Supporting Information

Long-Lived Charged States of Single Porphyrin-Tape Junctions Under Ambient Conditions.

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1. Break Junction Experiments

1.1. Sample preparation for single-molecule experiments. Each compound was deposited onto a freshly flame-annealed gold substrate from a 0.1–1.0 mM dichloromethane solution, using an immersion time of 30 minutes. After this time the substrate was removed and blown dry. To prepare the tip we mechanically cut a gold wire, rinse it with ethanol to remove any grease and then pass it briefly through a butane flame.

1.2. Single-Molecule Conductivity Studies. The conductance of each compound was measured using the STM-BJ method. All experiments were performed using a home-built STM, optimized for room temperature measurements in air. During the break-junction experiment, the tip is moved vertically in and out of contact with the substrate at a constant speed of approximately 10 nm/s, in 1 pm steps. For the conductance (G = I/V) versus distance measurements, a bias voltage V of between 0.1 and 0.2 V was applied between the tip and the substrate. A linear current-to-voltage converter with two amplification stages allows us to record conductance values over a large dynamic range which depends on the compound under investigation and chosen to explore the largest range of conductance according to the value of

the histogram peak. We also place a resistor in series with the main circuit which limits the total current when the junction resistance is low. The size of the resistor depends on the gain used. Please see Table S2 for a table of gains and resistor used for each measurement.

The motion of the tip and the conductance measurement are controlled by an in-house computer program to record conductance versus tip-displacement (*G* vs. *z*) curves. Typically, when moving out of contact, we move several nm after reaching our lower conductance limit. When in contact, the piezo moves a further 1–2 nm after reaching 1.0 G_0 . These limits guarantee that a broad gold contact is formed and broken in each cycle, and that any molecular junction is broken at the end of the cycle. We aim to carry out 5000–10000 approach and retraction cycles in each run, and we vary the location of the tip over the sample in order to avoid systematic errors in the data. We focus on the opening stages of the cycle. After data acquisition is complete, we first remove any blocks of traces in which there is a clear degradation in trace quality due (most likely) to tip blunting or excessive build-up of material between the electrodes. We then use an automated routine to separate traces displaying plateaus from those with tunnelling-only. This searches for regions of individual traces in which the conductance change is less than a certain amount across a minimum distance interval (for example, a plateau is identified when a $\Delta z > 0.1$ nm is needed to produce a change in conductance of $\Delta \log(G/G_0)$ < 0.1 at any region below 0.5 G_0). We use very similar criteria for all compounds.

1.3 I-V measurements. For the I-V measurements, we stop the piezo movement at regular intervals during the stretching of a single junction and perform a voltage ramp. This is done every 0.5 to 1 Å during an opening trace. A sweep rate of 0.7 Vs⁻¹ was used. Between each two ramps (+V to -V and -V to +V), we return the voltage to the predetermined value and continue

Compound	Voltage (V) for	Gains used	Series
	Gz measurement		Resistor (Ω)
	0.2	1.0 x 10 ⁷ /5.0 x 10 ⁹	205300
P1			
1	0.1	4.9 x 10 ⁶ /2.3 x 10 ⁸	47500
tP2			
(Tag	0.1	4.9 x 10 ⁶ /2.3 x 10 ⁸	47500
tP3			

recording the current as the piezo is moved, thus building a G(z) trace as for the fixed-bias measurement. All +V to –V traces are coloured black, all –V to +V traces are coloured red.

Table S1. Table of gains and series resistance values used for each measurement.



Figure S1. Representative *G-V* curves. Curves were recorded with a bias range of a-b) ± 0.8 V, c) ± 1.0 V and d-e) ± 1.2 V.

- **1.4.** Examples of reversible (uncharged) and hysteretic (charged) *G-V* curves for P1 and fP2.
- **P1** non hysteretic *G-V* curves



Figure S2. Individual G-z breaking trace for P1.





Figure S3. All G-V traces recorded for the junction shown in Fig. S2. The order of the traces reads from top to bottom and left to right.

P1 – hysteretic G-V curves

Figure S4. Individual G-z breaking trace for **P1**.

Figure S5. All G-V traces recorded for the junction shown in Fig. S4.

fP2 - non hysteretic G-V curves

Figure S6. Individual G-z breaking trace for **fP2**.

Figure S7. All G-V traces recorded for the junction shown in Fig. S6.

fP2 –hysteretic G-V curves

Figure S8. Individual G-z breaking trace for **fP2**.

Figure S9. All G-V traces recorded for the junction shown in Fig. S8.

Figure S10. Individual G-z breaking trace for **fP2**.

Figure S11. All G-V traces recorded for the junction shown in Fig. S10.

Figure S12. Further examples of junctions with two state-hysteretic switching behaviour for **fP3**.

