Replicating Partially Wet Phase molecular MCB junctions, what matters most?

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1 Summary, Audience and Scope

This guide consolidates practical, reproducible steps to create and measure single-molecule junctions in a partially wet phase (PWP) using a mechanically controllable break junction (MCB) setup. It emphasizes timing, mass production discipline, and a measurement protocol optimized for the approximate 10-minute window during which the PWP junction is stable. The document separates the mechanical setup, device fabrication, chemical preparation, breaking and draining procedure, self-assembly dynamics, and measurement strategies, with checklists and expected ranges to accelerate success for newcomers in the field.

Audience: Experimenters familiar with MCB concepts and basic laboratory skills, seeking a reproducible path to PWP single-molecule junctions. Scope: A practical, step-by-step protocol with parameters, expected ranges, and decision points.

2 Experimental Overview

High-level sequence:

(a) Prepare and mount the MCB device

(b) Inject solution (THF or BDT/THF)

(c) Break the junction under controlled electrical conditions

(d) Drain to achieve PWP

(e) Allow self-assembly

(f) Start measurements during the ∼10-minute PWP window

(g) Monitor conductivity and adjust equipment ranges when required

(h) Capture IV curves until PWP ends

3 The MCB Setup

3.1 A basic simple setup

The MCB setup for PWP MCB junctions consists of a basic setup. The piezoelectric element which is often used in MCB setups for fine adjustment is not required. This is because the experiment makes use of a self-assembly process. Taking the process steps in the right order will result in a single molecule junction lined with a PWP of fluid molecules. The default solvent of use is tetrahydrofuran (THF).

3.2 Requirements for the setup

Requirements for the MCB setup: A course adjustment for example an M4 screw (fine pitch) operated by a gearbox 1:120 moves a lever towards the bending beam. Due to design of the lever and the turning point, an approximate attenuation of 3:1 is realized. A motor with low revolution possibility, (40 revolutions/min) is used to operate the gearbox 1:1 [1].

