

Physisorption of Three Amine Terminated Molecules (TMBDA, BDA, TFBDA) on the Au(111) Surface: The Role of van der Waals Interactions

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Recently, the electronic properties and alignment of tetramethyl-1,4-benzenediamine (TMBDA), 1,4-benzenediamine (BDA) and tetrafluoro-1,4-benzenediamine (TFBDA), molecules were studied experimentally. Discrepancies were found for both the binding energy and the molecule tilt angle with respect to the surface, when results were compared with density functional theory calculations [1]. We have included the effect of vdW interactions both between the molecules and the Au(111) surface and find binding energies which are in very good agreement with experiments. We also find that at low coverages each of these molecules would adsorb almost parallel to the surface. N-Au bond lengths and charge redistribution on adsorption of the molecules are also analyzed. Our calculations are based on DFT using vdW-DF exchange correlation functionals. For BDA (since we are aware of experimental data), we show that for higher coverage, inclusion of intermolecular van der Waals interaction leads to tilting of the molecules with respect to the surface and formation of line structures. Our results demonstrate the central role played by intermolecular interaction in pattern formation on this surface.

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[1] M. Dell'Angela *et al.*, Nano Lett. **10**, 2470 (2010).

[2] M. Kamenetska *et al.*, J. Phys. Chem. C **115**, 12625 (2011).