Controlling hydrogen transfer rate in molecules on graphene by tunable molecular orbital levels

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Tautomerisation during scanning

When a STM topography is recorded, tautomerization events can be induced due to the excitation by tunneling electrons. Consequently, depending on the scanning parameters, tautomerization events can be observed in topographical images. In Fig. S1 we show an example of such events leading to the observation of clear cuts in the image of H$_2$TPP molecules.

![Figure S1: STM topography image of H$_2$TPP on pristine graphene with setpoint parameters of -1.8 V, 100 pA.](image)

Switching events induced at positive bias voltage

We have recorded the time dependent tunneling current with the STM tip placed above the center of a pyrrole group pointing upwards (α-pyr) with a current setpoint of 100 pA before opening the feedback loop. Fig. S2 shows typical telegraph signal below and above the LUMO energy position. The fitting signal was determined by detecting all the switching events between the various current levels observed in the signal.
Figure S 2: Telegraph signal in the tunneling current recorded at 3 different positive sample bias voltages.

**Image of H$_2$TPP at positive bias**

In Fig. S3 we show a STM image of the same area as in Fig. S1 measured at positive bias. A scheme of the molecules has been added as guide to the eye. At such bias voltage, the molecules appear as four lobes close to the phenyl groups, which corresponds to what has been previously reported.$^1$

Figure S 3: STM topography image of H$_2$TPP on pristine graphene with setpoint parameters of +1.8 V, 100 pA.
Absence of spontaneous tautomerization

In order to check whether H$_2$TPP undergoes a spontaneous tautomerization process at 4.6 K on graphene we have measured an area of molecular island on pristine graphene showing the random distribution of two types of tautomers (Fig. S4a). The tip was then retracted for 15 hours and approached again toward the surface on the same area. The image just after approach is shown in Fig. S4b. As can be observed, all the molecules have kept the same configuration except two of them. It is likely that those molecules have switched under the influence of the tip when it was in proximity. In case that this was due to a spontaneous switch, it means that the yield of spontaneous switch is very negligible as compared to the induced tautomerization. Note that in Fig. S4b some molecules are clearly switching under the influence of the tip as evidenced by sharp cuts in the image of these molecules. These switching are not spontaneous but induced by the tunneling current, similarly to the events described in Fig. S1.

Figure S 4: (a) STM image of a H$_2$TPP molecular array on pristine graphene (-1.5 V, 10 pA). (b) STM image measured 15 hours later.
References