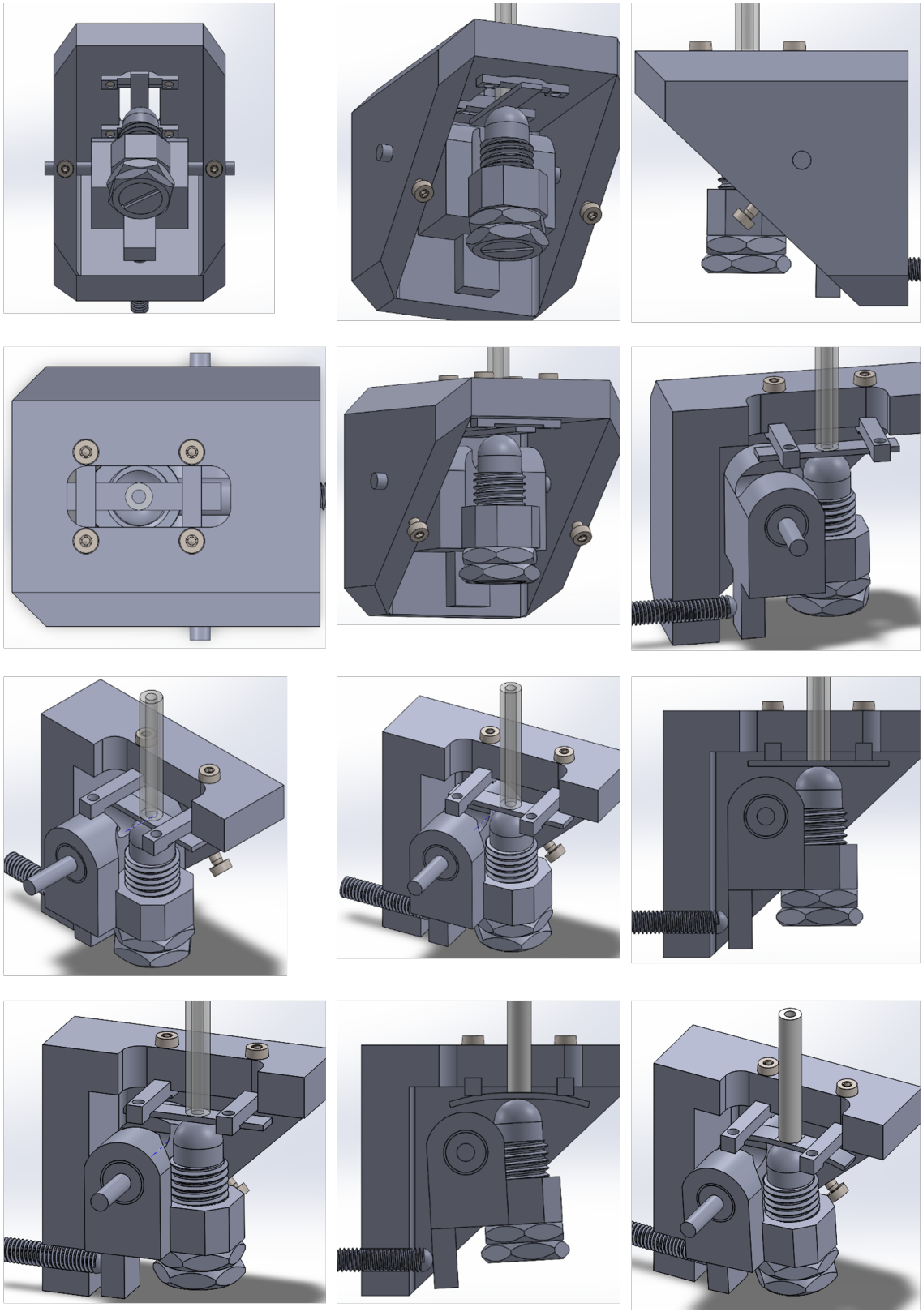

Figure 1: Detailed overview of the heart from the MCB setup. The M4 bolt operates a lever which in turn bends the bending beam with glass cell mounted to it.

3.3 The partially wet phase duration is finite

The junction is temporary. Its PWP layer changes over time. Initially, the layer may thicken as THF vapor redeposits from the glass cell wall on the junction area during initial drying. Progressing, the PWP layer decreases in thickness once the cell is completely dry, due to ongoing evaporation. At some point the last molecular layer of THF lining the electrode-molecule-electrode system will be evaporated. This reflects the end of the PWP which will destroy the specific advantages that this phase offers. The above indicates that timing is paramount. The molecular junction in the PWP is created at some point in time, lasts for about 10 minutes, and dies. The experimenter needs to acquire a good sense when to start the measurements.

4 The MCB device

4.1 Creation of the device

The MCB device is at the heart of the experimental setup. Devices are created, either by hand or mass produced on a wafer for example. Wafer produced devices still require manual handling in mounting the cell and leads to the attachment of the MCB setup. The method used has been elaborately detailed [2]. That method will work but requires building some skills. This choice is the experimenters to make. Experimenters should take note that micro machined MCB's in the PWP is uncharted territory. If the choice is to copy the notched filament device, make sure to copy exact. Use the 2 mm inner diameter 25 mm long glass cell and use the paper tip for draining.

The use of electrode material is either hard or soft tempered gold. No difference of the temper could be detected in any of the experimental results.

4.2 Mass production as a requirement

Mass production is an important aspect of the device manufacturing process. Having been emersed in mass production environments in wafer fabs for a large part of my professional life, this experience has been used in more than one way during my experimental years 2018-2021. The pros of mass production cater for honing a process that led to 100% success ratio, creating 25 or 30 devices in one go during a week or so. Having an abundant supply of good working devices allows for a very steep learning curve. A measurement day typically consumes 3 or 4 devices. Mass production implies sticking to the exact same process, no rework, no reuse and finding the root cause of every deviation in the process.

5 The measurement equipment

5.1 Facilitate your measurements

The 4155 has two possibilities to measure, "single" mode or "continuous" mode, where the indicated range is continuously scanned back and forth. The continuous mode offers an experimenter friendly option as it allows monitoring the progression of the junction as the PWP slowly increases or decreases. Resulting in a continuously increasing or decreasing average conductivity or equivalently current. Once structure becomes visible in the measurement trace it can be captured immediately. Measurements should continue during the PWP existence. Once the PWP is extinct the conductivity will be below 5 nA at 5 V. The changing conductivity over time may require an adjustment of the equipment range being used.

