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Substitution Pattern Controlled Quantum Interference in [2.2]Paracyclophane-Based Single-Molecule Junctions

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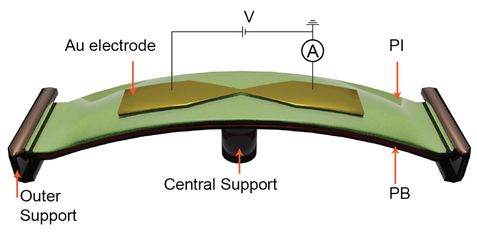
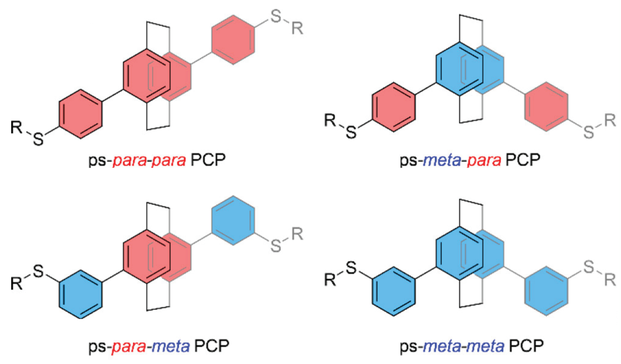
Single-molecule study on [2.2]Paracyclophane

- Mechanically-controlled break junction (MCBJ) forms atomically sharp electrodes by bending the flexible substrate.[1] The precise mechanical movement and atomic contact is ideal for single-molecule characterization.
- [2.2]paracyclophane (PCP) molecules are flexible molecules, which have been experimentally shown to host large mechanosensitivity, originated from quantum interference (QI).[2]
- Theoretical calculations predict that the type of QI, constructive or destructive, can be changed by different substitution patterns of the PCP core.[3,4]
- We create 4 different PCP molecules to study the substitution effect.





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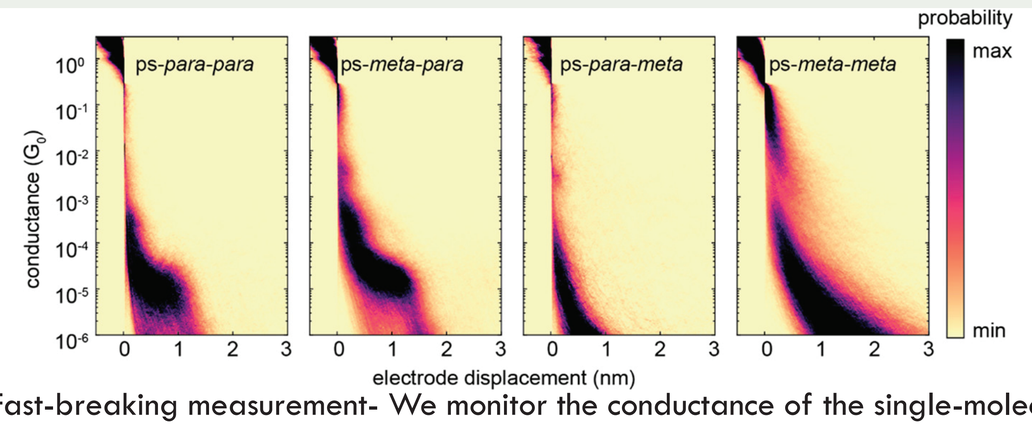
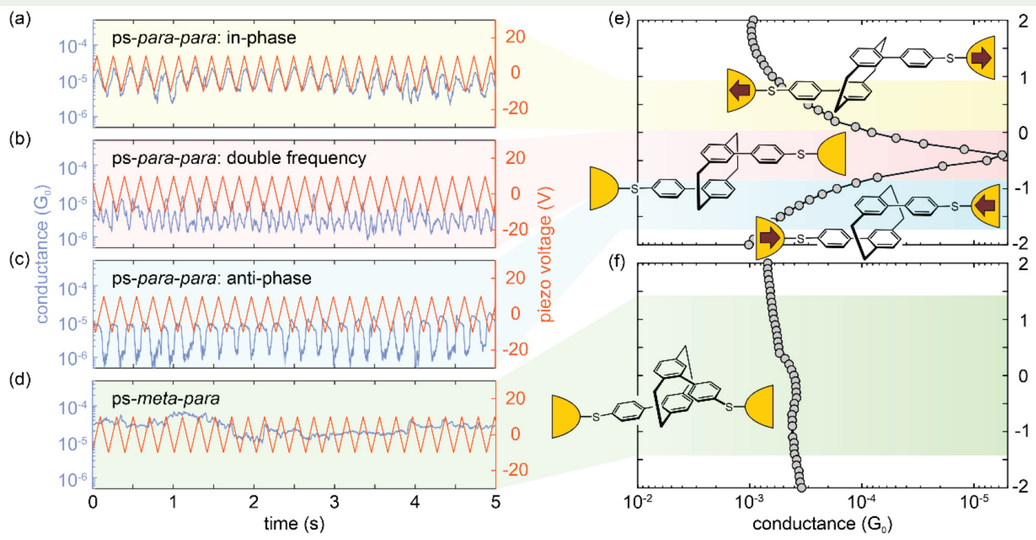
MCBJ conductance measurements

