

## Electronic Supplementary Information to

# “Impact of the reaction pathway on the final product in on-surface synthesis”

*Antje Kutz,<sup>a‡</sup> Md Taibur Rahman,<sup>b‡</sup> Ville Haapasilta,<sup>c</sup> Chiara Venturini,<sup>d</sup> Ralf Bechstein,<sup>b</sup> André Gordon,<sup>d</sup> Adam S. Foster,<sup>c,e</sup> Angelika Kühnle<sup>b\*</sup>*

<sup>a</sup> Institute of Physical Chemistry, Johannes Gutenberg University Mainz, Duesbergweg 10-14,  
55099 Mainz, Germany

<sup>b</sup> Physical Chemistry I, Faculty of Chemistry, Bielefeld University, Universitätsstraße 25, 33615  
Bielefeld, Germany

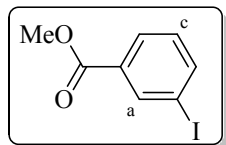
<sup>c</sup> Department of Applied Physics, Aalto University, PO Box 11100, FI-00076 Aalto, Finland

<sup>d</sup> CNRS, CEMES, Nanoscience Group, BP 94347, 29 Rue J. Marvig, 31005 Toulouse, France

<sup>e</sup> WPI Nano Life Science Institute (WPI-NanoLSI), Kanazawa University, Kakuma-machi,  
Kanazawa 920-1192, Japan

‡ These authors contributed equally to this work.

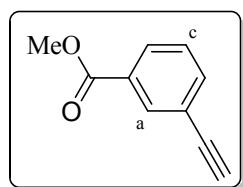
## Synthesis of methyl 3-iodobenzoate<sup>1</sup>



To a round-bottomed flask were added 3-iodobenzoic acid (2 g, 8.06 mmol), some drops of conc. H<sub>2</sub>SO<sub>4</sub> and MeOH (50 mL). The solution was heated under reflux overnight, then it was diluted with diethyl ether and washed with H<sub>2</sub>O, a saturated solution of NaHCO<sub>3</sub> and brine. The organic phase was dried over MgSO<sub>4</sub> and evaporated under vacuum. The product **7** (1.473 g) is a white solid and was obtained with a yield of 69.71 %.

<sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>): δ<sub>H</sub> 8.38 (1H, s, Ar-H<sub>a</sub>), 8.02-7.99 (1H, m, Ar-H), 7.90-7.87 (1H, m, Ar-H), 7.19 (1H, t, *J* = 7.8 Hz, Ar-H<sub>c</sub>), 3.92 (3H, s, -OCH<sub>3</sub>).

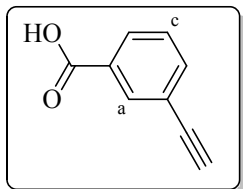
## Synthesis of methyl 3-ethynylbenzoate<sup>2-4</sup>



Methyl 3-iodobenzoate (1 g, 3.8 mmol), CuI (29 mg, 1.52\*10<sup>-1</sup> mmol), Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (53 mg, 7.55\*10<sup>-1</sup> mmol) were dissolved in degassed THF (10 mL) in a Schlenk flask. Then trimethylsilylacetylene (0.81 mL), NEt<sub>3</sub> (1.06 mL) were added and degassed again for some minutes. The solution was stirred at room temperature under argon atmosphere. After 3h (when the entire starting compound had reacted) were added TBAF in THF solution (7.65 mL) and some molecular sieves (3Å). The reaction was stirred under air atmosphere and at room temperature overnight. The mixture was then filtered on Celite, washing with Et<sub>2</sub>O. The residue was then purified by column chromatography (SiO<sub>2</sub>, EtOAc/ hex 0.5 : 9.5) to afford the product (0.392 g, 64.13 %).

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ<sub>H</sub> 8.16 (1H, s, Ar-H<sub>a</sub>), 8.03-8.00 (1H, m, Ar-H), 7.68-7.64 (1H, m, Ar-H), 7.41 (1H, t, *J* = 7.8 Hz, Ar-H<sub>c</sub>), 3.92 (3H, s, -OCH<sub>3</sub>), 3.12 (1H, s, -CH).

