

James M. Tour

MOLECULAR ELECTRONICS

Commercial Insights, Chemistry, Devices,
Architecture and Programming

ISBN 978-981-4327-08-0

World Scientific

Contents

Preface	vii
Chapter 1. Commercialization of Molecular Electronics	1
1.1. Introduction	1
1.2. Commercial Challenges of Molecular Electronics	2
1.2.1. Investments in Molecular Electronics	3
1.2.2. Molecular Electronics Market Insertion Strategy	8
1.3. Molecular Electronics-Focused Companies	11
1.4. Advice from the Trenches for the Wannabe Corporate Founder	16
1.5. From a Front Row Observer to the Aspiring CEO of an Academically Founded Startup	22
Chapter 2. Molecular Electronics	25
2.1. Introduction	25
2.2. The DNA and Quantum Computing Distinctions	29
2.3. Present Microelectronics Technology	29
2.4. Monetary and Fundamental Physical Limitations of Present Technology	30
Chapter 3. Chemical Synthesis	33
3.1. Iterative Approaches to oligo(2,5-thiophene ethynylene)s Molecular Wires, Properties and Experimental Details	33
3.1.1. Introduction	33
3.1.2. Results and Discussion	34
3.1.2.1. Monomer Syntheses	34
3.1.2.2. Controlled Oligomer Syntheses	35
3.1.2.3. Oligomer Characterization	37
3.1.2.4. Attachment of Thiol End Groups	38
3.1.3. Summary	42
3.1.4. Experimental Procedures	42

3.2.	Iterative Approaches to oligo(1,4-phenylene ethynylene) Molecular Wires, Properties and Experimental Details	56
3.2.1.	Introduction	56
3.2.2.	Results and Discussion	56
3.2.2.1.	Monomer Syntheses for Solution-Based Oligomerizations	56
3.2.2.2.	Oligomer Syntheses in Solution	59
3.2.2.3.	Monomer Syntheses for the Polymer Supported Approach	60
3.2.2.4.	Oligomer Syntheses on the Polymer Support	60
3.2.2.5.	Spectroscopic Reaction Monitoring Techniques on the Resin	62
3.2.2.6.	Assessing Solid Phase Reaction Yields	62
3.2.2.7.	Characterization of the Oligomers	68
3.2.2.8.	Attachment of Thiol End Groups	71
3.2.3.	Summary	73
3.2.4.	Experimental Procedures	74
3.3.	Shorter Phenylene-Based Molecular Wires and Devices and Experimental Details	110
3.3.1.	Synthesis of Molecular Scale Wires	110
3.3.1.1.	Synthesis of One-Terminal Oligo(phenylene ethynylene) Molecular Wires	110
3.3.1.2.	Synthesis of Two-Terminal Oligo(phenylene ethynylene) Molecular Wires	112
3.3.1.3.	Syntheses of Three-Terminal Molecular Scale Wires	113
3.3.1.4.	Molecular Wires with Internal Methylenes and Ethylene Transport Barriers	114
3.3.2.	Synthesis of Molecular Scale Devices with Heteroatomic Functionalities	119
3.3.3.	Porphyrin Containing Molecular Scale Wires	126
3.3.4.	Synthesis of Dipole-Possessing Molecular Wire SAMs to Control Schottky Barriers in Organic Electronic Devices	128
3.3.5.	Experimental	130
3.4.	Highly Functional Molecular Wires and Devices with Diverse Alligator Clips and Experimental Details	176
3.4.1.	Introduction	176
3.4.2.	Switches and Memory Components	177
3.4.3.	Alligator Clips	180

3.4.4. Conclusions	184
3.4.5. Experimental	184
3.5. Combinatorial Routes to Molecular Wires and Devices and Experimental Details	198
3.5.1. Introduction	198
3.5.2. Results and Discussion	198
3.5.2.1. Monomer Synthesis for the Combinatorial Approach	198
3.5.2.2. Oligomer Syntheses in Solution	199
3.5.2.3. Oligomer Syntheses on a Solid Support	200
3.5.3. Summary	205
3.5.4. Experimental Section	206
Chapter 4. Molecular Self-Assembly, Device Construction, and Testing	229
4.1. Self-Assembly and Molecular Ordering	229
4.2. Probe Addressing of Molecules	232
4.3. Switching and Memory in Molecular Bundles	238
4.4. Large Area Molecular Electronic Devices: The Large Area Contact Problem	249
4.5. Summary	250
Chapter 5. Architectures in Molecular Electronics	251
5.1. Introduction	251
5.1.1. Quantum Cellular Automata (QCA) and Electrostatics Architectures	252
5.1.2. Cross-Bar Arrays	256
5.1.3. The NanoCell Architecture	261
5.2. Summary	265
Chapter 6. Programming the Nanocell	266
6.1. NanoCell	266
6.1.1. Nanocell Design	267
6.1.2. Molecular Switches	268
6.1.3. Simulated Nanocell	272
6.1.4. The Nanocell as a Logic Gate	274
6.2. Training a NanoCell	279
6.2.1. NanoCell as an Optimization Problem	279

6.2.1.1. Nanocell Training	280
6.2.1.2. Omnipotent Training	281
6.2.2. Genetic Algorithms	282
6.2.3. Training Process	283
6.2.3.1. Testing the Molecule	284
6.2.3.2. Genetic Algorithm Used in Training Nanocells	295
6.2.4. Fitness Function	296
6.3. Trained Nanocells	298
6.3.1. Voltage In – Current Out	298
6.3.1.1. Trained Logic Gates	299
6.3.1.2. Observations	302
6.3.2. Voltage In – Voltage Out	304
6.3.2.1. Trained Logic Gates	306
6.3.2.2. Observations	312
6.3.3. Hooking NanoCells Together	313
6.4. NanoCell Proofs	317
6.4.1. Biconnected Components in a NanoCell	317
6.4.2. Observing Sufficient Conditions	320
6.4.3. Isolated Nanoparticles	320
6.4.4. Necessary and Sufficient Conditions for Inverters and NANDs	324
6.4.4.1. Inverters	324
6.4.4.2. NANDs	335
6.4.5. Defect- and Fault-Tolerance	337
6.4.6. Training More Robust Nanocells	339
6.5. Future Work	346
6.6. Conclusions	351
Bibliography	353
Index	365