● *Chapter 1*

Introduction

Although electroluminesence from organic materials[1] has been known for a long time, research on light emitting diodes based upon conjugated polymers, with quantum efficiencies attractive for consideration in real devices, is quite new[2] and currently growing into a topic commanding the attention of a wide variety of scientists and engineers, in both industry and academia, the world over[3]. A great deal of the physics, and especially the chemistry, which governs the behavior of polymer-LEDs, occurs at the polymer surface, or the near surface region. The details are greatly determined by the metalic contact. Information obtained from detailed studies of the chemical and electronic structure of conjugated polymer surfaces and interfaces with metals, is becoming a basic ingredient in understanding device behaviour and optimizing device performance.

In this book, we attempt to bring together in one place the results of a relatively large number of basic studies of conjugated polymer surfaces, as well as the 'early stages of metal–polymer interface formation', in an attempt to produce a simple and coherent picture of some of the unique features of these surfaces and interfaces; features which are important in understanding and controling the performance of polymer-based LEDs. Instead of presenting a series of detailed chronological accounts of individual studies, we have tried to take a more global approach, at least in part, where the nature of the

information allows, in order to make the book more comprehensible to readers from a range of different backgrounds. This 'compendium' is intended to be multi-level in content; different parts and chapters being of use to readers of different backgrounds and/or interests, as outlined below.

1.1   Background: towards molecular (based) electronics

Organic materials comprise most of the chemically identifiable materials on the earth. Despite this fact, *in*organic materials have occupied the traditional role as electronic materials in the modern information technology revolution. As the density of electronic components continues to increase, the characteristic size of the individual electronic elements (e.g., transistors) are rapidly approaching the molecular scale, ~ 10 Å. It is expected, however, that bulk-effect solid state physics devices will 'mature' at dimensions on the order of 400 atoms (i.e., around 50 to 60 nm)[4], at which point quantum-physics devices and molecular-based elements will come into play. Either individual organic molecules or molecular aggregates become attractive candidates for active elements; at first certainly in specialized electronic applications, later as major components. With only a few exceptions, molecular materials are organic, that is, based upon carbon.

Molecular electronics on a true molecular size scale is a technology with a future somewhere well into the next century[5]. On the other hand, on a larger size scale, bulk molecular materials, in thin-film form, have been in use for many years. As one example, organic photo-receptors have been at the heart of the photocopying industry for almost two decades[6]. More recent developments involve conjugated polymers[7], which have been the subjects of intense study, since, in 1977, Heeger, MacDiarmid, Shirakawa and co-workers were able to dope polyacetylene to a high electrical conductivity[8] of almost 10^{+3} S/cm. Although conjugated polymers attracted much initial interest based upon their electrical properties in the doped, electrically conducting state, new developments in device applications are based upon these polymers in the pristine, semiconducting state. Conjugated-polymer-based transistors, and especially conjugated-polymer-based light emitting diodes, or LEDs, developed at the University of

Cambridge, UK, are presently the focus of study in a large number of research laboratories, and topics of development in ever-growing numbers of both small and large industrial laboratories, world wide[9].

1.2   Surfaces and interfaces

It is perhaps trivial and obvious to state that communication with a material occurs through the surface, and that communication involving physical contact occurs through a physical interface. It also is clear that addressing the properties of a material involves understanding the nature of surfaces and interfaces of that material. Although the science of inorganic surfaces and interfaces is highly developed[10], the surface science of organic materials, and in particular polymeric materials, is less well developed[11]. Even then, most work reported to date involves the surfaces and interfaces on non-conjugated polymers. The early work was pioneered by Clark[12], while more recently the science is represented by the work of Pireaux and co-workers[13]. Some examples of applications have been documented[14] in the series of books edited by Mittal. The surface and interface science of conjugated polymers, although sparsely studied, is highly relevant to the present and rapidly developing areas of molecular electronics and molecular-based electronics[3].

1.3   Approach

This book represents an attempt to illustrate the state-of-the-art of the basic physics and materials science of conjugated polymers and their interfaces, as related more-or-less to a specific application, present polymer-based LEDs, as of the time of writing (March 1995). It is intended to illustrate the basic fundamental physical (and the specifically associated chemical) principles that apply to these materials, which in many instances are different than those encountered in their inorganic counterparts. The references provided are not exhaustive, but rather are representative of the state-of-the-art; as such, they should be sufficient to enable the interested reader to delve deeper into the area. Although by doing so some duplication occurs, references are grouped at the end of each chapter for

convenience. As history has shown in other areas of physics and chemistry, it may be that some presently 'known' properties might actually depend (at least to some extent) upon the experimental measurement used to study the property, or even the theoretical model used in the interpretation of measurement data. Therefore, the goals here are to point out specific issues and specific properties of polymer surfaces and interfaces, which may be relevant in the context of the emerging area of polymer-based electronics, in general, and polymer-based light emitting diodes in particular; and, in the process, discuss both the theoretical and experimental methods mostly commonly used in studies of these properties[15]. Generally, but especially in the introductory and background material, the discussions are made as short, concise and to-the-point as possible, pointing out the features relevant to the specific topics at hand.

