ORGANIC SEMICONDUCTORS

Reports on semiconductor devices based on organic materials, such as light-emitting diodes (LED), flat panel displays, field-effect transistors (FET), photovoltaic elements (solar cells), and photodetector arrays (PDA), are becoming conspicuous in the scientific and technical literature. Liquid-crystal-based optoelectronic devices are commonly used today in display technology as well as in spatial light modulators. Another principal electronics application of organic materials is in xerographic photoreceptors. Other applications such as organic LEDs have recently been introduced commercially. Although the organic optoelectronic devices are new, their progress is remarkable. The technological advantages of this class of materials consist, among others, of (1) tunability of the electronic bandgap by chemical synthesis, (2) processability of the materials on a large scale (large-area devices), (3) substantial reduction of production costs by large-scale production (typical of polymeric, “plastic” materials). Thus, the advantages of the chemical industrial production (as in the dye or the plastic industry) and the properties of semiconductors are combined in the organic semiconductor technology.

We first summarize organic semiconductor devices in general by discussing the electronic properties of molecular crystals and polymers with extended π electrons. The analogy will be drawn between the valence and conduction bands (VB and CB) in semiconductor physics and the π and π^* bands in organic chemistry, respectively. Transport properties as well as photophysical effects will be explained briefly. Detailed analysis of transport in organic crystals is given by Pope and Swenberg (see Reading List). Examples of devices and their operations will be reviewed. A treatment of photonic devices using molecular semiconductors closes this article.

ORGANIC SEMICONDUCTOR MATERIALS

Quite generally, organic semiconductor materials can be divided into three different classes:

1. Monomolecular solids (anthracene, fullerene, phtalocyanine, sexithiophene, etc.)
2. Donor–acceptor-type charge transfer solids (Bechgaard salts, one-dimensional metals, etc.)
3. Conjugated polymers [polyaniline, polythiophene, polysilane, poly(*para*-phenylene), etc.]

Monomolecular Solids

Figure 1 displays the crystal structure of fullerene (C_{60}) as an example of a typical molecular solid. Generally, solids consisting of one type of molecule are van der Waals crystals with a very small intermolecular overlap of different units’ wave functions. This results in the formation of narrow bands of the molecules’ outer valence orbitals. Because this electronic overlap between the molecules is small, the spectral features of such organic solids (absorption, emission, vibrational spectroscopy, etc.) are very similar to those of dilute solutions of the molecule itself.

For example, the outer p_z electrons of anthracene, which form a bonding molecular orbital (π, MO) and an antibonding molecular orbital (π^*, MO), thus form a narrow energy band in the crystal lattice. In the undoped pristine phase, these molecular solids are semiconductors with a filled π band and an empty π^* band, in full analogy with inorganic semiconductors with a filled valence band and an empty conduction band. The electronic bandgaps of these organic solids are variable

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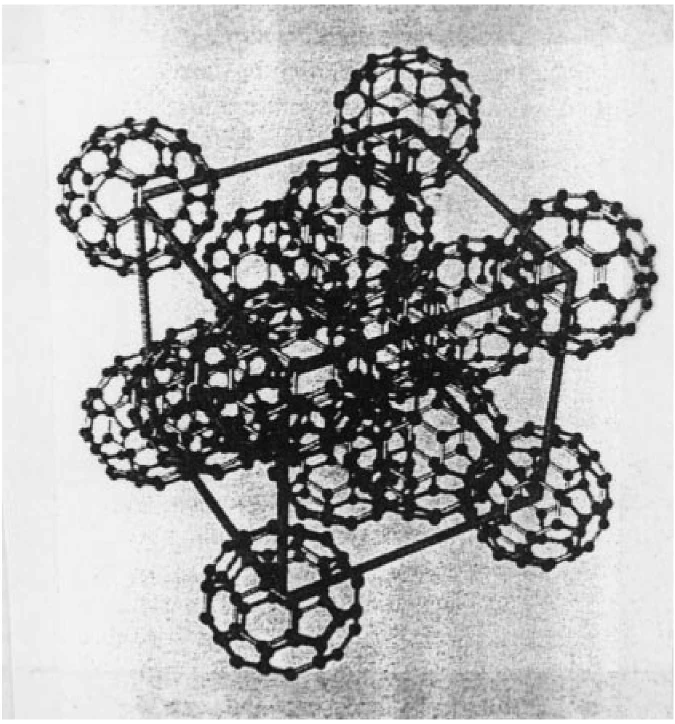

