

Organic materials with optical properties

D. Guillon*, J.-L. Gallani, L. Mager¹, S. Méry, J. Le Moigne, D. Navarro-Rodriguez and J.-F. Nierengarten

IPCMS, Groupe des Matériaux Organiques, UMR CNRS 7504, CNRS-ULP, 23, rue du Loess, 67037 Strasbourg Cedex, France

¹IPCMS, Groupe d'Optique Linéaire et d'Opto-électronique, UMR 7504, CNRS-ULP, 23, rue du Loess, 67037 Strasbourg Cedex, France

Microelectronics based on semi-conductors plays an important role in information technology since several decades. However, for the high rates needed for today's highly performing systems of telecommunications, the new optoelectronic technologies use processes involving the photon as well as the electron. Thus, what is usually called "Molecular Optoelectronics" has been developed since over the last ten years: it requires the expertise of both physicists and chemists. This molecular approach of information technology is based on a deep knowledge at the molecular level, from which are built complex supramolecular assemblies having specific physical properties. This area of investigation is nearly infinite since the choice of molecules able to supply the elementary bricks of the assemblies is unlimited. It has also to take into account the establishment of strong correlations between the structure and the optoelectronic properties of the supramolecular assemblies. Due to the large possibilities of molecular engineering, organic materials are very promising for many optoelectronic applications. In this chapter we will describe three of them. The first one deals with fullerene derivatives which can be used in photovoltaic cells. The second one concerns photorefractive polymers for recording and storage of optical informations in holograms. Finally, the third one concerns electroluminescent conjugated oligomers and polymers used in large flat displays. In connection with the latter, the way to prepare and to control the quality of thin films obtained by the Langmuir-Blodgett technique will be described.

Photochemical molecular devices based on fullerenes derivatives

Due to their unusual physical and chemical properties, fullerenes and their derivatives appear to be attractive candidates for the construction of supramolecular assemblies and advanced materials [1]. The recent progress in the C₆₀ chemistry allows the preparation of many fullerene derivatives covalently bonded to donor moieties. These systems provide entries into intramolecular processes such as energy and electron transfer [2]. It should be pointed out that the C₆₀ group appears to be a particularly interesting electron

acceptor in photochemical molecular devices because of its symmetrical shape, its large size and the properties of its π -electron system.

The efficient photogeneration of long lived charge-separated states by photoinduced electron transfer is of particular interest for initiating photocatalytic reactions or for solar energy conversion (photovoltaic cells). Photovoltaic devices using thin films of interpenetrating bicontinuous networks of C₆₀ itself or of a C₆₀ derivative and a number of conjugated polymers have been demonstrated to be promising for large-area photodetectors and solar cells [3]. The film morphology is of crucial importance for the device performance. It is also well known that donor and acceptor molecules are generally incompatible and tend to a strong and uncontrolled phase separation. An alternative approach which has been developed recently is to create the bicontinuous network by chemically connecting the donor and acceptor molecules.

The compound under consideration, a fulleropyrrolidine derivative substituted by an oligophenylenevinylene (OPV) moiety has been used for the construction of a solar energy conversion cell [4]. The fullerene-OPV hybrid material leads to a photoinduced charge separation by combining the C₆₀ electron acceptor and the OPV moiety electron donor within a unique molecular architecture (see chemical formula on figure 1). A photovoltaic cell has been prepared by spin-casting thin films of this C₆₀-OPV derivative on a glass substrate coated with indium-tin-oxide. The 100 μ m Al electrode was vacuum evaporated on the films. In such a configuration, this new material is not only able to generate electrons and holes when irradiated, but provides also pathways for their recombination on the electrodes, thus producing a photocurrent. This original chemical approach is in agreement with the basic concepts for obtaining a photocurrent, and is a good illustration of the large possibilities offered by organic chemistry to provide new materials able to be used in photovoltaic devices.

The light-collecting and energy-conversion efficiencies of this molecular photovoltaic system is not yet optimized, but further improvements could be expected if using new fullerene derivatives with a strong absorption in the visible range, able to achieve very fast charge separation and slow charge recombination.