Although it is not intended to provide here a detailed description of polymer-based LED devices, some background material is included, both as motivation as well as to set the context for, and develop the terminology for, the discussions of the surface and interface issues. Such an approach should enable a scientist entering this field to become familiar enough with the most applicable theoretical and experimental methods employed, so that he/she should be able to read and understand the basic scientific papers, and to understand the issues which are particularly relevant to addressing the underlying science and development of polymer-based light emitting diodes. The level of discussion is aimed at the intermediate graduate student level, which also should be sufficient for the established, but non-expert, scientist, new to the area of polymer surfaces and interfaces.

1.4   Structure and organization

In addition to the present *Introduction* chapter, the contents are organized and presented in chapters, and subdivided in such a way that, to the extent reasonably possible, each chapter comprises a free-standing unit, which may be read (by readers of appropriate backgrounds) as independent units, if or when necessary.

- *Theory and experimental methods*. Since the combined experimental–
  theoretical approach is stressed, both the underlying theoretical
  and experimental aspects receive considerable attention in chapters
  2 and 3. Computational methods are presented in order to
  introduce the nomenclature, discuss the input into the models,
  and the other approximations used. Thereafter, a brief survey of
  possible surface science experimental techniques is provided,
  with a critical view towards the application of these techniques to
  studies of conjugated polymer surfaces and interfaces. Next, some
  of the relevant details of the most common, and singly most useful,
  measurement employed in the studies of polymer surfaces and
  interfaces, photoelectron spectroscopy, are pointed out, to provide
  the reader with a familiarity of certain concepts used in data
  interpretation in the *Examples* chapter (chapter 7). Finally, the use
  of the output of the computational modelling in interpreting
  experimental electronic and chemical structural data, the combined
  experimental–theoretical approach, is illustrated.
- *Materials*. A detailed discussion of the chemical and electronic
  structure of conjugated molecules and polymers is unnecessary,
  since several recent and comprehensive reviews are available[16–18].
  A few of the aspects essential for the chapters which follow, however,
  are presented in chapter 4. First, a description of the concept of
  molecular and certain polymeric solids, in contrast to conventional
  three-dimensional covalently bonded semiconductors and insulators,
  is provided. This is in effect necessary in order to bring the language
  of physics and chemistry together. Thereafter, a brief description
  of the basic physical properties of π-conjugated polymers is included
  to set the context for discussions of the elementary optical excitations,
  and the nature of the charge bearing species in these systems.
  Then, the basic electronic structure of one-dimensional (linear)
  conjugated polymers is outlined in terms of the electronic band
  structure[19]. The use of model molecular solid (thin film) systems
  for conjugated polymer systems is described, but only to the extent
  necessary for some of the examples. Finally, key issues involved in
  optical absorption and photo-luminescence are outlined, empha-
  sizing the interconnection of the geometrical and electronic structure
  of π-conjugated systems.

- *Device motivation for interface studies,* and *Optical absorption and emission in conjugated oligomers and polymers.* The principles of device physics of metal insulator field-effect transistors (MISFETs) and light emitting diodes (LEDs) are outlined; mainly as motivation for the contents of the chapters which follow, but also to point out certain features relevant to developing an understanding of the nature of the polymer–metal interface (chapters 5 and 6). The basic principles of electro-luminescence are reviewed here, at the level consistent with the aims of this work.

- *Examples.* Combined experimental–theoretical studies lead to information at a level not easily obtainable from either approach separately[15]. Several detailed examples are provided in chapter 7 to illustrate this point, and to provide the basis for the conclusions drawn on relevant polymer surfaces and the early stages of metal–polymer interface formation. This portion of the book is for the reader who wants to become familiar with details upon which certain conclusions, in the final chapter, have been drawn.

- *The nature of organic molecular solid surfaces and interfaces with metals.* This is a summary containing a digest of the results of the investigations, where 'our view of polymer surfaces and interfaces', in the context of polymer-based LEDs, is summarized in a direct way. Sub-divisions include: polymer surfaces; polymer-on-metal interfaces; and polymer–polymer interfaces. Different (ideal) models of the interfaces are outlined.

