Individual Assembly of Radical Molecules on a Superconductor

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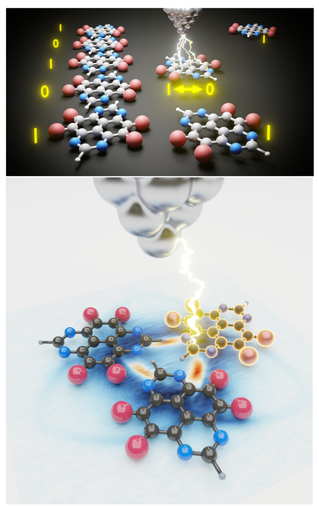
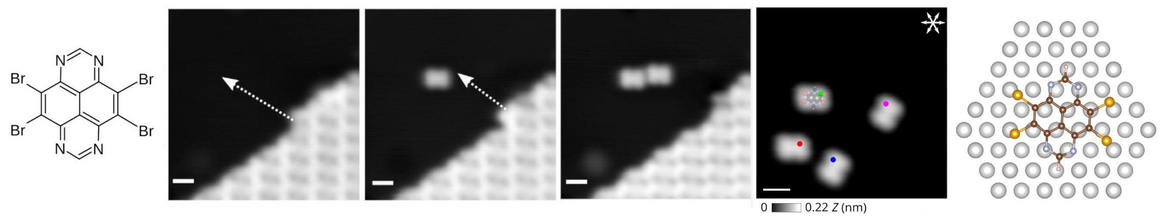
Motivation



- **Magnetic molecules on a superconductor**: tunable platforms to study the interplay of electronic correlations, quantum tunneling, magnetism, bound states, topology, entanglement and more.
- **Superconducting molecular spintronics**: nanoscale devices that are easy to manipulate, enable low-energy data storage and computing, and can serve as building blocks for logic gates.
- **Quantum-dot cellular automata (QCA)**: a transistor-free nanotechnology for ultra-high-density, low-power computing in which binary information is encoded in charge configurations rather than current.

TBTAP molecule on a superconducting surface



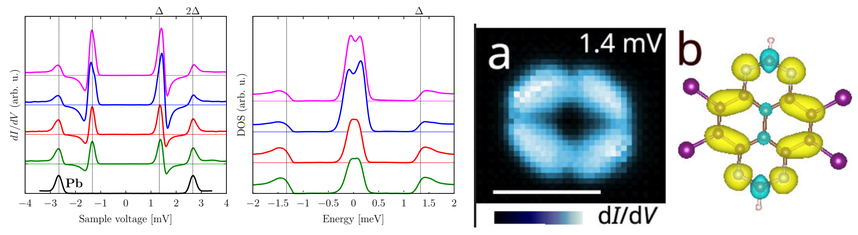
Individual molecules were removed from the island by lateral manipulation (pulling with the scanning tip).

4,5,9,10-tetrabromo-1,3,6,8-tetraazapyrene (TBTAP):

- Acceptor tetraazapyrene backbone decorated with four bromine atoms; **metal-free**.
- Isolated molecule: $TBTAP^{\bullet-}$ radical with a **spin-1/2** ground state on both Pb(111) and Ag(111) [1].
- Forms a densely packed supramolecular network when sublimed onto a Pb(111) surface.
- Stripes of charged (spin-1/2) and neutral (spin-0) molecules [2].

Tunneling spectra:

- Measured at $T_{exp} = 1\,K$ (2.6 K for the trimer) using a superconducting Pb tip to enhance resolution.
- Deconvolution performed via the **maximum-entropy method** (modified *ana_cont* package [3]).