Figure 1. Crystal structure of fullerene (C_{60}) as an example of organic solids.

and dependent on the difference between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of the molecule. This gives the unique possibility of chemically designing the desired energy gap by manipulating the electronic structure via the molecular structure.

Generally, the molecular solids do not show intrinsic charge carriers, since the bandgaps of organic semiconductors with small molecular units are larger than 3 eV. In addition to the large bandgap, the excitations in organic semiconductors are coulombically bound electron–hole pairs on one molecule (Frenkel excitons on a molecule). This property of having strongly bound and localized electron–hole pairs, which result in a localized energy level below the one-electron bandgap (energy level of the exciton, Fig. 2), is an important difference from the inorganic semiconductors, where excited electrons and holes are generally free at room temperature.

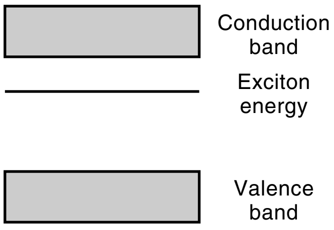

Figure 2. Schematic description of the exciton binding within the energy band diagram. The exciton energy level lies lower than the one-electron continuum at a distance roughly equal to the Coulomb binding energy of the excitonic electron–hole pair.

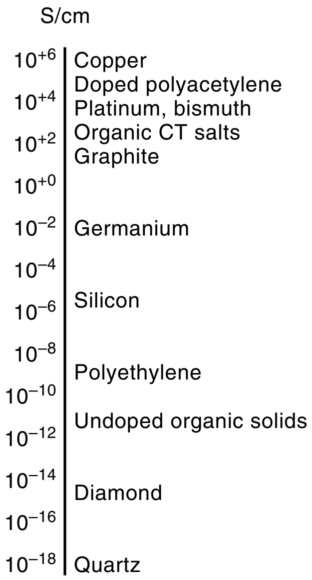

Figure 3. Room temperature conductivities of organic semiconductors together with some reference materials.

The overall conductivity defines the classical frontiers between metals, semiconductors, and insulators (Fig. 3). An undoped, classical semiconductor has room temperature dc conductivities around 10^{-2} S/cm to 10^{-4} S/cm. Within this definition, no intrinsic monomolecular organic semiconductors have been ever described. Organic solids form two distinct classes, belonging either to the metals (fully doped phases) or to the insulators (undoped, pristine phases).

The conductance equation is

$$\sigma = Zen\mu \tag{1}$$

where σ is the conductivity in $\Omega^{-1} \cdot \mathrm{cm}^{-1}$ (S/cm), Ze the net charge of the carriers, n the concentration of charge carriers, and μ the mobility in $\mathrm{cm}^2/\mathrm{V} \cdot \mathrm{s}$. Since the molecular solids have bandgaps larger than 3 eV and since the excitations are Frenkel excitons (coulombically bound, hydrogenlike, electrically neutral quasiparticles) the *intrinsic* charge carrier concentration (created mainly by thermal excitations) is negligible. Furthermore, in many molecular solids an electronic excitation of a molecule is immediately followed by structural relaxations of the molecular coordinates (lattice relaxations), which further lower the total energy and act as a trap. All these components together limit the charge carrier generation as well as migration and thus explain the fact that undoped organic solids are mostly insulators.