1.5   References

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● *Chapter 2*

Theory

2.1 Introduction

The purpose of performing calculations of physical properties parallel to experimental studies is twofold. First, since calculations by necessity involve approximations, the results have to be compared with experimental data in order to test the validity of these approximations. If the comparison turns out to be favourable, the second step in the evaluation of the theoretical data is to make predictions of physical properties that are inaccessible to experimental investigations. This second step can result in new understanding of material properties and make it possible to tune these properties for specific purposes. In the context of this book, theoretical calculations are aimed at understanding of the basic interfacial chemistry of metal-conjugated polymer interfaces. This understanding should be related to structural properties such as stability of the interface and adhesion of the metallic overlayer to the polymer surface. Problems related to the electronic properties of the interface are also addressed. Such properties include, for instance, the formation of localized interfacial states, charge transfer between the metal and the polymer, and electron mobility across the interface.

In this chapter we discuss theoretical modelling, approximation schemes, and calculation methods. The description of the methods is on the level where we focus on the main steps in the theoretical

8

development and not on details related to the solution of the
resulting equations. For details of the derivation and evaluation of
these equations we refer to some of the excellent books or reviews
that are available[1,2]. Special emphasis is put on quantities that are
subject to direct comparison with experimental data, for instance,
electron binding energies and how the approximations invoked in
the theory influence the accuracy of these quantities. The analysis
and evaluation of theoretical results in comparison with experimental
electronic structure data are discussed in chapter 7.

2.2   Schrödinger equation

The basis for studies of the electronic structure of materials is the
(non-relativistic) time independent Schrödinger equation, $H\Phi = E\Phi$,
where the Hamiltonian, H, in atomic units is:

$$H = -\sum_i \frac{1}{2}\nabla_i^2 - \sum_A \frac{1}{2M_A}\nabla_A^2 - \sum_{i,A}\frac{Z_A}{|r_i - R_A|} + \qquad (2.1)$$
$$\frac{1}{2}\sum_i\sum_j\frac{1}{|r_i - r_j|} + \frac{1}{2}\sum_i\sum_A\frac{Z_A Z_B}{|R_A - R_B|}$$

where r_i and R_A are the position vectors for the electrons and nuclei.
The two first terms in eq. (2.1) are the operators for the kinetic energy
of the electrons and the nuclei, respectively, the third term expresses
the Coulomb attraction between the electrons and the nuclei, and the
last two terms express the Coulomb repulsion between pairs of
electrons and pairs of nuclei. The solution of the time-independent
Schrödinger equations gives the stationary states of the system.

The experimental spectroscopic methods discussed below are
performed in the steady state, i.e., the time average of the nuclei
positions is fixed. This justifies the use of the time-independent
Schrödinger equation in the calculations. Dynamical systems are also
of some interest in the context of metal–polymer interfaces in studies
of, for instance, the growth process of the metallic overlayer. Also, in
the context of polymer or molecular electronic devices, the dynamics
of electron transport, or transport of coupled electron–phonon
quasi-particles (polarons) is of fundamental interest for the performance

of the device. However, in the context of this book we restrict
ourselves to studies of stationary states and to the situation when the
interface is already formed.

The first step in solving the Schrödinger equation is to apply the
so-called Born–Oppenheimer approximation. This approximation
makes use of the fact that the nuclei are much heavier than the
electrons and therefore move much slower. Any change in the
position of a nucleus leads to an immediate response of the electronic
system. The kinetic energy of the nuclei can therefore be neglected
in calculations of the total energy of the system. Consequently, the
total energy is expressed as a sum of an electronic part and a constant
nuclear repulsion energy term (the last term in eq. (2. 1) above). The
electronic energy is obtained by solving the electronic Schrödinger
equation $H_{el}\Psi = E_{el}\Psi$, where:

$$H_{el} = -\sum_i \frac{1}{2}\nabla_i^2 - \sum_i \sum_A \frac{Z_A}{|r_i - R_A|} + \frac{1}{2}\sum_i \sum_j \frac{1}{|r_i - r_j|} \qquad (2.2)$$

In the expression for the electronic energy the positions of the nuclei
can be regarded as parameters that can be set to any value we like. In
such a way one can explore the potential energy surface of the
system. Another common situation is that only the equilibrium
geometrical configuration is of interest. In this case the total energy
of the system has to be minimized with respect to the position of the
nuclei. The latter is an important part of the studies of how metal
atoms interact with carbon-based organic molecules. The procedure
of geometry optimization is discussed in Section 2.9 below.

If we are interested in the ground-state electronic properties of a
molecule or solid with a given set of nuclear coordinates we should
seek the solution to the Schrödinger equation which corresponds to
the lowest electronic energy of the system. However, the inter-
electronic interactions in eq. (2.2) are such that this differential
equation is non-separable. It is therefore impossible to obtain the
exact solution to the full many-body problem. In order to proceed, it
is necessary to introduce approximation in this equation. Two types
of approximations can be separated, namely, approximations of the
wavefunction, Ψ, from a true many-particle wavefunction to, in most