Figure S13. Corresponding G-z traces from Figure 1 c-e (a corresponds to 1c, b to 1d and c to 1e).

Figure S14. Corresponding *G*-*z* traces from Figure 5 c (left) and d (right).

Figure S15. dI/dV curve for 7 averaged I-V traces recorded on the junction shown in Fig. 2.

1.5 Clustering Analysis

The rationale for dividing traces into 'U'-shaped and non-'U'-shaped traces is as follows. We recognise that 'U'-shaped traces are typical for uncharged molecules (not just the porphyrins here, but in principle any other molecule except where destructive quantum interference plays a dominant role). When the molecule becomes charged, the shape of the G-V no longer has this 'U'-shape, although the precise shape can vary (see Figure S18 for example). As such we grouped the non-'U'-shaped traces into a single group (by hand) which represent the charged junction state. A few curves have shapes which can be considered hard to classify concretely. As, in our case, this was a low percentage, we decided to group these traces with the 'U'-shaped curves for the main analysis.

Figure S16. Summary of the clustering analysis for **fP3**. a) 'U'-shaped traces recorded for a bias window of ± 0.8 V. b) non-'U'-shaped traces recorded for a bias window of ± 0.8 V. c) 'U'-shaped traces recorded for a bias window of ± 1.0 V. d) non-'U'-shaped traces recorded for a bias window of ± 1.0 V. e) non-'U'-shaped traces recorded for a bias window of ± 1.2 V.

Bias range = ± 0.8 V non-'U'-shape log(G/G_n) -3 -1 -0.5 0 0.5 1 V (V) -1 -0.5 0 0.5 V (V) -1 -0.5 0 0.5 V (V) 1 1 hard to classify log(G/G_n) 2 -3 -4 -5 -1 -0.5 0 0.5 1 V (V) -1 -0.5 0 0.5 V (V) 1

Figure S17. Top panel: various individual clusters of non-'U'-shaped traces for **fP3** recorded for a bias window of ± 0.8 V showing distinct profiles. Bottom panel: traces with a flatter profile than the strongly 'U'-shaped traces which are difficult to classify.

Figure S18. Top panel: various individual clusters of non-'U'-shaped traces for **fP3** recorded for a bias window of ± 1.0 V showing distinct profiles. Bottom panel: traces with a flatter profile than the strongly 'U'-shaped traces which are difficult to classify.

Figure S19. a) 2D histogram for the bias window ± 0.8 V for **fP2**. The number of traces is 2623.

Bias range = ± 1.0 V

Figure S20. Top panel: 'U'-shaped traces recorded for a bias window of ± 1.0 V. The number of traces is 7450. Middle and lower panel: various individual clusters of non-'U'-shaped traces for **fP2** recorded for a bias window of ± 1.0 V showing distinct profiles. The number of traces is 109, 45, 69 and 198 from left to right. Bottom panel: traces with a flatter profile than the strongly 'U'-shaped traces which are difficult to classify. The number of traces is 182.

Figure S21. a) Percentage of G-V traces with 'U' and 'non-U' shapes within the various voltage ranges studied for **fP2**.

Bias range = ± 1.2 V

Figure S22. Top panel: 'U'-shaped traces for **P1** recorded for a bias window of ± 1.3 V. The number of traces is 6175. Bottom panel: various individual clusters of non-'U'-shaped traces recorded for a bias window of ± 1.3 V showing distinct profiles. The number of traces is 16, 26 and 23 from left to right.

1.6. Note on single molecule junction formation.

One of the fundamental issues with the breakjunction technique is that it can be considered as a blind approach to connecting to molecules. In the current work, we are quite sure that only single molecules are wired in any one junction for two main reasons. The percentage of molecular junctions we find for porphyrins is relatively low (normally between 15 to 30 % of all traces recorded and are fairly evenly distributed throughout the whole measurement). This fits into the regime whereby we have previously shown that single molecule junctions are most likely formed.⁶ Logically, in this situation it is unlikely to wire several molecules simultaneously. The second reason is due to the bulky substituents attached to the porphyrins. **P1** has two -Ph(OC₈H₁₇)₂ groups on the central ring while **fP2/3** have two -Ph(Si(C₆H₁₃)₃)₂ groups. This prevents aggregation of molecules and should promote isolated molecules on the surface. So even though we do not visualise molecule prior to wiring, as could be done in other STM experiments, we are confident that we wire only single molecules. During an *I-V* measurement, there is no difference between our measurement and that of an experiment in which a single molecule has been clearly identified beforehand on a surface. Both types of experiment are blind during the 'wired' phase.

