## **Supporting Information File**

# One-Way Rotation of a Chemically Anchored Single Molecule-Rotor

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1 Synthesis of 2-(2-methoxyphenyl)-1,3-dimethyl-1H-benzo[2,3-d]imidazol-3-ium iodide (o-MeO-DMBI-I)



Scheme S1: Synthesis of *o*-MeO-DMBI-I (1b).

Synthesis of 1a:



2-(2-methoxyphenyl)-1H-benz[d]imidazol

1,2-diaminobenzene (0.34 g, 3.19 mmol) was introduced to a 250 mL oven-dried flask equipped with a magnetic stirrer. Dry CH<sub>2</sub>Cl<sub>2</sub> (100 mL) and Et<sub>3</sub>N (0.6 mL, 4.3 mmol) were added, and the reaction flask cooled to 0 °C in an ice bath. Acyl chloride (0.48 mL, 3.29 mmol) was dissolved in 10 mL dry CH<sub>2</sub>Cl<sub>2</sub> and added dropwise over 30 min. Once the addition was completed, the reaction mixture was stirred for 4h at 0 °C, and then allowed to warm to rt. The volatiles were removed *in vacuo* to give a brown solid, which was then dissolved in glacial AcOH (25 mL). AcONa (0.27 g, 3.3 mmol) was added, and the mixture refluxed for 19 h before allowed to cool down to rt. Volatiles were removed *in vacuo*, the crude product partitioned between CH<sub>2</sub>Cl<sub>2</sub>/H<sub>2</sub>O and cooled in an ice bath. After the biphasic mixture was neutralized with solid K<sub>2</sub>CO<sub>3</sub>, the organic phase was separated, and the extraction was completed with additional portions of CH<sub>2</sub>Cl<sub>2</sub>. The combined organic extracts were dried with MgSO<sub>4</sub>, filtrated and concentrated *in vacuo*. The crude product was purified *via* to column chromatography on silica gel (CH<sub>2</sub>Cl<sub>2</sub>/EtOAc, 8/1), and **1a** obtained as a white solid (1.08 g, 89%). <sup>1</sup>H NMR (500 MHz, DMSO):  $\delta$  4.03 (s, 3H), 7.12 (t, 1H), 7.18 (br s, 2H), 7.25 (d, 2H), 7.46 (t, 1H), 7.62 (br s, 2H), 8.33 (d, 1H), 12.10 (br s, 1H) ppm.



2-(2-methoxyphenyl)-1,3-dimethyl-1H-benzo[2,3-d]imidazol-3-ium iodide

**1a** (0.5 g, 1.31 mmol) was added to a mixture of 10 mL 5N KOH and ethanol (3 mL). After dissolution, methyl iodide (3 ml, 82.5 mmol) was added dropwise. Then the reaction mixture was heated at 45°C overnight. A white solid precipitated, which was microfiltered using a nylon filter and washed with water. Recrystallization from ethanol gave the pure product **1b** in 53% yield. <sup>1</sup>**H NMR** (500 MHz, DMSO):  $\delta$  3.80 (s, 6H), 3.83 (s, 3H), 7.25 (t, 1H), 7.38 (d, 1H), 7.69 (m, 3H), 7.78 (t, 1H), 8.05 (dd, 2H) ppm. <sup>13</sup>C **NMR** (500 MHz, DMSO):  $\delta$  158.25, 148.82, 135.89, 132.58, 132.14,127.19, 121.80, 113.95,113.33, 109.39, 56.86, 33.18 ppm.



Figure S1. <sup>1</sup>H NMR Spectrum of 1b after recrystallization.



Figure S2. <sup>13</sup>C NMR Spectrum of 1b after recrystallization.

## 2 Methyl bond cleavage of o-MeO-DMBI-I monitored by NMR spectroscopy

The sublimation conditions used in STM experiments were simulated in lab. Compound **1b** (20 mg) was introduced to a 5 mL flask and heated to 225 C° under vacuum ( $10^{-2}$  mbar). Once the target temperature was reached, a light-yellow compound started to sublime to the top region of the glass flask. After 3min, a sample of the sublimed light-yellow compound was dissolved in DMSO and an <sup>1</sup>H NMR experiment carried out. After 60 min heating a second sample was characterized.



Figure S3. Sublimation experiment – transformation of 1b at 225 °C over time.

After heating at 225 °C for 3 min, the <sup>1</sup>H NMR spectrum in the methyl region clearly show the emergence of a new singlet (6 *H*) at  $\delta$  = 3.80 ppm next to the two characteristic signals of *o*-MeO-DMBI-I at  $\delta$  = 3.83, and  $\delta$  = 3.79 ppm (Fig. S4). This singlet can be attributed to DMBI-P. This indicates a partial thermal decomposition of the sample by cleaving Me-O bond.