Measurement time is defined as the integration time of the charge flowing through the junction. For the 4155 three preset measurement times are available: short: 0.64 ms, medium: 20 ms and long: 320 ms. While recording a measurement these times can be toggled between short and medium, "long" has never been used. This provides an easy way to study the resulting response of the quantum system. Modern equipment will be able to provide a range of measurement times as well as frequencies to study the response of the quantum system, possibly quantifying the entire quantum system in a single IV curve!

5.2 Relevant voltage range for the experiments

Do not try to capture the entire -10 V to 10 V range. The relevant action is in the high voltage regime, starting off in the 9-10 V or 7.5-10 V range only with scan speeds between 200 mV/s and 20 mV/s is recommended. Measurements are voltage biased and the resulting current is measured within an integration time in the short to medium range. Measurement equipment should have a resolution of 1 or 2 mV at high voltages to capture the displayed level of detail. The 4155 obtains a 1 mV resolution over a 1 Volt range up to 10 V.

5.3 Relevant current levels

Just after breaking the device in either THF or the BDT/THF solution the measured current level at 5 V is in the range 6-50 nA. In the drying phase that follows and endures approximately half an hour the current levels are expected to increase to approximately 100 nA at 5 V. A typical successful measurement cycle obtains current levels in the 50 nA at 10 V to 1 µA at 10 V depending on the exact stage in the drying process. This holds for THF only devices as well as BDT devices. In general, the BDT devices exhibit a somewhat (20-30%) higher conductivity as compared to THF only devices.

6 Mounting the bending beam assembly

Normally an MCB device will be mounted in a three-point bending configuration. Robust phosphor bronze bending beams can be easily stressed during mounting, enabling an adhesive-free fixture. This will not break the notched wire yet and fix the assembly in place against the counter supports. For electrical connections, copper leads (100 µm) are glued to the bending beam assembly, the gold wire leading to the notch has been wound tightly around the two copper leads at the bending beam end. Silver paint has been used at the gold-copper connection as an extra precaution. After mounting the assembly, the two copper leads can be tightly wound around two fixed connector-stubs on the MCB setup. This enables rapid swaps of bending beam assemblies to maximize measurement time.

7 Chemical preparations

7.1 Which solution to use?

A solution can be injected into the cell after the bending beam assembly is mounted and electrically connected. So far, the default has been an approximate 1mM BDT/THF solution which originates from the Yale "Atomic Probes" BDT/THF experiments.

Results from the past years, however, reveal that THF only devices show the same interesting physics as BDT/THF devices. Studying the THF only devices show a qe2 effect in S274 a qe1 effect in S279 and qe1 as well as qe2 in S280, qe1 and qe2 are defined in Ref. [3]. Therefore a simple start is to use THF only, interesting qe1,2 effects are still obtainable.

7.2 How to prepare the THF or BDT/THF solution?

If one would like to use the 1mM BDT/THF solution it has been consistently created in the following manner: The vial containing the BDT molecules is to be used repeatedly and therefore needs to be stored under Ar (inert gas) atmosphere in a fridge. It is known that BDT molecules degrade in air. Thus, the miniature glove box is used. With a spatula the molecules are transferred to a small glass vial which is subsequently closed with a white septum, in Ar atmosphere, see photo below.

The THF is used from small 25 ml septum sealed bottles, see photo. All THF handling is done outside of the glovebox. While extracting the THF a small amount of overpressure is realized by an Ar filled balloon attached to a syringe which needle ends above the fluid level. Another glass syringe with stainless needle ends inside the fluid, which can be extracted. Glass syringes are preheated in a furnace (>100 C) and cooled down prior to use to minimize water content in the THF.

Option A: THF only devices, use the extracted THF fluid in the glass syringe.

Option B: BDT/THF devices, the solution can be created by injecting the THF into the glass vial capped with a septum containing the molecules. The BDT/THF solution can also be extracted from this vial. In the glovebox one should estimate the quantity of molecules to transfer to the glass vial to end up with an approximately 1 mM BDT/THF solution.