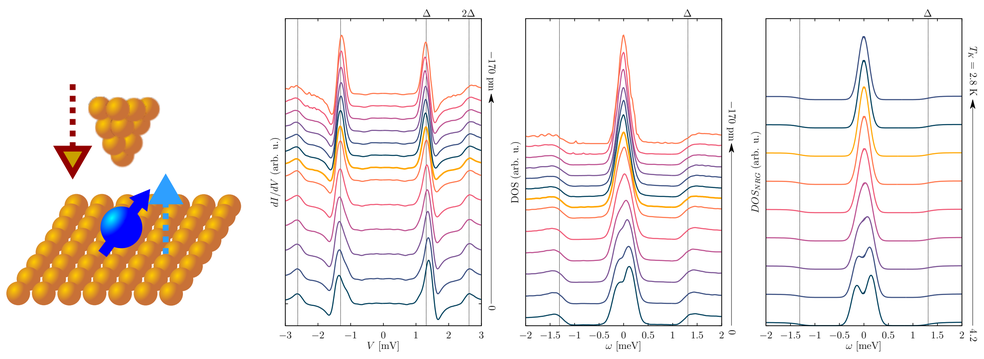


- Results show a gap $\Delta \approx 1.3\,meV$ and a single pair of **Yu–Shiba–Rusinov** (YSR) states along the molecular backbone, very close to zero energy.
- This indicates that TBTAP on Pb(111) is **naturally close to a singlet–doublet impurity quantum phase transition** (QPT).
- The Coulomb interaction $U \approx 200\,meV$, obtained from the gap measurement, places the system in the Kondo regime with $k_B T_K = 0.29\sqrt{\Gamma U}\exp[-\pi U/(8\Gamma)]$.
- For $U \gg \Delta$, one can use $k_B T_K^c \approx \Delta/(e^{5/3}-1) \doteq 0.23\Delta$ [4], giving $T_K^c = 3.5\,K$.

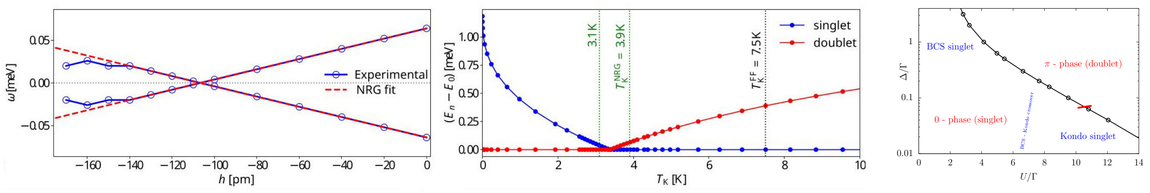
Triggering the QPT

Tunneling spectra at different tip heights:

- Decreasing the STM tip height reduces the coupling to the substrate, Γ_s, by lifting the molecule via attractive interaction.
- YSR states cross at the Fermi energy at $h \approx -110\,pm$—a hallmark of a QPT.



Extracting T_K^c from the YSR evolution



NRG [5] fits yield $\Gamma = 18.2$–$19.8\,meV$, corresponding to $T_K = 3.1$–$3.9\,K$, and $T_K^c = 3.4\,K$.

References and Acknowledgments

* C. Li, V. Pokorný, M. Žonda, J.-C. Liu, P. Zhou, O. Chahib, T. Glatzel, R. Häner, S. Decurtins, S. X. Liu, R. Pawlak, E. Meyer, *ACS Nano* **19**, 3403 (2025); * C. Li, V. Pokorný, P. Hapala, M. Žonda, P. Zhou, S. Decurtins, S. X. Liu, F. Song, R. Pawlak, E. Meyer, arXiv:2508.05575 (2025)

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QOpen
Many-body Open Quantum Systems

Model: Superconducting Anderson-Hubbard Impurity Model

An ensemble of N_d interacting impurities:

$$\mathcal{H}^{en} = \sum_{j=1}^{N_d}\sum_{\sigma}\epsilon_j n_{j\sigma} + \sum_{j=1}^{N_d} U_j n_{j\uparrow} n_{j\downarrow} - \sum_{i=1}^{N_d}\sum_{j=1}^{N_d}\sum_{\sigma} t_{ij} d_{i\sigma}^{\dagger} d_{j\sigma} + \sum_{i=1}^{N_d-1}\sum_{j>i}^{N_d} W_{ij}\left(n_{i\uparrow}+n_{i\downarrow}\right)\left(n_{j\uparrow}+n_{j\downarrow}\right)$$

N_l superconducting leads (tip and surface):

$$\mathcal{H}_l^{le} = \sum_{\mathbf{k}\sigma}\epsilon_{l\mathbf{k}} c_{l\mathbf{k}\sigma}^{\dagger} c_{l\mathbf{k}\sigma} - \Delta\sum_{\mathbf{k}}\left(e^{i\varphi_l} c_{l\mathbf{k}\uparrow}^{\dagger} c_{l,-\mathbf{k}\downarrow}^{\dagger} + \mathrm{H.c.}\right) + \sum_{\mathbf{k}\sigma}\left(V_{j,l\mathbf{k}} c_{l\mathbf{k}\sigma}^{\dagger} d_{j\sigma} + \mathrm{H.c.}\right)$$