The conductance equation further shows that good conductivity may be obtained when a large number of charge carriers are generated. This is the role of doping. An *extrinsic* semiconductor contains impurities capable of accepting or donating electrons. According to that analogy, charges have to be created from neutral organic molecules, and several pathways are possible:

1. Chemical doping
2. Electrochemical doping
3. Photodoping

Chemical doping is the incorporation of another chemical agent, capable of oxidizing (withdrawing electrons from) or reducing (injecting electrons into) the molecular semiconductor. Typical oxidizing agents are iodine (I_2) and $FeCl_3$, whereas typical reducing agents are alkali metals. The net reaction is a salt formation where the charges of the cationic and anionic molecules in the solid are compensated with the oppositely charged counterions within the crystal lattice. For example, for fullerene solids the chemical doping proceeds via reduction using alkali metal vapors (typically potassium):

$$\text{Fullerene} + 3\text{K} \rightarrow \text{Fullerene}^{3-} + 3\text{K}^{+} \quad (2)$$

Potassium cations are incorporated into interstitial crystal lattice spaces of the cubic lattice structures (Fig. 4) of fullerene (C_{60}). The resulting salt is not only conducting but also superconducting at low temperatures.

During electrochemical doping the oxidation and reduction processes are carried out on an electrochemical working electrode (typically a platinum foil) in an electrolyte. The first difference from chemical doping is therefore that the molecular semiconductor has to be prepared as a thin film on the electrode. Upon withdrawal or injection of the electrons in the electrochemical setup, the charge carrier concentration can be well monitored and controlled through Coulomb counting of the electrochemical Faraday current. This possibility is the greatest advantage of electrochemical doping over chemical doping. Upon creation of the charges, a counterion with opposite charge has to migrate from the electrolyte into the molecular film. Diffusion limits migration and forces the method of the electrochemical doping to use thin film samples. The resulting final state from electrochemical doping is in principle the same as from chemical doping. The materials become highly conducting.

During photodoping of a molecular solid consisting of one molecular moiety (such as anthracene or fullerene), an incident photon has to transfer an electron from one molecule to another. This implies that the same type of molecule (we are treating here monomolecular solids) has to be capable of occupying a stable anionic and a stable cationic state. Furthermore, the photoexcitation results from the creation of a molecular exciton on a specific molecule first. To separate the charges onto different molecules and get them free, one must overcome the Coulomb forces, which can be as strong as several hundred millielectron volts. Therefore, the geminate recombination of the photoexcited excitons is the main relaxation pathway, heavily limiting the photogeneration of free charges. If one excites the molecular solid with photon energies above the one-electron bandgap, which lies higher than the lowest absorption band due to Coulomb binding energy of excitons, then charge carrier generation with photodoping can be measured. Further mechanisms, such as exciton–exciton annihilation as well as exciton dissociation at impurity trap sites, can create charges. Putting a large electrical field across the thin film of a molecular solid helps the excitons to overcome the Coulomb barrier for separation and results in an nonlinear enhancement of the photocurrent at large fields.

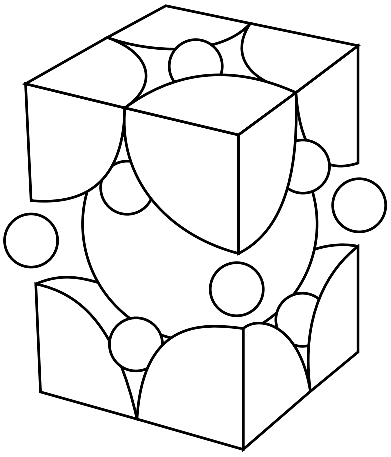

Figure 4. Schematics of K_3C_{60} crystal lattice structure.

