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Introduction*Guglielmo Lanzani*

The field of organic semiconductors is very old. Melvin Calvin, introducing a first comprehensive text on the subject, *Organic Semiconductors*, by Felix Gutman and Lawrence E. Lyons, published by John Wiley & Sons in 1966, says: “*It was just over thirty years ago that I became aware of the idea that electronic conduction might be observed in organic materials and might play a role in their biological function*”. This places the birth of the field somewhere between 1930 and 1940, when quantum mechanics was still young, inorganic semiconductors were in their early stages and physics was having a fantastic evolution. The book by Gutman and Lyons collects the results obtained from World War II until 1966. In spite of the size and completeness of their text, these authors already acknowledged at that time that a much larger, encyclopedic effort would have been required to cover the field fully. Since then much work has been done, making the “encyclopedia” even further out of reach. Important discoveries occurred in more recent years, especially conjugated polymers leading to the Nobel Prize in Chemistry in 2000. The continuous discovery of new classes of materials, new applications and new tools for investigation has kept the field in a state of flux, in spite of its long history. So in 2005 many of the issues reported in 1966 are still valid, such as the demand for a large interdisciplinary approach, the effort of physicists to develop a theory for weakly bounded systems and that of chemists for understanding property–structure relationships. Amid the spectacular development in science and technology of organic semiconductors, allowed by an exponential increase in the number of active researchers in the field, in both academies and industrial laboratories, many questions remain open.

When I decided to undertake the challenge of editing a book on molecular materials, I had one point fixed in my mind: to make something different from the cutting-and-pasting of published papers. I felt that a monograph was needed that puts new and exciting experimental techniques on a common footing whenever possible, showing their foundations, limitations and interconnections. This will help to intensify and specify communication among experts in different experimental fields.

I asked all the authors of this book to write a broad, exhaustive tutorial on their subject, with original contents, explanation and views. Something that could actu-

ally help the newcomers, instruct the students, support the researchers, not become obsolete too soon and yet have up-to-date contents. It sounds like a mammoth task and indeed it was. Of course, selection was needed, to keep the contents sufficiently focused while preserving these general aims. For instance, the book contains reviews mainly on experimental results, interpretation is based on relatively simple models, except for a few cases, and theory is not included. There are already many excellent books on quantum chemistry. A painful screening had to be done, to select a few topics out of a huge amount of high-quality work existing in the field. One unquestionable criterion guiding this process was, again, avoiding overlap with other reviews. Yet the bibliography received special attention, to compensate for deficiencies and provide as broad as possible review for consultation. I hope most of the existing literature is properly quoted in the references and I apologize in advance for missing any contributions.

In any dynamic science there are many areas of controversy. Experiments, however, “never deceive”, as Leonardo da Vinci said. Interpretation is often that of the authors, yet I hope the reader will have the opportunity to elaborate her or his own point of view.

Radiation–matter interaction is at the foundation of material science, since it is an integral constituent of the principal material characterization tools. Photophysics is the keystone of the subject. The wealth of processes that it includes may be useful for the interpretation of results and also for the design of new device concepts. This is particularly true for organic semiconductors, which have the properties to be highly reactive to light stimuli. Indeed, natural chromophores, light-harvesting systems or emitters are all based on π -conjugated carbon molecules. Mimicking nature has led to the amazing development of plastic electronics.

The book starts with molecular photophysics (Chapter 2). This is one important piece of the story of organic optoelectronics, for such materials often behave as molecular solids. In addition, single-molecule devices are at the heart of molecular electronics, refreshing old molecular concepts for future technology. While basic topic can be a century old, the experimental results reported here are updated to state-of-the-art techniques for single-molecule spectroscopy. This is an attractive way to collect information on molecular dynamics, which reveals surprises and opens up new perspectives towards nanotechnology. The innovative way in which molecular dynamics is investigated, probing single events of isolated species and not averages over large ensembles, provides a new point of view for looking at molecular photophysics. Next are presented studies on single polymer chains, a nascent field (Chapter 3). Here the system investigated has a large size, challenging the concept of localized states suitable to describe molecules and introducing the concepts and tools of the solid state, yet in low dimensions. Such a borderline area is very fertile for new ideas about how to describe phenomena which are neither typical of covalent solids nor of isolated molecules. Quantum confinement, from three- to one-dimensional space, has dramatic effects on the nature and dynamics of excited states, as is well known from inorganic nanostructure investigations. In spite of a high electronic density, screening is much less effective than in higher dimensions and correlation takes over. The resulting tight