## Synthesis of 3-ethynylbenzoic acid<sup>5, 6, 7</sup>

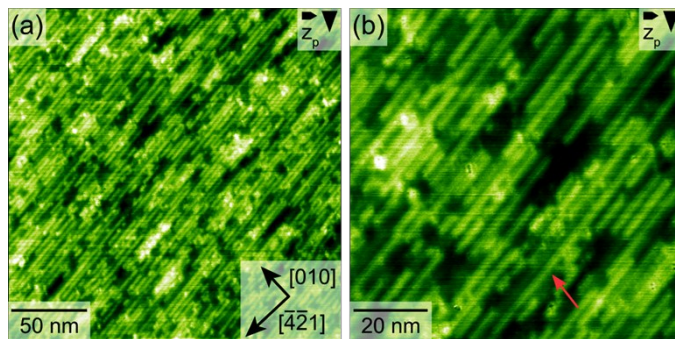


Methyl 3-ethynylbenzoate (91 mg,  $5.68 \times 10^{-1}$  mmol) was dissolved in MeOH (1.5 mL) under stirring and then a solution of LiOH (16 mg,  $6.68 \times 10^{-1}$  mmol) in H<sub>2</sub>O (1.5 mL) was added to the mixture. The reaction was stirred overnight. Then the solvent was removed *in vacuum*, then HCl 3M was added drop by drop until precipitate at pH 8; then adjusted at pH 2~3 and extracted with EtOAc. The organic phase was washed with brine and dried over an. MgSO<sub>4</sub>; removing of the solvent *in vacuum* afforded the target compound (0.045 g, 54.20 %).

<sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>)  $\delta_{\text{H}}$  8.23 (1H, s, Ar-*H<sub>a</sub>*), 8.10-8.06 (1H, m, Ar-*H*), 7.74-7.71 (1H, m, Ar-*H*), 7.46 (1H, t,  $J = 7.8$  Hz, Ar-*H<sub>c</sub>*), 3.14 (1H, s, -*CH*).

### Additional Image of Reaction Product

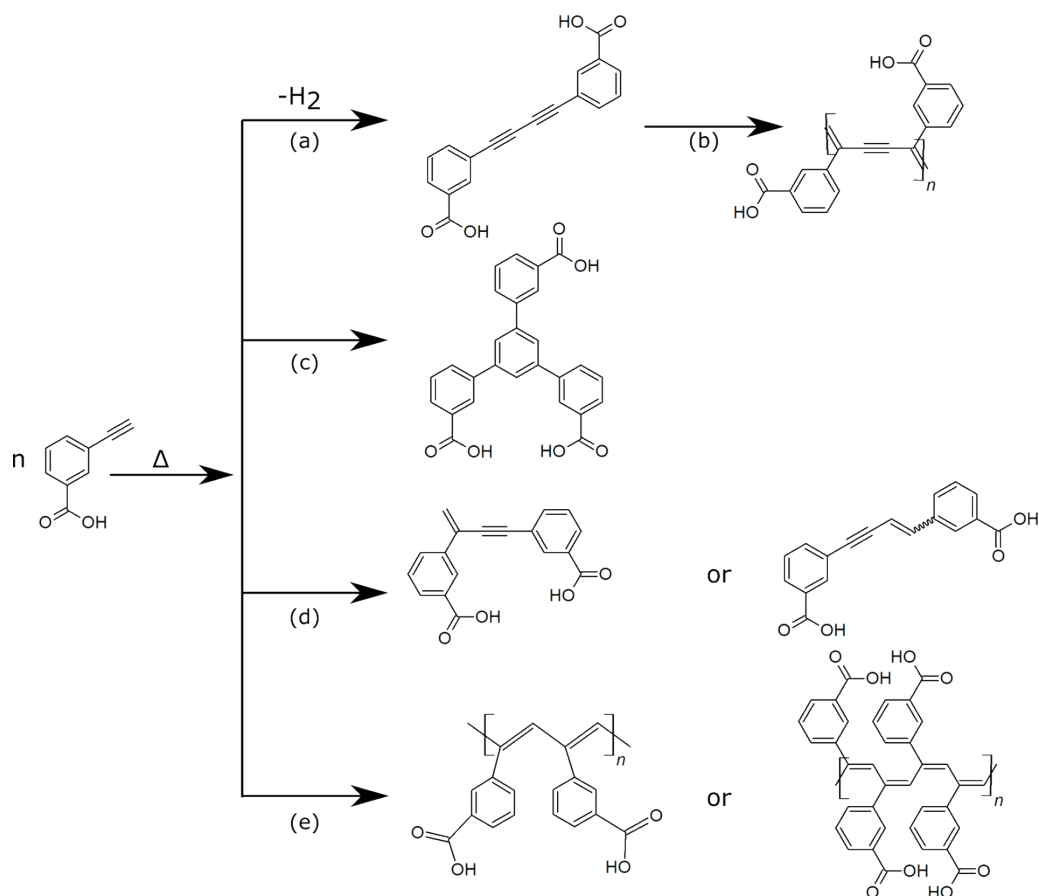
We have done the mentioned experiment more than 10 times and investigated a total area of more than 50,000 nm<sup>2</sup> on several calcite (10.4) surfaces. A further representative image is given below.