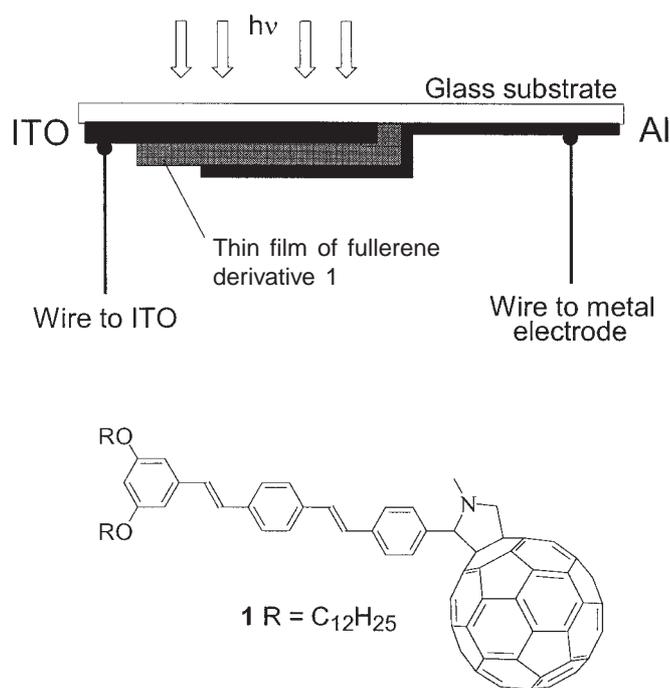


Figure 1. Top: Structure of the photovoltaic cell. Bottom: Chemical structure of compound 1.

The photorefractive polymers: a new class of photonic materials

Nowadays, the development of communications with optic fibers is related to the huge market of telecommunications (Internet, Intranet, TVs, phones...). It induces a strong demand in new materials and technologies. Organic materials begin to be used as passive optical devices (polymer fiber replaces silica fiber) as well as active optical devices (high frequency intensity modulator). However, some functions, such as line interconnection still requires electronic devices. Complete optical systems are under study, and among them the reconfigurable networks using photorefractive materials seem to be the most promising ones.

Known since the late sixties [5], these materials combine three properties: photoconduction, charges trapping, and electro-optic effect. By illuminating the material non uniformly, photoelectric charges are photogenerated in the illuminated areas. These charges then tend to concentrate in the dark areas, where they are trapped. Such a charge separation leads to the build-up of an internal electric field. Since the material is electro-optic, the internal electric field changes the refractive index of the material (see figure 2). As a result, the initial light distribution is optically engraved in the material as a refractive index pattern. Due to charges trapping, the refractive index pattern may have a life time ranging from a few milliseconds to several years, depending

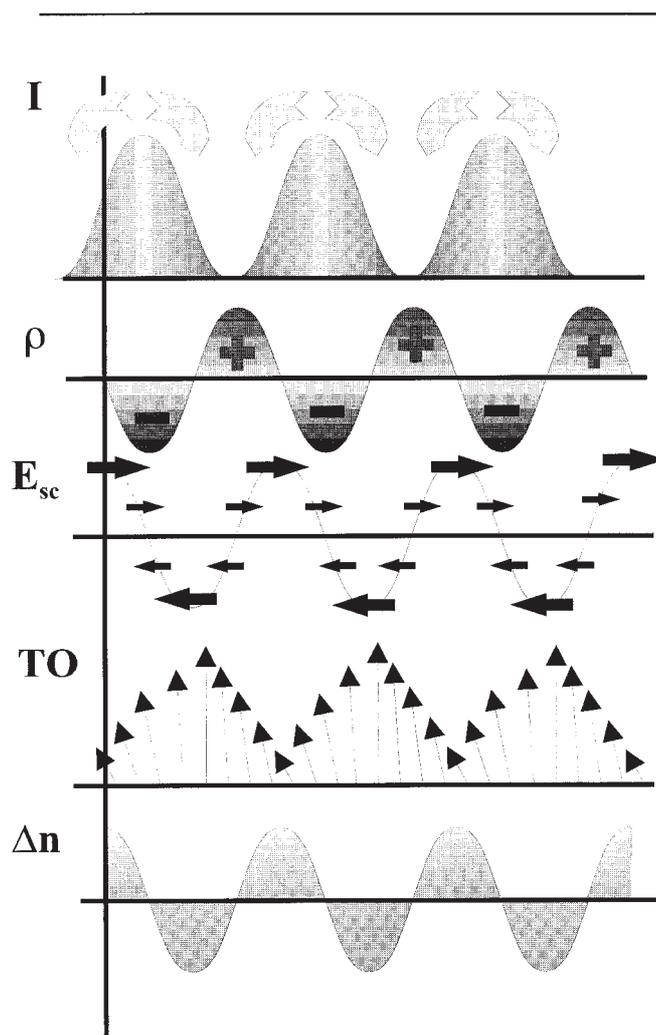


Figure 2. Photorefractive effect in an organic material: The initial periodic distribution of the light (I) leads to a redistribution of charges (ρ) within the material, inducing an internal electric field (E_{sc}). The electro-optic effect induces itself a modulation of the direction and of the degree of orientation of the chromophores (TO) leading to the creation of a spatial modulation of the refractive index (Δn).

on the system considered. These photorefractive materials are well suited for recording and storage of optical informations like in holograms. In the area of the technology used for transportation of optical informations, holographic storage leads to fast access time and to very large storage possibilities.