2. Theoretical Investigations

2.1 Porphyrin molecules in vacuum

As a first step in the theoretical calculations we relaxed the three Porphyrin structures shown in the main text of this article in vacuum. For that purpose, we chose slightly simplified molecules compared to the ones used for the measurements where we substituted the phenyl groups perpendicular to the transport direction with H. We plot the frontier orbitals of such simplified and relaxed molecules in Fig. S38, where we find that the symmetry of the MOs compare well with the results given in Fig. S32 of Ref. [1] for the molecules used in the measurements, which justifies our structural simplification. Therefore, no significant deviation in the coupling of the eigenstates to the electrodes with respect to the measured molecule can be expected.

We also show the corresponding eigen energies of the plotted MOs in Fig. S38. The reference energy for the eigenstates in vacuum is arbitrary, which leads to a constant shift in the absolute values compared to Figure S32 of Ref. [1]. However, the relative energy differences of the MOs match the results from [1] quite nicely with gap sizes of 1.36 (P1), 0.79 (fP2) and 0.58 (fP3) compared to 1.33 (P1), 0.77 (fP2), 0.57 (fP3) reported in Fig. S32 of Ref. [1], which again confirms that our structural reduction should have no significant impact on electron transport properties.

In principle the HOMO-1 of all three molecules is a prime candidate for bias driven switching, because it does not show any localization on the anchor groups and its distance to the electrodes is very similar to that found for a hysteresis inducing Mo-complex in Ref. [2].

We note that the gap size is reduced with molecular size, as expected. Since also the HOMO-1 comes closer to the Fermi level in energy with an increase of the molecular length, this provides a clear distinction between the three molecules, which makes stochastic switching most likely for **fP3** because here the HOMO-1 can be most easily reached with the bias window.

2.2 Junctions and transmission functions

In a next step in the theoretical work of our study we form the junction, which allows us to investigate the MO energies with respect to the electrode's Fermi level as well as to calculate the corresponding transmission functions. For this purpose we chose an adsorption configuration of the molecule's anchor groups bound to the electrodes in a threefold hollow site, which can be considered as the most stable i.e equilibrium one but this is of course a highly idealized setup of the junction compared with want we expect to happen in the actual experiments, where the surface structures and adsorption sites will vary from measurement to measurement and the electrode's surfaces will include steps of all shapes and sizes. Therefore, this is one of the major factors in making our simulations just semi-quantitative.

The transmission functions resulting from our simulations, as well as the corresponding molecular eigen energies with respect to the electrode's Fermi level are shown in Fig. S39. While the HOMO and the LUMO (as well as, the LUMO+1 in the **fP3** junction) of the molecules show broad distinctive peaks, the HOMO-1 is not a viable transmission channel for coherent electron tunnelling (which dominates the conductance) in any of the three junctions. In fact, no peak relating to the HOMO-1 is visible at all. This is a promising result regarding the role of this MO as a switching state, since this means that HOMO-1's coupling is orders of magnitude lower than e.g. the HOMO's.

We note that we find overall higher values of the conductance than those reported from the calculations in Ref. [2], where a scissor operator has been applied in order to increase the gap size and also models for the electrode's surface structure different from ours with a pyramid of Au atoms on top of the surface and on top adsorption of the molecules have been chosen.

2.3 Coupling of the HOMO-1

Fig. S25: Single MO transmission function of the HOMO-1 for all three compounds with both binding schemes. The calculated transmission function, shown in black, has been fitted with a Lorentzian of the shape

Since the HOMO-1 (of the bare molecule) is a promising candidate for conductance switching, we studied its electronic coupling to the electrodes for all three molecules in our study by fitting a Lorentzian to the corresponding single MO transmission function, where we also compared hollow with on top adsorption configurations.

The resulting peak and the fitted Lorentzian can be seen in Fig. S40. In all three compounds the coupling is minuscule, making them viable for conductance switching. Because all these peaks and the resulting values for the couplings, are very similar, however, we can conclude that the coupling of the MO is not the selective factor for the switching behaviour found for **fP2** and **fP3** only. This only leaves the distance of the localized MO from the electrode's Fermi level as the source of their differing behaviour. Also, the coupling magnitude does not seem to be influenced significantly by the adsorption configuration. This is plausible since the coupling of this state to the electrodes is mostly determined by the distance between the molecular core and the electrodes, which is increased only slightly in the top adsorption when compared to the hollow configuration.

2.4 Switching simulations

Parameters

The switching reaction rate is calculated via a Marcus-Hush-Chidsey approach as developed in earlier work [2-4]. This methodology needs three parameters inherent to the junction, namely the energy of the localized orbital with respect to the electrode's Fermi level (ϵ_0), the reorganization energy of the molecule in the junction (λ) and the electronic coupling of the localized orbital with the metallic bands (Γ). ϵ_0 and Γ have been determined as -0.40 eV and 3.5 10⁻⁹ eV for the **fP3** junction, respectively as shown in Figure S39 and S40.