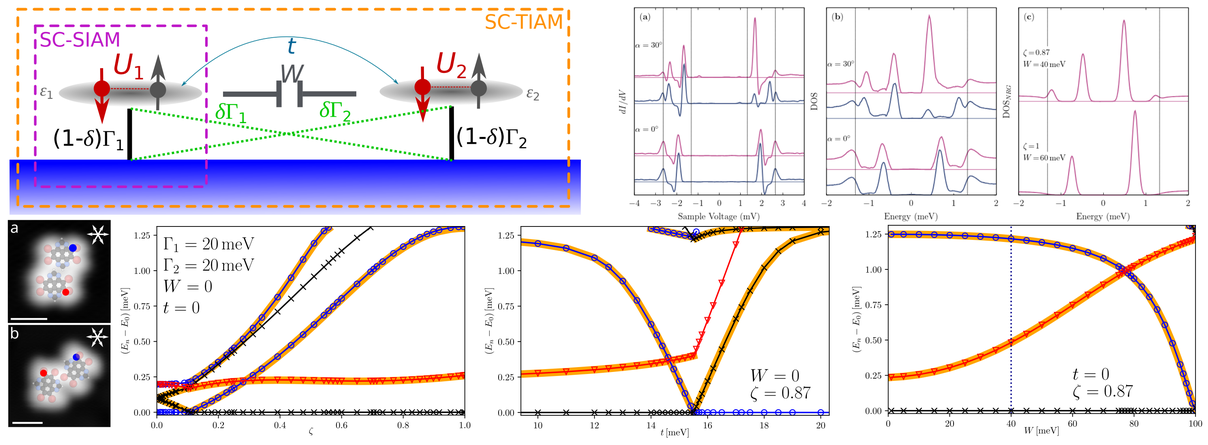
Local and non-local tunneling rates:

$$\Gamma_{j,l}(E) = \pi\sum_{\mathbf{k}}|V_{j,l\mathbf{k}}|^2\delta(E-\varepsilon_{\mathbf{k}}) = \Gamma_{jl},\ \ \Gamma_{ij,l}(E) = \pi\sum_{\mathbf{k}} V_{i,l\mathbf{k}}^{*} V_{j,l\mathbf{k}}\delta(E-\varepsilon_{\mathbf{k}}) = \zeta\sqrt{\Gamma_{il}\Gamma_{jl}}.$$

ζ parametrizes the distance: $\zeta = 0$ (large distance), $\zeta = 1$ (local, two-level impurity).