**Figure S1.** AFM images of stripe-like structures formed by 3-EBA on calcite (10.4) upon heating at 550 K for 10 hours (a). (b) Zoom into the image given in (a), the red arrow indicates a stripe, which has a length of approx. 80 nm.

## Discussion of Reasonable other Reaction Products

To elucidate the nature of the majority stripes formed after annealing, we here discuss the possible reaction pathways the precursor 3-EBA can undergo (Fig. S2).



**Figure S2.** (a) Overview of reaction pathways based on terminal alkynes, namely (a) homocoupling of terminal alkynes with possible subsequent (b) diacetylene polymerization, (c) alkyne cyclotrimerization, (d) alkyne dimerization and (e) acetylene polymerization.

Firstly, the 3-EBA monomers can form straight dimers (Fig. S2a), which are known to subsequently undergo a diacetylene polymerization reaction (Fig. S2b). Secondly, the 3-EBA monomers can undergo a cyclo-trimerization reaction (Fig. S2c) or dimerization reactions that would result in non-straight dimers (Fig. S2d). Finally, terminal alkynes are known to react *via* an

acetylene polymerization (Fig. S2e). Next, we discuss the nature of the majority stripes observed here upon annealing of 3-EBA on the basis of these reaction pathways. As detailed in the main text, the majority stripes are oriented along the  $[-4-21]$  direction and show a periodicity of 0.4 nm along this direction.

We discard option S2a, as we can directly compare with the outcome of our previous study:<sup>8</sup> Previously reported AFM images of the straight dimer molecules (3,3'-(1,3-butadiyne-1,4-diyl)bisbenzoic acid, 3-BBA) directly deposited onto calcite (10.4) revealed islands composed of rows running along the  $[010]$  direction. As our stripes are aligned perpendicular to the  $[010]$  direction, we discard this structure. However, in the previous work, we have observed that 3-BBA molecules can form a second island structure that is composed of rows oriented along the  $[-4-21]$  direction (see Fig. 5c in the main text). These rows, however, exhibit a periodicity of 0.8 nm along the row direction, which does not match the 0.4 nm periodicity found here for the stripes. From these experimental evidences, we conclude that the stripes are not composed of the straight dimers (ruling out the option shown in Fig. S2a). Moreover, we performed DFT calculations to further corroborate this experimental conclusion. To this end, we investigated whether the stripes could be formed 3-BBA molecules arranged side-by-side. Our DFT calculations revealed that it is energetically unfavorable for 3-BBA to be arranged side-by-side along the  $[-4-21]$  direction with a periodicity of 0.4 nm, giving further evidence for the conclusion that the stripes are not formed by side-by-side arranged molecular dimers.

As has been shown previously, the dimers can further react via a diacetylene polymerization (Fig. S2b).<sup>8</sup> The diacetylene polymer chain revealed a periodicity of 0.5 nm along the  $[010]$  direction on the calcite (10.4) surface. The comparison of the stripes observed here with this

diacetylene polymer chain discards the option of the type A stripes being formed from diacetylene polymers, as these two structures do not agree in orientation nor in periodicity.

Moreover, all non-straight and cyclic structures can be excluded, as the stripes observed here are linear. Thus, we additionally discard the options shown in Figs. S2c and S2d.

## References

- 1 D. A. Offermann, J. E. McKendrick, J. J. P. Sejberg, B. L. Mo, M. D. Holdom, B. A. Helm, R. J. Leatherbarrow, A. J. Beavil, B. J. Sutton and A. C. Spivey, *J. Org. Chem.*, 2012, **77**, 3197-3214.
- 2 E. Merkul, D. Urselmann and T. J. J. Müller, *Eur. J. Org. Chem.*, 2011, 238-242.
- 3 W. B. Austin, N. Bilow, W. J. Kelleghan and K. S. Y. Lau, *J. Org. Chem.*, 1981, **46**, 2280-2286.
- 4 Y. S. Feng, C. Q. Xie, W. L. Qiao and H. J. Xu, *Org. Lett.*, 2013, **15**, 936-939.
- 5 L. F. Jones, M. E. Cochrane, B. D. Koivisto, D. A. Leigh, S. P. Perlepes, W. Wernsdorfer and E. K. Brechin, *Inorg. Chim. Acta*, 2008, **361**, 3420-3426.
- 6 R. H. Pawle, V. Eastman and S. W. Thomas, *J. Mater. Chem.*, 2011, **21**, 14041-14047.
- 7 WO 2008/157844 Patent PCT/US2008/067951
- 8 A. Richter, V. Haapasilta, C. Venturini, R. Bechstein, A. Gourdon, A. S. Foster and A. Kühnle, *Phys. Chem. Chem. Phys.*, 2017, **19**, 15172-15176.