Field-effect transistors are the basic building block for solid state electronics. Currently silicon is and will remain the dominant technology in the foreseeable future. On the other hand, ‘plastic transistors’, i.e. transistors in which an organic material is used as the active semiconductor, may form the basis for new low-cost microelectronic technology on flexible substrates. The low process temperature and mechanical properties of organic semiconductors allow for innovative products such as fully printed contactless radio frequency identification (RFID) tags and flexible displays. Research in the field of organic electronics has been mainly focused on the development of new $p$-type semiconductors to improve environmental stability and charge carrier mobility. However to improve organic circuitry complementary logic is required for which $n$-type semiconductors are required. For the same reason there is a growing interest in ambipolar transistors. Ambipolar semiconductors support both hole and electron accumulation. The transistors can operate in either $p$-type or $n$-type mode or in a mode where both hole and electron accumulation coexist. The dual nature of ambipolar transistors have allowed integration into CMOS-like logic gates and integrated circuits without any increase in fabrication complexity.

In chapter two of this thesis, a model is developed to describe charge transport in disordered ambipolar organic field-effect transistors. It is shown that the model can be used to calculate all biasing regimes in unipolar as well as ambipolar organic transistors. By applying it to experimental data obtained from ambipolar organic transistors based on a small bandgap organic molecule excel-
lent fits were obtained. An excellent agreement between theory and experiment is observed over a wide range of biasing regimes and temperatures.

In the following step, the charge transport model is extended to describe the current voltage and the potential profiles. The potential profiles are given for unipolar as well as ambipolar field-effect transistors. By performing scanning Kelvin probe measurements on organic field-effect transistors the validity of this and other charge transport models is benchmarked. The potential profiles are predicted from the parameters obtained from the current-voltage characteristics. Finally the measured and calculated potential profile of ambipolar field-effect transistors show that the position of the recombination zone for various biasing can be accurately predicted.

Having electrically measured and analytically predicted the recombination behaviour of ambipolar field-effect transistors in the previous chapters, radiative recombination was investigated in ambipolar near-infrared light-emitting field-effect transistors. By employing an emissive small bandgap semiconductor (squarylium dye), the emission as a function of bias was investigated. Using the model previously developed, the emission behaviour could be accurately described. A tentative approximation of the width of the recombination zone is given.

An analytical model for the recombination profile in ambipolar organic field-effect transistors is presented in chapter 5. Results from the model are supported by both numerical calculations and measured surface potential profiles of an actual ambipolar device. The width determined from the model is found to be in the order of a few hundred nanometers, comparable to the values found for ambipolar near-infrared light-emitting transistors.

Last of all, real CMOS-like logic is demonstrated by combining ambipolar field-effect transistors into logic gates. By fabricating thin film transistors with an air-stable small bandgap semiconductor (nickel dithiolene) on PEN foil, flexible CMOS-like ring oscillators were obtained. The ring oscillators were shown to function properly at kilohertz frequencies in air and light over an extended period of time.

The second part of the thesis focuses on self-assembly and self-organization of molecular electronics. Two device geometries were investigated. First a two
terminal devices were studied in the form of molecular diodes. Secondly three
terminal devices were fabricated in the form of self-assembled monolayer field-
effect transistors.

Molecular diodes is one of the holy grails of molecular electronics. The ulti-
mate target of molecular electronics is to combine discrete junctions with func-
tional molecules into integrated circuits. The formation should be autonomous,
ence by self-assembly. Charge transport perpendicular through self-assembled
monolayers (SAM) has been investigated. The main issue was reliability and
yield. Electric shorts are formed upon vapor deposition of the top electrode.
Short-circuit formation in discrete junctions can be prevented by applying a
conducting polymer as barrier layer between the SAM and top electrode. We
demonstrate a technology to fabricate and integrate molecular junctions on 150-
mm wafers. On a single wafer over 20 000 molecular junctions are fabricated
simultaneously. Integration is presented in strings where up to 200 junctions are
connected in series with a yield of unity. The statistical analysis on these molec-
ular junctions, for which the processing parameters were varied and the influence
on the junction resistance was measured, allows for the tentative interpretation
that the electrical transport through these monolayer junctions is factorized.

In chapter 8, integrated circuits using a bottom-up approach involving self-
assembling molecules is demonstrated. The basic building block for such inte-
grated circuit is the self-assembled-monolayer field-effect transistor (SAMFET),
where the semiconductor is a monolayer spontaneously formed on the gate di-
electric. In the SAMFETs fabricated so far, current modulation has only been
observed in submicrometer channels, the lack of efficient charge transport in
longer channels being due to defects and the limited intermolecular $\pi - \pi$ cou-
pling between the molecules in the self-assembled monolayers. Low field-effect
carrier mobility, low yield and poor reproducibility have prohibited the realiza-
tion of bottom-up integrated circuits. We demonstrate SAMFETs with long-
range intermolecular $\pi - \pi$ coupling in the monolayer. We achieve dense packing
by using liquid-crystalline molecules consisting of a $\pi$-conjugated mesogenic core
separated by a long aliphatic chain from a monofunctionalized anchor group.
The resulting SAMFETs exhibit a bulk-like carrier mobility, large current mod-
ulation and high reproducibility. As a first step towards functional circuits, we
combine the SAMFETs into logic gates as inverters; the small parameter spread then allows us to combine the inverters into ring oscillators. We demonstrate complex logic functionality by constructing a 15-bit code generator in which hundreds of SAMFETs are addressed simultaneously.