The reorganization energy we calculated according to

 $\lambda = \lambda_{in} + \lambda_{out} + \lambda_{img}$,

where the three components are the inner and outer reorganization energy and the stabilization of the charged state due to image charges, respectively. Since the measurements we want to mimic were performed in air, λ_{out} will be neglected in the following. λ_{in} represents the change in Free Energy due relaxing the uncharged into the charged state geometry and vice versa. This contribution has been calculated as the potential energy difference of the different charge states for the molecule in the gas phase where the geometry was kept fixed to the equilibrium configuration of the neutral molecule. Vibrational contributions to the Free Energy were neglected in our calculations, since we assume that the change in the charging state might not alter them significantly.

A value of 18meV for the **fP3** molecule has been determined for λ_{in} , which is rather low. However, this is not surprising since the molecule is very large, leading to a delocalization of the added charge over an extended area. This reduces the effect of charging on the molecular geometry.

Since in the scheme applied for simulating the charged state of the junction we are only able to charge the HOMO and not the localized HOMO-1, the stabilization of the charged state due to screening on the metallic electrode (λ_{img}) is not directly accessible. However, we can estimate that as a stabilizing factor it will be negative in sign. In addition, the large magnitude of the localized orbital and its extended spatial distance from the electrode will lead to a rather small value. For our switching model we, therefore, approximated this contribution by an estimated value of -8meV.

Combining λ_{in} and our estimate for λ_{img} leads to a total value of 0.01eV for the reorganization energy, which was used in all our simulation runs for the switching in the **fP3** junction.

Running the algorithm

The parametrization described above was used in all switching simulations referred to in this article. In figures S41 and S42 a series of 16 independent *G-V* sweeps are shown, where in each of the 16 runs 50 subsequent sweeps were simulated. All sweeps ranged from -1V to 1V in the applied bias voltage with a sweeping rate of 10 V/s and T=298K.

Pronounced switching between the uncharged and charged state of the molecule has been found. This switching does not happen in every simulated run, but in 7 out of the 16 runs. The lifetime varies significantly between different runs, which is a consequence of the stochastic model used for the simulation. However, in general, the lifetime of the switching is remarkably high. For example, in run 2 the switching was stable for about 9 seconds. This is, however, an extreme example and on average the switching is stable for about 4-6 seconds.

For a more rigorous way of defining the mean lifetime of the charged state the actual switching reaction rate can be used. It has to be a mean lifetime rather than a well-defined value because our algorithm is stochastic in nature as is the physical process that it reproduces. The calculated reaction rate in dependence of the applied bias and the corresponding lifetime we show and discuss in the main text of this article.

Fig. S26: G curves resulting from eight independent runs of the switching algorithm. The parameters applied are: ε_{HOMO-1} =-0.40eV- E_f , Γ =3.5 10⁻⁹ eV, λ = 0.01eV, sweep rate = 10 V/s, switching range = [-1V:1V], T=298K

Fig. S27: G curves resulting from eight independent runs of the switching algorithm. The parameters applied are: ε HOMO-1=-0.40eV-Ef, Γ =3.5 10-9 eV, λ = 0.01eV, sweep rate = 10 V/s, switching range = [-1V:1V],T=298K

Figure S28. Conductance-voltage curves generated from the single level (resonant tunneling) model at T= 0 K (I-V curves were produced using the analytical formula for the current in the zero temperature limit⁵). ε_0 is the position of the single level with respect to the Fermi level. The level broadening Gamma (Γ) equals 10 meV in a) and 1 meV in b). Left and right gammas are equal.

Figure S29. Comparison between the single level model (SLM) and an experimental conductance-bias voltage sweep measurement. a) Two G-V curves generated from the SLM using $\Gamma_{l/r} = 1$ meV and $\varepsilon_0 = 0.4$ (black) and 0.05 (red). b) Experimental data reproduced from Figure 3c in the main text.

2.5 Projected density of states on the Zn atoms of P1, fP2, fP3

In order to unravel the role of Zn in the molecular bridges investigated in this study, we investigated the density of states projected onto Zn in the junction systems. The result is shown in figure S30. The Zn states are located well below and above the electrode's Fermi energy. Thus, the Zn does not directly participate in the tunnelling and charging processes of this study. Whether a change in the metal centre would provide an enhancing or diminish the junction's performance, was not a subject of this study and might inspire future investigations.

Figure S30. Projected density of states on the Zn ion in all three junctions. The experimentally investigated region ranges from -0.6 to 0.6 eV with respect to the Fermi level, which corresponds to an applied bias of 1.2V.

3. References

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