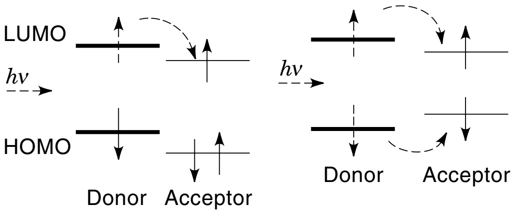

Figure 5. Electronic level description of typical energy/electron transfer donor–acceptor pairs.

Donor–Acceptor Charge Transfer Solids

In this subsection we consider molecular solids consisting of two different kinds of molecules. Sometimes molecular pairs have electronic levels that allow a charge transfer reaction between the units, either immediately in the ground state or as photoinduced charge transfer in the excited state. The molecular partner that is donating electrons and becomes positively charged is called the *donor,* and the opposite partner is called the *acceptor.* A well-known system forming a ground state charge transfer crystal with one-dimensional stacks of donors and acceptors in a crystal lattice is tetrathiafulvalene with tetracyanoquinodimethane (TTF–TCNQ). Several interesting phenomena such as charge density waves (CDW), spin density waves (SDW), and superconductivity have been reported on this class of organic charge transfer salts. A detailed description of this very interesting system goes beyond the scope of this article, and further reading is suggested in the list at the end.

An important class of donor–acceptor pairs is the group of materials that exchange charges not in the ground state but in the photoexcited state. Such donor–acceptor photoinduced charge transfer composites are important (e.g., for the photovoltaic conversion of solar energy), because they can transfer the excitation energy or the photoexcited electron similarly to the operation principle of the photosynthetic reaction center in natural green plants. Figure 5 shows examples of donor–acceptor electronic structures.

A practical example of a donor–acceptor pair performing a photoinduced electron transfer is oligothiophene and fullerene. For an energy transfer pair, two different phorphyrin derivatives as found in the photosynthetic reaction center can be mentioned.

Conjugated Polymers

At first glance a macromolecular crystal is just another kind of monomolecular solid (such as anthracene or fullerene) as

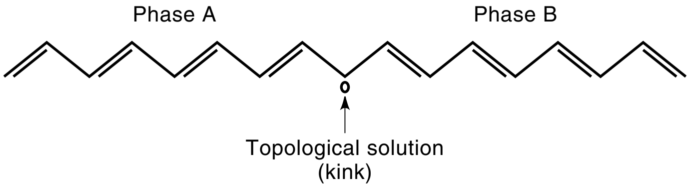

Figure 6. Topological soliton of a linear *trans*-polyacetylene chain.

described above. However, the existence of interesting physics on a long π-conjugated macromolecule itself deserves special attention. A *trans*-polyacetylene (PA) chain has two energetically degenerate ground state configurations with reversed double-bond–single-bond sequence. Therefore, a domain boundary between these two phases represents a topological soliton (Fig. 6). Such solitons can move along the chain nearly freely, together with the lattice distortion they create. Upon doping or removal or injection of electrons, charged solitons are created. Interaction of charged and neutral solitons results in quasiparticles such as polarons and bipolarons. These highly mobile charge carriers can also be photogenerated. Generally, the possibility of delocalization along the polymer backbone and the lattice relaxations in these one-dimensional systems enhances the stability of photogenerated charges over that obtained with small-molecule organic crystals.

There are, however, limitations to the overall conductivity in the conjugated polymeric semiconductors arising from the limitation of charge carrier mobility, especially due to disorder. The fundamental reason for the large concentration of defects in macromolecular solids can be expressed in thermodynamic terms by the expression of the free energy for crystallization per mole of crystallizing units, ΔF_c, as the sum of two opposing terms involving the enthalpy of crystallization (ΔH_c) and the entropy (ΔS_c):

$$\Delta F_c = \Delta H_c - T\,\Delta S_c \tag{3}$$

Compared to the enthalpy of crystallization in covalent, ionic, or metallic solids, the enthalpy of crystallization in molecular solids is very weak, for it is based only on weak van der Waals intermolecular forces. On the other hand, highly perfect crystalline polymeric solids have high entropies to pay for; e.g., the opportunity for disorder in a long chain with almost freely rotating segments is much higher than in small-molecule, covalent, or ionic crystals. As a consequence of the two unfavorable factors, low enthalpy and high entropy cost of crystallization, the net free energy of crystallization is very low in polymeric molecular solids. The consequent built-in disorder results in localization of the free charge carriers (the Mott–Anderson localization) and limits the conductivity.