Interestingly, increasing the reaction time leads to a full conversion of o-MeO-DMBI-I to *o*-MeO-MBI, a more stable form of the cleavage product (Scheme S2, Fig S5). This product was further characterized by <sup>1</sup>H (Fig. S6) and <sup>13</sup>C NMR (Fig. S7).



**Figure S4.** Methyl region of the <sup>1</sup>H NMR spectra of compound 1b before and after heating. Bottom: Pristine 1b at RT, visible are two peaks corresponding to the N-Me and O-Me functional groups (colour coded in green and blue, respectively). Top: Methyl region of the 1H NMR after subliming for 3 minutes at 225°C. Due to the elimination of CH<sub>3</sub>I, a mixture of two compounds is observed: 1b (colour coded in green and blue, respectively) and DMBI-P (colour coded in orange).



Figure S5. <sup>1</sup>H NMR spectra of the aromatic region of 1b at RT and after 3 min at 225 °C.



Scheme S2. Thermal decomposition process.



Figure S6. <sup>1</sup>H NMR Spectrum of the sample after heating for 60 min.



## 3 Thermal decomposition behaviour of o-MeO-DMBI-I

The thermal decomposition behavior of *o*-MeO-DMBI-I was studied by Headspace Gas Chromatography/Mass Spectrometry (GC/MS) and Thermogravimetric Analysis/Infrared spectrometry (TGA/IR) techniques.

## **Headspace GC-MS measurement**



Figure S8. Head Space GC isothermal chromatogram of 1b at 230°C.

*o*-MeO-DMBI-I was transferred to a sealed headspace vial and heated for 5 min at 220 °C. The mixture resulting from its thermal analyzed by GC-MS: An aliquot from the evolved vapor phase above the solid sample was transferred to the inlet of the gas chromatograph. Beside some impurities, the GC spectrum showed a peak with retention time 1.8–1.9 min. The latter was detected and identified by mass spectrometry (Fig. S9) to be methyl iodide (m/z 141.9).

The weight loss of 39% recorded at 230 °C (Fig. S10) indicates the decomposition of *o*-MeO-DMBI-I *via* the cleavage of the H<sub>3</sub>C-O bond and the formation of MeI as byproduct with DMBI-P.

The maximum decomposition temperature is 245 °C. Another decomposition peak appearing at 250 °C results from the degradation of DMBI-P. After that the rate of the weight loss quickly dropped to zero. The evolved gases collected from the degradation of *o*-MeO-DMBI-I were detected by FTIR (Fig. S11): The spectrum taken at 185 °C shows only the presence of water and CO<sub>2</sub>, while that taken at 236 °C starts revealing the presence of methyl iodide, CH<sub>3</sub>- stretch at v = 2971, 3060 cm<sup>-1</sup> and CH<sub>3</sub> deformation v = 1250, 1435 cm<sup>-1</sup>.

At temperatures above 245 °C The FTIR spectra indicates the presence of aromatic compounds  $(700 \text{ cm}^{-1})$  from the thermal decomposition of DMBI-P.



Figure S9. Mass detection of gaseous products from the thermal decomposition of 1b.



Figure S10. Weight loss of 1b by increasing the temperature.



**Figure S11.** FTIR spectrum of the gaseous products evolved from the thermal decomposition of **1b**.

## 4 Further STM images of DMBI-P on Au(111)



**Figure S12.** Overview STM image of DMBI-P on Au(111). Image dimensions:  $(60 \text{ nm})^2$ . Imaging conditions I = 49 pA, V = 480 mV.



**Figure S13.** Consecutive series of STM images showing the step by step clockwise rotation of a DMBI-P molecule. Image size  $10x10nm^2$ , image parameters I = 100 pA, V = 500 mV. Pulses -700 mV, ~-1nA



**Figure S14.** Voltage pulses applied at different molecule locations result in the same rotation. On all images on the left side (500 mV, 100 pA, (6 nm)<sup>2</sup>), voltage pulses were applied at the positions marked by the white circles. The tip was retracted to a position with a tunneling resistance >  $10^{12} \Omega$  before a pulse of -3V was applied to reduce the influence of the tip location on the rotation, resulting in < 1 pA tunneling current. For negative bias voltage, independent of the tip position on the molecule (left and right of the long molecule axis or at the "tail" end) the rotation is always clockwise, denying that the asymmetric position of the tip during a pulse is responsible for the directionality of the rotation.