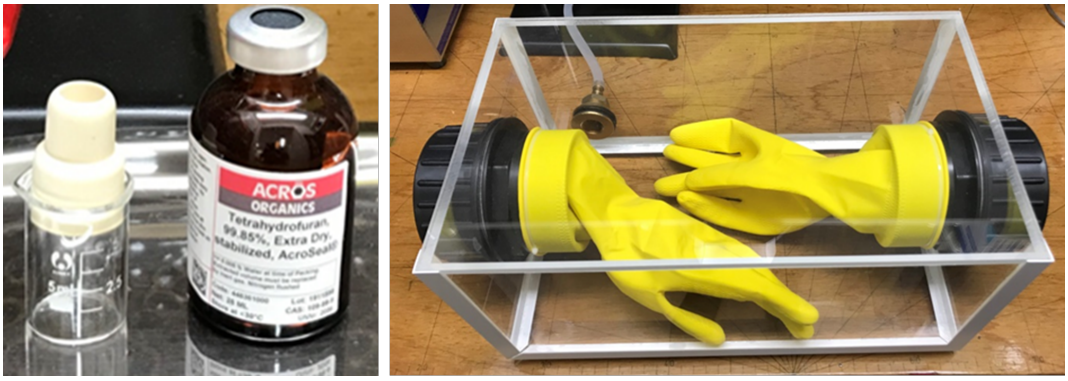

Figure 2: BDT molecules are handled and transferred to a glass vial in the glovebox under Ar atmosphere.

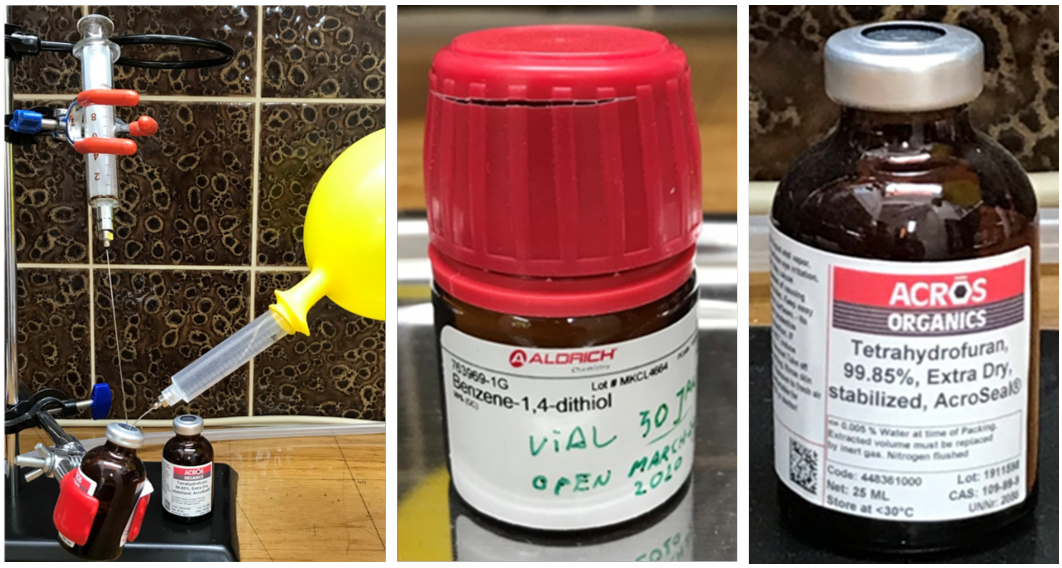

Figure 3: THF is transferred from a septum sealed bottle to a glass syringe.

8 Submitting the solution, breaking the notch and draining the cell

8.1 Submitting the solution

The solution is injected inside the 2 mm inner diameter cell by a glass syringe with stainless needle, only a few drops suffice. Default the cell was filled until halfway with fluid, about 12 mm of cell height.

8.2 Breaking the notch

The MCB can be broken by motor action. The variation in time until the notch breaks is a good gauge of the mass production skill level reached. To prevent large current densities during breaking use a compliance of +1 µA or -1 µA and a voltage scan in continuous mode from -100 mV to 100 mV.

Although it may seem a nontrivial action, breaking the notch in a certain manner is a crucial step in the following self-assembly process. Although the process of breaking is forgiving, it was always handled in a manner that the motor was immediately stopped after breaking by manually breaking the circuit. The human reaction time of 0.1-0.2 s together with the motor its 40rev/min, the gearbox 1:120 attenuation, the fine pitch of the M4 bolt, the approximate 1:3 attenuation of the lever and the estimated reduction factor of the MCB junction, leads to an electrode separation estimate of a few nm. This is sufficient to complete the self-assembly process and get the electrodes a molecule apart either by elasticity or by deformation in the drying process. After the notch is broken and the electrodes are formed some time is provided for molecules to settle on the fresh surfaces, one or a few minutes.

