface. For example, the orientation of the vanadyl group may be pointing downward towards the substrate, or upward towards vacuum.

Additionally, the proximity of the molecules to point defects or step edges may influence the degree of charge transfer, causing a shift in the energies of the molecular orbitals and thus the appearance in STM images. This deposition scheme can be applied to a wide variety of molecule samples and surfaces.

4. Introducing a decoupling layer: VOPc on TiOPc (QNS)

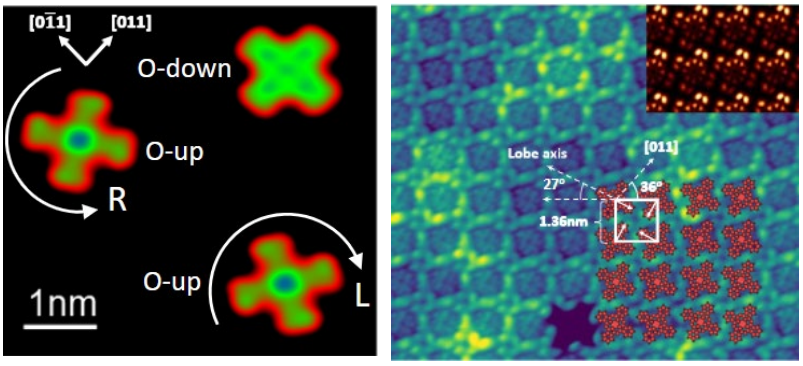


Figure 3. (left) STM image of three VOPc molecules on Ag(100), showing the O-up/down configurations, and the two chiralities for the O-up configuration. (right) STM image of a bilayer of VOPc, with overlays of the molecular structure and simulated DFT images from Wolf at QNS.

Selecting a substrate like Ag(111) or HOPG provides a way to control the adsorption geometry and the degree of hybridization of molecules on the surface. While VOPc molecules show well-localized molecular orbitals on Ag(111), which hints the molecules are decoupled from the metallic substrate, the same molecules on Ag(100) are much more hybridized with the substrate. No clear molecular orbital feature is observed in topographic images (Fig. 3). This difference of the electronic state of VOPc on Ag(111) and Ag(100) can be attributed to the symmetry between the VOPc molecule and the underlying substrate. The VOPc molecule with four-fold symmetry presumably couples more strongly with Ag(100) in four-fold symmetry rather than Ag(111) in three-fold symmetry.

Another way to decouple the molecular spins from the substrate electrons is to introduce a decoupling layer like a thin insulating film like MgO, NaCl, and Cu_2N. We found the TiOPc molecular layer can be served as a decoupling layer. A TiOPc molecule has the isostructure with VOPc, but with zero spin. While VOPc molecules directly on Ag(100) show 4 lobes with no clear molecular features, the molecules adsorbed on a self-assembled monolayer of TiOPc does show density of states localized to the molecular orbitals. Taking advantage of the self-assembly of molecular layers, using a molecular decoupling layer can provide a way to create a spin network of highly ordered molecular arrays.

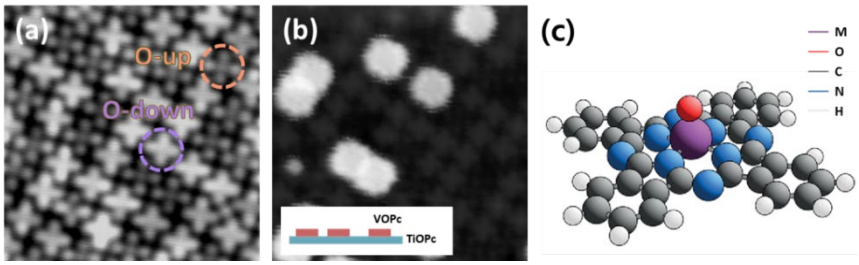


Figure 4. VOPc molecule on one monolayer of TiOPc molecules. (a) STM image of the first monolayer of TiOPc on Ag(001). The dashed circles show two different adsorption configurations of TiOPc molecules on Ag(001): Oxygen atom toward vacuum (O-up) and oxygen atom toward Ag (O-down) (scan size: 10x10 nm^2, V = 100 mV, I = 50 pA, T = 10 K). (b) VOPc molecule on TiOPc molecular layer. The VOPc molecules show 8 lob features of the density of state (scan size: 15 x 15 nm^2, V = 1 V, I = 50 pA, T = 10 K). (c) A schematic of the molecular structure of a single non-planar VOPc molecule.

