## Contents

1 Introduction .................................................. 1
  1.1 The Experimental Observations of 2D Supramolecular
      Monolayers ........................................... 3
    1.1.1 Melamine ......................................... 4
    1.1.2 PTCDA ........................................... 6
    1.1.3 PTCDI ........................................... 9
    1.1.4 NTCDA and NTCDI ................................. 9
    1.1.5 Mixed Phases PTCDA/PTCDI-Melamine ........... 11
  1.2 Theoretical Issues Related to 2D Supramolecular
      Monolayers ........................................... 12
  1.3 Experimental Techniques STM and AFM .................. 13
    1.3.1 STM ........................................... 14
    1.3.2 AFM Technique .................................. 17
  References .................................................. 18

2 Theoretical Methods ........................................... 23
  2.1 Solving the Schrödinger Equation ....................... 23
  2.2 The Hartree-Fock Method ................................ 25
  2.3 Density Functional Theory ................................ 27
  2.4 Technical Details of DFT Calculations .................. 28
    2.4.1 Choice of the Basis Set ......................... 29
    2.4.2 Pseudopotential Method .......................... 30
    2.4.3 Periodic Boundary Conditions and k-Point Sampling... 31
  2.5 Siesta Method .......................................... 31
    2.5.1 Definition of Useful Energies to Analyse
          Systems Stability .................................. 32
    2.5.2 Characterisation of the Hydrogen Bonds:
          “Kebab” Structures .................................. 33
  2.6 Diffusion Calculations .................................. 33
  2.7 Van der Waals Implementation in DFT Method .......... 33
3 Hydrogen-Bonding Templates in the Gas Phase .......................... 41
  3.1 Melamine ................................................. 41
     3.1.1 Dimer ........................................... 41
     3.1.2 Trimers ....................................... 48
     3.1.3 Tetramers ..................................... 50
     3.1.4 Comparison with Experimental Data .................. 53
  3.2 PTCDA .................................................. 55
     3.2.1 PTCDA Dimers .................................. 55
     3.2.2 One-Dimensional Chains Based on the PTCDA Pairs .... 57
     3.2.3 Two-Dimensional Structures Based on the PTCDA Pairs .. 59
     3.2.4 Going Beyond Two Molecules Per Cell ............. 63
  3.3 PTCDI .................................................. 66
     3.3.1 PTCDI Dimers .................................. 66
     3.3.2 One-Dimensional Chains Based on the PTCDI Pairs .... 68
     3.3.3 Monolayers Based on the PTCDI Dimers ............. 68
  3.4 NTCDA .................................................. 74
     3.4.1 NTCDA Dimers .................................. 74
     3.4.2 One-Dimensional Chain Based on the NTCDA Dimers .... 76
     3.4.3 Monolayers Based on NTCDA Dimers ................ 77
  3.5 NTCDI .................................................. 78
     3.5.1 NTCDI Dimers .................................. 78
  3.6 Mixed PTCDA-Melamine and PTCDI-Melamine .................. 79
     3.6.1 Melamine PTCDA/PTCDI Dimers ....................... 79
     3.6.2 One-Dimensional Chains and Two-Dimensional Monolayers Based on Melamine-PTCDA and Melamine PTCDI Dimers .... 81
     3.6.3 Going Beyond Two Molecules Per Unit Cell .......... 83
  3.7 Importance of vdW Interaction for Hydrogen Bonding Systems .... 86
  3.8 Conclusions .............................................. 88
References ..................................................... 88
4 Molecules on the Au(111) Surface

4.1 Melamine on the Au(111) Surface

4.1.1 Adsorption of Melamine on the Au(111) Surface

4.1.2 Commensurability of the Melamine Network and the Au(111) Surface

4.1.3 Corrugation of the Surface Potential

4.2 PTCDA/PTCDI and NTCDA/NTCDI on the Au(111) Surface

4.2.1 Adsorption of PTCDA, PTCDI, NTCDA and NTCDA on the Au(111) Surface

4.2.2 Corrugation of the Surface Potential

4.3 Importance of vdW Interaction for Stabilisation of the Molecules on the Gold Surface

4.3.1 Approximate Method with Sci-Fi: Analysis of Adsorption Energy and Corrugation Potential

4.3.2 vdW-DF Method (Quantum Espresso and Siesta) Applied to Molecules on the Au(111) Surface

4.3.3 Effect of vdW-DF Functional in the Electronic Charge Density Difference: PTCDA Case

4.4 Conclusions

References

5 Influence of Dynamics of Melamine with Au ad-Atom on the Au(111) Surface on Self Assembled Structures: Bright Spots

5.1 Diffusion of Au Atoms on the Au(111) Surface and Detachment from a Step Edge

5.2 Gas Phase Calculations: First Attempts

5.3 Interaction of a Melamine with an Au ad-Atom on the Au(111) Surface

5.4 Diffusion Calculations of Melamine and “Melamine + Au ad-Atom” Block

5.5 Melamine Clusters and a Au ad-Atom

5.6 The Final Stage of Formation of a Melamine Hexagon with a Au ad-Atom

5.7 Modelling the STM Images of the Hexagonal Cluster on the Au(111) Surface

5.8 Conclusion

References

6 Modelling of DNA Derivatives and Comparison with Experimental Results

6.1 Pairs Based on the DNA Derivatives in the Gas Phase

6.2 Pairs Based on the Guanine and Cytosine DNA Derivative Molecules in the Gas Phase
6.3 One-Dimensional Structures Based on the DNA Homo-Pairs in the Gas Phase ........................................ 143
6.4 Gas-Phase Two-Dimensional Structures Based on the DNA Pairs .................................................. 147
6.5 Interaction with the Au(111) Surface and STM Modelling .................................................. 151
   6.5.1 Single DNA Bases on the Au(111) Surface ......................... 151
   6.5.2 DNA Base Pairs on the Au(111) Surface ......................... 154
6.6 Comparison with Experimental Data .............................. 155
6.7 Conclusion ................................................... 160
References ..................................................... 160

7 Conclusions ................................................... 161
References ..................................................... 165

Index .......................................................... 167
Self-Assembly of Flat Organic Molecules on Metal Surfaces
A Theoretical Characterisation
Mura, M.
2012, XVI, 169 p., Hardcover
ISBN: 978-3-642-30324-1