Using on-surface synthesis to combine high-spin trapezoidal molecules into covalently coupled open- and closed-shell dimers

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Constructing trapezoidal molecules via on-surface synthesis allows for the formation of high-spin molecular structures with highly-tunable properties. Since the pioneering synthesis and imaging of olympicene by Mistry et al. in 2017,[1] trapezoids have become a popular motif used in high-spin molecules and their derived structures. Non-contact atomic force microscopy (nc-AFM) is an essential tool for determining the bonding structure within such molecules, especially when they have a spectroscopic zero-bias Kondo feature that obscures it in other bond-resolving techniques. Here, we demonstrate the on-surface synthesis of a novel extended trapezoidal structure that has a high spin of S = 1 due to its carbon sublattice imbalance, as predicted by Ovchinnikov's rule and Lieb's theorem. We then use the same precursor to form various dimers on Au(111), observing different levels of magnetic exchange coupling between their unpaired electrons, showing the strong dependence of these properties on the orientation and bonding between the sub-units.

We also utilize another precursor, previously used for the formation of aza-[5]triangulene,[2] to create larger nitrogen-doped trapezoids. A common side-product of this reaction is a structure with a 5-membered ring on one edge due to the extraction of an edge carbon. We use bond-resolving techniques, along with scanning tunnelling spectroscopy and theoretical calculations, to determine the effect of doping and edge modification on the spins and general electronic properties of these molecules in comparison to their all-carbon relatives.

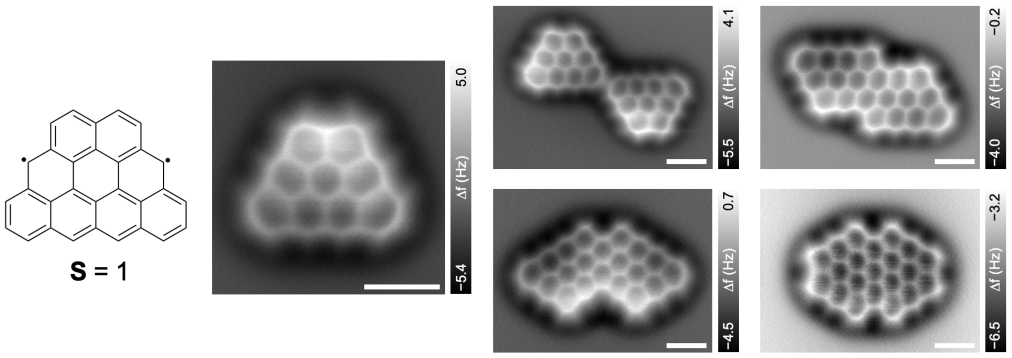

Figure 1. Chemical structure and nc-AFM image of the all-carbon trapezoid, alongside nc-AFM images of some of the dimers that are also formed when heating its precursor on Au(111). Scale bars are all 500 pm.

References

[1] A. Mistry, et al. Chem. – Eur. J. **21**, 2011-2018 (2015).

[2] J. Lawrence, et al. ACS Nano, **17**, 20237-20245 (2023).