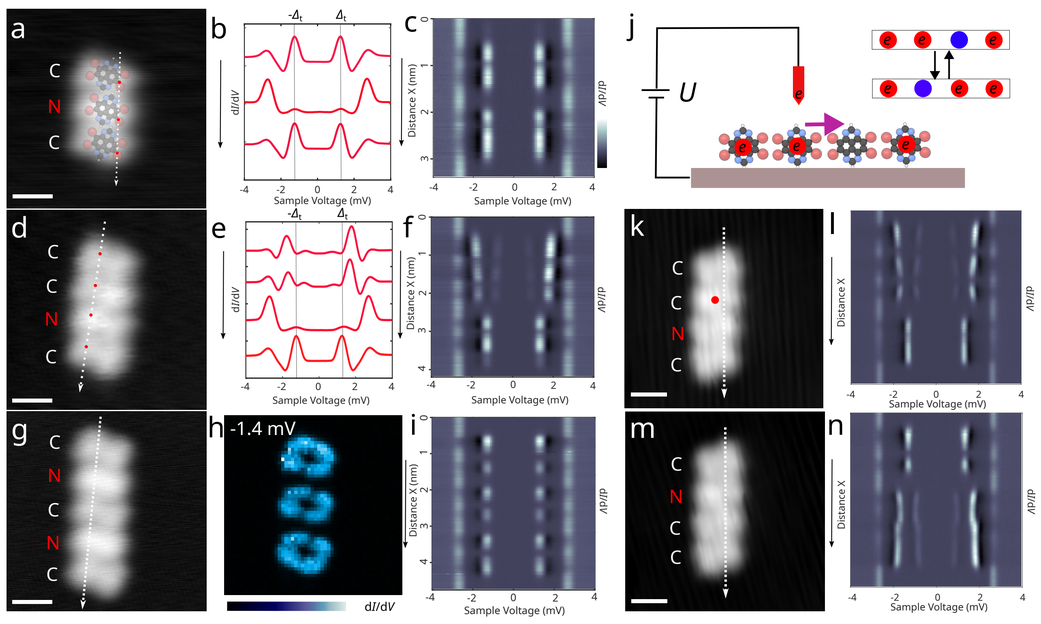
Short molecular chains

Two types of dimers engineered via lateral manipulation:



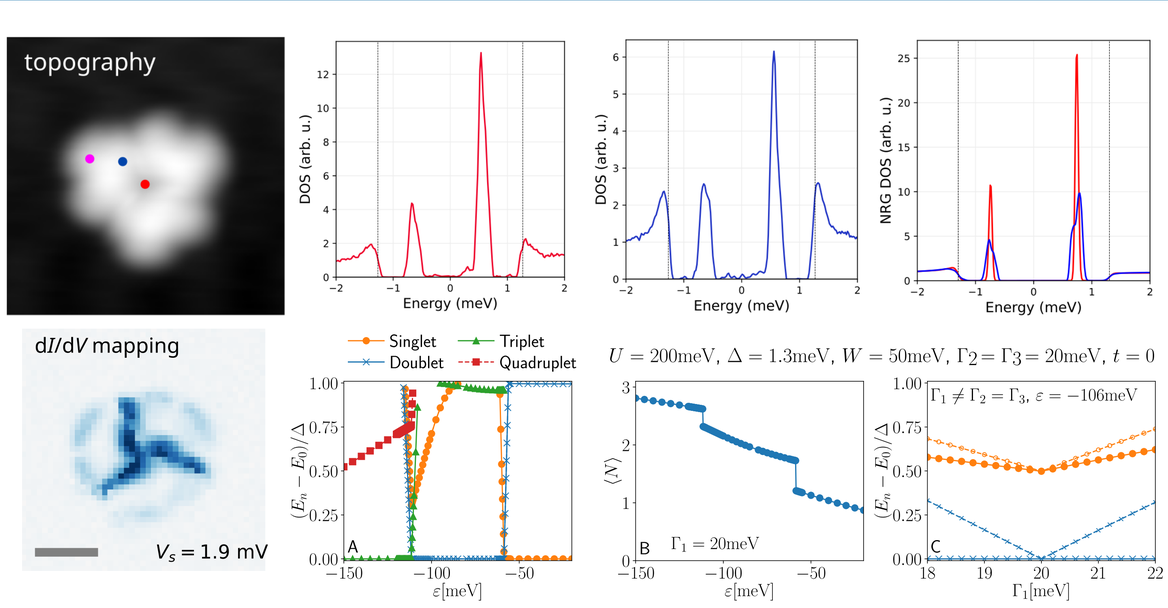
- Two pairs of YSR states for $\alpha = 30°$ and a single pair for $\alpha = 0°$.
- Large distance (small ζ): singlet with YSR states near the Fermi energy—alike an isolated molecule.
- Singlet–doublet QPT at $\zeta \sim 0.1$; three, two, and finally one pair of YSR states in the doublet phase.
- By fine-tuning ζ and W, we reproduce the experimental YSR positions in both cases; the **ground state is a doublet in both**.
- We observe an **effective ferromagnetic coupling** in the doublet phase.

Chains of 3, 4, and 5 molecules (same orientation with respect to the surface):



- Chains of odd length show a periodic arrangement of charged and neutral molecules.
- Molecules at the ends are always charged.
- The tetramer is frustrated: a dimer forms at one end.
- It can be switched between the two states using an STM tip, demonstrating information storage.

Trimer in a triangular arrangement



- NRG predicts approximately **two electrons** on the trimer and a **doublet** ground state due to sizable W, consistent with Pauli master-equation (PME) calculations.
- The eperimental YSR states are split by ≈ 0.1 meV; this is consistent with small differences in the Γ values.
- We develop an effective model describing the influence of molecular distance on YSR [6].

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