ORGANIC SEMICONDUCTOR DEVICES

Single-Layer Metal–Insulator–Metal Diodes

The simplest and most widely used organic semiconductor device is a metal–insulator–metal (MIM) tunnel diode with asymmetrical-work-function metal electrodes (Fig. 7). In forward bias, holes from the high-work-function metal and electrons from the low-work-function metal are injected into the organic semiconductor thin film. Because of the asymmetry of the work functions for the two different metals, forward bias currents are orders of magnitude larger than reverse bias currents at low voltages. The rectifying diode characteristic can be accompanied by radiative recombination of the injected electrons and holes within the molecular solid; the result is a light-emitting diode (LED). If radiative recombination of the injected charges as well as photoinduced free charge carrier generation are allowed at the same time, the device gives light emission in forward bias as well as a significant photocurrent under a reverse bias field. This dual functionality of organic thin film MIM devices is important for optoelectronic applications.

To enhance the charge injection at the metal electrodes as well as to bring the light-emitting material to a safe distance from the metal electrode, additional charge transport layers are used on both sides of the organic semiconductor thin film (Fig. 7). These electron–hole transport layers are organic molecular thin films. The operational principle of the MIM diode is not altered. However, achieved efficiencies for the LEDs are greatly improved by using these additional layers.

When using the devices for photodetection under reverse bias, the potential difference between the electrodes has to be high enough to overcome the Coulomb attraction barrier of the photogenerated excitons. Otherwise the absorbed photons will mainly create excitons, which decay geminately (either radiatively, with photoluminescence, or nonradiatively). Thus the photocurrent efficiency of such devices will be limited. In the photovoltaic mode, where no external voltage is applied and short-circuit conditions exist, the only potential difference available in the MIM device is the work function difference of the metal electrodes. In most cases (e.g. ITO and Al) the potential difference due to this work function difference is not high enough to give efficient photoinduced charge generation, limiting the operation of the photovoltaic cells.

To overcome the limitation on the photoinduced charge carrier generation in a monomolecular solid, a dual molecule approach has been successful. In the molecular thin film between the electrodes, a donor–acceptor molecular pair is introduced. For example, if the organic semiconductor used is a conjugated polymer (electron donor), fullerenes have been shown to be an excellent partner (electron acceptor). In such devices, consisting of a composite thin film with conjugated polymer–fullerene mixture, the photogeneration efficiency of charges is near unity because the electron transfer from the conjugated polymer onto fullerene takes place within 1 ps after the photoexcitation. Since this approach includes a mo-

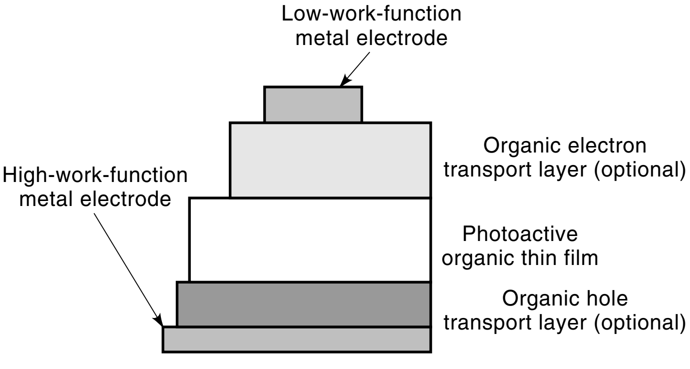

Figure 7. General scheme of a multilayer organic tunnel diode: a single-layer MIM device without the optional charge transport layers.

