Chalcogen bond at work on surface

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Larger molecular architectures can be formed on surfaces via a bottom-up strategy starting from smaller individual building blocks. Consequently, it is possible to finely tune the final molecular architectures' morphology and properties by *ad hoc* engineering such individual building blocks. Clearly, strong interactions are necessary for stabilizing these architectures. Among these, halogen bonding is currently the most common SIGMA-hole interaction that can be found in the literature [1]. However, very recent theoretical studies have suggested chalcogen bonding as a valuable alternative [2, 3].

Here we demonstrate on-surface synthesis of such molecular architectures via formation of chalcogen bonds. *Ad hoc* monomers have been synthesized and then sublimated in ultra-high vacuum conditions on an Au(111) substrate. These monomers diffuse on the substrate surface and form dimer structures in which the individual monomers are held together via chalcogen bonds. The polymerization reaction was studied experimentally by means of scanning tunnelling microscopy (STM), whereas density functional theory (DFT) has been used to simulate the STM images, to compute the interaction energy of two monomers and to investigate the dimer/substrate interaction. Bond-resolved STM (BRSTM) images have also been acquired that unequivocally confirm the geometrical configuration of the dimers.

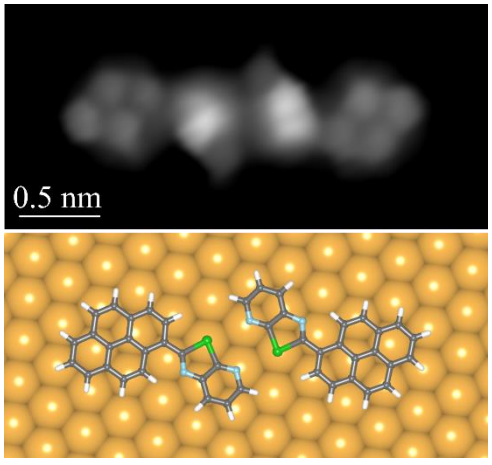

Fig. 1. BRSTM image of a dimer with double Se—N coordination (upper panel) and its geometrical model on an Au(111) substrate as optimized by DFT calculations (lower panel). Green balls represent Se atoms; cyan balls N atoms; grey and white balls C and H atoms respectively.

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[2] B. Ren *et al.*, Chemical Physics, **565**, 111763 (2023)
[3] S. Scheiner *et al.* J. Phys. Chem. A, **126**, 4025 (2022)