5. Spin-related features of VOPc on MgO(100)

Currently, the QNS team focuses on VOPc molecules on two-monolayers of MgO grown on Ag(100). The team found the VOPc molecules on MgO are adsorbed in two different configurations, O-up and O-down, and their electronic states are well decoupled from the substrate electrons thanks to the MgO decoupling layer reminiscent of the previous case (VOPc on TiOPc, Fig. 4b). The team prepared the spin-polarized STM tip by picking up several Fe atoms from the MgO surface. However, it is quite challenging to utilize the Fe-terminated STM tip to investigate the spin characteristics of VOPc since the VOPc molecules are weakly adsorbed to the MgO surface and, thus, prefer to be attached to the Fe tip. As one of alternative approaches, the team applied a short voltage pulse while the tip is located at the center of the VOPc molecule to remove the O-atom, resulting in VPc. This VPc molecule is found to be stable on the surface. The electronic and magnetic states of this VPc molecule are under investigation.

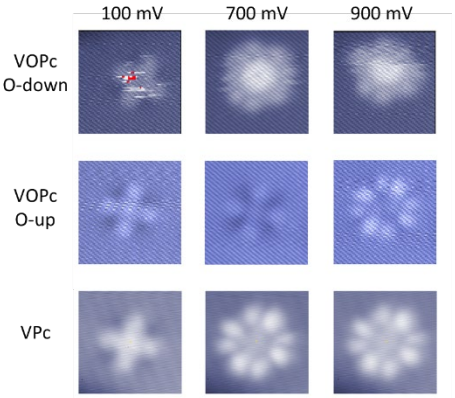


Figure 5. Constant heights STM images of VOPc and VPc on MgO obtained at different bias voltages.

Publication list

[4] S. Reale et al., “Electrically driven spin resonance of 4f electrons in a single atom on a surface”, arXiv:2309.02348 (2023) *under review*

[3] K. Noh et al., “Template-directed 2D nanopatterning of S = 1/2 molecular spins”, *Nanoscale Horiz.* 8, 624 (2023)

[2] J. Kim et al., “Anisotropic hyperfine interaction of surface-adsorbed single atoms”, *Nano Lett.* 22, 9766 (2022)

[1] J. Hwang et al., “Development of a scanning tunneling microscope for variable temperature electron spin resonance”, *Rev. Sci. Instrum.* 93, 093703 (2022)

Research Exchanges

During our performance period, the regulations and circumstances imposed by Covid-19 severely restricted our active exchange visits. Thus, we had collaborated through regular online meetings at the first year of this performance period. As threats and risks associated with travel abroad decrease with decreasing severe corona cases since 2021, we could have more active exchange of researchers between two groups. In fact, we hosted two research stays at QNS for researchers from the Ohio state university and one research stay at OSU for a researcher from QNS, which accelerated our collaboration.

Researcher for Stay	Period of Stay	Activities
Ferdous Ara (OSU)	2022/Mar15 – Apr15	- Knowledge exchange on a single molecular magnet and STM-based characterization of its electronic and magnetic states - Knowledge exchange on sample preparation (growth of two monolayers of MgO partially covered Ag(100) and low-temperature deposition of individual atoms and molecules) and set-up of electronics for ESR-STM - Characterization of individual copper-phthalocyanine (CuPc) molecules on two-monolayers of MgO on Ag(100) using ESR-STM
William Koll (OSU)	2022/Jun4-Jun23	- Knowledge exchange on electronic states of sub-monolayer and several monolayers of VOPc on Ag(100) - Updates on recent progress on graphene/hBN/graphene hetero-structure devices - Knowledge exchange on the set-up of electronics for ESR-STM studies
Corina Urdaniz (QNS)	2023/Mar/11~17	- Discussions on experimental results on VOPc multi-layers obtained by OSU team. - Discussions on theoretical approaches to understand the stacking configurations of VOPc layers and the origin of Moire patterns observed from the STM images of the multi-layered VOPc - Preparing a manuscript based on the results as an outcome of collaboration