bounded exciton states resemble more a molecular than a wave-like crystal excitation. Soft lattice and strong electron–phonon coupling, typical of organic semiconductors, gives an extra twist to the subject.

Once the building blocks, molecules and polymers, are known, one can move on to the solid state, where they interact. An interesting mixing of notions gets involved here, depending on the intermolecular coupling regime. In the weak-coupling regime, localized, molecular states are still a valid description of the elementary excitations. However, in solids new phenomena may occur: energy (excited states) can migrate, incoherently, giving rise to energy transfer, or dissociate, forming charge-transfer states. In the medium coupling regime, intermolecular “resonance” interaction may lead to delocalization of the wavefunction, thus generating completely new excitations with respect to the starting component, described as Frenkel excitons, which cohabit with localized states. In the strong coupling regime, typical of covalent bonding, weakly bound electron–hole pairs can be formed, named Wannier–Mott excitons, or sometimes delocalized charge carriers can appear. Morphology plays a crucial role in modulating the degree of intermolecular interaction. Starting from the molecular structure, it is still a challenge to predict how this happens and to what extent. A number of empirical rules, sometime true recipes, were developed over time. Yet it is well known that even the same molecular species can give rise to a variety of aggregation states, depending on a number of parameters not always under control. We then introduce, in Chapter 4, a specifically designed technique for addressing the relationship between photophysics and morphology, based on the local probing of the optical properties through confocal microscopy.

Elementary excitation dynamics, including generation, relaxation and deactivation, are the next step. First we address long-lived excitations in Chapter 5, which usually appear only in the solid state, where intermolecular processes are responsible for either their generation or slower recombination. Typically long-lived excitations are triplet states and charged states. On this time scale, typically milliseconds, a wealth of characterization techniques are available, including the magnetic degree of freedom, which is of critical importance in some assignments. The scenario one can obtain is fairly exhaustive. The phenomena considered here are those occurring in most optoelectronic devices, which work in quasi-steady-state conditions. Charged excitations, rarely encountered in isolated systems, become important. They play a key role in many applications, so charge transport is the next topic to be considered (Chapter 6), and the discussion is focused on transport in disordered media, suitable for most carbon-based π -conjugated materials. Free carriers, however, are rarely encountered, if they exist at all in soft condensed matter. The place to look for them is the far-infrared region, where “Drude-like” contributions to the radiation–matter interaction may arise. Using electromagnetic pulses in the THz frequency range can do this. It is a difficult experiment, yet appealing and new to this field. The basics and a review of results are reported in Chapter 7. The case of highly ordered systems, as in crystalline specimens, is addressed in Chapter 8. Strong intermolecular interactions lead to wavefunction delocalization, generating new, collective excitations, which involves

all the molecules in the crystal and carry properties peculiar to the crystal and not the constituents. Excitons and polaritons have to be considered. Their peculiar properties are discussed comprehensively and some exemplifying cases are reported. In the last two chapters (9 and 10), ultrafast spectroscopy is introduced. Early time dynamics embody fundamental properties of the materials. The branching ratio of the nascent population into a number of subspecies, which determines the final performance of the material, occurs within 100 fs. We consider standard pump–probe experiments with extreme time resolution and finally electric field-assisted pump–probe experiments, which are carried out on device structures. The latter provide a useful and rather unusual tool for investigating elementary excitation dynamics, which offers a straightforward way of comparison with the better known inorganic semiconductor counterpart.

Advance in science is a collective process, which nowadays involves millions of people. Even in our specific subject the number of active researchers is very large and steady increasing. The essential step that keeps the whole machine running is information exchange within the community. I hope that the publication of this book will contribute to this process.