

On-surface molecular recognition driven by chalcogen bonding

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The manipulation of organic architectures on surfaces through supramolecular interactions has recently gained remarkable attention.¹⁻⁵ Among them, secondary bonding interactions (SBIs) such as H-bonding and halogen bonding have been used with notable success.⁶⁻⁹ Chalcogen bonding interactions (ChBIs) belong to the same category of SBIs, yet they have only been employed in crystal engineering,¹⁰ while their ability to govern self-assembly on surfaces is yet to be demonstrated. The interest towards ChBIs relies on its orbital mixing nature¹¹ that provides semiconducting properties to the supramolecular assemblies.¹²

Two very recent studies have theoretically explored the use of intermolecular Ch \cdots N ChBI as a driving force for self-assembling chalcogenazole derivatives on surfaces, but experimental evidence is still absent.^{13, 14}

Here, we combine scanning tunnelling microscopy (STM) measurements and quantum chemistry calculations to present the first example of ChBI-driven molecular self-assembly on metal surfaces. Notably, we show that pyrene-based modules bearing chalcogenazole pyridine moieties (where Ch is either Se or Te) undergo self-assembly into dimers through double Ch \cdots N interactions on Au(111) and Ag(110). Furthermore, we confirm that reference benzochalcogenazole congeners, in which the N-pyridyl atom has been substituted by a C-H moiety, do not establish any ChBIs and instead assemble into irregularly shaped kinetic aggregates.

This study sheds light on a promising avenue for future research in the bottom-up engineering of two-dimensional monolayered supramolecular chalcogenide-type materials, as we delve into the novel role of ChBIs in surface-based molecular recognition.

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