

Contents

1	Introduction	1
1.1	The miniaturization of electronic devices	1
1.2	Molecular scale electronics	2
1.2.1	Concepts and prospects	2
1.2.2	Contacting single molecules and molecular assemblies	3
1.3	Semiconducting organic materials	5
1.4	Outline of the thesis	6
2	Theoretical fundamentals of molecular devices	9
2.1	The single molecule junction	9
2.1.1	A qualitative picture	9
2.1.2	Organic molecules and molecular orbitals	11
2.1.3	Non-resonant transport	11
2.1.4	Resonant transport	13
2.2	Semiconductivity in organic solids and thin films	17
2.3	Self-assembly of molecules on solid surfaces	19
3	Scanning tunneling microscopy and spectroscopy	23
3.1	The working principle	23
3.2	Theoretical description	24
3.3	Model calculations of tunneling spectra	28
3.4	Experimental details	30
4	Investigated organic compounds	33
4.1	Arylthio-substituted coronenes	33
4.2	Deposition of molecules	34
5	Substrates	37

5.1	Gold thin film substrates	37
5.2	Graphite	40
5.2.1	Basic properties	40
5.2.2	Superlattice phenomena	43
6	Self-assembly of Cor-H	49
6.1	Adsorption of Cor-H on graphite	49
6.2	Supramolecular self-assembly on Au(111)	50
6.3	Structural properties and aggregation behaviour in solution	53
7	Impact of molecular order on charge transport characteristics	57
7.1	Tunneling through undisturbed molecular states	57
7.1.1	Tunneling spectroscopy measurements	57
7.1.2	Empirical simulations of tunneling spectra	60
7.2	Formation of band-like electronic states	64
8	Analysis of structural and electronic properties based on DFT simulations	69
8.1	The geometrical structure of single Cor-H molecules	69
8.2	Energetics of adsorption on graphite	71
8.3	Electronic structure calculations	73
8.4	Analysis of the adsorbate structure on Au(111)	74
8.5	Summary	79
9	Substituent effects on structure formation and charge transport	81
9.1	Cor-OMe on Au(111)	82
9.1.1	Structural observations	82
9.1.2	Analysis of molecular conformations	84
9.1.3	Tunneling spectroscopy measurements	87
9.2	Cor-CF ₃ on Au(111)	92
9.2.1	Structural observations	92
9.2.2	Tunneling spectroscopy measurements	94
9.2.3	DFT calculations and discussion	96
9.3	Summary	100
10	Nanoscale structures for single molecule electronics	103

10.1 Fabrication of nanometer-spaced metal electrodes	103
10.1.1 Direct fabrication by electron-beam lithography	103
10.1.2 Suspended nanogap electrodes with self-aligned gate	107
10.1.3 Electromigration of metallic nanowires	110
10.2 Electrical transport through Cor-OMe between nanogap electrodes	117
10.3 Summary	120
11 Conclusion	123
11.1 Summary	123
11.2 Possible future directions	128
Bibliography	131