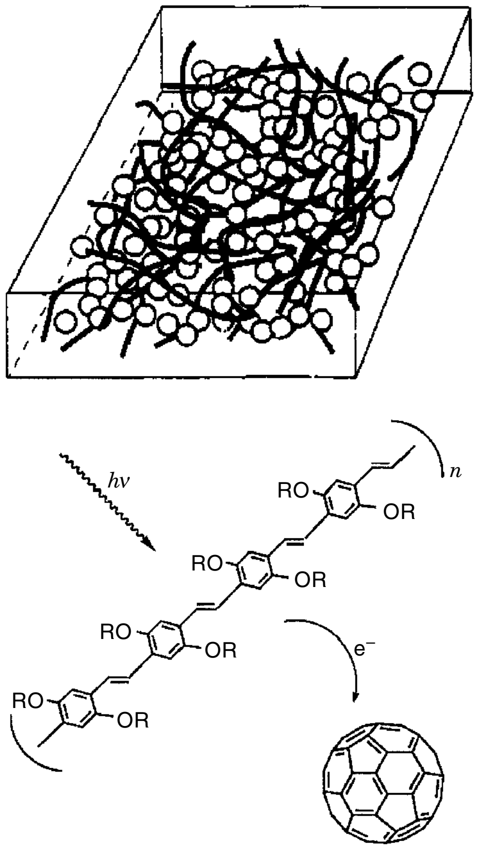

Figure 8. Bulk heterojunction formed within a conjugated polymer–fullerene composite film.

lecular-level interfacing of the two active units, it is called a *bulk heterojunction* (Fig. 8). Using donor–acceptor pairs with an efficient photoinduced charge transfer is generally a sound approach to enhancing the generation of photoinduced charges and has been successful with many other donor–acceptor pairs, either mixed (intermolecular charge transfer) or chemically attached together in a donor–bridge–acceptor supramolecule (intramolecular charge transfer). The limiting factor for the photovoltaic device efficiency is the migration of the photogenerated charges to the electrodes, and thus the mobility.

Heterojunction Diodes

Considering the energy band diagram in Fig. 9, the heterojunction formed at the interface between (for example) a conjugated polymer and a C_{60} should have a rectifying current–voltage characteristic even using the same metal contact on both sides (analogous to a *pn* junction). One bias direction of such a device (electron injection on the semiconducting polymer side and electron removal on C_{60}) is energetically unfavorable. This polarity of the device results in very low current densities. On the other hand, electron injection onto C_{60} and electron removal from the semiconducting polymer is energetically favorable, creating conducting species on both sides. This polarity of the device results in relatively high current densities. Thus, organic semiconductor devices using two layers with different electronic band structures as illustrated in Fig. 9 have rectifying diode characteristics. Molecular diodes based on the same principle were first proposed years ago by Aviram and Rattner for Langmuir–Blodgett donor–acceptor structures. It has been demonstrated that molecularly thin heterojunctions where each layer is only a few molecules thick (nanometers) have rectifying diode characteristics. Even a single donor–bridge–acceptor molecule layer has been reported to show rectification. These findings open up a new dimension in electronic devices and may be called *molecular-scale electronics.*

A photophysical interaction between the two molecular units (photoinduced electron and/or energy transfer) happens at the interface and gives rise to photocurrents as well as a photovoltaic effect.