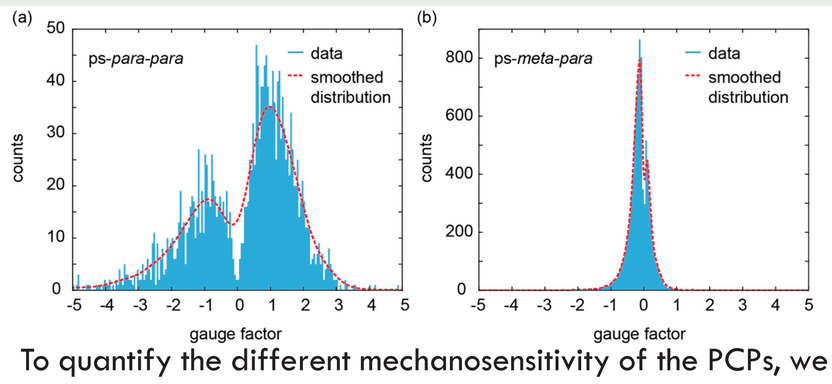


- Fast-breaking measurement- We monitor the conductance of the single-molecule junction at 100 mV (ps-*para*) and 250 mV (ps-*meta*), while opening the MCBJ. The recorded thousands of consecutive breaking traces are plotted in a two dimensional (2D) histogram, showing the single-molecule conductance distribution.
- *meta*-phenyl-anchored molecules show no clear conductance plateaus, different from the *para*-phenyl-anchored cases. It suggests that *meta*-phenyl-anchored molecules have such low conductance below detection limit.
- On the other hand, ps-*meta*-coupled PCP shows a higher conductance ps-*para*-coupled PCP, suggesting a possible substitution effect different from the phenyl-anchoring substitutions.

Mechanosensitivity & Gauge factor

- To probe the mechanosensitivity of ps-*para*-*para* and ps-*meta*-*para* PCP, we perform the distance modulation experiment. We first open the junction by 7.5 Å and further introduce a triangular wave of 5 Å at 5 Hz.
- Only ps-*para*-*para* shows responses to the modulation with 3 different phase behaviours: in-phase, anti-phase and double frequency. This corresponds to different initial positions in a conductance dip as a function of displacement. For example, double-frequency corresponds to the vicinity of a conductance dip where conductance increases whenever the molecule is stretched or compressed. These are the same behaviours seen in the reported long PCP, suggesting the presence of Destructive QI (DQI) in ps-*para*-*para* PCP.[2]