8.3 Draining the cell

The cell is ready to be drained by a paper tip, first most of the fluid is absorbed by a course paper tip. After that a sharp tip, which is bend at a straight angle for the last 3-4 mm is inserted in the cell for draining until an "outer ring" is observed [2]. Subsequently after a certain waiting time the single molecule junction in the PWP has been self-assembled.

9 Self-assembly and picking the right time to start the measurement

9.1 Self-assembly

Once the "outer ring" has been established nature creates a single molecule PWP MCB device. As an experimenter the right moment to start recording IV curves needs to be established.

In the 2021 Decoupling preprint it is phrased as follows: "A law of nature seems to hold for two electrodes spaced at nanometers distance during the drying process. Be it soft temper Au or hard temper Au used as the MCB electrode material, be it broken in air and after that immersed in fluid or broken directly in a THF environment, the shown electrode behavior upon the drying process is the same. Once the excess fluid has been drained, the continuous increase of the conductivity is attributed to a constantly decreasing distance between the two closest points on the opposing electrodes due to the lasting evaporation of the fluid on and between the electrodes. Apparently, there is enough elasticity in the nanometers separated electrodes such that the exact initial separation does not matter. The continuously decreasing amount of fluid between the electrodes pulls the electrodes ever closer together. This process continues until the fluid is getting depleted, and a molecule is squeezed between the electrodes, blocking any further movement. The adhesion forces of the molecules (either BDT or THF) to the gold electrode surface, together with the PWP layer which is lining the entire electrode-molecule-electrode system are such that a metal-molecule-metal junction is favored over a metallic junction."

9.2 Current levels as a manner to monitor

Current levels during the waiting time provide a view of the single molecule creation process. The absolute current level provides an indication when to start the measurements. Continuously monitoring the current level however may have adverse effects. It may direct bulk fluid towards the junction region, leaving the junction in an "emerged fluid" situation as opposed to a PWP situation. To prevent this situation, single (pulse) measurements are performed to gauge the current level every few minutes or so. A default voltage level of -5 V has been used to gauge the current level. Below the drying characteristic of a 1 mM BDT/THF solution is shown for both a hard temper and a soft temper Au junction.

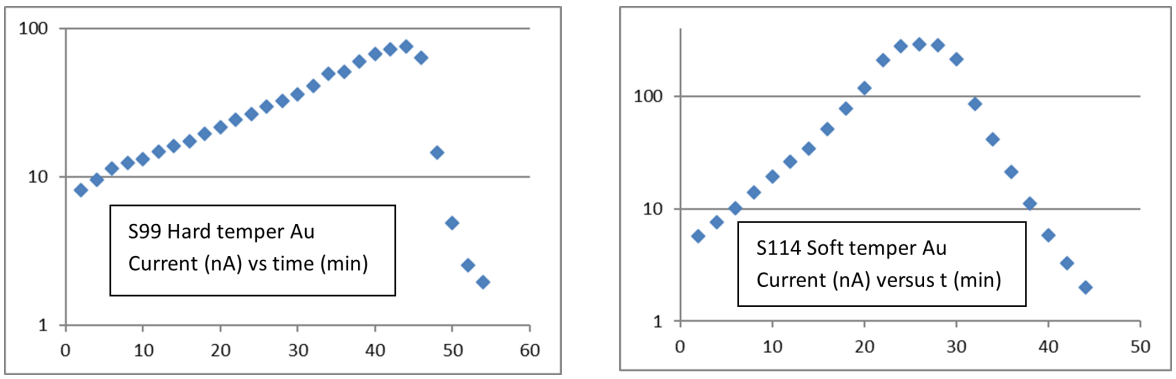

Figure 4: Drying characteristics of a BDT/THF solution in two different junctions, the |current| is measured at -5 V.

9.3 Combining the current level and the physical cell situation in the critical "start" decision

Starting too soon with the measurements will leave the junction in a "bulk" liquid situation, losing the advantages of the PWP. Starting too late will leave the experimenter with no time to measure. The above is the dilemma the experimenter is facing. Experience will help the experimenter in this situation. The visual check of the bottom of the cell provides an additional gauge to see if the THF fluid is almost gone. The experimenter needs to have a good understanding of the physical situations which the bottom of the cell obtains during the various drying stages [2].

References

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