Are Organic Semiconductor Heterojunction Devices Different from *pn* Junctions? The intrinsic charge carrier concentration of semiconductors arises from thermal excitation of the charge carriers across the energy gap. Upon doping, new energy levels are introduced in the gap, and the Fermi energy is no longer in the middle of the gap, but displaced towards the conduction band (*n* doping) or the valence band (*p* doping). If a *p*-doped and an *n*-doped semiconductor are joined at an interface, electrons flow from the *n*-type to the *p*-type semiconductor, creating an electric field V_{bi} (built-in potential) at the interface. The area of ionized dopants is called the space charge or depletion region. Because the Fermi energies on the two sides of the interface must be equal at equilibrium, the energy shift required to equalize the two Fermi levels is

$$\Delta E = E_F(n) - E_F(p) = eV_{bi} \tag{4}$$

Molecular crystals or conjugated polymeric systems have very low intrinsic conductivities. As an example, for a conjugated polymer with an energy gap of 4 eV, which is necessary for a blue-light-emitting polymer diode, the fraction of electrons excited across the gap at room temperature is of the order of 10^{-50}. This has fundamental consequences for the description of the organic semiconductor devices:

1. At a metal–polymer junction there is negligible charge exchange, and the extent of the space charge region as well as the band bending is very small.
2. At a heterojunction there are no charge carriers available to flow across the interface at room temperature; thus the depletion layer is confined to very few mono-

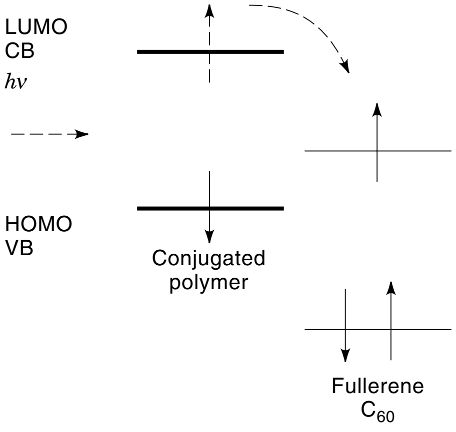

Figure 9. Schematic description of the electronic levels for conjugated polymer–fullerene heterojunctions.

layers at the interface, with nearly vanishing built-in potential.

In other words, for organic molecular devices, the MIM tunnel diode description as illustrated above is still more appropriate than classical *pn* junction and Schottky barrier descriptions.

ORGANIC PHOTONIC DEVICES

Liquid crystals for photonic applications are already on the market, and reviewing them goes beyond the scope of this article. Generally, organic materials as described in the previous section are good candidates for photonic applications such as optical frequency doubling, optical sum and difference frequency generation, parametric amplification, waveguiding, photorefractive elements, optical correlators, reverse-saturable absorbers (optical limiters), all optical switches, and electro-optical switches. As an example, only one photonic application of organic semiconductors is presented here, and further reading is recommended on this highly promising area of research and development.

Optical Limiters Using Nonlinear Absorption

After photoexcitation, the excited state of conjugated molecules exhibits absorption bands due to higher excitations of the singlet excitons, or due to absorption by the triplet state, or due to ionic state absorption of the photoinduced charges (with large oscillator strengths). In fullerene (C_{60}) solids there is a very rapid intersystem crossing to the triplet state with near-unity quantum efficiency. The resulting triplet state has intense absorptions within the triplet manifold, which is also long-lived. In another example of photoexcited molecules, donor–acceptor pairs that produce ultrafast (picosecond or less) photoinduced charge transfer have potential for nonlinear optical (NLO) applications. After a photoinduced electron transfer, there is a cation radical on the donor molecule and an anion radical on the acceptor molecule, which have generally intense absorption coefficients. During the lifetime of the charge-separated state, a second photon probing the system will encounter these strong excited state absorptions. These excited state absorptions of the organic semiconductors often lie within the electronic bandgap, in contrast to ground state absorptions, where only photon energies larger than the bandgap are absorbed.

Utilizing this effect of excited state absorption in the photoinduced electron transfer pair (conjugated polymers or fullerenes), optical limiters have been realized.

Further examples of photonic devices utilizing nonlinear optical properties of conjugated organic molecules can be found in the literature. The combination of unique electronic and optical properties promises a number of applications for organic semiconductors in future.

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