#### 5 Calculations of the rotational barrier

To analyze the rotation of the DMBI-P molecule-rotor, we have used two different calculation methods, based on different approximations: the semi-empirical ASED+ and DFT. While DFT allows precisely calculating the adsorption geometry and the corresponding potential energy curve for a few rotational steps, the ASED+ calculations is able to address several complete 360° turns of the molecule on a large supporting surface.



**Figure S15.** Potential energy curve for a  $120^{\circ}$  collective rotation  $\Theta$  of the molecule on the Au(111) surface around the O-Au axle clculated by DFT. The stations observed experimentally correspond to the energy minima visible every  $60^{\circ}$  when the molecule is oriented along the <110> directions, which are not equivalent due to the molecular asymmetry. Smaller minima appear also  $30^{\circ}$  after each station, corresponding to the <112> direction. The energy barrier along this minimum energy path of the total potential energy surface is about 50 meV. However, as the difference in zero-point energy between the minimum and maximum on the T rotation direction on the potential energy surface is 39 meV, the final rotation barrier is 50 meV – 39 meV = 11 meV, in reasonable agreement with the experimental Arrhenius plot. It is important to note that due to the difficulty of this many-degrees-of-freedom calculations, we cannot expect to have but qualitative agreement between theory and experiment.



**Figure S16.** Molecular mechanics (ASED+) simulations describing the rotational mechanics around the Au-O bond (collective rotation angle  $\Theta$ ) for two complete rotations of DMBI-P. 2x6 minima, corresponding to the observed stable positions of the molecule during its rotation induced by tunneling electrons are visible. The small fluctuations in energy indicate that the DMBI-P rotor is not a rigid body and  $\Theta$  is not a native degree of freedom. Lower panel: Series of six experimental STM images of the DMBI P molecule corresponding to the six consecutive minima.

#### 6 Variation of three characteristic main degrees of freedom as a function of $\Theta$

Ground state variations along the  $\theta$  rotation path on the PES calculated using the ASED+ semiempirical approximation of the bond length d(Au-O), the dihedral angle  $\Phi$ 1 and one of the multiple secondary angle's degrees of freedom. Those curves were calculated by  $\theta$  steps of 0.1° looking for the minimum energy configuration on each step. The fluctuations along those curves are a signature that all the degrees of freedom are contributing to the collective rotation angle  $\theta$ .



**Figure S17.** Ground state ASED+ calculated variation of the bond length d(Au-O), the dihedral angle  $\Phi 1$  and one of the multiple secondary angles (the methyl angle  $\Phi 3$  indicated on the molecular structure) as a function of the collective rotation angle  $\Theta$ .

The inelastic coupling between the transferred electrons and the O-Au bond incoherently populates the  $|S1-\rangle$  (respectively  $|S0+\rangle$ ) ro-vibronic manifold. The topology of the energy surfaces is such that, upon excitation, the trajectory escapes from the O-Au local paraboloid minimum to explore other directions. One possible direction is the collective rotation of the DMBI molecule around the O-Au bond. In other words, while the Au-O bond is vibrating, it is releasing the mechanical constrains on the two main angles: rotation and dihedral. Fig. S18 demonstrates the detail molecular mechanics while rotating step by step the molecule. The collective rotational angle  $\Theta$  depends on the Au-O distance and the detail molecular conformation since  $\Theta$  is a collective angle.

## 7 Statistical analysis

We have systematically analyzed the tip height traces time variations recorded during the time interval of a voltage pulse in constant current mode. This was recorded and analyzed for over 600 observed single step rotation events. A typical height trace is shown here:



**Figure S18.** Tip height measured as a function of time during a voltage pulse V = 0.4 V at a current I = 30 pA on a DMBI-P molecule positioning the tip in the area indicated in Fig. 4b. The observed jump after about 15 sec indicates the time needed to excite an event.

A jump in the trace indicates a sudden change in the conductance at the position of the tip. The time it takes for the jump to occur is in our case nearly constant and of the order of magnitude of several seconds.

## 8 Electronic resonances of a single DMBI-P molecule

Example of a dI/dV spectrum recorded with the tip located on the DMBI-P molecule. The |S0+> and  $|S1^->$  resonances are quite broad (about 0.4 eV half-width) and are the signature of mainly the HOMO and LUMO mono-electronic component of |S0+> and  $|S1^->$ .



**Figure S19.** Experimental scanning tunneling spectroscopy dI/dV plot recorded on the center of a single DMBI-P molecule. Two resonances are clearly visible at -2.5 V and +2.7 V. Differential conductance spectra were measured using lock-in detection with a modulation frequency of 833 Hz and a modulation amplitude of 20 mV.