For a long time inorganic crystals have been the only photorefractive materials. However, since the early nineties, some organic materials were found to be good candidates for photorefractivity [6]. These new materials are based on the association of different molecules ensuring the functions of photoconduction, charge trapping and electro-optic effect.

For example, a photoconducting polymer like polyvinylcarbazole can be associated with a “push-pull” chromophore exhibiting non-linear optical properties like DMNPAA [7] (respectively **a**) and **b**) in the figure 3).

The observation of the electro-optic effect is only possible with non-centrosymmetric materials. In photorefractive materials, this effect is obtained by orientating under electric field the chromophores having a permanent dipole moment. The applied electric field is also necessary for the observation of photoconduction in these materials. Owing to their ease of processability, photorefractive organic polymers are thus suitable materials; indeed, some of these polymers exhibit already non-linear optical properties as efficient as those of inorganic materials used so far [9]. Finally let us note that, unlike many other optical recording media such as silver halides, these photorefractive polymers are WORM type (write many read many) [9]; in other words, they are reconfigurable and do not need any post-exposure treatment.

Among the photorefractive polymers, one generally distinguishes those for which the glass transition (T_g) is high from those for which the glass transition is around room temperature. In the case of low T_g polymers [10], which are today the most efficient ones, the chromophores can be orientated under the internal electric field, thus inducing strong modulations of the refractive index. These low T_g materials are for example doped polymers (photoconducting polymers doped with non-linear chromophores), organic glasses [11] (low molar mass molecules exhibiting both photoconducting and non-linear properties), liquid crystals dispersed in photoconducting polymers [12]. In the case of high T_g polymers, the orientation of the chromophores under electric field is achieved at higher temperatures. The orientation of the molecules is then kept below the glass transition, and thus the molecules cannot be oriented by the internal electric field at room temperature. These materials which are generally less performing systems are fully functionalized polymers [13] (the photoconducting and electro-optic functions are grafted onto the polymer chain).

The future of these materials depends now on the optimization of some parameters, in particular the sensitivity and the response time. But it depends also on the development of novel technologies adapted for using the photorefractive materials in the forthcoming applications.

Electroluminescent organic materials

Since the discovery of electroluminescent properties with some organic materials [14], a large effort of research has been undertaken in many academic and industrial laboratories in order to obtain high performing materials able to be used in electroluminescent (EL) diodes. Indeed, such components can be used in a large number of applications, and in particular in large area flat displays. The structure of a EL diode consists essentially in a thin film of organic material sandwiched between two electrodes (indium-tin oxide

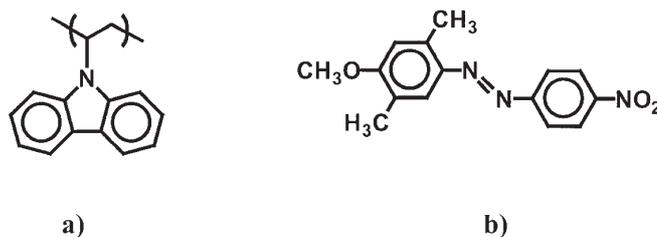


Figure 3. Association of polyvinylcarbazole **a**) with a chromophore; **b**) exhibiting non-linear optical properties.

(ITO) and a metal cathode). When a voltage is applied to such a device, holes and electrons are injected into the organic material from the ITO electrode and the cathode respectively. Holes and electrons recombine to produce excitons inducing then light emission.

The first efficient organic materials were conjugated polymers such as poly(p-phenylenevinylene) (PPV) [15]. Some derivatives of these polymers can be processed into thin films by spin-casting. Such flexible films, a few microns thick, can be obtained in more larger dimensions than the traditional polycrystalline inorganic materials. Since, many other families of conjugated polymers have been studied [16], and it was rapidly shown that these materials are able to emit light with a maximum in the absorption spectrum located at a defined wavelength ranging from near infrared to ultra-violet. The luminescence is generally remarkable and is obtained for relatively low voltages. These features are quite promising from the point of view of applications in the display domain [17].