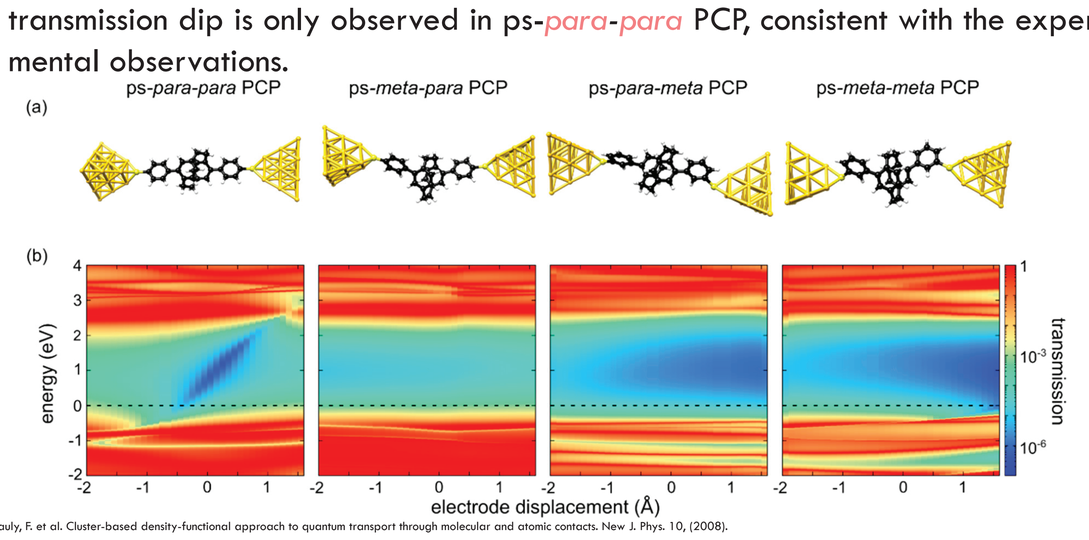
- To quantify the different mechanosensitivity of the PCPs, we use the notion of gauge factor (GF), which is essentially the fast Fourier transform (FFT) of the modulation response.
- The complex GF is defined as:

$$z(f) = r(f)e^{i\varphi(f)} = \frac{\mathrm{FFT}(\log(G/G_0))(f)}{\mathrm{FFT}(d/d_0)(f)} \quad .$$

The GF amplitude is large when G responds the modulations. It is evident that ps-*para*-*para* is more mechanosensitive than ps-*meta*-*para*. It also suggests the absence of DQI in the case of ps-*meta*-*para*.

Calculated transmission

- Density-functional theory (DFT) based transport calculations have been performed for the 4 PCP molecules.[5] The observed substitution effect are rationalized via the transmission maps.
- For the case of *meta*-phenyl-anchored PCPs, strong DQI is observed leading to low conductance level.
- *para*-phenyl-anchored PCPs both show higher conductance level. However, a transmission dip is only observed in ps-*para*-*para* PCP, consistent with the experimental observations.



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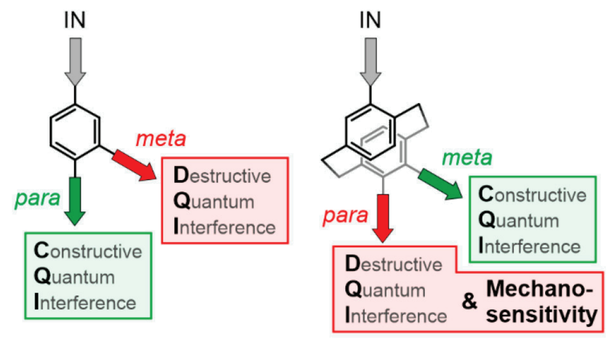
Summary

- Via the single-molecule study of PCPs we realize the substitution effects at the phenyl groups and PCP cores. This is summarized in the figure here.
- For phenyl rings, constructive QI (CQI) happens for *para* connection while *meta* connection gives DQI.
- For PCP cores, CQI happens for ps-*meta* connection and DQI occurs for ps-*para* connection, opposite to the case of phenyl rings.
- Our discovery is in agreement with reported substitution rules of phenyl-like molecule both experimentally and theoretically.[6-9] Within the same molecule, we further demonstrate the predicted substitution rules for PCP molecules.[3,4] This knowledge facilitates the future designs for DQI-based mechanosensitive molecules.



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