

## Substituent Controlled Orientational Order in Van-der-Waals Self-assembled Molecular Networks

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The self-assembly of molecules with functional groups is of fundamental interest for many fields like, for example, molecular electronics. In particular, for molecules lacking rotational symmetry, which can be exploited in rectifying electronical or optically active devices, it is important to assemble monolayers with high orientational direction. In most of the STM studies on self-assembled monolayers reported so far, the molecular self-assembly is driven by hydrogen-bonding mediated interactions [1, 2]. Within those networks the molecules have little or no rotational freedom due to the directionality of the hydrogen bonds [3]: the orientational and spatial ordering are, thus, strongly coupled. In contrast, molecular self-assemblies driven by van-der-Waals interactions are good candidates for independent control of spatial and orientational order. The non-directional van-der-Waals interactions ensure a close-packed geometry of the assembled monolayer, while allowing a certain degree of orientational freedom.

The scanning tunneling microscopy studies presented in this study focus on the orientational order of the assemblies of three related molecules on Cu(110). The three investigated molecules (HBHBC, PBPHBC, and PBHBC), which are based on the *peri*-hexabenzene-coronene molecule (HBC) [4], possess no polar groups and therefore do not form hydrogen bonds. Thus, the self-assembly mechanism is expected to be mainly driven by van-der-Waals interactions. The HBHBC molecule, which has rotational symmetry, is used as reference, whereas the PBHBC and PBPHBC molecules have a broken rotational symmetry due to different peripheral substituents [5] (see Figure 1).

As displayed in Figure 2, the spatial order within the networks is equivalent for all three molecules, which is in good agreement with van-der-Waals interaction driven networks. However, the PBHBC and PBPHBC molecules, which do not possess a rotational symmetry, show a rotational order which depends on the functional group. For the PBPHBC network the phenyl groups are all aligned in the same overall direction, whereas the direction of the functional group within the PBHBC network alternates.

The orientational order in the networks indicates a distinct long range order for molecules without rotational symmetry, which is not yet understood. Even though the nature of the self-assembly for these three molecules is not well understood, the assembly of molecules without polar groups and rotational symmetry into networks which clearly show a long range order might be relevant for molecular films with rectifying electronical or optically active properties which can be used in molecular electronics such as circuits with directional functions like e.g. diodes.