However, it is well known that one limitation of the conjugated polymers is their low solubility, which induces some difficulties in the thin film process. To overcome this problem, flexible side-chains have been grafted laterally onto the polymer backbone [18]. Another promising approach is to consider conjugated oligomers [19], in order for the material to be more soluble on one hand, and to control the organization of the active chemical moieties on the other one. In this respect, the Langmuir-Blodgett technique is an efficient tool to build-up active electroluminescent molecular assemblies. The molecular alignment thus obtained allows for polarized light emission [20]. The quality of the multilayer film obtained with this technique is analyzed by X-ray reflectivity (see below).

Langmuir-Blodgett films are promising materials, especially in the field of molecular electronics, since they permit complex architectures with molecular level resolution. These structures are built up by stacking organic layers, which may either be identical or have each one a precise function. The control of the material in the z -dimension (perpendicularly to the substrate) is therefore of prime importance. Grazing incidence X-ray reflectometry offers a probe of the structure of thin layered films.

For most materials, the mean refractive index for X-rays can be written as $n = 1 - \delta + i\beta$. The electronic density δ is very small, in the order of a few 10^{-6} and β , the imaginary part of the index, is related to dissipative processes (absorption). In the usual experimental setup, a planar X-ray beam falls onto the investigated surface at an angle θ_i , and a detector set at an angle $\theta_r = \theta_i = \theta$ counts the diffracted photons. This is the so-called "specular reflection geometry". During a typical measurement the scattered intensity is recorded as a function of the deviation angle 2θ (see figure 4). At very low angles of incidence, the index being slightly negative, one observes total reflection (the plateau at the very beginning of the spectrum). When the angle of incidence increases and exceeds the critical angle θ_c (θ_c ranges from 0.15° for water to 0.55° for gold), the reflected intensity decreases very rapidly, in a way which mainly depends on the surface roughness. The measure of θ_c gives access to δ with the use of the relation $\theta_c = \sqrt{2\delta}$. Curve (a) in the figure 4 shows a typical reflectivity pattern from a bare silicon wafer.

If a thin layer of material is deposited on this previous substrate, one usually observes interferences (Kiessig fringes) between the photons reflected at the different interfaces because of index mismatch. These interferences are the X-ray equivalent of equal inclination fringes observed with visible light. Curve (b) is the diffraction pattern of a two-layers film of Cadmium arachidate, deposited on a silicon wafer. Kiessig fringes are clearly seen. The 2θ -spacing of the fringes is inversely proportional to the film thickness, the contrast of the fringes is related to the index mismatch.

When the deposited layers have a periodic electronic density in the z -direction, Bragg peaks begin to appear, as evi-

denced by curve (c). Due to finite-size effects, the peaks are not resolution limited and may exhibit secondary maxima. They superimpose on the Kiessig fringes, giving rise to the complex fringe pattern in-between the Bragg peaks. Analysis of the diffraction pattern gives access to the electron density of the film as a function of z . Through X-ray reflectivity measurements it is then possible to get useful informations such as film thickness, surface roughness, layer spacing and structure.

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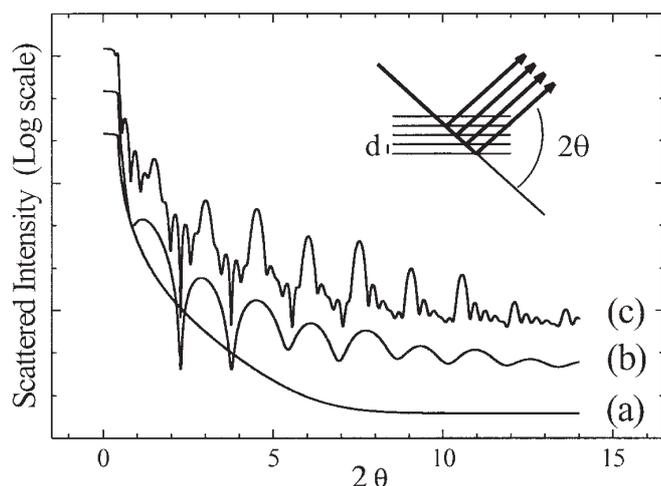


Figure 4. X-ray-Reflectivity patterns for: (a) bare silicon substrate, (b) 2 layers Cadmium arachidate film, (c) 10 layers Cadmium arachidate film. Curves (b) and (c) have been shifted for sake of clarity.